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An aerial photograph of a large body of water, likely a bay or estuary, with a prominent bridge spanning across it. The water is blue and reflects the sky. In the background, there are industrial buildings and a coastline. The image is partially obscured by a white circular graphic element.

**Poster  
Presentations**

# ABSTRACT BOOK

## Asymmetric 1,3,4-thiadiazoles as bridging ligands for bimetallic transition metal complexes

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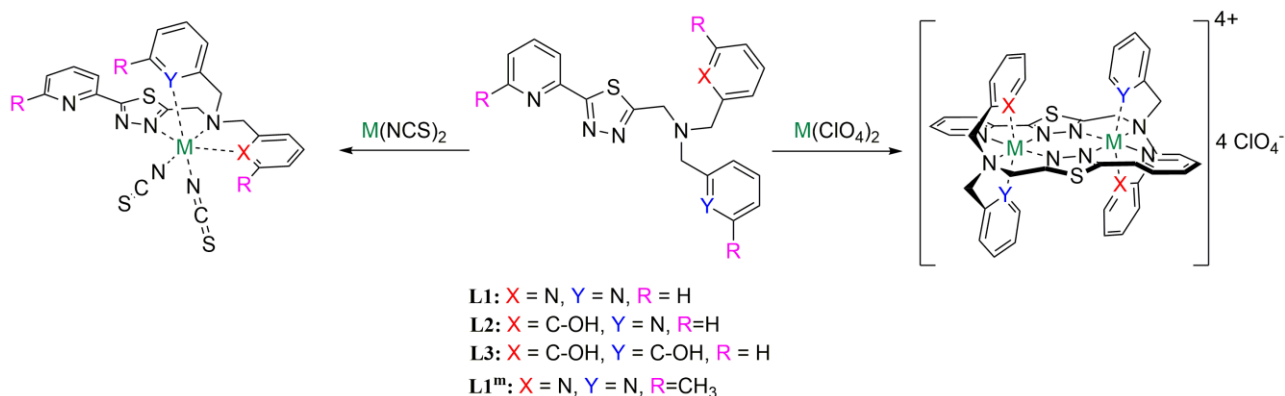
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Bimetallic complexes are expected to exhibit properties different from those observed for monometallic ones if electronic and magnetic interactions between metal ions are present. Bimetallic spin-crossover complexes can show successive high-spin low-spin transitions for both metal ions resulting in a multistep spin transition behavior with a symmetry broken mixed spin state.<sup>1</sup> Thus, a purposeful synthesis of complexes that provide asymmetric coordination modes for two metal ions allows for magnetic materials with three addressable spin states.

Thiadiazoles provide a feasible synthetic route for asymmetric ligands with adjustable coordination pockets, thus offer the opportunity to prepare bimetallic and hetero-bimetallic complexes with controllable magnetic exchange interaction. We synthesized three asymmetric ligands (**L1-L3**) based on 1,3,4-thiadiazoles, each bearing a bidentate and a tetradentate pocket. The latter was progressively altered in order to increase ion selectivity and the ability to stabilize metal ions in higher oxidation states. To further prevent formation of symmetric complexes, **L1<sup>m</sup>** with additional methyl groups was synthesized. We have prepared monometallic and bimetallic transition metal complexes, the x-ray structures and the magnetic properties are discussed here.



**Figure 1** Complexes based on asymmetric 1,3,4-thiadiazole ligands.

1 J. A. Kitchen, J. Olguín, R. Kulmaczewski, N. G. White, V. A. Milway, G. N.L. Jameson, J. L. Tallon, S. Brooker, *Inorg. Chem.*, **2013**, 52, 1185.



## Rational conception of Dysprosium-based complex featuring different Single-Molecule Magnets

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Lanthanide-based Single Molecule Magnets (SMMs) are fascinating objects for both fundamental science and potential applications.<sup>1</sup>The most used lanthanide to elaborate such molecular objects is undoubtedly the Dy<sup>III</sup> ion. The mononuclear Dy-based SMMs present a large magnetic hysteresis loop but closed in zero field due to the fast relaxation of the quantum effect while the polynuclear Dy-based SMMs present a narrower hysteresis loop but opened in zero field when the magnetic interaction are significant. So, it is natural to try to combine both mononuclear and polynuclear (with significant magnetic interaction) SMMs in the same compound in order to obtain as large as possible magnetic hysteresis loop. To do so, we start from two systems synthesized in our group: i) a binuclear Dy<sup>III</sup>-based SMM ([Dy(tta)<sub>3</sub>(L<sup>1</sup>)]<sub>2</sub> with L<sup>1</sup> = tetrathiafulvalene-3-pyridine-N-oxide and tta<sup>-</sup> = 2-thenoyltrifluoroacetate anion)<sup>2</sup> in which the antiferromagnetic coupling between axial magnetic moment leads to the opening of the magnetic hysteresis loop at zero field which closes in field (double butterfly) and ii) a mononuclear Dy<sup>III</sup>-based SMM ([Dy(tta)<sub>3</sub>(L<sup>2</sup>)] where L<sup>2</sup> = 4,5-bis(propylthio)-tetrathiafulvalene-2-(2-pyridyl)benzimidazole-methyl-2-pyridine)<sup>3</sup> with hysteresis opened in field only (butterfly). Then during this presentation, it will be exposed how the carefully designed TTF-based ligand L<sup>3</sup> (L<sup>3</sup> = 2-{1-Methylpyridine-N-oxide-4,5-[4,5-bis(propylthio)tetrathiafulvalenyl]-1H-benzimidazol-2-yl}pyridine) can guaranty the auto-assembly of the two previously presented systems in a unique molecule. Among other properties, the SMM behavior of the resulting tetranuclear complex [Dy<sub>4</sub>(tta)<sub>12</sub>(L<sup>3</sup>)<sub>2</sub>]<sup>4</sup> will be presented and explained.

1 a) R. Sessoli and A. K. Powell, *Coord. Chem. Rev.*, **2009**, 253, 2328. b) D. N. Woodruff, R. E. P. Winpenny, R. A. Layfield, *Chem. Rev.* **2013**, 113, 5510.

2 F. Pointillart, Y. Le Gal, S. Golhen, O. Cador, L. Ouahab, *Chem.-Eur. J.* **2011**, 17, 10397.

3 a) T. T. da Cunha, J. Jung, M.-E. Boulon, G. Campo, F. Pointillart, C. L. M. Pereira, B. Le Guennic, O. Cador, K. Bernot, F. Pineider, S. Golhen, L. Ouahab, *J. Am. Chem. Soc.* **2013**, 135, 16332. b) F. Pointillart, K. Bernot, S. Golhen, B. Le Guennic, T. Guizouarn, L. Ouahab, O. Cador, *Angew. Chem. Int. Ed.* **2015**, 54, 1504.

4 F. Pointillart, T. Guizouarn, B. Lefeuvre, S. Golhen, O. Cador, L. Ouahab, *Chem. Eur. J.* **2015**, 21, 16929.

## **Distant substitution effects on the magnetic properties of Dy-based single-ion magnets**

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Paramagnetic metal-ion complexes showing single-molecule magnet (SMM) behavior have potential applications in magnetic memory devices. The SMM behavior arises from a combination of large ground-state spin states and large magnetic anisotropies. The possibility of large numbers of unpaired electrons in the case of lanthanide ions in comparison to transition metal ions and the intrinsic anisotropies caused by these electrons makes 4f elements good candidates for SMMs. The magnetic properties of lanthanide ion-based SMMs are sensitive to the crystal field around the metal ions. Previous work to tune the slow relaxation of the magnetization by changing the crystal field was primarily focused on changing the coordinated atom<sup>1,2</sup> or changing the coordination geometry<sup>3</sup>. Herein a family of lanthanide complexes where peripheral of a ligand was substituted was investigated. Due to the distance from the metal ion, the substitution does not affect the coordination sphere of the metal ion, but it does affect the electronic structure of the ligand, inducing a slight change in the crystal field. To avoid any bias from the crystal packing, which can constrain the coordination sphere<sup>4</sup>, magnetic measurements were performed in solution. In the solution state, the structures of complexes are close to those in the gas phase, and the coordination geometry can be considered to be the same for each complex.

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3. J. Zhu, C. Wang, F. Luan, T. Liu, P. Yan, G. Li, Inorg. Chem., **2014**, 53, 8895
4. M. Ramos Silva, P. Martín-Ramos, J. T. Coutinho, L. C. J. Pereirac, J. Martín-Gild, Dalton Trans., **2014**, 43, 6752

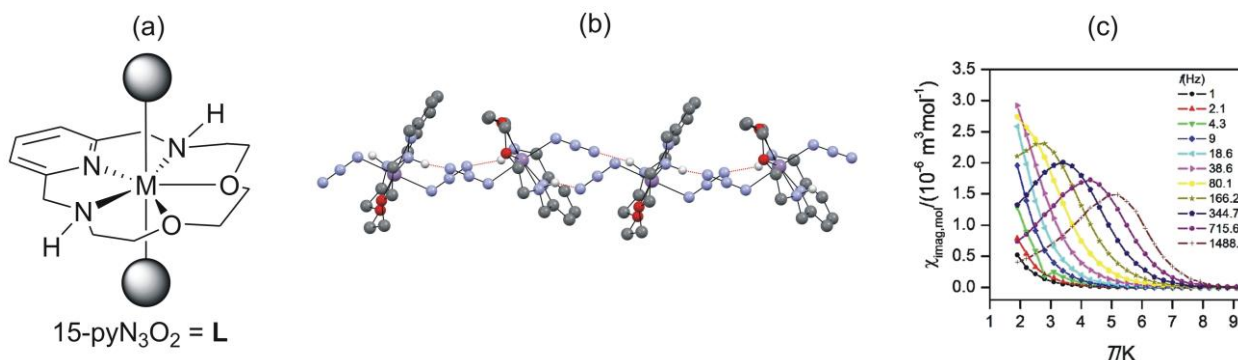
## Evaluation of magnetic properties in transition metal complexes containing 15-membered pyridine-based macrocycle

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Heptacoordinated complexes of selected transition metals have attained more attention during last years because of their interesting magnetic properties, e.g. large magnetic anisotropy, single-molecule and single-ion magnet properties.<sup>1</sup> We prepared two series of complexes containing pentadentate 15-membered pyridine-based macrocycle (15-pyN<sub>3</sub>O<sub>2</sub> = **L**, Fig. 1) of the general composition [M(**L**)X<sub>2</sub>] (where M = Mn(II) with X = Br<sup>-</sup>, I<sup>-</sup>, N<sub>3</sub><sup>-</sup>, NCS<sup>-</sup>, CN<sup>-</sup>; M = Co(II) with X = CN<sup>-</sup>, N(CN)<sub>2</sub><sup>-</sup>, C(CN)<sub>3</sub><sup>-</sup>). In both the series, the impact of the axial coligands (X) on magnetic properties has been studied. Magnetic data of Mn(II) complexes revealed that the coligands have negligible effect on magnetic anisotropy ( $|D| < 0.7 \text{ cm}^{-1}$ ), but magnetic features of the complexes are influenced by non-covalent contacts mediating a weak antiferromagnetic exchange. On the other hand, a large magnetic anisotropy has been observed in the case of Co(II) complexes ( $D \approx +40 \text{ cm}^{-1}$ ) which behave as field-induced single-ion magnets, with the best result ( $U_{\text{eff}} = 13.7 \text{ cm}^{-1}$ ) for [Co(**L**){C(CN)<sub>3</sub>}<sub>2</sub>]. The obtained results will be compared with the previously published data regarding the [M(**L**)Cl<sub>2</sub>] complexes, where M = Mn(II), Fe(III), Co(II), Ni(II), Cu(II).<sup>2</sup>



**Figure 1** (a) Structural representation of complexes with **L**, (b) Part of the supramolecular structure of [MnL(N<sub>3</sub>)<sub>2</sub>] showing hydrogen bonds (dashed lines), (c) ac susceptibility data for [CoL{C(CN)<sub>3</sub>}<sub>2</sub>].

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2. B. Drahoš, R. Herchel, Z. Trávníček, *Inorg. Chem.*, **2015**, *54*, 3352.



## Synthesis, characterization and magnetic study to Co (II) and Ni (II) complexes with cryptand type ligands

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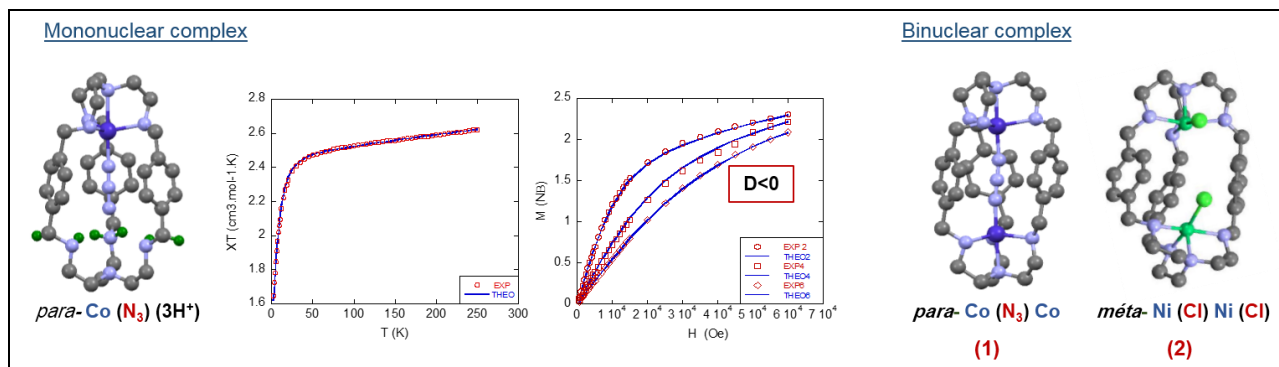
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Single molecule magnets (SMMs) exhibit a slow relaxation of their magnetization leading to a magnetic hysteresis at low temperature. Since this bistable behavior may ultimately lead to technological applications in the domain of data storage and quantum computing, the study of these objects has generated a considerable interest. This remarkable property arises from the existence of two ground states of different magnetization  $+M_s$  and  $-M_s$  separated by an energy barrier. The design of suitable SMMs therefore rests on the ability to synthesize new objects with larger and uniaxial magnetic anisotropy (Ising type magnetization, negative  $D$  parameter), and an as small as possible rhombic parameter  $E$ . In this context, SMM can be divided into two classes, the mononuclear complex, and the Homo or Hetero-Binuclear complex, where the metal ions communicate with each other by an exchange interaction or dipole interaction  $J$ .

Pentagonal complexes of Co (II) and Ni (II) were synthesized, and their magnetic behavior was investigated with a different bridging ligands (Cl<sup>-</sup>, Br<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, N<sub>3</sub><sup>-</sup>, imidazole, etc...). Magnetic susceptibility measurements of (1) indicated that the two Co (II) atoms are antiferromagnetically coupled which their anisotropy is Ising type ( $D < 0$ ), while its planar type for Ni (II) ( $D > 0$ ). This is due to the nature of the metal ion and mainly to the complexes geometries that are trigonal bipyramidal for (1) and very close to square pyramidal for (2) (figure 1).



**Figure 1** Pentagonal Complexes of Co (II) and Ni (II) and their magnetic behavior

## Field Induced Slow Magnetic Relaxation in Trigonal Planar Mononuclear Fe(II), Co(II) and Ni(I) Complexes

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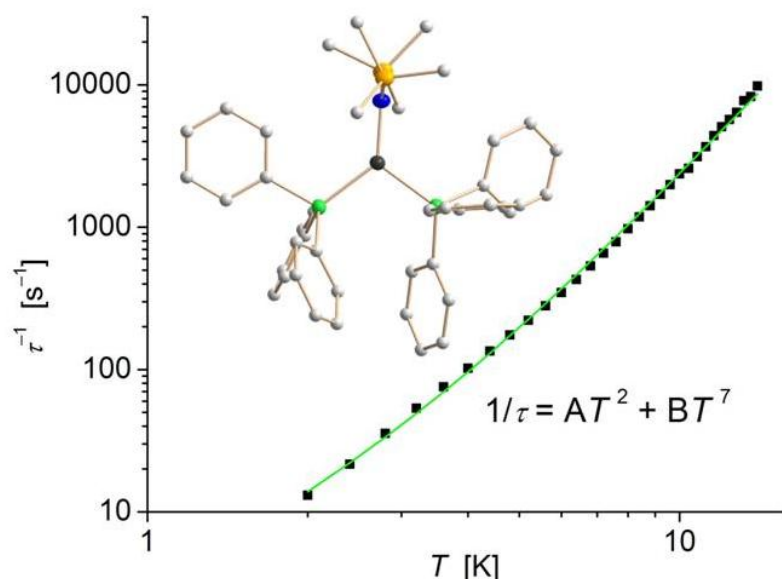
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Coordinationally unsaturated compounds of 3d transition metals are of increasing interest because of their magnetic properties. It was shown that iron complexes of this type can display unusual slow relaxation of the magnetization at low temperatures with numbers for the energy barriers of the spin reversal up to  $226 \text{ cm}^{-1}$  in  $[\text{Fe}(\text{C}(\text{SiMe}_3)_3)_2]^-$ .<sup>1</sup> In this respect we have studied the dc and ac magnetic properties of a series of trigonal planar complexes of Fe(II), Co(II) and Ni(I) namely  $[\text{Li}(15\text{-crown-5})][\text{M}\{\text{N}(\text{SiMe}_3)_2\}_3]$ ,  $[\text{M}\{\text{N}(\text{SiMe}_3)_2\}_2\text{thf}]$  and  $[\text{M}\{\text{N}(\text{SiMe}_3)_2\}_2(\text{PCy}_3)]$  ( $\text{M} = \text{Fe}, \text{Co}$ )<sup>2</sup> as well as  $[\text{NiCl}(\text{PPh}_3)_2] \cdot \text{C}_4\text{H}_8\text{O}$  and  $[\text{Ni}(\text{N}(\text{SiMe}_3)_2)(\text{PPh}_3)_2]$ .<sup>3</sup> DFT and ab initio wave function based multi configurational methods have been applied to model the electronic properties of the compounds.



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(2) Eichhöfer, A.; Lan, Y.; Mereacre, V.; Bodenstein, T.; Weigend, F. *Inorg. Chem.* **2014**, 53, 1962

(3) W. Lin, T. Bodenstein, K. Fink, A. Eichhöfer, *Inorg. Chem.* Submitted.

## Characterization of magnetic nano-objects by Planar Hall Effect

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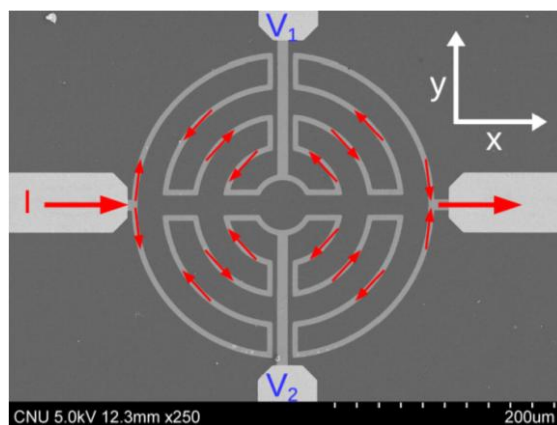
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The synthesis of small magnetic nano-objects of coordination compounds has allowed showing a modification of the material behavior at the nanometer scale. However, the magnetic characterization of these objects is still realized with classical techniques, which means characterize a large amount of matter. When the amount of matter decreasing, the interparticular interactions, matrix and the average effects are reduced, and new phenomena may be observed.

With this aim, we developed a planar Hall effect (PHE) sensor, which works at low and room temperature. It is sensitive to a small amount of matter, with a small magnetic susceptibility ( $\chi \geq 10^{-4}$ , see figure 1 b)).<sup>1,2</sup> Optimizing the sensor, we succeed to increase the sensibility of the PHE sensor, and by consequence we reduced the amount of studied matter. This magnetic sensor will be a real asset to understand the behavior of isolated objects.



**Figure 1** a) Image SEM of a PHE ring sensor, with the schematization of the current propagation.

1 T. Q. Hung, F. Terki, *et al.*, *Angew. Chem. Int. Ed.*, **2013**, *52*, 1185.

2 G. Félix, *et al.*, *submitted*, **2016**.



## **A modular design of molecular qubits to implement universal quantum gates**

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The physical implementation of quantum information processing relies on obtaining quantum bits and quantum gates that could be organized in such a way to carry out useful algorithms. To build useful devices two universal gates are needed – the CNOT gate and the SWAP gate. To achieve such gates it would be ideal if one simple module could be used in each, linked and addressed in different ways to achieve the gate operations. Here we show, as proof of principle, that {Cr7Ni} rings can be functionalized to provide modules that can be easily assembled into these two types of two-qubit gates; we fully characterize the two-qubit gates and use these parameters to perform simple simulations that indicate how such gates would operate. This provides a strong basis for future developments of molecular two-qubit gates towards quantum computation.

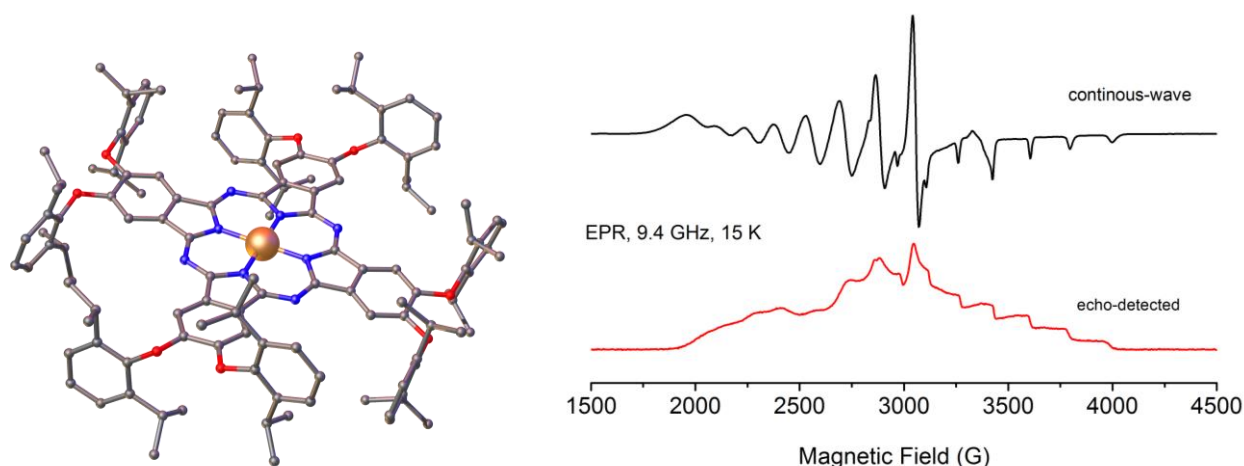
# Quantum Coherence Measurements in a Co(II)-Phthalocyanine Complex

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Metallo-phthalocyanines are used in a wide range of applications, from dyes and pigments to nonlinear optics and photodynamic therapy, and more recently they have been found to have long quantum coherence times that make them ideal candidates for quantum information processing [1].

Here we focus on a new cobalt(II) phthalocyanine complex synthesized in our laboratory, along with its pyridine-derivatives [2]. Quantum coherence was observed in these compounds over the temperature range 3-30 K, with phase memory times up to 3  $\mu$ s being measured at 15 K. Decoherence mechanisms involve hyperfine interactions to the  $^{14}\text{N}$  nuclear spins of the phthalocyanine macrocycle, which have been nicely determined through a combination of continuous-wave electron paramagnetic resonance (EPR) (Figure 1) and hyperfine sublevel correlation (HYSCORE) pulse-EPR spectroscopies. We further examine the impact of solvents, oxygen and temperature on both  $T_1$  and  $T_2$  relaxation times, to conclude on relaxation mechanisms in all these compounds.



**Figure 1.** (left) X-ray crystal structure and (right) X-band EPR spectra at 15K, of the cobalt-phthalocyanine compound

- [1] M. Atzori, L. Tesi, E. Morra, M. Chiesa, L. Sorace, R. Sessolini, *J. Amer. Chem. Soc.* **2016**, *138*, 2154.  
[2] C. G. Bezzu, B. M. Kariuki, M. Helliwell, F. Tuna, J.E. Warren, D. R. Allan, N. B. McKeown, *CrystEngComm*, **2013**, *15*, 1545.

## Beyond the single-molecule approaches: “teamwork” magnetic relaxation of some Ln(III)-based SMM

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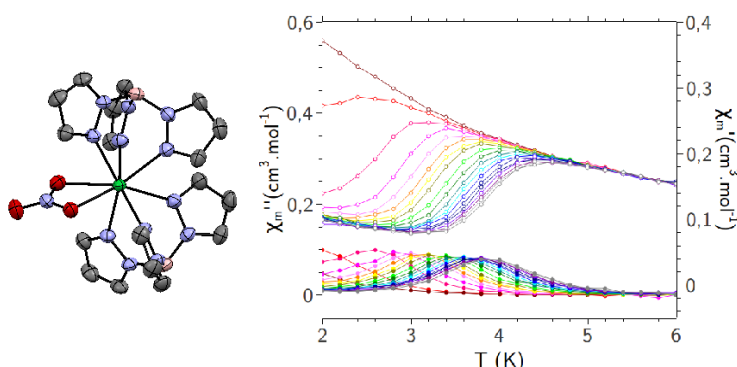
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In the last decade an intense research has been dedicated to the study of mononuclear lanthanide complexes behaving as a Single Molecule Magnet (SMM). They indeed display exotic behaviours, and noticeably it has lately been shown that the slow relaxation of magnetisation of these Ln-based SMM can be partially triggered by the lattice vibrations. In other words, what seems to be a molecular property actually conveys informations on the supramolecular organisation.



**Figure 1** *Left:* structure of the  $[\text{LnTp}_2\text{NO}_3]$  complexes. *Right:* susceptibility dynamics under a 0.2 T DC field, for frequencies ranging from 1 Hz (dark red) to 1400 Hz (grey).

We present here, to the best of our knowledge, the first example of a family of field induced Ln-based SMM whose slow relaxation of magnetisation is entirely controlled at the supramolecular level. Based on a combination of SQUID and luminescence measurements, we show the magnetisation dynamics of these  $[\text{LnTp}_2\text{NO}_3]$  complexes (with Ln = Dy, Er, Yb, Tp = hydro-trispyrazolylborate) does not involve an Orbach process, but rather direct and Raman relaxations. Furthermore, *ab initio* calculations allow to rationalise the observed temperature dependence of the Raman processes.

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2. E. Lucaccini *et al.*, *Chem. Commun.*, **2014**, 50, 1648.
3. K. W. H. Stevens, *Rep. Prog. Phys.*, **1967**, 30, 189.
4. G. Cosquer *et al.*, *Eur. J. Inorg. Chem.*, **2014**, 69
5. E. Pardo *et al.*, *J. Mater. Chem.*, **2006**, 16, 2702-2714.



## Six and seven coordinate Fe and Zn compounds with redox active ligands and remarkable magnetic behavior

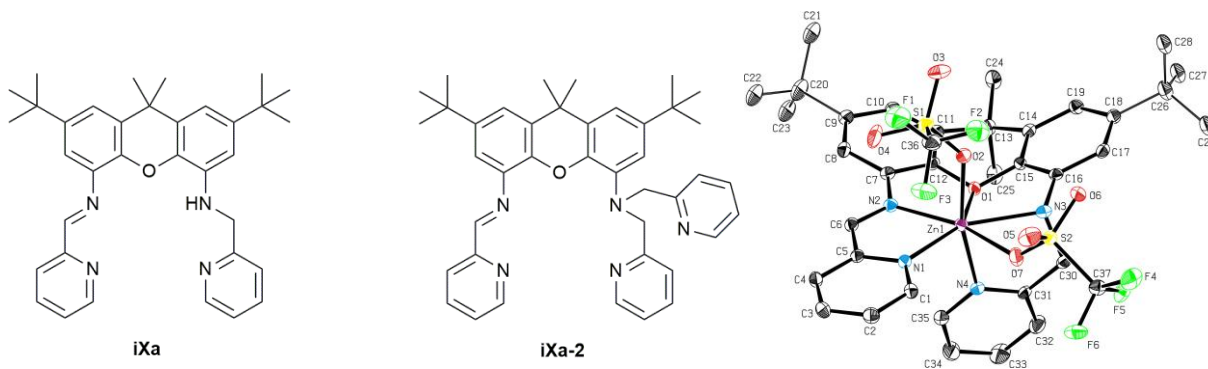
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Seven coordinate Fe complexes represent less than 1% of known Fe compounds; seven coordinate Zn complexes are even rarer.<sup>1</sup> In the following we present the syntheses of a novel series of asymmetric ligands containing a redox active imine alongside a redox inactive site with a aminopyridine group. These ligands were investigated and the corresponding metal complexes of Fe<sup>II</sup> and Zn<sup>II</sup> complexes were synthesized, yielding in all cases in pentagonal bipyramidal complexes. The complexes were characterised in the solid and in solution state by NMR spectroscopy and magnetic susceptibility measurements, supported by DFT calculations, to provide an insight into the magnetic behavior of the paramagnetic complexes. The redox activity of the compounds also was examined.

**Figure 1** Ligands, **iXa** and **iXa-2**, and Zn(iXa)(OTf)<sub>2</sub>



<sup>1</sup> D. Casanova, P. Alemany, J. M. Bofill, S. Alvarez, *Chem. Eur. J.*, **2003**, *9*, 1281.

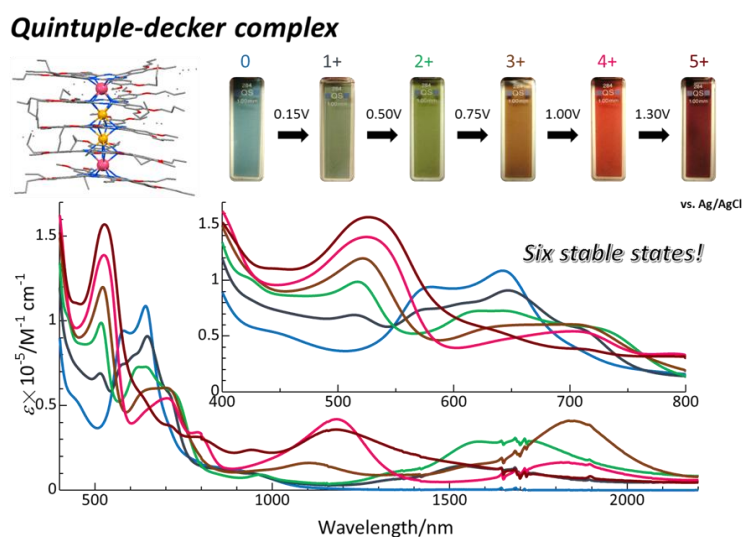
## Magnetic properties of stable terbium(III)-phthalocyaninato multiple-decker complexes in high valence states

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Tb(III)-phthalocyaninato complexes show single-molecule magnet (SMM) properties because of the strong magnetic anisotropy of the Tb(III) ion, which strongly correlates with the ligand field of phthalocyaninato ligands. Therefore, by tuning the ligand field strength, the SMM properties can be adjusted. According to Ishikawa et al., oxidation of the Tb(III) double-decker complex (TbPc<sub>2</sub>) affords a stronger ligand field as well as an improvement in its SMM properties.<sup>1</sup> Thus, we studied the SMM properties of Tb(III)-phthalocyaninato multiple-decker complexes after stepwise oxidation up to the +5 state. In contrast to TbPc<sub>2</sub>, the multiple-decker complexes exhibit several stable valence states.<sup>2</sup> To isolate and characterize these oxidation states, bulk electrolysis was used. We found that the number of stable valence states increased in relation to the number of stacked phthalocyaninato ligands. In case of the quintuple-decker complex, stable species with oxidation states of 1<sup>+</sup>–5<sup>+</sup> were isolated and characterized by using UV-Vis-NIR spectroscopy. We will discuss the magnetic properties for each valence state, which are currently being determined.



**Figure 1** Stepwise oxidation of a Tb(III) quintuple-decker complex.

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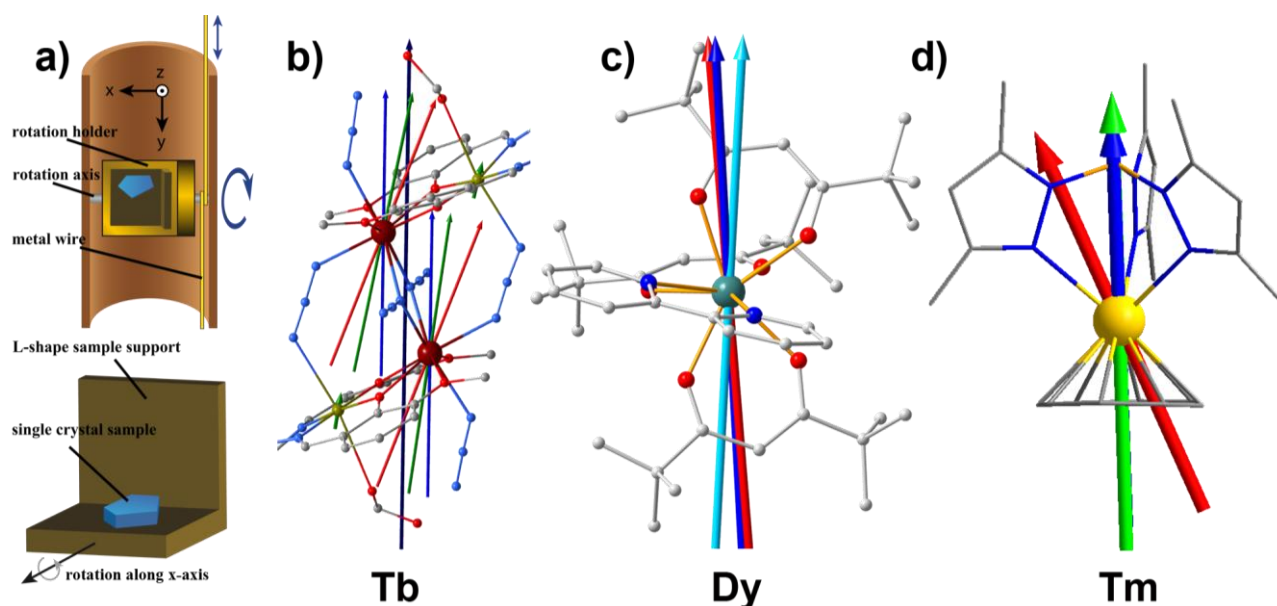
# Angular-Resolved Magnetometry as a Characterization approach for Single- Ion Anisotropy

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The experimental determination of the molecular magnetic principal axes is of fundamental importance in understanding the magnetic anisotropy. The angular-resolved magnetometry method has recently been generally applied for this purpose. This method measures the magnetization as a function of the rotation angle with respect to three orthogonal axes to determine the crystal magnetic susceptibility tensor. The rotator is figured in Figure 1a and the detailed introduction of this method was discussed herein. We have determined the magnetic principal axes of various lanthanide ions (Tb<sup>III</sup>, Dy<sup>III</sup>, Tm<sup>III</sup> Figure 1) based on this methods. The results reveal that the easy axial orientation is closely related to the distribution of the negative charges around the lanthanide ions.



**Figure 1** Description of the method of the angular-resolved magnetometry measurement.

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## Single-Molecule Magnet with Metallacrown

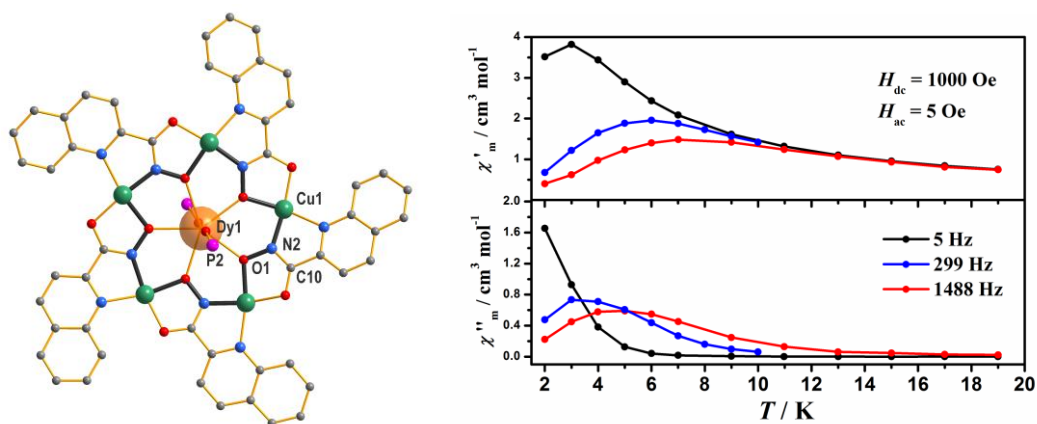
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Single-molecule magnets (SMMs) based on lanthanide complexes have received a considerable attention for their intriguing magnetic properties and potential applications in high-density data storage and quantum computation.<sup>1</sup> Both electron density distribution of crystal field and local symmetry of lanthanide ion, especially for those having only one paramagnetic center namely single-ion magnets (SIMs), are considered as the key parameters to suppress the quantum tunneling of magnetization.<sup>2</sup> In this regard, metallacrown (MC) was used to restrict the coordination environment to obtain the specific symmetry for lanthanide ion because of MCs' particular configurations such as [9-MC-3], [12-MC-4], [15-MC-5], etc. Recently, we have first reported two Yb(III) SIMs based on [12-MC<sub>Zn(II)</sub>-4] with YbO<sub>8</sub> geometry in  $D_{4d}$  symmetry.<sup>3</sup> Besides, We have also succeeded in preparing Dy(III) SMM based on [15-MC<sub>Cu(II)</sub>-5] with *quasi*- $D_{5h}$  symmetry lately (Figure 1). Probably this strategy will be regarded as an efficient way to develop SMMs with the specific coordination environment.



**Figure 1** (left) Structure diagram and (right) temperature-dependent ac susceptibilities under an indicated dc field of Dy(III) SMM with [15-MC<sub>Cu(II)</sub>-5].

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## Linking antiferromagnetic rings through lanthanide ions

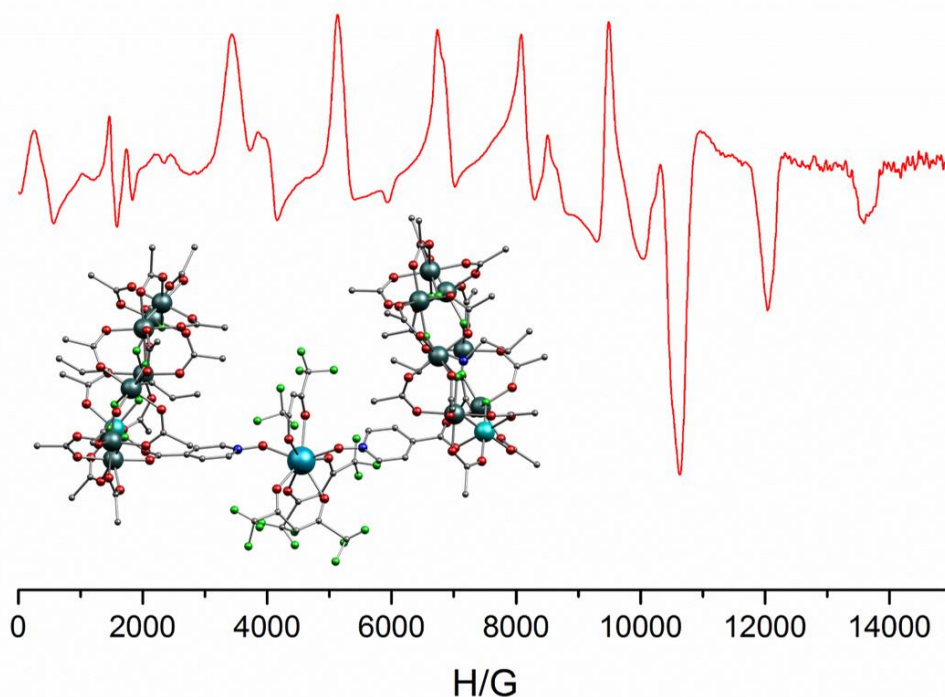
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The {Cr<sub>7</sub>Ni} rings have been previously proposed as quantum bits (*qubits*, the quantum equivalent of the bit used in conventional computing) for quantum information processing, based on their antiferromagnetic spin cluster nature<sup>1</sup>. The synthetic goal is to make supramolecular assemblies that contain a very large number of qubits. Starting with assemblies where there are two components (a qubit and a linker) our aim is to understand what happens to the communication between the qubits and determine which linkers are suitable. The aim of this work is to design the molecular components that could lead to complex assemblies and in the long term into useful devices<sup>2</sup>.

Herein we present some of the results obtained by functionalising the {Cr<sub>7</sub>Ni} rings with N-oxide ligands in order to synthesize dimers of wheels linked by lanthanide ions. Their magnetic properties have been probed using EPR spectroscopy and SQUID magnetometry.



**Figure.** K band CW powder EPR spectrum of  $[\{Cr_7Ni\}_2Gd(hfac)_3]$  measured at 4.2 K

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## **Towards Molecular Spintronics using Isolated Rare-earth Magnets**

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Molecular magnets have high potential for the next generation of nanospintronics devices. However, at present, there is still an important lack of understanding of how the spin and electronic degrees of freedom are coupled together. Therefore, we still do not know what metal centers are best suited to build perspective devices. This is because present methods (STM, break junction ect.) offer little insight into the fundamental physics of these systems, as current approaches do not allow the magnetization to be directly measured. We have overcome this problem by creating molecular magnetic systems where the bulk electrodes that are traditionally attached to the molecule are substituted by chemical groups. We examine electron flow-spin affects through a series of molecular magnets. Our novel design approach and preliminary synthetic and optical results will be presented.

## Single-Molecule Magnet Behavior in $[\text{ReCl}_4(\text{CN})_2]^{2-}$

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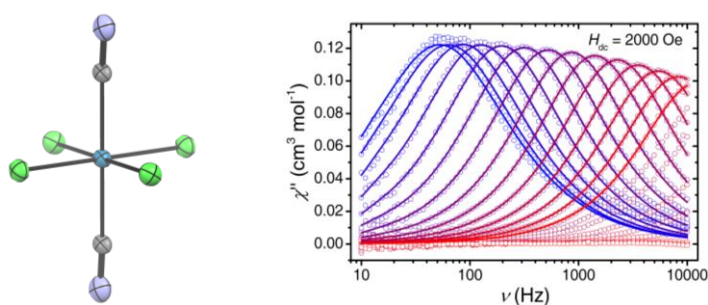
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Heavier elements provide enhanced spin-orbit coupling that potentially contributes to the larger magnetic anisotropy for single-molecule magnets (SMMs). Mononuclear 4d/5d cyano/halogeno complexes are useful building blocks towards SMMs and single-chain magnets. As an odd-electron ion, according to Kramers theorem,  $\text{Re}^{\text{IV}}$  possesses a ground-state doublet without magnetic field, regardless of the  $m_S$  of the ground doublet.

Herein we present a mononuclear  $(\text{Bu}_4\text{N})_2[\text{Re}^{\text{IV}}\text{Cl}_4(\text{CN})_2]\cdot 2\text{DMA}$  displaying SMM behavior, despite an easy-plane magnetic anisotropy, *i.e.* the axial zero-field parameter ( $D$ ) is positive.



**Figure 1** Structure of  $[\text{ReCl}_4(\text{CN})_2]^{2-}$  and out-of-phase ac susceptibilities.

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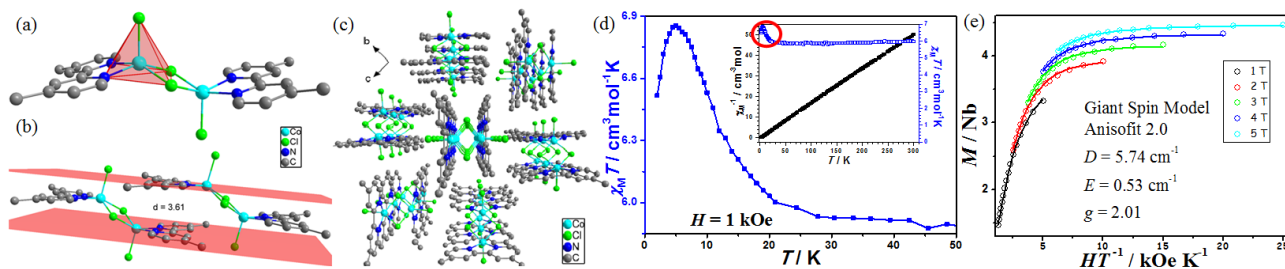
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# A Chloro-bridged Dinuclear Cobalt Complex with Ferromagnetic Coupling

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The azido anion, a pseudo-halide group, is widely employed in molecular magnetic materials to effectively bridge the spin carriers<sup>1</sup>. However, the investigation about the halide ions as bridging ligand is rarely reported<sup>2,3</sup>, even fewer of ferromagnetic coupled dimers. Herein we report a dinuclear-cobalt complex, [Co(4,4-mbpy)Cl<sub>2</sub>]<sub>2</sub>, with solely chloro-bridge. Single crystal structure (fig. 1(a-c)) shows that the Co<sup>2+</sup> located in a distorted square pyramid geometry coordinated by two N and three Cl atoms. The molecules are stacked by  $\pi$ - $\pi$  interaction and extended along *a*-axis. Temperature dependence of  $\chi_M T$  is plotted in fig. 1(d). Below 30 K, an increment of  $\chi_M T$  can be found upon cooling with a maximum of 6.85 cm<sup>3</sup>mol<sup>-1</sup>K at 5 K, indicating the existence of ferromagnetic interaction between the two cobalt ions within one molecule. The zero-field splitting of the *S* = 3 ground spin state can be viewed from the mismatching of *M* vs. *H/T* plots (fig. 1(e)) at various temperatures and *dc* fields.

The detailed characterizations are ongoing.



**Figure 1** (a) The molecular structure of the complex [Co(4,4-mbpy)Cl<sub>2</sub>]<sub>2</sub> (with all H atoms omitted). (b)  $\pi$ - $\pi$  stacking between adjacent molecules. (c) Packing structure viewed along *a*-axis. (d) The temperature dependence of  $\chi_M T$ . (e) The magnetization versus  $HT^{-1}$  plots.

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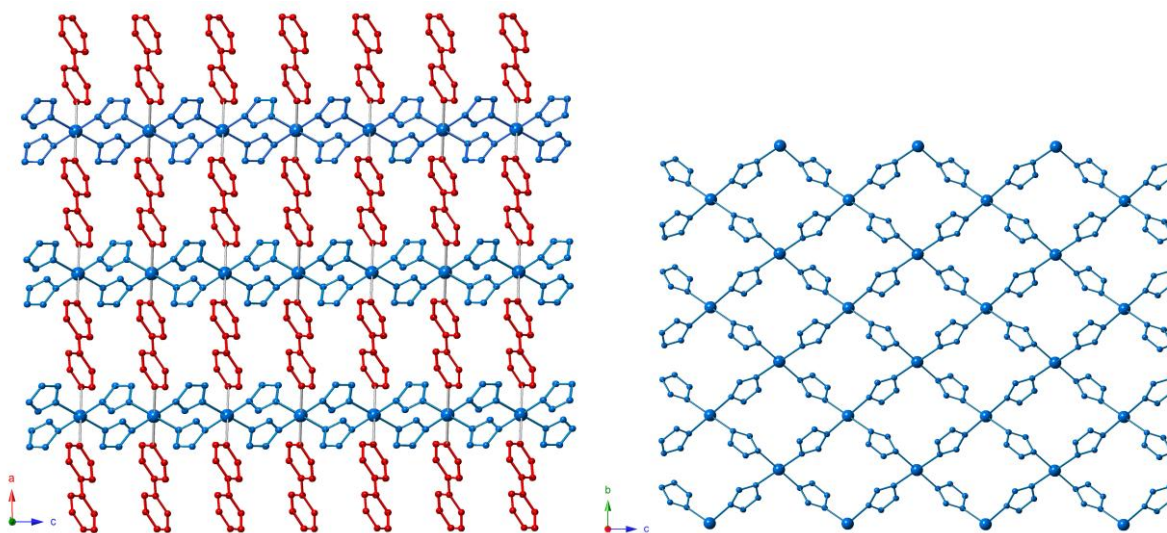
## Magnetic layered coordination polymers

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Coordination polymers and metal-organic frameworks (MOFs)<sup>[1]</sup> have shown great versatility in the design of crystalline materials with a wide range of properties. The tremendous efforts of these years have resulted in the expansion of the initial rigid systems into more flexible ones, as well as a movement from the presence of a singular physical property to the coexistence or synergy of different physical properties in the same material<sup>[2]</sup>. Among this large area, pillared-layer coordination polymers formed by neutral layers which are linked in the third direction by additional ligands present an attractive approach for the rapid modulation of the materials<sup>[3]</sup>. Another approach to these materials is that they can be exfoliated to obtain 2D magnetic compounds, allowing it to be deposited in a substrate for measure in a few layers the magnetic properties or to use in a device.



**Figure 1** . Left) View of the crystal structure of  $[\text{Fe}(\text{bipy})(\text{im})_2]$  along the  $b$  axis showing the neutral layers in blue and pillars connecting these layers in red; Right) Projection of the crystal structure onto the  $bc$  plane, with the bipy ligands omitted for clarity, showing the  $\text{Fe}(\text{im})_2$  square-like layer.

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## Slow magnetic relaxation in heterometallic Cu<sup>II</sup>-Dy<sup>III</sup> clusters of high nuclearity

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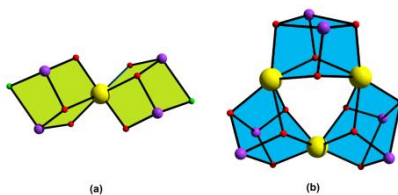
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The design and synthesis of high nuclearity 3d-4f clusters have recently seen a sweeping growth in the arena of coordination chemistry, magnetochemistry and molecular magnetic materials as evident by a constantly increasing number of publications in this area<sup>1-4</sup>. The syntheses, structures and magnetic properties of two heterometallic Cu<sup>II</sup>-Dy<sup>III</sup> clusters are reported. The first structural motif displays a pentanuclear Cu<sup>II</sup><sub>4</sub>Dy<sup>III</sup> [1] core, while the second reveals a nonanuclear Cu<sup>II</sup><sub>6</sub>Dy<sup>III</sup><sub>3</sub> [2] core. The differing nuclearities of the two clusters stem from the choice of imino alcohol arm in the Schiff base. The ligand systems utilized are such that they differ only by an additional spacer, allowing the topological conversion from unit Cu<sub>4</sub>Dy{2,4M5-1} core to fused Cu<sub>6</sub>Dy<sub>3}{3,6M9-1} core. Variable-temperature solid state magnetic susceptibilities results indicate that an overall ferromagnetic and antiferromagnetic interaction among the metal ions is operative for cluster 1 and 2, respectively. Under zero external field, both the clusters show a frequency dependence out-of-phase ( $\chi''$ ) signals, with two relaxation process, which indicates slow relaxation of the magnetization.</sub>



**Figure 1:** Metallic core of 1 and 2 described as (a) vertex Sharing [Cu<sup>II</sup><sub>4</sub>Dy<sup>III</sup>(O)<sub>2</sub>(OH)(Cl)] incomplete cubanes and (b) corner sharing [Cu<sup>II</sup><sub>6</sub>Dy<sup>III</sup><sub>3</sub>(O)<sub>2</sub>(OH)<sub>2</sub>] cubanes.

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## Heterospin 3d-4f, 2p-3d, 2p-4f, and 2p-3d-4f complexes. Synthesis, crystal structures and magnetic properties

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The heterospin homo- and heterometallic complexes are of high interest, especially because of their magnetic properties.<sup>1</sup> There are different strategies allowing to obtain coordination compounds, using metal-ligand and/or organic radicals building-block. In this context, the nitronyl-nitroxide radicals<sup>2</sup> and the Schiff-base ligands<sup>3</sup> are widely used in the synthesis of heterospin complexes showing SMM (single molecule magnet) and SCM (single chain magnet) behavior. We are currently developing an original strategy to obtain magnetic molecular compounds based on polydentate ligands including also new nitronyl-nitroxide derivatives. The new ligands are selective and can accommodate simultaneously 3d and 4f ions. Here, we present new families of 2p-3d-3d, 2p-4f, and 2p-3d-4f complexes containing the first nitronyl-nitroxide dissymmetric ligand, and hfac (hexafluoroacetilacetate) as a co-ligand. We also present three 1D coordination polymers constructed using a 3d-4f Schiff-base node and the isonicotinate anion as linker (Figure 1). Depending on the nature of the 3d metal, different molecular structures can be obtained. The magnetic properties are investigated and discussed.

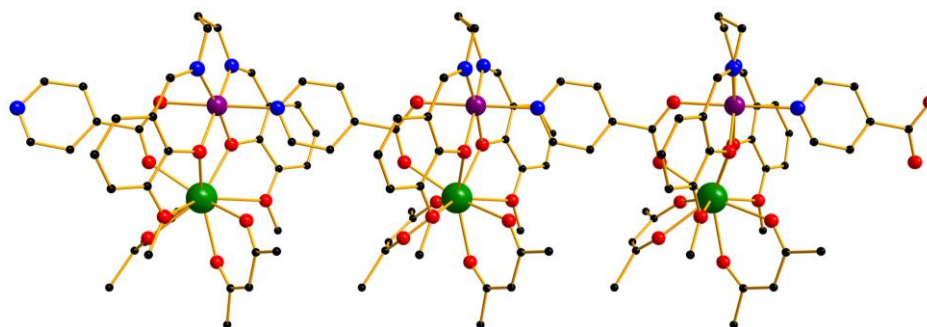


Fig 1 Crystal structure of  $\infty$ [Co(valpn)Gd(hfac)<sub>2</sub>(isonicotinate)]

### References:

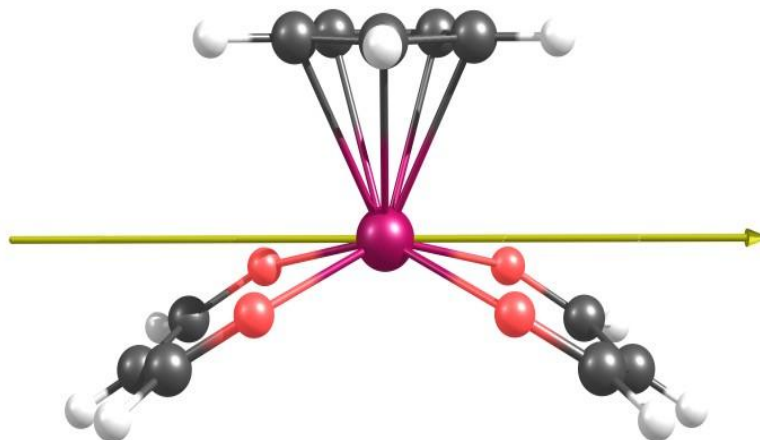
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## Effect of the ligand environment on the magnetic properties and relaxation barrier of Dy(III) complexes

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Single molecule magnets (SMM) are compounds that exhibit magnetic bistability purely of molecular origin. The control of anisotropy and suppression of quantum tunneling to obtain a comprehensive picture of the relaxation pathway manifold, is of vital importance with the ultimate goal of slowing the relaxation dynamics within single molecule magnets to facilitate their potential applications. In lanthanide elements particularly, understanding the anisotropic electronic structure of complexes is important in areas as diverse as magnetic resonance imaging, luminescent cell labeling and quantum computing. In the present work a series of recently synthesized<sup>1</sup> mononuclear Dy<sup>III</sup> complexes with *two-faces* structure were characterized theoretically using *ab-initio* wavefunction based methods like RASSCF and SO-RASSI. In the first step the nondynamical-correlated wavefunction were computed and in the second step the spin-orbit interaction is taken into account performing a state interaction calculation in an AMFI scheme of calculation. The calculations show that the ground Kramers doublet is strongly axial with  $g_z$  approaching to the value of 20 expected for a pure  $M_J = \pm 15/2$  state, and the magnetic anisotropy axes for all the complexes share a similar orientation which is perpendicular to the molecular pseudosymmetric axis.



**Figure 1** Molecular model used as a building block for Dy(III) complexes. The orientation of the magnetization axis is presented (yellow arrow)

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## A direct picture of the molecular magnetic anisotropy by polarized neutron diffraction

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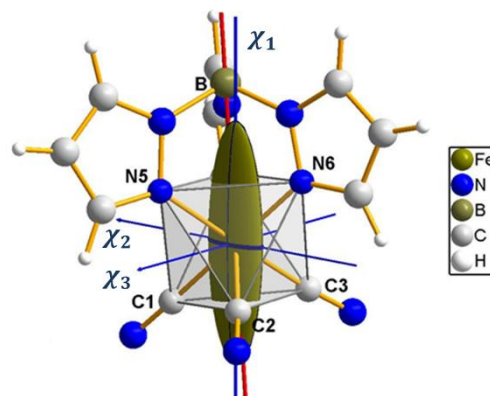
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Research in molecular magnetism has motivated a growing interest for the study of magnetic anisotropy in molecular complexes since a strong axial anisotropy is required for potential applications like high-density data storage. For this purpose, we used Polarized Neutron Diffraction (PND) combined with the so-called local site susceptibility tensor approach.<sup>1</sup> We report the PND results obtained on the mononuclear low-spin  $[\text{Fe}^{3+}(\text{Tp})(\text{CN})_3]^-$  complex<sup>2</sup> where Tp = tris(pyrazolylborate) and confront them with Electron Paramagnetic Resonance (EPR), SQUID magnetometry and quantum chemistry calculations.

The  $\text{Fe}^{3+}$  molecular magnetic susceptibility tensor (Figure 1) determined by PND shows that the magnetic anisotropy is driven by the  $C_3$  pseudo-axis of the molecule, which also corresponds to a trigonal elongation direction of the coordination octahedron, giving rise to molecular easy magnetization axis.<sup>3</sup>

This study demonstrates the capabilities of PND to provide a unique, direct and straightforward picture of the magnetic anisotropy, offering a clear-cut way to establish magneto-structural correlations in paramagnetic molecular complexes.



**Figure 1**  $\text{Fe}^{3+}$  magnetic susceptibility ellipsoid obtained from PND within its coordination octahedron at 2 K.

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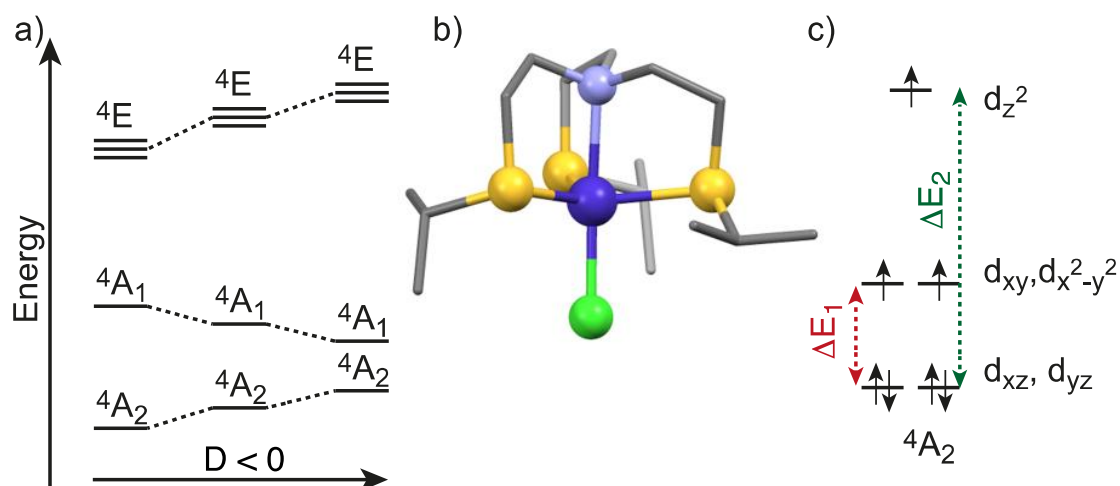
<sup>3</sup> K. Ridier et. al., submitted to *Angew. Chem. Int. Ed.*

## Engineering the Ising-type anisotropy in trigonal bipyramidal Co(II) complexes

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This work demonstrates the engineering of the Ising-type magnetic anisotropy in trigonal bipyramidal Co(II) complexes.<sup>1,2</sup> Employing a ligand that forces a trigonal bipyramidal arrangement with weak equatorial  $\sigma$ -donating atoms, increases the magnitude of the uniaxial magnetic anisotropy (large negative zero field splitting parameter  $D$ ). With these considerations in mind, we used a sulfur containing ligand ( $\text{NS}_3^{\text{iPr}}$ ), which imposes a trigonal bipyramidal geometry to the central Co(II) ion with equatorial Co-S bonds. Everything being equal, the resulting complexes exhibit a larger anisotropy barrier and a longer relaxation time in comparison to the complex prepared with a the nitrogen containing ligand ( $\text{Me}_6\text{tren}$ ).

**Figure 1** a) Schematic energy diagram of the lowest quadruplets for a trigonal bipyramidal Co(II) complex; b) X-ray crystal structure of  $[\text{Co}(\text{NS}_3^{\text{iPr}})\text{Cl}](\text{BPh}_4)$ : Co = purple; C = grey; N = lilac; S = yellow; Cl = green; H atoms and counter ions were removed for clarity; c) orbital energy diagram for a trigonal bipyramidal Co(II) complex.



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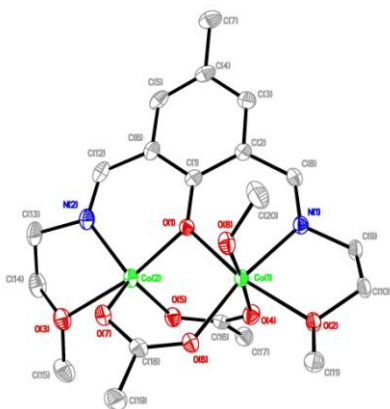
## Magnetic analysis of multinuclear octahedral high-spin cobalt(II) complexes

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Magnetic properties of octahedral high-spin cobalt(II) complexes are sometimes difficult to be interpreted because of the spin-orbit coupling.<sup>1</sup> Some of the cobalt(II) complexes show significant magnetic anisotropy.<sup>2-4</sup> The crystal anisotropy of monomeric cobalt(II) complexes can be interpreted as single-ion anisotropy; however, the anisotropy of magnetically coupled multinuclear cobalt(II) complexes is sometimes very complicated. In this study, in order to reveal the magnetic properties of hetero-geometrical dinuclear cobalt(II) complexes, crystal structure and magnetic properties of  $[\text{Co}_2(\text{L})(\text{MeCO}_2)_2(\text{MeOH})]\text{BPh}_4$  (**1**) were examined. In **1**, one of the Co(II) ion has a trigonal bipyramidal environment, but the other Co(II) ion has an octahedral environment. The cryomagnetic data could be analyzed assuming the local spin-orbit coupling on the octahedral Co(II) ion.



**Figure 1** Crystal structure of  $[\text{Co}_2(\text{L})(\text{MeCO}_2)_2(\text{MeOH})]^+$ .

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## A simple Schiff base for spin crossover, single-ion magnets (SIM) and homochiral bishelicates

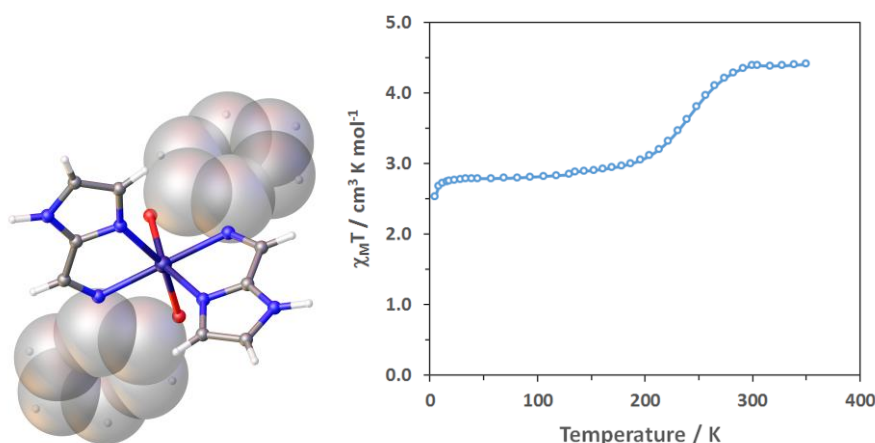
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The synthesis, crystal structures and magnetic characterization of novel octahedral Fe<sup>III</sup>, Co<sup>II</sup>, Co<sup>III</sup> and Ni<sup>II</sup> complexes, [Fe(2-Himap)<sub>2</sub>]<sub>2</sub>ClO<sub>4</sub> **1**, [Fe(2-Himap)<sub>2</sub>]<sub>2</sub>NO<sub>3</sub>·MeOH **2**, [Co(2-Himap)<sub>2</sub>] **3** and [Co(2-Himap)<sub>2</sub>]<sub>2</sub>NO<sub>3</sub>·MeOH **4** and [Ni<sub>2</sub>(2-Himap)<sub>2</sub>(2-H<sub>2</sub>imap)<sub>2</sub>][NO<sub>3</sub>]<sub>2</sub>·3H<sub>2</sub>O **5** (where Himap = 2-[(1*H*-imidazol-2-yl)methyleneamino]phenol) are reported.<sup>[1]</sup> X-ray crystallographic studies of three complexes at 123 K, show the Fe and Co centres have a N<sub>4</sub>O<sub>2</sub> donor set. In the case of **2** and **4**, π-π interactions and hydrogen bonds between the cation, nitrate and methanol are found. Interestingly, in **3** the packing consists of strong alternating N-H...O hydrogen bonds (1.63 Å) with significant bonding character. Magnetic studies reveal that **1** undergoes incomplete 50% spin crossover while the Co(II) complex **3** exhibits slow magnetic relaxation in the absence of an applied dc field, confirming the compound to be a rare octahedral single-ion magnet (SIM). In contrast, **4** is low spin at all temperatures, as expected for Co(III). Moreover, **5** exists as a dinuclear bishelicate held together via two strong O-H...O interactions. **1**



**Figure 1** SQUID of [Fe(2-Himap)<sub>2</sub>]<sub>2</sub>ClO<sub>4</sub> **1** (right) and structure [Co(2-Himap)<sub>2</sub>] **3** (left). The space filling moieties are phenyl groups.

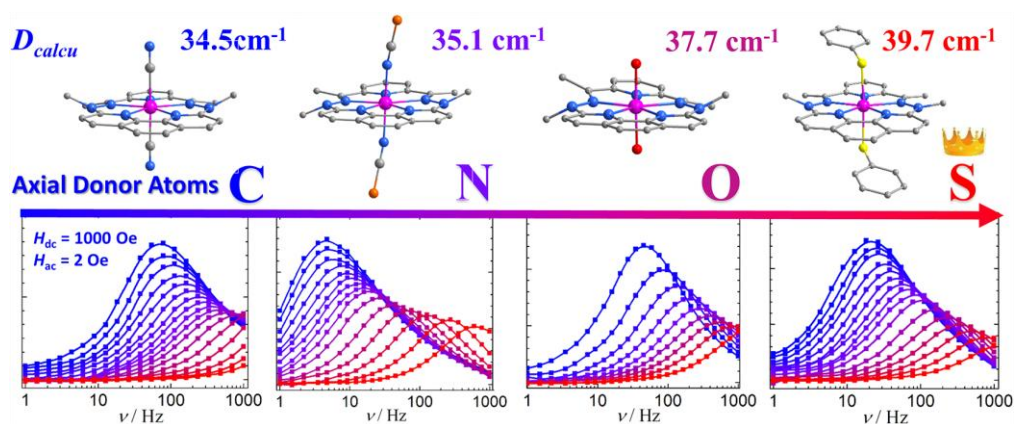
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# Probing the Effects of Axial Ligands on Easy-Plane Anisotropy of Pentagonal Bipyramidal Cobalt(II) Single-Ion Magnets

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Single-molecule magnets (SMMs) have attracted considerable interests in the field of molecular magnetism for their potential applications in high-density information storage and quantum computing.<sup>1</sup> The pursuit for better controlling of the magnetic anisotropy has inspired intensive studies, including the numerous reports of the mononuclear SMMs, also known as single-ion magnets (SIMs).<sup>2</sup> One year ago, our group reported the first observation of the field-induced SIM behavior in pentagonal bipyramid Co<sup>II</sup> compounds constructed from the pentagonal ligands.<sup>3</sup> As a continuing work on easy-plane magnetic anisotropy, we synthesized four air-stable mononuclear Co<sup>II</sup> complexes with various axial ligands (C, N, O, and S) using a rigid pentadentate macrocyclic ligand to eliminate other factors influencing the magnetic anisotropy. The effect of the axial ligands on the magnetic anisotropy of the Co<sup>II</sup> center in the pentagonal bipyramidal geometry were discussed by detailed magnetic measurements and *ab initio* calculations.



**Figure 1** Crystal structure of the four mononuclear Co<sup>II</sup> compounds and their frequency dependence of the  $\chi''$  part of the ac magnetic susceptibility.

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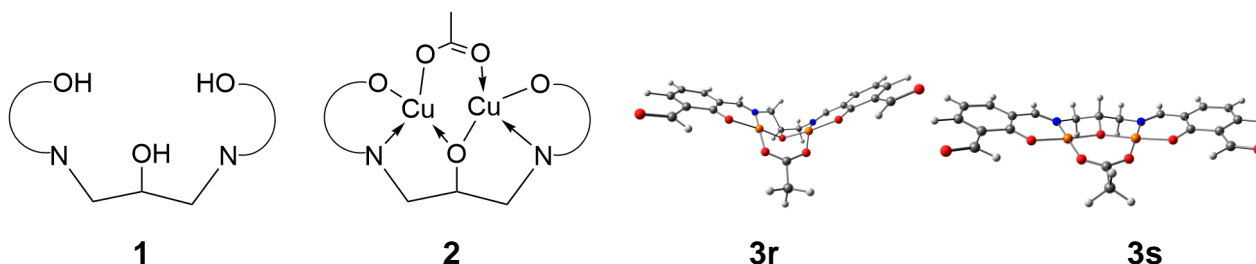
## Triggering of the magnetic exchange coupling sign in binuclear copper(II) complex by solvent molecule coordination

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Here we present experimental and theoretical study of magnetic properties of binuclear copper(II) complexes of the series of 1,3-diaminopropan-2-ol *bis*-azomethinys (**1**, fig.1) with acetate exogenous bridging group  $[\text{Cu}_2\text{L}^n(\text{CH}_3\text{COO})]$  (**2**), and products of their crystallization from DMSO solution -  $[\text{Cu}_2\text{L}^n(\text{CH}_3\text{COO})(\mu_2\text{-DMSO})]$  (**3**). It was observed that the products (**2**) obtained by the reaction in methanol solution exhibit antiferromagnetic coupling, whilst upon recrystallization from the DMSO solution compounds (**3**) are obtained with the ferromagnetic type of exchange coupling between Cu(II) centers [1].



**Figure 1.** Structures of the ligands (**1**) and complexes (**2**). Optimised structures of roof-shaped 3r (left) and «symmetric» 3s (right) conformations of exchange unit in **3**.

Based on the combination of experimental data (XRD, EXAFS) and theoretical calculations (first principle DFT calculations of singlet-triplet splitting within broken symmetry approximation) we can conclude that antiferromagnetic exchange coupling between copper(II) atoms is determined by “symmetric” conformation of the binuclear unit (fig.1, **3s**) while ferromagnetic one - by roof-shaped conformation (fig.1, **3r**). The role of the DMSO molecule in triggering exchange coupling sign in binuclear copper(II) complex is limited to stabilization of the roof-shaped conformation of the complex due to axial coordination to both copper centres.

The research was done under RFBR funding (grant No. 14-03-00788).

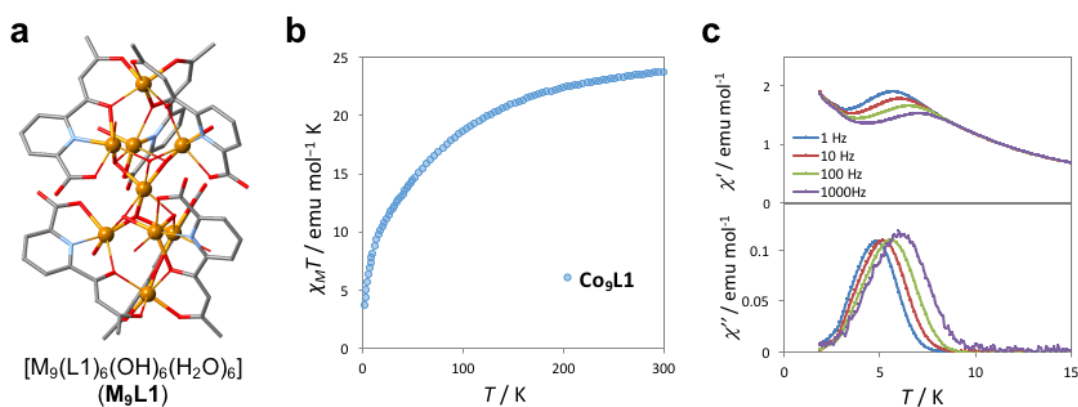
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# Synthesis and Magnetic Properties of Coordination Clusters Based on Tripod-type Complex Unit

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Metal cluster complexes have attracted much attention because of their unique magnetic properties such as large spin ground states, high magnetic anisotropy and single-molecule magnet (SMM) behavior, which is expected to be applied in molecular devices. Multidentate ligands have exhibited validity for deriving the objective cluster structure through a self-assembling process so far<sup>1</sup>. Here, we synthesized an asymmetric linear multidentate ligand 6-acetoacetyl-2-pyridinecarboxylic acid (H<sub>2</sub>L1) and its derivatives introduced either *tert*-butyl (H<sub>2</sub>L2) or methoxy group (H<sub>2</sub>L3), or both (H<sub>2</sub>L4), and systematically prepared new cluster complexes [M<sub>9</sub>(L<sub>n</sub>)<sub>6</sub>(OH)<sub>6</sub>(H<sub>2</sub>O)<sub>6</sub>] (**M<sub>9</sub>L<sub>n</sub>**; M=Ni, Co, *n*=1-4).

**M<sub>9</sub>L<sub>n</sub>** formed a unique [M-7M-M] type nonanuclear structure with a hydroxyl-bridged heptanuclear central core, [M<sub>7</sub>(μ<sub>3</sub>-OH)<sub>6</sub>]<sup>8+</sup>, that flanked with mononuclear sites, [ML<sub>n</sub>]<sup>4-</sup> (**Figure 1a**). In the Co complexes,  $\chi_M T$  values decreased at low temperature due to a weak antiferromagnetic interaction among Co<sup>II</sup> ions and contribution of spin-orbit coupling (**Figure 1b**). In the case of Ni complexes, only **Ni<sub>9</sub>L2** exhibited a magnetic anomaly in dc magnetic measurement and a SMM-like behavior with ac magnetic responses at low temperature (**Figure 1c**). Detailed magneto-structural correlation is now under consideration.



**Figure 1 (a)** Structure of **M<sub>9</sub>L1**, **(b)**  $\chi_M T$  vs.  $T$  plots, **(c)**  $\chi'$  and  $\chi''$  vs.  $T$  plots for **Ni<sub>9</sub>L2**

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## Field-induced slow relaxation in a mononuclear iron(III) compound

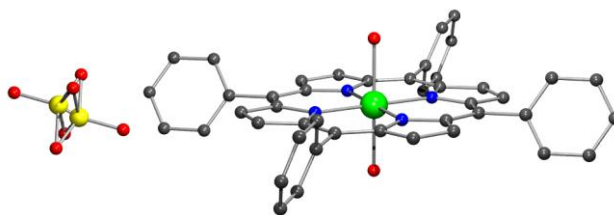
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Recent strategies to increase the anisotropy control on single-molecule magnets deal with the synthesis of mononuclear transition-metal complexes, especially from the first-row transition metals, with a proper ligand field.<sup>1,2</sup> Most of them are formed by cobalt(II) ions and/or also by ligands with soft donor atoms in a low geometry environment.

Porphyrins have been revealed as good ligands for the design of single-ion magnets.<sup>3</sup> In this work, we present preliminary results on the synthesis and characterization of a new iron(III) porphyrin showing field-induced slow relaxation.



**Figure 1** View of the compound  $[\text{Fe}(\text{TTP})(\text{H}_2\text{O})_2](\text{ClO}_4)$ .

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## Spreading Frustration with Molecular Magnets

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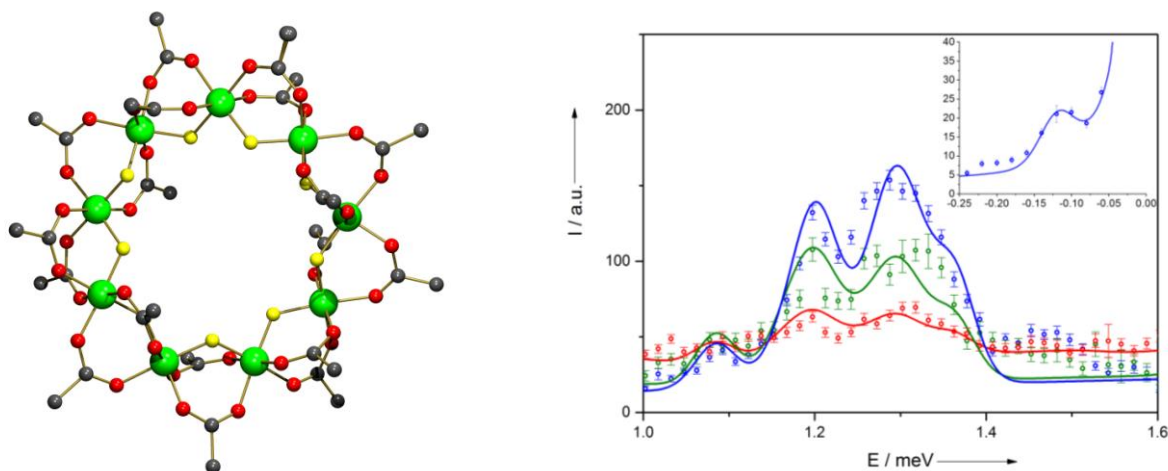
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Frustrated spin systems are of significant interest within the molecular magnetism community, both for the insight they shed on fundamental processes and for their potential applications in quantum computing.<sup>1,2</sup> The prototypical molecular system of a triangle of metals held together by bridging ligands has been extensively published,<sup>3</sup> but reports of frustrated systems with more than three metals are conspicuously sparse.<sup>4</sup>

We have synthesised a new family of odd numbered homometallic metal rings, including the first reported example of a regular nonametallc ring, via one pot templated self-assembly. Using X-ray crystallography, magnetometry, EPR spectroscopy and neutrons we have studied the differences in physical and electronic structure within this family along with the varying degrees of frustration and, along the way, developed a new way of classifying molecular spin frustration.<sup>5</sup>



**Figure 1:** Left – The X-ray crystal structure of  $[\text{CrF}(\text{tBuCO}_2)]_9$ . Right – Powder Inelastic Neutron Scattering data of  $[\text{CrF}(\text{tBuCO}_2)]_9$  at  $\lambda = 2.5 \text{ \AA}$  and  $\lambda = 1.0 \text{ \AA}$  (inset).

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## **Interconversion between hexanuclear and chain accompanying switchable magnetic interactions**

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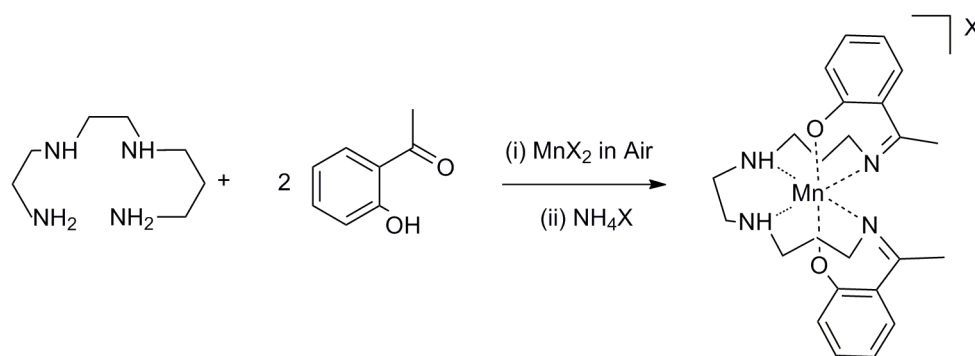
Porous coordination polymers (PCPs) are attracting increasing interest owing to their potential applications in catalysis, gas storage, and separation. One of the most important challenges in this area is the design and synthesis of PCPs with dynamic structures as well as switchable functional properties such as magnetism, conductivity, and photonics. Although great advances have been made in various cases of structural transformation, examples of single-crystal to single-crystal (SCSC) phase transformation are few in number. Most of them are dimerization or polymerization of unsaturated molecules or guest exchange of porous materials. Particularly rare are solid state reactions within the coordination spheres of transition metals involving the breaking and forming of coordination bonds, especially accompanying with structural dimensionality change. Such reactions have often accompanied by catastrophic failure of the crystal, thus preventing the identification of the products. Only limited SCSC transformations involving the dimensionality changes of coordination polymers have been reported. To the best of our knowledge, none of these examples involve porosity transformation from nonporous to porous. Utilization of topotactic reactions in the solid state enabled us to observe such an unusual phenomenon by exploiting directional supermolecular interactions. Here, we report a reversible SCSC transformation from hexanuclear clusters to a one-dimensional (1D) double-zigzag chain via the formation and breakage of coordination bonds<sup>1</sup>. The framework of the former is nonporous whereas that of the latter is porous and displays selective gas adsorption. Our results indicate that the transformation between nonporous and porous, and between monomer and polymer, is a reversible process, a very rare example in this field. Moreover, an important characteristic we should emphasize is that the magnetic functions can be reversibly switched between paramagnet in the hexanuclear cluster and antiferromagnet in the 1D chain.

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## A Spectroscopic Study of Spin State Switching in Manganese(III) Complexes

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Whilst the majority of examples of SCO complexes feature Fe(II) or Fe(III), there are also many reports with Co(II).<sup>1</sup> More rare are examples with the  $d^4$  ion Mn(III) which is an interesting spin transition candidate as high spin (HS) Mn(III) has a marked Jahn-Teller (JT) distortion. After a 25-year gap since the first reported example of abrupt SCO in [Mn(TAA)] by Sim and Sinn in 1981,<sup>2</sup> we discovered that X-Sal<sub>2</sub>323- type  $N_4O_2^{2-}$  Schiff base ligands can promote the SCO effect in Mn(III),<sup>3</sup> Scheme 1. To date we have focused on thermal spin state switching in both Fe(III) and Mn(III) but are interested now to examine the potential for optical switching in both ions. We have recently shown that long-lived LIESST effects are possible in Fe(III) and in preparation for our magneto-optical investigations on Mn(III) SCO complexes, we have initiated a study on the extent of spin state switching in solution where we also tried to probe the energy differences between the HS and low spin (LS) states. We chose a constrained ligand where the HS state is stabilised in the solid state but it was hoped that SCO would be switched on in solution.



**Scheme 1** Complex synthesis *via* condensation reaction between the amine 1,2 bis(3 aminopropylamino)ethane and the ketone 2'-hydroxyacetophenone and addition of manganese(II) in air.

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## Polymorphism in Mononuclear Fe(II) Complexes with *N'*-(2-pyridylmethylene)-3,5-dimethylaniline

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A new bidentate Schiff base ligand *N'*-(2-pyridylmethylene)-3,5-dimethylaniline (PM-3,5-DMA) was prepared and reacted with [Fe(NCS)<sub>2</sub>] precursor complex in methanol afforded two polymorphisms of a mononuclear iron(II) complex with the formula, [Fe(NCS)<sub>2</sub>(PM-3,5-DMA)<sub>2</sub>] (1 (major), 1' (minor)). Both polymorphs 1 and 1' crystallize in the triclinic space group *P*-1 with four (*Z* = 8) and six (*Z* = 24) molecules, respectively, in the asymmetric unit. The structure of 1 was solved at three temperatures 296, 175, and 100 K, whereas, the structure for 1' was determined at 296 and 85 K. The main differences between the structures of the two polymorphs are found in their crystal packing. Polymorph 1 exhibits gradual, one-step spin transition with *T*<sub>1/2</sub> ~ 150 K. and also displays LIESST effect when irradiated at 10 K temperature.

## Rationalization of the spin crossover (SCO) behavior in polypyridyl-based systems

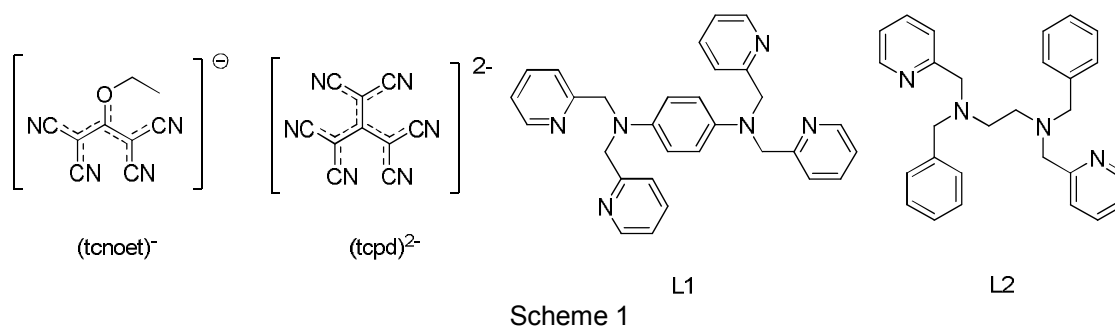
N. Cosquer,<sup>a</sup> K. Déniel,<sup>a</sup> S. Houille,<sup>a</sup> F. Conan,<sup>a</sup> S. Triki,<sup>\*a</sup> C. J. Gómez-García.<sup>b</sup>

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In recent years, our group focuses on design of new systems based on cyanocarbanion to elaborate new spin cross-over (SCO) systems. These anions exhibit several characteristics such as many potentially donor nitrile groups and  $\pi$ -conjugated system which allow transmission of electronic effects between the metal centers. So, these properties make them very interesting ligands for the preparation of new SCO materials for which the elastic interactions can be tuned by the nature and the geometries of such anions (Scheme 1).<sup>1,2</sup>



In this context, we have reported in the last few years the first SCO series based on such cyanocarbanion ligands together with abpt (4-Amino-3,5-bis(2-pyridyl)-1,2,4-triazole) chelating neutral ligand.<sup>1</sup> In this series, the single charge on the anion induces a terminal coordination mode for the cyanocarbanion unit, resulting in neutral discrete SCO complexes. Afterward, we have showed, in a second report, that the use of the  $(tcpd)^{2-}$  cyanocarbanion ( $(tcpd)^{2-}$  = 2-dicyanomethylene-1,1,3,3-tetracyanopropanediide anion) ligand bearing two negative charges induces bridging coordination modes to lead to an original thermo- and photo-switchable SCO chain.<sup>2</sup> With the aim to better explore the potential impact of such anionic ligands on the structural features of their complexes, and then on the switching properties (transition temperatures, hysteresis width, abruptness of the transition, photo-induced effects...), we have extended this work to the use of other polydentate neutral ligands such as the polypyridine ligands (Scheme 1).

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# Ultrafast pump probe IR Spectroscopy applied to a photoinduced SCO solid

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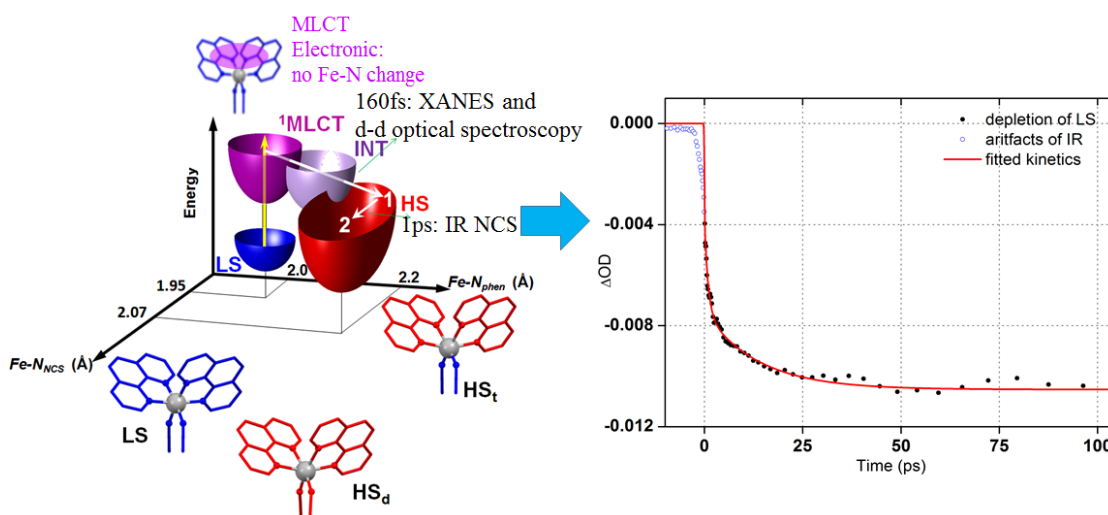
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The compound FeIIPhen, archetypal spin crossover (SCO) system, has been studied a lot and we know that the low spin state molecules can be excited to MLCT and they cross possible intermediate (INT) states before they settle in high spin state (HSS). In this process, the molecules undergo a sequence, whereby the breathing motion and the bending motion are activated at different times<sup>1</sup>. By exciting the high spin molecules with VIS pump, and probing the mid IR spectrum of the molecules<sup>2,3</sup>, it is possible to select a reporter group and observe its evolution in ultrafast time scales. The NCS ligand has a distinct fingerprint, not overlapping with other reporter groups, of the molecules in both spin states. With ultrafast IR spectroscopy we monitor the delayed bending motion on the temporal evolution of NCS mode.



**Figure 1** (left) potential energy surface (PES) of [Fe(phen)<sub>2</sub>(NCS)<sub>2</sub>] in the breathing and bending (D, Σ) coordinate space. (right) IR kinetic of a spin state sensitive mode.

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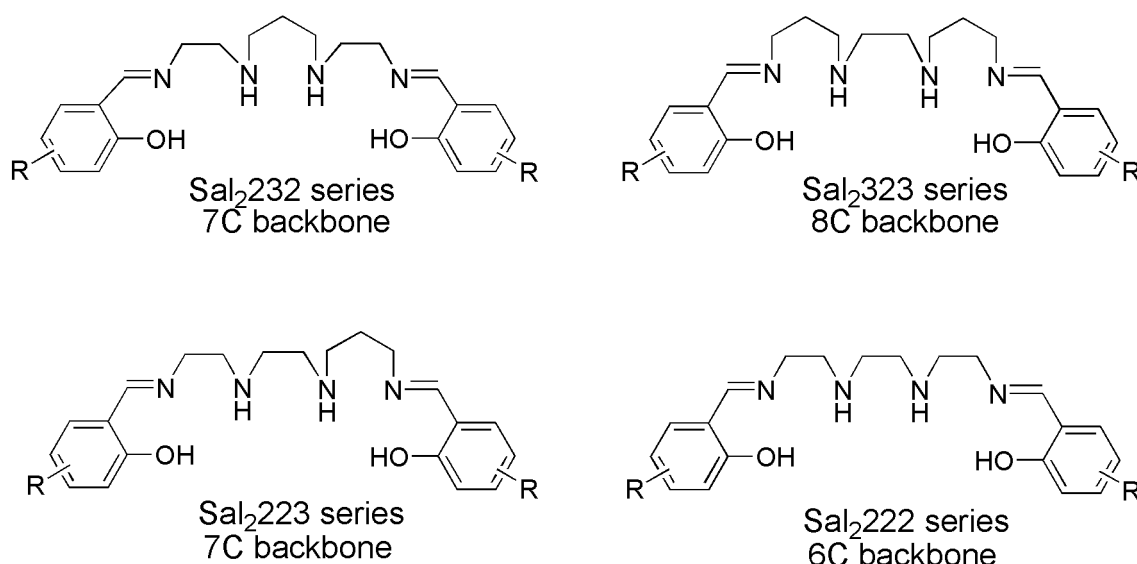
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## Introducing Asymmetry into Mn(III) Spin-Crossover Complexes with Schiff Base Ligands

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We have studied the spin state behaviour of iron(III) and manganese(III) complexes with Type I ligands (**Fig. 1**) with different phenolate substitution patterns and polyamine lengths. Four polyamine spacers have been used, resulting in the generic ligand families, Sal<sub>2</sub>222, Sal<sub>2</sub>323, Sal<sub>2</sub>232 and Sal<sub>2</sub>223 and these promote distinct choices of electronic spin state in Fe(III) and Mn(III). We present here examples of ordering phenomena in iron(III)<sup>1</sup> and manganese(III)<sup>2</sup> complexes and show how this is related to the symmetry of the starting amines in the ligand synthesis.



**Figure 1** Representation of the ligand sets used to probe SCO phenomena in Fe(III) and Mn(III), where R can be an electron withdrawing group (EWG) or an electron donating group (EDG).

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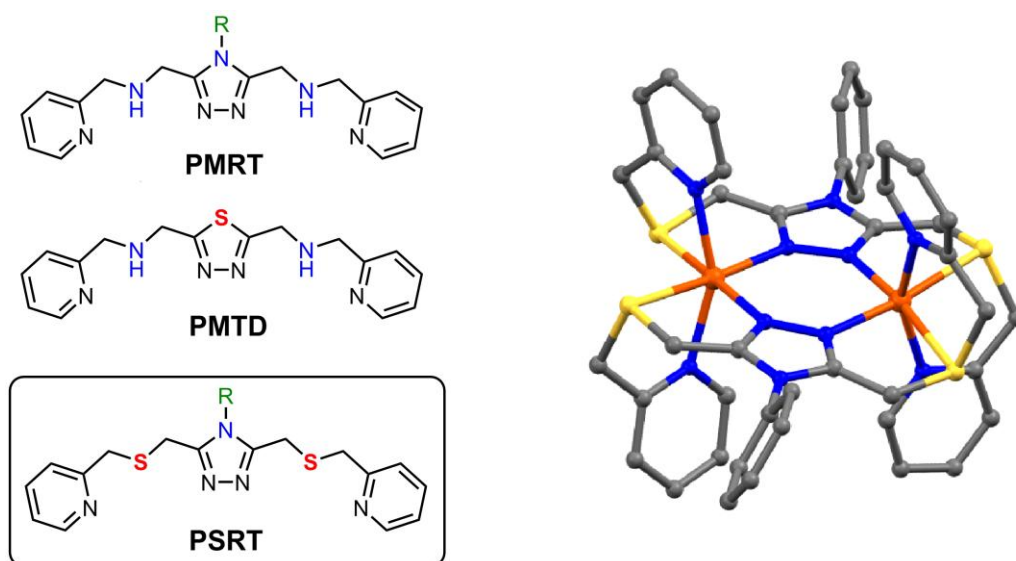


## Spin crossover in dinuclear $N_4S_2$ iron(II) complexes: access to [HS-HS], [HS-LS] and [LS-LS] spin states

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The spin crossover (SCO) phenomenon has attracted a lot of attention due to various potential applications, including as molecular switches.<sup>1</sup> While the majority of SCO active compounds contain Fe(II) in an octahedral  $FeN_6$  coordination environment, those with mixed donor coordination sets, such as  $FeN_4S_2$ , have also produced unique SCO activity.<sup>2</sup> Our previous in depth studies of  $[Fe^{II}_2(\mathbf{PMRT})_2]X_4$  complexes, varying R and/or X, gave switching between [HS-HS] and [HS-LS] states with remarkable SCO,<sup>3,4</sup> while others have isolated a [LS-LS] species using the related **PMTD** ligand (Fig. 1).<sup>5</sup> Our attention has now turned to designing new sulphur-containing analogues, **PSRT**, which impose an unusual  $N_4S_2$  coordination on the Fe(II) centres in the dinuclear  $[Fe^{II}_2(\mathbf{PSRT})_2](BF_4)_4$  complexes, and results in SCO between all three spin states: [HS-HS], [HS-LS], and [LS-LS].



**Figure 1.** **PMRT**, **PMTD**, and the new **PSRT** ligand systems (left), and  $[Fe^{II}_2(\mathbf{PSRT})_2](BF_4)_4$  structure (right).

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# New microscopic approach to the problem of spin crossover in molecular crystals

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A new theoretical model of spin crossover has been developed. For the first time both the interactions of spin crossover ions with the acoustic lattice phonons and molecular vibrations have been taken into account. The difference in the frequencies of the molecular vibrations in the low-spin (ls) and high-spin (hs) states is also accounted for in the model. Following the idea suggested in <sup>1</sup> it has been obtained that an effective coupling of the molecular modes with phonons appears. This bilinear interaction has been proved to be responsible for the cooperative spin transition accompanied by the structural reorganization. The transition is characterized by the two order parameters representing the mean values of the products of electronic diagonal matrices and the coordinates of the local modes for the hs- and ls- states of the spin crossover complex. To illustrate the validity of the suggested approach the cooperative  $ls(^1A_1) \rightarrow hs(^5T_2)$  transition in the  $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$  crystal has been examined since for this crystal the majority of parameters involved in the model can be determined from the experimental data. <sup>2</sup> It has been demonstrated that the main observed features of the spin crossover phenomenon in  $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$  can be reproduced by the suggested approach. For this crystal the approach provides a reasonable explanation of the temperature dependence of the high-spin fraction in a wide temperature range as well as the pronounced hysteresis loop.

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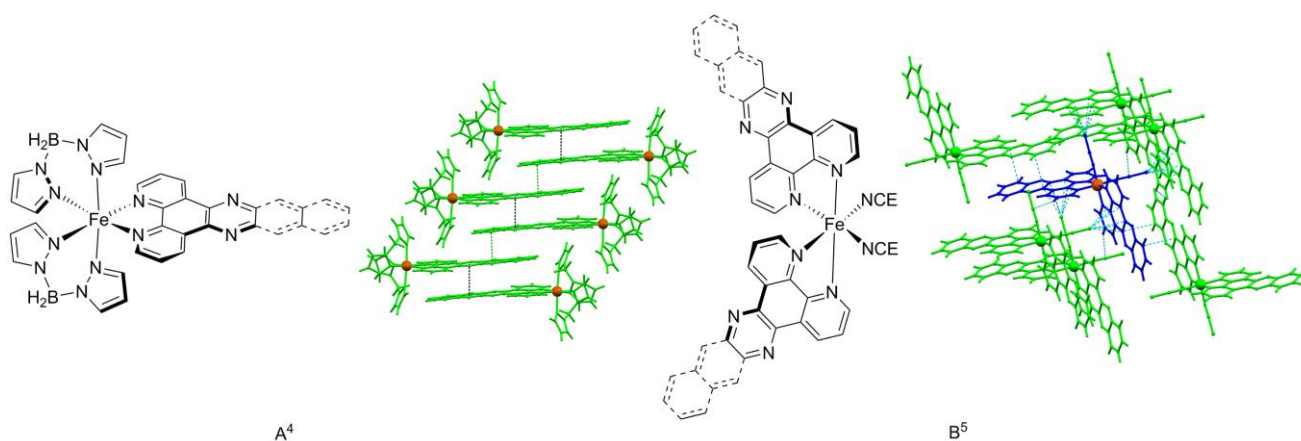
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## Structure:Function Relationships in Fe(II) Complexes with Annealated Bipyridyl Ligands.

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Abrupt spin crossover (SCO) is a result of cooperativity between the switching centres, and it might result in hysteresis.<sup>1</sup> The cooperativity itself is a function of the crystal lattice and its strength can be attributed to: hydrogen bonding,  $\pi$ - $\pi$  interactions and/or van der Waals forces. From the point of view of applications, systems undergoing transition with wide hysteresis loop centered at room temperature are desirable.<sup>2</sup> A recent review relating structure with function in SCO systems outlined that strong cooperativity might be achieved by the increase of mechanical coupling between spin centres.<sup>3</sup> We have investigated this argument by targeting the complexes with annealated bipyridyl ligands in which arene groups can interdigitate in solid state resulting in large surface contact areas and extended  $\pi$ - $\pi$  interactions throughout the lattice. As an example, iron(II) complexes A and B, shown in Figure 1, were structurally and magnetically characterised.<sup>4-5</sup> Detailed results showing the relationship between crystal packing ( $\pi$ - $\pi$  interactions) and magnetic properties will be discussed.



**Figure 1** Fe(II) complexes tested for structure:function relationship

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## Fe<sup>II</sup> spin crossover complexes for modulating lanthanide-centered luminescence

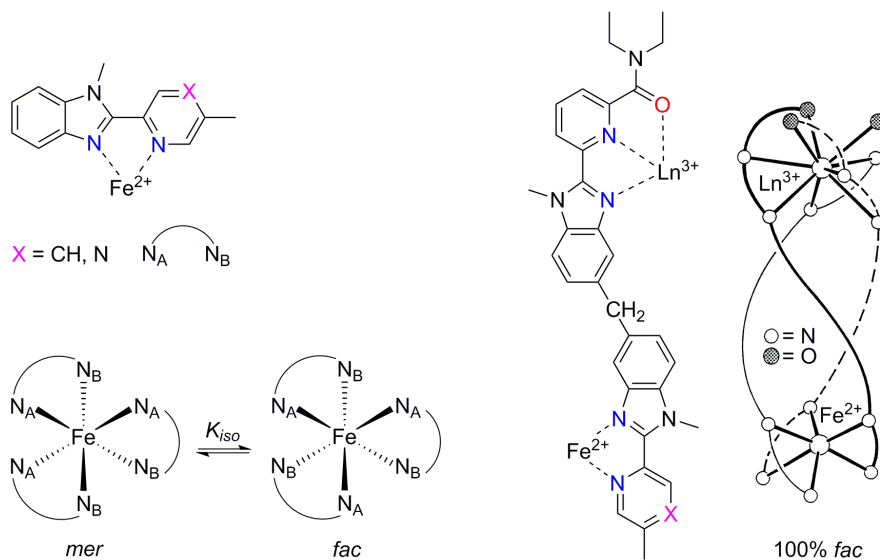
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Mononuclear pseudo-octahedral spin crossover Fe<sup>II</sup> complexes with unsymmetrical diimine ligands suffer from the existence of *facial* and *meridional* isomers, for which different thermal, magnetic and optical properties are expected (Figure, left).<sup>1</sup> When the didentate binding units are incorporated into dinuclear *d-f* helicates, the lanthanide cations act as a template and force the quantitative *facial* arrangement of the diimines moieties around Fe<sup>II</sup> (Figure, right), restoring spin crossover transitions characterized by linear van't Hoff plots.<sup>2</sup> Reciprocally, the thermal spin crossover transition can be exploited for modulating the lanthanide-centered luminescence via intramolecular energy transfer processes.



**Figure.** *Mer* → *fac* isomerization in Fe<sup>II</sup> tris-diimine spin crossover complexes (left) and quantitative *facial* complexation of Fe<sup>II</sup> in heterometallic dinuclear helicates (right).

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# Influence of the functional group of the ligand, the anions and the solvent molecules in Fe(III) Spin Crossover complexes

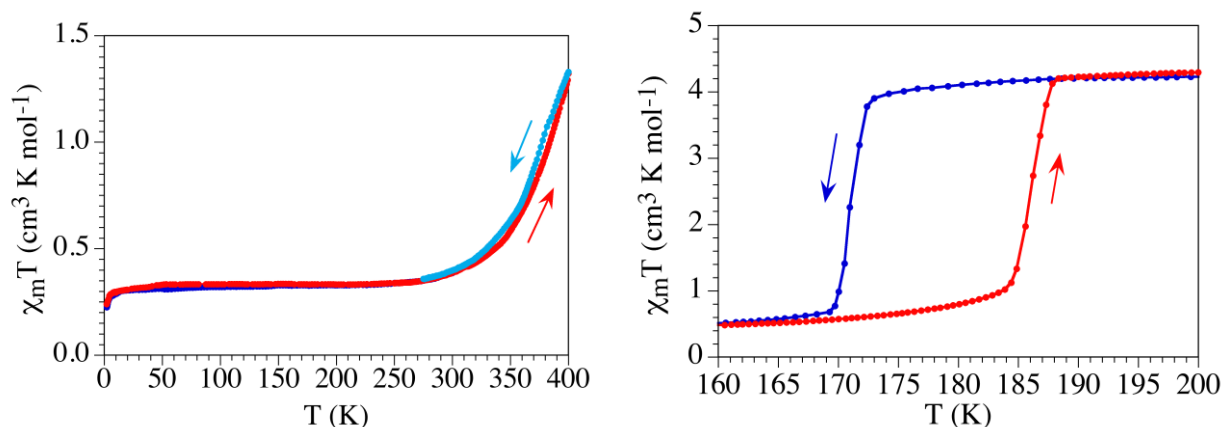
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Spin crossover (SCO) transitions with hysteresis around room temperature constitutes a very interesting example of bistability that can be used in data storage, sensors, molecular commutation, displays,....

In this communication we present two novel series of spin crossover (SCO) Fe(III) complexes with Schiff-base ligands derived from quinolylsalicylaldimines. We have analysed the role played by the different functional groups of the Schiff base ligand and we study in detail the role played by the intermolecular interactions in the parameters of the SCO transition. We will show the influence of (i) the functional group in the ligand, (ii) the counter-anion used to neutralize the charge of the Fe(III) SCO complexes  $[\text{Fe}(\text{L})_2]^+$  and (iii) the presence/absence of different solvent molecules in the parameters of the SCO transition. These parameters include the transition temperature, its abruptness, the presence/absence of hysteresis and the presence of different steps in the SCO transitions.



**Figure 1** SCO transitions in two Fe(III) complexes with two related Schiff base ligands

## Rational Design and Synthesis of Switchable Spin Crossover Materials: from 0D Cluster to 3D MOFs

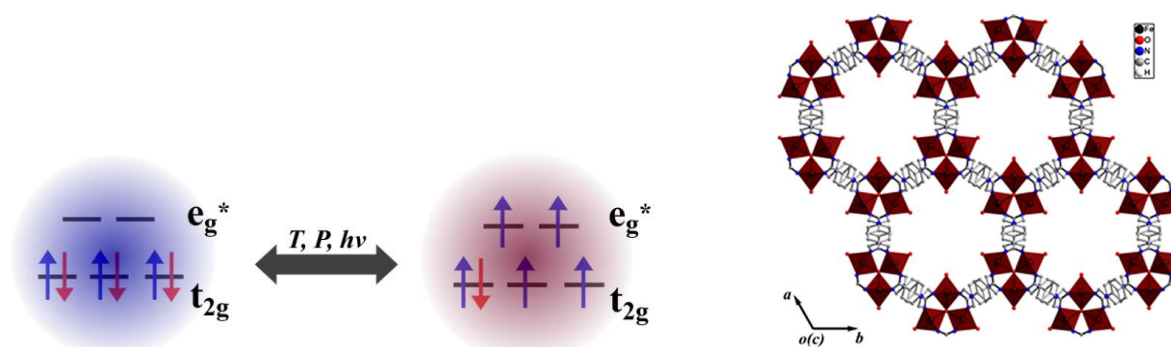
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Initially discovered in 1931, spin crossover (SCO) complexes and materials has been continually studied by research groups all over the world.<sup>[1]</sup> Numerous studies have been devoted to the origin of the cooperativity. As intermolecular interactions among complexes partly explain cooperativity, enhancement of abruptness should be possible by covalently linking the magnetic metal centers.<sup>[2]</sup> Based on this consideration, a variety of polynuclear systems has been introduced and extensively studied. As one of the most prospective systems for potential applications the iron(II) triazole coordination polymer has undergone extensive studies, yet only one structure has been determined very recently.<sup>[3]</sup> The promising approach in our project here is the well-designing of the 4-substituted 1,2,4-triazole ligand. We aim to modify the appropriate ligand field that triggers the SCO behavior on one hand, and to link the active magnetic centers via varieties of non-covalent interactions (H-bonding,  $\pi\cdots\pi$ , Halogen...Halogen, ... etc.) on the other hand. We thus perform SCO studies of 1,2,4-triazoles system from lower dimensional molecules to three-dimensional MOFs.



**Figure** Left, Spin state transition; right, 3-D Fe<sup>II</sup> MOFs

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## Towards MEMS/NEMS devices based on spin crossover materials

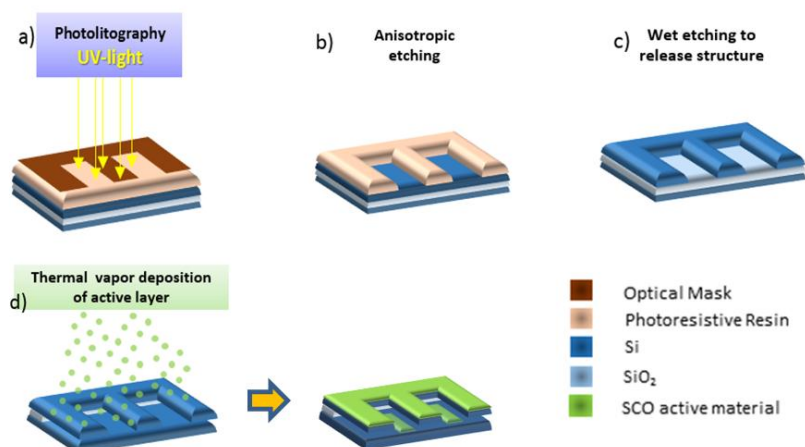
M. Dolores Manrique J.<sup>a,b</sup>, Sylvain Rat<sup>a</sup>, Gabor Molnar<sup>a</sup>, Liviu Nicu<sup>b</sup>, Lionel Salmon<sup>a</sup>, Thierry Leichle<sup>b</sup>, Laurent Mazenq<sup>b</sup>, Fabrice Mathieu<sup>b</sup>, Isabelle Seguy<sup>b</sup> and Azzedine Bousseksou<sup>a</sup>.

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Silicon-based microelectromechanical systems (MEMS) have become popular sensor, switching and actuator devices for their high sensitivity, low energy dissipation and fast operation.<sup>1</sup> Their further development towards the nanoscale is largely limited by the restricted range of materials used for their construction. In this context spin crossover (SCO) complexes present promising characteristics. In addition, these molecular phenomena can occur in single molecules presenting a new lower limit for miniaturization.<sup>2</sup> The proof of concept of SCO actuators have been already achieved using either single crystals or composite materials.<sup>3,4</sup> The next step is their successful integration into useful devices, which requires appropriate fabrication protocols. In this work we discuss our approach of fabricating MEMS and their mechanical response obtained by high frequency piezo actuation and interferometric detection.



**Figure 1** Si/SCO Actuators: Fabrication steps

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## The spin crossover profile in iron(III) Schiff-base compounds: halogen influence.

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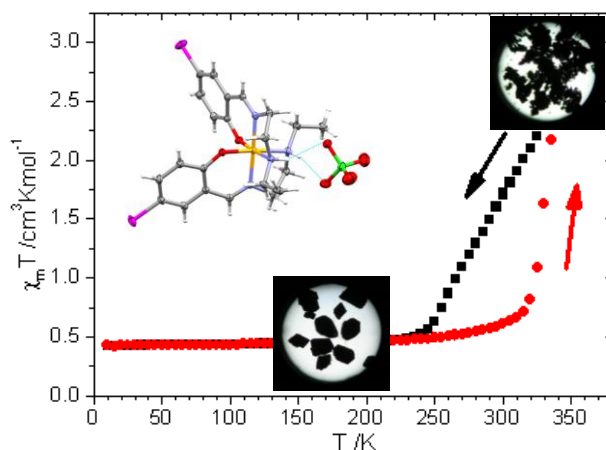
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Technological advances have been pushing the limits of chemistry for the last few years towards creating more efficient and multifunctional molecules and materials. A phenomenon that shows great promise in molecular electronics is spin crossover (SCO).<sup>1</sup> This switching can be harnessed to develop materials with a wide range of possible applications such as memory or sensing nano-devices.<sup>2</sup> Halogen derivatized SCO molecules are of great interest as they can interact with neighboring molecules through either halogen or hydrogen bonds and additionally they can be modified through substitution or coupling reactions conferring additional properties and high versatility to the SCO molecules.<sup>3,4</sup>

Here we report the synthesis and characterization of halogen derivatized SCO compounds with an Fe(III) metallic center coordinated to both tridentate (N<sub>2</sub>O) and hexadentate (N<sub>4</sub>O<sub>2</sub>) Schiff-base ligands. We have found that all compounds exhibit SCO with profiles ranging from gradual to abrupt with hysteresis and a detailed study on the halogen influence on these is also being carried out.



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## Pressure Tune of Spin-Crossover-Like Phenomenon in Cu(II)-Nitroxide Complexes

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Galina Romanenko,<sup>c</sup> and Victor Ovcharenko<sup>c</sup>

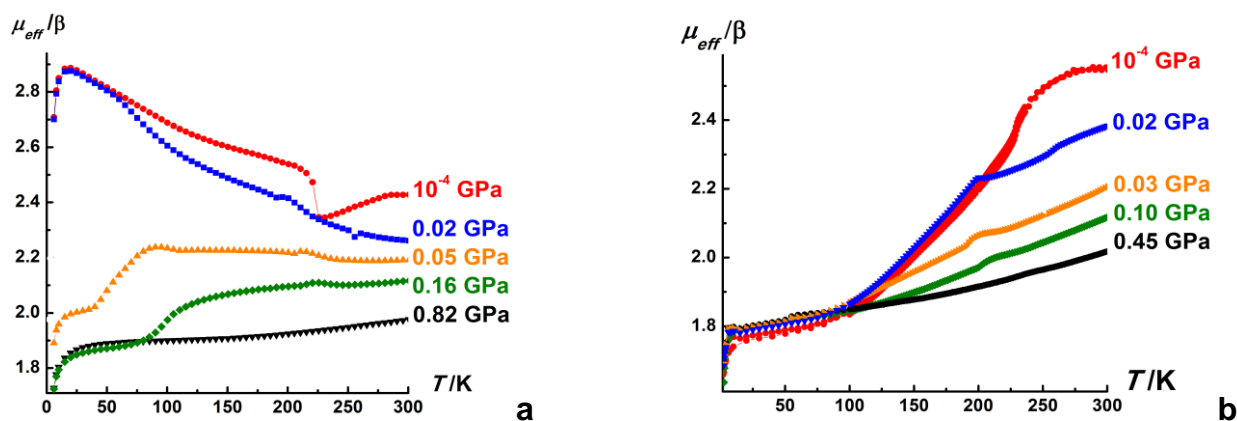
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Heterospin Cu(II)-nitroxide systems are of special interest for detailed studies of various thermally, pressure or light induced phase transitions that accompanied by magnetic anomalies similar with spin crossover.<sup>1</sup> Our study have shown that an increase in the hydrostatic pressure caused a significant changes at  $\mu_{\text{eff}}(T)$  dependences (fig. 1) that can serve as gentle and effective tuning of functional properties of spin-crossover-like complexes. An analysis of the effect of the external pressure on the physical characteristics of Cu(II)-nitroxide complexes can provide valuable information on the mechanism of the observed magnetic anomalies and serve as a basis for creating new highly efficient pressure sensors.



**Figure 1** Experimental dependences of  $\mu_{\text{eff}}(T)$  at different pressure for [Cu(hfac)<sub>2</sub>NN-PzEt] (a) and [Cu(hfac)<sub>2</sub>NN-PzPr] (b).

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## Spin Cross-Over (SCO) based on polypyridyl ligands

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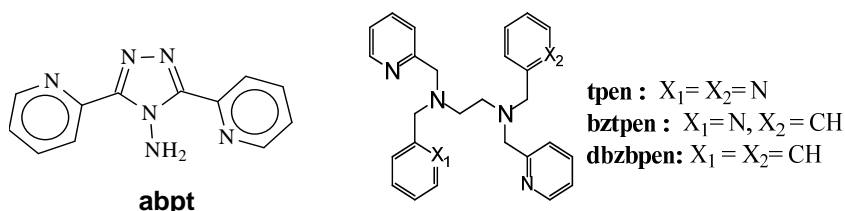
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The design of new coordination complexes exhibiting the spin crossover (SCO) phenomenon is one of the most relevant challenges in the field of magnetic molecular materials.<sup>1</sup> The SCO systems relate to the pseudo-octahedral  $d^4$ - $d^7$  transition metal complexes for which the high spin (*HS*) and the low spin (*LS*) electron configurations can be reversibly switched by external stimuli such as temperature, pressure, magnetic field or light irradiation.<sup>1</sup> Nevertheless, the primary investigated systems to date remain those based on Fe(II) ( $d^6$  configuration), for which a paramagnetic-diamagnetic transition from the *HS* ( $S = 2$ ) state to the *LS* ( $S = 0$ ) state is observed. In the last few years, we have reported the first SCO series based on the cyanocarbanions bearing one negative charge and abpt (4-amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole) co-ligand.<sup>2</sup> However, in this system, all the complexes display SCO transitions above room temperature, making difficult to reach any structural and electronic information on the *HS* state.



Thus, in order to better control the transition temperature and the cooperative effect between the active metal ions, we have substituted abpt co-ligand by other chelating co-ligands displaying various coordination modes and lower crystal field energies. We report herein syntheses, structural characterizations and magnetic properties of new series of formula  $[Fe(dbzbpn)_2(NCX)_2]$  ( $X = S, Se$ ).

1 Eds. Gütllich, P.; Goodwin, H. A., Spin Crossover in Transition Metal Compounds I-III, *Top. Curr. Chem.*, Springer Verlag, Berlin-Heidelberg-New York, **2004**, vol. 233-235.

2 G. Dupouy, M. Marchivie, S. Triki, J. Sala-Pala, J.-Y. Salaün, C. J. Gómez-García, P. Guionneau, *Inorg. Chem.*, **2008**, *47*, 8921.

## NO Responsivity of Magnetically-Bistable Fe(II)Pt(II) Porous Coordination Polymer

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A 3-D Hofmann-type porous coordination polymer {Fe(pz)[Pt(CN)<sub>4</sub>]} (**1**; pz = pyrazine) consisting of pillared Fe(II)Pt(II) layers exhibits a cooperative spin transition (ST) around room temperature and a chemo-responsive spin state change [1]. Magnetic behavior of **1** depends on adsorbates strongly, however gas molecules such as O<sub>2</sub>, N<sub>2</sub> and CO<sub>2</sub> do not affect it because of their weak interaction with the framework. To reinforce the host-guest

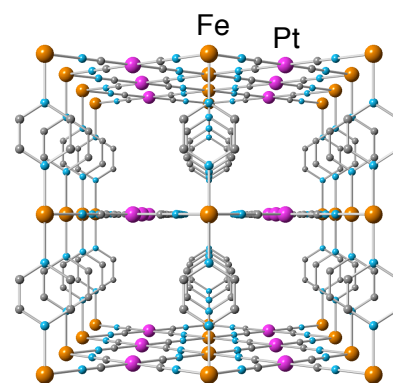


Fig. 1 Crystal structure of **1**

interaction we focus on NO having dipole moment, quadrupole moment and unpaired electron. At room temperature, **1** displayed a hysteretic adsorption isotherm, which suggests strong host-guest interaction. Magnetic susceptibility of **1** in the low-spin state (LS) gradually increased in association with NO adsorption at 298 K, which was confirmed by *in situ* magnetic measurement under NO. The NO clathrate (**1**⊃NO) exhibited two-step ST behavior, which was completely different from that of guest-free **1**. The structural and magnetic changes of **1** were carefully examined using *in situ* synchrotron powder X-ray diffraction (sXRPD) and IR spectroscopy measurement under NO. Temperature-dependences of sXRPD and IR spectra showed significant changes corresponding to the magnetic behavior as follows: (1) New stretching modes attributed to NO dimer appeared at low temperature, (2) the space group of **1**⊃NO changed to *P2/m* from *P4/mmm* at low temperature. These results corroborate specific interaction between **1** and NO, and arrangement change of NO in the pore.

[1] M. Ohba, J. A. Real, S. Kitagawa *et al.*, *J. Am. Chem. Soc.*, **135**, 4840 (2013).; *ibid.*, **134**, 5083 (2012).; *ibid.*, **133**, 8600 (2011).; *Angew. Chem. Int. Ed.*, **48**, 4767 (2009).; *ibid.*, **48**, 8944 (2009).

## Porous spin crossover networks for multifunctional materials

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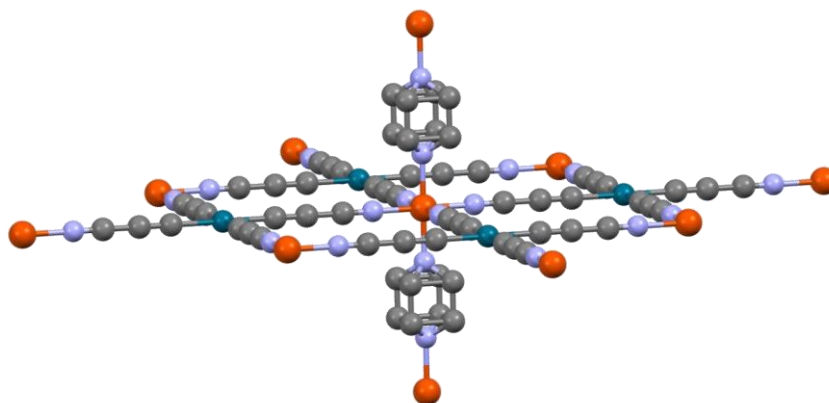
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A main objective of actual spin crossover (SCO) research is the development of materials suitable for technological applications. Multifunctional materials, combining the SCO effect with an additive property (luminescence, NLO, etc.) would notably broaden the scope of applicability.<sup>1</sup> Currently we focused on the development of spin-switchable metal organic frameworks with extended pore-size. The availability of such porous spin-switchable hosts could provide combinatorial materials by sole incorporation of a functional guest.

Different ligand systems, based on N-ligands (1-substituted tetrazoles, pyrazoles) were investigated. Although these approaches led to the desired porous switchable materials, due to the ligand's design no regular pore structure could be obtained. Therefore, an extension of the  $[M^{II}(\text{CN})_4]^{2-}$  (M=Ni, Pd, Pt) fragment of the well-known Hofmann-type networks<sup>2</sup> was performed. This led to second generation Hofmann-type networks with extended pore size (fig.1) and SCO behavior beyond room-temperature.



**Figure 1** Second generation Hofmann-type network, view along a-axis

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## Two-Dimensional Spin-Crossover (SCO) Hoffman-Like Metal-Organic Frameworks Based on Functionalized Triazole Ligands

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Spin crossover materials (SCO), in particular those exhibiting thermal and photo-induced magnetic bistability, are likely among the most studied switchable molecular solids in the last few years.<sup>1</sup> So far, The most studied examples are those based on Fe(II) ( $d^6$  configuration), for which a paramagnetic-diamagnetic transition from the high spin (HS) state ( $S = 2$ ,  $^5T_{2g}$ ) to the low spin (LS) state ( $S = 0$ ,  $^1A_{1g}$ ) is observed with temperature.<sup>1</sup> With the aim of growing networks with cyanide donors, we have investigated the inorganic tetracyanometallate anions ( $[M(CN)_4]^{2-}$ ,  $M = Ni(II), Pt(II), Pd(II)$ ) which can act as polybridging ligands through their nitrile groups. This led us recently to two series of molecular bimetallic coordination neutral chains formulated as  $[FeL_2][\mu_2-M(CN)_4]$  ( $M = Ni(II), Pt(II)$ ;  $L = 4\text{-amino-}3,5\text{-bis(pyridin-2-yl)-}1,2,4\text{-triazole (abpt), quinolin-8-amine (aqin)}$ ).<sup>2</sup> In this work, we have shown that the coordination mode of inorganic planar anions, and consequently the 1-D character of the bimetallic material, can be imposed by the choice of the iron (II)  $[Fe(L)_2]^{2+}$  precursor ( $L =$  bidentate ligand); where the ligand field of the Fe(II) centers can be tuned by the nature of the chelating co-ligand ( $L$ ). Based on such 1-D systems, we have extended our investigations to bimetallic systems involving the  $[Fe^II M^II(CN)_4]$  2-D layers and other mono-dentate or bridging aromatic N-donor co-ligands such as functionalized triazole ligands.

We report herein the synthesis, the thermal variation of the crystallographic structural data and magnetic properties of the SCO 2-D Hoffman-like system  $[Fe(L)_2\{Pt(CN)_4\}].nH_2O$  series, based on the N-donor functionalized triazole ligand ( $L$ ).

1 Halcrow, M. A. (Eds.), *Spin-Crossover Materials, Properties and Applications* **2013**, John Wiley & Sons Ltd, Oxford, UK.

2 a) F. Setifi, F.; C. Charles, S. Houille, F. Thétiot, S. Triki, C. J. Gómez-García, S. Pillet, *Polyhedron* **2013**, *61*, 242; b) F. Setifi, E. Milin, C. Charles, F. Thétiot, S. Triki, C. J. Gómez-García, *Inorg. Chem.* **2014**, *53*, 97.

## Ligand Substitution Effects on The Spin Cross-Over (SCO) Behaviour of Dinuclear Cyanocarbanions-Based Complexes

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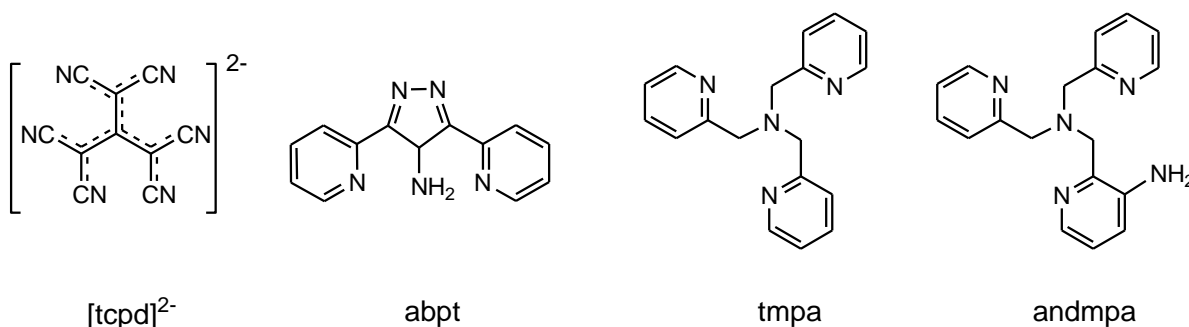
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In last few years, our group has been interested in the design of new series of spin crossover (SCO) compounds using polynitrile anionic ligands like the  $\text{tcpd}^{2-}$  dianionic ligand. Such anions are very attractive due to their high electronic delocalization and their cyano groups juxtaposed in such a way that they cannot all coordinate to the same metal ion.<sup>[1]</sup> With the two negative charges,  $\text{tcpd}^{2-}$  has the ability to act as a bridging ligand to produce original thermo- and photoswitchable Fe(II) SCO chain when combined to neutral polydentate ligand such as  $\text{abpt}$ .<sup>[2]</sup> In order to develop and characterize new systems with SCO behaviour, we investigate other neutral polydentate ligand based on coordinating polypyridine units :  $\text{tmpa}$ , a aza-tripodal base with three methylpyridine arms, and its analogue  $\text{andmpa}$  that possesses a aniline function in place of one pyridine group.



We present the synthesis, structural properties and magnetic measurements of new dinuclear iron(II) complexes exhibiting SCO behaviours using these two neutral polydentate ligands combined with  $\text{tcpd}^{2-}$  polynitrile dianionic ligand.<sup>[3]</sup> This work gives a good exemple of the influence of the ligand modulation on the SCO behaviour.

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3. E. Milin, F. El Hajj, V. Patinec, S. Triki, M. Marchivie, C.J. Gómez-García, S. Pillet, *Inorg. Chem*, Submitted.

## Molecular Spin Crossover (SCO) Coordination Polymers Based on Substituted Triazole ligands

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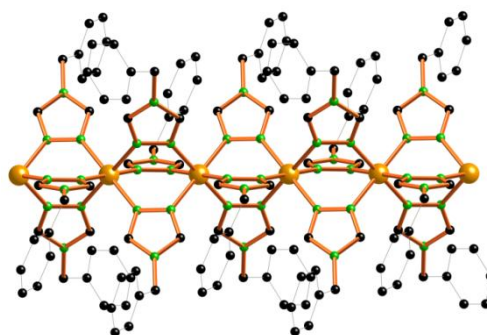
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Coordination Fe(II) polymers of general formula  $[\text{Fe}(\text{Rtrz})_3][\text{A}]_{2\text{or}1}$  ( where Rtrz = 4-substituted-1,2,4-triazole, and A = monovalent or divalent anion) are a unique class of spin-crossover (SCO) materials.<sup>1</sup> These SCO materials certainly have allowed the design of early optical devices prototypes and sensors in various forms i.e. nanoparticles, gels, thin films, and liquid crystals<sup>2</sup>. Those Fe(II) materials constructed through triple N<sub>1</sub>,N<sub>2</sub>-1,2,4-triazole bridges illustrate their dominance in SCO research with high synthetic versatility of which allows the possibility to modify the triazole ring at the 4th position. Even though this system is known for more than three decades, their crystallographic structure has been rarely established.<sup>2,3</sup>

In this context, our group is interested to investigate the structural properties involving 4R-1,2,4-triazole derivatives. Here, we report the first single crystalline SCO Fe(II) coordination polymer of formula  $\{\text{Fe}(\text{bntrz})_3[\text{Pt}(\text{CN})_4]\} \cdot \text{H}_2\text{O}$  (bntrz = 4-benzyl-1,2,4-triazole) with structural characterisations including the crystallographic data and magnetic properties.



**Figure 1.** Fe(II) spin crossover coordination polymer  $\{\text{Fe}(\text{bntrz})_3[\text{Pt}(\text{CN})_4]\} \cdot \text{H}_2\text{O}$ .

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## Spin crossover nanomaterials

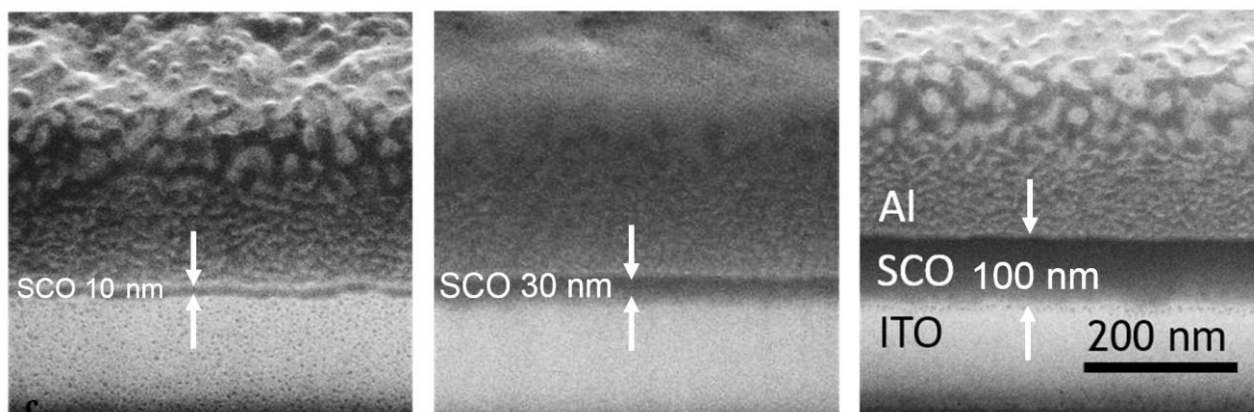
S. Rat<sup>a</sup>, C. Lefter<sup>a</sup>, P. Demont<sup>b</sup>, L. Salmon<sup>a\*</sup>, G. Molnár<sup>a</sup>, A. Bousseksou<sup>a\*</sup>

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The molecular spin crossover phenomenon (SCO), involving thermo-, photo-, magneto- and piezo-chromic properties of a class of transition metal complexes ( $3d^4$ - $3d^7$ ), is of growing importance in the area of functional materials, and have considerable prospects for technological applications in sensor, actuators, display or memory devices and as molecular switches<sup>1-2</sup>. Most of the appealing properties of these materials cannot be readily exploited for applications in bulk materials, but only as thin films or nano-objects. We have therefore developed a variety of top-down and bottom-up methods for the elaboration of spin crossover nano-materials. In this poster recent results concerning the synthesis, optical, electrical and mechanical characterization of SCO materials will be discussed.



**Figure 1** SEM images displaying the thickness control of a sublimated SCO film between Al and ITO electrodes.

<sup>1</sup> A. Bousseksou, G. Molnar, L. Salmon, W. Nicolazzi, *Chem Soc. Rev.* **2011**, *40*, 3313.

<sup>2</sup> M. D. Manrique-Juárez, et al. *Coord. Chem. Rev.* **2016**, *308*, 395.

## Diazine-Triazole Ligands for Spin-Crossover

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The phenomenon known as spin crossover (SCO), which is the switching between two different electron configurations, high spin (HS) and low spin (LS), has been attracting considerable attention over recent years due to its wide potential in applications, such as in data storage devices, optical displays, molecular switches, and sensors.<sup>[1]</sup>

Iron(II) complexes of dipyrizyltriazole ligands, **Rdpt** (Figure),<sup>[2][3]</sup> reveal a range of appealing and interesting spin crossover behaviour. Herein we present the synthesis of new diazine analogues, including **Rpdzt** (Figure), and the synthesis of characterisation of iron(II) complexes of them.

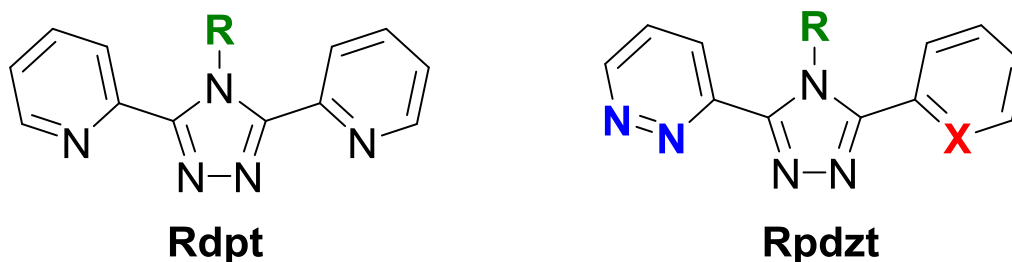


Figure. Literature **Rdpt** ligands (left)<sup>[2][3]</sup> and the new pyridazine-based **Rpdzt** analogues (right).

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## P- and/or T-Induced Structural Dynamics in Breathing Crystals

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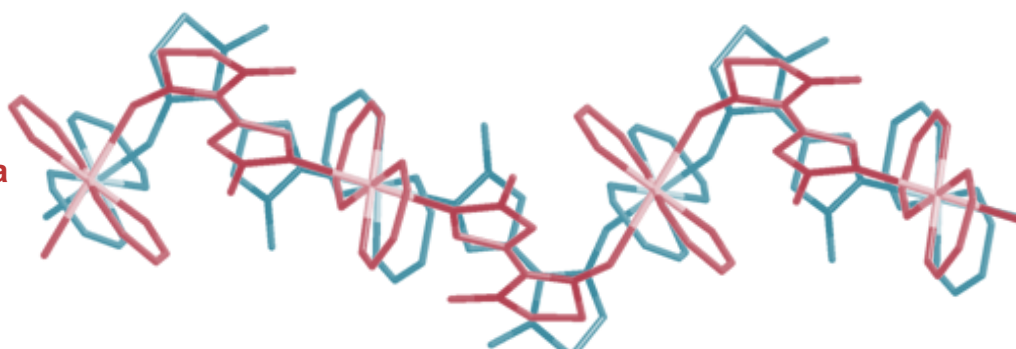
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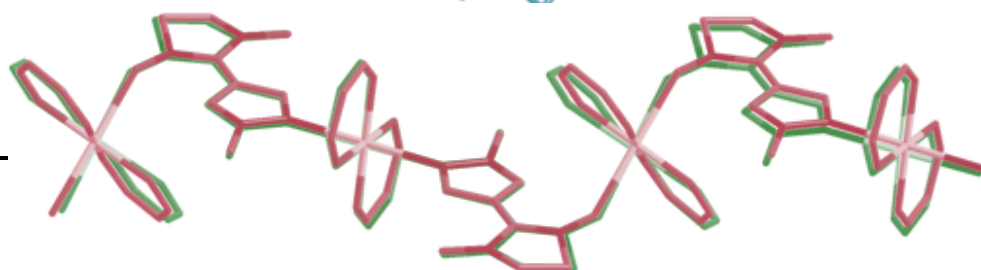
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'Breathing crystals' are compressible or expanded substances based on heterospin complexes of copper(II) hexafluoroacetylacetonate  $\text{Cu}(\text{hfac})_2$  with persistent nitronyl nitroxides  $\text{L}^{\text{R}}$ . Their ability to undergo reversible SC-SC phase transformations facilitates a detail investigation of solid dynamics. Phase transitions occur as a consequence of the P- and/or T-induced structural reorganization of exchange clusters 'Cu-O<sup>•</sup>-N' or 'N<sup>•</sup>-O-Cu-O<sup>•</sup>-N'. This reorganization causes an appearance of magnetic anomalies on the dependence of the effective magnetic moment vs temperature (or pressure). It was shown that pressure variation provokes another type of structural reorganization in compare with temperature induced structural changing.

**T = 295 K**  
**P = 0.0001 GPa**  
**P = 0.23 GPa**



**P = 0.0001 GPa**  
**T = 295 K**  
**T = 65 K**



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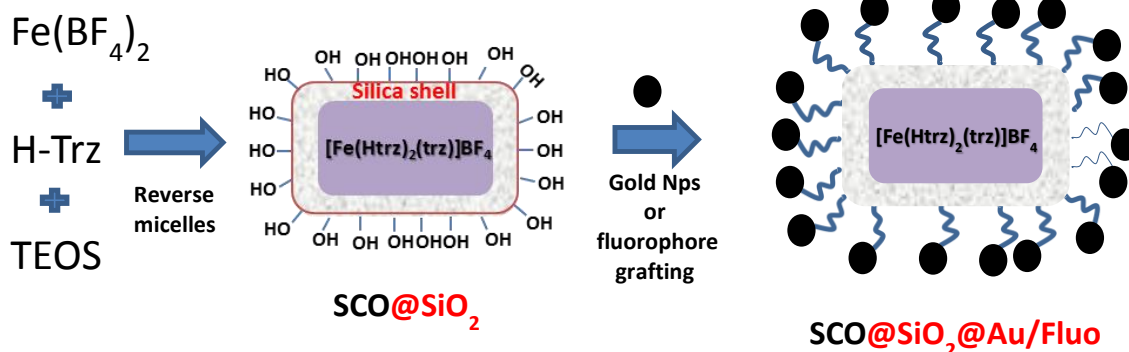
## Spin crossover nano-composites

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Among all compounds showing spin crossover (SCO) properties, 1-D iron (II) coordination polymers with 1,2,4-triazole-based ligands attract much attention because their spin-state switching is close to the room temperature.<sup>1</sup> This phenomenon is very attractive nowadays, in particular, in the field of molecular memory devices, information storage and sensors.<sup>2</sup> Most of the appealing properties of these materials cannot be readily exploited in bulk materials, but only if thin films or other nano-objects of the compounds are prepared.<sup>3</sup> In this communication we report on the synthesis, the characterization and the properties of nano-composite core-shell SCO particles based on the coordination polymer  $[\text{Fe}(\text{H-trz})_2(\text{trz})](\text{BF}_4)$  (H-trz = 1,2,4-triazole and trz = 1,2,4-triazolato), known to show a very abrupt spin transition and a wide thermal hysteresis loop, using silica shell for the grafting of gold nanoparticles (Nps)<sup>4</sup> or different fluorophores (organic molecule, quantum dots, rare earth).<sup>5,6</sup>



**Figure 1:** Synthetic pathway for the elaboration of  $\text{SCO}@\text{SiO}_2@\text{Au/Fluo}$  nano-composites

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3 A. Bousseksou, G. Molnár, L. Salmon, W. Nikolazzi, *Chem. Soc. Rev.*, **2011**, *40*, 3313.

4 I. Suleimanov, J. Sanchez Costa, G. Molnár, L. Salmon and A. Bousseksou, *Chem. Commun.*, **2014**, *50*, 13415

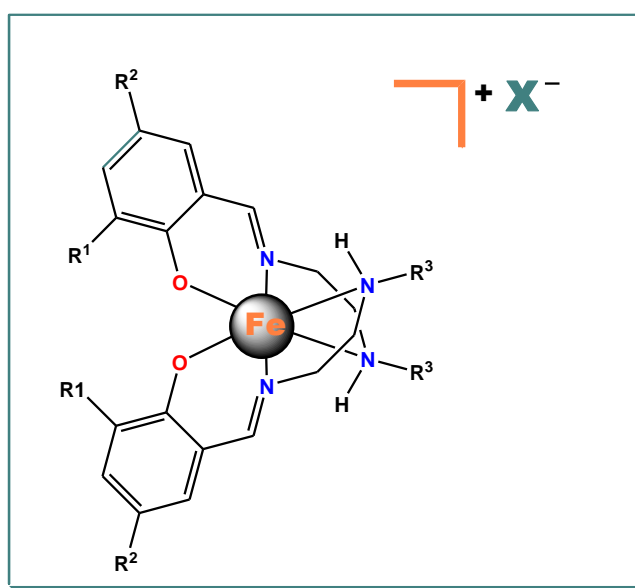
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## Development of Iron(III)-Based Cooperative Spin Crossover

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The upsurge in the development of spin-crossover materials is driven by the realization of their potential applications in information storage, molecular switches, displays and sensors. In the spin-crossover realm, iron(II) SCO complexes are the most prevalent and exhibit the most diverse range of spin-transition profiles. Contrariwise, iron(III) SCO complexes are much rarer with a mere handful known to display cooperative spin transformation. Indeed, of the bis-chelate iron(III)-salicylaldimine family of complexes (Figure 1) investigated over a period of three decades, only two members have been demonstrated to exhibit hysteretic spin crossover. Considering the various factors that affect spin crossover, in this work we have methodically modulated the spin-state behaviour within the  $[\text{Fe}^{\text{III}}\{(3,5\text{-R}^1, \text{R}^2)\text{-salRen}\}_2]\text{X}$  series of complexes by employing a wide range of permutations and combinations of ligand substituents and counter-ions. The resultant complexes have been characterized by pertinent techniques such magnetic susceptibility measurements, single-crystal X-ray analyses, Mössbauer spectroscopy, EPR spectroscopy and electronic absorption spectroscopy.



**Figure 1:** The ferric salicylaldimine family:  $[\text{Fe}^{\text{III}}\{(3,5\text{-R}^1, \text{R}^2)\text{-salRen}\}_2]\text{X}$

## Hidden Hysteresis Revealed by Photo-switching in a Multi-Stable Two-Dimensional Hoffman-Like Spin-Crossover Metal-Organic Framework.

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In some Spin crossover materials (SCO) complexes, the photo-conversion of the Low Spin (LS) stable state into the High Spin (HS) metastable state has been evidenced at low temperature and shown to be reversible in some complexes.<sup>1</sup> This allows a bidirectional photo-switching between a reference state (0) and an excited state (1) with a long lifetime, as long as the experiment is performed at low-temperature. Going further, it is of huge interest to be able to reach different states from the same reference state, with a high contrast in at least one physical property. Such multi-addressable systems with at least three states (0, +1, -1) are quite rare.<sup>2</sup>

In this context, we focused on the design of bimetallic systems involving the  $[\text{Fe}^{\text{II}}\text{M}^{\text{II}}(\text{CN})_4]$  Hoffman-like 2-D layers and mono-dentate or bridging aromatic N-donor co-ligands. Since the 2-D and 3-D Hoffman-type frameworks are essentially limited to the pyridyl N-donor ligands, we have focused our investigations on other aromatic N-donor ligands such as functionalized azole ligands involving two or more N-donor atoms.

We report herein the synthesis, the thermal variation of the crystallographic structural data and magnetic properties of the SCO 2-D Hoffman-like system  $[\text{Fe}(\text{trz-py})_2\{\text{Pt}(\text{CN})_4\}]\cdot 3\text{H}_2\text{O}$  (**1**) (trz-py = 4-(2-pyridyl)-1,2,4,4*H*-triazole), based on the N-donor functionalized triazole ligand.

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## Large Hysteretic Spin Crossover at High Temperature in 3D Hofmann-like Networks

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The design, synthesis and physicochemical characterization of new switchable magnetic materials is one of the major challenges in the pursuit of polyfunctional assemblies which can be applied for construction of highly efficient sensors and memory devices.<sup>1</sup> In this regard, iron(II) spin crossover (SCO) assemblies represent one of the best examples of such materials in which the Fe(II) centre can adopt two different states with spin  $S = 0$  or  $2$  depending on the size of energy gap between them.<sup>2</sup> Strong interest was directed towards the development of hybrid inorganic-organic networks represented by Hofmann-like networks. These systems usually reveal not only thermally, but also light- and solvent-induced switching between two states of Fe(II).

In this work, we present a complete investigation of the magnetic properties of new Hofmann-like coordination polymers based on silver (**1**) and gold (**2**) precursors. Both complexes are isostructural and form two 3D networks consisting of parallel stacks of 2D  $\{\text{Fe}^{\text{II}}[\text{M}^{\text{I}}(\text{CN})_2]_2\}_n$  grids linked by pyrazine through iron sites. Magnetic studies of **1** reveal a cooperative SCO with uncommonly large hysteresis with  $\Delta T$  of 60 K ( $T_{\text{SCO}}^{\text{down}} = 355$  K and  $T_{\text{SCO}}^{\text{up}} = 415$  K). Meanwhile, assembly **2** displays similar hysteretic behaviour with  $\Delta T$  of 18 K ( $T_{\text{SCO}}^{\text{down}} = 352$  K and  $T_{\text{SCO}}^{\text{up}} = 370$  K). These two coordination polymers are an interesting example of hysteretic SCO materials with one of the highest temperatures of work. To the best of our knowledge, assembly **1** reveals the largest hysteresis among Hofmann-like networks.

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## Trinuclear Fe(II) SCO Complexes Based on Functionalised Triazole and Cyanocarbanions

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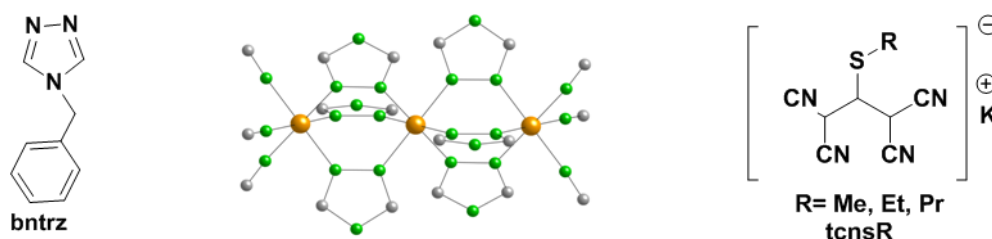
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Triazole based Fe(II) spin-crossover (SCO) materials of general formula  $[\text{Fe}(\text{Rtrz})_3][\text{A}]_2$  (Rtrz = 4-substituted-1,2,4-triazole and A is monovalent anion) constructed through triple  $\text{N}_1, \text{N}_2$ -1,2,4-triazole bridges are one of the best representative examples of molecular switchable materials.<sup>1</sup> Indeed, the SCO temperature and cooperative character for this system can be tuned by the nature of the 4-substituent on the triazole ligand and also the choice of the counter anion. The literature survey of those particular materials for the past three decades revealed that very few crystal structures have been reported up to now which make difficult to clearly establish structure-properties correlations.<sup>2</sup>

In this context, we have designed novel SCO materials using original polycyanocarbanions in combination with 4-R-1,2,4-triazole as ligands.<sup>3</sup> Noticeably, a unique class of Fe(II) polynuclear SCO complexes of formula  $[\text{Fe}_3(\text{bntrz})_6][\text{tcnsR}]_6$ ; (where bntrz = 4-benzyl-1,2,4-triazole and tcnsR = alkyl substituted thiocyanocarbanion) has been synthesized in single crystalline form with abrupt  $T_{\text{SCO}}$  around room temperature in which all the three Fe(II) centres are involved in SCO phenomenon. The original structural diversity in those triazole-based systems will be discussed with the full structural characterizations including the crystallographic structural data, and magnetic properties



**Figure 1.** Trinuclear Fe(II) SCO Complexes  $[\text{Fe}_3(\text{bntrz})_6(\text{tcnsR})_6] \cdot \text{H}_2\text{O}$ .

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## Study of thermal expansion behavior of rubidium manganese hexacyanoferrate

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In recent years, cyano-bridged metal assemblies have been aggressively studied to demonstrate various magnetic functionalities.<sup>1,2</sup> Among them, rubidium manganese hexacyanoferrate is an attractive material since it shows a various functionalities, e.g., thermal-induced phase transition, electronic-field induced phase transition, ferroelectric ferromagnetism, second harmonic generation, photogmantic effect, and so on.<sup>3-6</sup> In the present work, we prepare plate-shaped microcrystals of rubidium manganese hexacyanoferrate,  $\text{Rb}_{0.97}\text{Mn}[\text{Fe}(\text{CN})_6]_{0.99}\cdot 0.3\text{H}_2\text{O}$ , using a surfactant matrix<sup>6</sup>.

The prepared microcrystals show a charge transfer induced phase transition between the cubic  $\text{Mn}^{\text{II}}\text{-NC-Fe}^{\text{III}}$  and tetragonal  $\text{Mn}^{\text{III}}\text{-NC-Fe}^{\text{II}}$  phases. The  $\text{Mn}^{\text{III}}\text{-NC-Fe}^{\text{II}}$  phase exhibits a small negative thermal expansion (NTE) along the  $a_{\text{LT}}$  and  $c_{\text{LT}}$  axes with a thermal expansion coefficient of  $\alpha_{(a_{\text{LT}})} = -1.40 \pm 0.12 \times 10^{-6} \text{ K}^{-1}$  and  $\alpha_{(c_{\text{LT}})} = -0.17 \pm 0.13 \times 10^{-6} \text{ K}^{-1}$  over a wide temperature range of 15 K – 300 K. Such small  $|\alpha|$  materials are classified as ZTE materials. The far-infrared spectra show that NTE originates from the transverse modes  $\delta(\text{Fe-C}\equiv\text{N-Mn})$  of the transverse translational mode around  $304 \text{ cm}^{-1}$ , and transverse librational modes at  $253$  and  $503 \text{ cm}^{-1}$ , which are assigned according to first principle calculations. Molecular orbital calculations indicate that ZTE and the charge transfer phase transition both originate from the transverse mode. Additionally, an oriented film on  $\text{SiO}_2$  glass is prepared using a microcrystal dispersive methanol solution and a spin-coating technique. This is the first report of a ZTE film that maintains a constant film thickness over a wide temperature range of 300 K.

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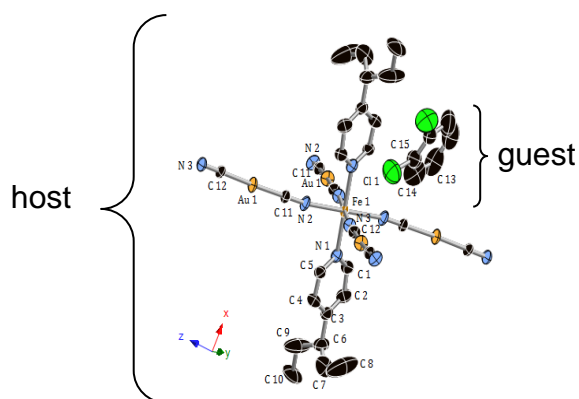
## Guest insertion into Hofmann-type coordination polymer

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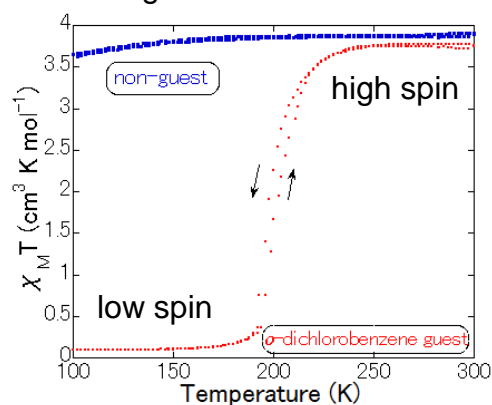
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Recently, novel spin crossover (SCO) coordination polymers have been developed by inserting the guest molecules into host  $\text{Fe}[4\text{-}(3\text{-Pentyl})\text{pyridine}]_2[\text{Au}(\text{CN})_2]_2$ . 4-(3-Pentyl)pyridine has been investigated as one of the guest molecules, which influences the magnetic property in the host complex [1]. In this presentation, we report the guest molecule *o*-dichlorobenzene insertion effect into the host  $\text{Fe}[4\text{-}(3\text{-Pentyl})\text{pyridine}]_2[\text{Au}(\text{CN})_2]_2$  which also modulates the host magnetic and electronic properties. From the analysis of single-crystal x-ray diffraction, we found that the host Fe ions are coordinated octahedrally with four nitrogen atoms in cyanide bridges and with two nitrogen atoms binding with the axial pyridine ligands. The guest molecules are positioned at the spaces surrounded by the host two-dimensional CN-bridged coordination polymer frameworks as shown in Fig.1. The crystal structure of this clathrate was determined to be the monoclinic space group *C2/c*. The SCO behavior with introducing the *o*-dichlorobenzene clathrate was observed as a rapid spin transition at around 200 K (Fig.2), which is considered to be the cooperative effects with the guest molecules.



**Fig.1.** Crystal structure of  $\text{Fe}[4\text{-}(3\text{-Pentyl})\text{pyridine}]_2[\text{Au}(\text{CN})_2]_2 \cdot o\text{-dichlorobenzene}$ .



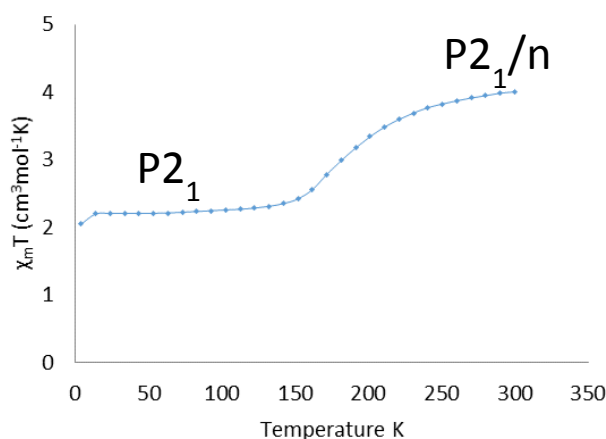
**Fig.2.** Magnetic properties of  $\text{Fe}[4\text{-}(3\text{-Pentyl})\text{pyridine}]_2[\text{Au}(\text{CN})_2]_2 \cdot \text{Guest}$  (Guest = non-guest, *o*-dichlorobenzene).

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## Chiral Resolution and Spin State Ordering in a series of Mononuclear Iron(III) Complexes

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Many small molecule complexes with chelating ligands have  $\Delta$  and  $\lambda$  optical forms depending on the direction of the ligand twist around the coordinated ion. Most of these crystallise in non-chiral space groups, with the pair of enantiomers related by an inversion centre. In our recent work we have studied several metal ligand combinations where spin crossover in either iron(III)<sup>1</sup> or manganese(III)<sup>2</sup> can be induced with judicious choice of chelating ligand. We now present a series of iron(III) complexes where spin crossover is accompanied by a structural phase transition which results in spin state ordering of high spin and low spin sites in a 1:1 ratio. During the ordering transition loss of the inversion centre between  $\Delta$  and  $\lambda$  forms also results in chiral resolution of the enantiomers, a rare example of combined spin state ordering and chiral resolution.<sup>3</sup> We report here our structural, magnetic and spectroscopic studies on the extent and reproducibility of the phenomenon in multiple crystals.



**Figure 1** Plot of  $X_M T$  versus  $T$  for mononuclear iron(III) complex showing spin state ordering and chiral resolution.

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# Ultrafast photoswitching in Fe-Co Prussian Blue Analogues investigated by femtosecond optical spectroscopy

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Fe-Co Prussian Blue Analogues are prototype bistable metallic cubic crystals. Among the great interests of these systems are their bistable chromic and ferromagnetic properties from the low spin (LS) ( $\text{Co}^{\text{III}}_{\text{LS}}\text{Fe}^{\text{II}}_{\text{LS}}$ ) to the high spin (HS) state ( $\text{Co}^{\text{II}}_{\text{HS}}\text{Fe}^{\text{III}}_{\text{LS}}$ ). The switching can be driven by light excitation and persists in nanocrystals. The bistability is associated with a charge transfer between the two metal sites (Fig.1a), accompanied by a structural relaxation stabilizing the new magnetic state. At  $T=10\text{K}$  under continuous laser irradiation the compound passes from the LS state to HS states. This transformation to a long-lived state characterized by magnetic measurements, optical or structural [1]. To understand the elementary mechanisms associated with this change of magnetic state induced by light, involving both a charge-transfer induced spin transition (CTIST) and structural reorganization, it is necessary to study this process on the time scale of electronic change and atomic motions [2]. We will present our first studies of this ultrafast dynamics of photo-switching. Our femtosecond optical pump-probe spectroscopy studies on nanocrystals in solution, revealed a multistep process (Fig 1b).

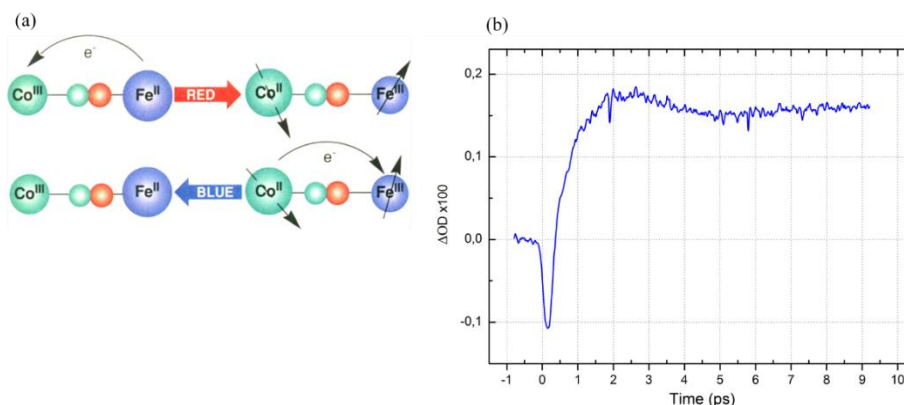


Figure 1 : (a) Schematic switching between low (left) and high spin (right) states, from Verdaguer, *Science* (1996) (b) OD change in  $\text{CsCo}^{\text{III}}\text{Fe}^{\text{II}}(\text{CN})_6$  nanoparticles after femtosecond excitation.

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## Magnetic Bistability in a Macrocycle-Based Iron (II) Complex

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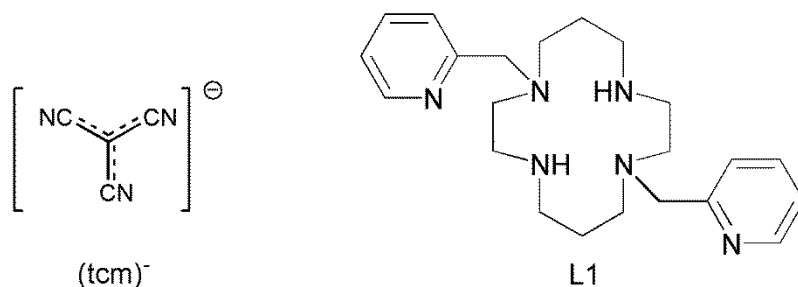
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The design of new coordination complexes exhibiting the spin scrossover phenomenon (SCO) is one of the most relevant questions in the field of magnetic molecular materials. One of the open challenge today is to obtain more cooperative materials and to increase the hysteresis width of their magnetic signature. In order to reach that aim, we develop an original approach based on the family of polyazamacrocycles to design new SCO materials. A first SCO Fe(II) complex **1** [Fe(L1)](BF<sub>4</sub>)<sub>2</sub>.H<sub>2</sub>O (L1 = 1,8-bis(2'-pyridinemethyl)-1,4,8,1-tetraazacyclotetradecane) has been described, exhibiting a spin transition (T<sub>1/2</sub>=150K) without hysteresis.<sup>1</sup>

In this communication, the synthesis, structural characterisation and magnetic properties of the complex **2** [Fe(L1)](tcm)<sub>2</sub>.H<sub>2</sub>O are displayed. The use of the high electronic delocalized polynitrile anion tcm<sup>-</sup> in place of BF<sub>4</sub><sup>-</sup> as the counterion has produced a SCO material presenting a 9K hysteresis loop, giving the first tetraazamacrocycle-based iron (II) compound exhibiting magnetic bistability. These results pointing out the effect of the counter-ion on the behaviour of the SCO conversion are discussed.



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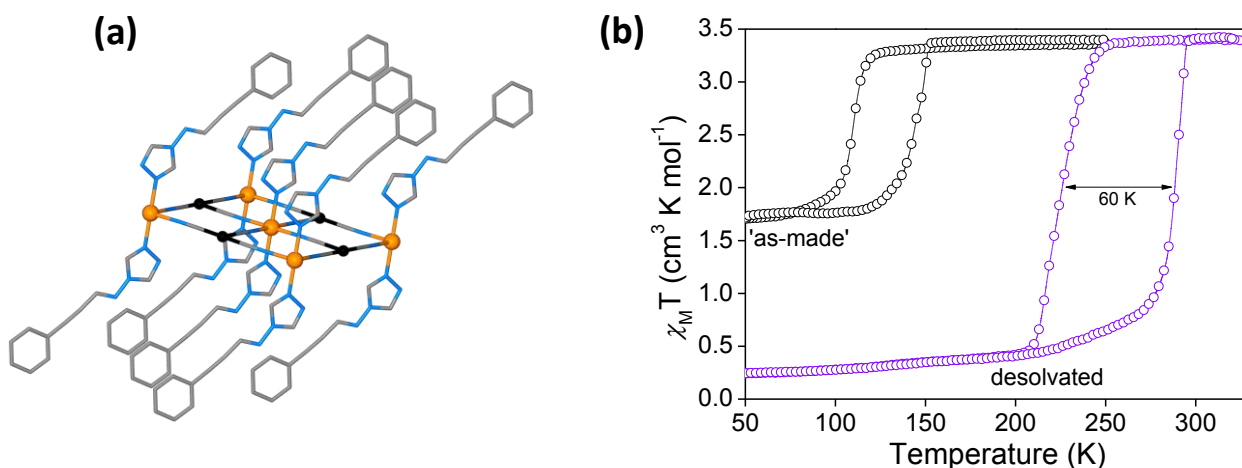
## Spin Crossover in Triazole-Based Two-Dimensional Framework Materials

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Spin crossover (SCO) is a type of magnetic switching where a  $3d^n$  ( $n = 4-7$ ) metal ion reversibly switches between a high spin (HS) and low spin (LS) state in response to temperature, pressure, or light.<sup>1</sup> One such example of materials that exhibit SCO behavior are 2-D Hofmann-type frameworks, which incorporate iron(II) SCO sites connected by rigid cyanide layers and separated by aromatic ligands. These types of materials have yielded interesting SCO behavior, such as hysteresis and room temperature spin transitions. Our focus has been to incorporate 1,2,4-triazole-based ligands into 2-D Hofmann-type materials, with recent work on the two-step SCO material  $[\text{Fe}(\text{thtrz})_2\text{Pd}(\text{CN})_4] \cdot (\text{EtOH})(\text{H}_2\text{O})$ .<sup>2</sup> To probe other interesting SCO behaviors, we have designed a longer aromatic ligand in the framework  $[\text{Fe}(\text{proptrz})_2\text{M}(\text{CN})_4] \cdot x(\text{guest})$  (proptrz = a propargyl-functionalized 1,2,4-triazole ligand, M = Pd or Pt). This material exhibits dramatic guest sensing behavior in which the guest-loaded material shows an incomplete, one-step SCO, while guest removal displays an ambient temperature spin transition with a wide hysteresis width (Figure 1).



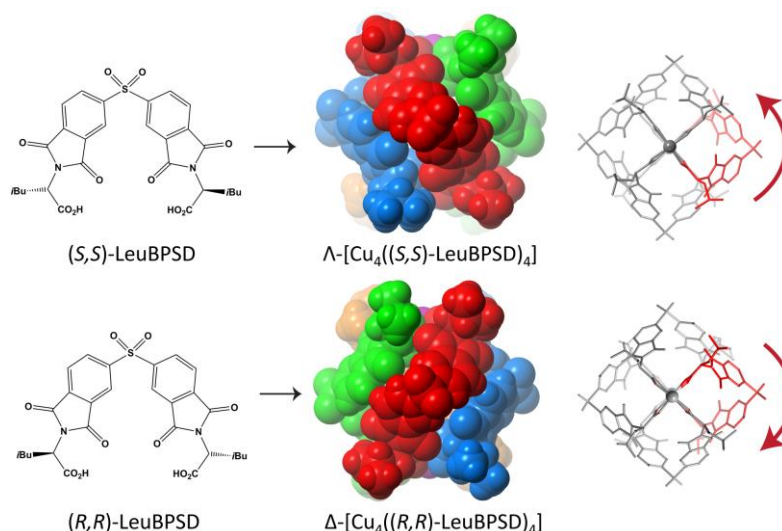
**Figure 1** (a) Single crystal structure; (b) thermal magnetic susceptibility of  $[\text{Fe}(\text{proptrz})_2\text{Pd}(\text{CN})_4] \cdot x(\text{guest})$  in the 'as-made' (black) and desolvated (purple) phases.

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# Self-Selecting Homochiral Quadruple-Stranded Helicates and Mesocates

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A series of quadruple-stranded  $\text{Cu}_4\text{L}_4$  cages have been synthesised using ligands containing a biphenylsulfonediimide core substituted with two amino acid groups. Analogous chiral complexes (helicates) and achiral complexes (mesocates) can be formed by controlling or removing the stereocentres within the ligands.<sup>1</sup> Helicates, complexes which have supramolecular chirality generated by a helical sense within the complex, are formed using enantiopure leucine-substituted ligands. These complexes contain copper paddlewheels at either end with the four ligands twisting between the  $\text{Cu}_2$  units. Changing the stereoisomer of the amino acid changes the handedness of the helicate, with *S*-leucine forming the  $\Lambda$  helicate and the *R*-leucine forming the  $\Delta$  helicate. The helicate cages are also shown to be self-selecting, as the reaction of a mixture of *S*-leucine and *R*-leucine substituted ligands forms a mixture the  $\Delta$  and  $\Lambda$  cages with no product containing both ligands. The chirality of the helicates can be disrupted by two different methods to form a mesocate. The achiral glycine derived ligand, and the racemic (*S,R*)-leucine-substituted ligand both form quadruple stranded mesocates, in which the ligands run straight 'up-and-down' the complex rather than twisting to form a helicate.



**Figure 1** Ligands containing stereocentres of opposing handedness form helicates with different supramolecular chirality.

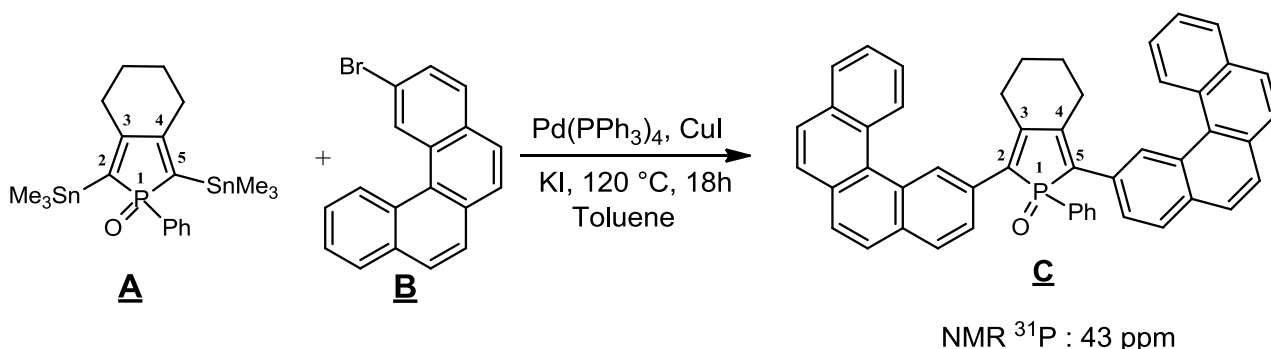
1 S. A. Boer, D. R. Turner, *Chem. Commun.*, **2015**, in press, DOI: 10.1039/C5CC07422C.

# Synthesis and physical characterization of helicene and phosphole based $\pi$ -systems

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The use of phospholes for the design of  $\pi$ -conjugated compounds provides an access to molecular materials exhibiting novel physicochemical properties. The weak aromaticity of these heterocycles favors the electron delocalization over  $\pi$ -systems usually offering a low HO-BV gap.<sup>1</sup> In addition, their properties can be easily tuned thanks to the presence of a reactive phosphorus atom.<sup>2</sup> In parallel, the inherent helical chirality of helicene skeletons provides with unique chiroptical properties (circular dichroism and high optical rotation values).<sup>3</sup> During this project, we have focused on the combination of physicochemical properties of phospholes and helicenes leading to the formation of new chiral  $\pi$ -conjugated molecules. The synthesis, photophysical and electrochemical properties of compounds such as **C** have been studied and will be described in this poster.



**Scheme 1.** Synthesis of 2,5 dibenzo[c]phenanthrenephosphole P-oxides **C**.

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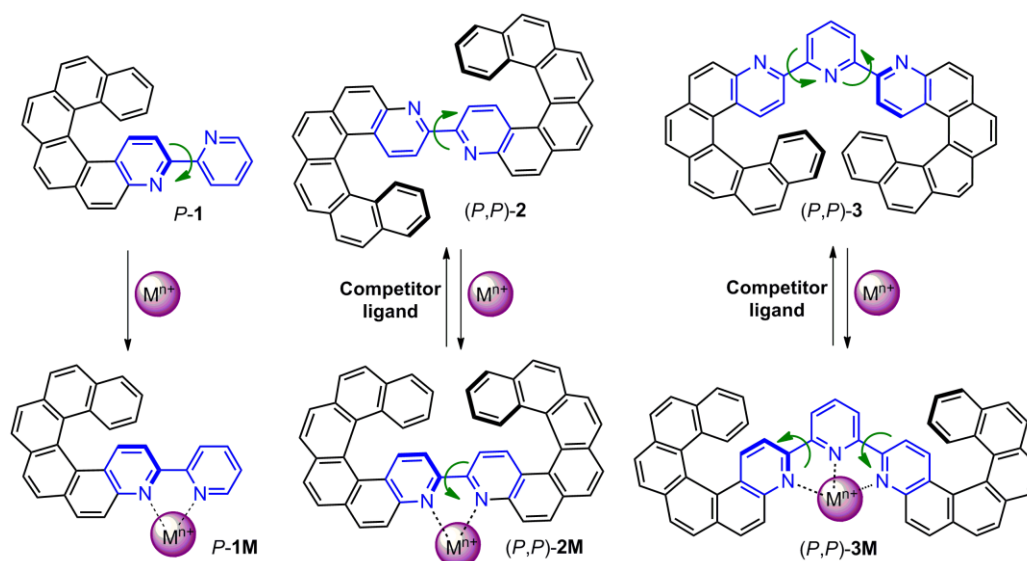
## Helicene-based chiroptical switches

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### Abstract:

The intrinsic chirality of helicenes combined with their extended  $\pi$ -conjugated system provides them with excellent chiroptical properties.<sup>1</sup> Among helicenes bearing heteroatoms, azahelicenes are especially interesting. The involvement of the nitrogen lone pair in coordination or protonation processes can induce a peculiar impact on the chiroptical properties of the helicene molecule. Our group has recently studied a [6]helicene incorporating a 2,2'-bipyridine moiety (**1**),<sup>2</sup> discovering very stable ligands with tunable chiroptical properties. Increasing the  $\pi$ -conjugated system with the aim of improving properties and switching quality, we designed structures bearing two aza-[6]helicenes, with bipyridine (**2**) and terpyridine (**3**) cores. The coordination process of the bpy- and tpy- cores involves conformational changes since the cores will rotate to accommodate the metal. In these bis-helicenic structures, we take the control of the chiroptical properties by controlling the molecular motion in the switching process.<sup>2c</sup>



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## Enantioselective Henry reaction of brominated and fluorinated nitroalcohols catalyzed by chiral oxazoline catalysts with nitromethane

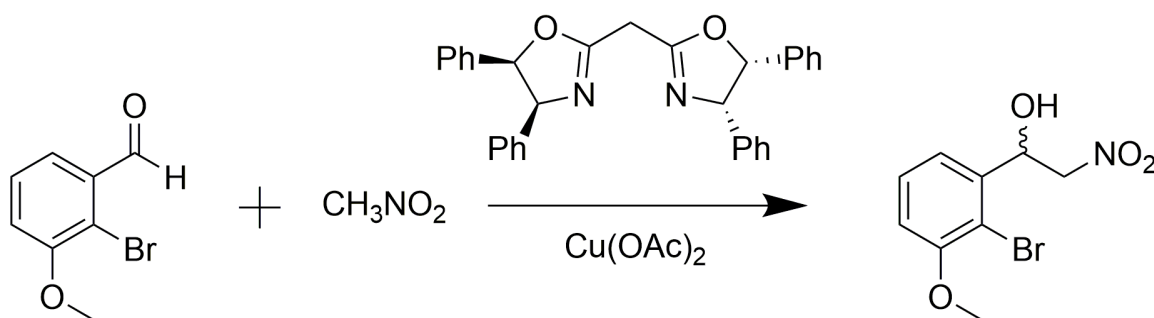
Cruz Ramírez, Harold<sup>a</sup>; Somanathan, Ratnasamy<sup>a</sup>; Aguirre, Gerardo<sup>a\*</sup>.

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Ballini and Bosica<sup>1</sup> report the Henry reaction in aqueous medium in the presence of a base, this methodology allows short reaction times, reporting yields between 66% and 95% with low costs and ecofriendly conditions.

Over the past years, recent efforts have focused on the development of catalytic enantioselective Henry reaction variants<sup>2</sup>. The current contributions to this area have been highlighted by the recent studies of Evans<sup>3</sup> and colleagues, they suggest to use oxazoline derivative complex and copper acetate as chiral catalyst in the Henry reaction, and reported enantiomeric excesses between 43 and 81%.

In this work a novel enantioselective Henry reaction are presented using a complex between different rings oxazoline (Ligand) and copper as catalyst, particularly in the reaction of nitromethane with monobrominated analogues of 3-methoxybenzaldehyde and fluorinated analogues of benzaldehyde.



**Figure 1.** Enantioselective Henry reaction.

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## When halogen bonding interactions influence the electronic properties of molecular conductors

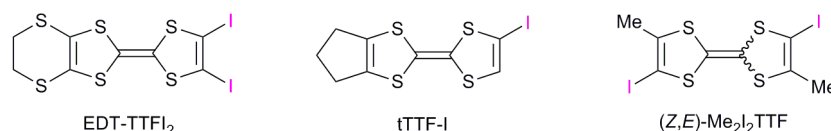
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In molecular conductors, weak intermolecular interactions taking place at the interface between the conducting stacks or slabs and the counter ion network often play a crucial role in the details of the overlap interactions, the band structure and the transport properties. Besides weak or strong hydrogen bonds,<sup>1</sup> halogen bonding interactions have been investigated for more than 15 years, at the organic/inorganic interface or within the anion layers.<sup>2</sup>

In this presentation we will highlight three different situations where halogen bonding strongly influences the structural electronic properties of charge-transfer complexes and cation radical salts. The correlation between the degree of charge transfer of the XB strength will be illustrated in (EDT-TTFI=)<sub>2</sub>(TCNQF<sub>n</sub>), where n = 0-2.<sup>3</sup> Interaction of iodo-trimethylenetetrafulvalene, tTTF-I with the non-centrosymmetrical ClO<sub>4</sub><sup>-</sup> anion favors the formation of bilayer systems with inter-layer charge disproportionation,<sup>4</sup> while Charge Order (CO) and Dimer Mott (DM) charge order processes are simultaneously observed in [(Z-Me<sub>2</sub>l<sub>2</sub>TTF)(E-Me<sub>2</sub>l<sub>2</sub>TTF)]Br phenomena.<sup>5</sup>



**Figure 1** The three iodinated TTFs used in charge transfer complexes and salts

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5 O. Jeannin, E. Canadell, P. Auban-Senzier, M. Fourmigué, *Chem. Commun.* **2016**, *52*, 308

## Synthesis of optically active P-stereogenic molecules

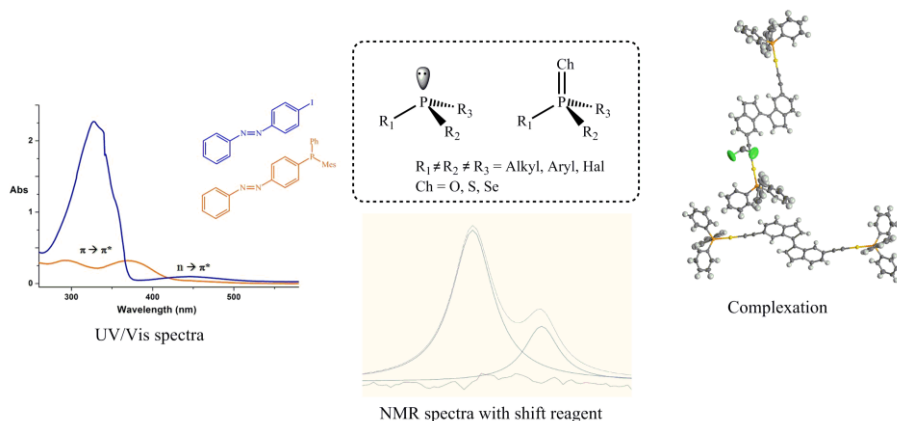
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Enantioselective reactions, especially by means of transition-metal based complexes e.g. in the context of hydroboration or olefin hydrogenation, are well known for decades.<sup>1</sup> Various P-stereogenic chiral ligands are known, containing tri- or pentavalent phosphorus atoms.<sup>2</sup>

We aspire the synthesis of asymmetrically substituted phosphorus(III)-compounds, which requires the separation of the resulting racemic mixture.<sup>3</sup> So far, many different and successful approaches regarding enantioselective syntheses and racemate resolution have been published.<sup>4,5</sup>

We were able to tailor phosphines with a variety of organic substituents with the structural motif of some P-chiral compounds shown in the figure below.



**Figure 1** Structural motif & examples for characterization and complexation.

Subsequent to the synthesis, we are interested in determining different quantitative and qualitative properties by various spectroscopic methods (NMR, UV/Vis, (PE)CD etc.).

