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ABSTRACT BOOK

DNA-mediated Signaling with Metalloproteins

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Many experiments have now shown that double helical DNA can serve as a conduit for efficient charge transport over long molecular distances. We have seen, for example, using tethered metal complexes as photooxidants, that oxidative damage to DNA can be promoted from a distance as a DNA-mediated redox process. Photophysical, electrochemical and biochemical experiments have been conducted to characterize this chemistry. This chemistry is exquisitely sensitive to perturbations in the DNA base stack, such as arise with base mismatches, lesions, and protein binding. We have now been exploring how this chemistry may be used within the cell for long range signaling. Increasingly, 4Fe-4S clusters are being found in DNA-binding proteins involved in genome maintenance. Studies are described to characterize DNA–mediated signaling by these metalloproteins. Experiments indicate that long range DNA charge transport can provide a first step in how DNA repair proteins may localize in the vicinity of lesions. DNA charge transport, in carrying out redox chemistry at a distance, offers a route for long range signaling and coordination of DNA repair and DNA-processing proteins across the genome.

Organometallic Macrocycles, Cages and Their Application

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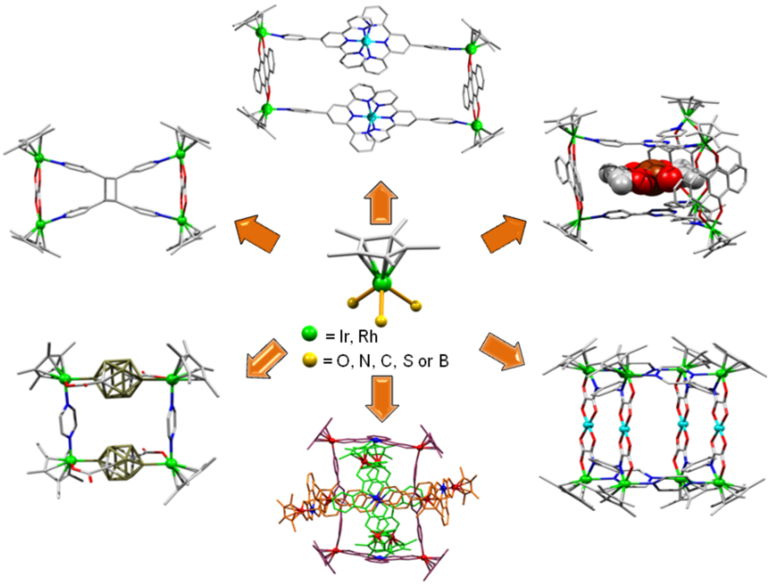
The construction of new inorganic and organometallic macrocycles and cages with interesting structural features and technologically useful functions have been topics of intense study with considerable potential.[1] One of the chief motivating factors to growth in this field is the development of new, functional and tunable donor building blocks that can bridge transition metals. Ideal building blocks should be easily accessible, exhibit high affinities toward transition metals, and possess facial coordination sites can undergo exchange reactions with various ligands. Half-sandwich transition metal complexes (Cp*M, Cp* = η^5-C_5Me_5) are useful model compounds in which one hemisphere of the coordination shell is blocked by the voluminous Cp* rings. In the protected space below the Cp* ligands, various bidentate or tridentate ligands can be accommodated.



Motivated by interest in supramolecular chemistry with organometallic half-sandwich complexes, we have initiated a new approach for preparing organometallic macrocycles via C-H and B-H activations with Terephthalate and dicarboxylate carborane.[2] We report herein an efficient method for synthesizing molecular macrocycles of half-sandwich iridium and rhodium complexes via C-H and B-H activation directed muticomponent self-assembly under mild condition.[3]

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Perspectives in Coordination Chemistry: From Metallo-Supramolecular Chemistry towards Adaptive Chemistry

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Supramolecular chemistry is actively exploring systems undergoing *self-organization*, i.e. systems capable of spontaneously generating well-defined functional supramolecular architectures by self-assembly from their components, on the basis of the *molecular information* stored in the covalent framework of the components and read out at the supramolecular level through specific non-covalent interactional algorithms, thus behaving as *programmed chemical systems*.

Supramolecular chemistry is intrinsically a *dynamic chemistry* in view of the lability of the interactions connecting the molecular components of a supramolecular entity and the resulting ability of supramolecular species to exchange their components. The same holds for molecular chemistry when the molecular entity contains covalent bonds that may form and break reversibility, so as to allow a continuous change in constitution by reorganization and exchange of building blocks. These features define a *Constitutional Dynamic Chemistry* (CDC) covering both the molecular and supramolecular levels. CDC takes advantage of dynamic diversity to allow variation and selection and operates on dynamic constitutional diversity in response to either internal or external factors to achieve *adaptation*.

CDC generates networks of dynamically interconverting constituents, *constitutional dynamic networks*, presenting *agonistic* and *antagonistic* relationships between their constituents that may respond to perturbations by physical stimuli or to chemical effectors.

The implementation of the features of CDC will be presented for *metallosupramolecular entities* involving the coordination of metal cations to dynamic ligand molecules formed by reversible reactions. Such entities present constitutional dynamics on both the molecular/covalent (the ligand) and the supramolecular/non-covalent (the cation binding) levels. They display adaptive features in response to metal cation effectors and form dynamic networks.

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Interfacial Coordination Programming of 1D and 2D Materials

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One of the final goals of the research on molecular electronics is to control electron conduction in molecular wires and networks at will by combining appropriate molecular units. Here I present interfacial coordination programming[1] to synthesize electro-functional one-dimensional (1D) nanowires and two-dimensional (2D) nanosheets.

A facile bottom-up method has been developed to fabricate 1D molecular wires of bis(terpyridine)metal oligomers on gold and silicon surfaces. The electron conduction properties of internal molecular segments as well as the resistivity at the electrode-molecular wire junction and the terminal hetero-redox molecular connection were quantitatively analyzed to evaluate the total performance of the molecular wires.[2,3]

Single layer nanosheet materials have attracted much attention because of their unique physical and chemical properties, which derive from their 2D nature. We are interested in using liquid-liquid and gas-liquid interfaces to synthesize coordination π-nanosheet, CONASH. We synthesized metalladithiolene π-nanosheet showing high electronic conductivity,[4-6] bis(terpyridine)metal nanosheet exhibiting electrochromism,[7] and bis(dipyrrinato)zinc nanosheet with photo-electronic conversation ability.[8]

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Recent Advances in Olefin Metathesis by Molybdenum and Tungsten Catalysts

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Among the several important developments in the last five years in olefin metathesis chemistry employing Mo or W catalysts has been the synthesis and application of M(NR)($CHCMe_2R'$)(OR)(Pyrrolide) (MonoAlkoxidePyrrolide or MAP) complexes, especially those in which OR is a sterically demanding terphenoxide such as 2,6-dimesitylphenoxide (OHMT). MAP species under the right circumstances have proven to be *Z*-selective in a variety of olefin metathesis reactions, among them enantioselective ring-opening/cross-metatheses, ROMP to give highly stereoregular polymers, ethenolysis of internal olefins such as oleates, coupling of terminal olefins, cross coupling of terminal olefins, and synthesis of macrocyclic natural products. A second important development has been the synthesis of a variety of tungsten oxo alkylidene complexes. Oxo complexes can be "activated" by binding $B(C_6F_5)_3$ to the oxo ligand and are likely to be analogs of metathesis catalysts found in classical metathesis catalyst systems. Applications of metathesis include stereoregular ring-opening metathesis polymerization to give *cis,isotactic* or *cis,syndiotactic* polymers and alternating AB copolymers. A third recent development is the discovery and development of "MAX" (monoaryloxide halide) complexes. MAX complexes can metathesize olefins that have a halide or other electron withdrawing group (e.g., CF_3) directly attached to the olefinic carbon atom.

Mixing spins and graphene: from coordination chemistry to electronic transport

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Controlling the dynamics of spins on surfaces is pivotal to the design of spintronic and quantum computing devices. Proposed schemes involve the interaction of spins with graphene to enable surface-state spintronics, but several challenges remain unsolved: how can molecular spins be assembled into hybrid structures? What is the influence of the graphene environment on the spin? Can molecules be used to control coherent currents in graphene devices? Here we answer these questions,[1] exploring spin-graphene interactions by using molecular magnetic materials.

We detail the assembly process and showcase the relevance of dynamic scaling theory and of graphene surface defects. We then show that, while the static spin response remains unaltered, the quantum spin dynamics and associated selection rules are profoundly modulated. The couplings to graphene phonons, to other spins, and to Dirac fermions are quantified using a newly-developed model. Coupling to Dirac electrons introduces a dominant quantum-relaxation channel that, by driving the spins over Villain's threshold, gives rise to fully-coherent, resonant spin tunneling. Eventually we show how molecular spins can be used to introduce bistable behavior into coherent spin currents. These findings provide the tenets for spin-manipulation in graphene nanodevices.