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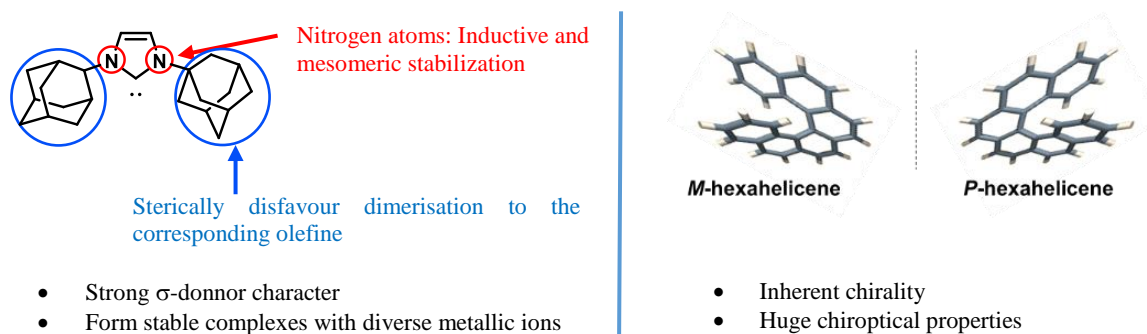
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## First NHC-helicenes complexes

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Helicenes possess a unique screw-shape and  $\pi$ -conjugated structure which provides them with particular properties such as huge optical rotation values. These helicene derivatives may have applications as chiroptical materials, in catalysis or in molecular recognition. In our group, we are investigating a diversity of applications by tuning the properties of helicenes, using either coordination or organometallic chemistry<sup>1</sup>. In order to obtain new original chiral materials with interesting properties we want to explore the association of helicenes with carbenes, namely N-heterocyclic carbenes (NHCs) in the preparation of metallic complexes. The NHC are known to have strong  $\sigma$ -donor character, to form stable complexes with a lot of metallic ions and thus to be efficient in catalysis.<sup>2,3</sup> By combining the properties of both helicenes and carbenes, our NHC-helicenes may have applications in enantioselective catalysis and in photoactive materials by association with a metallic ion. The strategy used is based on i) the synthesis of imidazolium salts with helicoidal chirality, and ii) generation of carbenic metallic complexes. Following this objective, we are synthesizing several NHC-helicene based Iridium and Gold complexes which will be tested after resolution in enantioselective catalysis reactions. Furthermore, by appropriate modifications we could obtain complexes which are expected to feature photophysical properties like luminescence.



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## Helicenes derivatives for chiral materials

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Introduction of chirality in tetrathiafulvalene (TTF) has been investigated by our group since several years and has recently provided the first experimental observation of the electrical magneto-chiral effect in a bulk molecular conductor.<sup>1</sup>

Helicenes<sup>2</sup> are original helical  $\pi$ -conjugated molecules with remarkable chiroptical properties.<sup>3</sup> Their association with the TTF unit provides new helical precursors with interesting chiroptical properties which can be modulated according to the TTF redox state. Also, we can expect original architectures in the solid state, with the presence of  $\pi$ - $\pi$  stacking between helicene units and S...S interaction between TTFs.<sup>4</sup>

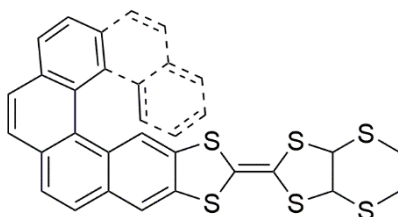


Figure 1 EDT-TTF-[n]helicene (n = 4, 6)

Such chiral electroactive precursors are of great interest since they might allow the preparation of chiral conducting materials.

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## Pd(III) Averaged Valence State above Room Temperature Induced by Hydroxy Groups of Ligand

M. R. Mian, H. Iguchi, S. Takaishi, M. Yamashita

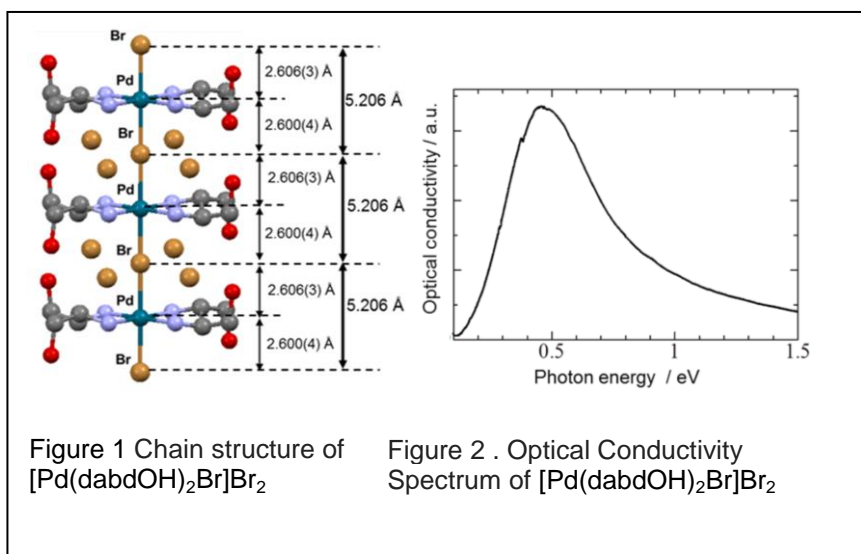
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One-dimensional halogen-bridged metal complexes (MX chains) are promising materials because of their optical and electronic properties. In addition, they have potential utility in devices, such as optical switching and computing. So far, most Ni-based MX chains are in a trivalent averaged valence (AV) state, whereas Pd and Pt-based MX chains are generally in  $M^{2+}/M^{4+}$  mixed valence (MV) states. Pd and Pt-based MX chains in AV states are promising for new strongly-correlated electron systems with small band gaps. Although Pd-based MX chains in AV state have been prepared by introducing counteranions with long alkyl chains,<sup>[1]</sup> their low crystallinities have prevented their use in optical applications.

We recently synthesized a bromo-bridged Pd-based MX chain,  $[\text{Pd}(\text{dabdOH})_2\text{Br}]\text{Br}_2$  (dabdOH = 2,3-diaminobutane-1,2-diol) (Figure 1), which is in AV state, confirmed by which was using X-ray crystal analysis, polarized Raman spectroscopy and scanning tunneling microscopy. In polarized optical conductivity spectrum of  $[\text{Pd}(\text{dabdOH})_2\text{Br}]\text{Br}_2$  (Figure 2), an intense absorption band at 0.44 eV, was observed and this is the smallest



band gap so far reported for Pd-based MX chains. Moreover, no phase transition to an MV state was observed up to 363 K. The complex shows semiconducting behavior with a high conductivity ( $0.36 \text{ Scm}^{-1}$  at 298 K) and small activation energy (81 meV).

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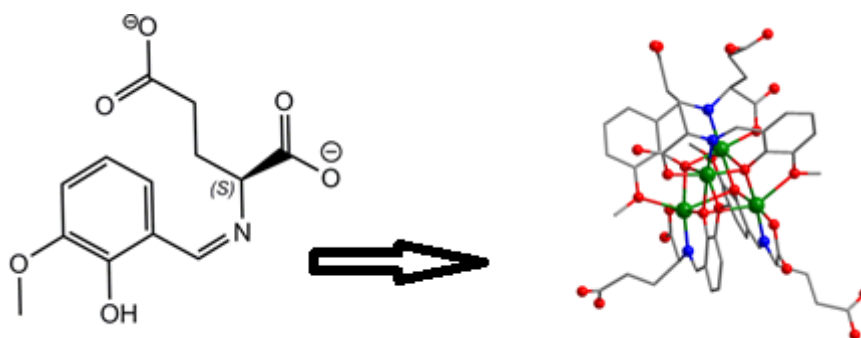
## Chiral Cubane-type $\text{Cu}_4\text{O}_4$ clusters. Synthesis, structures and chirality

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Enantiopure polynuclear complexes containing multi-metal centres represent a topic of growing interest for synthetic chemists [1]. Chiral magnets have opened up a new field of research on molecular materials which possess both magnetic and optical properties [2].

Our current research is focused on tridentate vaniline-type ligands [3] containing mainly glutamic amino-acid moieties. In this study we present the synthesis and NMR characterisation of new chiral Schiff base ligand containing glutamic acid as a chiral precursor. This ligand was further employed to obtain a chiral cubane type  $\text{Cu}_4\text{O}_4$  cluster. The physical properties (electronic, fluorescence, CD spectra) have been discussed for each compound.



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## Rational Study of the Supramolecular Self-Assembly of a Novel Family of Chiral and non-Chiral Zn(II)-Porphyrins

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Inspired by natural photosynthetic systems, which utilize chlorophylls to absorb light and carry out photochemical charge separation to use light energy, porphyrins and their derivatives are being explored as the active materials in initial OSC studies.<sup>1</sup> Studies indicate that the performances of OSCs often depend on the processing conditions, which mainly affect the non-covalent intermolecular interactions of the active materials or the morphology of the films.<sup>2,3</sup> It has been well documented that the formation of supramolecular self-assembly is an effective way for forming highly ordered structures.

In order to provide further insight in the supramolecular behavior of porphyrins, here we introduce metal ions into the central cavity of porphyrin with chiral or non-chiral substituents. Our goal is the rational design of porphyrin donors possessing (i) high solubility and strong intermolecular interactions, (ii) with chiral and nonchiral substituents attached to the tetrapyrrolic macrocyclic core as well as (iii) Zn(II) centers incorporated in the core and toward the study of their final supramolecular arrangements. Such factors might give different performances in solution-processed solar cells. We demonstrate that the supramolecular structures of the new porphyrins can be altered by the method conditions (e.g.: solvents), and for that we use single crystal X-ray diffraction.

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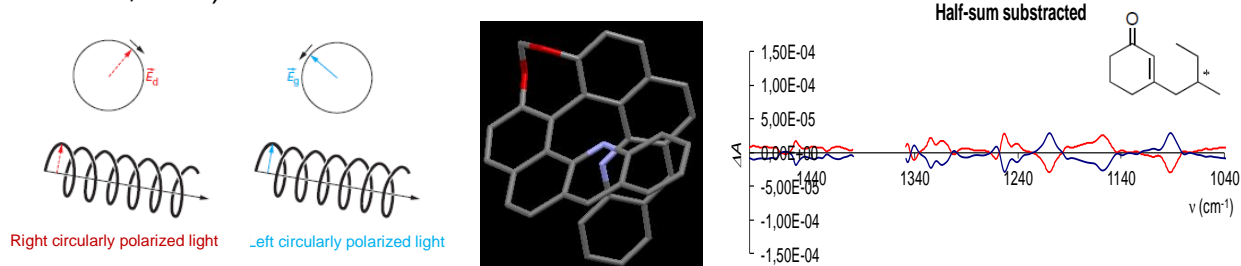
## Helicenes and chiral enones investigated by vibrational circular dichroism (VCD)

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Chirality is a crucial property for pharmaceutical development (biological recognition), organic chemistry (selective synthesis) and data transmission (polarized light). The determination of the absolute configuration of chiral molecules is crucial in those fields. Since the very first discovery by Pasteur and Biot that chiral molecules rotate the polarization of light, optical activity has been recognized to be the direct result of a geometrical arrangement and interaction of atoms in the molecules. In our group, we are investigating how the vibrational circular dichroism (VCD) spectroscopy can provide three-dimensional structural information. The VCD signal is the differences in absorption of left and right circularly polarized light passing through a sample. It is the extension of the electronic circular dichroism into the infrared region. The VCD method of analysis involves comparison of the experimentally measured VCD spectrum to the one calculated from ab initio quantum chemistry.

Here we show that thin films of helicene-like molecules can be measured and compared to the solution state. This project is conducted in collaboration with the groups of Laure Guy (ENS, Lyon), Monika Srebro (Krakow, Poland) and Jochen Autschbach (Buffalo, USA).[1] Absolute configurations of 1,4- and 1,6-adducts coming from the stereoselective conjugate addition of nucleophiles to dienones were determined and enabled to assess the stereochemistry of the reaction. This work was performed in collaboration with the groups of Marc Mauduit (ENSC Rennes) and Prasad Polavarapu (Nashville, USA).



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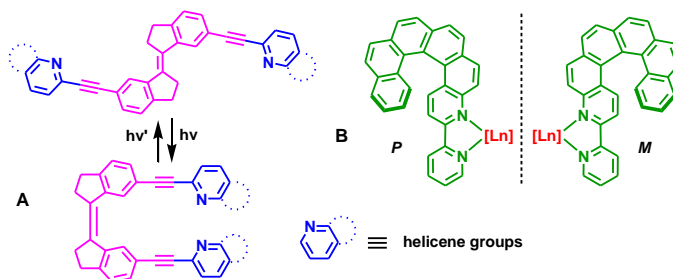
## Novel Photoresponsive switches and Emissive Complexes Based on Helicenes

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### Abstract:

Helicenes are polycyclic aromatic compounds with nonplanar  $\pi$ -conjugated skeletons which are formed by ortho-fused aromatic rings, and which show huge optical rotation (OR) and intense circular dichroism (CD) spectra.<sup>[1]</sup> Stiff stilbene exists as *E* and *Z* isomers separated by activation barrier of about 43 kcal/mol, thus making thermal isomerization negligibly slow at room temperature.<sup>[2]</sup> The combination of both helicene and stiff stilbene is expected to endow the chiral switch with appealing properties (**A**). Lanthanide coordination complexes are fascinating objects displaying peculiar magnetic and luminescent properties.<sup>[3]</sup> We successfully prepared new lanthanide complexes (**B**) based on helicene and studied their emission, magnetic properties, and chiroptical activity.<sup>[4]</sup>



**Figure 1.** Structures of photoresponsive switches and chiral lanthanide complexes.

### Reference:

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## Protonation and Binding of Substrates to $[\text{Fe}_4\text{S}_4\text{Cl}_4]^{2-}$

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Fe-S-based clusters are the active sites in a variety of enzymes including nitrogenases, aconitase and carbon monoxide dehydrogenase. How substrates are bound and transformed at these natural clusters remains poorly defined. In work presented in this poster we have focused on understanding the factors affecting substrate binding to synthetic Fe-S clusters operating in a protic environment using methodologies established earlier.<sup>1</sup> Recent DFT calculations suggest that protonation of a  $\mu_3\text{-S}$  is coupled to concomitant Fe-S bond cleavage as shown in the Figure and our results are discussed in terms of this proposal.<sup>2</sup>

Initial studies on the kinetics of the acid-catalysed substitution reactions of  $[\text{Fe}_4\text{S}_4\text{Cl}_4]^{2-}$  with PhSH in the presence of  $\text{NHR}_3^+$  (R = Me, Et, Pr<sup>n</sup> or Bu<sup>n</sup>) showed that with  $\text{NHBu}_3^+$  the mechanism involves rate-limiting proton transfer, presumably because of the bulk of the acid. In further studies the reaction between  $[\text{Fe}_4\text{S}_4\text{Cl}_4]^{2-}$  (0.2 mmol dm<sup>-3</sup>) and  $\text{NHBu}_3^+$  (10 mmol dm<sup>-3</sup>) with PhS<sup>-</sup> (2.5 mmol dm<sup>-3</sup>) was monitored in the presence of various concentrations of substrates {substrate = L = Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, RNH<sub>2</sub> (R = Me or Ph), Me<sub>2</sub>NNH<sub>2</sub>, pyridine, Bu<sup>t</sup>NC, NCS<sup>-</sup>, CN<sup>-</sup> or N<sub>3</sub><sup>-</sup>}. In all cases the rate law is that shown below and the mechanism is that shown in the Figure. The studies in the presence of the various substrates show that binding any substrate increases the rate of protonation of the cluster ( $k_1^L/k_1 > 1$ ) and the increase in rate depends on the electronic characteristics of the substrate.

### Figure

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## New photoactive Titanium based Metal-Organic Frameworks

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Metal-Organic Frameworks MOFs are one of the most recent classes of crystalline porous materials. They are currently considered as potentially useful multifunctional materials in various domains (gas storage, fluid separation, catalysis,<sup>1</sup> and more recently in biomedicine<sup>2</sup>). However, the literature on the photocatalytic activity of these solids remains scarce<sup>3,4</sup>, although the many advantages of using these materials as heterogeneous photocatalysts in comparison with classical semiconductors<sup>5</sup>. Considering the well-established photocatalytic properties of TiO<sub>2</sub>, it seems logical to focus on titanium in order to develop new MOFs for such applications. Nevertheless, because of the difficulty in controlling the reactivity of titanium ions Ti<sup>4+</sup> in solution (especially out of the very acidic conditions), very few crystalline 3D Titanium-based frameworks have been described<sup>6-8</sup>, among the thousands of MOFs known in the literature. Thus, obtaining Titanium-based crystalline solids in water and basic medium remains challenging.

We focused our interest on the exploration of the chemistry of Ti<sup>4+</sup> ions (Titanium alkoxides, complexes and oxo-clusters) with various polytopic ligands, especially hydroxycarboxylate and polycatecholate derivatives. Such ligands provide important advantages in comparison with pure carboxylates, such as a potentially higher structural diversity, stronger Ti-O bonds leading to an enhanced chemical stability in basic medium, and a strong absorption in the visible range ensured by ligand to metal charge transfer. Our recent results on the synthesis, structural characterization and properties of these new solids will be discussed.

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## Exfoliation in atomically-thin nano-sheets of 2D layered lanthanide-based MOFs

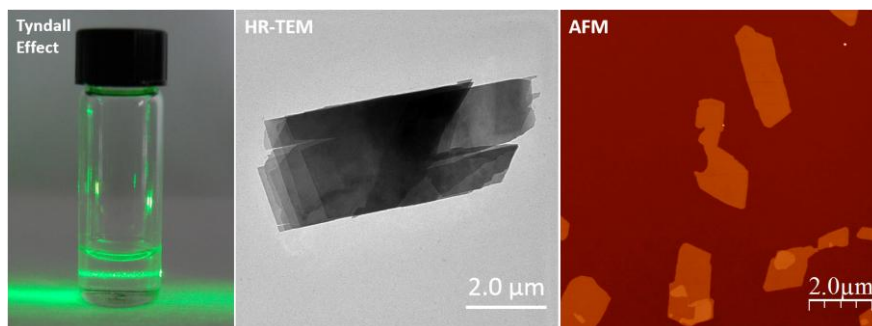
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The discovery of graphene by exfoliation of graphite resulted in a new explosion of interest in two-dimensional (2D) layered materials. The range of materials that can be exfoliated has been extended to transition metal dichalcogenides (TMDs), layered double hydroxides (LDHs) and, more recently, coordination polymers (CPs) such as metal-organic frameworks (MOFs). Here we present the exfoliation of a new family of 2D layered neutral MOFs based on lanthanide ions. These MOFs have been structurally characterized and their interesting absorption properties have been characterized. The presence of large interlayer cavities allow the intercalation of solvent molecules and the separation of the layers by solvent-mediated exfoliation. 2D flakes of nanometric thickness have been obtained by ultrasonication of the crystals in methanol and analyzed by HR-TEM and AFM measurements. These nano-sheets display lateral dimensions of several micrometers and thicknesses between 2 and 4 nm which correspond to a few layers of the material.[1]

The complete study of the exfoliation conditions have demonstrated that it is also possible to obtain small nano-sheets without ultrasonication by immersion of the crystals in a solvent, and by a micromechanical exfoliation method rarely used for the exfoliation of CPs. These results prove the ability of these MOFs to be easily exfoliated, which is essential for their integration into devices.



1 A. Abhervé, S. Benmansour, G. López-Martínez, C. J. Gómez-García, *to be submitted*.



## Noble metals containing polyoxoniobates

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The chemistry of polyoxometalates (POM) is a rapidly growing area of modern coordination chemistry. One of the emerging research lines in this field is chemistry of polyoxoniobates and tantalates, which offer various chemical challenges like generation of pentagonal building blocks<sup>1</sup>, nanosized catalysts for water splitting (WS)<sup>2</sup> etc.

We have found that reaction of  $[(C_6H_6)RuCl_2]_2$  and  $Na_8[Ta_6O_{19}]$  gives, depending on the reagent ratio, two new hybrid organometallic-POM complexes –  $Na_{10}[\{(C_6H_6)RuTa_6O_{18}\}_2(\mu-O)] \cdot 39.4H_2O$  (1:1 ratio) and  $Na_4(trans-\{(C_6H_6)Ru\}_2Ta_6O_{19}) \cdot 20H_2O$  (2:1 ratio). In both cases the half-sandwich fragments  $\{(C_6H_6)Ru\}^{2+}$  are coordinated as additional vertices to the  $\{Ta_3(\mu_2-O)_3\}$  triangles.

Reactions between  $[M_6O_{19}]^{8-}$  (M = Nb, Ta) and  $[Cp^*RhCl_2]_2$  gives  $trans-\{[Cp^*Rh]_2M_6O_{19}\}^{4-}$ , that was isolated and characterized with different methods as  $K_4[\{Cp^*Rh\}_2Nb_6O_{19}] \cdot 20H_2O$  and  $Cs_4[\{Cp^*Rh\}_2Ta_6O_{19}] \cdot 18H_2O$  correspondingly. Grafting of  $\{Cp^*Ir\}^{2+}$  fragments onto  $[M_6O_{19}]^{8-}$  (M = Nb, Ta) gives 1:1 and  $trans$ -1:2 complexes, which were fully characterized as sodium salts. These reactions also can be transferred to the recently started by us water solution chemistry of  $[(OH)TeNb_5O_{18}]^{6-}$ . We isolated and characterized  $trans-\{[Cp^*M]_2(OH)TeNb_5O_{18}\}^{2-}$  (M = Rh, Ir). Te atom locates in the central  $M_4$  plane that was found from x-ray and NMR.

In the present work complexation of platinum(IV) with  $[Nb_6O_{19}]^{8-}$  was studied with different techniques. Thus, a dimeric complex  $Cs_2K_{10}[Nb_6O_{19}\{Pt(OH)_2\}]_2 \cdot 13H_2O$  when hexaniobate  $[Nb_6O_{19}]^{8-}$  reacts with Pt(IV) in 1:1 molar ratio, while increasing of the Pt/ $Nb_6$  ratio to 2:1 gives crystals of a sandwich-type  $Cs_2K_{10}[(Nb_6O_{19})_2Pt] \cdot 18H_2O$  complex.

This work was supported by RScF 14-13-00645.

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## Syntheses and Physical Properties of Ni and Pt Nanoparticles Coated with the Metal-organic Framework HKUST-1

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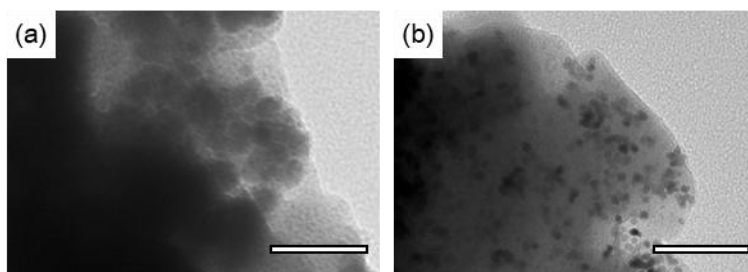
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Hybrid materials composed of metal nanoparticles and metal–organic frameworks (MOFs) have increasingly received attention in recent years because of their potential multifunctionality, such as material and energy conversion applications. Very recently, we reported Pd nanocrystals covered with the MOF, copper(II) 1,3,5-benzenetricarboxylate (HKUST-1) as a novel highly-efficient hydrogen storage material.<sup>1</sup> The hybrid material (Pd@HKUST-1) showed doubly enhanced hydrogen storage capacity and speed, compared to the bare Pd nanocrystals. The enhancement is considered to originate from a charge transfer from Pd to HKUST-1. The synergistic property of Pd and HKUST-1 promotes us to develop other hybrid material systems with HKUST-1. In this study, we focus on Ni and Pt where the constituent elements belong to the same 10 group of Pd as metal nanoparticles for hybrid materials with HKUST-1. The Ni@HKUST-1 and Pt@HKUST-1 were synthesized by a liquid phase method. The powder X-ray diffraction (XRD) patterns of Ni@HKUST-1 and Pt@HKUST-1 consisted of two kinds of Ni or Pt and HKUST-1 diffractions. The crystal sizes of Ni and Pt were estimated to be 3.4 nm and 5.1 nm from the Le Bail fitting, respectively. The TEM images revealed that the Ni or Pt nanoparticles were monodispersed (Figure). Their hydrogen storage properties were investigated and are presented.



**Figure** TEM images of (a) Ni@HKUST-1 and Pt@HKUST-1. The scale bar length is 50 nm.

1 G. Li, H. Kobayashi, H. Kitagawa, *et al.*, *Nature Materials*, **2014**, 13, 802.

## **Fluorene and spirobifluorene-based MOFs: synthesis, crystal structure and reactivity**

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Over the span of a decade, Metal-Organic Frameworks have become one of the most promising classes of synthetic materials. These compounds have potential applications in a large variety of fields, from gas storage and separation to heterogeneous catalysis, controlled drug delivery, and even chemical warfare agents neutralization. Their properties mainly rely on the framework design which can be controlled by making a judicious choice of the organic linkers and inorganic connecting units. Over the past few years members of our group focused their efforts on the synthesis and use of original di- and tetracarboxylate ligands, based on spirobifluorene or fluorene cores, exploring various sizes, geometries and dimensionalities<sup>1,2</sup>. In addition to a pure topological approach, we introduced functionalization to our MOF studies. We aimed to implement chirality for enantioselective heterogeneous catalysis and we thus synthesized new optically pure large carboxylate spacers containing chiral alkyl chains<sup>2</sup>. These ligands, when assembled through metal and rare earth building units, lead to new families of MOFs with various topologies, interpenetration degrees, stabilities, and potential porosities up to 60% of the cell volume. The systematic modulation of the size of the ligands and the number and position of the carboxylate functions will be discussed regarding the control of interpenetration and dimensionality of the obtained frameworks along with the investigation of MOF reactivity as a function of atmosphere and temperature.

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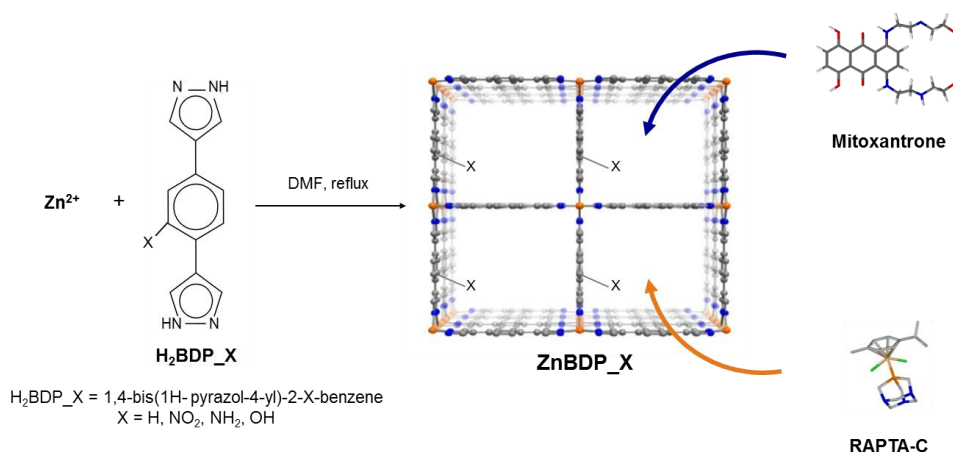
## Nanoscaled Pyrazolate PCPs as Drug Delivery Systems

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In recent years, there has been a growing interest in the design of new nanometric materials as carriers of challenging therapeutic agents, with the aim to solve important drawbacks associated with solubility, bioavailability and/or toxicity. In this regard, metal-Organic Frameworks at the nanometric scale (nanoMOFs) have emerged as promising materials for biomedical applications due to their exceptional porosity and highly tunable structures. In this context, we have optimized the synthesis of **ZnBDP\_X** nanoparticles (BDP\_X = 1,4-bis(pyrazolate-4-yl)-2-X-benzene; X = H, NO<sub>2</sub>, NH<sub>2</sub>, OH). The **ZnBDP\_OH** nanoparticles show a good structural and colloidal stability in simulated intravenous conditions as a consequence of the formation of an albumin corona on their surface that prevents aggregation. Furthermore, two antitumor drugs (mitoxantrone and [Ru(p-cymene)Cl<sub>2</sub>(pta)]; pta = 1,3,5-triaza-7-phosphaadamantane, RAPTA-C) were encapsulated within the pores of the **ZnBDP\_X**. The loading capacity of both drugs seems to directly depend on the surface area of the solids. Moreover, ligand functionalization significantly affects both the delivery kinetics and the total amount of released drug.<sup>1</sup>



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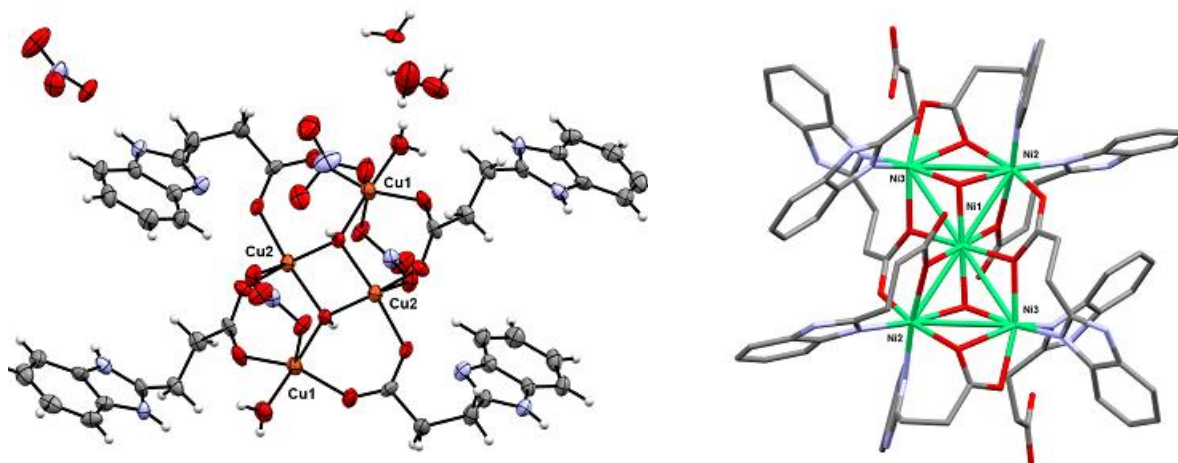
<sup>1</sup> S. Rojas, F. J. Carmona, C. R. Maldonado, P. Horcajada, T. Hidalgo, C. Serre, J. A. R. Navarro and Elisa Barea. *Inorg. Chem.*, submitted.

## Polynuclear coordination compounds with 2-benzimidazole carboxylic derivatives. Study of its chemical and structural properties.

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In recent years there has been a considerable interest in coordination compounds from benzimidazole derivatives and transition metals ions of the first and second series. A group of ligands with special features are the carboxylated derivatives, which may form mononuclear and polynuclear compounds. The number of ligands present in these coordination compounds may stabilize different geometries around the metal ion, due to the coordination modes that the carboxylate oxygen atoms may present <sup>1,2</sup>.

In this work, we investigated the coordination behavior the 2-benzimidazole propionic acid (Hbzpr) towards first transition metal ions. There were obtained polynuclear coordination compounds (dinuclear, trinuclear, tetranuclear and pentanuclear), (Figure 1). In these compounds there are several coordination modes of the carboxylate group: bidentate (chelate); bridging (one bifurcated oxygen) or via both oxygen atoms; forming a chelate ring through the imidazolic nitrogen atom and one oxygen from the carboxylate group.



**Figure 1.** Examples of the polynuclear coordination compounds with copper(II) (left) and nickel(II) (right) of bzpr.

<sup>1</sup> C. Camacho-Camacho, A. Esparza-Ruíz, A. Peña-Hueso, E. Mijangos, I. Ramos-García, R. Contreras, Flores-Parra; *Z. Anorg. Allg. Chem.* **2013**, 639, 7, 1122.

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## Porous coordination polymers based on Mn(II) and Mg(II)

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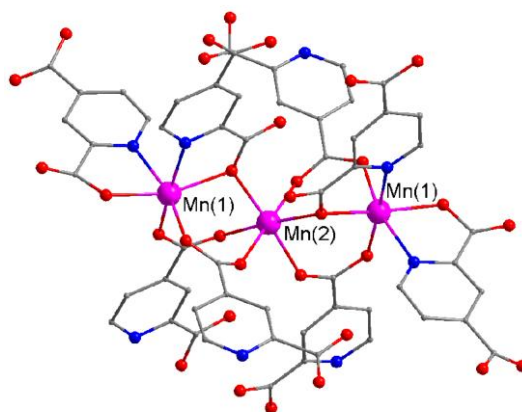
Metal–organic frameworks are a class of crystalline coordination compounds with 1, 2, or 3D structures consisting of metal ions or clusters connected by rigid organic bridging ligands. A great interest in the chemistry of these compounds comes from numerous possible applications in gas storage and separation, heterogeneous catalysis and the development of the photoactive materials. MOFs demonstrating magnetic properties can be considered for the creation of MOF-based sensors.

Herein we present two isostructural metal–organic coordination polymers  $[\text{Mn}_3(\text{pdc})_2(\text{Hpdc})_2] \cdot 3\text{DMF} \cdot 2\text{H}_2\text{O}$  (**1**) and  $[\text{Mg}_3(\text{pdc})_2(\text{Hpdc})_2] \cdot 4\text{DMF} \cdot 2\text{H}_2\text{O}$  (**2**). They were synthesized under solvothermal conditions from mixture of corresponding metal salt, 2, 4-pyridinedicarboxylic acid ( $\text{H}_2\text{pdc}$ ) and triethylamine in DMF. Crystal structure was determined by the single-crystal X-ray diffraction technique.

Compounds contain trinuclear secondary building blocks (**Fig. 1**), connected to each other by bridging  $\text{pdc}^-/\text{pdc}^{2-}$  fragments forming a microporous structure. According to the PLATON calculations, the accessible volume is 49%, and characteristic pore size is  $6 \times 4$  Å. Interestingly that compound **1** practically doesn't adsorb  $\text{N}_2$ , but adsorbs  $\text{CO}_2$ . Moreover, we observed a significant hysteresis between sorption and desorption isotherms, what was probably connected with some reversible structural rearrangements.

Magnetic measurements indicate the presence of antiferromagnetic interactions between paramagnetic atoms in compound **1** at lower temperature, and magnetic moment value corresponds to the cation  $\text{Mn}^{2+}$ .

*This work was supported by the Russian Megagrant Projects No. 14.Z50.31.0006 (Leading scientist M. Schröder).*



**Figure 1** Structure fragment of compound **1**



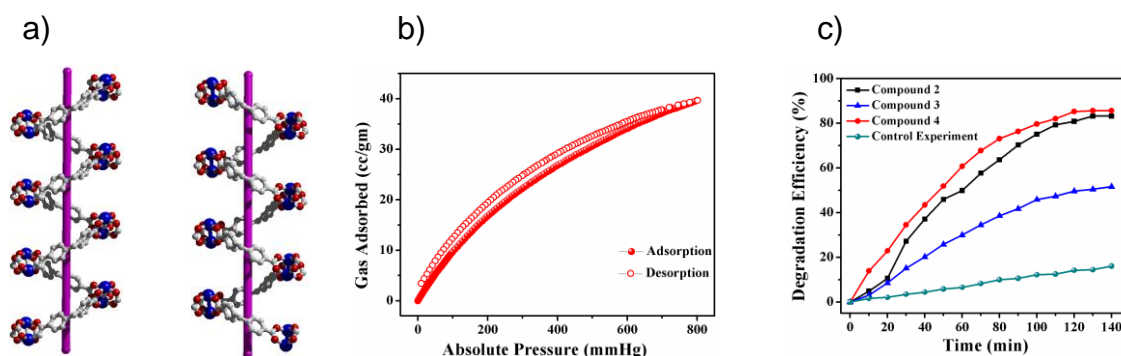
# Bis-Pyrazole Amide Based Chiral Co(II)-MOFs and their Utility in the Sphere of CO<sub>2</sub> Adsorption and Photocatalytic Waste Water Treatment

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Metal Organic Frameworks are of unabated interest in magnetism, gas adsorption, catalysis and in luminescence studies<sup>1</sup>. With interesting topology and architecture helical MOFs, in particular their chiral analogue has gained immense interest due to their application in asymmetric catalysis and chiral separation. We have constructed a series of multifunctional MOFs showing potential applications in environmental remediation. Four new Co-MOFs based on an amide based bispyrazole ligand and different carboxylic acids, with a wide variety of dimensionality, porosity and surface characteristics were exploited for this purpose. The unique bis-bidentate nature of the ligand with two chelating compartments along with a semi-rigid backbone leads to some interesting chiral MOFs. Detail self-assembly studies reveals that both helicity as well as local environments around the metal centres are responsible for chirality. The much improved photocatalytic degradation of a representative toxic dye molecule highlights the advantages of MOFs over the usual metal oxide based semiconductors as de-degrading materials. Furthermore, MOFs with an ability to capture CO<sub>2</sub> gas, offer a solution to environmental pollutions.



**Figure 1** a) Left handed and right handed helix, b) CO<sub>2</sub> adsorption isotherm collected at 298K, c) Degradation efficiency curve of Congo Red with respect to time in presence of MOFs.

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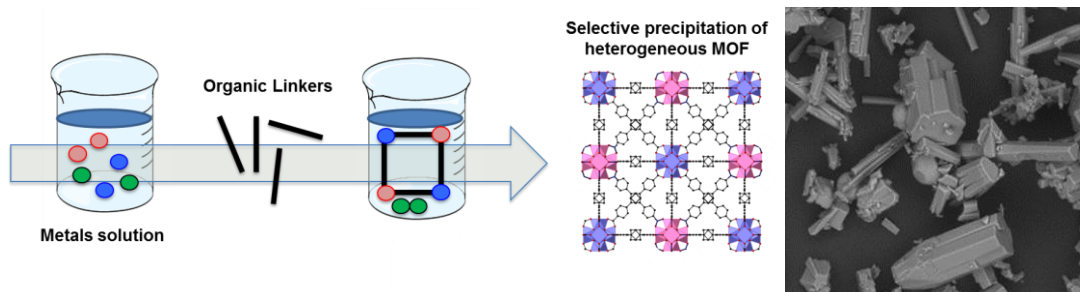
## In-Situ Precipitation of Metal-Organic Frameworks from a Simulant Battery Waste Solution

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Battery storage technologies are a crucial topic to develop clean energy. Due to new applications such as hybrid or fully electric vehicles, the production of batteries is growing dramatically. It is necessary to have an efficient metal recycling process to reduce the cost and to create a stable environmental resource management.

Metal–Organic Frameworks (MOFs) are an emerging class of porous materials constructed from metal containing nodes and organic linkers with a particular high porosity, stability and easy tunability. These materials have shown promise for diverse applications including catalysis, sensing, separations, or even as light-harvesting materials.<sup>1</sup> Our interest is to obtain a method for a selective metal precipitation to obtain MOFs that include different metals inside a same structure (Heterogenic crystalline material) that can potentially generate new activities<sup>2</sup> and give a new direction on the recycling process through the development of higher value products.



**Figure 1** Selective precipitation of porous material from multi-metallic solution<sup>3</sup>

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- 3 E. Perez, R. Navarro Amador, M. Carboni, D. Meyer, **Submitted**.

## **Control of particle size and morphology in MOFs: influence on drug encapsulation and delivery**

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CO is produced naturally in animals and acts as an important cell-signaling. However, the practical clinical use of exogeneous CO gas is currently hampered due to its strong binding to the haemoglobin. In this regard, the development of solid-storage forms of CO in combination with a specific trigger for the gas release is an important research goal.

On the other hand, metal-organic frameworks (MOFs) are considered as potential platforms for drug delivery due to the possibility of tuning their structures and pore functionalization for better drug interactions and high loadings. Not only biocompatible MOF matrixes are needed for this application. Indeed, the control of crystal morphology and particle size is of paramount importance as it strongly influences the amount of loaded drug as well as its releasing kinetics.

In this communication, we show that it is possible to control the shape and size of CYCU-3 ( $[Al(OH)(4,4'\text{-stilbenedicarboxylate})]_n$ ) particles, a biocompatible MOF showing 1D channels of 3 nm of diameter, using the coordination modulation method. Indeed, depending on the synthetic conditions, we have isolated a variety of materials ranging from small amorphous nanoparticles to highly crystalline needles in the micrometric range. In addition, we have also studied the incorporation of the CORM ALF794 ( $Mo(CO)_3(CNCMe_2CO_2H)_3$ ) in the CYCU-3 materials. Our preliminary results demonstrate that the hybrid materials ALF794@CYCU-3 are able to release CO in physiological media. Moreover, the stability of the framework as well as its adsorption capacity of ALF794 are highly affected by the crystallinity and size of the particles.

**Acknowledgement:** Spanish MINECO (CTQ2014-53486-R), Junta de Andalucía (P09-FQM-4981), COST Action CM 1105, UGR and CEI BioTic (FJC Movility grant) and JSPS (EB invitation fellowship) are acknowledged.

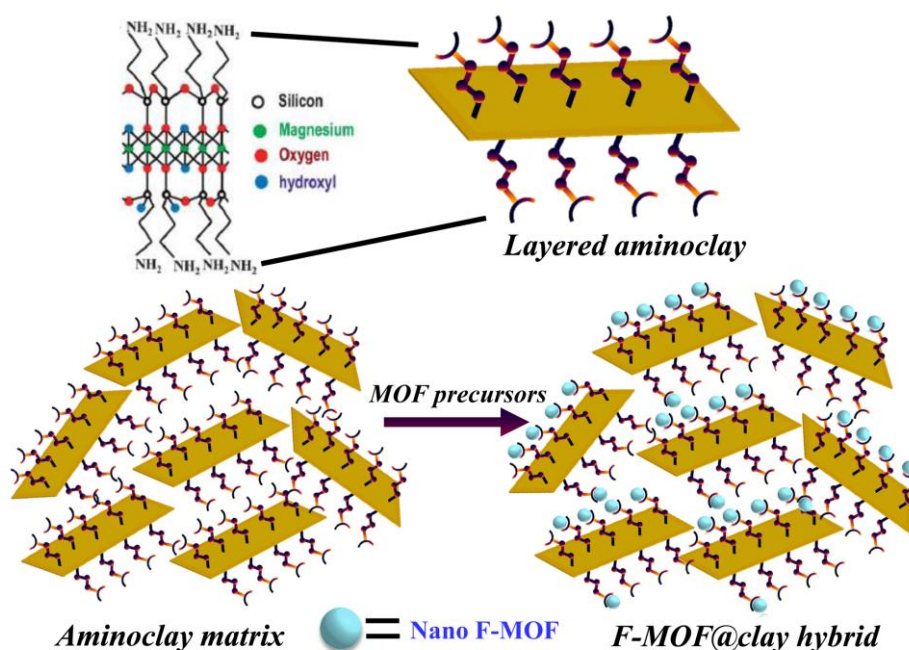
# Growth and stabilization of flexible MOF nanocrystals on aminoclay matrix towards novel MOF@clay nanohybrids

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Metal-organic frameworks (MOFs) have rapidly developed as a new class of hybrid materials with diverse functionalities.<sup>1-3</sup> Flexible MOFs (F-MOFs) can change their framework structure with guest removal/inclusion and have important applications in storage and separation. Nanoscale F-MOFs and their hybrids have emerged recently and remained largely unexplored. Here we present a novel and facile method to synthesize F-MOF nanohybrids in aminoclay matrix with enhanced gas adsorption properties. We demonstrate miniaturization of two different F-MOFs using aminoclay which acts as a functional matrix to grow and stabilize MOF nanocrystals. Several hybrids with various compositions were synthesized by varying the clay content. Enhanced guest adsorption with additional stepwise behaviour has been realized in certain hybrids. The strategy is expected to provide new route to prepare F-MOF nanohybrids with enhanced properties.



**Figure 1:** Synthesis of F-MOF@clay hybrid on layered aminoclay matrix

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## In Situ NMR Observation of Hydrogen Adsorbed inside $[\text{Cu}_3(\text{btc})_2]$ under Ambient Condition

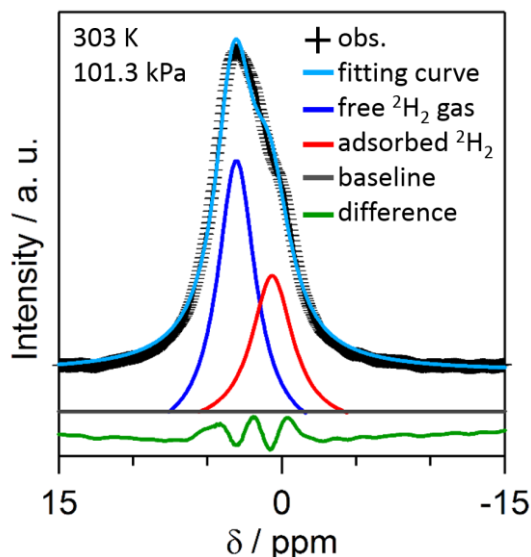
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Metal–organic frameworks (MOFs), which are porous crystalline solids composed of metal ions and organic linkers, have been studied for variable potential applications due to its high regularity and designability. In particular, MOFs have been studied as candidates for hydrogen-storage materials, and a lot of hydrogen-storage MOFs have been reported so far. In general, however, high hydrogen pressure and/or low temperatures are required to store large amounts of hydrogen in MOFs because of the low adsorption enthalpy involved in physisorption. MOFs can store very little amount of hydrogen at ambient conditions (at room temperature and below 1 atm). Under the circumstances, there are few detailed studies on the interaction between hydrogen and MOFs under ambient conditions. On the other hand, solid-state nuclear magnetic resonance (NMR) is very sensitive to hydrogen, so that NMR is expected to be powerful probe to investigate the hydrogen inside MOFs. In this study, we have focused on  $[\text{Cu}_3(\text{btc})_2]$  (HKUST-1<sup>1</sup>; btc = benzene-tricarboxylate), one of the famous hydrogen-storage MOFs, as the first investigation of hydrogen adsorption properties using in situ solid-state  $^2\text{H}$  NMR under controlled  $^2\text{H}_2$  gas pressure up to 101.3 kPa at 303 K. We first successfully observed the NMR signal of  $^2\text{H}_2$  adsorbed inside the pore, and revealed that adsorbed  $^2\text{H}_2$  molecules interacts with  $\text{Cu}^{2+}$  inside the pore.<sup>2</sup>



**Figure 1** Solid-state  $^2\text{H}$  NMR spectrum at 303 K and 101.3 kPa of  $^2\text{H}_2$  gas pressure with the fitting curves.

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## Co(II)-tricarboxylate Metal-Organic Frameworks for CO<sub>2</sub> and H<sub>2</sub> adsorption.

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Increasing environmental pollution and depletion of fossil fuel reserves<sup>1,2</sup> is creating an urgent need to find new ways to generate, store, and deliver energy while minimizing greenhouse carbon dioxide emissions. One option of doing this is to explore Metal-Organic Frameworks (MOFs) as possible reservoirs to store hydrogen for energy and for carbon dioxide adsorption. MOFs are porous crystalline materials that are formed by connecting metal ions or clusters with polytopic organic linkers. MOFs have a wide range of potential applications in gas storage, catalysis, drug delivery, sensing, separation and magnetism.<sup>3,4</sup>

In this work, two MOFs, {Co<sub>3</sub>(μ<sup>3</sup>-O)(BTC)<sub>2</sub>(H<sub>2</sub>O)<sub>4.5</sub>(EtOH)<sub>0.5</sub>(DMF)<sub>2</sub>}<sub>n</sub> (1) and {Co<sub>1.5</sub>(μ<sup>2</sup>-O)(BTB)(H<sub>2</sub>O)<sub>3.5</sub>(DMF)<sub>1.5</sub>}<sub>n</sub> (2) (BTC= 1,3,5-benzenetricarboxylate, BTB=4,4',4''-benzene-1,3,5-triyltrisbenzoate, DMF= N,N-dimethylformamide, EtOH=ethanol) were synthesized by solvothermal methods in the presence of proline (Pro) and glutamic acid (Glu) respectively. X-ray analysis reveals that (1) crystallises in the orthorhombic system with space group of *Iba2* (*a*=17.829(4), *b*=19.226(5), *c*=21.255(5) Å, *V*=7286(5) Å<sup>3</sup>, *Z*=8), while (2) crystallises in the orthorhombic system, space group *Pnma* (*a*=17.43(3), *b*=18.41(3), *c*=28.06(4) Å, *V*=9000(4) Å<sup>3</sup>, *Z*=8). The structures of these MOFs have been elucidated and their hydrogen and carbon dioxide adsorption properties will be investigated.

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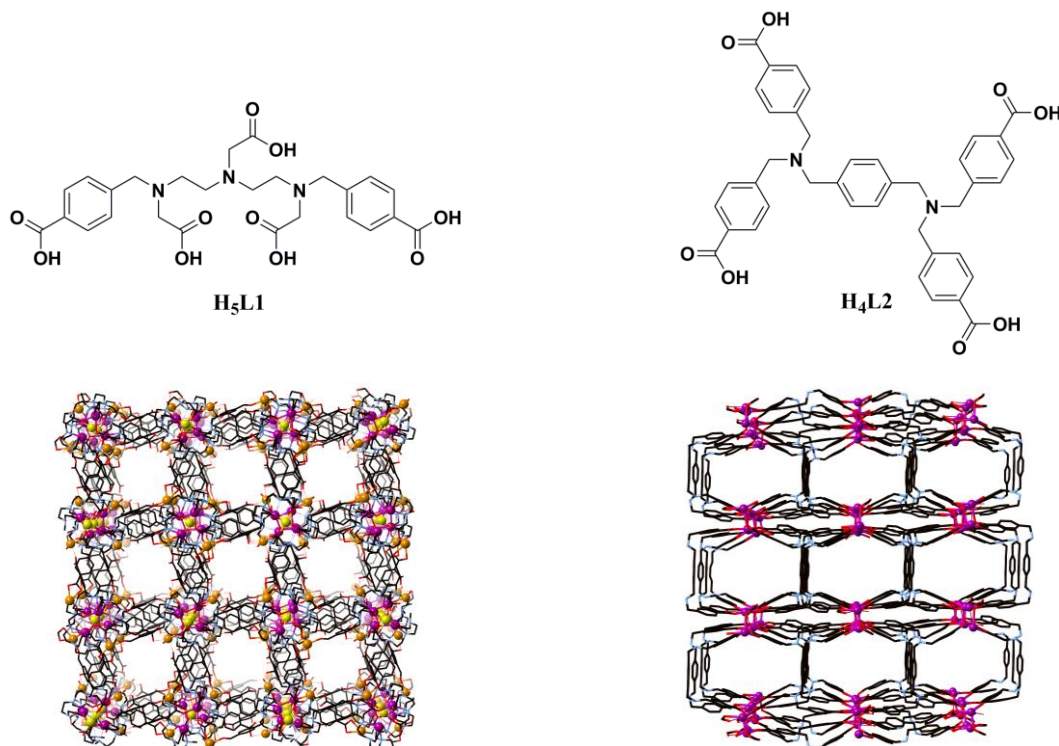
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## Coordination Polymers from Amine-Based Ligands

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By directly incorporating amine functionality into the ligand, the adsorption of CO<sub>2</sub> into porous coordination polymers has been shown to be increased in comparison to the unfunctionalised frameworks.<sup>[1]</sup> Using small polyamines such as diethylenetriamine and 1,4-bis(aminomethyl)benzene to synthesise the ligands N,N''-(4-carboxybenzyl)-N,N',N''-(carboxymethyl)-diethylenetriamine (H<sub>5</sub>L1) and N,N'-di(4-carboxybenzyl)-1,4-bis(aminomethyl)benzene (H<sub>4</sub>L2), which contain tertiary amines along the core of the ligand. Both L1 and L2 ligands are able to form three-dimensional coordination polymers which contain moderate solvent free void volumes. The framework poly-[Cd<sub>3</sub>(L1)(OH<sub>2</sub>)]·2H<sub>2</sub>O contains 1D square solvent channels with 23 % void volume, a CO<sub>2</sub> uptake of 66 cm<sup>3</sup>/g at 273 K and maintains crystallinity in water. The framework poly-[Cd<sub>2</sub>(L2)(OH<sub>2</sub>)] contains 1D hexagonal solvent channels with 37 % void volume.



**Figure 1:** The amine derived ligands H<sub>5</sub>L1 and H<sub>4</sub>L2 shown above the three-dimensional frameworks that the respective ligands form with cadmium.

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## Paramagnetic vanadium oxo complexes containing heterocyclic diimine ligands

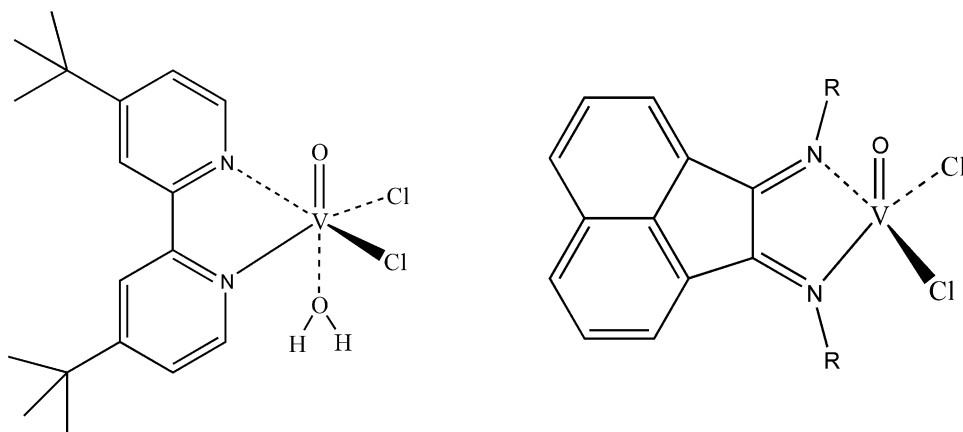
Fomenko Yakov,<sup>a,b</sup> Gushchin Artem,<sup>a,b</sup> Abramov Pavel,<sup>a,b</sup> Poryvaev Artem,<sup>b,c</sup> Sheveleva Alyona,<sup>b,c</sup> Bogomyakov Artem,<sup>b,c</sup> Sokolov Maxim<sup>a,b</sup>

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Vanadium oxo complexes represent one of the most ubiquitous classes of metal oxo functionalities and have found diverse and widespread utilization in fields ranging from bioinorganic chemistry to heterogeneous and homogeneous catalysis. In particular, vanadium oxo complexes have demonstrated efficient catalytic activity in a diverse array of transformations, including olefin epoxidation, aromatization of  $\alpha,\beta$ -unsaturated cyclohexanone derivatives, alcohol oxidations, C–C bond cleavage of glycols to the corresponding ketones, naphthol coupling, and  $\alpha$ -oxidation of hydroxyl esters and amides.<sup>1</sup> Herein we report synthesis and magnetic properties of mononuclear vanadium oxo complexes containing 4,4'-di-*tert*-butyl-2,2'-bipyridine (dbbpy) and bis(N-(2,6-diisopropylphenyl)imino)acenaphthene (R-bian), namely  $[\text{VOCl}_2(\text{dbbpy})(\text{H}_2\text{O})]$  and  $[\text{VOCl}_2(\text{R-bian})]$ , represented in Figure 1.



**Figure 1** The structure of mononuclear vanadium oxo complexes  $[\text{VOCl}_2(\text{dbbpy})(\text{H}_2\text{O})]$  (left) and  $[\text{VOCl}_2(\text{R-bian})]$ , R=2,6-diisopropylphenyl (right)

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## Guest-dependent single-ion magnet behaviour in a cobalt(II) metal–organic framework

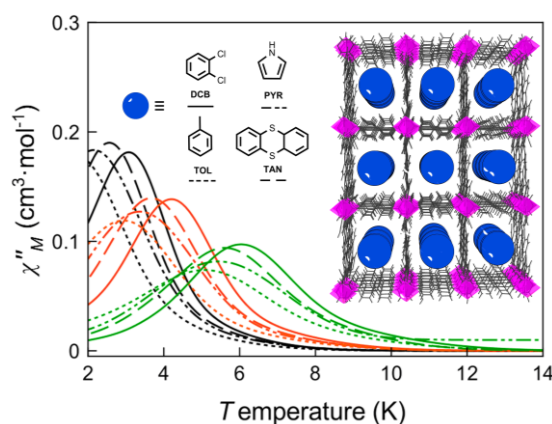
Francisco R. Fortea-Pérez<sup>a</sup>, Julia Vallejo<sup>a</sup>, Emilio Pardo<sup>\*a</sup>, Samia Benmansour<sup>a</sup>, Isabel Castro<sup>a</sup>, J. Krzystek<sup>b</sup>, Donatella Armentano<sup>c</sup> and Joan Cano<sup>\*ad</sup>

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Single-ion magnets (SIMs) are the smallest possible magnetic devices for potential applications in quantum computing and high-density information storage. Here we report a two-dimensional 2D MOF with a square grid topology built from cobalt(II) SIMs as nodes and long rod-like aromatic bipyridine ligands as linkers, and exhibiting large square channels capable to host a large number of different guest molecules. The organization of the cobalt(II) nodes in the square layers improves the magnetic properties by minimizing the intermolecular interactions between the cobalt(II) centres. Moreover, the SIM behaviour was found to be dependent on the nature of the aromatic guest molecules. The whole process could be followed by single-crystal X-ray diffraction, providing comprehensive evidence of the putative role of the solvent guest molecules that leave a “fingerprint” on the 2D structures and thus, on the cobalt environment.

**Figure 1** Such exciting properties as porosity and single-ion magnetic behavior are merged into a single unique material which affords the first in-depth study of guest-dependent SIM behavior in a MOF.



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## Synthesis and Characterization of Hexanuclear Molybdenum Clusters Containing Terminal Benzoate Ligands

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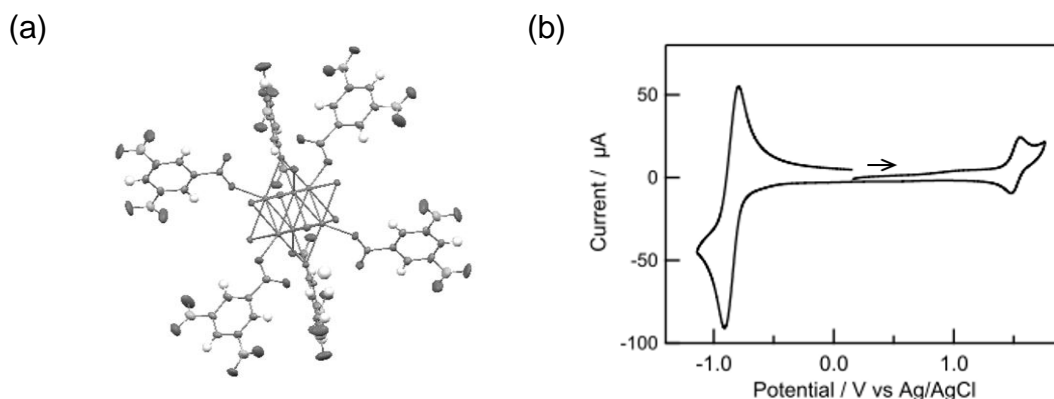
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Hexanuclear molybdenum clusters ( $\text{Mo}_6\text{X}_8\text{L}_6$ , X = Cl, Br, I; L = X, organic ligands) have been widely studied due to their long-lived electronic excited states and luminescence properties. In contrast, electrochemical studies on the clusters, in particular, electrochemical reduction characteristics, have rarely been reported because most of the clusters show irreversible reduction waves. Previously, it has been reported that the rhenium clusters with N-heterocyclic ligands exhibit stepwise one-electron reversible reduction waves<sup>1</sup>, while that with 4, 4'-bipyridine ligands show one-step two-electron reduction wave. Nonetheless, one-step multi-electron transfer beyond two electrons in the cluster has never been reported, which motivates us to design the cluster showing one-step multi-electron reduction.

In this study, we report electrochemical properties of new molybdenum clusters containing terminal benzoate ligands ( $\text{Mo}_6\text{Br}_8\text{L}_6$ ). The cluster with 3, 5-dinitrobenzoate (DNBZ,  $\text{Mo}_6\text{Br}_8(\text{DNBZ})_6$ , Figure 1a) shows one-step three-electron reduction wave as demonstrated by cyclic voltammetry (Figure 1b). We will discuss the details about the multi-electron transfer processes of  $\text{Mo}_6\text{X}_8\text{L}_6$ .



**Figure 1** (a) X-ray structure and (b) cyclic voltammogram of  $\text{Mo}_6\text{Br}_8(\text{DNBZ})_6$ .

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## Postsynthetic Improvement of the physical properties in a Metal-Organic Framework through a Single Crystal to Single Crystal Transmetalation

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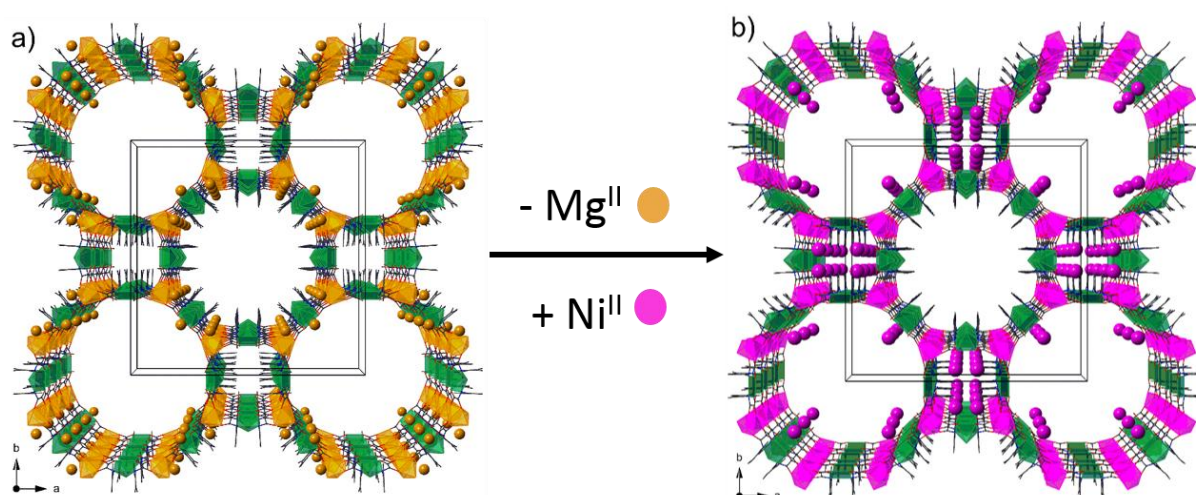
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In this work, we report the synthesis, structural characterization, and the magnetic and gas sorption properties of a novel oxamato-based three-dimensional (3D) MOF of formula  $\text{Ni}^{\text{II}}_2\{\text{Ni}^{\text{II}}_4[\text{Cu}_2(\text{mpba})_2]_3\}\cdot 50\text{H}_2\text{O}$ , where mpba is the *N,N'*-1,3-phenylenebis(oxamate) ligand. This system was obtained by a single-crystal to single-crystal transmetalation process from the previously synthesized ancestor of formula  $\text{Mg}^{\text{II}}_2\{\text{Mg}^{\text{II}}_4[\text{Cu}_2(\text{mpba})_2(\text{H}_2\text{O})_4]_3\}\cdot 45\text{H}_2\text{O}$ . After the complete replacement of the  $\text{Mg}^{\text{II}}$  ions within the covalent network and the  $\text{Mg}^{\text{II}}$  ions hosted in the large octagonal channels (Figure 1) of  $\text{Mg}^{\text{II}}_2\{\text{Mg}^{\text{II}}_4[\text{Cu}_2(\text{mpba})_2(\text{H}_2\text{O})_4]_3\}\cdot 45\text{H}_2\text{O}$  by  $\text{Ni}^{\text{II}}$  ions, an increase of the robustness occurs in the resulting 3D MOF, which is also reflected in a drastic improvement of the magnetic and gas sorption properties.[1]



**Figure 1** Perspective view of  $\text{Mg}^{\text{II}}_2\{\text{Mg}^{\text{II}}_4[\text{Cu}_2(\text{mpba})_2(\text{H}_2\text{O})_4]_3\}\cdot 45\text{H}_2\text{O}$  (left) and  $\text{Ni}^{\text{II}}_2\{\text{Ni}^{\text{II}}_4[\text{Cu}_2(\text{mpba})_2]_3\}\cdot 50\text{H}_2\text{O}$  (right) along the crystallographic *c* axis. Cu atoms are represented in green.

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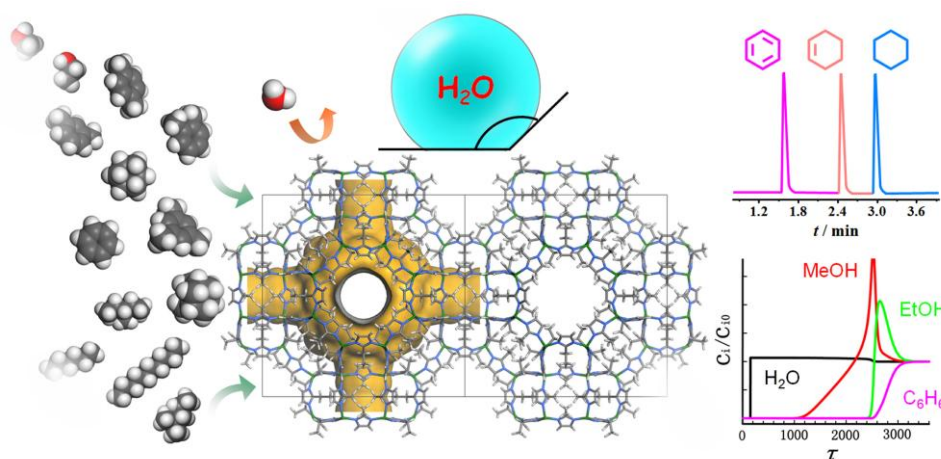
## Exceptional hydrophobicity of a large-pore metal-organic zeolite

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Porous materials combining high hydrophobicity, large surface area, as well as large and uniform pore size is very useful but rare. Here, by an in-depth study of the supramolecular isomerism of Zn(II) 2-ethylimidazolate, we achieved the bulk synthesis of high-quality MAF-6 with high purity and crystallinity, and thermal/chemical stability. Based on its unique RHO topology, this material possesses large surface area, pore volume, pore size, and aperture size,<sup>1</sup> as demonstrated by gas, vapour, liquid, and solid adsorption experiments. More importantly, it exhibits exceptional hydrophobicity on both the internal pore and external crystal surfaces, which are originated from its ethyl-lined pore surface and nanoscaled corrugation of the crystal surface. As a consequence, it can well separate organic molecules, such as alcohol and hydrocarbons, with molecular sizes ranging from methanol to C6 alkane isomers, xylene isomers, mesitylene, and adamantane, from each other and especially from water, by preferential adsorption/retention of the low-polarity guests, in a variety of application environments. These results suggest that MAF-6, an unusually large-pore and hydrophobic adsorbent consisting of cheap and non-toxic building blocks, can serve as a promising candidate for sorption and separation applications.<sup>2</sup>



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## Photoactive copper iodide clusters

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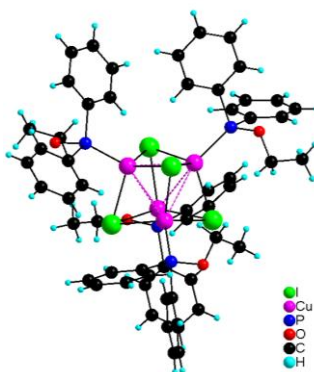
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In recent years, mechanochromic luminescent materials which exhibit reversible modification of the emission wavelength in response to external mechanical stimuli have attracted much attention because of their potential applications in optical memory devices, pressure sensing systems for instance.<sup>1</sup> Due to their promising development, the number of reported pressure sensitive luminescent compounds has exploded in the five last years with examples based on transition-metal complexes<sup>2</sup> still relatively limited compared to the organic molecules,<sup>3</sup> and mainly based on gold and platinum complexes.



**Figure 1.** Molecular structure of  $[\text{Cu}_4\text{I}_4\text{L}_4]$  (L = phosphine ligand) cubane clusters.

We report here the luminescence mechanochromism of molecular copper(I) iodide clusters of general formula  $[\text{Cu}_4\text{I}_4\text{L}_4]$  (Figure 1), whose photoemission properties are greatly modified upon mechanical solicitations. These compounds have the particularity of exhibiting both mechanochromic and thermochromic luminescence properties. In order to synthesize pressure-responsive materials, the incorporation of these clusters within polymeric matrices have been also studied.

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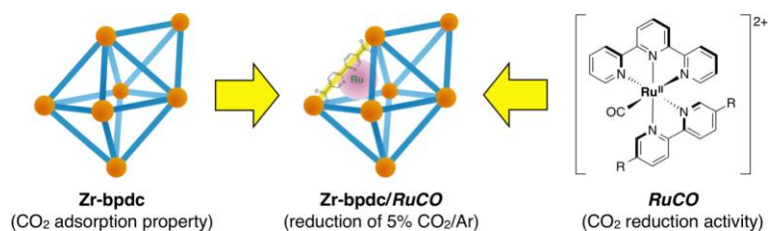
# Photochemical Reduction of Low Concentrations of CO<sub>2</sub> in a Porous Coordination Polymer with a Ru<sup>II</sup>-CO Complex

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In our current society, use of CO<sub>2</sub> as a C1 source is one of the most important topics from various aspects, such as reducing CO<sub>2</sub> emissions and developing an alternative energy resource to fossil fuels. Efficient catalytic systems for CO<sub>2</sub> reduction<sup>1</sup> and hydrogenation<sup>2</sup> using metal complexes have been developed. However, they usually need high temperature and/or high pressures of CO<sub>2</sub>. In this context, direct use of low pressures of CO<sub>2</sub> without concentration from gas mixtures, such as flue gas (5–15% CO<sub>2</sub>) is of great interest from the viewpoint of energy saving. Here we report that the integration of CO<sub>2</sub> adsorption properties of a porous coordination polymer (PCP) and CO<sub>2</sub> reduction activity of a metal complex catalyst realizes such a new catalyst system (Figure 1).

We synthesized a new PCP-Ru<sup>II</sup> complex hybrid material, **Zr-bpdc/RuCO**, by the post synthetic linker exchange method.<sup>3,4</sup> The gas sorption measurements at room temperature showed the potential of **Zr-bpdc/RuCO** for the selective adsorption from gas mixtures such as CO<sub>2</sub>/N<sub>2</sub> or CO<sub>2</sub>/Ar. The CO<sub>2</sub> reduction proceeded upon irradiation with visible light by using **Zr-bpdc/RuCO** as a catalyst, [Ru<sup>II</sup>(bpy)<sub>3</sub>]<sup>2+</sup> as a photosensitizer, and triethanolamine as an electron donor. Whereas the catalytic activity of the corresponding homogeneous catalyst decreased with lowering the CO<sub>2</sub> concentrations (diluted with Ar), that of **Zr-bpdc/RuCO** maintained even under 5% CO<sub>2</sub>/Ar gas mixture.<sup>5</sup>



**Figure 1** Integration of CO<sub>2</sub> adsorptive PCP and CO<sub>2</sub> reduction active Ru<sup>II</sup> catalyst

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## Adsorption of CO<sub>2</sub> Facilitated by Halogen Bond Interaction in the Nanospace of Porous Coordination Polymers

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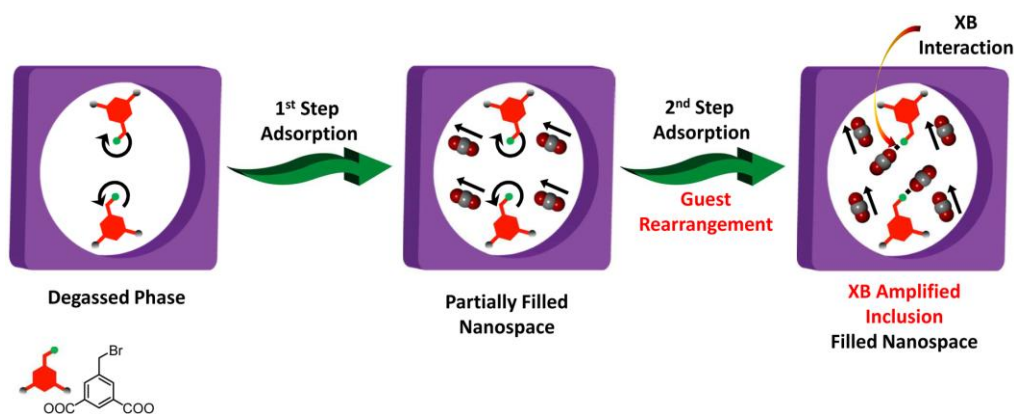
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The design and discoveries of porous coordination polymers (PCPs) during the past two decades or so have inspired materials scientists to look PCPs beyond the scope of traditional porous materials such as zeolites and porous carbon.<sup>1,2</sup> An intriguing property of the PCPs is flexibility,<sup>3,4</sup> the later combined with enormous opportunities to tune the nanospaces have made PCPs ideal candidates for applications in important areas such as gas technology, catalysis and biomedicines. Improving gas adsorption by utilizing weak interaction in flexible porous compounds is highly attractive for the design of energy efficient storage materials. Inspired with this idea, here we report a rational design to achieve such a adsorption process using synergistic functions between dynamic motion in a local module and weak host–guest interaction, viz. halogen bond (XB) in PCPs (Scheme 1).<sup>5</sup>



**Scheme 1:** Two step CO<sub>2</sub> adsorption in PCPs facilitated by XB interaction

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# Significantly Enhanced CO<sub>2</sub> Reduction Activity of Cu Nanocatalysts by Hybridization with a Metal-organic Framework

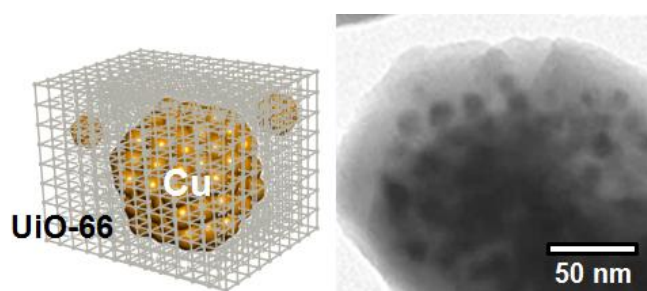
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Metal-organic frameworks (MOFs) have received much interest because of the highly versatile nature of the material, which are constructed from organic ligands connecting metal ions into a crystalline framework structure. A recent progress in the field of MOFs has been made to develop multifunctional composite materials by including metal nanoparticles to synergize with the MOF for new applications. This is an important development because the MOF can serve many functions around the metal nanoparticle, acting as a stabilizer, a discrimination filter, a co-catalyst and even acting to alter the surface reactivity of the metal nanoparticles.<sup>1</sup> Here we report novel Cu/MOF composites as an efficient CO<sub>2</sub> reduction catalyst. We selected [Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>(BDC)<sub>6</sub>] (BDC = benzenedicarboxylate) (UiO-66) with superior thermal (over 673 K), water and chemical stability as a MOF for hybridization with Cu nanoparticles.

The composite materials were synthesized by a thermal decomposition of Cu precursors in presence of UiO-66. The obtained Cu nanoparticles/UiO-66 composites were characterized by transmission electron microscopy (TEM), a powder X-ray diffraction, and N<sub>2</sub> adsorption/desorption isotherms. To investigate the catalytic activity of the composite materials for CO<sub>2</sub> reduction into methanol, we carried out activity tests using a fixed bed flow reactor. The XRD pattern of the composites consisted of two kinds of diffractions from Cu and UiO-66. TEM image revealed that the mean diameter of the Cu nanoparticles was ca. 15 nm (Figure). The hybrid catalysts demonstrated higher activity for methanol synthesis from CO<sub>2</sub> and H<sub>2</sub>, compared to Cu/γ-Al<sub>2</sub>O<sub>3</sub>.



**Figure** TEM image of Cu nanoparticles/UiO-66 composite.

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## Synthesis and reactivity of novel heterobimetallic cuboidal $\text{Mo}_3\text{CuS}_4$ clusters containing 4,4'-di-*tert*-butyl-2,2'-bipyridine

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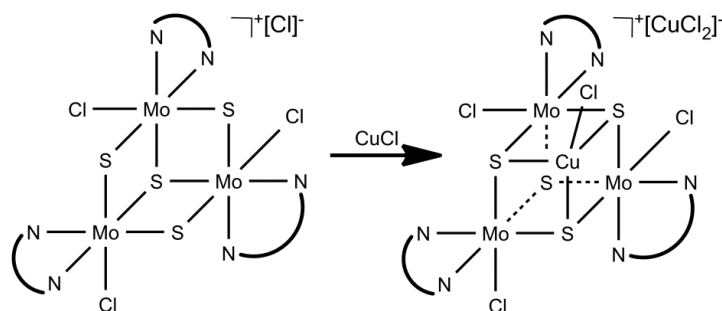
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A large variety of heterobimetallic cubane-type  $\text{M}_3\text{M}'\text{S}_4$  ( $\text{M} = \text{Mo}, \text{W}$ ) clusters was prepared in last 30 years, and their relevance in bioinorganic chemistry and organic catalysis has been demonstrated.<sup>1-3</sup> These heterometallic clusters are easily accessible by direct incorporation of a metal atom in low oxidation state into the homometallic  $\text{M}_3\text{S}_4$  clusters as shown in Figure 1.



**Figure 1** Simplified scheme for the synthesis of  $[\text{Mo}_3\text{S}_4(\text{CuCl})\text{Cl}_3(\text{dbbpy})_3](\text{CuCl}_2)$ . M-M bonds are omitted for clarity

Herein we report synthesis and reactivity of new  $\text{Mo}_3\text{CuS}_4$  diimino complexes, namely  $[\text{Mo}_3\text{S}_4(\text{CuCl})\text{Cl}_3(\text{dbbpy})_3]\text{X}$  ( $\text{X} = \text{PF}_6, [\text{CuCl}_2]^-$ ,  $\text{dbbpy} = 4,4'$ -di-*tert*-butyl-2,2'-bipyridine). Kinetic studies for  $[\text{Mo}_3\text{S}_4(\text{CuCl})\text{Cl}_3(\text{dbbpy})_3][\text{CuCl}_2]$  show that halide excess triggers the release of the cluster-bonded  $\{\text{CuCl}\}$  unit with an active role played by the  $[\text{CuCl}_2]^-$  counter-ion. The kinetic studies are supported by multinuclear NMR, ESI mass spectrometry, cyclic voltammetry and quantum chemical calculations.

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## Controlled synthesis of triol-decorated Cu-centered Anderson-Evans polyoxometalates

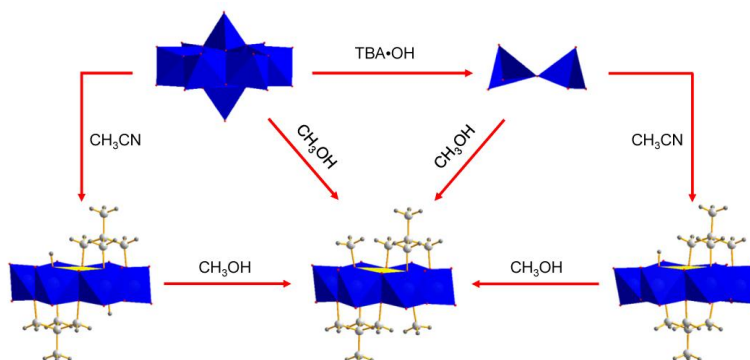
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Organic covalently decorated polyoxometalates (POMs) are one of the most important issues in POM chemistry due to its synergy between organic and inorganic materials.<sup>1</sup> As a type of disk-like POMs, Anderson-Evans POMs can be modified by triol ligands replacing partial or all  $\mu_3$ -O atoms surrounding heteroatom to form single or double-sided organic/inorganic hybrids.<sup>2</sup> Comparing with the widely investigated post-functionalization of triol ligand-grafted Anderson-Evans POMs, the reports concerning the structural types and transformations between different modification architectures, as well as the additional reaction positions, are rare.

Herein, we selected Cu<sup>II</sup> as heteroatom and synthesized a series of triol derivative-decoration Cu-centered hybrids, including a complex possessing new asymmetrical triol decoration fashion with one triol ligand replacing three  $\mu_3$ -O atoms on one side in regular position while the other replacing one  $\mu_2$ -O and two  $\mu_3$ -O atoms on the other side in malposition. In addition, we found that, by selecting as a proton solvent, methanol, the residue  $\mu_3$ -O atoms could also be replaced, to form a triol/solvent co-decorated Anderson-Evans POM (**Figure 1**).



**Figure 1** Synthesis and transformations of organically-modified Cu-centered Anderson-Evans clusters.

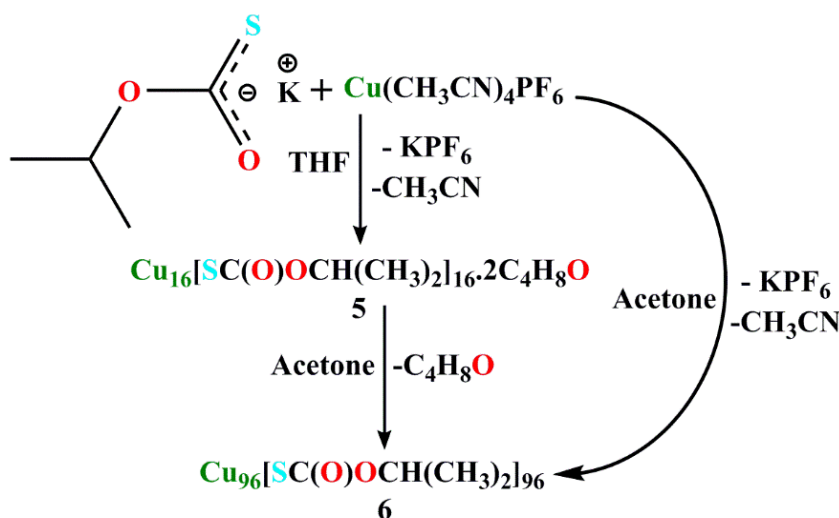
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## Hexadecanuclear Copper Monothiocarbonates: An Emissive Cluster Building Unit

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Clusters as the building unit or the network node combined with suitable linkers in the formation of supramolecules have been elegantly demonstrated recently. Herein we present a brand new cluster building unit, namely  $\text{Cu}_{16}\text{L}_{16}$ , in combination with N-donor ligands such as 4-phenylpyridine (**2**), 4,4'-bipyridine (**3**) and 2,2'-bipyridine (**4**) to yield a new series of polynuclear Cu(I) clusters stabilized by cyclohexyl monothiocarbonate ligands. Clusters **1-3** display photoluminescence (PL) ( $\lambda_{\text{max}}^{\text{em}} = 572, 568, 590 \text{ nm}$ ) while **4** displays no emission. It appears that emission properties of these clusters can be tuned by the added ancillary ligands. Intriguingly, a stoichiometric reaction of  $\text{Cu}(\text{CH}_3\text{CN})_4(\text{PF}_6)_2$  with  $\text{KSC}(\text{O})\text{OCH}(\text{CH}_3)_2$  in acetone affords a cuprous wheel,  $\text{Cu}_{96}[\text{SC}(\text{O})\text{OCH}(\text{CH}_3)_2]_{96}$  (**6**). An intermediate,  $\text{Cu}_{16}[\text{SC}(\text{O})\text{OCH}(\text{CH}_3)_2]_{16} \cdot 2\text{THF}$  (**5**), which restricted the growth of  $\text{Cu}_{96}[\text{SC}(\text{O})\text{OCH}(\text{CH}_3)_2]_{96}$  (**6**) via self assembly, was isolated in coordinated THF solvents. Both clusters **5** and **6** exhibit yellow emission in the solid state. Our results illustrate that the controlled formation of cuprous wheel  $\text{Cu}_{96}[\text{SC}(\text{O})\text{OCH}(\text{CH}_3)_2]_{96}$  from  $\text{Cu}_{16}[\text{SC}(\text{O})\text{OR}]_{16} \cdot 2\text{X}$  [ $\text{X} = \text{THF}$  (**5**), acetone (**1**)] depends on the steric bulk of the alkyl substituent on monothiocarbonates as well as the donor ability of solvents.



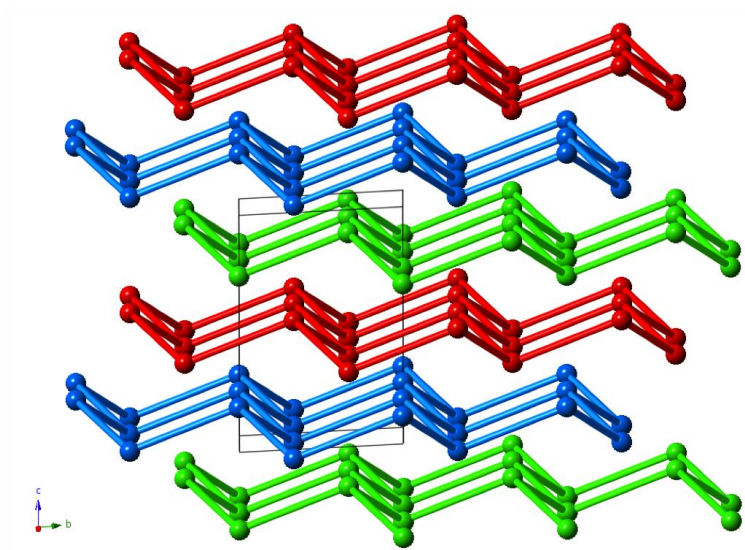
## Structures and properties of 2D porous lanthanide-based coordination polymers

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Coordination Polymers (CPs) and metal-organic frameworks (MOFs) are known for their interesting properties such as porosity, magnetism, luminescence and catalytic activity. They have been studied due to a wide range potential applications such as gas-storage, light-converting materials, sensor-development or catalysis. In this work, we elaborate a new serie of 2D lanthanide porous coordination polymers (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb) using oxygen donor aromatic ligands to prepare layered neutral coordination polymers. These CPs have been structurally characterized by X-ray diffraction analysis and present interesting absorption properties that allow insertion and exchange of different solvent and gaseous molecules. The magnetic susceptibilities of this family of layered porous networks have also been investigated.



**Figure 1.** Structure of the families of Ln-based 2D MOF used in this work



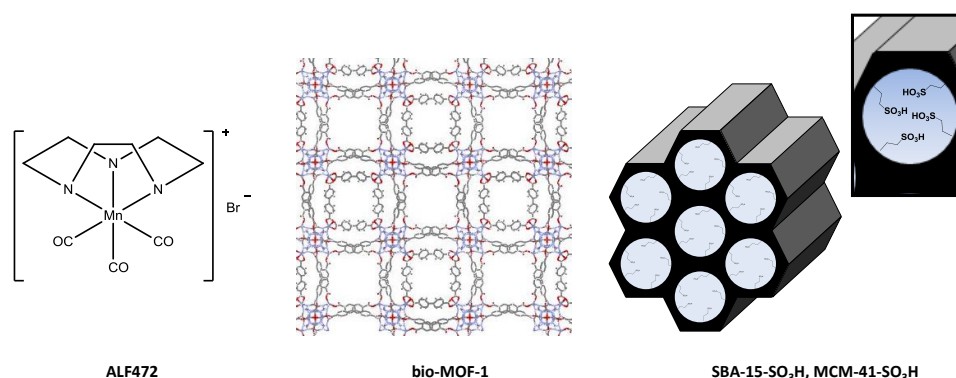
## Cation exchange strategy for the encapsulation of a photoactive CORM in anionic porous frameworks

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Carbon monoxide (CO) is known as the silent killer because of its toxicity. Nevertheless, despite its reputation as a toxic gas, CO is produced naturally in animals and plays an essential role in various important physiological as well as pathological cellular processes.<sup>1</sup> In order to exploit the therapeutic side of carbon monoxide, numerous CO releasing molecules (CORMs) have been designed for the specific delivery of exogenous CO to targeted locations. In this work, the encapsulation of a photoactive, water soluble and air stable cationic CORM [Mn(CO)<sub>3</sub>C<sub>6</sub>N<sub>3</sub>H<sub>15</sub>]<sup>+</sup>Br<sup>-</sup> (ALF472) in different inorganic porous matrixes, namely [Zn<sub>8</sub>(adeninate)<sub>4</sub>(BPDC)<sub>6</sub>]<sup>-</sup>·2(NH<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>)·8DMF·11H<sub>2</sub>O (bio-MOF-1) and the functionalized mesoporous silicas MCM-41-SO<sub>3</sub>H and SBA-15-SO<sub>3</sub>H has been performed by a cation exchange strategy. The CO-release from these loaded materials has been achieved by activation with visible light. The results show that the silica matrixes, which are unaltered under physiological conditions, slow down the kinetics of CO release allowing a more controlled CO supply, while bio-MOF-1 unstability leads to the complete leaching of the CORM.



**Figure 1.** Structures of the photoactive CORM ALF472, bio-MOF-1 and functionalized mesoporous silicas SBA-15-SO<sub>3</sub>H and MCM-41-SO<sub>3</sub>H

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## Synthesis and Rearrangement of Ring-Shaped Manganese-Substituted Phosphotungstates

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Polyoxometalates (POMs) are a large family of structurally well-defined anionic molecular metal-oxide clusters, and their chemical and physical properties can be finely tuned by selecting constituent elements, structures, or by introducing metal cations. Especially, ring-shaped POM oligomers show cation capturing behaviors due to their nucleophilic cavities, which leads to unique catalytic, magnetic, and redox properties.<sup>1</sup> Therefore, design of shape and size of ring structures is important. It is expected that chemical and physical properties of POMs can be drastically changed by transforming one oligomer into another oligomer, namely, rearrangement of POM oligomers. However, rearrangement of POM oligomers is difficult because 1) decomposition and/or isomerization of anion structures often occur or 2) stable POM oligomers hardly undergo transformation under mild conditions. Herein, we successfully demonstrated rearrangement of giant ring-shaped POM structures by utilizing organic-solvent-soluble hexavacant lacunary phosphotungstate (**I**). POM **I** was synthesized by cation exchange reaction of  $K_{12}H_2[P_2W_{12}O_{48}]$  with  $[(n-C_4H_9)_4N]Br$ , and a giant ring-shaped phosphotungstate (**II**) was successfully synthesized by the reaction of **I** with four equivalents of manganese cations in dichloromethane. The X-ray crystallographic analysis revealed that **II** consisted of a hexameric ring-shaped structure of manganese-substituted **I**. POM **II** possessed the largest inner diameter of the anion among the reported ring-shaped polyoxotungstates. By removing the organic ligands coordinated to manganese cations in **II** in chloroform, rearrangement of manganese-substituted units occurred and a smaller tetrameric ring-shaped phosphotungstate (**III**) was synthesized. In POM **III**, the anion structures of manganese-substituted **I** were maintained even after the drastic rearrangement. To the best of our knowledge, this is the first report of rearrangement of POM structures without decomposition or isomerization of monomeric anion frameworks.

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## Gas adsorption behavior in the narrow crystalline cavities of flexible peptide Ni(II)-macrocycles

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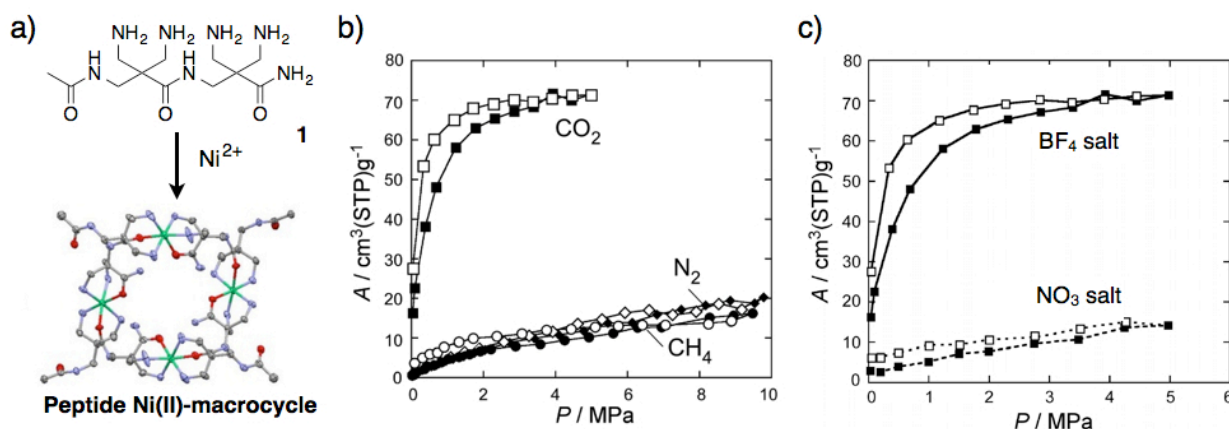
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We have recently reported crystalline tetranuclear Ni(II) cyclic complexes with a dipeptide ligand **1** possessing flexible nano-cavities.<sup>1,2</sup> Herein, we present gas adsorption behavior of the crystalline peptide Ni(II)-macrocycles and its relationship to structural transformation properties.

We revealed that the BF<sub>4</sub> salt of the peptide Ni(II)-macrocycle exhibited moderate CO<sub>2</sub> gas adsorption (ca. 6-7 CO<sub>2</sub> molecules per macrocycle), accompanied by the expansion of peptide framework<sup>1</sup>, although the diameter of narrowest part of the cavities is less than 2 Å.<sup>3</sup> In addition, the BF<sub>4</sub> salt demonstrated selective uptake of CO<sub>2</sub> gas in preference to CH<sub>4</sub> and N<sub>2</sub> gases. The estimated value for heat of adsorption of CO<sub>2</sub> gas suggested the existence of significant interactions between CO<sub>2</sub> molecules and the surface of the crystalline cavities. In contrast, NO<sub>3</sub> salt, which is pseudo-isostructural to the BF<sub>4</sub> salt in hydrated form but transforms to a densely packed structure in dehydrated form, adsorbed only a slight amount of CO<sub>2</sub> gas, suggesting that the nature of structural transformation is an important factor for gas adsorption behavior in narrow crystalline cavities.



**Figure 1** Ligand **1** and crystal structure of peptide Ni(II)-macrocycle (a) and adsorption isotherm curves of (b) various gases for the BF<sub>4</sub> salt at 293 K (c) CO<sub>2</sub> gas for the BF<sub>4</sub> salt and NO<sub>3</sub> salt at 293 K.

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## Polyoxovanadoborates Containing a $\{V_{10}O_{30}\}$ Ring and Occluded Protonated Diammines with Different Lengths

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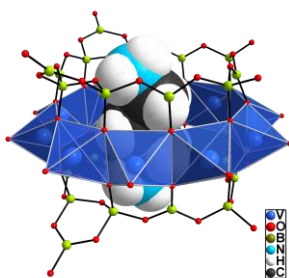
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Polyoxovanadoborates (VBO) are a class of polyoxometalates (POMs) that contain  $V^{IV}$  ( $d^0$ ) and/or  $V^V$  ( $d^1$ ) centers as five-coordinated entities  $[VO_5]$  in a square base pyramid coordination geometry, along with oxo-borate trigonal  $[BO_3]$  and tetrahedral  $[BO_4]$  units. The decanuclear open barrel-like cluster  $\{V_{10}B_{28}O_{74}H_8\}$ , and the recently reported non-centrosymmetric  $\{V_{10}B_{24}O_{66}H_8\}$ <sup>1</sup>, have the same central  $\{V_{10}O_{30}\}$  ring condensed to two polyborate crowns. The main difference between them is that the latter has an occluded protonated diammine ( $1,3\text{-DiapH}_2^{2+}$ ) within the center of the ring (Figure 1), while the former is empty. This structural difference is expected to cause an important effect in their electronic and magnetic properties. In this work, the electronic and magnetic properties of four  $\{V_{10}O_{30}\}$ -type crystalline systems are presented. The studied systems include on their central cavity on one hand only water molecules and on the other hand, protonated diamines with different lengths. Additionally, a theoretical DFT study of their electronic properties is presented.



**Figure 1.** VBO clusters of  $\{V_{10}B_{24}O_{66}H_8\}$  with a protonated diamine molecule occluded inside of it. The  $\{V_{10}O_{30}\}$  ring is shown in polyhedral representation.

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## Polyoxometalates entrapped in sol-gel matrices for reducing electron exchange column applications

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Electron exchange columns are analogous to ion exchange columns and comprise entrapment of a strong redox reagent that performs oxidation/reduction cycles with the substrate passing through the columns. Such columns are reversible in nature and are more advantageous as the entrapped redox reagent do not contaminate the products. The electron exchange columns reported so far were designed for oxidation processes and have significant drawbacks, such as relatively small redox reagents that result in leaching, and some organic ligands are more procumbent to redox sensitivity and decomposed with time.<sup>1-2</sup> Therefore in order to overcome these drawbacks, a redox active polyoxometalate was entrapped in silica sol-gel matrices for electron exchange column applications. Polyoxometalates (POMs) are the most suitable candidates for this purpose having the ability to accept/release several electrons without decomposing and changing their structure and moreover are expected to have stability for many redox cycles.<sup>3</sup> The properties of the columns strongly depend on the composition of the precursors used to prepare the matrices.<sup>4</sup> The columns exhibit good reversibility and are the first reducing electron exchange columns ever prepared.

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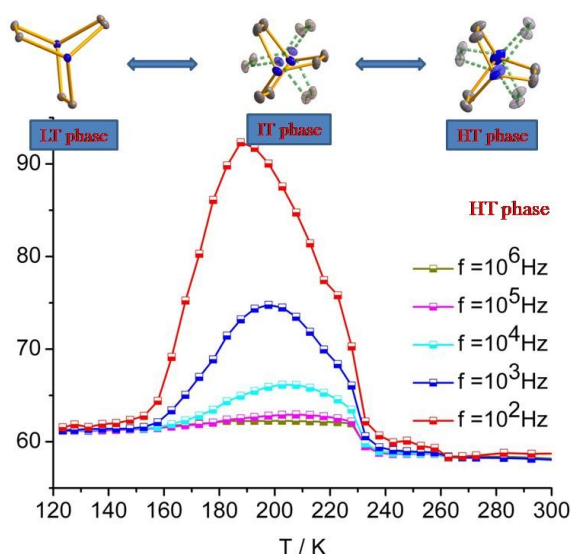
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## Two-step dielectric anomalies coupled with structural phase transitions in a co-crystal of 1,4-diazabicyclo[2.2.2]octane and 4,4'-biphenol

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The co-crystal of 4,4'-biphenol with 1,4-diazabicyclo[2.2.2]octane (**1**) was obtained using a mutual diffusion approach of a two component methanol solution at ambient temperature. DSC measurement detected that **1** undergoes two reversible phase transitions at 182 K/167 K and 236 K/229 K in a heating/cooling cycle. The phases are named: high-temperature (HT), intermediate (IT) and low-temperature (LT) ones in descending order of temperature. Each reversible phase transition corresponds to a dielectric anomaly. The single crystal structure analysis revealed that an isostructural phase transition occurs between the HT and IT phases while a symmetry-breaking structural phase transition undergoes between the IT and LT phases.



**Figure 1** Plots of dielectric permittivity versus temperature over the range 123–353 K and within frequency regions  $10^2$ – $10^6$  Hz

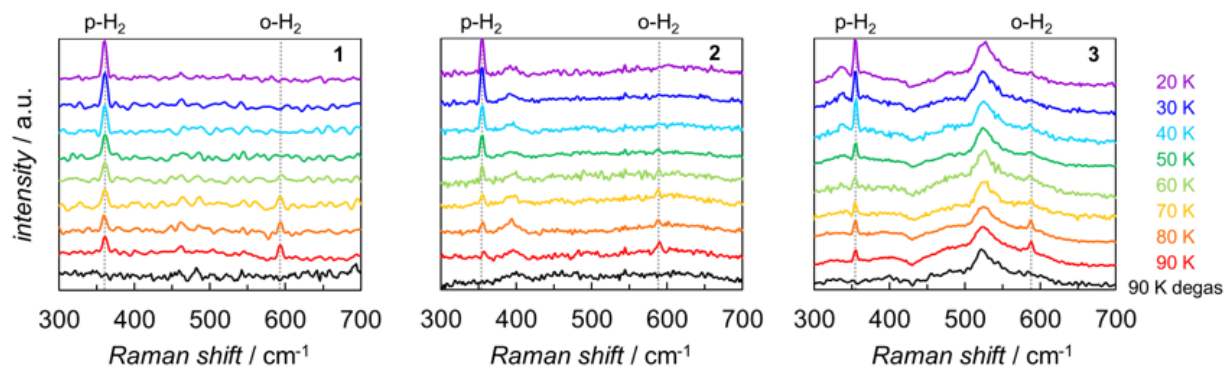
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## Nuclear Spin Conversion for Hydrogen in Porous Magnets

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Liquid hydrogen storage has a boil-off problem caused by the conversion of nuclear spin isomers for hydrogen, i.e. ortho-hydrogen (o-H<sub>2</sub>) and para-hydrogen (p-H<sub>2</sub>), in which the o-p conversion is a spin-forbidden process and exothermic reaction. To solve this problem, promotion of the o-p conversion before liquefaction using solid catalysts has been investigated so far. We have reported that a porous coordination polymer (PCP) {Fe(pyrazine)[Pd(CN)<sub>4</sub>] } accelerates the conversion greatly by perturbation of electric field gradient generated in the pores around 20 K [1]. To verify the effectiveness of PCPs for the conversion and improve the conversion temperature more, we prepared several Prussian blue analogues (PBAs) {M<sup>II</sup><sub>3</sub>[Cr<sup>III</sup>(CN)<sub>6</sub>]<sub>2</sub>} (M = Cr (**1**), Mn (**2**), Ni (**3**)) as porous magnets. These compounds are expected to accelerate the conversion at higher temperature by the inner electric and magnetic fields. We evaluated the nuclear spin state of hydrogen by in-situ Raman spectroscopy and observed two peaks around 355 and 590 cm<sup>-1</sup>, which were assigned to p- and o-H<sub>2</sub>, respectively (**Figure 1**). The peak intensity of p-H<sub>2</sub> increased with cooling, whereas that of o-H<sub>2</sub> decreased and vanished at low temperature for **1** and **2**. These results indicated that o-H<sub>2</sub> was converted to p-H<sub>2</sub> in less than 600 s, and especially in the cases of **1** and **2**, the conversion was completed around 30 and 40 K, respectively. Moreover, the conversion temperature increased by ca. 10 K after magnetization of PBAs, which suggested that the isomer ratio of absorbed H<sub>2</sub> in PBAs deviated from the Boltzmann distribution in the bulk gas state.



**Figure 1** Temperature-dependences of Raman spectra for **1**, **2** and **3**

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# Crystal Structure and Electronic Properties of Novel Four-legged MX-tube Typed Platinum Complex with Pyrazine Bridging Ligand

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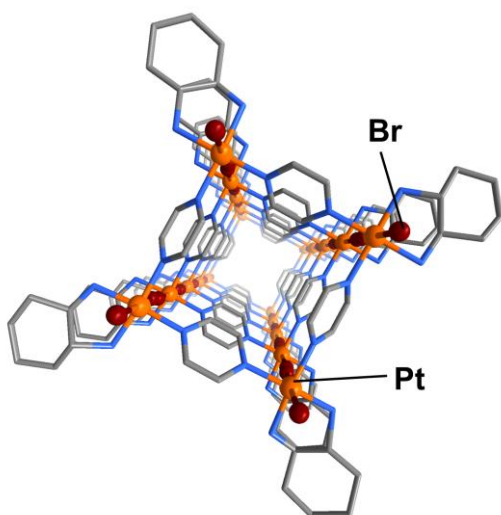
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One-dimensional halogen-bridged transition-metal complex, the so-called MX-chain, has been extensively investigated because of high tunability of their electronic states. Recently, we reported the synthesis and structural properties of two-legged MX-ladder and four-legged MX-tube complexes as extended systems of MX-chain. Moreover, we also found their unique electronic states that strongly depend on the number of constituent legs.<sup>1-4</sup> In order to investigate more variety of electronic states of the four-legged tube system, we have intended to introduce pyrazine as the bridging ligand of the four-legged platinum tube structure. In this work, we have successfully synthesized a novel four-legged MX-tube typed platinum complex [(dach)Pt(pz)Br]<sub>4</sub>(SO<sub>4</sub>)<sub>4</sub> (**1**; dach = (1R,2R)-(-)-1,2-diaminocyclohexane; pz = pyrazine). **1** has square prism-type tubular structures with a 1-D pore (pore-aperture size: ~5 Å) composed of four MX-chains and pz ligands (Figure



1). Its electronic properties were investigated using single-crystal X-ray diffraction, XPS, diffuse reflectance and Raman spectroscopic measurements. The electronic state of constituent chains of **1** was indicated to be charge-density wave (CDW: ...Pt<sup>2+</sup>...Br-Pt<sup>4+</sup>-Br...) state at low temperature. However, the valence state was strongly suggested to become close to Mott-Hubbard (MH: -Pt<sup>3+</sup>-Br-Pt<sup>3+</sup>-Br-) state above room temperature. Details of this study are reported.

**Figure 1.** Crystal structure of **1**

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## Tandem Reductive Amination between nitroarenes and aldehydes catalyzed by a Mo<sub>3</sub>S<sub>4</sub> cluster

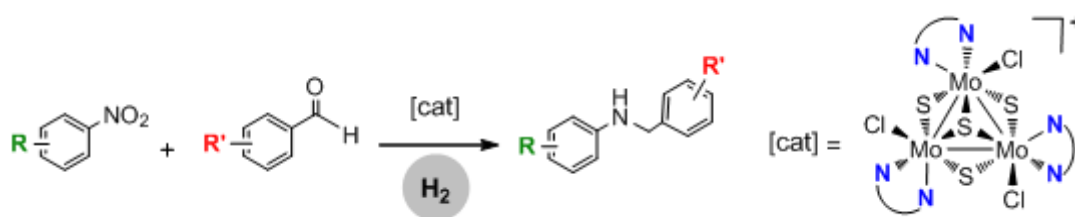
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The synthesis of amines is a very active field in industry and medicine, because they represent important building blocks in chemical and biological processes. For the synthesis of secondary amines, several methodologies have been reported, but the tandem reductive amination (Figure 1) using nitroarenes as starting materials is a clean and atom-economical alternative.<sup>1,2</sup>



**Figure 1.** Tandem Reductive Amination catalyzed by a Mo<sub>3</sub>S<sub>4</sub> cluster

Recently, we have investigated the reduction of nitroarenes under hydrosilylation conditions using a novel diamino Mo<sub>3</sub>S<sub>4</sub> cluster as catalyst.<sup>3</sup> Furthermore, this diamino complex has presented a high catalytic activity in the direct hydrogenation of nitroarenes under mild conditions.<sup>4</sup> Motivated by these results, we have studied the effectiveness of this molybdenum catalyst in the tandem reductive amination between nitroarenes and aldehydes. Herein, we present a chemoselective and environmentally attractive process to obtain a wide range of functionalized secondary amines.

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4 Unpublished results.

# Ligand Substituent-, Metal to Ligand Reaction Ratio-, Metal Starting Material- and Solvent-Control of the Metal Topology in Nickel(II) Coordination Clusters

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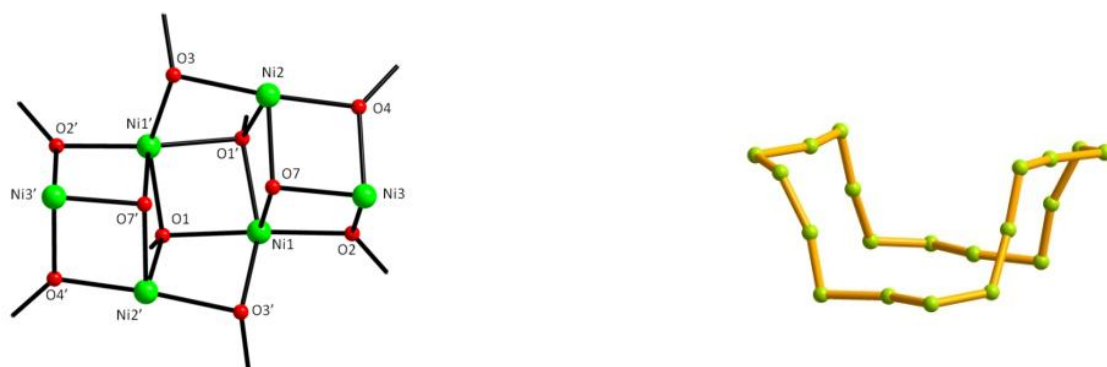
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There is currently an intense interest from many inorganic chemistry groups around the world for the synthesis, reactivity chemistry and physical study of molecular, high-nuclearity 3d-metal coordination clusters.<sup>1</sup> Nickel(II) coordination clusters have been receiving increasing attention in the areas of Single-Molecule Magnets and spin-phonon traps. We have been using more than ten ligand "blends" for the preparation of Ni<sup>II</sup> clusters. One of these consists of *N*-salicylidene-*o*-aminophenyl (saphH<sub>2</sub>) or its chloro derivative, *N*-salicylidene-4-chloro-*o*-aminophenol (4ClSaphH<sub>2</sub>), in combination with carboxylate ions (RCO<sub>2</sub><sup>-</sup>), the latter being terminal and/or bridging ligands.<sup>2</sup> We shall describe the synthesis and properties of families of clusters arising from this general reaction "blend" (Fig. 1) and we shall try to rationalize their metal topologies in terms of the ligand substituent, the metal to ligand reaction ratio, the nature of the Ni<sup>II</sup> carboxylate starting material and the reaction (but also crystallization) solvent.



**Figure 1** Structural data for Ni<sup>II</sup>/saph<sup>2-</sup> or 4ClSaph<sup>2-</sup>/RCO<sub>2</sub><sup>-</sup> clusters.

<sup>1</sup> C.J. Milios, R.E.P. Winpenny, *Struct. Bonding (Berlin)*, **2015**, 164, 1.

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# Dual Influence of Temperature and Co-existent groups on the Coordination Geometry of metal, network topologies & their properties

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During last two decades the synthesis and design of metal-organic frameworks (MOFs) or novel coordination polymers (CPs) has flourished as an emerging area of research because of their promising application in gas separation, magnetism, catalysis etc<sup>1</sup>. Recently there has been a great deal of interest in designing magnetic MOFs through the assembly of organic ligands and paramagnetic metal centers. Of particular interest is the molecular-based magnetic materials having a cryogenic magnetocaloric effect (MCE), because of their potential application as a magnetic refrigerant material.<sup>2</sup> Accordingly, a series of Co(II) MOFs are synthesized which showed different coordination geometries such as octahedral, tetrahedral, sq pyramidal, trigonal bipyramidal, and sq planar, controlled by external physical stimuli like temperature(Fig.1). All the MOFs show photocatalytic degradation of toxic dye molecules (Fig.2). On the other hand, magnetic behaviors specially to explore MCE in non-cluster-based SBU type Co MOF (MOF-2) have also been investigated (Fig.3).<sup>3</sup>

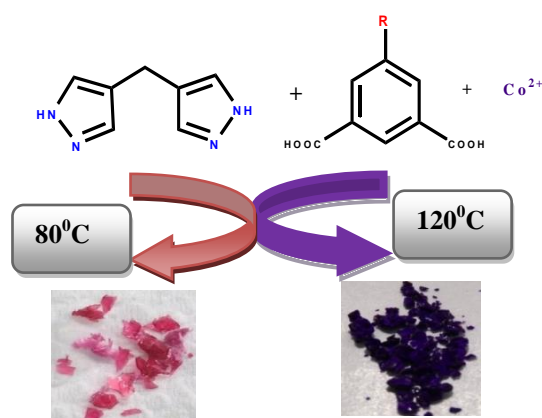


Figure 1

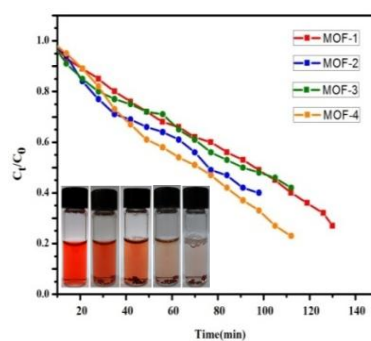


Figure 2

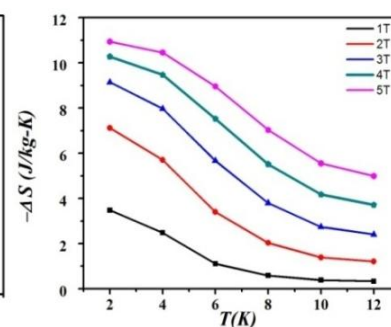


Figure 3

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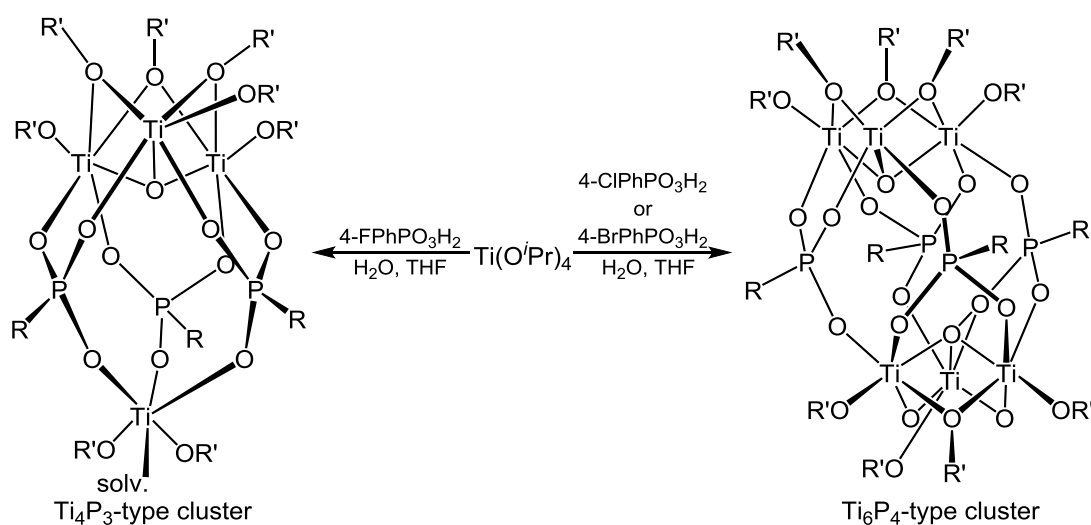
## Synthesis of titanium phosphonate clusters

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Titanium phosphonate clusters ( $Ti_4P_3$ -type cluster), which main framework comprises four titanium ions, three phosphorous ions and ten oxygen ions, are expected to one of the new raw materials to develop novel organic-inorganic hybrid materials. Main backbone of  $Ti_4P_3$ -type cluster is expected to have highly chemical and thermal stabilities due to nine strong Ti-O-P bonds. Another important point of  $Ti_4P_3$ -type cluster is the multi reaction points on titanium and phosphorus ions. These reaction points are profitable for the preparation of advanced materials by using many organic and inorganic synthetic methods. However, few studies are conducted on the investigation of the synthesis and structure analysis of titanium phosphonate clusters.

In this study, novel titanium phosphonate clusters were synthesized by the reaction of  $Ti(O^iPr)_4$  with  $RPO_3H_2$  ( $R = 4$ -fluorophenyl, 4-chlorophenyl and 4-bromophenyl) (Scheme 1).  $Ti_4P_3$ -type cluster was obtained when using 4-fluorophenylphosphonic acid. In the case of other phosphonic acid derivatives, novel titanium phosphonate clusters were obtained. These clusters comprise six titanium ions, four phosphorus ions and fourteen oxygen ions ( $Ti_6P_4$ -type cluster).  $Ti_6P_4$ -type cluster has highly symmetric structure compared with  $Ti_4P_3$ -type cluster. We also investigated their properties and preparation of organic-inorganic hybrid films utilizing  $Ti_4P_3$  and  $Ti_6P_4$ -type clusters.



Scheme 1 Synthesis of  $Ti_4P_3$  and  $Ti_6P_4$ -type clusters

## The Ag<sub>13</sub> centered cuboctahedral architecture in inorganic cluster chemistry: A DFT investigation

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Within the family of inorganic Group-11 metal clusters, the 13-atom centered icosahedral arrangement is well documented for gold<sup>1</sup> and has been also reported for silver.<sup>2</sup> This M<sub>13</sub> structure constitutes the kernel of stable mixed-valent closed-shell molecules called superatoms, in which this kernel is protected by an outer shell made of coordinated ligands and, in the case of chalcogenolate ligands, of peripheral M<sup>I</sup> cations. The stability of such superatoms is associated with “magic” electron numbers.<sup>1</sup>

An alternative pseudo-spherical arrangement for a 13-atom unit is the centered cuboctahedron, which is slightly less compact than the centered icosahedron. To our knowledge, this arrangement is very rare within the family of ligated Group-11 metal clusters. The only silver example is the [Ag<sub>13</sub>{μ<sub>3</sub>-Fe(CO)<sub>4</sub>}<sub>8</sub>]<sup>n-</sup> (n = 3, 4, 5) series.<sup>3</sup> In this communication, we rationalize by DFT calculations the electronic structure and the bonding within this series and other related hypothetical species, with emphasis on the interaction between the encapsulated atom and its host cage. Optical properties are also investigated, as well as the stability of the Ag<sub>13</sub> cuboctahedral arrangement with respect to the icosahedral one, for different electron counts.

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## Porous coordination polymers synthesis using carboxylate heterometallic complexes

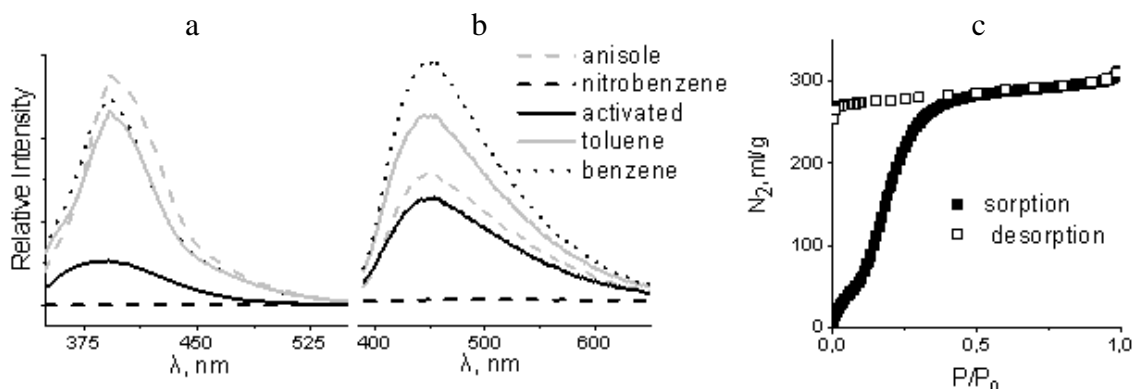
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Metal-organic coordination polymers are of interest due to practically unlimited possibilities for their structural design and important functional properties. Many porous frameworks are based on polinuclear building blocks forming by self-assembling from simple reagents (salts) during the synthesis. In this work we implement an idea of a step-by-step synthesis of coordination polymers based on pre-synthesized polinuclear heterometallic complexes. Such an approach allows more rational design of the compounds with a desired structure. Using various previously synthesized pivalate complexes as synthons we obtained a row of new metal-organic frameworks containing carboxylate fragments  $\{Zn_2Li_2(COO)_6\}$ ,  $\{Co_2Li_2(COO)_6\}$ . Their sorption properties, luminescence and framework dynamics were investigated as well (fig. 1 a,b,c). The inclusion of nitrobenzene results in complete luminescence quenching. Isotherm of  $N_2$  sorption of compound  $[Li_2Zn_2(bdc)_3(bpy)]$  contains hysteresis loop between sorption and desorption plots, what could be related to some structural rearrangement (fig. 1 c).



**Figure 1.** Luminescence spectra of compounds  $[Li_2Zn_2(bpdc)_3(dabco)]$  (a) and  $[Li_2Zn_2(bdc)_3(bpy)]$  (b), nitrogen sorption isotherm of compound  $[Li_2Zn_2(bdc)_3(bpy)]$  (c)

*This work was supported by the Russian Megagrant Projects No.14.Z50.31.0006 (Leading scientist M. Schröder).*

# New Photoresponsive Spiropyran and Spirooxazine-Polyoxometalate Hybrid Nanomaterials for High-Density Optical Data Storage

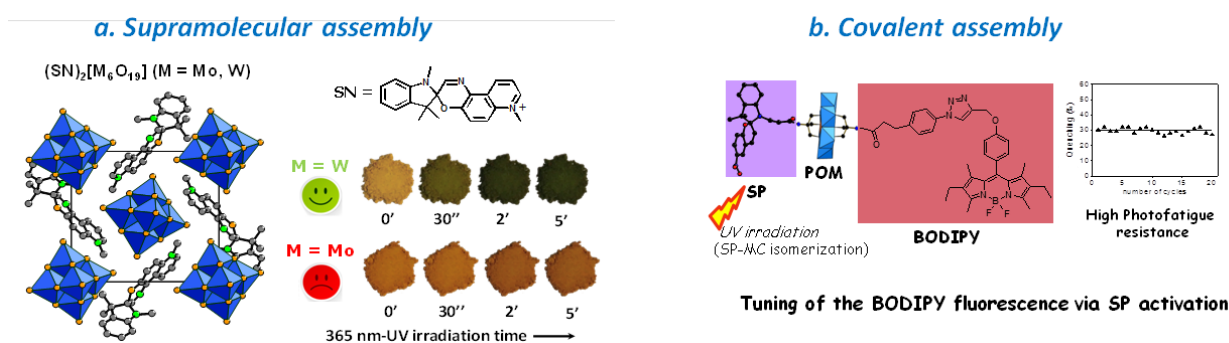
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The ionic<sup>1</sup> and covalent<sup>2</sup> combination of polyoxometalates (POMs) with photoswitchable spiropyran (SP) and spirooxazine (SN) molecules has recently led to new photochromic hybrid materials which are promising candidates in optical memory devices. Noticeably this innovative coupling constitutes an attractive opportunity to drastically improve photoisomerization of spiro-derivatives in the solid-state, which so far strongly limits their incorporation into photoaddressable devices. Some of the new hybrid systems are remarkably bistable, and the SP or SN photoconversion rate can be strongly tailored with the nature of POM units and the design of the hybrid framework (Figure 1a).

In addition, the covalent approach has recently opened up the way to new multifunctional material where a photochromic spiropyran can tune the fluorescence of a BODIPY when they are connected of the same Anderson  $[MnMo_6O_{18}]^{3-}$  platform<sup>3</sup>. These photochemically controlled systems offer a high photofatigue resistance compared to organic SP–BODIPY molecules.



**Figure 1.** a) Structure of  $(SN)_2[M_6O_{19}]$  with  $M = Mo$  or  $W$  with strong solid-state photochromism (under 365 nm excitation) in ambient conditions, b)  $(TBA)_3[MnMo_6O_{18}(SP)(BODIPY)]$  and the repeatable quenching of BODIPY fluorescence via SP photocommutation.

1a) K. Hakouk, O. Oms, A. Dolbecq, J. Marrot, A. Saad, P. Mialane, H. El Bekkachi, S. Jobic, P. Deniard, R. Dessapt, *J. Mater. Chem. C* **2014**, 1628; 1b) C. Menet, H. Serier-Brault, O. Oms, A. Dolbecq, J. Marrot, A. Saad, P. Mialane, S. Jobic, P. Deniard, R. Dessapt, *RSC Adv.* **2015**, 79635.

2a) A. Saad, O. Oms, J. Marrot, A. Dolbecq, K. Hakouk, H. El Bekkachi, S. Jobic, P. Deniard, R. Dessapt, D. Garrot, K. Boukheddaden, R. Liu, G. Zhang, B. Keita, P. Mialane *J. Mater. Chem. C* **2014**, 2, 4748; 2b) O. Oms, K. Hakouk, R. Dessapt, P. Deniard, S. Jobic, A. Dolbecq, L. Nadjo, B. Keita, J. Marrot, P. Mialane, *Chem. Commun.* **2012**, 48, 12103

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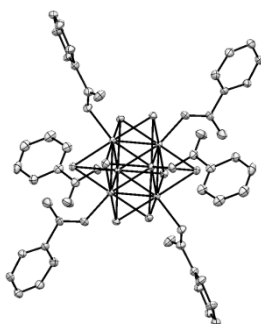


## Photophysical properties of hexamolybdenum(II) clusters having apical carboxylate ligands

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An octahedral hexanuclear cluster,  $[\{M_6(\mu-Q)_8\}L_6]^{n-}$ , shows long-lived emission (5 – 200  $\mu$ s) in the near-infrared region (600–800 nm) in both solution and crystalline phases. Owing to such emission properties, the cluster complexes have attracted wide interests in the fields of bio-imaging, organic light-emitting diodes, and so forth. However, the relationships between the structures and emission characteristics of the complexes are not necessarily investigated in detail, despite its importance toward developing highly luminescent materials. In this study, we focused our work on the emission characteristics of the  $\{Mo_6X_8\}^{4+}$  (X = Cl, Br, I) clusters having a series of apical carboxylate ligands with different  $pK_a$  values (Chart 1).









	Met	Pyv	Fur	Ben	Nap	FMet
Structure: RCOO <sup>-</sup>						
$pK_a$	4.76	5.03	3.16	4.20	3.69	0.52

Chart 1. Structures of  $[\{Mo_6X_8\}(OCOC_6H_5)_6]^{2-}$  (left) and apical ligands (right)

$[\{Mo_6X_8\}(OCOR)_6]^{2-}$  (X: halide, OOCR: carboxylate anion) was synthesized by similar procedures to those reported previously<sup>1</sup>. The emission spectra and lifetimes of these clusters were dependent on the  $pK_a$  value of the apical ligand and the emission spectrum shifted to the higher energy with a decrease in the  $pK_a$  value of the apical ligand. The spectroscopic, photophysical, and electrochemical properties of the clusters, including zero-magnetic-field splitting in the excited triplet states, will be presented.

1. M. N. Sokolov, M. A. Mihailov, E. V. Peresyphkina, K. A. Brylev, N. Kitamura, and V. P. Fedin, *Dalton Trans.*, **2011**, 40, 6375

## Colorimetric Alkane Sensing using Porous Coordination Framework

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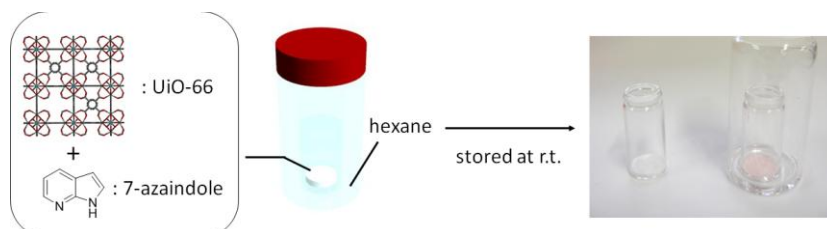
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Exceptional challenges have confronted the rational design of colorimetric sensors for saturated aliphatic hydrocarbons. The main reasons for this difficulty are the extremely nonpolar nature of these targets and their lack of functional groups that can interact with probes.

Porous coordination polymers (PCPs), or metal-organic frameworks, that are crystalline porous materials constructed from coordination bonds between metals and organic linkers, have attracted considerable attention not only for gas adsorption and separation but also for sensor applications, as it is possible to modulate their pore size, shape and functionality with the judicious choice of metal nodes, organic linkers.<sup>1</sup>

In this work, we show new synthetic strategy towards colorimetric alkane sensing with PCPs, in which the interactions between the defect site inside framework and 7-azaindole as guest molecule play a pivotal role.

The colorimetric alkane sensing was achieved with the mixed powder of Zr-based MOF, UiO-66:  $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bdc})_6]_n$  (bdc = benzene-1,4-dicarboxylate)<sup>2</sup> and 7-azaindole, whose color was changed from white to pink under hexane vapor atmosphere (Figure 1). In the case of other polar solvents such as methanol, no colorimetric change was observed, meaning that less polar solvents can induce the inclusion of 7-azaindole inside the framework, as confirmed by NMR measurements. The details of this unique colorimetric phenomena would be discussed in this poster presentation.



**Figure 1** Colorimetric change of the sample before and after hexane vapor exposure

1 S. Kitagawa, R. Kitaura and S. Noro, *Angew. Chem. Int. ed.*, **2004**, *43*, 2334.

2 M. J. Katz, Z. J. Brown, Y. J. Colón, P. W. Siu, K. A. Scheidt, R. Q. Snurr, J. T. Hupp and O. K. Farha, *Chem. Commun.* **2013**, *49*, 9449.

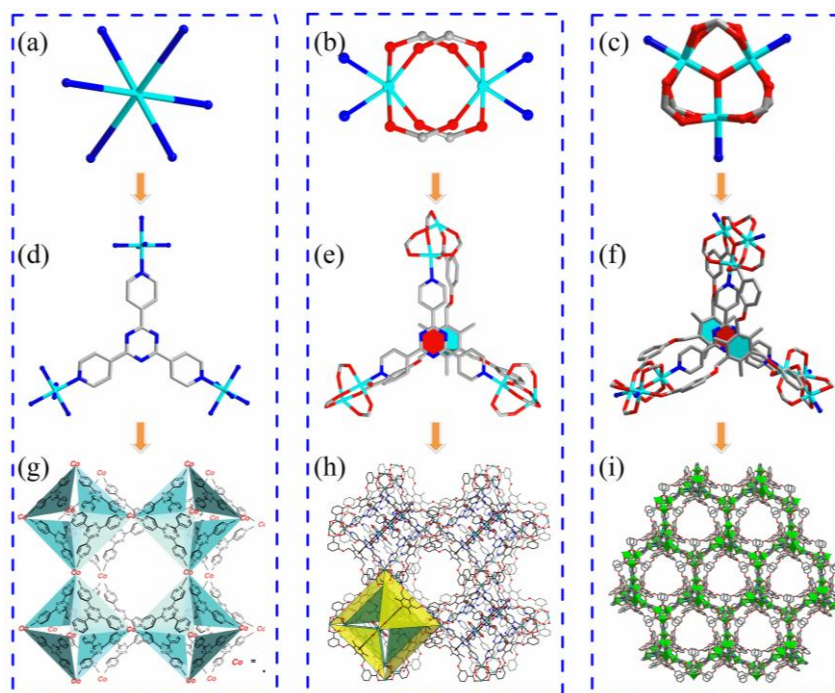
# A Mixed Molecular Building Block Strategy for the Design of Multi-walled Metal–Organic Frameworks

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Synthetic strategies of MOFs[1] play a significant part in preparing new and distinctive materials. One of the most attractive targets in this field is to adjust and control the geometry and recognition properties of the pore. Here, we present a mixed molecular building block (MBB) strategy for the syntheses of three multi-walled MOFs. The structural analyses of these the multi-walled MOFs indicate that the size-matching between different molecular building blocks plays an important role in the assembly procedure. We anticipate that the proposed mixed MBB strategy could not only offer a new platform for developing novel MOF structures, but also provide new insights into the functionalization of this class of crystalline materials.



**Figure 1** The single-, double- and triple-walled MOFs.

1 D. Tian , Q. Chen , Y. Li , Y. H. Zhang , Z. Chang, X. H. Bu\*, *Angew. Chem., Int. Ed.* **2014**, 53, 837.

2. D. Tian, J. Xu, Z.J. Xie, Z.Q. Yao, D.L. Fu, Z. Zhou, X.H. Bu\*, *Adv. Sci.* **2015**, 1500283.

# Magnetic and Guest Adsorption Properties of Hofmann-type Porous Coordination Polymer Solid Solutions

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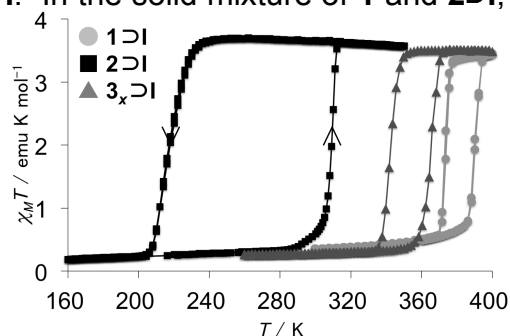
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Porous coordination polymers (PCPs) having designable and highly-ordered frameworks provide a multifunctional platform linking between uptake/release of guest molecules and physical properties of framework. We have systematically researched on Hofmann-type PCPs  $\{\text{Fe}^{\text{II}}(\text{pz})[\text{M}^{\text{II}}(\text{CN})_4]\}$  (pz = pyrazine;  $\text{M}^{\text{II}} = \text{Pt}$  (**1**), Pd (**2**)), showing spin transition near room temperature with a hysteresis width of 20 K. Their spin transition behaviors were drastically changed depending on guest molecules<sup>1</sup>.

Compounds **1** and **2** exhibited quite different spin transition behaviors with responding to  $\text{I}_2$  guest molecule<sup>2</sup>. In the case of **1**, iodine coordinated to the Pt(IV) centers as  $\text{I}^-$  and it formed a mixed valence  $\{\text{Fe}(\text{pz})[\text{Pt}^{\text{II/IV}}(\text{CN})_4(\text{I})]\}$  (**1** $\supset$ **I**), in which the spin transition temperature increased by 100 K ( $T_c^\uparrow = 398$  K). On the other hand, **2** confined iodine as  $\text{I}_2$  molecules in the framework through interactions with pz and Pd(II), and it formed a clathrate  $\{\text{Fe}(\text{pz})[\text{Pd}(\text{CN})_4] \cdot 0.95\text{I}_2\}$  (**2** $\supset$ **I**). Its hysteresis width increased to 94 K ( $T_c^\uparrow = 310$  K and  $T_c^\downarrow = 216$  K).

In this work, we prepared solid solutions incorporating Pt and Pd centers  $\{\text{Fe}(\text{pz})[\text{Pt}_x\text{Pd}_{1-x}(\text{CN})_4]\}$  (**3**<sub>x</sub>) and their  $\text{I}_2$  adsorbent **3**<sub>x</sub> $\supset$ **I**. In addition, we considered behavior of iodine molecules in the porous framework through magnetic measurements using solid mixture of **1** and **2** $\supset$ **I** as well as **2** and **1** $\supset$ **I**. In the case of solid solutions, their magnetic properties mainly reflected the features of **1** $\supset$ **I**. In the solid mixture of **1** and **2** $\supset$ **I**, iodine migrated from Pd(II) sites to Pt(II) sites with an oxidative addition forming Pt(IV)-I bonds. On the other hand iodine didn't migrate in the solid mixture of **2** and **1** $\supset$ **I**, which suggested iodine molecules were trapped at Pt sites as  $\text{I}^-$  preferentially. In addition, we tried to control their adsorption properties by post-synthetic modification using  $\text{I}_2$ .



**Figure 1** The magnetic behavior of **1** $\supset$ **I**, **2** $\supset$ **I** and **3**<sub>x</sub> $\supset$ **I** ( $x = 0.5$ )

1 M. Ohba, J. A. Real, S. Kitagawa et al., *Angew. Chem. Int. Ed.*, **2009**, 48, 4767.

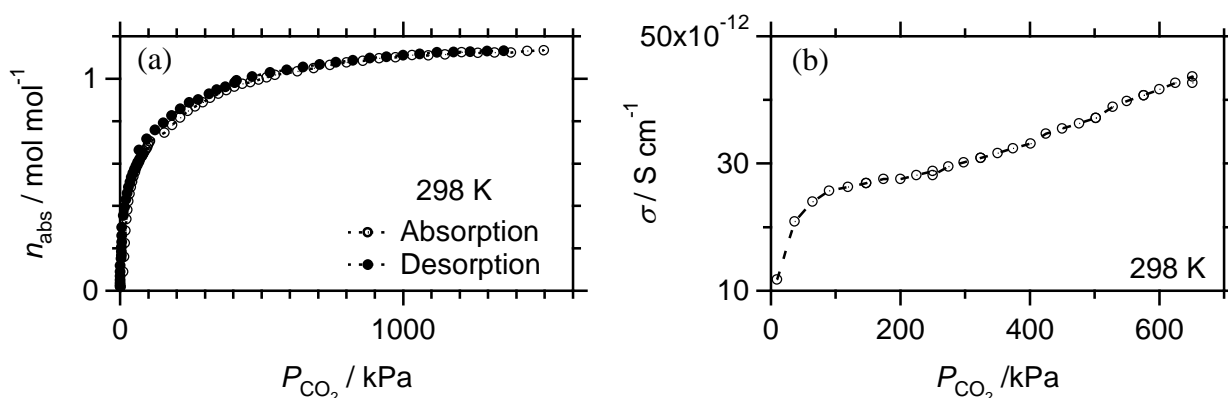
2 R. Ohtani, J.A. Real, M. Ohba et al., *J. Am. Chem. Soc.*, **2011**, 133, 8600.

## Enhancement in Proton Conductivity of a MOF under CO<sub>2</sub>

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Recently, metal–organic frameworks (MOFs) have attracted much interest as a candidate of proton conductor[1]. The advantages of MOFs among proton conductors such as polymers or perovskite-type oxides are their highly ordered structures, porosity, and high designability by choosing metal ions and organic ligands. It is known that some MOFs show the enhancement in the proton conductivity under humid condition. However, enhancement in the proton conductivity under gases that do not contain any protons has not been observed. Carbonic acid can be generated when CO<sub>2</sub> and water react and provides proton. Thus it is expected that CO<sub>2</sub> loading into hydrated MOFs will enhance the proton conductivity through the generation of carbonic acid. Here, we report enhancement of the proton conductivity of Co-MOF-74 [Co<sub>2</sub>(DOBDC)] (H<sub>4</sub>DOBDC = 2,5-dihydroxyterephthalic acid) by introducing CO<sub>2</sub>. Co-MOF-74 has 1D-pore and shows a good CO<sub>2</sub> uptake. CO<sub>2</sub> absorption measurement was performed to evaluate CO<sub>2</sub> uptake (Figure 1a) and AC-impedance measurement under CO<sub>2</sub> was carried out to investigate proton conductivity (Figure 1b). A large increase in CO<sub>2</sub> uptake under 100 kPa was observed and proton conductivity also increased in the same pressure region. These results suggest that carbonic acid was generated and its acidity enhanced proton conductivity.



**Figure 1** (a) CO<sub>2</sub> uptake of Co-MOF-74, (b) Conductivity of Co-MOF-74 under CO<sub>2</sub>

[1] P. Ramaswamy, N. E. Wong, and G. K. H. Shimizu, *Chem. Soc. Rev.*, **2014**, *43*, 5913.

## Development of recyclable organo-polyoxometalates for sustainable asymmetric acid

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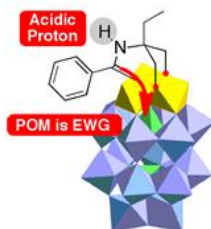
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Polyoxometalates (POMs) are anionic nanometric molecules made of highly oxidized metals and oxygen, whose structure can be easily controlled changing synthetic conditions. Thanks to their robustness, in general simple POMs are regularly used in industrial processes as Brønsted acids or oxidants. With the aim to rationally design new chiral hybrid POM-based Brønsted and Lewis acid catalysts for sustainable asymmetric catalysis (artificial enzymes), the introduction of organic moieties on the totally inorganic scaffold offers the opportunity of direct and post-functionalization reactions,<sup>1</sup> and also of chirality transfer between the organic ligand and the inorganic architecture.

With this challenge, we decided to focus our attention on two different polyoxometallic platforms to start our studies on the development of "artificial enzymes":

- two lacunary-POMs ( $\alpha_1/\alpha_2$ - $P_2W_{17}O_{61}$ )<sup>10-</sup> easily modifiable, to understand through high-field NMR and Molecular Modelling the critical factors governing supramolecular interactions between peptide chains and the highly negatively charged POM surface;
- a catalytically active trivanadic Dawson POM ( $P_2W_{15}V_3O_{62}$ )<sup>9-</sup>, to evaluate how the organic grafting affects the catalytic activity of amides and ureas, on the one hand and that of the inorganic cluster on the other hand.



<sup>1</sup> a) J. Li, I. Huth, L.M. Charmoreau, B. Hasenknopf, E. Lacôte, S. Thorimbert, M. Malacria; *Angew. Chem. Int. Ed.*, **2009**, 48, 2035; b) J. Oble, B. Riflade, A. Noël, M. Malacria, S. Thorimbert, B. Hasenknopf, E. Lacôte; *Org. Lett.*, **2011**, 13, 22, 5990.

## Toward the Understanding of the Delocalization on Mixed Valence Polyoxometalates: An Experimental and Theoretical approach

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Polyoxometalates constitute an extended family of polyanionic compounds containing oxygen atoms and transition metal atoms (V, Nb, Ta, Mo y W) in their higher oxidation states. These compounds highlight by presenting different topologies and electronic properties, which can be modified by incorporation of substituents. For instance, one of most studied polyoxometalates is the Lindqvist's structure  $[M_6O_{19}]^{n-}$ , known for Mo, W, Nb and Ta, while V cluster is only known in substituted or functionalized forms. An interesting set of compounds is the mixed valence Lindqvist's dodecamethoxovanadates  $[V_n^{IV}V_{(6-n)}^{V}O_7(OCH_3)_{12}]^{(4-n)-}$  ( $n=2-6$ ). Augustyniak-Jablokow *et al.*<sup>1</sup> studied the neutral mixed valence state,  $[V^{IV}_4V^V_2O_7(OCH_3)_{12}]$ , by single-crystal EPR, reporting a delocalized-to-localized structural phase transition about 190 K.

In order to understand the electronic properties of these mixed valence systems, we have carried out studies from spectroscopic, magnetic, electrochemical and theoretical viewpoints. Theoretical studies using DFT framework presented accurate results to describe and understand the electronic, magnetic and spectroscopic properties for different mixed valence states obtained from  $[V^{IV}_4V^V_2O_7(OCH_3)_{12}]$ . Furthermore, results indicate that methoxy substituents not only contribute in the cluster stabilization, also influence electron delocalization affecting several related properties.

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1 Augustyniak-Jablokow, M. A.; Borshch, S. A.; Daniel, C.; Hartl, H.; Yablokov, Y. V. *New Journal of Chemistry. Chem.*, 29 (8), 1064, (2005)



## Two-ligand approach for obtaining chiral coordination polymers

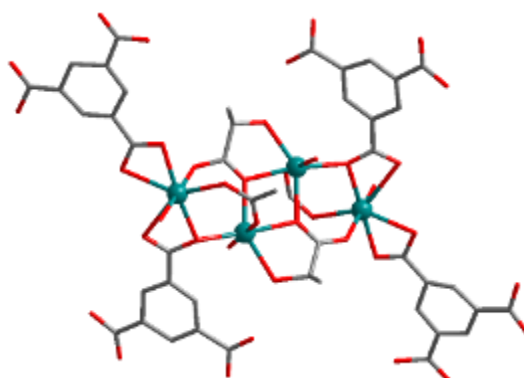
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Chiral coordination polymers built from metal cations and optically pure linkers demonstrate interesting features in addition to “typical” MOF properties like sorption, storage or catalysis, and that determines the great attention to such compounds. We used two-ligand approach for rational design of chiral coordination polymers. In this case one of the ligands is optically pure and bears asymmetric centers to the structure. Another one acts as a rigid linker and provides the formation of the polymer. Such approach guarantees non-centrosymmetric nature of the material and allows flexible control of both chemical composition and structural features of the coordination polymer.

Here we present a number of unique homochiral metal-organic frameworks based on lactic and mandelic acid derivatives. Malic acid also was used for its additional ability to act as bridging ligand. These oxo-carboxylic acids demonstrate different coordination modes thus giving various chiral building units with metal cations, connected through N-donor (trans-1,2-bis(4-pyridyl)ethylene, urotropin) or polycarboxylic (terephthalic, trimesic acids) linkers. New compounds were characterized by a number of analytical methods; guest-related properties of chiral coordination polymers are also investigated.

This work was supported by RFBR (grant number 16-33-00520).



**Figure 1** Structure fragment of Cd lactate with trimesic acid

# Luminescent MOFs with conjugated 1, 1'-ethynebenzene-3, 3', 5, 5'-tetracarboxylate ligand: syntheses, structures and photoluminescent properties

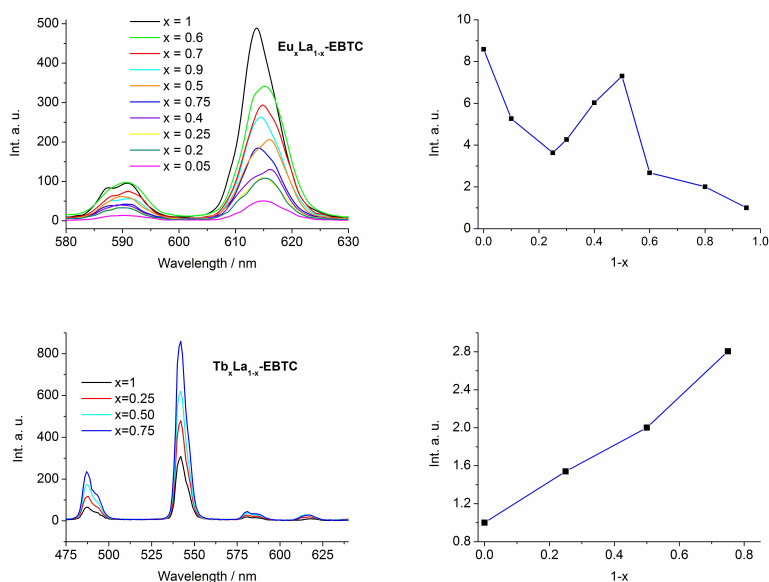
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## ABSTRACT

We systematically investigated the crystal structures and luminescence properties of nine new isostructural EBTC<sup>4-</sup> (EBTC<sup>4-</sup>=1,1'-ethynebenzene-3,3',5,5'-tetracarboxylate) based Ln-MOFs, which are capable of emitting from the visible to near-infrared wavelengths. Interestingly, compounds **6**(Ln=Eu) and **8**(Ln=Tb) emit intense red and green luminescence (visible by bare eyes), respectively and show microsecond time scale fluorescence lifetimes.<sup>1</sup> Therefore, two series of 3-D fluorescent lanthanide-MOFs-based molecular alloys RE<sub>x</sub>La<sub>1-x</sub>-EBTC (RE<sup>3+</sup>=Eu<sup>3+</sup> or Tb<sup>3+</sup>) have been successfully prepared by mixing Eu<sup>3+</sup>/Tb<sup>3+</sup> and La<sup>3+</sup> salts with the desired molar ratio in the starting material and showed photoluminescence property with divergent La<sup>3+</sup> ion dilute effect.



**Figure 1** Emission spectra and the corresponding plot of luminescence intensity of Eu<sup>3+</sup> or Tb<sup>3+</sup> against La<sup>3+</sup> ion concentration in the two series molecular alloys.<sup>2</sup>

1 L. Zhai, W.W. Zhang, *Dalton Trans.* 2015, 44, 5746.

2 L. Zhai, W.W. Zhang, *J. Solid State Chem.* 2015, 230, 14.

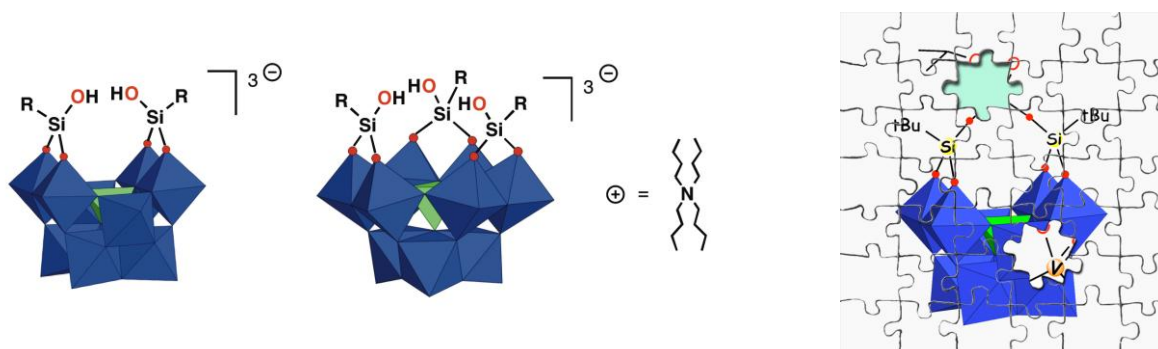
## Silanol-Functionalized Polyoxotungstates: The Generation and Synthetic Use of Metal Complexes

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Based on their inherent properties most applications of polyoxometalates (POMs) in catalysis refer either to acid catalysis linked to the superacidity of heteropolyacids or oxidation catalysis.<sup>1</sup> The functionalization of (multi)vacant polyoxotungstates by a covalent grafting of organic electrophiles opens the scope of their applications. It can either allow the preparation of *organic/inorganic* hybrids that present emerging properties<sup>2</sup> or may also provide new coordination sites of interest for catalysis by transition metals. As an example, reaction of organo-silanes onto the dilacunary  $\gamma$ -[PW<sub>10</sub>O<sub>36</sub>]<sup>7-</sup> or the trilacunary  $\alpha$ -A-[PW<sub>9</sub>O<sub>34</sub>]<sup>9-</sup> provides rigid and preorganized bis- or tris-silanol environments (Figure 1) that are well suited for the coordination of early and middle transition metal ions.<sup>3</sup>



**Figure 1** Silanol decorated polyoxotungstates.

The nature of the substituent at the silicon atoms (R) allows tuning the size of the sterical protection around the metal and thus allows the metal ion to fit in a well-defined single site. In this poster, we will report the ability of these platforms to bind high- and low-valent transition metals and will also discuss the reactivity of the resulting metal complexes with a careful attention to the role of redox mediator eventually played by the POM framework owing to its intrinsic electron acceptor properties.

1 Polyoxometalates in Catalysis (Ed. C. L. Hill), *J. Mol. Catal.* **2007**, 262, 1.

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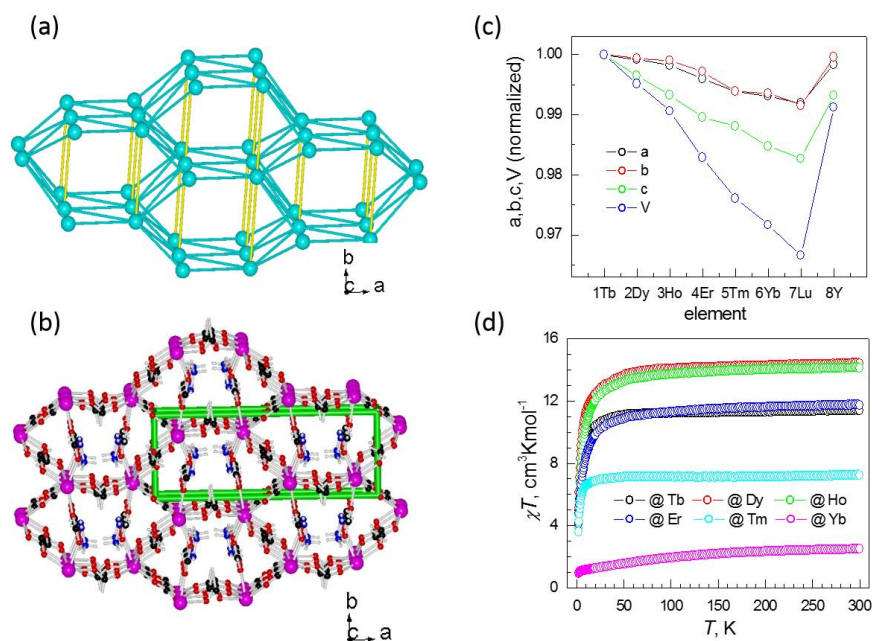
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## Frameworks of Hydrazinium Lanthanide Formate

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The isostructural compounds of  $[\text{NH}_2\text{NH}_3][\text{Ln}(\text{HCOO})_4]$  series (Ln = Tb, Dy, Ho, Er, Tm, Yb, Lu and Y) were prepared. They possess a diamond-like structure in space group  $Pca2_1$ . The unique  $\text{Ln}^{3+}$  ion is in a distorted square antiprism comprised eight *anti-anti*  $\text{HCOO}^-$ , in which six link other  $\text{Ln}^{3+}$  nodes to produce the diamond network showing hexagonal channels along the  $c$  direction and the other two act as two additional arrays acrossing the channels, occupied by  $\text{NH}_2\text{NH}_3^+$ . The unit cell parameters decrease from Tb to Lu. The compounds exhibit paramagnetism, and the  $\chi T$  values at 300K were 11.39 (Tb), 14.39 (Dy), 14.11 (Ho), 11.73 (Er), 7.24 (Tm), 2.50 (Yb)  $\text{cm}^3\text{Kmol}^{-1}$  respectively, close to the expected values for the isolated trivalent lanthanide ions. The  $\chi T$  values decreased slowly from 300 to 50K, then more rapidly and reached a minimum at 2K.



**Figure 1** (a) The topological view of the Ln-formate frameworks. (b) The diamond-like structure of  $[\text{NH}_2\text{NH}_3][\text{Ln}(\text{HCOO})_4]$ . (c) The element dependence of the unit cell. (d) The magnetism for Tb to Yb

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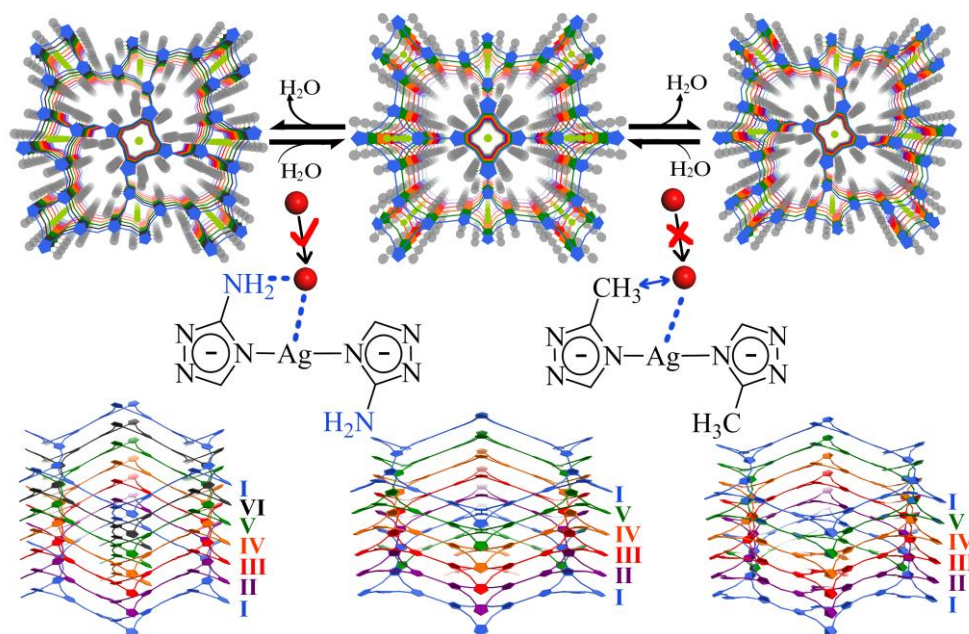
# Controlling Flexibility and Interpenetration Reconstitution Behaviors of Metal-Organic Frameworks

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Porous coordination polymer (PCPs) or Metal-organic frameworks (MOFs) have undoubtedly received wide attention due to their highly designable/controllable/tailorable framework structures.<sup>1</sup> Notably, MOFs are also unique for their flexibilities, which can be hardly designed or controlled, especially for some special flexibilities such as those require coordination bond cleavage and reformation. Herein, we designed and synthesized a series of isostructural interpenetrated MOFs.<sup>2,3</sup> By changing the substituent groups near the open metal sites from hydrophilic to hydrophobic, the structural reversible dynamism of these crystals changed from 5-fold to 6-fold interpenetration reconstitution to simple framework breathing, under stimuli of guest change.



**Figure 1** Controlling the framework breathing behaviors of isostructural MOFs. Simultaneous framework distortion and interpenetration reconstitution (between 5- and 6-fold) for R = NH<sub>2</sub>, and framework distortion without interpenetration reconstitution for R = CH<sub>3</sub>.

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## Construction of Porous Structure Based on Cyclic Metal Complexes and Polyoxometalates Composites

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Porous coordination polymers (PCPs) attract many attentions as a new porous materials having designable highly-ordered framework. One of their characteristics is the flexible framework. To construct more flexible and more functional porous structure, we focused on ionic crystals formed through the isotropic and long-range Coulomb interaction. Our key strategy for the ionic porous compounds is to make composites with cyclic metal complexes as 0-D porous units and polyoxometalates (POMs) as functional units.

In this work, we prepared a hexanuclear cyclic metal complex  $\{[\text{Cu}(\text{L})(\text{H}_2\text{O})]\text{BF}_4 \cdot n\text{H}_2\text{O}\}_6$  (**1**) by a self-assembling reaction using an asymmetric ligand (HL) and  $\text{Cu}(\text{BF}_4)_2 \cdot n\text{H}_2\text{O}$ . Compound **1** spontaneously formed a 1-D channel based on the cyclic structure in the lattice (Fig. 1). Since the 1-D channel was a very fragile construction, the structure was easily changed to amorphous when it was grinded. To reinforce the channel structure and construct new functional porous structure we used POMs as counter anions instead of  $\text{BF}_4^-$ . POMs are a subset of metal oxides with various physical and chemical properties.

Upon the addition of POMs during synthesis of **1**, we successfully prepared various types of objective composites **2** with **1** and POMs (Fig. 2). Stacking of cyclic structure gives a flexible channel, in which POMs play multiple roles of counter anion, fixer as “pillar” for the porous structure and interactive site. We will also present guest adsorption and redox properties of these composites.

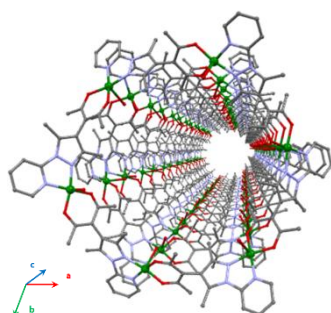


Fig. 1 Channel structure of **1**

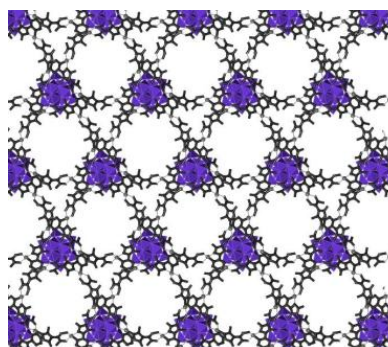


Fig. 2 Structure of **2**

## Controlling Induced-Chirality of Polyoxometalates via Supramolecular Bridging with Cyclodextrins

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Polyoxometalates (POMs) are a type of nano-scale inorganic objects, which possess various advantageous functions in both fundamental research and practical applications.<sup>1</sup> More important events in POM chemistry are related to their chirality because of the potentials in asymmetric catalysis, chiral chromism and nonlinear optics.<sup>2</sup> The construction of chiral POMs are generally carried out through hydrothermal, asymmetrically covalent modification or supramolecular interactions. Among the developed methods, complicated synthesis is often needed, and the quick attenuation of chirality is always a severe problem in the meantime. Through multi-supramolecular interactions we have succeeded in the fabrication of a simple, stable POM system with controllable chirality in solution. Herein, we would like to present the most recent results on single-side azobenzene functionalized Anderson-type POM hybrid, which were demonstrated to act as a bridge for combining cyclodextrin (CD) and cationic dyes through dual supramolecular interactions.<sup>3</sup> The observed induced-chirality migrates from CD to electrostatically adsorbed dye cations through the POM connector. Interestingly, the modulation of the chiral delivery can be done just by adjusting the host-guest recognition and electrostatic interactions within the three-component system. Following the cognition, guest cations are chosen as a bridge to combine both CD and POMs via the supramolecular interactions in aqueous solution. The induced chirality of POMs assigned to LMCT can be clearly observed to maintain stably. The well-retained redox property operating through electrochemistry endows the shuttling on-off variation of heteropoly blue corresponding to IVCT, generating switchable chiral electrochromism. Meanwhile, the multi-electron reduction of induced chiral POMs are disclosed for the first time. The present research findings imply that the supramolecular chiral POM complexes can be used in asymmetric catalysis and the film for electrochromic devices.

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## Rhenium(I) tricarbonyl complexes with 4,4''-azobis(2,2'-bipyridine)

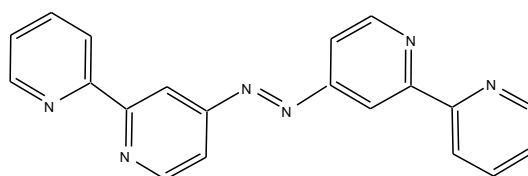
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Rhenium(I) tricarbonyl complexes have interesting optical and electrical properties that can be applied in the design of molecular devices.<sup>1</sup> We describe in this work the synthesis and spectroscopic and electrochemical characterization of new Re(I) species of formula:  $[\{\text{Re}(\text{CO})_3\text{Cl}\}_2\text{L}]$ , **1** and  $[\{\text{Re}(\text{CO})_3(\text{CH}_3\text{CN})\}_2\text{L}](\text{PF}_6)_6$ , **2**, where L = 4,4''-azobis(2,2'-bipyridine), whose structure is shown in Scheme 1. The IR spectrum of complex **2** shows the typical stretching frequencies  $\nu_{\text{CO}}$  at higher values than those of complex **1**, which can be attributed to the competition between  $\text{CH}_3\text{CN}$  and the CO groups for the metal electronic density. This effect is consistent with the shift observed in the absorption maxima corresponding to the MLCT  $d_{\pi}(\text{Re}) \rightarrow \pi^*(\text{L})$  bands in the UV-Visible spectra for both species in  $\text{CH}_3\text{CN}$ :  $\lambda_{\text{max}} = 450 \text{ nm}$  for **1** and  $\lambda_{\text{max}} = 380 \text{ nm}$  for **2**.

By adding L-cysteine to complex **2** (at pH = 7.5), the lowest-energy MLCT band is displaced to higher energies ( $\lambda_{\text{max}} = 350 \text{ nm}$ ), thus pointing to a reduction of the azo group. This colour change can be applied for sensing aminoacids. On the other hand, by irradiating complex **2** at  $\lambda_{\text{ex}} = 277 \text{ nm}$  for 1 hour, the shifts in the UV-visible bands to higher energies disclose a trans-cis isomerization process, sensitized by a low-energy MLCT state.

In conclusion, complex **2** can be used as a molecular switch for sensing biologically relevant compounds and as a model for controlling changes of molecular geometry induced by light.



**Scheme 1.** Structure of 4,4''-azobis(2,2'-bipyridine).

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## Polynuclear halide and polyhalide complexes of bismuth(III)

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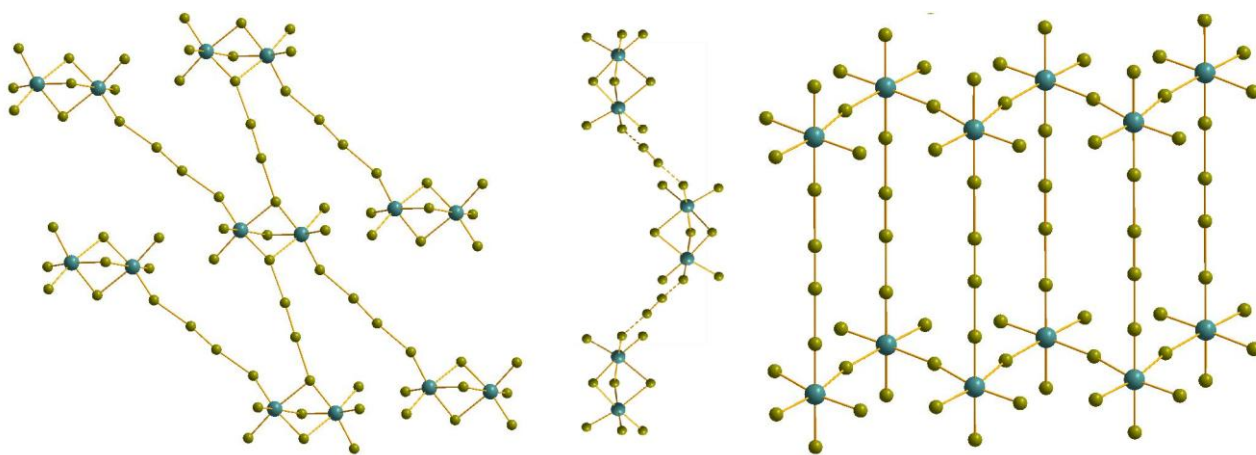
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The halide complexes of post-transition metals, in particular Bi(III), attract an interest due to their optical properties, i.a. luminescence and photochromism. In this work, we summarize our most recent research in this area.

The series of binuclear complexes  $(\text{HNNH})_2[\text{Bi}_2\text{X}_{10}]$  ( $\text{X} = \text{Cl}, \text{Br}$ , N,N = 4,4'-bipy (**1,2**), bpe (**3,4**) and bpen (**5, 6**)) has been obtained. All compounds reveal moderate luminescence properties. **1, 3** and **4** are obtained in form of solvates ( $\cdot 2\text{H}_2\text{O}$ ). In the case of **1**, the desolvation is irreversible, leading to the shift of intensity maximum (30 nm), while **3** and **4** may be desolvated reversibly, resulting in increasing of luminescence intensity [1-2].

The first examples of Bi(III) polybromide complexes have been synthesized and characterized. We found that reactions of  $[\text{BiBr}_6]^{3-}$  and various aromatic cations, when conducted in presence of  $\text{Br}_2$  in solution, may result in "inclusion" of  $\text{Br}_2$  molecules into the structure in form of polymeric  $\{\text{Br}_{4n}\}^{2-}$  ligands, building an extended 1D-or 2D coordination networks. At the moment, we have found 3 structural types of polybromides (Fig. 1). All complexes reveal remarkable thermal stability (release of  $\text{Br}_2$  proceeds above  $150^\circ\text{C}$ ) [3].



**Figure 1.** Polybromides of Bi(III): type 1 (left), 2 (middle) and 3 (right)

This work has been supported by Russian Science Foundation (Grant No. 14-23-00013)

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## Two-photon absorption and photochromism of new ruthenium complexes: applications to 3D optical data storage

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3D optical data storage is the term given to any form of optical data storage in which information can be recorded and/or read with three dimensional resolution (as opposed to the two dimensional resolution afforded, for example, by CD). This innovation has the potential to provide terabyte-level mass storage on DVD-sized disks<sup>1</sup>. One possible way to encode optical information consists in using two-photon isomerisation in a photo-assisted poling scheme followed by a simple second harmonic generation (SHG) read-out stage. We demonstrate in this work that the resulting localized loss in second harmonic generation efficiency can be exploited to store then read data using new scanning Second Harmonic Generation (SHG) microscopy imaging methods.<sup>2</sup>

We have developed innovative multicomponent molecules and materials for photo-induced nonlinear optical properties. We designed multifunctional transition metal-based photoactive heteroleptic  $[\text{Ru}(\text{bpy})_3]^{2+}$  complexes, combining a two-photon absorber (**TPA**: bipyridine ligands with high intramolecular charge transfer transitions) and a photochromic unit (**PC**: azobenzene unit). The linear and non linear optical characterization of these complexes, showing high two photon cross section, will be presented.<sup>3</sup> Their processing as active materials within matrices (PMMA) and the use of pulsed laser based methods to induce data encoding within the resulting photoactive materials in oriented films (second harmonic generation response) have been studied.

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## Defining the Electronic Structure and Bonding of the +3 Oxidation State of Thorium

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The concept of oxidation states is consistently used in order to rationalise the reactivity and the bonding regimes of atoms in different environments. Whereas the approach of formal oxidation states, where electron density is assigned to individual elements in compounds, gives a relevant approximation of atomic behaviour, the actual spin densities and electronic studies can be solved through comprehensive physical studies which are sparse for elements in uncommon formal oxidation states in the actinide series.

Although the first structurally characterized Th(III) complex was isolated decades ago, the oxidation state is not thoroughly understood. Here we focus on describing a novel Th(III) complex for comparison with a U(III) homologue and Th(IV) and U(IV) complexes in similar ligand environments.<sup>1-3</sup> The bonding in these complexes has been studied using single crystal XRD and NIR/Vis/UV spectroscopies together with c.w. EPR, pulse EPR and EXAFS spectroscopies and SQUID measurements to probe the electronic structures and valence orbital spin densities of these systems. These results for the first time provide an experimental measure of the varying extend of covalency in related systems containing Th(III), Th(IV), U(III) and U(IV) oxidation states.

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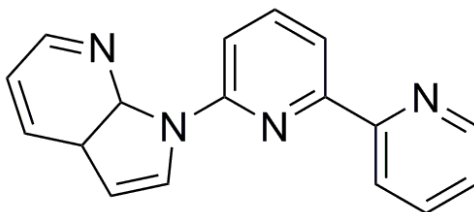
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## Anhydrous lanthanide salts for complexing neutral tridentate binding units with six-membered chelate rings

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Numerous large trivalent lanthanide cations were successfully coordinated not only with 5-, but also with 6- or even with 7-membered polyaromatic chelates. However, we note that 6- and 7-membered chelates systematically relied on negatively charged oxygen-containing ligands. For neutral polyaromatic tridentate ligands, only fused 5-membered chelates are known to give stable complexes with trivalent lanthanide cations. Beyond the investigation of these neutral soft receptors for the selective extraction of actinides over lanthanides in acidic nuclear wastes, only limited interest was focused on their potential selectivity along the lanthanide series. Recently, we reported on the preparation and some complexation properties of the unsymmetrical tridentate 6-(azaindol-1-yl)-2,2'-bipyridine (Figure 1).<sup>[1]</sup> The polyaromatic tridentate ligand combines one 5-membered chelate ring with a fused 6-membered chelate ring. It is designed to provide complexation properties intermediate between ligands with two fused 5-membered chelate rings and two fused 6-membered chelate rings.



**Figure 1** Chemical structure of the 6-(azaindol-1-yl)-2,2'-bipyridine.

We report here on the preparation of mononuclear lanthanide complexes with variable lanthanide to ligand ratios and unravel their complexation properties. Due to the expected low stability of these complexes in polar solvents, we used the weakly coordinating  $[Al(OC(CF_3)_3)_4]^-$  counter-anions.<sup>[2]</sup>

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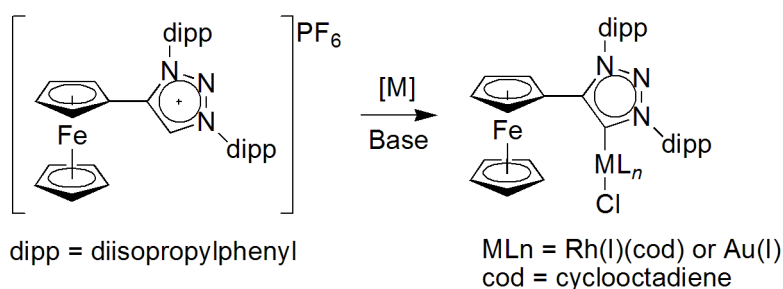
## Triarylated 1,2,3-triazolylidenes substituted with a redox-active ferrocenyl moiety

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Herein we present the synthesis of a triarylated 1,2,3-triazolium salt substituted with a ferrocenyl moiety, as a precursor to a stable mesoionic carbene (MIC) or 1,2,3-triazol-5-ylidene.<sup>1</sup> The electronic effect of the redox-active, electron-donating ferrocenyl<sup>2</sup> substituent is evaluated by coordination of the ligand to catalytically relevant transition metals such as Rh(I)<sup>3</sup> and Au(I).<sup>4</sup> The synthesis, characterisation and electrochemistry of the resultant metal carbene complexes are reported, as well as preliminary reactivity and catalytic results.



**Figure 1** Metalation of 4-ferrocenyl-triarylated-1,2,3-triazol-5-ylidene.

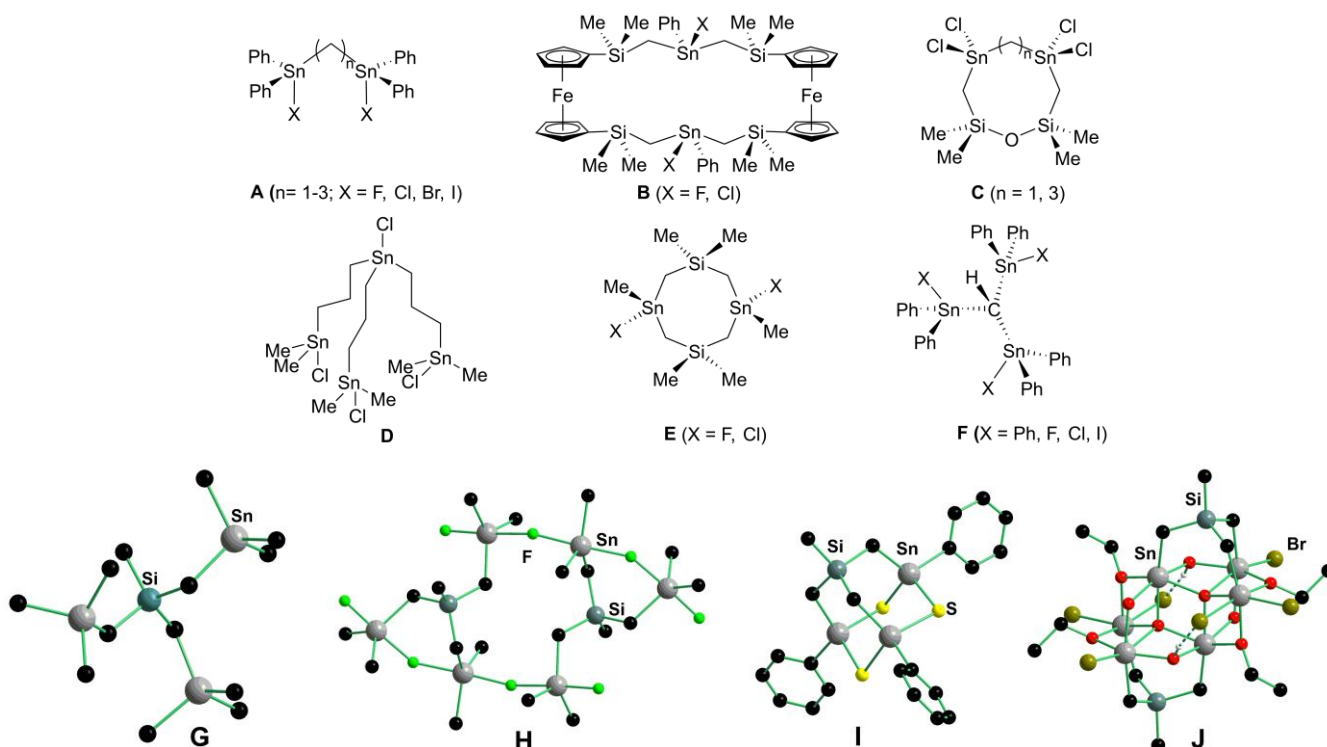
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# MeSi(CH<sub>2</sub>SnPh<sub>(3-n)</sub>X<sub>n</sub>)<sub>3</sub>: Syntheses, Complexation Behaviour Toward Anions, and Formation of Organotin Chalcogen Clusters

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In continuation of our systematic studies on multicentric tin-containing Lewis acids such as types **A** – **F**,<sup>[1]</sup> we present here the novel compound tris(triphenylstannylmethyl)silane **G**. By the reaction with elemental iodine and bromine, respectively, the latter can easily be converted into the corresponding halogen-functionalized derivatives MeSi(CH<sub>2</sub>SnPh<sub>(3-n)</sub>X<sub>n</sub>)<sub>3</sub> (**1**, X = I, n = 1; **2**, X = I, n = 2; **3**, X = Br, n = 3). These react with halide anions to give organostannate complexes such as compound **H**, with sodium sulfide providing the novel sila-tristanna-adamantane **I**, or with ethanol giving an unprecedented organotin oxo cluster **J**.



\*In part, phenyl substituents and ethanol solvate molecules are omitted for clarity.

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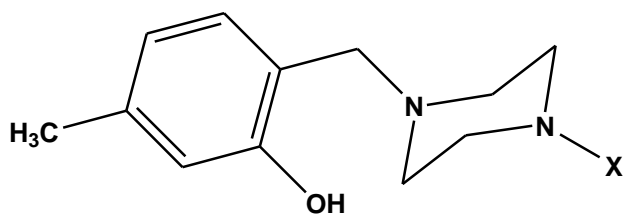


# Synthesis and Spectroscopic studies of some N-piperazyl Mannich bases and their Metal Complexes containing thiocyanate bridging ligands

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Corresponding Author\* (A.O. Ayeni)

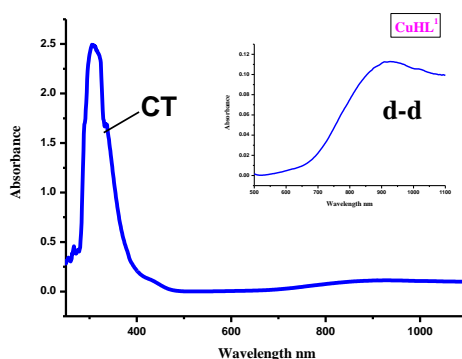
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Mannich bases derived from 1-(2-pyridyl)piperazine and 1-(4-nitrophenyl)piperazine have been synthesized by a slight modification to the classical Mannich reaction and were characterized by NMR spectroscopy, elemental analyses, FT-IR and electronic spectroscopy.



X = pyridine, p-nitrobenzene

Metal complexes and those containing thiocyanate bridging ligands have also been synthesized and characterized by FT-IR, UV, Electron Paramagnetic Resonance and cyclic voltammetry.



**Figure 1:** UV-Vis Spectrum of Cu(II) complex of 1-(4-nitrophenyl)piperazine Mannich Base

Intense bands around  $2080 - 2200\text{cm}^{-1}$  characteristic of  $\nu\text{NCS}$  are observed in all the thiocyanate complexes indicating bridging. The electronic spectra of the both ligands and complexes were recorded in DMSO. The spectra of the complexes show absorptions typical of charge-transfer (300 – 450nm) and d-d transitions (at about 910nm).

Preliminary screening of the ligands and their copper complexes showed minimal antibacterial activity against *S. aureus*. We will further investigate these compounds for their antimicrobial and antimalarial properties.

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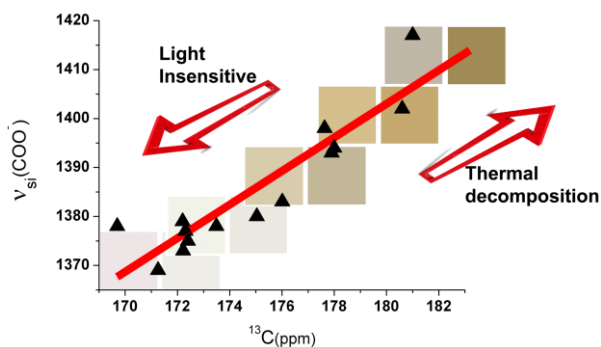
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## Light and thermal stability of silver carboxylate complexes: An infrared- $^{13}\text{C}$ NMR correlation

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Ag(I) complexes have been widely studied for their antibacterial properties for several decades<sup>1</sup>. However, a good candidate as an antibacterial agent in future medical applications should include some additional properties: light-insensitive, thermal stability, and poor solubility<sup>3</sup>.



Unfortunately, few researches have addressed the problem of stability and antibacterial activity simultaneously<sup>3</sup>, neither additional applications for the ligands used in the preparation of the metal complexes.

Here we present evidence to evaluate the light sensibility behavior of Ag(I) carboxylate complexes, and the influence in the nature of the Ag-OOC bond in order to demonstrate the importance of the ligands in these kind of antibacterial compounds. 12 new complexes with anti-inflammatory ligands were synthesized and characterized by FT-IR, elemental analysis and NMR ( $^1\text{H}$  and  $^{13}\text{C}$  in  $d^6$ -DMSO). Synthesized compounds were tested toward UV-c radiation (254 nm, 30 W) in order to characterize their light sensibility. Finally, the thermogravimetric analyses were performed in order to confirm and compare the thermal stability of the compounds.

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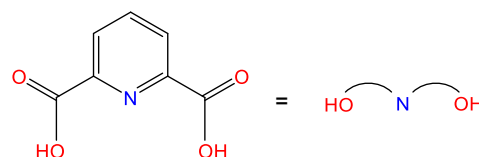
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## Reactions of Ruthenium Complexes Bearing 2,6-Pyridinedicarboxylate with Hydrazine

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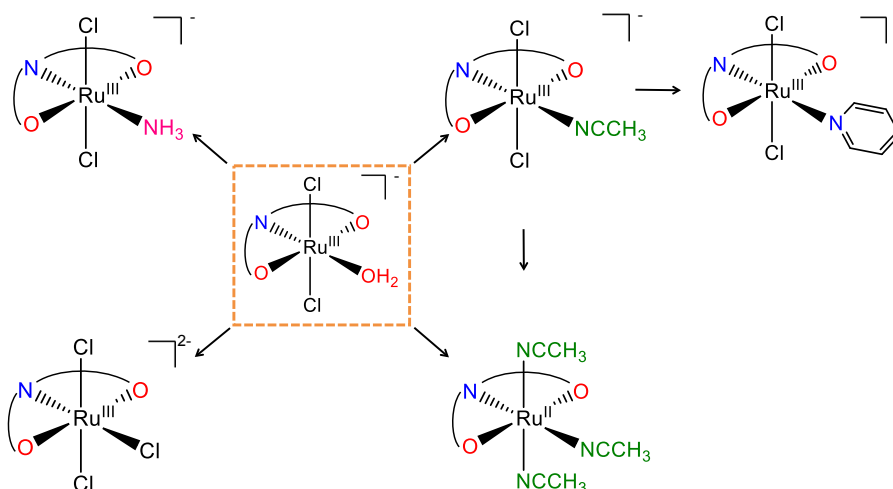
We have been investigating interactions of ruthenium complexes with biomolecules and nitrogen-containing compounds. To study a relationship between bioactivities and electronic structures of complexes, we synthesized



**Figure 1** 2,6-pyridinedicarboxylate

ruthenium complexes bearing 2,6-pyridinedicarboxylate (pydcH<sub>2</sub> **Figure 1**), which have high solubility toward water and stabilize high valence state of the metal center.

In this work, [Ru<sup>III</sup>(pydc)Cl<sub>2</sub>(X)]<sup>n-</sup>, in which pydc coordinates as an anionic tridentate ligand, were synthesized by substitution reactions of dichloridoaqua complex [Ru<sup>III</sup>(pydc)Cl<sub>2</sub>(H<sub>2</sub>O)]<sup>-</sup> and dichloridoacetonitrile complex [Ru<sup>III</sup>(pydc)Cl<sub>2</sub>(CH<sub>3</sub>CN)]<sup>-</sup> as shown in **Scheme 1**. A reduction reaction of [Ru<sup>III</sup>(pydc)Cl<sub>2</sub>(CH<sub>3</sub>CN)]<sup>-</sup> or [Ru<sup>III</sup>(pydc)Cl<sub>2</sub>(H<sub>2</sub>O)]<sup>-</sup> in CH<sub>3</sub>CN afforded Ru(II) complex [Ru<sup>II</sup>(pydc)(CH<sub>3</sub>CN)<sub>3</sub>]. [Ru<sup>III</sup>(pydc)Cl<sub>2</sub>(X)]<sup>n-</sup> reacted with hydrazine in CH<sub>3</sub>OH under reflux conditions to afford a light green complex. The light green complex showed an absorption band at 1994 cm<sup>-1</sup> in infrared spectrum and reversible oxidation and irreversible reduction waves in electrochemical measurements in aqueous solutions. We would like to report characterization and reactions of this complex.



**Scheme 1** Syntheses of ruthenium complexes bearing 2,6-pyridinedicarboxylate

## Functional Materials: synthesis and structural characterization of new precursors based on $M^{II}$ and 4-imidazoleacrylic acid

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During the last time, the coordination chemistry area has been mainly focused in the synthesis of new materials based on *nd* and *4f* cations which are bridged through organic ligands with different chemical nature.<sup>1,2</sup> In this type of functional materials it is possible to find interesting properties as luminescence, non linear optical and magnetism, among others.<sup>3,4</sup> Taking into account that many times the synthesis of these materials involve long reaction times, high temperatures and the use of solvents, the scientist continuously search for new synthetic alternatives. Mechanochemistry synthesis is a new synthetic procedure characterized mainly for the short reaction times and the use of minimum amount of solvents through which it is possible to obtain new compounds.

In this work we are presenting the synthesis and structural characterization of two new compounds of  $Ni^{II}$  and  $Cu^{II}$  based material, which was obtained by mechanochemistry synthesis from  $M(CH_3COO)_2 \cdot nH_2O$  and 4-imidazoleacrylic acid precursors. These materials have been analyzed by X-ray powder diffraction. They present structural analogies with relative molecular materials obtained by Baran et al. with  $Zn^{II}$  and  $Co^{II}$  where the metallic center is attached to two molecules of 4-imidazoleacrylic acid.<sup>5</sup> The assembly of these compounds with lanthanide cations could allow to obtain new *3d-4f* functional compounds. Details on the synthesis methodology and structural characterizations will be discussed in this work.

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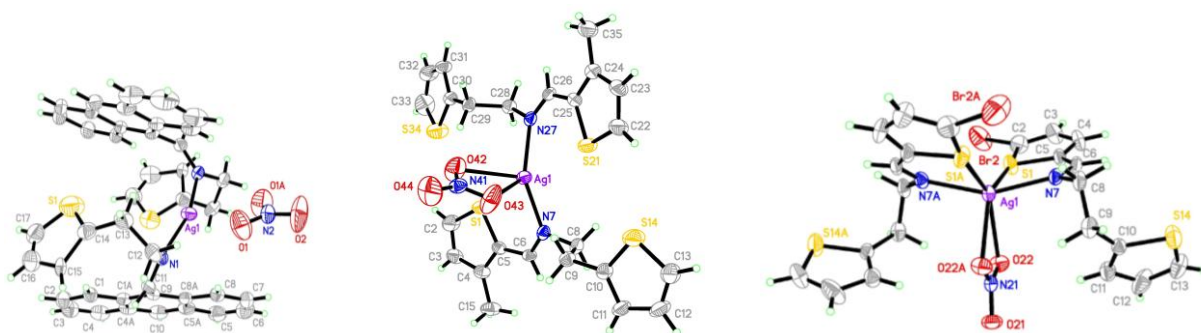
**Acknowledgments:** The authors acknowledge financial support from FONDECYT 1130643, Financial Support from Programa de Anillos en Ciencia y Tecnología Grant ACT1404. The authors also acknowledge the LIA-MIF 836 International collaborative project and ECOS/CONICYT grant. B.B thanks CONICYT scholarship n° 21140908.

## Ag(I) complexes with Schiff bases derived from 2- thiopheneethylamine and their thin layers

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Ag(I) complexes with Schiff bases derived from 2- thiopheneethylamine were used to obtain the thin materials. The ligands and complexes were characterized by UV-VIS, fluorescence, IR and  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra. The X-ray crystal structures for thet(9-anthracene) (**L1**),  $[\text{Ag}(\text{thet}(9\text{-anthracene}))_2]\text{NO}_3$  (**1**),  $[\text{Ag}(\text{thet}(3\text{-meth}))_2]\text{NO}_3$  (**2**) and  $[\text{Ag}(\text{thet}(5\text{-Brth}))_2]\text{NO}_3$  (**3**) were solved. (Fig. 1) The asymmetric unit of complex (**1**) contains Ag(I) ion with coordinated Schiff base (**L1**), and half of  $\text{NO}_3^-$  ion. The linear coordination sphere of Ag(I) ion is formed by the nitrogen atoms of two (**L1**) ligands. The distorted tetrahedral coordination sphere of Ag(I) in  $[\text{Ag}(\text{thet}(3\text{-meth}))_2]\text{NO}_3$  (**2**) is formed by two (**L2**) ligands coordinated *via* their imine N7 and N27 atoms and the bidentate nitrate ligand. Whereas, in the  $[\text{Ag}(\text{thet}(5\text{-Brth}))_2]\text{NO}_3$  (**3**) the coordination sphere of Ag1 might be described as the strongly deformed square pyramid with the  $\text{N}_2\text{S}_2$  base.

Thin layers of studied silver(I) complexes were deposited on Si(111) substrates by a spin and dip coating methods and characterized with a scanning electron microscopy (SEM/EDS), atomic force microscopy (AFM) and fluorescence spectroscopy.



**Figure 1** ORTEP diagram and atom labeling scheme for (**1**), (**2**) and (**3**) complexes.

### Acknowledgements

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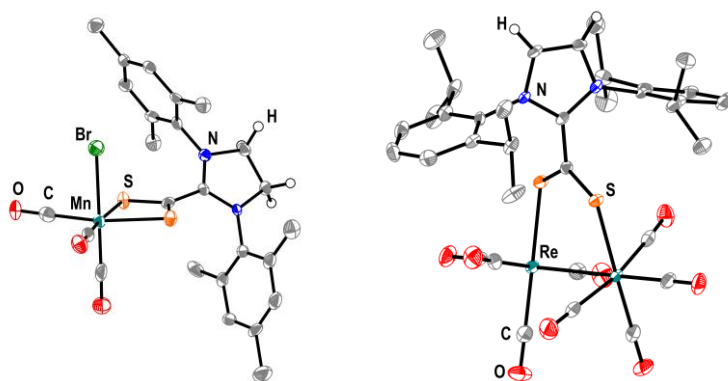
# Molecular Architecture of Transition Metal Complexes Containing Imidazol(in)ium-2-dithiocarboxylate Ligands

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Over the past fifty years, N-heterocyclic carbenes (NHCs) have evolved from laboratory curiosities to powerful organocatalysts and ubiquitous ligands for organometallic chemistry and homogeneous catalysis.<sup>1</sup> However, much of their potential to generate other ligand systems remains unexplored.<sup>2</sup> In 2009, our group reported on a series of transition metal complexes based on ruthenium, in which NHC·CS<sub>2</sub> zwitterions acted as κ<sup>2</sup>-S,S' chelating ligands.<sup>3</sup> Moreover, imidazol(in)ium-2-dithiocarboxylate adducts were also employed as bridging ligands in unprecedented homoleptic digold complexes of the type [Au<sub>2</sub>(S<sub>2</sub>C·NHC)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>.<sup>4</sup> The potential of NHC·CS<sub>2</sub> zwitterions to generate new molecular architectures prompted us to investigate the preparation of a large family of mono- and polynuclear complexes based on groups 6 to 8 transition metals bearing these ligands. In this communication, we shall discuss the coordination mode of NHC·CS<sub>2</sub> zwitterions in a series of new transition metal carbonyl complexes, on the basis of X-ray diffraction analysis and spectroscopic techniques.



**Figure 1** ORTEP representations of [MnBr(CO)<sub>3</sub>(S<sub>2</sub>C·SIMes)] (left) and [Re<sub>2</sub>(CO)<sub>8</sub>(S<sub>2</sub>C·IDip)] (right) (Ellipsoids drawn at the 50 % probability level).

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## Synthesis, structural characterization and catalytic properties of $[\text{Cu}_2(\text{VBA})_4(\text{CNCH}_3)_2]$ compound

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A new dinuclear copper(II) compound with 4-vinyl benzoic acid (VBA) and acetonitrile of formula  $[\text{Cu}_2(\text{VBA})_4(\text{CNCH}_3)_2]$  is presented here, for the preparation of this compound, a mixture of acetonitrile, copper nitrate, VBA and  $\text{C}_6\text{H}_{15}\text{N}$ , was stirred for 1 h at room temperature, then vacuum filtered off. The mother liquor obtained after the filtration was left under refrigeration to obtain blue single crystals<sup>1</sup> these were characterized by FT-IR, thermogravimetric analysis, single crystal X-ray diffraction, magnetic susceptibility, etc. The compound is evaluated as a catalyst on the oxidation of phenol. The oxidation of phenol was carried out in a glass reactor flask equipped with a reflux condenser. In a typical reaction the catalyst ( $[\text{Cu}_2(\text{VBA})_4(\text{CNCH}_3)_2]$  compound), was added into ethanolic solution of phenol. The reaction mixture was stirred at 35°C. Then a solution of  $\text{H}_2\text{O}_2$  (30 wt%) in ethanol was added dropwise over a period of 2 h. The reaction was stirred for another 7 h<sup>2</sup>. The products of the oxidation reaction, were initially identified by FT-IR. The vibrational spectra showed two signals corresponding to p-benzoquinone and hydroquinone at 1750 and 1550  $\text{cm}^{-1}$ , respectively.

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## Using Pincer Ligands to Study *s*- and *p*-Block Halides and Hydrides

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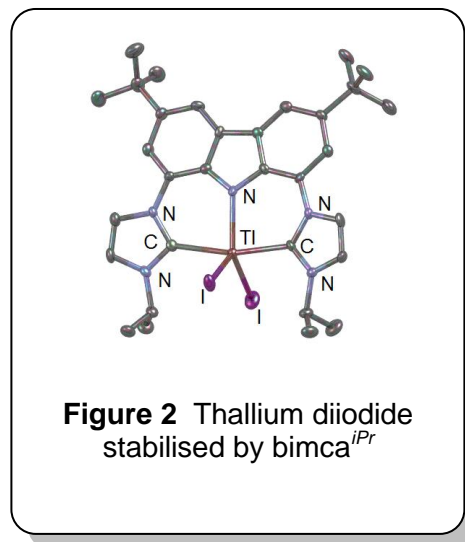
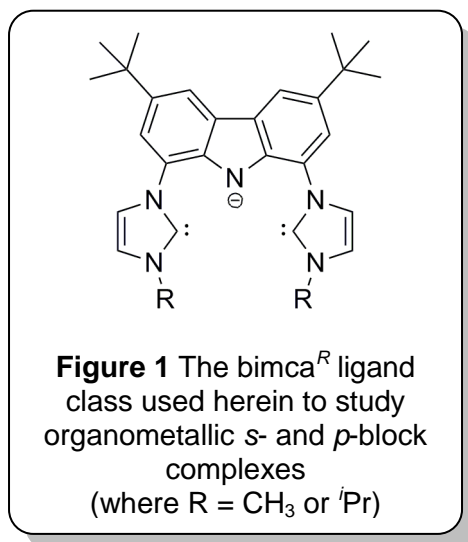
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Several key advancements regarding the stabilisation or activation of *s*- and *p*-block organometallic complexes have been reported to date, including (i) the use of tertiary amines or *N*-heterocyclic carbene (NHC) donors<sup>(1, 2, 3)</sup> to form highly stable Lewis-adducts and (ii) sterically enshrouding, anionic chelates, e.g. amidinates,<sup>(4)</sup> triazenides,<sup>(5)</sup> and  $\beta$ -diketiminates<sup>(6)</sup> to kinetically and electronically disfavour decomposition. The “bimca<sup>R</sup>” ligand class (Figure 1) provides a versatile tridentate bis(NHC) carbazolidide framework<sup>(7)</sup> that beneficially incorporates aspects of all the aforementioned donors.

This work showcases a variety of outcomes that are borne from the coordination chemistry of the bimca<sup>R</sup> ligand class with *s*- and *p*-block metals (Figure 2), ranging from the activation of group 2 and 14 halides, to the stabilisation of group 13 hydrides.



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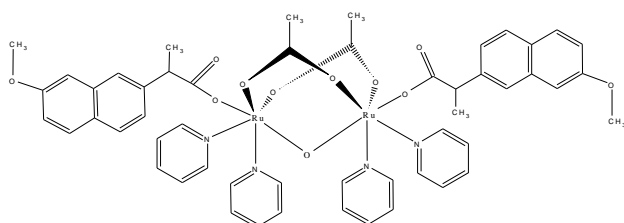
# Synthesis and characterization of a new binuclear ruthenium complex combined with the NSAID naproxen

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In recent years, interest in studying binuclear  $\mu$ -oxo bridged complexes has increased, due to the discovery that this type of structure is a part of the active site of hemerythrin. Arylpropionic acid derivatives are part of a relatively new class of nonsteroidal anti-inflammatory drugs (NSAIDs). These drugs have anti-inflammatory activity, analgesic and anti thermal properties, being widely used in the treatment of chronic pain, rheumatoid arthritis, osteoarthritis, among others<sup>1</sup>. Recent studies have shown that NSAIDs as ligand in metal complexes showed anti cancer activity<sup>2</sup>. This study aims to synthesize and to characterize new complexes of general formula  $[\text{Ru}_2\text{O}(\text{CH}_3\text{COO})_2(\text{NSAID})_2(\text{py})_4](\text{PF}_6)_2$  (**1**). In this particular paper, it is shown the results of synthesis and characterization for the new complex with naproxen  $[\text{Ru}_2\text{O}(\text{CH}_3\text{COO})_2(\text{C}_{13}\text{H}_{13}\text{O}_3)_2(\text{py})_4](\text{PF}_6)_2$ . The synthesis of this compound explored the lability of the trans positions to the oxo bridge<sup>3</sup> and it was purified by chromatography column of neutral alumina. The electronic spectrum of  $[\text{Ru}_2\text{O}(\text{CH}_3\text{COO})_2(\text{C}_{13}\text{H}_{13}\text{O}_3)_2(\text{py})_4](\text{PF}_6)_2$  consists of two bands at 317 nm and 588 nm assigned to charge-transfer and intra  $[\text{Ru}_2\text{O}]$  transitions, respectively<sup>3</sup>. The cyclic voltammetry of the complex shows two distinct redox couples at  $E_{1/2} = -0.48$  and 0.65 V versus Ag/AgCl, which are assigned to the  $\text{Ru}_2^{\text{II,III}}/\text{Ru}_2^{\text{III,III}}$  and  $\text{Ru}_2^{\text{III,III}}/\text{Ru}_2^{\text{III,IV}}$  processes, respectively. The fragmentation pattern observed from the mass spectrum is consistent with the proposed structure showing the fragments  $[(\mathbf{1}) - \text{PF}_6 - 1\text{py} - \bullet\text{CH}_3]$  m/z 1161,  $[(\mathbf{1}) - \text{PF}_6 - 2\text{py} - \bullet\text{CH}_3]$  m/z 1081 and  $[(\mathbf{1}) - \text{PF}_6 - 4\text{py} - 2\bullet\text{CH}_3]$  m/z 909.



**Figure 1:** Structure of  $[\text{Ru}_2\text{O}(\text{CH}_3\text{COO})_2(\text{C}_{13}\text{H}_{13}\text{O}_3)_2(\text{py})_4](\text{PF}_6)_2$ .

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CNPq, CAPES, FAPESP

## Rhenium (I) tricarbonyl complexes for marker prokaryotic and eukaryotic cells.

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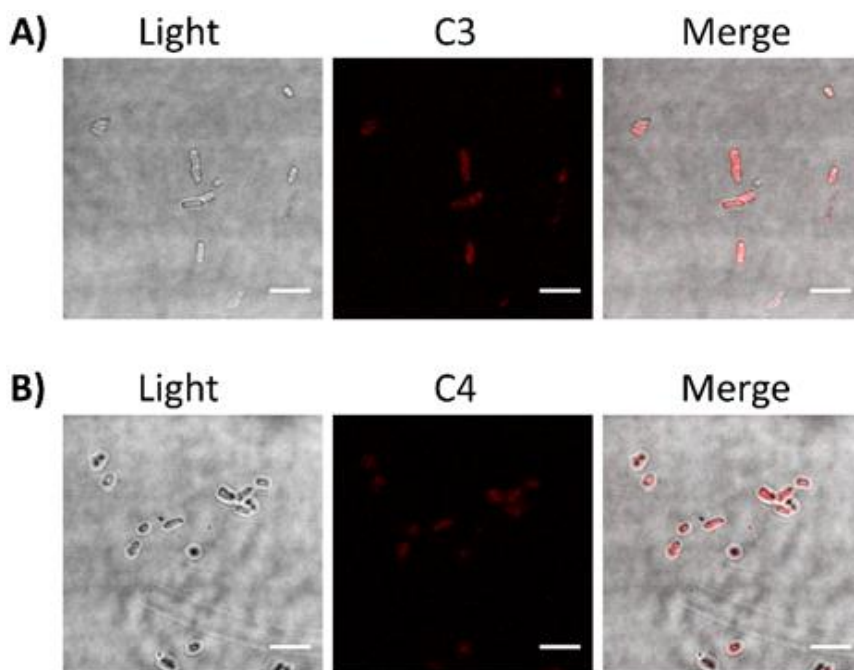
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The research of Rhenium(I) tricarbonyl diimine complexes of the general form *fac*-Re(CO)<sub>3</sub>(**N,N**)(**L**), where **N,N** are substituted bipyridine and **L** the ancillary ligand might be halogen or pyridine, dates back from the 1970s.<sup>1</sup> Since then, it has attracted much attention due to their appealing photophysical properties based on the Re<sup>I</sup> core which are adjustable, and might be optimized by the variation of the **N,N** ligand structure, or more subtly, by tuning the electronic nature of the ancillary ligand **L**.<sup>2</sup> In this work, two Rhenium(I) tricarbonyl complexes **C3** and **C4** of type *fac*-[Re(CO)<sub>3</sub>(**N,N**)**L**]<sup>+</sup>, where **L** is an ancillary ligand Schiff base (*E*)-2-((3-amino-pyridin-4-ylimino)-methyl)-4,6-diterbutylphenol,<sup>3</sup> which presents an intramolecular hydrogen bond, has been synthesized and characterized using chemical techniques such as UV-Vis, 1D and 2D NMR, TOCSY, FT-IR and cyclic voltammetry. The electron withdrawing nature of the ancillary ligand **L** in **C3** and **C4** explain the electrochemical behavior, which shows the oxidation of Re<sup>I</sup> at 1.84 V for **C3** and at 1.88 V for **C4**.

We also assessed the cytotoxicity of **C3** and **C4** in an epithelial cell line (T84). We found that 12.5 µg/ml of **C3** or **C4** is the minimum concentration needed to kill the 80% of cell population, as determined by neutral red uptake. Also, in this work, we explored the potential of **C3** and **C4** as biological dyes for use in fluorescent microscopy was assessed in bacteria (*Salmonella enteric*, Figure 1) and yeasts (*Candida albicans*).



**Figure 1.** Fluorescence confocal microscopy images showing bacteria (*Salmonella enterica*) stained with either **C3** (A) or **C4** (B). In all the cases, the microorganisms were observed fresh, using a 100X objective. White bars represent 5 µm.

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## Synthesis of AACVD precursors for Transparent Conducting Oxides

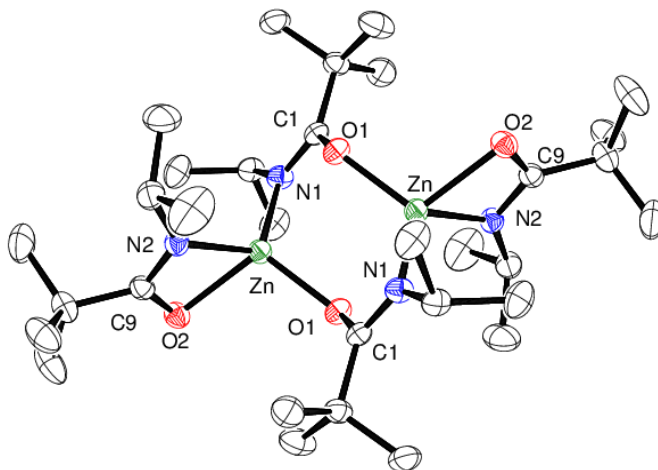
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Transparent conductive oxides (TCOs) are an important and unique class of materials in the photovoltaics industry; they have several key features such as high optical transparency in the visible region and good electrical conductivity.<sup>1</sup> While indium-doped tin oxide (ITO) is the most widely used material, due to the rarity and expensive cost of indium alternative materials need to be found. Research has been carried out to find alternative materials using low cost, abundant, non-toxic elements such as zinc, tin aluminium and magnesium.<sup>2</sup>

Aerosol Assisted Chemical Vapour Deposition (AACVD) would provide a simple method of depositing metal oxide on to a substrate and is potentially scalable as an industrial process.

Reported herein is a synthetic approach to suitable CVD precursors for the deposition of doped metal oxides. Amide ligands are reacted with metal precursors to produce metal amidate species. The resulting complexes will be analysed by NMR and X-ray crystallography (Figure 1) and the decomposition will be analysed by TGA.



**Figure 1** Crystal Structure of homoleptic zinc amidate complex

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## Niobium tetrahalide complexes with neutral soft donor ligands

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Neutral donor complexes of niobium chlorides are known in oxidation state V-II with wide range of stoichiometries and structures.<sup>1</sup> Recently, we have reported a series of niobium(V) and dimeric niobium(III) complexes with thio-, seleno- and telluro-ether ligands and investigated their application in low pressure chemical vapor deposition (LPCVD).<sup>2-3</sup> While thin films of crystalline NbS<sub>2</sub> and NbSe<sub>2</sub> were obtained from several of the Nb(V) complexes at elevated temperatures, LPCVD on the Nb(III) systems failed; this is most likely due to the extremely stable Nb-Nb bond present and their correspondingly high molecular weights. We have now investigated the preparation of niobium(IV) complexes with soft donor ligands; it was anticipated that the lower molecular weights of the monomeric species, together with the presence of the tetravalent oxidation state in the precursors might lead to improved CVD reagents .

The preparation of a small number of thioether complexes of NbCl<sub>4</sub> have been reported.<sup>4-5</sup> Both these and NbCl<sub>4</sub> complexes with other soft donor ligands such as phosphines have been shown to form six-, seven- or eight-coordinate species.<sup>6</sup> Other complexes with neutral bidentate ligands form [2:1] or [1:1] eight coordinate compounds.<sup>7-8</sup> Niobium tetrahalide complexes with neutral soft donor ligands are still unusual.

Here we report the preparation, spectroscopic and characterisation of a series of six- and eight- coordinate Nb(IV) monomer and dimer complexes with soft neutral diphosphine or dichalcogenoether ligands obtained by direct reaction from NbCl<sub>4</sub> or from [NbCl<sub>4</sub>(CH<sub>3</sub>CN)<sub>2</sub>].

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## Toward more efficient poly-*N*-donor-based iron complexes

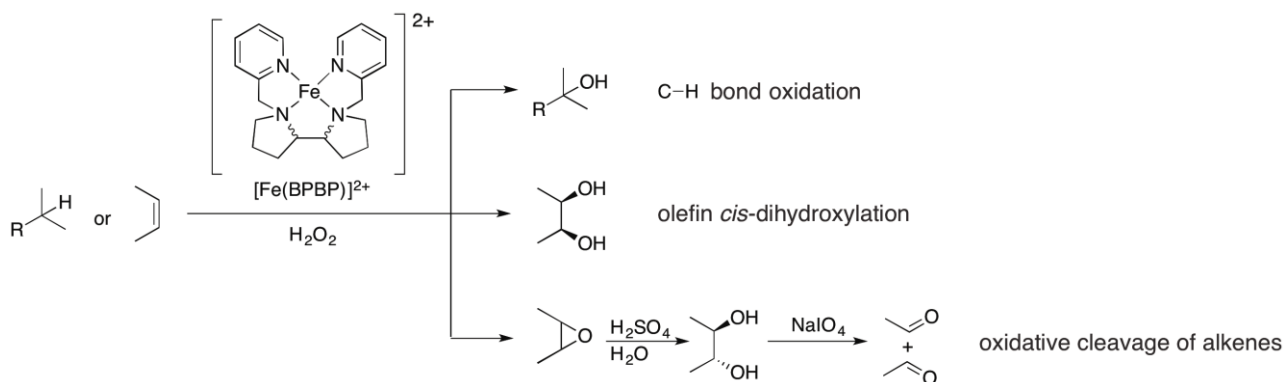
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Catalyst systems based on non-heme iron coordination complexes in combination with H<sub>2</sub>O<sub>2</sub> as oxidant are of particular interest due to the high availability and versatile redox chemistry of iron, and the benign nature of the H<sub>2</sub>O<sub>2</sub> oxidant. In the past decades, a large number of bio-inspired iron complexes have been reported that are capable of activating H<sub>2</sub>O<sub>2</sub> and catalyzing C–H bond oxidations and alkene oxidations, giving rise to various building blocks for organic bulk and fine chemicals. The requirement for chemo- and stereoselective C–H/C=C oxidations on a technical scale in modern chemistry stimulates researchers to develop more reactive, efficient and selective catalytic protocols.

Iron(II) complexes bearing the poly-*N*-donor ligand BPBP (BPBP = *N,N*-bis(2-pyridylmethyl)-2,2'-bipyrrolidine) have been found to be able to perform predictable selective C–H bond oxidations<sup>1</sup> and enantioselective olefin epoxidation and *cis*-dihydroxylation with H<sub>2</sub>O<sub>2</sub>.<sup>2</sup> Using a racemic version of this catalyst, the oxidative cleavage of unsaturated fatty acids into aldehydes and regioselective cleavage of dienes have also been achieved.<sup>3</sup> In this poster, we will describe the development of a new iron catalyst family based on a similar poly-*N*-donor ligand. Our research focuses on the structural and electronic properties of the ligand with the aim to develop more efficient iron-based catalytic oxidation protocols with increased chemo- and stereo-selectivities.



**Figure 1** Oxidative transformations catalyzed by the  $[\text{Fe}(\text{BPBP})]^{2+}/\text{H}_2\text{O}_2$  system

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## Characterization of new electro-polymerized bisphenol A Ferric complex material

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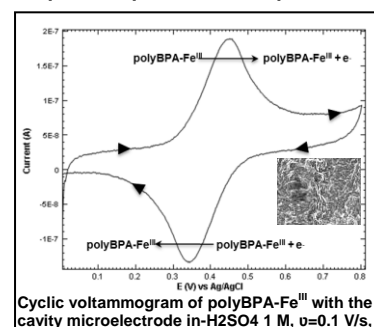
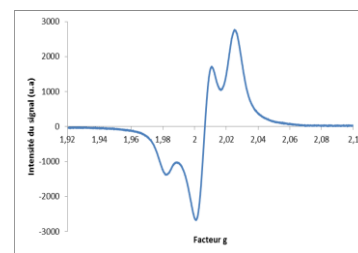
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During the treatment of bisphenol A by the electro-Fenton process at semi-pilot scale, consisting of pollutant oxidation by the hydroxyl radicals in the presence of a catalytic amount of Fe<sup>II</sup>, an electro-polymerized “bisphenol A – Ferric” complex powder material has been formed. In order to be valorized, this material was recovered, studied and characterized by different analytical and characterization techniques: DLS, MEB, TGA, IR, EA, XRF, AAS, UV-VIS, MEC, MS, ICP-OES, RMN and RPE. The solubility of the new material in the common organic solvents is very low. This material shows a thermal stability up to 160°C in an oxidizing atmosphere. The elementary composition by mass unit (C, H, N and S) was also determinate as respectively 57.22 %, 3.94 %, 0 % and 0.16 %. The presence of Fe<sup>III</sup> was studied by the electron paramagnetic resonance and the X-ray fluorescence techniques and quantified as 6.96 % by the atomic absorption spectroscopy and confirmed by the inductively coupled plasma optical emission spectrometry technique. The voltammetric study of the new material contained in the cavity microelectrode shows a reversible redox system probably related to the reduction of the ferric component, indicating that it is an electroactive material. The structure of this powder material was investigated also by the IR spectroscopy and different NMR methods. They indicate a high polymer compatibility structure to the parent molecule: the bisphenol A.



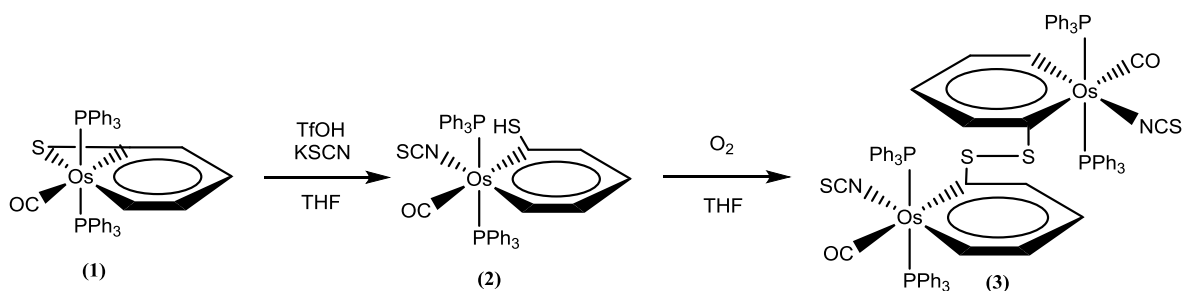
In the presented results, the new electro-polymerized “bisphenol A – Ferric” complex material (polyBPA-Fe<sup>III</sup>) was investigated in order to find an application to valorize a future scaling electro-Fenton process to the industrial scale.

## Chemistry of sulfur-functionalized osmabenzenes

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Metallabenzenes are a relatively new class of compounds, first being hypothesized in 1979 by Thorn and Hoffman<sup>1</sup>. The first metallabenzene, an osmabenzene (**1**) was synthesized in 1982. These compounds have attracted significant attention and show both similarities and differences in reactivity, when compared to that of traditional aromatic compounds.<sup>2, 3</sup>

While research into the reactivity of these compounds is still in its infancy, some definite parallels with their organic counterparts have emerged. Protonation of the S atom in **1** gives the osmathiol product without disruption of the aromaticity of the metallabenzene ring. When an isothiocyanate ligand is present at the metal centre, the thiol substituted osmabenzene **2** is oxidized in the presence of air to the corresponding disulfide, **3**. An analogous reaction is observed for many organic aromatic thiols. The osmabenzene dimer **3** has been found to undergo electrophilic aromatic substitution reactions without cleavage of the S-S bond. Nitration under Menke conditions and bromination with pyridinium tribromide both resulted in substitution at the position para to the disulfide linkage, on both metallabenzene rings. The analogous iridabenzene dimer  $[\text{Ir}(\text{C}_5\text{H}_4\{\text{S}\}-1)\text{Cl}_2(\text{PPh}_3)_2]_2$  can be prepared by treatment of the iridathiol  $\text{Ir}(\text{C}_5\text{H}_4\{\text{SH}\}-1)\text{Cl}_2(\text{PPh}_3)_2$  with the oxidant  $\text{I}_2$ .



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## 3D heterometallic coordination polymer based on Cu<sup>II</sup> and Gd<sup>III</sup>

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In the past years, the heterometallic 3d-4f coordination polymers (CPs) have gain considerable attention due their intriguing architectures and also their novel properties. In comparison with the other 3d cations, Cu<sup>II</sup> presents a wide variety of coordination numbers and more flexible coordination modes, which in addition with the interesting chemistry of lanthanides, makes the binding of these cations a rich field of research.<sup>1</sup>

In this work we present the synthesis and characterization of a new heterometallic Cu<sup>II</sup>-Gd<sup>III</sup> 3D CP, [Gd(H<sub>2</sub>O)<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)Cu(IDC)]·H<sub>2</sub>O **CuGd-1**, using 1H-imidazole-4,5-dicarboxylic acid (H<sub>3</sub>IDC) and oxalate (C<sub>2</sub>O<sub>4</sub><sup>2-</sup>) as auxiliary ligands. In the 3D structure, Cu<sup>II</sup> ions have a N<sub>2</sub>O<sub>4</sub> coordination sphere presenting axial Jahn-Teller distortion, and Gd<sup>III</sup> cations having an O<sub>8</sub> coordination sphere, with a square antiprism geometry. Structural, magnetic and electronic characterization of this coordination polymer will be discussed in this work.

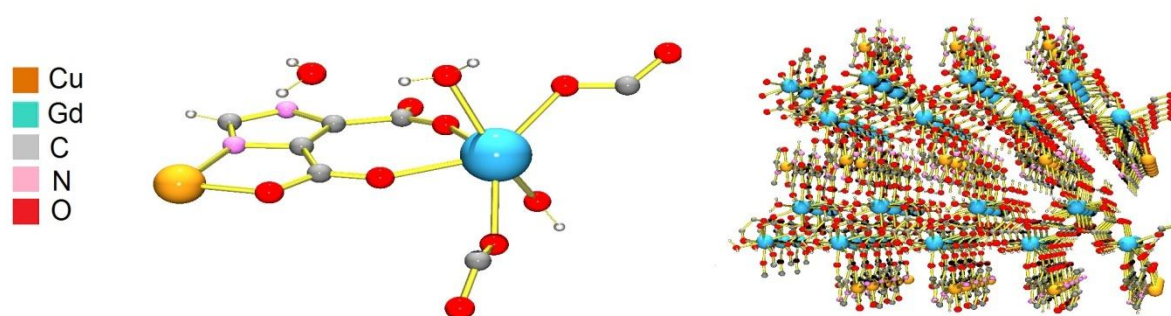


Figure 1. (a) Asymmetric unit and (b) visual of the extended structure of **CuGd-1**.

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## Coordination Compounds of Fe<sup>3+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Dy<sup>3+</sup>, and Gd<sup>3+</sup> with (1-Amino-1-methyl-ethyl)phosphonic Acid and a New Schiff Base Ligand

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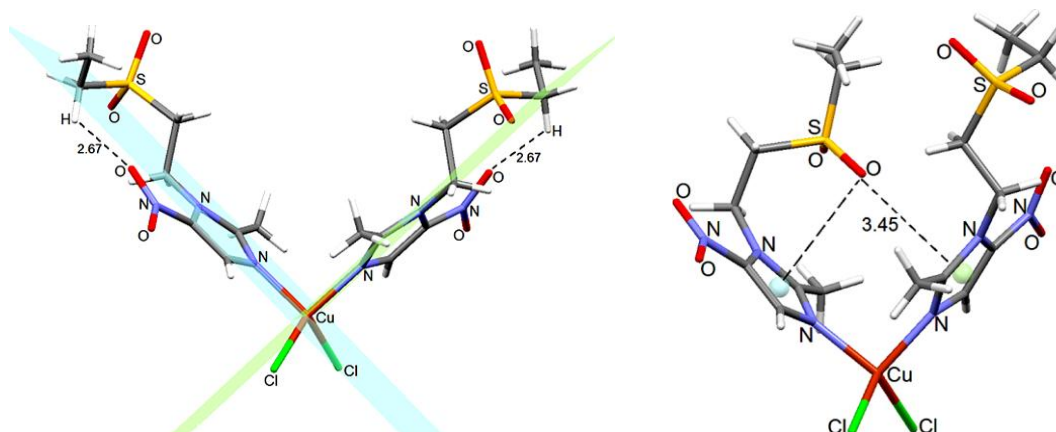
In the last decade, there has been a great interest in the phosphonic acid-based molecular complexes and coordination polymers. Because the M-O-P bonds are 1.5 times stronger than M-O-C bonds in carboxylates, phosphonates were used in the role of molecular precursors for the synthesis of new materials, such as polynuclear metal phosphonates, layered compounds, and porous metal-organic frameworks, with a wide range of properties and different applications. Phosphonate mononuclear complexes or molecular clusters with paramagnetic metal cations are very interesting objects because of their magnetic properties. We synthesized and isolated new molecular complexes and coordination polymers of AIPA ((1-amino-1-methyl-ethyl)phosphonic acid) and Na<sub>x</sub>SAA, x = 1, 2 (sodium hydrogen (2-[[*E*-(2-hydroxyphenyl)methylidene]amino]propan-2-yl)phosphonate, disodium hydrogen (2-[[*E*-(2-oxidophenyl)methylidene]amino]propan-2-yl)phosphonate) ligands with Fe<sup>3+</sup>, Ni<sup>2+</sup>, Co<sup>2+</sup>, Dy<sup>3+</sup>, and Gd<sup>3+</sup>. Their properties were studied by a variety of physicochemical methods including structural analyses by single-crystal X-ray diffraction methods. Their magnetic properties were studied on a SQUID magnetometer. Among the most interesting results obtained in this study are isolation and characterization of hexanuclear iron(III) phosphonate Fe<sub>6</sub>(NH<sub>3</sub>(CH<sub>3</sub>)<sub>2</sub>CPO<sub>3</sub>)<sub>12</sub>(OH)<sub>6</sub>·31H<sub>2</sub>O, a 1D coordination polymer of Fe with the SAA ligand, a series of heptanuclear Co<sup>2+</sup> phosphonates with a Star-of-David structural motif, and a coordination polymer of Ni<sup>2+</sup> with SAA ligands. Beside that, mononuclear isostructural complexes of Ni<sup>2+</sup> and Co<sup>2+</sup> with AIPA were obtained and characterized. The presence of non-coordinated amino groups in the complexes with AIPA makes these compounds potential precursors for the synthesis of new extended structures.

## Synthesis and characterization of new coordination compounds of 2-methyl-1-(2-(phenylsulfonyl)ethyl)-1H-imidazole and different metallic centers.

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Metals and metal-containing compounds have been extensively studied due to their important enzymatic, structural or reactive roles in biological processes. Over the years, their properties have awoken the interest in developing novel means to use metals or metal-containing agents to modulate biological systems searching for their potential use in medicine; imidazole and its derivatives are of special interest for their chemical and pharmacological properties. Thus, the widespread use of metal complexes as chemotherapeutic agents is well established; this is particularly true as antineoplastic, antihelmintic and antimicrobial compounds [1]. In this respect, we have synthesized the 2-methyl-1-(2-(phenylsulfonyl)ethyl)-1H-imidazole (2-mfsi) and a serie of novel  $\text{Fe}^{\text{II}}$ ,  $\text{Ru}^{\text{II}}$ ,  $\text{Co}^{\text{II}}$ ,  $\text{Ni}^{\text{II}}$ ,  $\text{Cu}^{\text{II}}$  and  $\text{Zn}^{\text{II}}$  coordination complexes to study the  $\text{S}=\text{O}\cdots\pi$  (imidazole ring) interaction and their antineoplastic effect [2]. The complexes were characterized by UV-Vis-NIR spectrophotometry, elemental analysis, infrared spectroscopy, molar conductivity, magnetic conductivity and magnetic susceptibility. In the coordination compounds these metals stabilize tetrahedral and octahedral geometries that in some cases are related to their in vitro anticancer or antimicrobial activity.



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## Squaramide-based dinuclear receptors for selective binding of phosphates

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Squaramides are outstanding four-membered ring structures derived from squaric acid that form up to four hydrogen bonds. This, together with the simultaneous increase in aromaticity of the ring, and with the structural rigidity, have been explored with a special relevance for its supramolecular chemistry applications.<sup>1</sup> On the other hand, dinuclear metal complexes used as receptors for anion substrates through formation of cascade species have been applied to numerous supramolecular systems. Indeed, the selective coordination of an anionic substrate bridging the two metal ions of a dinuclear complex has the advantage of the high energy of the coordination bond that confers higher affinities towards the anions.<sup>2</sup> Additionally, these receptors can easily be transformed in anion optical sensing systems, that can be used to monitor the presence, or/and the concentration of the anionic substrate.<sup>3</sup>

In the presented work, new squaramide-based dinuclear complexes were prepared, and their interactions with anionic substrates, namely phosphorylated anions, were studied through determination of the thermodynamic constants in aqueous solution. For this purpose, two new squaramide-based ligands were prepared. Moreover, the receptors and their cascade species containing the anions were studied in solution by a range of spectroscopic techniques with special emphasis on fluorescence, and in the solid state by single crystal X-ray diffraction determination.

### Acknowledgements:

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## Molecular design of Ag(I) $\beta$ -diketonate complexes for MOCVD application

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Silver-containing thin films are widely used in various fields such as microelectronics, catalysis, optics, etc. In the perspective, silver may be used as dopant of palladium membranes for hydrogen separation. One of the most suitable methods to form metal structures on difficult-shaped object is MOCVD (Metal-Organic Chemical Vapor Deposition). However, in the case of silver, the usage of MOCVD is strongly limited by only a few numbers of effective precursors because of the tendency of silver to form polymeric/oligomeric compounds. The solution of this problem could be achieved through molecular design.

From this point, the general idea of the work was the creation of monomeric Ag(I) complexes by the introduction of bulky substituent in the  $\beta$ -diketonate (RC(O)CHC(O)R') ligand. The mono- and mixed-ligand complexes were the objects of investigation. The hfac (R = R' = CF<sub>3</sub>) and ptac (R = CF<sub>3</sub>, R' = <sup>t</sup>Bu) were chosen as  $\beta$ -diketonates L and diamines with different steric rigidity (tetramethylethylenediamine (tmeda), 2,2'-bipyridil (bipy), 1,10-phenanthroline (phen)) were chosen as additional neutral ligands. The following series of complexes were synthesized: [Ag(ptac)]<sub>∞</sub> **1**, [Ag<sub>2</sub>(tmeda)<sub>2</sub>(hfac)]<sub>2</sub> **2**, [Ag<sub>2</sub>(tmeda)<sub>2</sub>(ptac)]<sub>∞</sub> **3**, [Ag(Q)(hfac)]<sub>2</sub> (Q = bipy **4**, phen **5**), [Ag(tmeda)(hfac)]<sub>∞</sub> **6**, [Ag(Q)(ptac)] (Q = bipy **7**, phen **8**, tmeda **9**). Compounds **1-3**, **5**, **7-9** were obtained for the first time. Complexes were characterized by elemental analysis, <sup>1</sup>H NMR and IR spectroscopy, single-crystal and powder XRD. Thermal properties of some compounds were investigated by mass-spectrometry, thermogravimetric analysis and differential scanning calorimetry.

In the case of flexible diamine tmeda the formation of mixed-ligand complexes with stoichiometry Ag:L = 1:1 and 2:1 was observed. It was also shown the great influence of introduction of <sup>t</sup>Bu-group in  $\beta$ -diketonate: in the case of mono- and mixed-ligand complex this modification led to the changing of polymeric structure from 2D to 1D while in the case of mixed-ligand complexes it led to the isolation of molecules from chains (diamine = tmeda) or dimers (bipy, phen). Among other complexes, **9** seems to be the most perspective MOCVD precursor. In total, the chosen approach appeared to be effective.



## Towards Nanoporous Hybrid Hydrides

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Among the various known MOFs, a family based on the imidazolate unit ( $Im^-$ ) and divalent metals shows typical zeolite topologies due to the structure-directing effect of the imidazolate ligand. In the other field of solid state chemistry, metal borohydrides  $M(BH_4)_n$  were intensively investigated for their high hydrogen content. Porous zeolite-like frameworks were synthesized with  $Mg^{2+}$  and  $Mn^{2+}$  [1, 2], where the  $BH_4^-$  unit has a structure-directing effect, bridging via its edges. Combining hydridic and classical ligands in the same structure could result in stable hydridic compounds showing specific guest-host interactions. Here we report on the strategy of obtaining porous hydridic MOFs and on the results obtained so far.

Firstly, we obtained a series of alkali metal imidazolate precursors,  $M/Im$ . The coordinative oversaturation of  $Im$  in the  $M/Im$  series ensures a coordination of the  $BH_4^-$  anion to metal atoms in the hybrid imidazolate-borohydrides. Indeed, in the first hybrid hydride,  $Li_2/ImBH_4$ , the borohydride group is linearly bridging two metal atoms. Its fast rotation manifested by neutron powder diffraction is decoupled from the Li-ion dynamics, unlike in metal borohydrides, where the two processes are linked by the paddle-wheel mechanism. The strong Li- $Im$  coordination is responsible for this partitioning, and the limiting ionic formula  $[Li_2Im]^+[BH_4]^-$  reflects the structural chemistry and the properties of this compound. Unfortunately, the structure of  $Li_2/ImBH_4$  is not porous.

Secondly, the  $Im$  linker was functionalized by benz- and methyl- substituents, which are known to favour porosity in ZIFs. The resulting  $Mb/Im$  and  $Mm/Im$  were combined with  $MBH_4$ , yielding hybrid hydrides. Thirdly, we explored the role of neutral bridging N-based ligands, obtaining a series of complexes with  $LiBH_4$ , where the borohydride group also plays a role of the bridging ligand. The highly ionic nature of the  $Li^+$  cation limits the directionality of the  $BH_4^-$  coordination, and thus leads to structures without porosity. Fourthly, we focused on Mg-based ZIFs and obtained  $Mg/Im_2$  in a form of the porous crystalline and amorphous phases.

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# Selective functionalization of iridabenzenoids

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\*Speaker

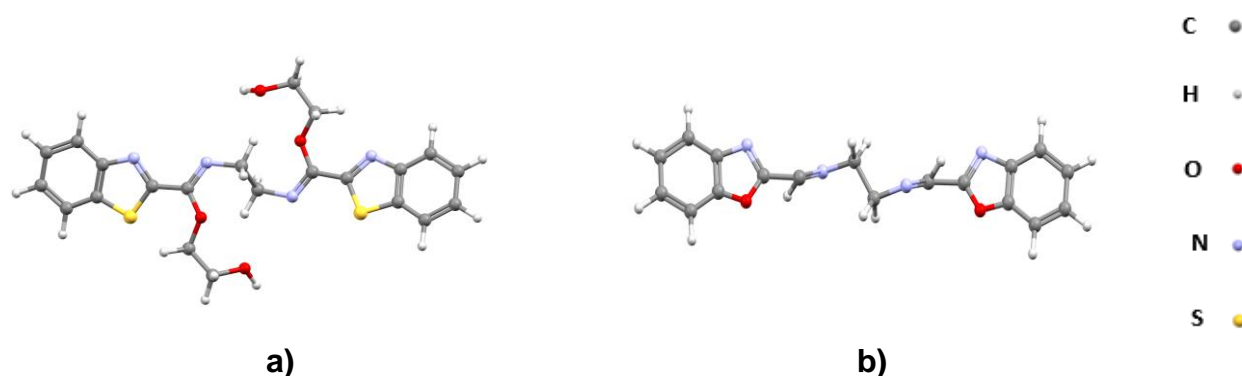
## Structural analysis of supramolecular arrangements of new benzoxazole and benzothiazole derivatives and their coordination compounds

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Benzoxazole and benzothiazole derivatives are organic molecules widely studied due to their important antibiotic<sup>1</sup>, antihelmintic<sup>2</sup>, antibacterial<sup>3</sup>, antitumor<sup>4</sup>, analgesic<sup>5</sup> and anticancer<sup>6</sup> biological activities.

Is for this reason, in our research group we have investigated coordination compounds that showed an increase in their biological activity with respect to the original organic molecules.<sup>7,8</sup>

In this work, it is presented the synthesis of new benzothiazole and benzoxazole derivatives (figure 1) which formed heteronuclear coordination compounds with transition metal ions of high nuclearity. These showed  $\pi$ -stacking interactions promoted by the aromatic rings, heteroatoms and electronic delocalization.



**Figure 1** Synthesized benzothiazole (a) and benzoxazole (b) derivatives.

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## Coordination Complexes of Plutonium (IV) and (VI) with Imidodiphosphinate Ligands

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There is a need to address the many environmental problems the nuclear age has brought about. In particular, the identification of radiotoxic actinide ions, their oxidation state and chemical form with regards to decommissioning, separation and environmental remediation. In this regard, we have previously shown that the TPIP (tetraphenylimidodiphosphinate) ligand stabilises neptunium and uranium exclusively in the +VI oxidation states.<sup>1,2</sup> Moreover, TPIP is able to form oligomeric species assembled by actinyl Lewis acid base adducts (cation-cation interactions) for uranyl (VI) ions that can be fingerprinted by emission spectroscopy and preliminary evidence suggests a mixed metal cation-cation aggregate occurs in mixtures of neptunyl (VI) and uranyl (VI). The study of cation-cation interactions is extremely important in evaluating and developing new separation processes based on new and simplified versions of the PUREX process.

Here we report the coordination chemistry of TPIP and its related counterpart with peripheral *iso*-propyl groups (TIPIP) with Pu(IV) and Pu(VI). The reaction of TPIP and TIPIP with Pu(VI) and TPIP with Pu(IV) yielded single crystals, XRD studies of which showed the Pu(VI) complexes to be  $[\text{PuO}_2(\text{HTIPIP})_2(\text{H}_2\text{O})][\text{NO}_3]_2$ , a rare example of bidentate HTIPIP coordination, and  $[\text{PuO}_2(\text{TPIP})(\text{HTIPIP})(\text{NO}_3)]$ , with monodentate HTIPIP coordination, and the Pu(IV) complex to be  $[\text{Pu}(\text{TPIP})_3(\text{NO}_3)]$ . Attempts to displace  $[\text{NO}_3^-]$  using coordinating solvents or  $\text{Ph}_3\text{PO}$  to form plutonyl(VI) cation-cation aggregates were unsuccessful. The complexes have been analysed by MS, UV-vis, IR, Raman and NMR spectroscopy that gave invaluable insights into the nature of the paramagnetic complexes in solution. Mixed metal systems of uranyl(VI) or neptunyl(V) with plutonyl(VI) and uranyl(VI) with plutonium(IV) were also investigated in order to establish whether mixed metal cation-cation aggregates formed. The results obtained will be discussed in detail.

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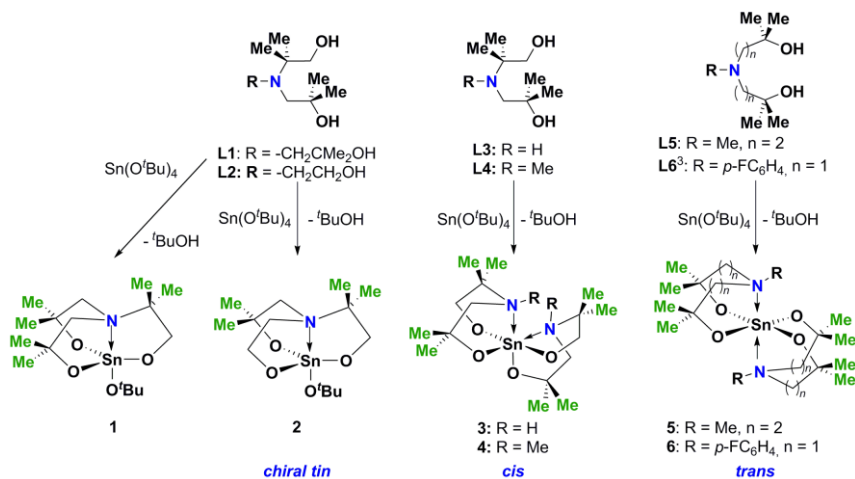
## Novel Alkanolamines and their Tin(IV) Derivatives

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Alkanolamines  $R_{3-n}N(CH_2CR'R''OH)_n$  ( $R, R', R'' = H, \text{alkyl, aryl}; n = 1-3$ ) are a structurally interesting class of chelate ligands.<sup>1</sup> Related to our investigation of their tin(IV) derivatives as versatile *delayed action* catalysts for polyurethane formation,<sup>2</sup> we synthesized novel alkanolamines such as  $RN(CH_2CMe_2OH)(CMe_2CH_2OH)$  (**L1**:  $R = CH_2CMe_2OH$ , **L2**:  $CH_2CH_2OH$ , **L3**:  $R = H$ , **L4**:  $R = Me$ ) and  $MeN(CH_2CH_2CMe_2OH)_2$  (**L5**). The reactions of  $Sn(O^tBu)_4$  with **L1-L4** and the fluorine-substituted representative<sup>3</sup>  $p\text{-FC}_6\text{H}_4N(CH_2CMe_2OH)_2$  (**L6**) gave the tin(IV)derivatives **1-6**, respectively (Scheme 1).

An important feature of these compounds is the intramolecular  $N \rightarrow Sn$  interaction the strength of which depends on different factors. Derivative **2** is the first *pseudo*-stannatrane with chirality at the tin atom as result of the unequal ligand arms. In contrast to the *cis*-coordination observed for compounds **3** and **4**, the nitrogen atoms in **5** and **6** are *trans*.



**Scheme 1** Selected alkanolamines and their tin (IV) derivatives.

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## Carboxylate Cd(II) complexes: synthetic approaches, structural rearrangement and special structure features

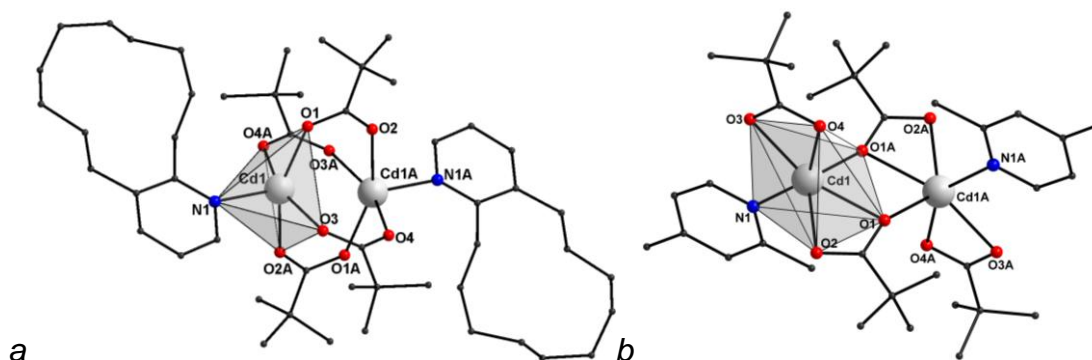
N.V. Gogoleva,\* M.A. Shmelev, M.A. Kiskin, G.G. Aleksandrov, A.A. Sidorov, I.L. Eremenko

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Specific of Cd(II) is connected with its big ionic radii and can influence on complexes structures [1], but was not systematically studied by now. We have found that In the reaction of  $[\text{Cd}(\text{piv})_2]$  ( $\text{piv} = {}^-\text{O}_2\text{CBu}^t$ ) and monodentate N-donor ligands (isoquinoline (iqn), 2,4-lutidine (lut), phenanthridine (phend), 2,3-cyclododecenopyridine (cpy)) gave mono- and binuclear complexes that structures are in a direct dependence of ligand steric factors (Figure 1). It appeared that homometallic Cd(II) complexes with  $\text{piv}^-$  are more stable than heterometallic, approaches to synthesis of that were found. As a result a series of complexes  $[\text{Cd}_2\text{M}(\text{piv})_6(\text{L})_2]$  ( $\text{M} = \text{Li}, \text{Mg}, \text{Ca}, \text{Sr}$ ) was characterized.

In the case of 3,5-di-tert-butylbenzoic acid anions ( $\text{bzo}^-$ ) Cd(II) complexes structures are similar to Zn(II) analogues and have compositions  $[\text{Cd}_3(\text{bzo})_6(\text{EtOH})_3(\text{H}_2\text{O})]$ ,  $[\text{Cd}_2\text{Mg}(\text{bzo})_6(\text{lut})_2]$ ,  $[\text{Cd}_2\text{Ln}(\text{bzo})_{6-7}(\text{Solv})_x]$ ,  $[\text{Cd}_2\text{Ln}(\text{bzo})_{6-7}(\text{Solv})_x\text{L}_2]$ . It should be mentioned that Cd can coordinate additional solvate molecules and EtOH can compete with N-donor ligands.

All the compounds were characterized by X-Ray diffraction analysis. Research of UV/Vis spectra and photoluminescence of the selected complexes was performed.



**Figure 1** Structure of  $[\text{Cd}_2(\text{piv})_4\text{L}_2]$  ( $\text{L}=\text{cpy}$  (a) or lut (b)) (H-atoms are not shown).

**Acknowledgements** - This study was supported by Russian Science Foundation (project 14-23-00176).

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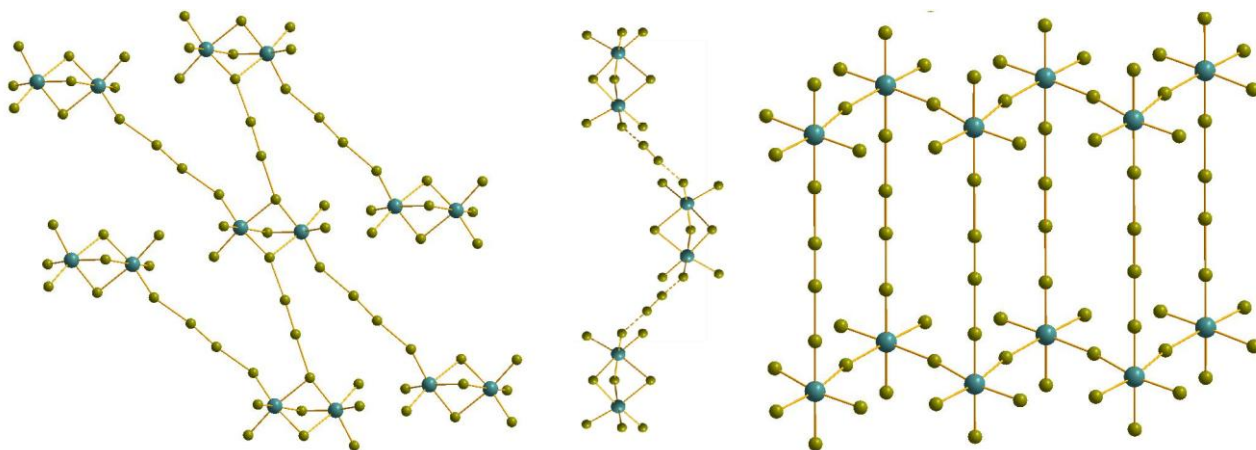
## Polybromide complexes of bismuth(III): new entry into the coordination chemistry of bismuth

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Over the last years, coordination compounds containing polyhalide ligands attract an interest of researchers. However, although there is a great variety of compounds containing polyiodide moieties, the number of polybromides is extremely limited. To date, there are known only several examples of polybromide complexes of Cu, Au, Pt, Sb and W. In this work, we present our recent advances in the chemistry of Bi(III) polybromides.

Reactions of  $[\text{BiBr}_6]^{3-}$  and different organic cations, conducted in HBr solutions in presence of  $\text{Br}_2$ , may yield in formation of polybromides ("inclusion" of  $\text{Br}_2$  molecules into the structure). Most commonly, it results in extended 1D- or 2D coordination networks. During our work, we discovered 4 structural types of polybromides. In some cases (Fig. 1),  $\{\text{Br}_2\}$  units connect the fragments which are common for Bi(III) bromide complexes, such as  $\{\text{Bi}_2\text{Br}_9\}$  or polymeric  $\{\text{BiBr}_5\}_n$ , via terminal or bridging Bi atoms. The  $\{\text{Br}_2\}/\text{Bi}$  ratio was found to be 0.5 or 1. All complexes display high thermal stability (release of  $\text{Br}_2$  proceeds above  $150^\circ\text{C}$ ) [1].



**Figure 1.** Polybromides of Bi(III): type 1 (left), 2 (middle) and 3 (right)

This work has been supported by Russian Science Foundation (Grant No. 14-23-00013)



## Syntheses and Electronic Properties of Novel Two-dimensional Nickel MX-ghost Leg Complexes

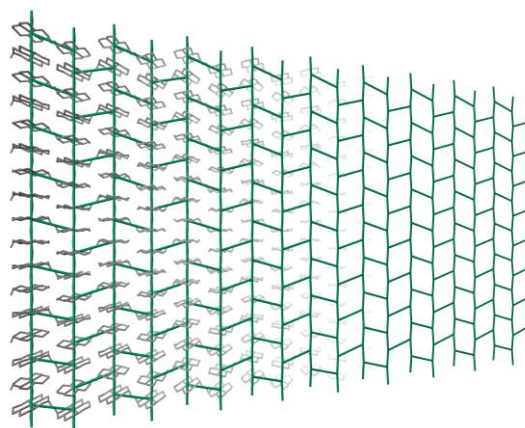
Ryota Hashiguchi,<sup>a</sup> Kazuya Otsubo,<sup>a,b</sup> Kunihisa Sugimoto,<sup>c</sup> Akihiko Fujiwara,<sup>d</sup>  
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One-dimensional (1-D) halogen-bridged transition-metal complexes (MX-chains) have attracted much attention for a long time because of their wide range of interesting physical properties. MX-chains are considered to be model compounds for studying a purely 1-D electronic system because they have well-isolated chain structures and systematically-controllable electronic states. Recently, studies of dimensional extension in MX type complex such as two-legged MX-ladders<sup>1,2</sup> and four-legged MX-tubes<sup>3</sup> have drawn significant attention. Compared with oxide ladder systems, these MX type complexes based on the coordination bond have many advantages for tunability of electronic properties through substitution of structural components. However, these MX type complexes are limited to platinum based ones. In this work, we have intended to study the electronic states of two-dimensional (2-D) sheet composed of nickel MX-chains.

We have successfully synthesized the first example of a nickel based 2-D MX type complex, namely MX-ghost leg,  $[\text{Ni}_2\text{X}_2\text{L}]\text{X}_4$  (L: 1,2-bis(1,4,6,8,11-pentaazacyclotetradecane-6-yl)-ethane, X: Br, Cl) and determined their crystal structures using single-crystal X-ray crystallography (Figure 1). These MX type complexes are not only the first nickel based MX-ladder type systems but also the first 2-D layered systems as MX type complex.

Their electronic states have been investigated using single-crystal X-ray diffraction, Raman and diffuse reflectance spectra measurements. The electronic state within one MX-leg was found to correspond to a CDW (charge-density-wave:  $\dots\text{Ni}^{\text{II}}\dots\text{X}-\text{Ni}^{\text{IV}}-\text{X}\dots$ ) state, which rarely occurs in nickel MX-chains. Details of this study are presented.



**Figure 1** Framework of nickel 2-D MX-ghost leg

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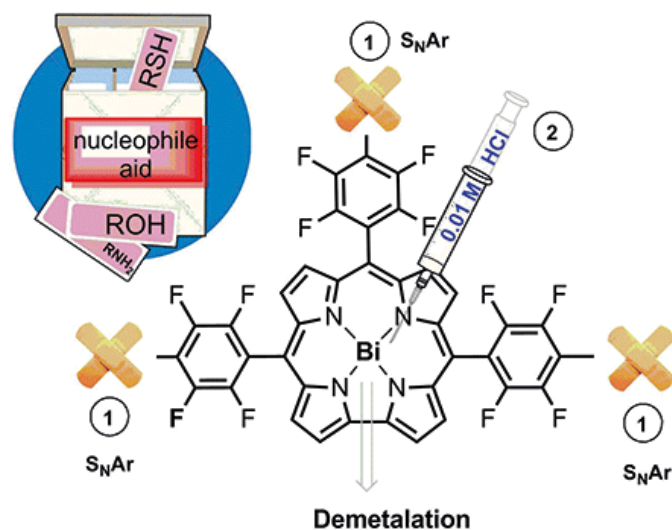
## Bismuth A<sub>3</sub>-corroles: Useful precursors for the development of meso-substituted free-base corroles

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We herein report our efforts to systematically study regioselective functionalization reactions employing oxygen-, nitrogen-, and sulfur- containing nucleophiles with bismuth A<sub>3</sub>-corroles under the influence of a strong non-nucleophilic base. In case of the thiols and dithiols we have established a high-yielding reaction procedure to obtain mono-, di-, and tri-functionalized corroles at room temperature within short reaction times. The described method offers a possibility to attach bi-functional linker molecules to the para-position of the meso-pentafluorophenyl-groups at positions 5, 10, and 15 of the corrole macrocycle. The described reaction strategy may serve as a versatile protocol for the covalent binding of corroles to proteins or antibodies and may be utilized to attach corroles on e.g. gold or titania surfaces to study surface supported reactions.<sup>1-3</sup>



**Figure 1:** 1) Functionalization of corroles by S<sub>N</sub>Ar reaction with nucleophiles and 2) the subsequent demetalation reaction with aqueous 0.01 M HCl solution.

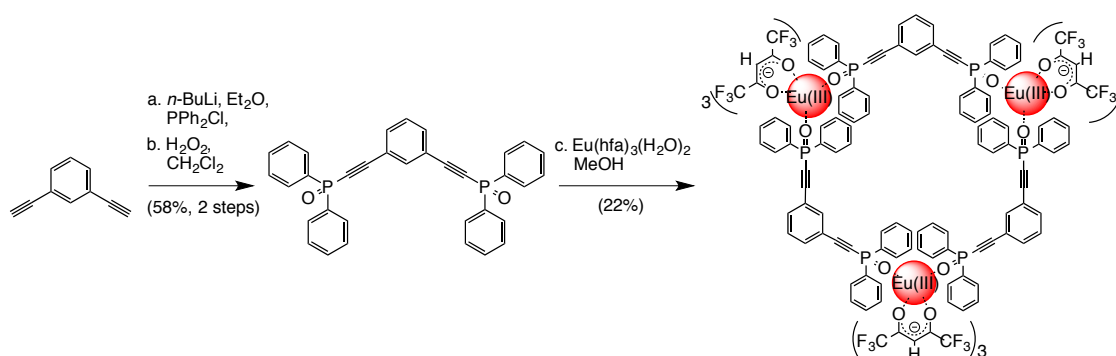
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## Design and synthesis of luminescent Eu(III) coordination glass

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Amorphous molecular materials have recently attracted attention as a novel class of functional materials with excellent processability, transparency, isotropic, and homogeneous properties for optical applications.<sup>1</sup> Organic molecules with  $C_3$  symmetrical axis are generally known to form stable amorphous solid.<sup>2</sup> We here report on design and synthesis of red-luminescent Eu(III) coordination glass composed of Eu(III) ions, 120° bite angle bridge, and hexafluoroacetylacetonate (hfa) ligands.<sup>3</sup> Lanthanide complexes exhibit line-like emission and have long emission lifetimes due to the forbidden nature of f-f transitions, which is attractive for optical materials.<sup>4,5</sup>



**Figure 1** Synthetic scheme of Eu(III) coordination glass.

We successfully synthesized the Eu(III) coordination glass (Figure 1), and FAB-MS spectrum and DFT calculation revealed the trimer structure. We also found strong red emission at around 613 nm due to the hypersensitive transition of Eu(III) ions ( $\Phi_{Ln} = 72\%$ ). Strong luminescent lanthanide coordination glasses, which can be processed at ambient temperatures, are expected as novel luminescent materials.

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## Mixed Amido-cyclopentadienyl Group 4 Metal Complexes

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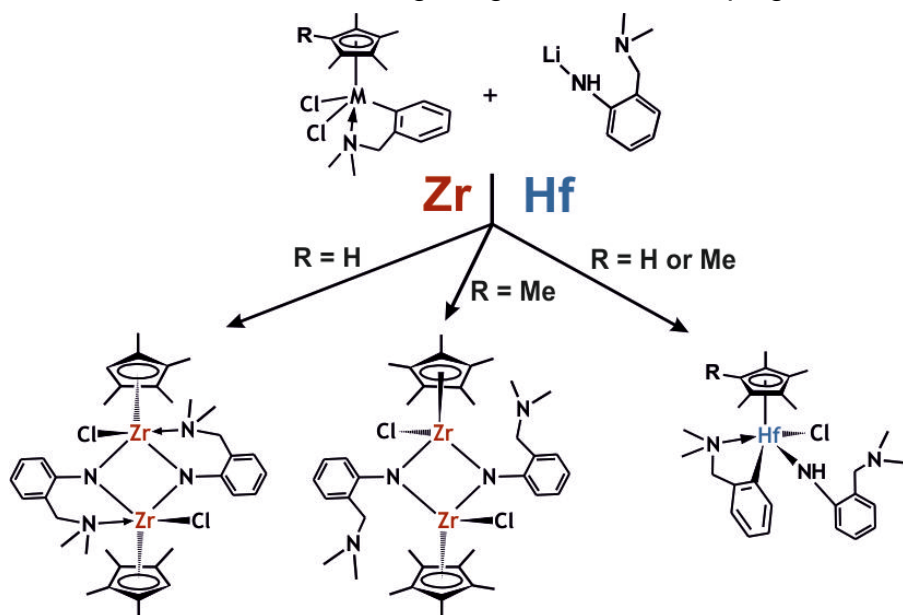
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Being interested in the preparation and potential use of bifunctional compounds of mainly group 4 metals, we described in our previous work a simple method for the preparation of compounds containing a highly substituted cyclopentadienyl ring and the C, N-chelating ligand<sup>1</sup> or bifunctional  $\beta$ -diketiminato ligands with the potentially coordinating methoxy groups<sup>2</sup>. Moreover the introduction of sterically demanding substituent as 2, 6-diisopropylaniline or N, N-chelating aniline led to the formation of dimeric compounds with arylimide bridges accompanied by release of C, N-chelating ligand.<sup>3</sup>

This contribution demonstrates variability of the group 4 metal coordination spheres where different kinds of nitrogen ligands and two Cp ligands with different electronic and



steric effects were employed. The results confirm anticipated differences in the chemical behaviour and properties of group 4 metals showing an increasing stability of amido- and imido-complexes from titanium to hafnium.

Scheme displays diversity of the reaction products for Zr and Hf in the reaction with Li[NHC<sub>6</sub>H<sub>4</sub>-2-(CH<sub>2</sub>NMe<sub>2</sub>)].

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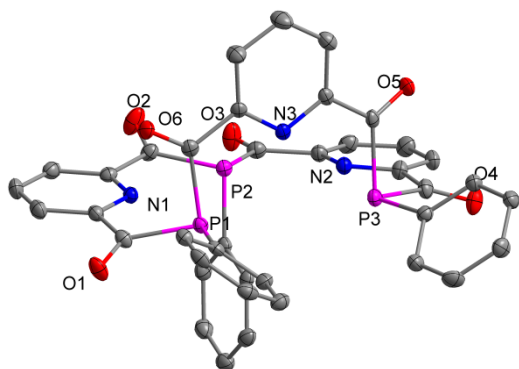
# Tri- and Tetraphosphametacyclophanes Containing Phosphomide Units: Synthesis, Structure and Coordination Chemistry

VITTHALRAO S. KASHID, MARAVANJI S. BALAKRISHNA\*

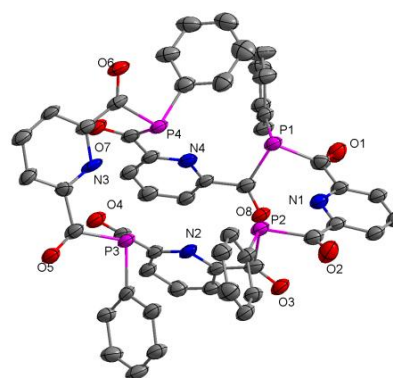
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One pot synthesis of phosphomide based tri- and tetraphosphametacyclophanes ( $m\text{-}\{C(O)\text{-}C_5H_3N(C(O)PPh)\}_3$ ,  $m\text{-}\{C(O)\text{-}C_5H_3N(C(O)PPh)\}_4$ ) was achieved by reacting phenylphosphine with 2,6-pyridinedicarbonyl dichloride in presence of a base. The molecular structures of these new cyclic ligands have been confirmed by various spectroscopic methods and single crystal X-ray diffraction analysis. Synthetic, spectroscopic and structural investigations along with coordination chemistry will be presented.



**Figure 1** Molecular structure of  $m\text{-}\{C(O)\text{-}C_5H_3N(C(O)PPh)\}_3$



**Figure 2** Molecular structure of  $m\text{-}\{C(O)\text{-}C_5H_3N(C(O)PPh)\}_4$

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# Organometallic complexes of phosphonomethylsulfonamides: Experimental and DFT studies

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## **Abstract:**

In recent years, there has been a rapid expansion in research and development of novel metal-based drugs to improve clinical effectiveness; however the choice of a suitable ligand is crucial in the design of new bioactive metal complexes [1]. The introductions of phosphate moiety in sulfonamides molecules improve bioavailability and biological activities of resulting compounds [2]. The aim of this work is to study the resulting complexes between the ligand and some metallic ions such as  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$  and the  $\text{Ni}^{2+}$  ions. The complexes formation was studied in solution and in solid state (Fig 1). In order to gain further insights into the interaction ligand-ion in this system the 1:1 and 1:2 complexes have been optimized by using DFT (B3LYP/6-311G) level of theory (Fig 2).

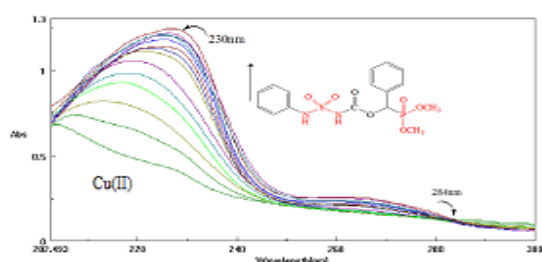


Fig 1: Evolution of absorption spectra of  $10^{-4}$  M Cu (II) in ethanolic solution with progressive addition of title ligand.

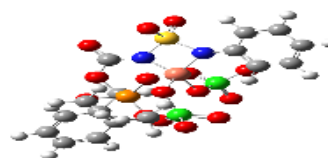


Fig 2: The optimization geometry CuL

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## Lanthanide fluorobenzoates for bioimaging and lighting applications

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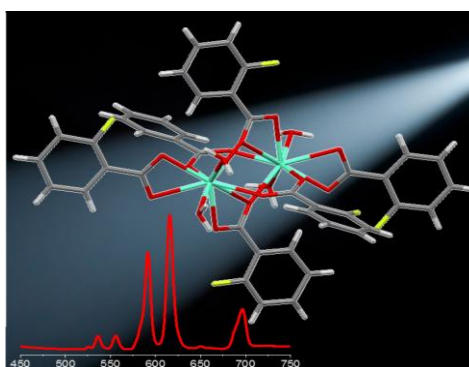
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The narrow emission lines from lanthanide ions has attracted great interest, particularly with regard to developing tools for bioimaging, where the long lifetimes of lanthanide excited state can be exploited to address problems arising from autofluorescence and sample transparency<sup>1</sup>. Moreover, the use of lanthanide complexes leads to the possibility of combining several functional properties in one molecule, such as high luminescence efficiency and the large paramagnetic moment for simultaneous optical and MRI imaging.

For this purpose bifunctional heterometallic Eu(III)-Gd(III) complexes are used. The search for the appropriate ligand was made among fluorinated derivatives of benzoic acid<sup>2</sup>. Therefore, 10 different ligands with variable number and positions of fluorine atoms were chosen and their chemical and functional properties (solubility, non-toxicity, stability and luminescence intensity in aqueous solutions) were investigated.

The most promising structures were modified further in order to attach a peptide for selective cell recognition. These aggregates were successfully engulfed by targeted cells and their luminescence was monitored *in cellulo*. To evaluate their potential as MRI contrast agents, their relaxation times were measured *in vitro*. Modified structures have been proposed to increase the signal intensity, and hence to reduce the concentration required for *in vivo* studies.



**Figure 1** The single crystal structure of Eu(III) 2-fluorobenzoate dihydrate and the luminescence spectra of its 0.003M aqueous solution

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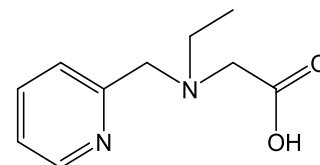


# Syntheses and Reactions of Ruthenium Complexes Bearing Ethyl(2-pyridylmethyl)aminoacetate

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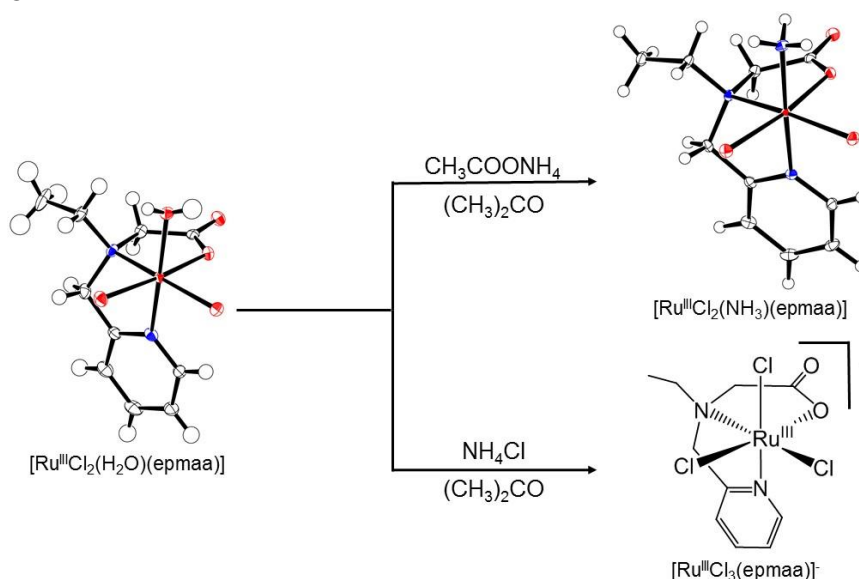
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Bis(2-pyridylalkyl)amine (bpa) coordinates to a ruthenium center as a neutral tridentate ligand by two pyridyl and amine nitrogen atoms in both *mer*- and *fac*- mode. The influences of configuration around a metal center on stability and reactivity of ruthenium complexes have been studied. Alkyl(2-pyridylmethyl)aminoacetate (Rpmaa), which has pyridyl and carboxylate groups connected by methylene arms was synthesized as an alternative tridentate ligand.



**Figure 1** Hepmaa

In this work, ethyl(2-pyridylmethyl)aminoacetate (Hepmaa) was synthesized by a reaction of 2-picolyl chloride hydrochloride with *N*-ethylglycine. Dichloridoaquaruthenium complex,  $[\text{Ru}^{\text{III}}\text{Cl}_2(\text{H}_2\text{O})(\text{epmaa})]$ , was obtained by a reaction of  $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$  and Hepmaa under reflux conditions. Reactions of  $[\text{Ru}^{\text{III}}\text{Cl}_2(\text{H}_2\text{O})(\text{epmaa})]$  with ammonium salts such as  $\text{CH}_3\text{COONH}_4$  and  $\text{NH}_4\text{Cl}$  were investigated to afford  $[\text{Ru}^{\text{III}}\text{Cl}_2(\text{NH}_3)(\text{epmaa})]$  and  $[\text{Ru}^{\text{III}}\text{Cl}_3(\text{epmaa})]^-$ , respectively (**Scheme 1**). These results indicated that products of reactions with ammonium salts depended on acidity of the conjugated anions of ammonium ion.



**Scheme 1** Reactions of  $[\text{Ru}^{\text{III}}\text{Cl}_2(\text{H}_2\text{O})(\text{epmaa})]$  with ammonium salts

## Structure and Properties of Hydrogen-bonded Solid Based on Metal Dithiolene Complex

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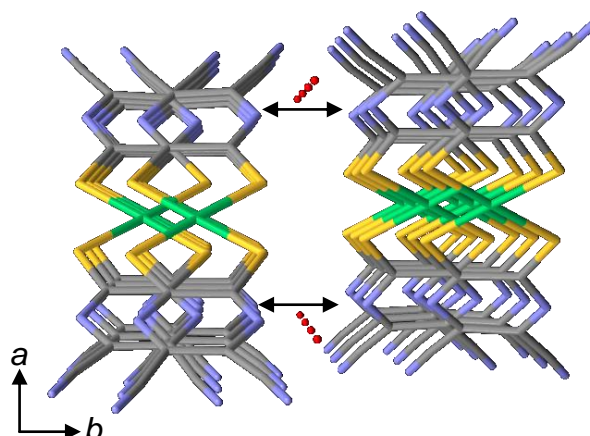
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There has been considerable interest in hydrogen-bonded solids because of their anomalous behavior in electrical, optical, and magnetic properties that are derived from curious electronic structures induced by not only proton but also proton-coupled electron transfers. Organic molecules having  $\pi$ -electrons have been mainly studied as the subject of hydrogen-bonded solids. On the other hand, metal complexes having both  $\pi$ - and d-electrons have been less studied regardless of their unique electronic structure. Among metal complexes, metal dithiolene complexes have characteristic molecular orbitals in which d-orbital and  $\pi$ -orbital are strongly hybridized. Therefore, they have a potential to show anomalous physical properties in a hydrogen-bonding lattice.

In this research, we focus on a metal dithiolene complex substituted by electron-withdrawing group (complex **1**). A novel hydrogen-bonded solid was successfully obtained (complex **1H<sub>2</sub>**). By X-ray diffraction and optical measurements, it was revealed that its crystal structure has one-dimensional  $\pi$ -stack columns connected with each other by hydrogen bonding. In this presentation, we discuss chemical and electrical properties.



**Figure 1** Crystal structure of complex **1H<sub>2</sub>**. Arrows represent hydrogen bonding between 1D columns.

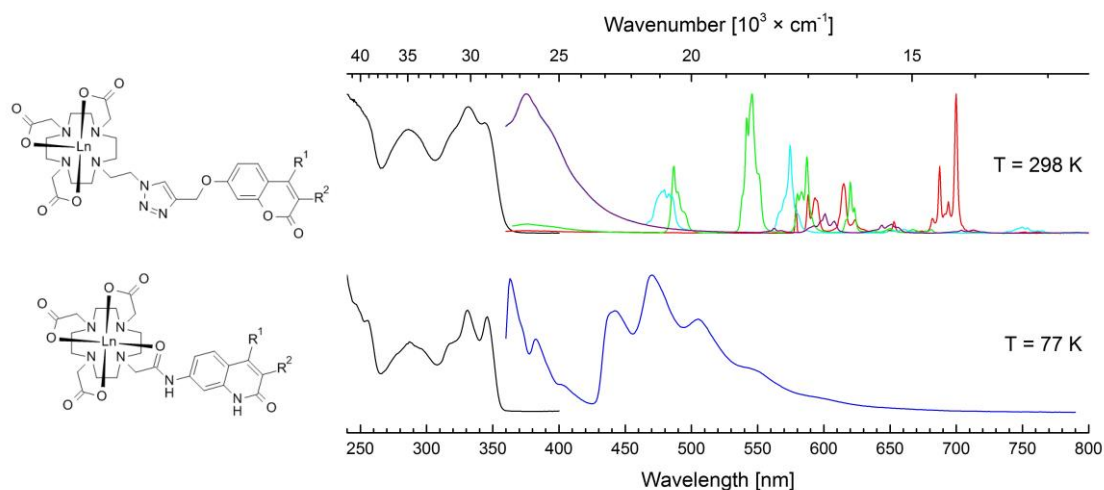
# Synthesis and critical evaluation of coumarin and carbostyryl-sensitized luminescent lanthanide complexes

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Noninvasive imaging techniques are increasingly in demand. Luminescence imaging offers high sensitivity and high resolution. Lanthanides (Ln) have long-lived, narrow, metal-specific emissions.<sup>1</sup> This is advantageous for multiplex detection, because overlap between these emission signals is minimal. Ln-luminescence is often sensitized through a light-harvesting chromophore ('antenna') as the metal ions' extinction coefficients are low. A large number of antennae have been tested in the past decades, but only a few possess the ability to sensitize several luminescent lanthanide ions to an appreciable extent.<sup>2-4</sup> Sensitizing the less emissive Dy and Sm in addition to Tb and Eu is still a challenge. Here, we present a family of functionalized coumarin and carbostyryl sensitizers linked to two different DO3A-type lanthanide binding units. We identified several antennae that were competent sensitizers for up to four visible-emitting lanthanides. The synthesis and photophysical characterization of these complexes will be presented.



**Figure 1.** Lanthanide complexes studied here. Excitation (solid black line, left) and steady-state emission spectra of Eu (red), Tb (green), Dy (cyan), Sm (purple) complexes at 298 K (top), and Gd-complex excitation and emission at 77 K (black and blue lines, bottom).

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## Synthesis and Characterization of TM Complexes Containing Organoantimony(I) Moieties

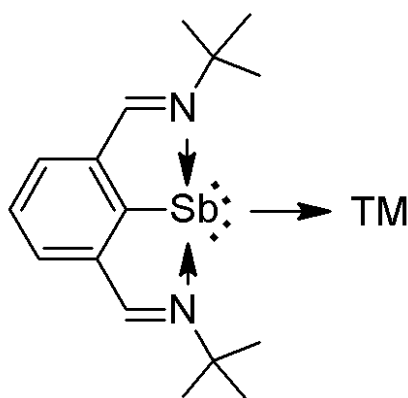
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Recently, our group successfully synthesized organoantimony(I) compounds stabilized by various types of NCN chelating ligand<sup>1</sup>. Increasing interest in chemistry of those species is due to their high reactivity and presence of two electron lone pairs. Those properties are predicting possibilities of using such compounds as ligands for transition metals (Figure 1).

We have done synthesis and full characterization of series of transition metal complexes based on coordination to organoantimony(I) moieties. Herein, we present the reactivity with selected transition metals of Group 9 – 11.



**Figure 1** Coordination of electron lone pairs of low-valent antimony to TM

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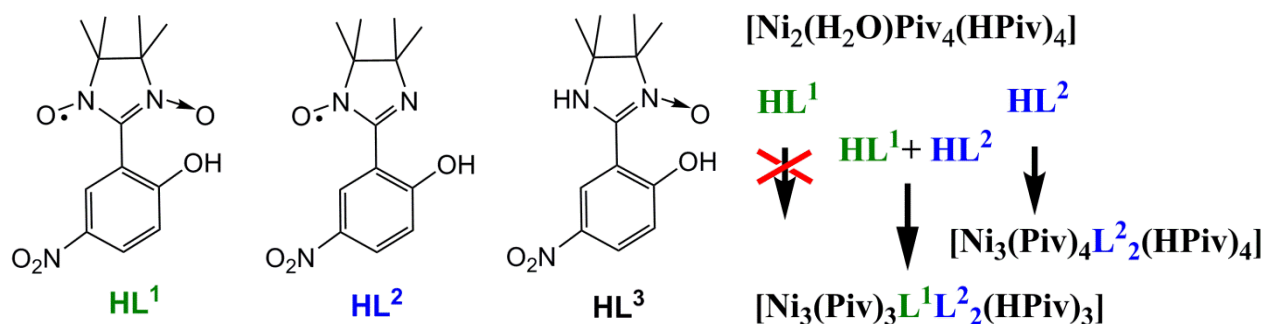
### Acknowledgement

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## Synthesis of Metal Complexes Containing Two Nitroxides

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Recently, a process called a “redox-induced change in the ligand coordination mode” was found<sup>1</sup>. It was shown reaction of **HL<sup>2</sup>** (2-(2-hydroxy-5-nitrophenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazole-1-oxyl) with  $[\text{Co}_2(\text{H}_2\text{O})\text{Piv}_4(\text{HPiv})_4]$  (Piv is trimethylacetate) gave rise to  $[\text{Co}_3(\text{Piv})_2\text{L}^2_2\text{L}^3_2]$ .  $[\text{Co}_3(\text{Piv})_2\text{L}^2_2\text{L}^3_2]$  formation indicates that exists an individual class of metal compounds with nitroxides whose ligand shell contains both the starting radical and the product of its reduction. The present study describes the complex  $[\text{Co}_5(\text{Piv})_4\text{L}^1_4\text{L}^2_2]$  formed in the reaction of  $[\text{Co}_2(\text{H}_2\text{O})\text{Piv}_4(\text{HPiv})_4]$  with nitronyl nitroxide **HL<sup>1</sup>**. This prompted us to introduce a known mixture of **HL<sup>1</sup>** and **HL<sup>2</sup>** in the reaction with  $[\text{M}_2(\text{H}_2\text{O})\text{Piv}_4(\text{HPiv})_4]$  where M = Co, Ni. Since both **HL<sup>1</sup>** and **HL<sup>2</sup>** are kinetically stable products, their binary mixtures can readily be prepared. The use of these mixtures in reactions with cobalt and nickel pivalates led to  $[\text{Co}_3(\text{Piv})_2\text{L}^1_2\text{L}^2_2]$  and  $[\text{Ni}_3(\text{Piv})_3\text{L}^1\text{L}^2_2(\text{HPiv})_3]$ , respectively<sup>2</sup>. Thus we found a new approach to synthesis metal complexes containing two different nitroxides.



The research was supported by the Russian Science Foundation (projects 15-03-00488, 15-33-20286), President's of Russian Federation Grant (MK- 2732.2015.3) and FANO RF.

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## Structural Investigation of Diphenic Acid/Nicotinamide Complexes with Co(II) Cu(II) and Zn(II) Cations

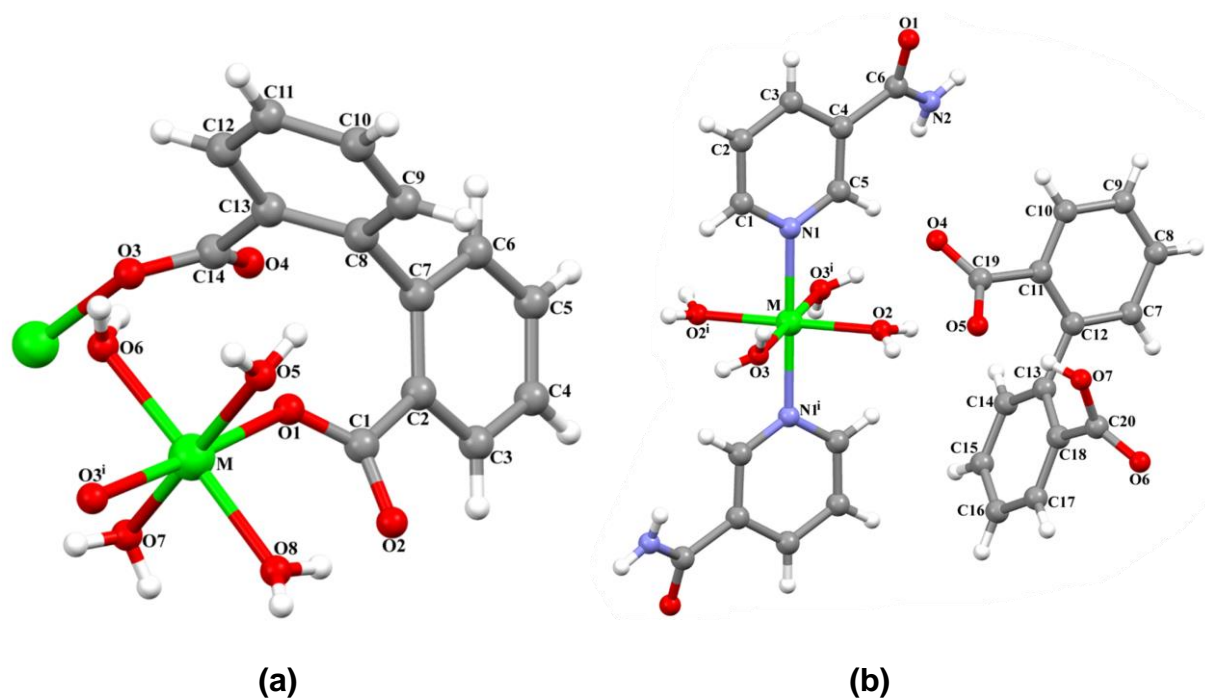
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<sup>a</sup>Hitit University Department of Chemistry, 19100, Çorum/Turkey

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In this study, Co<sup>II</sup>, Cu<sup>II</sup> and Zn<sup>II</sup> metal cation complexes were synthesized and investigated of their structural properties by FT-IR, TG/DrTG-DTA, UV-Vis spectroscopy, elemental analysis and single crystal XRD methods. The complexes were obtained with high purity. According to structural evidence, pure ligand complexes contain one mole metal cation and one mole dianionic diphenate ligand and four moles crystalized aqua ligands. The unit cell of complex contains four moles metal cation and four moles diphenate ligands. Each diphenate ligand was settled to two moles copper cations. The mixed ligands complexes include two moles nicotinamide and four moles aqua ligands in coordination sphere. The one mole diphenate anion was located outside of the coordination sphere as dianionic counter ion. The geometries of the all complexes are distorted octahedral. The molecule structures were shown in Figure 1.



**Figure 1.** (a) Pure ligand complex of Co<sup>II</sup> and Cu<sup>II</sup>(b) Mixed ligand complex of Co<sup>II</sup> and Zn<sup>II</sup>

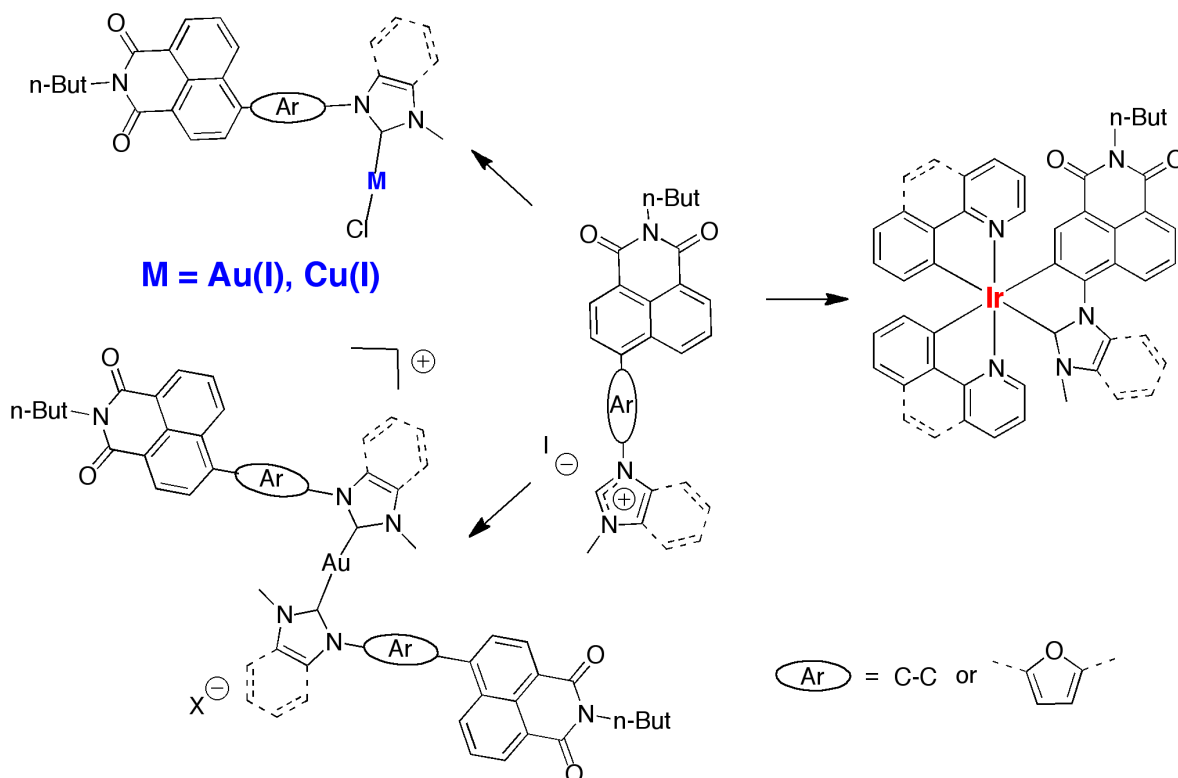
## Chromophoric N-heterocyclic carbene ligands for luminescent metal complexes: from blue to deep red emitters

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Luminescent N-heterocyclic carbene (NHC) complexes attract an increasing attention in the quest of new luminophore since the last decade.<sup>1</sup> In this context, we designed new ligands featuring a common naphthalimide moiety (NI) attached to the NHC framework and extended the  $\pi$ -conjugation in order to control the emission wavelength. In this communication, we describe a new family of luminescent carbene complexes with various transition metals spanning from coinage metals, such as Cu(I) and Au(I) to  $[\text{Ir}(\text{C}^{\wedge}\text{N})_2]$  moieties (see figure). While coinage carbene complexes are fluorescent at room temperature, in stark contrast the cyclometallating carbene complexes behave as strong red phosphores.



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<sup>2</sup> ) P.-H. Lanoë, J. Chan, F. Monti, N. Armaroli, A. Barbieri and H. Amouri, Submitted.



## Diradical Ni(II) complexes derived from *o*-PDA based ligands

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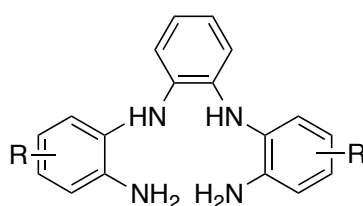
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Redox active ligands have recently received an increased attention in the field of catalysis since they can act as electron reservoirs.<sup>1</sup> The particular class of radical ligands exhibits the ability of abstracting hydrogen atoms, causing the C-H bond activation of small substrates. Such a property is well illustrated by metalloenzymes like Cytochrome P450 or Galactose Oxidase, where molecular O<sub>2</sub> plays also a prominent role. These ligands give rise to enormous perspectives since their association to base metals could lead to new and unsuspected reactivities. Therefore the design of new redox active radical ligands is challenging. In this context, ligands based on anilines and *o*-phenylenediamines (*o*-PDA) are promising since their deprotonated forms can be reversibly oxidized at low potentials. However, they have been poorly studied, probably due to their ability to oxidize easily and the absence of flexible synthetic methods.

Aiming at the development of sustainable catalytic oxidative methodologies, our research has mainly focused on the design, the characterization and the reactivity study of bio-inspired radical metal complexes derived from anilines and PDA.<sup>2</sup> Our latest results in relation with unprecedented bis(*o*-PDA) redox active ligands will be given (Scheme 1).



**Scheme 1** The bis(*o*-PDA) tetradentate coordinating pattern

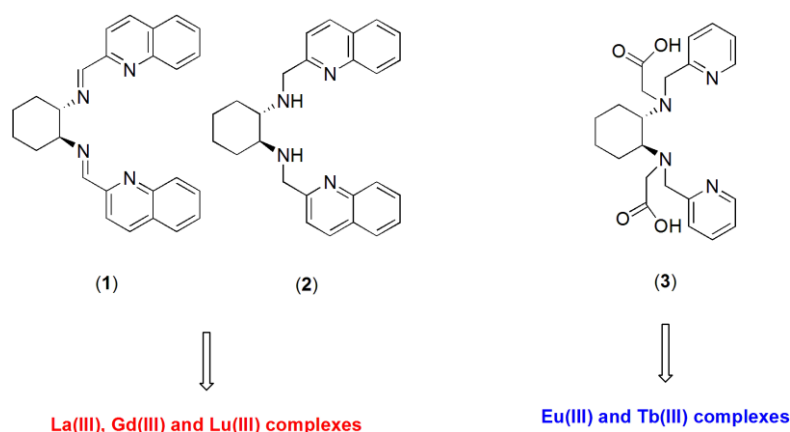
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## Luminescent Ln(III)-based complexes for multiple applications

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OLEDs represent the continuing generation flat displays due the low cost, ease of fabrication, low driving voltage, high contrast and wide viewing angle [1]. In this field, Ln-based complexes play a relevant role. When the light emitted is circularly polarized, it is possible to fabricate CP-OLEDs. In this context, the study of the chiral electroluminescence by Ln-based OLEDs is an emerging field of research [2]. In addition, the Circularly Polarized luminescence (CPL) is broadly exploited also in solution. In fact, the induced CPL upon binding to Ln chiral bioanalytes is of particular use to signal selectively the presence of chiral species, such as certain proteins [3] or chiral ions e.g. lactate or sialic acid [4]. With these multiple applications in mind, we have designed a new family of nitrogen-based chiral ligands and their Ln complexes (figure 1).



**Figure 1**

The total luminescence of La(III), Lu(III) and Gd(III) complexes with the ligands (1) and (2) is discussed, in detail. As far as the sensing in solution is concerned, we propose the Eu(III) and Tb(III) complexes with the ligand (3), as a new chiroptical probe. A preliminary study of their spectroscopy is presented.

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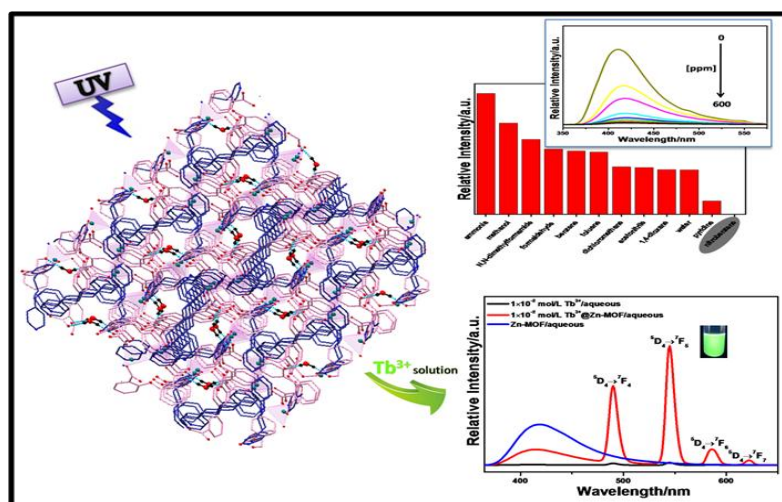
## Transition metal(II)–organic frameworks: preparation, crystal structures and luminescent properties

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The metal-organic frameworks attract more and more attention due to their intriguing architectures and their potential properties in separation, ion exchange, catalysis, sensors, magnetism and gas storage.<sup>1</sup> A series of coordination polymers, [Cd(DPDC)(BPP)·H<sub>2</sub>O]·H<sub>2</sub>O (**1**), Cd<sub>4</sub>(O-OBA)<sub>4</sub>(BPP)<sub>2</sub> (**2**), [Zn<sub>2</sub>(DPDC)<sub>2</sub>(BTB)(H<sub>2</sub>O)<sub>2</sub>]·H<sub>2</sub>O (**3**), [Zn(O-OBA)(BPP)]·0.5H<sub>2</sub>O (**4**) and Cu(DPDC)(BTB) (**5**) (DPDC = 2,2'-diphenyldicarboxylate, O-OBA= 2,2'-oxybis(benzoate, 1,3- di(4- pyridyl) - propane (BPP), and 1,4- bis (1,2,4- triazol -1- yl) butane (BTB)) were hydrothermally synthesized and structurally characterized. Complexes **1–5** exhibit diverse structural features based on the different coordination geometry of metal centers and different coordination modes and conformations ligands. The luminescent properties of the Zn-MOF (**4**) were investigated. The results showed that the Zn-MOF (**4**) could be used as a fluorescence probe to detect nitrobenzene and Tb(III) ion.



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## Perspective anticancer agents based on copper(II) complexes with 2-(N-acetylamino)pyridines

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Metal complexes have recently received considerable attention, as they have been shown to exhibit various types of biological activity. There is a strong need of the design of novel potential therapeutic candidates based on coordination metal complexes. This work will focus on the synthesis and characterization of new Cu(II) complexes with methyl-substituted 2-(N-acylamino)pyridine derivatives<sup>1,2</sup>. Constant interest to the pyridine derivatives is explained by the fact that many of them, natural and synthetic, display significant physiological activity.

All of the complexes have been identified and characterized by a set of methods including elemental analysis, IR-spectroscopy, single-crystal X-ray diffraction analysis, and magnetic susceptibility measurements in the range 5 – 300 K.

The cytotoxic activity some of the complexes in comparison with cisplatin was investigated *in vitro* against human cancer cell lines: HEK 293 (human embryonic kidney) and U937 (leukemic). Our results showed that cisplatin and complexes inhibit HEK 293 cell line in a dose and time dependent manner, toxicity of complexes is similar to that of cisplatin. The U937 cell line is significantly less sensitive to complexes compared to cisplatin. However, this selective sensitivity can be useful for the selection of drugs with reduced sensitivity to normal cells.

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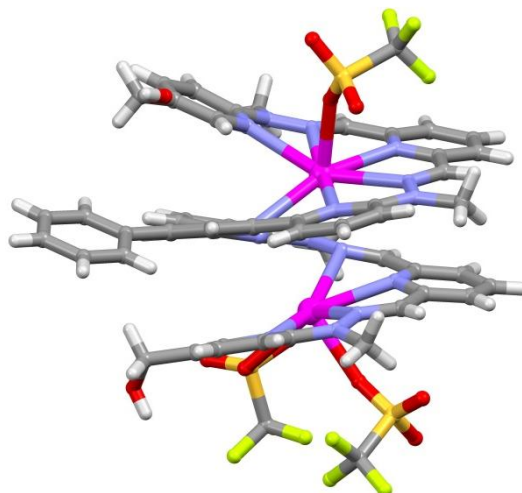
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## Helical Pyridine-Hyrazone Complexes

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Nature uses folded molecules such as proteins and nucleic acids to carry out complex functions including gene expression, membrane transport, and enzyme catalysis. The diverse chemistry of folded biomolecules has inspired the design of synthetic analogues that organise into discrete and thermodynamically stable structures in solution.<sup>1</sup>Oligopyridines connected by *trans* bonds act as helicating ligands when coordinated to metal ions.<sup>2</sup>Replacement of pyridine with a hydrazone isomorph facilitates the synthesis of long oligopyridine strands by aldehyde-amine condensation, while conserving the *trans* geometry that is required for helicity. A pyridine-hydrazone strand with seven pyridyl units formed a helical structure with two Pb(II) metals (Figure 1).



**Figure 1.** Crystal structure of pyridine-hydrazone with  $\text{Pb}_2(\text{CF}_3\text{SO}_3)_4$  (an uncoordinated  $\text{CF}_3\text{SO}_3$ , and  $\text{CH}_3\text{CN}$  removed for clarity)

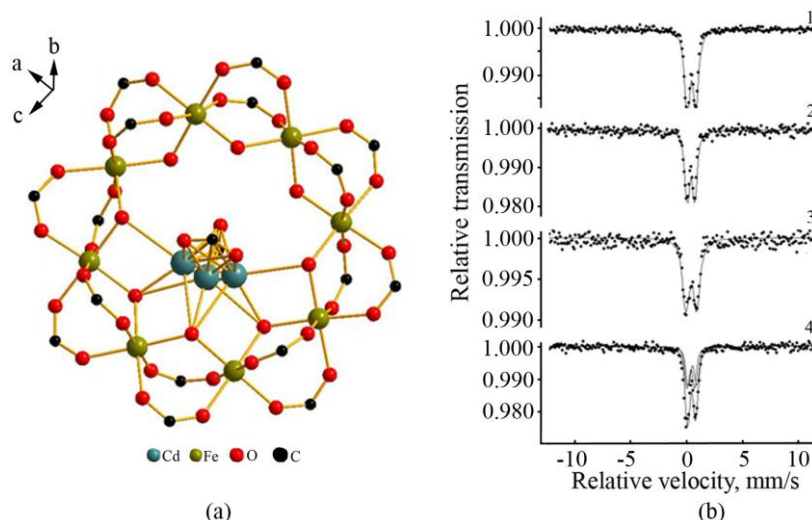
1. D.J. Hill; M.J. Mio; R.B. Prince; T.S. Hughes; J.S. Moore. *Chemical Reviews* **2001**, 101, 3893.
2. E.C. Constable. *Tetrahedron* **1992**, 48, 10013.

# Solid phase thermolysis as a method of new heteronuclear complexes forming

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All researches in the field of synthesis and determination of the physico-chemical properties of the heterometal complexes are of great interest in the development of coordination chemistry and materials on their basis. In this work we present an alternative synthetic way to form new polynuclear heterometallic complexes by solid phase thermolysis of known heteronuclear complexes or its mixture containing low boiling ligands ( $T_{\text{boil}} < 200\text{ }^{\circ}\text{C}$ ). It allows to remove the ligands from coordination sphere of metal atoms (without oxidation of other bridging organic ligands) with subsequent transformation of metal core due to a change in the coordination number of metal atoms and functionality of bridging ligands. Further crystallization of the product of thermolysis can give new compounds, the structure of which may depend on the nature of the solvent. By this method we synthesized new molecular pivalate complexes:  $[\text{Li}_2\text{Fe}_4\text{O}_2(\text{Piv})_{10}\text{H}_2\text{O}]$  (**1**),  $[\text{Fe}_2\text{Mn}_4\text{O}_2(\text{Piv})_8(\text{HPiv})_4]$  (**2**),  $[\text{Fe}_4\text{Zn}_3(\text{O})_3(\text{Piv})_{12}(\text{H}_2\text{O})]$  (**3**) and  $[\text{Fe}_8\text{Cd}(\text{OH})_8(\text{Piv})_{18}(\text{H}_2\text{O})]$  (**4**, Fig. 1a). These compounds were characterized by single-crystal X-ray diffraction, XRD, magnetochemistry and Mössbauer spectroscopy (Fig. 1b).



**Figure 1.** The molecular structural of **4** (a) and Mössbauer powder spectra of **1–4** (b).

This work was financially supported by the Russian Scientific Foundation (14-23-00176).

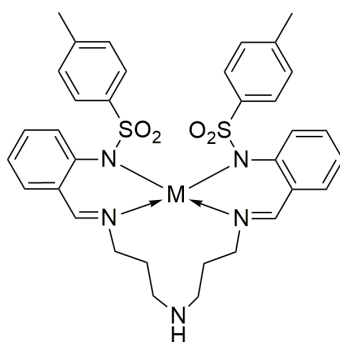
## Synthesis and structure of zinc (II) and cadmium (II) azomethine complexes

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The novel mononuclear Zn(II) and Cd(II) complexes with azomethine ligand 1 have been synthesized. The structures of the complexes were determined by elemental analysis, IR, <sup>1</sup>H NMR, UV spectroscopy, X-ray absorption spectroscopy and quantum chemical calculations. The structure of cadmium (II) complex was established by X-ray diffraction. In the complexes the metal ion is coordinated to the four nitrogen donor atoms of the ligand. From X-ray single crystal diffraction and EXAFS data of these complexes it was determined, that these complexes are characterized by pseudo radial distribution of atoms in the nearest coordination sphere around the absorbing metal atom. In both cases 1:1 (M:L) complex formation was confirmed by elemental analysis data.



1 M=Zn(a), Cd(b)

These complexes exhibit fluorescent properties ( $\lambda_{FL}=425-428$  nm) having photoluminescence quantum yields of 0.75 (1a) and 0.20 (1b).

Complexes are thermally stable. The melting points of the complexes are above 280 ° C. Due to its favourable characteristics these complexes can be used as the component of emissive layers in OLED devices.

The work was performed as part of the implementation of the Project goszadaniya in scientific research (project 4.742.2014 / K). We used a unique scientific equipment installation "Kurchatov synchrotron radiation source" with the financial support from the Ministry of Education and Science (project ID RFMEFI61914X0002).



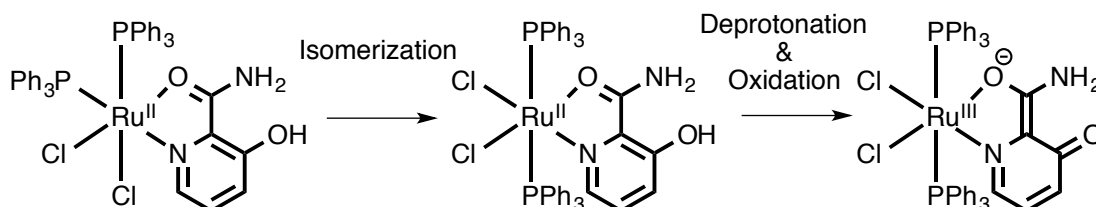
## Geometrical Isomerization and Redox Behavior of Ruthenium Complexes with Unsymmetrical Bidentate Ligand

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Electron transfer (ET) reactions of transition metal complexes are attracting much interest because they play fundamental role in energy conversion reactions in chemistry and biology.<sup>1</sup> Such ET reactions are generally accompanied by the change in protonation state of the ligand to accelerate the reaction. However, many of the ligands with proton-responsive group are unsymmetrical ligands, and consequently, they give geometrical isomers. In general, each geometrical isomer exhibits different redox behavior. In this study, we focused on the geometrical selectivity of  $[\text{RuCl}_2(\text{PPh}_3)_2(\text{L})]^{n+}$ -type complex with unsymmetrical ligand, and investigated the redox behaviors of some geometrical isomers upon deprotonation ( $\text{PPh}_3$ =triphenylphosphine, L=unsymmetrical bidentate ligand).

A stoichiometric reaction of  $[\text{RuCl}_2(\text{PPh}_3)_3]$  and Hpic (Hpic=3-hydroxypicolinamide) in ethanol afforded  $[\text{Ru}^{\text{II}}\text{Cl}_2(\text{PPh}_3)_2(\text{Hpic})]$ . X-Ray crystallographic analysis indicated that this complex is *cis(Cl,Cl),trans(P,N)*- $[\text{Ru}^{\text{II}}\text{Cl}_2(\text{PPh}_3)_2(\text{Hpic})]$  (**1**) as shown in Figure 1, left. By standing ethanol/ $\text{CH}_2\text{Cl}_2$  solution of **1** for a few weeks, *trans(P,P)*- $[\text{Ru}^{\text{III}}\text{Cl}_2(\text{PPh}_3)_2(\text{pic})]$  (**2**; Figure 1, right) were obtained. The cyclic voltammetry of **1** and **2** in  $\text{CH}_2\text{Cl}_2$  showed reversible  $\text{Ru}^{\text{III/II}}$  redox couple at  $E_{1/2} = -0.59$  and  $-0.05$  V vs.  $[\text{FeCp}_2]^{0/+}$ , respectively. Addition of base to **1** or acid to **2** gave only the  $\text{Ru}^{\text{III/II}}$  reduction waves. These results suggests that *trans(P,P)*- $[\text{Ru}^{\text{II}}\text{Cl}_2(\text{PPh}_3)_2(\text{Hpic})]$  and *trans(P,P)*- $[\text{Ru}^{\text{II}}\text{Cl}_2(\text{PPh}_3)_2(\text{Hpic})]$  are unstable and  $\text{H}^+/\text{e}^-$  transfer from  $[\text{Ru}^{\text{II}}\text{Cl}_2(\text{PPh}_3)_2(\text{Hpic})]$  was induced by isomerization from *cis(Cl,Cl),trans(P,N)*-isomer to *trans(P,P)*-isomer.



**Figure 1** Expected reaction scheme from **1** to **2**.

1 Y. Umena, K. Kawakami, J.-R. Shen, N. Kamiya, *Nature*, **2011**, 473, 55.

# Synthesis of Soluble Chalcogenide Precursors for the Development of Metal Sulfide Thin Films for Photovoltaics

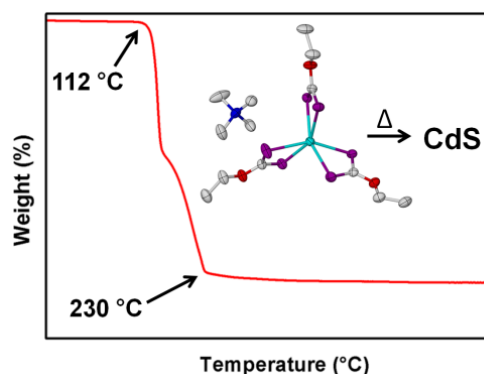
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Cadmium alkylxanthate complexes,  $[\text{Cd}(\text{S}_2\text{COR})_2]$ , and cadmium dialkyldithiocarbamate complexes,  $[\text{Cd}(\text{S}_2\text{CNR}_2)_2]$ , have found application as precursors for cadmium sulfide (CdS) thin film development and subsequent incorporation into photovoltaic devices. However, the polymeric nature of these complexes severely limits their solubility in green, organic solvents commonly used in solution deposition routes towards thin film formation.<sup>1</sup> A series of soluble, air and moisture stable, cadmium alkylxanthate salts,  $[\text{Cd}(\text{S}_2\text{COR})_3]^-$ , and cadmium dialkyldithiocarbamate salts,  $[\text{Cd}(\text{S}_2\text{CNR}_2)_3]^-$ , were developed for use as single source molecular precursors for CdS formation. The xanthate salts undergo facile and clean thermal decomposition to form the CdS thin films (Figure 1). Single crystal X-ray diffraction and *in situ* variable temperature synchrotron X-ray diffraction techniques were also used to examine CdS thin film formation.<sup>2</sup> The dialkyldithiocarbamate salts also showed clean decomposition pathways at low temperatures. Furthermore, some were synthesised to be ionic liquids through judicious choice of cation. These precursors possess significant potential for the development of metal sulfide thin films using solution based deposition techniques.



**Figure 1** TGA plot of  $\text{Me}_4\text{N}[\text{Cd}(\text{EtXn})_3]$  showing the low temperature decomposition profile generally exhibited by these salts to form CdS materials.

1 A. S. R. Chesman, N. W. Duffy, A. Martucci, L. De Oliveira Tozi, T. B. Singh, J. J. Jasieniak, *J. Mater. Chem. C* **2014**, 2, 3247.

2 L. K. Macreadie, H. E. Maynard-Casely, S. R. Batten, D. R. Turner, A. S. R. Chesman, *ChemPlusChem* **2015**, 80, 107.

## Synthesis, structure and interactions of ruthenium nitrosyl pyridine complexes

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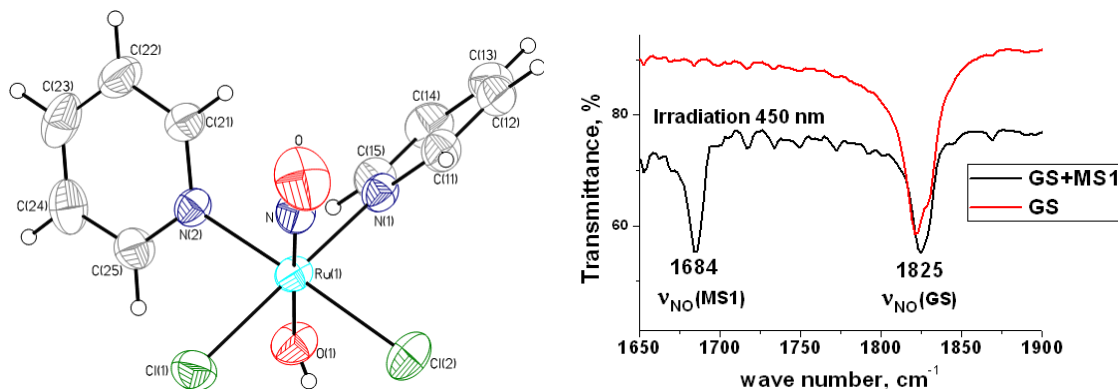
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Due to high affinity of ruthenium for NO, these complexes are currently being investigated as potential vasodilating, anticancer and antiparasite compounds<sup>1</sup>. Moreover, the ability of these complexes to form light-induced long-lived metastable linkage isomers is of interest as well. Due to the differences in the method of coordination of NO, ruthenium nitrosyls can be used as polyfunctional compounds for dynamic holography<sup>2</sup>.

We have studied the interactions of  $K_2[Ru(NO)Cl_5]$  in water-pyridine solution by using  $^1H$  NMR- and electronic spectroscopy, and have synthesized the series of ruthenium nitrosyl compounds containing the complex particles  $[Ru(NO)Py_nCl_{(4-n)}(OH)]^{(n-2)}$  or their aqua-forms  $[Ru(NO)Py_nCl_{(4-n)}(H_2O)]^{(n-1)}$   $n = 4,3,2$  (with yields 55-70%).



**Figure 1** Crystal structure of (I) and IR-spectra (upon irradiation and without).

Photoisomerization of  $cis-[Ru(NO)Py_2Cl_2(OH)]$  (I) at 80 K results in two metastable isomers detected by IR. The population of MS1 state is at least 60%, the kinetic parameters of its decay were calculated and determined.

1. E. Tfouni, D.R. Truzzi, A. Tavares et al, *Nitric Oxide*, **2012**, 26, 38.

2. D. Schaniel, M. Imlau, T. Weisemoeller et al, *Advanced Materials*, **2007**, 19, 723.

## **Synthesis, Characterization and Optical Properties of Cobalt(II) Metal-organic Frameworks**

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### **Abstract**

This paper reports on a synthesis of pink cobalt(II) coordination complex with 8-hydroxyquinoline and benzoic acid by slow evaporation of the organic media in the metal to ligands ratio, 1:1:1. The percentage yield was 74%, calculated based on the starting copper salt used. The complex was found to be stable at room temperature and insoluble in some organic solvents. The complex obtained was characterized by elemental analysis, scanning electron microscopy, Powder X-ray diffraction, ultraviolet-visible spectroscopy, FTIR and magnetic susceptibility measurements. The FTIR spectrum of this complex confirmed that complexation had taken place by the existence of COO<sup>-</sup> asymmetric and stretching symmetric peaks at 1644-1542 and 1456-1407 cm<sup>-1</sup>, respectively. Crystallite size was calculated by Debye Scherrer formula and the size and shape of this nanosized particle confirmed by Powder X-ray diffraction and scanning electron microscopy. The optical properties examined by ultraviolet-visible spectroscopy. The absorption peaks observed around 260, 310 and 395 nm by UV-Vis spectroscopy were assigned to energy band gap values of 4.77, 4.00, and 3.14 eV, respectively. This result demonstrate absorption within the ultraviolet region of the spectrum, a unique property of cobalt(II) nano-particles that can be used to fabricate semiconductor diodes.

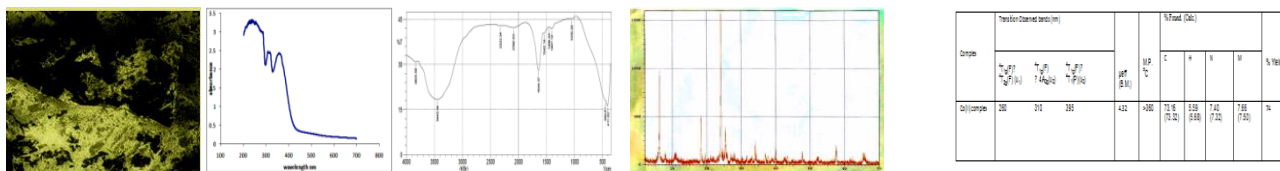


Fig.1: SEM micrograph Fig 2: Uv/ visible spectrum Fig.3: FTIR spectrum Fig. 4: PXRD diffractogram Table 1. Analytical data

1. Saugata, K., *et al.* (2011), Synthesis, Crystal Structure, Spectroscopic and Photoluminescence Studies of Manganese(II), Cobalt(II), Cadmium(II), Zinc(II) and Copper(II) Complexes with a Pyrazole derived Schiff base Ligand. *Polyhedron*. 30 2801–280.

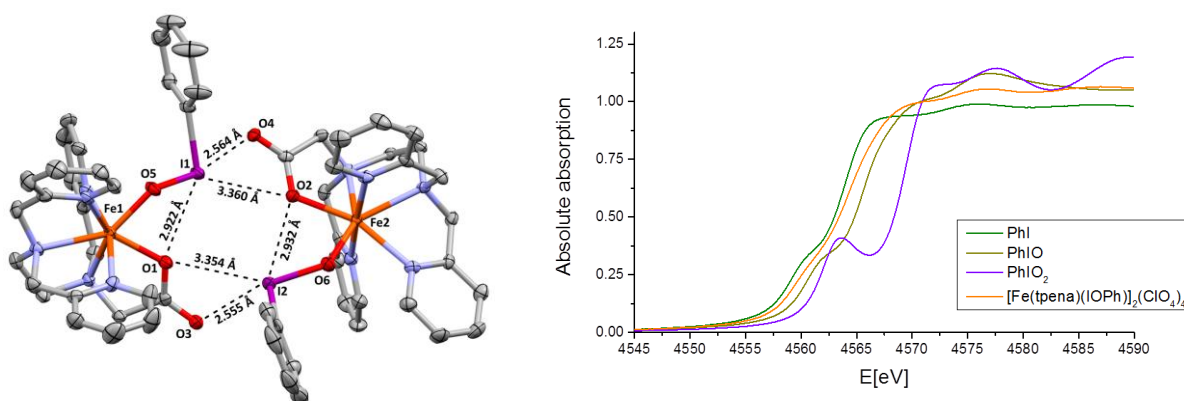
**Keywords:** Co(II) nanoparticles, characterization, optical absorption properties

## Iron Coordination and Halogen-Bonding Assisted Iodosylbenzene Activation

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The iron complex of the hexadentate ligand *N,N,N'*-tris(2-pyridylmethyl)ethylenediamine-*N'*-acetate (tpena) efficiently catalyzes selective oxidations of electron-rich olefins and sulfides by insoluble iodosylbenzene (PhIO).<sup>1</sup> Surprisingly, these reactions are faster and more selective than homogenous catalytic mixtures using soluble terminal oxygen transfer agents.<sup>2</sup> Isolation of a reactive iron-terminal oxidant adduct, an unique Fe<sup>III</sup>-OIPh complex, is facilitated by strong stabilizing supramolecular halogen-bonding (Figure 1a). L<sub>3</sub>-edge XANES (Figure 1b) suggests +1.6 for the average oxidation state for the iodine atom<sup>3</sup> in the iron(III)-coordinated PhIO. This represents a reduction of iodine relative to the original “hypervalent” (+3) PhIO. The equivalent of electron density must be removed from the {(tpena)Fe<sup>III</sup>O} moiety, however Mössbauer spectroscopy shows that the iron atom is not high valent.<sup>2,4</sup>



**Figure 1 (a)** Single crystal X-ray structure of Fe-OIPh complex of tpena showing strong intradimer halogen bonds. **(b)** Iodine L<sub>3</sub>-edge XANES spectra of the iron complex together with iodine reference compounds (PhI, PhIO, PhIO<sub>2</sub>).

1 A. Lennartson and C. J. McKenzie, *Angew. Chem., Int. Ed.*, **2012**, *51*, 6767.

2 D. P. de Sousa, C. Wegeberg, M. V. Sørensen, S. Mørup, C. Frandsen, W. A. Donald and C. J. McKenzie, *Chem., Eur. J.* **2015**, DOI: 10.1002/chem.201503112.

3 C. Wegeberg, C. G. Frankær and C. J. McKenzie, *in preparation*.

4 M. S. Vad, A. Lennartson, A. Nielsen, J. Harmer, J. E. McGrady, C. Frandsen, S. Mørup and C. J. McKenzie, *Chem. Commun.*, **2012**, *48*, 10880.

## Facile preparation of tetrakis(acetonitrilo)-*ortho*-metallated heteroaryls

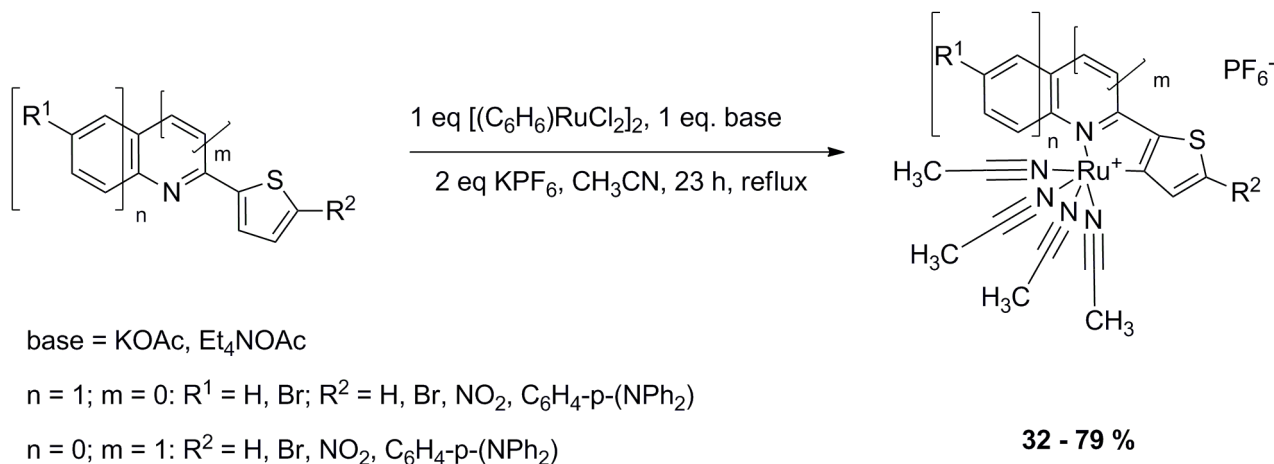
A.V. Medved'ko,<sup>a\*</sup> S.Z. Vatsadze,<sup>a</sup> S.A. Kurzeev,<sup>a</sup> S.A. Kozyukhin,<sup>b</sup> M.A. Kiskin,<sup>b</sup>  
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*Ortho*-metallated compounds are used as C-C coupling, water splitting and hydrolytic catalysts, sensibilizers in DSSCs and LEDs, anticancer agents and so on [1]. It is known, that the rate of direct cyclometallation reaction is limited by the substitution of the proton and reaction requires an external base like sodium hydroxide. This reagent is very cheap but the key problem is that it gives quite moderate yields mainly because of its limited solubility in organic solvents. Using of equimolar amount of commercially available potassium acetate or tetraethylammonium acetate tetrahydrate allows to overcome this problem.



**Figure 1.** Aryl/heteroaryls *ortho*-ruthenation.

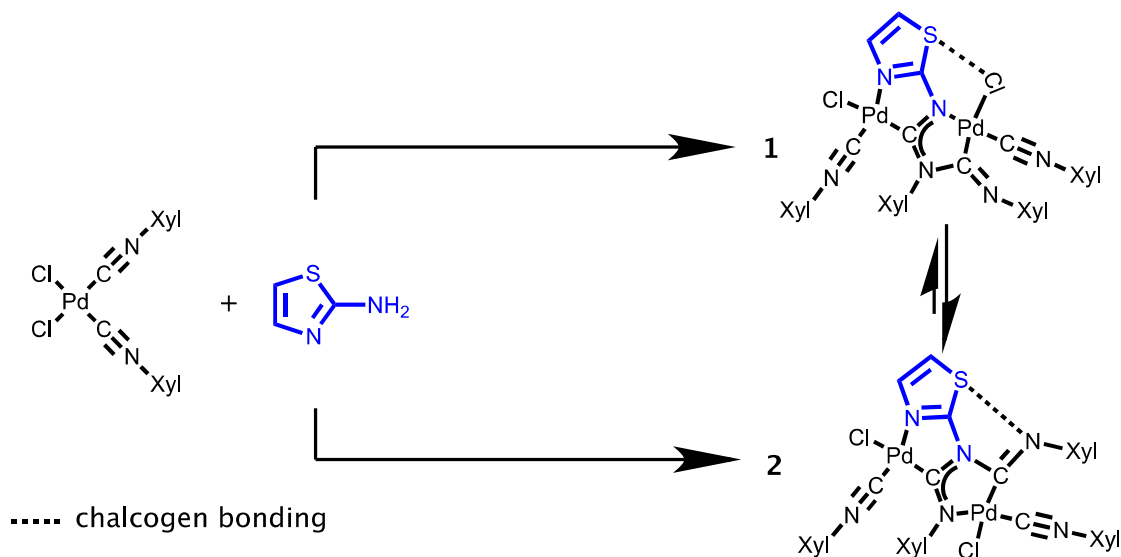
Reactions proceed smoothly with well-known 2-phenylpyridine as model compound and wide range of substituted thiophene-based imines and pyridines. Also, we found that while di- $\mu$ -chlorobis[( $\eta^6$ -benzene)ruthenium chloride] gives only tetrakis(acetonitrilo) complexes, di- $\mu$ -chlorobis[( $\eta^6$ -p-cymene)ruthenium chloride] reacts through intermediate formation of cyclometallated complexes containing  $\eta^6$ -p-cymene ligand.

1 I. Omae, Cyclometalation Reactions, **2014**, Springer Japan.

## Influence of chalcogen bonding on reversible regioisomerization of binuclear palladium carbene complexes

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Weak nonbonded interactions as halogen or chalcogen bonding play important roles in many chemical phenomena in coordination chemistry, e.g. conformational transformations or molecular packing in crystals. We study coupling of the palladium complex *cis*-[PdCl<sub>2</sub>(CNXyl)<sub>2</sub>] (Xyl = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) with thiazole-2-amine leads to the mixture of two regioisomeric binuclear diaminocarbene complexes **1** and **2** (Scheme 1). In course of time one of the isomers is able to reversible isomerize into another and in chloroform solution at RT the equilibrium is in favor of complex **2**. Inspection of the crystallographic data and DFT calculations suggests presence of chalcogen bonding S...Cl for **1** and S...N for **2** in these species. The difference in the orders of the chalcogen bonding may be one of causes for greater stability of complex **2** comparing with complex **1**. So we calculated the energies of chalcogen bonding in solid state and solution for binuclear carbene complexes **1** and **2** and estimated influence of chalcogen bonding on the regioisomerization.



**Scheme 1.** Coupling of *cis*-[PdCl<sub>2</sub>(CNXyl)<sub>2</sub>] with thiazole-2-amine

Acknowledgements: Physicochemical studies were performed at Center for Magnetic Resonance, Center for X-ray Diffraction Studies and Center for Chemical Analysis and Materials Research of SPbU. The authors thank RFBR (grant 14-03-00297), SPbU (grant 12.37.214.2016) and government of RF (grant of president of RF MK-7425.2016.3).



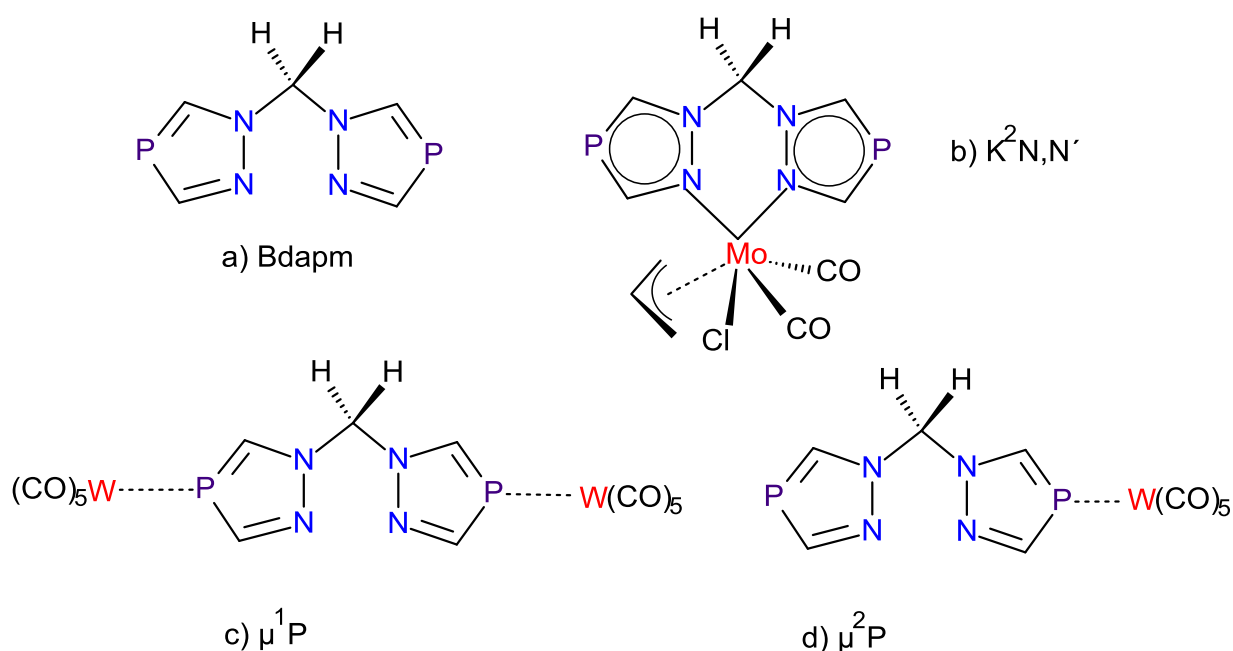
## Coordination behaviour of bis(1,2,4-diazaphospholyl)methane

Martin Mlateček<sup>a</sup>, Milan Erben<sup>a</sup>, Libor Dostál<sup>a</sup>, Zdeňka Růžičková<sup>a</sup> and Jan Honzíček<sup>b</sup>

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New anionic ligand, phenyl-tris(1,2,4-diazaphospholyl)borate (**PhTdap**), containing phosphorus heterocycle has been recently synthesised and characterized. [1] A series of transition and non-transition metal complexes have been prepared but only in one case the coordination *via* phosphorus atom was observed. Afterwards we synthesised neutral chelating ligand bis(1,2,4-diazaphospholyl)methane (**Bdapm**) and studied its properties. We find out, that **Bdapm** shows a variety of coordination modes that could yield multimetallic species. The structures and spectroscopic study of these new compounds will be discussed in presented contribution.



**Figure 1.** Observed coordination modes of **Bdapm**

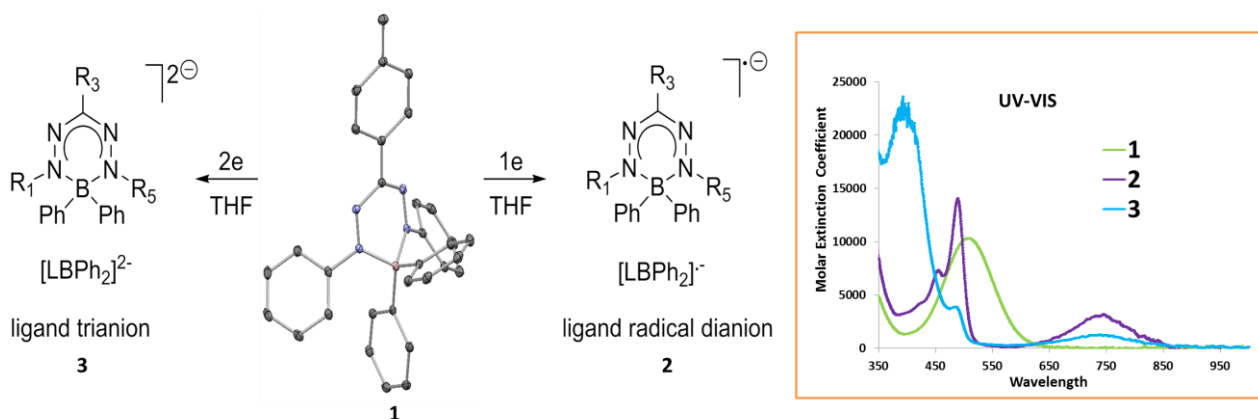
[1] M. Mlateček, L. Dostál, Z. Růžičková, J. Honzíček, J. Holubová and M. Erben. Dalton Trans., 2015, **44**, 20242

# Synthesis of boron diphenyl complexes containing redox-active formazanate ligands in three oxidation states

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We recently developed formazanates (containing a [NNCNN] backbone) as a novel class of redox-active ligands which show facile, reversible redox reactions and flexible coordination modes leading to 6-, 5- or 4-membered chelate complexes.<sup>1,2</sup> Both our group<sup>1</sup> and Gilroy and co-workers<sup>2</sup> recently synthesized and characterized formazanate boron difluoride complexes (LBF<sub>2</sub>). Cyclic voltammetry indicated ligand-based reductions to generate the redox series LBF<sub>2</sub><sup>0/-1/-2</sup>. While the radical monoanion [LBF<sub>2</sub>]<sup>-</sup> is sufficiently stable to be isolated,<sup>1a</sup> attempted chemical synthesis of the corresponding 2-electron reduction product [LBF<sub>2</sub>]<sup>2-</sup> results in loss of F<sup>-</sup> (as NaF) and (partial) ligand fragmentation.<sup>1c</sup> To remedy this, here we report the synthesis of formazanate boron diphenyl complexes (LBPh<sub>2</sub>). The replacement of B-F with B-Ph in these compounds allows access to the full redox series LBPh<sub>2</sub><sup>0/-1/-2</sup>, which were characterized by X-ray crystallography and spectroscopic methods (Scheme 1). For the first time we are able to isolate and characterize the product of ligand-based 2-electron reduction in a formazanate complex, which allows us to study the further reactivity of these compounds.



**Scheme 1.** Synthesis of mono(formazanate) boron diphenyl complexes and their reduction products(left) .

1 (a) Chang, M.-C.; Otten, E. *Chem. Commun.* 2014, 50, 7431. (b) Chang, M.-C.; Dann, T.; Day, D. P.; Lutz, M.; Wildgoose, G. G.; Otten, E. *Angew. Chem. Int. Ed.* 2014, 53, 4118. (c) Chang, M.-C.; Otten, E. *Inorg. Chem.* 2015, 54, 8656. (d) Travieso-Puente, R.; Chang, M.-C.; Otten, E. *Dalton Trans.* 2014, 43, 18035  
2 Barbon, S.M.; Price, J.T.; Yogarajah, U.; Gilroy, J.B. *Chem. Commun.* 2015, 5, 56316

## Unprecedented diradical iron complex: synthesis, characterization and reactivity

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In the past few years, there has been a renewed interest for redox active ligands (RAL) in the field of organometallic catalysis in association with *d*-transition metals. RAL behave as electron reservoirs thanks to their ability to undergo multiple electronic changes. They may also form radicals that allow H-atom abstraction and may enable the C-H bond activation. In Nature, metalloenzymes incorporate RAL in association with earth-abundant metals and perform sophisticated reactions, like oxidation or hydroxylation using molecular O<sub>2</sub>. The design of unprecedented redox active architectures is thus highly challenging: once coordinated to a metal, they could give rise to unsuspected reactivities.<sup>1</sup>

In this context, our laboratory is specialized in the design of new redox active architectures and the characterization of their transition metal complexes.<sup>2</sup> The course of our research led us to investigate the *o*-phenylenediamine moiety (*o*-PDA) because, once deprotonated, this redox entity is known for its ability to reversibly exchange two electrons at low potentials.

Recently, we have described the preparation of diradical Ni complexes based on original tetradentate bis(*o*-PDA) redox active ligands.<sup>3</sup> The elucidation of the electronic structures has exhibited a rich ligand-centered redox activity. In the current work, we will present our latest results concerning an analogous iron complex. The preparation and the extensive characterization as well as a reactivity study will be exposed.

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<sup>1</sup> a/ Chirik, P. J.; Wieghardt, K. *Science* **2010**, *327*, 794. b/ Lyaskovskyy, V.; De Bruin, B. *ACS Catal.* **2012**, *2*, 270. c/ Blanchard, S.; Derat, E.; Desage-El Murr, M.; Fensterbank, L.; Malacria, M.; Mouriès-Mansuy, V. *Eur. J. Inorg. Chem.* **2012**, *2012*, 376.

<sup>2</sup> a/ Orio, M.; Jarjayes, O.; Kansa, H.; Philouze, C.; Neese, F.; Thomas, F. *Angew. Chemie - Int. Ed.* **2010**, *49*, 4989. b/ Kochem, A.; Chiang, L.; Baptiste, B.; Philouze, C.; Leconte, N.; Jarjayes, O.; Storr, T.; Thomas, F. *Chem. Eur. J.* **2012**, *18*, 14590. c/ Kochem, A.; Gellon, G.; Leconte, N.; Baptiste, B.; Philouze, C.; Jarjayes, O.; Orio, M.; Thomas, F. *Chem. - A Eur. J.* **2013**, *19*, 16707. d/ Kochem, A.; Gellon, G.; Jarjayes, O.; Philouze, C.; Leconte, N.; van Gastel, M.; Bill, E.; Thomas, F. *Chem. Commun.* **2014**, *50*, 4924.

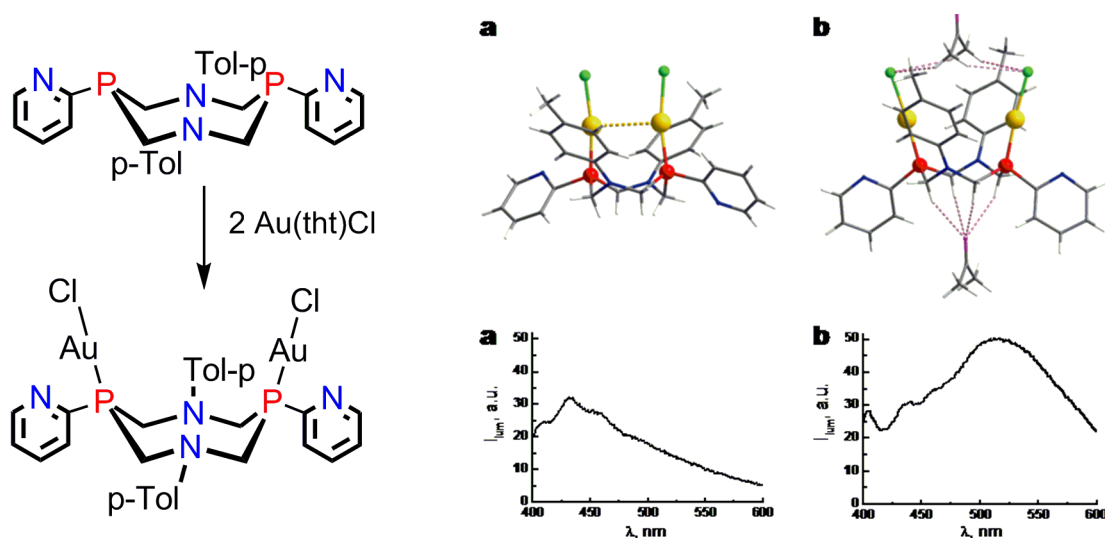
<sup>3</sup> a/ Leconte, N.; Ciccione, J.; Gellon, G.; Philouze, C.; Thomas, F. *Chem. Commun.* **2014**, *50*, 1918. b/ Ciccione, J.; Leconte, N.; Luneau, D.; Philouze, C.; Thomas, F. *Inorg. Chem.*, DOI 10.1021/acs.inorgchem.5b01947

## Luminescence solvatochromism of Au(I) complexes of 1,5-diaza-3,7-diphosphacyclooctanes

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The dinuclear gold(I) complex of cyclic aminomethylphosphine **1** was obtained by the reaction of gold(tht)chloride with 1,5-dipyridyl-3,7-di(p-tolyl)-1,5-diaza-3,7-diphosphacyclooctane. In the solid state molecule **1** demonstrates conformational isomerism related to formation of aurophilic bonding (a) and ability to form “host-guest” interactions with solvent molecules (b).



**Figure 1** Synthesis; X-Ray structures of **1** from  $\text{CH}_2\text{Cl}_2$  (a) and from acetone (b); and emission spectra of **1** in  $\text{CH}_3\text{CN}$  (a) and DMF (b).

The synthesized complexes exhibit luminescent solvatochromism in solutions. The emission spectra of complex **1** in different organic solvents is represented in Figure 1. The structure (a) with shortest Au-Au distance (3.13 Å) correlates with emission spectra, where short wavelength emission is more efficient than the longer wavelength one. This structure and luminescence behavior is predominant in acetonitrile and  $\text{CH}_2\text{Cl}_2$ . The spectral pattern (b) is observed in acetone and DMF. This spectral pattern correlates with the structure (b) with greater Au-Au-distance (5.38 Å). Moreover, the analysis of the spectra recorded in mixed solvents through Job plotting reveals tight 1:1 “host-guest” binding of the complex with DMF even in the excess amounts of other organic solvents.

**Acknowledgments.** This work is financial supported by the RSF grant № 15-13-30031.

# Families of Dinuclear Lanthanide(III) Complexes: Synthetic, Structural, Optical and Magnetic Studies

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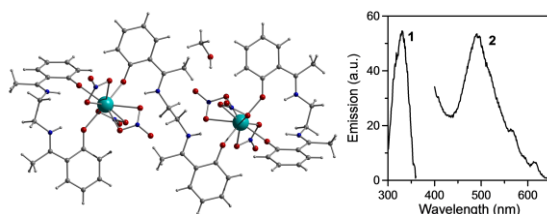
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Dinuclear lanthanide(III) [Ln<sup>III</sup>] complexes continue to attract the intense interest of coordination chemists<sup>1</sup> due to their involvement in diverse scientific fields/areas, for example, single-molecule magnetism, magnetic refrigeration, quantum computing, homogeneous catalysis, optics, organic transformations and in the chemistry of multifunctional (or "hybrid") molecular materials. In the latter area, Ln<sup>III</sup><sub>2</sub> molecular compounds allow scientists to investigate the dominance of one property over the other and -within a given property-to answer basic questions regarding single-ion behaviour *versus* behaviour arising from the molecule as an entity. One route for the preparation of dinuclear 4f-metal complexes is the simultaneous employment of capping nitrate or carboxylate groups and *neutral* or *anionic* organic ligands that bridge the two metal centers. Using polydentate organic ligands, we have prepared, structurally and spectroscopically characterized, and studied the magnetic and emission properties (Fig. 1) of Ln<sup>III</sup><sub>2</sub> complexes that belong to various structural motifs.



**Figure 1** Data for the [Ln<sub>2</sub>(NO<sub>3</sub>)<sub>6</sub>(acphen)<sub>3</sub>] family of ligands, where acphenH<sub>2</sub> is 2,2'-[1,2-ethanediylbis(nitrilo-1-ethyl-1-ylidene)]diphenol.

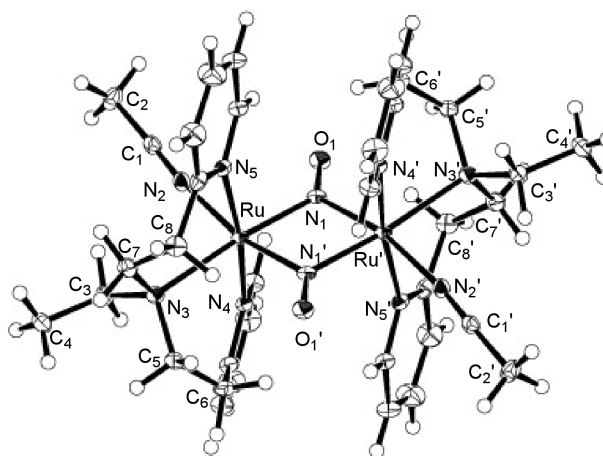
1. F. Habib, M. Murugesu, *Chem. Soc. Rev.*, **2013**, *42*, 3278.

## Formation and Reactions of Doubly Nitrosyl-Bridged Dinuclear Ruthenium Complex

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Small nitrogen-containing compounds such as  $N_aO_b^n$  and  $N_cH_d$  species with nitrogen atom(s) in the oxidation state(s) between  $-3$  and  $+5$  play many important roles in chemical and biochemical processes. Reduction of nitrate to give nitrosyl (NO) complexes and formation of  $N_2O$  from metal complexes having NO ligands are one of the most important processes in nature and have been investigated in connection with the reaction mechanisms in the nitrite reductase and the nitric oxide reductase. The mechanisms of the formation of nitrosyl complexes, however, have hardly been discussed on account of the difficulties in the isolation and characterization of the reaction intermediates.

In this work, we report a reaction of triacetonitrileruthenium(II) complex bearing ethylbis(2-pyridylethyl)amine (ebpea) with sodium nitrate in ethanol affording a dinuclear ruthenium complex in which the ruthenium centers are doubly bridged by two nitrosyl ligands,  $[\{Ru(NCCH_3)(ebpea)\}_2(\mu-NO)_2]^{2+}$  as shown in Figure 1. Electrochemical behavior of the diruthenium complex in  $CH_3CN$  shows two reversible one-electron oxidation waves at 0.03 and 0.57 V vs. Ag | 0.01 M  $AgNO_3(CH_3CN)$ . There is a strong interaction between two  $\{Ru(NO)\}$ -moieties of the dinuclear ruthenium complex. In a reaction with hydrochloric acid in  $H_2O-CH_3CN$  under air, an evolution of dinitrogen oxide ( $N_2O$ ) was also observed and triacetonitrileruthenium(II) complex was formed with dichloridonitrosylruthenium complex,  $[RuCl_2(NO)(ebpea)]^+$ . It is noteworthy that the present dinuclear framework functions as a precursor of the formation of dinitrogen oxide.



**Figure 1** Structure of  $[\{Ru(NCCH_3)(ebpea)\}_2(\mu-NO)_2]^{2+}$

## Cobalt(III) Complexes of 1, 10-Phenanthroline and N,O-Donor Ligands: Synthesis, Structures and Reactivity

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Transition metal complexes containing polypyridyl and N,O-donor ligands have been a subject of study in chemistry due to their biological activity, with Cu(II) complexes been the well-known examples.<sup>1,2</sup> In this work, cobalt(III) complexes with a general formula [Co(phen)(L)<sub>2</sub>][X] (phen = 1,10-phenanthroline, L = N,O-donor ligands, X = anions) were prepared. The complexes were obtained by reacting solutions of the ligands and the cobalt salt in the presence of a base. The complexes were characterized by spectroscopic and spectrometric techniques, microanalysis and X-ray crystallography. The chirality of the compounds was studied using circular dichroism. Some of these complexes were investigated for their biological activities. The preliminary results obtained from this work will be presented in this presentation.

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2. C.-H. Ng, W.-S. Wang, K.-V. Chong, Y.-F. Win, K.-E. Neo, H.-B. Lee, S.-L. San, R. N. Z. Raja Abd. Rahman, W. K. Leong, *Dalton Transaction*, **2013**, 42, 10233.

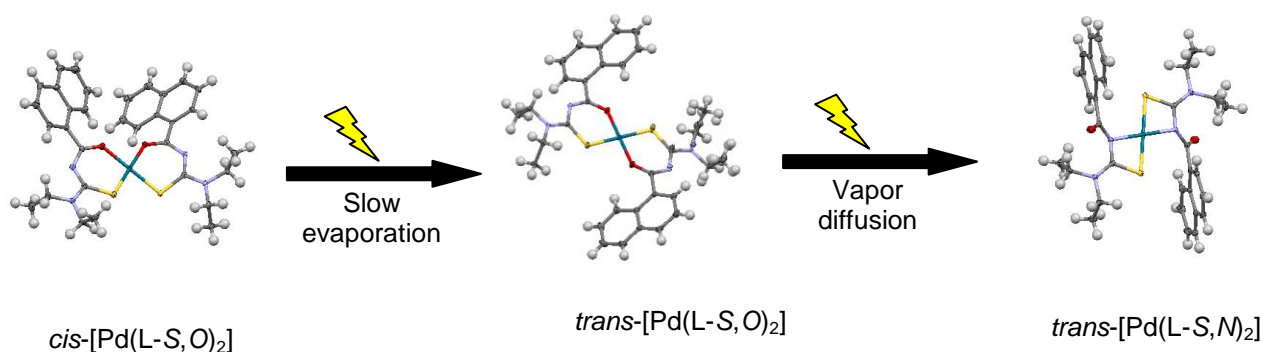


## Light-induced isomerization of *cis*-[Pd(L-S,O)<sub>2</sub>] (L=*N,N*-diethyl-*N'*-naphthoylthiourea); key to the preparation and isolation of *trans*-[Pd(L-S,O)<sub>2</sub>] and *trans*-[Pd(L-S,N)<sub>2</sub>] chelates

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Light-induced isomerization of *cis*-[M(L-S,O)<sub>2</sub>] (M=Pt(II) and Pd(II), HL = *N,N*-diethyl-*N'*-naphthoylthiourea) type complexes in acetonitrile upon irradiation with polychromatic light generates the corresponding *trans*-[M(L-S,O)<sub>2</sub>] isomers.<sup>1</sup> The qualitative rate of isomerization is dependent on the nature of organic solvent and ligand structure, as confirmed by the isolation of a series of *trans*-[Pd(L<sup>n</sup>-S,O)<sub>2</sub>] complexes by vapor diffusion-induced crystallization.<sup>2</sup> In acetonitrile *cis*-[Pd(L-S,O)<sub>2</sub>] subjected to similar light treatment not only results in the corresponding *trans*-[Pd(L-S,O)<sub>2</sub>] chelate, but also form a new previously not observed *trans*-[Pd(L-S,N)<sub>2</sub>] isomer. This is confirmed by the crystal structures of *inter alia* the novel *trans*-[Pd(L-S,N)<sub>2</sub>] complex isolated under prolonged exposure by polychromatic light, under conditions of vapor diffusion in acetonitrile/ether mixtures. Both the *trans*-[Pd(L-S,O)<sub>2</sub>] and *trans*-[Pd(L-S,N)<sub>2</sub>] isomers revert back to the *cis*-[Pd(L-S,O)<sub>2</sub>] complex in the dark, albeit at different relative rates shown by <sup>1</sup>H and <sup>195</sup>Pt NMR spectroscopy and reversed phase HPLC separations in acetonitrile solution. In summary, *light-induced cis*→*trans* isomerization of [Pd(L-S,O)<sub>2</sub>] complexes is the key to the formation of *trans* isomers. Unusually, for the *N,N*-diethyl-*N'*-naphthoylthioureaato ligand, the *trans*-[Pd(L-S,N)<sub>2</sub>] isomer is also obtained, unlike that for the corresponding *N,N*-diethyl-*N'*-benzoylthioureaato Pt(II) and Pd(II) complexes.



1 D. Hanekom, J. M. McKenzie, N. M. Derix, K. R. Koch, *Chem. Commun.*, **2005**, 767.

2 H. A. Nkabyo, D. Hanekom, J. M. McKenzie, K. R. Koch, *J. Coord. Chem.*, **2014**, 76, 4039.

## Uncatalyzed Reduction of Imines to Amines via Coordinated Hydrosilanes

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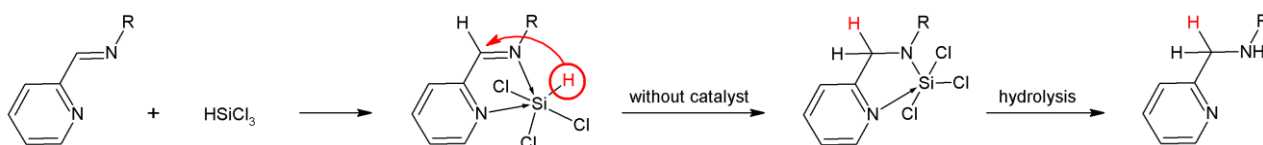
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The transformation of amines from imines is an important method in organic synthesis because of their versatile utility as intermediates for the synthesis of pharmaceuticals or agrochemicals. One of the commonly used methods for the synthesis of amines is hydrometallation of imines with various reducing agents. Mainly complexes of transition metals catalyze the most of these hydrometallation reactions.

Recently, we dealt with the synthesis of organohydrosilanes stabilized by anionic C,N-chelating ligands containing an C=N imine group in their structures. We found out that the Si-H hydrogen atom is activated by intramolecular N→Si coordination and this hydrogen atom is able to migrate to the carbon atom of the imine group very easily and the spontaneous hydrosilylation occurs.<sup>1</sup>

In this work we focused our attention to hydrosilylation of neutral ligands based on pyridine-containing C=N imine functional group (L<sup>py</sup>). We prepared a set of these ligands and reduced them with trichlorosilane HSiCl<sub>3</sub> to the corresponding amines. Trichlorosilane HSiCl<sub>3</sub> was used as hydrosilylating agent due to its Lewis acidity and possibility to form adducts L<sup>py</sup>·SiHCl<sub>3</sub>. Moreover, the organosilicon amides as one of the intermediates were isolated and fully characterized in some cases. Also discussed will be the mechanism for this reaction.



**Figure 1** Reduction of imines to amines via coordinated hydrosilanes

1 M. Novák, L. Dostál, M. Alonso, F. De Proft, A. Růžička, A. Lyčka, R. Jambor, *Chem. Eur. J.*, **2014**, *20*, 2542.

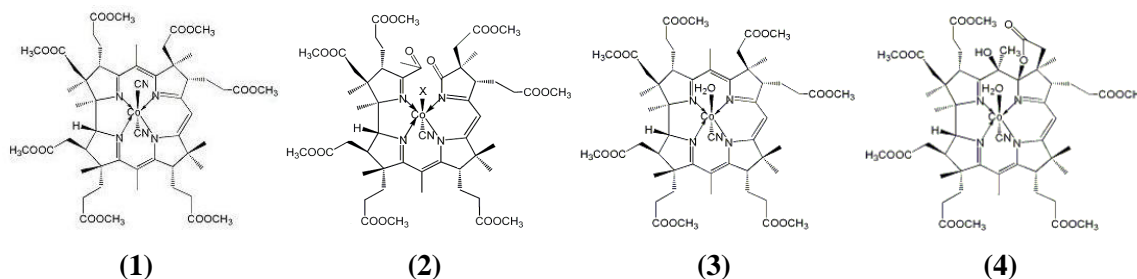
## The synthesis and reactions of a modified cobalt corrin

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The environment in which cobalt(III) finds itself in a corrin macrocycle such as vitamin B<sub>12</sub>, is powerfully activating. When coordinated to such a macrocycle, the typically inert cobalt(III) metal centre exhibits remarkable lability. The unexpected activity of cobalt(III) thus raises the fundamental question: how has the structure been manipulated to enhance the metal's inherent inactivity?

It is speculated that the partially delocalized electron cloud of the corrin ring transfers electron density to the cobalt(III) ion, thus imparting to it a degree of labile cobalt(II) character.<sup>1</sup> To test this hypothesis, the electronic structure of the corrin was perturbed by selectively cleaving Co $\alpha$ ,Co $\beta$ -dicyano-heptamethylcob(III)yrinate (dicyanocobester, DCCbs, **1**) by photosensitised oxygenation, resulting in 5-seco-dicyanocobester (5-seco-DCCbs) (**2**, X = CN). The secocobester was then converted to the aqua form, 5-seco-aquacyanocobester (5-seco-ACCbs) (**2**, X = H<sub>2</sub>O) for ligand binding and kinetic studies, in which axial H<sub>2</sub>O was replaced by a variety of exogenous ligands. These results were then used to compare the chemistry of a series of vitamin B<sub>12</sub> derivatives such as aquacyanocobester (ACCbs) (**3**) and aquacyano-stable yellow cobester (**4**). A comparison of the thermodynamic and kinetic results of the various systems indicate that the nature of the corrin ring materially affects the chemistry of cobalt(III). The implications of these structural modifications will be discussed.



**Figure 1:** The structures of DCCbs, 5-seco-DCCbs (X = CN) or 5-seco-ACCbs (X = H<sub>2</sub>O), ACCbs and ACSYCbs.

<sup>1</sup> S. M. Chemaly, M. Florczak, H. Dirr, Marques, H. M. *Inorg. Chem.*, **2011**, *50*, 8719.

# Reactivities and Electronic Properties of Nitrosylruthenium Complexes Bearing Pyridyl-containing Compounds

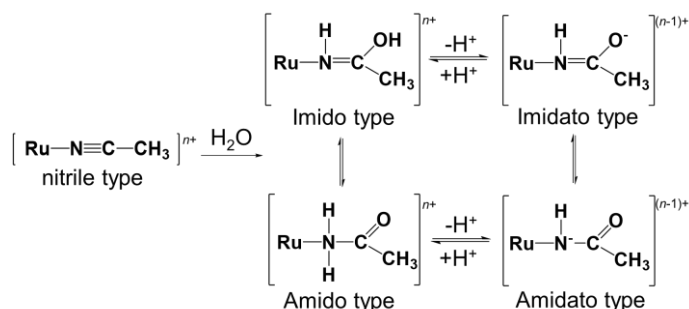
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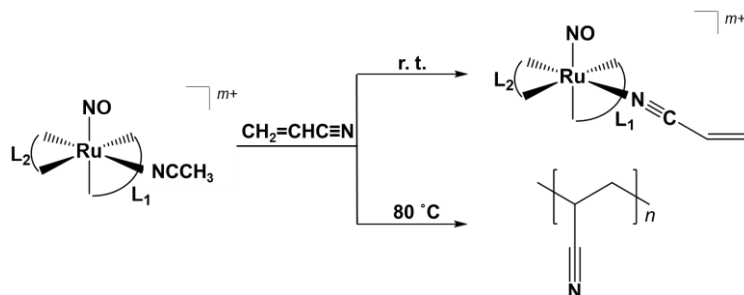
Email: h-nagao@sophia.ac.jp

We have been investigating syntheses and reactions of nitrilenitrosylruthenium complexes bearing pyridyl-containing compounds such as pyridinecarboxylate (pyc) and/or 2,2'-bipyridine (bpy) as supporting ligands. A coordinated nitrosyl ligand functions as a electron-drawing group, inducing a hydration reaction of nitrile on a ruthenium center to give imido or amido type (Scheme 1)<sup>1</sup>. Reactions of



**Scheme 1.** Hydration reaction of nitrile

nitrosylruthenium complexes  $cis-[Ru(NO)(H_2O)L_1L_2]^{n+}$  ( $L_1 = L_2 = pyc$ ;  $n = 1$ ,  $L_1 = pyc$ ,  $L_2 = bpy$ ;  $n = 2$ ,  $L_1 = L_2 = bpy$ ;  $n = 3$ ) with acrylonitrile afforded acrylonitrilenitrosylruthenium complexes at room temperature. The nitrosylruthenium complexes catalyzed for polymerization of acrylonitrile under heating conditions (Scheme 2). Polymerization reactions of acrylonitrile were carried out using nitrosylruthenium complexes  $[Ru(NO)XL]^{m+}$  as catalysts without initiators of polymerization to afford polyacrylonitrile (PAN). In this work, relationship between electronic properties and reactivities of nitrosylruthenium complexes for polymerization were investigated. We would like to discuss syntheses of nitrosylruthenium complexes using various supporting ligands (L) such as ethylbis(2-pyridylmethyl)amine (ebpma) and coexisting-ligands ( $X = Cl, NO_3^-, CH_3CN$  etc.), to control electric charge ( $n = -1 - 3$ ) and redox potential, and polymerization reactions.



**Scheme 2.** Reaction of nitrosylruthenium complex and acrylonitrile

1 H. Nagao, T. Hirano, N. Tsuboya, M. Mukaida, T. Oi, and M. Yamasaki, *Inorg. Chem.*, **2002**, *41*, 6267.

# PHOTOPHYSICAL AND ELECTRONIC PROPERTIES IN A SERIES OF IRIIDIUM COMPLEXES WITH TRIDENTATE 3{5}-SUBSTITUTED PYRAZOLE LIGANDS

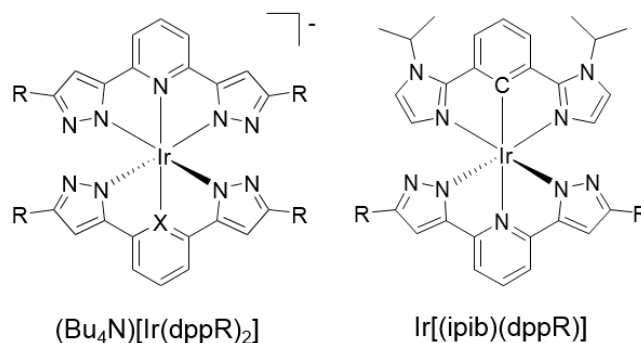
Tomoko ODAKA,<sup>a</sup> Hiroaki OZAWA,<sup>a</sup> Junichi MAEBA,<sup>b</sup> Koichi NOZAKI,<sup>b</sup> Masa-aki HAGA<sup>a\*</sup>

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Phosphorescent iridium complexes have been extensively investigated for the potential application to OLEDs and biomolecular imaging. The studies on phosphorescent Ir complexes containing tridentate ligands are still limited, compared to ones bearing bidentate ligands such as [Ir(ppy)<sub>3</sub>] derivatives. We have reported the synthesis and photophysical properties of highly phosphorescent Ir complexes containing N-heteroaromatic tridentate benzimidazole or imidazole ligand.[1] In this work, a series of iridium(III) homo- and heteroleptic bis-tridentate complexes with 3{5}-substituted pyrazole (see Fig. 1) were synthesized since pyrazole has a strong  $\sigma$ -donor property which induces a shorter wavelength shift on emission. Homoleptic complex (Bu<sub>4</sub>N)[Ir(dpp<sup>t</sup>Bu)<sub>2</sub>] showed high emission quantum yield,  $\Phi = 0.54$  at 523 nm. The quantum yields of heteroleptic complexes [Ir(ipib)(dppR)] were lower than those of homoleptic complexes [Ir(dppR)<sub>2</sub>]. Temperature dependent lifetime measurements and DFT calculation revealed that the deactivation process took place through the dd state closely lying the emissive excited state. The destabilized dd state due to the strong basicity of coordinated pyrazole nitrogen may prevent thermal deactivation process in typically homoleptic cases. Additionally the decrease of luminescence intensity induced by the effect of protonation on pyrazole nitrogen moiety will be discussed.



**Figure 1** Chemical structures (R = <sup>t</sup>Bu or CF<sub>3</sub>)

[1] (a) L. Yang, et al., *Inorg. Chem.*, **2008**, *47*, 7154. (b) M. Ashizawa et al., *Dalton Trans.*, **2009**, 1700.

## Synthesis, structures, and properties of mononuclear transition-metal complexes with Schiff base ligands derived from L-histidine

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L-Histidine residue exists in many kinds of enzymes, and its imidazole moiety acts as a key functional group for acid-base catalysis, proton transfer, and so on. In addition, multi-dentate Schiff-base ligands were known to stabilize various oxidation states of metal ion. In this study we deal with the Schiff-base ligands derived from L-histidine (Figure 1), because they are expected to show various kinds of coordination modes to a metal center.

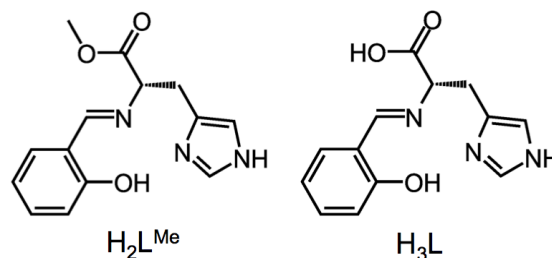


Figure 1 Ligand precursors

A reaction of L-histidine methyl ester di(hydrogen chloride),  $\text{NEt}_3$ , salicylaldehyde, and  $\text{M}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  ( $\text{M} = \text{Mn}$  or  $\text{Co}$ ) gave a  $[\text{M}^{\text{III}}(\text{HL}^{\text{Me}})_2]^+$ -type complex (Figure 2a). In the case of  $\text{Co}$  a hydrolysis product of  $[\text{Co}(\text{HL})(\text{hisOMe})]\text{ClO}_4$  (Figure 2b) was also isolated. In these complexes the ligand,  $(\text{HL}^{\text{Me}})^-$  coordinates to a metal center in *mer* configuration with a tridentate mode of  $\kappa^3\text{-O,N,N'}$ , and  $(\text{HL})^{2-}$  coordinates to a  $\text{Co}^{\text{III}}$  ion with a tetradentate mode of  $\kappa^4\text{-O,N,O',N'}$ . When  $\text{FeCl}_2$  was reacted with a mixture of L-histidine and salicyl-aldehyde, followed by the addition of  $\text{KPF}_6$ , a complex of  $[\text{Fe}(\text{H}_2\text{L})_2]\text{PF}_6$  was obtained, where  $(\text{H}_2\text{L})^-$  coordinates to a  $\text{Fe}^{\text{III}}$  ion in a tridentate  $\kappa^3\text{-O,N,O'}$  mode.

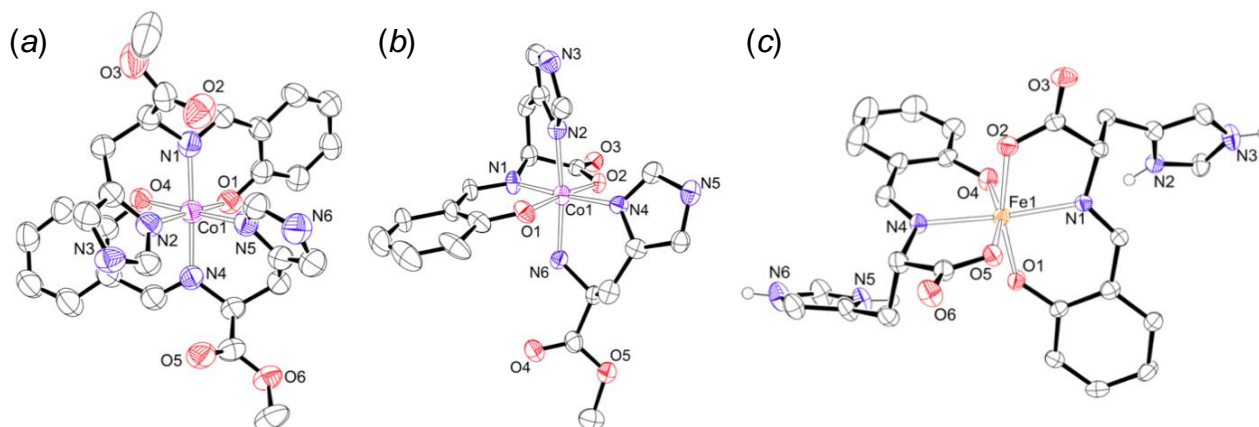


Figure 2 (a)  $[\text{Co}(\text{HL}^{\text{Me}})_2]^+$ , (b)  $[\text{Co}(\text{HL})(\text{hisOMe})]^+$ , and (c)  $[\text{Fe}(\text{H}_2\text{L})_2]^+$ .

## "Chiral" Complexes Containing $\beta$ -Enaminone and Carborane Skeletons

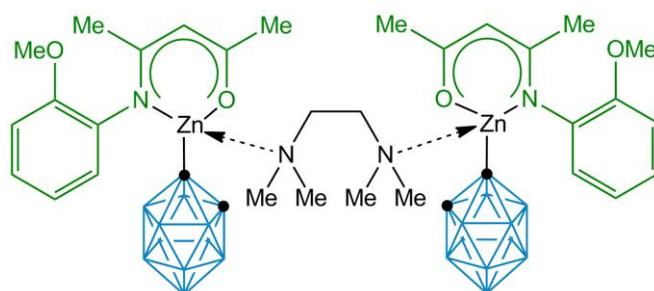
R. Olejník<sup>a\*</sup>, Z. Růžicková<sup>a</sup>, B. Štíbr<sup>b</sup>, A. Růžička<sup>a</sup>

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The chemistry of complexes containing carborane skeletons has attracted a significant interest in particular due to remarkable reactivity and possible wide range of applications starting from polymerization reactions<sup>1</sup> to various organic transformations.<sup>2</sup> On the contrary, tridentate  $\beta$ -enaminone (*BEN*) may be classified among the most widespread spectator systems which can stabilize metal centers and thus form six membered metallacycles. The central fragment consists of  $\text{NC}_3\text{O}$  entity and renders space for variation of its substituents with tunable steric demand. The combination of carborane and *BEN* parts forming "chiral" vicinity of metal in one specie open new area of coordination chemistry and could contribute to study of complexes with higher added value.



**Figure 1** The proposed structure of one of the compounds studied.

The synthesis of target species can be classified as a ligand exchange reaction between homoleptic *BEN* complex and lithium precursor (Figure 1) or as an addition of lithium specie to  $\text{NC}_3\text{O}$  fragment of *BEN*. Comprehensive study of selected complexes was supported by quantum chemistry calculations.

**Acknowledgement** We gratefully acknowledged the financial support of the Czech Science Foundation (project no. GA CR 16-01618S).