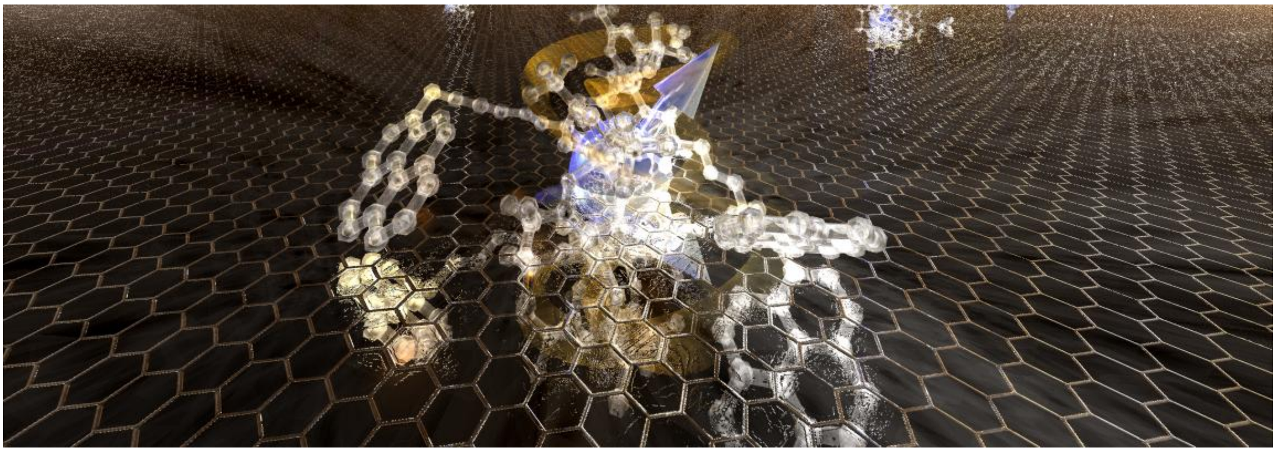

Figure 1 Molecular magnetic systems deposited on a graphene surface.

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Chromium-Lanthanide coordination complexes: single molecule magnet behaviour and magnetocaloric effect

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The first observation of a magnetic bistability phenomenon from a purely molecular origin has been reported by Sessoli & al.[1] in 1991, on a Mn_{12} acetate complex. Since this pioneering result, molecules exhibiting a slow relaxation of their magnetization are named single molecule magnets or SMMs and have been widely studied. Up to now, peculiar attentions have been devoted to the synthesis of 3d and heterometallic 3d-3d' complexes.[2] But recently, in the search for more efficient SMMs, it has been demonstrated that the incorporation of a highly anisotropic 4f ions into 3d matrices can enhance the SMM properties.[3] Furthermore, it has been demonstrated[4] that the combination of a highly anisotropic 4f ion with a highly isotropic 3d ion such as Cr^{III} ion can led to the formation of 3d-4f clusters with higher blocking temperature. We will present here a new family of Cr^{III}-Ln^{III} coordination complexes $[Cr_4Ln(CH_3COO)(pyCOO)((py)_2COO)_4]$ $(NO_3)_2{\cdot}nH_2O$ (with Ln = Gd^{3+}, Tb^{3+}, Dy^{3+}, and n = 19 or 20).[5] Single crystal X-ray studies revealed that the dysprosium derivative crystallizes as two different structural forms, a triclinic *P*-1 form and a monoclinic $P2_1/n$ form, as for the gadolinium and the terbium derivatives. Surprisingly, static and dynamic magnetic studies revealed that none of the synthesized complexes exhibit single molecule magnet behaviour, while Gd derivative displays a magnetocaloric effect (MCE). We will also discuss about the magnetic behaviour of a new neutral coordination complexes Cr^{III}-Ln^{III} $[CrDy_2(OCH_3)_4(dpm)_5(CH_3OH)]{\cdot}CH_3OH$ (dpm^- = deprototated dipivaloymethane ligand). Full magnetic investigations revealed that the complex exhibits single molecule magnet behaviour.

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Single Chain Magnets on Silicon surfaces

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Single chain magnets (SCMs) are an interesting class of molecular polymeric materials displaying slow relaxation of the magnetization. They provide, at low temperatures, a magnetic hysteretic behavior for a single polymeric chain. They behave as molecular magnetic nanowires and open interesting perspectives for storing information in low-dimensional magnetic materials.

Most often these materials are synthesized as micro(nano) crystalline powders. Their shaping as thin films is a key issue for the development of new devices.

In this work we study the growth of one SCM. These compounds are prepared by rational design by reaction of a mononuclear copper(II) complex with cobalt(II) cations. [1]

The growth is performed on Si surfaces functionalized by an organic monolayer tethered with functional groups able to coordinate the metal precursors, to favor the nucleation and the growth on the surface. [2,3] The formation of the films is monitored by AFM.

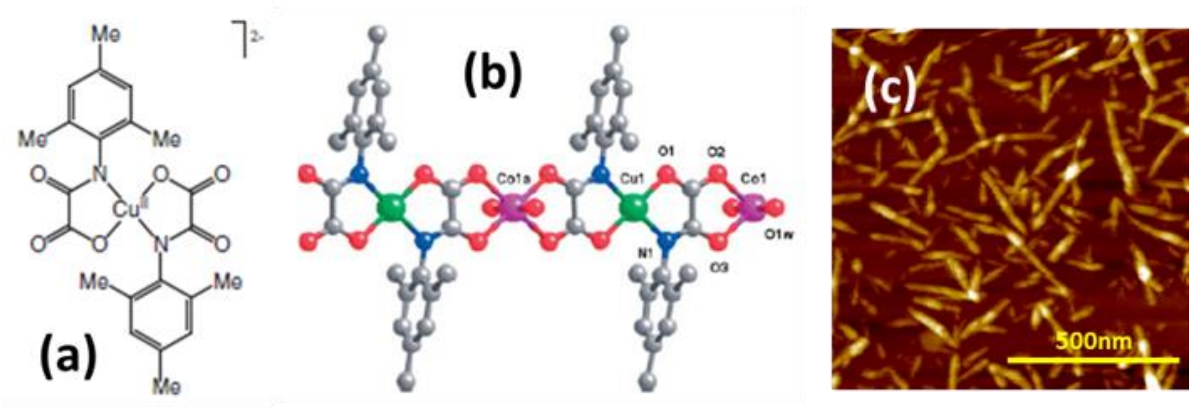

Figure 1 (a) Schema of the mononuclear Cu(II) entities precursors of the SCM ; (b) structure of the $Co^{II}Cu^{II}$ chain which is going to be grown as a thin film over the surfaces ; (c) AFM images showing the structure of this chain film grown on a Si surface with a pyridine-terminated functionalization.

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LANTHANIDE ION-CONTAINING COMPLEXES: A NEW FAMILY OF MOLECULAR MAGNETS

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Heterometallic and homometallic complexes containing lanthanide ions have been investigated with respect to their structure and magnetism. Of particular interest have been trimetallic complexes containing a central lanthanide ion and two peripheral open-shell transition metal ions or diamagnetic metal ions. In this talk emphasis will be given on the design of new polyfunctional ligands that have the capability to assemble both homo- and heterometallic complexes containing lanthanide ions.

Figure 1 A trinuclear complex containing a central Dy^{III} flanked on either side by diamagnetic Co^{III}

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Field-induced slow magnetic relaxation in a mononuclear Mn(III) complex: An ambient and high pressure study.

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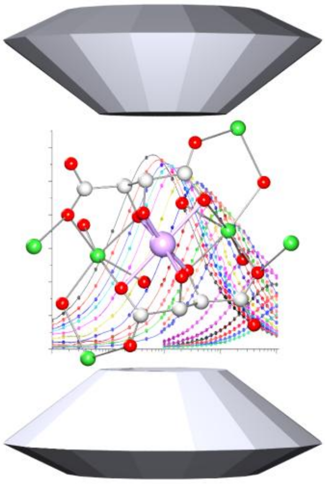
Slow relaxation of magnetisation arising from a single ion in a suitable ligand field,[1] and high pressure studies of metal complexes[2] are both hot topics in coordination chemistry. The former offers the possibility of using synthetic chemistry to achieve large magnetic anisotropy: sometimes an order of magnitude beyond that observed in polynuclear assemblies.[3] The latter have shown that pressure can flip the orientation of Jahn-Teller axes.[4] Herein, we will describe the magnetic anisotropy and field-induced slow relaxation of magnetisation observed in the compound $Na_5[Mn(L\text{-}tart)_2]\cdot 12H_2O$ (**1**, L-tart = L-tartrate).[5] The effect of hydrostatic pressure on the structure and magnetic properties of **1** will be detailed, revealing an unusual role played by the alkali metal ions.[6]



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Study of the self-assembly of the Single Molecule Magnet Fe_4Ph on Au(111) via a combined MM and QM approach

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The adsorbtion of inorganic magnetic systems on surface is a crucial step in the design of new materials, as spintronic devices or molecular qubits. Recently, a lot of efforts have been focused on the prediction, via ab initio calculations, of structure and electronic properties of isolated or single adsorbates. Such techniques are however unaffordable for the study at the mesoscale level, i.e. the self-assembly process. Here we present a study of the well known Single Molecule Magnet $[Fe_4(L)_6(dpm)_6]$ (Hdpm=dipivaloyl-methane and H_3L=2-hydroxymethyl-2-phenylpropane) or Fe_4Ph, for which we developed a full set of ad hoc classical potentials, allowing the study through Molecular Mechanics (MM) of large scale phenomena (temporally and spatially), combined with Density Functional Theory (DFT). The new potentials have been tested on a series of benchmarks to verify the reliability of the model. With this MM and QM integrated approach, we studied three systems: a single Fe_4Ph on surface[1], the half coverage and the full coverage monolayer. We identified and magnetically characterized new stable conformers and we gained insights on the process of clusterization. The computed hexagonal 2-D lattice was in very good agreement with STM results was and “edge effects” due to the finite dimension of the domains on surface were found.