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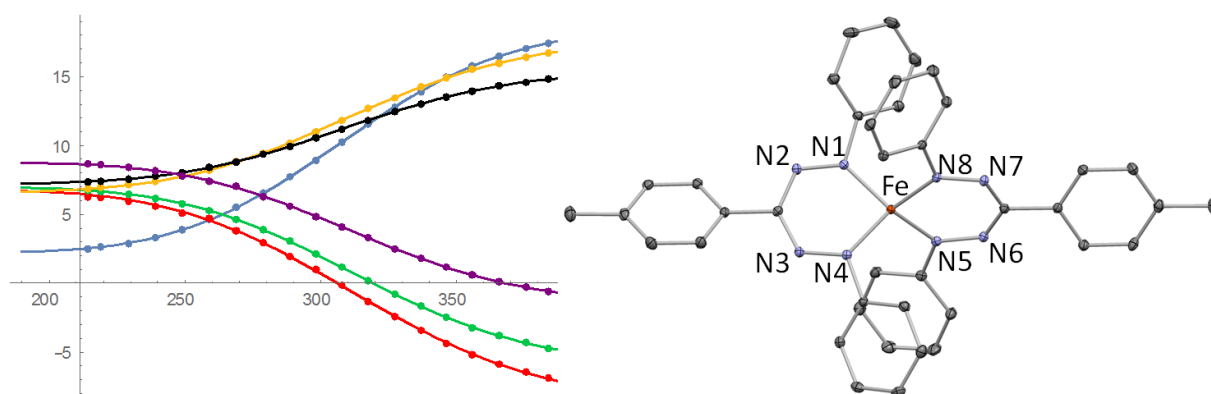
# Reversible Spin-State Changes in a Tetrahedral Iron Complex

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Coordination compounds that show electronic bistability are of interest for applications such as molecule-based data-storage, switches and sensors.<sup>1</sup> Complexes that show spin cross-over are well-known for 6-coordinate, octahedral geometries for which the ligand field strength is such that two spin states are close in energy and may be reversibly addressed (by applying pressure, light or heating). Due to a much weaker ligand field in 4-coordinate complexes, these (with very few exceptions)<sup>2</sup> lead to high spin-states only.

We recently developed formazanates (based on a [NNCNN] backbone) as a novel class of redox-active ligands that are accessible in the anionic ( $L^-$ ), radical dianionic ( $L^{2-}$ ) and trianionic ( $L^{3-}$ ) form.<sup>3</sup> Here, we report a bis(formazanate)iron complex ( $L_2Fe$ ) and present X-ray crystallographic, magnetic and spectroscopic evidence spin cross-over behavior that allows thermal switching between  $S=0$  and  $S=2$  states. Fitting of variable-temperature NMR data (Figure 1) suggests that the transition is driven by entropy changes and takes place with  $T_{1/2} = 345$  K. The neutral compound may be reduced to the corresponding radical anion ( $[L_2Fe]^-$ ,  $S=1/2$ ). The observation of spin cross-over in a (pseudo)tetrahedral iron compound presents a new design principle for materials with electronic bistability.



**Figure 1.** Temperature-dependence of  $^1H$  NMR shifts of compound **1** (right, X-ray)

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## Novel mononuclear Re(II) nitrosyl complex with 3,5-pyridinedicarboxylic acid: crystal structure, magnetic properties and potential application as metalloligand

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Coordination compounds of Re(II) are known to have large magnetic anisotropy due to an important spin-orbit coupling, turning them a potential source for the discovery of new molecular magnets<sup>1,2</sup>.

Here we report the synthesis and crystal structure of a novel Re(II) complex of formula **(NBu<sub>4</sub>)[Re(NO)Br<sub>4</sub>(H<sub>2</sub>pydc)]·i-prOH** (H<sub>2</sub>pydc = 3,5-pyridinedicarboxylic acid). The crystal structure of these complexes contains NBu<sub>4</sub><sup>+</sup> cations, mononuclear [Re(NO)Br<sub>4</sub>(H<sub>2</sub>pydc)]<sup>-</sup> units and an isopropanol as crystallizing molecule. Besides the anion-cation interaction there is a double hydrogen bond between adjacent carboxylic group which connects units [Re(NO)Br<sub>4</sub>(H<sub>2</sub>pydc)]<sup>-</sup> into pairs (O...O distances of 2.59 Å). The magnetic properties of the compounds were examined over the temperature range of 2-300 K. The thermal dependence of  $\chi T$  is in line with one unpaired electron and a large temperature independent paramagnetic contribution (TIP). In addition, antiferromagnetic interactions are present between the [Re(NO)Br<sub>4</sub>(H<sub>2</sub>pydc)]<sup>-</sup> units. What is more, we show how the [Re(NO)Br<sub>4</sub>(H<sub>2</sub>pydc)]<sup>-</sup> unit can act as building block to afford heterobimetallic compounds in a rational manner using the complex-as-ligand strategy. It has been possible to obtain the novel polynuclear complex **[{Re(NO)Br<sub>4</sub>( $\mu$ -Hpydc)}Cu(dmbipy)<sub>2</sub>](CH<sub>3</sub>)<sub>2</sub>CO** (dmbipy = 4,4'-Dimethyl-2,2'-dipyridyl). The crystal structure is made up of neutral dinuclear Re(II)-Cu(II) units where the metal ions are connected through a pydc ligand. This bridging ligand act as monodentate towards the Re(II) atom through the aromatic nitrogen, and as monodentate to the Cu(II) atom through only one of the carboxylate groups.

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## Highly endothermic azido and nitrate complexes of main group elements

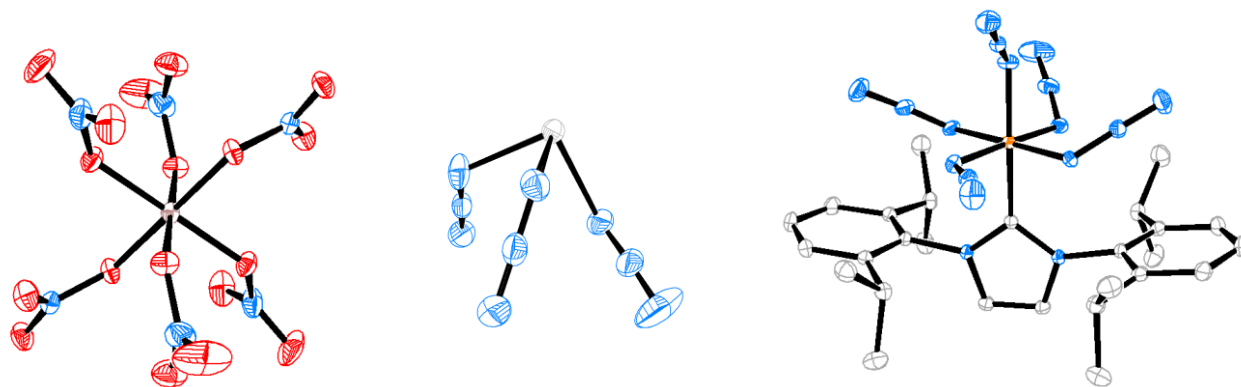
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Explosophoric ligands represent a method of increasing the endothermicity of coordination complexes for their potential use in energy storage.<sup>1</sup> Nitrogen and oxygen rich ligands such as the azide anion,  $\text{N}_3^-$ , and the nitrate anion,  $\text{NO}_3^-$ , fall into this category due to their propensity to decompose with release of  $\text{N}_2$  and  $\text{NO}_2$ , respectively. Our research aims to produce stable homoleptic and base-stabilized main group complexes bearing these ligands. By combining appropriate ligand exchange reactions, bulky counterions and strong Lewis bases, such as N-heterocyclic carbenes (NHC), we have been able to prepare several previously unreported, stable, hypercoordinate and low-valent polyazido and polynitrate complexes including  $\text{Ge}(\text{N}_3)_3^-$  (Fig. 1 centre),  $\text{Sn}(\text{N}_3)_3^-$ ,<sup>2</sup>  $\text{Si}(\text{ONO}_2)_6^{2-}$  (Fig. 1 left),  $\text{Ge}(\text{ONO}_2)_6^{2-}$ ,<sup>3</sup>  $\text{Al}(\text{N}_3)_3(\text{NHC})$ ,  $\text{Si}(\text{N}_3)_4(\text{NHC})$  and  $\text{P}(\text{N}_3)_5(\text{NHC})$  (Fig. 1 right). The complexes were fully characterized including, amongst others, thermochemical and crystallographic methods (Fig. 1) and their reactivity studied toward reducing agents in attempts to access low-valent azido complexes of the lighter *p*-block elements.



**Figure 1** Thermal ellipsoid diagrams (50%) of the complexes  $\text{Si}(\text{ONO}_2)_6^{2-}$  (left),  $\text{Ge}(\text{N}_3)_3^-$  (centre) and  $\text{P}(\text{N}_3)_5(\text{NHC})$  (right) obtained from single crystal XRD investigations; carbon (grey), nitrogen (blue), oxygen (red), silicon (mauve), phosphorus (orange), germanium (light grey). H atoms are omitted for clarity.

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3 B. Peerless, P. Portius, *manuscript in preparation*.

# Interesting Metal Ion-Assisted Transformations of Carbonyl- and Oxime-Containing Ligands

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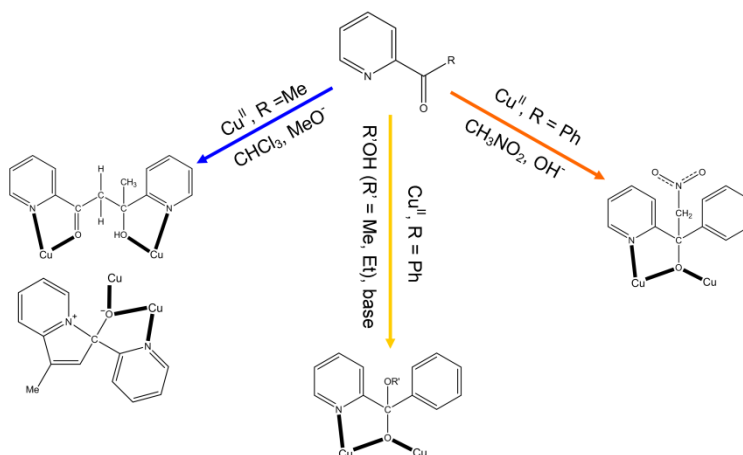
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Nowadays, the altered reactivity of inorganic or organic ligands as a consequence of their coordination to a metal ion is an interesting research theme in contemporary transition-metal chemistry, because it forms the basis for the use of coordination complexes as stoichiometric reagents and also as homogeneous catalysts in organic chemistry.<sup>1</sup> Our groups have had a strong interest over many years in the reactivity chemistry of coordinated ligands of the general types X-CO-X, X-CO-CO-X, X-CO-X-CO-X, X-C(NOH)-X, X-CO-Ψ and X-C(NOH)-Ψ, where X and Ψ are donor and non-donor groups, respectively.<sup>2</sup> In our presentation we shall describe interesting Co<sup>II</sup>-, Ni<sup>II</sup>-, Cu<sup>II</sup>-, Zn<sup>II</sup>- and Ln<sup>III</sup>- assisted/promoted transformations of various 2-pyridyl aldehydes/ketones (Fig. 1) and 2-pyridyl oximes (Ln = lanthanide).



**Figure 1** Cu<sup>II</sup>-assisted transformations of 2-acetylpyridine and 2-benzoylpyridine.

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## Interactions of novel Ru(II) polypyridyl complexes with G-quadruplex DNA

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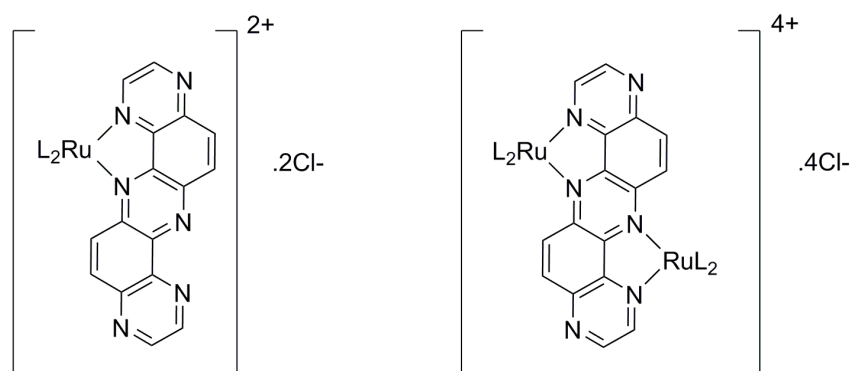
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Over the years, extended planar polycyclic aromatic ligands have been used in various applications<sup>1,2</sup> due to their abilities to form supramolecular assemblies or complexes with transition metals. Recently, such complexes have also displayed features of desirable G-quadruplex stabilisers<sup>3,4</sup>. However, due to the lack of novel syntheses, only a few new extended planar polycyclic aromatic ligands have been published recently. In our lab, we achieved the synthesis of the dipyrazino[2,3-a:2',3'-h]phenazine (dph) containing five fused cycles, three of them being pyrazinic rings, through a novel reaction.

In this work, we report on the syntheses of novel mononuclear and dinuclear Ru(II) complexes bearing dph ligand (figure 1). The affinity for G-quadruplex DNA is currently investigated by Surface Plasmon Resonance and some early results suggest a selectivity for G-quadruplex versus duplex DNA.



**Figure 1** Ru(II) - dph complexes

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## A Multimodal and Functional Cu(II) Complex Targeting G-quadruplex DNA

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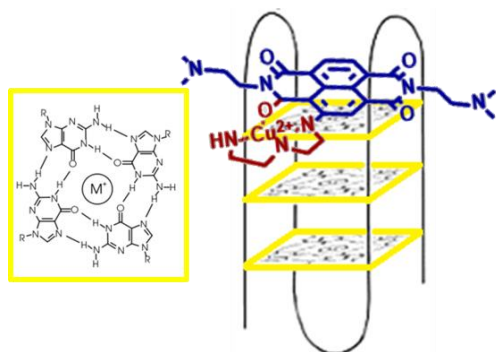
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Nucleic acid sequences rich in guanine are able to fold into G-quadruplex (G4) structures have received increasing attention as they may be involved in genomic instability, telomerase dysfunction, regulation of gene expression and viral transcription.<sup>1</sup> Consequently, G4 selective ligands represent potential anticancer and antiviral agents.

In this frame, we synthesized and characterized a tri-substituted naphthalene diimide (NDI) with a diethylenetriamine (Tren) substituent, which strongly coordinate Cu(II) at physiological pH (apparent constant of 17.3(1) log units; **Cu-Tren-NDI**).

Tri- and tetra-substituted naphthalene diimides (NDIs) are known as important small molecules able to bind G4 structures with high affinity and reversibility,<sup>2</sup> while the copper complex presence could potentially oxidize and cleave G4 nucleic acids by application of a catalytic metallodrug strategy. The selective oxidation is a ROS mediated process catalysed by Cu(II) under oxidative stress. In the present study, we have investigated ligand stability using ascorbate (1 equiv.) and H<sub>2</sub>O<sub>2</sub> (4 equiv.) at neutral pH, confirmed that Cu-Tren-NDI interaction with G4 is fundamental to maintain the ligand undamaged.



Furthermore, the **NDI-Cu-Tren** ligand delivers the copper coordination sphere in close proximity to G4s, opening the opportunity to achieve their selective cleavage. Accordingly, a detailed characterization of the structural modifications of G4s induced directly by ROS is addressed.

**Figure 1.** Schematic representations of the interaction between G-quadruplex and **NDI-Cu-Tren** ligand.

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## Beryllium chelation

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Beryllium (Be), the first of the group 2 alkali-earth elements, is a silver-gray metal possessing an unmatched combination of physical and mechanical properties, which are vital for a variety of applications that offer tremendous benefits to society.<sup>1</sup> Unfortunately, beryllium is also problematic. It is brittle, hard to machine, expensive and extremely toxic. It is a suspected human carcinogen, an initiator of chronic beryllium disease (CBD) and is regarded as the most toxic non-radioactive element in the periodic table.<sup>2</sup> Surprisingly, this has not deterred its production and usage, making it imperative to gain a better understanding of this element. This presentation will describe recent progress we have made in developing selective ligands for the beryllium cation.<sup>3</sup>

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## New trinuclear ruthenium complex coordinated to nitric oxide

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Nitric oxide (NO) is known by its properties like anticancer activity, vasodilation and antiparasitic action<sup>1</sup>. Nitrosyl ruthenium complexes are example of compounds which can deliver NO by electrochemical and light stimulus<sup>2</sup>. In this context, nitrosyl trinuclear ruthenium complexes are good options as NO delivers, since they have three biologically accessible electrochemical processes, photochemical release of NO happens in the visible region<sup>3</sup>, and the complex can carry more two functional ligands, as presented by this work trough the synthesis of the complex  $[\text{Ru}_3\text{O}(\text{CH}_3\text{COO})_6(\text{thiq})_2\text{NO}]\text{PF}_6$ , where thiq is 5,6,7,8-tetrahydroisoquinoline. The synthetic route was different from the usual<sup>3</sup> because it employed the complex  $[\text{Ru}_3\text{O}(\text{CH}_3\text{COO})_6(\text{CH}_3\text{OH})_2\text{NO}](\text{CH}_3\text{COO})$  as a precursor, eliminating the need for carbonyl intermediate complex. 200 mg of the precursor were stirred with four times of ligand excess at room temperature and protected from light. By the end of 48 hours,  $\text{NH}_4\text{PF}_6$  was added and the reaction medium was dried using a rotative evaporator. The resulting brownish purple complex was purified by column chromatography using neutral aluminum oxide as stationary phase and a 7:3 DCM:ACN mixture as mobile phase. Absorption spectrum in UV-visible region showed the three characteristic bands presented by this kind of complex<sup>3</sup>: a CLCT (Cluster to Ligand Charge Transfer) band at 458.5 nm ( $\log \epsilon = 3.27$ ), a CLCT band at 548.5 nm (3.25) and an intracuster band at 694.5 nm (3.14). Qualitative photolysis (performed using a 365 nm lamp) presented a spectral behavior in agreement with NO release and formation the solvated complex<sup>3</sup>. The characteristic stretching of coordinated NO occurs at  $1874 \text{ cm}^{-1}$ . The cyclic voltammogram (acetonitrile, 0.1 M TBABF<sub>4</sub>, 0.001 M of complex) showed three reversible processes:  $E_{1/2} 0.85 \text{ V (0/+1)}$ ,  $E_{1/2} 0.13 \text{ V (+1/+2)}$ ,  $E_{1/2} 1.30 \text{ V (+3/+4)}$ , any of which is correspondent to  $\text{NO}^0/\text{NO}^+$  process. Given the results presented, it is reasonable to assume that the new complex is a good candidate to continue the photochemical studies aiming its application as a NO donor. FAPESP, CAPES, CNPq

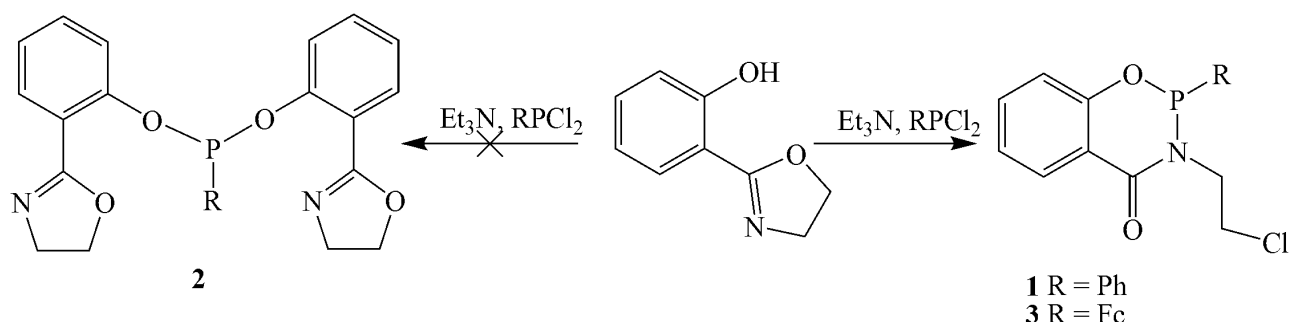
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## Synthesis and Transition Metal Chemistry of Ferrocenyl-benzo-oxazaphosphininone

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The reaction of 2(2'-hydroxy)phenyloxazoline and dichlorophenylphosphine led to the isolation of an unexpected cyclic product 3-(2-chloroethyl)-2-phenyl-2H-benzo[e][1,3,2]oxazaphosphinin-4(3H)-one (**1**)<sup>1</sup> instead of an expected bis(phosphinite) (**2**). The P-Cl bond induced oxazoline ring opening followed by cyclization resulted in the formation of six-membered  $\gamma$ -lactam (**1**). The extension of this methodology to bis(dichlorophosphino)ferrocene<sup>2</sup>,  $\text{Fe}(\eta^5\text{C}_5\text{H}_4\text{PCl}_2)_2$  yielded ferrocenyl benzo-oxazaphosphininone derivative  $[\text{Fe}\{\text{C}_5\text{H}_4\text{P}(\text{OC}_6\text{H}_4)(\text{CO})\text{N}(\text{C}_2\text{H}_4\text{Cl})\}_2]$  (**3**). The details of reactions, synthesis, transition metal chemistry and structural aspects will be presented.



**Scheme 1** The reaction of oxazoline with  $\text{RPCl}_2$ .

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## Synthesis and Characterization of Homoleptic $[M(C^N^N)_2]$ Complexes Where M = Ruthenium or Osmium

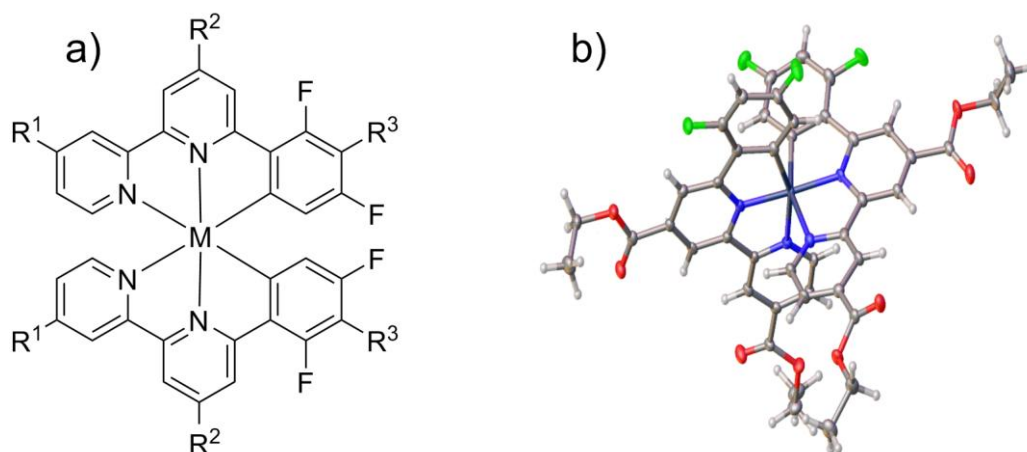
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Organometallic complexes containing cyclometalated  $C^N^N$  ligands are well known in the literature. Complexes of this kind have shown promising properties for applications, including medicine, and optoelectronic devices.<sup>1,2,3</sup> There are however very few examples of homoleptic  $C^N^N$  complexes. We have designed and synthesized a new family of organometallic compounds in order to investigate their properties.

Our complexes are based on a metal center (either ruthenium or osmium) coordinated to two identical phenylbipyridine ligands, with strongly electron withdrawing substituents.



**Figure 1** a) General structure of the investigated complexes, where M = Ru or Os, R<sup>1</sup> and R<sup>2</sup> = CO<sub>2</sub>Et or CF<sub>3</sub>, and R<sup>3</sup> = H or CF<sub>3</sub>, b) Example x-ray crystal structure.

This talk will focus on the synthetic challenges involved in accessing the complexes, the methods used to solve these issues, as well as characterization of the compounds by UV-Vis absorption, cyclic voltammetry and X-ray crystallography.

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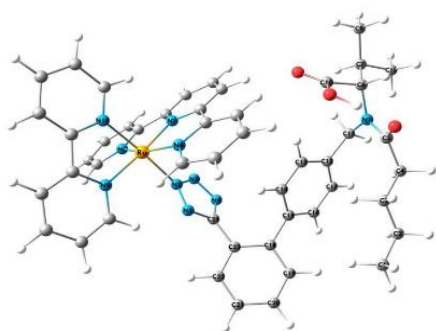
## Synthesis and interaction studies with human serum albumin of a new ruthenium complex with valsartan.

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The ruthenium polypyridyl complex, [Ru(val)(bpy)(terpy)](PF<sub>6</sub>) (**RuVal**, Fig.1), which contains the antihypertensive drug valsartan was synthesized without any noticeable drug degradation.



**Fig. 1** Structural representation of **RuVal** at BP86/def2-TZVPP level.

**RuVal** was characterized by CHN, ESI-MS, <sup>1</sup>H and <sup>13</sup>C NMR, FTIR, UV-Vis, and cyclic voltammetry techniques. NMR spectra suggest that coordination of valsartan to Ru(II) occurs by tetrazol ring. Electronic-structure calculations performed at DFT level showed that valsartan adopts an anti-configuration and a Ru-N<sub>tetrazole</sub> bond length of 2.050 Å.

Fluorescence spectroscopy binding studies with human serum albumin (HSA) indicate spontaneous interaction. The static quenching mechanism is predominant, as can be inferred by the dependence of K<sub>sv</sub> with temperature and the high values of k<sub>q</sub>. Moreover, high values of K<sub>b</sub> observed (Table 1) demonstrate that this compound can be efficiently stored and transported by this protein in a living organism. The analysis of the thermodynamic parameters shows a predominance of hydrophobic interactions<sup>1,2</sup>.

Table 1. Stern-Volmer, quenching rate and binding constants and thermodynamic parameters for HSA-RuVal system, at different temperatures.

T (K)	K <sub>sv</sub> × 10 <sup>4</sup> (L mol <sup>-1</sup> )	k <sub>q</sub> × 10 <sup>12</sup> (L mol <sup>-1</sup> s <sup>-1</sup> )	K <sub>b</sub> × 10 <sup>5</sup> (mol <sup>-1</sup> L)	n	ΔG (kJ mol <sup>-1</sup> )	ΔH (kJ mol <sup>-1</sup> )	ΔS (kJ mol <sup>-1</sup> )
298	5.92	5.92	0.04	0.77	-20.6		
305	6.39	6.39	1.08	1.05	-29.4	36	1.28
312	5.87	5.87	28.70	1.35	-38.6		

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CAPES, CNPq, FAPESB, FAPESP

## Structural Aspects of Molecular Coordination Compounds of Tin(II) Thiocyanate, $\text{Sn}(\text{NCS})_2$

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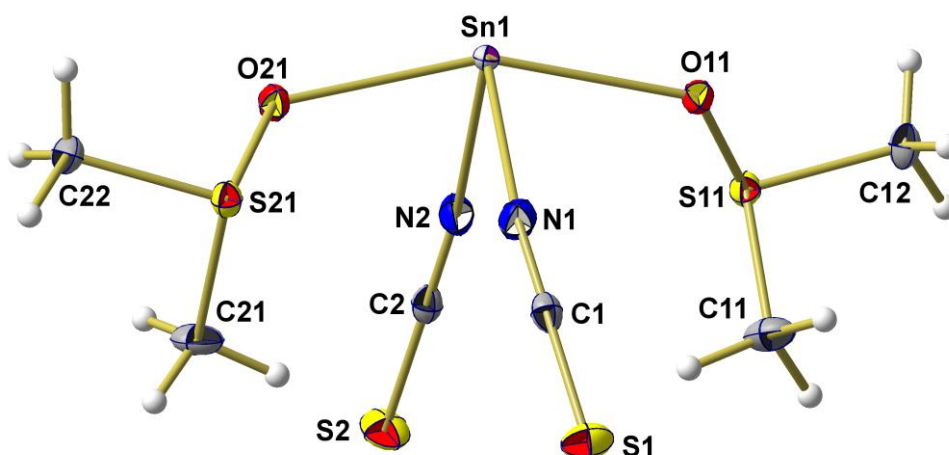
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Complexes of tin(II) compounds with Lewis bases (LB) are well documented in literature covering a broad range regarding stoichiometry (1:1, 1:2), complexity (monomeric, dimeric, polymeric) and stereochemistry (tetrahedral = tetr, trigonal-bipyramidal = tbpy, octahedral = oct) at the tin(II) center with its non-bonding (pseudo =  $\Psi$ ) electron pair. With the aim to study the influence of different Lewis bases on some of these factors in case of one and the same tin(II) compound we prepared several molecular complexes using tin(II) thiocyanate,  $\text{Sn}(\text{NCS})_2$ , **1** as target molecule.

In summary, the unidentate O- and N-Lewis bases dimethyl sulfoxide (DMSO), diphenyl sulfoxide ( $\text{Ph}_2\text{SO}$ ), triphenylphosphine oxide (TPPO), 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (DMPU), pyridine-*N*-oxide (PyNO), pyridine (Py), as well as the chelating, bidentate N,N-complex ligands 1,10-phenanthroline (Phen), and 2,2'-bipyridine (Bipy) have been applied resulting in the formation of the following 1 : 2 complexes **1** · 2DMSO ( $\Psi$ -tbpy, Fig. 1), **1** · 2Py ( $\Psi$ -tbpy), **1** · 2PyNO ( $\Psi$ -tbpy), **1** · 2DMPU ( $\Psi$ -tbpy), **1** · 2 $\text{Ph}_2\text{SO}$  · EtOH (EtOH disordered, non-complexing), and **1** · Phen · DMSO ( $\Psi$ -oct); as well as the 1 : 1 complexes **1** · Bipy ( $\Psi$ -tbpy), **1** · Phen ( $\Psi$ -tbpy), **1** · TPPO ( $\Psi$ -tetr) which have been all structurally characterized by single crystal X-ray diffraction.



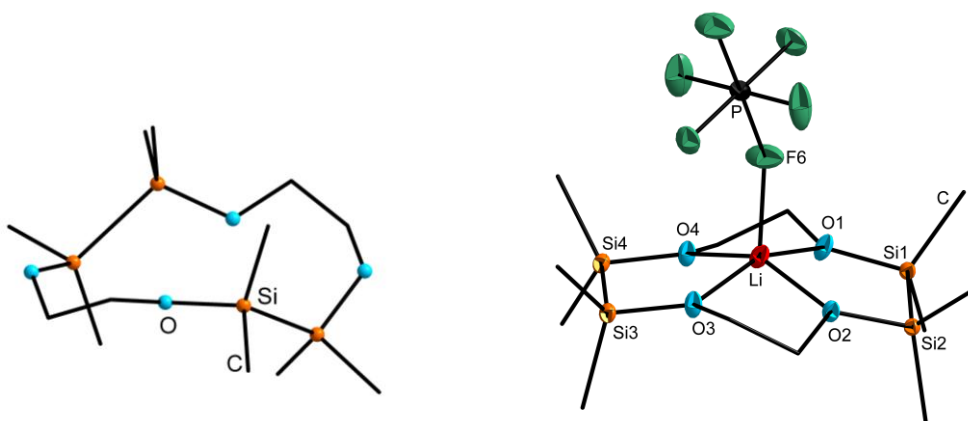
**Figure 1:** Ball-and-stick model of the  $\Psi$ -trigonal-bipyramidal complex  $\text{Sn}(\text{NCS})_2 \cdot 2\text{DMSO}$ .

## Metal Complexes of Disilane Substituted Crown Ethers

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Compared to crown ethers cyclosiloxanes barely interact with lewis acids like  $\text{BCl}_3$  and  $\text{BF}_3$ .<sup>[1–3]</sup> Until today, complex formation with cyclosiloxanes as ligands has only been successful by use of the salts of large, weakly coordinating anions.<sup>[4][5]</sup> However, the basicity of cyclic silaethers bearing  $\text{Si}_2$ -units is higher compared to cyclosiloxanes due to a lower impact of negative hyperconjugation. We therefore synthesized hybrid crown ethers containing disilane as well as ethylene fragments in between the oxygen atoms to determine their binding affinity to alkaline metal ions.



**Figure 1** *Left*: Optimized geometry of 1,2,7,8-tetrasiladecylcrown-4 calculated by means of DFT at the def2-TZVP level; *Right*: Molecular structure of  $[\text{Li}(1,2,7,8\text{-tetrasiladecylcrown-4})]\text{PF}_6$ ; thermal ellipsoid represent a 50% probability level; hydrogen is omitted for clarity.

1,2,7,8-Tetrasiladecylcrown-4 was synthesized via Williamson ether synthesis of 1,2-dichlorodisilane and ethylene glycole and interacts willingly with lithium salts like  $\text{LiPF}_6$ . Using [12]crown-4, 1,2,7,8-tetrasiladecylcrown-4 and  $\text{LiPF}_6$  in 1:1:1 ratio we discovered via  $^1\text{H}$  NMR spectroscopy that the silylated ligand has a similar binding affinity compared to the organic crown ether. These results have additionally been confirmed by quantum chemical methods and indicate that crown ethers made up of  $\text{Si}_2$ -units act as excellent ligands.

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## Synthesis, crystal structures and properties of complexes based on new zoledronic acid analog with 3d metal ions.

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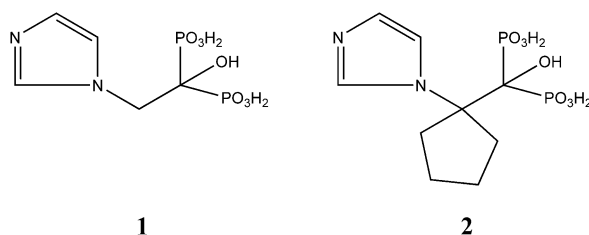
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Bisphosphonic acids are a class of compounds which main application is associated with antiresorptive properties and high affinity for cations, and for that reason have been successfully used in clinical treatment of diseases such as osteoporosis or Paget disease<sup>1</sup>. A characteristic feature of bisphosphonates is their ability to form highly complex hydrogen-bonded networks due to the tetrahedral geometry of phosphonate and phosphonic groups and their donor/acceptor potential. This allows them to create with metal ions structures with different architecture, promising properties and potentially wide range of applications<sup>2,3</sup>. Among the commercially available compounds of this class, the highest activity is displayed by zoledronic acid (**1**). Apart from interest of pharmaceutical industry and medical sciences, for nearly a decade this compound has been an object of interest of supramolecular chemistry.

As a part of our ongoing studies, herein we present crystal forms of Co(II) and Ni(II) phosphonate coordination compounds based on new  $\alpha,\alpha$ -disubstituted analog of zoledronic acid (**2**) comprising coordination polymers and tetranuclear isolated coordination units. Furthermore, properties of obtained compounds were characterized by thermogravimetric analysis (TGA) and spectroscopic (FT-IR, FT-Raman) techniques.



**Figure 1** Zoledronic acid (**1**) and his  $\alpha,\alpha$ -disubstituted analog (**2**).

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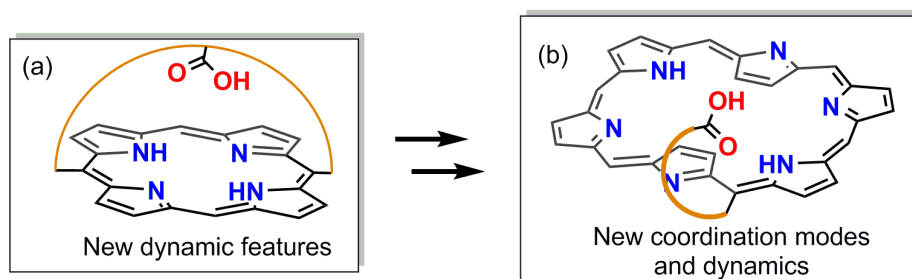
## Hexaphyrins with coordinating arms: a new path to control the topology, aromaticity and metallation behavior of expanded porphyrinoids?

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Porphyrins have been largely used as metal ligands, with a paramount importance in various fields: bioinspired models, catalysis and supramolecular chemistry. In the laboratory, we have developed porphyrins bearing coordinating arm(s) and strap(s) delivering a COOH group above the macrocycle (Figure 1a). Those functionalizations allow new types of metal complexes with unprecedented dynamic behaviors.<sup>1</sup> Thus, fast kinetic of metallations, control of the entrance/departure of the metallic cation(s) *in* and *out* of the macrocycle by transmetallation or translocation processes, formation of hetero or homobimetallic complexes, and control of the nuclearity, are innovative features defining a new supramolecular coordination chemistry. Moving forward with coordinating arms, we have decided to extend the size of the macrocycle to 6 pyrroles. Physical and chemical properties of hexaphyrins<sup>2</sup> are different from those of porphyrins. For instance, the formers exhibit large conformational flexibility of the macrocycle,<sup>3</sup> naturally two coordination sites, NIR and two-photon absorptions. However, hexaphyrins suffer from unpredictable metallation behaviors and side reactions. Herein, we show that hexaphyrins with a pendant coordinating arm (Figure 1b) allow the formation of new metal complexes with group 12 cations.



**Figure 1.** Simple representation of a strap porphyrin ligand with an overhanging COOH group (a) and of an hexaphyrin ligand with a coordinating arm (b).

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## Photoluminescence Color Adjustment of Co-deposited CuI Complexes

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Copper(I) complex has attracted much attention in organic light-emitting diodes (OLEDs) for its theoretical maximum internal quantum efficiency of 100% as well as that of noble metal (i.e. Ir and Pt) complex.<sup>1,2</sup> Among copper(I) complexes, (CuX)<sub>m</sub>L<sub>n</sub> (X = I, Br, or Cl; L = pyridine derivatives) are well-known for their rich photophysical behavior, and high photoluminescence quantum yield (PLQY). However, most of them are thermal unstable and hence not amenable to the vacuum deposition methods typically used to fabricate OLEDs. To solve this problem, a co-deposition route to prepare CuI-pyridine coordination complexes for OLEDs has been proposed.<sup>3-7</sup>

Since the pyridine derivative serves a ligand for forming the emissive complex in the co-deposition route, the electronic and chemical structures of the ligands are responsible for the photoluminescence property of the co-deposited copper(I) complex. Herein, a series of novel bicarbazole (BCz) compounds were designed and synthesized to tune the emission color of the *in situ* formed copper(I) complex. By systematically studying these compounds and their co-deposited CuI:BCz films, it is found that with the introduction of more nitrogen atoms into the heterocyclic arylene, or expansion of conjugation system, the corresponding CuI:BCz films showed a red-shifted photoluminescence spectrum, ranging from 517 nm to 564 nm, realizing the adjustment from green to yellow.

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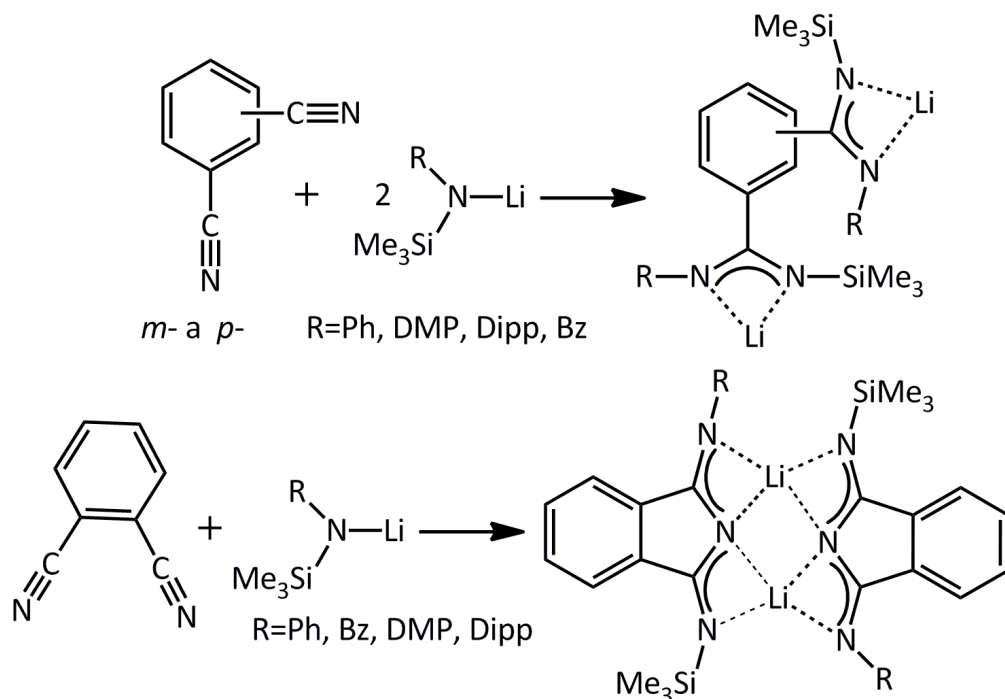
## Addition of main group metal amides to various nitriles

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The activation of small molecules together with reactions of main group metal complexes and organometallics with unsaturated systems is one of the hottest topic of nowadays chemistry. In this paper, we would like to demonstrate the reactivity of various lithium, magnesium, aluminium and tin complexes with unsaturated systems such as alkynes and various aliphatic and aromatic nitriles and dinitriles. These reactions are usually connected to the presence of lowest possible oxidation state of the central metal atom as well as the possibility of the trimethylsilyl group, present in the amide backbone, migration process to the nitrogen atom(s) of parent nitrile group. Various organic molecules or natural products can be synthesized by our approach.



**Figure 1** Example of reactivity of lithium amides with various dinitriles.

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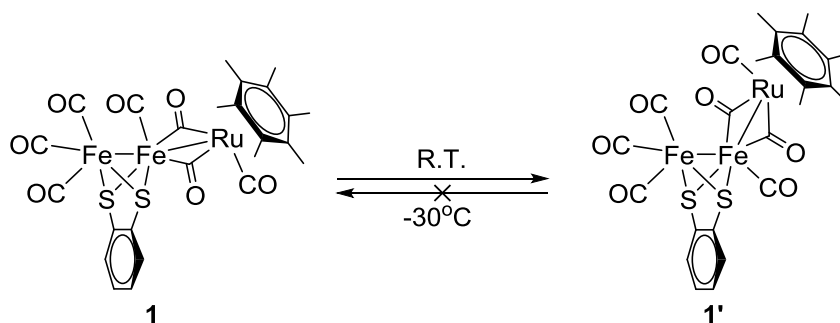
## Synthesis and properties of Fe-Ru trinuclear dithiolene complex

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Metalladithiolene complex have five-membered ring which is composed of a metal center, two sulfur atoms, and two unsaturated carbon atoms. This complex has a 16-electron metal center, indicating electronically unsaturated coordination. Because of this feature, the addition reaction of various chemical species on metalladithiolene ring is reported. For example, synthesis of mixed metal dithiolene complexes from mononuclear metalladithiolene complexes and metal carbonyls has been well studied.<sup>1</sup> We previously reported the synthesis of carbon monoxide coordinated ruthenium dithiolene complex,  $[(C_6Me_6)Ru(CO)(S_2C_6H_4)]$ , from  $[(C_6Me_6)Ru(S_2C_6H_4)]$  with  $Fe(CO)_5$ .<sup>2</sup> We also recognized generation of Fe-Ru trinuclear dithiolene complex **1** in the above reaction. However, detailed structure and properties of **1** has not been investigated.

In this study, we will report the structure and properties of **1**. The structure of the trinuclear complex **1** was successfully determined by single crystal X-ray structure analysis. We found that the single crystal of **1** prepared at  $-30\text{ }^\circ\text{C}$  converted to **1'** by standing for 1 week at room temperature. On the other hand, the single crystal of **1'** didn't convert to **1** at  $-30\text{ }^\circ\text{C}$ . We also found that **1** is working as an electrocatalyst for proton reduction. It is indicating that **1** has a potential to become a novel model complex for the active site of [FeFe]-hydrogenase.



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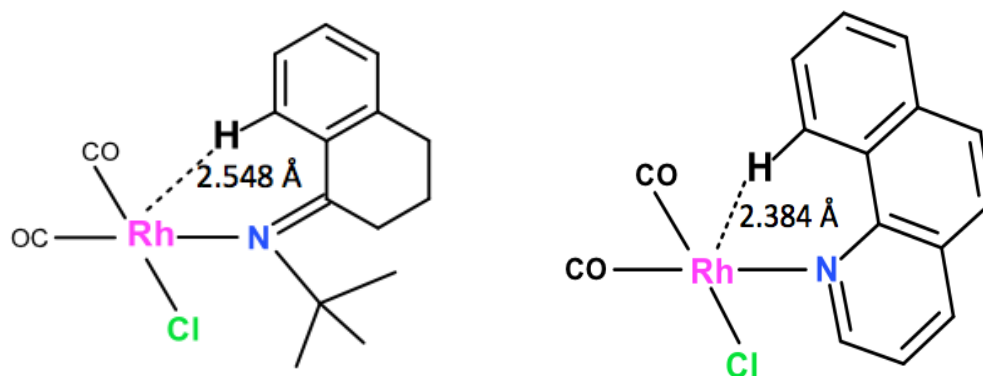
## Understanding the Nature of Anagostic Interactions - a Synthesis by Computation Approach

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C-H functionalization by transition metal cyclometallation reactions is an important area of research in organic transformations. The primary interaction in a cyclometallation reaction after a ligand coordinates is the anagostic approach in which a metal interacts with a hydrogen attached to an alkyl or aryl carbon. We have carried out a comprehensive computational study which addresses how steric and electronic effects influence the anagostic interaction using the 'synthesis by computation' approach<sup>1</sup> which gives information on the structure and nature of the interaction without resorting to bench syntheses. DFT calculations using the PBE-D3 functional for the rhodium complexes  $[\text{RhCl}(\text{CO})_2(\text{L})]$  ( $\text{L} = 1\text{-tetralone oximes and imines}$ ) show that (N)-OH and (N)-Me groups position the anagostic hydrogen more over the metal and (N)-OCMe<sub>3</sub> and (N)-CMe<sub>3</sub> groups more out towards the chloro ligand. QTAIM analysis indicates electrostatic dominance for the Rh····H separation and  $\sigma$  and  $\pi$ -withdrawing substituents on the ligand aromatic ring lengthen the Rh····H separation whereas  $\sigma$  and  $\pi$ -donating substituents shorten the Rh····H separation, and an attractive Rh····C interaction can develop. The  $\text{RhCl}(\text{CO})_2(\text{L})$  complexes ( $\text{L} = \text{isoquinoline}$ ) show much shorter Rh····H separations and severe distortion of the aromatic ring system occurs as the ligand moves to avoid the close approach.



**Figure 1** Rh····H close approaches in 1-tetralone oxime and isoquinoline complexes.

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## Cadmium and mercury complexes with phosphine chalcogenides: Synthesis, characterization and structural study

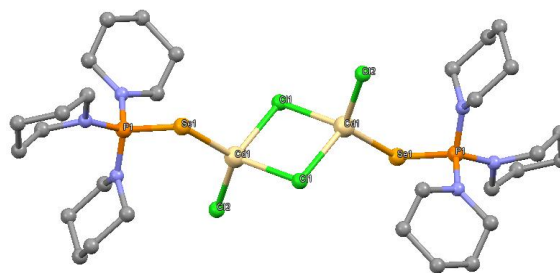
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The coordination chemistry of organophosphine chalcogenides of the formula  $R_3PE$  ( $E = O, S, Se$  or  $Te$ ) is attracting considerable interest due to the selective complexation properties of these ligands towards 'hard/soft' metal cations [1,2] and to their use as suitable single-source precursors for the production of nanocrystals of metal chalcogenides, for example  $ME$  ( $M = Cd, Zn$  or  $Hg; E = S$  or  $Se$ ) [3,4]. As a continuation of our work on the coordination properties of organophosphorus ligands of the type  $R_3PE$  ( $E = O, S, Se$  or  $Te$ ) towards various metal cations [5,6], we report herein on the synthesis of new  $Cd$  and  $Hg$  complexes with  $Pip_3P(E)$  and  $Pyrr_3P(E)$  ( $Pip =$  piperidinyl,  $Pyrr =$  pyrrolidinyl ;  $E = S$  or  $Se$ ). These complexes were fully characterised by multinuclear ( $^1H, ^{31}P, ^{77}Se, ^{113}Cd$  and  $^{199}Hg$ ) NMR, IR spectroscopies and in some cases by X-ray analysis and conductimetry. Our results show that both the nature of the chalcogen atom and the minor changes in the substituents on the phosphorus atom of the ligand could lead to significant effects on the stability of the complex formed. The X-ray structures of the piperidinyl derivatives show that they exist as dimers with bridging chlorine atoms producing a structure of the type  $M_2Cl_4(Pip_3PE)_2$ .



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## Characterization of one-electron oxidized metal(II) di(*p*-methylthiophenolate) complexes

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The Cu(II)–phenoxy radical formed during the catalytic cycle of galactose oxidase (GO) attracted much attention, and the structures and properties of a number of metal–phenoxy radical complexes have been studied.<sup>1</sup> Some of functional model system of GO have been reported previously that the Cu complexes showed the oxidation of primary alcohols to aldehydes, and formation of the Cu(II)-phenoxy radical species was revealed in the catalytic cycle. The phenoxy radical in GO has carbon-sulfur covalent bond at ortho-position of the phenol ring. However, properties and detailed electronic structures of the methylthiooxy radical coordinated metal complexes have been reported only a few.

As an extension of the studies on one-electron oxidized Cu(II)–phenolate species and a clarification of role of the methylthio group of phenoxy radical in GO, we synthesized one-electron oxidized square-planar Cu(II) and group 10 metal(II) complexes of di(*p*-methylthiophenolate) Schiff base ligands and characterized their geometric and electronic structures and reactivity. The geometric and electronic structures difference dependent with the central metal ion in di(*p*-methylthiophenolate) Schiff base ligands will be mainly discussed in this presentation.

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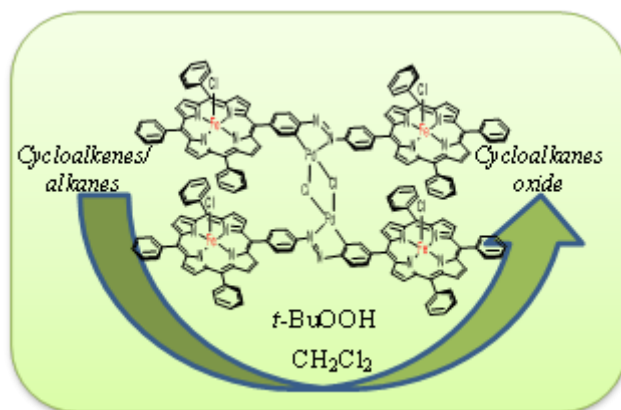
## A new Organopalladium Compound Containing Four Iron (III) Porphyrins in the Selective Oxidation of Alkanes/ Alkenes by *t*-BuOOH

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Two iron(III) tetraphenyl porphyrin catalytic units are connected by an azo-link to form the dimeric compound **A**. The compound **A** was then reacted with Pd<sup>2+</sup> to make a tetrameric iron(III) porphyrin complex **B** with all four iron(III) catalytic sites open to the substrates and reactants. Both the compounds are characterized spectroscopically and the results of homogeneous oxidation of some alkanes and alkenes with *t*-BuOOH in presence of catalytic quantities of **A** and **B** has indicated remarkable improvement in selectivity and efficiency of **B** over **A** and **A** over the monomeric catalyst.



**Figure 1** New tetrameric soluble iron(III) porphyrins and their remarkable catalytic oxidation of several alkenes by *t*-BuOOH.

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## Pt(C<sup>^</sup>N) motif as a block for supramolecular construction: luminescent [Pt(C<sup>^</sup>N)(μ-CN)<sub>2</sub>M(PPh<sub>3</sub>)<sub>n</sub>]<sub>2</sub> squares (M = Cu<sup>I</sup>, Ag<sup>I</sup>)

V.V. Sivchik,<sup>a,\*</sup> L. Schneider,<sup>a,b</sup> I.O. Koshevoy<sup>a</sup>

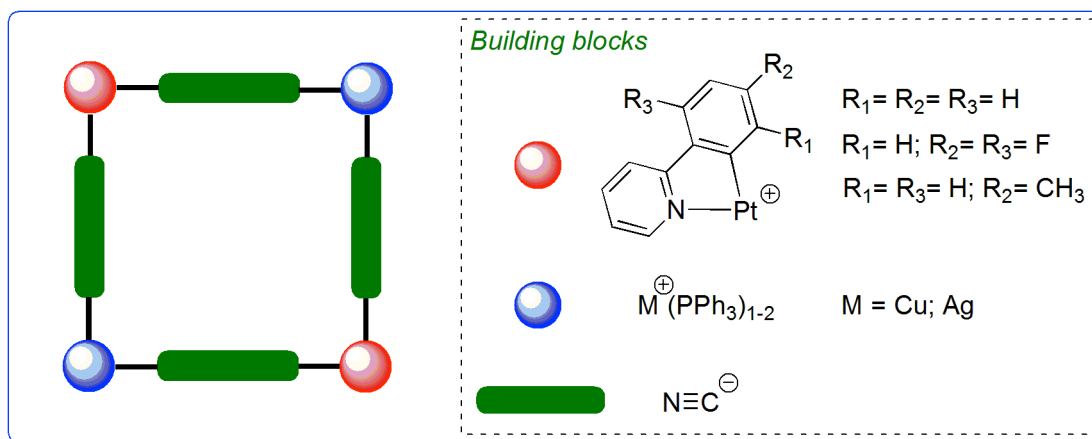
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Ligand-assisted self-assembly of platinum(II) building blocks has been intensively studied over past two decades.<sup>1</sup> The predictable coordination behavior of the metallic center allows to construct the variety of two- and three-dimensional topologies, which are able to generate light, to encapsulate small chemical species and to catalyze chemical transformations.

The square motif [Pt(μ-L)<sub>2</sub>]<sub>4</sub> is a well-known assembly since the first example described in 1994.<sup>2</sup> Surprisingly, heterometallic square aggregates [Pt(μ-L)<sub>2</sub>M]<sub>2</sub> remain scarce.<sup>3</sup> Moreover, highly emissive cycloplatinates containing (C<sup>^</sup>N)-carbometalating ligands have not been used in the construction of such systems.



**Figure 1** Structures of synthesized molecular “squares”.

Herein, we present a self-assembly approach to a family of novel square heterometallic tetranuclear complexes (Fig. 1). The synthesis, structural elucidation and photophysical properties of these compounds will be discussed.

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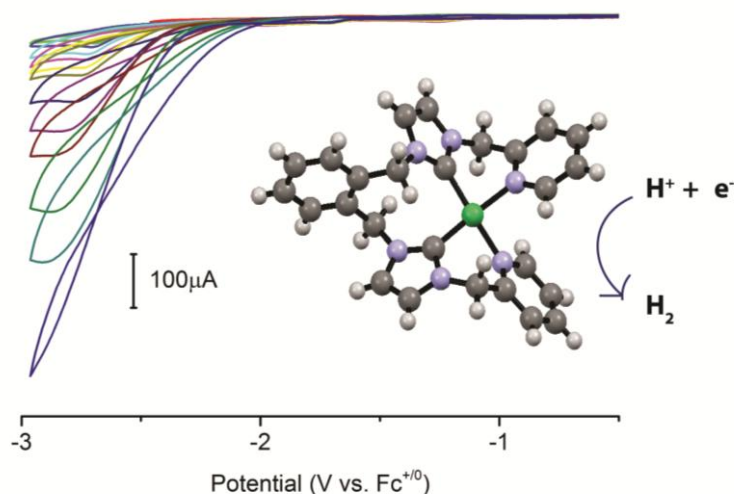
## Syntheses, Structures, and Electrocatalytic Hydrogen Production of S/N-Functionalized Ni-NHC Complexes

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We have synthesized of four pyridine-functionalized Ni-NHC complexes and investigated their efficiency in the electro catalytic reduction of protons. Although Ni-NHC complexes have found various applications in organometallic chemistry, the electrocatalytic properties of this kind of compounds so far mostly have been neglected by researchers working in the field of organocatalysis. The handful of publications related to proton reduction with metal-NHC compounds mostly addressed cobalt-NHC complexes.<sup>1,2</sup> With the aim to develop new electrocatalysts for proton reduction, several novel thiolate or pyridine-functionalized NHC-Ni complexes have been synthesized and were characterized by various methods. The synthesis and structures of the compounds, as well as their redox properties and electrocatalytic activity for proton reduction in organic solvent will be reported.



**Figure 1** Cyclic voltammograms of 1 mM solutions of one of the pyridine-functionalized NHC-Ni complexes with various amounts of acetic acid (0-120 eq) in 0.1M TBAP-DMF at 0.1 V/s.

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# Synthesis and NMR study of paramagnetic pyridine-based NAMI-A-type ruthenium complexes

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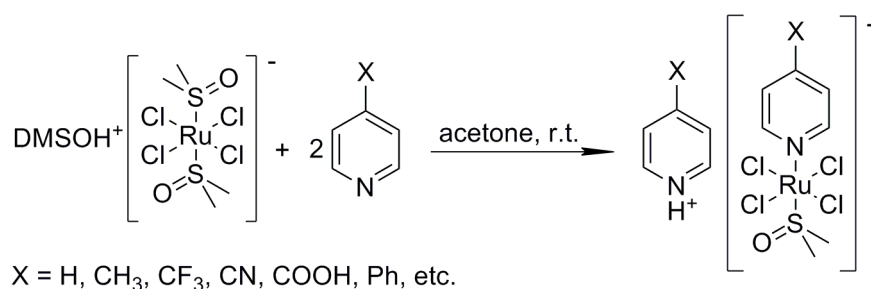
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We are interested in the synthesis of new Ru(III)-based complexes with promising anticancer activity. The paramagnetic nature of Ru(III) compounds usually makes routine 2D NMR experiments inapplicable and complicates the unambiguous interpretation of 1D NMR spectra. Thus, the assignment of experimentally detected <sup>1</sup>H and <sup>13</sup>C NMR resonances is performed with close support of advanced quantum-chemical calculations.

Hereby we report a study of NAMI-A-type Ru(III) complexes with selected pyridine derivatives. For our NMR experiments we synthesized a series of Ru(III) complexes with pyridine ligands (Figure 1)<sup>1</sup> and their Rh(III) analogs. To determine the temperature-independent part of the NMR chemical shift (orbital contribution) we performed temperature-dependent NMR experiments and characterized the closed-shell Rh analogs. The experimental values will be compared with theoretical data obtained from DFT calculations employing SO-ZORA approximation and implicit model of solvent.

**Figure 1** General synthetic approach for synthesis of Ru(III) NAMI-A-type complexes



*This work was supported by the Czech Science Foundation (15-09381S).*

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## Optical Properties of Eu(III) macrocyclic complexes

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D. Venegas-Yazigi<sup>b,e</sup>, J. Manzur<sup>b,f</sup>

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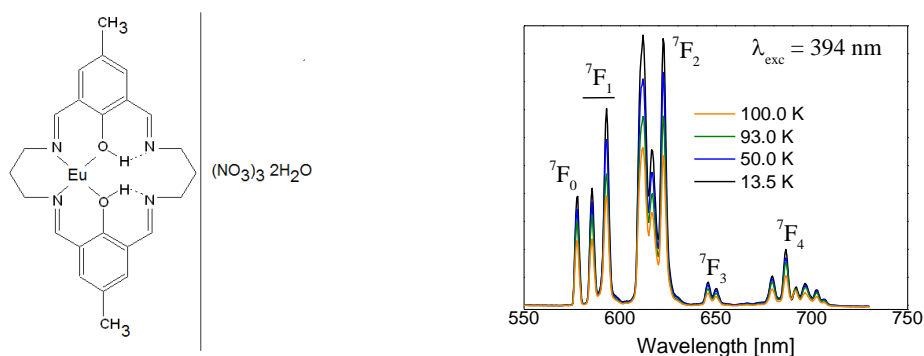
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In coordination chemistry, lanthanide(III) macrocyclic complexes are being studied because these compounds have interesting optical properties<sup>1,2</sup>. Herein, the optical properties of a family Eu<sup>III</sup> complexes are presented.

Mononuclear [2+2] macrocyclic complexes have been synthesized by a template reaction. The used ligands are derived from 2-hydroxy-5-methyl-1,3-benzenedicarbalddehyde and aliphatic or aromatic amines (Fig.1). Absorption and emission spectra were recorded in solution at room temperature, while emission spectra were obtained in solid state at different temperatures and under different excitation wavelengths. In solution, only the emission band of the ligand is observed at ca.520 nm; complexes with aromatic amine having a greater quantum yield than the ones derived from aliphatic amines. Thus, the intense emission band of the aromatic ligand overlaps the emission of the Eu<sup>III</sup> ion. In the solid state only the spectra of complexes with aliphatic amines show the Eu<sup>III</sup> emission (Fig. 2).



**Fig. 1** Scheme of the Eu<sup>III</sup> complex **Fig. 2.** Emission spectra at different temperatures.

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### Acknowledgements.

The authors thank FONDECYT project 1120001 and Proyecto Basal FB 0708 (CEDENNA)

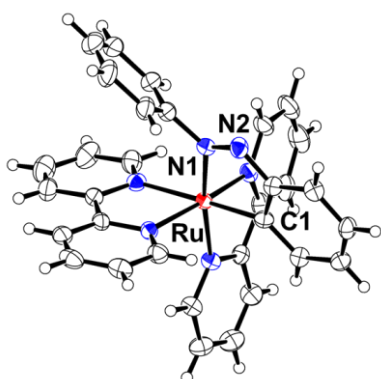
# Conversion Reactions of Nitrogen-containing Compounds on Ruthenium Complexes

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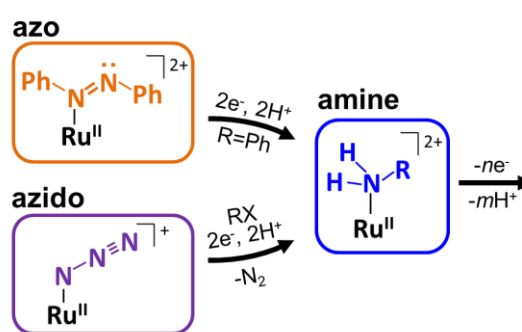
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Nitrogen-containing compounds are converted on metal enzymes under mild conditions in nature (nitrogen cycle). We have focused on nitrogen-containing compounds whose oxidation number of the nitrogen atom(s) was from -3 to 0. Formation of imine and amine complexes by reactions of azido ( $\text{N}_3^-$ ) ligand with haloalkane has been reported.<sup>1</sup> In this work, properties and reactions of the azo ( $-\text{N}=\text{N}-$ ) compound and amine ( $\text{RNH}_2$ ) on ruthenium complexes was studied.

A reaction of azobenzene with ruthenium(II) complex afforded cyclometalated complex  $[\text{Ru}^{\text{II}}\kappa(\text{N},\text{C})(\text{N}(\text{Ph})=\text{NC}_6\text{H}_4)(\text{bpy})_2]^+$  (Figure 1), which had a lone pair at the azo group and whose LUMO was centered on  $\pi^*$  orbital of the azo group. The cyclometalated complex reacted with nitric acid to form nitration compound of the phenyl group. Reduction of cyclometalated complex under acidic condition afforded bisaniline complex  $[\text{Ru}^{\text{II}}(\text{NH}_2\text{Ph})_2(\text{bpy})_2]^{2+}$ , which showed characteristic oxidation behavior. The oxidation reaction of bisaniline complex was multi-electron process due to intramolecular electron transfer and proton dissociation from aniline ligands. The details of these reaction and functions of these complexes as redox mediators were investigated.



**Figure 1** Structure of cyclometalated complex



**Scheme 1** Reactions of nitrogen-containing compounds on ruthenium complexes

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## C,N-chelated Organotin(IV) Azides as Building Blocks within the Click Chemistry

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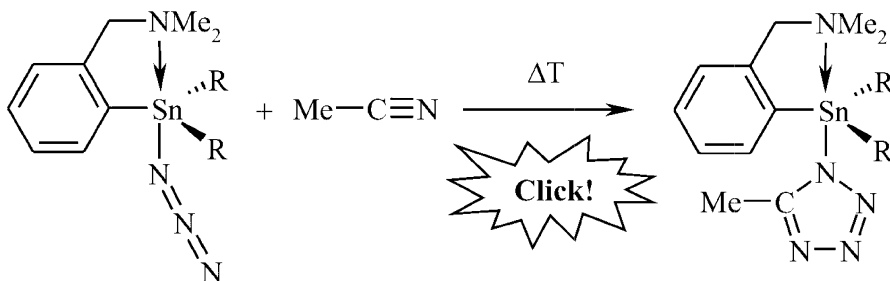
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Organotin species containing the 2-(*N,N*-dimethylaminomethyl)phenyl- moiety as a *C,N*-chelating ligand are studied since seventieth of the last century.<sup>1</sup> Significant N→Sn intramolecular coordination is the typical phenomenon of this class of compounds. For example, we have recently described the synthesis and structural characterization of some novel *C,N*-chelated organotin(IV) pseudohalides.<sup>2</sup> Moreover, the potential use of the respective triorganotin(IV) azides within the click chemistry has been explored (Figure 1).<sup>3</sup>

As a continuation of our work we would like to introduce some novel *C,N*-chelated organotin(IV) tri- or tetrazolides. These species are accessible *via* the [3+2] cycloaddition reactions of the *C,N*-chelated organotin(IV) azides with nitriles or alkynes. Synthesis and structural characterization of such complexes will be discussed in detail within the poster presentation.



**Figure 1** Reactivity of *C,N*-chelated organotin(IV) azides towards acetonitrile (R = *n*-Bu, Ph)

**Acknowledgement:** The authors would like to thank the Czech Science Foundation (project P207/12/0223) for the financial support of this work.

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## Copper(II) Schiff base complexes studies and application in ZnO nanoparticles doped thin layers preparation

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Cu(II) complexes with Schiff bases derived from ethylenediamine (en) and 2-pyridinecarboxaldehyde (pyca), 2,5-dimethoxybenzaldehyde (dmbaH) or 4-imidazolecarboxaldehyde (4Him) were obtained and studied by elemental analysis, UV-VIS and IR spectra. The ligands were also characterized by  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{15}\text{N}$  NMR spectroscopy. Zinc oxide was synthesized using a homogeneous precipitation method with zinc acetate as a starting material. Thin layers of studied copper(II) complexes were deposited on Si(111) or ZnO/Si(111) substrates by a spin coating method and characterized with a scanning electron microscopy (SEM/EDS), atomic force microscopy (AFM) and fluorescence spectroscopy. For copper(II) layers the most intensive fluorescence bands from intra-ligand transition were observed between 462 and 503 nm. The fluorescence intensity of thin layers was related to the rotation speed. In the case of the  $[\text{Cu}(\text{II})((\text{en})(4\text{Him})_2)(\text{Cl}_2)](\mathbf{2a})/\text{ZnO}/\text{Si}$  and  $[\text{Cu}(\text{en}(\text{dmbaH})_2)\text{Cl}_2](\mathbf{3a})/\text{ZnO}/\text{Si}$  layers the quenching of the emission fluorescence band from ZnO at 440 nm associated with various intrinsic or extrinsic lattice defects was noted ( $\lambda_{\text{ex}}=330$  nm).

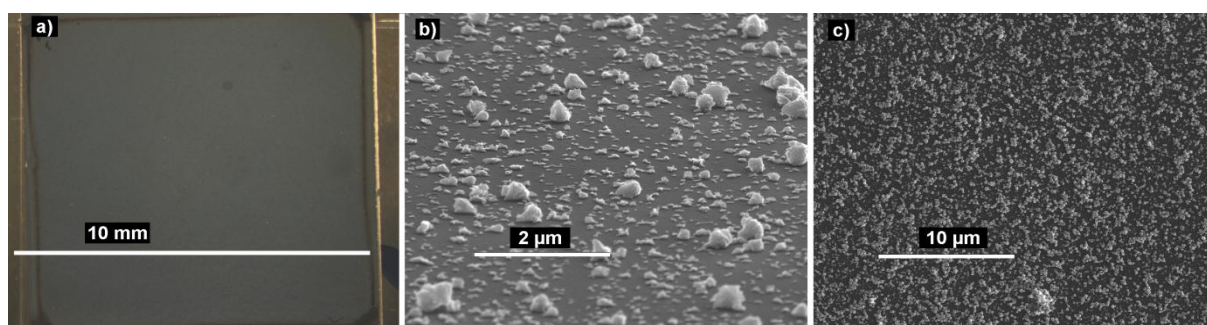


Figure 1 The ZnO layers: optical microscopy (a) and SEM (b; cross-section) images of sample **A4** (3000 rpm, 3min); (c) SEM image of sample **A6** (5000 rpm, 3min).

### Acknowledgement

Authors would like to thank the National Science Centre (NCN), Poland for financial support (grant no. 2013/09/B/ST5/03509).

## Synthesis and Reactions of Azidoruthenium(III) Complex Having 2-Pyridinecarboxylate and 2,2'-Bipyridine

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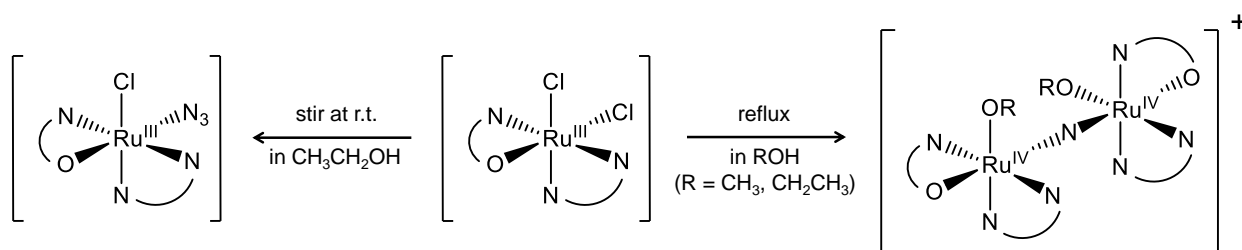
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Reactions of nitrogen containing compounds on ruthenium complexes having 2,2'-bipyridine (bpy) and 2-pyridinecarboxylate (pyc) have been investigating. Reactions of nitrosylruthenium complexes,  $cis\text{-}[\text{Ru}(\text{NO})\text{Cl}(\text{bpy})_2]^{2+}$  and  $cis\text{-}[\text{Ru}(\text{NO})\text{Cl}(\text{pyc})(\text{bpy})]^+$ , with  $\text{NaN}_3$  afforded diazidoruthenium(II) complex,  $[\text{Ru}^{\text{II}}(\text{N}_3)_2(\text{bpy})_2]^{2+}$ , and nitrido-bridged diruthenium(IV) complex,  $[\{\text{Ru}^{\text{IV}}(\text{OR})(\text{pyc})(\text{bpy})\}_2(\mu\text{-N})]\text{PF}_6$  ( $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5$ ), respectively. Formation of imine<sup>1</sup>, amine, and ammine ligands has been reported in reactions of diazidoruthenium(II) complex with haloalkanes.

In this work, azidoruthenium(III) complex,  $cis\text{-}[\text{Ru}^{\text{III}}(\text{N}_3)\text{Cl}(\text{pyc})(\text{bpy})]$ , was synthesized by a reaction of dichloridoruthenium(III) complex,  $cis\text{-}[\text{Ru}^{\text{III}}\text{Cl}_2(\text{pyc})(\text{bpy})]$ , with  $\text{NaN}_3$  under stirring conditions in ethanol, while nitrido-bridged diruthenium(IV) complex was formed under refluxing conditions in ROH ( $\text{R} = \text{CH}_3, \text{CH}_2\text{CH}_3$ ) (**Scheme 1**). The formation mechanism of nitrido-bridged diruthenium(IV) complex and reactions of azidoruthenium(III) complex with iodoalkanes  $\text{RCH}_2\text{I}$  ( $\text{R} = \text{H}, \text{CH}_3, \text{CH}_2\text{CH}_3$ ) were studied.



**Scheme 1** Reactions of  $cis\text{-}[\text{Ru}^{\text{III}}\text{Cl}_2(\text{pyc})(\text{bpy})]$  with  $\text{NaN}_3$

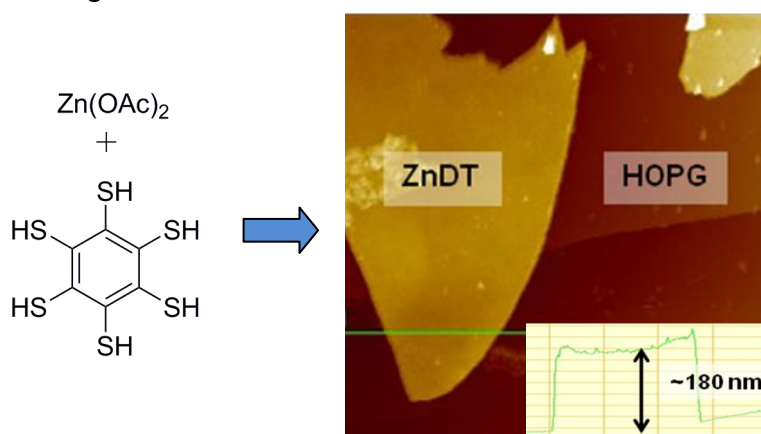
1 H. Nagao, T. Kikuchi, M. Inukai, A. Ueda, T. Oi, N. Suzuki, and M. Yamasaki, *Angew. Chem. Int. Ed.*, **2006**, *45*, 3131.

## Interfacial Synthesis of Zinc(II) Dithiolene Coordination Nanosheet

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Two-dimensional coordination nanosheets (CONASHs) utilizing the benzenehexathiol ligand have been previously reported, showing desirable properties such as high conductivity and redox-tunability.<sup>1,2</sup> Exotic CONASHs with novel physical properties are created by simply changing the metal ion or ligand (termed the 'bottom-up' approach). However, the non-innocent benzenehexathiol poses problems especially for high redox potential metal ions such as Pd(II), which are easily reduced.<sup>3</sup> In our search to analyze this problem, the use of redox inactive Zn(II) ions for comparison studies serendipitously generated flat Zn(II) dithiolene CONASH (named 'ZnDT'). This is considerably different from the metal ions used in previous reports, which were specifically chosen to coordinate in a square-planar geometry, such as Ni(II). The unusual formation of flat ZnDT with the  $d^{10}$  Zn(II) ion, together with its characterization studies and physical properties will be presented. It is foreseen that the use of redox-inert Zn(II) should allow us to better understand the chemical and physical properties of the dithiolene CONASHs formed using the benzenehexathiol ligand.



**Figure 1** AFM image of ZnDT

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## Tautomerism in arsoranes derived from carbohydrates

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Experimental and theoretical studies give evidence of stereochemical nonrigidity of p-block elements. Furthermore, fluxional equilibrium in arsoranes is the principal model for understanding their pentacoordination phenomena. Thus, changes in the stereochemical configuration of arsenic atom generally take place by means of polytopal equilibria.<sup>1</sup> However, it is possible that fluxional equilibrium of arsoranes could take place through tautomeric phenomena when restricted ligands are used (Figure 1).

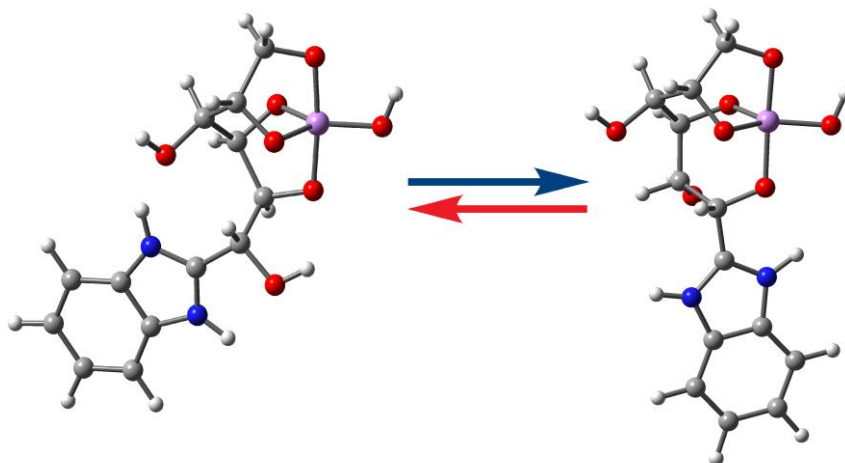


Figure 1

Arsoranes **1** and **2** were synthesized by means of the condensation of 2-(*D*-glycero-*D*-gulo-hexahydroxyhexyl)-benzimidazole or *N*-ethylglucamine with AsCl<sub>3</sub>. NMR studies showed that **1** and **2** quickly epimerize in aqueous solution. Moreover, HPLC revealed that this process occur via the formation of several structural intermediaries at acid media. On the other hand, theoretical studies at B3LYP/6-311++G(2d,2p) level demonstrated that fluxional equilibrium of arsoranes **1** and **2** is a tautomeric phenomenon where chemical species with tetrahedral arsenic atom are produced.

Authors thanks SEP-CONACyT for financial support (169010).

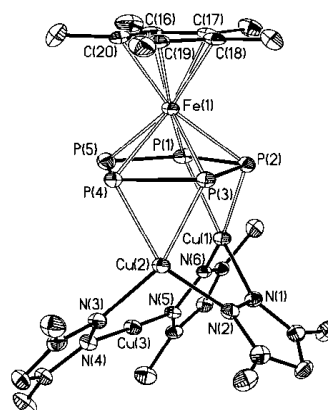
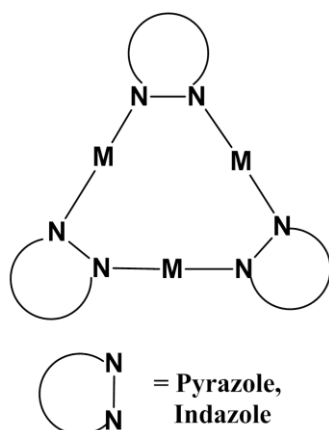
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## Complexation of the $d^{10}$ metal azaheterocyclic macrocycles with Lewis bases

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Complexes of coinage metal ions such as Cu, Ag with fluorinated N-based ligands, in particular pyrazolates, and their chemistry have recently attracted strong attention because of their interesting luminescence properties,  $\pi$ -acid/ $\pi$ -base chemistry and ability to form supramolecular aggregates through metallophilic  $d^{10}$ - $d^{10}$  closed-shell interactions.<sup>1,2</sup> Herein we report on the synthesis of several  $d^{10}$  metal azaheterocyclic macrocycles, and the investigation of complexation of these compounds with bases.



According to spectroscopic (NMR, IR, UV-vis) study the interaction of  $[\text{Cp}^*\text{Fe}(\eta^5\text{-P}_5)]$  and  $[\text{Cb}^*\text{Co}(\eta^5\text{-(C}_4\text{(Me)}_4\text{P))}]$  with trimeric pyrazolates yields new complexes which are astonishingly stable in solution. The single crystal X-ray analysis reveals the unprecedented folding of the macrocycle plane to  $90^\circ$  that makes the copper atoms able to behave both as Lewis acid and Lewis base in the interaction with *cyclo*- $\text{P}_5$  ligand.<sup>3</sup>

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## Interaction of pincer iridium hydrides with acids and bases

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Despite an extensive exploration of “(PCP)Ir” chemistry,<sup>1</sup> the ligand exchange for these complexes and the coordination of neutral ligands other than CO is almost unexplored.<sup>2</sup> In this contribution we present the results of NMR, IR and UV spectroscopic studies in a wide temperature range (190-290K) on the coordination of different bases, such as pyridines, nitriles as well as amines and amino-boranes to iridium complex (<sup>t</sup>BuPCP)IrHCl (**1**). Upon coordination of different molecules to **1** a mixture of several isomeric hydrides was obtained depending of the nature of the ligand and reaction conditions.<sup>3</sup>

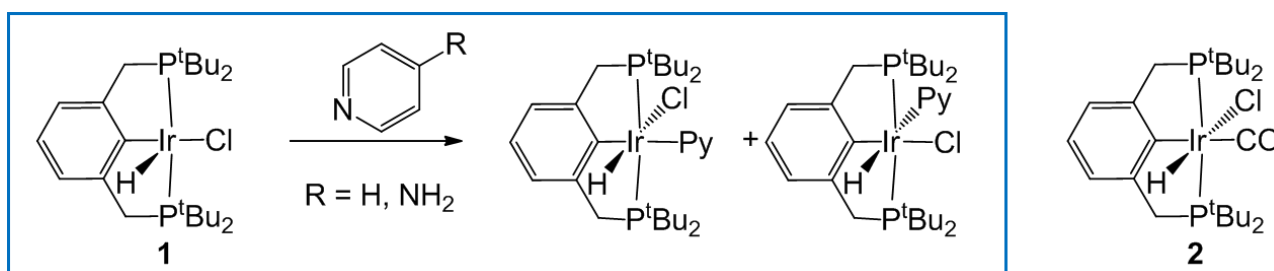


Figure 1

Both hydride and chloride ligands can serve as proton accepting sites in the interaction with proton donors. To figure out this possibility and compare their proton accepting ability in five and six coordinated iridium complexes **1** and **2** their interaction with different acids (fluorinated alcohols, phenols, NH-acids) was investigated and thermodynamic parameters were determined. The kinetics of amine-boranes dehydrogenation catalyzed by **1** was also studied.

**Acknowledgements:** The work was supported by the Russian Science Foundation (grant № 14-13-00801).

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## Structures and Luminescent Properties of Trinuclear Lanthanide Complexes with Triple-arch-type Ligand

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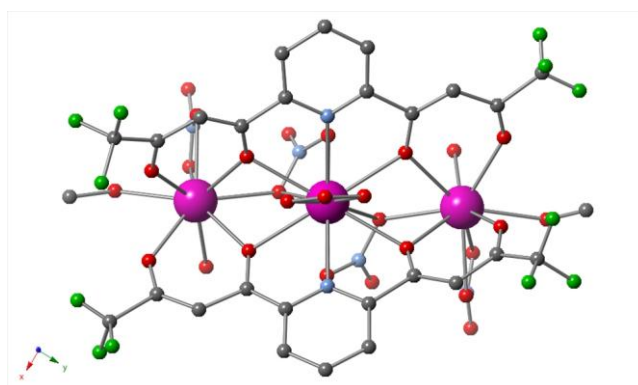
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Multinuclear lanthanide complexes are expected to show unique magnetic and luminescent properties due to 4f electrons and intermetallic interaction. We have reported 3d-4f-3d complexes using a triple-arch type ligand, 2,6-di(acetoacetyl)pyridine ( $H_2Paa$ ) having two terminal  $\beta$ -diketone sites and one central tridentate 2,6-diacetylpyridine site.<sup>1</sup> These results presented one of the rational strategies for constructing oligo- and poly-nuclear metal assembled structures. Here we report tri-nuclear lanthanide complexes using the triple-arch type ligands  $H_2L$  and a fluorinated derivative, 2,6-di(1,1,1-trifluoro acetoacetyl)pyridine ( $H_2L^F$ ) which suppresses vibration of the ligand.

Two Eu(III) complexes,  $Eu_3L$  and  $Eu_3L^F$  were prepared by a one-pot reaction of  $Eu(NO_3)_3 \cdot 6H_2O$  and the ligands. They formed almost same structure with three Eu(III) ions, two ligands, five nitrate anions, and four solvents (Fig. 1), but luminescent quantum yield (QY) of  $Eu_3L^F$  was more than tenfold that of  $Eu_3L$ . QY is responsive to thermal vibration of the ligand. Because the vibration frequency of C-H bond is much higher than that of C-F bond, excitation energy of Eu(III) ion was lost by thermal vibration in  $Eu_3L$ . On the other hand, the deactivation was suppressed in  $Eu_3L^F$  because of the replacement the  $CH_3$  groups to  $CF_3$  ones. Characterization of other  $Ln_3$  analogs is in progress.



**Fig. 1** Crystal structure of  $[Eu_3(L^F)_2(NO_3)_5(H_2O)_2(MeOH)_2]$  ( $Eu_3L^F$ )

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## A new 2-D coordination polymer of Co(II) based on functionalized terpyridine ligand. Synthesis, Structure and Properties

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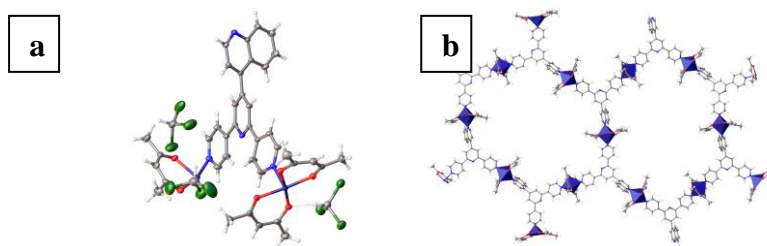
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Investigation of the synthesis and properties of coordination polymers and metal-organic frameworks (MOFs) have attracted intense interest due to their intriguing architectures and potential applications as functional materials, mainly thanks to their useful solid-state properties, such as magnetism, catalysis, molecular sorption, luminescence, etc. The best strategy to build these compounds depends on the selection of metal centers and ligands.<sup>1</sup> The functionalized terpyridine ligands are considered versatile building blocks for the construction of stable coordination compounds with various metal ions, giving rise to 1-, 2- or 3- dimensional structures. Therefore, 4'-(quinolin-4-yl)-4,2':6',4''-terpyridine ligand (**L**) has attracted our interest as a good candidate to synthesize coordination polymers and MOFs.<sup>2</sup>



**Fig.1.** a) Asymmetric unit

b) 2D Structure

We report herein a new coordination polymer,  $\{[C_{78}H_{74}Co_3N_8O_{12}]\cdot 6CHCl_3\}_n$  (**1**). In the solid state, the system exhibits a 2D network of octahedral nodes  $trans\text{-}\{CoN_2(acac)_2\}$ ; the paramagnetic centres are connected by the ligand **L** through the outer two N-donors of terpyridine and the N's of substituent quinoline. (See **Fig. 1.a**) and **b**). Adjacent sheets are associated by various hydrogen bonds:  $CH\cdots O$  and  $CH\cdots N$  and  $\pi\text{-}\pi$  interactions. The synthesis, crystal structure, thermal stability, sorption and magnetic properties of the system will be discussed.

**Acknowledgments:** FONDECYT 1130433; LIA-MIF n°836; CONICYT n°21120148, UNAB DI-773-15/R

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## Indium complexes derived from 2-(aminomethyl)benzimidazolyl amides

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Indium is a toxic metal that interacts easily with molecules containing lone pair electrons. However, indium complexes are useful compounds with industrial and medicinal applications. Thus, indium coordination complexes are used in organic synthesis or the manufacture of semiconductors. Moreover, some of these complexes have anticancer activity. It is known that the utility of indium in medicine depend of the ligand nature. For example, peptides (and their derivatives) could yield kinetic stable coordination complexes with  $\text{In}^{3+}$  and adjust the biological activity of this ion. Thus, the synthesis of new indium complexes with pseudopeptides becomes an important topic.

### Scheme 1

Complexes **6-10** were synthesized by means the coordination of  $\text{InCl}_3$  with amino-amides **1-5** (Scheme 1). NMR and IR studies showed that  $\text{In}^{3+}$  selectively interact with carbonyl and amine groups. Thus, the reaction of  $\text{InCl}_3$  with amino-amides yields *O,N*-chelate complexes. But, in any case benzimidazole groups interact with the metal ion. These results were confirmed by crystallographic studies, and they are interesting because could explain the behavior of indium ions toward some proteins.

Authors thanks SEP-CONACyT for financial support (169010).

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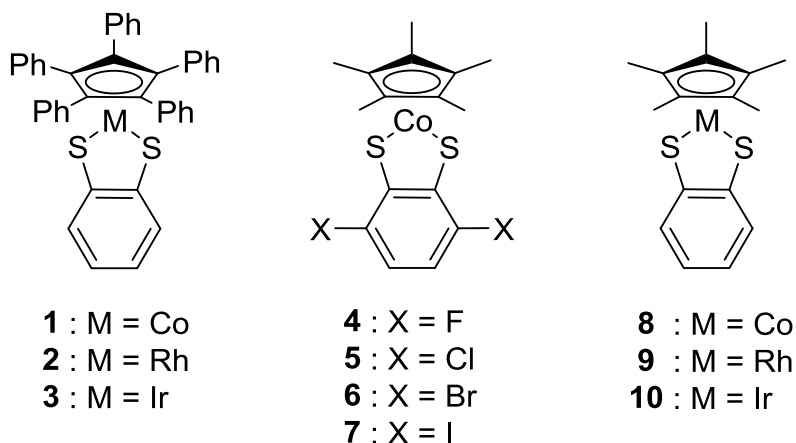
## Electronic state control of nine group metalladithiolene complexes by ligands

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Late transition metal dithiolato complexes have been extensively studied because they show remarkable properties such as reversible redox activity, absorption of visible light, and addition reactions on the metalladithiolene ring. Their unique properties depend on the electron density on metal center. For example, catalytic activity of metalladithiolene complexes change drastically depend on the electronic state on metal which is controlled by the substituent group on ligand.<sup>1</sup> However, it has not been systematically investigated on the effect of electronic state on the metal center by substituents on ligand.

To investigate the effect on metal center by ligand, novel nine group metalladithiolene complexes **1-7** were synthesized. Their properties were compared with **8-10** using cyclic voltammetry and UV-vis spectroscopy. As a result, reduction potentials of **1-7** largely shifted compared to **8-10**. The absorption peak that attributed to LMCT (Ligand to Metal Charge Transfer) of **1-3** showed red-shift compared to **8-10**. In contrast, blue-shift was observed in **4-7**. These results suggested that it is possible the precisely control of electronic state on metal center of dithiolato complexes by substituents on ligand.



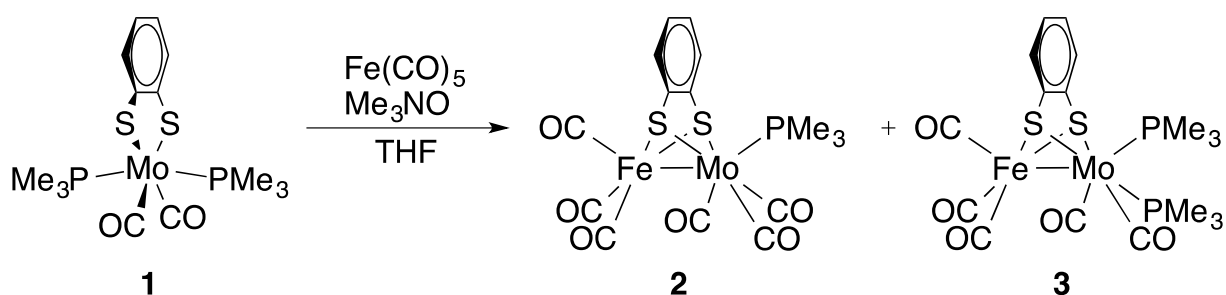
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## Synthesis and properties of Fe-Mo dinuclear dithiolene complexes

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Nitrogen fixation under mild condition is one of the most important goals for chemists. In the natural world, nitrogenase enzymes catalyze the conversion of nitrogen into ammonia. The active site of nitrogenase is known by FeMo-cofactor (FeMoco) that X-ray structural model has been recently reported.<sup>1</sup> FeMoco is a cluster that comprises seven iron ions, one molybdenum ion, and nine sulfides. Although structure of FeMoco is clear, the precise reaction mechanism is still unclear. Synthesis of model complex for FeMoco is one of the methods for understanding of reaction mechanism. In this study, we synthesized dithiolato bridged Fe-Mo dinuclear complexes,  $[\text{FeMo}(\text{S}_2\text{C}_6\text{H}_4)(\text{PMe}_3)(\text{CO})_6]$  (**2**) and  $[\text{FeMo}(\text{S}_2\text{C}_6\text{H}_4)(\text{PMe}_3)_2(\text{CO})_5]$  (**3**), as model complex for a part of FeMoco (Scheme 1). Complexes (**2**) and (**3**) were synthesized by a reaction of molybdenum dithiolene complex (**1**)<sup>2</sup> and  $\text{Fe}(\text{CO})_5$  in the presence of  $\text{Me}_3\text{NO}$  in THF. The combination of  $\text{Fe}(\text{CO})_5$  and  $\text{Me}_3\text{NO}$  is effective in generating a reactive fragment. The molecular structure of (**2**) and (**3**) were successfully determined by single crystal X-ray diffraction analysis. Other chemical and physical properties were also analyzed.



**Scheme 1** Synthesis of Fe-Mo dinuclear dithiolene complexes

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## New alkoxo-bridged Co/Cu, Co/Mn, Co/Ni, Co/Zn heteroclusters. Synthesis, Crystal structures, Magnetic properties.

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The chemistry of homo- and heterometallic clusters is extremely rich. The main interest in such compounds arises from their magnetic properties, some of them acting as Single Molecule Magnets (SMMs) [1-3].

As part of our continuing search for new preparative routes leading to homometallic clusters based on aminoalcohols [4, 5], we have recently turned our attention towards alkoxo-bridged 3d-3d' heterometallic clusters. Three new heptanuclear complexes [Co<sup>III</sup><sub>3</sub>Co<sup>II</sup>Cu<sup>II</sup><sub>3</sub>(dea)<sub>6</sub>(CH<sub>3</sub>COO)<sub>3</sub>](ClO<sub>4</sub>)<sub>0,75</sub>·(CH<sub>3</sub>COO)<sub>1,25</sub> **1**, [Co<sup>III</sup><sub>3</sub>Co<sup>II</sup>Mn<sup>II</sup><sub>2</sub>Mn<sup>III</sup>(dea)<sub>6</sub>(CH<sub>3</sub>COO)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>](ClO<sub>4</sub>)<sub>3</sub> **2**, and [Co<sup>III</sup><sub>4</sub>Co<sup>II</sup>Zn<sup>II</sup><sub>2</sub>(tea)<sub>2</sub>((CH<sub>3</sub>)<sub>3</sub>CCOO)<sub>6</sub>(HO)<sub>2</sub>(CH<sub>3</sub>O)<sub>4</sub>·3H<sub>2</sub>O **3**, with diethanolamine (H<sub>2</sub>dea), triethanolamine (H<sub>3</sub>tea) and carboxylato anions as coligands have been synthesized and characterized. The magnetic properties of these complexes will be discussed. A new topology of Co<sup>III</sup>/Cu<sup>II</sup> ions in a pentanuclear complex, [Co<sup>III</sup><sub>3</sub>Cu<sup>II</sup><sub>2</sub>(Hedtp)<sub>3</sub>(OH)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>·2(ClO<sub>4</sub>)·H<sub>2</sub>O **4** with N,N,N,N-tetrakis(2-hydroxypropyl)ethylenediamine (H<sub>4</sub>edtp) has been observed. Three other complexes, [Co<sup>II</sup><sub>2</sub>Co<sup>III</sup><sub>6</sub>Cu<sup>II</sup><sub>6</sub>(tea)<sub>4</sub>(Htea)<sub>2</sub>(piv)<sub>6</sub>(HO)<sub>6</sub>(H<sub>2</sub>O)<sub>4</sub>·2ClO<sub>4</sub>·8H<sub>2</sub>O **5**, [Co<sup>II</sup><sub>6</sub>Co<sup>III</sup><sub>4</sub>Ni<sup>II</sup><sub>3</sub>(dea)<sub>8</sub>(CH<sub>3</sub>COO)<sub>4</sub>(HO)<sub>8</sub>·2ClO<sub>4</sub>·10H<sub>2</sub>O **6** and, [Co<sup>III</sup><sub>10</sub>Co<sup>II</sup><sub>2</sub>Zn<sup>II</sup><sub>9</sub>(dea)<sub>16</sub>(CH<sub>3</sub>COO)<sub>4</sub>(CO)<sub>3,2</sub>(O)<sub>4</sub>·4(ClO<sub>4</sub>)·3H<sub>2</sub>O **7** will be also presented.

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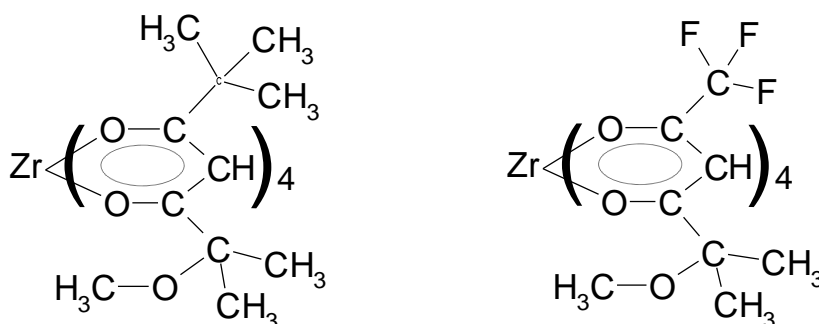
## New Zr(IV) complexes with functionalized $\beta$ -diketonates

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Two new Zr complexes with bulky  $\beta$ -diketonates, containing a donor group in the substituent, have been prepared:  $ZrL_4$  ( $L=C(CH_3)_3COCHCOC(CH_3)_2OCH_3$ ) and  $ZrL'_4$  ( $L'=CF_3COCHCOC(CH_3)_2OCH_3$ ) (Figure 1). The compounds sublime in a vacuum without decomposition. According to TG/DTA, complexes evaporated in a single step with residue <1%. Fluorinated complex is more volatile. The mass spectrum of the compounds obtained is characterized by presence of a molecular ion and the fragmentation under EI proceeds with cleavage of methoxy-group.

Comparison of  $ZrL_4$  with  $Zr(thd)_4$  ( $thd=(C_4H_9COCHCOC_4H_9)$ ) shows that volatility of the new complexes is higher with lower melting point that apparently can be explained by a more loose packing of the molecules in the new compounds.

This work was supported by Russian Foundation for Basic Research, Project No. 15-03-06588a



**Figure 1 Structural formulas of the reported compounds**

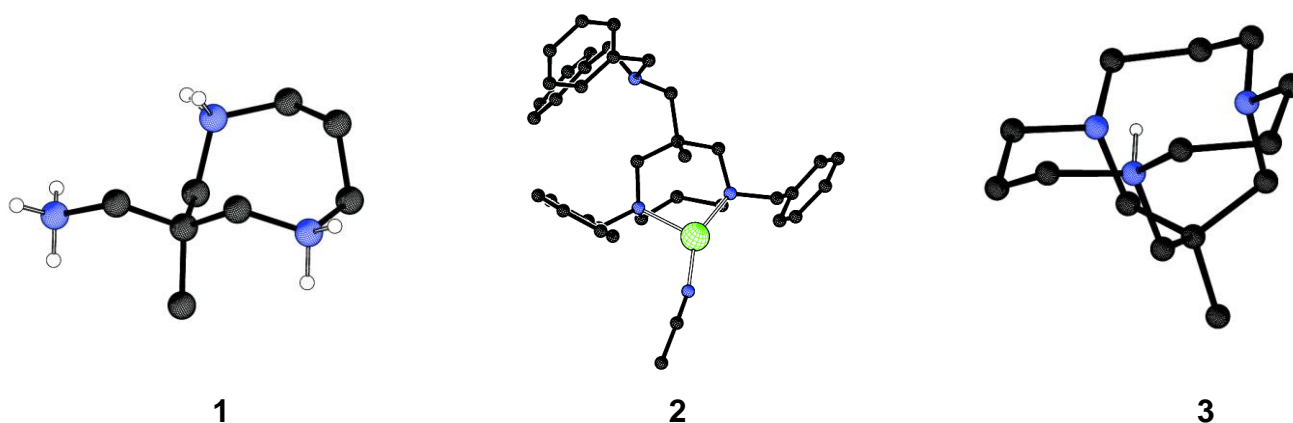
# Design and Synthesis of a Novel Class of Tripodal, Triamine Ligands

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Owing to their high basicity, four coordinate nitrogen donor ligands have been utilised to great success in stabilising the highly oxidising metal-centres of transition metal-oxo complexes.<sup>1</sup> Ligand field theory predicts that lowering the coordination number of the ligand to three will allow for the stabilisation of late transition metal-oxos.<sup>2</sup> Here, we report the synthesis of aminomethylDACO (**1**).<sup>3</sup> Importantly, we have demonstrated that this mesocyclic tripodal, triamine ligand reacts with metals to form 1:1 complexes; overcoming the problems associated with other 3-coordinate ligands. Furthermore, we have shown that **1** is readily functionalised through reaction with alkyl halides. The *tetra*-benzylated analogue of **1** has been synthesised and used in the preparation of the 1:1 Cu(I) complex **2**. Finally, utilising **1**, we have been able to synthesise the sterically encumbered macrocyclic ligand, **3**. We believe that the ligands described will be capable of stabilising metals in high oxidation states.



**Figure 1 – 1)** X-Ray crystal structure of N,N-dimethyl-1-(1,3,5-trimethyl-1,5-diazocan-3-yl)methanamine. **2)** X-ray crystal structure of a Cu(I) complex containing an alkylated derivative of **1**; **3)** X-ray crystal structure of the macrocycle **3**. (Counter ions have been omitted for clarity)

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# Mn-mediated “umpolung” of methylenephosphonium ions aimed at the synthesis of NHC core-based pincer-type ligands

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The modification of the chemical properties of organic molecules upon interaction with transition metals, leading to the stabilization of transient molecules or to the exaltation the intrinsic reactivity of others, constitutes the basis of coordination chemistry. The present work will provide an illustrative example that such a modification may go as far as a formal polarity reversal of polar molecules with practical consequences.

It had indeed been shown that the reactivity of free methylenephosphonium ions is governed by the electrophilicity of the phosphorus atom leading to the corresponding phosphorus ylide upon reaction with nucleophiles.<sup>1</sup> By contrast, we have observed that methylenephosphonium *ligands* in the manganese complexes  $\text{Cp}(\text{CO})_2\text{Mn}(\eta^2\text{-R}_2\text{P}=\text{C}(\text{H})\text{Ph})\text{J}^+$  undergo regioselective addition of nucleophiles *at the carbon center* to produce phosphine complexes,<sup>2</sup> from which the phosphine may be eventually released upon visible light irradiation.<sup>3</sup>

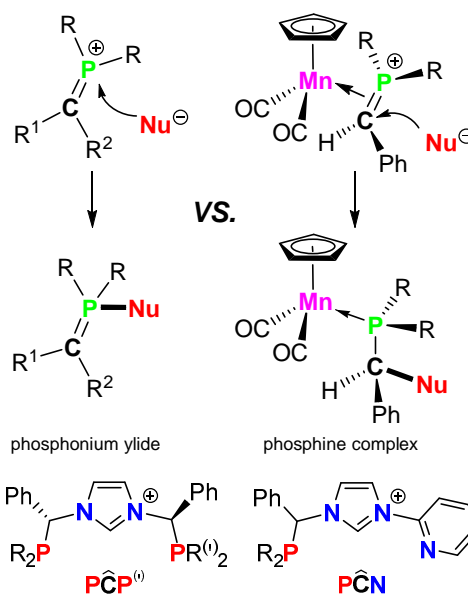
We shall demonstrate that this formal “umpolung” of methylenephosphonium ions could be exploited in the prospect of organic synthesis offering a simple, modular, and efficient route to  $\text{P}\hat{\text{C}}\text{P}^{(i)}$  and  $\text{P}\hat{\text{C}}\text{N}$  NHC core-based pincer-type ligands on a preparative scale. Theoretical studies related to the structure and reactivity of methylenephosphonium manganese complexes as well as the coordination chemistry of the target NHC-core pincer ligands will be also presented.

We thank the MENSUR for a Ph.D. fellowship to JW. DAV thanks the IDEX-UNITI for a starting grant and the French Embassy in Moscow (Program André Mazon) for a travel grant. OAF is grateful to the RSF (grant 14-13-00801) for a financial support of DFT calculations.

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3 D. A. Valyaev, S. Bastin, K. I. Utegenov, N. Lugan, G. Lavigne, N. A. Ustynyuk, *Chem. Eur. J.* **2014**, 20, 2175.



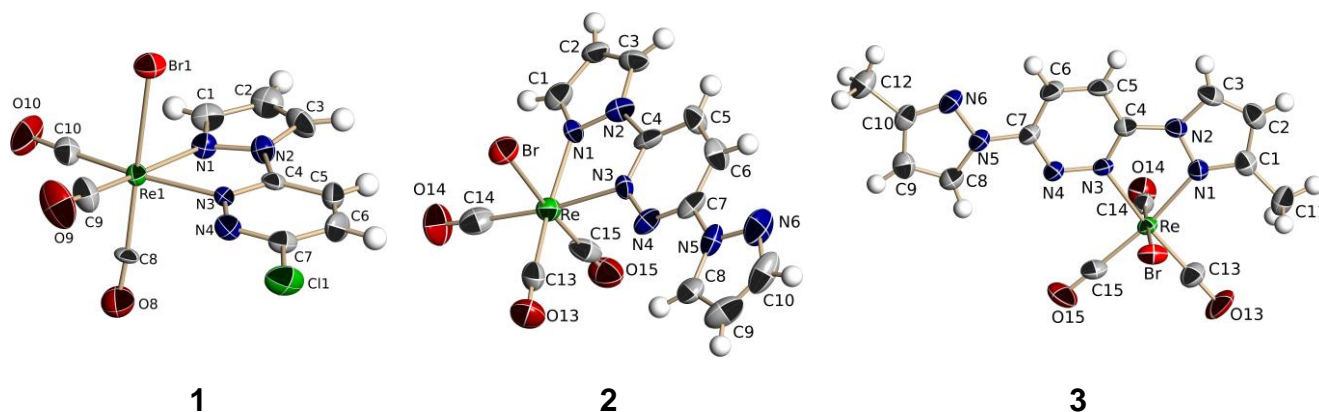
# Substitution effect on the photophysical properties of Re<sup>I</sup> complexes with pyrazolpyridazine derivatives as ligands

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Rhenium(I) tricarbonyl complexes as *fac*-[(N<sup>^</sup>N)Re(CO)<sub>3</sub>X] (N<sup>^</sup>N = diimine and X = halides) have been extensively studied<sup>1</sup> as they may be used as electroluminescent materials in organic light-emitting diodes (OLEDs),<sup>2</sup> solar energy conversion,<sup>3</sup> and/or photocatalytic CO<sub>2</sub> reduction.<sup>3</sup> It has been established that their luminescent properties are directly related with the nature of the diimine ligands. In this work we report the structural, electrochemical and photophysical properties of three mononuclear complexes of Re<sup>I</sup> with pyrazolpyridazine: *fac*-[LRe<sup>I</sup>(CO)<sub>3</sub>Br], where L is 3-chloro,6-N-pyrazolylpyridazine (**1**), 3,6-bis(N-pyrazolyl)pyridazine (**2**), 3,6-bis(N-3-methylpyrazolyl)pyridazine (**3**). These complexes are interesting due to the different N,N'-ligand as well because they offer the possibility to coordinate to a second transition metal center. The absorption and emission properties were evaluated using steady state and time resolved techniques.



**Figure 1.** X-rays determined structure for each complex.

AV is a member of Financiamiento Basal para Centros Científicos y Tecnológicos de Excelencia FB0807.

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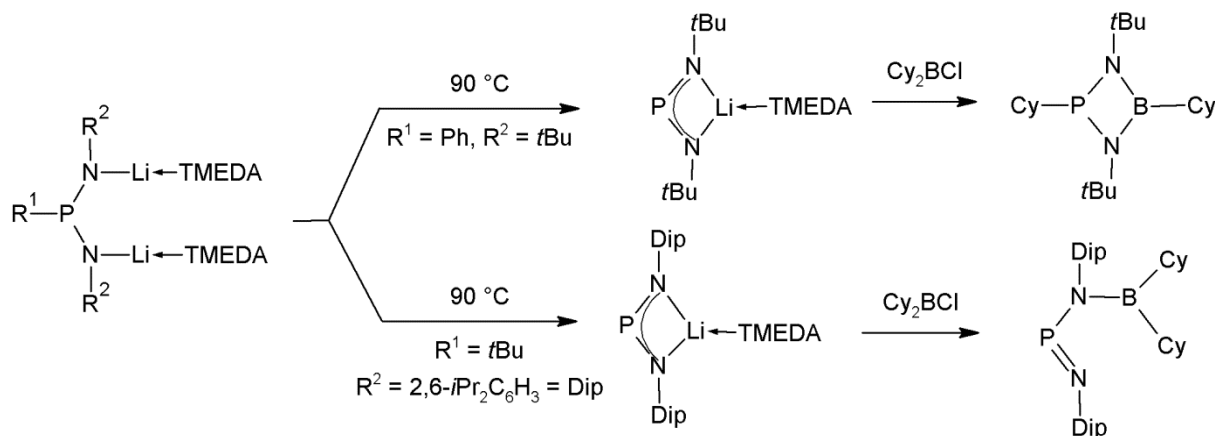
## Different pathways for preparation of diverse compounds bearing amidophosphane ligand

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Boramidates<sup>1</sup> and amidates<sup>2</sup> were used as suitable ligands for both transition and main group metals. Analogical compounds, bis(amido)phosphanes, were also proven to be useful ligands in organometallic and coordination chemistry<sup>3</sup>, but their chemistry was studied in significantly lower extent. Bis(amido)phosphanes may have a wide range of bonding properties, since they can act as both monoanionic and dianionic<sup>4</sup> ligands, where the ligand is bonded by either covalent or coordination bond to the central atom. Novel lithium and potassium complexes were prepared using various methodologies. Further reactivity of these compounds was studied as well.



**Figure 1.** Thermal decompositions of bis(organoamido)phosphanes and subsequent reactions of their products.

### References

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# Preparation of the stibinidenes and bismuthinidenes and their use as ligands for TM

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Our group has recently succeeded in the synthesis and structural characterization of the first monomeric organoantimony(I) and organobismuth(I) compounds stabilized by coordination of the *N,C,N*-pincer type of ligand.<sup>1</sup> The present work includes a comparison of the reduction of organoantimony(III) and organobismuth(III) compounds. The reduction of the *N,C,N*-chelated bismuth(III) chlorides  $[C_6H_3-2,6-(CH=NR)_2]BiCl_2$  (where R = *t*-Bu, 2',6'-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub> and 4'-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>) gave monomeric *N,C,N*-chelated bismuthinidenes<sup>2</sup>. In contrast, the structure of the compounds resulting from the reduction of the *N,C,N*-chelated antimony(III) chlorides depends on the reducing reagent and the nature of stabilizing ligand (Figure 1). Thanks to these findings, we were able to obtain new monomeric stibinidenes and bismuthinidenes, which contain two electron lone pairs available for TM coordination (Figure 1). In this contribution, the reactivity of monovalent stibinidenes and bismuthinidenes with selected TM complexes will be presented.

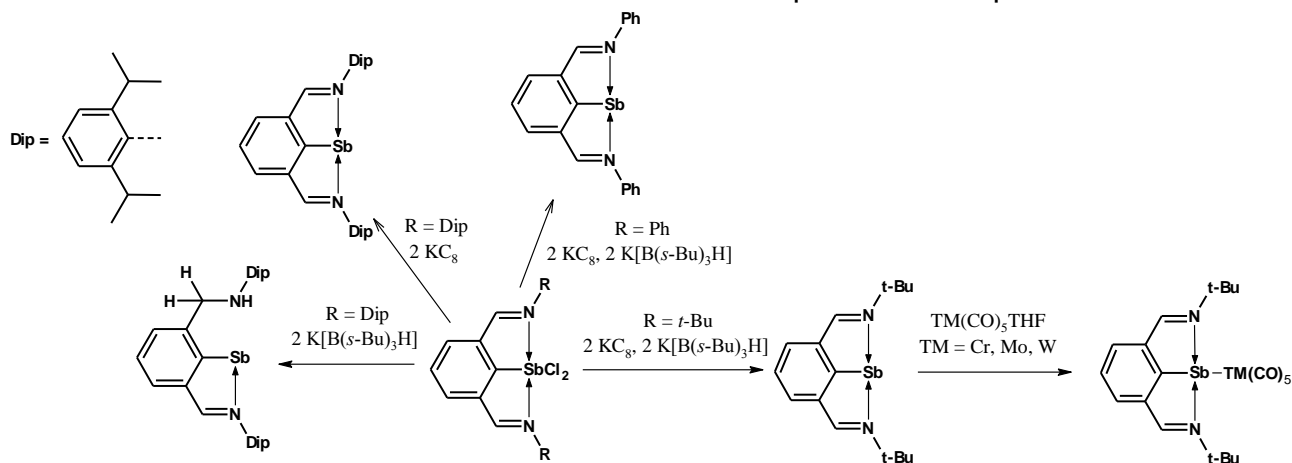


Figure 1

## References

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**Acknowledgements:** The authors thank the Grant agency of Czech Republic project no. P207/15-06609S.

## Synthesis of Heterometallic Complexes of Rhenium (I) and Oxorhenium (V) Based On A Click-To-Chelate Approach

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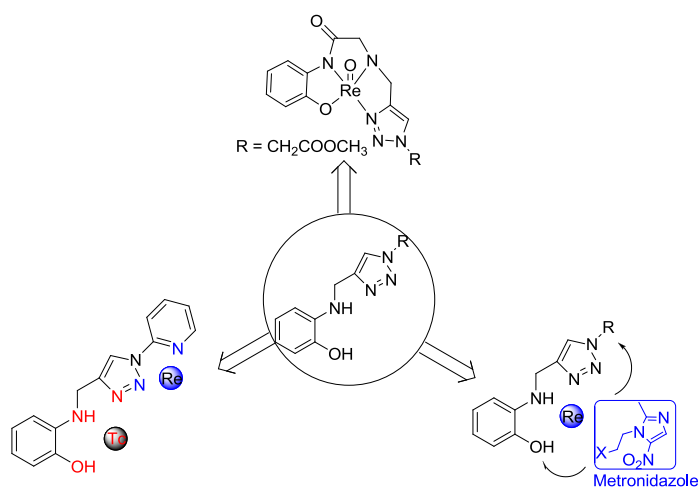
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Bifunctional Chelating Agents (BCAs), are widely used for the preparation of luminescent sensors, MRI contrast agents and target-specific radiopharmaceuticals. To prepare BCAs, Cu-catalyzed azide–alkyne cycloaddition (so-called CuAAC) becomes one of the most efficient ways due to its mild, fast and efficient reaction, requiring neither protecting groups nor fastidious purification steps and lead exclusively to one isomer (1,4-disubstituted triazolyl ring) which has shown to be extraordinarily good chelators for Tc and Re cores in order to develop nuclear imaging or therapeutic purposes, respectively.<sup>[1]</sup>

Recently, we reported the synthesis of an original tridentate N<sub>2</sub>O BCA, *via* a click chemistry approach and first *in vivo* evaluation of the corresponding technetium-99m complex exhibited promising properties (rapid clearance, no long-term retention in healthy organs...), making this compound a promising <sup>99m</sup>Tc chelating system.<sup>[2]</sup>

In this communication, a general synthetic approach for a novel range of semi-rigid bifunctional chelating agents (BCAs) including an aromatic ring and a triazolyl moiety in the chelating unit, for [Re(CO)<sub>3</sub>]<sup>+</sup> and [ReO]<sup>3+</sup> cores was investigated. In addition, some chelators containing metronidazole (Mtz) can be potential <sup>99m</sup>Tc-radiopharmaceuticals for imaging hypoxia.



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# Luminescent pH Sensor Based on Europium(III) Complex in Aqueous Solution

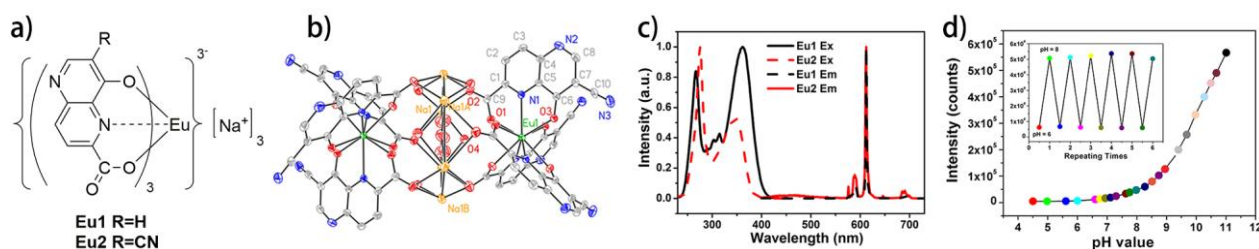
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The luminescent sensor has received much attention due to high sensitivity, miniaturized probe size, and a wide variety of material choices. Among them, lanthanide complexes exhibit some special photophysical properties including large Stokes shift for easy separation of excitation and emission light, long luminescence lifetime and characteristic narrow emission band to distinguish from shorter-lived background present in most biological systems, which make them attractive as sensor.<sup>1,2</sup>

We here report two novel water-soluble, highly efficient luminescent europium (Eu(III)) complexes, **Eu1** and **Eu2** (shown in Figure a), with pH sensing character. The composition and structure of Eu(III) complexes have been studied by fluorescence titration experiments along with the single crystal analysis for **Eu2** (Figure b). Both complexes show strong Eu(III) ion emission in aqueous solution (Figure c) with best photoluminescence quantum yield of 30 and 15% for **Eu1** and **Eu2** respectively and they exhibit good pH sensing property. Especially, **Eu1** shows 100 times increase of emission intensity from pH 4 to pH 11 (Figure d). The significant enhancement of Eu(III) emission with increasing pH is possibly due to the suppression of N-H quenching of ligand and absorption reinforcement. The results demonstrate that these novel Eu(III) complexes can be as stable and highly sensitive pH probes and have potential application in intracellular pH sensing area.



**Figure 1.** (a) Chemical formula of Eu(III) complexes and (b) ORTEP diagrams of **Eu2**. (c) Excitation and emission spectra of Eu(III) complexes in aqueous solution. (d) Emission intensity of **Eu1** at 615 nm as a function of pH. The inset shows reversible luminescence intensity change between pH 6 and pH 8.

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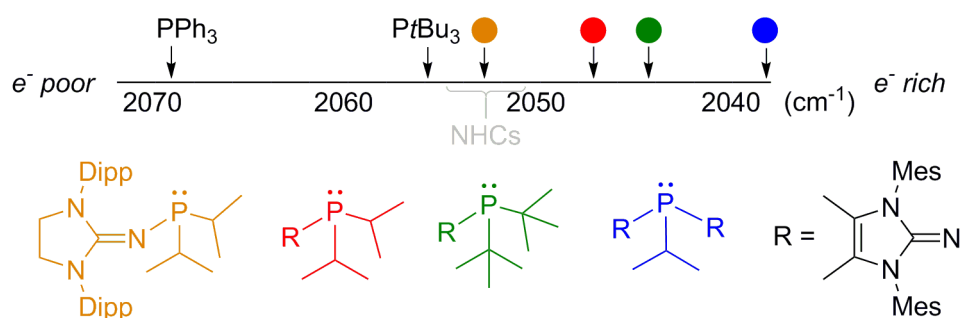
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## Sterically demanding imidazolin-2-ylidenaminophosphines

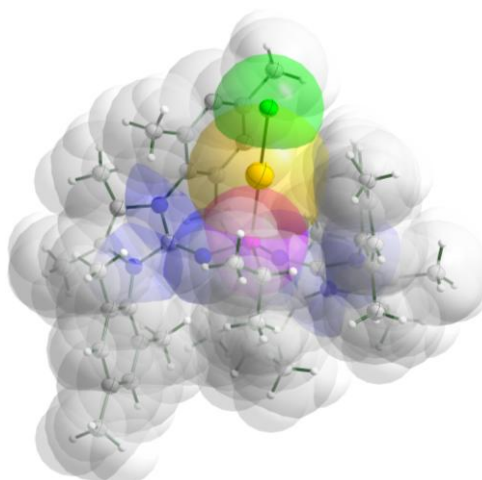
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Phosphines are important ancillary ligands with broad application in transition metal catalysis due to their variable donor strength and steric demand. We recently developed a new class of strong electron-donating ancillary ligands, namely imidazolin-2-ylidenaminophosphines (IAPs). These IAPs show donor abilities higher than alkylphosphines and N-heterocyclic carbenes (NHCs).<sup>1</sup> The steric demand can be efficiently increased by using diisopropylphenyl (Dipp) and 2,4,6-trimethylphenyl (Mes) substituents at the imidazolium backbone (Figure 2). Several sterically demanding IAPs have been synthesized (Figure 1) and coordinated to gold(I) atoms. These complexes are interesting precursors for catalysts in hydroamination reactions.



**Figure 1** Tolman electronic parameter of  $\text{PPh}_3$ ,  $\text{PtBu}_3$  and IAPs.



**Figure 2** Molecular structure of  $[\text{AuCl}(\text{PR}_2i\text{Pr})]$  that contains a very bulky phosphine ligand which resembles the steric demand of Buckwald-type phosphines.

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## Coordination Compounds of Acesulfame/Nicotinamide Complexes with Co(II), Cu(II), Zn(II) and Mn(II) Cations

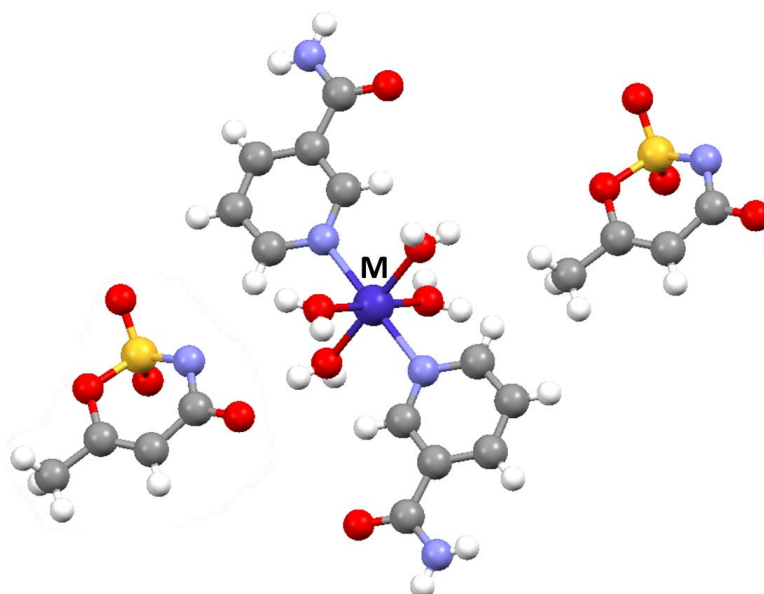
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The mixed ligand complexes of Co<sup>II</sup>, Cu<sup>II</sup>, Zn<sup>II</sup> and Mn<sup>II</sup> metal cations with acesulfame/nicotinamide were synthesized and characterized by FT-IR, TG/DrTG-DTA, UV-Vis spectroscopy, elemental analysis and single crystal XRD methods. The complexes were synthesized with high purity. The results of the elemental analysis indicated that the structure of complexes contain two molecules nicotinamide and four molecules coordinated aqua ligand in coordination sphere. The two moles of acesulfame mono-anion are established in outside of the coordination sphere as counter ion fo metal cation. The acesulfame ions connect to fragment of the unit cell with hydrogen bonds as a bridge. According to thermal investigation, aqua ligands firstly remove from the structures. The coordination geometry of the metal cations are distorted octahedral. The molecular structure of the complexes are shown in Figure 1.



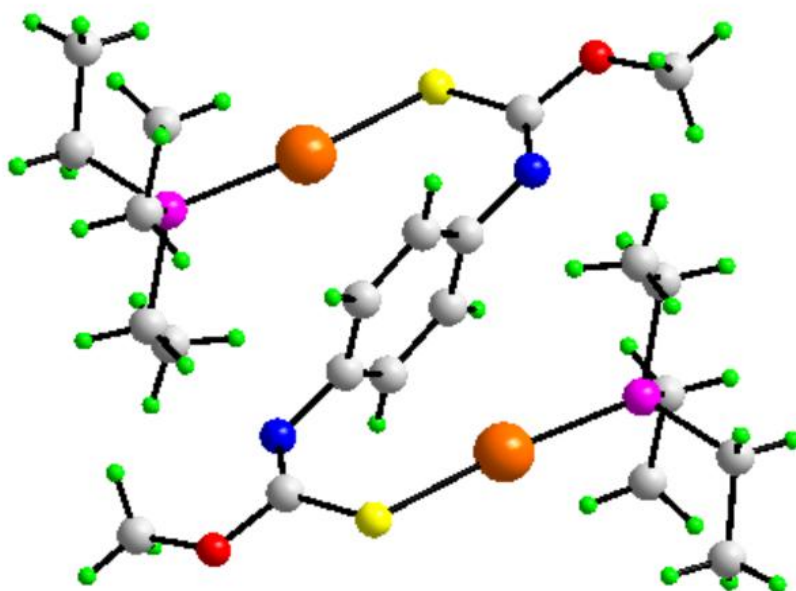
**Figure 1.** The molecular structure of the metal complexes.

## Binuclear Phosphanegold(I) Thiocarbamates: The importance of Au... $\pi$ (aryl) interactions and their anti-microbial activity

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A series of three binuclear phosphanegold(I) complexes of a bipodal thiocarbamate dianion,  $(R_3PAu)_2L$ , R = Et (**1**), Ph (**2**) and Cy (**3**), where  $LH_2$  is  $\{1,4-[MeOC(=S)N(H)]_2C_6H_4\}$  were prepared. Each of the complexes features a linear gold atom geometry defined by the phosphane-P and thiolate-S atoms, with the gold atoms oriented toward the central ring to form intramolecular Au... $\pi$ (aryl) interactions. This phenomenon has been evaluated by a computational study for **1** which revealed that the geometry optimised species with two Au... $\pi$ (aryl) interactions is more stable by at least 12 kcal mol<sup>-1</sup> compared to conformations having one or more Au...O interactions. Complexes **1–3** were further investigated for their inhibitory effect against a panel of Gram-positive and Gram-negative bacteria using the disk diffusion, minimum inhibitory concentration (MIC) and minimum bactericidal concentration (MBC) methods. The disk diffusion results demonstrated that **1** exhibited a broad spectrum of anti-bacterial activity but the anti-bacterial activity of **2** and **3** was only limited to Gram-positive bacteria.

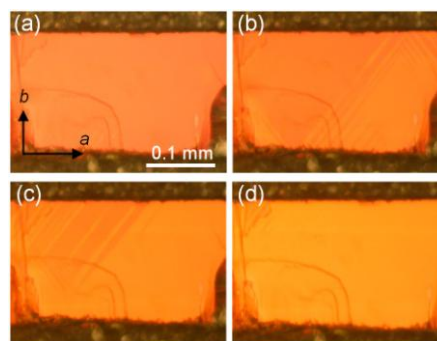


**Figure 1** Perspective view of molecule of complex  $(Et_3PAu)_2\{1,4-[SC(OMe)=N]_2C_6H_4\}$ .

## Optically Visible Phase Separation between Mott-Hubbard and Charge-Density-Wave Domains in a Pd-Br Chain Complex

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Charge bistability in solid-state complexes is a key property for functional materials. There has been great effort to switch physical properties via charge transfer phase transitions (CTPT), by using optical, thermal, and electrical stimuli. However, there are still many challenges in designing materials which undergo phase-transition phenomena by controlling molecular charge bistability. Quasi-one-dimensional halogen-bridged metal complexes are good motif for the switching because they potentially have charge bistability, which is between averaged valence Mott-Hubbard (MH) state and mixed valence charge-density-wave (CDW) state. Ni complexes show  $\text{Ni}^{3+}\text{-Ni}^{3+}$  MH state, whereas Pd and Pt complexes are in  $\text{M}^{2+}\text{-M}^{4+}$  CDW state. Although, more than 300 compounds have been so far reported, all Ni compounds are in the MH ground state, and all Pd and Pt compounds are in the CDW ground state, except for a Pd complex which stabilized by “chemical pressure” between alkyl chains introduced as counterions<sup>1</sup>. In this work, we have firstly realized the MH state in Pd complex (**1**) without the alkyl chain with a phase transition between CDW and MH states, and we successfully visualized the local electronic state of the both state by temperature dependent scanning tunneling microscopy (STM) measurement. To the best of our knowledge, this is the first example to visualize a change of the local electronic state accompanied by CTPT using STM. We also observed phase separation with a stripe pattern over a wide temperature range, which can be clearly observed using optical microscope (Figure 1). This is very interesting phenomenon from the viewpoint of cooperation and competition between two phases.



**Figure 1** Optical images of **1** at (a) 130 K, (b) 120 K, (c) 100 K and (d) 50 K.

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# Molecular Arrangements and Emission Color Controlled by the Chirality in Dinuclear Pt(II) Complexes with Tartrate

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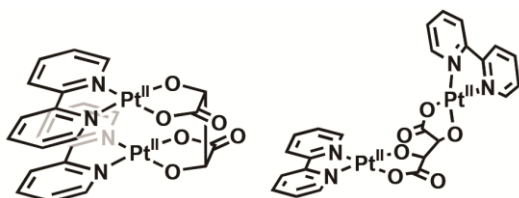
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Dinuclear Pt(II) complexes with aromatic-type chelates and bridging ligand(s) exhibited unique phosphorescence due to the intramolecular interactions in solution, and different emission was seen in the solid state, for which the intermolecular interactions are responsible.<sup>1</sup> We intended to introduce the chirality in the bridging ligand to control the molecular arrangements causing the change in the emission color, and to disclose the interactions affecting on the luminescence in the solid state.

We have prepared new dinuclear Pt(II) complexes  $[\{Pt^{II}(R_2bpy)\}_2(\mu\text{-}x\text{-tart})]$  ( $\text{tart}^{4-}$ : tartrate;  $R_2bpy$ : bipyridine derivatives; **1**:  $R = H$ ; **2**:  $R = Me$ ; **a**:  $x = L$ ; **b**:  $x = DL$ ; **c**:  $x = meso$ ). Molecular structures of **1a-b** showed clamshell-like form through intramolecular Pt–Pt and/or  $\pi$ – $\pi$  interactions, while **1c** exhibited twisted structure without those interactions (Figure 1). In crystals, **1a** stacked through both intermolecular Pt–Pt and  $\pi$ – $\pi$  interactions, **1b** stacked through only intermolecular  $\pi$ – $\pi$  interaction, and **1c** constructed dimer structure with adjacent one through both interactions. The structural differences were induced by the chirality of tartrate. These crystals showed diverse emission colors depending on intra- and inter-molecular interactions (Table 1).

The molecular and crystal structures are controlled by the chirality in the bridging ligand, and the intra- and inter-molecular stacking cause significantly different emission colors. Now, we attempt to reveal the effect of R on their structures and luminescence.



**Figure 1** Clamshell-like form of **1a-b** (left) and twisted structure of **1c** (right).

	<b>1a</b>	<b>1b</b>	<b>1c</b>
Pt–Pt (Intra-) (Å)	av. 3.45	3.54	-
Pt–Pt (Inter-) (Å)	av. 3.36	-	3.34
Luminescence (nm)	647	569	621

**Table 1** Intra- and inter-molecular Pt–Pt distance (Å) and luminescence ( $\lambda$  / nm) of **1a-c** in the solid state at r.t.

<sup>1</sup> B.C. Tzeng, *Cryst. Growth Des.*, **2009**, 9, 5356; M. Kato, *Bull. Chem. Soc. Jpn.*, **2007**, 80, 287.

## Hybrid phosphinoferrocene ligands with a methylene spacer

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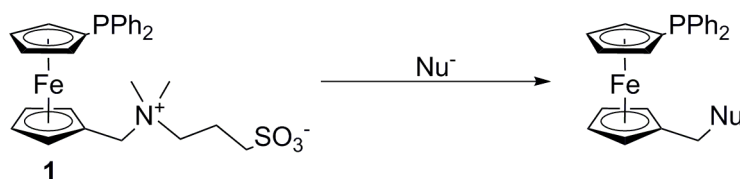
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Considerable attention has been invested into the development of novel catalytic systems that could be used for catalytic processes conducted in aqueous reaction media. The reasons for increased use of water as a solvent are plentiful,<sup>1</sup> environmental, economic and technological aspects being mentioned most often. Hybrid<sup>2</sup> bifunctional ferrocene phosphines<sup>3</sup> can become constituents of such systems if modified with a polar secondary donor group that renders the ligand and its complexes water-soluble.

Ferrocene core is often employed in ligand design due to its conformational variability which can broaden the range of accessible coordination modes. We have attempted to build upon this approach and decided to increase the ligand flexibility even further by inclusion of an additional, conformationally flexible methylene spacer. To this end, a route toward methylene-spaced phosphinoferrocene donors bearing various secondary donor groups has been developed based on nucleophilic substitution reactions on compound **1** (Figure 1).<sup>4</sup> Depending on the nucleophile, this reaction gives rise to new hybrid phosphinoferrocene donors that will be reported in this contribution along with the results of coordination studies with these compounds.

**Figure 1**



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3 P. Štěpnička in *Ferrocenes: Ligands, Materials and Biomolecules*, ed. P. Štěpnička, WILEY, Chichester, 2008, chapter 5, 177.

4 M. Zábranský, I. Císařová, P. Štěpnička, *Dalton Trans.*, **2015**, 44, 14494.

# Proton Responsive Pyridone-Containing *N,N,N*-Palladium(II) Pincer Complexes

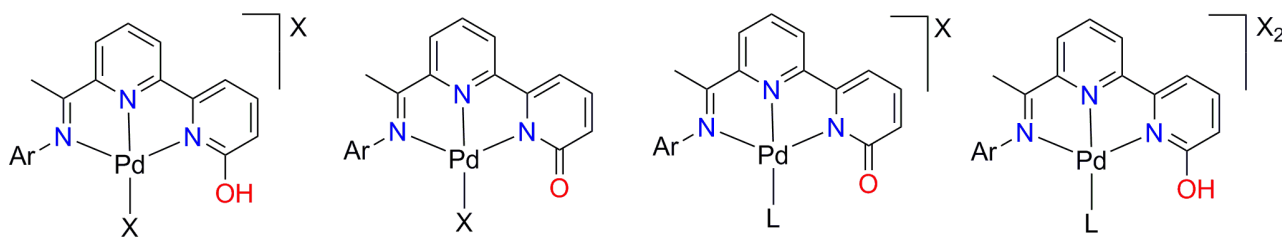
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Platinum group-containing complexes bearing hydroxy-substituted pyridine ligands (or as the pyridone tautomer) have been the subject of some interest in recent years due, in part, to the intriguing properties of the pendant hydroxyl group and the active role the functionality may play in a catalytic process.<sup>1,2</sup> For example, iridium complexes containing such functionalised ligands have shown great potential in the oxidation of alcohols to ketones and aldehydes; a fundamental organic transformation of considerable industrial importance.<sup>3</sup>

Elsewhere, *N,N*-pyridylimine ligands appended with suitable functionality are currently being investigated in a wide range of homogeneous catalytic applications including processes involving C-H bond activation.<sup>4</sup> The capacity to modify the *N*-aryl group of the imino unit makes these ligands particularly attractive as the electronic and steric properties can be systematically varied as can the solubility properties of the resultant complexes.

Herein, we report the synthesis of a range of novel *N,N,N*-Pd(II) pincer complexes incorporating pyridylimines appended with an active pyridone unit. Their interconversions between protonated (*pyridinol*) and deprotonated (*pyridonate*) forms on the palladium centre are systematically probed.



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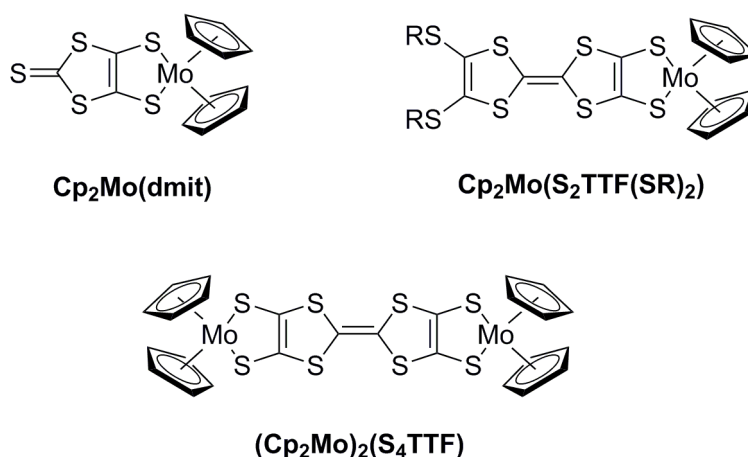
## Bis(cyclopentadienyl)molybdenum dithiolene tetrathiafulvalene complexes : interplay between electrophores

N. Bellec,\* A. Vacher, F. Barrière, Z. Xu, T. Roisnel, D. Lorcy

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Tetrathiafulvalenes (TTF) and bis(cyclopentadienyl) molybdenum dithiolene complexes,  $\text{Cp}_2\text{Mo}(\text{dithiolene})$  complexes, are known separately to act as good electron donor molecules. For an investigation of the interaction between both electrophores, two types of complexes were synthesized and characterized. The first type has one  $\text{Cp}_2\text{Mo}$  fragment coordinated to one TTF dithiolate ligand, and the second type has one TTF bis(dithiolate) bridging two  $\text{Cp}_2\text{Mo}$  fragments. Comparisons of the electrochemical properties of these complexes with those of models of each separate electrophore provide evidence for their mutual influence. All of these complexes act as very good electron donors with a first oxidation potential 430 mV lower than the tetrakis(methylthio)TTF. DFT calculations suggest that the HOMO of the neutral complex and the SOMO of the cation are delocalized across the whole TTF dithiolate ligand. The X-ray crystal structure analyses of the neutral and the mono-oxidized  $\text{Cp}_2\text{Mo}(\text{dithiolene})(\text{bismethylthio})\text{TTF}$  complexes are consistent with the delocalized assignment of the highest occupied frontier molecular orbitals. UV-vis-NIR spectroelectrochemical investigations confirm this electronic delocalization within the TTF dithiolate ligand.



1 N. Bellec, A. Vacher, F. Barrière, Z. Xu, T. Roisnel, D. Lorcy, *Inorg. Chem.*, **2015**, *54*, 5013.



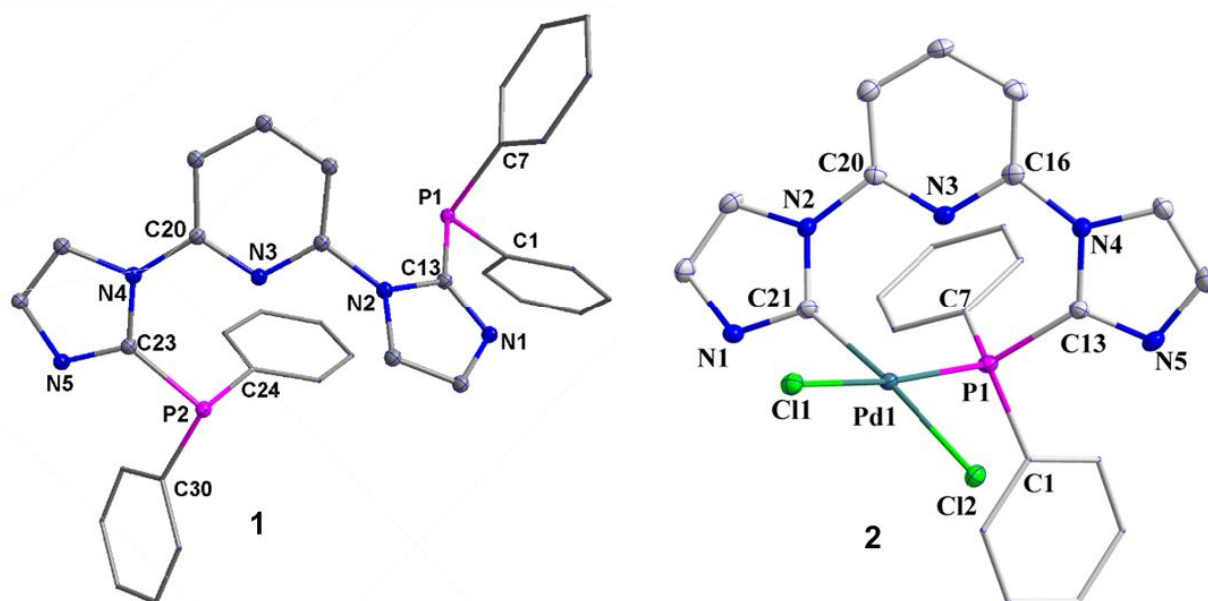
## Imidazole-based Bisphosphine: Synthesis, Structure and Coordination Chemistry

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The bisphosphine [2,6-(PPh<sub>2</sub>-C<sub>3</sub>H<sub>2</sub>N<sub>2</sub>)<sub>2</sub>C<sub>5</sub>H<sub>3</sub>N] (**1**) was synthesized by the treatment of 1,3-bis(imidazol-N-yl)pyridine with <sup>n</sup>BuLi followed by the addition of chlorodiphenylphosphine.<sup>1</sup> The reaction of **1** with one equivalent of silver perchlorate followed by the addition of [Pd(cod)Cl<sub>2</sub>] afforded 9-membered neutral palladacycle (**2**), with the cleavage of a C-P bond.<sup>2,3</sup> The structures of **1** and **2** have been confirmed by single crystal X-ray diffraction studies. Detailed coordination chemistry of this ligand will be presented.



**Figure** X-ray structures of **1** and its palladium complex **2**.

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- (2) Y. Canac, N. Debono, C. Lepetit, C. Duhayon, R. Chauvin, *Inorg. Chem.*, **2011**, 50, 10810.
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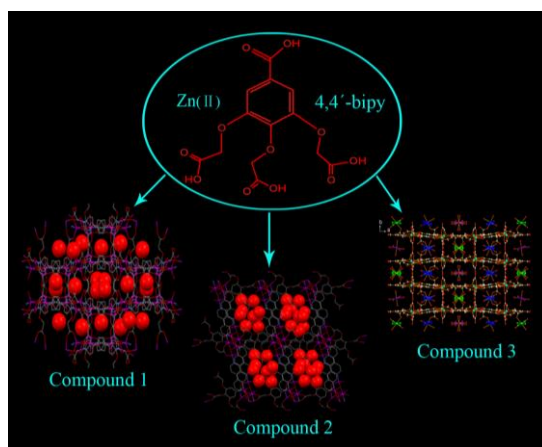
## Three Microporous Zn Coordination Polymers Constructed by 3,4,5-Tris(carboxymethoxy)benzoic Acid and 4,4'-bipyridine: Structures, Topologies, and Luminescence

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Recently, much attention has been paid to the design and synthesis of novel MOFs due to their intriguing topologies and potential properties in separation, ion exchange, sensors, gas storage and fluorescence.<sup>1,2</sup> Three new microporous Zn MOFs,  $[\text{Zn}_3(\text{OH})_2(\text{TCBA})(4,4'\text{-bpy})]\cdot 5.5\text{H}_2\text{O}$  (1),  $[\text{Zn}_3(\text{OH})_2(\text{TCBA})(4,4'\text{-bpy})1.5]\cdot 5\text{H}_2\text{O}$  (2), and  $[\text{Zn}_4(\text{TCBA})_2(4,4'\text{-bpy})_2(\text{H}_2\text{O})_8]\cdot 11\text{H}_2\text{O}$  (3) ( $\text{H}_4\text{TCBA}$  = 3,4,5-tris(carboxymethoxy)benzoic acid, 4,4'-bpy = 4,4'-bipyridine), have been hydrothermal synthesized and structurally characterized. 1 presents an uncommon 2-nodal (4,10)-connected network with  $\{3\cdot 4^5\}_2\{3^4\cdot 4^{12}\cdot 5^{10}\cdot 6^{14}\cdot 7^3\cdot 8^2\}$  topology; 2 can be described as a 2-nodal (3,8)-connected tfz-d net with symbol of  $\{4^3\}_2\{4^6\cdot 6^{18}\cdot 8^4\}$ , both networks construct from hexameric  $[\text{Zn}_6(\mu_3\text{-OH})_4]^{8+}$  clusters. While 3 shows an interesting 4-nodal (3,3,3,4)-connected network with  $\{8\cdot 10\cdot 12\}_2\{8\cdot 10^2\}_2\{8^4\cdot 10\cdot 12\}$  topology. Complexes 1-3 all own 3-D frameworks with 1-D channel, and in 1-3 lattice and/or coordinated water molecules occupy the channels, especially in 3 Zn-bipy chains reside the channels. Furthermore, the thermal stabilities and photophysical properties of complexes 1-3 were also investigated.



**Figure 1** Three microporous Zn coordination polymers based on 3,4,5-Tris(carboxymethoxy)benzoic Acid and 4,4'-bipyridine

1. Gao-Shan Yang, Chong-Bo Liu, Hui-Liang Wen, Sheng-Shui Tan and Z. John Zhang, *CrystEngComm*, 17, 2015, 1518.
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## Orthometalations in platinum(II) complexes with tertiary phosphine ligands – a mechanistic study

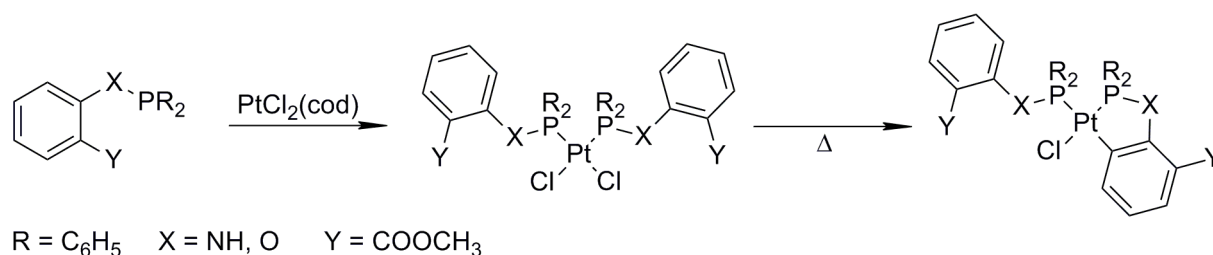
Zdeněk Štěpánek <sup>a,\*</sup>, Martin Sojka <sup>a,b</sup>, Jaromír Toušek <sup>b</sup>, Marek Nečas <sup>a,b</sup>

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Intramolecular activation reactions of C-H bonds in transition metal complexes are frequently studied since resulting orthometalated products are tested and applied in variable areas of research.<sup>[1,2]</sup> We recently performed C-H thermal activation reactions in Pt(II) complexes with several phosphinoamine ligands to evaluate the importance of ligand substitution on the structure and properties of the orthometalated complexes. Unexpectedly, the presence and positioning (*ortho* and *para*) of the substituents was found to be crucial for a successful orthometalation. We have therefore prepared a series of organophosphorus ligands and synthesized their *cis*-Pt(II) complexes from PtCl<sub>2</sub>(cod). By means of <sup>31</sup>P NMR spectroscopy we investigated their propensity for orthometalation via thermal C-H bond activation on aromatic moieties as well as possible isomerization of *cis* complexes into *trans* isomers. We support our experimental findings by single crystal X-ray diffraction and quantum-mechanical calculations.

**Figure 1** Synthetic route to orthometalated Pt(II) complexes



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# Fluorescence and Ferroelectric Properties of Pyrene Derivative bearing Alkylamide Group

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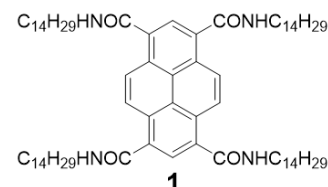
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<sup>b</sup> Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku Univ.

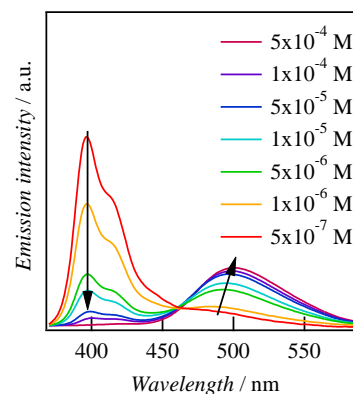
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Alkylamide-substituted benzene derivatives showed hydrogen-bonding molecular assembly, ferroelectricity and liquid and crystalline (LC) phase.<sup>1</sup> On the other hand, LC phase of pyrene derivatives bearing long alkylester chains have been reported.<sup>2</sup> Herein, we successfully obtained a novel pyrene derivative (**1**), which showed novel molecular assemblies, LC properties, dielectric responses, carrier transport properties, and optical properties.<sup>3</sup>

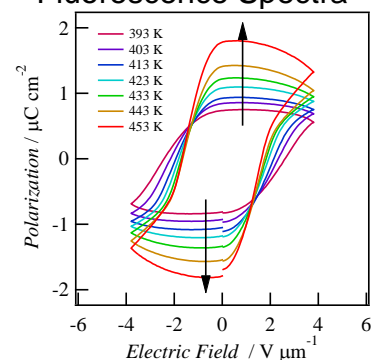


Concentration-dependent fluorescence spectra in the chloroform showed the molecular aggregation properties of **1**. The monomer emission with a maximum emission wavelength of ~400 nm was observed at dilute solution. Increasing in the concentration suppressed the fluorescence intensity around 400 nm and appeared a new emission band around ~500 nm at the concentration over  $5 \times 10^{-6}$  M. The latter band was assigned to the excimer emission. Since the excimer band of pyrene was observed at the concentration over  $5 \times 10^{-3}$  M, high molecular aggregation ability of **1** was confirmed through the  $\pi$ -stacking and hydrogen-bonding interactions. Molecule **1** also showed the hexagonal columnar LC phase, where the  $\pi$ -stacking and intermolecular hydrogen-bonding interaction played an important role to form LC phase. The polarization - electric field ( $P$ - $E$ ) hysteresis curve of **1** was measured for the LC cell at 393 K ( $f = 0.5$  Hz,  $E_{max} = 3.8$  V/ $\mu$ m), resulting in the ferroelectric behavior with coercive electric field of 2.6 V/ $\mu$ m and remnant polarization of 0.75  $\mu$ C/cm<sup>2</sup>. These dielectric switching phenomena were also associated with the dipole inversion of hydrogen-bonding chains along the column.



**Figure 1**

Fluorescence Spectra



**Figure 2**

$P$ - $E$  hysteresis

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3 H. Anetai, T. Akutagawa *et. al*, *J. Phys. Chem. Lett.* **2015**, *6*, 1813.

## Selective Methane and Ethane Storage in the Porous Magnesium Borohydride Framework

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Borohydride-based materials have recently received much attention owing to their high gravimetric hydrogen content and straightforward synthesis through both mechanochemical and solution-based methods. Magnesium borohydride,  $\text{Mg}(\text{BH}_4)_2$ , is one of the most promising materials for hydrogen-storage applications, as it has a relatively low decomposition temperature, reversible hydrogen desorption and high gravimetric hydrogen content of 14.9 wt %  $\text{H}_2$ . Among all the four existed polymorphs of  $\text{Mg}(\text{BH}_4)_2$ , the porous  $\gamma\text{-Mg}(\text{BH}_4)_2$  polymorph, the first porous hydride ever obtained, seems to be the most intriguing since it has about 33% of empty space in a form of small pores available to guest molecules, such as  $\text{H}_2$ ,  $\text{N}_2$  or  $\text{CH}_2\text{Cl}_2$  [1]. It is expected that the hydridic nature of the borohydride ligands, exposed by  $\text{H}^{\delta-}$  into the pores, gives rise to specific host-guest interactions and thus to a selectivity of absorption.

Herein we report absorption properties of  $\gamma\text{-Mg}(\text{BH}_4)_2$  towards a series of hydrocarbons. *In situ* X-ray diffraction data showed that methane and ethane are exclusively absorbed into pores, while propane and butane are too large to enter. Variable temperature diffraction under different gas pressures allowed us not only to localize the guests, but also for the first time to extract the isosteric heats of absorption directly from the diffraction data. Moreover, neutron powder diffraction was performed on doubly isotopically substituted  $\gamma\text{-Mg}({}^{11}\text{BD}_4)_2$ , loaded with  $\text{CD}_4$  and  $\text{C}_2\text{H}_6$ . This allowed accurate localization of the guest molecules and to determine the nature and the role of the host-guest interactions.

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## Luminescent Lanthanide-based Single-Molecule Magnets: from dimers to 3D-networks and ordered magnetic films

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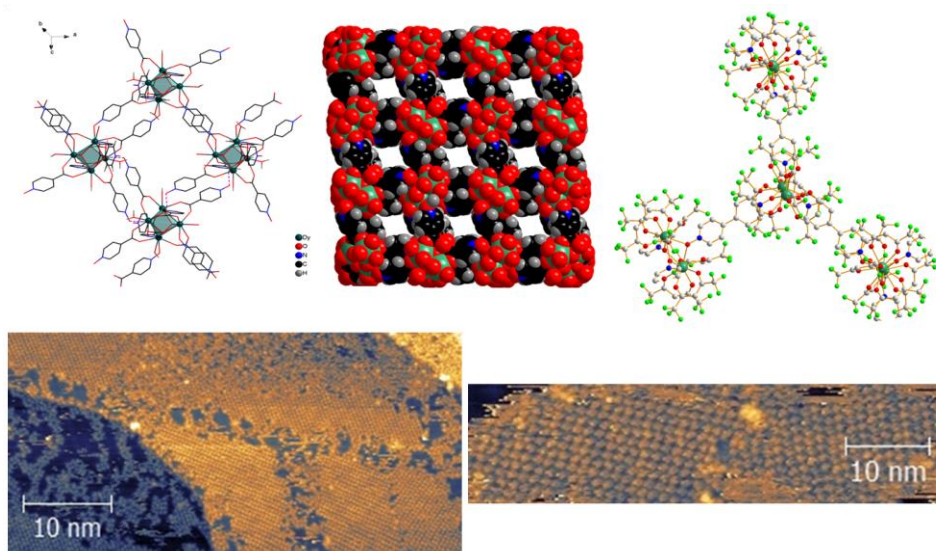
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A set of investigations on Dy-based dimers<sup>1</sup> single-molecule magnet (SMM) is presented. Modification of the dimers gives rise to extended 3D-network of SMM with significant cell volume ( $\approx 24500 \text{ \AA}^3$ ). The advantage of the interplay between luminescence, ab-initio calculations and magnetic measurements will also be demonstrated.<sup>2</sup>

Last, the very good evaporability of the dimers allow for their surface deposition as sub-monolayers, thin and thick films. XPS, TOF-SIMS, and AFM demonstrate that these molecules remain intact after evaporation. XMCD and XNLD measurement highlight ordering of dimers within the thin film as confirmed by STM images. Finally, low-energy muon spectroscopy (LE- $\mu$ SR), a unique technique that permits to investigate the depth-dependence of the magnetic behavior on thick films, show no degradation of the relaxation time at the neighboring of the surface.



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## Two bisthienylethene-Ir(III) complexes showing acid/base-induced structural transformation and on-off luminescence switching in solution

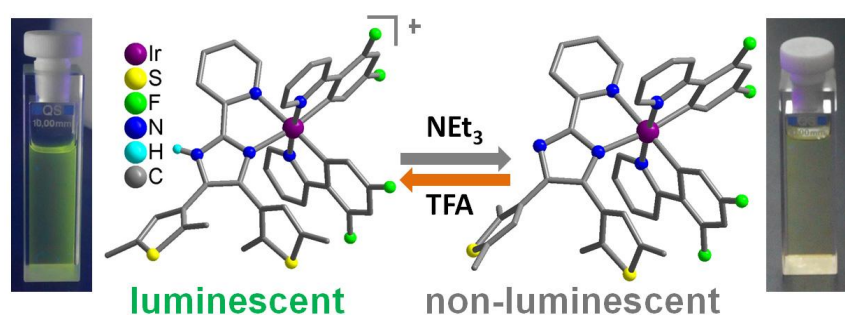
Deng-Ke Cao,<sup>\*a</sup> Jiong-Sheng Hu,<sup>a</sup> Min-Qiang Li,<sup>a</sup> Xiao-Xiong Li,<sup>a</sup> Michael D. Ward<sup>b</sup>

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Complexes  $[\text{Ir}(\text{dfppy})_2(\text{pbdtiH})](\text{PF}_6) \cdot 2\text{CHCl}_3$  (**1-H**) and  $[\text{Ir}(\text{dfppy})_2(\text{pbdti})]$  (**1**) were synthesized by the reaction of bisthienylethene pbdtiH and  $[\text{Ir}(\text{dfppy})_2\text{Cl}]_2$  dimer under the neutral and basic condition, respectively. Thus, the  $\{\text{Ir}(\text{dfppy})_2\}^+$  unit is coordinated by pbdtiH in **1-H**, while pbdti<sup>-</sup> in **1**, which are confirmed by their crystal structures. The structures of **1-H** and **1** could be interconverted in solution, upon alternately adding  $\text{NEt}_3$  and TFA, thus resulting in reversible luminescence switching between on-state of **1-H** and off-state of **1** at room temperature. In addition, both **1-H** and **1** show solid-state luminescence, with a broad emission at 534nm and 525 nm, respectively. Free pbdtiH ligand shows photochromic behavior in  $\text{CH}_2\text{Cl}_2$  solution. However, no photochromism has been observed in **1-H** and **1**, indicating that the coordination of pbdtiH/pbdti<sup>-</sup> ligand to  $\{\text{Ir}(\text{dfppy})_2\}^+$  unit could suppress their photochromic behaviors.



**Figure 1**  $\text{NEt}_3$ /TFA-induced structural transformation and on-off luminescence switching between **1-H** (left) and **1** (right).

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## Photoswitchable dinuclear copper(II) compounds as building-blocks for the synthesis of hexanuclear complexes

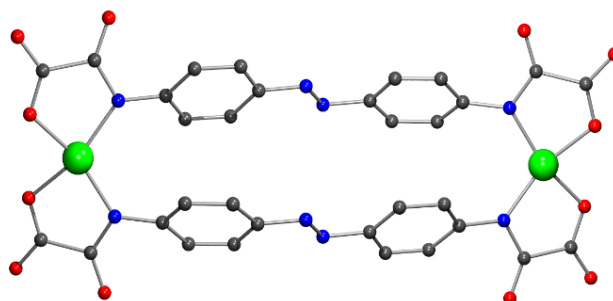
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Molecular magnetic photoswitches are attractive due to the applications that can present, such as data storage, drug delivery or sensors,<sup>1</sup> since their chemical and magnetic properties can be reversibly tuned by electromagnetic radiation.<sup>2</sup> Among all the photoswitches, stilbene and azobenzene groups are very well-known for their photoreactivity.

In a first approach, we have synthesized dinuclear copper(II) compounds with bis-oxamate ligands bearing stilbene and azobenzene groups.<sup>3</sup> They present a relatively moderate magnetic coupling between very distant copper(II) ions, that can be tuned when irradiated. In a second approach, we exploit the possibility of their self-assembly to obtain polynuclear compounds. Herein, the syntheses, physical characterization, photoactivity and magnetic studies of dinuclear and hexanuclear copper(II) compounds with these ligands are presented.



**Figure 1** Structural view of an anionic dinuclear copper(II) compound with a photoactive azobenzene derivative ligand. Color code: copper, green; oxygen, red; nitrogen: blue; carbon, grey.

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3 J.M. Carbonell-Vilar, M. Viciano-Chumillas, J. Cano, F. Lloret, M. Julve, ms in preparation.

# Oxalato-Bridged 2D Copper(II)-Pyrazol Nets as Chromogenic and Magnetic Sensors for Amine Vapour Detection

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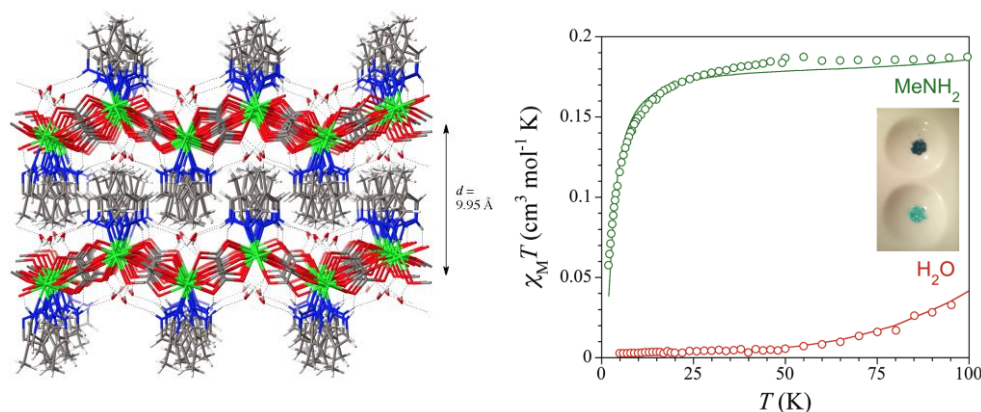
<sup>a</sup>Instituto de Ciencia Molecular (ICMol), Universitat de València, c/ Catedrático José Beltrán 2, E-46980 Paterna (València), Spain

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Metal-organic frameworks (MOFs) are one of the most challenging issues among the diverse class of molecular multifunctional materials because of their applications for chemical sensing.<sup>1</sup> The main goal in this area is to tune their optical, electronic, and/or magnetic properties by the inclusion of selected guests for future applications in the detection of volatile organic compounds resulting from food degradation.<sup>2</sup>

Our strategy in this field is based on the use of oxalate (ox) and 4-methylpyrazole (H-4-Mepz) as bridging and terminal ligands, respectively, towards Cu<sup>II</sup> ions. Such strategy has allowed us to synthesise a 2D copper(II) coordination polymer of formula Cu(ox)(H-4-Mepz)·1/3H<sub>2</sub>O (**H<sub>2</sub>O@1**) exhibiting a dynamic vapochromic and magnetic switching behaviour, which is accompanied by a colour change from light blue greenish to deep blue, upon adsorption of methylamine to give the new adsorbate of formula Cu(ox)(H-4-Mepz)·MeNH<sub>2</sub> (**MeNH<sub>2</sub>@1**) (Figure 1).



**Figure 1.** (left) Perspective view of the crystal packing of the hydrated precursor **H<sub>2</sub>O@1** showing the zipper-like interpenetration of the parallel disposed corrugated layers. The water molecules occupy the small pores. (right) Magnetic properties of the hydrated precursor **H<sub>2</sub>O@1** and the methylamine adsorbate **MeNH<sub>2</sub>@1**. The inset shows a photograph illustrating the colour change upon adsorption of methylamine.

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# COORDINATION-ORGANOMETALLIC HYBRID MATERIALS BASED ON THE HETEROMETALLIC M(II)-Ru(II) (M=Cu AND Cd) COMPLEXES: SYNTHESIS, SPECTROSCOPIC CHARACTERIZATION, LUMINESCENCE AND NLO PROPERTIES

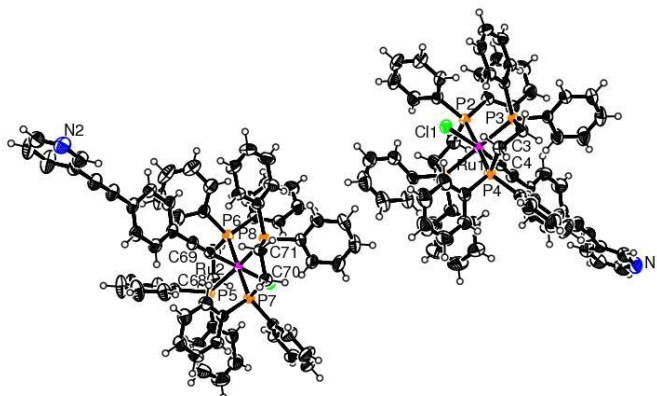
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## Abstract

Some heterobimetallic complexes of the type  $[\text{Cu}(\text{L}_{1-3})(\text{NC}_5\text{H}_4\text{C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CRu}(\text{dppe})_2\text{Cl})]$  (**1a-c**) and  $[\text{Cd}(\text{L}_{1-3})(\text{NC}_5\text{H}_4\text{C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CRu}(\text{dppe})_2\text{Cl})]$  (**2a-c**) have been prepared by the reaction of *trans*- $[\text{RuCl}(\text{dppe})_2(\text{C}\equiv\text{CC}_6\text{H}_4(\text{C}\equiv\text{C-py-3}))]$  (**1**) with Cu(II) and Cd(II) in presence of Schiff base ligands  $\text{L}_{1-3}$  (Where  $\text{L}_1$ =2-(pyrrole-2-yl-methylidene)aminophenol,  $\text{L}_2$  = 5-bromo-2-(pyrrole-2-yl methyl dine)aminophenol and  $\text{L}_3$  = 5-nitro-2-(pyrrole-2-ylmethylidene)aminophenol. All the complexes were characterized on the basis of elemental analysis, IR, UV-visible,  $^1\text{H}$  NMR, and  $^{31}\text{P}$  NMR spectral studies. Quassireversible redox behavior is accounted for all complexes corresponding to Cu(I)/Cu(II) and Ru(II)/Ru(III) for **1a-c** and Ru(II)/Ru(III) for **2a-c**. All complexes exhibit intra-ligand ( $\pi\rightarrow\pi^*$ ) fluorescence with high quantum yield in dimethylformamide. The second harmonic generation (SHG) efficiency of the complexes was measured by Kurtz-powder technique indicating that all the complexes appear to be a good candidate for NLO material.



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## Magnetic and Photophysical Properties in Multiple Functionalized TTF-based Complexes of Lanthanides.

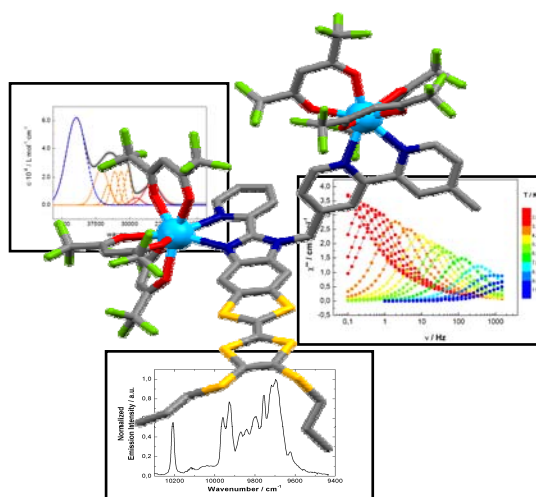
H. Douib,<sup>\*a</sup> S. Speed,<sup>a</sup> M. Feng,<sup>a</sup> F. Pointillart,<sup>a</sup> B. Lefeuvre,<sup>a</sup> B. Le Guennic,<sup>a</sup> S. Golhen,<sup>a</sup> O. Cador,<sup>a</sup> O. Maury,<sup>b</sup> L. Ouahab<sup>a</sup>

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Lanthanide ions are well-known to exhibit large magnetic moments and strong magnetic anisotropy and therefore they are considered good candidates for the elaboration of Single Molecule Magnets (SMMs). And they also possess interesting luminescence properties, emitting light when adequately sensitized by an appropriate ligand. It has previously been demonstrated in our group that the TTF-based ligands play the double role of structural agent for SMM<sup>1</sup> behaviour and organic chromophore for an antenna effect.<sup>2</sup> So by coordinating a lanthanide ion to a TTF-based ligand we have obtained two new complexes which exhibit SMM behaviour and luminescence. These behaviours have been rationalized by TD-DFT calculations.



**Figure 1** TTF-based dysprosium complex and its magnetic and photophysical properties.

1 F. Pointillart, Y. Le Gal, S. Golhen, O. Cador, and L. Ouahab, *Chem. Eur. J.*, **2011**, *17*, 10397.

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## Novel hybrid coordination networks based on imidazolium dicarboxylate salts and 3d transition metal salts.

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Metal-organic coordination networks are hybrid compounds built from inorganic part (3d metal or lanthanide based building units...) linked together by organic part (ligands). The synthesis of such hybrid compounds has known a growing interest for the last decades due to the versatility of their synthesis and their potential applications (for gas storage/separation, catalysis, drug delivery...).[1-3]

Coordination networks are usually obtained by solvothermal synthesis and more recently by ionothermal synthesis where solvents are replaced by ionic liquids (ILs).[4, 5] This approach has already proved to be efficient to obtain new functional materials. Yet, in the examples of the literature the role of the IL is not well-defined since it can play the role of solvent, charge balancer and/or structuring agent. In our group, we have decided to synthesize hybrid materials from ILs bearing specific coordination functions, developing a solvo-ionothermal synthesis, to control the role of the ILs as ligand.

The synthesis and complete characterization of new hybrid frameworks based on imidazolium and first row transition metal ions will be presented (see Figure 1). We will specially emphasize the effect of the solvent and the kind of metal salt on the formation of new hybrid compounds and their physical properties.<sup>6</sup>

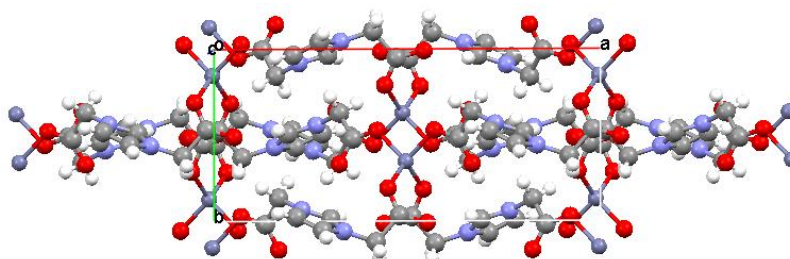


Figure 1. Crystal structure of  $[(\text{MimCO}_2)_2]_2\text{Co}$  along the a axis.<sup>6</sup>

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4. P. J. Calderone, P. M. Forster, L. A. Borkowski, S. J. Teat, M. Feygenson, M. C. Aronson, J. B. Parise, *Inorg. Chem.* **2011**, 50, 2159.
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6. P. Farger, R. Guillot, F. Leroux, N. Parizel, M. Gallart, P. Gilliot, G. Rogez, E. Delahaye, P. Rabu, *Eur. J. Inorg. Chem.*, **2015**, 5342.



## Anilate ligand as building block for new multifunctional materials

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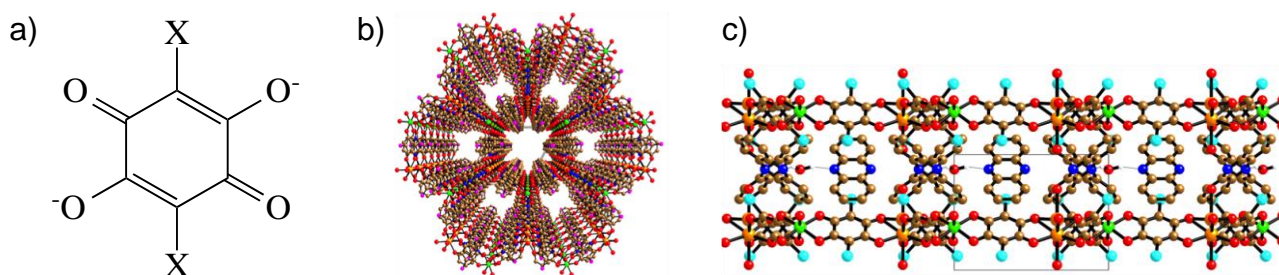
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In the last years, the search for multifunctional molecule-based materials has been one of the most interesting topics in molecular magnetism. The popular oxalate-based magnetic compounds are now being reinvented with the anilate ligand (*fig a*) that has the same coordination modes but can be easily functionalized changing the X group (X = Cl, Br, NO<sub>2</sub>, OH, H....).

We present a whole new family of 2D compounds (*fig b, c*) with different functional cations (chiral, luminescent...). The magnetic properties can also be altered by changing the divalent and trivalent metal ions and the X group of the anilate ligand, which is not possible with the oxalate ligand. This adds a new variable to easily modify multifunctional materials.

Moreover, we are able to prepare 0D structures by combining the  $[M^{III}(C_6O_4X_2)_3]^{3-}$  (X = Br, Cl; M<sup>III</sup> = Cr) unit with functional cations (luminescent, spin crossover,...) with aromatic rings, thanks to the  $\pi$ - $\pi$  interactions, also impossible with the oxalate ligand. As a result we obtain paramagnetic compounds with an extra functionality.



**Figure 1** a) Anilate ligand. b) Perspective view of the hexagonal channels of a 2D honeycomb layer c) view of the alternating anionic and cationic layers

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# Assembly Enhanced Emission by Bismuth Complexes in Dendritic Poly(phenylazomethine)s: Fine Tunable Intensity and Switching Functionality

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Dendrimers have unique properties due to their branched three-dimensional architectures. The most important feature is the encapsulation ability of chemical units within their inner coordination sites. This feature enables precise synthesis of the metal nanoparticles as a dendrimer reactor. On the other hand, dendrimers with some compounds are also used as nano-capsules, which are expected to provide unique catalytic, optical and optoelectronic features derived from the branched structure.

Assembling photoluminescent components within the dendrimers is of particular interest for understanding the dendritic skeletons, light harvesting properties, sensors with signal amplification, *etc.* However, a quenching effect generally prevents enhancement of the luminescence because the local concentration of the luminescent components is too high. In addition, general dendrimers demonstrate a random coordination behavior with metal ions. Such systems have difficulties in controlling the optical properties.

In our previous study, we reported that various metal salts such as PtCl<sub>4</sub>, SnCl<sub>2</sub>, GaCl<sub>3</sub>, FeCl<sub>3</sub>, AuCl<sub>3</sub>, CuCl<sub>2</sub> and VCl<sub>3</sub> could be assembled in dendritic polyphenylazomethines (DPAs) with specific atom numbers.<sup>1</sup> They have been much developed for the fabrication of metal clusters in the DPAs, however, the luminescent property has not been demonstrated yet. In this study, we attempted to utilize the typical elements, and achieved fine-controllable phosphors by the complexation to the DPAs.

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# Multicolor Control of a Transparent Film Incorporating ( $\beta$ -Diketonato)lanthanide(III) Complexes by Proton Concentration

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A transparent film incorporating Ln<sup>III</sup>- $\beta$ -diketonato complexes, [Ln<sup>III</sup><sub>2</sub>( $\mu$ -PBA)<sub>2</sub>(PBA)<sub>4</sub>]@Nafion (Ln = Eu, Tb, Dy; HPBA = *N*-(2-pyridinyl)benzoylacetamide; Figure 1)<sup>[1]</sup> whose emission color can be controlled by external pH condition, has been developed. Nafion is known as a cation exchange and highly proton-conductive membrane, where hydrophilic SO<sub>3</sub>H groups forms cavities of ca. 4 nm diameter when they are swollen with water.<sup>[2]</sup> Thanks to the cation exchange property, Nafion can conveniently provide transparent films with multifunctionality.

The emission color of dual component film incorporating the green light-emitting [Tb<sup>III</sup><sub>2</sub>( $\mu$ -PBA)<sub>2</sub>(PBA)<sub>4</sub>] only in acidic condition and red light-emitting [Eu<sup>III</sup><sub>2</sub>( $\mu$ -PBA)<sub>2</sub>(PBA)<sub>4</sub>] only in basic condition, abbreviated as Eu/Tb@Nafion, was reversibly controlled by pH as can be seen in Figure 2. Likewise, remarkable changes were observed in the quantum yield and emission lifetime depending on pH. Based on the result thereof, the emission color of the transparent film may be controlled by proton flow induced by applied voltage. In this presentation, magnetic properties of Ln<sup>III</sup>-PBA complexes in the crystalline and film states will be discussed.

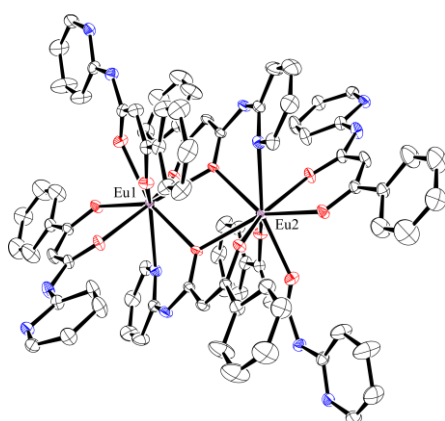


Figure 1. Crystal structure of [Eu<sup>III</sup><sub>2</sub>( $\mu$ -PBA)<sub>2</sub>(PBA)<sub>4</sub>].

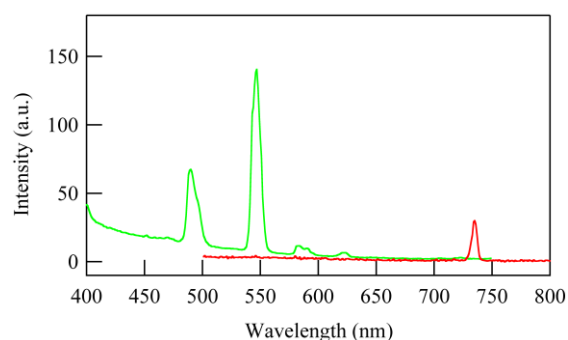


Figure 2. pH dependence of emission spectra in Tb/Eu@Nafion. (Green: pH 3, red: pH 10.)

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## Fine-tuned Multifunctionality in Halogen-bonded Molecular Conductors $(\text{DIETSe})_2\text{FeBr}_{4x}\text{Cl}_{4(1-x)}$

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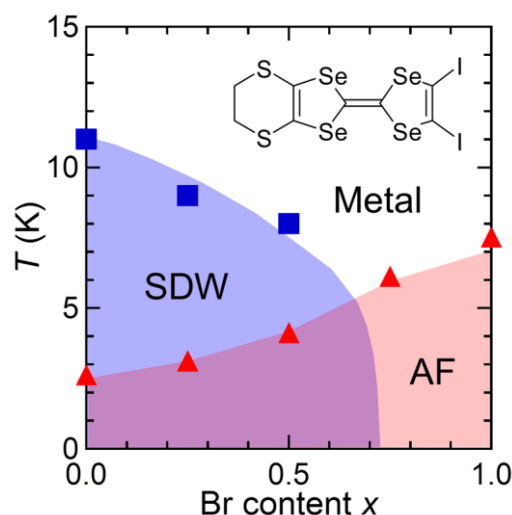
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Towards multifunctionality, various supramolecular systems have been studied, where designing intermolecular interactions can control electronic functions as desired. To tune both spin and charge degrees of freedom and explore spin–charge interactions, we focus on halogen-bonded  $\pi$ – $d$  molecular conductors,  $(\text{DIETSe})_2\text{FeX}_4$  [DIETSe = diiodo(ethylenedithio)tetraselenafulvalene (Fig. 1 inset) ; X = Br, Cl],<sup>1</sup> where halogen bonds link donors and magnetic  $d$ -spins of  $\text{Fe}^{3+}$ . They show much different electronic states by halogen species, despite the isostructure supported by halogen bonding.

To systematically control the electronic states, we considered to modulate halogen-bonding interactions by synthesizing the halogen-mixed salts  $(\text{DIETSe})_2\text{FeBr}_{4x}\text{Cl}_{4(1-x)}$ . We found that with increasing Br, spin-density-wave (SDW) transition was suppressed and antiferromagnetic ordering of  $d$ -spins was enhanced (Figure 1). These results indicate fine-tuning of dimensionality of  $\pi$ -electrons and  $\pi$ – $d$  interactions by halogen bonding modulation. We also discovered mixing-induced hysteresis in magnetic moment and resistivity in  $(\text{DIETSe})_2\text{FeBr}_2\text{Cl}_2$ , which is attributed to random magnetic interactions by halogen mixing.<sup>2</sup> In this study, we will also present physical controls of  $(\text{DIETSe})_2\text{FeBr}_{4x}\text{Cl}_{4(1-x)}$  under multi-extreme conditions.



**Figure 1** Phase diagram of  $(\text{DIETSe})_2\text{FeBr}_{4x}\text{Cl}_{4(1-x)}$ .

1) T. Shirahata, M. Kibune, M. Maesato, T. Kawashima, G. Saito, T. Imakubo, *J. Mater. Chem.*, **2006**, *16*, 3381.