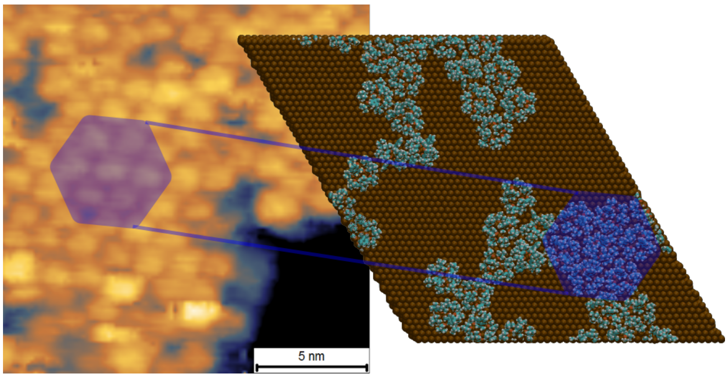

Figure 1. Comparison between experimental STM image and half coverage simulation

[1] G. Fernandez Garcia, A. Lunghi, F. Totti, R. Sessoli, *manuscript in preparation*

Geometric Modulation of the Jahn-Teller Distortion in Highly Anisotropic Manganese(III) Complexes

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High spin (HS) Mn^{III} in an octahedral field exhibits a strong Jahn-Teller (JT) effect which can confer considerable magnetic anisotropy or directionality. Magnetic anisotropy and its effect on the overall assembly of spins has been widely exploited in the design of single molecule magnets.[1,2] We were particularly interested in exploring the magnetic anisotropy in Mn^{III}, as our previous spin crossover complexes,[3-5] the JT distortion in the HS form is non-classical: we have typically observed a HS axial compression (equatorial elongation), presumably due to the relative ordering of the orbitals in the low spin (LS) state which would place the $d_{x^2-y^2}$ lower in energy than d_{z^2}. The addition of strain on the flexible ligand backbone previously used[3] is explored here, leading to the formation of trigonal prismatic complexes, Figure 1, with varying degrees of geometrical distortion. The counter anion has a marked effect on the degree of distortion and therefore on the trigonal prismatic character of the complex. This rare geometry could be integral in yielding interesting complexes that are both; magnetically and electronically atypical. This is due to the JT distortion manifesting itself in a peculiar way, a *cis* Jahn-Teller distortion, which results in the elongation of both tertiary amine donors. The magnetic anisotropy has been probed by high field/frequency EPR, magnetization and, DC and AC susceptibility measurements.

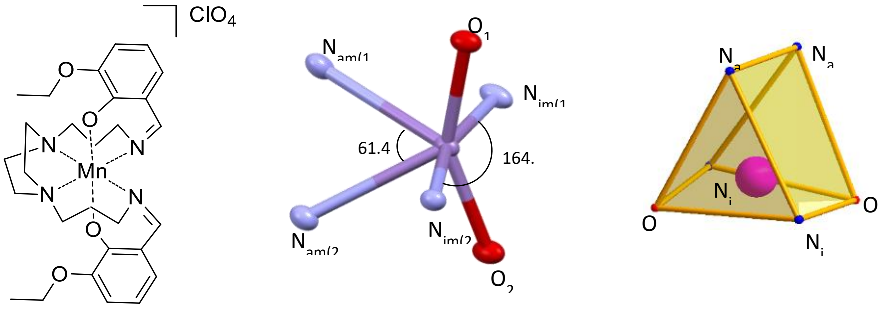

Figure 1: Mn(III) complex exhibiting a rare trigonal prismatic geometry

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Assessing the role of Ln^{III} (Nd^{III}, Sm^{III}, Gd^{III}, Tb^{III}, Dy^{III}) in $Co^{II}_2Ln^{III}$ systems : SMM behaviour of Sm^{III}, Gd^{III}, Tb^{III}, Dy^{III} analogues

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Since the first single-molecule magnet (SMM), $Mn_{12}OAc$, was discovered in the 1990s, many magnetic molecules exhibiting a slow relaxation of magnetization have been synthesized and magnetically characterized[1] with potential technological applications.[2] Much of the current SMM research has been inclined towards 3*d*-4*f* aggregates as the strong magnetic anisotropy of 4*f* ions is an essential basis for tuning the properties of SMMs.[3] As Co^{II} possesses significant magnetic anisotropy, thus the combination of Co^{II} with Ln^{III} ions might present a potentially interesting protocol to design SMMs. Here, we wish to convey the syntheses and investigation of SMM characteristics of a series of trinuclear $Co^{II}_2Ln^{III}$ complexes **1 – 5** with an aim to assess the contribution of Ln^{III}. The $Co^{II}_2Ln^{III}$ assembly was obtained from $Ln(NO_3)_3.xH_2O$: $Co(OAc)_2$: H_2vab : NaOMe in 0.4:0.5:1:1 ratio in methanol.

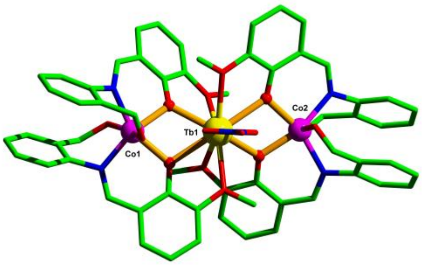

Figure 1 Crystal structure of $Co_2Tb(HVab)_4(OAc)](OAc)_2$ (**1**)

The isostructural $Co^{II}_2Ln^{III}$ complexes have a core structure with general formula, $[Co_2Ln(HVab)_4(OAc)](OAc)_2$, (where H_2vab = 2-[(2-Hydroxymethyl-phenylimino)-methyl]-6-methoxy-phenol and Ln^{III} = Nd^{III} **1**, Sm^{III} **2**, Gd^{III} **3**, Tb^{III} **4**, Dy^{III} **5**). Single crystal X-ray diffraction study reveals that complexes **1 − 5** crystallize in the triclinic system *P-1* bearing almost linear arrangement. The contribution of Ln^{III} is evidenced by the different magnetic behaviour of the $Co^{II}_2Ln^{III}$ compounds; Co_2Nd: no SMM characteristics; Co_2Sm: SMM; Co_2Gd: SMM; Co_2Tb: weak SMM; Co_2Dy: weak SMM.

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Influence of counterions on magnetism of dinuclear lanthanide(III) complexes with pentadentate Schiff base

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A series of dinuclear complexes of the general formula $[\{Ln(\mu\text{-}L5)A\}_2]$ (Ln = Gd-Er, H_2L5 = *N*,*N*-bis(salicylidene)diethylenetriamine, A = NO_3^- and Cl^-) was prepared and appropriately characterized. Although some of these compounds were already reported,[1-2] their detailed magnetic study is missing. Therefore, static and dynamic magnetic properties were investigated by dc magnetometry, and ac susceptibility measurements, respectively, complemented by the study of magnetocaloric effect (Ln = Gd). Moreover, *ab initio* calculations based on CASSCF were employed in order to better understand the magnetic properties of the complexes. Moreover, the impact of different counterions (NO_3^- vs. Cl^-) and different coordination numbers (8 vs. 7) are discussed.