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## Association of photoswitches and/or redox active units with 4f ions for luminescence and magnetism control

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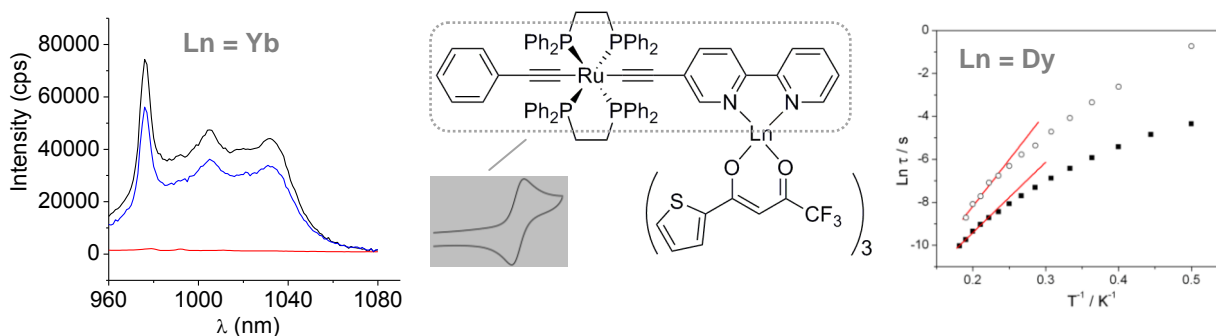
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We present our strategies to build efficient molecular switches based on 4f ions in order to switch either their luminescence or their slow relaxation of magnetization by two type of external stimuli: redox potential and light.

Ruthenium(II) acetylide complexes can be incorporated in 4d-4f bimetallic complexes (Figure 1) with excellent redox-switching behavior for i) the ON/OFF switching of NIR emission in the case of ytterbium(III) and neodymium(III) ions,<sup>1-2</sup> and ii) the modulation of the slow relaxation of magnetization in the case of the dysprosium(III) ion.<sup>3-4</sup>

Photochromic ligands (spiropyran or dithienylethene), easily interconverted between two isomers with different coordination abilities, are ideal candidates for light switching of slow relaxation of magnetization. We will show that they can also produce original 4f complexes with a strong magnetic anisotropy.



**Figure 1** Redox switching of luminescence (left) and magnetization relaxation time (right) in ruthenium(II)-lanthanide(III) complexes.

1 E. Di Piazza, L. Norel, K. Costuas, A. Bourdolle, O. Maury, S. Rigaut *J. Am. Chem. Soc.* **2011**, *133*, 6174.

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4 L. Norel, M. Feng, K. Bernot, T. Roisnel, T. Guizouarn, K. Costuas, S. Rigaut *Inorg. Chem.* **2014**, *53*, 2361

## Organic Cations Conduction in Coordination Polymers

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Design of ion conductive crystalline structures is important because of the applications for various electrochemical devices and catalysis.<sup>1</sup> Coordination polymers (CPs) have highly designable framework architecture and have attracted the attention as a new class of ion conductor. There are many reports on CPs showing H<sup>+</sup>, Li<sup>+</sup> ion conductivity, which more readily integrated into functional device such as fuel cell and secondary battery.<sup>2</sup> On the other hand, fundamental developments of other ionic conductors such as multivalent metal cations, monoanions (H<sup>-</sup>, OH<sup>-</sup>), and organic ions are also of important for future energy devices and electrochemical applications.

Here, we report a new 1-D CP incorporating organic cations from ionic liquid (Figure 1). Organic cations, 1-ethyl-3-methylimidazolium, are located densely between robust CPs composed of Zinc (II) and sulfate. The optimized structure of the CP shows close to 10<sup>-3</sup> S cm<sup>-1</sup> of organic cation conductivity at 210 °C. We investigated the mechanism of organic cations conduction by use of X-ray, AC impedance and solid state NMR.

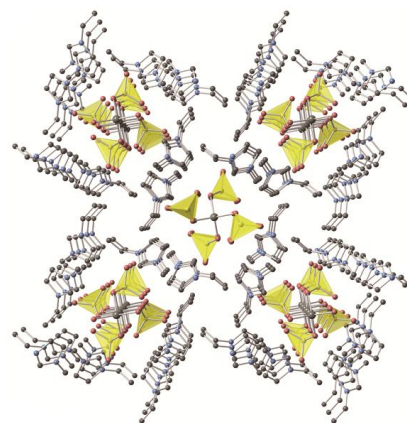


Figure 1. **Crystal structure of the cation conductive CP.**

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2. S. Horike, D. Umeyama, S. Kitagawa, *Acc. Chem. Res.*, **2013**, 46, 2376.

## Lanthanides-TTF complexes displaying Single Molecule Magnet behaviour and Luminescence

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Lanthanide-based complexes have greatly contributed to the development of molecular magnetism in the last decade and more particularly in the branch of single molecule magnets (SMMs)<sup>1</sup>. The main reasons are their large magnetic moments associated to their intrinsic large magnetic anisotropy. The splitting of the multiplet ground state of a single-ion in a given environment is responsible of the trapping of the magnetic moment in one direction in SMMs. However, the analyses of the crystal field effects on the magnetic anisotropy are not so common<sup>2</sup>. A better understanding of the magneto-structural correlations in lanthanide-based complexes should provide tools to improve their potentialities.

In this presentation we will focus on the specific magnetic properties of TTF-based lanthanide mononuclear and polynuclear complexes. We will show how optimize the SMM behavior playing on i) the modulation of the supramolecular effects via chemical modifications of the TTF ligand<sup>3</sup>, ii) simple molecular engineering modifying the electronic distribution and symmetry of the coordination polyhedron, iii) magnetic dilutions (solution and doping) and iv) isotopic enrichment of the dysprosium<sup>4</sup>.

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- 3 T. T. da Cunha, J. Jung, M.-E. Boulon, G. Campo, F. Pointillart, C. L. M. Pereira, B. Le Guennic, O. Cador, Kevin Bernot, F. Pineider, S. Golhen, L. Ouahab, *J. Am. Chem. Soc.* **2013**, 135, 16332.
- 4 F. Pointillart, K. Bernot, B. Le Guennic, S. Golhen, O. Cador, L. Ouahab, *Angew. Chem. Int. Ed.* **2015**, 54, 1504-1507.

### Acknowledgements

This work was supported by the CNRS, Rennes Métropole, Université de Rennes 1, Région Bretagne, FEDER and Agence Nationale de la Recherche (N° ANR-13-BS07-0022-01).

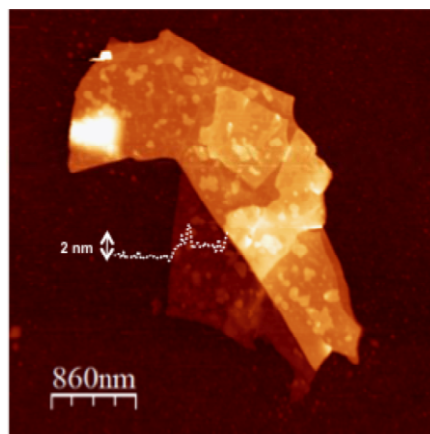
## Multifunctional materials based on single-molecule magnets, spin-crossover complexes and magnetic extended networks

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In this communication, we report the preparation and characterization of compounds that combine oxalate and anilate-based anionic extended networks with small cations such as spin-crossover complexes, single-molecule magnets, Pt<sup>II</sup> luminescent complexes and trialkylammonium proton conducting molecules. In the case of the anilate-based networks, the reduction of size of the templating cations together with the increase of size of the ligand have afforded a novel type of structure, in which the cations are placed into the hexagonal channels of the 2D network and not between the layers as usual for this type of compounds. These compounds present a ferrimagnetic ordering at around 10 K. The insertion of the cations within the channels of anilate-based networks confers a neutral character to the layers. These layered materials can be exfoliated in atomically-thin layers with heights down to 2 nm by using the well-known Scotch tape method.<sup>1</sup>

As a second strategy, we have explored the formation of covalent links between the two functional subunits by preparing Fe<sup>II</sup> complexes of magnetic polyoxometalates (POMs) with organic ligands. This has given rise to coexistence of a single-molecule magnet behavior and photo-induced spin-crossover.<sup>2</sup>



**Figure 1** AFM image of a flake of  $[\text{Fe}^{\text{III}}(\text{acac}_2\text{-trien})][\text{Mn}^{\text{II}}\text{Cr}^{\text{III}}(\text{Br}_2\text{An})_3]$

1 A. Abhervé, S. Mañas-Valero, M. Clemente-León, E. Coronado *Chem. Sci.*, **2015**, *6*, 4665.

2 A. Abhervé, M. Palacios-Corella, J. M. Clemente-Juan, R. Marx, P. Neugebauer, J. van Slageren, M. Clemente-León, E. Coronado, *J. Mater. Chem. C* **2015**, *3*, 7936



## Luminescent Yb<sup>III</sup>-Based Single Molecule Magnets

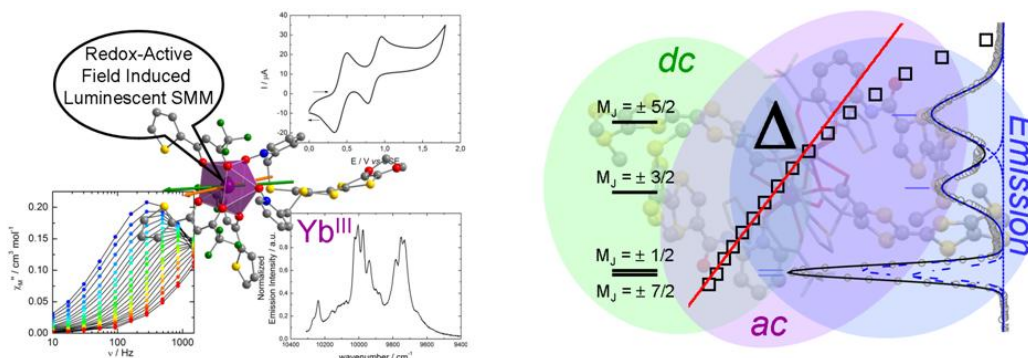
F. Pointillart,<sup>\*a</sup> B. Lefeuvre,<sup>a</sup> B. Le Guennic,<sup>a</sup> S. Golhen,<sup>a</sup> O. Cador,<sup>a</sup> O. Maury,<sup>b</sup> L. Ouahab<sup>a</sup>

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Lanthanide-based complexes have greatly contributed to the development of molecular magnetism in the last decade and more particularly in the branch of single molecule magnets (SMMs).<sup>1</sup> The main reasons are their large magnetic moment associated to their intrinsic large magnetic anisotropy. The splitting of the multiplet ground state of a single-ion in a given environment is responsible of the trapping of the magnetic moment in one direction in SMMs. The energy splitting of the ground multiplet state in a given crystal field is responsible for the magnetic moment blocking along one direction. An analysis of the crystal field effect on the magnetic anisotropy<sup>2</sup> and a good understanding of the magneto-structural correlation are key points in the enhancement of the potential applications of this kind of coordination complexes. For example, the lanthanide luminescence is a photography of the  $M_J$  splitting and can be directly correlated with magnetic data.<sup>3</sup> In this presentation, we will present two redox-active luminescent Yb<sup>III</sup>-based SMM for which we will correlate magnetic and optical properties.<sup>4</sup> TD-DFT and ab initio calculations are helpful to rationalize our interpretations.



**Figure 1** Correlations between magnetic and optical properties in Yb<sup>III</sup>-based SMM

1 R. Sessoli and A. K. Powell, *Coord. Chem. Rev.* **2009**, 253, 2328.

2 J. D. Rinehart and J. R. Long, *Chem. Sci.* **2011**, 2, 2078.

3 G. Cucinotta, M. Perfetti, J. Luzon, M. Etienne, P.-E. Car, A. Caneschi, G. Calvez, K. Bernot, R. Sessoli, *Angew. Chem. Int. Ed.* **2012**, 51, 1606.

4 a) F. Pointillart, B. Le Guennic, S. Golhen, O. Cador, O. Maury, L. Ouahab, *Chem. Commun.* **2013**, 49, 615. b) K. Soussi, J. Jung, F. Pointillart, B. Le Guennic, B. Lefeuvre, S. Golhen, O. Cador, Y. Guyot, O. Maury, L. Ouahab *Inorg. Chem. Front.* **2015**, 2, 1105.



## Multifunctionality in lanthanide-based dimers: single-molecule magnetism and photo-induced tuning of color emission

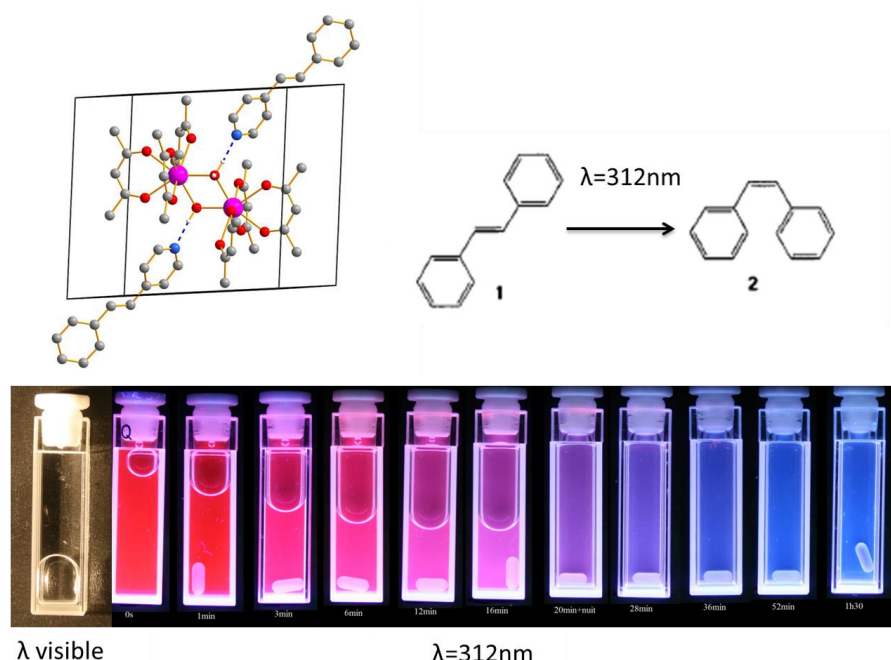
Marin Puget,<sup>a\*</sup> Julien David-Viffantzeff,<sup>a</sup> K. Bernot,<sup>a</sup> G. Calvez,<sup>a</sup> C. Daignebonne,<sup>a</sup> O. Guillou,<sup>a</sup>

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Lanthanide-based coordination chemistry offer tremendous potentialities for luminescent and magnetic materials.<sup>1</sup> The control of these properties by external stimuli is a challenging task.

In this work we report the synthesis<sup>2</sup> and photophysical characterization of lanthanide-based dimers that can be associated with photoactive ligands (namely 4-Styrylpyridine). The resulting compounds of formula  $[(Ln(hfac)_3)_2(4\text{-styrylpyridine})_2(H_2O)_2]$  are stable in most organic solvent. Moreover, once dissolved in solution, exposition to UV light induces an isomerization of the photoactive ligand. For  $Eu^{III}$  derivative this induces a significant emission color change (from red to blue). The  $Dy^{III}$  derivative shows ferromagnetic interaction between the two lanthanide ions and behave as Single Molecule Magnet (SMM).<sup>2</sup> The modification of the coordination environment of the lanthanide is also expected to induce changes in the SMM behavior.



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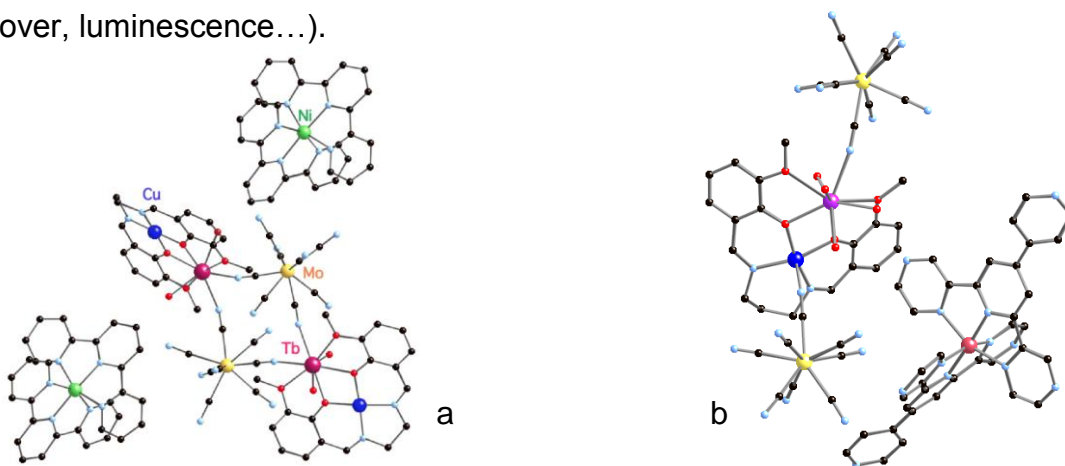
## Functional hetero-tetra-metallic architectures

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One of the main challenges in coordination chemistry is the synthesis of hetero-tri or hetero-tetra-metallic species. Indeed such molecules are promising for the development of poly-functional compounds integrating magnetic properties. This presentation will highlight some recent achievements in the field of single molecule magnets and photo-switchable high spin molecules<sup>1,2,3</sup>.

Relying on the concept of “polynuclear complexes as ligands”, we synthesized a large family of hetero-poly-metallic complexes. The main building blocks we used are (i) Molybdenum/Tungsten complexes such as MoCu<sub>n</sub> (n = 2, 4, 6), MoZn<sub>2</sub> or WZn<sub>2</sub> whose magnetic properties can be modified by light, (ii) CuTb bimetallic Schiff base compounds<sup>4,5,6</sup>, well known for their single molecule magnet property, and (iii) polypyridines complexes that are of interest for their luminescent properties.

Our strategy demonstrates the relevance of using these polynuclear complexes as valuable building blocks for the rational design of hetero-poly-metallic supramolecular architectures mixing several properties (single molecule magnets, photomagnetism, spin crossover, luminescence...).



**Figure 1** : hetero-tetra-metallic architectures : a) Mo<sub>2</sub>Cu<sub>2</sub>Tb<sub>2</sub>-Ni<sub>2</sub> b) MoCuTb-Ru

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## The first heterometallic [M(III)M'(III)(L)<sub>3</sub>] 2D lattice with anilato-based ligands

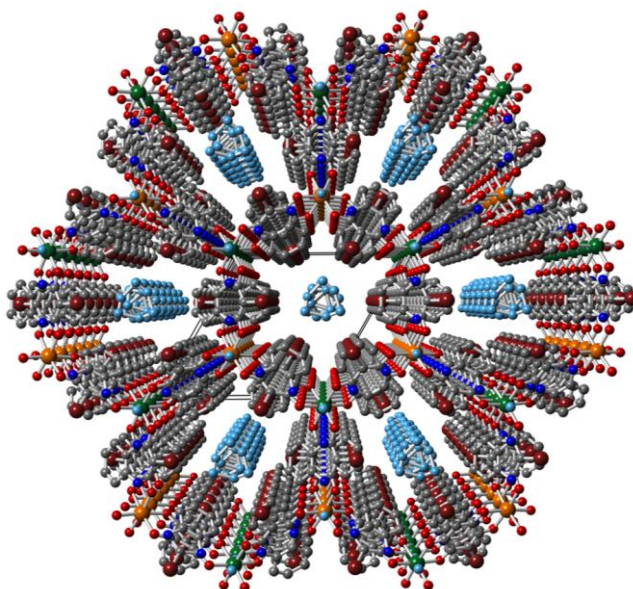
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The last twenty five years have witnessed a fruitful search of multifunctional molecular materials using the well-known anionic hetero-metallic lattices based on the oxalato ligand formulated as  $A[M^II M^III(C_2O_4)_3]$ . In this family of compounds the anionic lattice furnishes the long range magnetic ordering whereas the  $A^+$  cations provide an extra functionality as paramagnetism, spin crossover, luminesce, chirality, proton conduction,...

Following a parallel approach we and others have recently prepared multifunctional molecular materials based on anilato-type ligands presenting chirality, porosity and long range magnetic ordering with critical temperatures easily tuned.<sup>1</sup> Albeit, the anionic charge of these honey-comb layers prevents their delamination in order to prepare single layer devices. In order to achieve this goal we have prepared the first neutral 2D hetero-metallic honey comb layers by combining two trivalent metal ions as Fe(III) and Cr(III). Here we present the synthesis, structure and magnetic properties of this first example.



**Figure 1** Structure of the first neutral [M(III)M'(III)(L)<sub>3</sub>] hetero-metallic honeycomb 2D lattice made with anilate-based ligands

<sup>1</sup> S. Benmansour, C. J. Gómez-García et al. *Inorg. Chem.* **2013**, *52*, 10031-10040.

# Spin, Photon and Molecule: Experimental Demonstrations from Fundamentals to Applications

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Chemistry and Physics of Coordination Compounds can give rise to beautiful, attractive demonstrations: bright colours, colour changes and light emission, shiny crystals, laboratory experiments, new demonstrators and devices. Beyond the necessity to develop citizen awareness and to present complex results in a simple manner, such demonstrations can help attracting curious and talented students towards science.

Based on our experience of research<sup>1</sup>, of teaching<sup>2,3</sup> and of spreading the understanding of chemistry to various audiences through experiments,<sup>4-7</sup> we propose to present such experiments, playing with spins, photons and molecules (everyday molecules, Prussian blue analogues, ruthenium and other transition metal complexes) going from fundamental principles to their applications in the fields of colour, light, luminescence, thermodynamics, energy, molecular magnetism, from the Si-Nan compass to oscillating and rotating molecular magnets, from photosynthesis to molecular photovoltaic solar cells.



**Figure 1** Demonstrations are attractive for children, students and large audiences: bench of a Friday Evening Lecture at the Royal Institution of Great Britain, London. 2005

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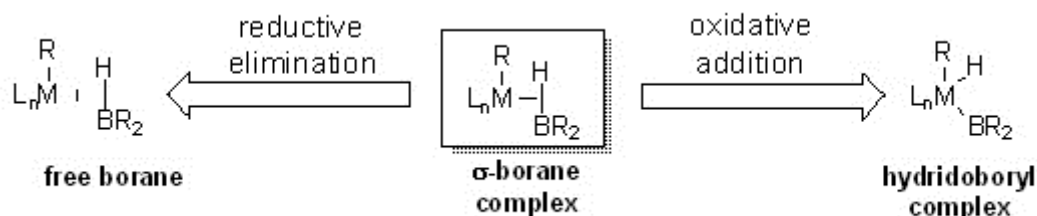
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## Borane engineering in B-H activation

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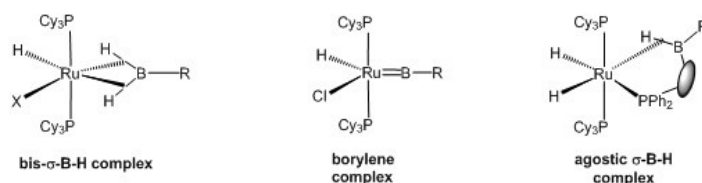
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Metal boron chemistry is an active field of investigation generally involving standard disubstituted boranes  $\text{HBRR}'$  ( $\text{R}, \text{R}' = \text{Pinacol, catechol, alkyl}$ ).<sup>1</sup>  $\sigma\text{-B-H}$  metal complexes can be seen as a snapshot in the oxidative addition pathway of the metal in the B-H bond and have now emerged as pivotal intermediates in number of catalytic processes (Figure 1). Since the first report in 1996 by Hartwig et al.,<sup>2</sup>  $\sigma\text{-borane}$  complexes have emerged as a species of strong potential.



**Figure 1** oxidative addition pathway of the metal in the B-H bond

In this prospect, borane engineering has proven particularly useful for mapping the different scenarios in the B-H activation.<sup>3</sup>



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## Capture and activation of CO<sub>2</sub> by metal-organic structures

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Currently hydrocarbon fuels are the most important source of energy because of their ready availability, stability, and high energy density. The increasing atmospheric concentration of CO<sub>2</sub> has been predicted by models which suggest dramatic and irreversible changes if actions are not taken urgently. It is now well established that CO<sub>2</sub> may be sequestered and stored as liquid CO<sub>2</sub> or solid carbonate but both solutions are energetically demanding and financially costly.<sup>1</sup> Recently reports of reaction of pressurised CO<sub>2</sub> with epoxides to form polycarbonates<sup>2</sup> or cyclic carbonates<sup>3</sup> have attracted both academic and industrial interest, but generally, the recycling of CO<sub>2</sub> to produce high value products via low-cost catalysts has not been exploited. Nelson's cryptands<sup>4</sup> are an example of a dynamic structure with useful applications, which demonstrated the ability to capture and convert CO<sub>2</sub> to carbonate and methyl carbonate following its coordination to encapsulated metal ions. Here we explore the fixation chemistry of CO<sub>2</sub> by derivatised dinuclear Cu(II), Ni(II), Zn(II) and Co(II) cryptands (Figure 1) where the phenyl ring was modified towards engineering these metal-organic structures into supramolecular assemblies. Attaching electron withdrawing groups to the phenyl ring proved to not affect their ability to capture CO<sub>2</sub>.

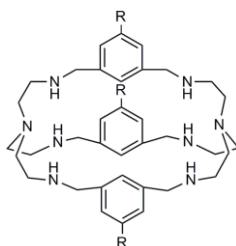


Figure 1 Derivatised cryptands.

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## Experimental and theoretical investigations on the stability of phosphine chalcogenides (R<sub>3</sub>PE) by <sup>31</sup>P NMR and DFT calculations

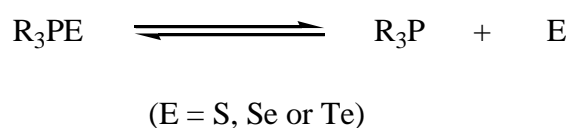
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Tertiary phosphine chalcogenides (R<sub>3</sub>PE) are suitable chalcogenide sources used in colloidal nanocrystal syntheses and remain one of the most common precursors [1]. Their wide use is due to the ease of preparation, high solubility, and desirable reactivity in many organic solvents [2,3]. Despite that no chalcogen is detected in solution upon preparation of R<sub>3</sub>PS and R<sub>3</sub>PSe [4], phosphine tellurides show an equilibrium between R<sub>3</sub>P<sub>2</sub>Te and tellurium which significantly depends upon the phosphine substituents [4-6]. In this context, we report herein on the stability of phosphine chalcogenides of the type R<sub>3</sub>PE (R = dialkylamino, alkyl or alkoxy group; E = S, Se or Te) using experimental <sup>31</sup>P NMR and theoretical DFT studies. Our experimental NMR data and DFT calculations (in solution and in the gas phase) show that the stability of the phosphine chalcogenide clearly depends on both the nature of the chalcogen and the solvent considered. The results of this study will be discussed and compared with those already reported in the literature.



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## Proton Reduction at Bimetallic Dithiolate Complexes of Nickel

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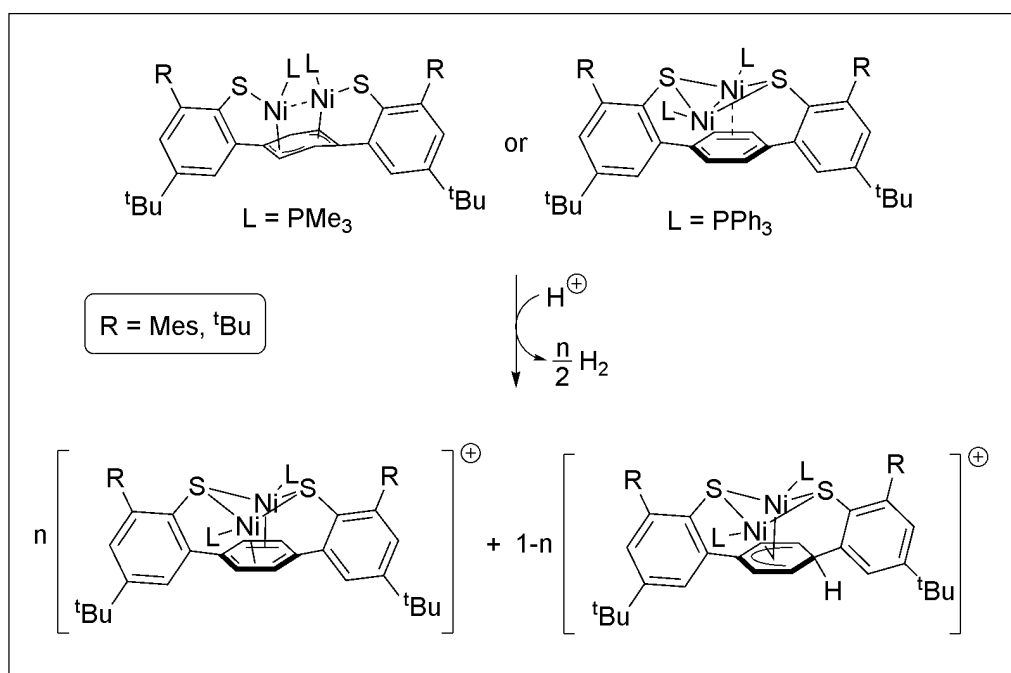
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The catalytic generation of hydrogen from a proton source is a cornerstone in sustainable energy conversion schemes. First-row transition-metals are suitable to function as reactive sites in light of their relatively high redox-flexibility and abundance. In this context, studies of synthetic nickel thiolate complexes are motivated by the fact that nickel is relevant to the function of metalloproteins.<sup>1</sup>

Our research aims at studying the ability of bimetallic fragments to mediate two-electron processes. First model systems which incorporate low-valent nickel sites were prepared from structurally and electronically flexible 1,4-terphenyldithiophenol ligands.<sup>2</sup>



In this contribution the results of a mechanistic study of the stoichiometric reaction of above complexes with acids will be presented. The ligand plays a pivotal role in coupling the redox-chemistry of the nickel sites for substrate turnover.

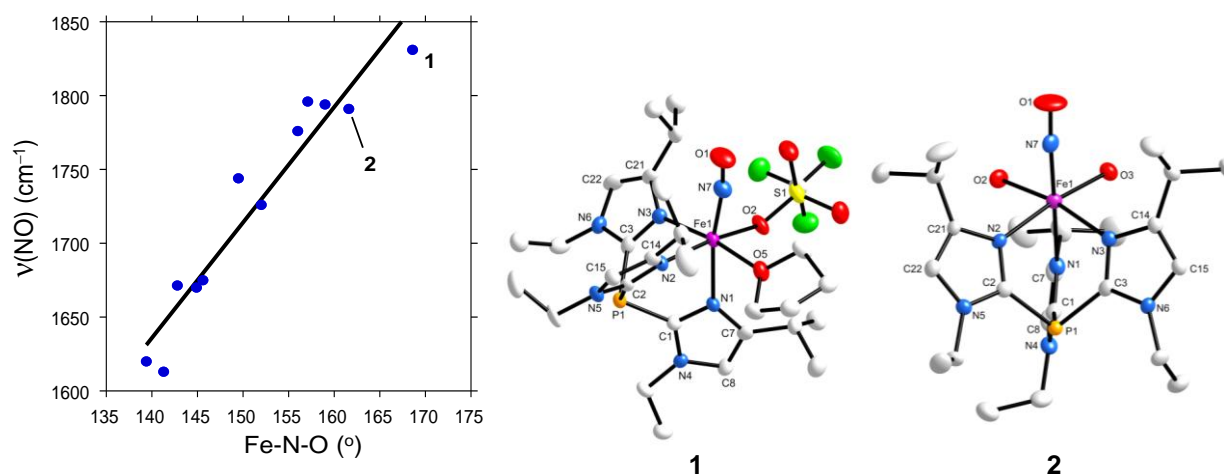
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## Structural and Functional Models for Bioremediation Enzymes

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Class III dioxygenases, contains His<sub>3</sub> iron (II) binding sites in contrast to Class I and II sites possessing 2His-1-Carboxylate metal binding sites. Enzymes containing His<sub>3</sub> metal binding sites include gentisate 1,2-dioxygenases (GDO), salicylate 1,2-dioxygenase (SDO), and 1-hydroxy-2-naphthoate dioxygenase (HNDO). Nitric oxide has been used to study ferrous active sites since they are spectroscopically silent and do not exhibit low energy absorption bands. Although many nonheme enzymes form stable Fe-NO complexes, a number of them are known to react reversibly with formation of paramagnetic nitrosyl-iron centers which according to the Enemark and Feltham notation are of the {FeNO}<sup>7</sup> type. In our efforts to synthesize models that reproduce the reversibility of iron-nitrosyl formation, we have synthesized [Fe(T1Et4iPrIP)(OTf)<sub>2</sub>] (T1Et4iPrIP = tris(1-ethyl-4-isopropyl-imidazolyl) phosphine) which reversibly binds nitric oxide to afford [Fe(T1Et4iPrIP)(NO)(THF)-(OTf)](OTf) (**1**), the first example of a 6-coordinate {FeNO}<sup>7</sup> S = 3/2 complex containing a linear Fe–N–O group and exhibiting the highest  $\nu(\text{NO})$  for compounds in this class (1831 cm<sup>-1</sup>). DFT studies reveal an enhanced degree of  $\beta$  electron transfer from the  $\pi^*(\text{NO})$  to the iron d orbitals accounting for the large stretching frequency. Reaction of **1** with 2 equiv water affords [Fe(T1Et4iPrIP)(NO)(H<sub>2</sub>O)](OTf)<sub>2</sub> (**2**) which is more electron rich and has a lower  $\nu(\text{NO})$  (1791 cm<sup>-1</sup>).



**Figure 1** Plot of Fe-nitrosyl Fe-N-O bond angle vs  $\nu(\text{NO})$  [1].

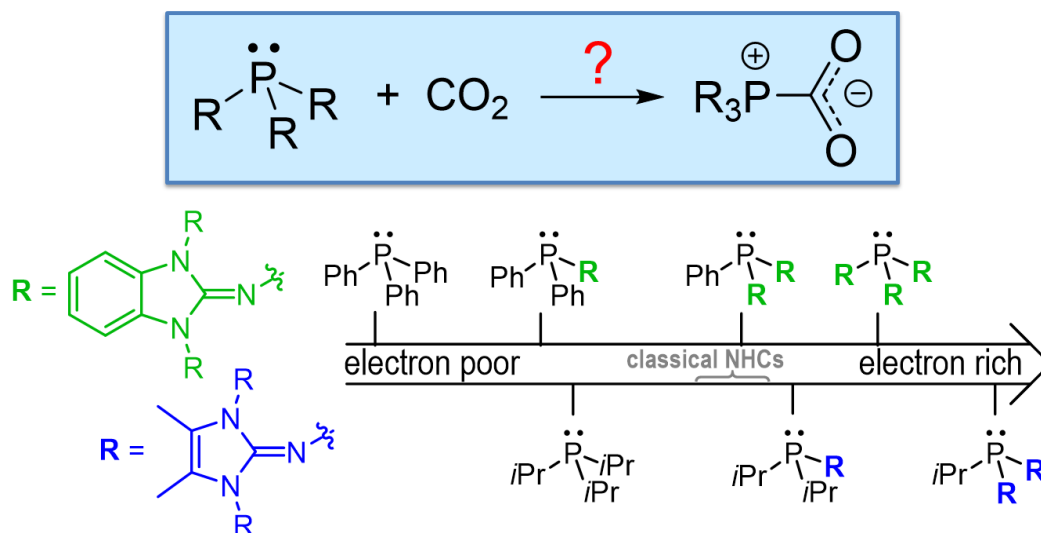
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## Highly electron-rich phosphines for the activation of strong bonds and small molecules

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Phosphines are arguably the most versatile ligands to modulate the steric and electronic properties of metal complexes. Particularly owing to their stronger  $\sigma$ -donor properties, N-heterocyclic carbenes nowadays rival phosphines as ligands across organometallic chemistry. As part of our program to enhance the donor strength of phosphines we report a new approach to highly electron-rich phosphines based on the use of imidazolin-2-ylidenamino groups directly attached to the phosphorus atom.<sup>1</sup> These imidazolin-2-ylidenaminophosphines (IAPs) depict excellent donor abilities, which exceed that of N-heterocyclic carbenes. Furthermore, the steric and electronic properties are easily varied owing to the facile and modular synthesis. With these features, IAPs provide new perspectives for the development of transition metal catalysts and for the activation of small molecules such as carbon dioxide (Figure 1).<sup>2</sup>



**Figure 1** CO<sub>2</sub> binding with electron-rich phosphines.

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## Nucleophilic Reactivity of a Nitride-Bridged di-Uranium(IV) Complex: CO<sub>2</sub> and CS<sub>2</sub> Functionalization

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Uranium nitrides have been identified as worthy candidates for stoichiometric and catalytic N-atom transfer reactions, small molecules transformation<sup>1</sup> and for advanced nuclear fuels. In recent years an increasing number of molecular nitride compounds of uranium has been synthesized.<sup>2</sup> Most of these nitride complexes contain a bridging nitride but the reactivity of such compounds has only been reported once for a nitride-bridged diuranium(V) complex.<sup>3</sup> N-C bond formation reactions are particularly attractive for the construction of value-added chemical compounds such as amino acids, pharmaceuticals or agrochemicals.<sup>4</sup> Synthetic methods using cheap and largely available feedstock such as carbon dioxide are particularly desirable.<sup>5</sup> However, N-C bond formation reactions from a nitride as nitrogen source and CO<sub>2</sub> as carbon source are rare and so far, described only for transition metals. Our group has recently shown that *tert*-butoxysiloxides are very effective ligands in supporting the reactivity of low valent f elements with small molecules.<sup>6,7</sup> In particular the reaction of [U(OSi(OtBu)<sub>3</sub>)<sub>3</sub>]<sub>2</sub> with azides provides a convenient route to nitride-bridged diuranium complexes.<sup>8</sup> Here we will report nucleophilic reactivity of the nitride-bridged diuranium(IV) complex Cs{(μ-N)[U(OSi(OtBu)<sub>3</sub>)<sub>3</sub>]<sub>2</sub>}. This complex reacts rapidly with CS<sub>2</sub> and CO<sub>2</sub> in ambient condition, affording N-C bond formation, cyanate and unprecedented dicarbamate products. The high reactivity with electrophiles contrasts with the inert character of nitride-bridged transition metal complexes. This reactivity, unprecedented in f element chemistry, will be discussed to highlight the potential of uranium nitrides in promoting N-C bond formation reactions.

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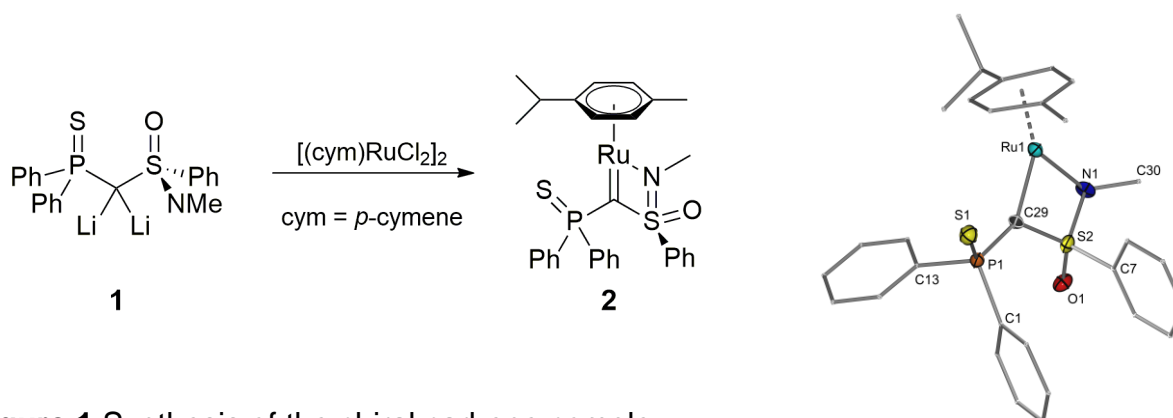
# Preparation and Isolation of a Chiral Methandiide and its Application as Cooperative Ligand in Bond Activation

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Transition metal carbene complexes have found a wide variety of applications in synthesis and catalysis. Thereby, the electronic and sterical properties of the substituent R significantly influence the nature and reactivity of the carbenic carbon atom  $M=CR_2$ . In this context, carbene complexes derived from methandiides have gained special interest, as they seem to contradict the typical Fischer and Schrock classification pattern showing a formal double donation of four electrons from the ligand to the metal.<sup>[1]</sup> However, so far only a small number of different geminal dianions has proven to be suitable ligands for the synthesis of transition metal carbene complexes.

Our group has focused on the synthesis of novel methandiides to enable the variation of the substituent R at the carbenic carbon atom. Recently, we succeeded in the synthesis of a new methandiide derived ruthenium carbene complex, which could be applied in the activation of a series of E–H bonds.<sup>[2]</sup> Here we present the synthesis of the enantiomerically pure chiral dilithiated species **1** (Figure 1). This methandiide gives way to chiral transition metal carbene complexes such as **2**.<sup>[3]</sup> These complexes may be applied in stereoselective bond activation reactions and catalysis.



**Figure 1** Synthesis of the chiral carbene complex.

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## Tuning of redox properties of phenoxo-bridged dinuclear copper models of oxygenases

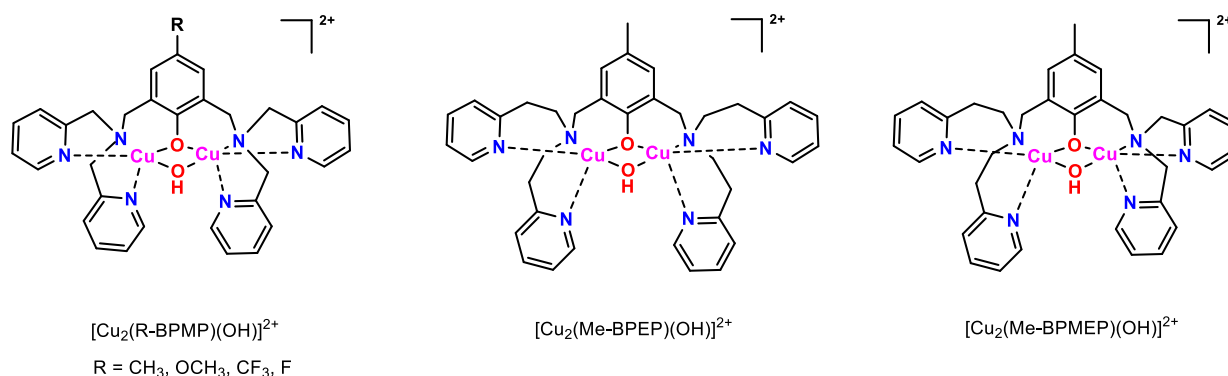
F. Gennarini,<sup>a,\*</sup> I. Lopez,<sup>a</sup> C. Belle,<sup>b</sup> H. Jamet,<sup>b</sup> R. David,<sup>b</sup> Y. Le Mest,<sup>a</sup>,  
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The galactose-oxidase (GAO) is a fungal copper enzyme that catalyzes the selective aerobic oxidation of primary alcohols to aldehydes with formation of hydrogen peroxide. In its active (oxidized) form, the enzyme displays a single copper (II) ion bound to a tyrosine radical, two histidine residues and a tyrosine anion. Oxidative formation of the free tyrosine radical is essential for substrate coordination and catalytic activity.<sup>1</sup> Many synthetic mononuclear models of GAO have been developed for which the copper (II) ion is directly linked to a phenolate moiety to mimic the active site of the protein in its reduced form.<sup>2</sup> We have investigated the spectroscopic and electrochemical properties of symmetrical and unsymmetrical dinuclear Cu complexes in which metal ions are bridged by phenolate and hydroxo groups.<sup>3</sup> Their reactivity towards organic substrates has been explored, demonstrating the influence of slight structural modifications on oxidation properties.



**Figure 1:** Symmetrical and unsymmetrical dinuclear phenoxo-bridged Cu complexes

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# Triggering the Oxidizing Power of Nitrous Oxide with Low Valent Cobalt Complexes

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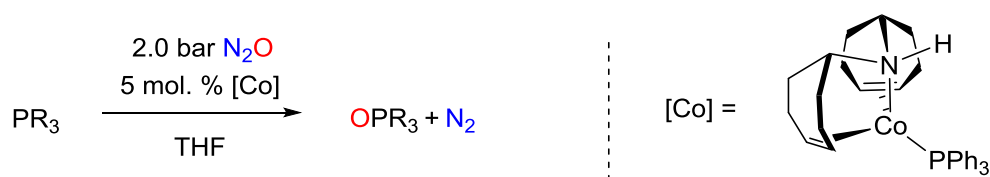
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Nitrous oxide (N<sub>2</sub>O) is industrially obtained as a by-product which has been recently identified as one of the largest global ozone depleting agents<sup>[1]</sup> and a greenhouse gas 300 times more powerful than CO<sub>2</sub>.<sup>[2]</sup> Its transformation to less harmful chemicals is of particular interest but very challenging,<sup>[4]</sup> since even if thermodynamically unstable, nitrous oxide is kinetically inert.<sup>[3]</sup> Phosphine oxides are an important class of compounds with several applications: ligands in metal-catalyzed cross-coupling reactions (secondary phosphine oxides, O=PHR<sub>2</sub>),<sup>[5]</sup> contact doping for silicon wafers and nanostructures, photoinitiators.<sup>[6]</sup> Traditional routes to their preparation (e.g. peroxides) are useful but present problems such as selectivity, functional group tolerance, complicated work-up and generation of chemical waste, and these route are not suitable for highly reactive or sensitive phosphines. The present work illustrates the use of zerovalent amino-olefin cobalt complexes in the selective oxidation of highly reactive phosphines using nitrous oxide as oxidant under mild reaction conditions.

**Figure 1**



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## Highly active Iron Catalyst for Ammonia Borane Dehydrocoupling

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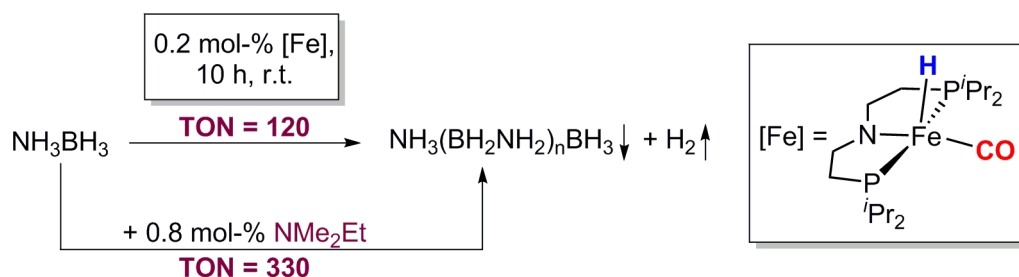
<sup>b</sup> Insitut für Anorganische und Analytische Chemie, Goethe-Universität, Max-von-Laue-Straße 7, 60438 Frankfurt am Main, Germany

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Ammonia borane (NH<sub>3</sub>BH<sub>3</sub>, AB) is a potential hydrogen storage material due to its high gravimetric H<sub>2</sub> content (19.6 wt-%).<sup>1</sup> The release of H<sub>2</sub> from AB requires elevated temperatures<sup>2</sup> or catalysis. Base metal catalysts generally suffer from low turnover numbers and –frequencies and require high catalyst loading (≈5 mol-%), elevated temperatures (≈60°C) or photochemical activation.<sup>3</sup>

Here we describe the use of FeH(CO)(PNP) (PNP = N(CH<sub>2</sub>CH<sub>2</sub>P<sup>i</sup>Pr<sub>2</sub>)<sub>2</sub>) for AB dehydrocoupling at room temperature to mainly linear polyaminoborane with unprecedented activity for a base metal catalyst. The catalyst deactivation mechanism was examined. Catalyst deactivation to Fe(BH<sub>4</sub>)H(CO)(HPNP) can be delayed upon addition of small amounts of an amine (0.8 mol-%) leading to a three times higher TON at the same reaction rates. Kinetic studies afford for a mechanistic model which will be discussed.<sup>4</sup>



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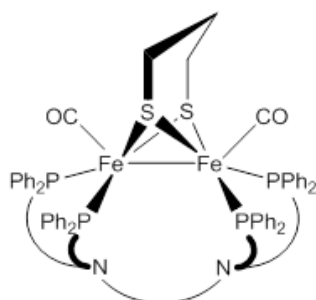
## Using tetraphosphine ligands for synthetic models of the active site of the [FeFe]-Hydrogenases

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In nature, [FeFe]-H<sub>2</sub>ases have the ability to catalyze, with a high efficiency, both hydrogen oxidation and production ( $2\text{H}^+ + 2\text{e}^- = \text{H}_2$ ). Inspired by the structure of the active site of these enzymes, many model systems were synthesized and studied focusing mainly on the nature of the ligands used. Indeed, electronic, steric and geometric effects related to ligand exhibit a decisive influence on the efficiency and catalytic mechanism for the production of H<sub>2</sub>. Furthermore, the presence of a protonation site on one of the ligands (amine cofactor) facilitates reduction of protons to form H<sub>2</sub>.

The main objective of this work is to prepare a diiron unit with a tetrabridging ligand to impose a particular geometry system and generate a cavity near the active site. We then propose to join four phosphines on the same ligand to give a discrete Fe<sub>2</sub>(tetraphosphine) species. At first, we will study the complexation of a simple tetraphosphine *N,N,N,N*-tetra(diphenylphosphinomethyl)-1,2-ethylenediamine with the diiron compound [Fe<sub>2</sub>(CO)<sub>6</sub>(pdt)] (pdt = 1,3-propanedithiolato) and then the possible application of the complex formed for the hydrogen production.



**Figure 1** Schematic representation of the expected complex [Fe<sub>2</sub>(tetraphosphine)(CO)<sub>2</sub>(pdt)].

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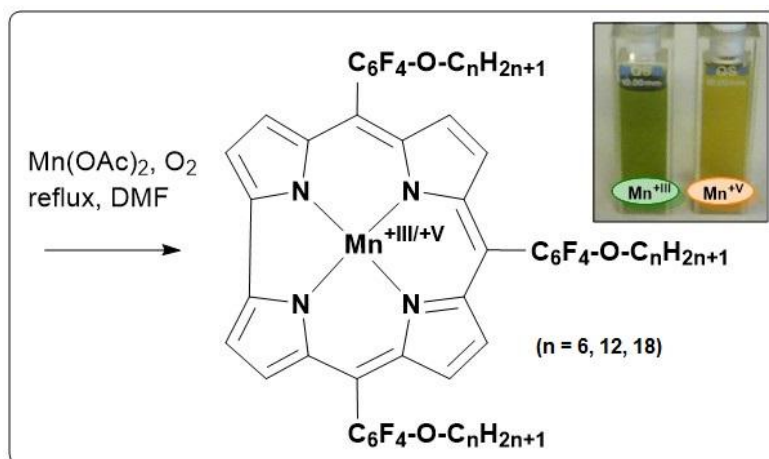
## Observation of high-valent manganese(V)-corrole complexes during metalation of *meso*-functionalized A<sub>3</sub>-corroles under aerobic conditions

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We report the synthesis of alkoxy-functionalized Mn(III)-A<sub>3</sub>-corrole and Mn(V) corrole complexes. Depending on the length of alkoxy-chain attached to the *meso*-tetrafluoropenyl moiety, the oxidation state of the central manganese ion could either be tuned to +III in case of O-C<sub>6</sub> or O-C<sub>12</sub> chains, or to +V in case of -O-C<sub>18</sub> chains. The Mn(V) corrole displays metal-centered redox chemistry in solution. Reduction with SnCl<sub>2</sub> or PPh<sub>3</sub> leads to the clean conversion yielding the corresponding Mn(III)-derivative.<sup>1-4</sup>



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## Effects of Ferric Ions on the Regioselectivity of Pictet-Spengler Reactions

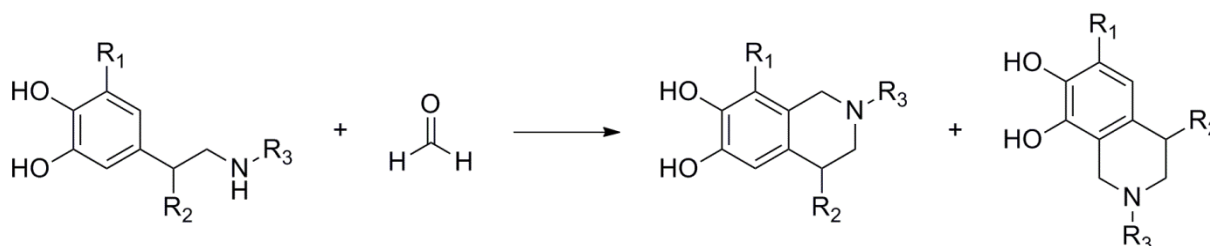
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Catecholamine is a widespread class of neurotransmitter in the central nervous system. Dopamine and adrenaline are naturally secreted *in vivo* but are also commonly used as medicines, especially in hospital or emergency circumstances. It is known that such catecholamines could decompose giving formaldehyde which can in a second step lead to a secondary reaction called the Pictet-Spengler Reaction (PSR)<sup>1</sup>.

The PSR consists in the condensation of formaldehyde with an arylalkylamine type compound leading to one or two bicyclic products depending on the substituents of such molecules. In the case of catecholamines, two regioisomers of tetrahydroisoquinolines (THIQ) can be obtained<sup>2</sup>.



**Figure 1** Formation of two regioisomers of tetrahydroisoquinolines through a Pictet-Spengler reaction

In a previous work<sup>3</sup>, it was shown that the kinetic and stereoselectivity of the PSR reaction was affected by the presence of transition metals, namely  $\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$ , two ions typically encountered *in vivo*. In the present work, we will discuss our work on the influence of the presence of ferric ions on the PSR regioselectivity with several catecholamines.

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## A High-Valent Iron(IV) Peroxo Core Derived from O<sub>2</sub>

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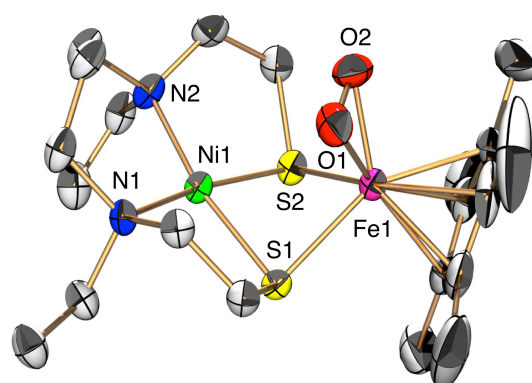
<sup>a</sup>Center for Small Molecule Energy, Kyushu University, Japan.

<sup>b</sup>Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, Japan.

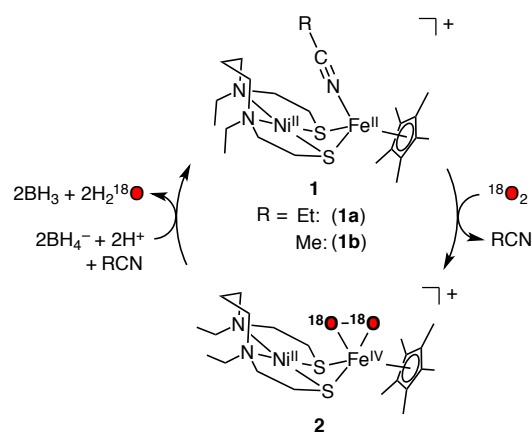
<sup>c</sup>International Institute for Carbon-Neutral Energy Research (WPI- I2CNER), Kyushu University, Japan.

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O<sub>2</sub>-tolerant [NiFe]hydrogenases ([NiFe]H<sub>2</sub>ases) are bifunctional enzymes that are able to act as both oxidases and H<sub>2</sub>ases. Although we previously reported an H<sub>2</sub>-oxidizing Ni<sup>II</sup>Fe<sup>II</sup> complex, it was not capable of also reducing O<sub>2</sub>.<sup>1</sup> We have now developed this catalyst into a mimic of O<sub>2</sub>-tolerant [NiFe]H<sub>2</sub>ases with the ability to reduce O<sub>2</sub>.<sup>2</sup> The solvent-coordinated Ni<sup>II</sup>Fe<sup>II</sup> complexes [Ni<sup>II</sup>LFe<sup>II</sup>(RCN)(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)]<sup>+</sup> (**1a**: R = Et, **1b**: R = Me) are reactive towards O<sub>2</sub> to form an O<sub>2</sub> adduct **2** (Figures 1 and 2). X-ray analysis demonstrated the formation of an Fe–O<sub>2</sub> complex, where the O<sub>2</sub> ligand is bound to the Fe center in an η<sup>2</sup>-fashion (Figure 1). The O–O bond length of 1.381(3) Å is within the region typical for side-on metal peroxo complexes and similar to that of biological side-on Fe<sup>III</sup> peroxo species. Complex **2** is capable of reducing the coordinated peroxide to H<sub>2</sub>O by supplying additional electrons and protons, as confirmed by an <sup>18</sup>O isotope-labeling experiment. Based on these results, we proposed a catalytic cycle for O<sub>2</sub> activation by our O<sub>2</sub>-tolerant [NiFe]H<sub>2</sub>ase model (Figure 2).



**Figure 1** Crystal structure of **2**.



**Figure 2** Activation of O<sub>2</sub> by **1**. The formation of H<sub>2</sub><sup>18</sup>O<sub>2</sub> was confirmed by an isotope-labeling experiment using <sup>18</sup>O<sub>2</sub>.

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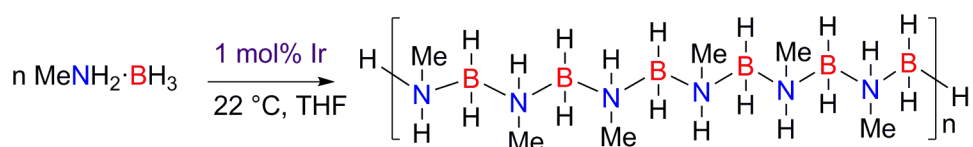
## Linear Diborazane Redistribution Reactions Relevant to the Catalytic Dehydrocoupling of Amine-Boranes

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Boron-nitrogen analogues of widely used carbon based compounds (ethane, olefins, aromatic hydrocarbons) and materials (graphene, polyolefins) have attracted much attention in the past decade due to their potential as hydrogen storage and transfer materials, precursors to ceramic thin films, and materials with piezoelectric properties.<sup>1</sup> Polyaminoboranes,  $[RHN-BH_2]_n$  (R = alkyl), isoelectronic analogues of linear polyolefins  $[RHC-CH_2]_n$ , one of the most important synthetic polymers today, are an exciting class of main-group polymers with potentially interesting properties. These polymers are accessible from a limited range of amine-borane adducts, facilitated by a homogeneous iridium catalyst under mild conditions,<sup>2</sup> but are also formed in the presence of other metal catalysts as well as in the absence of metal catalysts<sup>3</sup> *albeit in much lower molecular weight*. In an effort to better understand the mechanism(s) of the catalytic dehydrocoupling of amine-boranes we investigated the thermal and catalytic dehydrocoupling of various linear diborazane model complexes ( $R_2R'N-BH_2-RR'N-BH_3$  R, R' = H, Me).<sup>4</sup> Our mechanistic findings from these studies will be discussed.



**Figure 1** The Catalytic Dehydrocoupling of Methylamine-Borane

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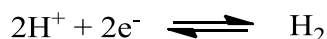
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## Study of the complex $[\text{Fe}_2(\text{CO})_4(\kappa^2\text{-dmpe})(\mu\text{-adt}^{\text{Bn}})]$ , model of the active site of $[\text{FeFe}]$ hydrogenases

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In the nature, there is a class of enzymes named hydrogenases, which has the capacity to efficiently catalyze both the production of dihydrogen and its oxidation in soft conditions according to the following reaction:



The crystallographic studies have revealed that the active site of  $[\text{FeFe}]$  hydrogenases features a diiron organometallic subsite in which one iron atom adopts a specific conformation<sup>1</sup>, called inverted or rotated and proposed as a structural key of the catalytic mechanism. In this context, many studies have been undertaken to reproduce this structure with synthetic models.

Our group has recently reported the complex  $[\text{Fe}_2(\text{CO})_4(\kappa^2\text{-dmpe})(\mu\text{-adt}^{\text{Bn}})]$  ( $\text{adt}^{\text{Bn}} = \{\text{SCH}_2\}_2\text{NCH}_2\text{C}_6\text{H}_5$ ,  $\text{dmpe} = (\text{CH}_3)_2\text{PCH}_2\text{CH}_2\text{P}(\text{CH}_3)_2$ ) which is described the first example of  $\text{Fe}^{\text{I}}\text{Fe}^{\text{I}}$  model with the rotated conformation<sup>2</sup>.

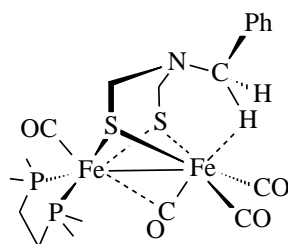


Figure 1

This unprecedented structure prompted us to look at its electrochemical behavior by voltammetry cyclic. The oxidatively induced reactivity of this complex towards various substrates ( $\text{CO}$ ,  $\text{P}(\text{OMe})_3$ ,  $\text{RNC}$ ) will be presented.

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# Synthesis of a Dinuclear Tantalum Tetrahydride via Hydrogenolysis of Tantalum Hydrocarbyl Complexes

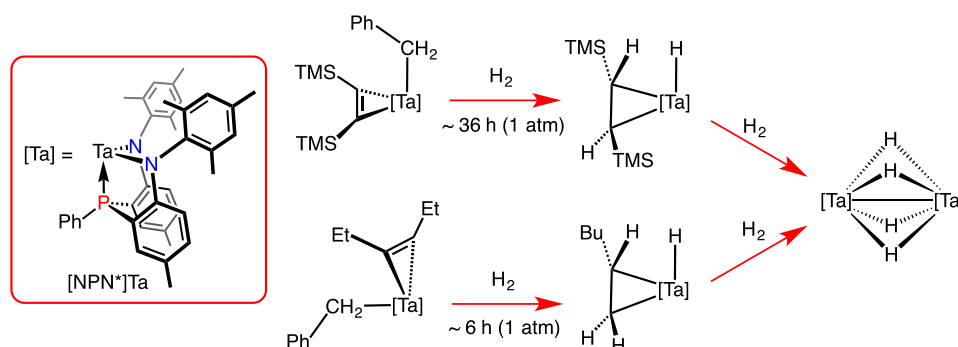
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The preparation of high value organo-nitrogen compounds via the reaction of metal-coordinated dinitrogen ( $N_2$ ) ligands with organic substrates is an ambitious goal for many synthetic chemists. Unfortunately, the synthesis of metal- $N_2$  complexes generally requires the use of strong reducing agents,<sup>1</sup> which complicates their use alongside electrophilic reagents in catalytic systems.<sup>2</sup> Several groups have investigated the use of dinuclear group 5 polyhydrides as reductants for  $N_2$ .<sup>3</sup> Previous work in our group resulted in the synthesis of the reactive dinitrogen complex  $([NPN^{Si}]Ta)_2(\mu-H)_2(\mu-\eta^2:\eta^1-N_2)$ , generated by exposing the dinuclear Ta tetrahydride complex  $([NPN^{Si}]Ta)_2(\mu-H)_4$  to  $N_2$ ; the formally Ta(IV) tetrahydride is generated by reacting the corresponding  $[NPN^{Si}]Ta$  trimethyl complex with  $H_2$ , a relatively mild reducing agent.<sup>4</sup>

In an effort to further develop this hydride route for  $N_2$  reduction, we present the synthesis of a Ta tetrahydride complex supported by a new *ortho*-phenylene linked diamidophosphine ligand set,  $[NPN^*]$ . We also detail the reactivity of several  $[NPN^*]$  tantalum alkyl and alkyne complexes with  $H_2$ .<sup>5</sup> While the resulting dinuclear tetrahydride does not react with  $N_2$  under ambient conditions, we have studied the hydrogenolysis process, and isolated and characterized several intermediates formed therein.



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## Catalysis of CO<sub>2</sub> and H<sup>+</sup> Reduction by a Low Valent Fe-Porphyrine With a Distal Superstructure: Electrochemical and Spectroscopic Investigation of The Mechanism.

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The current goal is to address the global carbon imbalance by exploring ways of recycling CO<sub>2</sub> to formate, formic acid or CO a potential feedstock in the classical Fischer Tropsch synthesis to generate fuels. Savéant et. al. has popularised the use of Fe porphyrins for this catalytic reaction with impressive efficiency.<sup>1</sup> In our pursuit, we have explored porphyrins with distal superstructures having H-bonding pocket for this important conversion of CO<sub>2</sub> to CO under homogeneous conditions both chemically and electrochemically. Absorption spectroscopy suggests the involvement of Fe(0) porphyrin as the active form for CO<sub>2</sub> activation consistent with the electrochemical data. Resonance Raman (rR) spectroscopic data suggests the involvement of at least two intermediates during the course of the conversion. These intermediates are only stable at cryogenic temperatures. The resonance Raman data of intermediate I, which could only be stabilized at -95 °C, indicates that it is a Fe(II)-CO<sub>2</sub><sup>2-</sup> adduct and is followed by another intermediate II at -80 °C where the bound CO<sub>2</sub> in intermediate I is protonated to form a Fe(II)-COOH species. While the initial protonation can be achieved using weak proton sources like MeOH and PhOH, the facile heterolytic cleavage of the C-OH bond in intermediate II requires strong acids like PTSA.<sup>2</sup>

Another important cathodic reaction relevant to energy is proton reduction to hydrogen,<sup>3</sup> which can be utilized as carbon free source of fuel. The Fe-porphyrin catalyzes HER in its formal Fe(0) state which is a well-known phenomenon. Whereas, an iron porphyrin complex bearing four distal triazoles catalyze HER in its formal Fe(I) state, in both organic and aqueous mediums which lowers the overpotential of HER by iron porphyrin by 50% not only aid the kinetics but also alter the thermodynamics of the reaction.

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## Novel Dinuclear Nickel *N*-heterocyclic Carbene Complexes for the Activation of Small Molecules

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Cooperative effects<sup>1</sup> in di- and multinuclear metal systems play a key role in many enzymatic reactions as for example in urease, hydrogenase, nitrogenase and methane monooxygenases.<sup>2</sup> Such cooperative effects can lead to a more efficient, selective transformation and conformational control of substrates, to a higher local reagent concentration at the metal centers, a stabilization of reactive species and complex intermediates.<sup>3</sup> Additionally, they can facilitate accessibility of bimolecular reaction pathways and be used to overcome entropic control.<sup>3</sup> Organometallic catalysis might conceptually benefit from exploiting these functional principles in a bioinspired approach, and cooperative effects in bimetallic systems have indeed been successfully applied in, e.g., epoxidation reactions<sup>4</sup> and olefin hydrogenations.<sup>5</sup>

We have been working on the development of various dinuclear metal complexes based on bridging pyrazole-based ligands and their use for the cooperative transformation of small molecules, such as water oxidation and dioxygen activation.<sup>6</sup> Here the syntheses and characterization of novel dinuclear nickel complexes based on compartmental pyrazole/NHC hybrid ligands will be presented, and first reactivity experiments towards the cooperative activation of small molecules will be discussed.

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## Electronic effect of ligand on high-spin $\mu$ -oxodioxodiiron(IV)

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We have reported that upon reaction of  $\mu$ -oxodiiquaquadiiron(III) (**1**) (Figure 1) stabilized by 6-hpa with  $\text{H}_2\text{O}_2$ ,  $\mu$ -oxo- $\mu$ -peroxodiiron(III) (**1a**) (Figure 2) is formed in the beginning of reaction, and rapidly converted to high-spin  $\mu$ -oxodioxodiiron(IV) (**1b**) (Figure 2) via O-O bond scission.<sup>1</sup> On the basis of the detailed kinetic studies, DFT studies, and catalytic alkane oxidation, we proposed a two-step mechanism where **1b** undergoes syn-to-anti transformation to form anti-dioxo form as the real active species that cleaves a strong C-H bond. We further synthesized  $\mu$ -oxodiiquaquadiiron(III) (**2**) with 6-hpa<sup>R</sup> (R = 4-OMe-3,5-Me<sub>2</sub>) (Figure 1) where four pendant pyridyl groups are substituted by electron donating groups, 3,5-dimethyl-4-methoxy. Here, we report electronic effect on the formation and reactivity of high-spin  $\mu$ -oxodioxodiiron(IV) on the basis of spectroscopic characterization and substrate oxidation.

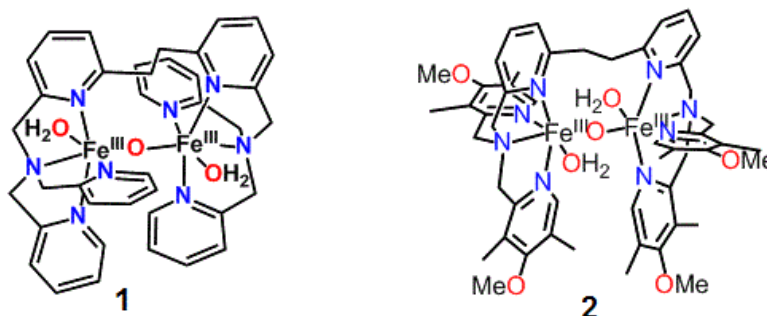


Figure 1 Chemical structures of **1** and **2**

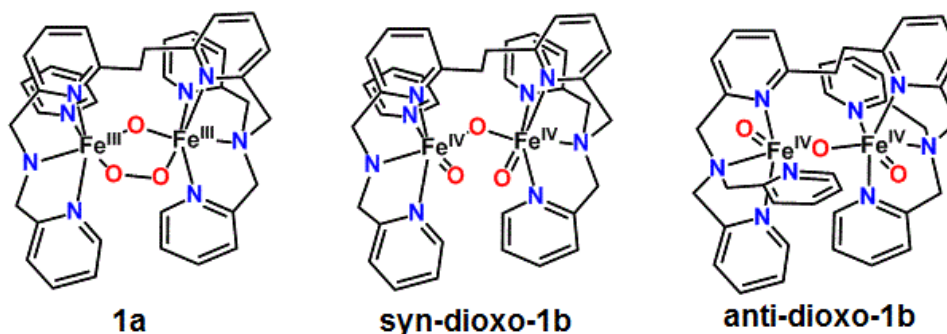


Figure 2 Chemical structures of **1a** and **1b**

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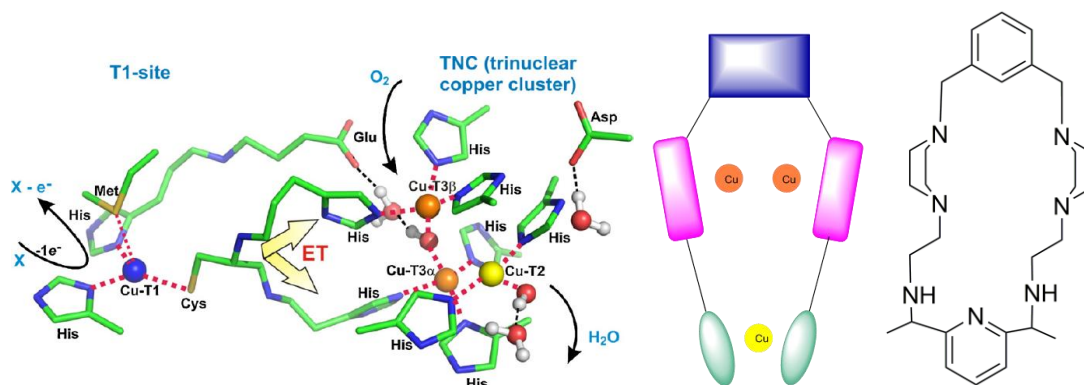
## Oxygen reduction: a biomimetic approach

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Fuel cells are electrochemical devices capable of producing electric energy from the chemical energy generated through the oxidation of hydrogen and the reduction of molecular oxygen, avoiding the production of polluting byproducts. Both the reactions are catalysed with platinum-based catalysts, making fuel cells technology quite expensive for large scale diffusion. Nature is capable of catalysing the oxygen reduction reaction using metalloenzymes with earth-abundant elements; multicopper oxidases couple the oxidation of organic substrates with four-electron reduction of molecular oxygen<sup>1</sup> (Figure 1, left).



**Figure 1** General scheme of multicopper oxidases<sup>1</sup> (left) and schematic model of a biomimetic complex of the trinuclear copper cluster (center), with the synthesized ligand (right).

Biomimetic catalysts are developed taking inspiration from the trinuclear copper cluster of multicopper oxidases, mimicking its T3/T2 motif capable of efficiently reducing molecular oxygen (Figure 1, center). On the way to the tricopper system (Figure 1, right), a bis-piperazinic binucleating ligand has been synthesized and characterized by NMR techniques. Its complexation of Cu<sup>I</sup> and Cu<sup>II</sup> and the redox properties of the complexes will be reported in relation to the oxygen reduction reaction.

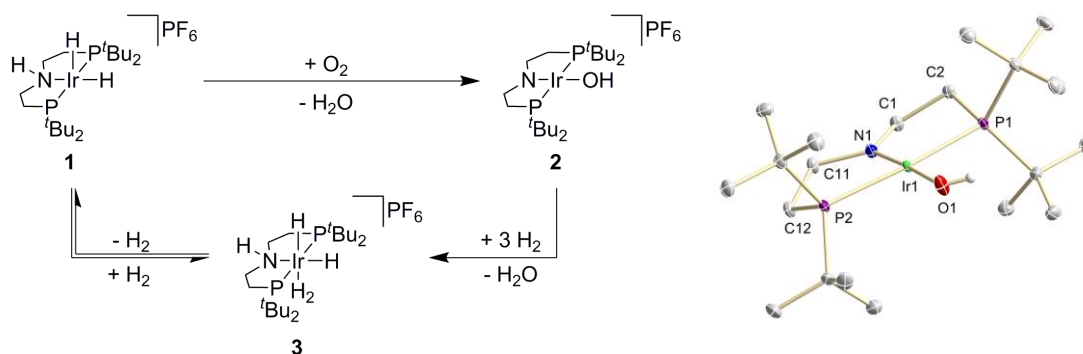
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# Oxygen Reduction with a Bifunctional Iridium Dihydride Complex

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The oxygen reduction reaction (ORR), while of great interest in regards to sustainable catalysis and energy conversion processes, imposes particular challenges: the delivery of four protons, which is addressed in catalyst design by acidic groups in proximity of the O<sub>2</sub> reducing site, as well as four electrons for reduction of O<sub>2</sub>, which need to be provided by multiple redox centers.<sup>1-3</sup> The Rauchfuss group reported an Ir<sup>III</sup> complex capable of catalyzing the ORR via a bimetallic mechanism within a synthetic cycle without change of the formal oxidation state of iridium by storing two electrons in a metal-hydride bond.<sup>3</sup>



**Figure 1** left: synthetic ORR cycle, right: molecular structure of **2** (C-H hydrogen atoms and anion omitted for clarity. ORTEP plot with ellipsoids at 50% probability).

Inspired by this, we examined whether a single metal center ORR-catalyst can be designed by storage of the electrons within two covalent metal-hydride bonds: [Ir<sup>III</sup>(H)<sub>2</sub>{NH(CH<sub>2</sub>CH<sub>2</sub>P<sup>t</sup>Bu<sub>2</sub>)<sub>2</sub>}]PF<sub>6</sub> **1**, using a bifunctional meridial, tridentate ('pincer') ligand, splits dioxygen with formation of water and the highly unusual square planar hydroxo complex [Ir<sup>III</sup>(OH){N(CH<sub>2</sub>CH<sub>2</sub>P<sup>t</sup>Bu<sub>2</sub>)<sub>2</sub>}]PF<sub>6</sub> **2**. Heterolysis of H<sub>2</sub> completes the synthetic cycle. A mechanism, which is first order in **1** as well as O<sub>2</sub>, is proposed based on kinetic studies, isotope labeling experiments and computations.<sup>4</sup>

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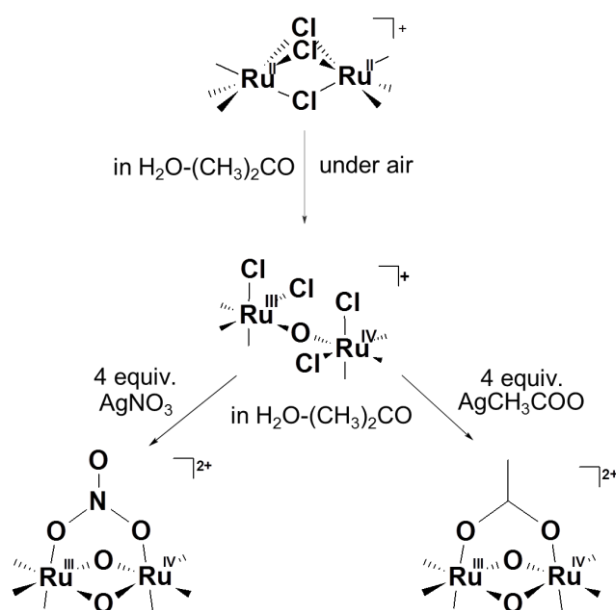


# Mixed-Valence Dinuclear Complexes of Ru(III)-Ru(IV), Triply Bridged by Two Oxido and One Nitrato or Acetato Ligands

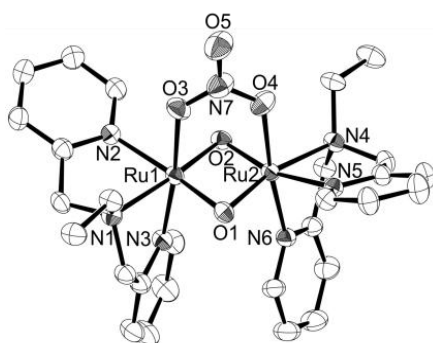
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We have been investigating syntheses of various dinuclear ruthenium frameworks to develop multi-center and multi-electron reaction systems for conversion of inert small molecules such as H<sub>2</sub>O.<sup>1,2</sup> Singly oxido-bridged diruthenium complexes bearing ethylbis(2-pyridylmethyl)amine (ebpma), in a mixed-valence state of Ru(III)-Ru(IV)  $[\{Ru^{III,IV}X_2(ebpma)\}_2(\mu-O)]^+$  (X = Cl, Br), were synthesized from the Ru(II)-Ru(II) triply halogeno-bridged dimer,  $[\{Ru^{II,II}(ebpma)\}_2(\mu-X)_3]^+$ , *via* oxidation under air (**Scheme 1**). Their catalytic activity for water oxidation has been reported.<sup>2</sup>



**Scheme 1** Synthesis of Diruthenium Complexes



**Figure 1** ORTEP Drawing of Nitrato Complex

An alternative type of diruthenium complexes having doubly oxido-bridged core in the Ru(III)-Ru(IV) mixed-valence state,  $[\{Ru^{III,IV}(ebpma)\}_2(\mu-O)_2(\mu-L)]^{2+}$  (L = NO<sub>3</sub><sup>-</sup>; Nitrato complex (**Figure 1**), CH<sub>3</sub>COO<sup>-</sup>; Acetato complex), were isolated from reactions of the singly oxido-bridged complex with 4 equimolar amounts of AgL in water-acetone. Nitrato and Acetato complexes show multi-step redox processes (involving proton transfers in aqueous solutions) in electrochemical measurements. We will report their properties and reactivity toward acid, as well as syntheses, structure and electrochemical and spectroscopic properties in organic and aqueous solutions.

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## The role of spin states in the catalytic mechanism of intra- and extradiol cleavage of catechols

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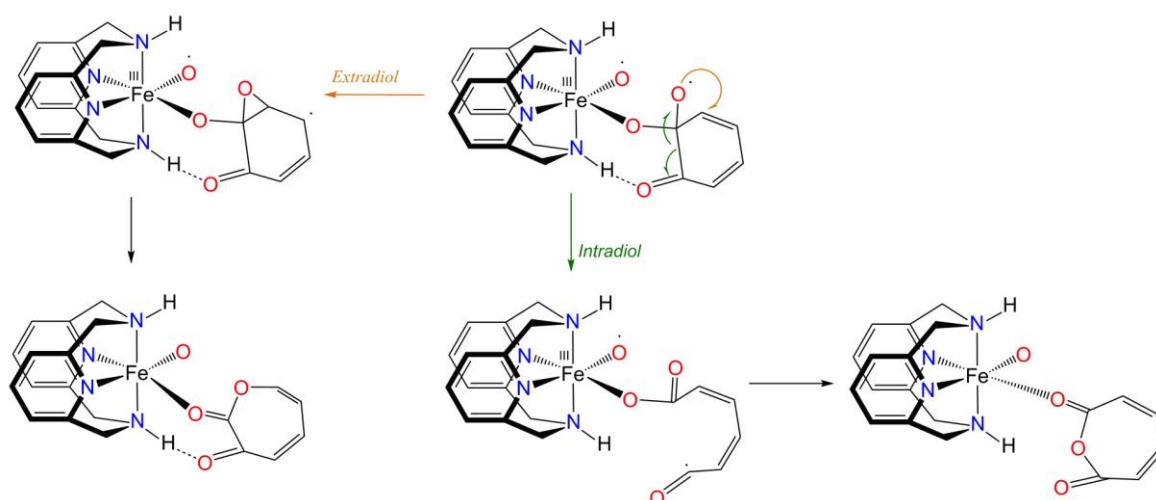
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Iron-dependent enzymes and biomimetic iron complexes can catalyze the ring cleavage of very inert, aromatic compounds. The mechanism of these transformations and the factors that lead either to extradiol or intradiol cleavage are not fully understood. By using Density Functional Theory we have elucidated<sup>1</sup> the mechanism of the catalytic cycle for two biomimetic complexes, and explained the difference in the experimentally obtained products.<sup>2</sup>



**Scheme 1.** Reaction scheme for competing extra- and intradiol pathways

It is also shown that, although the sextet state is the ground state at the beginning and at the very end of the catalytic cycle, the quartet state governs the reaction and determines the product distribution.

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## Valorization of Small Molecules

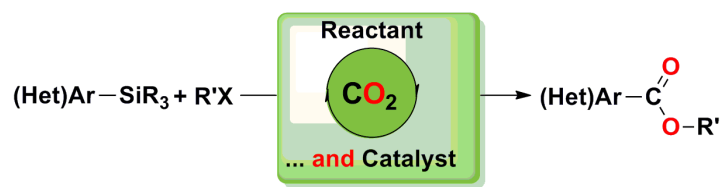
### From Mechanism to New Reactions

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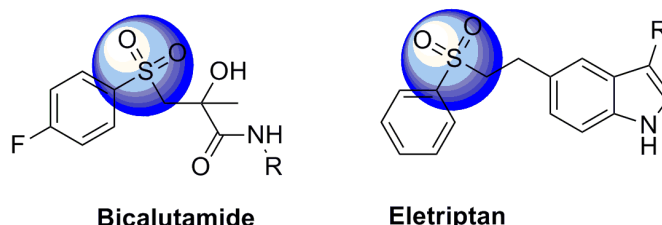
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Small molecules, such as CO<sub>2</sub>, SO<sub>2</sub>, or nitrous oxides NO<sub>x</sub> are generally regarded as pollutants and wastes. However, recent developments made it possible to think about small molecules as building blocks for organic synthesis, especially using CO<sub>2</sub>. As C–C bonds are universal in organic chemistry, the formation of these bonds from CO<sub>2</sub> is of key interest. We herein report a novel reaction of unactivated organosilanes with CO<sub>2</sub> to form esters and a polyester material for the first time, where CO<sub>2</sub> plays both the role of the reactant and a catalyst.<sup>1</sup>



**Figure 1** CO<sub>2</sub> acts both as reactant and catalyst in the formation of esters from heteroarylsilanes as demonstrated by DFT calculations.

Understanding this reaction and the unique catalytic role of CO<sub>2</sub> using DFT calculations enabled the development of a novel transformation involving SO<sub>2</sub>. For the first time, SO<sub>2</sub> is incorporated in a one-pot one-step process to form aryl alkyl sulfones, a major class of compounds in the organic chemistry with wide applications in synthesis, from pharmaceuticals to natural products.<sup>2</sup>



**Figure 2** Examples of pharmaceuticals bearing the sulfonyl group

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## Polyoxometalate assisted electroreduction of CO<sub>2</sub>

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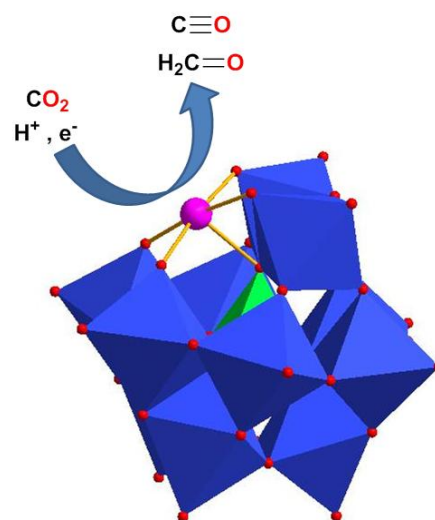
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The capture and transformation of carbon dioxide is a major environmental and economical issue to respond both to its greenhouse effect and to the depletion of fossil fuels reserves. The reduction of CO<sub>2</sub> into valuable fuels has thus been addressed photo- and electrochemically.<sup>1</sup> The direct electro-assisted reduction of CO<sub>2</sub> on a bare electrode is a kinetically slow process characterized by large overpotentials. Thus, a variety of molecular catalysts have been tested, and, in the case of iron-porphyrin electro-catalysts, investigations of the reduction mechanism have pointed out the efficiency of the proton coupled electron transfer (PCET) mechanism.<sup>2</sup>

Transition metal substituted polyoxometalates (TMSPs) fulfill several of the relevant criteria for being competitive CO<sub>2</sub> electro-catalysts: (i) (multi)vacant polyoxometalates (POMs) act as all-inorganic ligands towards extra transition metal cations, that in turn could fix CO<sub>2</sub>; (ii) many POMs display reversible redox processes sensitive to the presence of protons and have been used as electro-catalysts for the multiproton-multielectron reduction of NO<sub>3</sub><sup>-</sup> to NH<sub>3</sub>,<sup>3</sup> or for hydrogen production; (iii) *albeit* weak bases, POMs could promote the formation of hydrogen bond networks at the vicinity of the CO<sub>2</sub> coordination center to favor PCET.

We will present our recent results on Co-substituted-POM assisted electroreduction of CO<sub>2</sub> to CO and HCHO, its seldom observed 4-electron reduced product.<sup>4</sup>



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## New D- $\pi$ -A-Conjugated metal-free Organic Sensitizers Based on $\alpha$ -Pyranylidene Donors for Dye-Sensitized Solar Cells

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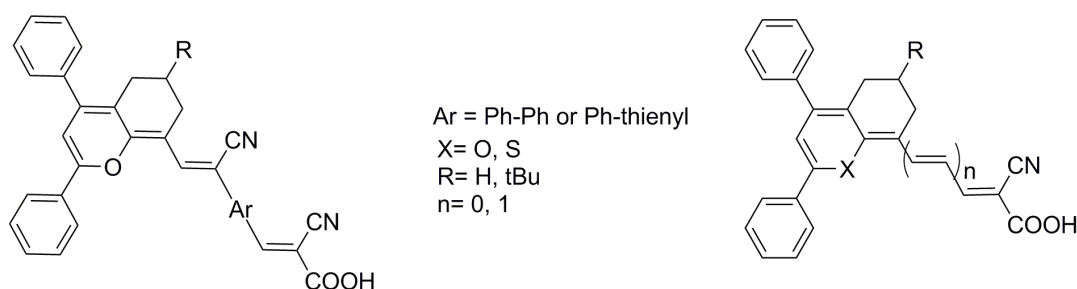
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Dye-sensitized solar cells (DSSCs) have received significant attention for converting solar energy into electrical energy, and to become an alternative to conventional silicon based solar cells, due to their low cost, ease of manufacturing and relatively high power conversion efficiency.<sup>1</sup> Organic dyes, as an alternative to the noble Ru complexes sensitizers, exhibit many advantages as low cost and structural design flexibility.<sup>2</sup> The donor- $\pi$ -acceptor (D- $\pi$ -A) type of organic sensitizer is the most commonly used framework to improve the light harvesting.

Since interesting photovoltaic results were obtained with pyranylidene donors,<sup>3</sup> we have designed and synthesized a series of new  $\alpha$ -chalcogenomethylenepyrene donor-based chromophores (D), with aromatic or non aromatic spacers. The acceptor group (A) was the commonly used cyanoacetic acid. Electrochemical and optical properties will be presented, as well as photovoltaic measurements.



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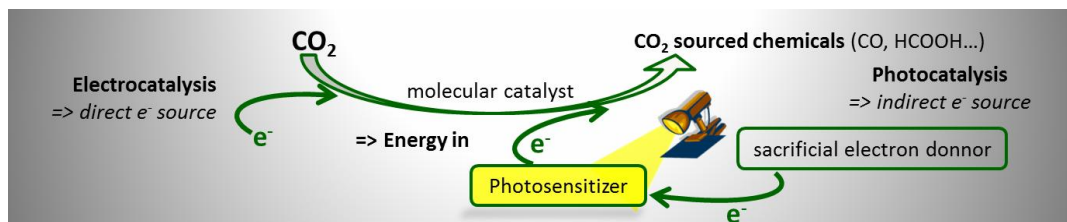
## Photo and electrocatalytic activation of CO<sub>2</sub> with molecular catalysts based on Mn carbonyl coordination complexes

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Carbon dioxide Capture and Utilization (CCU) is increasingly gaining attention as CO<sub>2</sub> can be regarded as a precursor for synthesis of a wide range of value added commodities such as useful chemical raw materials, energy rich products or materials that do not rely on petrochemical source. However, the inherent chemical stability of CO<sub>2</sub> poses a challenge to its efficient transformation. For instance, its conversion by a reduction reaction requires energy, a catalyst and high yield. Among various methodologies, ElectroCatalytic and PhotoCatalytic Reduction (ECR and PCR) have promise.



It is well known that electrochemically-driven CO<sub>2</sub> reduction can be accomplished on bulk metallic cathodes but their use have their downsides. Using molecular catalysts is an alternative. Several transition metal (e.g. Re, Ru, Os, Ni ...) coordination complexes, able to activate the CO<sub>2</sub> ECR, have been described since the 80s, nonetheless few molecular electrocatalysts based on non-noble metals have been reported. As solar light is a direct carbon-free energy source, research on CO<sub>2</sub> PCR with molecular catalysts has also been growing. Nevertheless efficient molecular based photocatalytic systems are scarce.

At present, much of our work is focused on developing new Mn based molecular catalysts and understanding their CO<sub>2</sub> reduction catalytic properties.<sup>1</sup> In both PCR and ECR, pathways often differ in their mechanisms. Gaining a better understanding of catalytic mechanisms is essential in improving and advancing this field of catalytic activation of CO<sub>2</sub> reduction. Herein we present an overview of our latest studies of ECR and PCR of CO<sub>2</sub>.

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## Mechanism and reactivity with dioxygen of Ni-containing carbon monoxide dehydrogenase

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and V. Fourmond<sup>a\*</sup>

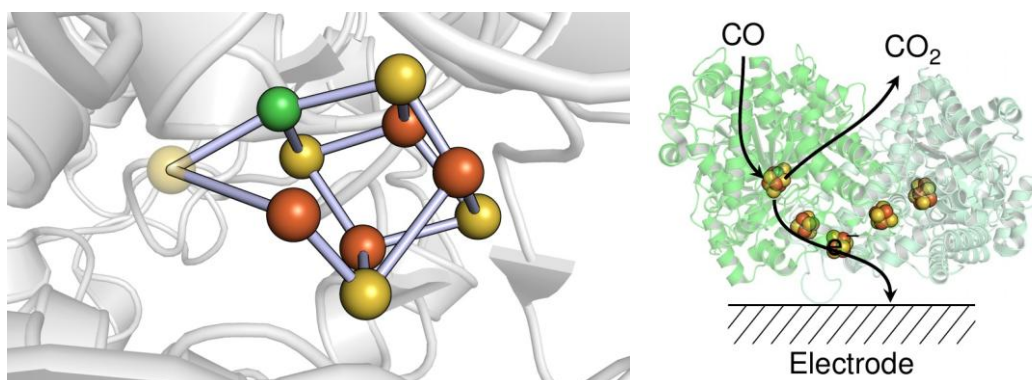
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In the context of the depletion of fossil fuel resources and accumulation of CO<sub>2</sub> in the atmosphere, the reduction of CO<sub>2</sub> to carbonaceous fuels appears as a solution to both problems. However, CO<sub>2</sub> is extremely stable, and man-made catalysts for its reduction are both slow and too demanding in terms of energy. In contrast, natural catalysts such as carbon monoxide dehydrogenase (CODH) are both fast and energy-efficient. CODH catalyzes the reduction for CO<sub>2</sub> to CO at a unique NiFe<sub>4</sub>S<sub>4</sub> active site; it is believed it could be used to build biotechnological devices for CO<sub>2</sub> reduction if it were less O<sub>2</sub>-sensitive.

We used protein film voltammetry<sup>1</sup>, and electrochemical technique in which an enzyme is adsorbed onto an electrode in a configuration in which electron transfer is direct, to probe the mechanism and reactivity with O<sub>2</sub> of two distinct CODHs, CODH II from *Carboxydotherrnus hydrogenoformans*<sup>2</sup> and the previously uncharacterized *Desulfovibrio vulgaris* CODH<sup>3</sup>. We show that they greatly differ in terms of reactivity with O<sub>2</sub>, which opens the possibility of finding O<sub>2</sub>-resistant CO dehydrogenases for biotechnological uses<sup>4</sup>.



**Figure 1** Left: active site of the CODH (green Nickel, red Iron, yellow Sulfur). Right schematic view of protein film voltammetry.

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## Photoelectrochemical analysis of metal complexes in solution

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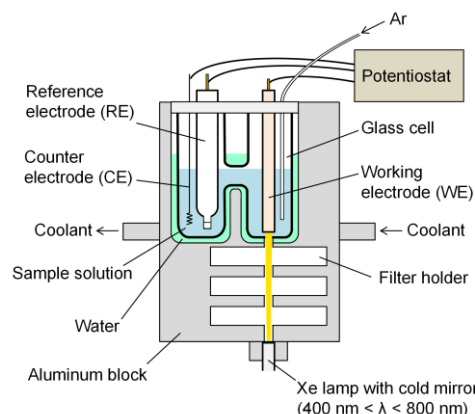
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The development of efficient catalysts for reactions involving multi-electron transfer is essential to construct the solar-energy conversion system. The analysis of the electrochemical response of the catalyst under photoirradiation should be a powerful method to understand the detailed reaction mechanisms, which provides concrete strategies to design efficient catalysts. In this study, we developed a novel method for the electrochemical measurement of solution under photoirradiation.<sup>1,2</sup>

The electrochemical measurements were performed with a custom-made photoelectrochemical cell (Figure 1). The electrochemical behaviour of ferrocene, which exhibits reversible redox behaviour and is photochemically inactive, was investigated. Although the reversible redox wave was observed in the dark, a sigmoidal-shaped voltammogram was obtained under photoirradiation. This result suggests that the photoirradiation may have generated the convection, and it affected the electrochemical responses. To overcome this problem, we performed electrochemical measurements under several conditions and succeeded to suppress these unfavourable responses by adopting well-established electrochemical techniques including thin layer voltammetry.<sup>1</sup>

As a further extension of our study, the electrochemical analysis of photoreactions of metal complexes in solution was also achieved.<sup>2</sup> The results pave a new way to analyse various catalytic reactions under photoirradiation.



**Figure 1** Schematic illustration of a custom-made photoelectrochemical cell.

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# A structural and functional [NiFe] hydrogenase mimic with unprecedented Ni-centered reactivity

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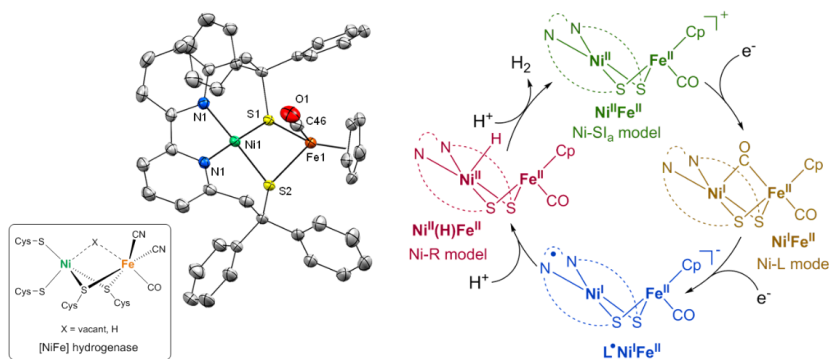
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Hydrogenases catalyze the reversible reduction of protons into dihydrogen at high rates and close to the thermodynamic equilibrium. For this reason, they certainly remain among the most investigated enzymes, reflecting the current interest in sustainable fuel production and energy storage.<sup>1</sup> The active site of [NiFe] hydrogenase features an original organometallic NiFe complex,

whose H<sub>2</sub>-evolving activity occurs at the Ni site, the Fe-center simply modulating the electronic properties of Ni. Surprisingly, none of the heterodinuclear NiFe mimics reported so far reproduces this Ni-centered reactivity.<sup>2</sup>

Here, we report on the first structural and functional NiFe

mimic (Figure 1) displaying Ni-centered chemistry and, in parallel, the best performances for electrocatalytic H<sub>2</sub> production for such bio-inspired systems ( $k_{\text{cat}} = 2.5 \pm 0.3 \cdot 10^4 \text{ M}^{-1} \cdot \text{s}^{-1}$ ). Two intermediate species have been generated, mimicking the Ni-L and Ni-R states of the enzyme. The full mechanism of electrocatalytic H<sub>2</sub> production by Ni<sup>II</sup>Fe<sup>II</sup> has been elucidated (Figure 1), and compared to the proposed mechanism for [NiFe] H<sub>2</sub>ase.



**Figure 1.** Molecular structure of the obtained NiFe mimic (Ni<sup>II</sup>Fe<sup>II</sup> state, left), with the corresponding catalytic cycle for H<sub>2</sub> evolution (right).

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## O<sub>2</sub> reduction reaction at a carbon-nanotube-supported mononuclear copper(phenolato) *Galactose oxidase* mimic

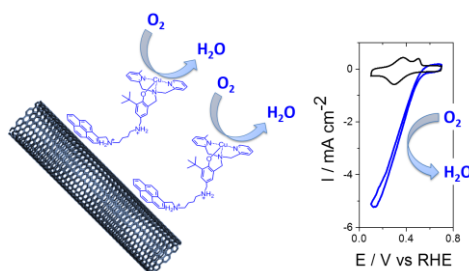
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The research of efficient electrocatalysts for oxygen reduction reaction (ORR) has increased with the demand for new cathodic electrode materials employing non-noble metals for application in fuel cell technologies. In Nature, this catalytic reaction is, in particular, managed by copper metalloenzymes<sup>1</sup>. Immobilized on electrode, multicopper oxidases perform the four-electron reduction of dioxygen by using a 3 + 1 arrangement of copper centers<sup>2</sup>, while mononuclear enzymes, such as *Galactose oxidase* (GOx), catalyzes the two-electron reduction of dioxygen into hydrogen peroxide.<sup>3</sup>

We have designed an original copper-phenolate complex, mimicking the active center of galactose oxidase, featuring a pyrene group.<sup>4</sup> Supramolecular pi-stacking allows its efficient and soft immobilization at the surface of a Multi-Walled Carbon Nanotube (MWCNT) electrode. This MWCNT-supported galactose oxidase model exhibits a four-proton-four electron electrocatalytic activity towards oxygen reduction at a redox potential of 0.60 V vs. RHE at pH 5.



**Figure 1** (a) Scheme of the copper(phenolato) pyrene complex immobilized onto MWCNT electrode. (b) Electrocatalytic behaviour towards O<sub>2</sub> reduction.

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## Synthesis and Characterization of [NiFe] Complexes as Biomimetic Models of Hydrogenases

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Hydrogenases are enzymes that play an important role in the metabolism of bacteria, as these enzymes catalyze the reversible oxidation of dihydrogen.<sup>1</sup> Three types of hydrogenases are known and are classified based on the metal in the active site: [NiFe], [FeFe] and [Fe] hydrogenases. From these three classes [NiFe] hydrogenase is the most studied one. Hydrogenases have gained the attention of synthetic chemists in the past decades, since dihydrogen gas may be used as a sustainable source of green energy. In order to produce dihydrogen gas and apply it in fuel cells, new catalysts can be developed by using biomimetic and functional models of the hydrogenase active site.<sup>2</sup>

The aim of our study is the synthesis of novel ligands with different flexibility and electronic properties to be used in the synthesis of [NiFe] compounds as hydrogenase models. New tetradentate S<sub>2</sub>Se<sub>2</sub> ligands have been synthesized and nickel complexes of these ligands have been prepared and characterized. By using these nickel complexes, new [NiFe] complexes have been synthesized and characterized. The electrochemical properties and electrocatalytic activity of these heteronuclear complexes will be discussed as functional models for [NiFeSe] hydrogenase.

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## The Role of the Local Proton Source in Electrocatalytic CO<sub>2</sub> Reduction by Mn(bpy-R)(CO)<sub>3</sub>Br Complexes

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The sustainability and encouraging performance displayed by the electrochemical conversion of carbon dioxide into value-added chemicals, which is mediated by transition metal complexes, has attracted growing interest in recent years.<sup>1,2</sup> Many organometallic catalysts have been found to selectively reduce CO<sub>2</sub> into two-electron products, such as CO and HCOOH, in non-aqueous systems. However, most of the reported homogeneous catalysts for CO<sub>2</sub> electrochemical reduction are selective towards CO formation, whereas only a few of them give formate in high yields. Novel chlorotricarbonyl Re(I) complexes containing a highly fluorescent group, covalently attached to common polypyridyl ligands, show promising electro- and photocatalytic performances.<sup>3</sup> Nevertheless abundant and cheaper transition metals are commercially more attractive with respect to catalysts based on rare precious transition metals. In this perspective, the use of Group VI transition metals (Cr, Mo, W) with polypyridyl ligands as potential electrocatalysts for CO<sub>2</sub> reduction is particularly attractive.<sup>4</sup> The availability of local proton sources is known to greatly enhance the selectivity and the redox catalytic activity for CO<sub>2</sub> reduction to CO. Novel polypyridyl Mn(I) catalysts (e.g. [Mn(dhbpy)(CO)<sub>3</sub>Br] (dhbpy = 4-phenyl 6-(1,3-dihydroxybenzen-2-yl)-2,2'-bipyridine) containing two acidic OH groups in proximity of the purported metal binding site for CO<sub>2</sub> redox catalysis show enhanced catalytic activity and clear mechanism pathway.<sup>5</sup>

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## Cobalt tetra and penta-aza-macrocyclic complexes as efficient catalysts for photoinduced hydrogen production in water

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Solar light-induced water-splitting into hydrogen (H<sub>2</sub>) and oxygen is a very attractive way to produce H<sub>2</sub>, one of the most promising clean and renewable fuels for the future.<sup>1</sup> During the past decade, numerous efficient molecular homogeneous photocatalytic systems have been reported based on the association of a photosensitizer (PS), a hydrogen evolving catalyst (Cat), and a sacrificial electron donor.<sup>2,3</sup> Only a few of them are active in fully aqueous solution – a highly desirable condition for their subsequent coupling to water oxidation systems in photo-electrochemical water-splitting devices. This communication will present our recent results on efficient photocatalytic systems for hydrogen production in water, which use cobalt tetra- and penta-aza-macrocyclic derivatives,

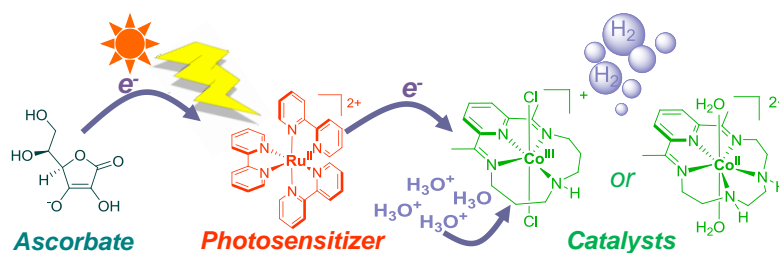


Figure 1

[Co(CR)(X)<sub>2</sub>]<sup>n+</sup> as Cat and [Ru(bpy)<sub>3</sub>]<sup>2+</sup> or quantum dot as PS, in presence of the ascorbate/ascorbic acid couple as the electron source and proton source respectively (Figure 1).<sup>4-6</sup> We report also the quantitative electro-generation of the low-valent Co<sup>I</sup> species in CH<sub>3</sub>CN, their reactivity toward protons reduction and a theoretical investigation of their electronic structures.<sup>5</sup>

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# Water Oxidation by Dinuclear Molecular Catalyst

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Visible light-induced water splitting involving four electrons oxidation of water is one of the most crucial steps and difficult process in both natural and artificial photosynthesis. In this context, it is important to develop new sustainable energy schemes based on highly efficient and robust water oxidation catalysts.

The molecular water oxidation catalysts based on transition metal complexes (Mn, Ru, Ir, Co,Cu,Fe) both in homogeneous and heterogeneous phase have the potential to tune their properties by modifying the ligands in the coordination sphere of the metallic site and therefore, they offer a wide range of possibilities to improve their catalytic activity and robustness.

In particular, dinuclear ruthenium complexes became very attractive since the first water oxidation catalytic activity of the blue dimer<sup>1</sup> was reported. Since then, many developments have been done based on this type of complexes<sup>2</sup>, however many challenges still remain, including high speed catalysis and robustness

In this work, we present the synthesis, characterization and water oxidation activity of ligand modified dinuclear ruthenium catalyst and also the mechanistic studies for the formation of the O-O bond.

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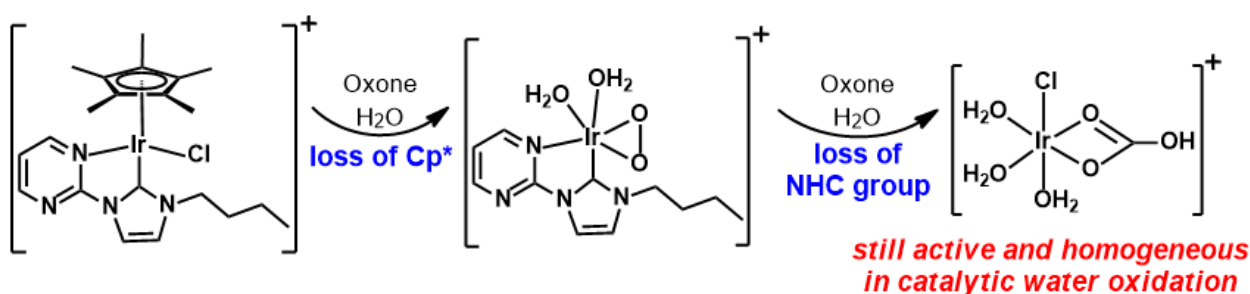
## Transformation of a Cp\*-Iridium Carbene Catalyst in Water Oxidation Using Oxone as Primary Oxidant

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Fundamental understanding of the real catalytic species in water oxidation is a major knowledge gap that must be overcome in order to develop artificial water splitting systems and produce chemical fuels from solar energy. In an effort to analyze the transformation and catalytic resting state of  $[\text{Cp}^*\text{Ir}(\text{pmNHC})\text{Cl}]\text{Cl}$  (pmNHC=1-(2-pyrimidyl)-3-n-butyl)imidazol-2-ylidene,  $\text{Cp}^*$ =pentamethylcyclopentadienyl) in water oxidation using potassium peroxymonosulfate (Oxone) as primary oxidant, we found the precatalyst evolved into blue solution when a small amount of Oxone was added while further oxidation yield purple solution. These species have been proven to be homogeneous and they remain active in water oxidation.  $^1\text{H}$  NMR profiles and MALDI-MS data suggested a rapid oxidation of the  $\text{Cp}^*$  ligand to acetone, formic and acetic acid.  $^1\text{H}$  NMR, TEM-EDX as well as MALDI-MS data indicated a continuous degradation of pyrimidyl, butyl and NHC groups. Possible structures for components in the blue species and catalytic resting purple species are proposed based on these results along with XANES and  $^{17}\text{O}$  NMR investigation.



**Figure 1** Transformation of Ir-complex in water oxidation with Oxone

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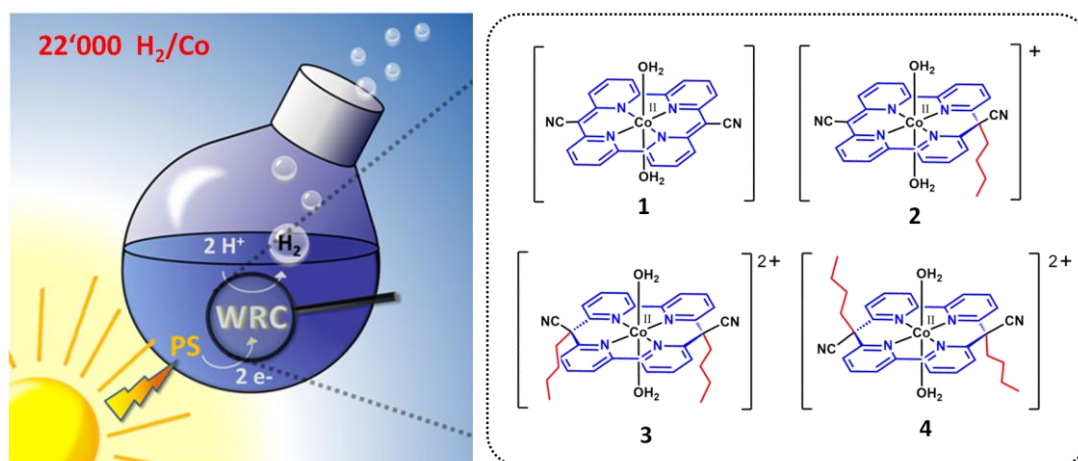


# Cobalt Complexes Based on Bipyridine Macrocycles: Properties and Photocatalytic Proton Reduction

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We present a series of novel cobalt(II) complexes that are highly efficient H<sup>+</sup> reducing catalysts for photocatalytic hydrogen evolution in water (Fig. 1).<sup>1</sup> The ligand framework is bipyridine-based as in our previous work.<sup>2</sup> But this time it features a macrocyclic scaffold and is thus called “pyrphyrin” due to the similarity to porphyrins.<sup>3</sup> We report on the synthesis and full characterization of non-alkylated, mono- and dialkylated Co(II)-pyrphyrin complexes. The physico-chemical properties of complexes **1–4** substantially depend on their degree of alkylation. Furthermore, the performance of **1–4** in aqueous photocatalytic H<sub>2</sub> production is presented. Although there are considerable differences in the rate and total amount of hydrogen evolution, all complexes **1–4** showed distinct H<sup>+</sup> reducing activity. With [Ru(bpy)<sub>3</sub>]<sup>2+</sup> as photosensitizer and TCEP/NaHasc as sacrificial electron donor and shuttle,<sup>4</sup> turnover numbers (TONs, H<sub>2</sub>/Co) up to 22'000 were achieved.



**Figure 1** Flask: Photocatalytic hydrogen evolution with a water reduction catalyst (WRC) and a photosensitizer (PS). Right: Series of non-, mono- and dialkylated Co(II)-pyrphyrin complexes. Highlighted in blue: Pyrphyrin scaffold.

<sup>1</sup> E. Joliat, S. Schnidrig, B. Probst, C. Bachmann, B. Spingler, K. K. Baldrige, F. von Rohr, A. Schilling, R. Alberto, *Dalton Trans.*, **2016**, 45, 1737.

<sup>2</sup> C. Bachmann, M. Guttentag, B. Spingler, R. Alberto, *Inorg. Chem.*, **2013**, 52, 6055.

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<sup>4</sup> C. Bachmann, B. Probst, M. Guttentag, R. Alberto, *Chem. Commun.*, **2014**, 50, 6737.

## Synthesis, Characterization and Reactivity of a Series of Co(Mabiq) Complexes

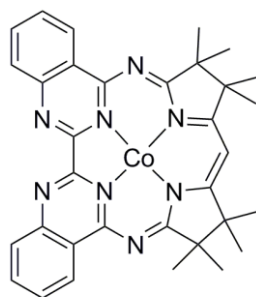
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Solar fuel production is vital for the future energy supply and storage, as renewable energy sources, such as sunlight and wind are not available on demand. Hydrogen production via water splitting is a promising approach to effectively store the energy provided by our environment. In the quest for cheap, efficient and sustainable systems for catalytic hydrogen production, macrocyclic Cobalt complexes have emerged as encouraging system over the past years.<sup>1-2</sup>

Against this background we will present the synthesis and characterization of a series of cobalt complexes, coordinated by a redox-active macrocyclic ligand (Mabiq), which supports formal metal valences from 0 to +3. The formally Co(III), Co(II), Co(I) and another low-valent compound have been successfully isolated and were characterized using different spectroscopic methods as well as magnetic susceptibility studies. With the low-valent complexes in hand reactivity studies with respect to hydrogen production as well as activation of other small molecules have been carried out.



Co(Mabiq)

**Figure 1** Structure of the low-valent Co(I) complex.

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## Multicopper Oxidases immobilized on functionalized carbon nanomaterials and their integration in hydrogen/air enzymatic fuel cells

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Carbon nanotube (CNT)-based electrodes combine many advantages for enzyme wiring: excellent conductivity, high specific surface, versatile functionalization techniques and strong interactions with redox enzymes [1]. CNTs can be modified with functional groups to achieve enzyme attachment and favor electron tunneling. We have especially investigated the covalent and non-covalent functionalization of CNTs for the rational immobilization of metalloenzymes such as multicopper oxidases to promote direct electron transfer between the copper active site and the electrode [2-4]. Efficient and stable direct bioelectrocatalytic reduction of O<sub>2</sub> was achieved at low overpotentials, demonstrating that CNT modification by functional groups represents a versatile and soft technique to achieve copper enzyme wiring on CNT sidewalls. These nanostructured bioelectrodes were combined with nickel-iron hydrogenase-based bioanodes in hydrogen/air enzymatic fuel cells based on gas-diffusion electrodes [5].

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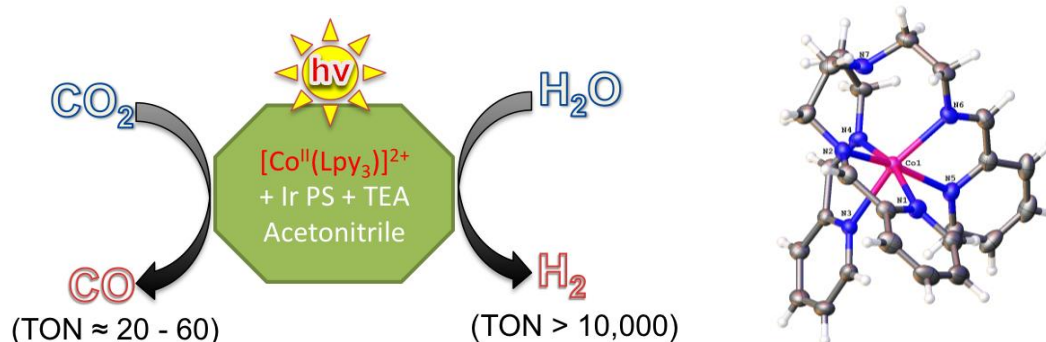
## Visible Light-driven Solar Fuels Generation with Cobalt(II) Tripodal Iminopyridine Complexes

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The cobalt(II) complexes  $[\text{Co}^{\text{II}}(\text{Lpy}_3)](\text{ClO}_4)_2$  ( $\text{Lpy}_3 = \text{tris-[4-(2-pyridyl)-3-azabut-3-enyl]}$  amine (**1**) and *cis,cis*-1,3,5-tris(pyridine-2-carboxaldimino)cyclohexane (**2**)) catalyze the light-driven ( $\lambda > 420\text{nm}$ ) reduction of water in the presence of  $[\text{Ir}^{\text{III}}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{dmbpy})](\text{PF}_6)$  (where  $\text{dF}(\text{CF}_3)\text{ppy} = 2\text{-(2,4-difluorophenyl)-5-trifluoromethylpyridine}$  anion and  $\text{dmbpy} = 4,4'\text{-dimethyl-butyl-2,2'-dipyridyl}$ ) as photosensitizer (PS) and triethylamine (TEA) as the sacrificial donor (D). Catalytic activity of the two complexes has been compared and was found to be limited by the stability of the PS. Similar  $\text{H}_2$  turnover number ( $\text{TON} > 10,000$ ) has been obtained for both catalysts in aqueous acetonitrile (10%  $\text{H}_2\text{O}$ ) with additional PS provided, whereas  $\text{H}_2$  is generated at a faster rate when **2** is used in place of **1**. The effects of solvent, proton sources and PS concentration on the catalytic activity have also been investigated. The photoreduction of carbon dioxide ( $\text{CO}_2$ ) to carbon monoxide ( $\text{CO}$ ) using the complexes is also discussed.



**Figure 1** Light-driven  $\text{H}_2\text{O}$  and  $\text{CO}_2$  reduction on  $[\text{Co}^{\text{II}}(\text{Lpy}_3)](\text{ClO}_4)_2$  catalysts; ORTEP drawing of **1**.

**Acknowledgement:** The work described in this paper is financially supported the Hong Kong University Grants Committee Early Career Scheme (HKIEd 28300014) and General Research Fund (HKIEd 18300715). HKIEd is also acknowledged for the Dean's Research Fund (04024).

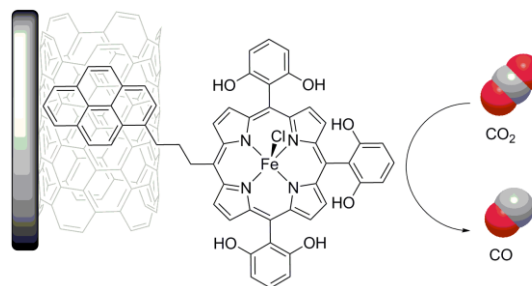
## NONCOVALENT IMMOBILIZATION OF AN IRON BASED MOLECULAR CATALYST ON CARBON ELECTRODES FOR SELECTIVE CO<sub>2</sub>-TO-CO CONVERSION IN WATER

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The transformation of carbon dioxide (CO<sub>2</sub>) to fuels and commodity chemicals is one of the most important contemporary energy and environmental challenge. The electrochemical reduction of CO<sub>2</sub> to carbon monoxide (CO) is a potentially useful step towards this



transformation. Recently, a number of molecular catalysts have been developed for this particular reaction. Among these, iron porphyrin-based complexes bearing pendant hydroxyl groups exhibit the highest catalytic activity and specificity towards the formation of CO<sup>1,2</sup>. Transferring the catalytic activity of these systems from homogeneous solution to the surface of a carbon electrode, via attachment of the molecular catalyst would be an essential step towards the conception of applied devices for the reduction of CO<sub>2</sub>. It is however highly challenging and still few studies report such supported catalysis.

A pyrene-appended iron triphenyl porphyrin bearing six pendant OH groups on the phenyl rings was synthesized, immobilized on carbon nanotubes via non covalent interactions, and further deposited on glassy carbon (see Scheme above). X-ray photoelectron spectroscopy and electrochemistry confirm catalyst immobilization, and bulk electrolysis demonstrates the remarkable stability and selectivity of the system.

The modified electrodes exhibit well-defined, reversible, electrochemical signals, characteristic of an immobilized redox system. When performing bulk electrolysis with these modified electrodes, selective and rapid catalysis of the reduction of CO<sub>2</sub> into CO occurs in pure water (pH 7) with an overpotential of 500 mV. Catalysis could be sustained for hours without loss of activity and selectivity, and high turnover numbers were obtained. The behaviour of these catalytic electrodes will be discussed.

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# Light Driven Hydrogen Atom Release from a Ruthenium Complex

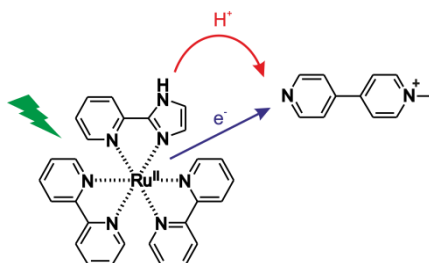
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Hydrogen atom transfer (HAT) is important in enzymes and in synthetic organic chemistry, for example for hydrogenations of unsaturated compounds such as ketones and imines. It would be attractive to use visible light as an energy resource to perform HAT reactions under mild reaction conditions. We therefore explored the (formal) HAT chemistry of photo-excited  $[\text{Ru}(\text{bpy})_2\text{pyimH}]^{2+}$  (bpy = 2,2'-bipyridine; pyimH = 2-(2'-pyridyl)imidazole).<sup>1,2</sup> Upon photo-excitation into the long living  $^3\text{MLCT}$  state, the formal bond dissociation free energy of the imidazole N-H bond drops by 50 kcal mol<sup>-1</sup> reaching a value comparable to typical ground state hydrogen atom donors on metal hydride basis.<sup>3,4</sup> Photo-induced formal HAT to monoquat (*N*-methyl-4,4'-bipyridinium) was investigated. Three different regimes for  $^3\text{MLCT}$  quenching were observed depending on the pH of the solution.



**Figure 1** Light driven formal hydrogen atom transfer from  $[\text{Ru}(\text{bpy})_2\text{pyimH}]^{2+}$  to *N*-methyl-4,4'-bipyridinium.

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# Coordination compounds of the earth abundant metals as novel sensitizer for DSSC

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One of the effective ways of the alternative energy utilization is direct conversion of the solar irradiation to electric power. The most promising type of photovoltaic convertor is dye-sensitized solar cell (DSSC) [1]. The wide search of the photosensitizers with suitable photochemical properties represents one of the most important directions of DSSC improvement, and its objective is the preparation of compounds capable of efficient light absorption in a wide spectral range and providing electron injection upon excitation to the conduction band (CB) of the supporting semiconductor. Until now the low efficiency of solar radiation conversion and high price of Ru-based sensitizers make the production of DSSC economically unfavorable compared to other types of solar cells. The replacement of the Ru(II) in the sensitizer by one of the earth abundant metals (Fe(II), Cu(I)) seems promising for the purpose of decreasing the final cost of the DSSC. Recently, we have synthesized and studied new sensitizers - Fe and Cu coordination compounds of the Schiff base ligand, bis-azomethine of 2,6-diformyl-4-methyl-phenol (see Figure). We will present the results of experimental physicochemical study and quantum chemical modeling of ligand and complexes and the discussion of observations and insights into the photochemical properties of dyes and their function in the solar cells.

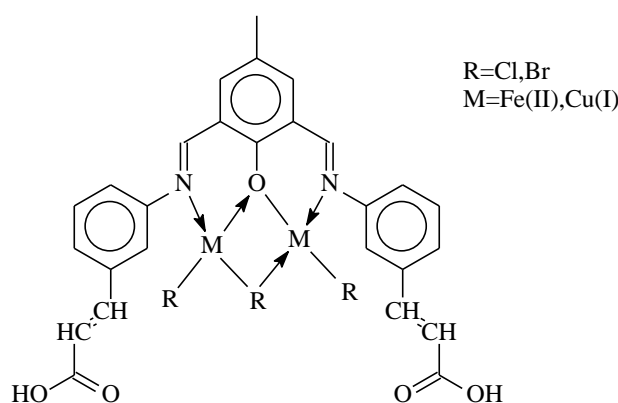


Figure 1

Work was founded by the basic part of internal SFedU grant, project № 213.01-2014/005

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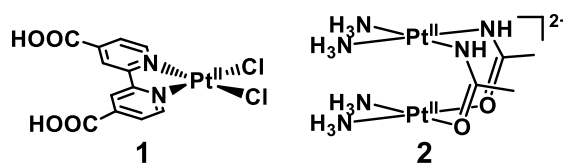
# Platinum(II)-Catalyzed Hydrogen Evolution via Formation of Hydridodiplatinum(II,III) Intermediates.

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Hydrogen energy has attracted great attention as an alternative energy to fossil fuels, because it does not emit greenhouse gases upon combustion. In this context, one of our interests over the past years has been the study of Pt(II)-based H<sub>2</sub>-evolving catalysts. Among these studies, it was proposed that hydrogen evolution reaction (HER) catalyzed by dinuclear Pt(II) complexes proceeds via the proton-coupled electron transfer (PCET) pathway (i.e. Pt(II)<sub>2</sub> + H<sup>+</sup> + e<sup>-</sup> → Pt(II)(III)-H). However, there has been no experimental evidence of that mechanism. In this study, we have carried out the kinetics studies on Pt(II)-based molecular catalysis for HER by MV<sup>+•</sup> (one-electron-reduced form of methylviologen). The decay of MV<sup>+•</sup> in the presence of mononuclear and dinuclear Pt(II) complexes was monitored spectrophotometrically inside a glovebox, where MV<sup>+•</sup> was electrochemically prepared as previously described.<sup>1</sup> Very interestingly, the bleaching rate of MV<sup>+•</sup> shows a second-order dependence on the concentration of **1**, consistent with our previous suggestion that the HER catalyzed by

**1** proceeds via formation of a dinuclear Pt(II)(III)-H intermediate. The results of our kinetic studies on a diplatinum(II) catalyst (**2**) will be also presented.



**Figure1** Platinum(II) complexes

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## Affecting the Catalytic Activity of the Known [Ru(tpy)(bpy)(OH<sub>2</sub>)]<sup>2+</sup> Complex in Water Oxidation by Utilization of a Hangman Ligand

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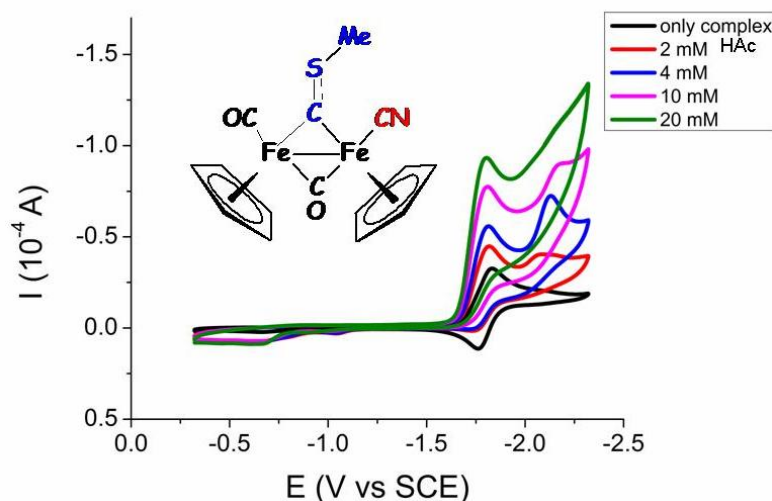
Major fuel sources for the world's energy supply are carbon-based (gas, oil, coal), with an associated emission of climate-damaging carbon dioxide.<sup>[1-3]</sup> Therefore, we need a change from a fossil fuels based energy system to a system of renewable energy. The solution of these energy problems is the development of clean and sustainable fuel technologies. One possible pathway is the splitting of water into hydrogen and oxygen to drive a hydrogen based society. The oxidation of water into protons and dioxygen by a proton-coupled electron transfer (PCET) is the critical - high-energetic - half reaction of this process<sup>[4]</sup>. [Ru(tpy)(bpy)(OH<sub>2</sub>)]<sup>2+</sup> (bpy = 2,2'-bipyridine, tpy = 2,2';6',2''-terpyridine) is the archetype of many known single-site ruthenium complexes used for catalytic water oxidation. Its efficiency is likely influenced by installing a proton-donor/acceptor functionality in proximity to the catalytic site because the reaction mechanism is believed to occur by nucleophilic attack of a water molecule on a high-valent metal-oxo species assisted by hydrogen-bonding interactions. Thus, a new metal complex based on the „Hangman“ motive was synthesized and characterized.<sup>[5]</sup> The known [Ru(tpy)(bpy)(OH<sub>2</sub>)]<sup>2+</sup>-unit is connected to a xanthene backbone with a carboxylic acid-function in proximity to the catalytic site. The proof of the catalytic activity and mechanistic investigations are the target of current work.

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## Beyond the iron-dithiolate mimics paradigm: diiron complexes with $\mu$ -carbyne ligands as electrocatalyst for proton reduction

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Increasing attention to sustainability has produced an exponentially grown interest toward iron mediated reactions. In this field, diiron complexes can play a distinctive role due to the presence of two adjacent iron centres.<sup>1</sup> Herein we report on diiron complexes containing bridging hydrocarbyl ligands (and also Cp and CO), as potential electrocatalysts for H<sub>2</sub> production. The aim is to demonstrate that the search for efficient, iron based, catalysts for H<sub>2</sub> production, is not necessarily restricted in the realm of iron dithiolates model systems, which closely resemble natural [Fe-Fe]-H<sub>2</sub> ases.



**Figure 1** Cyclic voltammograms of the diiron complex with increasing amounts of HOAc.

We found that in a few cases the electrocatalytic properties are comparable to those of many common dithiolate systems.<sup>2</sup> As an example, in figure 1 it is reported the CV of a diiron  $\mu$ -thiocarbyne complex ( $2 \times 10^{-3}$  M), recorded in CH<sub>3</sub>CN (glassy carbon electrode,  $0.05 \text{ V s}^{-1}$ ), in the presence of increasing concentrations of acetic acid, which is the usual way to demonstrate electrocatalytic ability for H<sub>2</sub> evolution.<sup>3</sup>

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## Electronic structure and optical properties calculation of Zn-porphyrin with N-annulated Perylene adsorbed on $\text{Ti}_{16}\text{O}_{34}\text{H}_4$ for Dye-Sensitized Solar Cell applications

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The current work scrutinizes the chemical behavior of a set of promissory DSSC, the dye Zn-porphyrins with N-annulated Perylene,<sup>1</sup> as electron donor, **WW3m-WW8m**, inside the more important steps on the performance of the solar cell photoexcitation, electron injection and dye regeneration.<sup>2</sup> In this direction, we have found through TD-DFT framework that the most important electronic transition in **WW3m** present the orbital contribution centered in the central ring porphyrin, while in **WW6m**, the HOMO is localized in the perylene, and the LUMO in the anchoring group. On the other hand, we studied two adsorbed modes on the  $\text{Ti}_{16}\text{O}_{34}\text{H}_4$  cluster model. Adsorption energies show that the bidentate is more stable than the monodentate coordination mode. This is due to the narrow band gap determined through the density of states (DOS), and to the high charge transfer since the porphyrin to the  $\text{TiO}_2$  model obtained by NPA charges, highlighting that **WW6m@TiO<sub>2</sub>**, who exhibit the most high overall efficiency of the solar cell, present the narrowest band gap (1.53 eV). In other context, the dye regeneration was studied through of the free energy, associated,  $\Delta G_{\text{regen}}$ , the values are between -6.61 to -6.93 eV for **WW3m@TiO<sub>2</sub>-WW8m@TiO<sub>2</sub>** which shows that this step is similar in all the porphyrins.

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## A photoactive Ru(II) centre intimately linked by bridging cyanide to a [FeFe]-hydrogenase subsite analogue

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The maturase HydF accommodates the synthetic diiron subsite precursor  $[\text{pdt-Fe}_2(\text{CO})_4(\text{CN})_2]^{2-}$  **A** by formation of a bridging cyanide link to an iron of the protein-bound  $\{4\text{Fe}4\text{S}\}$ -cubane cluster<sup>1</sup>, surprisingly this appears to involve linkage isomerism of the CN. Certain borane Lewis acids will also bind through the cyanide to this same diiron dithiolate unit<sup>2</sup>, substantially modifying its oxidation and protonation chemistry. This prompted us to explore the possibility of directly linking a light-harvesting Ru(II) antenna **B** to the synthetic subsite analogue *via* formation of a Ru-N≡C-Fe bridge. It was achieved by the route shown in figure 1 which allowed the isolation of the red crystalline *zwitterionic* complex **C**. Crystallographic analysis revealed the structure shown in figure 1, which established the retention of the carbon-bound Fe of the precursor subsite. The (electro)chemistry and photophysics of **C** together with its potential for photogeneration of dihydrogen<sup>3</sup> will be presented.

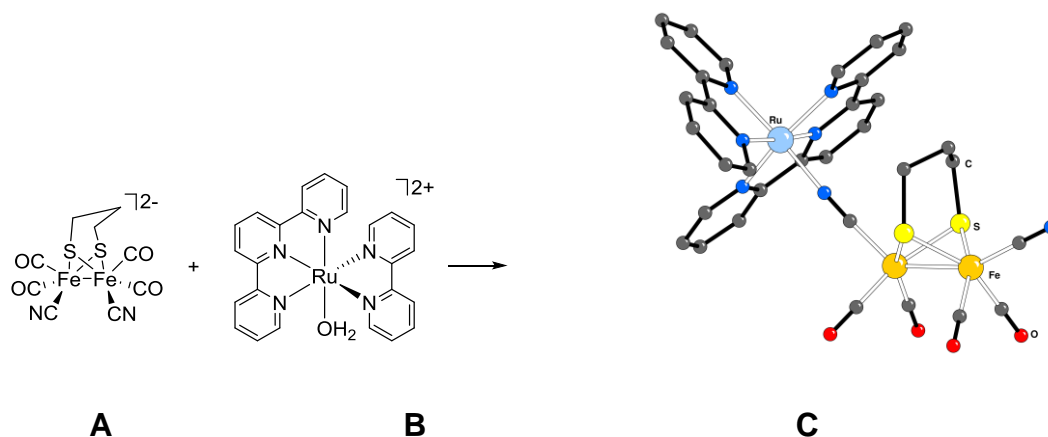


Figure 1 Synthesis and X-Ray structure of  $\text{pdt-Fe}_2(\text{CO})_4(\text{CN})_2\text{Ru}(\text{trpy})(\text{bpy})$

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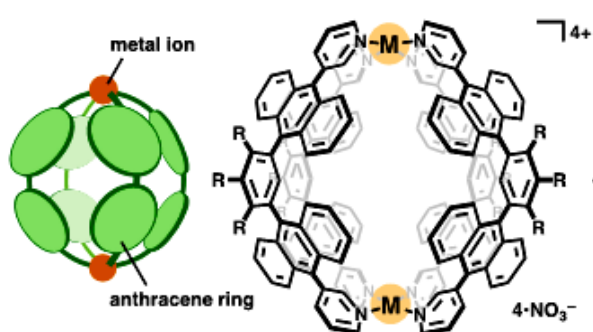
## M<sub>2</sub>L<sub>4</sub> metallosupramolecular capsules with improved therapeutic potential for cancer treatment

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Herein, we present the first data on biological activity of anthracene based coordination capsules **1<sup>M</sup>** (where M= Pd or Pt) that have recently been designed and synthesised <sup>1-3</sup>. The capsules have an M<sub>2</sub>L<sub>4</sub> composition and provide large, hydrophobic cavity with an average volume of ~580 Å<sup>3</sup>. The use of the capsules' interior as molecular containers for safe storage of highly reactive radical-initiators has recently been demonstrated <sup>4</sup>. Inspired by the potential biomedical applications of metallosupramolecules, we evaluated the cytotoxicity profiles of these coordination nano-capsules **1<sup>M</sup>** against human cancer cell lines (HL-60, SKW-3 and T-24), cisplatin resistant cells HL-60/CDDP and non-malignant cells HEK-293. The capsules showed higher anticancer activities (up to 5-fold) against the human leukemic cells and high potency to circumvent the multi-drug resistance (up to 125-fold) when compared with cisplatin, and very high selectivity that is ~10- times more toxic to the cancer cells over the non-malignant cells. These findings illustrate the Pt and Pd capsules potencies for improved therapeutic applications<sup>5</sup>.



**Figure 1.** Cartoon and molecular structure of the metallosupramolecular capsules **1<sup>M</sup>** (M= Pd or Pt).

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## Self-Assembly of cationic surfactant platinum(II) complexes: synthesis and luminescent properties

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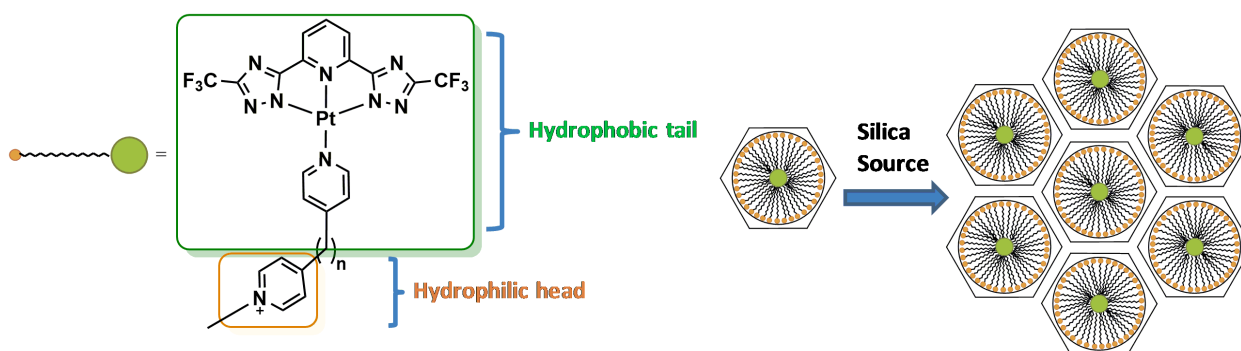
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Transition metal complexes have been intensively studied due to their interesting luminescent properties. In particular, square planar platinum (II) complexes have the ability to self-assemble thanks to its square planar geometry, resulting in dramatic changes in their luminescent properties.<sup>1,2</sup> Here we show the self-assembly properties of platinum(II) complexes bearing a cationic ligand, that are then used as templates for the synthesis of mesoporous silica nanoparticles following a procedure described previously in our group based on a modified Stober method (**Figure 1**).<sup>3,4</sup> The formation of this confined space should provide to the complex after irradiation more rigidity and therefore less distortion, leading to an improvement of the luminescent properties.



**Figure 1** Synthetic strategy using cationic Pt(II) complexes as templates for the synthesis of mesoporous silica nanoparticles.

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# Transformable Nanostructures of Luminescent Platinum-Containing Organosilane Hybrids: Non-Covalent Self-Assembly of Polyhedral Oligomeric Silsesquioxanes Assisted by Pt...Pt and $\pi$ - $\pi$ Stacking Interactions of Alkynylplatinum(II) Terpyridine Moieties

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A luminescent alkynylplatinum(II) terpyridine complex functionalized with polyhedral oligomeric silsesquioxanes (POSS) moieties has been demonstrated to exhibit self-association behavior to give different luminescence properties as well as various distinguishable nanostructures with interesting morphological transformation from rings to rods in response to solvent conditions through the stabilization of Pt...Pt and  $\pi$ - $\pi$  stacking interactions as well as hydrophobic-hydrophobic interactions. These changes can be systemically controlled by varying the solvent composition and have been studied by <sup>1</sup>H NMR, electron microscopy, UV-vis absorption and emission spectroscopies.

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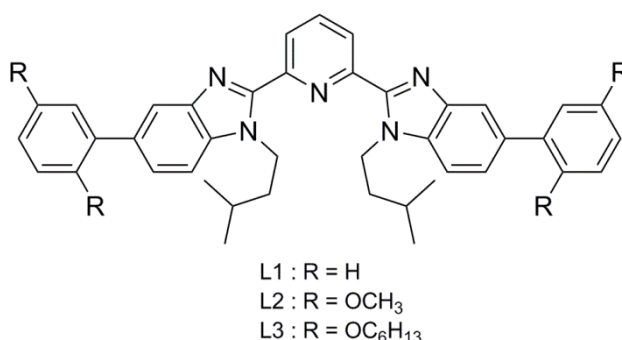
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## A Novel Thermodynamic Analysis of Intermolecular Association Processes

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Thermodynamic laws consider solvent as having a constant activity in binding equilibria occurring in diluted solutions, but the neglect of solvent molecules involved in the solvation reactions may be detrimental to the comprehension of intermolecular association processes. In this context, Castellano and Eggers<sup>1</sup> introduced a new thermodynamic model, in which solvent molecules were introduced as co-reactants in the development of a general binding equation. The explicit consideration of solvent contribution to the complexation equilibria results in significant deviations in the law of mass action. Stability constants, which characterize the formation of coordination complexes, are therefore dramatically affected. Bearing all these elements in mind, we established theoretical and experimental methods, which aim at separately evaluating solvent effects and “pure” binding affinity accompanying the reaction of tridentate ligands (**L**<sub>1</sub>, **L**<sub>2</sub> and **L**<sub>3</sub>) with saturated trivalent lanthanide carriers [Ln(hfac)<sub>3</sub>(diglyme)]. Changes in solvent polarity, in ligand lipophilicities and in metallic sizes are investigated for decrypting robust trends in binding selectivity.<sup>2</sup>



**Figure 1** Chemical structures of the tridentate ligands **L**<sub>1</sub>, **L**<sub>2</sub>, **L**<sub>3</sub>

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## 2,2'-Bisdipyrin based assemblies: linear helicate and beyond

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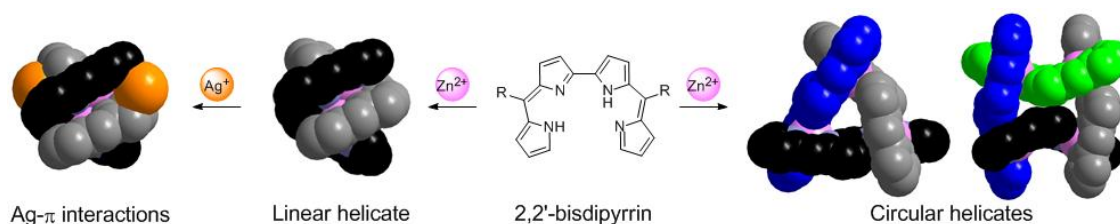
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Known since the 1920s,<sup>1</sup> dipyrins ligands<sup>2</sup> have, particularly over the past decade, demonstrated their ability to promote the formation of metal-organic frameworks (MOFs).<sup>3</sup> Indeed, these bis-pyrrolic species can be rather easily synthesized and functionalized, and form monoanionic chelates under mild basic conditions. In particular, the 5-aryl-dipyrin derivatives bearing a peripheral coordinating group have been successfully used. These ligands can form either homometallic MOFs upon self-assembly of their complexes or heterometallic M'MOFs upon sequential reaction with different metal centres.

Interestingly, investigations on the 2,2'-bisdipyrin derivatives (Figure 1), incorporating two chelate moieties directly bound through a C-C bond, have been mostly centered on their assembly with Zn(II) cations, affording binuclear linear helicates.<sup>4</sup> To our knowledge, no compounds of higher nuclearity and showing circular helicity have been reported with these ligands. Furthermore, they have not been employed for the construction of coordination networks, in contrast with the mono-dipyrin analogues.

We will present here our recent results demonstrating not only that discrete cyclic species can be formed but also that the linear helicates can be employed to prepare heterometallic infinite crystalline architectures by Ag- $\pi$  interactions.<sup>5</sup>



**Figure 1** Supramolecular assemblies based on 2,2'-bisdipyrin ligands

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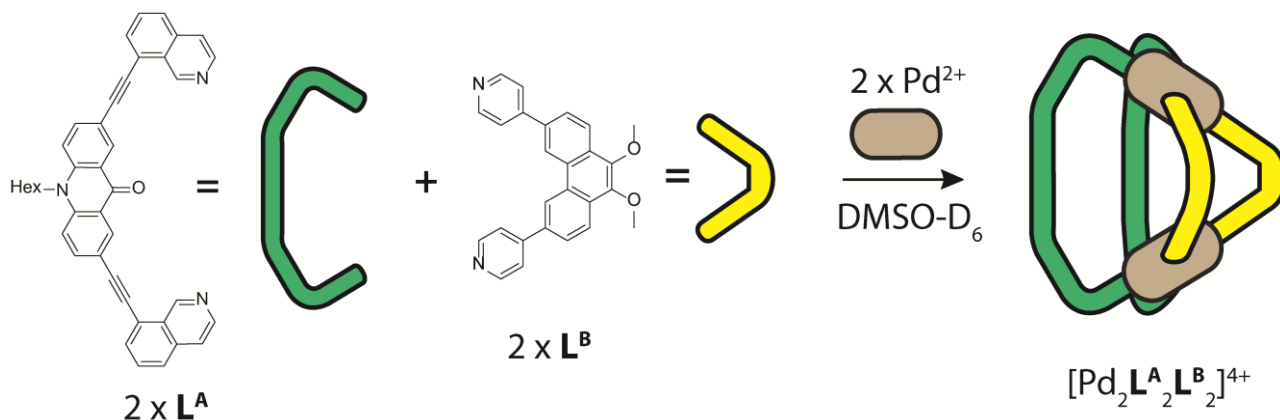
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## Assembly of a Heteroleptic Coordination Cage by Geometric Complementarity

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Coordination cages assembled from banana-shaped ligands have received much attention in the past decade due to their fascinating and dynamic properties, for example, stimuli triggered guest binding, energy transfer, structural re-organizations and more.<sup>[1]</sup> With the focus of the field of coordination cages shifting progressively from structure towards function, chemists are seeking strategies to bring together more than one type of ligand, i.e. to achieve controlled heteroleptic self-assembly from multiple components.<sup>[2]</sup> Here we introduce the approach of geometric complementarity as a strategy to access heteroleptic coordination cages. Upon combination of two complementary-shaped pyridyl ligands ( $L^A$  and  $L^B$ , Fig. 1) with  $[Pd(CH_3CN)_4](BF_4)_2$  we observe by  $^1H$  NMR spectroscopy and mass spectrometry almost exclusive formation of a  $[Pd_2L^A_2L^B_2]^{4+}$  coordination cage despite the unfavorable entropy of the assembly pathway. When the individual homoleptic cages from  $L^A$  and  $L^B$  are mixed in a 1:1 ratio a slow conversion (>4 days) to the desired heteroleptic  $[Pd_2L^A_2L^B_2]^{2+}$  is observed. We attribute this to the lower steric strain of the heteroleptic system which is achieved through careful ligand design.



**Figure 1** A scheme showing the self-assembly of a heteroleptic  $[Pd_2L^A_2L^B_2]^{4+}$  cage from two complementary-shaped pyridyl ligands.

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## Induced Self-Assembly of Alkynylplatinum(II) Complexes by Variations of Solvent Compositions and Addition of Polyelectrolytes

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Water-soluble cationic alkynylplatinum(II) 2,6-bis(benzimidazol-2'-yl)pyridine (bzimpy) complexes have been synthesized and demonstrated to undergo self-assembly with anionic polyelectrolytes in aqueous buffer solution. The self-assembly processes have been shown to give rise to the formation of metal–metal-to-ligand charge transfer (MMLCT) absorptions and triplet MMLCT (<sup>3</sup>MMLCT) emissions. The supramolecular assemblies exhibit different photophysical properties and excited state chemistry, which has been rationalized by the difference in Förster resonance energy transfer (FRET) efficiency, extent of polymer–metal complex aggregate formation, photo-induced charge transfer (PCT), and Dexter triplet energy back transfer (TEBT) quenching.

In addition, a new class of amphiphilic platinum(II) terpyridine-based polymers has been prepared and demonstrated to give different morphologies in various solvent compositions. The morphological changes could induce drastic UV-vis and emission spectral changes due to the formation of Pt...Pt and  $\pi$ - $\pi$  interactions. The morphological changes have been studied by electron microscopy, UV-vis absorption, and emission spectroscopy.

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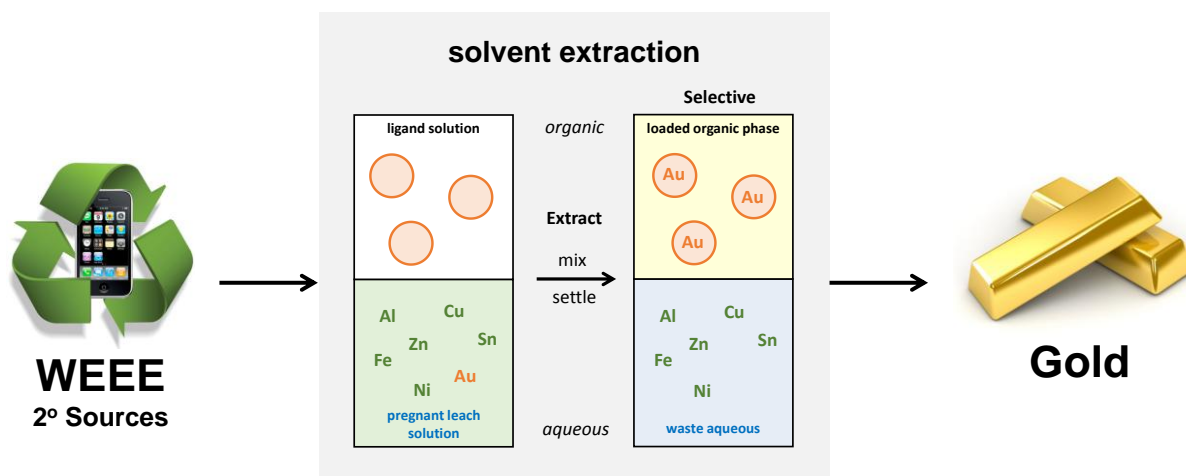
## Selective Recovery of Gold from Secondary Sources: Solvent Extraction and Supramolecular Chemistry

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Waste electrical and electronic equipment (WEEE) such as mobile phones contain a variety of metals,<sup>1</sup> often in higher concentrations than is found in primary mineral deposits.<sup>2</sup> Efficient recovery and recycling of these metals from secondary sources would reduce the environmental impact of energy and emission intensive mining processes.<sup>3</sup>

The recovery of gold, the most valuable metal in mobile phones to recycle, is plagued by hazardous processing conditions, including cyanide leaching and volatile solvents.<sup>4</sup> We report the use of a new class of simple, non-toxic, recyclable solvent extractants<sup>5</sup> for the selective separation of gold from a mixture of metals typically found in secondary source feeds (Figure 1).

The reagent exploits supramolecular chemistry to extract gold into an organic phase, showing remarkable selectivity over other metals that are present in higher concentrations, and with marked advantages over existing commercial reagents.



**Figure 1** Recovery of gold from secondary (WEEE) sources using solvent extraction.

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## SOLID STATE EMISSIVE CU(I) POLYMETALLIC ASSEMBLIES

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K. Costuas<sup>c</sup>, G. Calvez<sup>d</sup>, V.W.W. Yam<sup>b</sup>, C. Lescop<sup>a,d\*</sup>

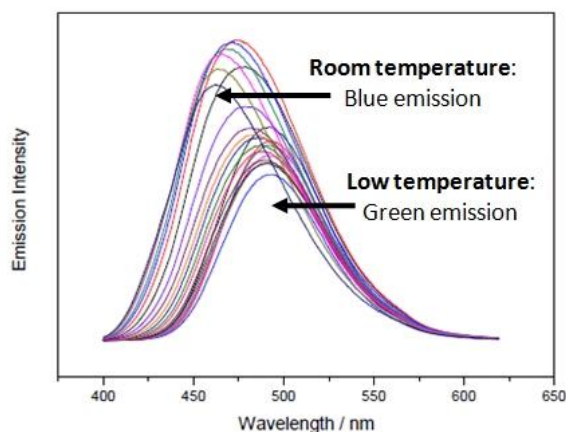
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An increasing interest is devoted to Cu(I) metal complexes in order to design brightly emissive cheap material for lighting applications.<sup>[1]</sup> To date, the most remarkable class of such derivatives is mostly based on Cu<sub>4</sub>I<sub>4</sub> cubane cores.<sup>[1c-e]</sup> Using a very general supramolecular chemistry synthetic approach previously developed in our group,<sup>[2]</sup> a new series of polymeric Cu(I) assemblies Cu<sub>n</sub> (n = 4, 6, ∞) has been recently obtained. Their syntheses, solid-state characterizations will be presented together with the study of their emissive behaviors (including thermochromism, vapochromism and mechanochromism).



**Figure 1** Emission spectra of Cu(I) complexes at different temperatures

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# Self-Assembly of Platinum(II) Polypyridine Complexes with L-Valine Units: A Delicate Balance Between Pt···Pt, $\pi$ - $\pi$ and Hydrogen-Bonding Interactions

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A series of platinum(II) polypyridine complexes with L-valine-containing ligands has been synthesized and characterized. In sharp contrast to the organic peptide-containing alkynes which only showed gelation with up to three valine units, a complex with an unsubstituted terpyridine and just one valine on the alkynyl ligand was found to display gelation properties in acetonitrile solution. Upon sol-gel transition, a color change from yellow to red could be observed, indicative of the presence of Pt···Pt and  $\pi$ - $\pi$  stacking interactions in driving metallogel formation. More interestingly, another series of L-valine-containing platinum(II) diimine complexes was found to aggregate at low temperatures, leading to supramolecular chirality. Their aggregation behaviors have been investigated by UV-vis, emission, circular dichroism and  $^1\text{H}$  NMR spectroscopies, with their morphologies studied by electron microscopies.

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## **Coordination polymers assembled from $[\text{Re}_4\text{Q}_4(\text{CN})_{12}]^{4-}$ (Q = S, Se, Te) cluster anions, $\text{Ln}^{3+}$ cations and 1,10-phenanthroline**

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The design of self-assembling systems from pre-made building blocks is an area of intense interest as a route to the generation of functional materials. The aim of present research is synthesis and structural investigation of supramolecular compounds composed of  $[\text{Re}_4\text{Q}_4(\text{CN})_{12}]^{4-}$  (Q = S, Se, Te) cluster anion as rigid building block and  $\text{Ln}^{3+}$  cations as functional sites possesses magnetic and luminescence properties. Additionally, N-donor organic ligands such as 1,10-phenanthroline (phen) can probably act as antennas for  $\text{Ln}^{3+}$  cations and as structural modifiers with to the ability to form  $\pi$ -stacking. It was shown that reactions of  $[\text{Re}_4\text{Q}_4(\text{CN})_{12}]^{4-}$  (Q = S, Se, Te) cluster anions,  $\text{Ln}^{3+}$  cations and 1,10-phenanthroline (phen) led to self-assembly of numerous compounds having ionic, oligomeric and polymeric structures. Two synthetic approaches are suitable for obtaining of such compounds: solvothermal reaction in  $\text{H}_2\text{O}/\text{EtOH}$  mixtures at 120-150°C and counter diffusion of the reagent solutions in  $\text{H}_2\text{O}$  and  $\text{EtOH}$ . 1D polymeric chains having three main topologies— linear, helical and ladder-type – were observed as the most common structural types for obtained compounds. Polymeric chains are constructed from cluster anions connected with each other through  $\{\text{Ln}(\text{H}_2\text{O})_x\text{phen}_y\}^{3+}$  or binuclear  $\{\text{Ln}(\text{H}_2\text{O})_x\text{phen}_y(\mu\text{-OH})\}_2^{4+}$  cationic fragments. Presence of phen molecules in the inner sphere of  $\text{Ln}^{3+}$  ion has a significant influence on the structures: packing of the polymeric chains strongly depends on the number and position of phen and  $\text{H}_2\text{O}$  molecules. Compounds have black or dark-brown color and showed no photoluminescence being irradiated by UV.

This work is financially supported by the Russian Science Foundation (project No 14-23-00013)

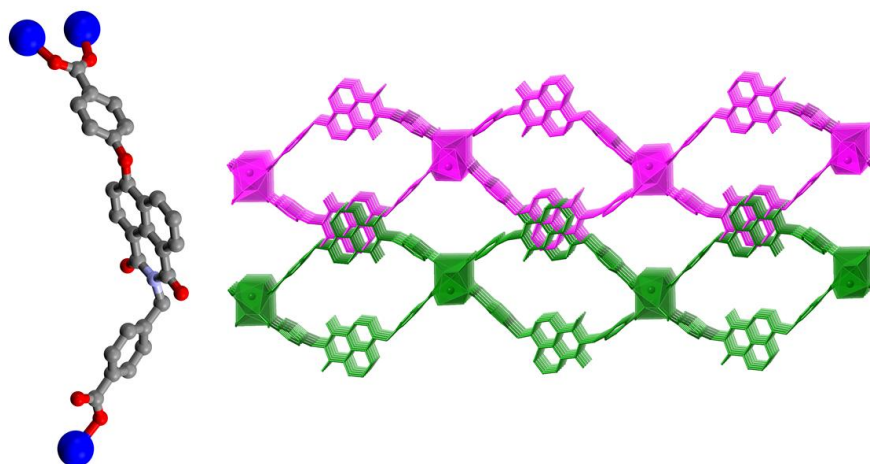
## Fluorescent Coordination Polymers for Molecular Detection

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The exploitation of molecular confinement phenomena within open framework materials has in recent years led to important discoveries in areas such as catalysis, separation and structure elucidation.<sup>1</sup> In each case, the geometric constraints imposed on a substrate by the size and orientation of the internal volume are crucial in dictating selectivity, and can seemingly give rise to greatly enhanced recognition properties compared with those observed in the bulk phase. Our aim is the incorporation of organic fluorophores with known tendencies towards environment-dependent emission behavior in the solution phase, particularly 1,8-naphthalimides and fused pyrroles, into porous coordination polymer materials. In particular, the effects of framework confinement on the anion recognition properties of these materials are of interest. Herein we report the synthesis, structural chemistry and spectroscopic properties of a series of coordination polymers derived from these organic fluorophores, and the effect of polar and ionic guests on their fluorescence behavior.



**Figure 1** Example of a porous coordination polymer containing fluorescent 1,8-naphthalimide moieties within the backbone

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## Elaboration and control of a switchable coordination polymer using $\pi$ -radicals as electrochemical switches

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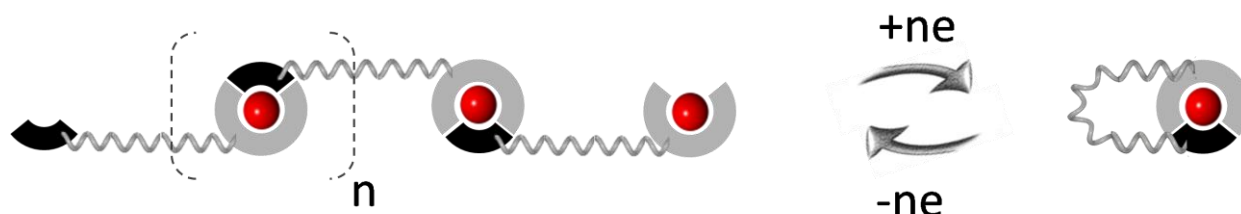
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The ability to control the structure and organization of molecular materials has emerged in the past decade as a major scientific objective that is mainly motivated by exciting foreseeable applications in nanoscience. Enormous technologic interests are indeed at stake in being able to devise molecular objects or supramolecular materials that could respond to external stimuli by changes in structure and function. These particular properties can lead to applications in various domains as (i) in molecular electronics, (ii) in analytic science, with switchable hosts allowing the controlled binding/release of pollutants or drugs, (iii) in materials science with the development of adaptive supramolecular polymers.

In this communication, the synthesis and physico-chemical properties of a switchable coordination polymer whose movements are triggered by electrochemically driven self-assembly of organic radicals will be presented<sup>1</sup>. The redox switchable tecton involved in the supramolecular assembly involves a zinc porphyrin and an imidazole ring as the self-complementary building units. The key electron-responsive component, capable of provoking a large amplitude folding motion in response to an electron transfer, is a bis-viologen hinge involving two 4,4'-bipyridinium salts linked through a short, albeit flexible, covalent linker. The properties of these dynamic architectures will mainly be discussed on the basis of electrochemical, spectroelectrochemical and ESR experiments supported by quantum chemical calculations.



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2 A. Iordache, M. Retegan, F. Thomas, G. Royal, E. Saint-Aman, C. Bucher, *Chem. Eur. J.*, **2012**, *18*, 7648.

3 Manuscript in preparation.

## Syntheses and crystal structures of new $M_2L_4$ cage type complexes constructed by bis-imidazole type ligands

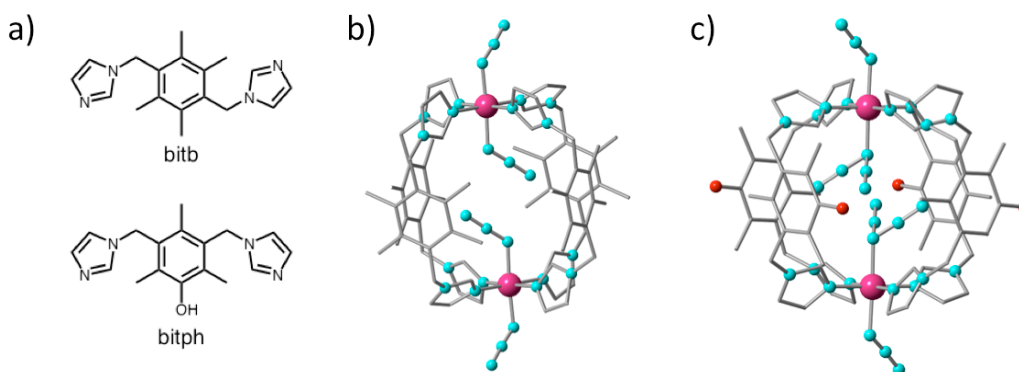
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Bis-imidazole type ligands have been studied for many  $M_2L_4$  cage type complexes for anions. Various anions such as  $ClO_4^-$ ,  $NO_3^-$ ,  $SO_4^{2-}$ , have been trapped in the cationic cages. We have focused on syntheses of molecular capsules by using 1,4-bis(imidazol-1-ylmethyl)-2,3,5,6-tetramethylbenzene (bitb).<sup>1</sup> In this work, we have synthesized and structurally characterized two new  $M_2L_4$  cage type complexes that encapsulate two anions in the cage by using bitb and a new ligand, 3,5-bis(imidazole-1-yl-methyl)-2,4,6-trimethylphenol (bitph). The ligand structures are illustrated in Figure 1a.

The target complex  $[(N_3)_2 \subset Co_2(bitb)_4](N_3)_2$  (**1**) was isolated as dark green and red crystals from the reaction mixture of  $Co(NO_3)_2 \cdot 6H_2O$  with bitb and  $NaN_3$ . Similar complex  $[(N_3)_2 \subset Co_2(m-bitph)_4](N_3)_2$  (**2**) was also obtained by treatment of  $CoCl_2$  with bitph and  $NaN_3$ . Single crystal diffraction studies have shown that the two  $N_3^-$  are trapped in the  $M_2L_4$  cationic cages (Figure 1b and c). The shortest N---N distance observed between the  $N_3^-$  ions is about 3.0 Å, which is slightly shorter than sum of van der Waals radii of nitrogen atoms (3.1 Å). Their syntheses and structures are described.



**Figure 1** Structures of the two bridging ligands, bitb and bitph (a). Molecular structures of  $M_2L_4$  cages of **1** (b) and **2** (c).

1. (a) T. Hirakara, M. Kondo, et al., *Chem. Lett.*, **2009**, 38, 290. (b) T. Inoue, K. Yamanishi, M. Kondo, *Inorg. Chem.* **2013**, 52, 4765.

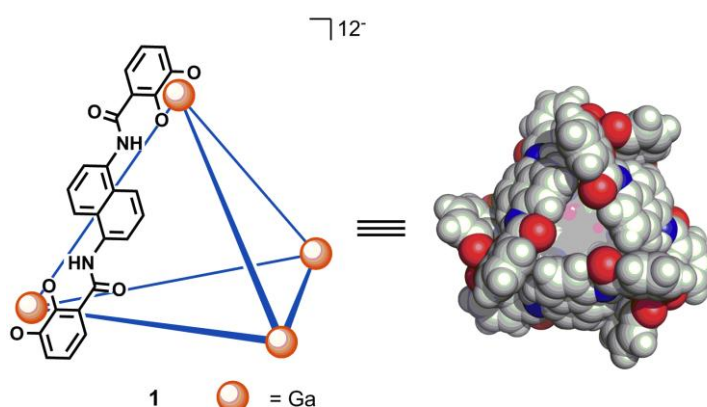
## A supramolecular microenvironment strategy for transition metal mediated cross coupling

D. M. Kaphan,<sup>a</sup> M. D. Levin,<sup>a</sup> R. G. Bergman,<sup>a\*</sup> K. N. Raymond,<sup>a\*</sup> F. D. Toste<sup>a\*</sup>

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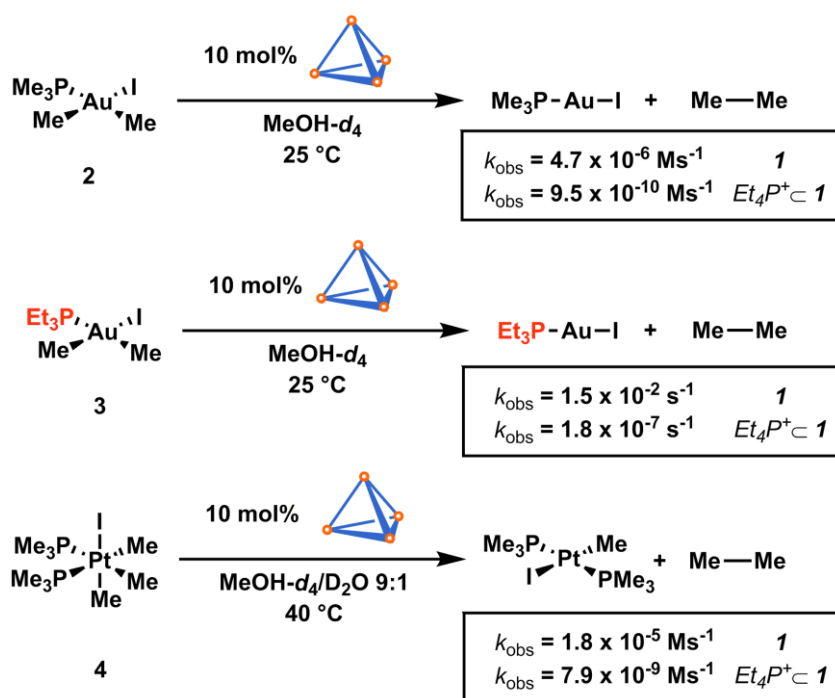
A self-assembled supramolecular metal-ligand architecture (**1**) was shown to catalyze alkyl-alkyl reductive elimination from high-valent transition metal complexes. This reactivity was general to two metals [Au(III), Pt(IV)] and the behavior of a variety of participating functional groups was explored. The cavity of the supramolecular assembly



**Figure 1** M<sub>4</sub>L<sub>6</sub> supramolecular assembly **1**

acts as a functional enzyme mimic, applying the concepts of enzymatic catalysis to a reactivity manifold not represented in biology. Kinetic experiments are presented which delineate a Michaelis-Menten type mechanism and reveal the highest measured

acceleration ( $k_{\text{cat}}/k_{\text{uncat}} = 1.9 \times 10^7$ ) for any synthetic supramolecular catalyst to date, well within the regime of enzymatic rate acceleration. This stoichiometric reactivity was incorporated into a dual-catalytic cross coupling reaction wherein both the transition metal precatalyst and the supramolecular cluster are necessary for the reaction to proceed on a reasonable timescale.



**Figure 2** Supramolecular cluster catalyzed reductive elimination from Au(III) and Pt(IV).

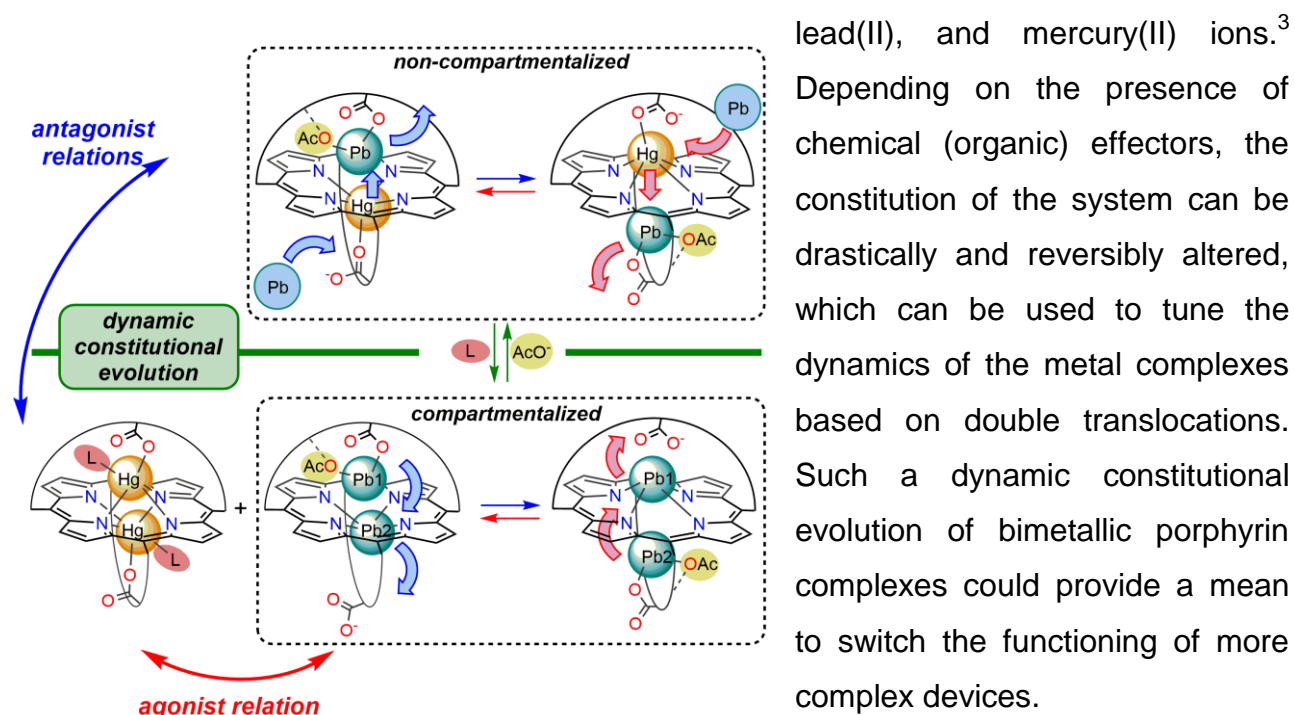
# Bimetallic Porphyrin Complexes: Double Translocations Tuned by Dynamic Constitutional Evolution

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Molecular compounds able to change their constitution as a response of a modification of their environment open new perspectives in the fields of complex systems and smart materials.<sup>1</sup> In addition to dynamic covalent chemistry, coordination chemistry has widened the possibilities to form such adaptive systems as coordination-driven assemblies allow reorganization of subcomponents in a well-defined manner.<sup>2</sup> Recently, our group has explored a different strategy where metal ions do not behave as nodes but rather as the subcomponents of an adaptive system. As shown in Figure 1, homo- and heterobimetallic complexes are selectively formed using a particular porphyrin ligand,



**Figure 1** Switching between non-compartmentalized and compartmentalized double translocations in bimetallic porphyrin complexes through a dynamic constitutional evolution process (adapted from ref 3).

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2 S. Zarra, D. M. Wood, D. A. Roberts, J. R. Nitschke, *Chem. Soc. Rev.*, **2015**, *44*, 419.

3 S. Le Gac, L. Fusaro, T. Roisnel, B. Boitrel, *J. Am. Chem. Soc.*, **2014**, *136*, 6698.

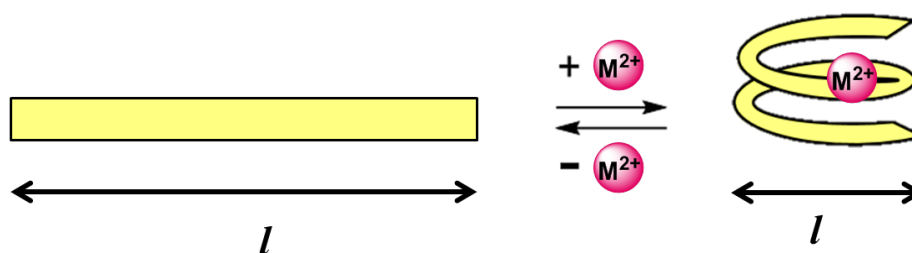


## Triazine-Hydrazone Ligand Strands: Coordination Chemistry and Incorporation into Polymer Gels

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The construction of molecular machines, such as molecular scale actuators, which mimic the motions demonstrated by nature's vast array of nanoscale machinery continues to be one of the many challenges facing chemists. While there is an abundance of natural molecular scale actuators, artificial molecular scale actuators are scarce. Ligand strands which undergo a conformational change upon complexation to suitable metal ions are of great interest for the use of molecular scale actuation as the conformational change is usually accompanied by a change in length of the ligand strand (figure 1).



**Figure 1** Cartoon showing the change of length associated with the change in conformation between helical and linear.

The coordination chemistry of such a ligand strand consisting of repeating trz-hyz units has been proven rich and diverse and holds potential for the use of synthetic building blocks and for molecular scale actuation. The use of molecular actuators on a macroscopic scale requires that they can be organized and integrated into larger actuating systems such as polymer gels. Polymer gel actuators are becoming increasingly popular as they are cheap, light and flexible.<sup>1</sup> It has been shown that they hold potential to be used in muscle replacement therapy, intelligent drug delivery systems and other extraordinary applications.<sup>2</sup> New trimer and pentamer ligands consisting of repeating trz-hyz units and containing acryloyl arms for incorporation into polymer gels have been synthesised and their coordination chemistry with Zn(II), Ag(I) and Pb(II) will be described. The structural changes upon coordination will be investigated.

1 Ahn, S.-K; Kasi, R.M; Kim, S C; Sharma, N; Zhou, Y. *Soft Matter*, **2008**, 4, 1151-1157.

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## Cp\*Rh-Based Heterometallic Borromean Rings

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Interest in Borromean rings architectures is rapidly growing not only because of their intriguing structures and topological importance, but also because of their potential applications as smart materials and nanoscale devices.<sup>1</sup> Our research focused on using the metallaligand complex (Pd<sup>2+</sup>) as building blocks to construct heterometallic macrocycles (Fig. 1).<sup>2-3</sup> By adjustment of the pyridyl arm length, the distance between two Pd<sup>2+</sup> ions can be controlled. Meantime, enlargement of the pyridyl arm length (L<sub>3</sub> and L<sub>4</sub>) could lead to the isolation of Borromean rings architectures (Fig. 1). Through enhancing the pyridyl arm width (L<sub>2</sub>), monomeric rectangles with empty void space could be instead of the Borromean ring architectures (Fig. 1). These results may help better understand self-assembly Borromean ring architectures and prompt future studies on the application of the heterometallic macrocycles on bimetallic cooperative catalysis.

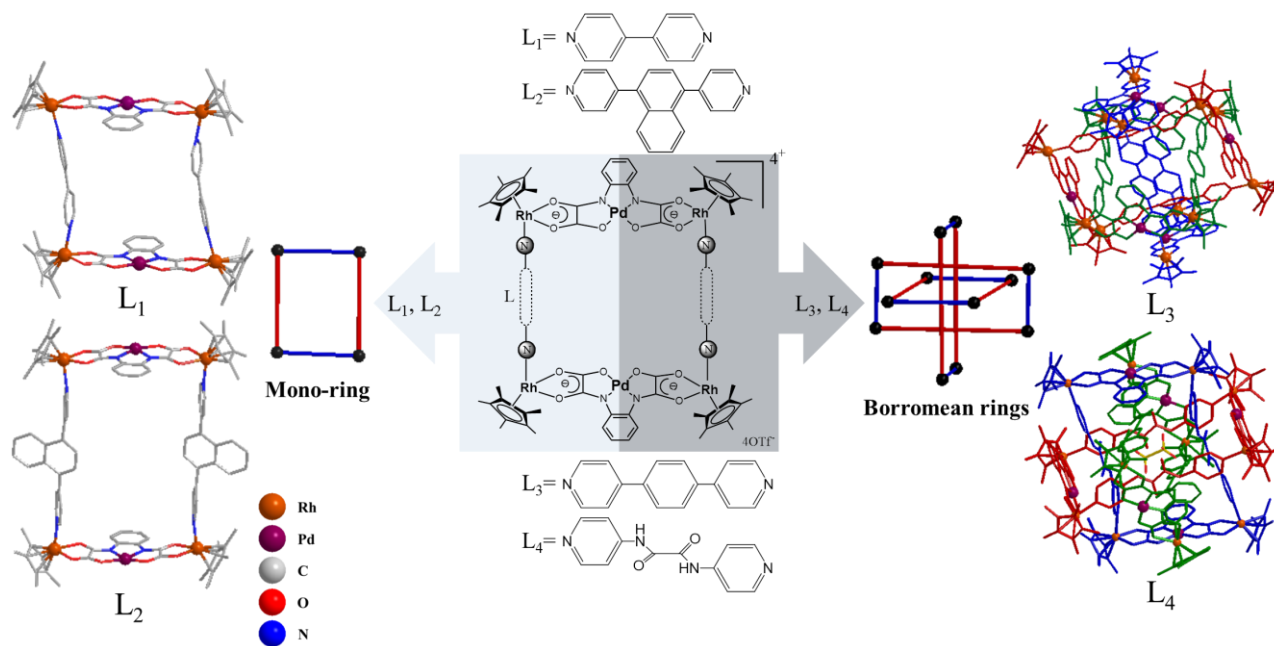


Figure 1

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- 2 S-L. Huang, Y-J. Lin, Z-H. Li, G-X. Jin, *Angew. Chem. Int. Edit.* **2014**, *53*, 11218.
- 3 S-L. Huang, Y-J. Lin, T. S. A. Hor, G-X. Jin, *J. Am. Chem. Soc.* **2013**, *135*, 8125.

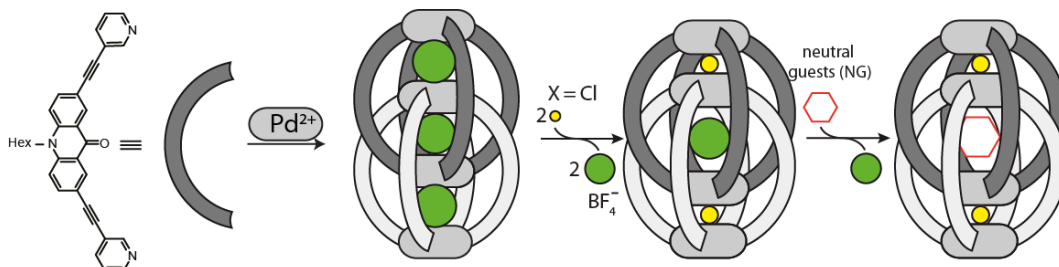
## Encapsulation of Neutral Guest Molecules by Interpenetrated Coordination Cages

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Supramolecular coordination cages have become a popular research area, due to their versatile usage. The cavity of self-assembled cages can serve as container for guest molecules or as environment for catalytic reactions similar to enzymatic processes. Interpenetrated double cages are of special interest, because they offer three mechanically coupled cavities, which are able to incorporate anionic guest molecules.<sup>1</sup>

In this poster we will present the formation of an interpenetrated double cage based on an acridone derived ligand, which is capable of allosteric anion binding in their outer two pockets. Surprisingly, halide binding enables the double cage to encapsulate various neutral guest molecules (e.g. benzene or norbornadiene) in its central pocket.<sup>2</sup>



**Figure 1** Schematic representation of the halide binding in the outer pockets of the double cage that triggers the uptake of neutral guest molecule in the central pocket.

We furthermore will show that the introduction of a bulky adamantyl group to this acridone ligand prevents dimerization and results in the clean formation of a monomeric cage [Pd<sub>2</sub>L<sub>4</sub>]. The ligand shows a flipping dynamic between two energetically degenerated conformers in the free ligand and astonishingly in the cage.<sup>3</sup>

Currently, we are studying the application of those systems in the context of double-input receptors, molecular logic gates and switchable catalysis inside confined cavities.

1 M. Han, D. M. Engelhard, G. H. Clever, *Chem. Soc. Rev.*, **2013**, 43, 1848–1860.

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3 S. Löffler, J. Lübben, A. Wuttke, R. A. Mata, M. John, B. Dittrich, G. H. Clever, *to be submitted*.

## Self-assembled Helical Ti(IV)-based Architectures controlled by Nitrogen Ligands

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Titanium alkoxides are extensively employed as precursors for sol-gel chemistry and materials science.<sup>1</sup> These compounds are also essential in numerous organic transformations. Concerning their reactivities, titanium alkoxides are generally water-sensitive and their chemistry is highly difficult to predict. In order to circumvent these particular features, we rationally designed a flexible stable chiral monomeric titanium(IV) complex. This  $C_2$ -symmetric octahedral complex incorporates two substituted 2,2-biphenolato entities and two labile isopropanol molecules.<sup>2</sup> We have showed that this precursor displays a rich coordination chemistry through the substitution of the alcohol ligands by various nitrogen bidentate ligands, permitting to generate a large library of  $TiO_4N_2$ -based complexes.<sup>3</sup> Having demonstrated the titanium coordination sphere control, we extended this chemistry to the generation of molecular multicomponent self-assembled  $TiO_4N_2$ -based architectures in the presence of a bis-biphenol strand<sup>4</sup> and several nitrogen ligands. Thus, we will present some helical complexes built around  $TiO_4N_2$ -nodes. In particular, we will show that the nature of the nitrogen ligands deeply influences the structures of the resulting metallo-supramolecular assemblies. This will be illustrated by recent results obtained by our group such as a bowl-shaped circular trinuclear helicate incorporating the bipyrimidine chelate (see Figure 1).<sup>5</sup>



**Figure 1** A  $TiO_4N_2$ -based bowl-shaped circular trinuclear helicate

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- 3) D. M. Weekes, N. Baradel, N. Kyritsakas, P. Mobian, M. Henry, *Eur. J. Inorg. Chem.*, **2012**, *34*, 5701.
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## Structure and properties of self-assembled copper and manganese 12-metallacrown-4 complexes

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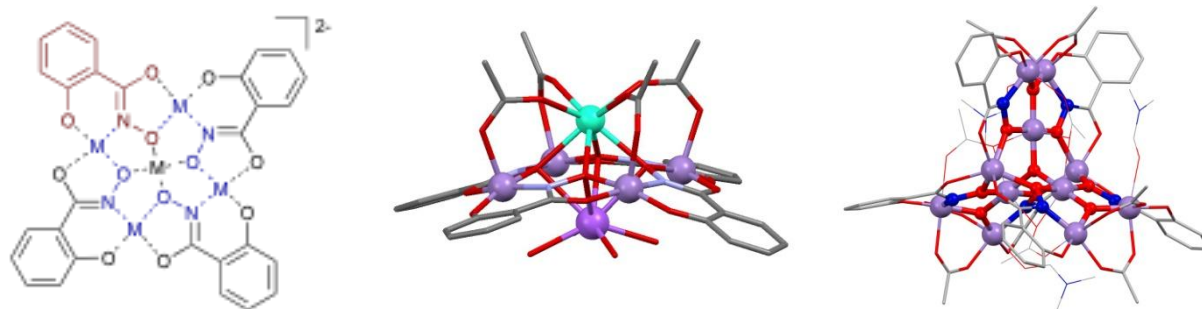
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Metallacrowns(MC) are defined as inorganic analogs of crown ethers. They are complexes with high nuclearity where aminohydroxamic acids act as bridging ligands between metal centers, allowing to confine a large number of metals into a small molecular framework (Fig. 1 left)<sup>1</sup>. Metallacrowns are investigated as molecular recognition agents, as luminescent probes, as single-molecule magnets (SMMs) and as building blocks of large porous assemblies.



**Figure 1** Left: Scheme of a 12-metallacrown-4 complex of salicylhydroxamate ( $H_3ShiHA$ ); center: X-ray structure of  $LnNa(OAc)_4[12-MC_{MnIII(N)shi-4}]^{2-}$ ; right:  $Mn_{11}L_6$  metallacryptate of  $Mn(II/III)$  and  $ShiHA^{3-}$ .

We report here the  $^1H$  NMR characterization in solution of self-assembled heterotrimetallic  $Ln(III)/Mn(III)/Na(I)$  MCs, showing how the paramagnetic shift of the signal correlates with the non-spherical distribution of the 4f-electron density of the lanthanide (Fig. 2 center).

The study of the structure of a  $Mn_{11}L_6$  metallacryptate, which bears a  $Mn_3(\mu_3-O)$  core (Fig. 3 right) and of the stability in solution of copper(II) metallacrowns will be also discussed.

The research leading to these results have received funding from the European Community's Seventh Framework Programme (FP7/2007-2013) under grant agreement n° 611488. The MAE (Italian Ministry of Foreign Affairs) is also acknowledged for support through the Bilateral Italy-USA Joint Declaration on S&T Cooperation 2016-2017.

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## Multiple Ion Sensing Quinoxalinone Derivatives

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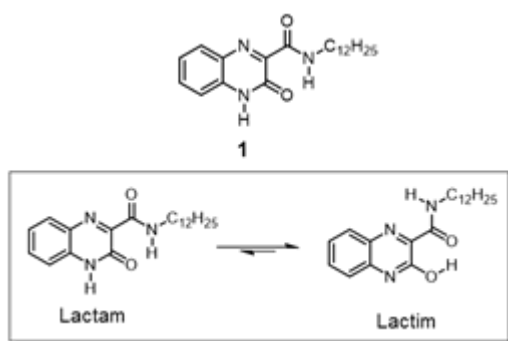
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<sup>b</sup> Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai, Japan

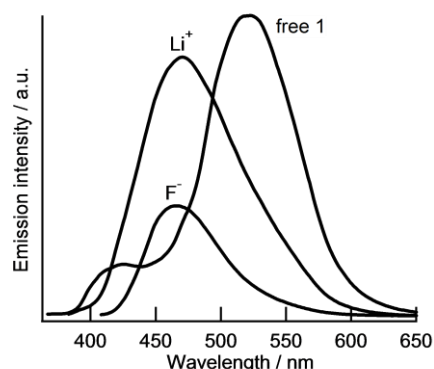
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The fluorescent sensors to recognize two kinds of different ions have been attracted much attentions from a viewpoint of the logic gate application. Herein, we designed and synthesized new fluorescent quinoxalinone derivative (1) bearing both the cation and anion sensing sites. The lactam-lactim tautomerism of quinoxalinone derivative has a potential to show interesting optical response coupled with ion recognitions (Figure 1). The synthesis and optical responses of 1 for cations and anions were examined.

From the <sup>1</sup>H NMR spectra, lactim form was stable in contrast with lactam one in THF. When F<sup>-</sup> anion was added into solution 1, the fluorescence quenching of lactam form was observed. On the contrary, the addition of Li<sup>+</sup> cations increased the lactam form accompanying in the emission enhancement. These emission responses were achieved by the change in the lactam - lactim equilibrium through the ion recognition. The crystal structures of the supramolecular complexes will be discussed for the ion-sensing mechanism of 1, and the multiple ion sensing of crown-ether fused new quinoxalinone derivative will be also reported in triple ion recognition system.



**Figure 1.** The structure and tautomerism of quinoxalinone derivative 1



**Figure 2.** Emission spectra of 1 and those by additions of Li<sup>+</sup> and F<sup>-</sup> ions

[1] Y. Nakane, K. Sakai, and T. Akutagawa *et al.*, *J. Phys. Chem. A*, **2015**, 119, 6223-6231.



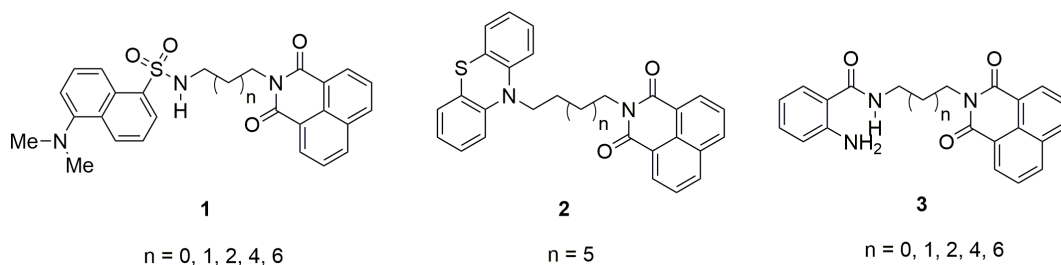
## Novel naphthalimide-aminobenzamide dyads as OFF/ON fluorescent supramolecular receptors in metal ion binding

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A series of novel naphthalimide-aminobenzamide (NAPIM-2ABZ) dyads **3** connected by different length polymethylene chains were synthesized and studied as fluorescent supramolecular receptors in metal ion binding.<sup>1-3</sup> The photophysical properties were evaluated and compared with separated chromophores. The electronic absorption spectra of dyads **3** showed no interaction between chromophores in ground state. The fluorescence quantum yields were lower in dyads **3** in comparison with *N*-propyl-2-aminobenzamide and *N*-propylnaphthalimide. The fluorescence quenching is attributed to a PET mechanism between fluorophores (from 2ABZ to NAPIM), which is dependent of the polymethylene chain length. In metal binding study was found response toward transition metal ions as Hg(II), Cu(II), Zn(II) and Ni(II). Dyad **3b** presented selectivity toward Cu(II). The UV-Vis, IR and <sup>1</sup>H-NMR studies demonstrated the interaction with 2ABZ moiety in the ground state and interestingly, dyads with shorter polymethylene chains **3a** (*n*=0), **3b** (*n*=1) and **3c** (*n*=2) exhibited an OFF/ON fluorescence behavior due to the PET inhibition and the quenching of 2ABZ fluorescence. Dyads **3d** (*n*=4) and **3e** (*n*=6) presented opposite response ON/OFF in the complex with metal ions evidencing the absent of PET in these dyads.



**Figure 1.** Fluorescent dyads designed for metal ion binding.

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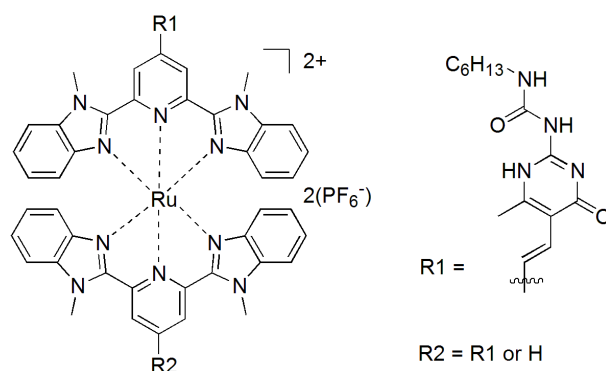


# SUPRAMOLECULAR STRUCTURES AND ELECTROCHEMICAL PROPERTIES OF H-BONDED RUTHENIUM COMPLEXES ON HOPG SURFACE

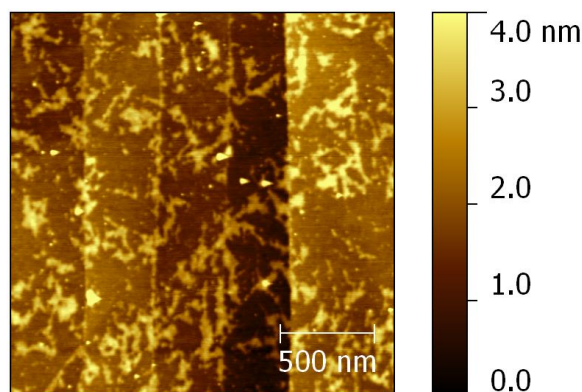
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Chemical functionalization of nano-carbon materials such as graphene and carbon nanotubes by metal complexes has attracted much attention due to many potential applications for efficient energy conversion and storage devices. We are interested in the surface modification of nano-carbon materials by functional complexes having pyrene groups through noncovalent  $\pi$ - $\pi$  interaction. In this study, novel Ru complexes having different number of H-bond sites were synthesized. (Figure 1) After the immersion of a HOPG substrate into the solution of the Ru complex, the HOPG surface revealed a supramolecular polymer network morphology by AFM measurements only for the Ru complex having H-bond sites at both ends. (Figure 2) Therefore, the formation of the H-bonded supramolecular coordination



**Figure 1** Chemical structure of Ru complexes having H-bond sites



**Figure 2** AFM image of supramolecular polymer network on HOPG surface

polymer was responsible for the adsorption of the Ru complex on a HOPG surface. Cyclic voltammogram of the modified HOPG electrode showed a well-defined adsorbed Ru(II/III) couple with the surface coverage of  $2.11 \times 10^{-13}$  mol/cm<sup>2</sup>. The detailed of structure formation and adsorption behavior of Ru complex onto the HOPG surface will be reported at the meeting.

## New Zn(II) coordination polymers with exo-bidentate ligands assembled in the presence of amino-alcohols

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<sup>b</sup> "Petru Poni" Institute of Macromolecular Chemistry, Romanian Academy, Aleea Grigore Ghica Voda 41-A, RO-700487, Iasi, Romania

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The synthesis of coordination polymers with mixed linkers has been attempted not only to generate diverse topologies, but also to give multifunctional systems, and numerous multitopic organic ligands with specific binding strength and directionality have been used. Among them, oxygen or nitrogen containing ligands such as aromatic polycarboxylic acids or bis(4-pyridyl) derivatives have been extensively employed, due to the tunability of the obtained structures and their suitability for hydrogen storage, sorption, separation and sensing.<sup>1</sup> On the other hand, amino-alcohols have received much less attention, in spite of the variety of coordination modes or their capability for formation of hydrogen bonds.<sup>2,3</sup>

In the present work we report on the synthesis and characterization of new Zn(II) coordination polymers self-assembled under solvothermal conditions from amino-alcohols and rigid rod-like organic linkers. Their crystal structures, photoluminescence and thermal behavior will be discussed.

Aknowledgements: This work was supported by a grant of the Romanian National Authority for Scientific Research, CNCS – UEFISCDI, project number PN-II-RU-TE-2012-3-0390.

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## Palladium and Platinum Phosphine Bio-conjugates

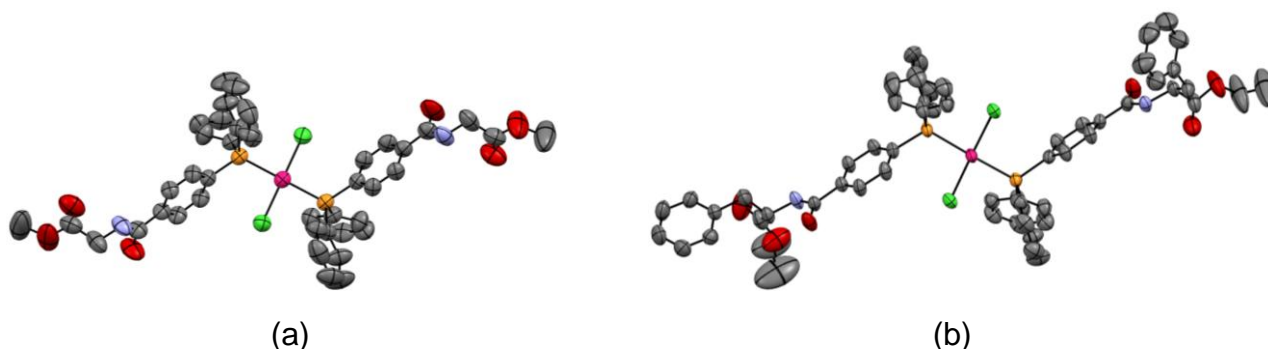
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Transition metal complexes that incorporate amino acids or short peptides have been extensively studied with focus on structural diversity of the complexes or selectivity towards metal ions.<sup>1</sup> Despite the vast literature work with almost all transition metals up to now, the crystal structures of oligopeptide complexes are scarce, probably due to the high flexibility and many coordination modes of peptide molecules.<sup>2</sup>

In expanding our research on Rh bioconjugates<sup>3</sup> to other transition metals, herein, we report novel Pd(II) and Pt(II) complexes with triphenylphosphine ligands bearing different amino acids. Structure of the complexes was studied in detail by means of spectroscopic methods and X-ray crystallography. NMR measurements in chloroform indicate predominant formation of *cis* and *trans* isomers for Pt and Pd complexes, respectively. Upon changing the solvent to acetonitrile, a significant increase in *cis* isomer is observed for Pd. Only *trans* Pd bioconjugates were found in the crystal structures of Gly and Phe derivatives.



**Figure 1** Molecular structures of (a) glycine and (b) phenylalanine Pd bioconjugates.

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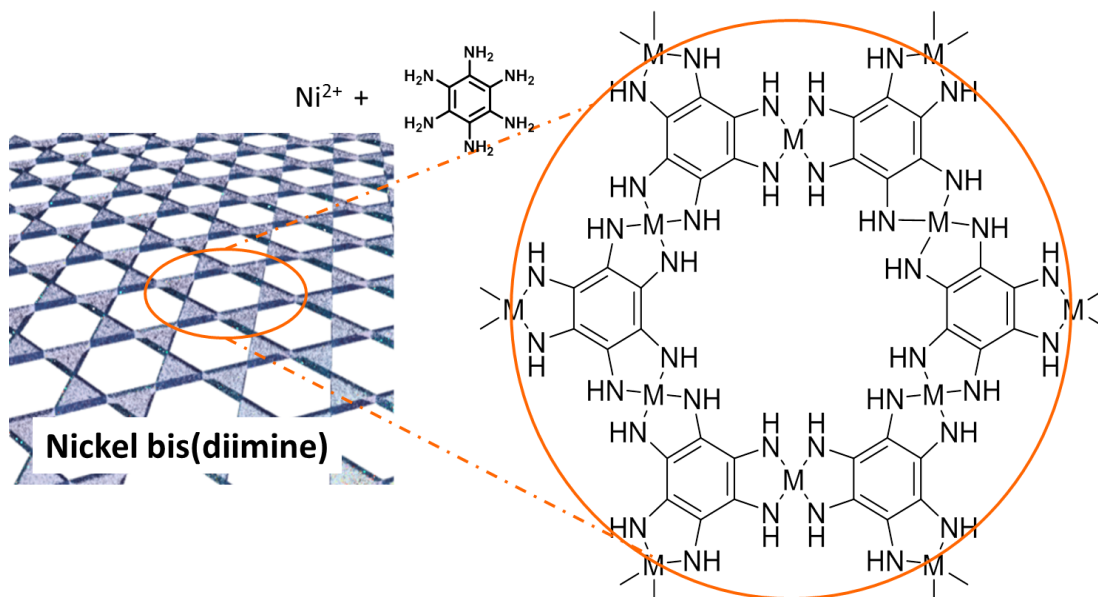
## Synthesis of Nickel Bis(diimine) Coordination Nanosheets

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The research on the chemistry of two dimensional compounds has been developing rapidly since the discovery of graphene in 2004, but the ability to tune and control these 2D materials' properties has been limited since most of these materials have been fabricated from a top-down method. Coordination nanosheets, or CONASH, are two dimensional sheets consisting of metal ions connected by bridging ligands via coordination bonds, synthesized from a bottom up method.

This work focuses on the study of one type of CONASH, the nickel bis(diimine) nanosheets, synthesized using hexaaminobenzene ligand and nickel(II) ions (Figure 1), the amine analogue of the bis(dithiolato)nickel complex nanosheet previously synthesized by Kambe et. al.<sup>1</sup> Crystalline black sheets obtained from a newly optimized gas-liquid interfacial reaction were characterized using pXRD, XPS, AFM, SEM and TEM. Other physical properties such as conductivity and magnetic susceptibility have also been investigated.



**Figure 1** Structure of nickel bis(diimine) CONASH synthesized.

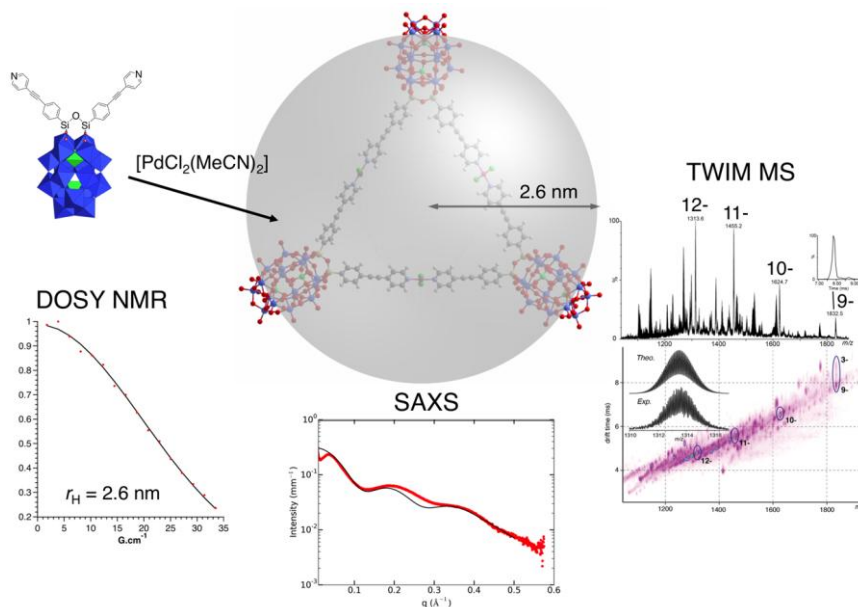
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## Coordination-directed Polyoxometalates Self-assemblies

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The development of nanostructured molecular materials is a major scientific challenge for various contemporary societal issues. In this context, the elaboration of materials of suitable properties integrating polyoxometalates (POMs) as molecular building blocks is particularly attracting owing to their various properties and potential applications. In particular, their functionalization into organic-inorganic hybrids makes them suitable for coordination-directed self-assemblies, which is a simple and effective way to control the formation of nanostructured materials. By using the synthetic functionalization strategies developed in the group to build POM-based hybrids of required topologies,<sup>1</sup> we recently developed their metal-directed self-assemblies as molecular polygons.<sup>2</sup> Owing to the large size of the resulting architectures, new characterization tools have been investigated. In some case, the resulting molecular polygons can further assemble into multi-scale architectures due to electrostatic interactions between the POMs and the cationic metallic linkers. We herein described synthesis of the POM-based building blocks and the characterization of the resulting coordination-directed self-assemblies.



<sup>1</sup> A. Proust, B. Matt, R. Villanneau, G. Guillemot, P. Gouzerh, G. Izzet, *Chem. Soc. Rev.* **2012**, *41*, 7605-7622.

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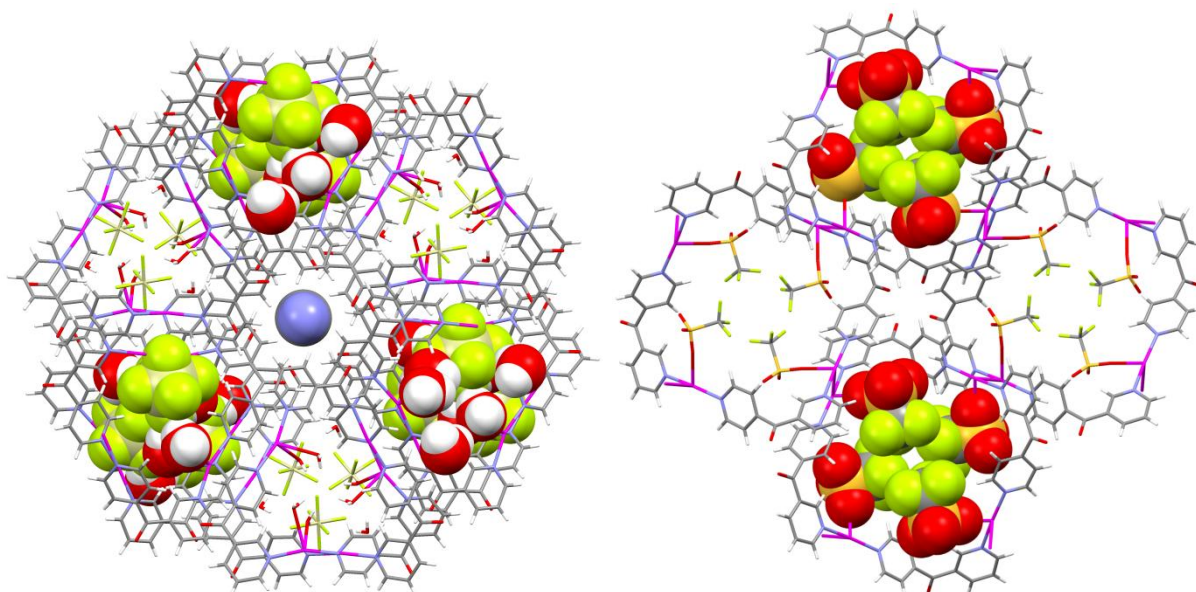
## Formation of networks with Ag(I) salts and the flexible unsymmetrical ligand 3,4-dipyridyl ketone

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The use of flexible ligands in coordination polymer chemistry gives rise to a diverse range of interesting and novel architectures with highly variable networks. The unpredictable nature of these complexes is further exacerbated when formed using ligands that are also unsymmetrical. Previous research involving flexible dipyriddy ketone ligands has revealed the formation of a wide range of assembly motifs, in part due to pyridyl ring rotation. This introduces a degree of chirality, as the ligands form two-bladed chiral propellers in the solid state. X-ray crystallography has shown that a range of differing architectures can be formed by altering the substitution of the pyridyl rings, the counter ion or metal cation.

We shall describe the use of the unsymmetrical flexible ligand 3,4-dipyridyl ketone in the formation of a range of networks when coordinated to varying Ag(I) salts (**Figure 1**). These systems make use of multiple cooperative weak interactions such as hydrogen bonding,  $\pi$ - $\pi$  stacking and van der Waals contacts. Some of the networks contain channels, which demonstrate a potential application for future storage devices.



**Figure 1** Two of the structures formed from complexation of 3,4-dipyridyl ketone and varying Ag(I) salts.

## Synthetic Complexes of new Quino[7,8-*h*]quinoline Derivatives

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The properties and applications of supramolecular cages and complexes are dependent on the synthons they are built from. Like 1,10-phenanthroline, the proton sponge quino[7,8-*h*]quinoline<sup>1</sup> is an attractive target as a functionalisable base structure for new synthons. Recently a new quino[7,8-*h*]quinoline derivative, 4,9-dipyridylquino[7,8-*h*]quinoline has been developed.<sup>2</sup> This presentation will explore the metallo-organic structures formed with this new molecule, and its potential for supramolecular cage formation.

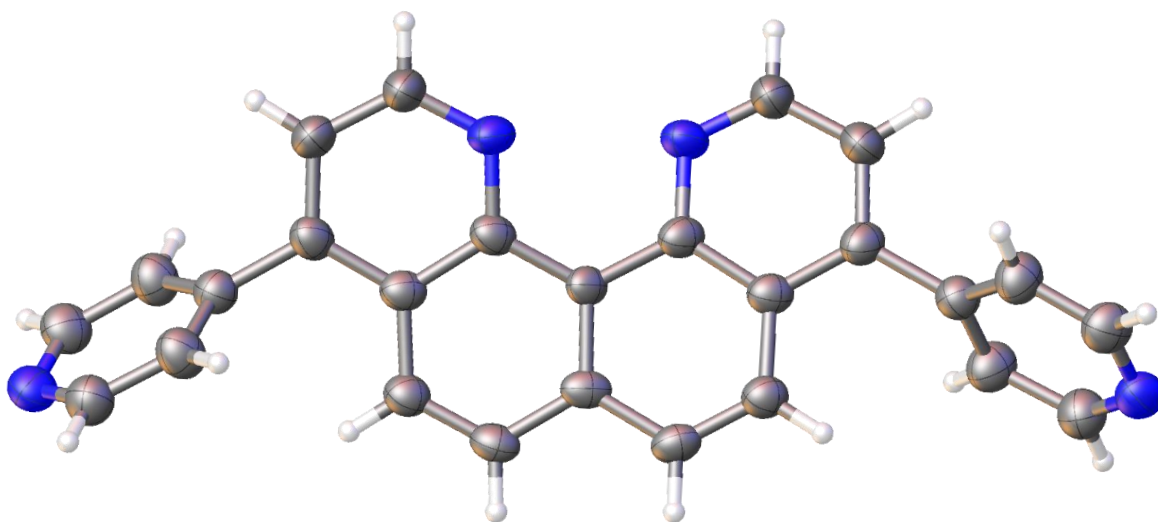


Figure 1 X-ray structure of 4,9-dipyridylquino[7,8-*h*]quinoline.<sup>2</sup>

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## Investigating pressure induced phase changes of porous organic molecular cages

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Porous organic materials offer synthetic advantages due to their solubility, mobility and diversification.<sup>1</sup> Work within the Cooper group has yielded a number of porous organic molecular cages, including shape persistent Covalent Cage 3 (**CC3- $\alpha$**  Figure 1) which can be used in a number of applications, including rare gas separation.<sup>2,3</sup>

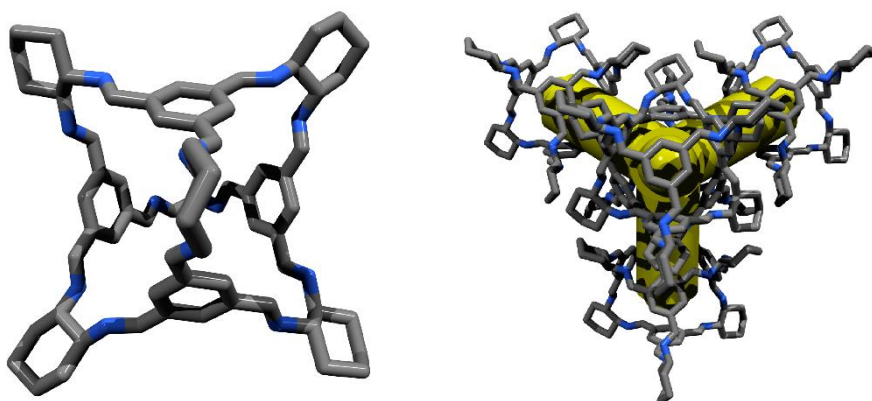


Figure 1 Left: Solitary **CC3** molecule, with the imine bonds illustrated in blue.  
Right: Tetrahedral network of the **CC3- $\alpha$**  crystal structure in cubic *F* space group  $F4_131$ ,  $a = 24.8569 \text{ \AA}$

Traditionally novel polymorphs of imine-based organic molecular cages, possessing different properties, can be accessed by varying crystallisation solvents.<sup>4</sup> By contrast, this work will induce and isolate novel phases using high pressures in order to modify the porosity. Previous work by Little *et. Al* has shown that the polymorph **CC3- $\beta$**  can be directed using diethylether.<sup>5</sup> It has been demonstrated using powder X-ray diffraction that post-exposure to high pressures the thermodynamically favourable **CC3- $\alpha$**  phase retains its structure. However the meta-stable polymorph of the same cage, **CC3- $\beta$**  converts to the thermodynamic **CC3- $\alpha$**  phase after exposure to pressures  $> 100 \text{ bar}$ .

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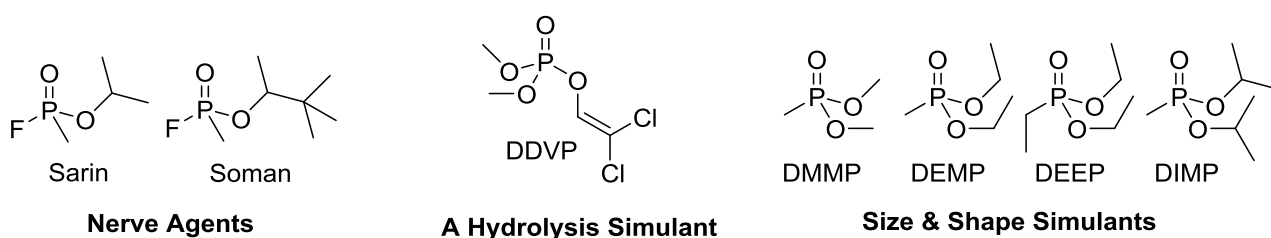
## Trapping, Detection and Destruction of Nerve Agent Simulants within Supramolecular Cages.

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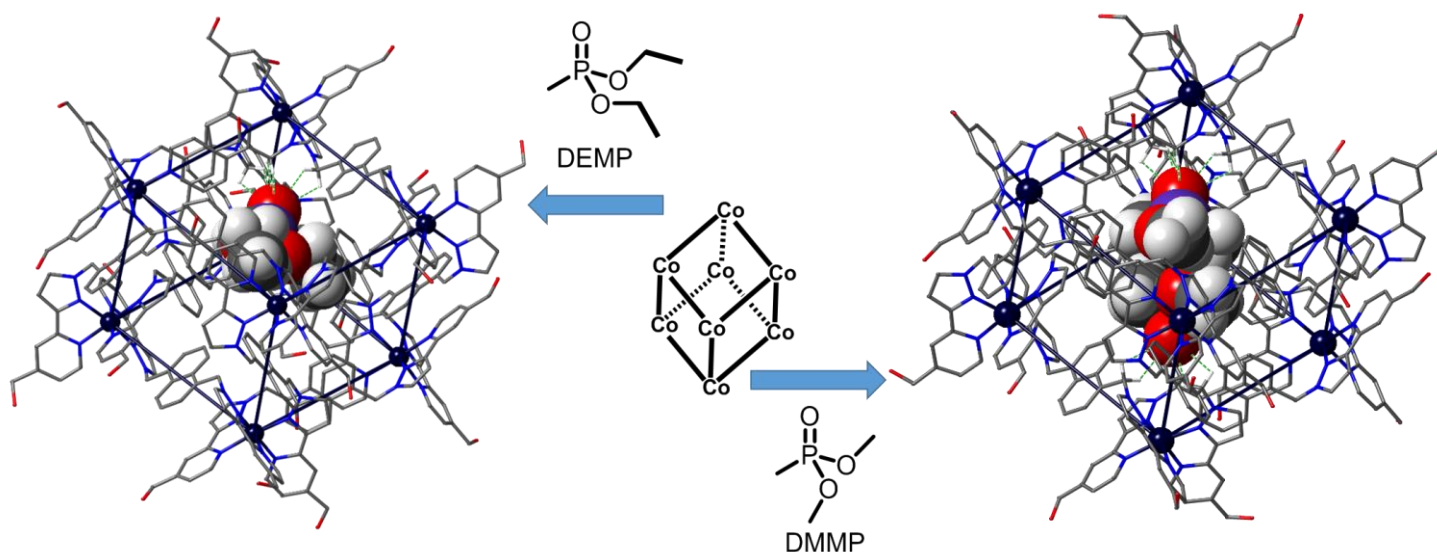
An increasing number of examples of self-assembled metal coordination cages have the ability to bind guests within an internal cavity allowing applications such as drug delivery or even the control of a reaction.

G-series nerve agents, such as Sarin, are colorless, odorless and deadly. A series of nerve agent simulants have been investigated and bound inside the Cage-Host.



**Figure 1** Structures of two G-series nerve agents and various chemical or physical simulants.

The single crystal x-ray structures of Host-Guest complexes have been obtained – two examples are displayed below (Fig 2). The binding of various simulants within the Cage-Host has been investigated. Additionally, the effect of cage binding upon the hydrolysis reaction of a simulant is under investigation.



**Figure 2** X-ray structures of simulants DEMP and DMMP within the Cage-Host.

## Coordination driven lanthanide capsules.

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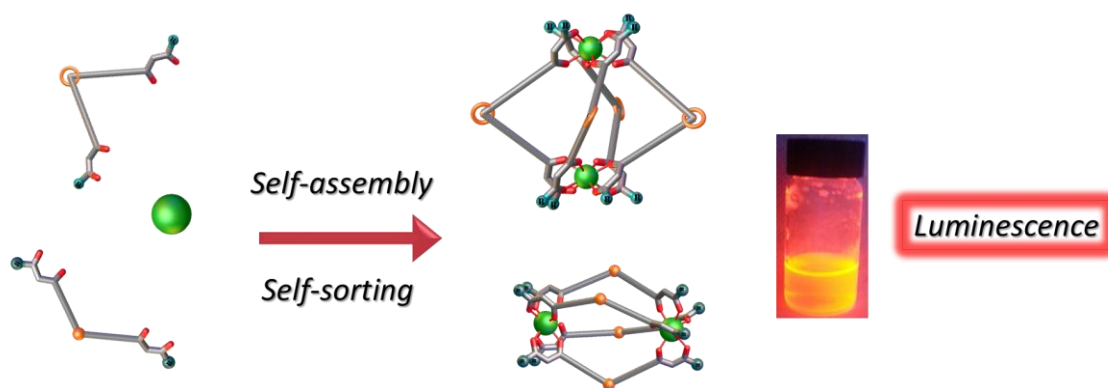
<sup>a</sup> Dept. of Chemical Sciences, University of Padova, Via Marzolo 1, 35131 Padova, Italy

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Self-assembly and self-sorting are a key step to obtain functional supramolecular objects towards complex matter. Herein, we present the synthesis and characterization of innovative classes of metal-organic capsules (MOCs) where the structural features of MOCs are combined with the peculiar optical properties of lanthanoid ions, in order to obtain luminescent coordination-driven capsules. To this aim,  $\beta$ -diketone based ligands have been combined with Eu(III) as metal center. A series of bis-1,3-diketone ligands (DPX-R library) have been designed with different scaffold units to tune the ligand geometry and in order to be easily functionalized. Self-assembly and self-sorting of  $[\text{Eu}_2(\text{DPX-R})_4]^{2-}$  capsules have been studied through ESI-MS and NMR analyses. Luminescence, quantum yields and lifetimes have been characterized. The stability and the emission properties of the capsules have been investigated in both water and organic solvents, down to nanomolar concentration.



**Figure 1** Self-assembly and self-sorting of luminescent europium-based supramolecular capsules.

## Synthesis and characterization of a Cu(I)-rotaxane stoppered by [2+2]cycloaddition-retroelectrocyclization with TCNQ

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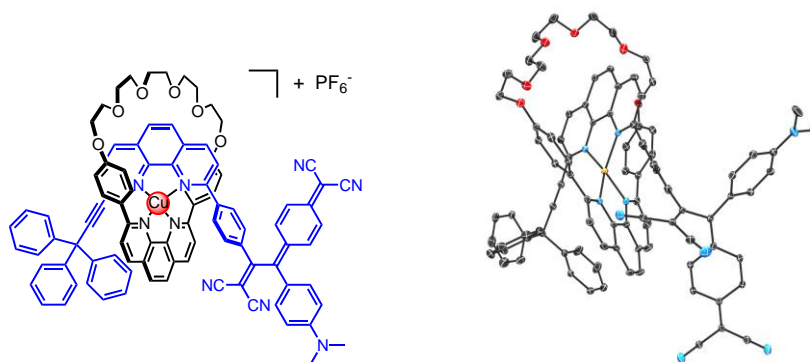
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A new Cu(I)-rotaxane has been synthesized by copper-template strategy.<sup>1</sup> The stoppering reaction involved a [2+2]cycloaddition-retroelectrocyclization (CA-RE) sequence between an aniline-functionalized pseudorotaxane and 7,7,8,8-tetracyanoquinodimethane (TCNQ). This rotaxane was characterized by NMR and UV-vis spectroscopies, mass spectrometry, electrochemistry and X-ray crystallography.

The UV-vis spectrum of this rotaxane shows two bands in the visible range with  $\lambda_{\max} = 471$  and 686 nm possessing extinction coefficients about  $14000 \text{ M}^{-1} \cdot \text{cm}^{-1}$  and  $23000 \text{ M}^{-1} \cdot \text{cm}^{-1}$  respectively. Particularly noteworthy is also the fact that this system absorbs light on the whole visible region and until near infrared region, with an extinction coefficient over  $10000 \text{ M}^{-1} \cdot \text{cm}^{-1}$  from 400 to 800 nm.



**Figure 1** Chemical and X-ray structures of the new rotaxane.

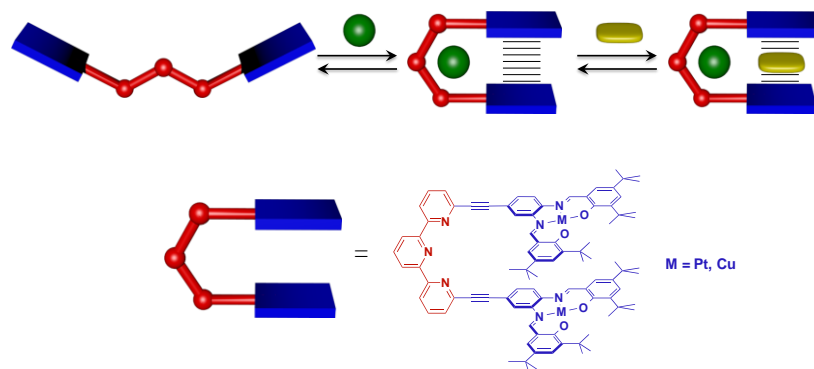
<sup>1</sup> Y. Trolez, A. Finke, F. Silvestri, F. Monti, C. Boudon, J.-P. Gisselbrecht, W. B. Schweizer, N. Armaroli, J.-Pierre Sauvage, F. Diederich, *manuscript in preparation*

## Switchable Luminescent or Magnetic Molecular Tweezers

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In the field of nanosciences, the control at the molecular level of physical or chemical properties represents an important challenge. Designing modular systems for the reversible switching of optical or magnetic properties via a mechanical motion is an innovative approach. We are interested in the design of molecular tweezers<sup>1</sup> that are switchable by metal coordination to perform such tasks. Our system is based on a terpyridine ligand substituted in 6 and 6'' positions by two arms bearing functional moieties (Figure 1). The terpyridine unit can switch upon metal coordination between a "W" shaped open form and a "U" shaped closed form bringing the two functional units in close proximity and an optimal geometry for binding substrates. Upon decoordination the tweezers will reopen, releasing the intercalated substrate. The functional units are based on salen complexes with magnetic or luminescent properties depending on the metallic center.

The synthesis and reversible switching of luminescent tweezers based on Pt-salen complexes will be presented as well as the impact of the intercalation on the luminescence properties.<sup>2</sup> The switching of magnetic interaction via a mechanical motion in Cu-salen based tweezers<sup>3</sup> will also be highlighted.



**Figure 1** Switchable molecular tweezers

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## The Significance of C-H $\cdots$ $\pi$ (metalloaromatic) Interactions in Stabilising Crystal Structures

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Secondary interactions provide crucial stabilisation in molecular packing. Most commonly, attention has been paid to hydrogen bonding, halogen bonding and  $\pi\cdots\pi$  stacking. Less studied are C-H $\cdots$  $\pi$  interactions, especially involving metalloaromatic chelate rings. In fact, C-H $\cdots$  $\pi$ (chelate) interactions also contribute to crystal stability.

Palladium(II) xanthates were studied as a model system for this supramolecular interaction. Thus, a series of 12 palladium(II) xanthates with varying side chains up to derivatives of hexyl, including species with primary, secondary or tertiary carbon atom. Surprisingly, 11 out of the 12 structures show the presence of the C-H $\cdots$  $\pi$ (PdS<sub>2</sub>C) interactions, with up to six interactions per molecule. DFT calculations were performed to further investigate this interaction: the C-H $\cdots$  $\pi$ (PdS<sub>2</sub>C) interactions were found to provide a similar energy of stabilisation as provided by intermolecular Pd $\cdots$ S interactions.

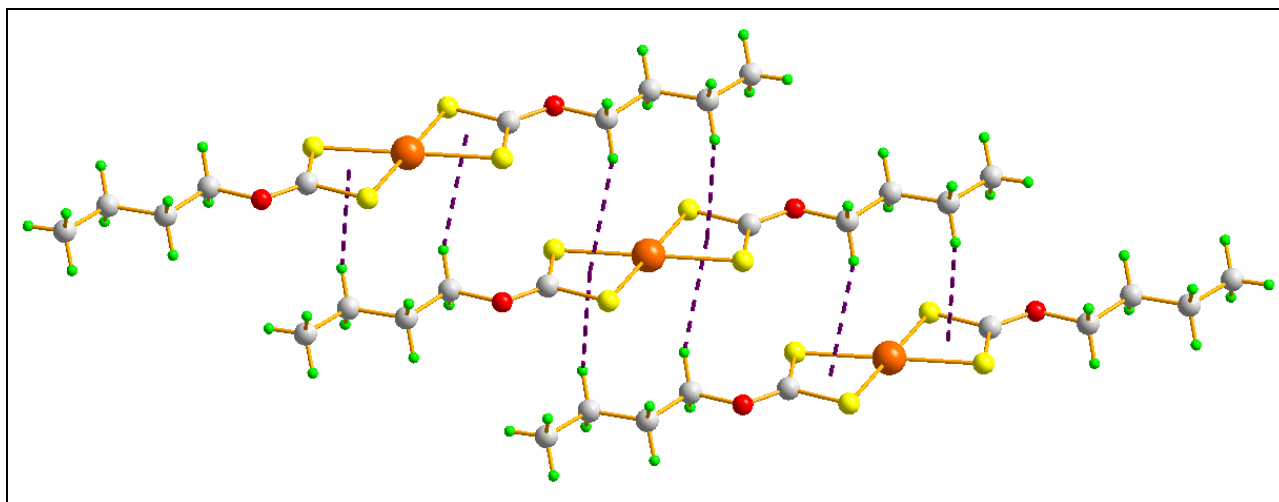


Figure1: Four cooperative C-H $\cdots$  $\pi$ (PdS<sub>2</sub>C) interactions per [Pd(S<sub>2</sub>COnBu)<sub>2</sub>] molecule.



## Syntheses and crystal structures of 1D coordination polymers constructed by bis-imidazole type ligands

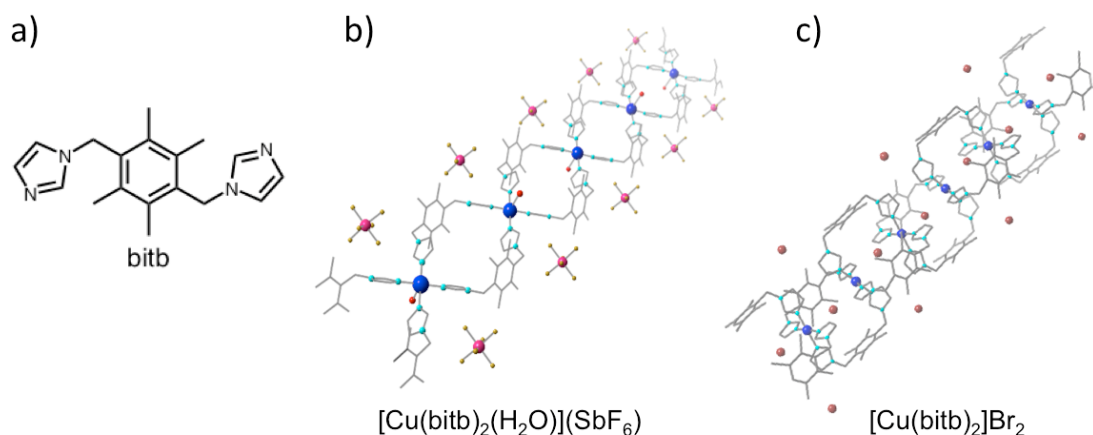
Yusuke Sugiyama,<sup>a</sup> Shiori Koike,<sup>a</sup> Moeko Sato,<sup>a</sup> Mitsuru Kondo<sup>a,b,\*</sup>

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Bis-imidazole type ligands have been used for syntheses of many metal complexes, which are cage type complexes and coordination polymers. The obtained structures are largely affected by kinds of metal ions, ligand structures, and counter anions. We have found that combination of Cu<sup>II</sup> ion and 1,4-bis(imidazol-1-ylmethyl)-2,3,5,6-tetramethylbenzene (bitb) provides a M<sub>2</sub>L<sub>4</sub> cage type complex responding to ClO<sub>4</sub><sup>-</sup> ion.<sup>1</sup> In this work, we have synthesized and structurally characterized the two new coordination polymers with bitb.

Reaction of CuSO<sub>4</sub>·5H<sub>2</sub>O with bitb and NaSbF<sub>6</sub> produced a coordination polymer [Cu(bitb)<sub>2</sub>(H<sub>2</sub>O)](SbF<sub>6</sub>)<sub>2</sub> (**1**) as blue crystals. Similarly, another coordination polymer [Cu(pbibt)<sub>2</sub>]Br<sub>2</sub> (**2**) was obtained by treatment of CuBr<sub>2</sub> with bitb. These compounds show 1D coordination frameworks as shown in Figure 1b and 1c. We have found that these compounds converted to the M<sub>2</sub>L<sub>4</sub> cage type complexes by contact with ClO<sub>4</sub><sup>-</sup>. Their structures and the conversion reactions are described.



**Figure 1** Structure of bitb (a). Crystal structures of **1** (b) and **2** (c).

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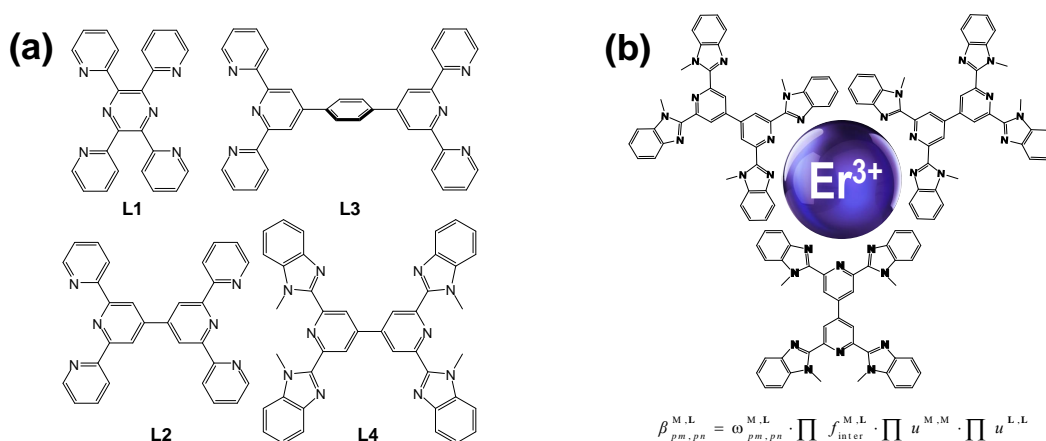


## Dual behavior of trivalent erbium with ditopic ligands in coordination compounds

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Back-to-back bis(tridentate ligands) such as **L1**= tppz, **L2**=btpy, **L3**=bptpy and **L4**= bbzpy (Figure 1a) have been mainly used for complexing kinetically inert Ru(II) entities, thus producing processable dinuclear discrete entities displaying attractive energy- and electron-transfer properties.<sup>1</sup> The complexation behavior becomes more tricky when labile d-block, or even f-block cations are reacted with **L1-L4**, and only few attempts have been made to explore their reactivity and speciation in solution.<sup>2</sup> In this context, the outstanding luminescence properties of trivalent lanthanides complexes, such as long excited state lifetimes, large antenna-generated pseudo-Stokes shifts, narrow emission bands and high emission quantum yields could be modulated by the complexation to back-to-back **L1-L4** ligands.<sup>3</sup> As a first step toward this goal, we report here on the thermodynamic properties of their complexation processes with  $\text{LnX}_3$  ( $\text{X} = \text{CF}_3\text{SO}_3^-$ ,  $\text{NO}_3^-$ ). Application of the site-binding model sheds light on the allosteric cooperativity factors produced by the successive fixation of two triply-charged cation  $\text{Ln}^{3+}$  on the same ligand and on its consequence for the formation of metallosupramolecular oligomers and polymers (Figure 1-b).



**Figure 1** (a) Schematic structures of ditopic ligands **L1**, **L2**, **L3** and **L4** and (b) of a saturated  $[\text{Er}(\text{L4})_3]^{3+}$  complex. The thermodynamic site-binding model is depicted.

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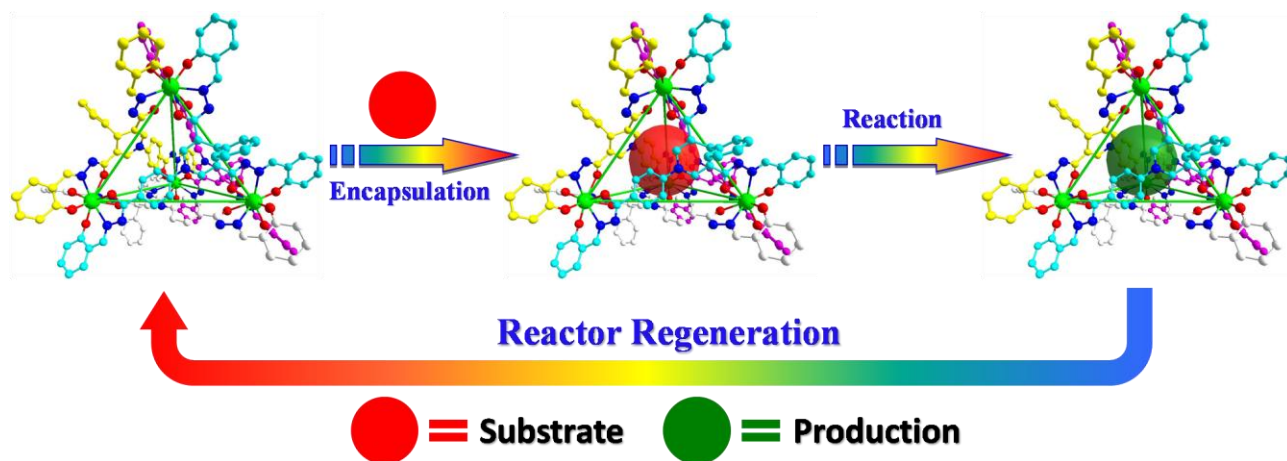
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## Construction of Renewable Metal-organic Supramolecular Reactor and Their Photochemical Properties

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The design of these artificial catalysts is a subject of intensive research because of they can compete with the catalytic proficiency of enzymes. The conventional route to fabricating an effective artificial enzyme is functionalized to mimic the environment and catalytic centers by reproducing structure of the enzyme's active site into mother structure of organic linkers. Accordingly, self-assembly molecular reaction vessels based on reversible interactions have been considered a new phase of matter, in which the physicochemical properties of the molecules contained in the "molecular flask" are considerably modified with respect to those exhibited in the solid, liquid, or gas phase. Nevertheless, in spite of the advances made in the process of functionalized of molecular reaction vessels in recent years, so far all know regeneration of functionalized molecular reaction vessels is still a very difficult problem. Developing a renewable functionalized molecular reaction vessels for a series of important and high-value chemical reaction is still a great challenge in the field of metal-organic supramolecule.



**Figure 1** The process of encapsulation, reaction and regeneration of molecular reactor.

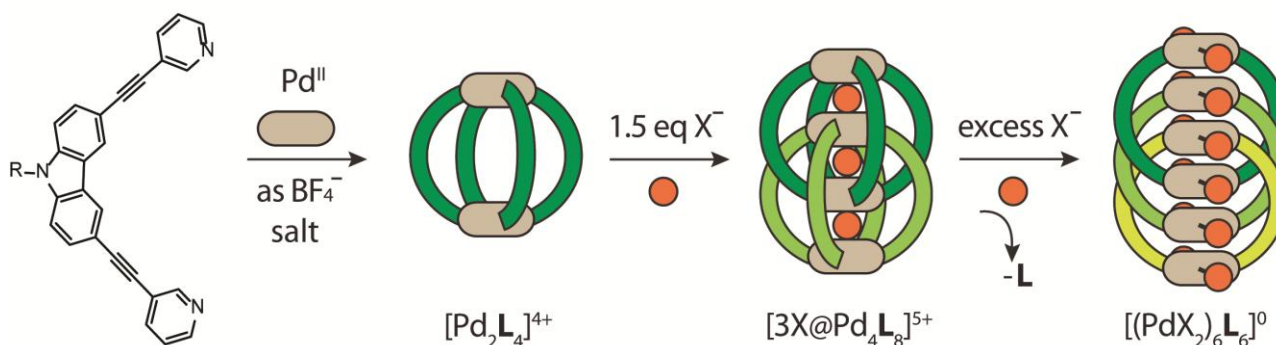
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## Stepwise Halide-triggered Double- and Triple-Catenation of Self-Assembled Coordination Cages

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The self-assembly of supramolecules driven by metal coordination has been intensely researched because of its extraordinary characteristics and potential applications. Researchers have studied anion binding widely in recent years due to its important roles in chemical and biological processes.<sup>1</sup>



**Figure 1:** Stepwise assembly of the monomeric cage [Pd<sub>2</sub>L<sub>4</sub>], the halide templated double-cage [3X@Pd<sub>4</sub>L<sub>8</sub>] (X = Cl<sup>-</sup>, Br<sup>-</sup>) and the triple-catenane {*trans*-[(PdX<sub>2</sub>)<sub>2</sub>L<sub>2</sub>]<sub>3</sub>} (X = Br<sup>-</sup>).

We have designed a structurally related but slightly shorter bis-pyridyl ligand based on a carbazole backbone compared with dibenzosuberone<sup>2</sup> and phenothiazine<sup>3</sup> in our previous work and reacted it with the palladium salt [Pd(CH<sub>3</sub>CN)<sub>4</sub>](BF<sub>4</sub>)<sub>2</sub> to obtain stable monomeric cage [Pd<sub>2</sub>L<sub>4</sub>] which shows no tendency to dimerize (Figure 1). Interestingly, the addition of stoichiometric amounts of halide anions resulted in the formation of dimeric cages containing halide anions in all of the three pockets. Surprisingly, excess amounts of the same anion (i.e. bromide) leads to a second structural transition generating a triply-catenated link structure.<sup>4</sup>

In conclusion, a thermodynamic stable monocage is obtained and two different self-assembled complexes are formed by variation of the concentration of a small anionic additive.

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## Self-assembly synthesis of sheet-type coordination polymer bearing cationic $M_2L_4$ cage type complexes

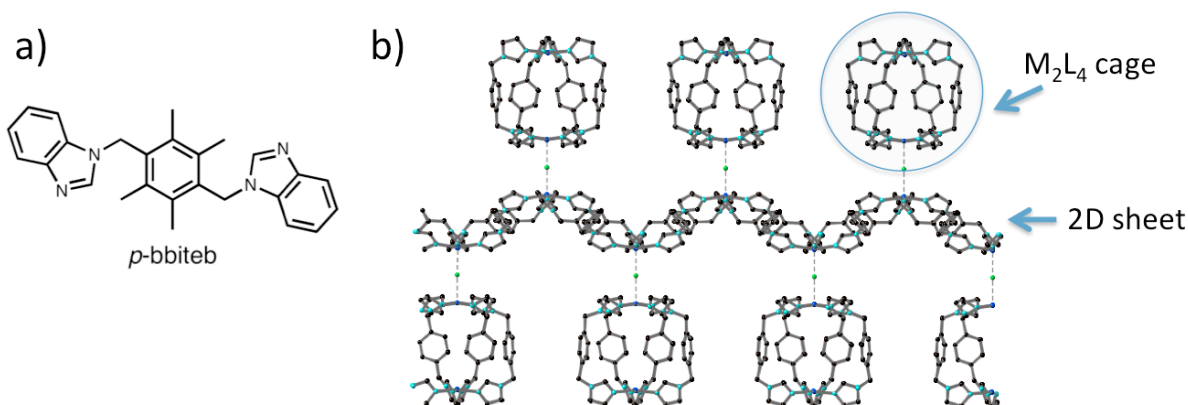
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Bis-benzimidazole type ligands have produced cage type complexes as well as coordination polymers.<sup>1</sup> Kinds of metal ions, ligand structures, and kinds of counter anions affect which type of compounds is obtained. Recently, we have found that 1,4-bis(benzimidazol-1-yl)-2,4,5,6-tetramethylbenzene (*p*-bbiteb) produces a new 2D coordination polymer,  $[Cu(p\text{-bbiteb})_2(-\mu\text{-Cl}[\text{Cl}\cdot(\text{H}_2\text{O})_2 \subset \text{Cu}_2(p\text{-bbiteb})_4])]\text{Cl}_4$  (**1**), whose main sheet framework bears cationic  $M_2L_4$  type cages on it.<sup>2</sup> This paper describes the unique one-spot self-assembly synthesis and crystal structure of the compound.

Treatment of  $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$  with *m*-bbitrbb produced the compound as blue crystals. The crystal structure was determined by single crystal X-ray diffraction analysis. Figure 1 shows crystal structure of the compound. This compound consists of cationic 2D coordination framework  $[\text{Cu}(p\text{-bbiteb})_2]^{2+}$  and  $M_2L_4$  type cationic cages  $[\text{Cl}\cdot(\text{H}_2\text{O})_2 \subset \text{Cu}_2(p\text{-bbiteb})_4]^{3+}$ . The cages are connected to the layer via  $\mu\text{-Cl}^-$  bridge. The overall structure created channels between the  $M_2L_4$  cages. The space are filled with  $\text{Cl}^-$ . It has been shown that the counter anions were preferentially exchanged with  $\text{ClO}_4^-$  and  $\text{NO}_3^-$  to remove these anions from aqueous solutions.



**Figure 1** Structure of *p*-bbiteb (a). Crystal structure of **1** (b).

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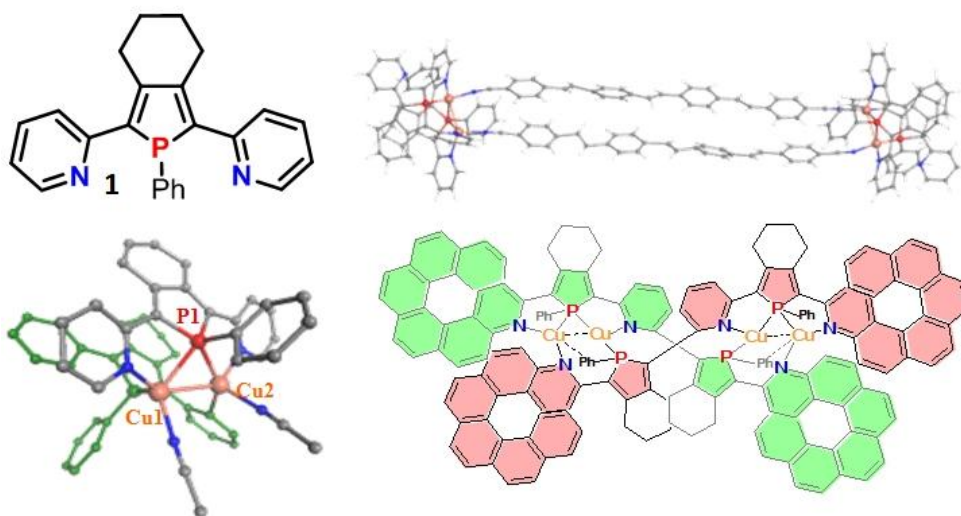
## Supramolecular assemblies based on pre-assembled polymetallic precursors bearing organophosphorus ligands

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Examples of stable polymetallic complexes bearing a bridging phosphane moiety are still very scarce and the reactivity of the such derivatives remains mainly unexplored. We have described a family of air stable bimetallic Cu(I) and Ag(I) complexes bearing the 2,5-bis(2-pyridyl)phosphole derivative **1** as bridging phosphane ligand.[1] These complexes can be used as versatile molecular clip in order to control the coordination-driven self-assembly of a variety of  $\pi$ -conjugated systems into  $\pi$ -stacked supramolecular metallocyclophanes.[2] Such results highlight the interest of pre-assembled polymetallic precursors for coordination-driven self-assembly processes as well as of the use of multidentate ligands bearing bridging phosphane coordination modes in order to obtain functional polymetallic supramolecular assemblies. Recent advances in this field will be presented



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## Cyclen-based macrocycles for the complexation of Bi<sup>3+</sup> for $\alpha$ -radioimmunotherapy

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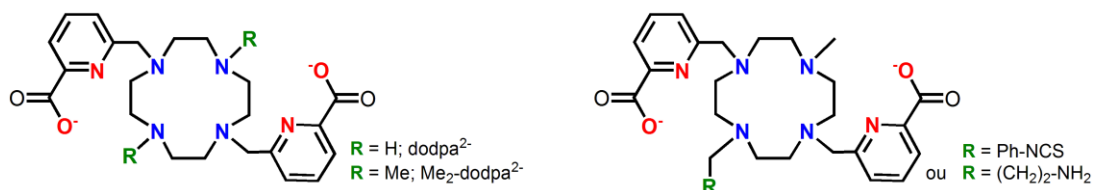
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Alpha-radioimmunotherapy ( $\alpha$ -RIT) represents an emerging therapeutic modality for tumour treatment.<sup>1</sup> The energy emissions of  $\alpha$ -particle decays are directly deposited over a very short distance (40-100  $\mu$ m), resulting in high linear energy transfer with limited toxicity toward normal tissues adjacent to the tumour. <sup>212</sup>Bi and <sup>213</sup>Bi are among the most studied radionuclides for  $\alpha$ -RIT applications. Therefore, our aim is to synthesize ligands that can trap hot bismuth and carry the  $\alpha$ -emitter selectively to the tumours to destroy.

Cyclen-based ligands bearing pyridine-2-carboxylic acid pendant arms were studied as chelates for bismuth(III) (Figure 1). The <sup>nat</sup>Bi<sup>3+</sup> complexes obtained present remarkably high thermodynamic stability constants. The labelling of **Me<sub>2</sub>-dodpa<sup>2-</sup>** with <sup>213</sup>Bi also resulted in a stable complex *in vitro*.

The ligand design allows easy introduction of bioconjugation functions by replacing one of the *N*-methyl group without altering the coordinating properties of the ligand (Figure 1). Isothiocyanate or amine derivatives were synthesized to obtain Bifunctional Chelating Agents (BCAs). The efficiency of the resulting radiopharmaceutic, specially its efficiency to target cancer cells will be examined.



**Figure 1** (a) Cyclen-based ligands and (b) BCAs derivatives for Bi(III) complexation.

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## New approaches to target the copper imbalance and toxicity in the brain affected by Alzheimer's disease

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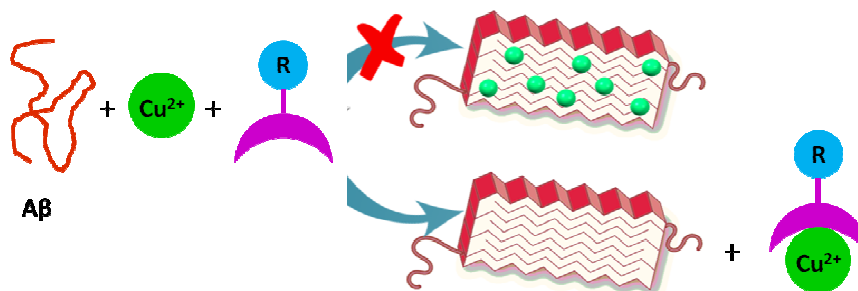
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Increasing evidence relates metal dyshomeostasis –especially, copper, iron and zinc– with the advent of neurodegenerative disorders such as Alzheimer's disease (AD).<sup>1</sup> Copper ions can interact with amyloid beta (A $\beta$ ) fragments and modulate their aggregation pathway, A $\beta$  aggregates being one of the hallmarks of AD. What is more, several studies suggest that the binding of copper ions promotes the formation of soluble oligomeric species, which are considered the most toxic form of A $\beta$ .<sup>2</sup>

Our research focuses on the restoration of the balance of copper ions *via* the administration of molecules acting as metal ionophores or “shuttles”. By trapping the excess of copper(II) ions that are loosely-bound in the extracellular media, we aim to block their redox activity and prevent the formation of toxic A $\beta$  aggregates and oxidative stress.

In this communication, we present our latest results regarding the use of small peptides and the strategies applied to tune their properties, including the ability to cross the blood-brain barrier, and to extend their potential applications.<sup>3</sup>



**Figure 1** Schematic representation of the proposed therapeutic approach.

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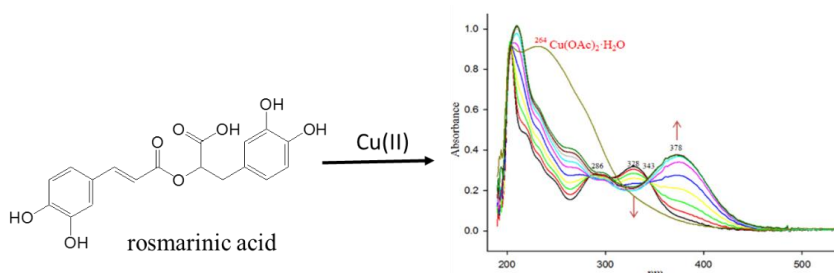
## Neutralization of toxic heavy metal ions using catechol-based materials isolated from comfrey

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Many metal ions are known to be toxic to humans and difficult to purge out from the body. For the effective reduction of poison caused by metal ions, the chelating agent such as EDTA analogs and dimercaprol is commonly used in the clinic treatment. However, EDTA is considered as a toxic material in biological systems. In order to neutralize the toxicity of these heavy metal ions, we have developed a new type of reagent to approach the detoxification of heavy metal ions. The strategy is based on the use of natural products containing catechol moieties to achieve the complexation. For instance, comfrey species are important therapeutic herbs for a long and widespread usage. The plant contains the small organic molecule allantoin, which is thought to stimulate cell growth and repair while simultaneously depressing inflammation. However, it contains dangerous amounts of hepatotoxic pyrrolizidine alkaloids (PAs) but is removable.



**Figure 1 Structure of rosmarinic acid and its binding study with Cu(II) ion**

In our lab, rosmarinic acid was successfully isolated from comfrey and demonstrated as one of the important components in biological effect achieved by using HPLC, DPPH method, NMR techniques (HMQC and HPBC), and zebrafish experiment. The binding constants of rosmarinic acid with Cu(II), Zn(II), Ni(II), Pb(II), and Fe(II) ions showed an approximated value of  $\sim 10^4 \text{ M}^{-1}$  measured by UV titration. As well, the binding sites of rosmarinic acid and a variety of metal ions were determined using NMR titration. In order to enhance the binding strength toward metal ions, a derivative of rosmarinic acid was designed and synthesized to assemble as nanoparticles. A further detail will be discussed.

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## Biocompatible nanohydrogels incorporating conventional MRI contrast agents: simple design, huge performances.

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Due to its high anatomical resolution, magnetic resonance imaging (MRI) is one of the most powerful non-invasive techniques for clinical diagnosis. However, information obtained from a simple unenhanced MR image is often not sufficient to highlight the areas of interest. Then, the contrast has to be improved by administering paramagnetic contrast-enhancing agents, mainly gadolinium chelates (GdCAs). Nevertheless at medical fields, their contrast enhancing capacity (quantitatively represented as relaxivity  $r_1$ ) is low.

To circumvent this important limitation, our objective is to tune the sensitivity of commercially available GdCAs into hypersensitive MRI probes. On the basis of SBM theory<sup>1</sup>, we have developed a series of biocompatible polysaccharide-based nanohydrogels for the encapsulation of GdCAs (GdCA<sub>c</sub>NPs)<sup>2</sup>. These nanohydrogels elaborated by an easy and robust ionotropic gelation process<sup>3</sup>, encapsulate various GdCAs<sup>4</sup> in a highly hydrated nanostructure. In the presentation, we will demonstrate that according to the nature of the polymer matrix,  $r_1$  relaxivities per Gd centre as high as 100 s<sup>-1</sup> mM<sup>-1</sup> at 30 MHz can be reached. The NMRD profiles will confirm that GdCA molecular motions are restricted and water access to the inner core of these nanogels not limited.  $T_1$ - and  $T_2$ -weighted images recorded at 3 T will show that this relaxation enhancement is clearly translated into a magnified contrast, demonstrating the powerful dual mode imaging ability of such nanosystems. Finally, cytotoxicity studies will demonstrate GdCA<sub>c</sub>NPs safety and their use for lymph node imaging will be addressed.

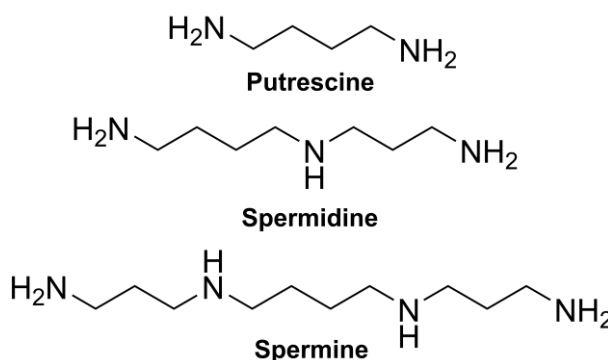
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## Can polyamines be used to deliver chemotherapeutic transition metal complexes?

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The naturally occurring polyamines putrescine, spermidine and spermine are found in almost all living cells. They are crucial to cell viability and play a key role in proliferation. Many cancer cell lines exhibit an upregulated polyamine transport system (PTS). As such, polyamine-drug conjugates are currently being evaluated as an approach toward cancer cell specific delivery of chemotherapeutic drugs.<sup>1</sup> Polyamines have been shown to enter the cell by endocytosis and be sequestered into acidic vesicles.<sup>2</sup> Acid labile linkers could provide a mechanism to selectively release chemotherapeutic drugs at the target site.



**Figure 1** The naturally occurring polyamines.

Cancer targeting chelating ligands bearing a polyamine group have been synthesised using Sonagashira coupling, diazo transfer and copper(I) catalyzed azide-alkyne cycloaddition, and coordinated to various metal centres. The luminescent properties of the complexes will be explored, and initial biological evaluations reported.

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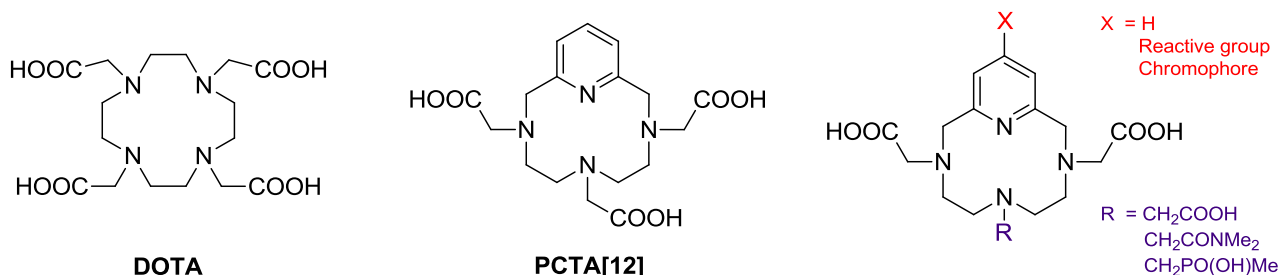
## Toward bimodal imaging through PCTA scaffold

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Among imaging techniques, some are characterized by high sensitivity but low resolution (optical imaging), and others by high resolution but low sensitivity (magnetic resonance imaging, MRI). Introduced about fifteen years ago, the bimodal imaging concept aims to combine two modalities in order to have both high sensibility and high resolution. This concept leads to the development of bimodal contrast agents, usually based on metal complexes. In this area of research, the well-known DOTA family plays a leading role but surprisingly, the heptadentate ligand PCTA[12], received far less attention.<sup>1</sup> Its potentiality to act as MRI contrast agent ( $Gd^{III}$  complex) has been reported over twenty years ago and more recently some of its derivatives were successfully evaluated for optical imaging ( $Tb^{III}$  complex) or nuclear imaging ( $Cu^{64}$ ,  $Ga^{68}$  complex for TEP and  $In^{111}$  complex for SPECT).<sup>2-4</sup>



We report here several PCTA derivatives and the relaxometric and fluorescent properties of their lanthanide complexes. Our interest in this family of chelators is based on their unique multimodal imaging potential as it offers the opportunity to adapt the coordination environment through functionalization and the heterocyclic moiety can act as a light collector to photosensitize the lanthanide ions. Moreover, functionalizing this unit for bioconjugation purposes should have very few effect on the chelating ligand properties.

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## Conception of radiopharmaceuticals radiolabelled with $^{188}\text{Re}$ for hepatocellular carcinoma targeting

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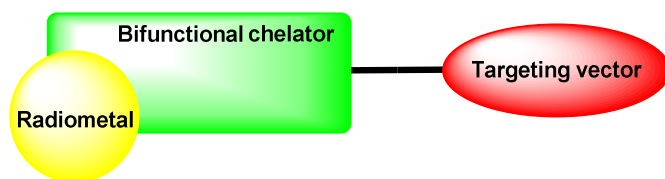
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Since 2008, Hepatocellular carcinoma (HCC) is the cancer with the highest mortality rate (0.95).<sup>[1]</sup> Nowadays, the only systemic treatment that has demonstrated a real benefit in advanced HCC is Sorafenib, but it remains associated with many side effects and this therapy is still very expensive. So, it is desirable to offer a more efficient, and cheaper, treatment.

An alternative is to develop radiotracers, so-called radiopharmaceuticals, to localize or destroy cancer cells selectively (*magic bullet concept*).<sup>[2]</sup>



**Figure 1** : Simplified representation of a radiopharmaceutical

Consequently, our challenge is to develop a targeting radiopharmaceutical with Rhenium-188 as destructive part, a tripodal  $\text{N}_2\text{O}$  bifunctional chelator and as biovector, a synthetic somatostatin analogue.

In this communication, we reported our first results related to the development of this radiopharmaceutical including: (i) the synthesis and the structural study of non-radioactive tricarbonylrhenium complexes involving BCAs based on a triazolyl moiety<sup>[3]</sup>, (ii) the conjugation of our BCAs to the biovector (iii) the first trials of  $^{188}\text{Re}$ -labelling of the tripodal ligand (proof of concept).

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## Nucleoside bis-(thio)phosphate analogues as metal-ion chelators with promising pharmacological properties

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Although involved in various physiological functions, nucleoside bis-phosphate analogues and their metal-ion complexes have been scarcely studied. Hence, we explored various properties of 2'-deoxyadenosine/guanosine-3',5'-bisphosphates, d(pNp), adenosine/guanosine 2',3'-bis(thio)phosphates, pNp, and the corresponding thiophosphate analogues, d(pSNpS) and pSNpS. These properties include their solution conformation, Zn(II)/Mg(II) binding-sites and binding-mode, acidity constants, stability constants of their Zn(II)/Mg(II) complexes, and species distribution. d(pNp) in solution adopted S ribose conformer, *gg* conformation around C4'-C5' and C5'-O5' bonds, and glycosidic angle in the *anti*-region. EPR and UV spectra indicated formation of a ML d(pNp)-Cu(II) complex (4O equatorial ligands) and ML d(pSNpS) and pSNpS -Zn(II)/Cu(II) complexes. <sup>1</sup>H-/<sup>31</sup>P-NMR spectra showed that Zn(II) was coordinated by P5' and P3' groups of d(pNp) but not by N7, and by both thiophosphate groups of d(pSNpS) and pSNpS. DFT calculations established that Zn(II) binds with O2S2 ligands in d(pSNpS) and pSNpS. d(pNp) formed ca. 100-fold more stable complexes with Zn(II) vs. Mg(II)-ions. Stability constants of Zn(II)/Mg(II) complexes of d(pNp) ( $\log K_{ML}^M=4.65-4.75/2.63-2.79$ , respectively) were similar to those of ADP/GDP complexes. Explicit solvent MD simulations of the complexes showed that the unexpectedly low  $\log K$  values of Zn(II)-d(pNp) vs. Zn(II)-NDP complexes are due to outer-sphere coordination in Zn(II)-d(pNp) vs. inner-sphere in NDP-Zn(II). d(pNp) and pNp inhibited OH<sup>•</sup> formation in Fe(II)-H<sub>2</sub>O<sub>2</sub> solution (IC<sub>50</sub> 24 - 40 μM). d(pSNpS) and pSNpS (IC<sub>50</sub> 50 – 92 μM), exhibited a dual antioxidant activity as both metal-ion chelators and radical scavengers (ABTS assay data). A turbidity assay showed that pSNpS dissolves Aβ<sub>42</sub>-Zn(II)/Cu(II) aggregates. Furthermore, d(pSNpS) and pSNpS reverted Aβ<sub>42</sub>-M(II) structure, back to that of free Aβ<sub>42</sub>, as observed by CD. Cryo-TEM/TEM images confirmed re-solubilization of Aβ<sub>42</sub>/Aβ<sub>42</sub>-M(II) aggregates by pSNpS. Hence, nucleoside bis(thio)phosphates are pharmacologically promising antioxidants and agents for solubilization of Aβ<sub>42</sub>-M(II) aggregates, acting by Cu(II)/Zn(II)-chelation.

## Molecular Gd(III) theranostic agent employing MRI and two-photon PDT

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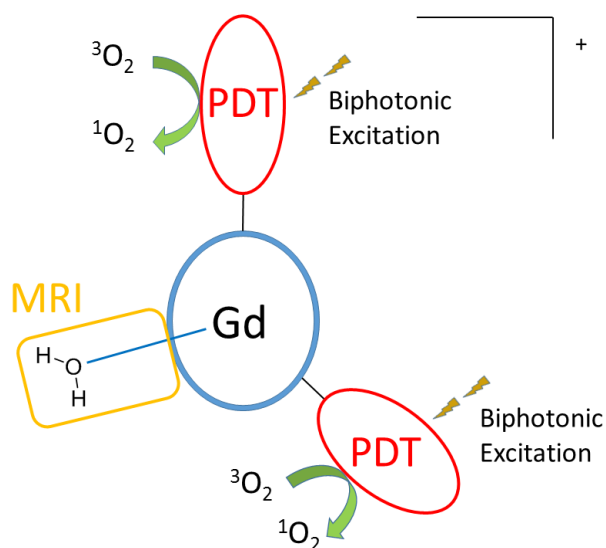
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Theranostics is a recent approach which combines in one entity a way to diagnose a disease and a way to treat it.<sup>1</sup> This can be achieved by using an imagery function for diagnosis and a therapy function for treatment.

We are currently developing molecular systems combining MRI (Magnetic Resonance Imagery) contrast agents and two-photon PDT (PhotoDynamic Therapy) photosensitizers generating singlet oxygen so as to kill cells. Indeed, monophotonic excitation suffers from the high absorption and diffusion of visible light by tissues while two-photon absorption permits to work in the near infra-red biological transparency window and to benefit from the high spatial resolution of the excitation.<sup>2</sup>



We present a new water-soluble molecular theranostic probe. It is composed of a triaza-cyclononane (TACN) platform substituted by two-photon PDT photosensitizers previously studied by our team<sup>3</sup> and complexed with Gd(III). The synthesis and spectroscopic studies will be presented.

**Figure 1** Molecular Gd(III) theranostic probe

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## New class of the NIR emitters beyond 1000 nm for theranostic applications: cytotoxic and luminescent 1D Pt-cyanoximates

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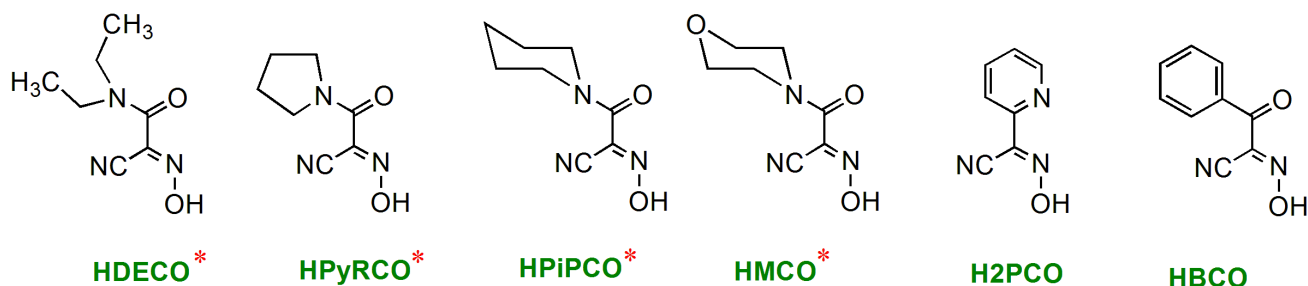
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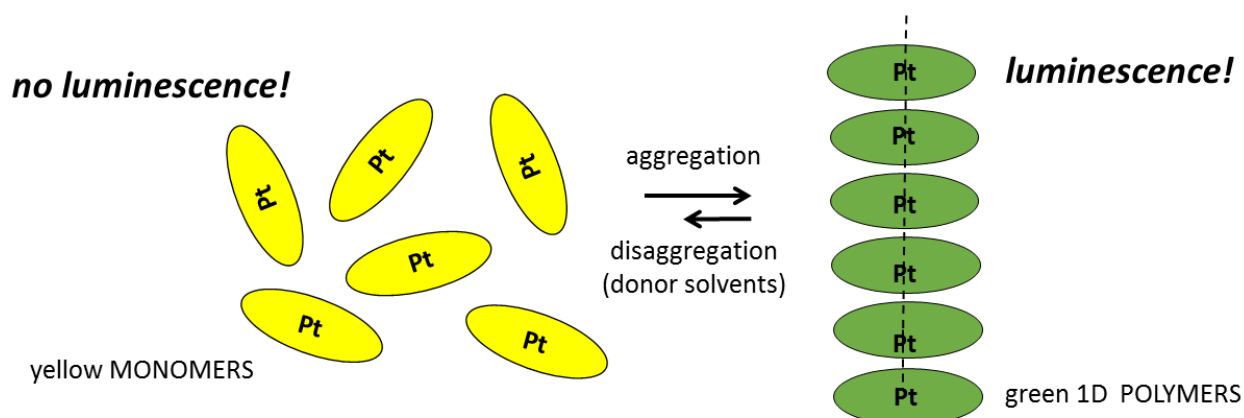
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We have discovered and initiated studies<sup>1</sup> of a unique class of platinum complexes of PtL<sub>2</sub> composition (L<sup>-</sup> = is a deprotonated ligand, Figure 1). In solutions yellow monomeric complexes spontaneously aggregate to form dark-green 1D mixed valence [PtL<sub>2</sub>]<sub>x</sub> polymers (Figure 2) in which individual units are held together via metallophilic Pt---Pt interactions. These polymeric Pt-cyanoximates strongly absorb in the 600 – 850 nm range and luminesce at 1000-1300 nm. Transparency of the biological tissue at 1060-1150 nm allows these complexes to be applied as theranostic agents because some studied Pt-cyanoximates exhibit pronounced cytotoxicity (ligands marked with \*). Chemistry and imaging properties of this new class of compounds are discussed in detail.



**Figure 1** Cyanoximes that form dark-green Pt-complexes.



**Figure 2** Self-assembly of Pt-cyanoximates into luminescent 1D polymers.

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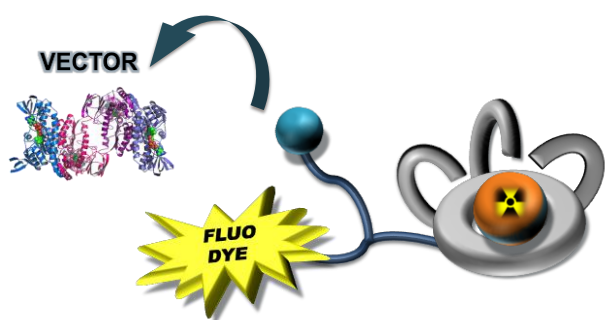
## BODIPY: a highly versatile platform for the design of Monomolecular Multimodal Imaging Probes

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Molecular imaging is a highly promising field of research and innovation with potential in a wide range of applications, including prognostic, diagnostic, drug discovery and development of theranostics.<sup>1</sup> The combination of two molecular imaging techniques can provide synergistic advantages and compensate the drawbacks of each imaging system while taking advantage of their individual strengths. In particular, combining optical and nuclear imaging may find important preclinical and clinical applications. For example, the radionuclide component can provide early quantitative data in a target tissue, and subsequent events can be monitored longitudinally by an optical method. In clinic, such bimodal imaging can be used for surgery assistance. Indeed, preoperative PET/SPECT scan will allow the localization of the tumor, while intraoperative optical imaging will help for a better delineation of tumor margins and resection of the tumor tissues.

In this context, we are developing Monomolecular Multimodal Imaging Probes (MOMIP) based of one promising fluorophore, BODIPY.<sup>2</sup> Versatile multimodal platforms were thus designed by tuning the luminescent properties of the dye, the coordination properties of the macrocyclic chelator and the nature of the functional group for bioconjugation. Some



of these MOMIP have been attached to biomolecules such as antibodies, peptides or lipopolysaccharides, and investigated *in vivo*.<sup>3</sup> The synthesis, photophysical studies and the *in vivo* validation of these bimodal systems will be presented.

**Figure 1:** General structure of the MOMIP

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## Polyazamacrocycles bearing methylthiazolyl pendant arms for Cu(II) complexation for potential medical applications

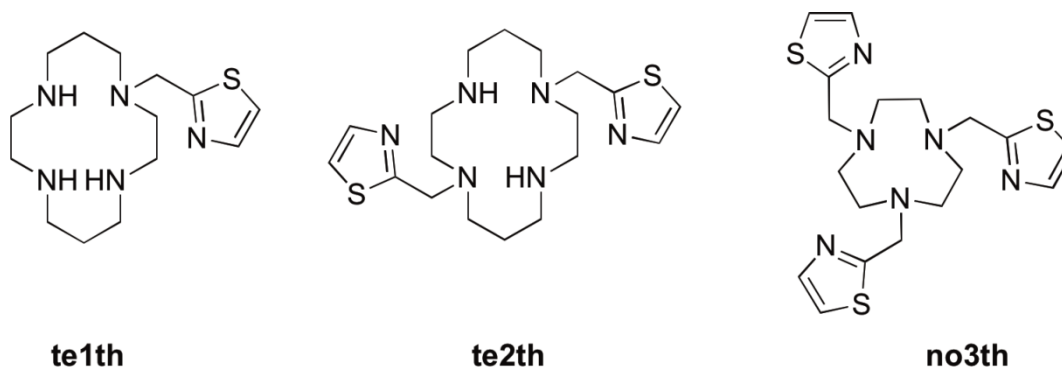
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Nuclear medicine is a new booming alternative because it enables, according to the selected radionuclide, to do either imaging or therapy. PET is a non-invasive imaging technique based on the emission of  $\beta^+$  particles by a radionuclide such as  $^{11}\text{C}$ ,  $^{18}\text{F}$ ,  $^{64}\text{Cu}$  etc...

In spite of a good kinetic process of metal complexation, a thermodynamic stability and a good selectivity of the acetate *N*-functionalized polyazamacrocycles (*ie nota*, *dota*, *teta*) for copper cations towards other metals, one of the current biggest concern is the redox stability of copper complexes in the biological environment.<sup>1,2</sup>

It is indeed assumed that the reduction of  $^{64}\text{Cu(II)}$  in  $^{64}\text{Cu(I)}$  by biological reductive enzymes could lead to the complex demetalation. Our group chose to alkylate polyazamacrocycles with *N,S*-ambident thiazolyl arms to study if this *N/S* coordinating group could permit to prevent any disassociation of the  $\text{Cu(I)}$  complex thanks to the sulphur- $\text{Cu(I)}$  affinity.

New chelating derivatives (figure 1) of cyclam, functionalized by either one or two methylthiazolyl arms (**te1th** or **te2th**)<sup>3</sup> and a triazacyclononane derivative functionalized with three methylthiazolyl arms (**no3th**) and their corresponding  $\text{Cu(II)}$  complexes have been synthesized. Complex properties in solution and in solid state will also be discussed.



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## New *tris*(hydroxypyridinone) chelators for $^{68}\text{Ga}$ PET imaging

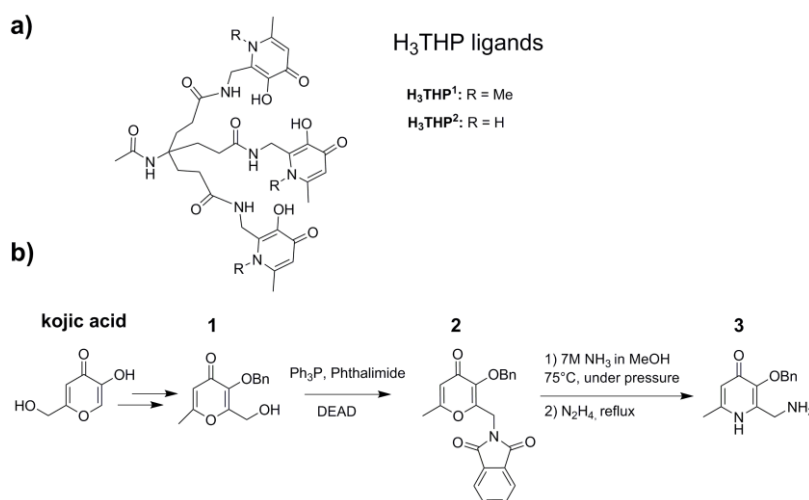
Cinzia Imberti<sup>a</sup>, Michelle T. Ma<sup>a</sup>, Brett M. Paterson<sup>a</sup>, Jennifer D. Young<sup>a</sup>, Vincenzo Abbate<sup>b</sup>, Robert C. Hider<sup>b</sup>, Philip J. Blower<sup>a</sup>

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Molecular diagnostic PET imaging agents based on  $^{68}\text{Ga}$ -complexes are gaining increasing interest in clinics because of the suitable decay profile of  $^{68}\text{Ga}$  ( $t_{1/2} = 68$  min, 90% positron yield) and its ready availability from a long-lived  $^{68}\text{Ge}/^{68}\text{Ga}$  generator. The *tris*(hydroxypyridinone) ( $\text{H}_3\text{THP}^1$ ) chelator developed in our group proved to be efficient in binding  $^{68}\text{Ga}^{3+}$  under mild conditions<sup>1</sup> and radiolabeled peptide derivatives were found to effectively target tumours *in vivo*<sup>2</sup>. However, persistent retention of such peptide derivatives in non-target tissue suggests that modification of the chelator – to increase its hydrophilicity – would improve biodistribution of the radiotracers.

Herein we report the synthesis and complete characterization of a second generation *tris*(hydroxypyridinone) chelator ( $\text{H}_3\text{THP}^2$ ) where the N-methyl group in the hydroxypyridinone unit has been replaced by hydrogen. Due to the different reactivity of the new hydroxypyridinone precursor, a new synthetic strategy has been developed.

$\text{H}_3\text{THP}^2$  coordinates  $^{68}\text{Ga}^{3+}$  under mild conditions and at low ligand concentration, achieving quantitative radiochemical yield.



**Figure 1** **a)** Chemical structures of  $\text{H}_3\text{THP}$  ligands. **b)** New synthetic strategy for the hydroxypyridinone precursor **3**. Compound **1** was synthesized in 4 steps from Kojic acid following literature procedures<sup>1</sup>.

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## Generation of Reactive Oxygen Species by Iron- and Manganese-based SOD Mimics

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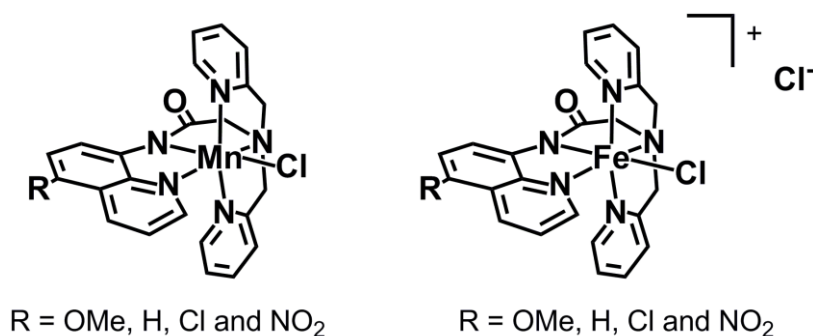
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Superoxide anion ( $O_2^{\cdot-}$ ) is one of unwanted by-products that are generated through oxidative life processes such as the mitochondrial respiratory chain. It is quickly decomposed to dioxygen and hydrogen peroxide by superoxide dismutases (SODs). However, generation of  $O_2^{\cdot-}$  exceeding over the enzymatic capacity leads to oxidative damage of biomolecules and subsequently to inflammatory disorder or neurodegenerating disease [1]. In this scenario, artificial SOD mimics that can significantly decrease the level of  $O_2^{\cdot-}$  have been extensively studied because they are potential anti-oxidative drugs that protect cells against oxidative stress. However, recent studies have revealed that anti-oxidative SOD mimics act as pro-oxidants in the presence of reducing agents [2].

We have prepared a series of iron(III) and manganese(II) complexes supported by pentadentate monocarboxylamido ligands,  $[Fe^{III}(dpaq^R)Cl]Cl$  and  $[Mn^{II}(dpaq^R)Cl]$  (Figure 1). These complexes have different substituents at 5-position of the quinoline ring ( $dpaq^R$ , R = OMe, H, Cl, or  $NO_2$ ) in order to modulate their redox potentials. In this study, we have examined the anti-oxidant and pro-oxidant activities of  $[Fe^{III}(dpaq^R)Cl]Cl$  and  $[Mn^{II}(dpaq^R)Cl]$  to access their structure and activity relationship [3,4].



**Figure 1** Chemical structure of  $[Mn^{II}(dpaq^R)Cl]$  and  $[Fe^{III}(dpaq^R)Cl]Cl$ .

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## A new generation of organometallic antitumor compounds : Ferrocifens as precursors to novel quinone methide metabolites

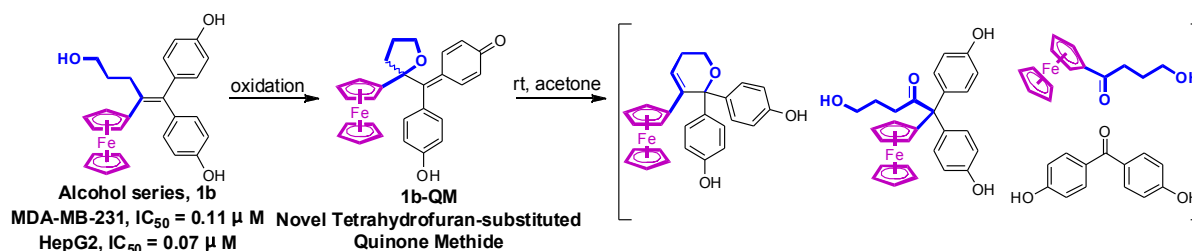
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In the search for novel therapeutic strategies, a new medicinal chemistry based on the unique behavior of organometallic complexes of transition metals may provide a breakthrough<sup>1</sup>. A strategy to overcome cancer cell resistance is to generate new types of organometallic prodrugs addressing several targets. Among the usable organometallic complexes, iron derivatives occupy a privileged position owing to the abundance of this metal in the body and the particular nature of ferrocene, which is a non toxic, compact and stable aromatic metallocene with redox properties.



We report the synthesis and chemical metabolic profile of a new generation of ferrocifen derivatives with strong antiproliferative behavior *in vitro*. In particular, the hydroxypropyl derivative **1b**, exhibited exceptional antiproliferative activity against cancer cells (IC<sub>50</sub> around 0.1  $\mu$ M).<sup>2</sup> Chemical oxidation of **1b** yielded an unprecedented tetrahydrofuran-substituted quinone methide (QM) *via* an internal cyclization of the hydroxy-alkyl chain. The ferrocenyl group in **1b** plays a key role not only as an intramolecular reversible redox “antenna” but also as a stabilized carbenium ion “modulator”. The presence of the oxygen heterocycle in **1b-QM** enhances its stability and leads to a unique chemical metabolic profile, which reveals crucial clues that may help us to decipher its mechanism of action *in vivo*.

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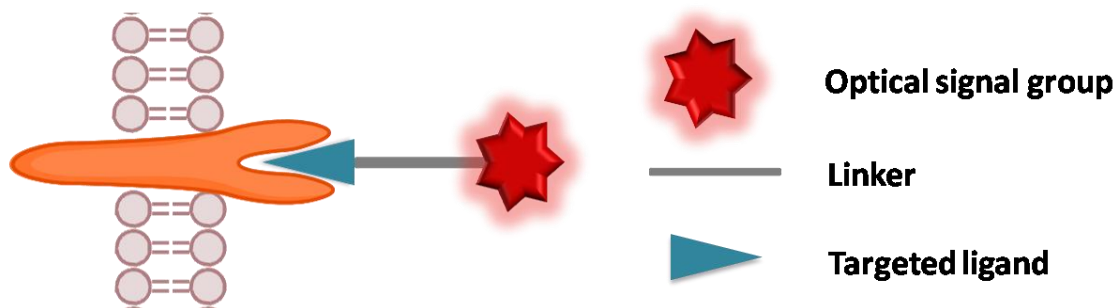
## Cell-Membrane Receptor Targeted Fluorescent Imaging and Early Diagnosis of Cancer

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Cell-membrane receptor is an important marker for early diagnosis of cancer. Different types of cell-membrane receptor over expressed in varying tumor cells. We designed and synthesized diverse Off-On switch mode receptor targeted fluorescent sensors which could identify the targeted cell membrane receptor. These sensors include three parts which are targeted ligand, linker and optical signal group. They have good biological compatibility and could go through the cell membrane. The sensors could have specific identification with the cell membrane receptor targets. Moreover, the sensors are fluorescence quenching in the body fluids, and the fluorescence of sensors shows significantly enhanced on the cell membrane which include targeted ligand receptor when the targeted ligand of sensors is combined with targeted ligand receptor. In the summary, these sensors have high sensitivity and selectivity towards cell membrane receptors, and they provide an effective means of early diagnosis of tumor cells and the formation mechanism of early cancer.



**Figure 1** Schematic diagram of sensor combined with targeted ligand receptor

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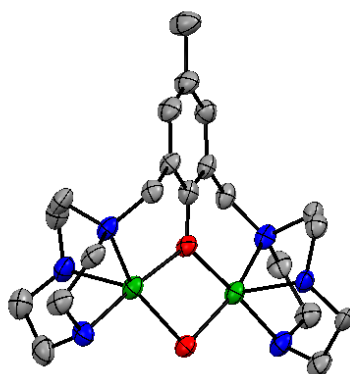


## DNA cleavage activity and Cell Insertion of Dinuclear Metal Complexes as Anti-Cancer Drugs

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Cisplatin is one of the most popular anticancer drugs. However, since this type of anticancer drugs has no selectivity between cancerous and normal cells for the binding to DNA, it generally causes strong side effects. Therefore, it is important to develop a new anticancer drug that selectively binds to the DNA in the cancerous cell and decreases the side effects.

We have synthesized a dinucleating ligand where two 1,4,7-triazacyclononane (TACN) donors are attached at 2 and 6 position of *p*-cresol. The ligand forms dinickel and dicopper complexes (Fig.1). We carried out DNA cleavage using these complexes, and found that these complexes showed high activity for the DNA cleavage at specifically low pH region (pH 5-6). Further, we measured binding constants of these dimetal complexes with DNA, and found that these complexes showed high binding constant of  $10^5 \text{ M}^{-1}$  in the low pH region. It is suggested that this type of dimetal complexes act as a minor groove binder. Here, we report that this type of dimetal complex enhances the DNA cleavage activity through the DNA-binding as a minor groove binder. The N-H groups in the TACN moieties play an important role for the activation of phosphate ester of DNA. The binding  $\text{H}_2\text{O}$  molecule is essentially important as a nucleophile for the hydrolytic DNA cleavage. In this study, moreover, we designed a new dinucleating ligand that has cationic groups that enhance the cell insertion of the complex. We will discuss the DNA-cleavage and cell insertion.



**Figure 1** ORTEP view of  $\text{Cu}_2(\mu\text{-H}_2\text{O})\text{bcmp}$

## Water-Soluble and Hydrophilic Gold(I) NHC Complexes: Synthesis and Biological Properties

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Organometallic gold(I) compounds have proven great potential in the treatment of cancer. Within this scope different families such as gold(I) alkynyl and gold (I) N-heterocyclic carbene (NHC) complexes are included.<sup>1</sup> In particular, NHC bearing Au(I) compounds have been successful exhibiting promising cytotoxic and enzyme inhibiting properties. One of the auspicious targets for Au(I) NHC compounds is the selenoenzyme thioredoxin reductase, TrxR.<sup>2</sup>

In spite of the promising properties, the so far investigated gold(I) NHC complexes are limited in their solubility in aqueous media which is accompanied by reduced bioavailability. Based on these considerations, we present here a new series of water-soluble and hydrophilic gold(I) NHC complexes which have been characterized for their different chemical and physical properties and antiproliferative effects *in vitro*. Moreover, their inhibition properties against the seleno-enzyme TrxR have been studied, and the obtained results discussed in terms of the possible mechanisms of cytotoxic action.

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## Water soluble rhenium(I) complexes for two-photon imaging

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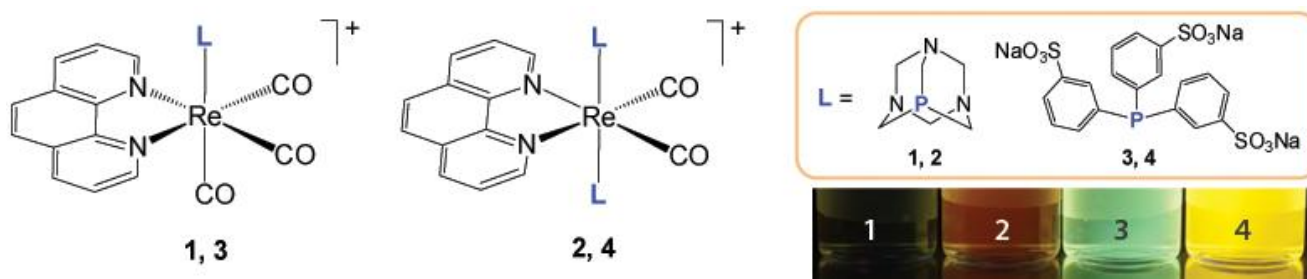
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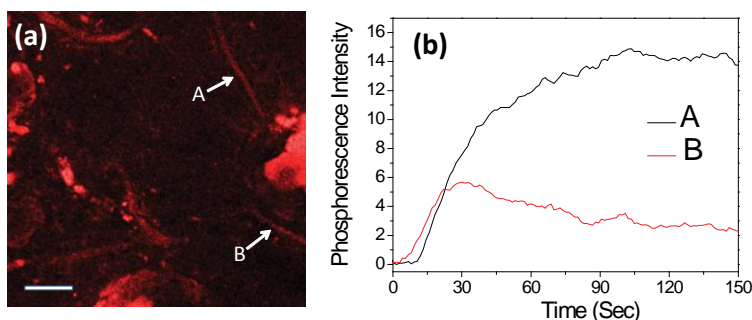
The luminescent metal complexes have been intensively investigated during the last two decades due to their attractive physical properties, which open new horizons for a number of technological applications, including luminescent analytical methods.<sup>1</sup>

The novel water soluble rhenium(I) complexes were obtained following a protocol of one-step thermal substitution carried out in a pressure autoclave (Figure 1).<sup>2</sup>



**Figure 1** Schematic representation of the rhenium (I) complexes **1–4**. The photo shows solutions of **1–4** under UV radiation ( $\text{H}_2\text{O}$ ,  $\lambda_{\text{ex}} = 365 \text{ nm}$ ).

The complex **4** is intensely luminescent in aqueous solution at 298 K ( $\Phi_{\text{em}} = 20\%$ ,  $\lambda_{\text{em}} = 583 \text{ nm}$ ). Moreover, it demonstrates very high two-photon absorption cross-section ( $\sigma = 2200 \text{ GM}$ ,  $\lambda_{\text{ex}} = 780 \text{ nm}$ ) and high intensity of two-photon induced emission. This feature in combination with very small toxicity and high stability allows for using **4** as an efficient nonlinear optical imaging agent in physiological medium (Figure 2).



**Figure 2** (a) Two-photon fluorescence image in the skin of mice ear ( $\lambda_{\text{ex}} = 800 \text{ nm}$ , monitoring at 550-650 nm). A – vein, B – artery. (b) Kinetics of the two-photon emission intensities after injecting **4**.

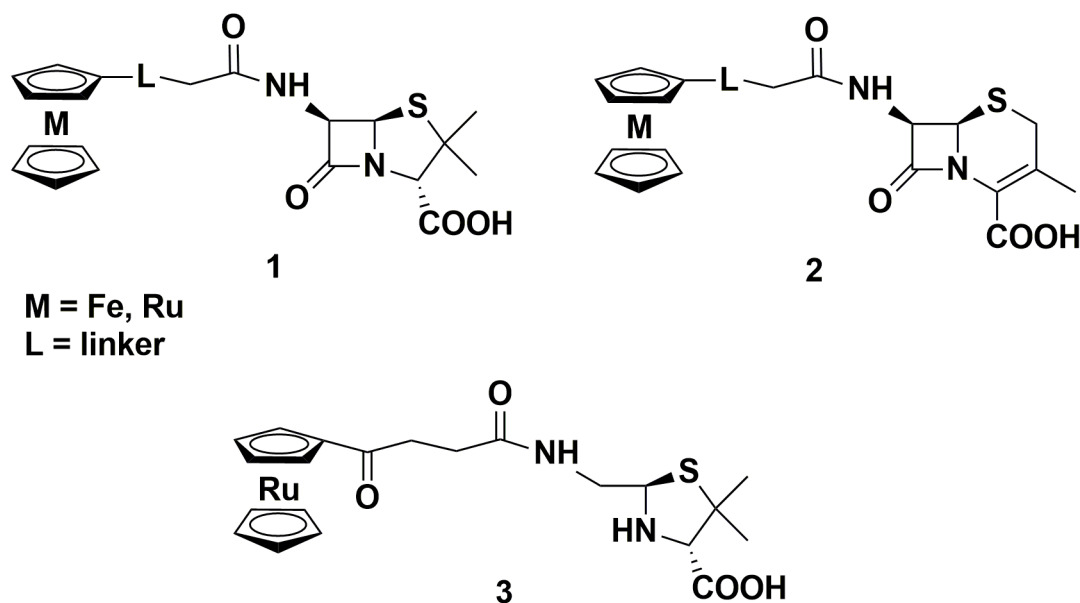
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## Ferrocenyl and ruthenocenyl $\beta$ -lactam antibiotics - antibacterial activity, DD-carboxypeptidase inhibition, and X-ray crystal structures with CTX-M $\beta$ -lactamase

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The  $\beta$ -lactam antibiotics inhibit Penicillin Binding Proteins which are involved in bacterial cell wall synthesis. In this poster presentation we report the antibacterial activity studies of ferrocenyl and ruthenocenyl  $\beta$ -lactams **1**, **2** and the X-ray crystal structure of the thiazolidine-derived inhibitor **3** with CTX-M  $\beta$ -lactamase<sup>1,2</sup>. Inhibition of the DD-carboxypeptidase and penicillinase bacterial enzymes by **1** and **3** will also be discussed.



**Figure 1** Structures of complexes **1-3**

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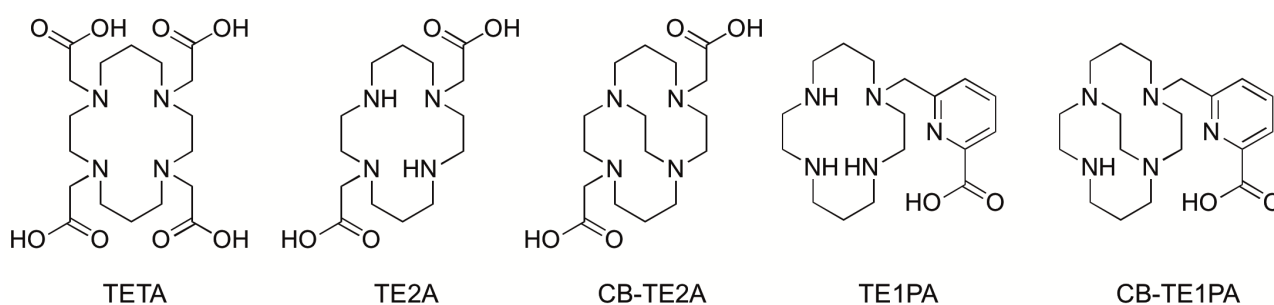
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## Synthesis of Bifunctional Chelating Agents. C-Functionalized Cyclams for Nuclear Medicine

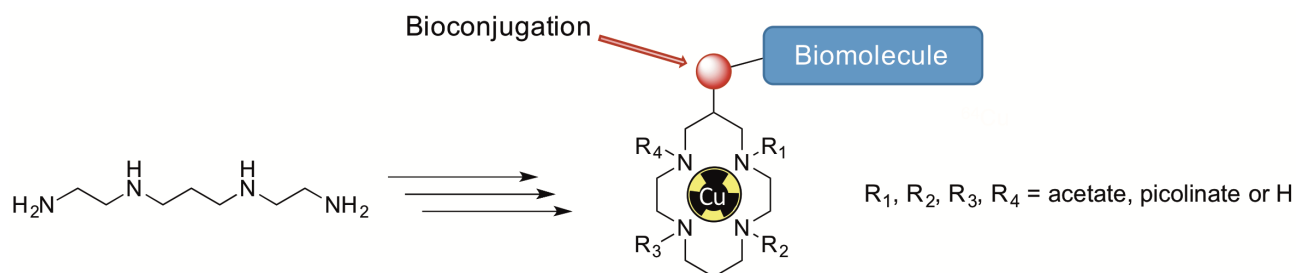
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The development of nuclear medicine techniques involves the use of isotopes of different metals. Copper has two interesting isotopes :  $^{64}\text{Cu}$  ( $\beta^+$  emission for PET imaging) and  $^{67}\text{Cu}$  ( $\beta^-$  emission for RIT). Cyclam derivatives as TETA, TE2A, CB-TE2A<sup>1</sup> or TE1PA<sup>2</sup> and CB-TE1PA<sup>3</sup> have shown good properties for the Cu (II) complexation.



**Figure 1** Structure of compounds described in the literature

However, for nuclear medicine applications, the macrocycle has to be conjugated to a biomolecule to target tumoral cells. “Transformation” of an existing N-functionalization is damaging to a good complexation of Cu (II). So we recently described new synthetic ways to introduce the grafting function on a carbon atom of the macrocycle<sup>4,5</sup>. In that case, the C-functionalization does not affect the coordinating properties of cyclam derivatives proved by coordination studies and PET-CT imaging results.



**Figure 2** From the linear tetraamine to the radiopharmaceutical

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## <sup>90</sup>Y-PCTMB: a promising chelate for vectorized radiotherapy

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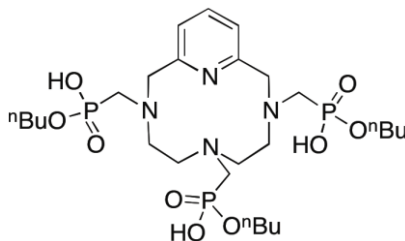
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A pyclen derivative, PCTMB (Figure 1), was investigated as chelator for  $\beta^-$  emitters such as <sup>90</sup>Y, <sup>177</sup>Lu or <sup>166</sup>Ho. Previously described for lanthanide complexation (Eu<sup>3+</sup>, Tb<sup>3+</sup>, Gd<sup>3+</sup>)<sup>1,2</sup> as well as radionuclide complexation (<sup>64</sup>Cu, <sup>111</sup>In, <sup>67</sup>Ga, <sup>68</sup>Ga),<sup>3</sup> PCTMB proves to be an interesting ligand for both imaging and therapy applications.

Polyazamacrocyclic ligands are well known for their capacity to form stable and inert complexes with metal ions.<sup>4</sup> In order to be used in nuclear medicine, the chelate has to present various properties: a fast complexation kinetic, a kinetic inertness, and a thermodynamic stability. These properties are required to avoid the toxicity induced by the release, in a biological medium, of a radionuclide by transchelation or transmetallation.

The choice of a radionuclide is determined by its emission type, energy rate, range of emission, half-life and availability. <sup>90</sup>Y, <sup>166</sup>Ho and <sup>177</sup>Lu, three  $\beta^-$  emitters, are potential candidates for vectorized radiotherapy. Their various emission path lengths can be used to treat tumors of variable size.

Y-PCTMB, Ho-PCTMB and Lu-PCTMB complexes were synthesized and studied in the solid state by X-Ray diffraction. The Kinetic of complexation, kinetic inertness, structure in solution, and thermodynamic stability of the Y-PCTMB complex, were investigated by UV-visible and NMR spectroscopies and potentiometric titration. <sup>90</sup>Y radiolabelling and serum stability were also performed.



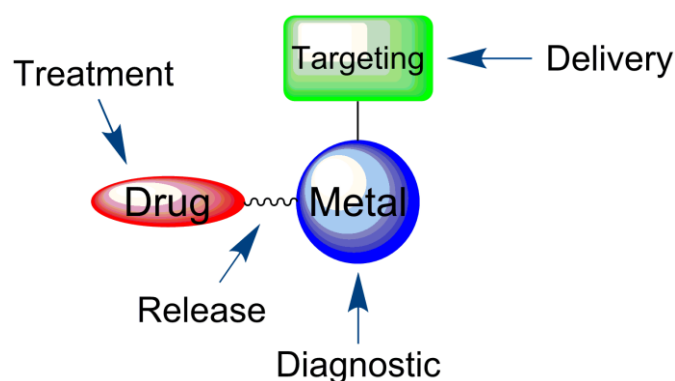
**Figure 1** : PCTMB

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## Can Polyamines be used to Deliver Diagnostic and Chemotherapeutic Agents?

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The ability of cells to actively transport polyamines is a ubiquitous phenomenon displaying major differences between normal and cancerous cells. Exploitation of polyamine transport to effect intracellular delivery of diagnostic and chemotherapeutic agents to cells expressing high levels of the polyamine transport system (PTS), represents a novel approach to getting molecules across the plasma membrane.<sup>1</sup> Precise molecular details of polyamine cellular uptake are unclear, but the capacity for polyamines to facilitate transmembrane transport of a range of molecular payloads has been established. We demonstrate that this promiscuity extends to transporting diagnostic and therapeutic transition metal complexes, showing that polyamines can deliver (and release) therapeutic agents. Using luminescent metal conjugates (confocal microscopy), these offer bright, long-lived luminescence (for cellular imaging) and can be used to deliver a chemotherapeutic payload. A range of complexes will be presented.



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## Thermodynamic and kinetic study of Cu(II) complex of cross-bridge cyclam ligand with two pyridine pendant arms

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Copper(II) complexes of tetraazamacrocyclic ligands exhibit both high thermodynamic stability as well as considerable kinetic inertness and, therefore, they can be employed for theranostics (<sup>64</sup>Cu with half-life 12.8 h for PET, <sup>67</sup>Cu with half-life 62 h for radio-immunotherapy). In order to find the best macrocyclic bifunctional ligands for possible *in vivo* applications of their complexes, it is necessary to study the thermodynamic and kinetic properties (dissociation/formation rate constants) of metal complexes.<sup>1</sup>

Here, thermodynamic and kinetic properties of Cu(II) complex with macrocyclic cross-bridged *cyclam* ligand with two 2-pyridylmethyl pendant arms will be presented. The results will be compared with analogous cross-bridged *cyclen*<sup>2</sup> and *cyclam* ligands with two phosphonic pendant arms.<sup>3,4</sup> Results of this study could help in design of new bifunctional chelators for possible *in vivo* applications.

### Acknowledgement:

Financial support from the Grant Agency of the Czech Republic (No. 13-08336S, 13-32167P), the Ministry of Education, Youth, and Sports of the Czech Republic (M NPU LO1305 ) and EU program (CEITEC CZ.1.05/1.1.0/02.0068) are acknowledged.

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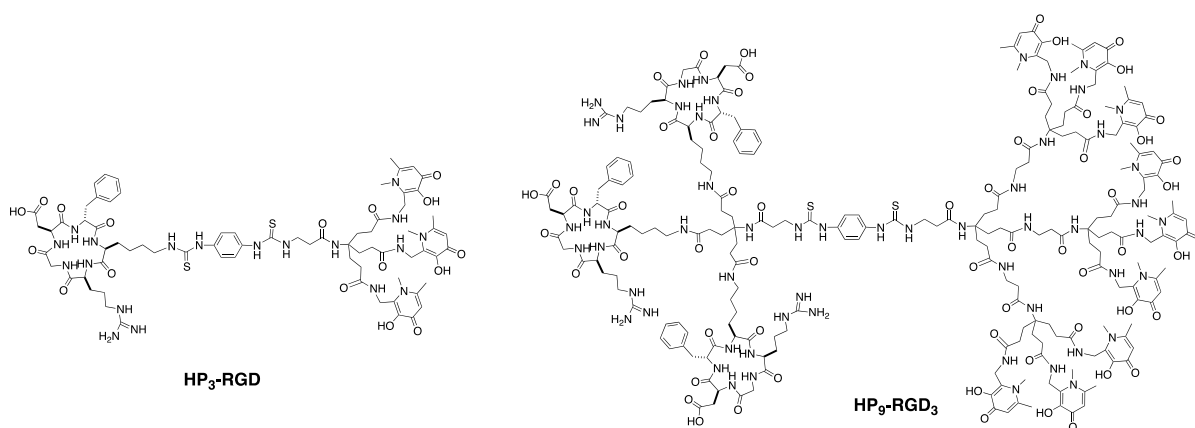
## Bifunctional hydroxypyridinone chelators for molecular radiopharmaceuticals

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Hydroxypyridinones are efficacious ligands for coordinating oxophilic metal ions. We have synthesised bifunctional chelators based on 1,6-dimethyl-3-hydroxypyridin-4-ones for coordination of the PET radiometals  $^{68}\text{Ga}^{3+}$  and  $^{89}\text{Zr}^{4+}$ , and the radiotherapeutic isotope,  $^{213}\text{Bi}^{3+}$ . Hexadentate tris(hydroxypyridinone) (THP) derivatives coordinate  $^{68}\text{Ga}^{3+}$  efficiently under mild conditions and low concentrations of chelator. PET scans using  $^{68}\text{Ga}$ -labelled THP peptide conjugates<sup>1</sup> can delineate neuroendocrine and prostate tumours, glioblastomas and arthritic synovial joints. A dendritic hydroxypyridinone derivative (HP<sub>9</sub>-RGD<sub>3</sub>, Figure 1) can coordinate up to three metal ions per molecule, and the highest achievable specific activity of the dendritic conjugate is three times that of its monomeric homologue (HP<sub>3</sub>-RGD, Figure 1). In vivo, the amount of localised radioactivity at target tissue is higher for the radiolabelled dendrimer than the monomer. Whilst THP also coordinates  $^{89}\text{Zr}^{4+}$ ,  $^{89}\text{Zr}$ -THP-antibody conjugates are unstable to demetallation in vivo.<sup>2</sup> To increase the stability of a hydroxypyridinone complex of  $^{89}\text{Zr}^{4+}$ , octadentate tetrakis(hydroxypyridinone) derivatives have been synthesised. We also report the utility of multidentate hydroxypyridinone ligands for coordination of  $^{213}\text{Bi}^{3+}$ .



**Figure 1** Monomeric HP<sub>3</sub>-RGD, and dendritic HP<sub>9</sub>-RGD<sub>3</sub>. The latter possesses three targeting peptides and three coordinating THP groups.

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## Potential MRI contrast agents for neuroimaging

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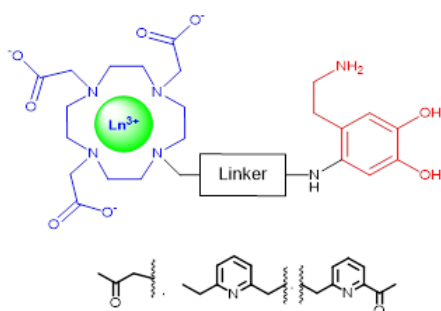
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Despite the role of neurotransmitters in the central nervous system, their non-invasive detection *in vivo* remains a major challenge. Recently, many methods for neurotransmitters detection, mapping and measurement are developed in molecular imaging.<sup>1</sup>

Magnetic Resonance Imaging (MRI) is a powerful technique due to its high resolution and depth tissue penetration. In this context developing MRI smart imaging agents for the *in vivo* visualization of neurotransmitters would be crucial but remains challenging, due to the small concentration of the neurotransmitter.

We propose here a strategy to assess the presence of dopamine by the detection of enzyme activities involved in its degradation or metabolism. Indeed, the detection of enzymatic activities by MRI, due to the catalytic action of the enzyme, is more realistic. We chose to develop ParaCEST smart agents. Those contrast agents are based on the detection of exchangeable protons present on the ligand of a paramagnetic complex, and/or on the proton of the water molecule linked to the paramagnetic cation.<sup>2</sup>



For this purpose, new molecules (*cf.* figure) are developed. They include a macrocyclic polyamine moiety for  $\text{Ln}^{3+}$  ion complexation linked to a dopamine derivative, through different type of spacers. The dopamine derivative constitutes the substrate of the targeted enzymes. After enzymatic recognition of the substrate, the

latter is modified leading to a change of the contrast agent molecular structure, detectable by paraCEST MRI.

We present here the synthetic pathway of different potential contrast agents including a dopamine-like derivative linked to a macrocyclic moiety through different spacers. ParaCEST measurements have been performed to underline their contrast agent ability.

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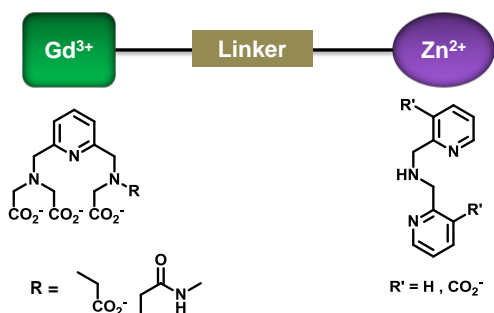
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## Zinc responsive contrast agents

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Zinc is the second most abundant transition metal in human body. It is mostly bound to proteins that play a central role in controlling gene transcription and metalloenzyme function. However, its quantitative distribution and its exact role in the brain (neuronal transmission) are not well understood. It has also been shown that disturbances in  $Zn^{2+}$  homeostasis is implicated in neurodegenerative diseases such as Alzheimer's, Parkinson's diseases and diabetes.<sup>1</sup> Therefore, monitoring  $Zn^{2+}$  *in vivo* by non-invasive technique such as Magnetic Resonance Imaging (MRI) is important in biomedical research to understand its biological role, and to provide earlier diagnosis for specific pathologies.

MRI has long been devoted to obtain anatomical images. Recently the development of molecular imaging, which always requires the use of a probe, has open new possibilities, and  $Zn^{2+}$  detection has led to the conception of new  $Gd^{3+}$ -based MRI contrast agents.<sup>2-4</sup> The efficacy (relaxivity) of these agents is mainly influenced by the number of water molecules directly coordinated to the  $Gd^{3+}$ ,  $q$ , and the rotational correlation time of the complex,  $\tau_R$ ; these parameters being the easiest to tailor by the chemist. Consequently, the two main strategies to modulate relaxivity through  $Zn^{2+}$  sensing rely on a change in one of these two parameters.



Here, we propose novel pyridine-based  $Gd^{3+}$  complexes for  $Zn^{2+}$  sensing. The design of the ligand combine a pyridine unit with aminocarboxylate moieties for  $Gd^{3+}$  complexation attached through a linker to a  $Zn^{2+}$  coordinating unit derived from the well-know dipicolylamine (cf. scheme). Those contrast agents have shown their potential interest for zinc detection.

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## Multimodal Magnetic and Luminescent Nanoparticles for Biomedical and Data Storage Applications

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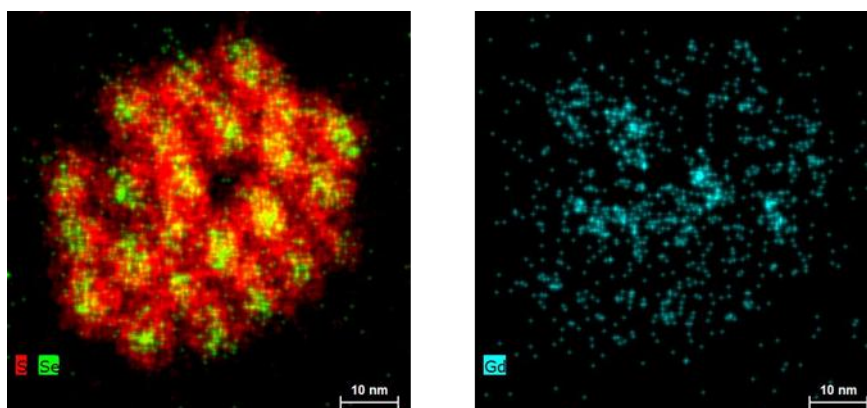
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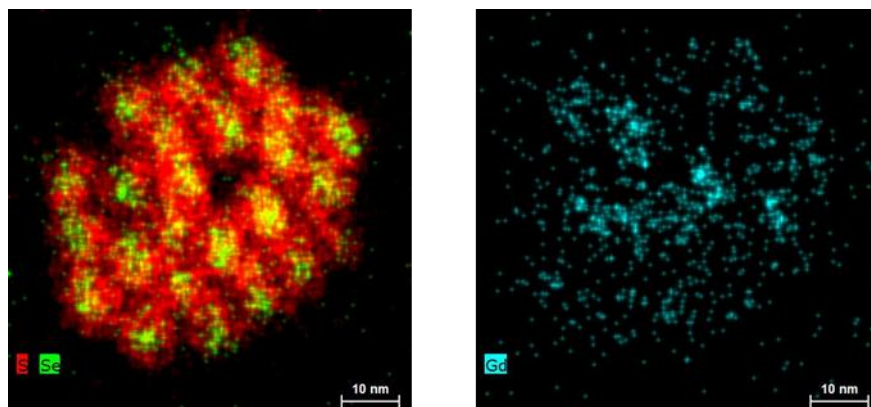
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Dual functioning nanoparticles will likely be key to future imaging, diagnostics, and treatments. Combining magnetic and optically active components would allow both MRI and fluorescent imaging with a single imaging probe. Semiconductor nanocrystals, or 'quantum dots (QDs)', are promising fluorescent probes with size-tunable optical properties and high photoluminescent quantum yields. However, QDs typically emit in the visible, and hence lack the tissue penetration of NIR. Conversely, lanthanides, in addition to paramagnetism, have sharp emission bands ranging from the UV to NIR. Modifying QDs with lanthanides would create attractive magnetic and luminescent hybrids well-suited for biomedical applications. Here, we have combined bright CdSe/CdS/ZnS QDs with a paramagnetic Gd complex<sup>1</sup> to form a multimodal hybrid with potential applications in dual MRI-fluorescence imaging (figure 1).



**Figure 1.** Energy-dispersive X-ray spectroscopy of CdSe/CdS/ZnS quantum dots (left) functionalised with a Gd complex (right).

1. Lewis *et al.*, *J. Am. Chem. Soc.*, **2011**, 133 (4), pp 1033.



**Figure 1.** Energy-dispersive X-ray spectroscopy of CdSe/CdS/ZnS quantum dots (left) functionalised with a Gd complex (right).

1. Lewis *et al.*, *J. Am. Chem. Soc.*, **2011**, 133 (4), pp 1033.

## Radioactive copper probes for diagnostic imaging of Alzheimer's disease

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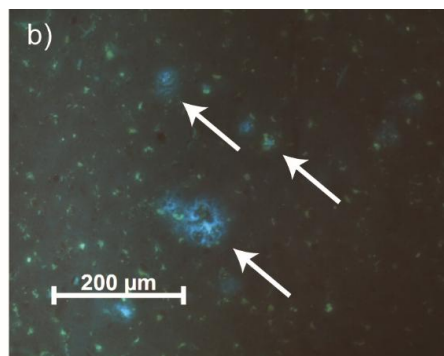
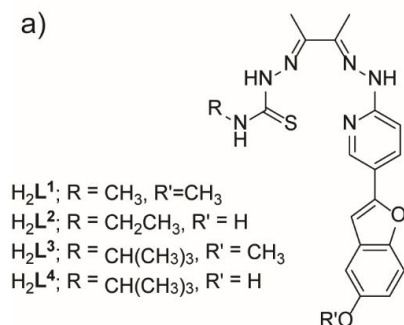
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One of the characteristic pathologies of Alzheimer's disease (AD) is the presence of extracellular cerebral plaques. The major constituent of these plaques is aggregated amyloid- $\beta$  ( $A\beta$ ) peptide. A radioactive tracer that selectively binds to  $A\beta$  plaques would allow estimation of plaque burden in suspected AD patients. A potential  $A\beta$  tracer must be small, lipophilic, stable *in vivo* to be able to cross through the blood brain barrier (BBB).

Copper has a range of useful isotopes for diagnostic applications. In particular,  $^{61}\text{Cu}$  ( $\beta^+$ ,  $\tau_{1/2} = 3.4$  h) and  $^{64}\text{Cu}$  ( $\beta^+$ ,  $\tau_{1/2} = 12.7$  h) are able to be visualised *in vivo* by positron emission tomography (PET).

Complexes based in the hybrid thiosemicarbazone-pyridylhydrazone ligands provide a sufficiently stable coordination environment for copper (II) while allowing functionalisation of the pyridyl group to include a targeting motif for  $A\beta$ .<sup>1</sup> The ligands  $\text{H}_2\text{L}^{1-4}$  (Figure 1(a)) have been synthesised to probe the effect of substitution on biodistribution with respect to membrane and BBB permeability. The interaction with  $A\beta$  has also been investigated by assessing the binding of the copper complexes  $[\text{CuL}^3]$  and  $[\text{CuL}^4]$  to fibrillar  $A\beta$  in solution and plaque  $A\beta$  in human brain tissue. (Figure 1(b))

a)



<sup>1</sup> J.L. Hickey, S. Lim, D. J. Hayne, B. M. Patterson, J. M. White, V. L. Villemagne, P. Roselt, D. Binns, C. Cullinane, C. M. Jeffery, R. I. Price, K. J. Barnham and P. S. Donnelly, *J. Am. Chem. Soc.*, **2013**, *135*, 16120



## NIR-Photothermal properties of nickel-bis(dithiolene) complexes : control of gelation properties and cancer therapy.

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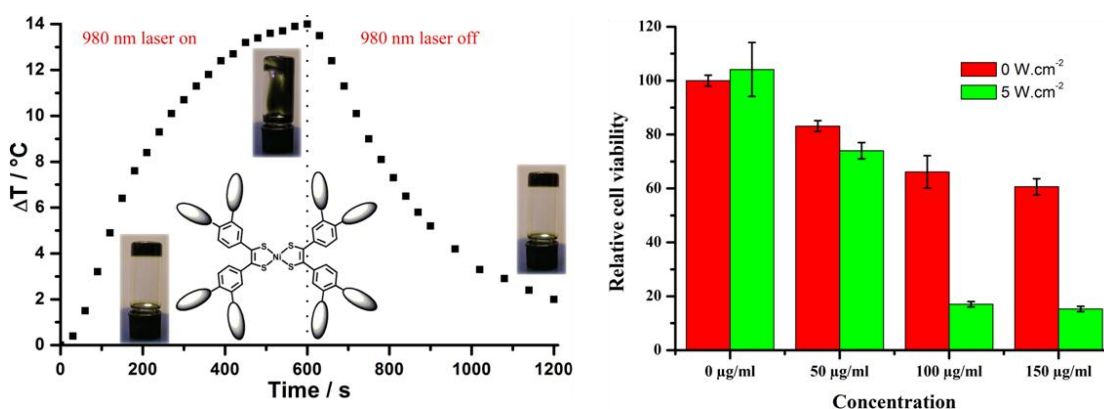
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Metal-bis(dithiolene) complexes are known as strong NIR absorbers with high thermal- and photostability. In their neutral state, they display high absorption coefficients (around  $30\,000\text{ M}^{-1}\cdot\text{cm}^{-1}$ ) in a wide range of NIR wavelengths, from 900 to 1600 nm, depending upon the choice of metal center and dithiolene substituents. Furthermore, these complexes are non-luminescent, implying that all the absorbed energy is released in the environment as heat. This peculiar feature has found applications for photothermal laser printing on thin films.<sup>1</sup>

Recently, we have first synthesized an original series of organogelator (metallogelator) built around a nickel-bis(dithiolene) core with 8 pendant cholesteryl fragments and demonstrate that the photothermal properties of these complexes in the NIR region can be efficiently used to control the degelation of the robust gels.<sup>2</sup>

More interestingly, we have also synthesized water-soluble nickel-bis(dithiolene) carrying polyethylene glycol chains at the periphery. These complexes were found to be biocompatible and were proved to be efficient photothermal agents able to induce cell death *in cellulo* under NIR Irradiation.<sup>3</sup>



**Figure 1** a) Control of the gelation properties by NIR irradiation. b) Relative Cell viability of malignant cells treated in presence of the water-soluble dithiolene complex

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## Photo-induced NO Transport from Composites of Lipophilic Ruthenium Salen Complexes and Liposomes

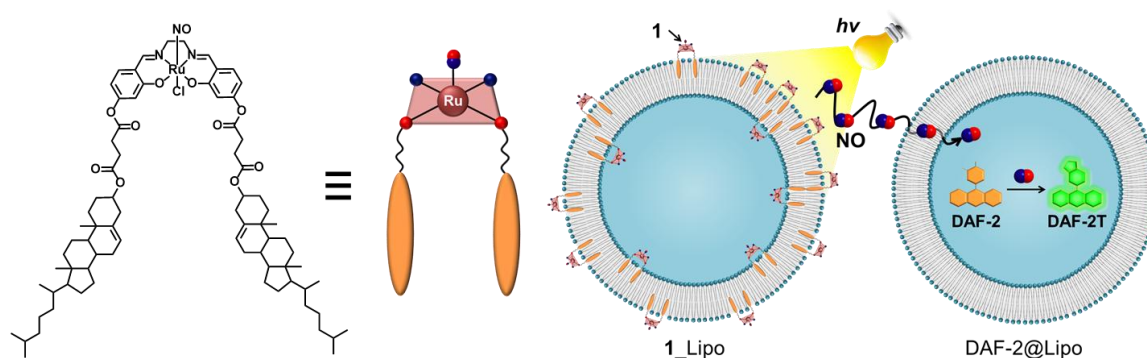
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Nitric oxide (NO) has been known to act as a cellular signaling molecule in mammals. However, half-life of onset of action of NO is short, so techniques to deliver stable NO to the target site and to control NO release are required. Here we developed NO transport system by integrating a [Ru(salen)Cl(NO)] derivative, which releases NO induced by light, into lipid vesicle, liposomes. We synthesized [Ru(salen-cho)Cl(NO)] (**1**) which have lipophilic cholesteryl part, and incorporated them into liposomes (**1\_Lipo**). We also evaluated their photo-induced NO transport property through the lipid bilayer [1].

**1\_Lipo** were prepared according to Bangham method. Incorporation of **1** into liposomes was confirmed by UV-Vis spectra and confocal laser scanning microscope (CLSM) observation. NO release and transport capacity of **1\_Lipo** was evaluated by emission spectra measurement using diaminofluorescein-2 (DAF-2) which emitted fluorescence at 515 nm excited by the light at 495 nm after reaction with NO.

From UV-Vis spectra of **1\_Lipo**, a peak around 376 nm derived from **1** was observed. Formation of liposomes was confirmed by CLSM. After Xe light irradiation to mixture of **1\_Lipo** and DAF-2, intensity of emission at 515 nm increased as irradiation time increased ( $\lambda_{\text{ex}}=495$  nm). Moreover, we prepared liposomes encapsulating DAF-2 (DAF-2@Lipo). From observation of mixture of **1\_Lipo** and DAF-2@Lipo with CLSM after Xe light irradiation, green fluorescence from inside of DAF-2@Lipo was observed. We successfully observed NO transportation from **1\_Lipo** to DAF-2@Lipo triggered by Xe light irradiation.



**Figure 1** Structure of **1** and schematic model for NO transportation between liposomes

1 K. Nakanishi, T. Koshiyama, S. Iba, M. Ohba, *Dalton Trans.*, **2015**, *44*, 14200.

## **Simple green synthesis of CdTe/CdSe/ZnSe core-multi shell with reduced cytotoxicity for bio imaging**

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We herein report a simple, economical and green synthesis of highly water soluble and stable CdTe/CdSe/ZnSe multicore-shell nanoparticles (NPs) via a one pot synthetic route. The synthesis was carried out under ambient conditions in the absence of an inert environment and involved the use of  $K_2TeO_3$  and  $Na_2SeSO_4$  as a stable tellurium and selenium precursor respectively. The temporal evolution of the optical properties and stability of the growing nanocrystals was monitored in detail by varying the refluxing time, pH and storing the NPs under ambient condition for several days. The as-prepared NPs were characterised using UV-Vis absorption and photoluminescence (PL) spectroscopy, Fourier transform infrared spectroscopy (FTIR), transmission electron microscopy (TEM), and high resolution transmission electron microscopy (HRTEM). The optical analyses showed an enhancement in the fluorescent intensity after the addition of the shell solution accompanied by red-shifting of the absorption and emission maximum. The stability study revealed an increase in the emission intensity as the ageing days increased. The TEM analysis showed that the materials are small, monodispersed, spherical and highly crystalline. The cytotoxicity of the NPs investigated on KM-Luc/GFP cell line at different concentrations showed a decrease in cell viability as the concentration of the NPs increased with the highest value of 88 % at 0.1  $\mu\text{g/mL}$ . Furthermore, the as-synthesised NPs prepared at longer reaction time showed lower cytotoxicity compared with those prepared at shorter reaction time. The results show variation in cell viability from 88 % to 57.6 % for the NPs produced at 7 h compared with those produced at 30 min as the concentration increased from 0.1  $\mu\text{g/mL}$  to 60  $\mu\text{g/mL}$ . The fluorescent imaging performed using confocal fluorescent microscope indicated that the as-synthesised NPs were taken up by the cells.

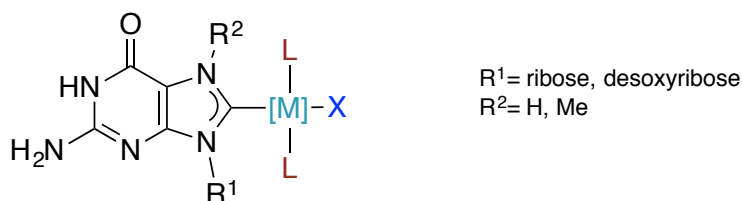
## Synthetic Approaches for N-heterocyclic Carbenes Derived from Nucleosides:

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Alkylation of DNA nucleobases to form DNA adducts, resulting from endogenous or exogenous sources is a crucial modification of the genome involved in regulating many cellular processes, from epigenetics to the formation of carcinogenic mutations.<sup>1</sup> Once formed, DNA adducts derived from methylation are formally N-heterocyclic carbene precursors and readily undergo exchange with deuterium<sup>2</sup>,.

Therefore DNA adducts can easily form stable carbenes upon proton loss, an in fact NHCs are proposed as intermediates in a variety of processes leading to mutagenic lesions.<sup>3</sup> Their role is nevertheless poorly understood.



**Figure 1** Nucleoside based NHC derived from guanine

Our group has developed methodologies for the formation of NHCs derived from nucleobases and nucleosides, by means of oxidative addition from the corresponding halogenated precursors. These complexes were evaluated for they behavior in physiological media and will be discussed in this communication.

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- (3) Gates, K. S. *Chem. Res. Toxicol.* **2009**, 22 (11), 1747.

## **Modified Ruthenium Bipyridines as Photoactive Molecular Artificial Retinas**

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Loss of photoreceptors due to retinal degenerative diseases, such as retinitis pigmentosa (RP) and age-related macular degeneration (AMD), is a major cause of blindness, for which there is no cure and few ameliorative treatments. Vision loss occurs when photoreceptors have deteriorated and are often beyond repair, yet a significant number of the inner retinal cells survive and remain capable of delivering visual information to the brain. We aim to develop a molecular artificial retina (MAR) that may be injected into or applied to the photoreceptor-degenerate eye and embed in the membrane of surviving retinal neurons to impart light sensitivity. By delivering the MAR to the membrane of functioning ganglion cells in the eye, the damaged photoreceptor cells are bypassed. Upon illumination of the embedded MAR, negative charge builds up on the outside of the ganglion cell membrane near Na<sub>v</sub>1.6 ion channels, forcing them to gate and pass an electrical signal to the brain. Ruthenium(II) bipyridine transition metal complexes have been extensively studied for many decades and are highly tunable to specific biological systems. Indeed, we have shown that a modified Rubpy MAR with a C17 tail (Rubpy-C17), where bpy is 2,2'-bipyridine and bpy-C17 is 2,2'-4-heptadecyl-4'-methyl-bipyridine, is able to incorporate into the plasma membrane of mammalian cells, and impart light sensitivity to the cells. In the presence of representative concentrations of the reducing agent ascorbate, illumination triggers membrane depolarization in non-excitabile HEK 293T cells, and action potential firing in excitable, neuronal-like, chromaffin cells. Furthermore, the Rubpy-C17 MAR confers light-driven increases in action potential firing in neural networks such as leech ganglia and wholemount rat retina. Most exciting, injection of the MAR into eyes of blind rats confers visually induced electrical activity in the superior colliculus. The predictable and reproducible light-induced membrane depolarization and subsequent action potential firing in the presence of exogenous reductants demonstrates the viability of a molecularly-driven artificial retina.

## Rapid Chelation of Gallium-68 at Neutral pH

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Gallium-68 is a useful isotope for positron emission tomography (PET) imaging due to its generator-based production.<sup>1</sup> Whilst the 1, 4, 7, 10-tetraazacyclodecane–N, N', N'', N'''-tetraacetic acid (DOTA) chelate is often seen as the “gold standard” for gallium-68 chelation,<sup>2</sup> it requires harsh conditions (pH 3.5 and 90 °C) to achieve modest yield (58% in 4 minutes).<sup>3</sup> 1, 4, 7-triazacyclononane–N, N', N''-triacetic acid (NOTA) is able to complex gallium-68 under milder conditions (pH 3.5, room temperature, 95% in 10 minutes),<sup>4</sup> but still requires acidic conditions for radiolabeling. This study demonstrates the viability of a selection of new chelates for the coordination of gallium-68 under mild conditions – physiological temperature and neutral pH.

In this study, 3 new chelates were tested for their ability to complex gallium-68 in 15 minutes at room temperature at pH 7.4. The chelate EDTA-bisamide-His was particularly suitable for rapid gallium-68 coordination with a 72% RCY achieved by 50 nmol of chelate, and a yield of 69% by 10 nmol. In addition, 50 nmol of EDTA-bisamide-Meth achieved a RCY of 52% under these conditions. Additional complexation of gallium-68 was seen in all cases, likely due to the formation of dimers or alternative coordination modes. The stability of the resultant complexes was assessed in a trans-metalation challenge with apo-transferrin, with 61% of the <sup>68</sup>Ga-EDTA-His complex remaining intact after 60 minutes. While these results have not yet been optimized, they are highly promising for future development due to the mild radiolabeling conditions used – this may make potential *in vivo* application possible without the need to adjust the solution pH after radiolabeling, and will allow for a range of targeting motifs to be employed in future studies.

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<sup>2</sup> G. J. Stasiuk, N. J. Long, *Chem. Comm.*, **2013**, 49, 2732

<sup>3</sup> G. J. Meyer, H. Mäcke, J. Schihmacher *et al.*, *Eur. J. Nucl. Med. Mol. Imaging*, **2004**, 31, 1097

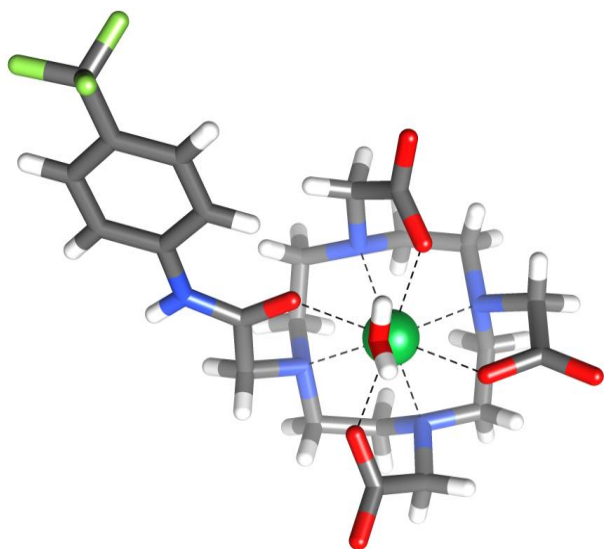
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## Lanthanide Complexes as Potential Bimodal $^{19}\text{F}/^1\text{H}$ MRI Probes

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Lanthanide complexes with polyamino-polycarboxylate ligands are the subject of intense research efforts due to their application as contrast agents in magnetic resonance imaging (MRI).<sup>1</sup> Classical MRI contrast agents are  $\text{Gd}^{3+}$  complexes with a high stability to avoid the release of the toxic free metal ion. In the last decade, paramagnetic  $\text{Ln}^{3+}$  complexes providing Chemical Exchange Saturation Transfer (PARACEST) effect have emerged as an attractive alternative to the classical  $\text{Gd}^{3+}$ -based agents.<sup>2</sup> Besides,  $^{19}\text{F}$ -based MRI agents have been also proposed as an alternative to  $^1\text{H}$  MRI contrast agents, since the  $^{19}\text{F}$  nucleus can be directly detected, has the second highest NMR sensitivity after  $^1\text{H}$  and is almost absent in tissue, which resolves the problem of ambiguous background signal.<sup>3</sup>



Herein, we report a series of  $\text{Ln}^{3+}$  complexes based on a DO3A unit containing a 4-(trifluoromethyl) phenylacetamide pendant arm (Figure 1). The ligand was designed to provide contrast at the  $^{19}\text{F}$  frequency and CEST contrast through the exchangeable amide NH proton. A full characterization of the complexes in the solid state and in solution will be presented, including CEST and  $^{19}\text{F}$  NMR studies.

**Figure 1** X-ray structure of  $[\text{YbL}]$

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## A new $^{89}\text{Zr}$ bifunctional chelator for immunoPET imaging

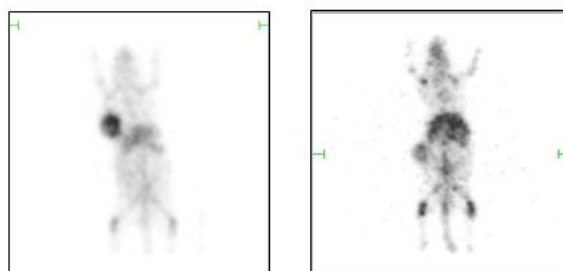
Rudd, S. E.,<sup>a\*</sup> Roselt, P.,<sup>b</sup> Cullinane, C.,<sup>b</sup> Hicks, R. J.,<sup>b</sup> & Donnelly, P. S.<sup>a</sup>

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$^{89}\text{Zr}$  is a useful radioisotope for immunoPET imaging as its decay half-life matches well with the pharmacokinetic half-life of antibodies. Desferrioxamine B (DFO) is commonly used as a chelator for Zr, and various DFO-based bifunctional chelators have been reported. Each bifunctional chelator incorporates a reactive functional group for bioconjugation to an antibody, however their stability is not ideal. For example, bioconjugation of the recently reported *p*-isothiocyanatobenzyl-desferrioxamine (DFO-Bz-NCS) results in a thiourea linkage, which is susceptible to cleavage through radiolysis.<sup>1</sup> Furthermore, the coordination sphere of  $\text{Zr}^{\text{IV}}$  is not saturated by most DFO-based chelators, suggesting the stability of the complex may be improved by ligand modification.

In order to address these issues, we have investigated a novel DFO-based bifunctional chelator using an alternative bioconjugation linkage (DFOX). The synthesis, characterisation, radiolabelling and small animal PET imaging of this  $^{89}\text{Zr}$  complex will be presented.



**Figure 1** Example PET images of SKOV3 xenograft-bearing mice 96 hours post administration with the radiotracers (left)  $^{89}\text{Zr}$ -DFOX-trastuzumab and (right)  $^{89}\text{Zr}$ -DFO-Bz-NCS-trastuzumab.

1. Perk, L., et al, *Eur. J. Nucl. Med. Mol. Imaging*, **2009**, 37 (2), 250

## Copper(II) coordination chemistry of C-alkylated dioxocyclam and cyclam ligands

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Medical imaging is one of the fastest growing areas within medicine at present and plays a central role in global healthcare systems as it clearly contributes to improve patient outcome. Among the different imaging modalities Positron Emission Tomography (PET) plays a pivotal role in diagnosis and staging of diseases, and follow-up of therapies as well. This nuclear imaging technique is associated with an adapted radiopharmaceutical *i.e.* a targeted vector bearing a positron emitting radionuclide ( $^{11}\text{C}$ ,  $^{18}\text{F}$ , radiometals as  $^{64}\text{Cu}$ ,  $^{68}\text{Ga}$ , for example). With a half-life of 12.7 h,  $^{64}\text{Cu}$  acquires an increasing interest as PET radioisotope and it must be incorporated by a bifunctional chelator (BFC), allowing the coordination of the metal ion and the creation of a covalent bond with a targeting agent.

Classical cyclen-, cyclam- and triazacyclononane-based BFCs (DOTA, TETA and NOTA, respectively) are *N*-functionalized displaying thus *tertiary amines*, which reduces the strength of the radiometal sequestration potentially leading to a loss of the radiometal *in vivo*. Moreover, heating for dozens of minutes is necessary to complex the radiometal. Thus, there is a need to develop innovative BFCs with optimized complexation properties: fast kinetics of complexation at RT and inertness of the complex.

The aim of this work is to develop new C-functionalized cyclam macrocycles displaying a complexation framework of four macrocyclic *secondary amines* and two additional coordinating pendant arms with N/O-donor atoms. An efficient synthetic pathway to C-alkylated cyclams anchored with non-functionalized “inverse” triazoles will be presented. Preliminary encouraging complexations properties with non-radioactive Cu(II) have already been observed and will also be presented (fast complexation at ambient temperature).<sup>1</sup>

1. A.-S. Felten, N. Petry, B. Henry, N. Pellegrini-Moïse and K. Selmeczi, *New J. Chem.* **2015**, DOI: 10.1039/C5NJ01927C.

## Prospects of octahedral rhenium cluster complexes as X-ray contrast agents

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Radiocontrast agents are used in medicine to improve visibility of inner body structures in X-ray imaging techniques. To date, the most of radiocontrast agents are based on 1,3,5-triiodobenzene derivatives. Low toxicity and high solubility allowed these compounds to integrate into a medical field. However, their application has some drawbacks like cardiovascular, anaphylactic (allergic), painful effects, and probability of emergence contrast-induced nephropathy. We believe that octahedral chalcogenide rhenium cluster complexes with the general formula  $[\{\text{Re}_6\text{Q}_8\}\text{L}_6]^n$  (Q = S, Se or Te; L = apical organic or inorganic ligands) may become alternative radiocontrast materials. In these compounds a cluster core  $\{\text{Re}_6\text{Q}_8\}$  may potentially act as a radiocontrast component and the apical ligand environment similar to substituent in 1,3,5-triiodobenzene radiocontrast agents may provide biocompatibility.

Thus, the aim of our research was to study radiopacity, cytotoxicity, intracellular localization *in vitro* and acute intravenous toxicity *in vivo* of several octahedral rhenium cluster compounds with different inner (Q) and outer (L) ligands, namely,  $\text{Na}_4[\{\text{Re}_6\text{Q}_8\}(\text{CN})_6]$  and  $\text{Na}_2\text{H}_8[\{\text{Re}_6\text{Se}_8\}(\text{P}(\text{CH}_2\text{CH}_2\text{CONH}_2)(\text{CH}_2\text{CH}_2\text{COO})_2)_6]$ , to evaluate which cluster complex is more promising for the application as X-ray contrast agent.



**Figure 1** Angiography of the mouse blood vessels with  $\text{Na}_4[\{\text{Re}_6\text{Te}_8\}(\text{CN})_6]$

This work was supported by the Russian Foundation for Basic Research (Grant 15-33-20083) and by the Grant of President of the Russian Federation (MK 4054.2015.3).

## Novel europium-based luminescent pH-responsive probes for lysosome targeting

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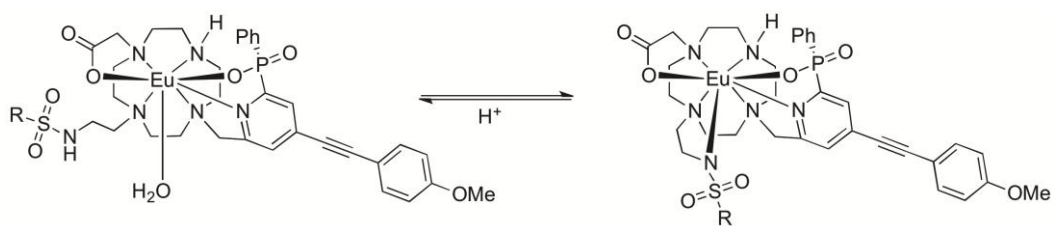
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Selective targeting of lysosomes is crucial for a better understanding of processes occurring inside these organelles. Certain inherited metabolic diseases, called lysosomal storage diseases (LSD), result from malfunctioning of lysosomes and are accompanied by pH changes inside this organelle from standard values. Therefore, lysosome-selective probes, able to provide a reversible pH-response, are desirable tools for biological studies.

Previously, we have reported pH-responsive lysosome-selective luminescent europium-based probes using a 12-N<sub>4</sub> system, bearing an azaxanthone chromophore<sup>1</sup>. However, brighter complexes can be derived by using alkyl-pyridine chromophores, as used in a 9-N<sub>3</sub> system for the selective targeting of the endoplasmic reticulum with a pH-responsive europium complex<sup>2</sup>.

Europium complexes based on a 12-N<sub>4</sub> platform bearing this chromophore, have been synthesized. The sulfonamide moiety binds reversibly to Eu<sup>3+</sup> as a function of pH, modulating the intensity of europium emission. The pH range of the reversible response, depends on the nature of substituent, R, and relative position of the ring substituents. The latter fact, supported by B3LYP/3-21G calculations, has been rationalised by differences in the steric demand around the lanthanide ion.



R = Me or *p*-MeO-Ph

**Figure 1** Reversible binding of the sulphonamide arm on changing pH

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## nanoMIL100: a novel efficient tool to target lung cancer

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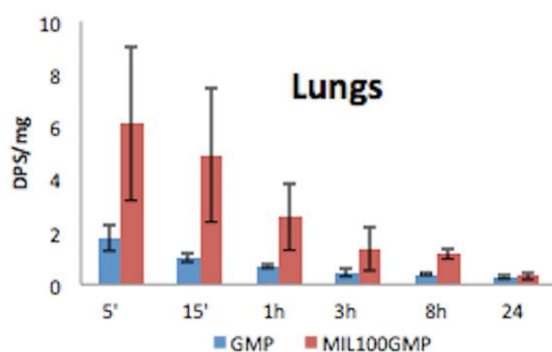
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Lung cancer (LC) is a major health problem, accounting for near 27% of all cancer deaths. Each year, more people die of LC than colon, breast, and prostate cancers combined (1). This fact evidences the urgent need to improve current available therapy. To increase LC therapy and to reduce its toxicity we propose the use of MOF-based nanoparticles (NP). In particular, we have developed a formulation that passively targets the lungs without any visible signs of toxicity based on MIL-100(Fe), a mesoporous iron(III) trimesate MOF.

NP were prepared and characterized as described elsewhere (2). To evaluate their *in vivo* biodistribution and toxicity at early times (up to 24 h), a first study was performed in Sprague-Dawley rats. An important accumulation of the NP was observed in the lungs by measuring the iron concentration by atomic absorption spectroscopy. In accordance with our previous data, animals did not present any signs of toxicity. This result encouraged the evaluation of the impact of the loading of Gemcitabine-monophosphate (GMP), a well-known drug used in LC treatment, into MIL100 NP, on drug organ accumulation.

Tritiated-GMP was encapsulated by the impregnation method as previously described (3).



C57BL/6JRj mice were treated iv with 10 mg/kg of the free drug and the equivalent dose of MIL100 encapsulated drug. When administered in NP, GMP concentration in lungs was five-fold higher than free GMP after 15 min and remained three-fold larger after 8h (Figure 1).

**Figure 1** Drug accumulation (measured as disintegrations per second per mg of organ).

Thus, MIL100 NP appear as an efficient tool to target the lungs to treat pulmonary diseases.

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## Evaluation the Tumor Specificity of a Herceptin- Conjugated {Mo<sub>6</sub>I<sub>8</sub>}@SiO<sub>2</sub> Nanoparticles In Vitro

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Molybdenum Complexes with {Mo<sub>6</sub>I<sub>8</sub>}<sup>4+</sup>-cluster core incorporated in silica nanoparticles are considered as attractive candidates for bioimaging (luminescent diagnostic), biolabeling and photodynamic therapy because the clusters exhibit red phosphorescence with high quantum yields and, as a consequence, may generate the singlet oxygen. To improve the cancer cell specific delivery the drug are conjugated with antibody. Here we describe a conjugate of {Mo<sub>6</sub>I<sub>8</sub>}@SiO<sub>2</sub> NPs with Herceptin (anti - HER2/neu antibody) for enhancing drug accumulation and HER2-positive cancer cell specific delivery.

Two cell populations were used in these experiments, one tumor cell line expressing HER2/neu (SKBR-3) and the other control cell line, negative for HER2/neu (Hep2). We demonstrate that {Mo<sub>6</sub>I<sub>8</sub>}@SiO<sub>2</sub>@Herceptin exhibit high and selective binding affinity for HER2-positive SKBR-3 cancer cells. Maximum SKBR-3 cellular uptake of {Mo<sub>6</sub>I<sub>8</sub>}@SiO<sub>2</sub>@Herceptin was observed after 15 minutes of incubation. As compared to SKBR3 cells Hep 2 cells contain much less fluorescence intensity even after 24 hours of incubation with {Mo<sub>6</sub>I<sub>8</sub>}@SiO<sub>2</sub>@Herceptin.

To determine intracellular localization of {Mo<sub>6</sub>I<sub>8</sub>}@SiO<sub>2</sub>@Herceptin the fluorescent confocal microscopy were applied. Luminescent imaging clearly showed that {Mo<sub>6</sub>I<sub>8</sub>}@SiO<sub>2</sub>@Herceptin was localized in the cell cytoplasm into endosome-similar structures on the periphery of the cell and in the perinuclear space.

Thus, {Mo<sub>6</sub>I<sub>8</sub>}@SiO<sub>2</sub> NPs were conjugated successfully with the herceptin antibody. {Mo<sub>6</sub>I<sub>8</sub>}@SiO<sub>2</sub>@Herceptin was internalized selectively into the target cells (SKBR3).

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## Dual-modal PET/fluorescent zinc-sensing probes for prostate cancer detection and screening

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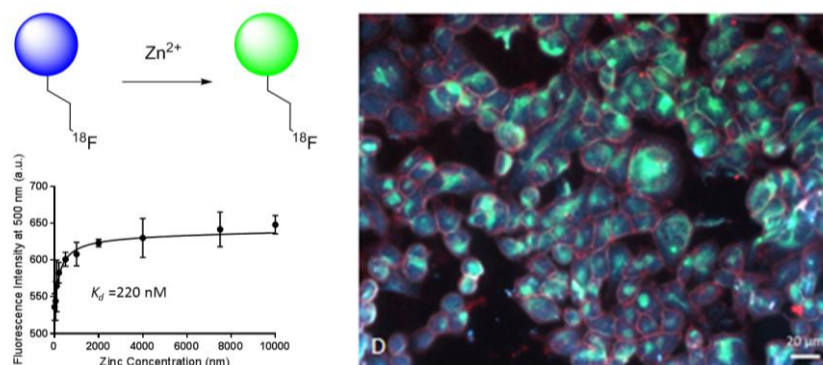
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Prostate cancer (PCA) is commonly diagnosed upon presentation with clinical symptoms relating to its metastatic spread to bone or during screening assessment for prostate specific antigen (PSA). Inaccurate diagnosis, based on serum levels of this secreted protease, and lack of effective treatment for metastasis, necessitates the development of improved diagnostics for early detection and monitoring of the disease. Zinc levels decrease during the early stages of PCA, consolidating its role as a *bona fide* biomarker.<sup>1</sup> In this study a dual-modal PET/fluorescence probe that senses alterations in zinc concentration has been synthesized and validated in a 3D cellular model of early PCA progression.<sup>2</sup> The <sup>18</sup>F radioisotope-based probe modified with organic fluorophores and zinc-sensing motifs<sup>3,4</sup> displays ratiometric fluorescence with a large Stokes shift upon zinc chelation (from  $\lambda_{em} = 400$  nm to  $\lambda_{em} = 500$  nm) and has a  $K_d$  of 220 nM, which is in the ideal range for monitoring changes in zinc concentrations in prostate glandular tissue.



**Figure 1.** Zinc-sensing using a dual modal fluorescent probe in a tumour cell line: Zn (II) (green) no Zn (II) (blue) and concanavalin A (red).

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## Synthesis, coordination and $^{64}\text{Cu}$ radiolabelling of cyclam picolinate chelators and phenotypic PET imaging of their conjugated derivatives

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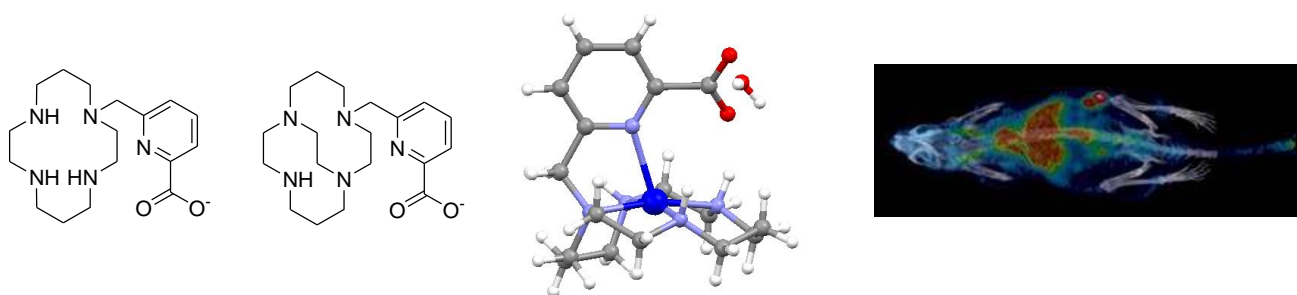
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In the frame of PET-phenotypic imaging or radioimmunotherapy a major issue is the *in vivo* instability of radiometals labelling.

Concerning  $^{nat}\text{Cu}(\text{II})$  complexation and  $^{64}\text{Cu}(\text{II})$  radiolabelling, *N*-functionalized cyclams are now recognized as the most promising chelates for these applications compared to other chelators as DOTA (the most commonly used commercial ligand) since they offer better physicochemical properties. Monopicolinate cyclam derivatives have previously demonstrated to form astonishing stable and inert  $\text{Cu}(\text{II})$  chelates.<sup>1</sup> The resultant  $^{64}\text{Cu}$  complexes were associated, *in vivo*, with a huge resistance to transchelation, especially in the liver, with an important clearance over 24 h post-injection.<sup>2</sup>

The conjugation of both ligands to a monoclonal antibody (mAb) was then investigated for future phenotypic imaging applications. Results are promising when compared to other chelates but a better conjugation mode must be found to preserve the coordination properties of the chelates when used as radiopharmaceuticals.<sup>3</sup>



**Figure 1** Picolinate cyclams for  $^{64}\text{Cu}$  PET imaging

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## pH-sensitive Angiographic Contrast Agents for MRI

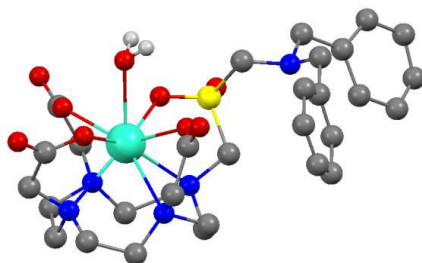
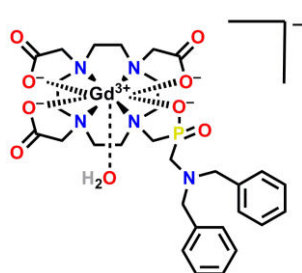
Peter Urbanovský,<sup>a\*</sup> Jan Kotek,<sup>a</sup> Petr Hermann,<sup>a</sup> Fabio Carniatio,<sup>b</sup> Mauro Botta<sup>b</sup>, Daniel Jiráček<sup>c</sup>

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Magnetic resonance imaging (MRI) angiography is commonly used diagnostic techniques. It shows circulatory system of patient, *i.e.* blood in veins. Some blood components can be utilized to achieve suitably long residence of a contrast agent (CA) in blood pool, *e.g.* hydrophobic cavities of the most abundant protein in plasma, human serum albumin (HSA). Lipophilic group like 4,4-bis(phenyl)cyclohexyl in clinically used Ablavar<sup>®</sup> (former Vasovist<sup>®</sup>) interacts with both cavities and, thus, the CA persists in blood<sup>1</sup> and MRI scans show the blood vessels. However, this interaction is so strong that excretion half-time is prolonged from tens of minutes to hours<sup>2</sup> and release of central ion, a heavy metal Gd<sup>3+</sup> (LD<sub>50</sub>(mouse, i.v.) is 0,35 mmol/kg)<sup>3</sup> is possible.

CA with bis(benzyl)amino group (Figure) has versatile properties due to presence of protonable amino group. Its deprotonated form interacts with HSA and observed relaxivity is several-fold increased, whereas its protonated form is almost exclusively present as HSA



**Figure:** The drawing (left) and solid-state structure (right) of the pH-sensitive CA.

non-bounded form. The HSA-bounded deprotonated CA remains in blood and the non-bound form is easily excreted through kidneys. The Gd(III)-complex side arm is protonated with  $pK_A$  5.6. One directly

coordinated water molecule was determined by luminescence, HR UV-VIS, DIS of <sup>17</sup>O-NMR and abundance of isomers from <sup>31</sup>P-NMR measurements of Ln(III)-complex analogues. Due to labilized coordinated water molecule in the deprotonated Gd(III)-complex, CA has very fast water exchange rate ( $\tau_M = 6,0 \pm 0,2$  ns). Hydrophobicity of pendant arm side chain is tunable and, furthermore, new optimized CA was prepared and tested *in vitro* and *in vivo*.

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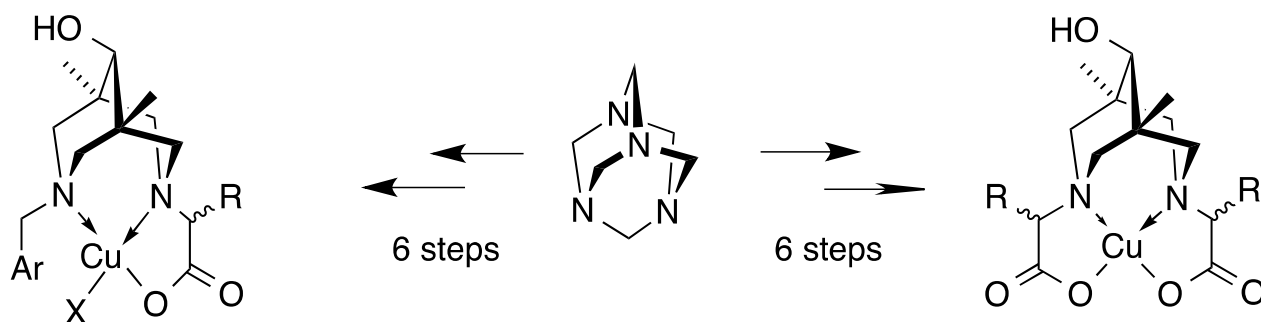
## Copper bispidinate as novel PET reagents

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This report summarizes the results of our long time work in the field of 3,7-diazabicyclo[3.3.1]nonane's (bispidine) coordination chemistry<sup>1</sup> and points out novel directions of research for the future<sup>2-4</sup>. We will discuss the ways of the possible application of bispidines and their complexes as bioactive compounds. The radiation therapy is one of the modern and useful methods for the treatment of the oncological diseases, particularly, for the brain, head and neck tumors as well as for the tumors of some other localization. The problem of short decay time can be solved by use of new radiopharmaceuticals containing long-lived isotopes, particularly, <sup>64</sup>Cu. To do this, the elaboration of easily modified ligand systems with high affinity to the metal cation and with wide possibilities of chemical modifications including the conjugation to the biological vectors is proposed. We will talk about two families of tri- and tetradentate bispidine-based ligands that are derived from the same commercially available starting compound, urotropine (scheme). The solubility, stability constants, spectroscopy, electrochemistry and current stage of using copper complexes, as new PET reagents, will be discussed in details.



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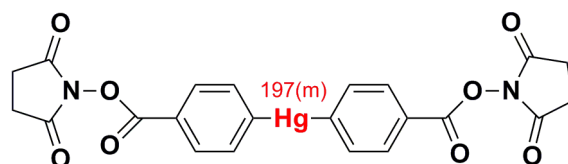
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## Comeback of Mercury as $^{197(m)}$ Hg for Theranostics

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The no-carrier-added (NCA) radionuclide  $^{197(m)}$ Hg is accessible in adequate quantity and quality for radiopharmaceutical research through the proton irradiation of gold using a cyclotron.<sup>1</sup> The interest in this mercury isotope was prompted primarily by the decay characteristics of both nuclear isomers, like convenient half-life ( $^{197m}$ Hg = 23.8 h,  $^{197}$ Hg = 64.14 h), low energy gamma radiations useful for diagnosis ( $^{197m}$ Hg = 133.98 keV, 33.5% ,  $^{197}$ Hg = 77.4 keV, 18.7%) and numerous Auger- and conversion electrons with high potential for cancer therapy. Additionally, the unique chemical properties of mercury allow for the development of promising radiolabeling tools and new radiopharmaceuticals. In addition to the typical metal properties to form coordination compounds with sulfur, nitrogen and oxygen containing ligands, mercury has the special ability to build water stable carbon-metal bonds. The reactivity of the mercury(II) ions towards sulfur containing ligands, solvomercuration of alkenes and electrophilic aromatic substitutions were investigated to prepare a stable labeling unit at NCA level with  $^{197(m)}$ Hg. While both the mercury thiolate complexes and the products of solvomercuration exhibited low stability in the presence of competing thiol ligands and are therefore unsuitable for radiopharmaceutical applications, symmetric diarylmercury compounds showed high stability against competing ligands. The development and application of a prelabeling tool based on a bis-benzoyl-mercury derivative as succinimidyl ester will be reported.



**Figure 1**  $^{197(m)}$ Hg-labeled Bis-succinimidyl Benzoate-Quicksilver (BBQ)

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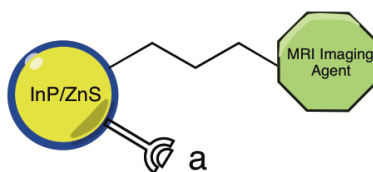
## Development Of A Multimodal Bio-imaging Platform for Detecting the Switch to Aggressive Prostate Cancer

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State-of-the-art multi-modal bio-imaging agents with the potential to predict the progression of prostate cancer (PCa) from an indolent to aggressive state have been developed in this project. The basis of this work follows the discovery of a novel bio-molecular switch for *de novo* cell invasiveness in the prostate gland.<sup>1,2</sup> The bio-imaging probes have been designed to detect an ectodomain-specific conformational change in the collagen receptor Endo180, as it switches from being a suppressor to promoter of epithelial-to-mesenchymal transition (EMT), that results in metastasis and decreased patient survival.<sup>1,2</sup> The novel bio-imaging system involves conjugation of epitope-mapped human Endo180 monoclonal antibodies<sup>2</sup> to the surface of quantum dots (QDs) (Figure 1). For this purpose, InP/ZnS core/shell QDs have been used as they are non-toxic and have highly tunable fluorescent properties, with the added advantage of facile incorporation of multiple Gd(III) MRI agents and targeting motifs on a single platform.<sup>3,4</sup> Following evaluation of their chemical and physical properties, and proof-of-principle application in biological models of tumour progression, the probes will be assessed for their application in the diagnosis, prognosis and personalised treatment of PCa patients.



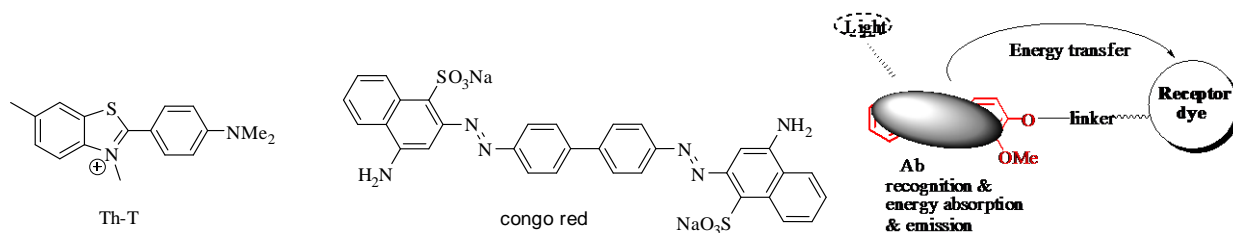
**Figure 1** shows InP/ZnS core/shell QD which have undergone surface functionalization to allow for the design of a multi-modal bio-imaging agent. Surface modification generates the ability for domain specific antibodies (**a**) to also be added.

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Transition metals have many important functions in biology but also responsible for few serious metal-induced diseases due to their imbalance. Disruption of these metal-peptide interactions using chemical agents holds considerable promise as a therapeutic strategy to combat these incurable diseases [1-4]. Recent efforts in studying the A $\beta$ -metal interactions have focused on small molecules, multifunctional chelators (MFCs), which can interact with the more than one target [3,4]. We are interested to use a combination of unique properties rendered by various molecular scaffolds to generate a new class of MFCs. Some of the well known molecular scaffolds are stilbene, thioflavin-T (ThT), clioquinol, phenylbenzothiazole etc. Although congo-red (CR) is an important dye but MFC based on CR is rare. We are particularly interested in design of new MFC based on CR azo-function. Azo-stilbene-imine based scaffold are being synthesized. These modified scaffolds will be further functionalized in order to add metal chelating arms for the purpose of metal chelation from various amyloids causing oxidative stress. In addition, DYADs based on amyloid binding molecular scaffold linked to other fluorophore suitable for energy donor-acceptor phenomena and subsequently we would like to use them as FRET based imaging agents. Initial results of these projects will be presented in this conference.



**Figure 1** Scheme 1. Structures of Thioflavin-T and congo red (top) and schematic representation of linked supra-molecule and energy transfer (bottom).

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# Biomimetic reactivity of dioxygen in iron (II) and copper (II) complexes for activation of C-H bonds.