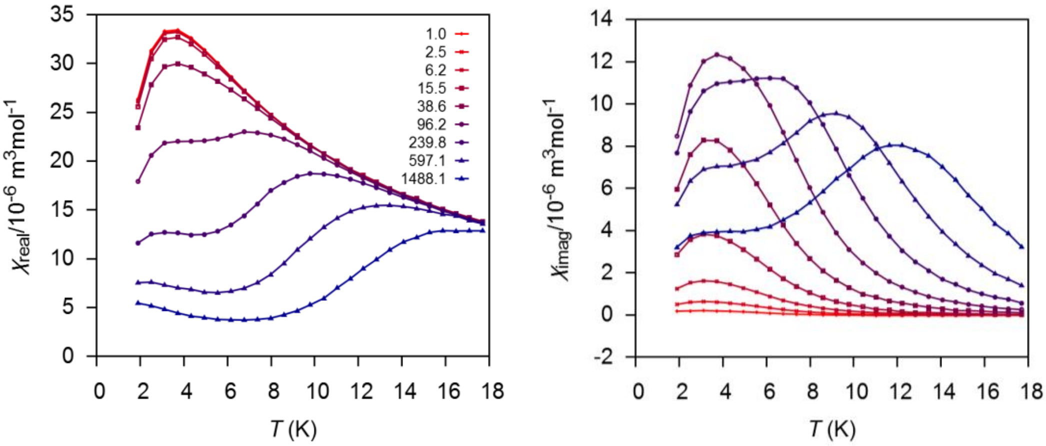

Figure 1 The ac susceptibility data measured at zero static magnetic field for $[\{Dy(\mu\text{-}L5)Cl\}_2]$

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Structure-Property Studies in Bistable Cyanometalates

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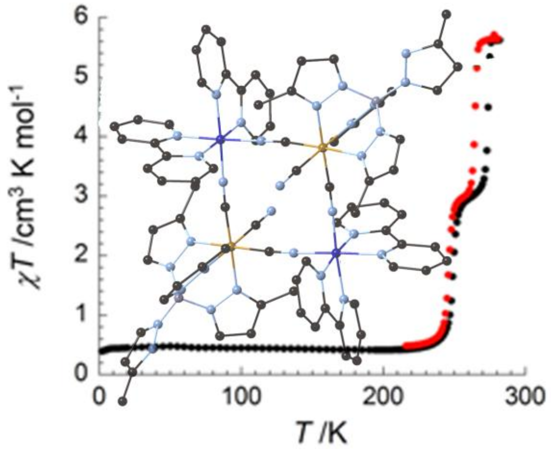

Figure 1. Magnetic data and structure for a new $\{M_2M'_2\}$ square.

Multifunctional materials are receiving considerable world-wide attention as potential switchable elements in information storage and molecule-based device technologies. The first photoswitchable Prussian blue was reported by Hashimoto in 1996, where dramatic color and magnetism changes are seen owing to thermally- and light-induced electron transfer that interconverts diamagnetic $Fe^{II}_{LS}/Co^{III}_{LS}$ and paramagnetic $Fe^{III}_{LS}/Co^{II}_{HS}$ pairs.[1] In 2008, we reported a molecular $\{Fe_4Co_4\}$ box that mimics the thermally- and optically-induced changes seen in thermo- and photochromic Fe/Co Prussian blues, ($T_{1/2}$ ~ 252 K); a remarkably long-lived photo-induced state is also seen (τ ~ 10 y at 120 K).[2] Later in 2010, we discovered a bistable $\{Fe_2Co_2\}$ square that displays qualitatively similar behavior ($T_{1/2}$ ~ 177 K; τ ~ 3 d at 120 K).[3] The temperature- and light-dependent magnetic, spectroscopic, and structural data indicate that intramolecular electron transfer may be tuned as a function of ancillary ligand donor strength and in some cases, their solid state contacts.[4] Several structurally related bistable clusters will be described in the frame of their intermolecular contacts and thermo- and photochromic behavior.

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Controlling and Sensing Spin States of Magnetic Porphyrin Molecules Using Scanning Tunneling Microscopy and Spectroscopy

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Binding and unbinding between small molecules and metallo-porphyrin are key processes for biological functions such as neuro-transmission, muscle-relaxation, and respiration. They can be also used to control spin states of magnetic metallo-porphyrin molecules. Controlling and sensing spin states of magnetic molecules in such reactions at the single molecule level is essential for spintronic molecular device applications. Here, we demonstrate that spin states of metallo-porphyrin on surfaces can be controlled over by binding and unbinding of small molecules, and be sensed using scanning tunneling microscopy and spectroscopy [1-4]. Kondo localized state of metallo-porhyrin showed significant modification by the binding of small molecules, implying that the spin state was changed. Our density functional theory calculation results explain the observations with the hybridization of unpaired spins in d and π^* orbitals of metallo-porphyrin and small molecules, respectively. Our study opens up ways to control molecular spin state and Kondo effect by means of molecular binding and unbinding reactions on surfaces.

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Highly anisotropic octanuclear SMMs based on Mn^{III} and Re^{IV}

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The magnetic properties of hexachlororhenate(IV) salts based on cationic $[Mn^{III}_6]^{2+}$ single-molecule magnets (SMMs) have been recently studied.[1] In these $[Mn_6][ReCl_6]$ systems, the energy barrier to magnetization relaxation of the $[Mn_6]^{2+}$ SMM is increased by effect of the highly anisotropic Re^{IV} metal ion.[1]

To step up our previous results we have also obtained a family of octanuclear $[Re^{IV}_2Mn^{III}_6]$ complexes, which have been prepared by using several mononuclear Re^{IV} precursors as metalloligands toward the $[Mn_6]^{2+}$ SMMs. One of these precursors is the highly anisotropic $[ReCl_4(ox)]^{2-}$ complex,[2] which exhibits here an oxalate coordination mode (μ_3) that is unusual in polynuclear 0D complexes containing this precursor (Fig. 1).

All family members show SMM behavior, this evidence being supported by micro-SQUID measurements performed on single crystals (Fig. 1).

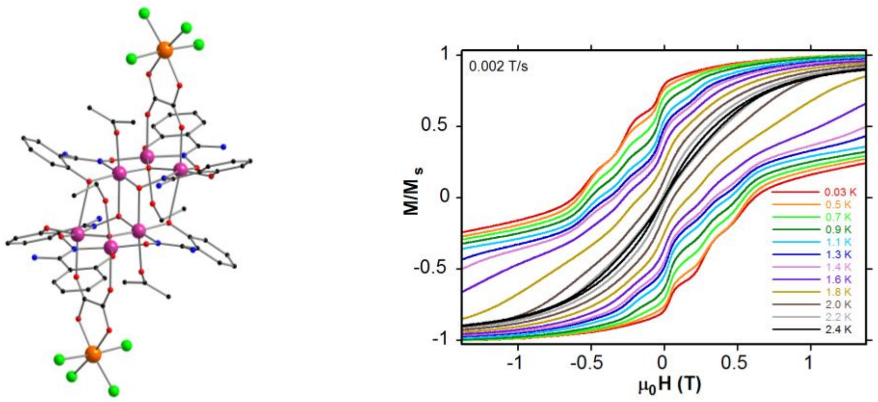

Figure 1. Molecular structure of an anionic octanuclear $[Re_2^{IV}Mn^{III}_6]^{2-}$ complex (left) and its plot of the magnetization vs. applied field recorded on a single crystal (right).

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Mixed-metal complexes based on ruthenium pivalate and octacyanidotungstate

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Mixed-metal complexes based on dinuclear ruthenium(II,III) carboxylates, $[Ru_2(O_2CR)_4]^+$, are interesting systems to construct molecular magnetic compounds, because mixed-valent $[Ru_2(O_2CR)_4]^+$ unit can be used as spin source [1,2]. Previously, we reported on mixed-metal complexes of dinuclear ruthenium(II,III) carboxylate with dicyanidoargentate(I) [3] or tetracyanidonickelate(II) [4] which showed a weak antiferromagnetic interaction between 3/2 spins of dinuclear ruthenium units. This is in contrast with the case for the system with octacyanidotungstate(V) $[\{Ru_2(piv)_4\}_3(H_2O)W(CN)_8]$ (Hpiv = pivalic acid), which showed a ferrimagnetic behavior with T_c = 44 K [5]. In this study, we extended this system by using some counter cations in the hope of obtaining ferrimagnetic compound with high T_c (Figure 1). We will discuss the structures and magnetic properties of the complexes together with those of the related mixed-metal complexes.

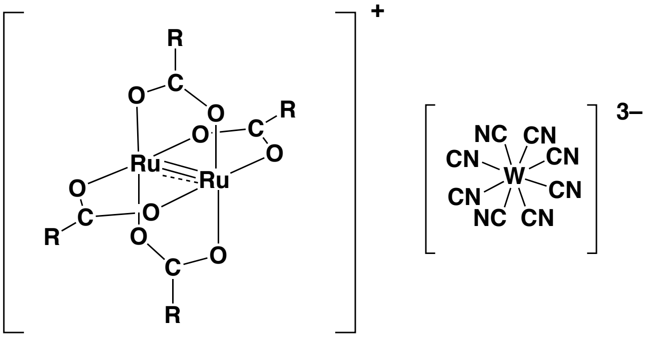

Figure 1 Dinuclear ruthenium carboxylate and octacyanidotungstate

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Symmetry Strategy to Enhance the Magnetic Anisotropy of Single-Molecule Magnets

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Inspired by the large intrinsic magnetic anisotropy of lanthanide ions[1], great synthetic efforts have been devoted to, not only the pure 4*f* single-molecule magnets (SMM), but also *d-f* SMMs since 2003[2]. We have focused on the employment of molecular engineering and magnetic engineering to synthesis novel molecular magnets with large magnetic reversal barrier and high blocking temperature[3]. We report herein the symmetry strategy to enhance the magnetic anisotropy of SMMs, in which the lanthanide centres with some special symmetries can hold both large energy barriers and record magnetic hysteresis temperature up to 20 K (Figure 1) as suggested by *ab initio* calculations.