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Dioxygen activation by iron enzymes is responsible for many metabolically important transformations in biology. Oxygen-coordinating metal species, such as metal-peroxo, -hydroperoxo, and -oxo complexes, have been frequently invoked as reactive intermediates in the catalytic cycles for dioxygen activation by metalloenzymes.<sup>[1]</sup> The chemistry of soluble methane monooxygenase (sMMO), which catalyzes the selective oxidation of methane to methanol (C-H bond activation) is of particular interest for biotechnological applications. The sMMO enzyme involves three components (Figure 1): a hydroxylase (MMOH), a regulatory protein (MMOB) and an oxidoreductase (MMOR).<sup>[2-4]</sup>

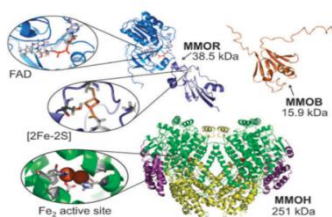


Figure 1

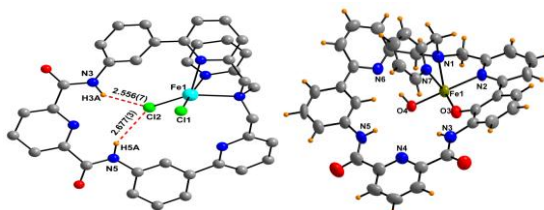


Figure 2

Figure 3

In order to model the ditopic active site of MMOH,<sup>[5-6]</sup> we are exploring the coordination chemistry of a novel asymmetric dinucleating

ligand  $\text{LH}_2$  Tris(2-methylpyridyl)amine-6-diphenyl-1,3-pyridyldicarboxamide associating a neutral tripodal site and a potentially dianionic pyridyldicarboxamide donor set with various metal centers. Iron and copper complexes have been prepared and characterized by NMR, EPR, UV-Vis, IR spectroscopy and X-ray Crystallography (Figure 2). In the chemistry of iron complexes, the reaction of  $\text{O}_2$  with  $\text{Fe}^{\text{II}}(\text{LH}_2)$  in a MeCN solution at room temperature generates an hydroperoxo- $\text{Fe}^{\text{III}}(\text{OOH})$  species which has been characterized by X-ray crystallography (Figure 3). This species can carry out an H-atom abstraction from a C-H bond hydroxylation

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## Zinc complexes with non-steroidal anti-inflammatory drugs: Synthesis, Characterization and Crystal Structures

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Till now, and since the approval of the use of *cis*-[PtCl<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>] in clinical practice as antitumor agent, many efforts have been made to develop novel platinum and non-platinum based antitumor drugs in order to improve effectiveness, to reduce the systemic and organospecific toxicities and to broaden the spectrum of activity of metal complexes as anti-carcinogenic species<sup>1</sup>.

As a vital metal ion for cellular processes, zinc (Zn), the second most important transition metal in the human body, is essential for cell growth and cell division. However, little attention has been paid to the biological roles of synthetic Zn-based compounds, especially those containing bioactive molecules exhibiting both effective antitumor and DNA-targeted activities<sup>2</sup>.

Non-steroidal anti-inflammatory drugs (NSAIDs) are commonly used anti-inflammatory, analgesic, and antipyretic agents. They have also exhibited anti-tumorigenic activity by reducing the number and size of carcinogen-induced colon tumors as well as a synergistic role on the activity of certain antitumor drugs<sup>3</sup>. The combination of two or more active parts into the same compound can generate a multi-therapeutic agent which can expand its potency by the synergic action of the metal residue once the coordination compound has dissociated inside the target tissue.

In this work we present our results on the synthesis and characterization of new Zn complexes coordinated with NSADs. The compounds have been prepared using a standard procedure and were characterized by elemental analysis, UV-visible (UV-vis), IR spectra, thermal gravimetric analysis, and single crystal X-ray analysis.

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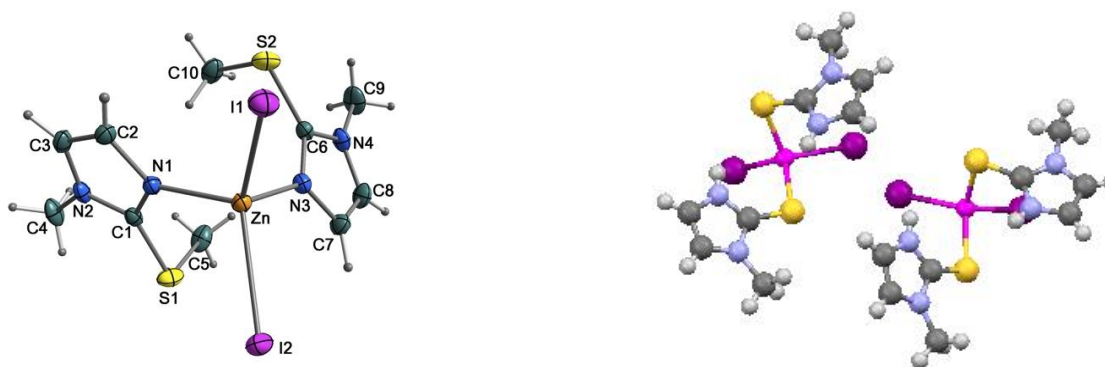
## Reactivity at the zinc-coordinated methimazole anion

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Zinc is an essential metal ion for living organisms, its presence being fundamental in catalytic, structural, and regulatory biological processes.<sup>1</sup> For these reasons, the exposure to coordinating drugs like methimazole (1-methyl-3*H*-imidazole-2-thione; MelmHS), which is currently the standard treatment for Graves' disease,<sup>2</sup> can potentially interact/interfere with zinc buffering systems and Zn-metalloenzyme activities either causing zinc deficiency, and/or potentially reducing the efficacy of the drug.

We recently synthesized the complex of stoichiometry  $[\text{Zn}(\text{MelmS})_2]$  (MelmS = anion methimazole acting as (*N,S*)-chelating ligand.).<sup>3</sup> Its reaction with  $\text{CH}_3\text{I}$  separates the novel complex  $[\text{Zn}(\text{MelmSMe})_2\text{I}_2]$  (MelmSMe = *S*-methylmethimazole) whose X-ray diffraction analysis shows a  $\text{ZnI}_2\text{N}_2$  core, with the methyl thioethers uncoordinated to zinc (figure, left). Conversely, the reaction of  $[\text{Zn}(\text{MelmS})_2]$  with HI led to the formation of the complex  $[\text{Zn}(\text{MelmHS})_2\text{I}_2]$  having a  $\text{ZnI}_2\text{S}_2$  core with the neutral methimazole units *S*-coordinating the metal centre (figure, right). The Zn-coordinated methimazole can markedly modify the coordination environment when changing from its thione to thionate form, and *vice versa*. These results underline that methimazole shows a reactivity, and a variety of coordinating modes that may in some way alter the biological processes that are based on the zinc ion.



**Figure 1** View of the complexes  $[\text{Zn}(\text{MelmSMe})_2\text{I}_2]$  (left), and  $[\text{Zn}(\text{MelmHS})_2\text{I}_2]$  (right).

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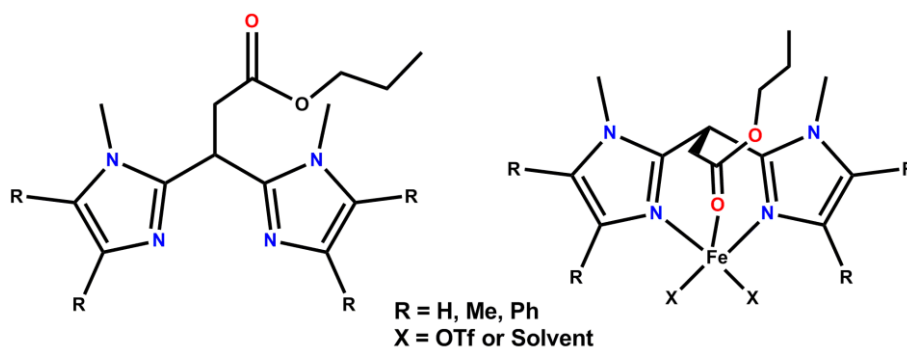
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## Mimicking the 2-His-1-Carboxylate Facial Triad using Bulky N,N,O-ligands

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Mononuclear non-heme iron enzymes featuring a 2-His-1-carboxylate facial triad active site have received particular attention primarily due the stunningly diverse oxidative catalytic transformations that are catalyzed by these enzymes. Many efforts by synthetic inorganic chemists have been devoted to biomimetic modeling studies of the facial triad enzymes in order to understand the immense oxidative power of these enzymes and to develop new synthetic catalysts. Initial studies have focused on the development of functional models of the different subfamilies and employed mostly polydentate all-N donor ligands. While impressive results have been obtained, limited effort has been devoted to the design of models that more faithfully reproduce the coordination environment of the 2-His-1-carboxylate facial triad, i.e. that contain combined N,N,O donor ligands.

In this presentation, the development of a new class of facial triad N,N,O ligands based on the bis(alkyl-imidazolyl)propionate (BAIP) architecture for the synthesis of bio-inspired mono-nuclear non-heme iron(II) complexes is described. Our studies have in particular focused on the use of bulky BAIP ligands for the construction of mono-N,N,O ligand complexes (shown in Figure) and on the ability of the resulting complexes to selectively catalyze challenging oxidative transformations of organic compounds using oxidants like H<sub>2</sub>O<sub>2</sub> or O<sub>2</sub>.



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## The New Ag-N-Heterocyclic Carbene Complexes Having Antitumor Potential

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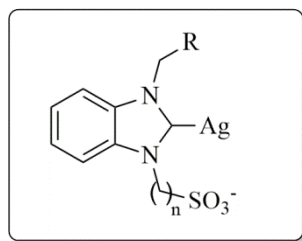
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Metal-NHC complexes are mostly used in catalytic applications.<sup>1</sup> Recently, NHCs came into the focus as carrier ligands for cytotoxic metal complexes because they perfectly fit prerequisites for an efficient drug design and fast optimization. NHCs are readily accessible in few steps and their substituents can be widely varied allowing an easy fine-tuning of both the physicochemical properties and the reactivity in biological medium of the final metal-NHC complexes. Additionally, their high stability and ease of derivatization make them suitable candidates for drug development.<sup>2-3</sup> Importantly, the great potential of metal-NHCs in the pharmaceutical domain is highlighted by several recent patents taken by universities and “big Pharma”.<sup>4</sup>

In this study sulphonated functionalized Ag-NHC complexes were synthesized and characterized. The antitumor activity of these metal-carbene complexes was tested in cancer cell lines HEP3B and SHSY5Y.



**Figure 1** Ag N-heterocyclic carbene complex

This work was financially supported by the TÜBİTAK-MHESR [114Z624].

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## Binuclear copper complexes based on a 1,8-naphthyridine ligand used as models for copper oxygenase.

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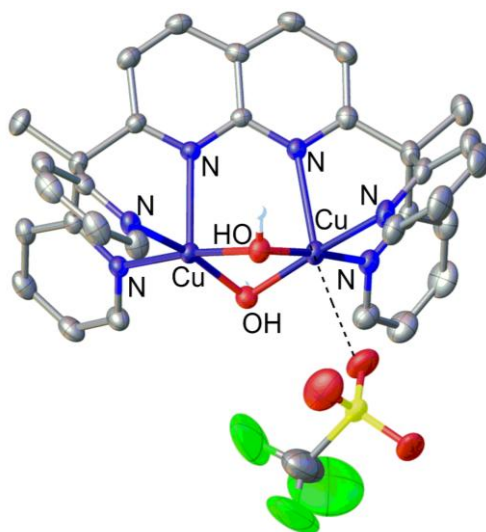
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The aim of this project is to generate a model for the dicopper centre present at the active site of particulate methane monooxygenase (pMMO),<sup>1</sup> an enzyme able to oxidise methane to methanol. The active species in pMMO is heavily debated, but a mixed valence  $\text{Cu}^{\text{II}}\text{Cu}^{\text{III}}$  species has been proposed,<sup>2</sup> so efforts are focused on stabilizing this species.

A symmetric  $\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}$  complex (**A**) has been synthesised using the ligand 2,7-bis(1,1-dipyridylethyl)-1,8-naphthyridine.<sup>3</sup> The complex contains a bis( $\mu\text{-OH}$ ) $\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}$  species. The complex has been characterised by crystallography (Figure 1), electron paramagnetic resonance (EPR) and NMR spectroscopy, UV-visible, electrochemical and theoretical studies. The  $\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}$  has been mono-oxidised to form a localized mixed valence  $\text{Cu}^{\text{II}}\text{Cu}^{\text{III}}$  species characterised by UV-visible, EPR...Theoretical calculations also confirm this result.



**Figure 1:** Crystal structure of cation **A**.

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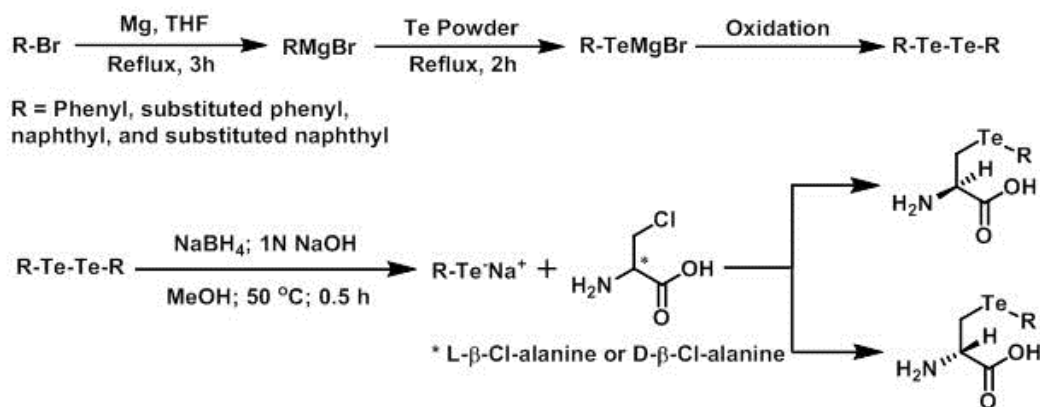
# Synthesis and Antioxidant Activity of D- and L-tellurocysteine Derivatives

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Selenocysteine (Sec) known as 21<sup>st</sup> proteinogenic amino acid, is at the active site of several selenoenzymes. The widely studied selenoenzymes are glutathione peroxidase (GPx), iodothyronine deiodinase and thioredoxin reductase etc.,<sup>1</sup> The synthesis of tellurocysteine (Tec) was reported in 1997.<sup>2a</sup> There are a few reports on bioincorporation of tellurocysteine into protein, such as, glutathione transferase and tellurosubtilisin.<sup>2b</sup> Tellurium containing proteins and compounds were shown to be much more effective antioxidants than their corresponding selenium and sulfur analogues. Especially, aliphatic tellurium compounds exhibit interesting and promising biological applications. For example, trichloro(ethane-1,2-diolato-O,O')tellurate(IV) (AS101) which is an aliphatic tellurium compound is promising as an immune-modulating drug for the treatment of AIDS.<sup>2c</sup> Our interest is to explore the tellurocysteine chemistry. In the poster, we mainly discuss about synthesis and characterization of tellurocysteine derivatives and their antioxidant properties (**Scheme 1**).



**Scheme 1.** Synthesis of D- and L-tellurocysteine derivatives

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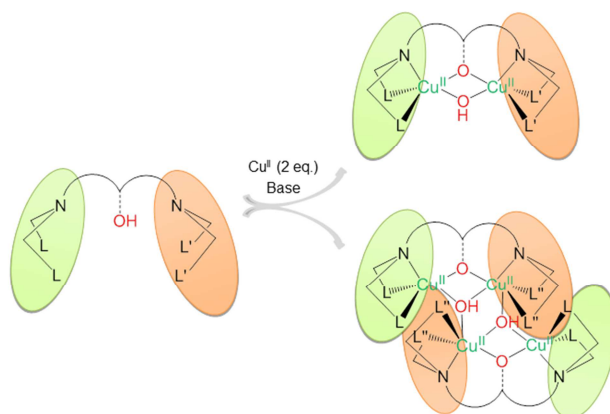
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## Di- and Tetranuclear copper(II) complexes derived from new unsymmetric ligands: synthesis and properties.

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Particulate methane monooxygenase (pMMO) is a copper enzyme which catalyzes the direct conversion of methane to methanol in the presence of oxygen under mild conditions.<sup>1</sup> Recent studies suggest the active site contains a non-symmetric dicopper site<sup>2</sup> and the possible involvement of a mixed valent Cu<sup>II</sup>Cu<sup>III</sup> active species.<sup>3</sup> In this context, dinucleating ligands that confer different coordination environments for the two copper atoms and different properties such as redox behavior is highly desirable.

We have recently prepared different unsymmetric ligand with different cavities in order to stabilise different oxydation states for copper. They were characterized by using X-ray crystallography, elemental analysis, UV-Vis, magnetic measurements, cyclic voltammetry and theoretical calculations. Depending on the nature of the ligand, a structural diversity (Figure 1) has been shown as well as a correlation between structural data and magnetic data. Some studies of reactivity will be also presented.



**Figure 1** Illustration of the structural diversity of the complexes obtained with ligands based on different functions.

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## Characterization and biological studies of organotin(IV) complexes with tris[hydroxymethyl]aminomethane] ligands

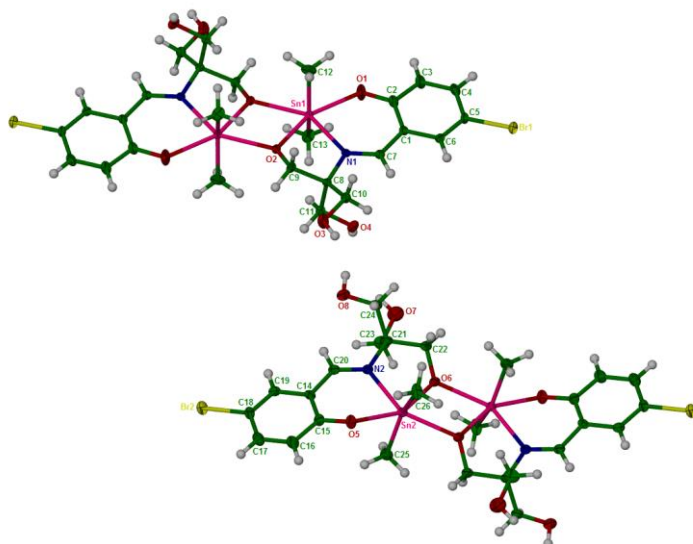
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Metal complexes have been successfully used in the treatment of numerous human diseases including cancer. Among these metal complexes, organotin complexes have been widely studied for their biological activities such as anticancer, antihistamine, antifungal and many others. *Tris*(hydroxymethyl)aminomethane (TRIS) and its Schiff base derivatives are known to have a broad spectrum of biological activities including antitumour, antibiotic, anticancer, antihistamine, antifungal, anti-inflammatory, etc. In the present studies, several ligands were prepared by reacting TRIS with substituted salicylaldehydes. As the ligands are found to have potential biological properties, it is our objective to focus on the investigation of the structural features and biological properties of the prepared diorganotin complexes. The *in vitro* cytotoxic activity of the ligands and complexes had been evaluated against several cancer cell-lines such as *HT-29*, *SKOV-3* and *MCF7*.



**Figure 1** Molecular structure of **1**

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## Enabling new isotopes for mass cytometry

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Development of metal-containing reagents for the simultaneous detection of multiple biomarkers in individual cells at high throughput in conjunction with mass cytometry<sup>1</sup> represents a significant interest. In mass cytometry, cells are injected stochastically into the plasma torch of an inductively coupled argon plasma, where they are vaporized, atomized, ionized and analyzed by time-of-flight mass spectrometry. It is a powerful tool for quantitative analysis of the biomarkers at the single cell level, particularly in multiplexed assays without interferences and with large dynamic range.

To carry out multiplexed immunoassays by mass cytometry, we developed metal-chelating polymer (MCPs) as antibody-tagging reagents and used them in such a way that each distinct antibody, targeted to a specific cell biomarker, is labeled with a different metal isotope.<sup>2</sup> We started from MCPs able to bind naturally occurring Lanthanide (Ln) isotopes having low background in cells and similar binding chemistry.

The Ln-MCPs have now enabled > 30-plex routine analysis using the mass cytometry instrument. With this success has come a growing need to increase multiplicity. We are developing MCPs that bind other metal ions thus expanding capabilities of mass cytometry. Here we will present the preparation and characterization of novel MCP reagents coordinated with Zirconium (Zr) and Rhenium (Re). They are subsequently conjugated to antibodies and functionally tested for their feasibility as reagents for high parameter mass cytometry analysis of single cells.

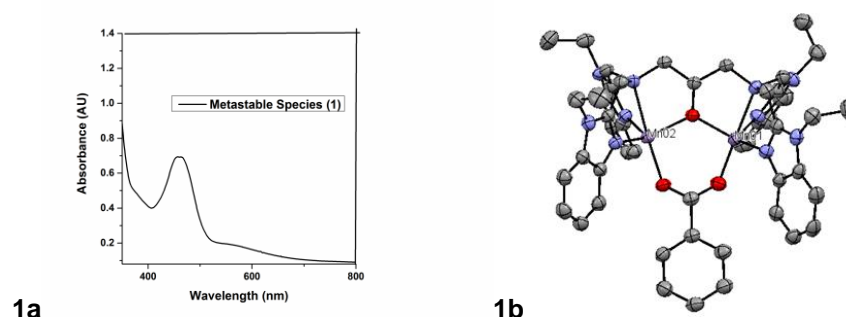
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## Biomimetic Dinuclear Manganese Complexes and Superoxide

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Ribonucleotide Reductases (RNRs) are proteins that are extremely important for DNA biosynthesis. An important breakthrough in RNRs chemistry has been the identification of a dimanganese-core in class Ib RNRs. In this enzyme, superoxide is involved in the process of conversion of nucleotides to deoxyribonucleotides. An enzymatic generation of superoxide was found to be required for this enzyme.<sup>[1]</sup>

We used biomimetic complexes to gain insight into the reactivity of dimanganese complexes towards superoxide. We have identified intermediates that we postulate mimic the reactive intermediates in ribonucleotide reductases. A series of dimanganese complexes supported by different carboxylate bridges were synthesised and characterised by IR, Elemental Analysis and Mass Spectrometry which is further supported by X-Ray Crystallography and EPR data. The crystal structure of one of the dimanganese complexes can be seen in fig. **1b**. The reactivity of these complexes towards superoxide at -40° C was monitored by UV-Vis, EPR spectroscopies and ESI-MS. The treatment of complexes with superoxide formed a metastable species at ~460 nm (fig. **1a**). The metastable species showed no electrophilic or nucleophilic reactivity. EPR was used for the characterisation showing the formation of an EPR silent species, suggesting the formation of a Mn<sub>2</sub>(III)-peroxo species. The peroxo-Mn<sub>2</sub><sup>III</sup> has also been identified by direct injection ESI-MS.



**Figure 1- a)** UV-Vis spectra of the Mn<sub>2</sub>(III)-peroxo species formed at ~460 nm **b)** Crystal Structure of [N-Et-HPTB(Mn<sub>2</sub>)(O<sub>2</sub>CCH<sub>3</sub>)](ClO<sub>4</sub>)<sub>2</sub> ( H atoms and perchlorate anions omitted for clarity)

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## Cysteamine-based water-soluble CO-releasing molecules for medicinal applications

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The lethal toxicity of CO seems to be incompatible with a therapeutic role, but the degradation of heme yields  $\text{Fe}^{2+}$ , biliverdin and CO, the latter being an essential signaling molecule with several beneficial physiological effects. Due to the fact that CO inhalation is challenging in therapeutic applications, CO-releasing molecules (CORMs) are necessary as carriers to administer the gas. These CORMs have to fulfill certain requirements such as solubility in aqueous solutions, thermal stability, triggered CO release at the disease site at a predetermined time, and non-toxicity of the metal complexes as well as of their inactive products (iCORMs).<sup>1</sup> The WESTERHAUSEN group is concentrating on 3d-metal-based photoCORMs with substituted thiolato ligands.<sup>2a</sup> In order to limit toxicity of CORMs and their degradation products, we used cysteamine as a ligand and started with the investigation of the iron-based CORM-S1 [dicarbonyl-bis(cysteamine)iron(II)], however, this photoCORM is only sparingly soluble in water.<sup>2b</sup> Therefore, we intended to synthesize and study a salt-like CORM with low toxicity and high solubility in aqueous media. The reaction of  $[\text{Mn}(\text{CO})_5\text{Br}]$  with cysteamine leads to the photoactive, non-toxic and highly water-soluble CORM-EDE1  $[\{(\text{OC})_3\text{Mn}_2(\mu\text{-SCH}_2\text{CH}_2\text{NH}_3)_3\}\text{Br}_2]$ .<sup>3</sup> This novel photoCORM fulfills all mentioned requirements. Moreover we are examining further cysteamine-based manganese carbonyl complexes that possess the same promising properties.

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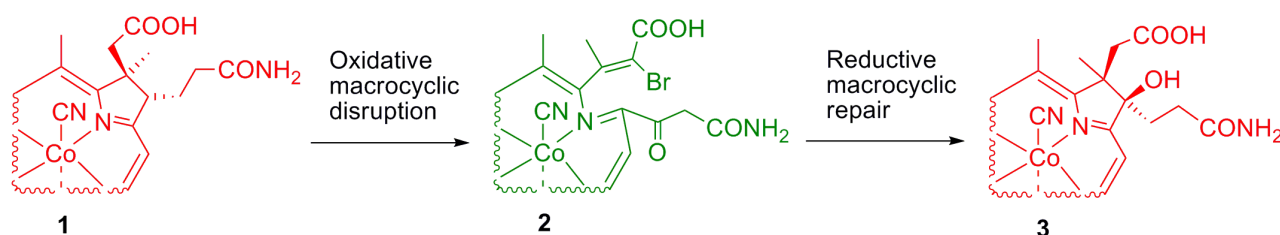
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## Metal and Ligand Centered Reactivity of Modified Cobalamins

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Vitamin B<sub>12</sub> (**1**) is a cobalt-containing nutrient that plays a fundamental role in numerous enzymatic processes amongst almost all forms of life.<sup>1</sup> Cofactor derivatives with tailored modifications of the basic corrin framework show enormous potential for medicinal applications.<sup>2</sup>



**Figure 1** Reversible chemical modifications of vitamin B<sub>12</sub> based on oxidative and reductive macrocyclic alterations.

Herein, we present high-yielding procedures to disrupt and repair the corrin macrocycle of vitamin B<sub>12</sub>, obtaining modified corrinoids **2** and **3** with altered properties and functions.<sup>3,4</sup> In particular, our endeavors focus on metal vs. ligand centered reactivity of the new cofactor derivatives. Biological evaluation of these new compounds is currently underway.

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## New Copper(II) Complexes with DNA-bases: Synthesis, Characterization and Crystal Structures

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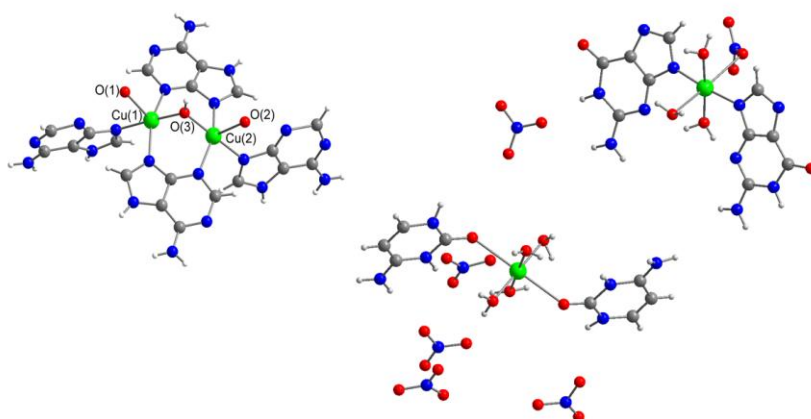
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Complexes of almost all transition metal elements in what concerns bio-sciences are getting more and more importance due to the role they are involved either in biochemical, pharmacological or medicinal chemistry. Their different stereo-electronic properties which depend on the metal centre, oxidation state and the coordinated ligand type afford them a wide and versatile spectra of applications. Among transition metal coordination compounds those with copper, mono, bi or multi-centred, have reached today a prominent place in the research for new metal drugs with enormous potential.<sup>1</sup> Nucleobases are multidentate ligands with different binding sites which vary with metal ions and physiological conditions. Thus it is of it is of immense interest to understand the underlying principles which dictate the propensity of the binding sites of nucleobases to metals.<sup>2,3</sup>

Here results on the synthesis and characterization of new copper(II) complexes coordinated with DNA bases (adenine, cytosine and guanine) (Figure 1) coordinated either in mono or bridging mode are presented. The DNA-bases have been used as models for interaction of coordination metal drugs with DNA by covalence. The new copper(II) complexes have been prepared using standard procedures and were characterized by EA, FTIR, UV-VIS, TGA and single crystal X-ray analysis.



**Figure 1** Cu(II) complexes with adenine, guanine and cytosine DNA bases

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## Nitrosylation of Biomimetic [2Fe2S] Clusters

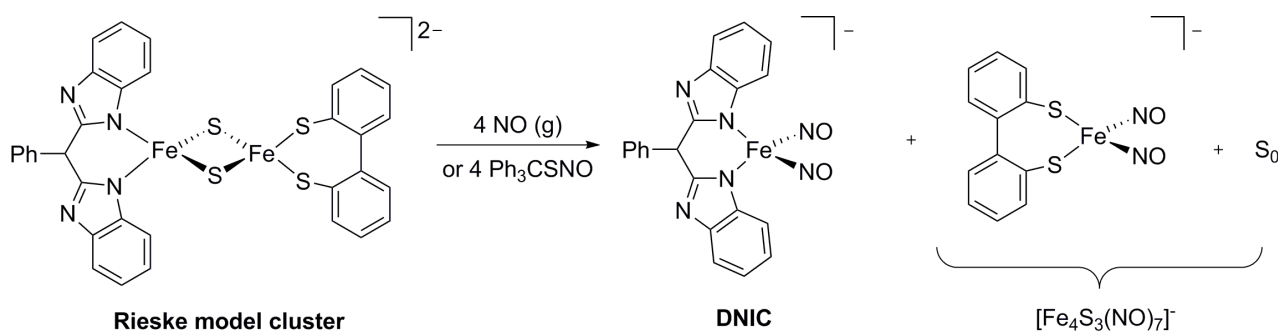
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The Rieske center is a [2Fe2S] cluster first discovered in 1964.<sup>[1]</sup> However, structural and functional synthetic analogues that emulate its heteroleptic coordination sphere have been reported only recently.<sup>[2-4]</sup> After isolating and characterizing the complexes in their diferric, mixed valent and protonated states, we were now interested in exploring their reactivity towards nitric oxide (NO). NO is a neurotransmitter and plays an important role in cardiovascular regulation.<sup>[5]</sup> On the other hand, its release can also lead to cytotoxicity. Studies on biological and synthetic iron-sulfur clusters suggest that NO triggers the degradation of the iron-sulfur core and formation of dinitrosyl iron complexes (DNICs).<sup>[6,7]</sup> The results of studies on the reactivity of the Rieske models and of a first model of the redox-active [2Fe2S] cluster of the integral membrane protein mitoNEET<sup>[8]</sup> which features a {His<sub>3</sub>Cys} ligation will be presented, together with insight into the electronic structure of the DNICs obtained from DFT calculations.



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## ***In vitro* evaluation of a new NO releaser based on trinuclear ruthenium complex: cytotoxicity studies and interaction with target biomolecule**

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In human body, depending on NO (nitric oxide) concentration, a number of different biological functions can be obtained, from immunological response and neurotransmission to relaxation of the blood vessel<sup>1</sup>. Besides that, it has been suggested the NO modulates different cancer-related events<sup>1</sup>. The chemical aspects of nitrosyl trinuclear ruthenium complexes have been explored by our research group showing potential NO release in physiological conditions<sup>2</sup>. In addition, these nitrosyl complexes demonstrated significant cytotoxicity against melanoma cancer cells<sup>2</sup>. The effect of the novel nitrosyl  $[\text{Ru}_3\text{O}(\text{CH}_3\text{COO})_6(4\text{-acpy})_2(\text{NO})]^+$  (1) was evaluated by performing “*in vitro*” cytotoxicity assays with B16F10 and L929 cell lines. Also, complex interaction with HSA (human serum albumin) was addressed, due to its importance as a metallodrug-protein carrier<sup>3</sup>. Different concentrations of the complex were incubated with the cell lines for 24 h, in absence of light. The cell viability was evaluated using the colorimetric method, MTT<sup>2</sup>. Comparing the concentration of 25  $\mu\text{M}$  on both cell lines, the complex was less toxic to healthy cells (fibroblast cell line - L929) than to B16F10 melanoma cells, lowering cancer cells viability to 60%. The interaction of the complex with HSA was assessed by fluorescence quenching experiments and Stern-Volmer analysis<sup>3</sup>. At 32°C, the value of the binding constant ( $K_b$ ) of the complex with HSA was  $3.05 \times 10^2$ , wherein the quenching efficiency ( $K_{sv}$ ) value and the number of sites (N) involved in the interaction were  $4.7 \times 10^3$  and 0.76. These data suggest that HSA is able to transport the complex. In summary, these previous studies suggest that this nitrosyl complex is a potential antitumor agent.

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## Fe<sup>II</sup> complexes covalently grafted on gold electrodes via thioctic based self-assembled monolayers : coordination chemistry and exogenous ligand exchange at the surface

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Cyt-P450 and MMO are Fe containing enzymes which are efficient to catalyse selectively the oxidation of robust C-H bonds using O<sub>2</sub> with 2 e<sup>-</sup> and 2 H<sup>+</sup>. This O<sub>2</sub> activation requires an electron transfer to an Fe(II)-O<sub>2</sub> adduct thereby generating an Fe(III)-peroxo intermediate.<sup>1</sup> The use of O<sub>2</sub> as oxidant implies to control the intake of electrons to avoid the reduction of the oxidizing generated intermediates. Starting from a nonheme Fe(II) complex, it has been possible to directly generate Fe(IV)-oxo and Fe(III)-(hydro)peroxo intermediates with chemical oxidants.<sup>2</sup> Using O<sub>2</sub> and a chemical reductant, the same intermediates have been generated but they readily reacted with the reductant or its side-product thus preventing any catalysis.<sup>3</sup> Deduced from a thorough cyclic voltammetry study, we recently proposed an O<sub>2</sub> activation mechanism by [Fe(TPEN)]<sup>2+</sup> which displayed similarities with the one of P450.<sup>4</sup> In the aim of controlling electron transfer, we have covalently grafted a similar (N<sub>5</sub>)Fe<sup>II</sup> complex on a gold electrode using a SAM procedure. We will present the synthesis and characterisation of these electroactive surfaces and describe the possibility of realizing exogenous ligand exchange at the electrode surface.

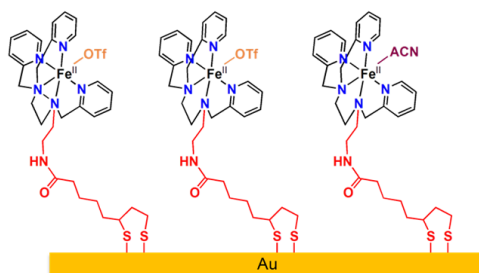


Figure 1 New SAM gold electrode

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## **Dissociation Kinetics of Pb(II) Diazacrowns and Cryptates**

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Ligands selective for Pb<sup>2+</sup>, relative to essential biological cations such as Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup> and Cu<sup>2+</sup>, would be useful for detoxication or development of sensors. Macrocyclic diazacrowns and cryptands have the desired selectivity in terms of thermodynamic stability<sup>1</sup>; however, the complexation kinetics have received little attention. We have measured the dissociation kinetics and stability constants for Pb<sup>2+</sup> in 95% MeOH/H<sub>2</sub>O for a family of related macrocycles, shown in the Figure 1 below.

The dissociation kinetics obeyed the rate law;  $-d\{\text{Pb}(\text{Cryp})\} / dt = k_d + k_H [\text{H}^+]$

The rate constants  $k_d$  and  $k_H$  both decreased in the following order; 2.2 > 2.2MM > 2.2DD > 2.2EAEA > 2.2C<sub>8</sub> >> An2.2.2 > 2.2.2 ~2<sub>D</sub>.2.2.

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### **Figure 1 Structures of diazacrown and cryptand ligands discussed in this study**

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## Characterization of oxidovanadium(IV) complexes with quinolones

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Vanadium compounds exhibit a wide variety of pharmacological properties, like antidiabetic and antitumor<sup>1</sup>. A class of very promising compounds consists of neutral  $V^{IV}O^{2+}$  species with bidentate anionic organic ligands  $L^-$  (named carriers) with composition  $VOL_2$ . The recent efforts have been oriented toward the synthesis of new compounds with high activity and low toxicity.

Quinolonecarboxylic acids or 4-quinolones, commonly termed as quinolones, are a group of synthetic antibacterial agents containing a 4-oxo-1,4-dihydroquinoline skeleton<sup>2</sup>.

The advantages of quinolones as carrier with respect to the other organic ligands are as follows: they are non-toxic, have overcome all the clinical tests for its use in medicine and easily penetrate the body membranes.

In this work the interaction of different quinolones with  $V^{IV}O^{2+}$  ion in aqueous solution was studied using spectroscopic and computational methods.

Moreover the biotransformation in the blood was investigated in order to clarify how these species are transported in the bloodstream; this is an important aspect of the drug metabolism because can affect the form transported to the target organs and, therefore, the efficiency and mechanism of action.

In particular the interaction of quinolone complexes with high and low molecular mass components of the blood serum (transferrin and albumin among the former, lactate and citrate between the latter) was evaluated and the results will be presented.

The subsequent goal of this work is to test these complexes as insulin-mimetic or antitumor species.

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## The synthesis of magnesium-selective ligands for incorporation into fluorescence and NMR-based sensors

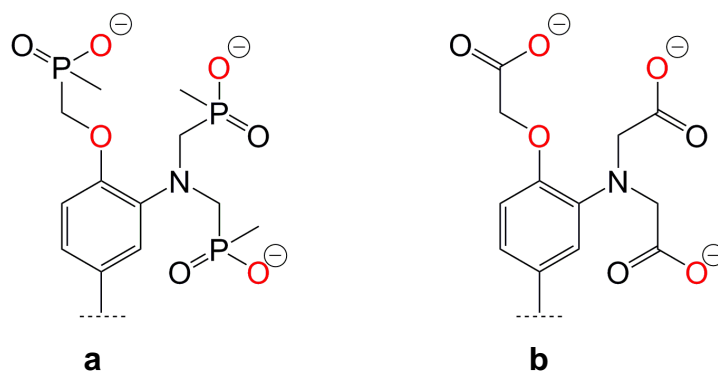
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Compared to other biologically relevant cations such as  $\text{Ca}^{2+}$  and  $\text{Na}^+$ ,  $\text{Mg}^{2+}$  homeostasis *in vivo* is poorly understood.<sup>1</sup> This is somewhat surprising, considering  $\text{Mg}^{2+}$  is the most abundant divalent cation in cells, and the second most abundant cation behind potassium.<sup>1</sup> Current commercially available fluorescent probes for  $\text{Mg}^{2+}$  suffer selectivity problems with other metal ions, particularly  $\text{Ca}^{2+}$ .<sup>2</sup> It is crucial, therefore, that new ligands are developed displaying a higher selectivity for  $\text{Mg}^{2+}$ .

We shall describe our recent work on the synthesis of a range of new, potentially  $\text{Mg}^{2+}$ -selective ligands. The systems are based on pyridines or aminophenols functionalised with carboxylate and / or phosphinate groups for multidentate coordination, as represented in **Fig.1**. The relative merits of P-O (**Fig. 1a**) versus C-O (**Fig. 1b**)<sup>3</sup> coordination in optimising the selectivity for  $\text{Mg}^{2+}$  over  $\text{Ca}^{2+}$  will be considered. Strategies for incorporation of these new metal-binding units into luminescent or magnetic resonance- based probes will be discussed.



**Figure 1**  $\text{Mg}^{2+}$  binding framework containing both phosphinate (**a**) and carboxylate (**b**) binding groups

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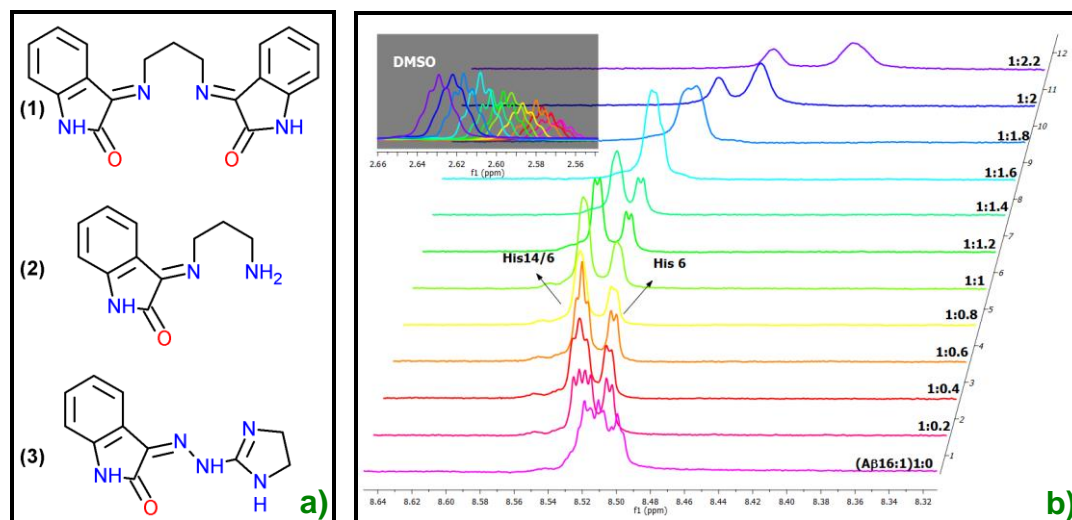
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## Imine Ligands as Complexing Agents of Copper and Zinc in Alzheimer Disease

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Alzheimer disease (AD) is characterized by the formation of  $\beta$ -amyloid ( $A\beta$ ) fibrils as a consequence of APP protein cleavage in the brain. Peptides  $A\beta_{40/42}$  are the remarkable frames of AD by formation of soluble and insoluble aggregates that could prevent synaptic activity and generate elevated fibrillar deposits. AD may be aggravated by means of metal ions overage, such as copper and zinc, by ROS formation and increase aggregation.<sup>1</sup> The imine ligands **1**, **2** and **3** (Fig1.a) were investigated as competitive chelators against the Cu/Zn $A\beta_{16}$  formation. NMR spectra (Fig1.b) and fluorescence analysis showed that those ligands are capable of interacting with  $A\beta_{16}$  peptides, particularly with histidine residues at strategic points, since it has been proved that these are preferential coordination positions for these ions.<sup>1</sup> The corresponding stability constants, at pH 7.4, for species [Cu(**L1**)](ClO<sub>4</sub>)<sub>2</sub> and [Cu(**L2**)](ClO<sub>4</sub>)<sub>2</sub> are (4.4±0.2) and (3.5±0.2), respectively, while for the  $A\beta_{16}$ .(**L3**)<sub>2</sub>, in water, the determined value is (8.8±0.2). Other stability constants for different ligands are under study, in order to correlate its structure and reactivity.



**Fig1.a)** Structures of Ligands **1**, **2** and **3**. **b)** Histidine signal shifting at  $A\beta_{16}$  spectra with ligand **1** increase. Conditions: Phosphate buffer pH 7.4, and DMSO max. 30%.

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## Carbohydrate scaffolds for coordination compounds - biological and synthetic applications.

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Carbohydrates have been widely incorporated into drug design to facilitate targeted delivery and improve characteristics such as solubility.<sup>1,2</sup> Carbohydrates also form one of Nature's diverse and readily accessible chiral pools, and they can be manipulated with relative ease to prepare chiral molecules of interest. Recently, this inherent property has been exploited in constructing chiral catalysts.<sup>3</sup> The process of modifying carbohydrates can be perceived to be challenging. However, the aforementioned characteristics make it worthwhile to explore their potential as scaffolds for both biological therapeutics and asymmetric catalysis.<sup>4,5</sup>

We will present our recent work on preparing carbohydrate scaffolds for use in ligand synthesis and complexation of these ligands with an assortment of transition group metals. Investigations into potential applications will also be described.

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## Water Soluble Silver-N-Heterocyclic Carbene Complexes

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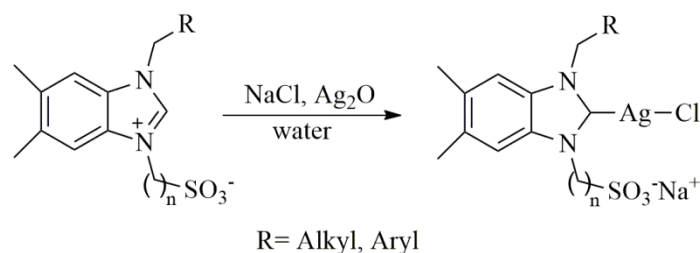
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Metallopharmaceuticals have a potent importance in therapeutic and diagnostic medicine. The much-familiar cisplatin, *cis*-(NH<sub>3</sub>)<sub>2</sub>PtCl<sub>2</sub>, along with its second generation analogue, carboplatin, are still among the most widely used chemotherapeutic agents worldwide today for 35 years. The use of these drugs is limited because of disadvantages, and side effects.<sup>1-2</sup> These negative factors lead to synthesis of new metal complexes can be alternative to cisplatin.<sup>3</sup> Recently, with the contributions of EU, various research networks have been established for synthesis of metal complexes having superior biological activity. These global activities clearly show the importance of metal complexes. In the search for anticancer agents containing metals other than platinum, ruthenium compounds turned out to be the most promising ones.

Aim of this work is synthesis, characterization and investigation of anticancer activities and interaction with biomolecules of water soluble Ag-N-heterocyclic carbene (NHC) complexes which are offering a combination of superior characteristics specified NHCs and silver metal.



**Figure 1** Method for synthesis of water soluble silver N-heterocyclic carbene complexes

This work was financially supported by COST 2515-CM1105 action TÜBİTAK [114Z036].

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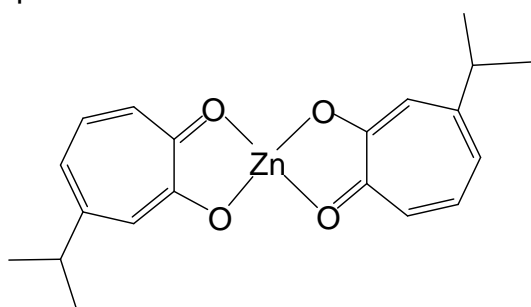
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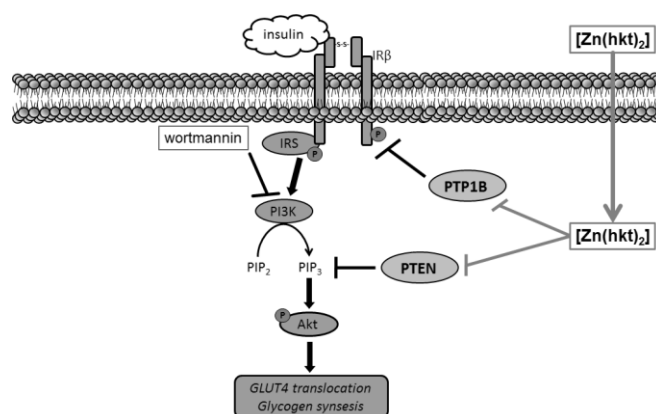
## Bis(hinokitiolato)zinc complex ( $[Zn(hkt)_2]$ ) affects the insulin signaling pathway in an insulin-independent manner

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Diabetes mellitus (DM) is a chronic disease characterized by hyperglycemia. Zinc (Zn) has been shown to exhibit the insulin-like effects. Since many Zn(II) complexes have been developed to enhance the insulin-like activity and increase the exposure of Zn in the animal body, these complexes are recognized as one of the new candidates with action mechanism different from existing anti-DM drugs. However, the molecular mechanism by which Zn(II) complexes exert an anti-DM effect is unknown. Therefore, we evaluated the activity of Zn(II) complexes, especially related to the protein phosphorylation of insulin signaling pathway components. We focused on the insulin-like effects of the bis(hinokitiolato)zinc(II) complex,  $[Zn(hkt)_2]$  (Figure 1), using 3T3-L1 adipocytes<sup>1</sup>.  $[Zn(hkt)_2]$  was taken up into cells and induced Akt phosphorylation in a time-dependent manner. Additionally, it showed inhibitory activities against PTP1B and PTEN, which are major negative regulators of insulin signaling. Actually, it enhanced the phosphorylation of IRS (insulin receptor substrate)-1 in combination with insulin. Molecular docking simulation data suggested that  $[Zn(hkt)_2]$  binds directly to these enzymes. We conclude that  $[Zn(hkt)_2]$  has anti-DM effects via the activation of the insulin signaling pathway and the promotion of insulin function (Figure 2), and  $[Zn(hkt)_2]$  may be the new candidate for improved DM treatments.



**Figure 1** Estimated structure of  $[Zn(hkt)_2]$



**Figure 2** Proposed effects of  $[Zn(hkt)_2]$  in cells

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## Highly efficient hydrosilylation reactions catalysed by iridium (III) metallacycles.

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The catalytic reduction of C-C and C-heteroatoms insaturations is one of the most used chemical reaction in synthetic organic chemistry.<sup>1a</sup> The hydrosilylation reaction which can be operated in mild conditions, at atmospheric pressure, is an interesting alternative to hydrogenation and silanes have a modular reactivity.<sup>1b</sup> Through a collaboration between our Lille and Strasbourg laboratories, Ir(III) metallacycles<sup>2</sup> have been shown to catalyze the hydrosilylation of a large substrate panel like ketimines, aldimines,<sup>3a</sup> aldehydes, ketones, esters and amides<sup>3b</sup> offering after hydrolysis the related products in high yields. These reactions could be performed rapidly and with low catalyst loadings, in mild and green conditions (e.g. silane, solvent and temperature). Our recent results<sup>3</sup> will be here highlighted with a focus on the efficient and selective reductions of amides into amines and of enamides into amides. The reaction mechanisms will be detailed on the basis of NMR and HRMS experiments as well as on the isolation of key intermediates.

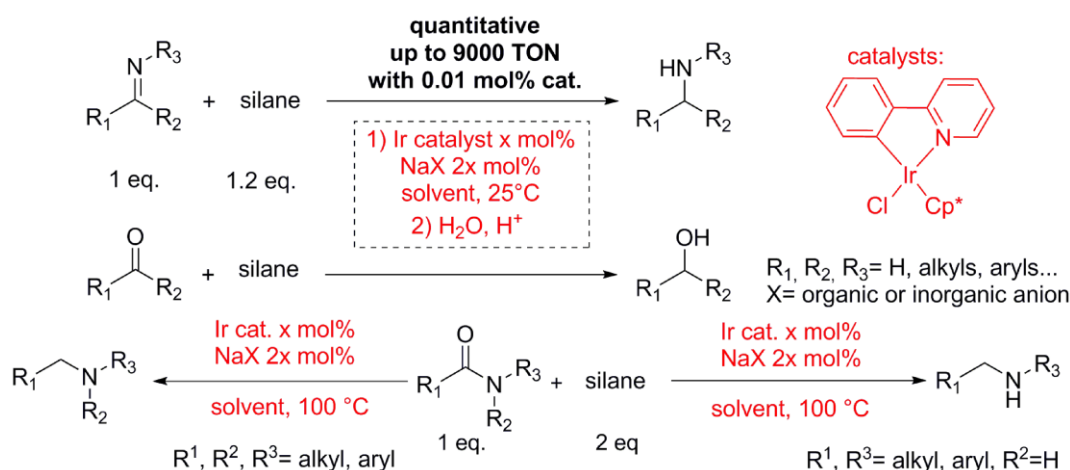


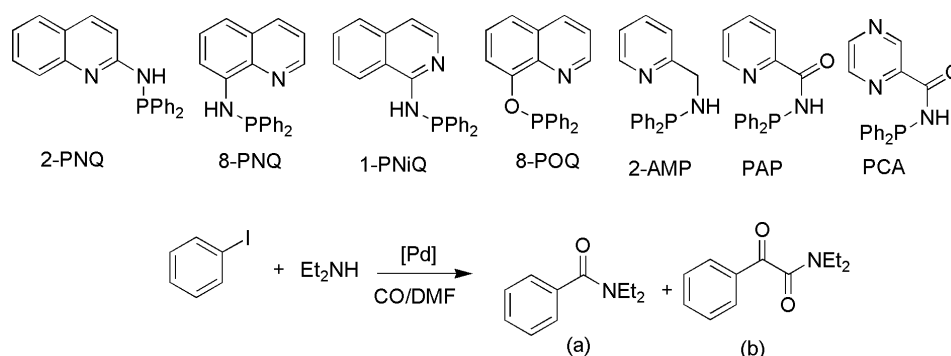
Figure 1. Hydrosilylation reactions catalysed by Ir(III) metallacycles.

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Arylhalide aminocarbonylation using Pd(II)/P<sup>A</sup>N systemsP. Aguirre<sup>\*a</sup>, B. Aranda, G. Valdebenito.

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In this work we report the aminocarbonylation of arylhalides using Pd(II) systems containing P<sup>A</sup>N ligands. This reaction is widely used in fine chemistry to functionalize steroidal skeletons, among other synthetic applications<sup>1</sup>. These P<sup>A</sup>N ligands, based from quinoline and pyridine, were synthesized using techniques described in literature<sup>2,3</sup>. For this work, iodobenzene was selected as benchmark substrate for its simplicity<sup>1,4</sup>. Overall, *in situ* systems containing aminoquinoline-based ligands achieve higher activities compared to PPh<sub>3</sub> (a ligand commonly used in this kind of reaction<sup>1,4</sup>) and pyridine-based P<sup>A</sup>N ligands, and in all cases with a chemoselectivity towards the formation of ketocarboxamide (b).



**Figure 1** P<sup>A</sup>N ligands (above) used in the aminocarbonylation of iodobenzene (below)

Run	System	Time (h)	Conv. (%)	Selectivity		Run	System	Time (h)	Conv. (%)	Selectivity	
				a	b					a	b
1	PPh <sub>3</sub>	4	96	29	71	10	Pd + 2AMP	3	99	25	75
2	Pd + 2-PNQ	2	97	14	86	11	Pd + PAP	3	98	40	60
3	Pd + 8-PNQ	2	98	16	84	12	Pd + PCA	3	96	39	61
4	Pd + 1-PNiQ	3	93	14	86	13	Pd(2-AMP)Cl <sub>2</sub>	4	97	28	72
5	Pd + 8-POQ	3	96	25	75	14	Pd(PAP)Cl <sub>2</sub>	4	97	32	68
6	Pd(2-PNQ)Cl <sub>2</sub>	2	93	34	66	15	Pd(PCA)Cl <sub>2</sub>	3	99	28	72
7	Pd(8-PNQ)Cl <sub>2</sub>	3	99	40	60						
8	Pd(1-PNiQ)Cl <sub>2</sub>	2	94	14	86						
9	Pd(8-POQ)Cl <sub>2</sub>	2	96	34	66						

Pd: Pd(OAc)<sub>2</sub> (0.075mmol), ligand 0.075mmol, Iodobenzene 7.5mmol, Et<sub>2</sub>NH 22.5mmol, Et<sub>3</sub>N 1.5mL, DMF 10mL, CO 30bar.

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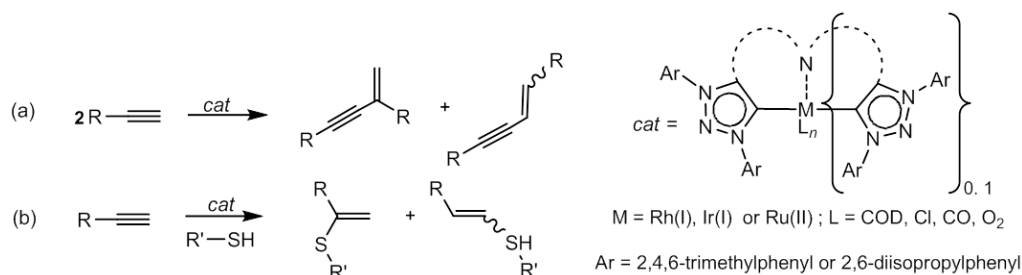
## Bi- and tridentate N-donor functionalized mesoionic carbene ligands for catalytic application in selective alkyne functionalizations

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The products of alkyne dimerization and hydrothiolation (enynes and vinyl sulfides, respectively) have found various applications, especially as biologically active compounds. However, chemo-, regio-, and stereoselectivity still remain a major challenge during the synthesis of these compounds, with *E*- and/or *Z*-enyne/alkene formation favoured over *gem*-enyne/alkene synthesis.



**Scheme 1** Alkyne (a) homo-dimerization and (b) hydrothiolation promoted by bi- and tridentate N-donor functionalized MICs

1,2,3-triazol-5-ylidene complexes have been investigated to a lesser extent than other N-heterocyclic carbenes (NHCs), particularly due to their more recent discovery<sup>1</sup> but have shown unique catalytic possibilities due to their mesoionic nature and potential for ligand cooperativity.<sup>2</sup> Herein we disclose a series of bidentate neutral and/or cationic N-donor functionalised triazol-5-ylidene complexes, and tridentate bis(1,2,3-triazol-5-ylidene)amido pincer<sup>3</sup> complexes of Rh(I) / Ir(I) as highly selective alkyne dimerization and hydrothiolation catalysts.

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## TWO COMPETING PRECATALYSTS IN IRON-CATALYZED CROSS-COUPLING REACTIONS.

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The use of palladium dominates the field of metal-catalyzed cross-coupling, but its inherent cost can make synthesis costly. While the use of catalysis is essential in the drive towards greener chemistry the catalysts themselves should also be both environmentally and biologically benign. For these reasons simple iron salts have recently gained a lot of interest.<sup>1</sup> However their chemistry is less well explored, and there remain many questions regarding the exact functioning mechanism(s) in the catalytic cycles.<sup>2-3</sup>

This work explores the mechanism operating in iron-catalyzed Kumada couplings; the iron mediated reaction between halogenated hydrocarbons and Grignard reagents.<sup>4</sup> Stoichiometric reaction of Fe(acac)<sub>3</sub> with Grignard reagents generates two separate iron species including a novel intermetallic complex (Figure 1.) A variety of characterization methods are employed including; <sup>1</sup>H NMR and IR spectroscopy, X-ray crystallography and magnetic susceptibility measurements. Furthermore, the catalytic competence of these precatalysts has been explored in a range of cross coupling-reactions.

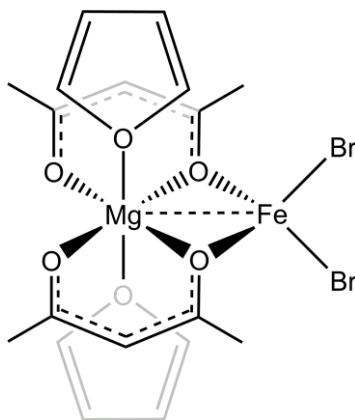


Figure 1. Intermetallic precatalyst: (THF)<sub>2</sub>Mg(μ-acac)<sub>2</sub>FeBr<sub>2</sub>.

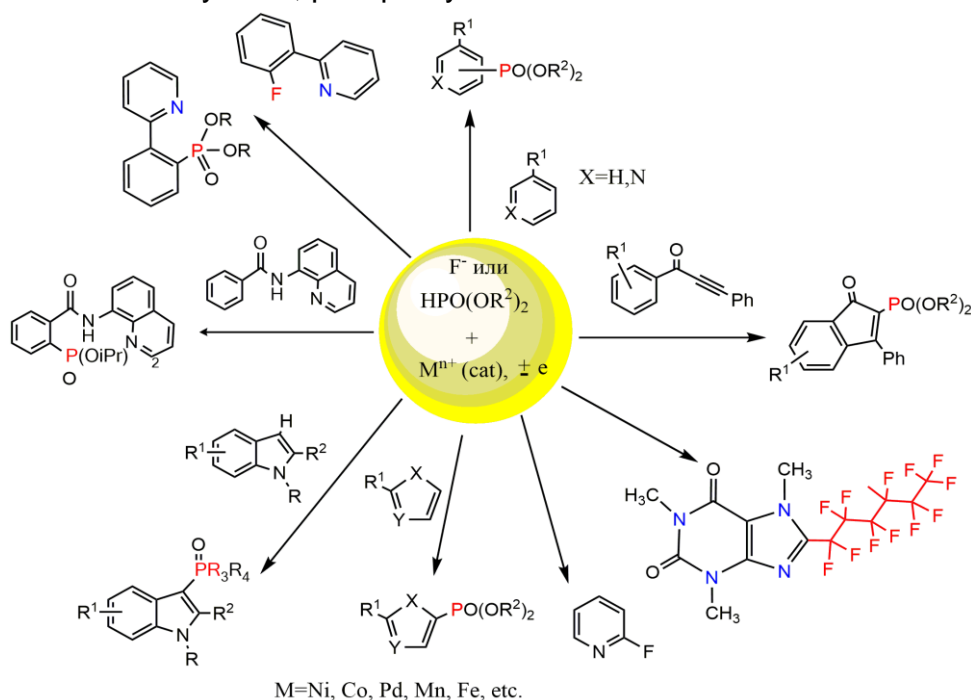
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# METAL CATALYSED ELECTROCHEMICALLY ASSISTED PHOSPHONATION AND FLUORINATION (FLUOROALKYLATION) OF AROMATIC C-H BONDS

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New methods that allow for the incorporation of fluorine or phosphorous synthons into a molecule at late synthesis stage are desperately needed. Metal-catalyzed coupling procedures would greatly facilitate the construction of fluoro- or phosphorous organic molecules; however they have been slow to develop. Achieving site selectivity in C–H functionalization reactions is a significant challenge. We propose a one-step catalytic method for introduction of fluorine- and phosphorus-containing functional groups to different compounds with C(sp<sup>2</sup>)-H bonds assisted by electrochemical reduction or oxidation of metal complexes under mild conditions. The catalytically active form of metal is generated and regenerated on the electrode without specially added reducing agents (or oxidants). We aimed to develop a mild method for the functionalization of simple arenes and more complicated substrates (for example, caffeine) and to utilize relatively inexpensive perfluoroalkyl iodides as RF precursors and dialkylphosphites as P-precursors and rarely used accessible, reasonable and nontoxic iron and silver compounds as catalysts. Possibilities and advantages of directed metal-induced aromatic C-H-fluoroalkylation, phosphorylations etc. are demonstrated.



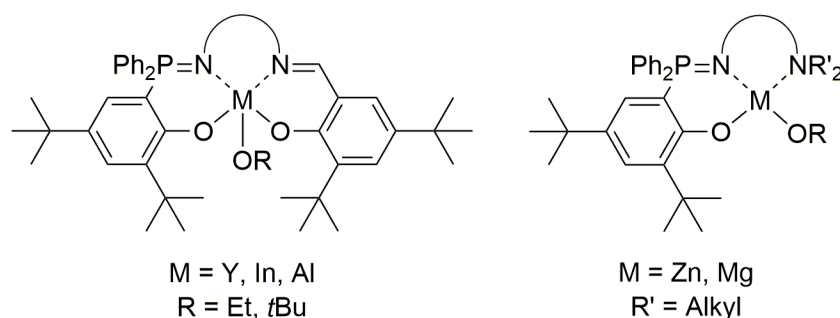
Acknowledgements  
 - This work was supported by Russian Science Foundation (grant № 14-23-00016).



## Hybrid phosphasalen/salen initiators for the ring-opening polymerisation of *rac*-lactide

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Poly(lactide) (PLA) is a bio-derived aliphatic polyester made from lactic acid and has suitable properties as a 'green' replacement for polyolefins, whilst also being compostable/degradable. The ring-opening polymerisation (ROP) can be initiated by Lewis acidic metal alkoxides, which control features such as the rate, molecular weight and stereochemistry of the polymer chain. Stereoselective initiators are of particular interest as the tacticity of the resulting PLA allows tuning of chemical-physical properties such as melting temperature/degradation rate. This work applies new types of phosphasalen ligands and more industrially viable metals as initiators for *rac*-lactide ROP.



**Figure 1** General structure of the phosphasalen ligand systems.

This presentation will describe the synthesis and characterisation of novel half-phosphasalen and mixed phosphasalen/salen ligands and the coordination chemistry with Zn(II), Mg(II), Group 13 and Group 3 metals (Figure 1). Polymerisation kinetics, multinuclear NMR studies and structure-activity relationships have been conducted in order to allow comparisons with known phosphasalen and salen initiators. The hybrid nature of the mixed phosphasalen/salen ligands allows easier access to metal centres which have been previously hard to synthesise within the phosphasalen or salen motifs. As a result, this new ligand class offers exciting opportunities, for lactide, other cyclic lactones and carbon dioxide/epoxide co-polymerisation, investigated here for the first time.

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# Catalytic dehydrocoupling of phosphine-boranes using low coordinate Fe(II) complexes

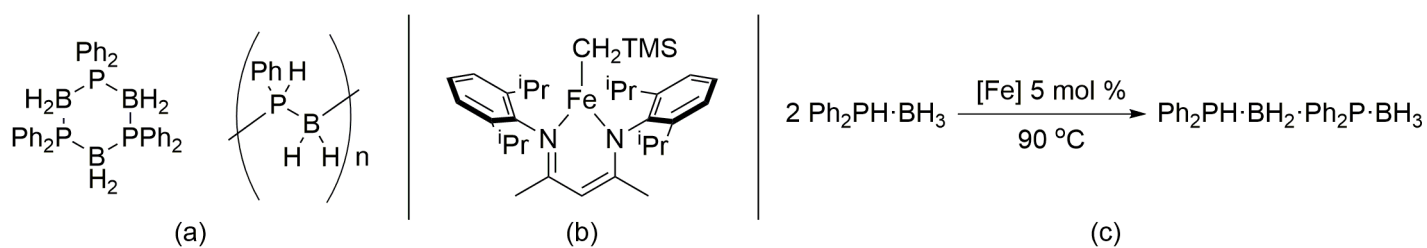
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Main group polymers are of interest as functional materials, due to their more unusual properties when compared to traditional polymers, such as acting as surface modifiers.<sup>1</sup> Manners *et al.* have previously shown that dehydrocoupling (DHC) of phosphine-boranes (PBs) is possible with Fe, Rh and Ru catalysts.<sup>2,3</sup> It has also been shown that with select substrates it is possible to form rings or polymeric chains (**fig. 1a**).<sup>1,4</sup>

Recent work by our group has shown that DHC between phosphines is possible using a cheap and easily synthesised low coordinate Fe(II) complex (**fig. 1b**).<sup>5</sup> Due to the success of this catalyst system we have investigated its activity in the DHC of PBs.

Preliminary work has shown that DHC with a variety of three coordinate Fe(II)  $\beta$ -diketimate complexes is possible. Optimisation of the catalyst has been undertaken along with varying the structure of the PB substrate. Preliminary mechanistic studies are underway and these results will also be presented.



**Figure 1** a) Possible DHC products. b) The catalyst used in DHC of phosphines. c) DHC reaction using the catalyst shown in **fig. 1b** (C<sub>6</sub>D<sub>6</sub>, 90 °C, 72 h, 100% conversion).

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# Synthesis of New PC(sp<sup>3</sup>)P iridium complexes possessing various stabilizing OR arms, for alkane transfer dehydrogenation

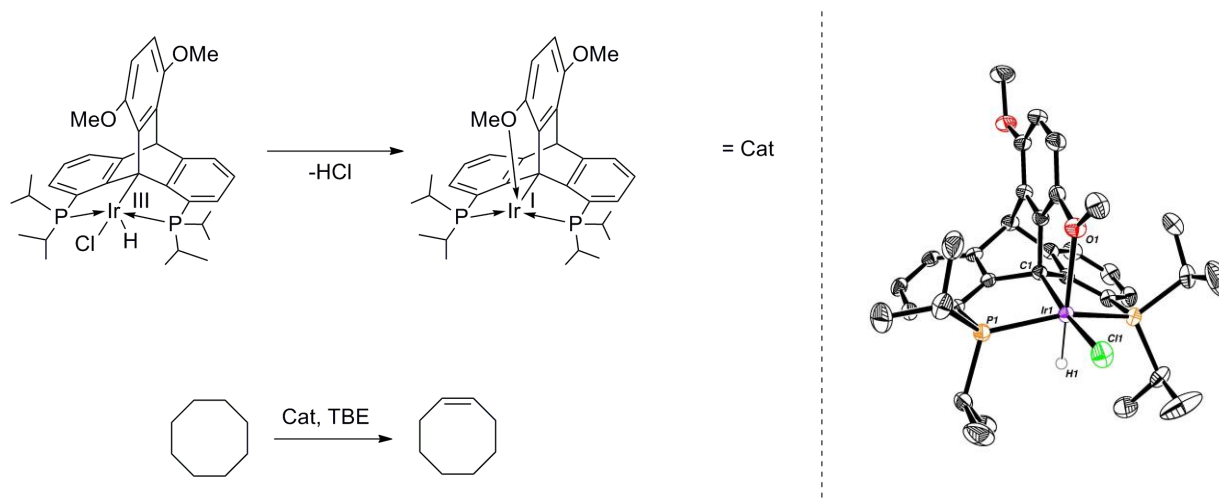
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Activation and functionalization of nonreactive C-H bonds is one of the major goals in homogeneous catalysis because conversion of cheap components of natural gas and petroleum into more versatile products is of great academic and industrial importance. The general term of "catalytic activation of nonreactive C-H bonds" comprehends several kinds of reactions that proceed via different mechanisms depending on the transition metal catalyst involved. *Inter alia*, low valent complexes of late transition metals (e.g. Ru, Rh, Ir, Pt, etc.) are known to activate C-H bonds via the oxidative addition pathway, giving hope to develop selective and efficient functionalization pathways. The simplest way is via alkane dehydrogenation; with or without the aid of a hydrogen acceptor (e.g. sacrificial alkene such as *tert*-butylethylene, norbornene). The major development in the field of homogeneous-transfer-dehydrogenation reactions was achieved using pincer complexes, highly thermally stable catalysts.

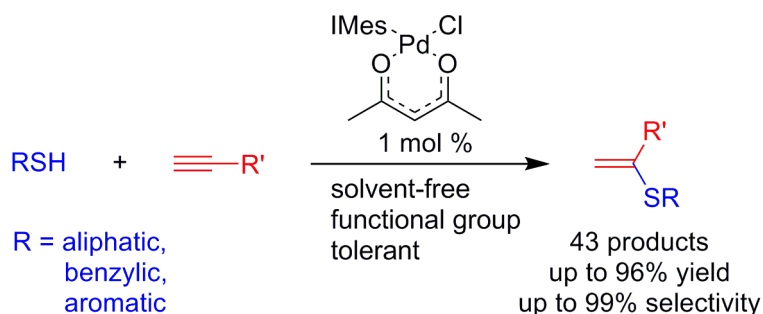
Our study focuses on the triptycene based-PC(sp<sup>3</sup>)P pincer complexes of iridium possessing alkoxy side-arms (e.g. R = OMe, O<sup>i</sup>Pr, MOM, etc.) as hemilabile stabilizing ligands (figure 1). Their synthesis and catalytic properties will be discussed.



**Figure 1** Ir-catalysts containing OR arms for alkane transfer dehydrogenation (left), X-ray structure of OMe-Ir-complex (right).

## Pd-NHC as Universal Catalytic System for Alkynes Hydrothiolation

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Branched Markovnikov-type vinyl sulfides can be synthesized by selective catalytic hydrothiolation of alkynes. For that process different metal-based ([Ni], [Pd], [Rh], [Zr], [Sm], [La], [Th], [In]) catalytic systems were developed.<sup>1</sup> Despite such catalyst variety, most of the described systems are extremely sensitive to the nature of thiol and require complicate experimental technique.

We have investigated Pd-NHC system in the hydrothiolation process, which exhibited high performance with all of the studied thiols (aromatic, benzylic and aliphatic).<sup>2</sup> All of the vinyl sulfides, even “unreactive” tertiary aliphatic, were obtained selectively in good to excellent yields. The catalyst demonstrated high air and moisture stability and operated in a wide (35 – 100 °C) temperature range. That is providing an excellent opportunity to render the transformation with various reagents.

The results of detailed mechanistic studies will be presented and discussed.

This work was supported by Russian Science Foundation (RSF grant 14-50-00126).

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# The Kinetic Stabilisation of Main Group and Transition Metal Complexes with a Super Bulky Diiminopyridine

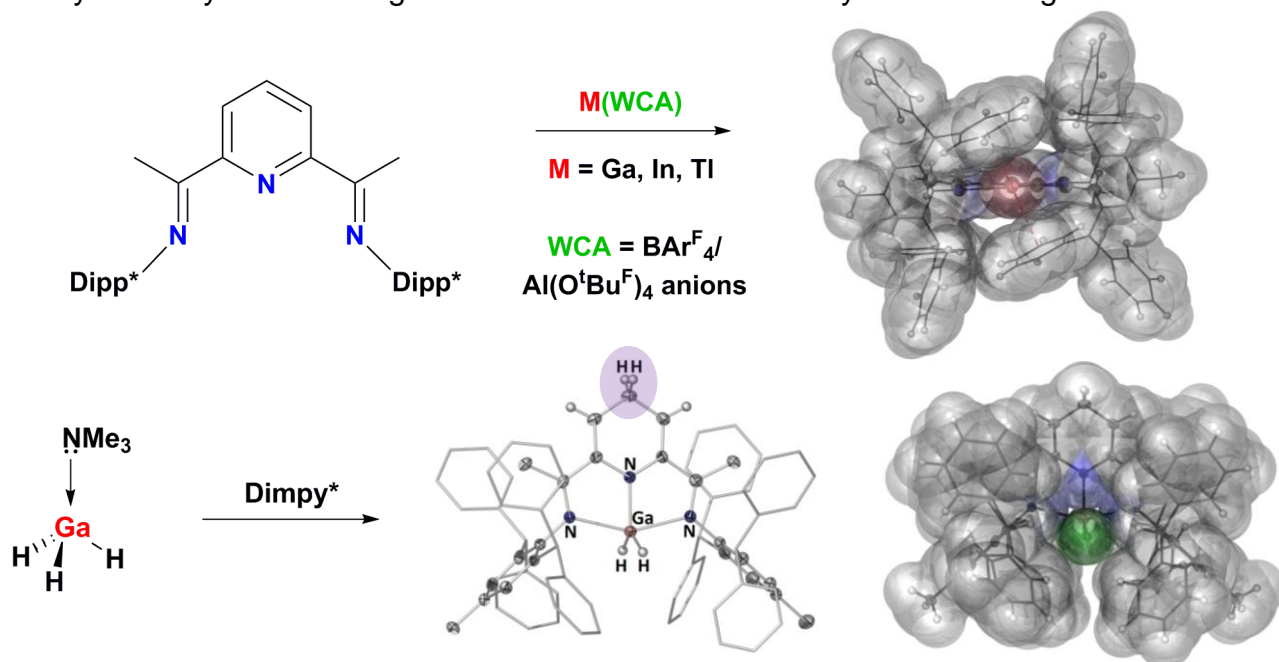
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Diiminopyridines are neutral, tridentate  $N,N',N''$ -donors that have been widely used in main group and transition metal chemistry. This class of ligand offers the advantages of thermodynamic stabilisation through tridentate chelation and kinetic stabilisation through highly modifiable imine substituents. They have been recently shown to stabilise otherwise highly reactive species, including low and even zero oxidation state group 13 and 14 complexes.<sup>1</sup> Thus, sterically bulky diiminopyridines are promising frameworks for the kinetic stabilisation of low oxidation state main group complexes, main group hydride complexes, and first row transition metal complexes as potential redox active catalysts.

Herein, a super bulky diiminopyridine (Dimpy\*), with 2,6-dibenzhydryl-4-methylphenyl (Dipp\*) substituents, has been developed and its coordination chemistry with group 13 halides, alkyls and hydrides explored; as well its coordination chemistry with first row transition metals. Additionally, the kinetic stabilisation of low valent group 13 and 14 complexes with weakly coordinating anions (WCAs) has been explored, with future investigation into its reactivity with low basicity hydride sources as a possible route to heavy metal hydrides through oxidative addition or halide-hydride exchange.



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## Dinuclear Rhodium(I) Complexes of Two-In-One Pincer Ligands

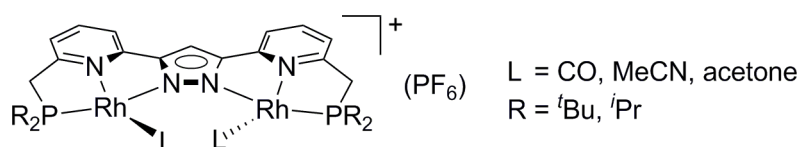
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Pincer ligands and the corresponding metal complexes are well known and widely used in catalysis. The complexes have been shown to enable various substrate activations as well as catalytic reactions.<sup>1</sup> The high stability and a variable ligand design of these complexes are responsible for the great academic and industrial interest. In addition, metal ligand cooperativity (MLC) was found for some pyridine based pincer ligands with a CH<sub>2</sub> spacer connecting the donor sites<sup>2</sup> which enables unusual substrate activations via bifunctional catalysis.<sup>3</sup>

We have now combined two pincer-type subunits in a binucleating ligand scaffold having two {PNN} pockets in close proximity.<sup>4</sup> These two-in-one pincer ligands are expected to support, in beneficial synergism, both MLC and metal-metal cooperativity (MMC). An iron(II) complex of the two-in-one pincer ligand indeed shows interesting spin state switching in solution through reversible ligand exchange processes.<sup>4</sup>

Here we present a first modification of the ligand system and rhodium complexes of the two-in-one pincer ligands HL<sup>*t*Bu</sup> and HL<sup>*i*Pr</sup> (Figure 1).



**Figure 1** Some dinuclear Rh(I) complexes of pyrazolate-based two-in-one pincer ligands.

Several rhodium complexes have been isolated and fully characterized, their dynamics and ligand exchange have been investigated, and first reactivity studies have been performed. Some key results will be presented.

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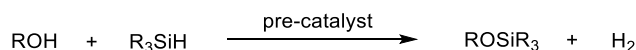
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**CATALYSIS PROMOTED BY A LEWIS PAIR IRIDACYCLE INTERMEDIATE:  
A COMBINED STUDY TOWARD MECHANISM UNDERSTANDING**

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Many recent reports highlighted the catalytic potential of PhPy-IrCp\*Cl metallacycles (PhPy =  $\kappa$ C,  $\kappa$ N-Phenylenepyridine, Cp\* = Pentamethylcyclopentadienyl) toward a wide range of transformations including hydroamination of alkynes<sup>1</sup>, hydrosilation of imines<sup>2</sup>, and water oxidation catalysis<sup>3</sup>, thus opening promising perspectives for such simple organometallic complexes. In order to gain insight into the complex mechanism operating for the tandem hydroamination/hydrosilation of alkynes published by our group<sup>1</sup>, a systematic study was undertaken aiming at “husking” each key catalytic step involved in the mechanism. In this communication, we describe a combined experiment/theory methodology which was conducted in the aim of rationalizing the catalytic performance of an ionic iridacycle (isolated) in the dehydrocoupling of alcohols and silanes (equation below).



An unprecedented iridium-silane adduct intermediate has been characterized, which according to its chemical reactivity and DFT-D (dispersion-corrected density functional theory) calculations can be formulated as the first nonacoordinate Ir<sup>III</sup> complex displaying an ionic Lewis pair structure.

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# Characterisation and Reactivity of $\sigma$ -Complexes of Copper(I) with Zinc and Magnesium Hydrides

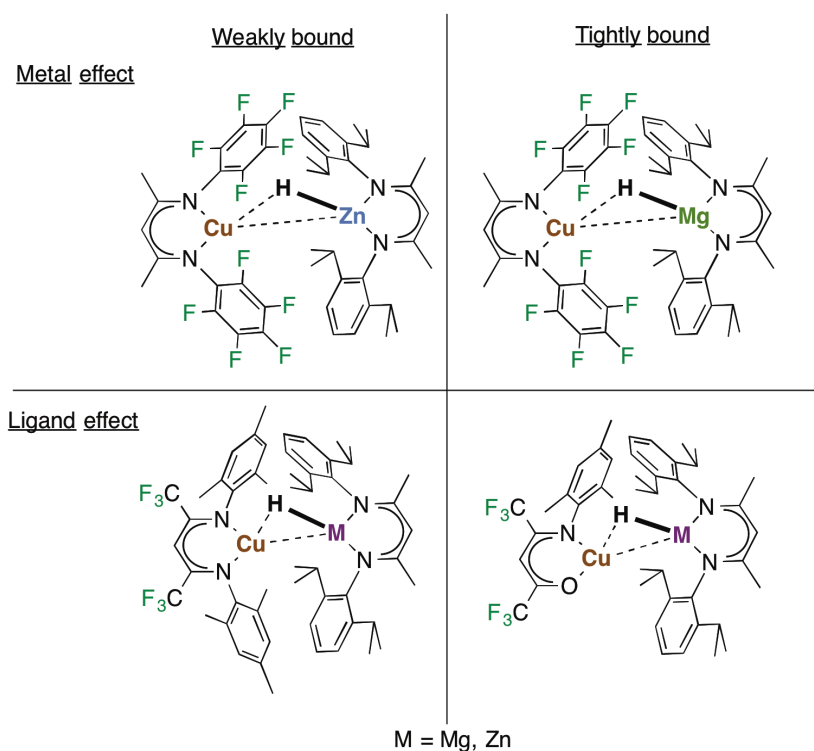
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We recently documented the synthesis of a series of  $\sigma$ -complexes of copper in which M–H (M = Al, Zn) and E–H (E = B)  $\sigma$ -bonds reversibly coordinate to a copper(I) fragment.<sup>1,2</sup> Here we report a new series of copper(I) arene complexes containing fluorinated ligands along with a phosphine stabilised copper(I) complex.<sup>3</sup> In solution, displacement of the arene or the phosphine with molecular magnesium and zinc hydrides has allowed the generation of new heterobimetallic complexes of copper(I), including the first examples that incorporate a Mg–H bond. In many cases, our data are consistent with tightly bound molecular hydride species with no evidence for ligand dissociation in solution. We expect these species to serve as useful starting materials to explore new reactivity.



**Figure 1** The effect of changing metal and ligand on the formation of  $\sigma$ - and molecular hydride complexes of copper(I)

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# Coupling Reactivity of Carbon Dioxide and Acetylene Mediated by Iron Phosphine Complexes

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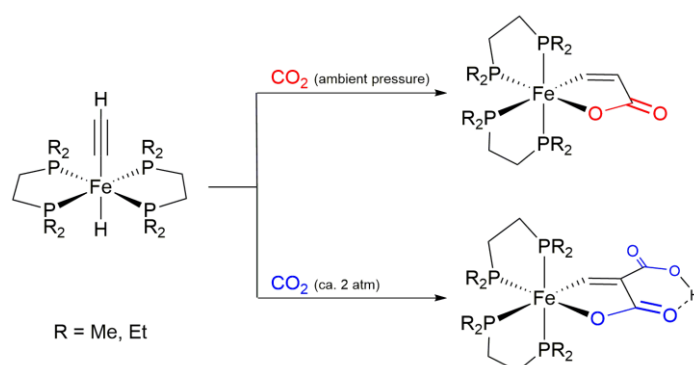
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The utilisation of carbon dioxide as a chemical feedstock in the synthesis of fine chemicals presents an attractive approach to emissions mitigation. However, due to the high thermodynamic stability of carbon dioxide, there are currently few viable industrial processes capable of utilising the compound on a meaningful scale.<sup>1</sup> Use of energetic unsaturated organic substrates such as alkynes is one approach to facilitate reactivity, providing a synthetic route to products such as 2-pyrones<sup>2</sup> and  $\alpha,\beta$ -unsaturated carboxylic acid derivatives.<sup>3</sup>

In this work, the reaction of carbon dioxide toward acetylene mediated by the iron phosphine complexes  $[\text{Fe}(\text{dmpe})_2]$  and  $[\text{Fe}(\text{depe})_2]$  (dmpe = 1,2-bis(dimethylphosphino)ethane, depe = 1,2-bis(diethylphosphino)ethane) is found to exhibit differing synthetic outcomes based upon  $\text{CO}_2$  substrate pressures (Figure 1). Herein we present efforts to gain mechanistic insight into these outcomes in order to better understand patterns of reactivity.



**Figure 1** Reaction of iron hydrido acetylide complexes toward carbon dioxide at varied substrate pressures resulting in differing synthetic outcomes

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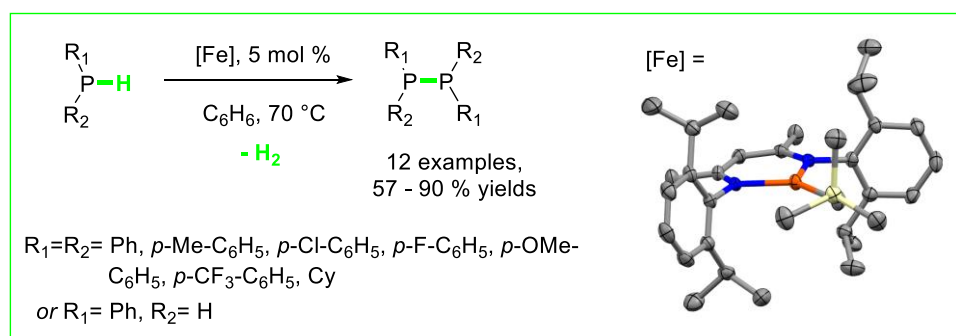
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# Facile, Catalytic Dehydrocoupling of Phosphines Using $\beta$ -Diketiminate Iron(II) Complexes

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Catalytic dehydrocoupling is an attractive and a well developed methodology for the synthesis of bonds between main group elements, with  $H_2$  being produced as the only by-product.<sup>1</sup> In particular the synthesis of P–P bonds *via* dehydrocoupling has previously been achieved using late transition metal catalysts.<sup>2-5</sup>

Iron catalysis is an ever expanding field due to the high abundance and low cost of the metal. In reactions with three coordinate iron  $\beta$ -diketiminate complexes we have shown high catalytic dehydrocoupling activity. This has been achieved under relatively mild conditions without the need for any additives (Scheme 1).



**Scheme 1** Dehydrocoupling of phosphines using a three coordinate iron  $\beta$ -diketiminate pre-catalyst.

To the best of our knowledge, this is the first example of catalytic dehydrocoupling of primary and secondary phosphines with an iron catalyst.<sup>6</sup> The synthetic catalytic methodology will be presented along with preliminary mechanistic details, which demonstrate that the reaction is most likely radical mediated.

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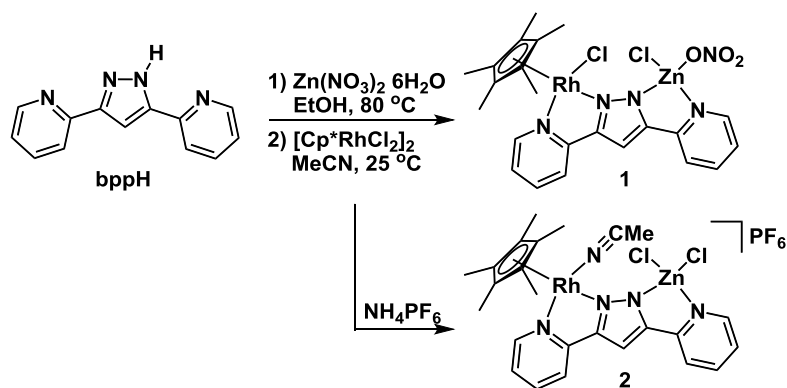
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# Synthesis of Rh-Zn heterobimetallic complexes and their catalytic activity for reduction reactions used by formic acid as a reductant

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Reduction is one of the most fundamentally important reactions in organic synthesis. H<sub>2</sub> and organometallic reagents such as NaBH<sub>4</sub> and LiAlH<sub>4</sub> are generally used for the reactions. However, these reductants have some problems. H<sub>2</sub> is an explosive gas, and needs large costs to store and transport. Organometallic reagents can be only carried out the equivalent reactions and wastes derived from the reductant are produced after the reaction. Therefore, safety and low environmental load reductant are desired. Formic acid is known as a reductant, and uses in mild conditions. In the transition metal complex-catalyzed reduction of organic compounds using formic acid, some carbonyl compounds such as aldehydes and ketones, imines, and NAD<sup>+</sup> can be reduced, however, reduction of carbonic acid derivatives such as esters and amides are still not achieved. To develop the high active catalyst for the formic acid using reduction reactions, we designed the Lewis acid-introduced heterobimetallic complex. Lewis acid can activate the carbonyl compounds, therefore such a heterobimetallic complex may be able to reduce the substrates which are difficult to reduce so far. In this study, we report the synthesis of new heterobimetallic complexes containing two metals, rhodium which can generate the hydride from formic acid and zinc which works as a Lewis acid, and the catalytic activity of the complexes for the reduction of carbonyl compounds using formic acid as a reductant.

New heterobimetallic complexes containing Rh and Zn bridged by 3,5-bis(2-pyridyl)pyrazolate (bpp<sup>-</sup>) were synthesized by the reaction shown in Scheme 1. **1** work as a catalyst for HCO<sub>2</sub>H/HCO<sub>2</sub>NH<sub>4</sub>-used reduction of ketones and imines in MeOH. Other results will be also reported.



**Scheme 1.** Synthesis of complexes **1** and **2**.

## Picolinohydrazides: a new class of ligands for the Zn-catalyzed hydrosilylation of ketones

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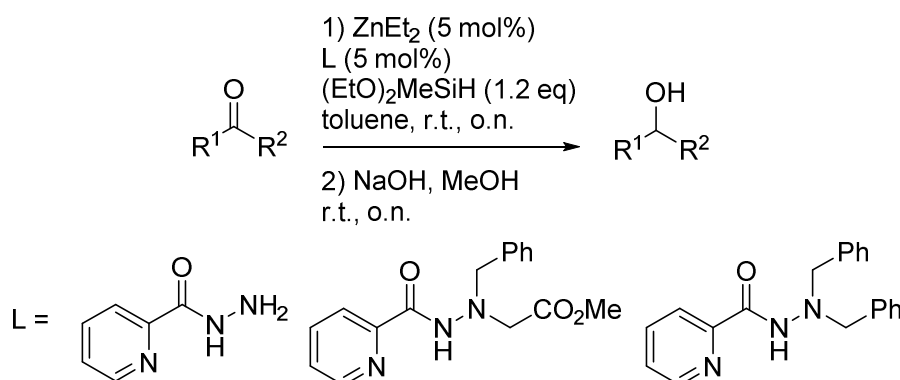
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The catalytic hydrosilylation of ketones is an important method for the synthesis of secondary alcohols. In a general concern to substitute expensive metals by low-toxic and cheap biorelevant metals, several research groups have demonstrated the abilities of zinc catalysts in this hydrosilylation reaction.<sup>1</sup> Frequently and suitably stabilized by bidentate ligands featuring amine or imine functional groups, these zinc complexes have shown excellent activities in the reduction of various aldehydes and ketones. *Herein we present the use of simple picolinohydrazides as a new class of ligands for the Zn-catalyzed hydrosilylation of carbonyl compounds* (Scheme 1).



**Scheme 1** Hydrosilylation of ketones catalyzed by Zn-picolinohydrazide complexes in the presence of diethoxymethylsilane.

The preparation of some representatives of this new class of ligands will be presented starting from picolinic acid (or esters) and modified hydrazines, as well as their evaluation in the hydrosilylation of acetophenone as the model substrate. The most efficient tested ligands were then used to explore the scope and limitations of this reaction on various ketones.<sup>2</sup>

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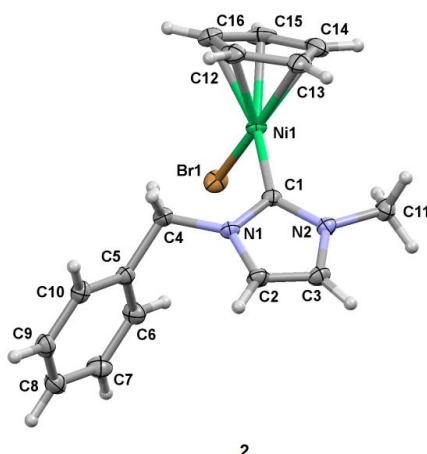
2 Manuscript in preparation

## Facile Suzuki-Miyaura coupling of activated aryl halides using new CpNiBr(NHC) complexes

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In homogeneous catalysis, Ni-NHCs can be employed in a number of carbon-carbon and carbon-heteroatom organic transformations to yield an array of valuable molecules which could previously be obtained only *via* expensive Ru and Pd catalysts [1,2]. The Suzuki-Miyaura reaction is one of the most studied catalytic reactions due to its tolerance of functional groups and low toxicity of its by-products [3]. [CpNiX(NHC)] (X = halide) and related systems have shown equal or improved catalytic activity in C-C coupling reactions compared to the traditional Pd catalysts [1,2]. However, the bromo complexes in the series of [CpNiBr(NHC)] compounds reported are limited when compared to their chloro- and iodo-analogues [1]. New Ni(II)-NHC complexes, [CpNiBr(NHC)], were synthesized containing symmetric or asymmetric N-substituents (for example Figure 1). The series of [CpNiBr(NHC)] exhibited catalytic activity in the Suzuki-Miyaura coupling of activated aryl halides with phenylboronic acid to give the respective biphenyl and biphenyl-containing products. In general, the more electron-donating NHC-bearing Ni complexes showed higher activity with aryl halides bearing electron-withdrawing functionalities, including carboxaldehyde moieties.



**Figure 1** Crystal structure of asymmetric [CpNiBr(NHC)] complex

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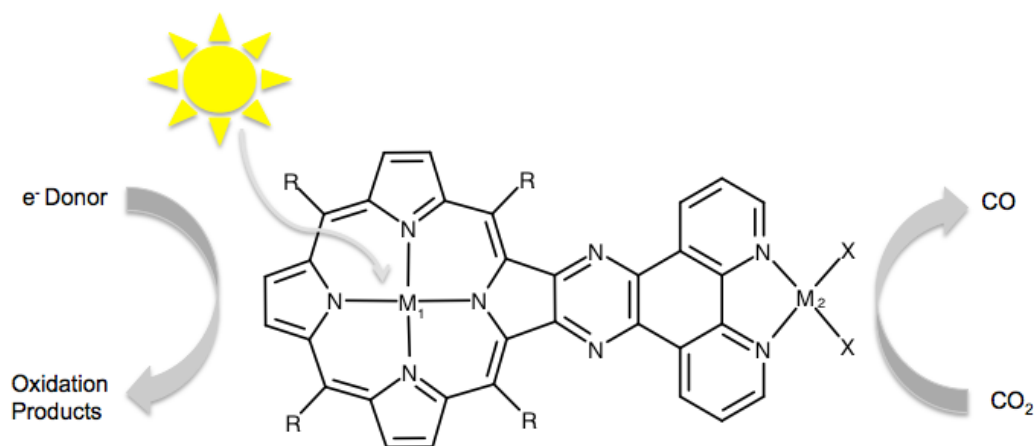
## Mono- and Dinuclear porphyrin complexes in light-driven CO<sub>2</sub> reduction catalysis

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The increasing energy consumption, the running short of fossil fuels, the associated price hikes and a growing CO<sub>2</sub>-pollution led to an increased international interest in secure and sustainable energy supply. In order to achieve this goal and to combat global warming a focus of research in renewable energy is essential.

Converting CO<sub>2</sub> into CO using sunlight as the driving force and earth-abundant metal complexes as the catalysts is an exciting challenge.<sup>[1]</sup> We here present a comprehensive study on the light-induced catalytic CO<sub>2</sub> reduction employing mono- and dinuclear phenanthroline-fused porphyrin complexes.<sup>[2]</sup> As metals in the porphyrin cavity we used redox active and inactive metals, e.g. Zn, Cu, Co and Fe. We report the photocatalytic behavior of the complexes in DMF/TEA solution by irradiation with visible light depending on the second metal center attached to the phenanthroline side, and compare the results with structurally related complexes. These catalysts were developed to selectively reduce CO<sub>2</sub> to CO with no detectable amounts of dihydrogen forming as a possible side-product.



**Figure 1:** Molecular Scheme of the synthesized compounds

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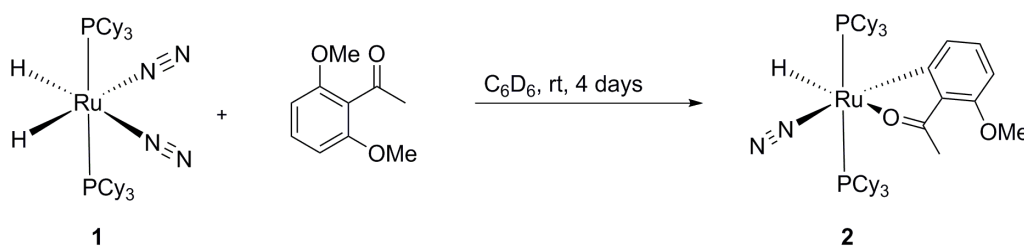
## Room Temperature Ruthenium-Mediated C–O Bond Activation

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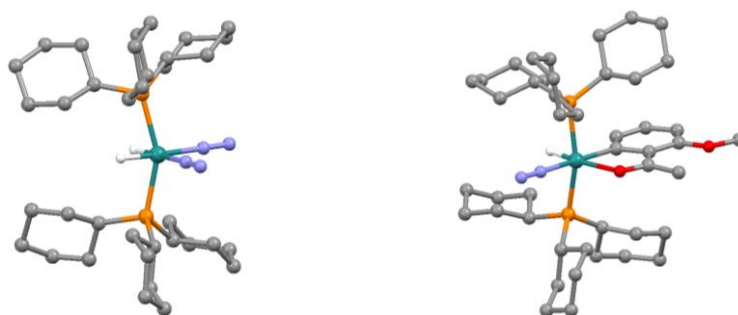
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Contemporary interest in organometallic catalysts capable of carbon–oxygen bond cleavage stems from a broad desire to upgrade low-value bio-derived chemical feedstock to more useful molecules. While a number of phosphine supported ruthenium catalysts are now known for C–O bond cleavage little is known about the fundamental steps surrounding these reactions.<sup>1,2</sup> Although oxidative addition of the C–O bond to a reactive organometallic intermediate is often proposed as key step in the mechanism there are only a few well studied examples this reaction in literature.<sup>3,4</sup>



**Figure 1** Ru catalyzed room temperature C–O cleavage

Here we show that, under an atmosphere of N<sub>2</sub>, [RuH<sub>2</sub>(N<sub>2</sub>)<sub>2</sub>(PCy<sub>3</sub>)<sub>2</sub>] can be isolated,<sup>5</sup> and that this complex is capable of room temperature C–O bond cleavage of the *sp*<sup>2</sup>C–O bond of 2,6-dimethoxyacetophenone to generate the cyclometallated intermediate **2** (Figure 1).



**Figure 2** X-ray crystal structure of **1** and **2** respectively

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## Exploring thallium organoamide/organometallic coordination chemistry

A. R. Leverett,<sup>a</sup> M. L. Cole\*

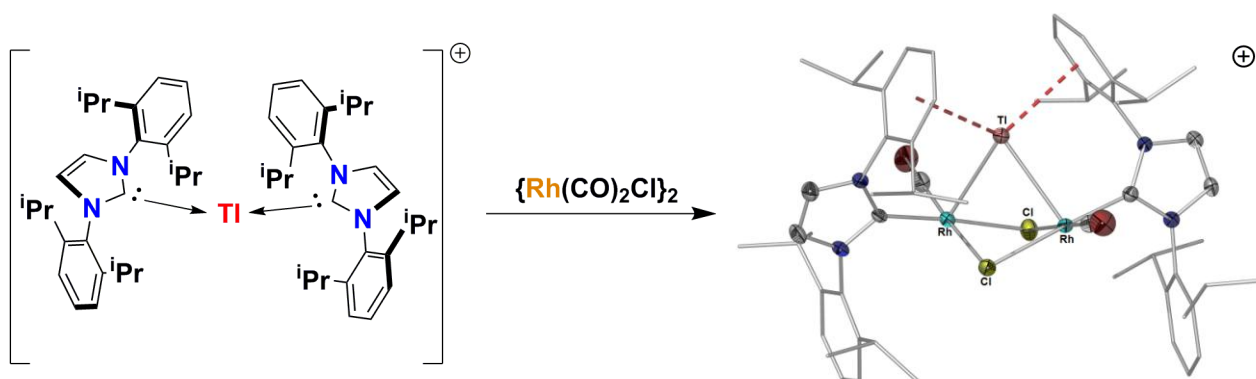
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Thallium is a major by-product of Australia's mining industries, particularly those of uranium, the rare earths and Cu/Sn/Zn. It is therefore a cheap and plentiful national resource. Regrettably, thallium's uses have been stunted by concerns regarding its toxicity which, while factually credible, have blinkered industry to its substantial synthetic and electronic potential. For example, aside from thallium, the metals of group 13 are a mainstay of functional optoelectronic devices,<sup>1</sup> and the lighter metals; aluminium and gallium, are finding increasing non-redox catalytic applications.<sup>2</sup> Against this, the most well reported application of thallium is, like its 6th period neighbours (Hg and Pb), as a non-catalytic desulfurizing agent (Claus process).

The 5th and 6th period p-block metals possess a favourable characteristic over their lighter metal counterparts; ready access to two stable oxidation states (+1 and +3 for group 13). This radically enhances indium and thallium's prospects for redox based catalytic applications akin to those of group 8-10 metals. To bring this step change closer, we have begun a research program pitched at addressing the underdevelopment of thallium's organometallic, hydrido and organoamide chemistry.

Herein we report the preparation of some thallium(I) bis(NHC), triazenide and formamidinate complexes and attempts to use these as precursors to hydridothallanes and as transmetallating agents for rhodium(I).



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## Reactivity of Protic *N*-Heterocyclic Carbene Iridium(III) Complexes

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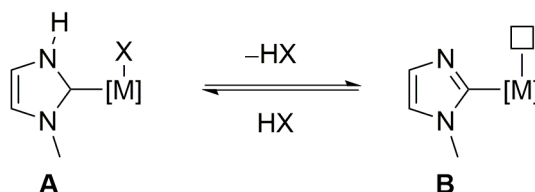
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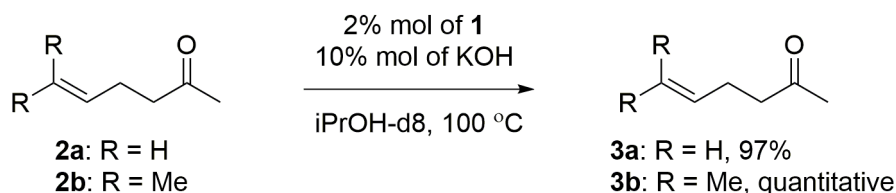
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A Protic *N*-Heterocyclic Carbene (PNHC) ligand in a metal complex could act as an assistant ligand activating and/or recognizing substrates by hydrogen bonding.<sup>1</sup> The NH group in the beta position to the metal center (**A**) as well as the basic nitrogen of the conjugate base (**B**) provides an adequate structure for bifunctional catalysis, containing a Brønsted acid and a Lewis base near to the metal center (Figure 1).<sup>2</sup>



In this contribution we report a non functionalized bis(imidazole) ligand precursor that has been directly metalated using IrCp\*(OAc)<sub>2</sub>, leading a bis(PNHC)iridium(III) complex (**1**). Studies on organometallic chemistry of the bis(PNHC)iridium(III) (**1**) includes ligand exchange, beta hydride elimination and catalytic selective hydrogenation of either 6-methyl-5-hepten-2-one (**2a**) or 5-hepten-2-one (**2b**) to give the 5-alken-2-ol (**3a** or **3b**).



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## Efforts Toward Isolation and Characterization of Active Species Present in Iron-Mediated Catalytic C-C Cross-Coupling with Alkyl Grignards

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Structural and spectroscopic investigations of novel iron based molecules isolated from catalytically relevant reaction mixtures is detailed. *In situ* reaction studies, as well as those performed with alkenyl bromides and material isolated from a mixture of ferric chloride and methyl Grignard, were conducted to gain mechanistic insight. A host of spectroscopic methods including electron paramagnetic resonance, magnetic circular dichroism, Mössbauer and X-ray diffraction were employed to aid in identifying potential precatalysts. Evidence points to the presence of low valent iron species formed by the reduction of ferric salts by the alkyl Grignard at low temperatures.

## HYDROGEN TRANSFER REACTION OF N-BENZYLIDENEANILINE CATALYZED BY Ni(II) BEARING PINCER LIGANDS

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Catalytic hydrogenation plays a very important role for generating fine chemical products<sup>1</sup>. In this reaction, various metals have been used, such Ru<sup>2</sup> and Ir<sup>3</sup>, but nickel compounds have not been reported as catalysts for this reaction. In this paper we report the synthesis, characterization and catalytic activity in the hydrogenation transfer reaction of complexes Ni(II) with ligands of the type pincer ([NiPPh<sub>3</sub>(PNP)](CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> (**1**), ([Ni(PNP)Cl]Cl (**2**) and ([Ni(PNP)Br]Br (**3**) PNP= PPh<sub>2</sub>-NH-Py-NH-PPh<sub>2</sub>). The characterizations of the catalysts were carried out by FT-IR, <sup>1</sup>H-NMR, and <sup>31</sup>P-NMR. The catalytic study was carried out using N-benzylideneaniline as substrate dissolved in acetonitrile and formic acid was used as hydrogen donor source. The systems were tested using two different ratios of substrate/catalyst (S/C = 200/1 and 400/1). The temperature in all experiments was 80°C. The results (Table 1) indicate that the Ni(II) complexes show catalytic activity in short reaction times.

**Table 1.** Results of the catalytic activities of (1), (2) and (3) complexes.

Hours (h)	% Conversion					
	<b>(1)</b>		<b>(2)</b>		<b>(3)</b>	
	200/1	400/1	200/1	400/1	200/1	400/1
1h	66	48	51	26	86	44
2h	80	73	78	92	100	74
3h	-	-	90	97	-	90

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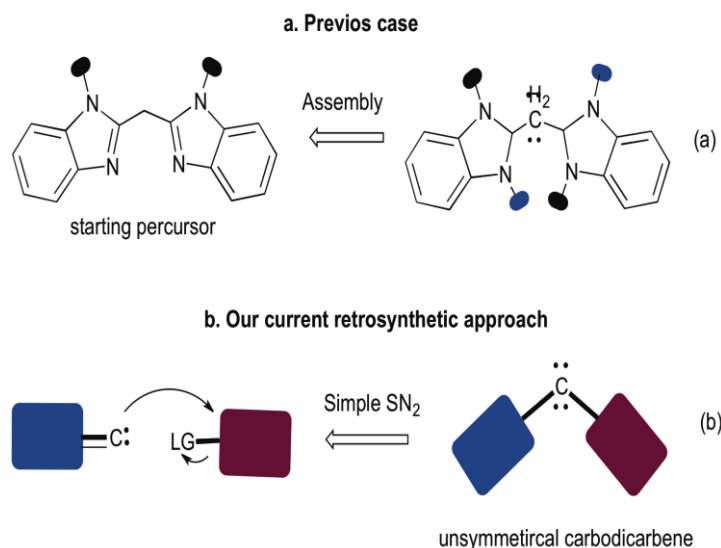
## Main Group Chemistry and Catalysis through Tinkering the Ligand Framework

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In describe the development of a synthetic protocol for the preparation of carbodicarbenes with unsymmetrical side arms and investigate their late transition metal complexes and intrinsic reactivities. The ligand carbodicarbene was used for possible catalysis application and main group chemistry.



1. Wen-Ching Chen, Jiun-Shian Shen, Titel Jurca, Chun-Jung Peng, Yen-Hsu Lin, Yi-Ping Wang, Wei-Chih Shih, Glenn P. A. Yap, Tiow-Gan Ong\* *Angew. Chem. Int. Ed.*, **2015**, *54*, 15307-15212.

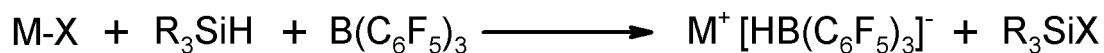
## Activation of transition metal complexes with $R_3Si-H-B(C_6F_5)_3$ adduct and its application in catalysis

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The activation of Si-H bond in hydrosilanes by strong Lewis acid  $B(C_6F_5)_3$  has attracted a widespread utilization in catalysis in recent 15 years.<sup>1</sup> As a key step of these reactions was proposed formation of hydrosilane-borane adduct  $R_3SiH \cdot B(C_6F_5)_3$ , which enhanced the polarization of hydrosilane moiety and boosted its reactivity towards various substrates. Although the adduct was proved by DFT calculation to be energetically feasible its isolation and even spectroscopic characterization remained elusive until recently.<sup>2</sup> The enhanced electropositivity of silicone atom in a hydrosilane-borane adduct allows an abstraction of anionic  $\sigma$ -ligand X (halide or pseudohalide) from early transition metal ( $M = Sc, Zr$ )<sup>3</sup> complexes, which leads to a formation of cationic metal centre and corresponding Si-X silane as schematically depicted in Scheme 1. The reaction is accompanied by hydride transfer from hydrosilane to boron center supported by the formation of compensating borate anion  $[HB(C_6F_5)_3]^-$ .



**Figure 1** Activation of metal-halide bond with hydrosilane- $B(C_6F_5)_3$  adduct

In our contribution, we will report a polymerization of ethylene by ternary zirconocene dihalide/hydrosilane/ $B(C_6F_5)_3$  system, which represents the first catalytic system based on group 4 halide complex activated with a non-aluminum cocatalyst or activator. In addition, we will present an extending of the methodology for activation of other early (Ti, Hf) and late (Ni) transition metal complexes and additional processes (eg. hydrodefluorination).

Acknowledgment: Authors thank the Czech Science Foundation for financial support (M.H, V.V. and J.P by project P207/12/2368 and M.L by project 14-08531S).

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## Ferrocene Polyfunctionalization towards Innovative Hybrid Phosphorus-based Ligands

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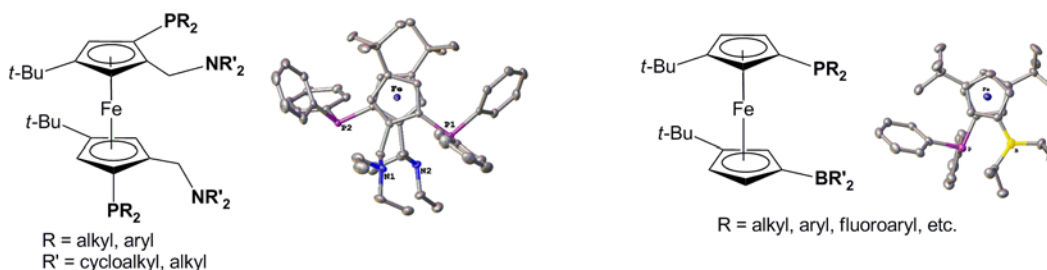
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Attachment of various heteroelements on a ferrocenylphosphine platform that can be used as a well-defined rigid but mobile linker is an interesting strategy for studying the interactions between a phosphanyl group and another heteroelement (B, Al, N, O, S). Because this platform could normally freely rotate around the iron atom, the disubstitution of the ferrocene by congesting groups may hamper this rotation and thus provides a way to better control the mutual position between other substituents on the Cp rings. In order to learn more about their potential cooperative and/or hemilabile coordination behaviour,<sup>1</sup> we chose two specific targets that combines :

- i) **Lewis acidic and basic sites (P, B):** these ambiphilic compounds which can show either a frustrated or an interacting behavior are topical for the activation of small molecules like hydrogen or carbon dioxide and for coordination with metals.
- ii) **Soft and hard donor sites (P, N):** these derivatives which can have varied electronic and steric effects due to substitution may provide additional benefits to multidentarity such as hemilabile behavior of great interest for catalytic reactivity.



Converging and diverging synthetic strategies to tetradentate (P,N)- and bidentate (P,B)-ferrocenyl ligands and their coordination chemistry will be reported in this poster.

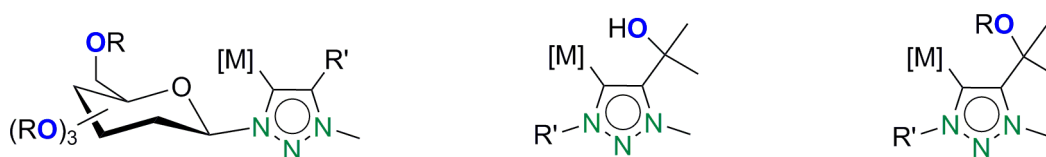
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## O-Functionalized 1,2,3-Triazolylidene Metal Complexes for Redox Catalysis

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1,2,3-Triazolylidenes are a unique class of carbenes which have many advantages over classical N-heterocyclic carbenes (NHCs) including ease of synthesis and modification, and increased  $\sigma$ -donation properties.<sup>1</sup> Since O- and N-functionalisation of classical NHCs has been shown to enhance the catalytic activity of the metal center, in particular for (transfer) hydrogenation reactions.<sup>2,3</sup> We aimed to explore the implication of such functional groups in combination with triazolylidene ligands. To this end, we have synthesised a range of metal complexes bearing O-functionalised 1,2,3-triazolylidene ligands. In this presentation, we will discuss the effects of this functional group, and the catalytic applications of the corresponding complexes in transfer hydrogenation and dehydrogenation reactions.



**Figure 1:** O-functionalised 1,2,3-triazolylidene metal complexes

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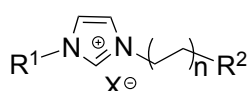
## Synthesis and characterization of mono- and bis-functionalized NHC complexes of Nickel(II) and their application in catalytic oligomerization and C-C bond formation

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A series of bis(ether-, alcohol-, ester-, acid-, or amine-mono-functionalized NHC) nickel(II) complexes were obtained by direct synthesis from the imidazolium salts, or by silver transmetallation. The length of the alky spacer between the imidazolium nitrogen and the R<sup>2</sup> function was varied to provide comparisons with related ligands and complexes.<sup>1</sup> We could also isolate corresponding mono-NHC nickel(II) complexes and some of them show interesting paramagnetic NMR features.<sup>2</sup> New bis-functionalized imine, ether or imine, amine NHC nickel(II) complexes were also synthesized to examine the possible competition between the various donor groups. All these complexes have been fully characterized and in most cases, their structures as well as that of the free carbene 1-(2-isopropylphenyl)-3-(3-methoxypropyl)-imidazole-2-ylidene, have been elucidated by single crystal X-ray diffraction.

The Ni complexes were also evaluated in catalytic ethylene oligomerization and C-C bond formation.<sup>3</sup>



R<sup>1</sup> = DiPP, Mes, Me, Octyl, Imine  
 R<sup>2</sup> = OMe, C(O)OH, C(O)OEt, OH,  
 NMe<sub>2</sub>, H  
 n = 0, 2, 3  
 X = Cl, Br, BF<sub>4</sub>

### Scheme 1 Mono- and bis-functionalized imidazolium salts used as precursors to NHC Ni(II) complexes

We thank the CNRS, the MESR (Paris), Unistra, and the China Scholarship Council for financial support and the Service de Radiocristallographie (Unistra) for the determination of the crystal structures.

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## Rh(I) Fischer carbene complexes and their application in hydroformylation catalysis

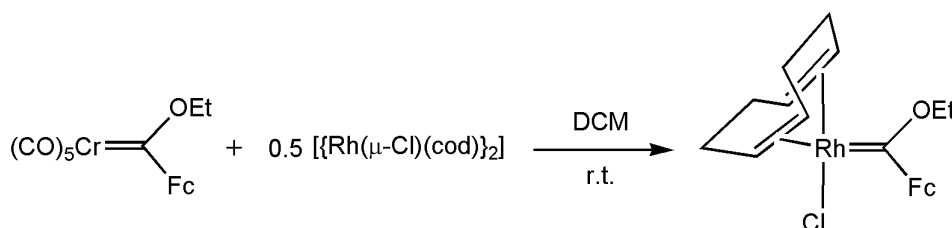
G. Kabelo Ramollo,<sup>a</sup> María J. López-Gómez,<sup>a</sup> Gregory S. Smith<sup>b</sup> and Daniela I. Bezuidenhout<sup>a\*</sup>

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Rh(I) complexes of the form  $[\text{Rh}(\text{LL}')\text{Cl}\{\text{C}(\text{OEt})\text{Fc}\}]$   $\{\text{LL}' = (\text{cod}), (\text{CO})_2, (\text{CO})(\text{PR}_3) (\text{R} = \text{Ph}, \text{Cy}, \text{OPh}) \text{ and } (\text{CO})(\text{AsPh}_3)\}$  bearing ferrocenyl Fischer carbene ligands were synthesized by means of transmetallation from the Group 6 transition metal carbene precursor<sup>1</sup> as depicted below (Scheme 1) and subsequent substitution of the cod ligand. Aminocarbene derivatives  $[\text{Rh}(\text{LL}')\text{Cl}\{\text{C}(\text{NHPr})\text{Fc}\}]$   $\{\text{LL}' = (\text{cod}) \text{ and } (\text{CO})_2\}$  were prepared by simple aminolysis of the transmetallated product and substitution of the cod ligand.



Scheme 1 **Preparation of a Rh(I) Fischer (ethoxy)ferrocenylcarbene complex via transmetallation.**

Many examples of rhodium-NHC complexes have been applied in the hydroformylation of olefins,<sup>2-4</sup> however, there have been no reports of the utilization of the mono-heteroatom substituted rhodium(I) Fischer carbene complexes in the hydroformylation reaction to date. We herein report the first example of the hydroformylation of 1-octene promoted by Rh(I) Fischer carbene complexes.<sup>5</sup>

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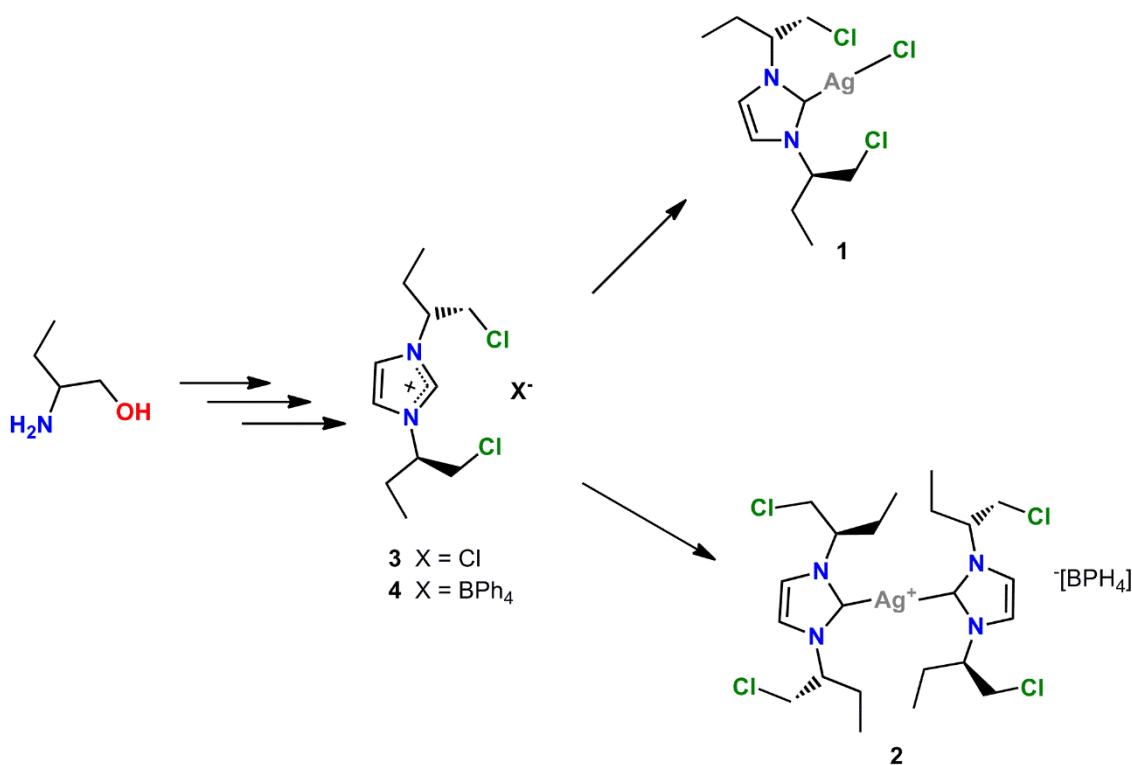
## Synthesis and catalytic activity in $A^3$ -coupling reaction of chiral N-heterocycliccarbene-silver complexes derived from [(R) - 1-chloro- butan-2-amine].

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Herein, we report the synthesis of the two new chiral carbene-silver complexes: (1,3-di{(R) 1-chloro-2-butyl}-[1,3]-imidazolin-2-ylidene) silver(I) chloride (**1**) and bis-(1,3-di{(R) 1-chloro-2-butyl}-[1,3]-imidazolin-2-ylidene)silver(I)tetraphenylborate (**2**), prepared from (1,3-di{(R) 1-chloro-2-butyl}-[1,3]-imidazolium)chloride (**3**) and (1,3-di{(R) 1-chloro-2-butyl}-[1,3]-imidazolium)tetraphenylborate (**4**), respectively. X-Ray diffraction structures of compounds **1** and **2** were obtained and the silver-chloride potential interactions were analysed. In the structure of **2** were observed rotamers where the chlorine atoms are directed to the metallic centre. Nevertheless, the Cl-Ag lengths are near than the van der Waals radii sum, and were found short Ag-H lengths. These lengths and rotamers observed in the structure suggest weak Cl-Ag and preagostic interaction. The silver complexes **1** and **2** were tested as catalyst in the synthesis of propargylamine derived by  $A^3$ -coupling reactions at room temperature and in presence of different solvents. The best yields were obtained with the catalyst **1** in THF or DMF.



**Figure 1** Synthesis of carbene-silver complexes

## MOLYBDENUM COMPLEXES AS CATALYSTS IN EPOXIDATION AND SULFOXIDATION REACTIONS

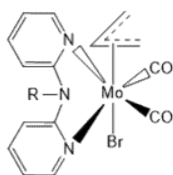
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New molybdenum complexes from the family  $[\text{MoBr}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{L})]$  were synthesised by reaction of the precursor  $[\text{MoBr}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{CH}_3\text{CN})_2]$  with a family of bidentate ligands derived from 2,2'-dipyridylamine, as shown in Figure 1. All new compounds prepared were characterized by FTIR, NMR of  $^1\text{H}$  e  $^{13}\text{C}$  as well as elemental analysis. All complexes were tested as homogeneous pre-catalysts in the oxidation of olefins and sulfides, such as cis-cyclooctene, styrene, cis-3-hexen-1-ol, trans-2-hexen-1-ol, geraniol, methylphenylsulfide and diphenylsulfide, using hydrogen peroxide, tert-butyl hydroperoxide or cumene hydroperoxide as the oxidant. These studies were carried out in order to determine the influence of the length of the alkyl chains of the ligands on the complexes catalytic activity.



**Figure 1.** Molybdenum complexes from 2,2'-ddipyridylamine derivatives.

Acknowledgements: We thank Fundação para a Ciência e Tecnologia for financial support (PEST UID /MULTI/00612/2013). MSS thanks FCT for Grant SFRH / BPD / 88082 / 2012.

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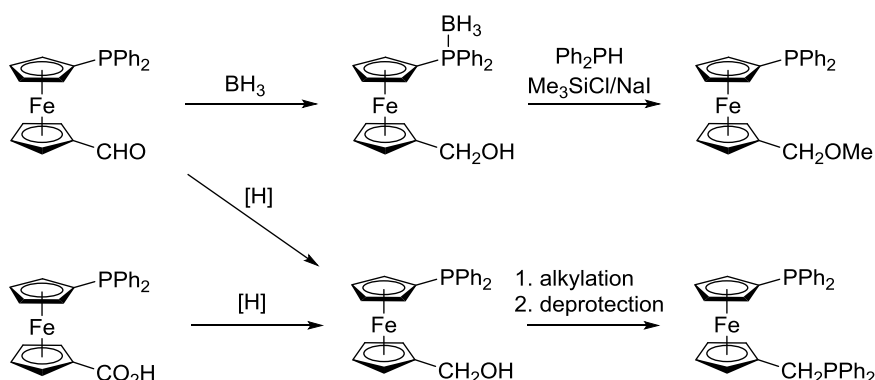
# Synthesis and Coordination Properties of Semihomologous Phosphinoferrocene Donors

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Phosphinoferrocene donors have attracted attention as versatile donors for coordination chemistry and catalysis. In addition to 1,1'-bis(diphenylphosphino)ferrocene (dppf), an archetypal bidentate ligand, there have been reported various chiral phosphinoferrocene dppf analogues, compounds modified with a polar functional group and other similar donors.<sup>1</sup> Much less attention has been paid to dppf congeners in which one of the donor groups is separated from the ferrocene unit *via* a spacer (e.g., methylene group). This contribution will detail the synthesis of such compounds (see Figure 1) and the results of our coordination studies with these conformationally flexible donors.<sup>2</sup>



**Figure 1** Synthesis of representative of semi-homologous phosphinoferrocene donors.

The research leading to these results has received funding from the Czech Science Foundation (Project No. 15-11571S).

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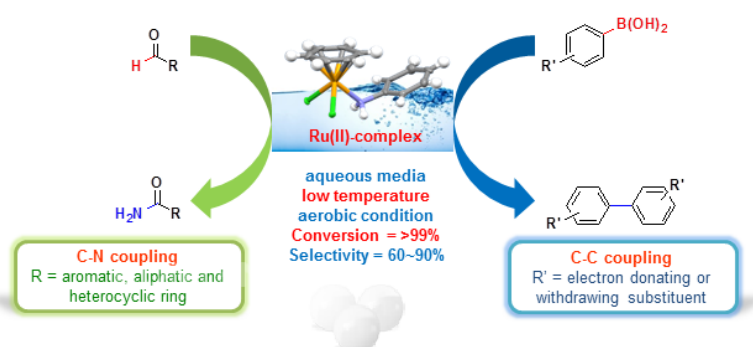
## Ru(II)-catalyzed C-N and C-C coupling reactions in water

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Devising developmental methods of catalytic C-N and C-C coupling reactions has turned out to be a fascinating dimension of current research owing to potential applicability in pharmacological and industrial ventures.<sup>1,2</sup> Earlier reports on these coupling reactions involve the expensive metals (Au, Pd etc.) and wasteful procedures using different organic solvents which are responsible for raising potential environmental threats.<sup>3</sup> As a part of our continuing efforts in development of homogeneous complexes, we investigated highly efficient and cost effective water soluble arene ruthenium complexes with versatile catalytic activities such as aldehyde to amide synthesis and homocoupling of arylboronic acids. We developed phosphine-free water soluble ruthenium complexes having different -NH<sub>2</sub> functional arene ligands which efficiently catalyzed both reactions such as one pot substituted aldehyde to substituted amide synthesis (C-N coupling) and symmetric biaryls (aryl C-C (sp<sup>2</sup>-sp<sup>2</sup>) coupling) from substituted arylboronic acids under green reaction conditions using water as solvent at low temperature with high conversion and selectivity of the desired products.<sup>4</sup>



**Figure 1** Scheme for the Ru(II) catalyzed C-N and C-C coupling reactions.

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2 P. Pillaiyar, S. Palaniswamy, P. Kasi, *Green Chem.*, **2014**, *16*, 2865.

3 S. Chunlou, Q. Panpan, L. Feng, *Catal. Sci. Technol.*, **2014**, *4*, 988.

4 T. Deepika, R. Rohit K., D. Ambikesh D., M. Shaikh M., S. Sanjay K., *Inorg. Chem. Front.*, **2015**, *2*, 116.

## Pd (II) with fosforous-nitrogen ligands as catalysts in styrene methoxycarbonylation

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Carbonylation reactions are an important tool for the activation of low-cost substrates, in order to synthesize esters, acids and aldehydes<sup>1</sup>. Methoxycarbonylation reaction catalyzed by palladium complexes containing phosphorus-nitrogen ligands activates various olefins under mild conditions of pressure and temperature <sup>2</sup> (75°C, 50 bar CO). This work reports the synthesis and characterization of palladium (II) with a new generation of phosphorus-nitrogen ligands, these compounds are synthesized by direct reaction between PdCl<sub>2</sub> in refluxing acetonitrile and 1 equivalents of phosphorus-nitrogen ligand. The compounds were studied in the styrene methoxycarbonylation reaction using batch reactors and monitored by gas chromatography. Tested compounds showed activity catalysts for the methoxycarbonylation reaction with high selectivity to branched ester.

Table 1. Results for the styrene methoxycarbonylation reaction.

Pd (II) P-N catalyst	Conversion to ester (%)	Chemoselectivity to ester (%)	Conversion to ramified ester (%)
PdCl <sub>2</sub> (1)	93	97	96
PdCl <sub>2</sub> (2)	57	97	95
PdCl <sub>2</sub> (3)	93	98	97

Catalytic reaction: The catalytic reaction was performed using  $4 \times 10^{-2}$  mmol of catalyst,  $4 \times 10^{-2}$  mmol of triphenylphosphine,  $4 \times 10^{-1}$  mmol of p-toluenesulfonic acid and the substrate / catalyst ratio of 1: 400. The reaction was performed in an autoclave at 75 ° C with a CO pressure of 50 bar and was monitored by gas chromatography.

1 C. Zuñiga, S. A. Moya. P. Aguirre, *Catal Letters*, **2009**, 130, 373.

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## Organometallic complexes incorporating a triazenido ligand functionalized with quinoline

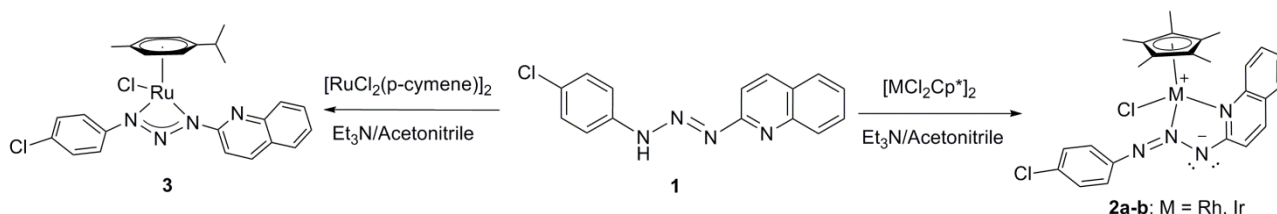
A. F. Velázquez-Ham,<sup>a</sup> M. P. Parra-Hake<sup>a</sup>, V. Miranda-Soto<sup>a\*</sup>

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Triazenes are organic molecules containing three contiguous nitrogen atoms, and their use as ligands in coordination compounds is well known.<sup>1</sup> In this work, a triazenido ligand functionalized with quinoline and a chlorinated aryl reacted with the dimers  $[MCl_2Cp^*]_2$  [ $M = Rh(III), Ir(III)$ ] and  $[RuCl_2(p\text{-cymene})]_2$  in acetonitrile at room temperature to generate three mononuclear complexes (**2a-3**).



**Figure 1.** Synthesis of organometallic complexes.

The complexes were tested as catalysts in transfer hydrogenation reactions. The catalytic reactions were performed at 70 °C in 2-propanol as solvent, 10 mol% of KOH and 2 mol% of complex.<sup>2</sup> In the hydrogenation of acetophenone, complex **2a** was the most effective, giving 1-phenylethanol in 98% yield after 5 h. Also, the hydrogenation of unsaturated ketones was tested, the selectivity of the catalyst to hydrogenate only the carbonyl group in the presence of an olefin fragment was one of the most satisfactory results.



**Figure 2.** Influence of the base on the hydrogenation products.

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2 R. Noyori, S. Hashiguchi, *Acc. Chem. Res.* **1997**, *30*, 97.

## Synthesis and characterization of a novel catalyst based on dendrimer of core-POSS and its applications in epoxidation of olefins

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In this research we report the preparation and characterization of a new dendrimer of second-generation with a core of silsesquioxane (POSS-DG2.0). Polyhedral oligomeric silsesquioxanes (POSS), are nanoplateforms with one to eight reactive or nonreactive organofunctional groups (R) anchored to the eight possible vertices of the cubic silsesquioxane. In this nanomaterial was anchored six tungsten organometallic complexes ( $[W(CO)_3Br_2(NCMe)_2]$ ) for application in catalytic epoxidation of olefins.

To the best of our knowledge, this study is the first that has reported the preparation of POSS-DG2.0- $[W(CO)_3Br_2]$  for catalytic epoxidation of 1-octene, cyclooctene, (S)-limonene, cis-3-hexen-1-ol, trans-3-hexen-1-ol and styrene. The material was characterized using infrared spectroscopy, elemental analysis, solid-state  $^{29}Si$  and  $^{13}C$  nuclear magnetic resonance and scanning electronic microscope (SEM) coupled to an energy dispersive spectroscopy (EDS).

The new organometallic nanomaterial POSS-DG2.0- $[W(CO)_3Br_2]$  was tested as a catalyst in the epoxidation of 1-octene, cyclooctene, (S)-limonene, cis-3-hexen-1-ol, trans-3-hexen-1-ol and styrene.

The catalyst behaved as an excellent catalytic precursor for the epoxidation of cyclooctene and styrene using TBHP (tert-butyl hydroperoxide).

The material selectively catalyzed the epoxidation for the corresponding epoxides, with and without formation of diols depending on the substrate, with high conversions and TOFs. No reaction took place without a metal containing catalyst.

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## Ruthenium Mediated Dual Catalytic Reactions of Isoquinoline via CH Activation Manifold.

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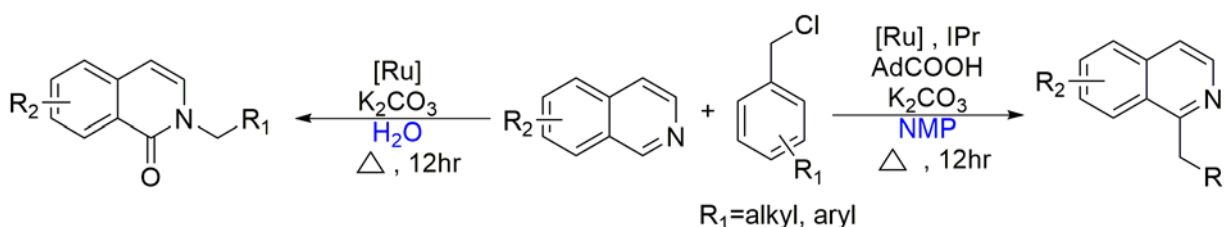
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<sup>c</sup> Nano Science and Technology Program, Taiwan International Graduate Program, Academia Sinica and National Tsing Hua University, Taiwan, Republic of China.

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We unravel the Ru-promoted prototype reaction based on C-C bond formation through the C-H activation of isoquinoline and other nitrogen containing heteroarenes with alkyl halide, leading to the 1-substituted isoquinoline products. Simultaneously, we are also able to chemically toggle the reaction mode towards producing isoquinolone by adding water. The detail of the reaction pathway will be discussed in poster presentation.



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3. L. Liu,\* M. Wan, and H. Lou, *Chem. Commun.*, **2015**, 51.13953.
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## Ruthenium(II) O-alkyl(aryl) dithiocarbonate complexes. Synthesis, characterisation, and catalytic properties

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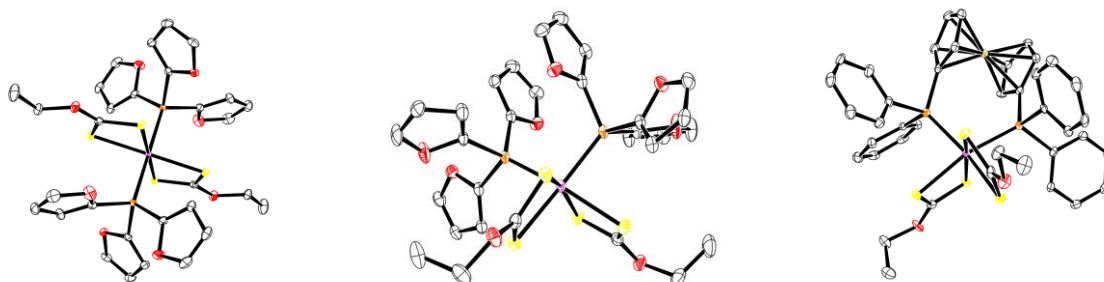
<sup>a</sup> Laboratory of Macromolecular Chemistry and Organic Catalysis, Department of Chemistry University of Liège, Sart-Tilman (B.6a), B-4000 Liège, Belgium

<sup>b</sup> Unidad de Difracción de Raios X, Edificio CACTUS Universidad de Santiago de Compostela, Campus Vida, 15782 Santiago de Compostela, Spain

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Interest in mononuclear complexes with sulfur-containing ligands has been sustained by their relevance as models for redox-active metalloproteins. Compared to dithiocarbamate complexes, dithiocarbonate complexes are less well-known. Only very few examples have been reported for ruthenium, using  $[\text{RuCl}_2(\text{PPh}_3)_3]$  and potassium O-ethyl dithiocarbonate as starting compounds. Subsequent treatment of  $[\text{Ru}(\text{S}_2\text{COEt})_2(\text{PPh}_3)_2]$  with a variety of tertiary phosphines  $\text{PR}_3$  or diphosphines  $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$  ( $n = 1$  or  $2$ ) provided *cis* derivatives, except for the complex with  $\text{PMe}_2\text{Ph}$  that gave the *trans* isomer.<sup>1</sup>

In this communication, we present a straightforward and versatile method for the synthesis of ruthenium dithiocarbonate complexes, starting from the readily available ruthenium dimer  $[\text{RuCl}_2(p\text{-cymene})]_2$  (*p*-cymene = 4-isopropyltoluene), potassium or sodium O-alkyl(aryl) dithiocarbonate, and phosphine, diphosphine or phosphite ligands. Depending on the reaction conditions, pure *cis* or *trans* complexes were formed. Finally, their catalytic activity was assessed in olefin cyclopropanation, atom transfer radical reactions (Kharasch addition), and in the synthesis of enol esters.



**Figure 1** ORTEP representations of *trans*- $[\text{Ru}(\text{S}_2\text{COEt})_2(\text{P}(o\text{-furyl})_3)_2]$ , *cis*- $[\text{Ru}(\text{S}_2\text{COEt})_2(\text{P}(o\text{-furyl})_3)_2]$  and  $[\text{Ru}(\text{S}_2\text{COEt})_2(\text{dppf})]$  complexes (from left to right).

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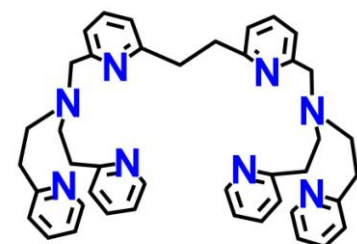
## Direct Oxidation of Benzene to Phenol with H<sub>2</sub>O<sub>2</sub> Catalyzed by Dinickel Complexes Stabilized by Dinucleating Ligands

Antonius Andre Zaoputra, Tomokazu Tsuji, Yutaka Hitomi, Masahito Kodera\*  
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 1-3 Tatara Miyakodani, Kyotanabe City, Kyoto Prefecture, Japan 610-0394  
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The conversion of benzene to phenol via the direct oxidation is an important target in the chemical industry. Cumene process, the industrial process used nowadays has many problems such as high temperature and pressure, low yield, and so on. Therefore, in order to solve these problems, it's important to develop a new efficient pathway, for example by using metal complex as catalyst.

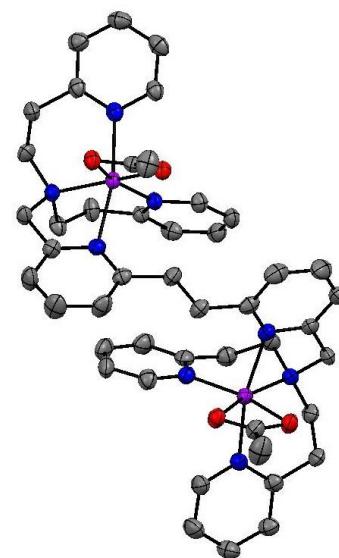
Itoh et al. reported that mononickel complexes supported by pyridylalkylamine ligands achieved direct oxidation of benzene with TON of 749,<sup>1</sup> where a dinuclear species was proposed as the active intermediate.

We have developed various dinucleating ligands to stabilize dinuclear structures.<sup>2</sup> To obtain dinickel complexes that is capable to efficiently catalyze the oxidation of benzene to phenol, we synthesized a new dinucleating ligand, 6-hpea, shown in Figure 1. It forms a dinickel(II) complex, [Ni<sub>2</sub>(6-hpea)(AcO)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (**1**). The crystal structure is shown in Figure 2, where a Ni ion takes distorted octahedral geometry, and two Ni ions are connected by a 1,2-dipyridylethane of 6-hpea.



**Figure 1** Chemical structure of 6-hpea

This may be advantageous for the benzene oxidation because 6-hpea may stabilize a dinuclear structure proposed as the active species. So, we carried out the oxidation of benzene with H<sub>2</sub>O<sub>2</sub> catalyzed by **1**, and found that turnover number of **1** in the phenol production exceeds two thousand. Here, we report the synthesis, crystal structure, and high catalytic activity of **1**.



**Figure 2** ORTEP drawing of cation part of [Ni<sup>II</sup><sub>2</sub>(6-hpea)(AcO)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>•C<sub>6</sub>H<sub>6</sub> (**1**)

1 S. Itoh; *J. Am. Chem. Soc.* **2015**, 137, 5867-5870

2 M. Kodera; *Angew. Chem. Int. Ed.* **2005**, 44, 7104–7106

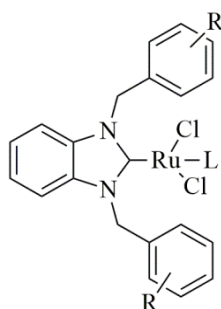


## Synthesis and Catalytic Properties of Palladium-NHC-PPh<sub>3</sub> Complexes

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After discovery of Arduengo, who isolated and characterized the first stable free NHC in 1991,<sup>1</sup> *N*-heterocyclic carbenes (NHC) and their different metal complexes have led to important evolution in homogeneous catalysis. Although there are numerous metal complexes of NHCs, Pd-NHC complexes come into prominence due to robustness against air, moisture and high temperature.

Carbon-carbon bond formation reactions are very important and useful catalytic transformations for modern synthetic chemistry.<sup>2</sup> Suzuki coupling is commonly preferred reaction in C-C bond formations reactions because it has mild reaction condition and non-toxic chemistry. Aim of this work is synthesis and investigation of catalytic activity of novel palladium-NHC-PPh<sub>3</sub> complexes.



L = NHC, Pyridine, PPh<sub>3</sub>

**Figure 1** synthesis of palladium NHC complexes

This work was financially supported by İnönü University Research Fund (İ.Ü. B.A.P: 2014/54).

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## Halogenation of aromatics by N-ligand directed selective C–H activation with Palladium catalysis

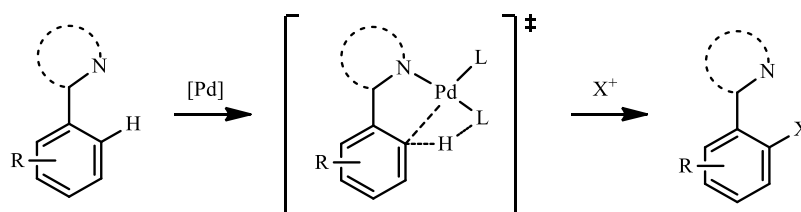
J. Roger,<sup>a</sup> C. Testa,<sup>a</sup> E. Gigot,<sup>a</sup> B. Darenne,<sup>a</sup> S. Schieb,<sup>a</sup> R. Decreau,<sup>a</sup> P. Fleurat-Lessard,<sup>a</sup> and J.-C. Hierso<sup>a,b</sup>

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Halogenation of aromatic rings is a widely used strategy for synthetic elaboration in the field of materials and biomedical applications. These starting materials are classically used as precursors to organolithium<sup>1</sup> and Grignard reagents<sup>2</sup>, and more recently, directly in cross-coupling reactions to form new C–C, C–N, C–O or C–S bonds<sup>3</sup>. In addition, halogenated organic compounds, especially aryl fluorides or aryl chlorides have shown important biological activities of potential pharmaceutical and agrochemical agents.<sup>4</sup>

In the past few years, transition metal catalyzed methods, especially palladium catalyst, emerged as an efficient method to directly functionalize C–H bonds on (hetero)aromatics bearing a N-ligand directing group to create a new C–halide bond (I, Br or Cl).<sup>5</sup> C–X bond formation are more difficult to form but using electrophilic halide reagent such as NXS, selectfluor, DAST or NFSI, such functionalization was efficiently achieved. We have recently demonstrated that the direct *ortho*-fluorination of highly substituted pyrazole derivatives proceeds in moderate to high yields.<sup>6</sup>



Scheme 1

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2. G. S. Silverman, P. E. Rakita, *Handbook of Grignard Reagents*; Eds.; Dekker: New York, NY, **1996**.
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# Synthesis of Heteroarenes Dyads from Heteroarenes and Heteroarylsulfonyl Chlorides *via* Pd-Catalyzed Desulfitative C–H bond Heteroarylations

B. Saoudi<sup>a,b</sup>, A. Debache<sup>b</sup>, J.F.Soulé<sup>a</sup>, and H. Doucet<sup>a</sup>

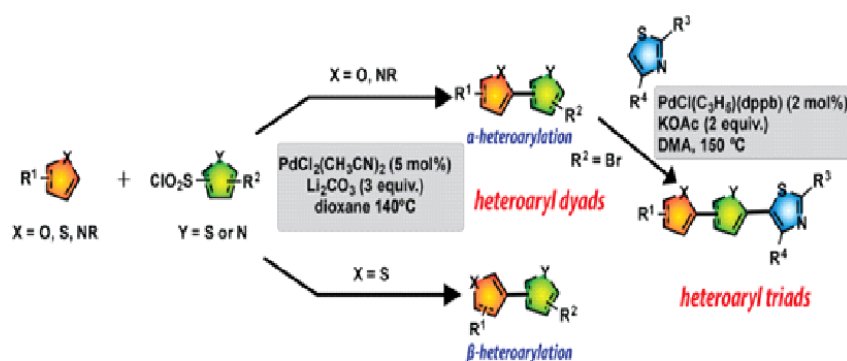
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The abundance of polyheteroaromatic structures in organic compounds led to intense efforts to develop new methods for their synthesis over the last few decades. Palladium catalysis is a very useful tool for the C–C bond formation. The synthesis of heteroaryl dyads has been widely reported using palladium catalysis from organometallic reagents with heteroaryl halides.

As part of our ongoing research towards on the palladium-catalyzed direct heteroarylation of heteroarenes (e.g., pyrroles, furans, and thiophenes) in which heteroarylsulfonyl chlorides are used as coupling partners through a desulfitative cross-coupling. These C–H bond functionalizations occurred at the  $\alpha$ -position in the case of pyrrole and furan derivatives, while in the case of thiophenes the C–H bonds at  $\beta$  position have been heteroarylated. The following Scheme summarizes the achieved works published in our paper <sup>1</sup>



**Scheme**

B. Saoudi, A. Debache, J.F. Soulé and H. Doucet, RSC Adv, **2015**, 5, 65175.

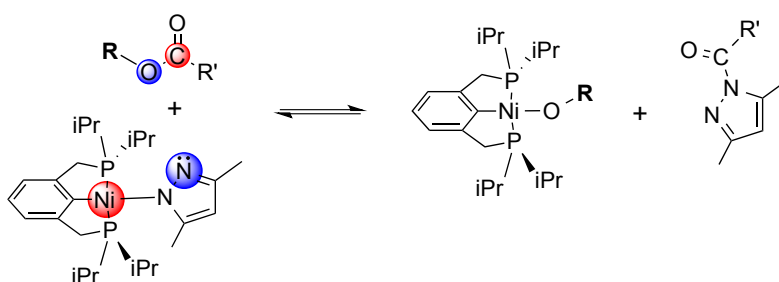
## Metal-Ligand Cooperative System in Azolate-Pincer Complexes: Bifunctional Catalysis

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In this contribution we discuss the reactivity of Nickel (II) complexes containing terminally bound azolate (pyrazolate, imidazolate or 1,2,4-triazolate) and tridentate pincer ligands. Azole heterocycles are known to act as organocatalysts in acyl transfer reactions<sup>1</sup>. In our compounds, the pincer ligand saturates three coordination positions of the square-planar metal center, enforcing the terminal coordination of the azolate. This leaves a nitrogen atom with significant nucleophilic character in the vicinity of the 16e<sup>-</sup> nickel atom, which retains residual Lewis acidic character. This situation is akin to Frustrated Lewis pairs (FLP)<sup>2</sup>, which emerged in the past decade as an innovative tool for the development of new catalytic transformations.

In order to evaluate the cooperative metal/ligand effect and to extend the concept of FLP to catalysis, we have studied the ability of our compounds to activate esters affording reactive combinations of nickel alkoxides and acylazolates (Scheme 1). We have exploited this reactivity pattern in the catalytic transesterification of alkyl carbonates, or the generation of reactive nickel species from unsaturated molecules (heterocumulenes, alkynes...), as potential intermediates in synthetically useful catalytic processes.



**Scheme 1**

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2. Erker, G., Stephan, D. W. *Frustrated Lewis Pairs I: Uncovering and Understanding. Topics in Current Chemistry*, Vol. 332. Springer, Berlin, 2013.

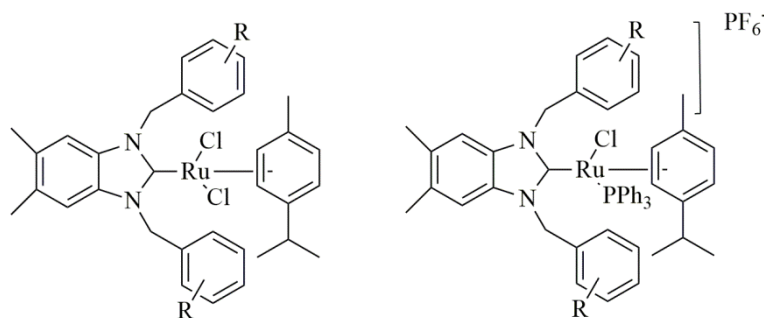
## Alkylation Reaction Catalyzed by Ruthenium-N-Heterocyclic Carbene Complexes

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N-heterocyclic carbenes (NHC) and their different metal complexes have led to important evolution in homogeneous catalysis.<sup>1-2</sup> The basis of this interest lies in strong  $\sigma$ -donor and weak  $\pi$ -acceptor ability and ease of adjusting the steric effects of NHC by nitrogen atoms. Complex bearing sterically bulky and electron-rich ligands perform enhanced catalytic activity in oxidative addition and reductive elimination reaction which are key step of many catalytic reaction on homogeneous catalyse.<sup>3-4</sup>

Aim of this work is synthesis and investigation of catalytic activity of novel ruthenium-N-heterocyclic carbene (NHC) complexes for alkylation of amines.



**Figure 1** Ruthenium N-heterocyclic carbene complexes

This work was financially supported by İnönü University Research Fund (İ.Ü. B.A.P: 2014/54).

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4 W.A. Herrmann, *Angew. Chem. Int. Ed.* **2002**, 41, 1290.

## Cross metathesis of unsaturated epoxides for the synthesis of polyfunctional building blocks

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Antoine Dupé<sup>b</sup>, Zahia Kabouche<sup>a</sup>, Christian Bruneau<sup>b</sup> and Cédric Fischmeister<sup>b\*</sup>

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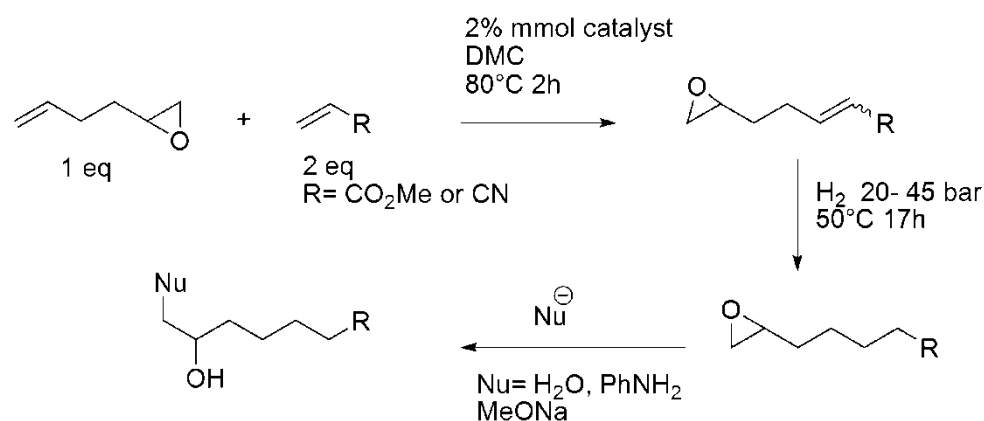
<sup>b</sup>UMR 6226 CNRS, Institut des Sciences Chimiques de Rennes, Université de Rennes 1,  
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<sup>c</sup>Charles University in Prague, Faculty of Science, Department of Physical and  
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Metathesis of renewable compounds with electron-deficient olefins was developed as a straightforward way for the synthesis of difunctional compounds suitable for polymer syntheses,<sup>[1,2]</sup> or as key synthetic tool in multistep syntheses of complex molecules.<sup>[3,4]</sup> Cross-metathesis with functional olefins is of great interest as it offers the possibility for post transformation of the functional group. We will present our results on cross-metathesis transformations of 1,2-epoxy-5-hexene with functional olefins in dimethyl carbonate as green solvent and subsequent transformation into multifunctional building blocks by tandem hydrogenation transformations and epoxide ring-opening.



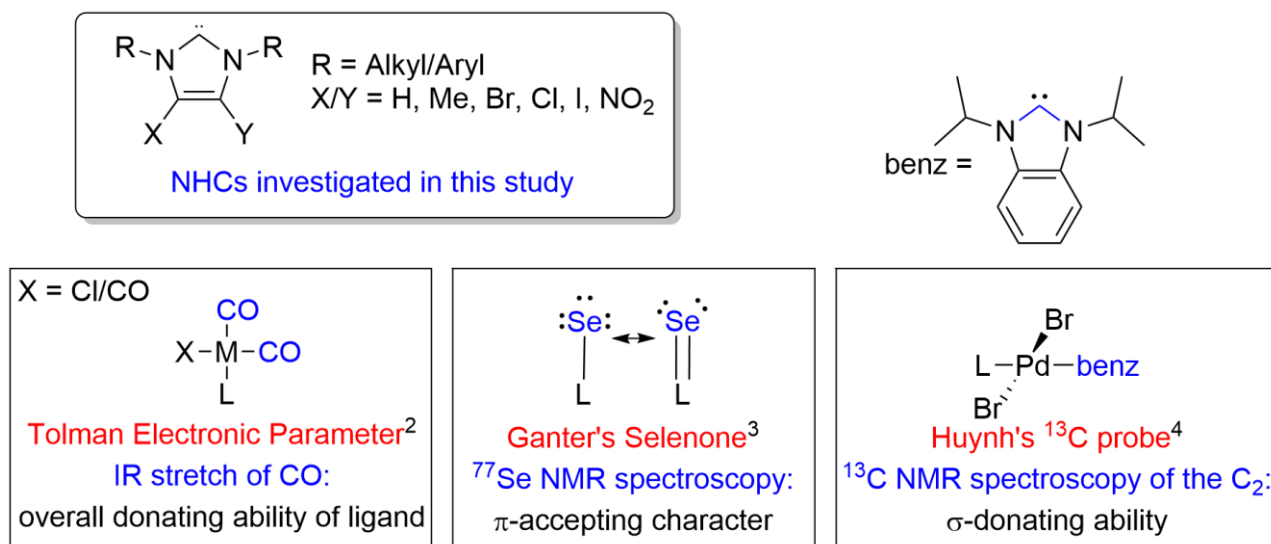
**Figure 1** Sequential transformations

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Control of *N*-heterocyclic carbene propertiesC. D. Barnett,<sup>a</sup> J. B. Harper,<sup>a</sup> M. L. Cole<sup>a</sup><sup>a</sup>University of New South Wales, Sydney,  
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*N*-Heterocyclic carbenes (NHCs) are widely used in chemistry, with numerous applications in organocatalysis and as support ligands for metallo-catalysis. Whilst much effort has been put into the evaluation of steric and electronic properties of NHCs,<sup>1</sup> a systematic evaluation of the effect of these properties on the performance of the NHCs in metallo- and organo- catalysis is lacking. The work that has been done only compares classes of NHC, such as triazolylidene vs imidazolylidene vs thiazolylidene rather than the much finer control that can be achieved through altering substituents. There is also no real emphasis placed on the steric nature of the systems compared, despite the potential importance of sterics on the properties of an NHC.

The study presented here describes the synthesis and stereoelectronic evaluation of a range of 4,5-substituted imidazol-2-ylidene NHCs (Figure, top left). Employing consistent nitrogen substituents (R in Figure), the electronic properties of a wide range of NHCs have been evaluated using a suite of established ligand donor probes (Figure), and NHC steric properties have been quantified through crystallography. Progress made towards improving the understanding of how to control the properties of NHCs, allowing selection of properties desirable in a given organocatalysis, will be described. A methodology has been developed allowing the tuning of the  $\sigma$ -donation and  $\pi$ -acceptor characteristics of the NHC motifs investigated by selection of the *N*-substituents and the 4,5-substituents.



**Figure 1** The techniques used in this study to probe the electronics of NHCs.

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## **Role of Au(III) coordination by chitosan and its N-containing derivatives in mechanism of “green” synthesis of gold nanoparticles**

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Biogenic synthesis of metal nanoparticles attracts an increasing interest due to its compliance with the principles of “green” chemistry, non-toxicity, and biocompatibility of fabricated materials. Among other biopolymers used simultaneously as reducing agents and stabilizers aminopolysaccharide chitosan is particularly favorable for gold nanoparticles synthesis, since, on the one hand, it effectively binds  $[\text{AuCl}_4]^-$  ions, and on the other hand, stabilizes formed nanoparticles due to the high affinity of N-containing functional groups to the surface of metallic gold. In many cases the mechanism of “green” metal reduction is not understood that makes particle size control problematic.

We have shown that complexation of Au(III) ions with chitosan and hydrolysis of adjacent glycoside bond are crucial steps in mechanism of Au(III) reduction to Au(0) in chitosan solution. This suggests that variation of strength of Au(III) complexation with chitosan can be used to control hydrolysis rate and, thus, morphology of gold nanoparticles formed without external reducing agents. Investigations of kinetics of gold nanoparticles formation in solutions of chemically modified chitosan derivatives - N-2-(2-pyridyl)ethylchitosan (2-PEC), N-2-(4-pyridyl)ethylchitosan (4-PEC), and N-(5-methyl-4-imidazolyl)methylchitosan (IMC) have revealed strong dependence of Au(III) reduction rate and size of the gold nanoparticles on polymer-Au(III) complex stability and metal/ligand ratio. It was found that stability of Au(III) complexes changes in the row  $\text{IMC} \gg 4\text{-PEC} > 2\text{-PEC} > \text{chitosan}$ . The higher was the Au(III)-polymer complex stability the smaller gold nanoparticles were obtained. Introduction of imidazole fragments to chitosan allowed fabrication of gold nanoparticles with average size of 2 nm, which exhibit strong luminescence but no plasmon resonance properties and have high catalytic activity.

Financial support from Russian Science Foundation (project № 14-13-00136) is gratefully acknowledged.

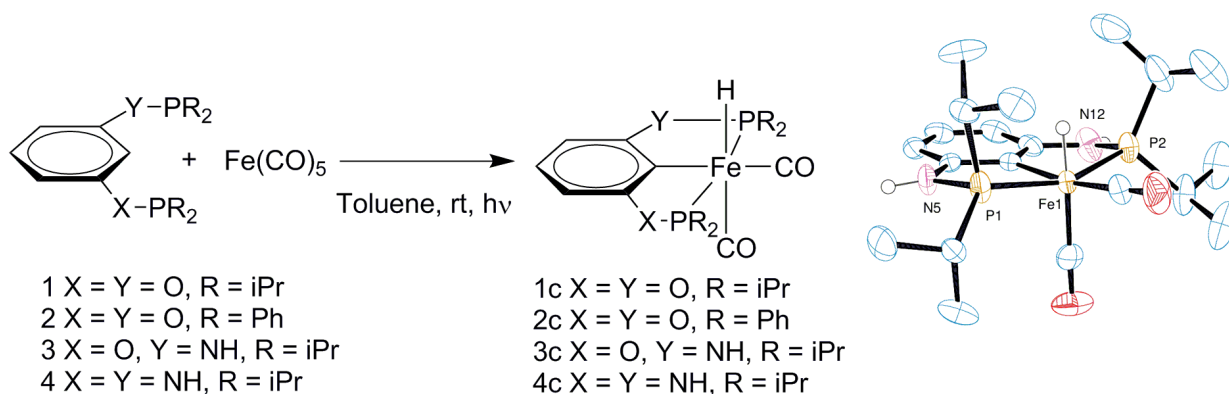
## Iron complexes with anionic PCP pincer ligands

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Cyclometalated complexes with iron are relatively rare compared to cyclometalated complexes based on other late transition metals.<sup>1</sup> The recent development of the orthometalation of imines with  $\text{Fe}(\text{PMe}_3)_4$ ,<sup>2</sup> followed by the extension to iron (0) precursors and related iron (II) precursors ( $\text{Fe}(\text{PMe}_3)_4$ ,  $\text{Fe}(\text{PMe}_2\text{Ph})_4$  and  $\text{Fe}(\text{PMe}_3)_4(\text{Me})_2$ ) allowed the orthometalation of a series of ligands.<sup>3</sup> Herein, a new efficient method based on simple  $\text{Fe}(\text{CO})_5$  metalating reagent has been developed for the straightforward synthesis of well-defined cyclometalated PCP iron carbonyl pincer complexes which have been fully characterized.<sup>4</sup>



**Figure 1** Examples of synthesis of PCP-iron hydride carbonyl complexes

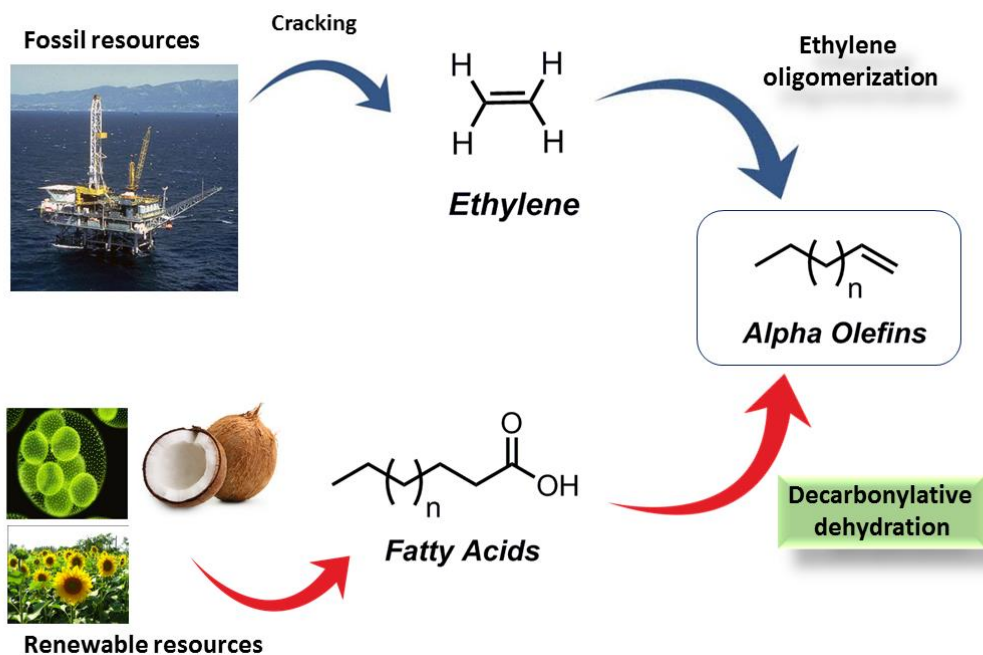
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4. A. Bruneau-Voisine, S. Jiang, S. Quintero-Duque, M. Grellier, S. Sabo-Etienne, C. Darcel, J.-B. Sortais, Submitted results

## New Organometallic Catalyst for Biomass Valorization

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Linear alpha-olefins count among the most important industrial intermediates and are used in the production of polymers and other materials and chemicals. Currently, these olefins are almost exclusively produced from fossil resources. As the world's oil reserves continue to diminish and global warming looms, production of alpha olefins from renewable feedstocks is an important goal. One of the most promising routes in this respect is transition-metal-catalyzed decarbonylative dehydration of fatty acids. However, the decarbonylative dehydration reaction is still poorly understood and the existing catalysts and processes are not efficient enough for industrial implementation.<sup>1-3</sup> Here we present new and more efficient organometallic catalysts for this reaction, catalysts that, under mild conditions, reach higher TOFs and require less phosphine excess than previously reported<sup>1-3</sup> catalysts (Figure 1).



**Figure 1** Synthesis of commodity chemicals from renewable fatty acids.

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# Catalyst Development for Green Oxidation Chemistry

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Traditional oxidants such as  $\text{Cl}_2$ ,  $\text{HOCl}$ , or  $\text{ClO}$  are polluting to the biosphere due to the formation of persistent organochloride pollutants on reaction with organic material. These organic pollutants can be bio-accumulative, and act as potent endocrine disruptors.<sup>1</sup> Therefore, there is an increasing need to design and develop more selective, greener oxidation systems that can replace those that use these traditional oxidants. The research being pursued focuses upon the development of new efficient green catalysts for the oxidation of organic compounds with hydrogen peroxide. The design of these catalysts is based on the reported iron-tetraamido macrocyclic ligand complexes (Fe-TAMLs, Figure 1). They are designed to activate hydrogen peroxide towards the oxidation of substrates via the formation of high oxidation state iron centres, therefore paving the way for hydrogen peroxide to be used as an environmentally friendly oxidant.<sup>2</sup>

This research looks at enhancing the catalytic properties of Fe-TAMLs through changes to the ring systems to influence in a rational way the overall electron donating/withdrawing effects of the nitrogen donors as well as the overall electrostatic charge of the iron complex (Figure 2). Details of progress towards synthesising new complexes of this type will be presented along with preliminary studies of the ability of the new compounds to catalyse oxidations with hydrogen peroxide and the possibility of anchoring the target catalyst onto solid support systems.

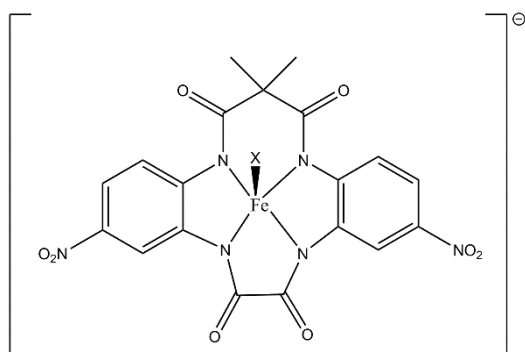


Figure 1: Fe-D\*

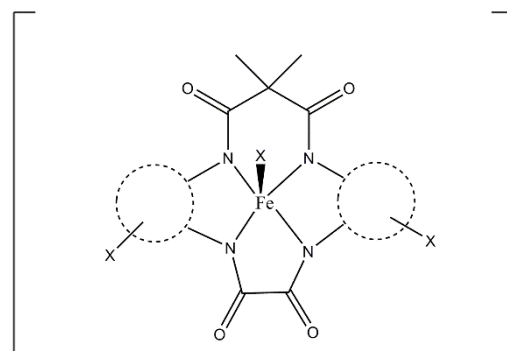


Figure 2: Target Catalyst

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## Synthesis of fluorinated polyheteroaromatic through palladium catalyzed iterative C(sp<sup>2</sup>)-H bonds Arylations

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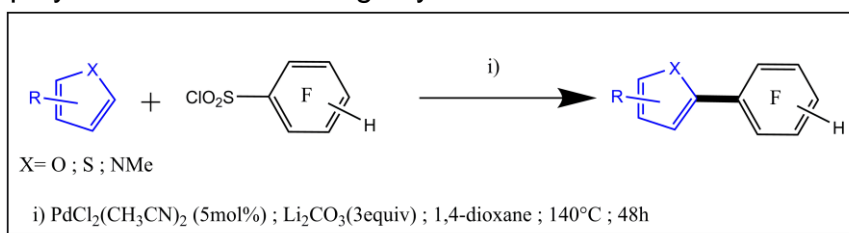
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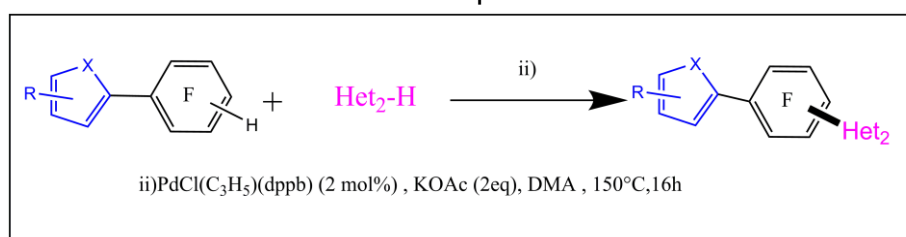
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Palladium-catalyzed direct C-H bonds arylation has appeared as one of the most reliable and straightforward protocols towards the synthesis of poly(hetero)arenes in high yields in only a few steps with the respect of the environment.

We have developed a new strategy for the synthesis of fluorinated  $\pi$ -conjugated oligomers involving palladium-catalyzed iterative C-H bonds arylations. Palladium-catalyzed desulfitative arylation of heteroarenes using  $\text{PdCl}_2(\text{CH}_3\text{CN})_2$  and fluorinated benzosulfonyl chloride as the aryl sources allowed in a first step the synthesis of heteroarylated polyfluorobenzenes in high yields.<sup>1</sup>



The direct desulfitative arylation allowed the regioselective arylation of thiophene and benzothiophene respectively at C3 or C4 positions, which are challenging positions to functionalize using aryl bromide as the coupling partners.<sup>1</sup> The next steps involved direct regioselective arylation with aryl bromides using  $\text{PdCl}(\text{C}_3\text{H}_5)(\text{dppb})$  as catalyst to deliver the desired triad or tetrad heteroaromatic compounds.<sup>1</sup>



In summary, we have developed an efficient synthesis of complex heteroaryl triads and tetrads through palladium-catalyzed iterative direct arylations. Tri-, di-, and monofluorophenyl substituted heteroarenes were synthesized in high yields and high regioselectivities through a desulfitative direct arylation of several heteroarenes using fluorinated arylsulfonyl chlorides.

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# Catalysed C-H bond activation/functionalization in water

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Ruthenium(II) catalysts associated to a carboxylate partner are able to promote the selective  $sp^2$  C-H bond activation of functional arenes and heterocycles to selectively lead to cross-couplings from heteroaromatic halides via C-H bond deprotonation.<sup>1,2</sup> It is possible now to show that such processes, due to the stability of both Ru(II) species in water, can be performed in water as renewable solvent without surfactant and with higher catalyst activity.<sup>3,4</sup>

It will be shown that

- i) this catalytic  $sp^2$  C-H bond activation in water can be applied to the functionalisation of imines and the synthesis of polydentate ligands containing nitrogen coordinating groups,<sup>5</sup>
- ii) water solvent favours selective monoarylation thus allowing sequential mixed arylation or successive monoarylation and alkenylation,<sup>5</sup> and that
- iii) catalytic annulation of heterocycles with alkynes in water can lead to the synthesis of pyrrole and indole fused isocoumarins.<sup>5</sup>

New perspectives of C-H bond functionalisation in water will be pointed out

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## Biomimetic catalyst design based on the structural model of carbonic anhydrase

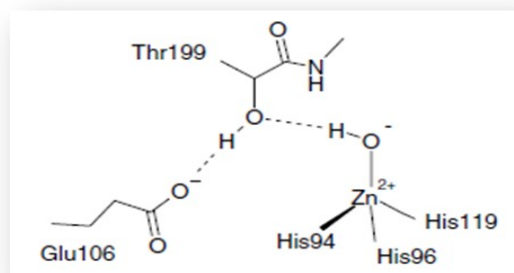
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Targeting low temperature and efficient processes for CO<sub>2</sub> activation, led us to a bio-inspired approach using the structural and functional model of the carbonic anhydrase, a metalloenzyme that is involved in the breathing mechanism <sup>1</sup>.



**Figure 1:** Active center of carbonic anhydrase: His = Histidine, Thr = Threonine et Glu = Glutamic acid.

Analogue counterparts of the enzyme active site are proposed here, using mesoporous silica <sup>2</sup> to mimic the enzymatic cavity and the molecular stencil patterning method <sup>3</sup> to isolate a tethered polyamine ligand using a monopodal silane (Trimethylsilyl) before its complexation by divalent metals (Zn<sup>2+</sup> and Cu<sup>2+</sup>). The structural and textural properties of the different materials were investigated using various techniques. Also, carbon dioxide adsorption behaviors on different catalysts were investigated.

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## Design and preparation of recyclable nano-catalysts

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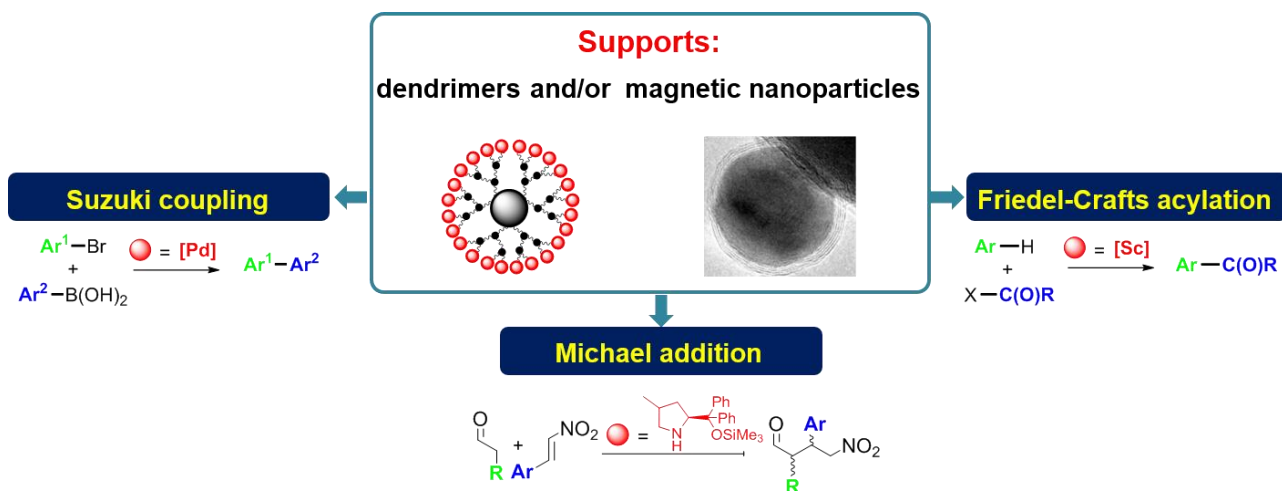
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The development of efficient and eco-compatible catalytic systems enabling the preparation of organic compounds is of great concern.

One possible approach to reach this objective consists in rendering the catalysts recyclable by grafting them onto nanometric supports. Here we report the preparation of several supported nano-catalysts<sup>1-4</sup> involving either dendrimers<sup>5</sup> or magnetic nanoparticles as the supports, as well as their applications in various reactions (examples in Figure 1). Besides their high activity and recyclability, some of the reported systems are moreover able to avoid metal leaching contrary to their corresponding molecular counterparts, thus allowing to prepare organic products free from metal traces.



For all examples: until 12 consecutive uses - recycling by precipitation or with a magnet

**Figure 1** Some applications of nano-sized metal-based or organo-catalysts

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- 5 hyperbranched and perfectly defined nano-sized polymers: a) A.-M. Caminade, A. Ouali, R. Laurent, C.-O. Turrin, J.-P. Majoral, *Coord. Chem. Rev.*, **2016**, 308, 478. b) *ibid*, *Chem. Soc. Rev.*, **2015**, 44, 3890. c) A.-M. Caminade, S. Fruchon, C.-O. Turrin, M. Poupot, A. Ouali, A. Maraval, M. Garzoni, M. Maly, V. Furer, V. Kovalenko, J.-P. Majoral, G. M. Pavan, R. Poupot, *Nature Commun.*, **2015**, DOI: 10.1038/ncomms8722.

# CO<sub>2</sub> Capture and Conversion using Functionalized Fibrous Nanosilica (KCC-1): Insights into the Effect of Silica Morphology

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CO<sub>2</sub> emissions need to be tackled urgently to avoid potentially dangerous climate change, which may not be reversible afterwards. To mitigate the emission, CO<sub>2</sub> capture and conversion is one of the best solution. In this regard, our recently discovered fibrous nanosilica (KCC-1) can yield efficient CO<sub>2</sub> sorbents due to their high surface area and unique fibrous morphology.<sup>1</sup> Such fibrous morphology observed in KCC-1 has not been seen before in silica materials and showed excellent catalytic activities.<sup>1-9</sup> In this work, we have synthesised hybrid nanomaterials by functionalization of KCC-1 for efficient CO<sub>2</sub> capture. Functionalization was achieved by simple physisorption of various amine molecules on KCC-1 as well as by their covalent attachment with silanols on KCC-1 surface. Their CO<sub>2</sub> capture efficiency was studied using various parameters such as CO<sub>2</sub> capture capacity, kinetics of adsorption, stability of the sorbent, and regeneration-reuse. Best of the KCC-1 sorbents was compared with its MCM-41 counterpart. KCC-1 based sorbents was found far better in terms of CO<sub>2</sub> capture capacity, rate of adsorption and stability. Improved performance of KCC-1 based sorbents was due to the unique fibrous morphology of KCC-1, accessible surface area and pore volume, which was retained even after functionalization.<sup>10</sup> We have also designed KCC-1 based hybrid system to capture and convert CO<sub>2</sub> in one pot.

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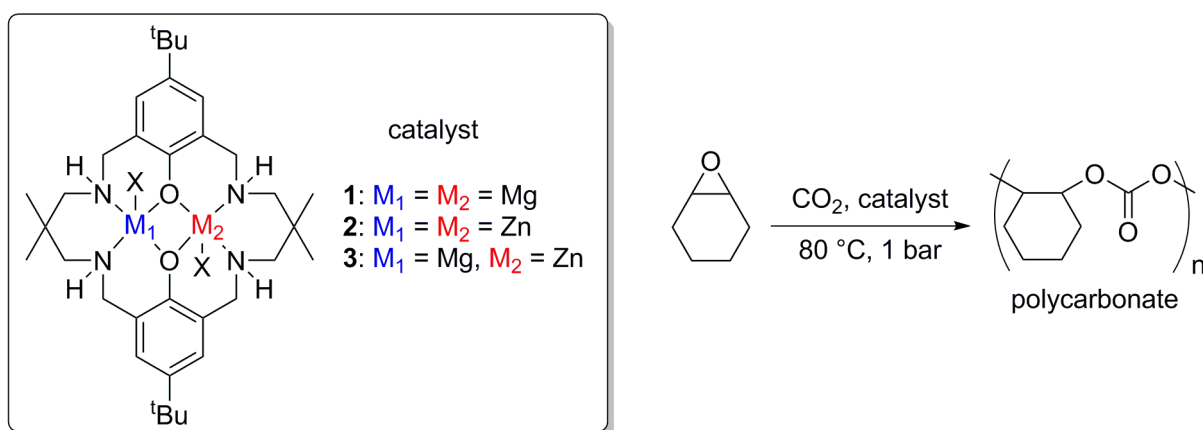
# CO<sub>2</sub>/Epoxide Copolymerization: Novel Heterodinuclear Catalysts and Mechanistic Investigations

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The ring opening copolymerization (ROCOP) of epoxides with CO<sub>2</sub> provides a promising route to the synthesis of renewable polycarbonates (and polyurethanes) which adds value to captured CO<sub>2</sub>.<sup>1</sup> Previous work in the field has focused on mononuclear or homodinuclear catalysts, most of which operate at high CO<sub>2</sub> pressures. The development of active catalysts for CO<sub>2</sub>-epoxide ROCOP, under reduced CO<sub>2</sub> pressures, is therefore highly desirable.