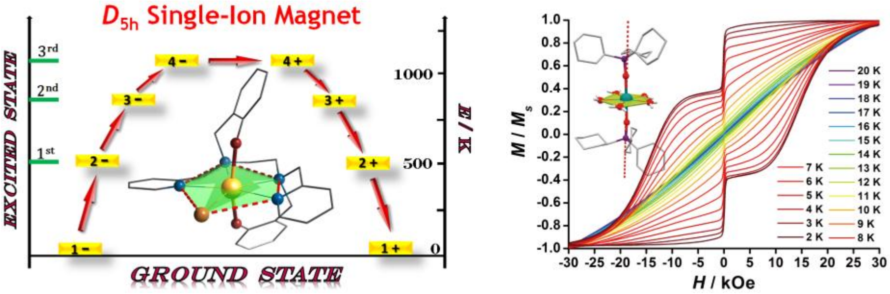

Figure 1 Mononuclear dysprosium SMMs with D_{5h} local symmetry, which show magnetic relaxations proceeding through the 2nd and 3rd excited Kramers doublet exhibiting a record energy barrier of over 1000 K (left) and a record magnetic blocking at 20 K (right).

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Magnetic Sponges for Solvents and Gases

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Metal-organic frameworks (MOFs) composed of electron-donors (D) and/or –acceptors (A): we call this group “D/A-MOFs” or “Redox-active MOFs” [1]. Since the charge transfer (CT) and electron transfer (ET) of $D^0A^0 \leftrightarrow D^{\square +}A^{\square -}$ can be rationally controlled by tuning the ionization potential of D and the electron affinity of A, they are really intriguing targets for functional materials with magnetic, conducting, and their synergistic properties (*Strategy-1*), as well as their porous nature for molecular adsorption. We have designed such materials in the combinations of paddlewheel-type diruthenium(II, II) complexes ($[Ru_2^{II,II}]$) as D and TCNQ or DCNQI derivatives as A, and demonstrated the rational control of CT/ET on D/A-frameworks to obtain electronic and magnetic functionalities [1-7]. On the other hand, these D/A-MOFs provide nano-sized pores surrounded by redox-active frameworks, which enable the absorption of specific gas molecules such as CO_2[8], NO [9,10], and O_2. Especially, the use of redox-active porous D/A-MOFs is advantageous not only to the specific separation of redox-active molecules[9,10] but also to the control of electronic/magnetic functionalities of frameworks[11] as guest-induced functionalities (*Strategy-2*).

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Breathing and Jumping Crystals

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Heterospin solids provide new opportunities for understanding of phase transition peculiarities. The results of studies on the synthesis and magnetostructural correlations of a specific group of heterospin complexes of $Cu(hfac)_2$ with stable nitroxides will be presented. When the temperature changes, the solid compounds undergo structural rearrangements accompanied by magnetic effects similar to spin crossover.

The high mechanical stability of the crystals, i.e., their ability of being reversibly compressed and expanded in the temperature range of phase transition, underlies the term "breathing crystals." The methods of modifying the character and temperature of spin transition for compounds from the given class are discussed. An analysis of the thermally induced phase transformations revealed a relationship between the structural rearrangement of $Cu(hfac)_2L\cdot 0.5Solv$ and the form of the magnetic anomaly on the $\mu_{eff}(T)$ curve and between the structural rearrangement of the solvate and the temperature of the magnetic effect.

The crystals of heterospin complexes $[M(hfac)_2L_2]$ (M=Cu, Ni, Co, or Mn; and L is nitronyl nitroxide), were found to make unusual jumping motions (lasted for several weeks under ambient conditions). The jumping was accompanied by the spontaneous elimination of oxygen, the source of which was the nitronyl nitroxyl fragment of coordinated radical. It was shown that the packing of $[M(hfac)_2L_2]$ was critical to the mechanical activity.

The crystals of several compounds were found to be capable of a reversible topotactic polymerization–depolymerization coordination reaction during repeated cooling–heating cycles.

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Coordination polymers based on carboxylate ligands. Structural and magnetic characterization

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The combination of organic and inorganic components into the same backbone has captivated many researchers probably as a consequence that the multiple choices of the components and also of the different synthetic strategies, permit to obtain and endless group of materials.[1,2] In the field of the coordination chemistry, beyond the wide variety and beautiful topologies which are characteristic of the coordination polymers, the different properties associated to the components and structural characteristic are obviously relevant. While the presence of the cavities or pores are desired for the applications in gas storage, sensing and separation, the type of metal ions and chemical identity of the organic ligand can be associated with the active catalytic center or optical properties of this material. Moreover, the type of paramagnetic metal ions and the organic linkers are significant in the magnetic properties. The use of lanthanide ions is interesting not only for their coordination environments, but also by the magnetic and luminescent properties. The last, clarify the importance of the constituents, both organic and inorganic in the different functionalities that a coordination polymer can acquire.

Taking into account the above paragraphs, we chose the carboxylate-based ligands as consequence of the coordination versatility and capability to bind 3d or 4f cations. Furthermore, using different synthetic procedures novel coordination polymers with different dimensionalities and presenting interesting topologies and magnetic characteristics were obtained. Details of the correlation of the structure and the observed properties, should be discussed in this work.

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Iridates from the molecular side

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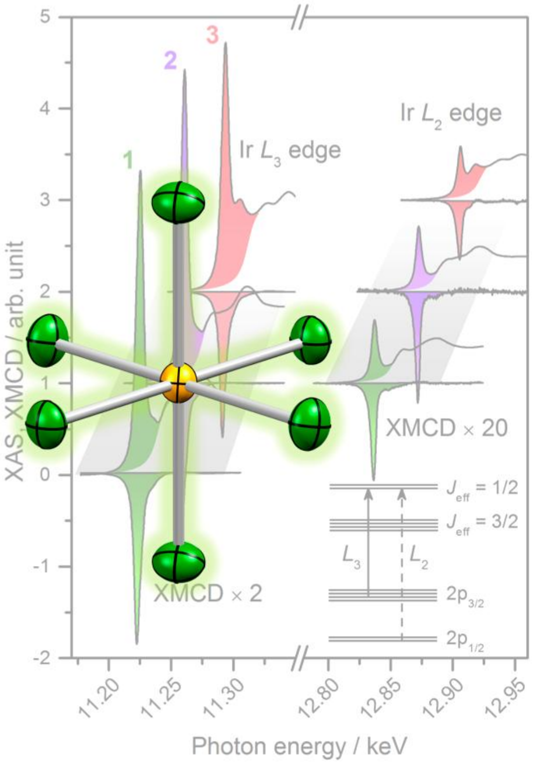
The interest in the heavier, 4d and 5d, transition metal ions recently blossomed due to the observation of exotic quantum phenomena in their oxides; most predominantly based on Ir^{IV}, the so-called 'iridates'.[1] Their singular properties originate at the microscopic level from the presence of exceedingly strong spin-orbit coupling within the $5d^5$ electronic configuration. The complex interplay of ionic Ir^{IV} properties and extended interactions hinders the understanding of the single-ion physics masking its full potential in novel quantum materials. Fluoride is key for the realization of a realistic model system for iridates due to its similar electronegativity, mass and redox-innocence, to the isoelectronic oxide. Herein, we determine the orbital and spin angular magnetic moments carried by the 5d electrons in the ultimate dimensional reduced iridate analogue: $[IrF_6]^{2-}$, by means of X-ray magnetic circular dichroism. Having established its electronic similarity to the iridates, the single-ion magnetic anisotropy, hyperfine interactions and its intrinsic slow relaxation of magnetization are unraveled. The resemblance of isolated Ir^{IV} complexes to its extended oxide analogues and its chemical robustness paves the way for application of molecular Ir^{IV} entities for bottom-up approaches towards novel electronic and magnetic quantum materials.



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Magneto-Structural Correlations in Organodysprosium Single-Molecule Magnets

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Single-molecule magnets (SMMs) are discrete molecular nano-magnets that, unlike bulk magnets, retain magnetization in ways that do not rely on long range magnetic ordering. SMMs offer unique properties with potential applications as device materials.[1] Our group has pioneered the use of organometallic chemistry in single-molecule magnetism,[2] and we have recently focused on developing unconventional ligand environments based on heavier p-block elements.

We now report a synthetic route to rare-earth complexes of primary pnictogen adducts **(1)**, and show how these complexes can be used to access rare-earth complexes of both monoanionic $[R_2E]^-$ **(2)** and dianionic $[RE]^{2-}$ **(3)** ligands (E = P,[3] As[4], Sb[5]), with the latter two types of ligand being unprecedented in rare-earth chemistry (Figure 1). We have found that varying the pnictogen donor atom in **1-3** produces systematic changes in the SMM properties, which has allowed a general design model for bis(cyclopentadienyl)-dysprosium complexes to be developed.

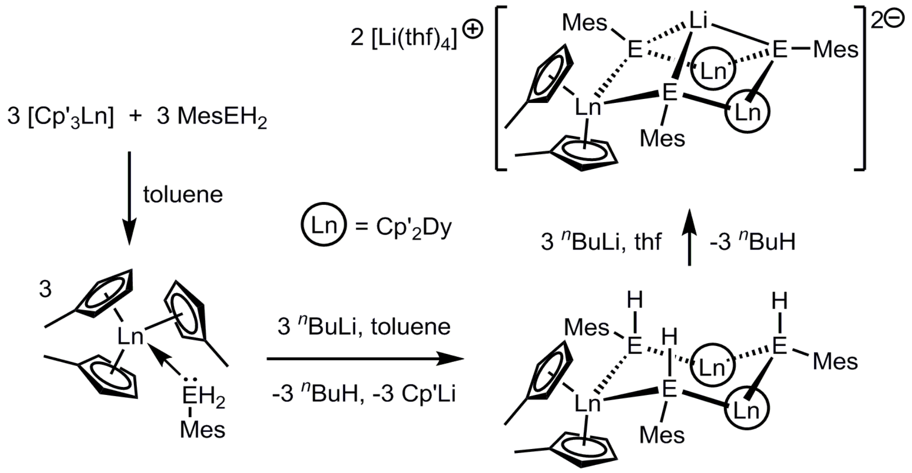

Figure 1 Complexes **1-3** (E = P, As, Sb,Ln = Dy, Y).

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Mn(III) single ion magnet with a tridentate Schiff-base ligand

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Single ion magnets (SIMs) are a class of materials with potential application as high-density magnetic memories and quantum-computing devices in spintronic field.[1] The size of the barrier of the reversal magnetization (U_{eff}) is the determining factor to the suitability of a single ion magnet to be applied in data storage devices. Efforts aiming at maximizing the anisotropy by an appropriate ligand field have been made to achieve high barriers.[2] Manganese(III) is a d^4 metal ion displaying a Jahn-Teller (JT) distortion when in an octahedral coordination environment. This feature turns Mn(III) into an promising ion to study its magnetic properties, namely spin crossover[3] and single ion magnet[2]. We report the synthesis of Mn(III) Schiff base cationic complexes (Figure 1) using different counter anions. SQUID magnetometry showed that all compounds are in the high-spin state with one pair of bond lengths (Mn-N_{amine}) considerably longer than the others (Figure 1). AC susceptibility measurements carried out using a MagLab2000 system showed that one of the new compounds displays single ion magnet behaviour, thus making it a good candidate for further investigation and possible application in data storage.

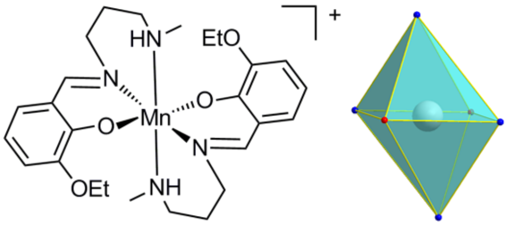

Figure 1

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Metallacrown based 3d-4f Complexes showing slow relaxation at high temperature

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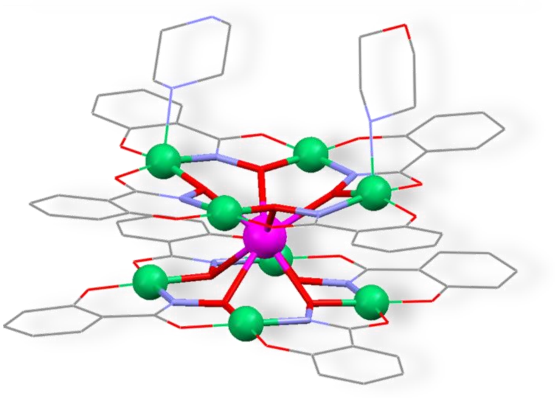
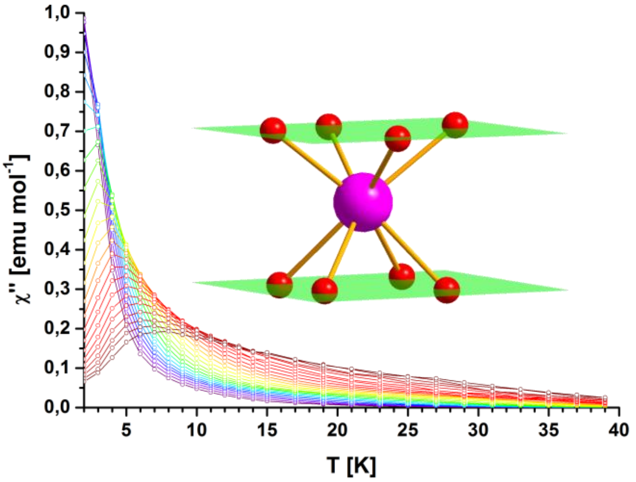
Over the last decade, SMMs containing lanthanide ions have gained more and more interest due to their strong anisotropy that creates high energy barriers preventing their molecular spin from reorientation. Lanthanide complexes have continuously pushed the records in the energy barrier and the highest hysteresis temperature. Sandwich complexes, such as $[Pc_2Tb]^-$, rank among the molecular compounds with the highest energy barriers due to their optimal ligand field.[1]

Tuning the magnetic anisotropy of lanthanides by adjusting their crystal field is of most importance. Here, we present a new approach based on enhancing the overall magnetic anisotropy of lanthanide sandwich complexes by the help of 3d-metal ions. For this purpose, we have studied 3d-metallacrowns functioning as η^4-complex ligands binding lanthanide ions in a sandwich-type coordination sphere. Metallacrowns are easily modified.[2] Our present concept allows to generate square antiprismatic coordination spheres for the lanthanide ions that allows for a slow relaxation of the magnetization above room temperature.





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Optically active molecule-based high temperature magnets

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Prussian blue (PBs) type materials are the molecule-based magnets with highest ordering temperatures discovered up to date. These non-stoichiometric solids of general formula $A_xM_y[M'(CN)_6].nH_2O$ (A = alkali cation; M, M' = transition metal), and face-centered cubic structure, are formed by homo- or heterometalic combinations of transition metals in multiple oxidation states, bridged by cyanide ligands. Magnetic ordering critical temperatures (T_C) over room temperature have been reported when V^{n+} and/or Cr^{n+} are the constitutive metals, although these derivatives usually exhibit poor stability to air in ambient conditions.[1,2]

In the search for chiral molecule-based magnets, a successful strategy has been implemented by the incorporation of chiral building blocks in synthesis of PB-based magnets.[3] This powerful strategy has not been so useful with the high T_C counterparts, because of the instability and difficult handling of these materials.

In this communication we will report successful strategies for the preparation of high T_C chiral molecule-based magnets in the PB family. For example, we have been able to synthesize a new cyanide-bridged chromium-vanadium magnet that orders above 120 K, and that exhibits optical activity.

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Investigation of magnetic anisotropy and relaxation processes in lanthanide complexes

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The common observation of slow relaxation of the magnetization in mononuclear lanthanide complexes can be due to mechanisms different from the usually invoked Orbach one involving a magnetic anisotropy barrier, such as quantum tunneling of magnetization (QT), Raman and direct processes, each of them being characterized by specific field and temperature dependences. These relaxation phenomena need to be rationalized and controlled to improve the properties of these complexes in term of blocking temperatures. In turn, this requires a detailed picture of their electronic structure which can only be obtained by using a combined spectroscopic, magnetic and *ab initio* characterization. We present here two examples for which, thanks to this approach, it was possible to evidence the role of the different processes in magnetization relaxation.[1-3] For Ln(trensal), (Fig. 1, left; H_3trensal = 2,2',2''-tris(salicylideneimino)triethylamine); Ln= Er, Dy,) it could be demonstrated that the observed slow relaxation of the magnetization is not related to the magnetic anisotropy barrier in the investigated temperature range. On the other hand for Dy(LH)$_3$ complex (Fig.1, right; LH is the anion of 2-Hydroxy-N’-[(E)-(2-hydroxy-3-methoxyphenyl) methylidene] benzhydrazide) the relaxation behavior in the high temperature range could be correctly reproduced using a master matrix approach based on *ab initio* results, which were on their turn validated by the outcome of single crystal magnetic measurements.