It has recently been shown that heterodinuclear catalysts can increase the activity of epoxide-anhydride ROCOP by up to 40 times in comparison to their homodinuclear analogues and these catalysts are highly active for CO<sub>2</sub>-epoxide copolymerization under low (1 bar) CO<sub>2</sub> pressures.<sup>2,3</sup> This presentation will discuss the synthesis, characterization and copolymerization reactions of novel heterodinuclear catalysts for CO<sub>2</sub>-cyclohexene oxide ROCOP, focusing on magnesium and zinc complexes (Figure 1). Kinetic investigations for the heterodinuclear and homodinuclear systems will also be illustrated to provide mechanistic insights.



**Figure 1.** Homo- and heterodinuclear catalysts for CO<sub>2</sub>-cyclohexene oxide ROCOP.

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## Water Purification Using a Green Chemistry Approach

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As the world's population increases and industrial and agricultural activities intensify, the availability of clean water is becoming a rapidly growing global problem.<sup>1</sup> The increasing shortage of clean water has already necessitated the widespread adoption of water reuse and recycling.<sup>2</sup> In these situations, the need for removal of trace contaminants such as pesticides, herbicides, active pharmaceutical ingredients, personal care products and endocrine disruptors is particularly important. While various technologies are available such as filtration, ozone, UV and chemical dosing, there are various drawbacks of each including cost, lack of specificity to contaminants, and issues with residual chemicals.<sup>3</sup>

We have developed an innovative smart film that enables the efficient removal of dilute organic pollutants in large volumes of water by catalytic oxidative destruction. Purification is achieved as the water simply runs over the surface of the new material. The system eliminates the need to dose (and hence contaminate) the water to be purified with chemical oxidants or catalysts. In preliminary experiments we have demonstrated that a wide range of harmful organic pollutants including EE2, triclosan and BPA can be successfully removed by this technology. Details of the synthesis of the new film, the chemistry behind the way it operates and details of how it performs will be presented.

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## $\pi$ -Complexes of Copper(I) with the Aromatic Rings catalyzed oxidation of Phenol with atmospheric Oxygen

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Phenol and phenol derivatives are carcinogens, and their presence in wastewater, even at small concentrations, is therefore a major concern.

The apparent stability constants of the complexes of Cu(I)<sub>aq</sub> with several aromatic compounds have been published<sup>1</sup>.

From the experimental published results (N.M.R, E.S.R, UV-vis and electrochemistry) it is clear that the complexes formed are due to  $d \rightarrow \pi^*$  interactions between the copper d orbital's and the aromatic  $\pi$  system.

It seems that these kind of complexes resemble an excited state of the aromatic system due to charge transfer from the bonding orbital of the aromatic system to the Cu<sup>+</sup>, and back donation to the  $\pi^*$  anti bonding of the aromatic system.

The finding that Cu<sup>+</sup><sub>(aq)</sub> forms  $d \rightarrow \pi^*$  complexes with aromatic compounds might explain the catalytic activity of copper(I) in copper catalyzed oxidation of aromatic compounds. The complex Cu(I)-Phenol in aqueous solutions react with molecular oxygen to form highly active intermediate that oxidize the phenol<sup>2</sup>.

The reaction was monitored by HPLC and UV-Vis spectroscopy.

This finding approves previous results that proposed mechanism for the Ullmann Reaction that involve formation of Cu(I) Aromatic ring complex in first stage<sup>3</sup>.

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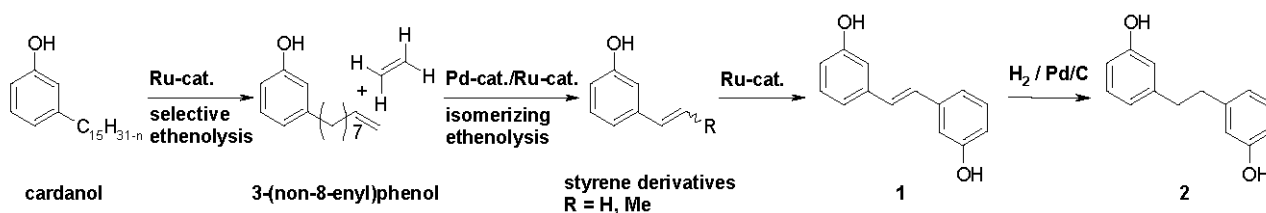
## Polymer building blocks from cashew nut waste

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Isomerizing olefin metathesis recently emerged as a valuable tool for the valorization of renewables.<sup>1</sup> In the presence of a bimetallic palladium / ruthenium catalyst system, fatty acids are converted into industrially useful olefinic blends with a tunable chain length distribution<sup>2</sup>. A similar synthetic approach was successfully applied in the synthesis of valuable styrenes from naturally occurring allylarenes<sup>3</sup> and in the synthesis of tsetse fly attractants from cashew nut shell liquid (CNSL).<sup>4</sup>

CNSL is an inedible waste by-product of cashew nut processing and it is an excellent example of a renewable resource for which no competition occurs between land use for food or raw materials.<sup>5</sup> Technical CNSL consists mainly of cardanol, a mixture of phenols with a side chain containing a varying degree of unsaturation. Starting from cardanol, we have developed a synthesis of polymer building blocks with isomerizing metathesis as the key step. After a selective ethenolysis delivering 3-(non-8-enyl)phenol, the isomerizing ethenolysis furnishes a mixture of styrene derivatives. A subsequent self- and / or cross-metathesis of this mixture leads to the 3,3'-hydroxystilbene **1** and, after hydrogenation, **2**. Stilbene derivatives have been frequently employed in the synthesis of polymers,<sup>6</sup> therefore building blocks **1** and **2**, used either in polycarbonate synthesis or thiol-ene polymerization, represent sustainable alternatives to ill-reputed bisphenol A.<sup>7</sup>



**Figure 1:** Synthesis of polymer precursors from cardanol

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## Catalytic transformations of carbohydrate-derived platform chemicals

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The sustainable utilisation of biomass as a renewable source of raw materials is a domain of strong economical and environmental interest in a context of fossil resource shortage.<sup>[1]</sup> Catalytic transformations of renewables have been reported for the production of derivatives with a broad scope of applications ranging from raw chemicals to polymer precursors and fine chemicals.<sup>[2]</sup> In continuation of our researches in the field of the catalytic transformation of fats and oils<sup>[3]</sup> we are now exploring catalytic processes for the transformation of platform chemicals arising from carbohydrates and we will present our recent results on catalytic transformations of levulinic acid.

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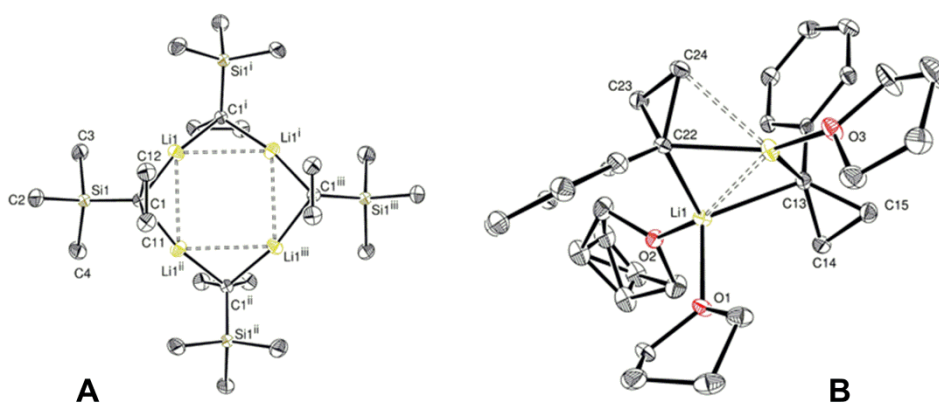
## Cyclopropyl derivatives of s-block metals

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Organolithium compounds are amongst the most used reagents in organic chemistry.<sup>1</sup> However, isolation and characterization of these species can be difficult due to their lability and oxophilicity. Although known for more than 50 years, cyclopropyllithium  $\text{Li}(c\text{-C}_3\text{H}_5)$  has never been fully characterized.<sup>2,3</sup> Beyond its use in synthesis, the cyclopropyl moiety is of interest due to its ability to engage in rare CC, rather than CH, agostic distortions when interacting with strongly electropositive metals.<sup>4,5</sup> Furthermore, while only a few organocalcium compounds have been prepared,<sup>6</sup> cyclopropyl calcium complexes are also anticipated to engage in similar CC agostic interactions.

The new 1-(trimethylsilyl)cyclopropyllithium (**A**) and 1-phenylcyclopropyllithium (**B**) were synthesized and characterized (XRD structures in figure 1). Compound B is the first example of an organolithium compound bearing a CC agostic distortion. Interestingly, this complex is not symmetric, with a CC agostic distortion occupying the coordination site of a THF molecule on a tricoordinate  $\text{Li}^+$ . Preliminary results on the synthesis of  $\text{Ca}(c\text{-C}_3\text{H}_5)(\text{I})(\text{THP})_n$  will also be presented.



**Figure 1** XRD structures of compounds A and B

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## Activation of methane at an unsaturated niobium center

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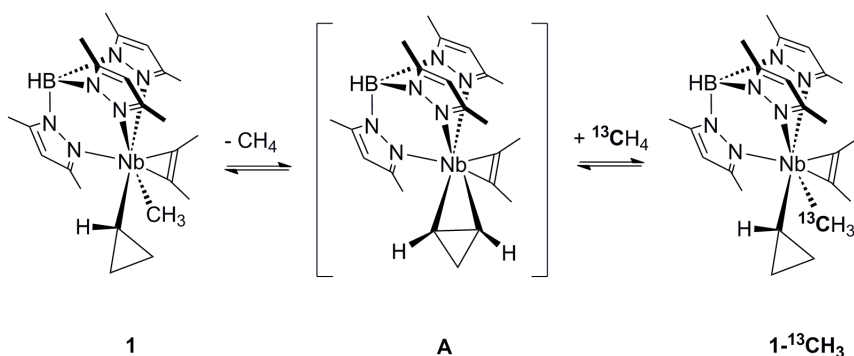
<sup>b</sup> Université de Toulouse; UPS, INPT; LCC; F-31077 Toulouse Cedex 4, France.

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Despite unabated efforts, efficient catalytic functionalization of methane by soluble metal complexes remains a long term goal on scientific, environmental and economic grounds.<sup>1</sup> Early transition metal complexes activate methane by either  $\sigma$ -bond metathesis<sup>2</sup> or 1,2-CH addition across an unsaturated M=NR (imido)<sup>3</sup> or M $\equiv$ CR (alkylidyne) bond.<sup>3</sup>

In this presentation, we report on mechanistic investigations of CH<sub>4</sub> activation by a transient unsaturated  $\eta^2$ -cyclopropene / metallabicyclobutane complex of niobium stabilized by hydrotris(pyrazolyl)borate and alkyne ligands [Tp<sup>Me2</sup>Nb( $\eta^2$ -c-C<sub>3</sub>H<sub>4</sub>)(MeCCMe)] (**A**). Isotopic labelling together with high pressure NMR and kinetic studies are used to elucidate the mechanism of the degenerate exchange of methane with [Tp<sup>Me2</sup>NbCH<sub>3</sub>(c-C<sub>3</sub>H<sub>5</sub>)(MeCCMe)] via intermediate **A**. Productive methane activation is also realized from the mesityl complex that reacts with CH<sub>4</sub> to give the methyl complex. It is the second example of methane example of methane activation via a 1,3-CH addition.<sup>4,5</sup>



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## Development of Dicopper Complexes as a Cathode Catalyst for Polymer Electrolyte Fuel Cell: Control of the Redox Potential

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A polymer electrolyte fuel cell (PEFC) is a method to convert chemical energy for the reaction between H<sub>2</sub> and O<sub>2</sub> molecules into electrical energy. The best catalyst for the cathode electrode is platinum metal. However, the high cost of platinum provides a strong motivation for development of less expensive alternatives. Laccases are multi-copper proteins having four copper ions in the active site, and efficiently catalyze four-electron reduction of O<sub>2</sub>-molecule. However, it is quite difficult to apply laccase as the cathode catalyst of PEFC because it only works in a neutral aqueous solution.

We have developed a bis-tmpa type dinucleating ligand 6-hpa having two tmpa units connected by a -CH<sub>2</sub>CH<sub>2</sub>- tether, which specifically stabilizes dimetal complexes.<sup>1</sup> It forms dicopper complex [Cu<sub>2</sub>(μ-OH)(6-hpa)](ClO<sub>4</sub>)<sub>3</sub> (**1**), which shows relatively high redox potential of Cu(I)/Cu(II), and accelerated the four-electron reduction of O<sub>2</sub>. Here, we report formation of end-on peroxodicopper(II) complex upon reaction of the dicopper(I) complex stabilized by 6-hpa with O<sub>2</sub>, and efficient four-electron reduction of O<sub>2</sub> toward application as a cathode catalyst of PEFC. Moreover, we synthesized a new dinucleating ligand 6-hpea shown in Figure 2, which has two pmap units. It forms dicopper complex [Cu<sub>2</sub>(6-hpea)](ClO<sub>4</sub>)<sub>4</sub> (**2**). The redox properties, formation of peroxy species, and four-electron reduction of O<sub>2</sub> are presented.

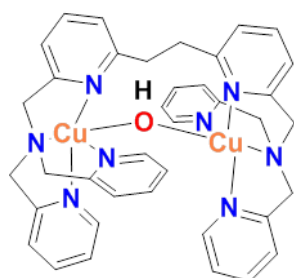


Figure 1 [Cu<sub>2</sub>(μ-OH)(6-hpa)](ClO<sub>4</sub>)<sub>3</sub>

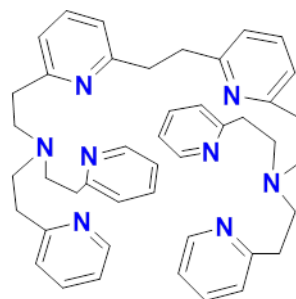


Figure 2 Structure of 6-hpea

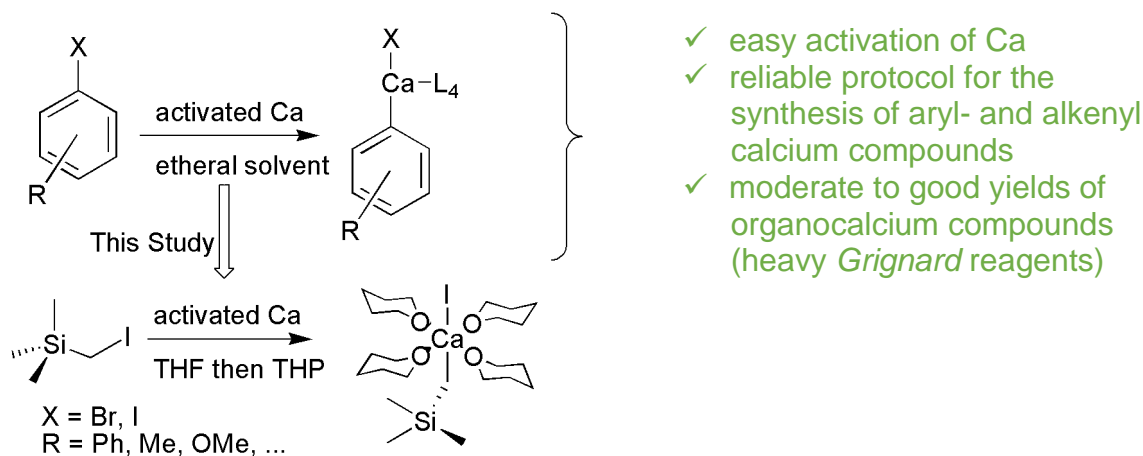
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## Extending the Limit: *Grignard*-Analogous Synthesis of Substituted Alkylcalcium Compounds

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Since *V. Grignard* has developed organomagnesium compounds at the end of the 19<sup>th</sup> century, these reagents have been established in a wide field of organic and organometallic chemistry. In contrast, the chemistry of the heavier analogs, calcium, strontium and barium, with the exception of the cyclopentadienyl derivative, has remained underdeveloped. On the one hand, the inexpensive and easy synthesis of *Grignard* compounds is attractive; on the other hand, the enormous discrepancy of the inertness of the heavier alkaline earth metals and the extremely high reactivity of their organometallics hampered a vast development. Nevertheless, successful attempts via salt metathesis and co-condensation of metal and substrate were developed [1].



Recently we were able to develop a routine protocol, including activation of the calcium metal as well as use of etheral solvents, which allows the direct synthesis of aryl- and alkenyl calcium halides with Ca-C  $\sigma$ -bonds to  $\text{sp}^2$ -hybridized carbons [2]. Recently, we used a modified protocol to reduce even (chloro/iodo-methyl)trimethylsilane [3].

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## Group 4 Metal Cationic Complexes with Bifunctional Ligands – Preparation and Reactivity

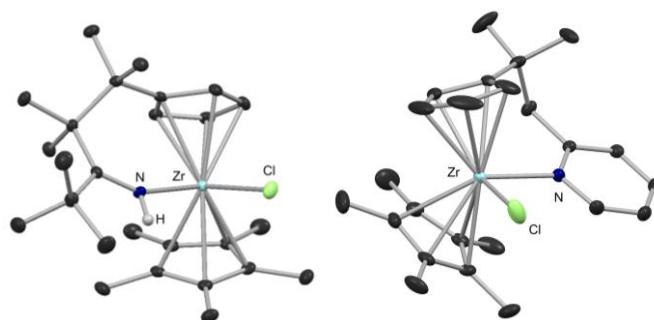
M. Večeřa,<sup>a</sup> V. Varga,<sup>a</sup> R. Gyepes,<sup>a,b</sup> J. Pinkas,<sup>a</sup> M. Horáček,<sup>a</sup> M. Lamač,<sup>a,\*</sup>

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Our previous work focused on transformations of functional moieties attached to group 4 metal complexes,<sup>1,2</sup> including conversion of the nitrile group into a ketimide moiety.<sup>2b</sup> We have recently introduced a new type of versatile bifunctional cyclopentadienyl-ketimide ligand.<sup>3</sup> Complexes of these ligands featuring group 4 elements were investigated in ethylene polymerization catalysis. Herein, we would like to report on the preparation of cationic species generated from functionalized group 4 bent metallocene complexes by different approaches (e.g., protonation of a bound ketimide or abstraction of a chloride anion from the metal center). Several types of starting complexes bearing predominantly tethered nitrogen-donor groups were synthesized and the formation of cationic species was investigated as well as their subsequent reactivity as Lewis acid-base pairs.



**Figure 1** Solid-state structures of cationic zirconocene complexes with coordinated imine (left) or pyridine (right) pendant moieties. The  $[B(C_6F_5)_4]^-$  anions are omitted.

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<sup>3</sup> M. Večeřa, V. Varga, I. Císařová, J. Pinkas, P. Kucharczyk, V. Sedlářík, M. Lamač, submitted manuscript.

# Single-component allyl *ansa*-lanthanidocenes catalysts for highly syndioselective polymerization of styrene

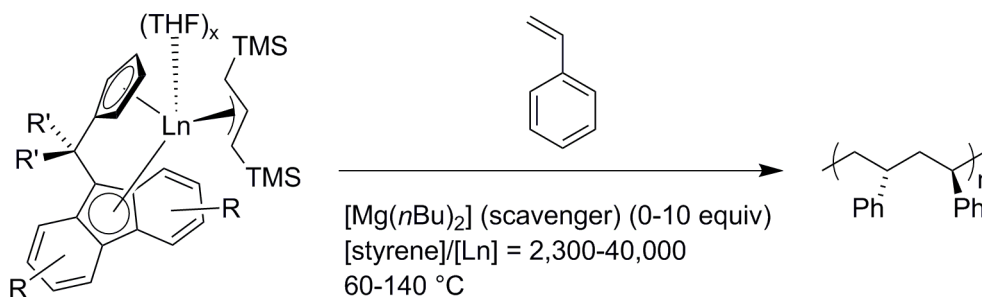
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Since its discovery in 1985, syndiospecific polymerization of styrene has been extensively investigated and wide range of Group 4 metals based catalytic systems (in combination with MAO or with molecular activators) has been developed.<sup>1</sup> On the other hand, very few examples of highly syndioselective *single-component* Group 3 based catalysts have been disclosed so far. Our group has reported that the allyl neodymium complex  $[(\text{Cp-CMe}_2\text{-Flu})\text{Nd}(\text{C}_3\text{H}_5)(\text{THF})]$  is an active and highly syndioselective ( $[\text{r}]^6 > 99\%$ ,  $T_m = 250\text{-}270\text{ }^\circ\text{C}$ ) catalyst for styrene polymerization.<sup>2</sup> In this contribution, we report new modifications of such catalysts that are aimed at improving the catalytic performances.

Thus, a new series of allyl *ansa*-lanthanidocenes complexes incorporating modified  $\{\text{Cp/Flu}\}$  ligands and metal centers have been synthesized and scrutinized in styrene polymerization (Figure 1). The influence of the ligand substitution and the nature of the metal center on catalytic performances as well as the polymer properties will be discussed.



**Figure 1** Syndioselective polymerization of styrene catalyzed by allyl *ansa*-lanthanidocenes complexes

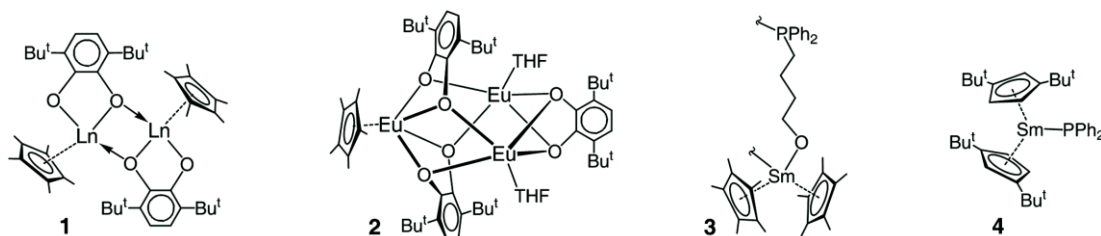
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## Metal- and ligand-assisted reduction by lanthanocenes (Sm, Yb, Eu): influence of solvent, sterical and electronic factors

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Lanthanocenes of the formula  $\text{LnCp}^x_2\text{L}$  ( $\text{Ln}$  = lanthanide ion 2+ or 3+;  $\text{Cp}^x$  = substituted cyclopentadienide;  $\text{L}$  = additional ligand(s)) are „classical“ organometallic species, largely studied in the field of organolanthanide chemistry for interesting structural, catalytical, and magnetic properties. We studied the reductive interactions of lanthanocene(II) complexes  $\text{LnCp}^*_2(\text{thf})_n$  (Sm, Yb, Eu) and  $\text{SmCp}''(\text{thf})$  ( $\text{Cp}'' = \text{C}_5\text{H}_3\text{Bu}^t_2$ ) with two series of substrates. First, with the redox-active ligand 3,6-di(*t*-butyl)-*o*-benzoquinone (dbbq),<sup>1</sup> which can act as 1 or 2-electron oxidant, and is reduced to the catechololate (dbcat, 2-) state, accompanied by the oxidation of  $\text{Ln}^{2+}$  to  $\text{Ln}^{3+}$  and  $\text{Cp}^{*-}$  to  $\text{Cp}^*_2$ . For Sm and Yb, the dimeric complexes  $[\text{LnCp}^*(\text{dbcat})]_2$  are formed (**1**). For Eu, the increase of  $\text{Eu}^{2+/3+}$  potential leads to the formation of mixed-valence trinuclear complex  $[(\text{EuCp}^*)(\text{Eu}(\text{thf}))_2(\text{dbcat})_3]$  (**2**) with  $2\text{Eu}^{2+} + \text{Eu}^{3+}$  ions. Interestingly, the reaction media greatly influences the latter interaction: in a coordinative solvent (thf) the ligand is reduced only to the semiquinolate (dbsq, 1-) state. Second, the reaction of samarocenes of different sterical bulk with diphosphine  $\text{P}_2\text{Ph}_4$  leads to reduction of the latter to the phosphido ( $\text{PPh}_2^-$ ) anion, thus forming either solvated ( $\text{SmCp}^*_2(\text{PPh}_2)(\text{thf})$ , which is further transformed to a coordination polymer  $[\text{SmCp}^*_2(\mu\text{-O}(\text{CH}_2)_4\text{PPh}_2)]_n$  (**3**) by ring opening of thf) or solvent-free complexes ( $\text{SmCp}''_2(\text{PPh}_2)$ , **4**), depending on the steric bulk of the  $\text{Cp}^x$  ligand. Again, the role of the solvent is very important, for the complex **4** being not formed in thf but only in unpolar solvents. All the major factors governing these redox processes are discussed.



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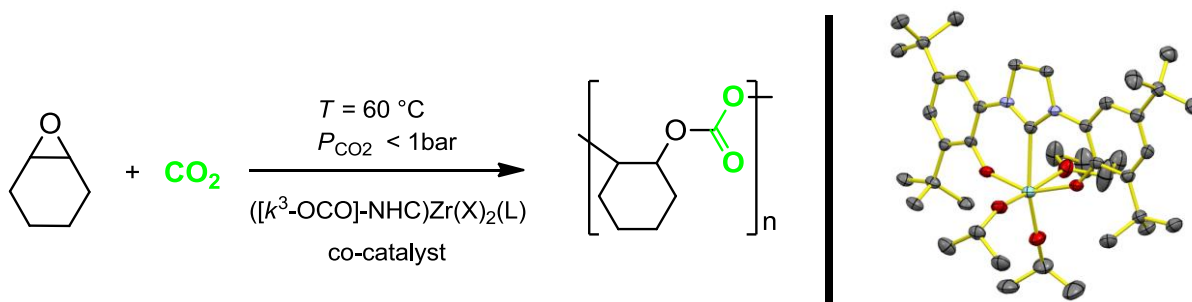


## Copolymerization of cyclohexene oxide with CO<sub>2</sub> Catalyzed by *N*-Heterocyclic Carbene Zirconium Complexes

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Since the first report of zinc catalysts for the copolymerization of epoxides/CO<sub>2</sub>,<sup>1</sup> the pursuit of a molecular catalyst able to copolymerize epoxides with CO<sub>2</sub> has been an area of intense research.<sup>2</sup> To date, a variety of efficient catalysts for the copolymerization of epoxides with CO<sub>2</sub> have been reported.<sup>2</sup> In 2011, Nozaki and co-workers were the first group to report active and highly selective catalysts based on tetravalent metals (Ti, Zr, Ge and Sn) for the copolymerization of epoxides/CO<sub>2</sub>.<sup>3</sup> Later, our research group reported the use of bisphenolate *mer*-tridentate *N*-heterocyclic carbene ( $\kappa^3$ -[OCO]-NHC) pincer ligand combined with tetravalent titanium metal as catalyst for the copolymerization of cyclohexene oxide (CHO) with CO<sub>2</sub>.<sup>4</sup>



**Figure 1** NHC Zr(IV) complexes catalyzing CO<sub>2</sub>/CHO copolymerization

Following this lead, a series of ( $\kappa^3$ -[OCO]-NHC)zirconium(IV) complexes<sup>5</sup> were synthesized and were tested as catalyst for the copolymerization of CHO with CO<sub>2</sub> (Fig. 1). All tetravalent zirconium precatalysts showed moderate activity under mild conditions and gave high selectivity in alternating copolymer.

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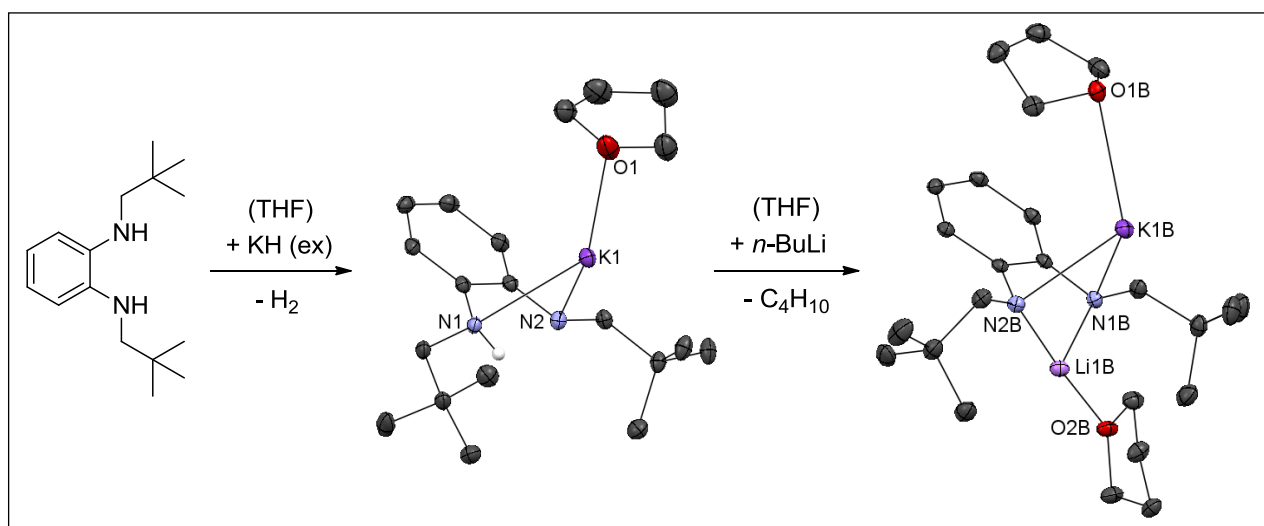
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## Hydrofunctionalization with s-Block-Metal Catalysts

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Hydrofunctionalization (hydroelementation, addition of H–E fragments [E = N, P] to alkynes and heterocumulenes) represents an atom efficient way to generate amines and phosphanes and related molecules. Due to the fact that this reaction is entropically unfavored and that electron-rich multiple bonds have to react with Lewis bases, a catalyst is required. For the catalysis, especially heavy s-block-metals such as potassium and calcium gained tremendous interest in recent years.<sup>[1]</sup> Especially calcium seems to be attractive because it is worldwide available, inexpensive, non-toxic and represents a strong Lewis acid. The calcium-based catalysts represent amides, phosphanides and phosphinites that are available via metalation, transamination, transmetalation, and metathetical approaches. We could demonstrate that amides<sup>[2]</sup> and phosphanides<sup>[3]</sup> of potassium and calcium and other s-block-metals are suitable catalysts for hydroelementation reactions. Recently, we also investigated the structures of *ortho*-phenylene diamides of potassium and heterobimetallic lithium/potassium derivatives (see figure 1).<sup>[2]</sup>



**Figure 1** Synthesis and molecular structures of metalated *ortho*-phenylene diamines

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## Design Approaches to Blue and White Light Emitting Gold(III) Complexes

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Transition metal complexes exhibiting interesting luminescent properties have been extensively investigated for applications in phosphorescent organic light emitting devices (PHOLEDs).<sup>1</sup> Gold(III) complexes have been gaining increasing attention for their emission properties.<sup>2</sup> Recently, our group has demonstrated stable complexes based on monocyclometalated gold(III) structural motif display emission properties that rival the isoelectronic platinum(II) complexes.<sup>3</sup> Utilizing a rational design approach, we have been able to render gold(III) complexes with blue and white light emission properties that has been previously unprecedented.<sup>4</sup> These complexes have been characterized by detailed photophysical studies and selected complexes by fabrication of devices. The tailored novel luminescent properties opens up further possibilities of applications of gold(III) complexes in light-emitting devices.

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## Functionalization of nanostructured silicon surfaces with luminescent lanthanide complexes

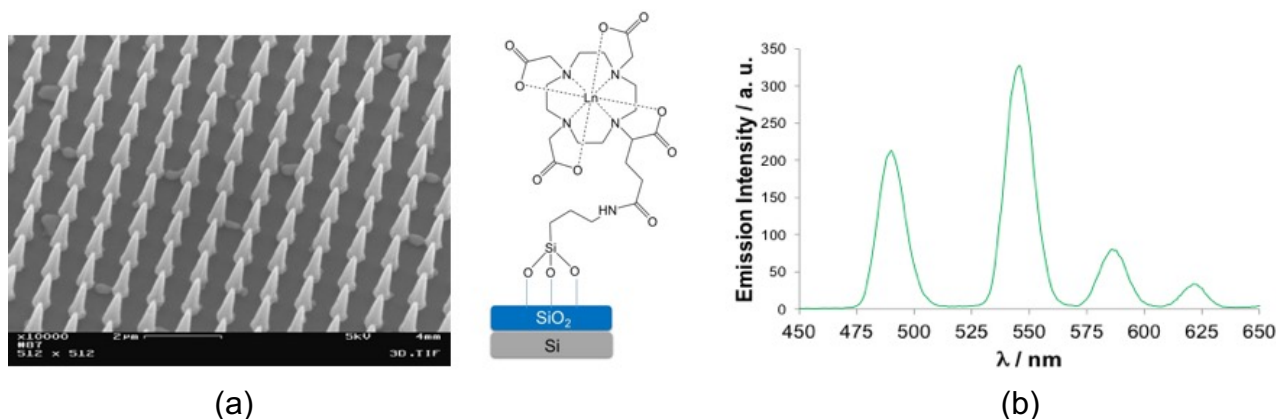
B. K. Bahuleyan,<sup>a</sup> S. Thomas,<sup>b</sup> A. Gwiazda,<sup>c</sup> M. Stoffel,<sup>d</sup> H. Rinnert,<sup>d</sup> G. Lerondel,<sup>c</sup> M. Molinari,<sup>b</sup> F. Chuburu,<sup>a</sup> J. Mallet,<sup>b</sup> C. Cadiou<sup>a\*</sup>

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In this presentation, we will describe the results of a study concerning the covalent anchoring of luminescent lanthanide complexes onto nanostructured silicon surfaces. The aim of this work is to design new sensors for gases based on the following principle: an alteration of the optical signal should occur when the analyte is in contact with the modified solid substrate.

The nanostructuring of Si wafer into an array of nanocones has been achieved by a two-step process combining Interferential optical Lithography and dry Reactive Ion Etching of the Si substrate.<sup>1</sup> Lanthanide complexes were designed in order to show reactivity towards the silica layer that covers the surface of the silicon.<sup>2,3,4</sup> The following figure shows an example of the results obtained with a terbium(III) complex:



**Figure 1** SEM (a) and luminescence (b) of Si nanocones functionalized with a Tb<sup>III</sup> complex

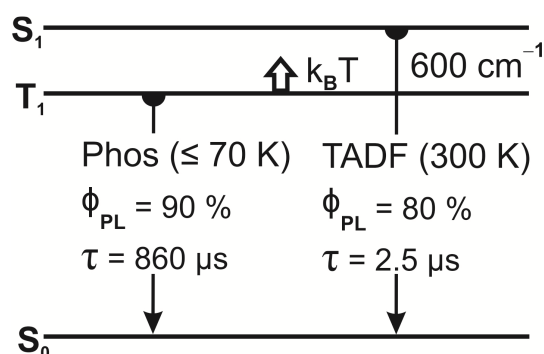
The preparation of the nanostructured surfaces, the synthesis of the ligands and lanthanide complexes, their anchoring onto the surfaces and the first results of the optical study in the presence of NO<sub>x</sub> gases will be discussed.

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## Highly Efficient Thermally Activated Delayed Fluorescence of Silver(I) Complexes.

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Recent progress in the chemistry and photophysics of copper(I) complexes led to strongly emissive materials for use in OLEDs according to the singlet harvesting effect.<sup>1-3</sup> Owing to small energy separations between the lowest excited singlet and triplet states  $\Delta E(S_1-T_1)$ , the compounds show thermally activated delayed fluorescence (TADF) at ambient temperature. Applied in OLEDs, this luminescence mechanism enables to harvest all singlet and triplet excitons for light generation and provides fast radiative decay of the excited emitters, necessary to improve stability and to reduce saturation effects at high brightness. In this contribution, a series of neutral silver complexes showing intense and short-lived TADF is presented. Their photophysical properties are compared with the results obtained for their copper-based analogues and the benefits of the Ag(I) materials are highlighted.



Emission properties of an exemplary silver(I) complex (powder).  
Emission maximum at  $T = 300 \text{ K}$  lies at  $508 \text{ nm}$ .

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## Iridium complexes: Unavoidable candidates for the design of high efficiency electroluminescent devices?

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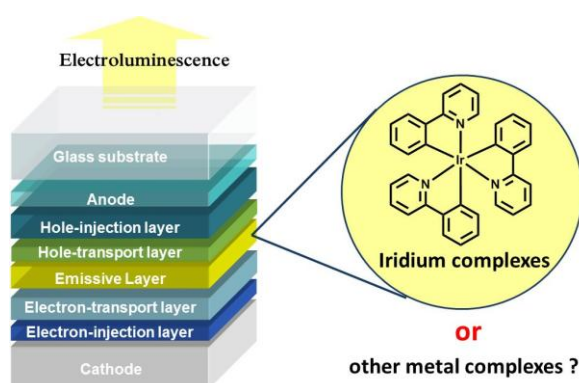
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During the past decade, luminescent materials have gained a particular interest due to their potential applications in optoelectronics including organic light-emitting devices (OLEDs), luminescence-based sensors and photocatalysis. Among all phosphorescent materials investigated for OLEDs, iridium (III) complexes are without contest the most widely studied materials due to their high luminescence quantum yields and relatively short luminescence lifetimes.<sup>1,2</sup> However, if highly emissive dopants are already reported, search for new emitters with higher brightness and power-to-light conversion is still ongoing.

Although iridium complexes are appealing candidates for electroluminescent devices, this metal is not very abundant in the Earth's crust and therefore relatively expensive. Much cheaper, more abundant and less toxic metals such as zinc<sup>3,4</sup> or copper<sup>5</sup> have thus been proposed. However, are these metals a realistic alternative to iridium?



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## Thermodynamic and Photophysical Properties of Dual VIS/NIR Luminescent Erbium Complexes

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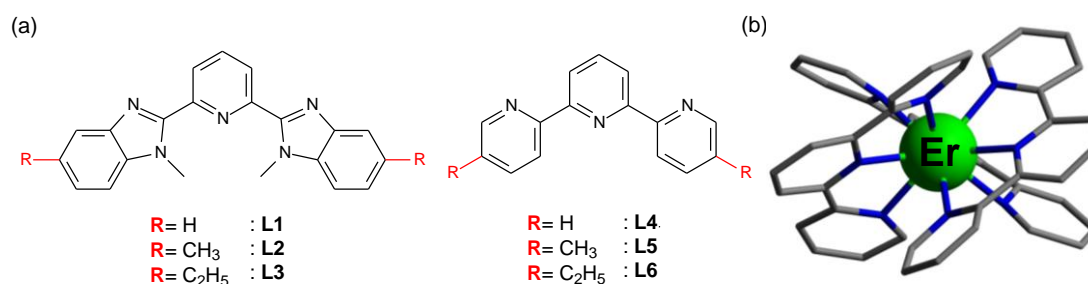
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The luminescence properties of lanthanide complexes are a subject of great interest mainly due to their applications as building blocks for construction of functional materials.<sup>1</sup> Since the Er(III) ion possesses several closely spaced excited states that cover the infrared to ultraviolet range, Er(III) complexes have been exploited as activators in linear optics for molecular up-conversion.<sup>2</sup> In this perspective, a series of nine- and eight-coordinated mononuclear Er(III) complexes with tridentate ligands of increasing steric demand **L1-L6** (Figure 1) have been synthesized and characterized. Spectrophotometric titrations with  $\text{ErX}_3$  ( $\text{X} = \text{CF}_3\text{SO}_3^-$ ,  $\text{ClO}_4^-$ , tetra-perfluoroalkoxyaluminate) in aprotic organic solvents show the successive formation of  $\text{ML}$ ,  $\text{ML}_2$  and  $\text{ML}_3$  complexes, the speciation of which can be rationalized by using the site-binding model. Photophysical investigations reveal a very unusual dual VIS/NIR Er-centered emission sensitized via ligand excitation. Whereas the NIR emission arising from the  $\text{Er}(^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2})$  may be classified as 'standard', the nanosecond green emission occurring at 540 nm ( $\text{Er}(^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2})$ ) is much more challenging and rarely reported for coordination complexes possessing high-energy oscillators. The special conditions required for implementing Er-centered visible emission in coordination complexes will be discussed in this work.



**Figure 1.** a) Chemical structures of the ligands **L1-L6**. b) Crystal structural of  $[\text{Er}(\text{L4})_3](\text{CF}_3\text{SO}_3)_3$

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## DITHIENYLETHENE-BASED CYCLOMETALATED PLATINUM COMPLEXES: EFFICIENT OPTICAL PHOTO-SWITCHES

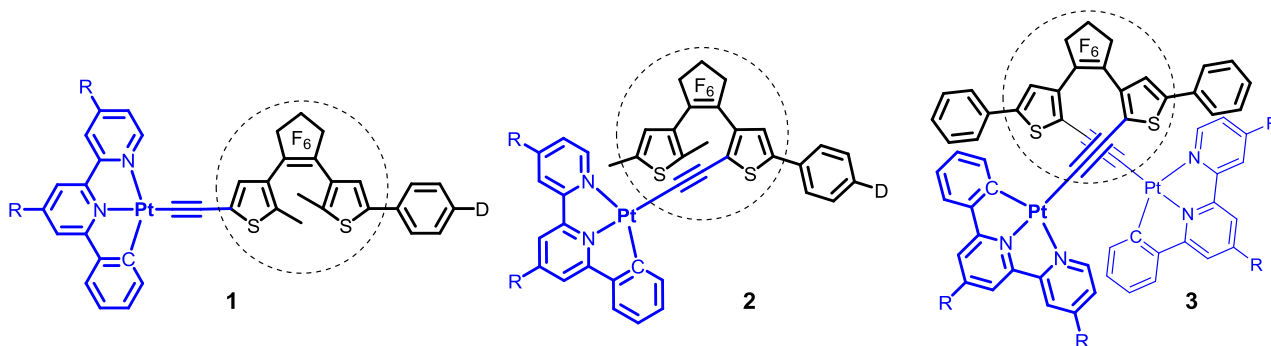
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Organometallic systems with commutable optical response (luminescence, nonlinear optic (NLO)) are of growing interest due to their potential application in photonics technologies. In the course of finding new strategies for molecular photo-switches, our group has been investigating dithienylethene-based cyclometalated platinum complexes with the aim of combining the optical properties of (N<sup>2</sup>C)Pt(II) acetylide complexes<sup>1</sup> with the well-known photochromic performances of dithienylethenes (DTE)<sup>2</sup>. We have designed and synthesized *classical* (**1**) and *non-classical* (**2**) mono-nuclear DTE-based Pt(II) complexes, and their related di-nuclear complexes (**3**).



Here, the influence of the design (*i. e.*, the position and the number of Pt(II) fragments as well as the nature of the end group D) on the photochromic reactivity will be discussed. We will also demonstrate the photo-regulation of the NLO response in solution and in thin films.<sup>3,4</sup>

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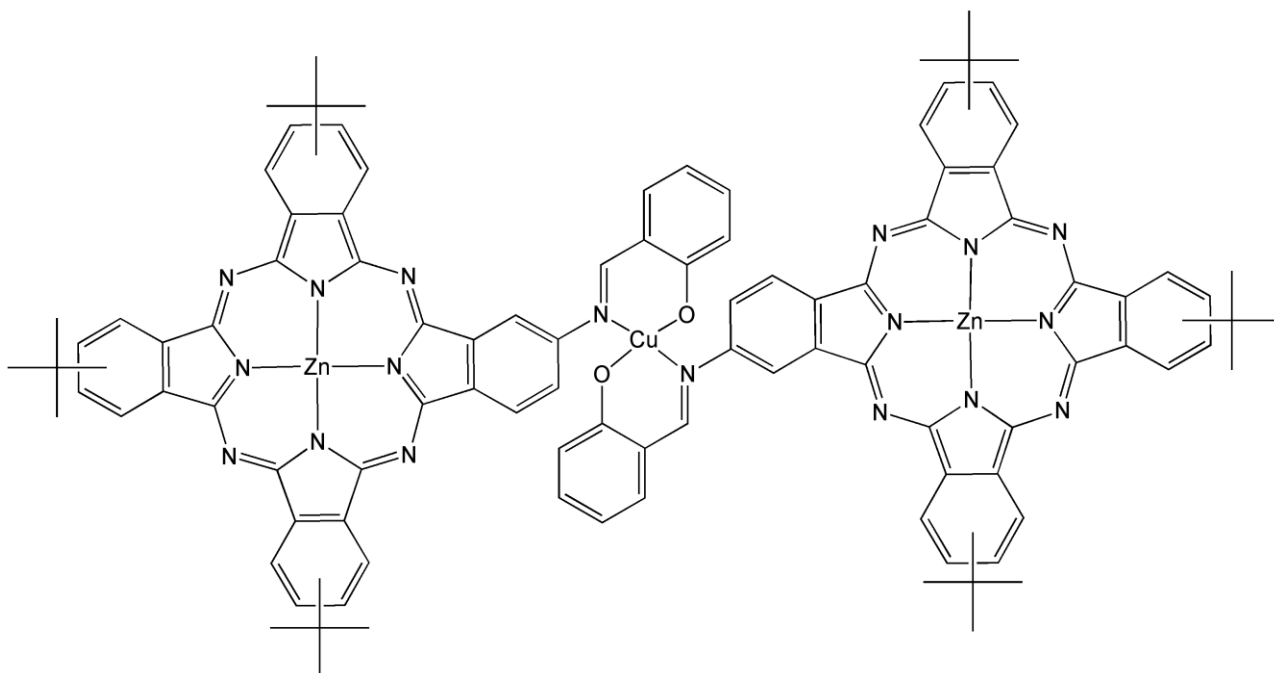
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## A fused ligand with phthalocyanine and Schiff-base coordination sites and its trinuclear Zn<sub>2</sub>-Cu complex

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Much interest has been devoted to phthalocyanine (Pc) complexes as blue dye stuffs, where the extended  $\pi$ -conjugated system in the Pc ligands gives rise to an intensive absorption band (Q band) around 680 nm ( $\epsilon = \sim 10^5 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ ).<sup>1</sup> Schiff-base (Sb) complexes have been widely investigated for their physicochemical properties based on the d electrons in the complexes.<sup>2</sup> We have ever reported on a tetranuclear copper(II) complex with a Pc-Sb fused ligand framework.<sup>3</sup> In this study, we newly prepared a trinuclear heterometal complex with a different fused Pc-Sb ligand framework (Figure 1) and evaluated the effect of d electrons in the Cu(Sb) site on the absorption and fluorescence spectral properties of Zn(Pc) sites. Details will be discussed on the optical behaviors in the presentation.



**Figure 1** Structure of trinuclear  $\{\text{Zn}(\text{Pc})\}_2\text{-Cu}(\text{Sb})$  complex

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## Enhanced Luminescence of Gold Complexes with Stable Luminescent Radical Ligands

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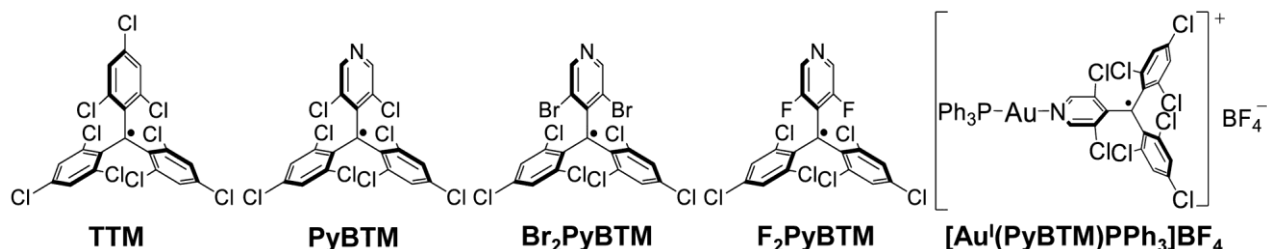
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Luminescent radicals are promising candidates for new types of future luminescent materials. Unique properties owing to their characteristic spin-multiplicity, i.e., the ground and excited doublet states, are expected. For example, luminescent radicals are expected to show superior characteristics for application to OLED and NIR emitter.

However, low stability of radicals in their ground and excited states has been a serious problem. We have developed a novel luminescent radical, (3,5-dichloro-4-pyridyl)bis(2,4,6-trichlorophenyl)methyl radical (PyBTM, Figure 1).<sup>1</sup> By the introduction of a pyridine ring into a tris(1,3,5-trichlorotriphenyl)methyl radical (TTM) skeleton, PyBTM realizes higher photostability; that is up to 115 times that of TTM in solutions.

We also reported effects of the halogen atoms on the pyridine ring.<sup>2</sup> Br<sub>2</sub>PyBTM showed superior photostability, and F<sub>2</sub>PyBTM displayed higher photoluminescence quantum yield (4%) than that of PyBTM (2%) in CH<sub>2</sub>Cl<sub>2</sub>. Furthermore, coordination of the nitrogen atom of PyBTM to a gold(I) enhanced luminescent properties.<sup>3</sup> [Au<sup>I</sup>(PyBTM)PPh<sub>3</sub>][BF<sub>4</sub>]<sup>-</sup> displayed enhanced photostability and quantum yield (8%).

In this study, we aimed at improving fluorescence quantum efficiency and prepared a novel gold(I) complex based on the combination of our established approaches: coordination to a metal ion and substitution of halogen atoms. The complex exhibited the highest fluorescence quantum efficiency among the related radicals.



**Figure 1** Chemical structures of TTM, PyBTM, Br<sub>2</sub>PyBTM, F<sub>2</sub>PyBTM, and [Au<sup>I</sup>(PyBTM)PPh<sub>3</sub>][BF<sub>4</sub>].

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# Impact of the Use of Sterically Congested C<sup>^</sup>N Ligands on the Photoluminescent Properties of Iridium(III) Complexes

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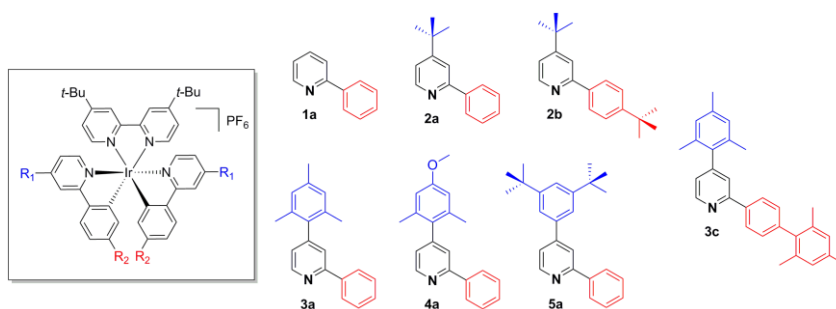
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In recent years light-emitting electrochemical cells (LEECs) utilizing ionic transition metal complexes (iTMCs) as luminophores<sup>1</sup> have been attracting interest in the area of solid-state lighting. One popular species of iTMCs in LEECs are cationic iridium(III) complexes of the form [Ir(C<sup>^</sup>N)<sub>2</sub>(N<sup>^</sup>N)]PF<sub>6</sub> (C<sup>^</sup>N is a cyclometalating ligand, N<sup>^</sup>N is a diimine ancillary ligand). Excited state self-quenching during the operation can limit the lifetime of the device. A strategy to circumvent this issue is to decorate the Ir-complexes with bulky, hydrophobic substituents that increase the intermolecular distance while also hindering the disadvantageous attack of small molecules. For example, introduction of bulky substituents on the N<sup>^</sup>N ligand leads to more stable LEECs.<sup>2,3</sup>

In this context, we will present a family of cationic Ir(III) complexes [Ir(C<sup>^</sup>N)<sub>2</sub>(d<sup>^</sup>t<sup>^</sup>bubpy)]<sup>+</sup> with bulky substituents R<sub>1</sub> and R<sub>2</sub> on the C<sup>^</sup>N ligands. We will show the impact of the steric bulk on their photophysical, electrochemical, and photoluminescent properties.



**Figure 1** Structure of the synthesized cationic Ir(III) complexes.

C.H. acknowledges the Région Bretagne for a grant.

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## Solid State Luminescence vs. Photo-isomerisation in Cyclometallated Ir(III) Complexes

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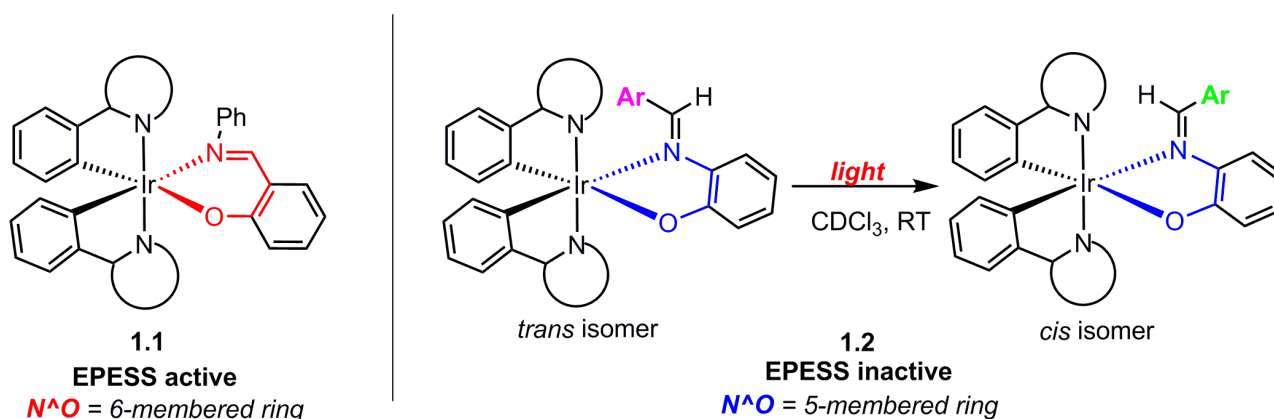
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Previously, we have shown that cyclometallated Ir(III) complexes (**1.1**) containing 6-membered N<sup>^</sup>O chelate rings undergo distortion in the triplet state and consequently emission is not observed in solution.<sup>1</sup> However, in the solid state they show EPESS (Enhanced Phosphorescence Emission in the Solid State).

To probe the effect of ring size on EPESS, we synthesised novel cyclometallated Ir(III) complexes (**1.2**) with a 5-membered N<sup>^</sup>O chelate ring. Complex **1.2** (Ar = Ph) was isolated as a mixture of *cis* and *trans* isomers differing in the geometry around the imine bond. The *trans* isomer (Ar = Ph) was characterised by X-ray crystallography. A similar situation was found in some related thiol imine complexes.<sup>2</sup> The mixture of isomers only shows very weak emission in solution. Synthesis of **1.2** in the absence of light led to only the *trans* isomer being formed. This suggests that the *trans* isomer is stable in the dark; however when exposed to room light it converts to a mixture of *cis* and *trans* isomers.

Here, we will present results on the effect of imine substituent and cyclometallating ligands on the *cis/trans* ratio. DFT calculations will be used to explore the mechanism of isomerisation and how this is affected by irradiation.



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## Design and Synthesis of a New Class of Alkynylplatinum(II) Complexes for Solution-Processable Organic Light-Emitting Devices

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A novel class of luminescent cyclometalated platinum(II) 1,3-bis-(*N*-alkylbenzimidazol-2'-yl)benzene (bzimb) complexes has been designed and synthesized.<sup>1-3</sup> The emission color can be readily tuned by the introduction of various substituents to the anionic phenyl rings of the bzimb ligand.<sup>2,3</sup> Their photophysical, electrochemical and electroluminescence properties have been investigated. Efficient organic light-emitting devices (OLEDs) have been fabricated based on this class of complexes using vacuum deposition and solution-processing techniques.<sup>2,3</sup>

To further improve the solution-processable device performance, dendritic pendants have been successfully incorporated into the platinum(II) complexes. The dendritic platinum(II) complexes show remarkable photoluminescence quantum yields of up to 80 % in spin-coated thin films. The solution-processable OLEDs show remarkable performances with high EQEs, suggesting a promising class of dendritic platinum(II) complexes for solution-processable OLEDs.

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## Luminescent diphosphine fluorophenylthiolate silver(I) compounds

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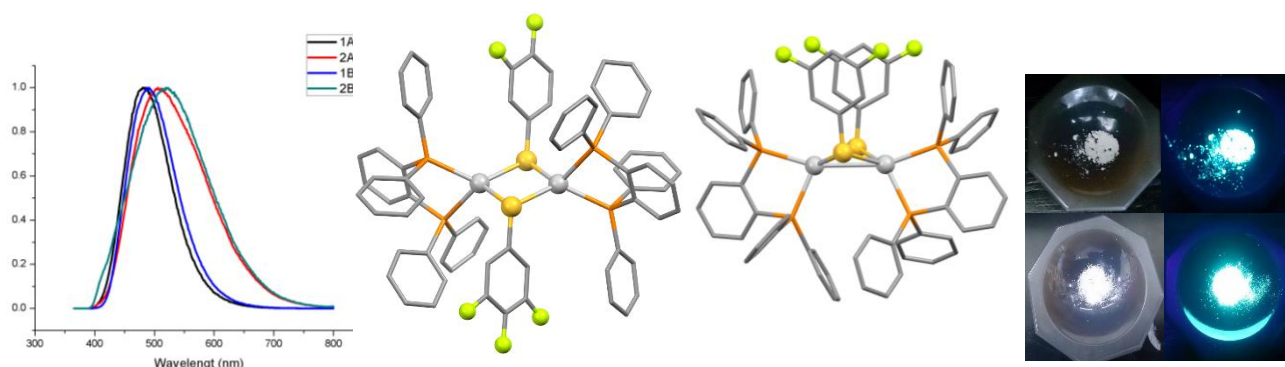
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In last decades luminescent behavior of gold compounds has been one of the important topics in gold chemistry, recently this interest is extending to the use of other d10 metal ions as luminescence sources<sup>1</sup>, for gold luminescence it's known that ligand and aurophilic interactions have a central role<sup>2</sup>, however, the luminescence properties of binuclear Ag(I) complexes and the influence of argentophilic interactions and ligand properties over it are less explored<sup>3</sup>.

Four new luminiscent discret diphosphine fluorothiolate silver(I) compounds had been synthesized using two geometrically analogue diphosphines: 1,2-bis(diphenylphosphine)benzene (dppBz) **1** and 1,2-cis-bis(diphenylphosphine)ethylene (dppE) **2**, and two difluorophenylthiolate ligands: 3,4-difluoro-phenylthiolate (3,4-dfpt) **A** and 3,5-difluoro-phenylthiolate (3,5 dfpt) **B**, in this compounds light variations in the fluorophenylthiolate ligand structure, changing a fluorine atom position, brings a change in observed crystal structures giving place to argentophilic interactions and different conformations and shifting luminescence emission maxima.



**Figure 1** Left: R.T. solid state normalized emission spectra of the four compounds  $\lambda_{ex}=310$  nm. Arbitrary units for y-axis. Center: XRay structures of 1A and 1B respectively Right: Visible luminescence of compounds 1A (top) and 1B (down) under 365 nm UV lamp.

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# Direct and switch NLO-2 response of new chromophores based in Schiff base complexes containing Ni<sup>II</sup> and Cu<sup>II</sup> coordinated by ONO ligands. Experimental and theoretical approach.

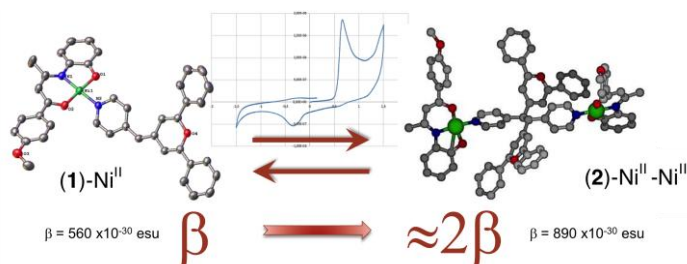
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The design and construction of novel molecular architectures displaying enhanced second-order nonlinear optical (NLO-2) properties has attracted considerable interest because of their potential applications in emerging optoelectronic and photonic technologies.<sup>1</sup> For this aim we have chosen build novel push-pull chromophores with tunable NLO-2 response, we have designed and constructed a new family of ONO square-planar complexes containing pyridine derivatives as ancillary ligand.<sup>2</sup> In addition, these ONO complexes were used for obtaining new building blocks containing methylenpyran units (MTPU).<sup>3</sup> The electro-active MTPU contained in (1) allows modulate the NLO-2 response by a *quasi-reversible* redox behavior (figure 1). These compounds exhibit a significant improvement in the hyperpolarizability values (see  $\beta$  in figure 1). Finally, the properties of this new family of complexes have been rationalized by DFT and TD-DFT theoretical calculations.



**Figure 1.** Direct and Switch NLO-2 response of selected square-planar complexes of Ni<sup>II</sup>.

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**Acknowledgments:** We thank the financial support from FONDECYT (Chile), Grant No. 1130105, FONDEQUIP EQM130154, the LIA-MIF N° 836, and the Vice-Rectoría de Investigación y Estudios Avanzados, PUC Valparaíso, the CNRS and the Université de Rennes 1 is gratefully acknowledged. N. N. thanks CONICYT for granting doctoral scholarship, BECAS-CHILE for Joint Supervision Scholarship and the Rennes Metropole for the 2013 scholarship awarded doctoral internship.

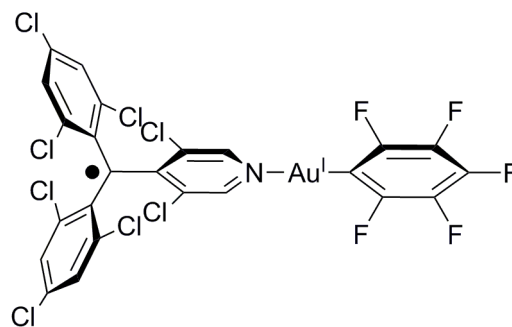
# Luminescent Properties of a Pentafluorophenyl Gold(I) Complex with an Open-Shell Fluorescent Radical Ligand

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## Introduction

We have developed a novel organic radical PyBTM, which is a rare example of open-shell luminescent radicals with high photostability.<sup>1</sup> The nitrogen atom of PyBTM acts as a coordination site to metal ions. The studies on a PyBTM-ligated Au<sup>I</sup> complex [Au<sup>I</sup>(PyBTM)PPh<sub>3</sub>][BF<sub>4</sub>] showed that the



**Figure 1.** Chemical structure of **1**.

coordination to metal ions is one promising strategy to develop novel luminescent properties based on the doublet (or multiplet) excited state.<sup>2</sup> In this study, we synthesized a new organometallic Au<sup>I</sup> complex with PyBTM as the ligand, [Au<sup>I</sup>(C<sub>6</sub>F<sub>5</sub>)(PyBTM)] (**1**) and investigated its optical properties to develop novel emission characteristics based on the weak Au<sup>I</sup>-N bond,<sup>3</sup> and to elucidate the effects of the counter-ligand in the Au<sup>I</sup> complexes.

## Results and Discussion

Single-crystal X-ray diffraction analysis confirmed the two-coordinate linear structure around the Au<sup>I</sup> ion. **1** in CH<sub>2</sub>Cl<sub>2</sub> displayed fluorescence with the emission peak wavelength  $\lambda_{em}$  of 625 nm at the excitation wavelength  $\lambda_{ex}$  of 412 nm;  $\lambda_{em}$  was bathochromically shifted compared with that of PyBTM ( $\lambda_{em}$  = 585 nm), while the shift was smaller than that of [Au<sup>I</sup>(PyBTM)PPh<sub>3</sub>][BF<sub>4</sub>] ( $\lambda_{em}$  = 653 nm). The decay of the fluorescence versus time was analyzed to afford two components with different lifetimes. The fluorescence spectrum of **1** depended on the temperature and excitation wavelength. These results, as well as the time-resolved fluorescence spectra, suggest the dual-emission character of **1**, which is presumably due to the dissociation of PyBTM from **1** in the photoexcited state.

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## Phosphole-based iridium cyclometalated complexes

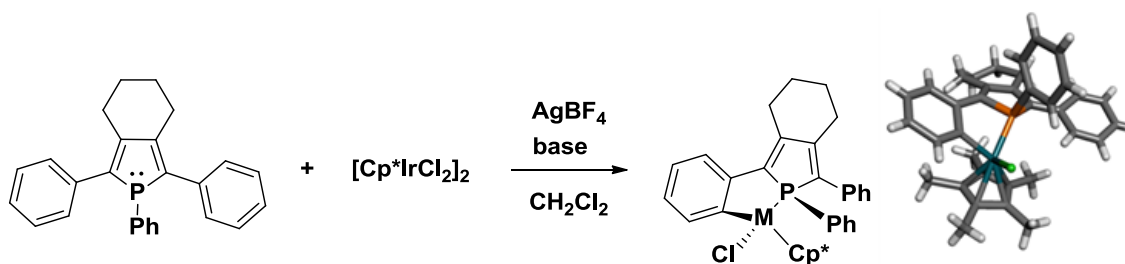
O. A. Mocanu,<sup>a</sup> W. Delaunay,<sup>a</sup> L. E. E. Broeckx,<sup>b</sup> E. Abou Nakad,<sup>a</sup>  
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Iridium complexes containing cyclometalated 2-phenylpyridines have received considerable attention since they behave as efficient organometallic catalysts for oxidation of water or as efficient triplet emitter in organic light-emitting diodes (OLEDs).<sup>1</sup> Replacing pyridine by a phosphole ring will create new functional coordination compounds. Effectively, the phosphole is known as a basically nonaromatic heterole because of insufficient  $\pi$ -conjugation between the cis-dienic  $\pi$ -system and the lone pair of the P-atom. Thus, the phosphole ring possesses a reactive lone pair which can coordinate different metal centers. Consequently, phospholes exhibit characteristic coordinating properties that differ significantly from those of pyridines and have been employed as reliable phosphine ligands in transition-metal catalysts.<sup>2</sup> The specific properties of the phosphole ring led us to use phosphole-based ligands in order to prepare a new family of cyclometalated complexes (Scheme 1) and study their optical and electronic properties.



**Figure 1.** Synthesis and X-ray structure of cyclometalated complex based on phosphole

In this contribution, we report new Ir(III). These complexes have been carefully characterized by NMR spectroscopy, HRMS and single crystal X-ray diffraction. The optical and electrochemical properties of the complexes and their intermediates have been studied.

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## [Cr(ddpd)<sub>2</sub>]<sub>3+</sub>: a molecular, water soluble, highly emissive ruby analogue

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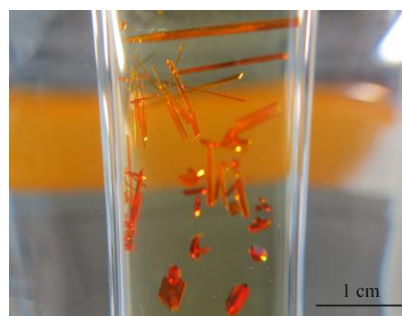
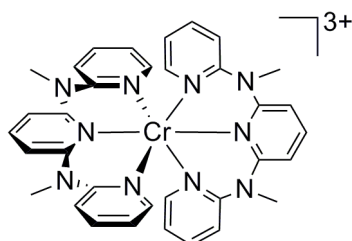
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NIR emission from 3d metal complexes is difficult to achieve. If emission is observed, it is generally short-lived and of low efficiency. By using the ddpd-ligand (*N,N*-dimethyl-*N,N*-dipyridin-2-ylpyridine-2,6-diamine) with its large N-M-N bite angle and its strong  $\sigma$ -donor properties we obtained a chromium(III) complex which, to the best of our knowledge, outperforms every 3d metal complex in that respect.<sup>1,2</sup>

The photophysical properties of [Cr(ddpd)<sub>2</sub>]<sup>3+</sup> have been investigated via spectroscopic (UV-VIS spectroscopy, steady-state and time-resolved emission spectroscopy at room temperature, 77 K, in solution and single crystal) and theoretical techniques (DFT and time-dependent DFT calculations). This combination of experimental and theoretical methods enables an understanding of the photophysical and photochemical properties within the ligand field theory framework.<sup>3</sup>



**Figure 1** Molecular structure of [Cr(ddpd)<sub>2</sub>]<sup>3+</sup> and a photograph of single crystals of [Cr(ddpd)<sub>2</sub>](BF<sub>4</sub>)<sub>3</sub>

The chemical and photochemical properties render [Cr(ddpd)<sub>2</sub>]<sup>3+</sup> a very promising candidate for biological and sensing applications.

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# Synthesis, Properties and LEEC Device Fabrication of cationic Ir(III) complexes Bearing Electron Withdrawing Aryl Ligands

Amlan K. Pal,<sup>a</sup> Nail M. Shavaleev,<sup>a</sup> David B. Cordes,<sup>b</sup> Alexandra M. Z. Slawin,<sup>b</sup> Antonio Pertegas Ojeda,<sup>c</sup> Henk Bolink,<sup>c</sup> and Eli Zysman-Colman<sup>\*,a</sup>

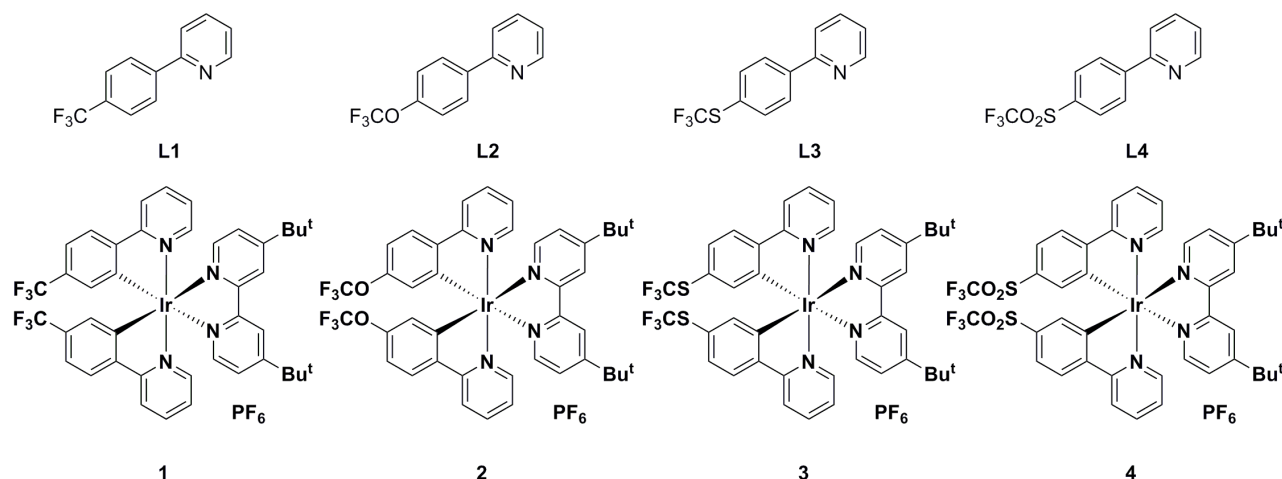
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Cationic luminescent Ir(III) complexes bearing cyclometallating C<sup>^</sup>N and ancillary N<sup>^</sup>N type ligands continue to gain widespread attraction in the fields of photo- and electro-luminescent devices,<sup>1,2</sup> photocatalysts<sup>3</sup> and biolabelling.<sup>4</sup> In this context, our present study involves design and synthesis of four Ir(III) complexes (**1-4**) bearing increasing electron-withdrawing groups on the C<sup>^</sup>N ligands (**L1-L4**) (**Figure 1**). The photophysical investigations reveal these complexes as sky-blue-to-green emissive luminophores that do not adhere to the paradigm where increasing electron-withdrawing character translates to bluer emission. We demonstrate how these complexes can act as emitters in light-emitting electrochemical cell (LEEC) devices.



**Figure 1** Structures of cyclometallating ligands (**L1-L4**) and cationic Ir(III) complexes (**1-4**) under study.

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## Unsymmetrical Pt(II) bis-acetylides as potential NLO chromophores: Synthesis, characterization and optical properties.

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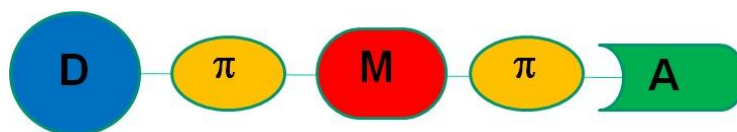
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Push-pull organic chromophores, in which a  $\pi$ -conjugated bridge is end-capped by an electron-donor (D) and an electron-acceptor (A) groups have been extensively studied over the last decades due to their wide applications as efficient materials in organic electronics and optoelectronics.

$\gamma$ -methylenepyran heterocycles, which acquire the aromatic character of pyrylium upon internal charge transfer, are particularly attracting as D part in push-pull structures. The use of such molecular fragments in the structure of Non-linear optical (NLO) chromophores has already been described in the literature.<sup>1</sup>

Diazines, such as pyrimidine and pyrazine, are very attractive electron accepting building blocks (A) for the synthesis of push pull structures.<sup>2</sup>

Due to the linear geometry of the alkynyl unit and their conjugated character, platinum acetylide complexes have displayed interesting properties such as NLO responses. Although a great number of organometallic complexes have been studied, only some examples have been reported in which electron withdrawing and electron donor fragments had been combined with the metal in the center of the structure in order to obtain high intramolecular charge transfer.<sup>3</sup>



**Figure 1** Design of the studied platinum complexes.

In this communication, we will describe the synthesis, redox properties, linear and non-linear optical properties of a new series of push-pull structure incorporating methylenepyran as pro-aromatic donor groups, di-acetylide platinum conjugated linkers and diazine rings as electron-attracting groups (Figure 1).

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## Electronic excited states of unsubstituted and methylated transition metal mixed sandwich complexes

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A unique spectroscopic property of metallocenes and related sandwich systems consists in a presence of clearly-defined Rydberg transitions in their gas-phase absorption and ionization spectra [1, 2]. Rydberg excitations originate at the non-bonding metal  $d_z^2$  orbital and provide valuable information on the molecular symmetry, electron density distribution, excitation energies and configuration interactions. Rydberg parameters of the gas-phase sandwich molecules provide, therefore, a powerful instrument to verify the results of quantum chemical calculations. In this work, the interpretation of the electronic absorption spectra of the transition metal mixed sandwich complexes  $(\eta^7\text{-C}_7\text{H}_7)(\eta^5\text{-C}_5\text{H}_5)\text{M}$  ( $\text{M} = \text{Ti}, \text{Mo}, \text{V}, \text{Cr}$ ) and the methylated mixed sandwich complexes of chromium and molybdenum  $((\text{C}_5\text{H}_5)(\text{C}_7\text{H}_6\text{CH}_3)\text{Cr}, (\text{C}_5\text{H}_4\text{CH}_3)(\text{C}_7\text{H}_7)\text{Cr}, (\text{C}_5\text{Me}_5)(\text{C}_7\text{H}_7)\text{Mo})$  in the gas phase has been made for the first time. Comparison of experimental data with time-dependent density functional theory (TD DFT) calculations provides new information on the nature and energies of electronic excited states of these compounds. The calculated parameters of electronic excited levels of mixed sandwich complexes were obtained including both valence-shell and Rydberg electronic excitations. The influence of methyl groups in the 5- or 7- membered carbocycles on the structure of electronic levels of sandwich molecules was evaluated. The role of the carbocycle size was analysed. Based on the Rydberg parameters of the mixed complexes the ionization potentials were determined and the influence of the carbocycle on the electron detachment energies was studied.

Acknowledgements: The spectroscopic studies were supported by the RFBR-MOST Russian-Taiwan joint research Project 15-53-52008. The computations were performed within the frames of Project 16-33-00893 supported by the Russian Foundation for Basic Research.

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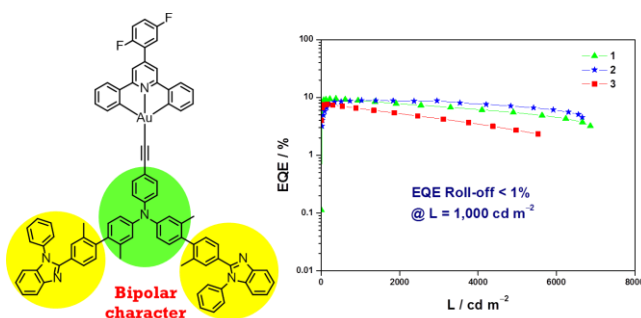


## Bipolar Gold(III) Complexes for Solution-Processable Organic Light-Emitting Devices with a Small Efficiency Roll-Off

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A new class of bipolar alkynylgold(III) complexes containing triphenylamine and benzimidazole moieties has been synthesized, characterized, and applied as phosphorescent dopants in the fabrication of solution-processable organic light-emitting devices (OLEDs). The incorporation of methyl groups in the central phenyl unit has been found to rigidify the molecule to reduce nonradiative decay, yielding a high photoluminescence quantum yield of up to 75% in spin-coated thin films. In addition, the realization of highly efficient solution-processable OLEDs with an extremely small external quantum efficiency (EQE) roll-off has been demonstrated. At practical brightness level of  $1000 \text{ cd m}^{-2}$ , the optimized devices exhibited a high EQE of up to 10.0% and an extremely small roll-off of less than 1%.<sup>1</sup>



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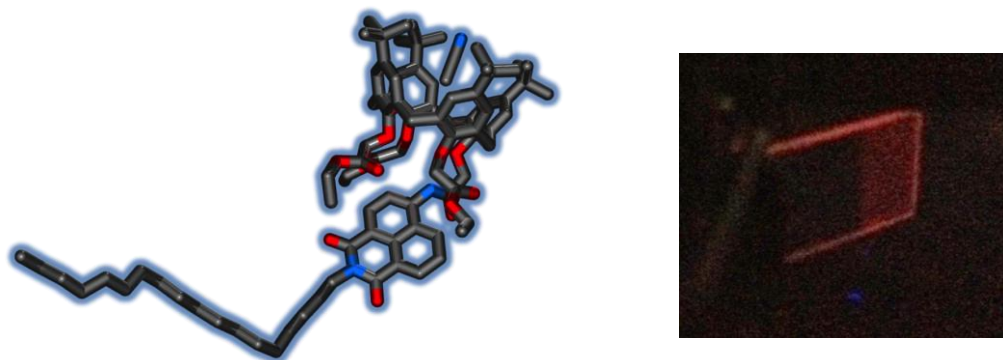
## Development of Ln<sup>III</sup> based luminescent surfaces for sensing applications

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The development of functional metal-based supramolecular sensors is an active area of research and there is an ever increasing move towards incorporating such systems into functional devices.<sup>1</sup> In order for this to be realised, these sensing systems must be immobilised without loss of function and one such method is to use the Langmuir-Blodgett (LB) technique to generate luminescent surface bound monolayers.<sup>2</sup> Luminescent lanthanide receptor-reporter systems capable of acting as chemical sensors have great potential for real-time monitoring of exposure to hazardous compounds. The Kitchen supramolecular group has recently developed families of Ln<sup>III</sup> based monolayer molecular sensors using Eu<sup>III</sup> and Tb<sup>III</sup> containing amphiphiles. Here we will present the synthesis and surface immobilisation studies of amphiphilic calix[4]arene lumiphores containing analyte recognition groups, highlighting the utility of the Langmuir-Blodgett deposition method to generate highly sensitive on-surface supramolecular chemosensors.



**Figure 1:** Structure of an amphiphilic ligand (**left**) and luminescent surface prepared through LB methods (**right**).

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## Material Selection for Donor Materials in Small Molecular-Based Bulk Heterojunction Organic Photovoltaic Devices

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Organic photovoltaic (OPV) devices are considered as a promising renewable energy source due to their distinct properties over the inorganic counterparts. Extensive efforts on the development of smart materials and innovative device architecture have boosted the power conversion efficiency up to 12 %. In particular, bulk heterojunction consisting of a spatially distributed donor/acceptor interface is the most efficient approach, in which almost all excitons can be effectively dissociated into free carriers to yield 100 % exciton dissociation efficiency and generate high photocurrent. However, the major challenge for achieving high power conversion efficiency is the relative poor charge carrier mobilities in the blended layer; especially the charge carrier mobilities in the blended layer are orders of magnitude lower than those of homogeneous layers. Recent demonstration on the use of a modified bulk heterojunction opens up a new avenue for improving the performance of OPV devices, in which a non-absorbing donor material at very low dopant concentration is doped into fullerene matrix to form the bulk heterojunction. Surprisingly, the doping of non-absorbing organic materials (i.e. 5 %) can dramatically improve the photovoltaic responses including short-circuit current, open-circuit voltage ( $V_{OC}$ ), and fill factor, which is the highest ever reported for a cell with fullerene as the sole absorber. On the other hand, the exact mechanism for the performance improvement is not well-understood. The common energy gap law for  $V_{OC}$  cannot be applied. Here, the effects of different non-absorbing organic materials as donor on the performance of OPV devices with the modified bulk heterojunction have been systematically studied and the correlation between the physical and energetic properties of donor materials and the photovoltaic responses will be discussed.

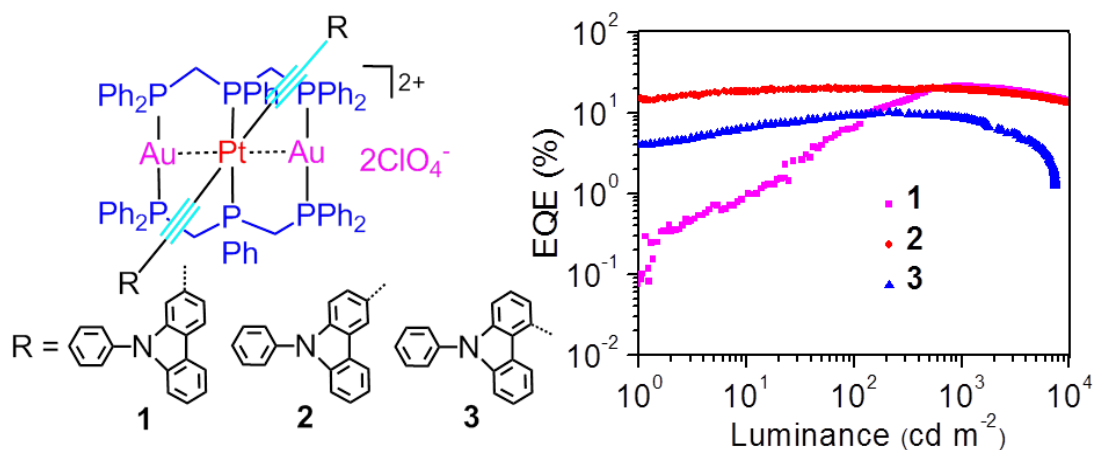
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# Solution-Processed High-Efficiency Phosphorescent OLEDs Based on Cationic PtAu<sub>2</sub> Complexes with Different Positioned Carbazole-Acetylide Ligands

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Ionic metal complexes as phosphorescent materials display some advantages over neutral cyclometallated iridium(II), platinum(II) and gold(III) complexes, including easy preparation under mild conditions in high yields, high thermal and photochemical stability, good solubility in organic solvents. Herein we describe solution-processed high-efficiency OLEDs based on cationic PtAu<sub>2</sub> heterotrimeric complexes with different positioned carbazole-acetylide ligands as dopants. The PtAu<sub>2</sub> cluster complexes show intense phosphorescence in fluid solution, powder and film with quantum yield as high as 0.73. As demonstrated experimentally and theoretically, the phosphorescence originates from [ $\pi$  (aromatic acetylide)  $\rightarrow \pi^*$  (dmpm)] LLCT and [ $\pi$  (aromatic acetylide)  $\rightarrow$  s/p (PtAu<sub>2</sub>)] LMCT triplet states. Solution-processed OLEDs gave highly efficient electroluminescence with current efficiency (CE) of 78.2, 78.3 and 30.0 cd/A and external quantum efficiency (EQE) of 21.5%, 20.2% and 10.1% for complexes **1**, **2** and **3**, respectively.



**Figure 1.** External quantum efficiency vs luminance for solution-processed OLEDs based on complexes **1–3**.

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# Iodobismuthates with One-Dimensional $\text{BiI}_4^-$ Anions: Synthesis, Structure, and Optical Properties of Prospective Light-Harvesting Materials

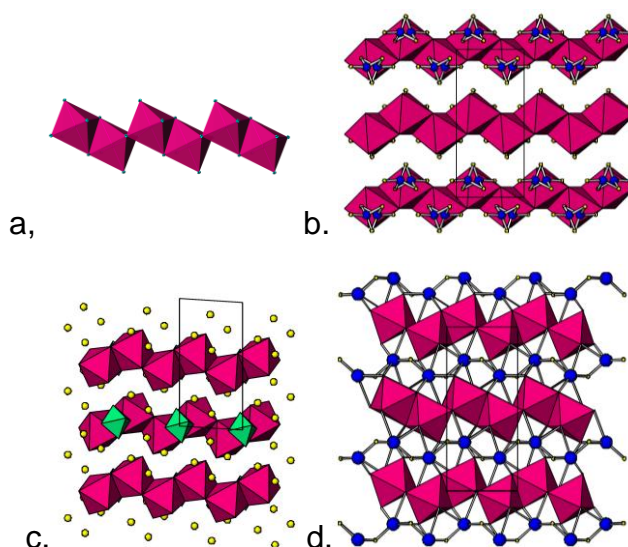
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As the alternative to widely studied Pb- and Sn-based perovskites for photovoltaics<sup>1,2</sup> we have investigated the Bi-based complex iodides. Four new compounds,  $\text{LiBiI}_4 \cdot 5\text{H}_2\text{O}$  (**1**),  $\text{MgBi}_2\text{I}_8 \cdot 8\text{H}_2\text{O}$  (**2**),  $\text{MnBi}_2\text{I}_8 \cdot 8\text{H}_2\text{O}$  (**3**), and  $\text{KBiI}_4 \cdot \text{H}_2\text{O}$  (**4**), featuring 1D  $(\text{BiI}_4)^-$  anionic chains (Figure 1a) have been obtained. Synthesis, thermal stability, crystal and electronic structure, and optical properties of these compounds will be presented. One-dimensional Bi/I substructures (fig.1b-d), appropriate band gaps (1.70–1.76 eV), facile fabrication via solution synthesis, and moderate thermal stability make the title compounds prospective light-harvesting materials.



**Figure 1.** a. A fragment of a 1D  $(\text{BiI}_4)^-$  chain. Bi, magenta; I, cyan; Crystal structures: b. View along the *a* axis in **1**; c. View along the *b* axis in **2** and **3**; d. View along the *a* axis in **4**.  $[\text{BiI}_6]$  octahedra and Bi atoms, magenta; water oxygen atoms, yellow; Li and K atoms, blue;  $[\text{Mg}(\text{H}_2\text{O})_6]$  and  $[\text{Mn}(\text{H}_2\text{O})_6]$  octahedra, green; I atoms, cyan.

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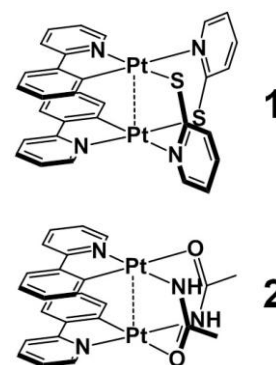
## Mixed-valency and Electrochromism of Redox-active Multinuclear Platinum Complexes

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Multinuclear Pt<sup>II</sup> complexes have attracted considerable attention owing to their outstanding luminescent properties and rich redox behavior that arises from electronic Pt...Pt interactions. We have developed cyclometalated dinuclear Pt<sup>II</sup> complexes bridged by pyridine-2-thiolate (**1**, Figure 1),<sup>1</sup> which exhibit intense luminescence from the <sup>3</sup>MMLCT (metal-metal-to-ligand charge transfer) state. Although **1** exhibited redox-bistability of the emissive Pt<sup>II</sup>-Pt<sup>II</sup> state and the non-emissive Pt<sup>III</sup>-Pt<sup>III</sup> state, any other oxidation states such as mixed-valent states could not be obtained. In order to construct mixed-valent Pt complexes bearing cyclometalating ligands, we focused on the  $\mu$ -acetamidato bridge for stabilize partially oxidized multinuclear system via intramolecular hydrogen bonding. Herein, we report the first example of redox-multistable Pt complex **2** (Figure 1) that is switchable between luminescent multicolored and nonluminescent colorless states by electrochemical means.<sup>2</sup>

Complex **2** was successfully synthesized from mononuclear Pt<sup>II</sup> precursor [Pt(ppy)(MeCN)<sub>2</sub>]<sup>2+</sup> in three stable oxidation states (i.e., Pt<sup>II</sup>, Pt<sup>+2.33</sup>, and Pt<sup>III</sup> states). Interestingly, **2** exhibited multistep electrochromic behavior, while other reported cyclometalated Pt dimers including **1** exhibited only one well-defined redox couple. Moreover, the reduction of **2** led to the strongly emissive Pt<sup>II</sup> state. In addition to the above results, mixed-valency and electrochromic behavior of other multinuclear Pt<sup>II</sup> complexes will also be reported.



**Figure 1** Dinuclear motifs of **1** and **2**.

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## Luminescence intensity switching of tetracyanonitridorhenium(V) complexes by mechanochemical reactions and exposure of water

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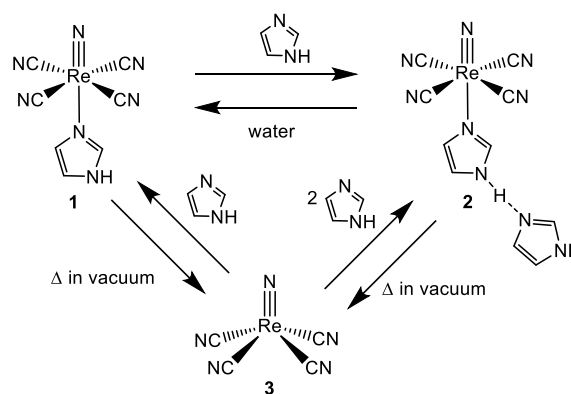
<sup>c</sup>Department of Chemistry, Graduate School of Science, Osaka-city University, Osaka 558-8585, Japan, <sup>d</sup>Chemistry and Materials Engineering Program, School of Engineering, Nagasaki University, Nagasaki, 852-8521, Japan, <sup>e</sup>Department of Chemistry, Graduate School of Chemical Sciences and Engineering, Hokkaido University, 060-0810, Japan

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Mechanochemical reactions giving a solid product from a solid substance and a solid reactant under solvent-free conditions are attractive because of treatment without harmful organic solvents. Reactions of solid compounds in a minimal amount of water that afford a solid compound in high yield are also useful methods. In the present study, significant luminescence intensity switching by mechanochemical reactions and exposure of water was conducted using five- and six-coordinate tetracyanonitridorhenium(V) complexes.

The complexes,  $(\text{PPh}_4)_2[\text{ReN}(\text{CN})_4\text{L}]$  (L = imidazole (Him) (**1**) and 1-methylimidazole (Mim) (**4**)) and  $(\text{PPh}_4)_2[\text{ReN}(\text{CN})_4\text{Mim}] \cdot \text{Mim}$  (**5**) showed intense luminescence ( $\Phi_{\text{em}} = 0.65 - 0.75$ ) in the solid state at 296 K. Luminescence of  $(\text{PPh}_4)_2[\text{ReN}(\text{CN})_4\text{Him}] \cdot \text{Him}$  (**2**) was very weak ( $\Phi_{\text{em}} < 0.01$ ) in the solid state at 296 K. The mechanochemical reaction of **1** with 1 equiv. of Him in the solid state produced **2**. The complex **2** was also obtained by the reaction of  $(\text{PPh}_4)_2[\text{ReN}(\text{CN})_4]$  (**3**) with 2 equiv. of Him in the solid state. The compound **1** could be reproduced by placing solid

**2** in water. The compound **3** was produced under vacuum at 185°C from **1** and **2** for several days, respectively. Both **4** and **5** showed intense luminescence with similar intensities. The weak photoemission of **2** will be due to quenching by the vibronic relaxation of the N-H...N hydrogen bond between the coordinate and free Him molecules.



**Scheme 1** The reversible reactions with significant luminescence intensity switching in the solid state.



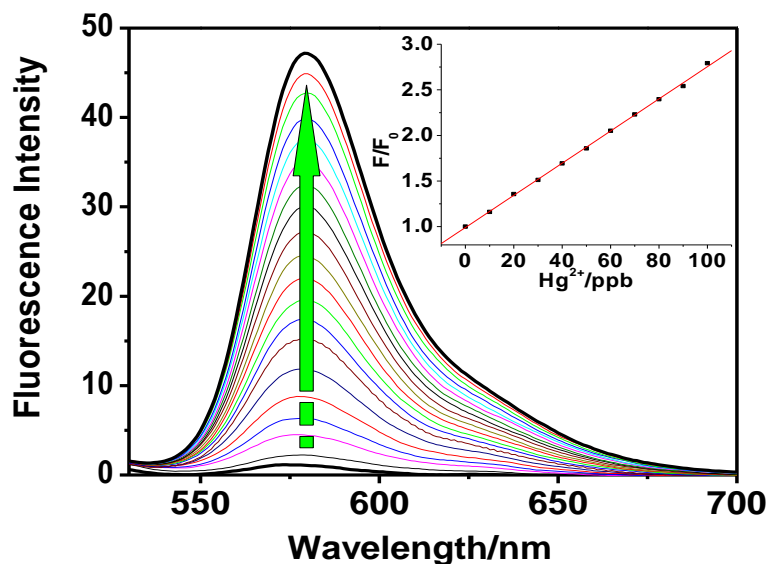
## Highly sensitive fluorescence probe based on Rhodamine Derivatives for selective detection of Hg<sup>2+</sup>

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Mercury is one of the most dangerous pollutants, and its contamination arises from a variety of natural and anthropogenic sources. Accordingly, the development of new or improved analytical methods for sensing and removing of Hg<sup>2+</sup>, applicable in a wide range of different sites and environments, is highly desirable<sup>[1,2]</sup>.

An inorganic–organic hybrid fluorescence sensor (RB-SBA-15) was prepared by covalent immobilization of a Rhodamine B derivative within the channels of mesoporous silica material SBA-15 via triethoxysilane groups. The primary hexagonally ordered mesoporous structure of SBA-15 was preserved after the grafting procedure. RB-SBA-15 can detect Hg<sup>2+</sup> with high selectivity to Cd<sup>2+</sup>, Cr<sup>3+</sup>, Co<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Pb<sup>2+</sup>, Mn<sup>2+</sup>, Ni<sup>2+</sup>, Ag<sup>+</sup>, and Mg<sup>2+</sup>, Ca<sup>2+</sup>, Na<sup>+</sup>, K<sup>+</sup> in water and excellent sensitivity to environmentally relevant mercury levels lower to ppb range.



**Figure 1.** Fluorescence spectral changes of RB-SBA-15 with different concentrations of Hg<sup>2+</sup>. Excitations were at 520 nm. Inset: the changes of fluorescence intensity of RB-SBA-15 upon addition of Hg<sup>2+</sup>

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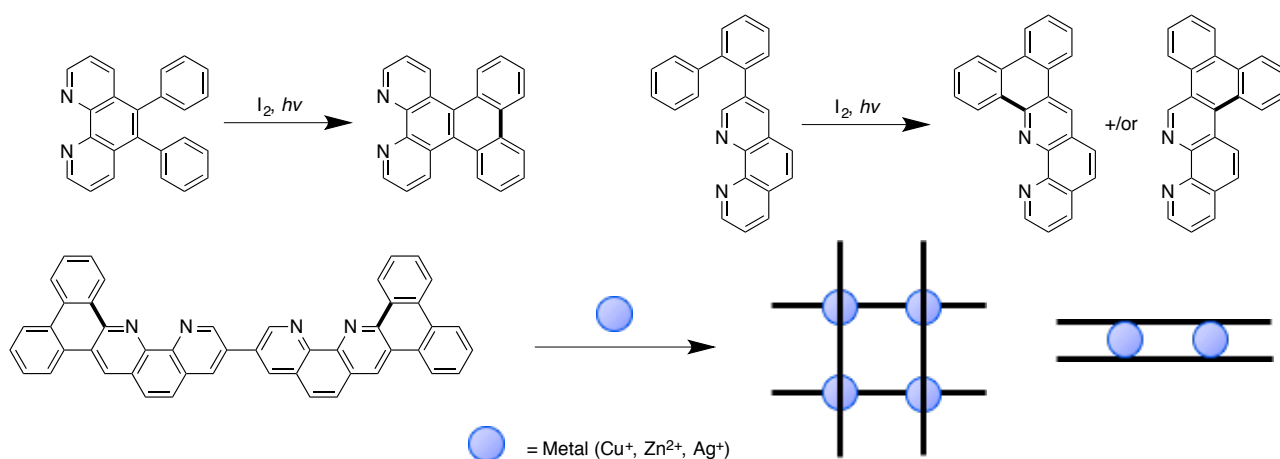
## Heteroaromatic Analogues as Supramolecular Materials

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Over the past twenty years, remarkable progress has been made in the design and construction of organic electronic devices.<sup>1,2</sup> Small molecules with large aromatic surfaces, such as polycyclic aromatic hydrocarbons, have been successfully used in the construction of a range of organic semiconductors.<sup>2</sup> The design and development of new and innovative procedures for the preparation of heteroaromatic analogues, where the periphery sites contain nitrogen atoms is the target of this research. The metal complexes of these molecules display novel chemical and physical properties due to their planar structures and high degree of electronic delocalization. We have been investigating the potential of photochemical cyclisation as a synthetic tool to augment the current chemical methods used for the preparation of these large aromatic ligands, as shown in figure 1. The resultant heteroatom containing molecules have been complexed with a variety of metals including ruthenium(II), silver(I), copper(I) and zinc(II). The potential of this route to allow the preparation of a series of novel supramolecular and functional molecules will be discussed.



**Figure 1** Potential photochemical reactions and cartoon representations of possible complexes that can form with the chosen  $d^{10}$  metals.<sup>3,4</sup>

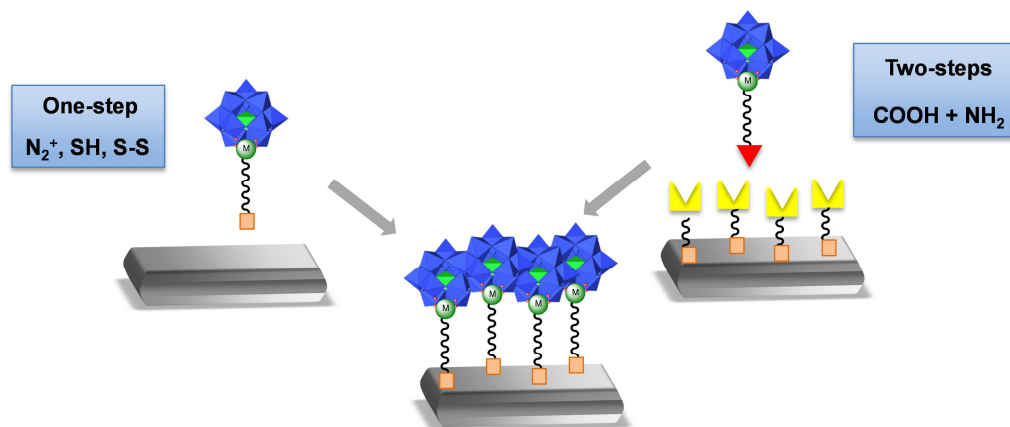
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## Processing of Polyoxometalates toward Molecular Memory

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Electroactive molecules can be incorporated inside molecular memory devices for their charge storage properties. Porphyrines<sup>[1]</sup> and ferrocene<sup>[2]</sup> have already been studied and polyoxometalates are good candidates as they present successive and reversible reduction processes, with low structure rearrangement. Electron delocalization is expected to favour their endurance toward charging/discharging cycles. We are focussing on Keggin and Wells-Dawson types and we are playing with the nature of the metallic centers to access to higher reduction potentials that means energy saving in future devices.



**Figure 1** POMs grafting by direct and indirect routes.

To graft such metal-oxide clusters onto surfaces, we have chosen POM hybrids functionalized with various organic tethers. Two approaches are then conceivable to make SAMs of POMs on surfaces (Figure 1). The first is a direct grafting by using adequate functionalized POMs, thiol on gold and diazonium on Si.<sup>[3]</sup> The second is to prepare readymade SAM on Au (thiol) and Si ( $-N_2^+$ ) bearing terminal amine group and a POM hybrid with terminal carboxylic acid group to assure a peptide coupling. Further, electron transfer kinetics will be studied at the solid state and compared with studies in solution.

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## MOLECULAR SWITCHES WITH ORGANOMETALLIC CARBON-RICH COMPLEXES

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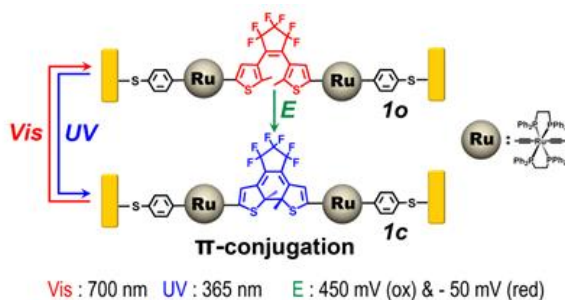
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Carbon-rich ruthenium complexes have been involved in the building of original redox-active molecular wires and junctions, owing to their excellent ability to promote a strong electronic coupling between the metal centers and the conjugated ligands, as well as for their fast electron transfer dynamics associated to discrete oxidation events at low potentials.<sup>1,2</sup>

Combinations of such metal complexes with carefully chosen functional units also lead to original properties valuable to achieve functional materials that present effective switching behaviors. For instance, association of dithienylethene with the ruthenium(II) complexes affords materials that gather efficient and suitable photo/electrochromism to achieve unique switchable multifunctional nanodevices.<sup>3-5</sup>



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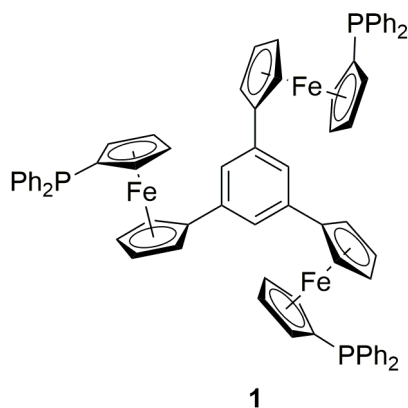
# A Redoxactive C<sub>3</sub>-Symmetric Tris-Phosphine Ligand– Synthesis, Characterisation and Coordination Behaviour

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Ferrocene has proven a very successful building block for ligand design, in particular owing to its conformational flexibility, the possibility of incorporating planar chirality and its amenability to organic transformations.<sup>1</sup> More recently, their reversible redox activity has rendered ferrocenyl-based ligands very interesting for redox-switchable catalysis (RSC).<sup>2</sup> Starting from simple molecular building blocks, a three-step synthesis is presented which opens a highly modular way to C<sub>3</sub>-symmetric tris-phosphine ligands.

The exemplary ligand **1** (Fig. 1) together with its transition metal complexes are discussed in terms of structural and redoxchemical features.



**Figure 1** Ferrocenyl-based tris-phosphine **1**

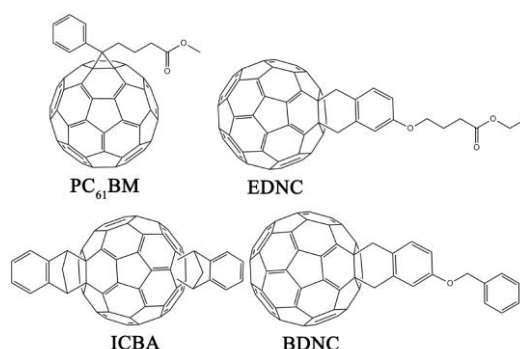
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## Searching for electron transporters of fullerene for perovskite solar cells

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A series of fullerene C<sub>60</sub> derivatives, such as [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester (PCBM), 2-(3-ethoxycarbonylpropyloxy)-(5,8)-dihydronaphthyl-(6,7)-[6,6]-C<sub>60</sub> (EDNC), and 2-benzyloxy-(5,8)-dihydro-naphthyl-(6,7)-[6,6]-C<sub>60</sub> (BDNC) as well as indene-C<sub>60</sub> bisadduct (ICBA), are introduced into inverted planar heterojunction perovskite solar cells as the electron transport materials (ETMs) to systematically investigate the correlation between electrochemical, charge-transporting and film-forming properties of these fullerene ETMs and the resulting photovoltaic performance. Power conversion efficiency (PCE) of 15.04% is achieved using PCBM as the ETM, while device employing ICBA as the ETM (with similar electronic mobility and surface roughness but ~0.2 eV higher LUMO energy level as compared to PCBM) obtains a decreased PCE of 1.45%. Due to better surface morphology, the EDNC-involving device shows better performance (12.64%) than that of BDNC-based device (7.36%) despite of their similar LUMO energy level, electron mobility, optical properties and electrochemical properties. Moreover, electronic mobility of PCBM is approximately one order of magnitude higher than that of EDNC, which leads to slightly higher short-circuit current density and fill factor for PCBM-based device. This work demonstrates that factors such as LUMO energy level, electron mobility, and surface morphology should be envisaged in searching for fullerene derivatives as efficient ETM in perovskite solar cells.



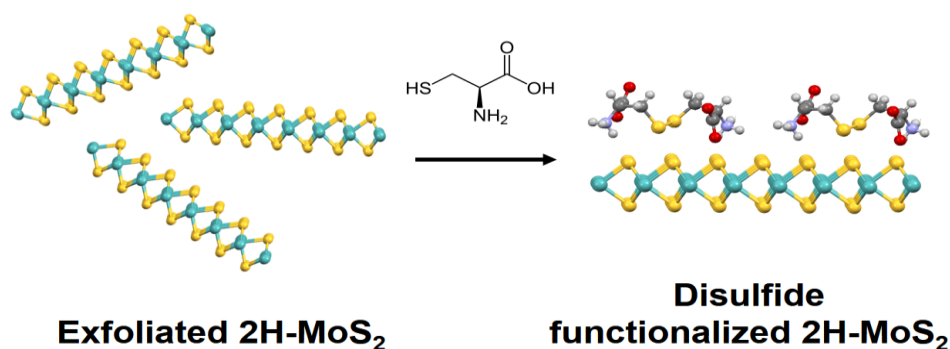
**Figure 1** Molecular structures of PC<sub>61</sub>BM, ICBA, EDNC, and BDNC

## Functionalization of Two-Dimensional MoS<sub>2</sub>: On the Reaction Between MoS<sub>2</sub> and Organic Thiols

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In recent years, two-dimensional transition metal dichalcogenides (2D TMDs) have aroused enormous interest in both fundamental and technological research due to their intriguing physical and chemical properties as well as potential applications.<sup>[1-4]</sup> To further tune their properties, and fully harness their capabilities, it is essential to develop routes to functionalize 2D TMDs. Here, we demonstrate a general route to functionalize layered 2H-MoS<sub>2</sub> with cysteine. The resulting functionalized 2H-MoS<sub>2</sub> was characterized by UV-Vis, XPS, TGA, DRIFT-IR and Raman and exhibited a good solubility and stability in water. Critically, MoS<sub>2</sub> was found to be facilitating the oxidation of the cysteine to its dimerized product cystine during functionalization. The resulting cystine was weakly physisorbed on 2H-MoS<sub>2</sub>. Similar oxidation processes were observed when employing other organic thiol substrates and other TMDs. Our findings suggest that instead of adsorption of thiol monomer covalently or datively on sulfur vacancies, functionalization of 2D MoS<sub>2</sub> with organic thiols, tends to produce the corresponding disulfide species physisorbed on the surface of nanosheets.



**Figure 1** Schematic illustration of functionalization of layered 2H-MoS<sub>2</sub> with cysteine.

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## Selective oxidation of cycloalkanes in neat water using metal nanoparticles

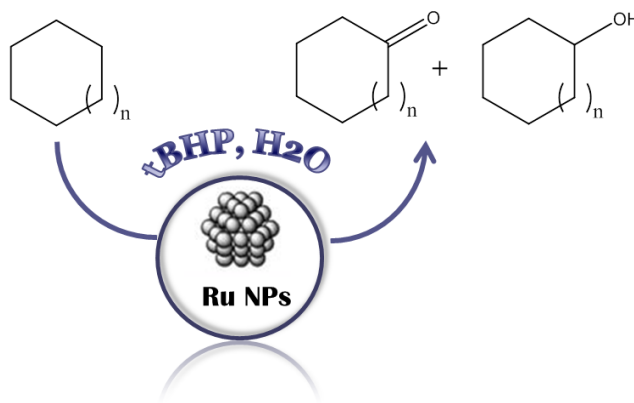
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Hydrocarbon functionalization via selective oxidation remains an important research area in catalysis. Among the great number of reactions, the oxidation of cyclohexane is of great interest from the industrial point of view, leading to the production of the corresponding ketone and alcohol, intermediates of Nylon-6 and Nylon-6,6. However, up to now, the industrial conditions are drastic in terms of energy consumption, the conversion being low to achieve interesting selectivity.

In the present work, the oxidation of cyclohexane in neat water was investigated as a model and relevant reaction, using metallic nanospecies (such as Ru, Ag, Au, Fe) and tBHP as an oxidant. After optimization of the reaction conditions, high conversions, combined with pertinent selectivities towards the ketone (up to 90%), were achieved. The presence of radical species was proved through kinetic and mechanistic studies. The catalyst lifetime was checked through several runs; with no significant loss of activity and selectivity. The catalyst was also characterized with different techniques (TEM, HRTEM, DLS, XANES, SAXS), revealing nanospecies with sizes around 1.5-1.75 nm.



**Figure 1** Cycloalkane oxidation over Ru nanospecies

(1 eq. Cycloalkane, 6x0.5 eq. tBHP, 0.01 eq. Ru catalyst, 3mL H<sub>2</sub>O, r.t. 9h)

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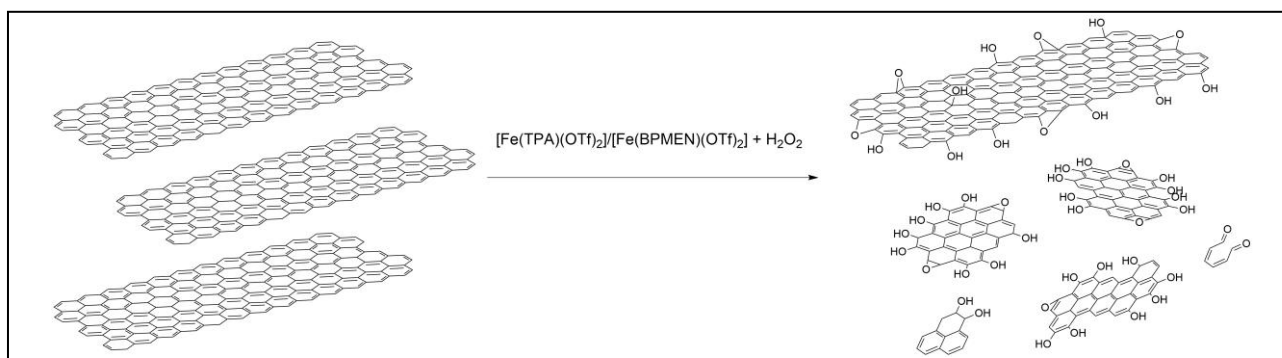
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## Towards the Oxidative Degradation of Graphene using Biomimetic Iron Complexes

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Graphene has been cited as the next 'wonder material' and many groups have invested time and money into its mass production and modification. A large amount of graphene research has been devoted to altering the structure of graphene via functionalisation for use in transistors, biosensors, inkjet printing, and many other applications for which pristine graphene is not suitable.<sup>1</sup> The possible industrial use of graphene in future also raises the question of how it will interact with, and could be broken down by, bacterial enzymes when released in the environment.<sup>2</sup>

To this end, we investigated the reactivity of some biomimetic Fe catalysts towards dispersed few-layer graphene and graphene oxide, using hydrogen peroxide as an oxidant. The complexes<sup>3,4</sup> used in this study were initially developed by Que's group to mimic Rieske dioxygenases,<sup>5</sup> which are known to be capable of breaking down aromatic compounds in bacteria via a (L)Fe<sup>V</sup>(O)(OH) intermediate. Viewing graphene as an extended polyaromatic system, these catalysts should hold the potential to catalytically functionalise or degrade graphene and other carbon nanomaterials as well.



**Figure 1** Postulated oxidation of graphene by H<sub>2</sub>O<sub>2</sub>, [Fe<sup>II</sup>(BPMEN)(OTf)<sub>2</sub>] and [Fe<sup>II</sup>(TPA)(OTf)<sub>2</sub>].<sup>6</sup>

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## Synthesis and Characterization of Dy acetylacetonate complexes encapsulated in Carbon nanotube

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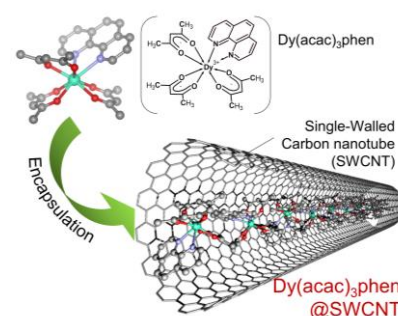
Single-molecule magnet (SMM) is a molecule which shows slow relaxation of the magnetization of purely molecular origin, which is expected to be applied such as next-generation data storage devices. However, any real application of SMM requires their communication with the outside macroscopic world to allow read-and-write processes. Simultaneously, smaller spin-spin interaction between each SMM is important to be used as an isolated magnet. Here, we focused on single-walled carbon nanotube (SWCNT) because the high electric conductivity offers a unique solution to linking SMM to the outside world<sup>1</sup> and the internal nano-space can reduce intermolecular interaction from three- to one-dimensionally. We tried to obtain the SMM encapsulated in SWCNT via sublimation method in order to achieve higher filling yield.

For sublimable SMM, we chose Dysprosium(III) acetylacetonate complexes  $[\text{Dy}(\text{acac})_3]^{2-}$ .  $\text{Dy}(\text{acac})_3 \cdot n\text{H}_2\text{O}$  was purchased and the water molecules were replaced to 1,10-phenanthroline (phen) in order not to be removed during the sublimation. The  $\text{Dy}(\text{acac})_3\text{phen}$  is sealed into a glass tube with SWCNTs (made by e-DIPS method<sup>3</sup>) under high vacuum, and encapsulated into them with heating at 423 K. We could confirm Dy atoms inside SWCNT from transmission electron microscope (TEM) observation, which indicates the  $\text{Dy}(\text{acac})_3\text{phen}$  was successfully encapsulated in SWCNT (Fig. 2). We also measured AC magnetic susceptibility and the differential of the SMM properties could be confirmed before and after the encapsulation, then the detailed characterization will be discussed.

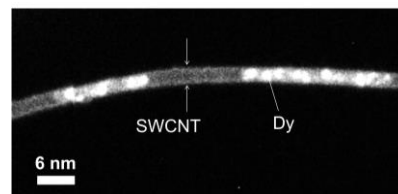
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**Figure 1** Structure model of  $\text{Dy}(\text{acac})_3\text{phen}$  and  $\text{Dy}(\text{acac})_3\text{phen}$  encapsulated in SWCNT.



**Figure 2** High-angle annular dark field - Scanning TEM image of  $\text{Dy}(\text{acac})_3\text{phen@SWCNT}$ .

# ***Bis*(2-hydroxy-1-naphthalenehydrato) Metal Complexes as Source of Face-Centered-Cubic Trioctylphosphine Oxide-Capped ZnO and CdO Nanoparticles Using Oleylamine as Dispersion Medium**

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Researchers have developed a great interest in the synthesis of metal oxide nanoparticles due to their potential applications in various fields of science and industry, especially in catalysis due to their high surface activities. The metal oxide nanomaterials such as ZnO and CdO are extensively used as catalysts and supports [1]. [*Bis*(2-hydroxy-1-naphthaldehyde)zinc(II)] and cadmium(II) complexes were prepared, characterized to confirm the bidentate bonding to metal centre by aldehyde ligand through the two oxygen atoms. The complexes used as precursors for the synthesis of zinc and cadmium oxide nanoparticles *via* thermal decomposition method using oleylamine as a dispersion medium of the complexes prior to injection into trioctylphosphine oxide (TOPO) as a capping agent at 210 °C. The 4-coordinate complexes were confirmed by a combination of FTIR spectroscopy, elemental analysis and thermogravimetric analysis (TGA). The synthesized metal oxide nanoparticles gave the face-centered cubic phase (as shown in Fig. 1) of materials with average particle sizes of 4.12 ( $\pm$  1.23) and 7.02 ( $\pm$  2.57) nm for zinc and cadmium oxide nanoparticles, respectively.

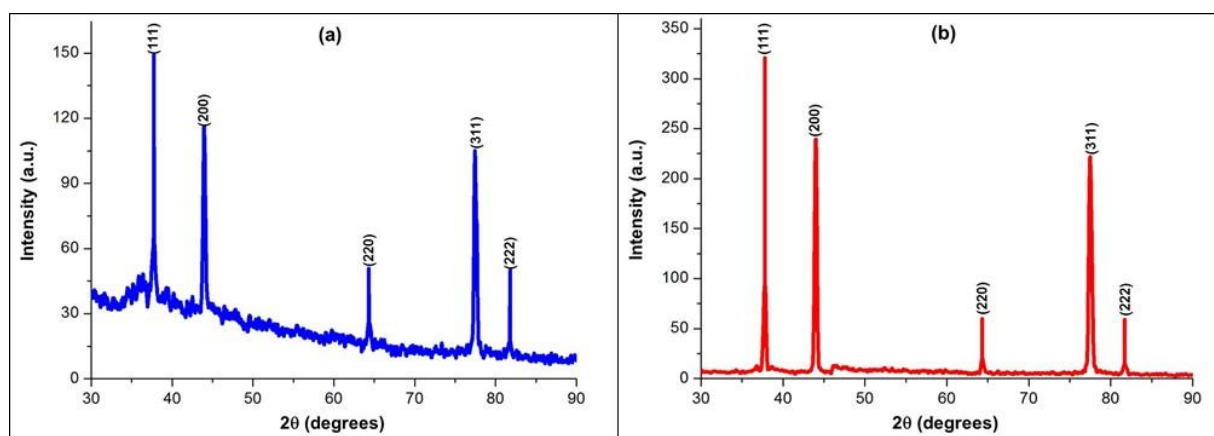


Figure 1: X-ray diffraction patterns of TOPO capped ZnO (a) and CdO (b) nanoparticles.

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## Theoretical study on molecular structures, electronic states and optical properties of bis(dipyrinato)zinc(II) complexes

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Recently, it has been reported that some heteroleptic bis(dipyrinato)zinc(II) complexes (Figure 1) having two different dipyrinato ligands show high fluorescence quantum yields ( $\Phi$ ).<sup>1</sup> They exhibit strong absorption and emission bands in the visible light region, so that they are expected to be promising compounds for functional materials. Theoretical calculations elucidated that the HOMO and LUMO of the fluorescent complexes are distributed in the same dipyrinato ligand. It suggests that the localization of the frontier orbitals is essential for the high quantum yields. On the other hand, the fluorescence of homoleptic bis(dipyrinato)zinc(II) complexes ( $R_1=R_5, R_2=R_6, R_3=R_7, R_4=R_8$  in Figure 1) is found to be weak especially in polar solvents. This feature is understood by the fact that a charge-separated (CS) state tends to suppress the fluorescence of the homoleptic complexes (Figure 2).<sup>1,2</sup> Very recently, Trinh and co-workers experimentally obtained the CS state by a transient absorption spectrum.<sup>2</sup> Their result suggested that the  $S_1$  state of the homoleptic compounds immediately changes to the CS state in polar solvents. However, a detailed mechanism of their optical properties has not been clarified. In this study, therefore, we investigate the relationship between molecular structures, electronic states and optical properties of several bis(dipyrinato)zinc(II) complexes by density functional theory (DFT) and time-dependent DFT calculations.

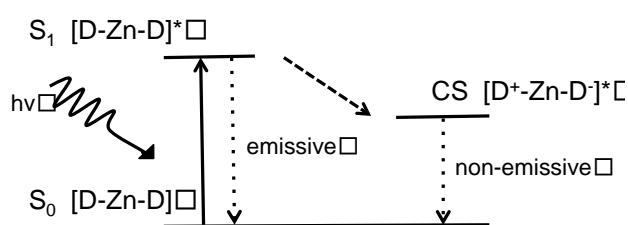
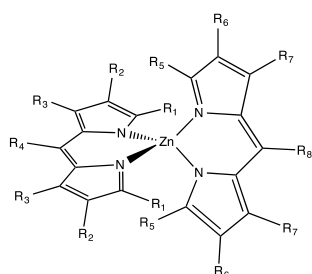


Figure 1. Framework of bis(dipyrinato)zinc(II) complex Figure 2. Illustration of the charge-separated state.

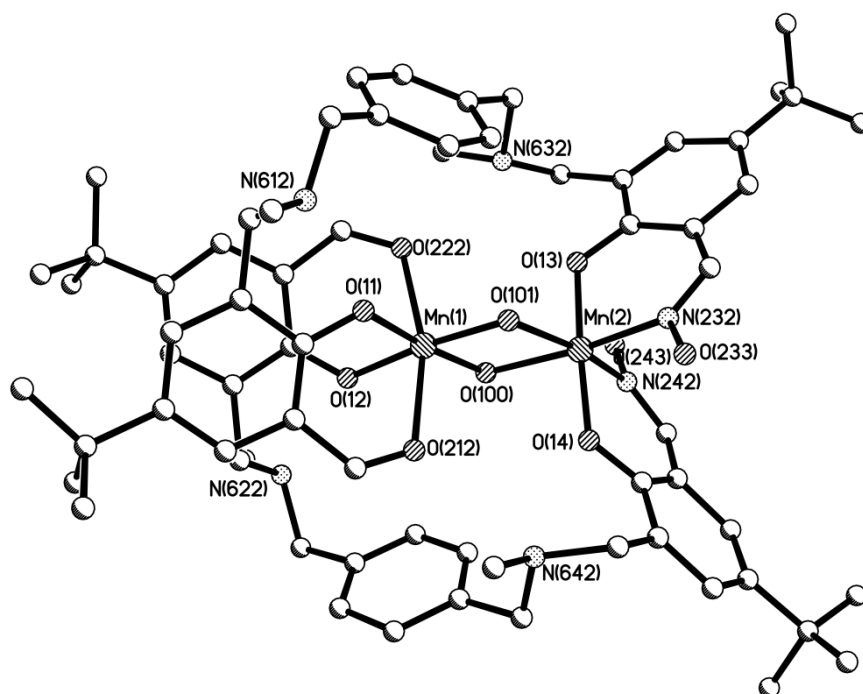
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## Exploring a Dinuclear Complex with Possible Jahn-Teller Compression and Elongation

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Complexes that possess both Jahn-Teller compression and elongation effects at metal centres within the same molecule are extremely rare with only nine examples known in the literature.<sup>1-9</sup> An X-ray crystallographic analysis of a di-manganese coordination compound serendipitously synthesised by Willoughby in 2011 suggested that this complex might possess both Jahn-Teller compression and elongation.<sup>10</sup> This presentation will describe the steps taken to complete the structural and magnetic characterisation of this complex.



**Figure 1** X-ray structure of the dinuclear complex synthesised by Willoughby.<sup>10</sup>

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## Symmetry in spin-orbit coupling and magnetic anisotropy in mononuclear transition metal complexes

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Magnetic anisotropy in transition metal (TM) complexes is essentially governed by the splitting of the  $M_S$  (or  $M_J$ ) levels of the electronic ground state. This zero-field splitting (ZFS) is mainly caused by the spin-orbit coupling (SOC). In TM with orbitally non-degenerate ground state, the SOC occurs at the 2<sup>nd</sup> order of perturbation theory and couples the ground state with some excited electronic states. In order to rationalize the magnetic properties of TM complexes, the identification of these excited states is crucial and represents a first step to design complexes with the wanted magnetic properties. Here we show that selection rules for spin-orbit interaction in molecules can be easily applied to identify which excited states are coupled to the ground state and how they act on the ZFS. Furthermore, since the crystal field in high spin complexes is weak, we show that, for the isolated metal cation, the spin-orbit selection rules are not (totally) quenched by the ligand field, further reducing the number of excited states to consider.

This idea has been illustrated by *ab initio* calculations (CASSCF/SO-RASSI) on the model complexes  $[\text{Co}(\text{NCH})_5]^{2+}$  and  $[\text{Co}(\text{NCH})_4\text{Cl}]^+$  and on the  $[\text{Co}(\text{tren})\text{Cl}]^+$  complex showing that very small distortions can lead to large changes in magnetic properties, regardless of the ligands nature. For instance, lowering the symmetry of cobalt(II) complexes from  $D_{3h}$  to  $C_{3v}$  leads to the apparition of new couplings between ground and excited states that progressively switch the easy-plane type magnetization to an easy-axis type. The combination of these selection rules and simple crystal-field theory has led to the synthesis of a series of  $C_{3v}$  cobalt(II) complexes with a controlled axial anisotropy ranging from -2 to -20  $\text{cm}^{-1}$ .



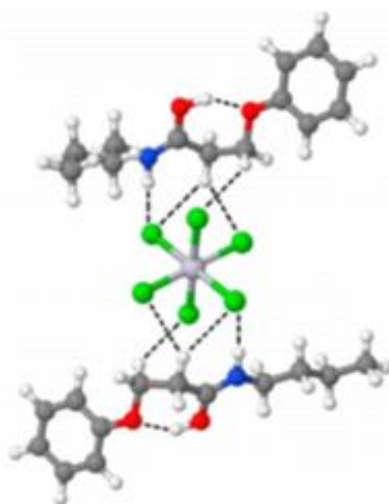
## Computational Modelling Techniques for the Design of Solvent Extractants for Metals

I. Carson, E. D. Doidge, K. J. MacRuary, C. A. Morrison, P. A. Tasker and J. B. Love.  
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Computational techniques have proven highly valuable in the design of reagents for solvent extraction of metals,<sup>1</sup> both as a means of screening potential extractants before experimental work is undertaken, and as an analytical tool to probe the modes of action of established solvent extractants.

We have successfully applied geometry optimisation and molecular dynamics methods to the design of solvent extractants targeting a variety of metals in acidic media. An example is the recently-reported development of a novel class of amidoamine and amidoetherextractants for platinum (Figure 1),<sup>2</sup> for which DFT formation energy calculations were able to reproduce and rationalise experimentally-observed trends in extractant strength, as well as the observed selectivity of these reagents for platinum chloridometalates over chloride. Classical and quantum mechanical molecular dynamics methods also show significant promise as means of investigating the mode of action of solvent extractants, particularly where the formation of supramolecular assemblies (such as reverse micelles) plays an important role in the extraction process.<sup>3</sup>



**Figure 1:** Assembly formed by outer-sphere complexation of  $\text{PtCl}_6^{2-}$  anion by amidoetherextractants, with key hydrogen-bonding interactions shown as dotted lines.<sup>2</sup>

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## Chain coordination polymers: topological taxonomy, basic correlations and prediction methods

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The one-periodic coordination polymers attract a great attention due to their electron and ionic conductivity, adsorption, catalytic and magnetic properties<sup>1</sup>. However, the accumulated crystallographic information is poorly used for finding general principles of their structural organization, developing the models of their formation and searching for the 'structure-property' correlations. The main goal of our work was to create the general geometrical-topological taxonomy for one-periodic coordination polymers.

Using the ToposPro program package<sup>2</sup> we have extracted from the CSD (version 5.36) and analyzed the crystal data for 26975 one-periodic coordination polymers. As a result, we have found topological correlations driving structural organization of the coordination polymers. For example, we have enumerated all observed rod-packings and correlations between the local characteristics of the inter-rod interactions and the type of the rod-packing. Interestingly, many types of rod packings are observed in MOFs.<sup>3</sup> Further, we have classified the coordination polymers according to their composition and topological type, as well as coordination properties of central atoms and ligands. The values of the geometrical and topological descriptors were stored in the knowledge database on coordination polymers. We have shown that these data can be used for prediction of new compounds with specified properties and composition.

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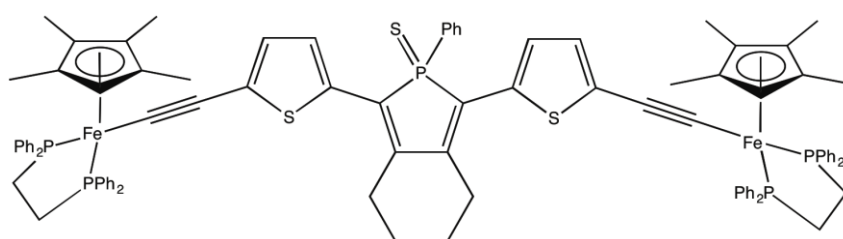
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## Computational Study of Electronic and Optical Properties of Phosphole-based Wire-like Iron Complexes

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Over the last years,  $\pi$ -conjugated systems with heteroatoms like carbazoles, pyrroles or thiophenes heterocycles have known a great success owing to their potential for optoelectronic application (OLED, photovoltaic cells...). More recently, phosphole rings were pointed out as an interesting alternative building block for the conception of  $\pi$ -conjugated systems due to its low aromatic character and its phosphorus reactivity.<sup>1,2</sup> Hissler's group has shown that optical properties of such systems can be tuned depending upon the organic groups tethered to the phospholes.<sup>2</sup> Alternatively, based on previous works by Lapinte and coworkers on redox-active organoiron wires in which different carbon-containing units span two transition metal groups,<sup>3</sup> new systems containing phosphole in the bridge such as the iron complex  $[(\text{Fe}(\text{Cp}^*\text{dppe})-\text{C}\equiv\text{C}-\text{C}_4\text{H}_2\text{S})_2-\text{C}_8\text{H}_8\text{PPhS}]$  ( $\text{Cp}^*$  = pentamethylcyclopentadiene, dppe = 1,2-bis(diphenylphosphino)ethane) (Scheme 1) can also be envisaged. Density Functional Theory (DFT) calculations were carried on this system and derivatives in order to discuss their electronic and optical properties. Main results will be presented.



**Scheme 1**

1 See for example: Kira, A.; Shibano, P.; Kang, S.; Hayashi, H.; Umeyama, T.; Matano, Y.; Imahori, H. *Chem. Lett.* **2010**, 39, 448.

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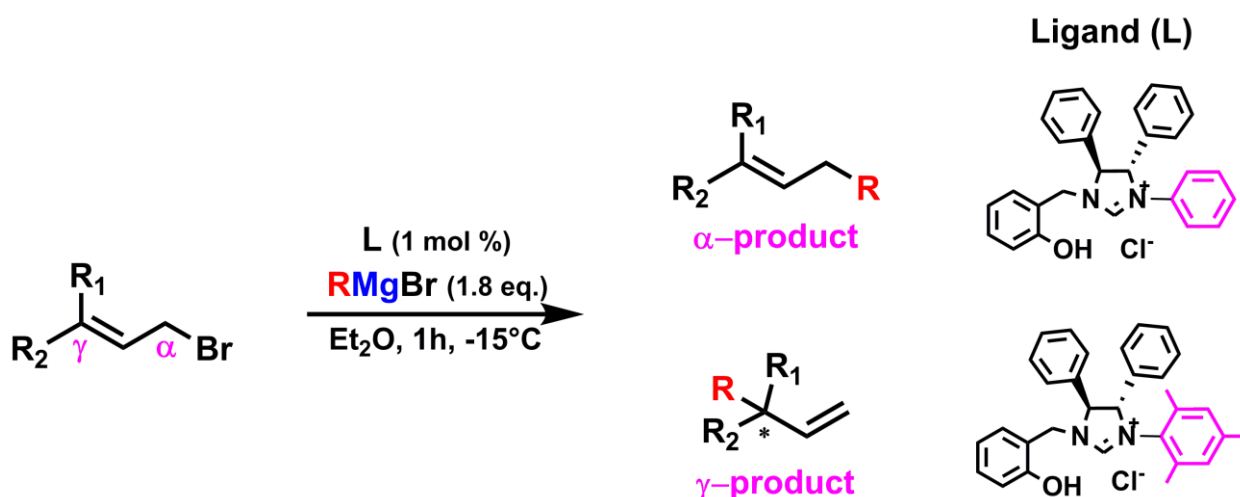
## Mechanisms and selectivity of the Cu-free Asymmetric Allylic Alkylation: a computational study.

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The asymmetric allylic alkylation (AAA), using copper and a chiral ligand is a powerful tool to reach an enantioenriched compound with a high level of regioselectivity. Recently, the Cu-free AAA was reported with Grignard reagent as nucleophile and NHC ligands exhibiting an efficient catalytic activity<sup>1</sup>. The design of the NHC ligand plays a key role in the regio- and enantioselectivity of this reaction (**Figure 1**).



**Figure 1:** The regioselectivity of the NHC-catalyzed AAA reaction of a Grignard reagent.

Theoretical studies were carried out to understand the mechanistic aspects and the selectivity of this reaction. In this study, the supposed mechanism was calculated with the Density Functional Theory (DFT). We will expose the complexity of this reaction due to the modelling of magnesium-carbene species, which are strongly dependent of the solvent effect and can aggregate.

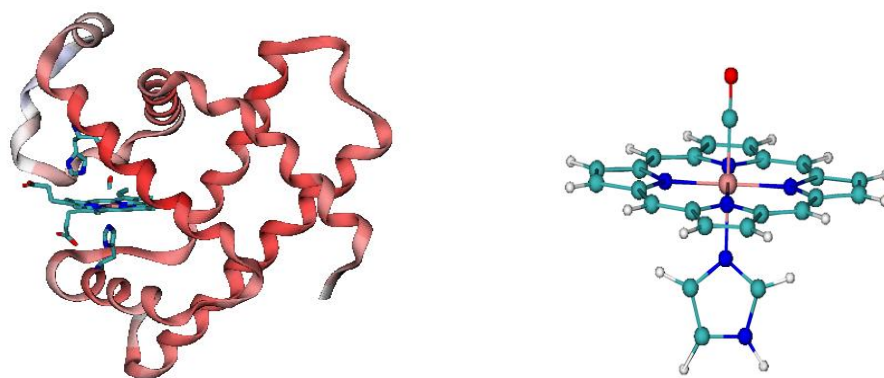
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## Ultrafast Heme-CO dissociation is triggered by vibronic couplings

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Hemoproteins are well known metalloproteins responsible for the transportation of gaseous diatomic molecules such as molecular oxygen, carbon monoxide (CO), etc. These molecules can be dissociated photochemically in an ultrafast scale ( $< 50$  fs) by a mechanism which is yet not fully characterized.<sup>1,2</sup> In this study, we determine the photochemistry for a cofactor model of myoglobin containing a histidine, the heme group and CO. We perform electronic structure and full quantum dynamics simulations to show that excitation to the Q-band of porphyrin leads to an ultrafast energy transfer to iron-centered states, mainly triggered by strong vibronic couplings in the singlet manifold.<sup>3</sup> In a second step, spin-orbit coupling acts allowing the spin crossover mechanism typical of such iron complexes.<sup>4</sup>



**Figure 1** (left) Myoglobin protein with the position of the prosthetic group. (right) Model used in our simulations.

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## Reliable calculations of redox potentials for dinuclear copper complexes

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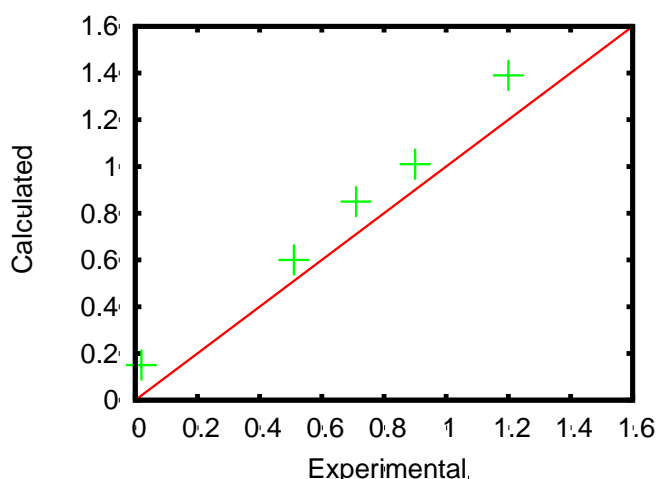
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Particulate methane monooxygenases (pMMO) accomplishes the direct conversion of methane into methanol at ambient temperature and atmospheric pressure.<sup>1</sup>To obtain new copper-based catalysts efficient for alkane oxidation, dinuclear copper(II) species inspired by the structure and function of this copper enzyme have been synthesized and characterized by X-ray crystallography and cyclic voltammetry.

In this communication, we will describe a calibration of DFT calculations to obtain a good correlation between experimental and theoretical data for these systems (Figure 1). We use a computational reference redox couple, calculated by using identical conditions (e.g. same level of theory and solvent parameters) to reduce systematic errors as it was shown before.<sup>2</sup>Reliable calculations of redox potentials would be used in the following to design new dinuclear copper complexes.



**Figure 1** Correlation between experimental and calculated  $E^\circ$  redox potential in V vs  $[\text{FeCp}_2]^{0/+}$  for the first oxidation for some dinuclear copper complexes

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## Group 15 Elements as Vertex Atoms in Metallaboranes

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Phosphorus has been recognized as a "carbon copy" owing to the similar electronegativities of phosphorus and carbon relating to their diagonal relationship in the Periodic Table. Welch et. al. have synthesized<sup>1</sup> an isomer of the cobalt complex CpCoP<sub>2</sub>B<sub>9</sub>H<sub>9</sub>. DFT results on the complete series of cobaltadiphosphaboranes CpCoP<sub>2</sub>B<sub>n-3</sub>H<sub>n-3</sub> (n=8-12) show that the central CoP<sub>2</sub>B<sub>n-3</sub> polyhedra are the most spherical closo deltahedra. Low-energy structures are found to avoid P-P edges with the phosphorus atoms preferring lower degree vertices<sup>2</sup>. However, for the analogous cobaltadibismaboranes CpCBi<sub>2</sub>B<sub>n-3</sub>H<sub>n-3</sub> (n=10-12) structures, Bi-Bi edges are energetically preferred with the lowest energy structures always having a CoBi<sub>2</sub> face<sup>3</sup>. Furthermore, in the 11-vertex deltahedral CpCoBi<sub>2</sub>B<sub>8</sub>H<sub>8</sub> lowest energy structures, a bismuth atom rather than a cobalt atom is located at the unique degree 6 vertex<sup>3</sup>.

A comprehensive DFT study of the complete series of cobaltaazaboranes CpCoNHB<sub>n-2</sub>H<sub>n-2</sub> (n = 8-12)<sup>4</sup> related to the experimentally reported<sup>5</sup> CpCoNHB<sub>9</sub>H<sub>9</sub> led to the discovery of low-energy structures for the 8- and 9-vertex systems based on non-spherical deltahedra providing a degree 3 vertex for the nitrogen atom and thus violating expectations from the Wade–Mingos rules<sup>5</sup>.

Using the anion [CH<sub>3</sub>PCHB<sub>8</sub>H<sub>8</sub>]<sup>-</sup> as a precursor, the 12-vertex ferraphosphacarborane CpFeCHP(CH<sub>3</sub>)B<sub>8</sub>H<sub>8</sub> was synthesized<sup>6</sup>. The complete CpFeCHP(CH<sub>3</sub>)B<sub>n-3</sub>H<sub>n-3</sub> (n=8-12) series have now been studied by DFT methods<sup>7</sup>. The low-energy structures are characterized by having adjacent iron and phosphorus atoms and non-adjacent phosphorus and carbon atoms. One of the low-energy 11-vertex CpFeCHP(CH<sub>3</sub>)B<sub>8</sub>H<sub>8</sub> structures, with a degree 6 iron vertex, was found to exhibit a fragile Fe–B bond readily elongating to ~3.1 Å, in agreement with experimental observation<sup>6</sup>.

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# Electronic Underpinnings of Phosphido-Bridged Pt<sub>3</sub> Clusters and the Questioned Stereochemistry of the Uniquely Reported 46e<sup>-</sup> Species

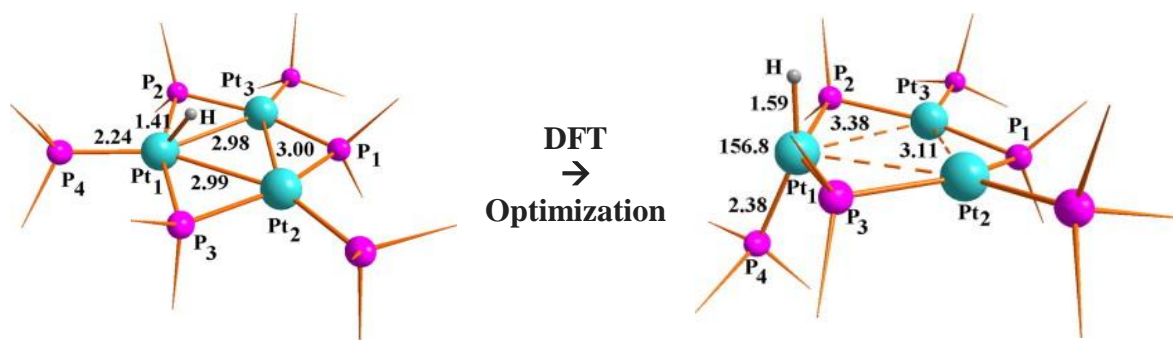
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The compound  $\text{H}(\text{PEt}_3)_3\text{Pt}_3(\mu\text{-PPh}_2)_3$  is the unique example of a 46e<sup>-</sup> phosphido-bridged triangular cluster, but its X-ray assigned stereochemistry appears questionable. In particular, the H-free  $\text{P}_3\text{Pt}_3(\mu\text{-P})_3$  metal core is identical to that of the 44e<sup>-</sup> cation  $[(\text{PEt}_3)_3\text{Pt}_3(\mu\text{-PPh}_2)_3]^+$  in two salts of the same publication. Also, the lack of a distortional effect due to the upright and strongly-bound hydride ligand is suspicious and intriguing aspects emerge from the inconsistent electronic structure. Although  $\text{H}(\text{PEt}_3)_3\text{Pt}_3(\mu\text{-PPh}_2)_3$  is fully validated by IR and NMR spectra, DFT optimizations never reproduced the proposed experimental structure but highlighted a different stereochemistry still consistent with the spectroscopic response. Here, a formal Pt(II) ion is essentially isolated and has square-planar coordination, completed by two *trans*-axial ligands (H and Et<sub>3</sub>P) out of the Pt<sub>3</sub> plane. Given the chemical reliability of the *in silico* molecule, the crystals of the experimental structure have likely contents other than the hydridic cluster and a co-crystallized Ph<sub>2</sub>PH molecule. As a working hypothesis, the Pt-H and P-H linkages of the distinct components may have reacted together with H<sub>2</sub> release, and subsequent crystallization of the salt whereas the ion pair  $[(\text{PEt}_3)_3\text{Pt}_3(\mu\text{-PPh}_2)_3]^+ / [\text{Ph}_2\text{P}]^-$ . This would explain the equal geometries of the putative 46e<sup>-</sup> cluster and the H-free 44e<sup>-</sup> cation. In the lack of any experimental X-ray dataset, the proposed crystal formulation could not be fully validated, but in the paper various aspects support its reliability. Essentially, the problem may arise from the misplacement of two H atoms (those of the mentioned Pt-H and P-H linkages), which does not affect the structural refinement but determines the chemical inconsistency.



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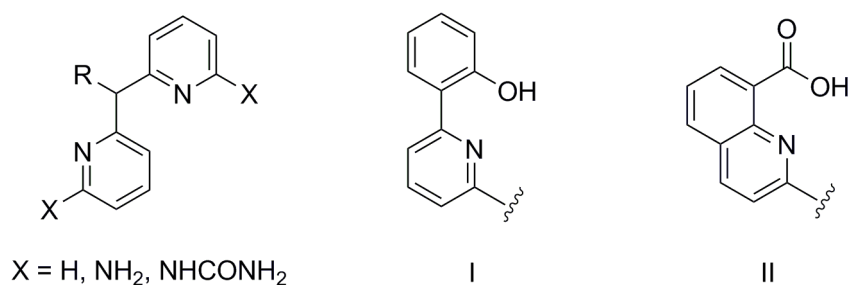
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## Second-sphere hydrogen bond tuning of receptors for the encapsulation of beryllium

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Beryllium is a crucial metal in the automotive, aviation, nuclear and consumer industries. It is considered to be the most toxic non-radioactive element, a class I carcinogen, and the cause of life-threatening chronic beryllium disease.<sup>1</sup> Previous efforts have been made to develop effective beryllium receptors.<sup>2</sup> This presentation will describe the effect that second-sphere hydrogen bonding on the binding strength of tetradentate pyridine-based ligands towards Be(II), B(III) and Al(III) using computational methods. We show that the intra-ligand H-bond interaction therefore imposes a strong influence on the structure and stability of the complex by providing a buttress to the coordination pocket.



**Figure 1** Motifs of studied ligands

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## Surface coordination chemistry on MgO: how dissociated water improves the basic catalysis of alcohol conversion

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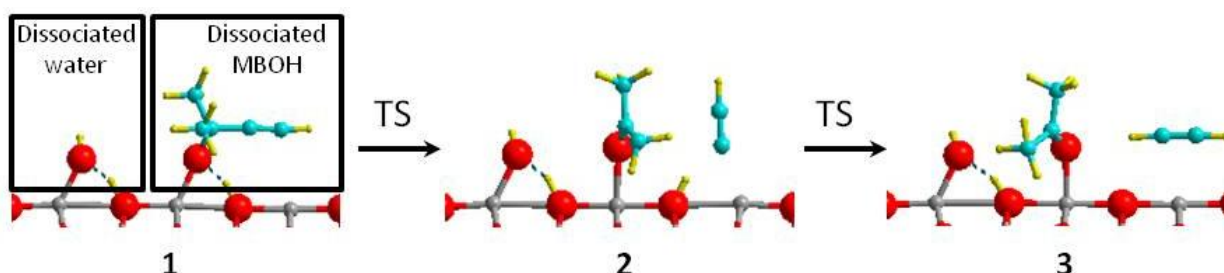
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Basic metal oxides play a major role as solid catalysts in valorization of alcohols from biomass. Those catalysts show a typical behaviour: Strong basic sites are not always needed for an efficient conversion of alcohols. Interestingly, surface hydroxo ligands are often involved in the most active sites catalyzing alcohol conversions, even when stronger basic sites are available on the surface. That role of hydroxo ligands was specifically proved on MgO from structure-activity relationships built with a model reaction, the conversion of 2-methylbut-3-yn-2-ol (MBOH), into acetone and acetylene.<sup>1</sup>



**Figure 1** Intermediates of MBOH conversion on a partially hydroxylated MgO edge: 1. dissociated MBOH, 2. ads. acetone near dissociated C<sub>2</sub>H<sub>2</sub>, 3. ads. acetone and ads. C<sub>2</sub>H<sub>2</sub>.

This presentation aims to explain with periodic DFT modeling (GGA, VASP code) why hydroxylated MgO surfaces catalyze basic conversion of MBOH more efficiently than bare MgO surfaces do. We modeled the MgO active site with the edge of a di-atomic step, largely used for rationalizing basic reactivity of MgO.<sup>2</sup> We calculated the reaction pathways on that MgO edge by varying the coverage of MBOH and preadsorbed OH.<sup>3</sup> In conclusion, the OH ligands improve the active site reactivity via an original mechanism in which the OH ligands hinder the geometric surface relaxation and destabilize the reactant.

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# Mechanistic Studies on Cooperative Bond Activation Reactions with a Carbene Ruthenium Complex

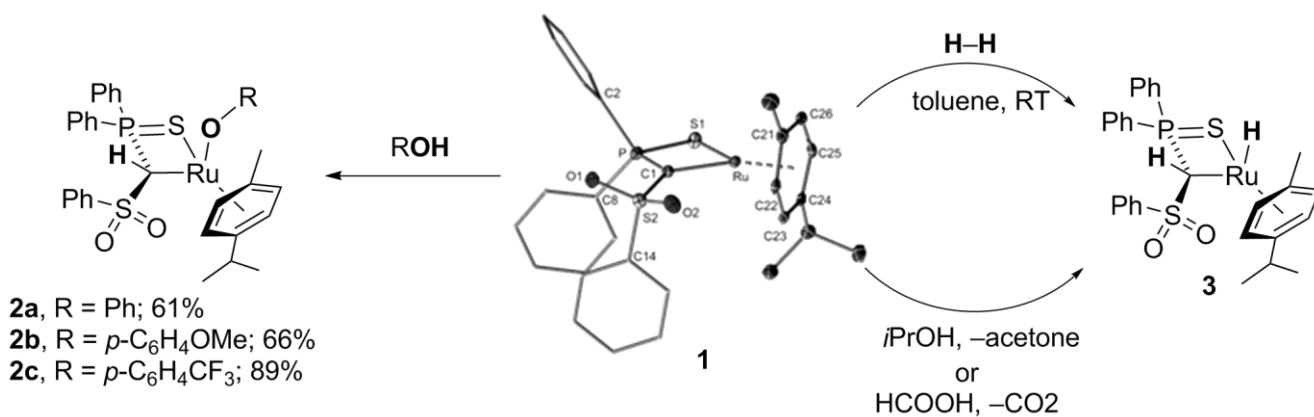
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In the past years, carbene complexes formed from methandiides have been subject of extensive research. Differing from the well-known Fischer- and Schrock-type carbene complexes by formally donating four electrons to the metal,<sup>1</sup> they exhibit a flexible metal carbon interaction. Depending on the bonding situation these complexes allow for the activation of element-hydrogen as well as element-element bonds by means of metal-ligand cooperation.<sup>2</sup>

The ruthenium complex **1** prepared in our group is able to activate a variety of different substrates, such as molecular dihydrogen, alcohols and silanes (see Figure 1).<sup>3,4</sup> Quantum mechanical calculations are used to investigate the mechanisms involved in the addition of different species to complex **1**. So far, two pathways have found to be active: a) a concerted 1,2-addition or b) an oxidative addition with a subsequent fragment transfer. Here, we discuss cooperative bond activation reactions with **1** and mechanistic details.



**Figure 1** Bond activation reactions with ruthenium complex **1**.<sup>3,4</sup>

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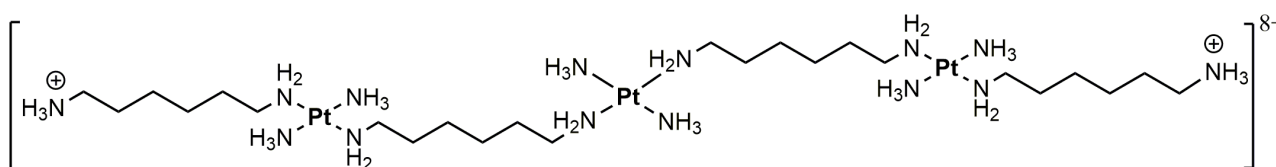
## Theoretical study of non-covalent interactions between trinuclear platinum(II) complexes and DNA.

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<sup>a</sup>Núcleo de Estudos em Química Computacional (NEQC), Dep. Química, ICE, Universidade Federal de Juiz de Fora - CEP 36036-900 - Juiz de Fora - MG - Brazil

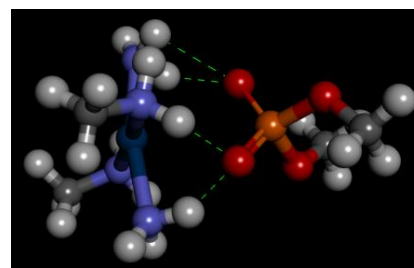
\*luiz.costa@ufjf.edu.br

Since the discovery of cisplatin antitumor properties the study of metallic complexes as chemotherapy agents has increased. Polinuclear platinum(II) compounds are very promising molecules against cancer cells due to its more rapid and effective interactions (high affinity) with DNA when comparing with mononuclear complexes. Within this class, trinuclear platinum complexes, such as AH78 (Fig. 1) and its analogues,<sup>1</sup> shows a unique non-covalent binding properties, due to the absence of good labile ligands. The goal here is to investigate and describe those interactions at molecular level through density functional theory (DFT) using a mimetic model and a full DNA dodecamer structure.



**Figure 1.** Triplatin structure AH78<sup>1</sup> of  $[\{trans\text{-Pt}(\text{NH}_3)_2(\text{NH}_2(\text{CH}_2)_6\text{NH}_3)\}_2-\mu\text{-}(trans\text{-Pt}(\text{NH}_3)_2(\text{NH}_2(\text{CH}_2)_n\text{NH}_2)_2\}]^{8+}$ .

In order to compare with the interactions reported by Qu and co-workers<sup>2</sup> a mimetic model of the phosphate clamp with the central Pt(II) of AH78 has been created. This model was obtained by optimization and harmonic frequencies calculations in aqueous solution (IEFPCM) at B3LYP/6-31G(d,p)/LANL2DZ level of theory.



**Figure 2.** Phosphate clamp mimetic model.

Four hydrogen bonds have been formed between the amino groups directly coordinated to the Pt center and the oxygen atom from the phosphate group. A largest model containing a DNA fraction is being studied aiming to evaluate these interactions in order to evaluate force constants and molecular orbitals, in a deeper analysis.

1. A. Prisecaru; *et. al. Nucleic Acid Research*, **2014**, *42*, 13474.
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## Electronic Structure of iron carbenes and their reactivity with alkenes: Alkene cyclopropanation vs. alkene metathesis

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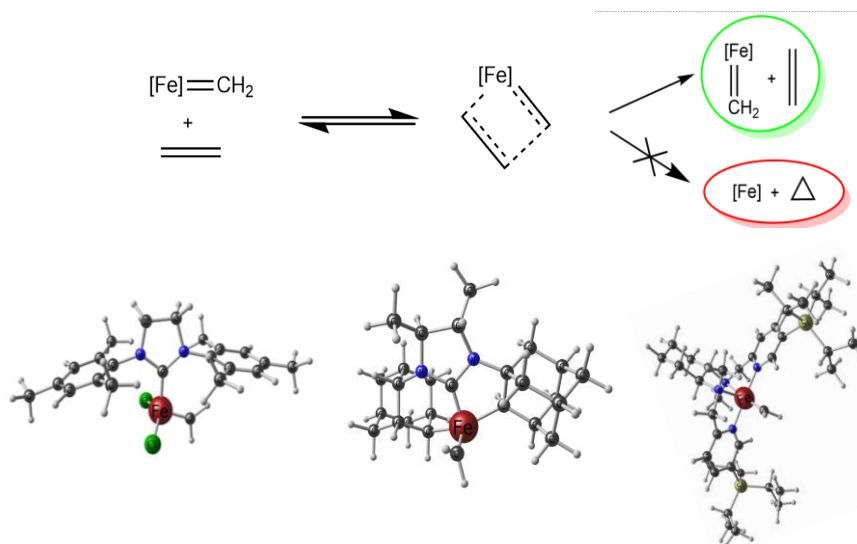
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The olefin metathesis reaction is one of the most efficient C=C double bond forming reactions. Mo, W and Ru based molecular catalysts have been synthesized with outstanding activities and selectivity.<sup>[1]</sup> However, cheap and eco-friendly catalysts are desired. One option would be to design iron-based olefin metathesis catalysts, since iron is inexpensive and has a low toxicity.<sup>[2]</sup> Unfortunately, the up-to-date existing iron carbenes undertake alkene cyclopropanation instead of metathesis.<sup>[3]</sup>

In this contribution, we use a DFT approach to study the electronic structure and reactivity of several existing as well as *in silico* designed iron carbenes. We analyze the factors that make alkene cyclopropanation more feasible than alkene metathesis with the aim of determining the nature of the ligand, coordination sphere and oxidation state of iron that could lead to a potential olefin metathesis catalyst (Figure 1).



**Figure 1** Catalysts studied in order to achieve a environment which promotes olefin metathesis instead of cyclopropanation.

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**N-(3-chlorophenyl) -4-{N-(3-cyclohexylthio propyl)} piperazinium chloride (L<sup>1</sup>) and N-(chlorophenyl)-4-(N-phenylseleno propyl) piperazinium chloride(L<sup>2</sup>); Synthesis and complexation with mercury (II), cadmium (II) and zinc (II). Crystal structures of(L<sup>2</sup>), [L<sup>1</sup>(NO<sub>3</sub>)], [L<sup>2</sup>(NO<sub>3</sub>)].**

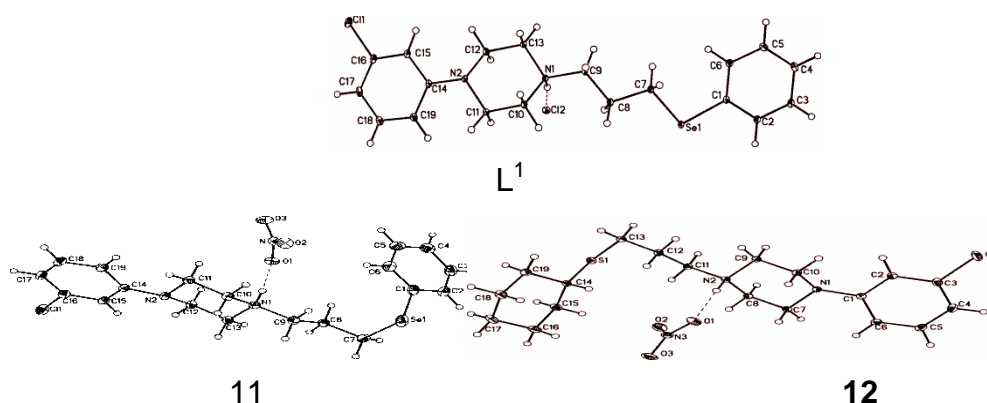
Muzzaffar Ahmad Bhat<sup>a\*</sup>, Sanjay K. Srivastava<sup>a</sup>, R.J. Butcher<sup>b</sup>

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Graphical abstract



*Abstract. Cadmium(II), Mercury(II) and Zinc(II) complexes of novel [N-(3-chlorophenyl) -4-{N-(3-cyclohexylthio propyl)} piperazinium chloride] (L<sup>1</sup>) and [1-(chlorophenyl)-4-(3-phenylseleno propyl) piperazinium chloride] (L<sup>2</sup>) having the formulae [CdCl<sub>2</sub>.(L<sup>1</sup>)] (1), [CdI<sub>2</sub>.(L<sup>1</sup>)] (2), [HgCl<sub>2</sub>. (L<sup>1</sup>)] (3), [ZnCl<sub>2</sub>. (L<sup>1</sup>)] (4), Cd(NO<sub>3</sub>)<sub>2</sub>.(L<sup>1</sup>)] (5) [CdCl<sub>2</sub>.(L<sup>2</sup>)] (6), [CdI<sub>2</sub>.(L<sup>2</sup>)] (7), [HgCl<sub>2</sub>. (L<sup>2</sup>)] (8), [ZnCl<sub>2</sub>. (L<sup>2</sup>)] (9), [(C<sub>6</sub>H<sub>5</sub>)HgCl. (L<sup>2</sup>)] (10) [(NO<sub>3</sub>). (L<sup>2</sup>)] (11) and [(NO<sub>3</sub>). (L<sup>1</sup>)] (12) were prepared and characterized on the basis of physico-chemical and spectral (FT-IR, Mass, <sup>1</sup>H, <sup>13</sup>C, DEPT 135° <sup>13</sup>C {<sup>1</sup>H} and <sup>77</sup>Se NMR) studies. Decomposition followed by anion exchange had taken place on keeping the complexes for crystallization. L<sup>2</sup> and the decomposed products 11 and 12 crystallized in monoclinic and orthorhombic systems with space groups P 21/c and P bca. The geometry around N is distorted tetrahedral. The intramolecular and intermolecular hydrogen bonding O-----H-N, Cl-----H-N exists in all structures and accounts for the supramolecular nature and stability.*

*Keywords Crystallization; anion exchange; monoclinic; orthorhombic; hydrogen bonding; supramolecular; crystal structure*



## When Amidinato-Methylaluminium Chloride Met N-Heterocyclic Carbenes... Normal or Abnormal???

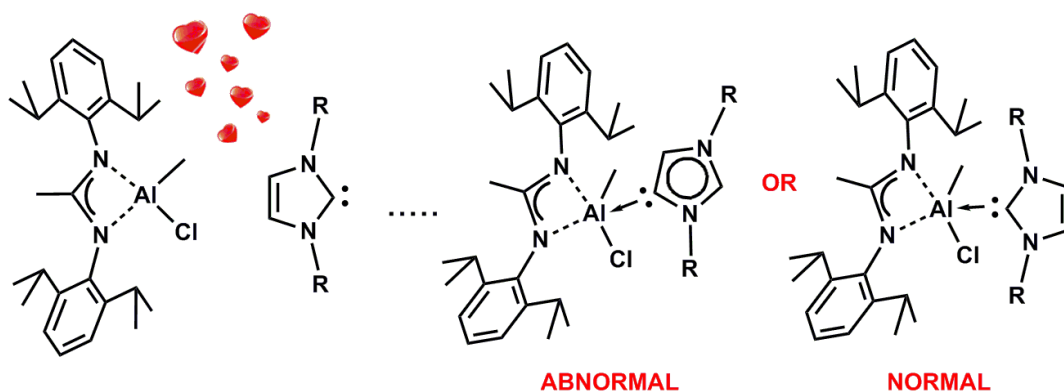
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The propensity of highly electron-deficient aluminium(III) compounds to interact with such Lewis bases as amines, phosphines or donor solvents is one of the cornerstones of classical organometallic chemistry. The first unusual example of congested Lewis adducts built up from the N-Heterocyclic carbene as a  $\sigma$ -electron donating system and aluminium(III) species was reported by Arduengo<sup>1</sup> in early 1990s. However, since then only little attention has been directed toward aluminium-carbene complexes and only a handful of examples of abnormal carbenes of main group metals<sup>2</sup> and zinc<sup>3</sup> are known.

The direct synthesis and structure of normal vs. abnormal amidinato-aluminium N-heterocyclic carbenes supported by a series of theoretical calculations will be demonstrated.



**Figure 1** When amidinato-methylaluminium chloride met N-heterocyclic carbenes.

**Acknowledgements:** Financial support from the Grant Agency of Czech Republic (grant nr. P207/12/0223) is acknowledged.

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# ASYMMETRIC GRIGNARD SYNTHESIS OF TERTIARY ALCOHOLS

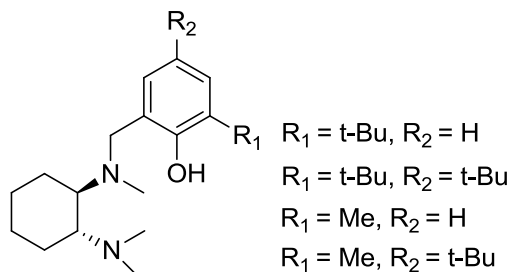
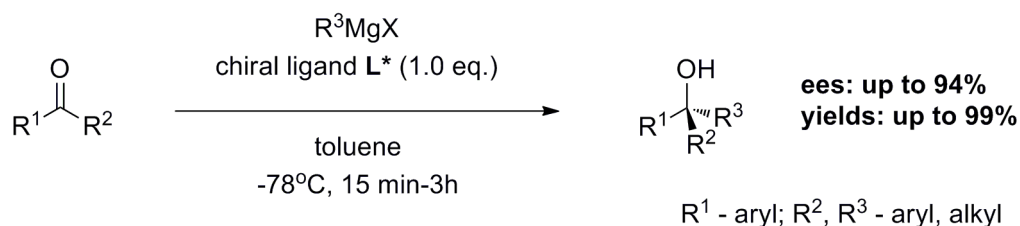
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Chiral tertiary alcohols constitute an important class of biologically active molecules.<sup>[1]</sup> Most conveniently they can be prepared by a stereoselective addition of organometallic reagents to ketones. Among organometallics, the Grignard reagents present the widest scope and greatest versatility. However, stereoselective synthesis of tertiary alcohols by direct 1,2-addition of Grignard reagent to ketones is extremely challenging and most of the successful cases involve transmetalation using transition metals.<sup>[2]</sup> To best of our knowledge, only a single case was reported to date where high enantioselectivity was obtained in the absence of metals other than magnesium.<sup>[3]</sup>

The challenges of asymmetric Grignard synthesis of tertiary alcohols lie in: the reduced enantioface discrimination between the prochiral sides of a ketone (as compared to an aldehyde), competitive non-stereoselective reactions, low yields due to enolization/reduction side reactions, and dynamic processes originating from the Schlenk equilibrium.<sup>[4]</sup>



We followed on from previously successful research in the group which employed a chiral ligand to produce tertiary alcohols stereoselectively via 1,2-addition of Grignard reagents to a range of ketones. Subsequent research has involved synthesizing variants of the general ligand structure and testing it under previously established conditions as chiral ligands. Future research will involve testing more exotic ligand structure, expanding the substrate scope, mechanistic investigation, and attempting to render the system catalytic. The chiral ligand **L\*** can easily be recycled from the crude reaction mixture.

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<sup>[4]</sup> B. Bieszczad, D.G. Gilheany, manuscript in preparation

## Total attribution of paramagnetic compounds signals by comparison of three Fe<sup>(III)</sup>(Cp\*)(dppe)-C≡C-P(O)Ar<sub>2</sub> analogues

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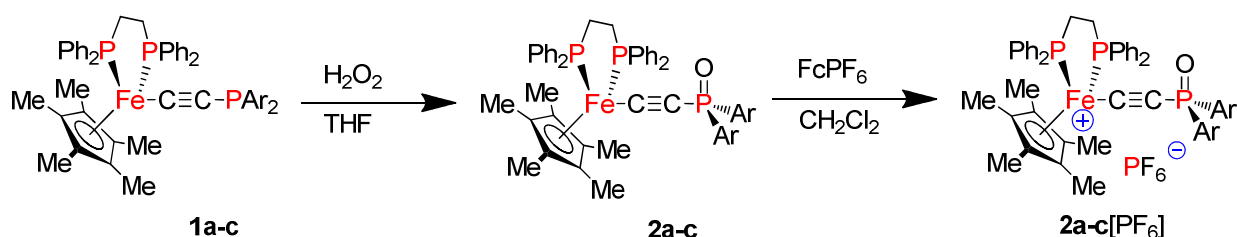
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We have reported previously the synthesis of Fe<sup>(III)</sup> species from the corresponding [Fe<sup>(III)</sup>(Cp\*)(dppe)(C≡CC<sub>6</sub>H<sub>4</sub>PAr<sub>2</sub>)] compounds.<sup>1</sup> All the <sup>1</sup>H NMR signals could be identified by analogy with those of their related complexes, supplemented by integration. More recently, we made a new kind of Fe<sup>(II)</sup> species without the 1,4-phenylene spacer (**1a**; Figure 1; Ar = Ph) and wanted to characterize it under its Fe<sup>(III)</sup> state. An unexpected formation of biphosphane (Fe<sup>(II)</sup>) species was observed upon oxidation.<sup>2</sup> In order to inhibit the formation of P-P bond, we have removed the doublet on the phosphorous center by making the corresponding oxide (**2a**). Accordingly, the corresponding Fe<sup>(III)</sup> species (**2a**[PF<sub>6</sub>]) turned out to be stable and isolable (Figure 1). This paramagnetic (low spin) compound presents a quite shifted <sup>1</sup>H NMR spectrum. Partial attribution of the signals could be proposed based on 2D-NMR. In order to remove any uncertainty on this attribution, two analogues of [Fe<sup>(III)</sup>(Cp\*)(dppe)(C≡CP(O)Ar<sub>2</sub>)] [PF<sub>6</sub>] have been synthesized (Ar = *o*-Tol and *p*-Tol). These two new compounds have been fully characterized,<sup>3</sup> allowing us to ascertain the proposed attribution for the <sup>1</sup>H NMR signals detected.



**Figure 1** Synthesis of the Paramagnetic Phosphine-Oxide Fe(III) Complexes.

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## Synthesis of Tetradentate Ligands starting from Carborane-substituted 1,2-Diphosphetanes

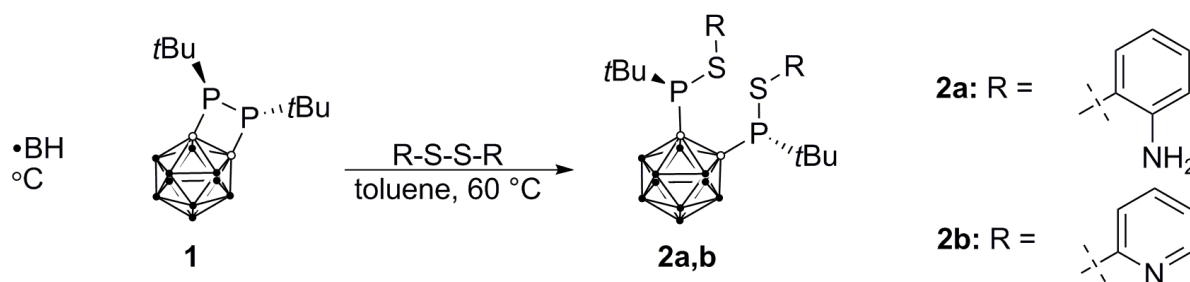
P. Coburger,<sup>a</sup> M. Sárosi,<sup>a</sup> E. Hey-Hawkins<sup>a\*</sup>

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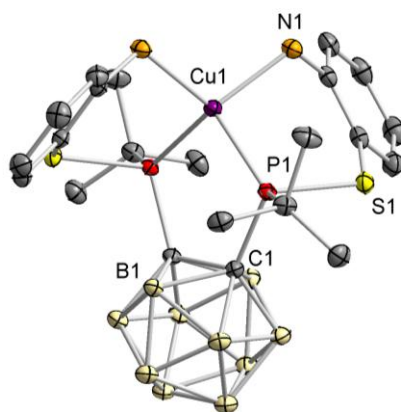
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Hemilabile ligands based on phosphanes have gained attention since they are capable of improving metal-catalysed homogeneous reactions when compared to traditional bisphosphanes.<sup>1,2</sup> This effect could be attributed to the weak coordination of one of the donor atoms to the metal atom which can then be readily displaced by a substrate molecule during a catalytic process.

A new approach towards this class of ligands is the stereoselective reaction of 1,2-diphosphetane **1** with functionalised diaryl disulfides to yield **2a,b** in good yields. Their ability for tetra-coordination is demonstrated by formation of copper complex **3**.



**Scheme 1:** Synthesis of tetradentate ligands **2a,b**.



**Figure 1:** Molecular structure of **3** with ellipsoids drawn at 50% probability level. Hydrogen atoms and iodide counterion are omitted for clarity.

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## *P*-<sup>t</sup>Bu oxaphosphirane complexes and products derived thereof – going for small to enable new reactivity

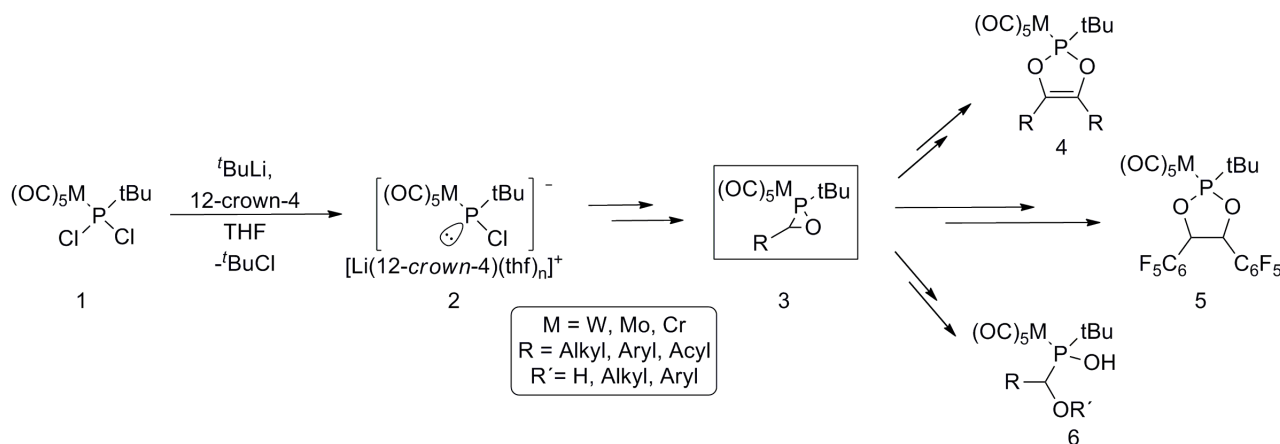
J. Fassbender,<sup>a</sup> R. Streubel\*<sup>a</sup>

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Despite oxaphosphirane complexes are known since 1990,<sup>1</sup> only recently their chemistry took off, as the use of Li/Cl phosphinidenoid complexes<sup>2</sup> has enabled broad studies. Since then a wide range of oxaphosphirane-derived products could be made accessible including new P-heterocyclic<sup>3</sup> and phosphalkene complexes.<sup>4</sup>

Herein, the synthesis and reactivity of *P*-<sup>t</sup>Bu substituted oxaphosphirane complexes **3**, readily available from dichlorophosphane complexes **1**,<sup>5</sup> will be described. Transient complexes **3** show enhanced reactivity (compared to previously known sterically demanding derivatives) as the facile ring expansion (to **4** and **5**)<sup>5</sup> as well as hydrolysis and alcoholysis reactions illustrate. Studies on decomplexation reactions will be reported, too.



**Figure 1** Generation and reactivity of *P*-<sup>t</sup>Bu-substituted oxaphosphirane complexes **3**

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# Methane and Methanol Steam Reforming in Catalytic Inorganic Membranes for Hydrogen Production and Continuous Fuel Cell Utilization.

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The aim of this paper is the description and analysis of new findings and results on catalytic membrane reactors and other catalytic reactor materials for the steam reforming reactions of methane and methanol, for hydrogen production and use in power generation systems and fuel cells. New inorganic polymeric materials are considered as membranes for the reactors. The current communication, continues this research by giving emphasis in the so-called "Improved Reaction" and "Reforming-Fuel Cell" systems.

We examine the use of methane/methanol based feed-stocks (hydrogen generating feed-stocks) as sources for Power/Electricity generation via Fuel Cell Technology (i.e., PEMFCs and SOFCs). The work focuses on the analysis of methane steam reforming data from two types of reactors. We also examine different inorganic polymeric materials as reactor and/or separator wall materials. The membrane based reformer and the conventional catalytic plug flow reformer. It was found that the catalytic inorganic membrane reformer offers higher yields of hydrogen than the catalytic plug flow reformer<sup>1,2,4,5,6</sup>. The same is true for the offered methane conversions and the CO<sub>2</sub> product yields. It is expected that the integration of the membrane reformer into the fuel cell network will offer an improved technical and economic design for this process operation. Moreover, the developed inorganic membrane-fuel cell designs offer reduced pollutant emissions (e.g., NO<sub>x</sub>, SO<sub>x</sub>, HCs) in comparison with conventional combustion systems.

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## (Poly)-propylene and hydrogen cogeneration using novel alternative technologies via smart inorganic and polymeric membranes

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Several types of process and reactor configurations have been considered and their polymeric reactions with the corresponding conditions have been studied in details. Their applications are reported for each case. The polypropylene production is analyzed in details and other polymers are discussed as well. All the conditions involved in the polymeric reactions are presented and compared to show the performance, taking into account the key parameters such as: increased polymer yield, hydrogen yield, recycling ratio, reaction rate constants, and reactor and separator intrinsic parameters. Smart polymeric processes that can save energy and show economical advantages as well, have been searched and analyzed. New catalytic reactors and separator/separation techniques are utilized to achieve higher efficiencies and yields for polymer (e.g., polypropylene) production. Two and three dimensions figures are presented for both conventional and novel permeable reactors. Reaction and catalytic characteristics are also examined. Novel inorganic polymeric materials and process configurations are also considered for suitable applications<sup>1,2,3</sup>. Optimization techniques have been employed to find the best achievable polymeric processes that provide interesting new results. Isomerization reactions of paraffins are employed to show the maximum performance in terms of yield and selectivity. Such a work is going to contribute to interesting new applications of polymers and ideas for further research<sup>4</sup>. It is also going to highlight the accomplishments of the important area of research for new inorganic polymeric materials. These processes are going to introduce new polymeric materials with dynamic applications such as polymer-catalyst and sensors, semiconducting nano-wires and more.

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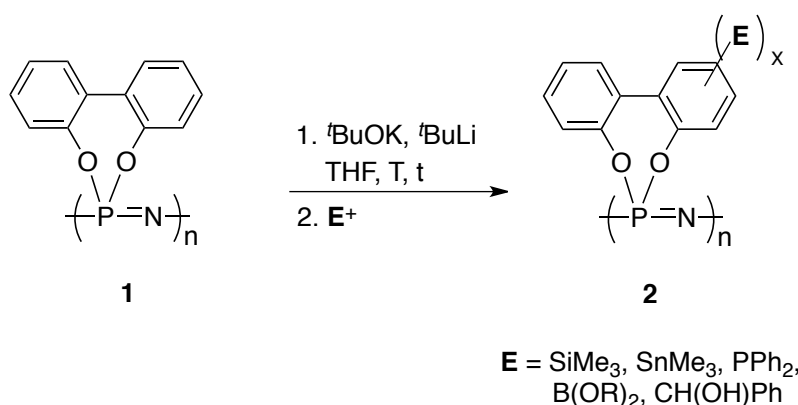
## Direct Functionalization of Poly(biphenoxyphosphazene) via Lithiation of the Aromatic Ring

Raquel de la Campa,<sup>a</sup> Diego García,<sup>a</sup> Gabino Carriedo Ulé,<sup>a</sup> Alejandro Presa Soto<sup>\*,a</sup>.

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The incorporation of useful chemical functions to linear polyphosphazenes or their surfaces is a subject of increasing interest and very relevant to the design of materials with predetermined properties including the immobilization of enzymes. The chemical derivatization of polyphosphazenes by secondary reactions on side groups is an important alternative to the classical macromolecular substitution for the introduction of functionalized groups on the polymeric chains. In earlier works<sup>1</sup> we reported the preparation of the soluble polyphosphazene  $[NP(O_2C_{12}H_8)]_n$  (**1**). So far, however, the study of its chemical reactivity has been limited to the acidic degradation,<sup>2</sup> nitration,<sup>3</sup> and halogenation.<sup>4</sup> Herein, we present a new direct functionalization reaction by metallation with the Schlosser's base ( $t\text{-BuLi/KOt-Bu}$ ) of the aromatic group present in the structure of a polybiphenoxyphosphazene (**1**). This reaction leads to a variety of functionalized polyphosphazene controlling the degree of functionalization and without any chain degradation (see Figure 1).



**Figure 1.** Direct functionalization of polybiphenoxyphosphazene (**1**)

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