Figure 1 Molecular structure of Ln(trensal) (left) and Dy(LH)$_3$ (right)

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Polyimido Sulfur Scorpionates in Molecular Magnetism

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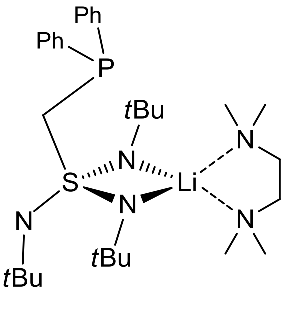
To further augment the coordination abilities of SN ligands, the diimidosulfinates[1] $RS(NR)_2^-$ and triimidosulfonates[2] $RS(NR)_3^-$, provide a rich platform. They chelate the main group[3] and transition metal[2] with two imido nitrogen atoms only and hold it tight like a scorpion its booty with the two claws. An additional coordination site, comparable to the sting of the scorpion, can be introduced if the sulfur di- or triimide is reacted with an organometallic compound providing an additional donor site, e. g. a phosphorus atom. In this talk we will discuss the facile linkage of the sulfur triimide with lithium diphenylphosphanyl methanide motif to give the lithiated ligand $[(tmeda)Li\{(N\mathit{t}Bu)_3SCH_2PPh_2\}]$ (**1**). The structural and geometrical differences to its sulfur(IV) diimide analogue $[(tmeda)Li\{(NSiMe_3)_2SCH_2PPh_2\}]$ are marginal but the advantages from the stronger redox stability of the first and the additional non-chelating imido group are obvious. We will also present an easy pathway to transition metal complexes via simple transition metal halides. The ligand gives rise to a remarkable cobalt containing Single Molecular Magnet complex $[Co\{(N\mathit{t}Bu)_2SMe(N\mathit{t}Bu)\}_2]$ **2** ($\chi_M T$ 2.9 [$cm^3mol^{-1}K$]; $U_{eff.}$ 75 [cm^{-1}]) with a hysteresis at 2K presumably due to the acute NSN bond angle.[4]



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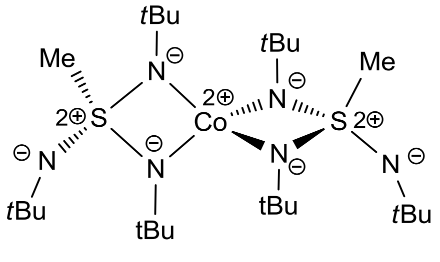

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How to deal with magnetism at nanoscale : Room temperature ultrasensitive magnetometry device

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This talk is driven by two reasons: (*i*) nanomagnetism investigation on switchable molecules *ie* (SCO) [1]. The development of these new, tailored architectures is central for the exploration of the physical properties of these materials, at the mesoscopic scale [2]. (*ii*) Up to now, the observations are essentially reduced to the simple investigation of the temperature dependence of the magnetisation or the optical absorption in a huge ensemble of nanoparticles by using high sensitivity conventional systems such as (SQUID) and/or dynamical light scattering measurements. The novel experimental approach based on ultra sensitive Planar Hall Effect (PHE) device can overcome theses drawbacks [2,3]. Compared to SQUID, the PHE approach has advantages of room temperature operation, detection of few amount of materials (μg), and hence more portable and flexible implementation. This innovation with high field resolution (micro to nanotesla) could detect a magnetic moment down to 10^{-13}*emu* at 300K. Interestingly, the resolution is 4 orders of magnitude higher than SQUID system. The ultimate target is the detection of single object by combining the forces from French, Korean, Vietnamese and Mexican researchers.

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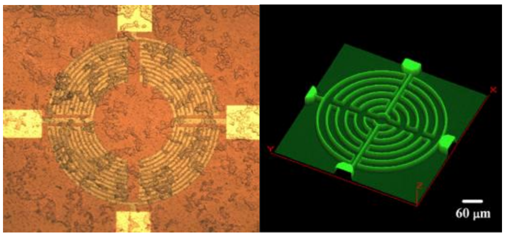
a)  b)

Figure 1 a) PHE ring sensor image & SCO nanoparticles, b) SEM image 11 rings sensors

Structures and relaxation dynamics of lanthanide single-molecule magnets

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Lanthanide compounds have become of increasing interest in the field of Single-molecule magnets (SMMs) due to the large inherent anisotropy of the metal ions.[1] Particular emphasis of our recent research efforts was placed on investigating the spin feature and relaxation dynamics of 4f SMMs. A series of new coordination compounds based on highly anisotropic lanthanide ions were designed and structually and magnetically characterized.[2] The synthetic strategy illustrated in our work represents a promising approach to steer the structural and spin features and design new molecular materials.

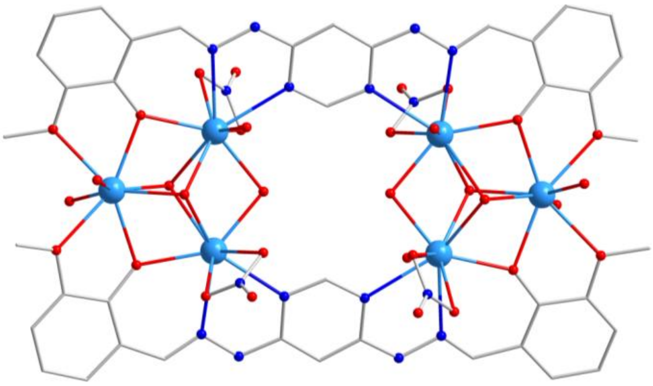

Figure 1 Molecular structure of Dy_6 compound.

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DESIGN OF MOLECULAR MAGNETIC MATERIALS USING THE RADICAL APPROACH

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The search for new molecular magnetic materials is motivated by their potential application in high-density information storage or multifunctional systems as well as the challenge to understand the factors that governs the nature and magnitude of the magnetic exchange interactions and magnetic anisotropy. In this talk will be reported the synthesis and study of coordination compounds containing organic radicals linked to paramagnetic metal ions. In particular, we will show the influence of changing the rigid cyclicpolyaromatic substituents of thenitronyl-nitroxideradicals, metal ions as well as the co-crystallization solventson the magnetic properties of single chain magnets (SCMs) containing 3d or 4f metal ions. One of the chains shows strong metal-radical exchange coupling with large blocking temperature and a very high coercive field.The influence of solvents in the crystal network onstatic and dynamic magnetic properties will be discussed based on defects created by the desolvation of lattice solvents. In addition, the synthesis and magnetic properties of new radicals-based heterobimetallic complexes will be also presented.

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Giant exchange interaction in mixed lanthanides

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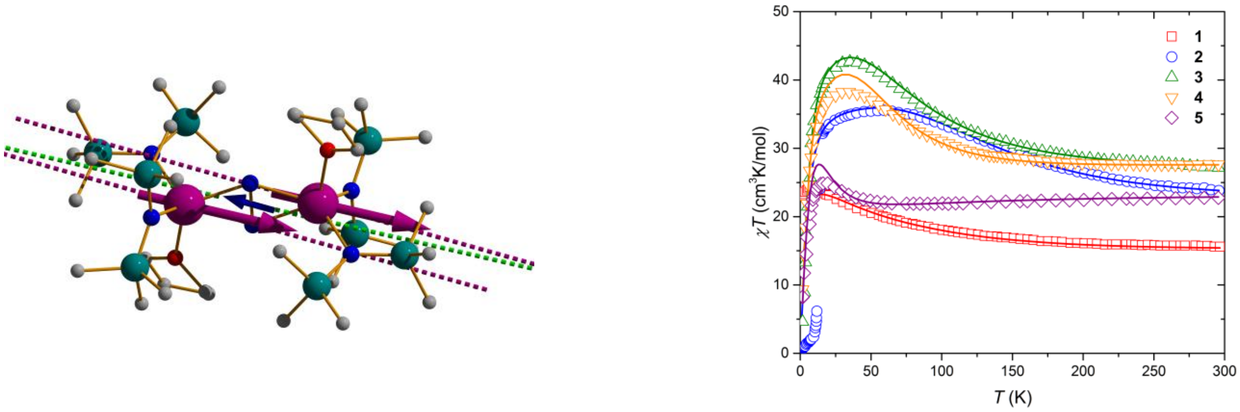
Combining strong magnetic anisotropy with strong exchange interaction is a long standing goal in the design of quantum magnets. The lanthanide complexes, while exhibiting a very strong ionic anisotropy, usually display a weak exchange coupling, amounting to only a few wavenumbers. Recently, an isostructural series of mixed Ln-R-Ln complexes with R the N_2^{3-} radical have been reported,[1,2] in which the exchange splitting is estimated to reach hundreds wavenumbers. The microscopic mechanism governing the unusual exchange interaction in these compounds is revealed here by combining detailed modeling with DFT and *ab initio* calculations.[3] We find it to be basically kinetic and highly complex, involving non-negligible contributions up to seventh power of total angular momentum of each Ln site. The performed analysis also elucidates the origin of magnetization blocking in these compounds. Contrary to general expectations the latter is not always favored by strong exchange interaction.



a

b

Figure 1. a) Molecular structure of Ln^{3+}-N_2^{3-}-Ln^{3+} complexes, with Ln=Gd (**1**), Tb (**2**), Dy (**3**), Ho (**4**) and Er (**5**). Dashed lines are the main magnetic axes on Tb ions (violet) and in the ground exchange Kramers doublet of the complex **2** (green). Arrows show the magnetic moments on Tb^{3+} ions and on the radical N_2^{3-}; b) Experimental (symbols) and calculated (solid line) magnetic susceptibility in **1-5**. The anisotropic exchange interaction used in the simulations was derived from *ab intio* and DFT calculations.

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Heterometallic low dimensional assemblies involving 4(5)*d* cyanometallates and displaying magnetic dynamics

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Low-dimensional magnetic materials demonstrating a slow relaxation of magnetization are significant from the outlook of fundamental and applied science, and have possible applications such as information storage and quantum computing.[1] Their magnetic behavior is determined by an energy barrier *U* that have to be surmount to reverse the magnetization. The *U* value for a single-molecule magnet (SMM) depends on the uniaxial anisotropy energy of a single molecule. For a chain of ferromagnetically coupled Ising spins the appearance of slow magnetization dynamics at finite temperatures was predicted by Glauber.[2] The experimental proof of single chain magnet (SCM) behavior was a discovery of magnetic relaxation in an Co–radical chain.[3] Contrary to SMMs, the energy barrier in SCMs depends not only on the magnetic anisotropy energy but also on the intrachain magnetic interaction.[4] Hence, it should be easier to increase *U* for SCMs than those for SMMs. After fruitful theoretical prediction that a use of orbitally degenerate 4d and 5d cyanometallates with a strong spin-orbit coupling as highly anisotropic synthones[5] is very promising in design of quantum molecular magnets, a row of SMMs with such building blocks were obtained.[6] The origin of magnetization dynamics in these objects is a presence of anisotropic exchange interactions between high spin 3*d* metal ions complexes and heavier cyanometallates.[7] However, to the best of our knowledge, there are no reports of SCMs based on anisotropic building units, $[M(CN)_n]^{m-}$, M = 4(5)*d* metal ions and n=6÷8 and m=3÷4. We present the synthetic approaches for the preparation of chain like coordination heterobimetallic polymers displaying slow magnetic dynamics and hysteresis > 2 K.

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Giant- and Tunneling-Magnetoresistance Based on Single-Molecule Magnets

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Spintronics is a key technology in 21st century based on the freedoms of the charge, spin, as well as orbital of the electron. The MRAM systems (magnetic random access memory) by using Giant Magnetoresistance (GMR) or Tunneling Magnetoresitance (TMR) have several advantages such as no volatility of information, the high operation speed of nanoseconds, the high information memory storage density, and the low consuming electric power. Usually in these systems, the bulk or classical magnets composed of the transition metal ions are used, while in our study we will use Single-Molecule Magnets (SMMs), which are usually composed of multi-nuclear metal complexes and nano-size magnets. Moreover, SMMs show the slow magnetic relaxations due to the double-well potential defined as $|D|S^2$ and the quantum tunneling. In our study, we hope to realize the new quantum molecular spintronics such as GMR and TMR by using SMMs.

According to such a strategy, we have synthesized the conducting SMM such as $[TbPc_2]Cl_{0.6}$, whose blocking temperature is 47K. The hysteresis is observed below 10K. This SMM shows the negative magnetoresistance below 8 K. As for the second strategy, we try to input/output one memory into/from double-decker Tb(III) SMM ($TbPc_2$) by using the spin polarized STM (Scanning Tunneling Microscopy). In this research, we have observed Kondo peak by using STS (Scanning Tunneling Spectroscopy) for the first time. We have succeeded in controlling the appearance and disappearance of Kondo peak by the electron injection using STS, reversibly. This is considered as the first single-molecule memory device.1) As for the third strategy, we have made the FET (Field Effect Transistor) devices of SMMs. The $DyPc_2$ device shows the ambipolar (n- and p-type) behavior, while the $TbPc_2$ device shows the p-type behavior.2) As for the fourth strategy, we have made doping of Cs atoms onto Pc_2Y, where Kondo peaks have not observed by coupling between the radical of Pc and 6s electron of Cs atom to make a single pair, while other Pc_2Y sites show Kondo peak due to the radicals. As for the fifth strategy, we have succeeded to write the letters of T and U, which are the initials of Tohoku University as shown in Figure.3-4)

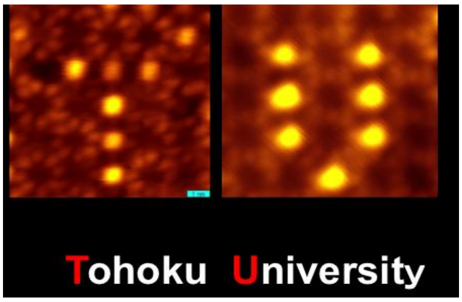

Fig. Initials of Tohoku University

As for the sixth strategy, we have evaporated $TbPc_2$ SMM on the magnetic Co surface, and by using the magnetic Cr tip, we have observed the GMR (200 %) for the first time. Finally, we have evaporated the Co film and $TbPc_2$ on Au surface, and by using the magnetic Cr tip, we have observed the TMR with the double butterfly structure for the first time.

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[2] K. Katoh, M. Yamashita, et al., **J. Am. Chem. Soc**., 131, 9967(2009)
[3] Z.Wei-Xiong, M. Yamashita, et al., **J. Am. Chem. Soc.**, 134, 6908(2012)
[4] T. Komeda, K. Kaoth, M. Yamashita, et al., **J. Am. Chem. Soc.**, 135, 651(2013)

Magnetic Relaxation in Organometallic Lanthanide and Actinide Complexes

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In recent years remarkable results have been obtained from studies of the magnetic relaxation of lanthanide and actinide complexes. A large number of such complexes were found to show single molecule magnet (SMM) behavior derived from their immense single-ion magnetic anisotropies. Some of these compunds, as for example terbium(III) bis(phthalocyanine) complexes, were reported to have spin-inversion barriers much larger than those of d-block SMMs,[1] while a blocking temperature to 14 K was reported for a N_2^{3-} bridged di-terbium complex.[2] These properties make f-SMMs attractive candidates for quantum-based devices.

This keynote lecture will focus on comparative studies amongst lanthanide and actinide organometallic single-molecule magnets, using original examples of Dy(III)-SMMs with high spin-inversion barriers of 700-840 K[3,4] and record blocking temperatures to 16 K,[4] along with the first clear-cut examples of U(III) and Th(III)-SMMs showing Rabi oscillations and quantum spin coherence at 125 K and below.[5] Relaxation mechanisms will be discussed and compared to exchanged-coupled UMn_2 SMMs.[6]

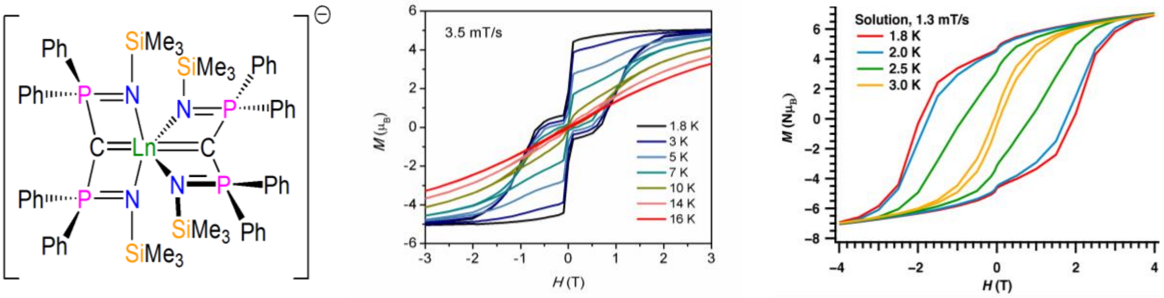

Figure 1. M(H) for (**left**) Dy-bis(carbene) SMM (ref 4) and (**right**) UMn_2-SMM (ref 6)

1. N. Ishikawa, M. Sugita, T. Ishikawa, S.-Y. Koshihara, Y. Kaizu, *J. Am. Chem. Soc*. **2003**, *125*, 8694.
2. J.D. Ribehart, M. Fang, W.J. Evans, J. R. Long, *J. Am. Chem. Soc*. **2011**, *133*, 14236.
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Spectroscopic Investigation of the Origin of Magnetic Bistability in Molecular Nanomagnets

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Molecular nanomagnets (MNMs) are coordination complexes consisting of one of more transition metal and/or f-element ions bridged and surrounded by organic ligands. Some of these can be magnetized in a magnetic field, and remain magnetized after the field is switched off. Because of this, MNMs have been proposed for magnetic data storage applications, where up to 1000 times higher data densities than currently possible can be obtained. Other MNMs were shown to display quantum coherence, and, as a consequence, are suitable as quantum bits. Quantum bits are the building blocks of a quantum computer, which will be able to carry out calculations that will never be possible with a conventional computer. The magnetic bistability of MNMs originates from the magnetic anisotropy of the magnetic ions, which creates an energy barrier between up and down orientations of the magnetic moment.

Currently, most work in the area focuses on complexes of either lanthanide ions or low-coordinate transition metal ions. Synthetic chemical efforts have led to a large number of novel materials, but the rate of improvement has been slow. Therefore a better understanding of the origin of the magnetic anisotropy is clearly necessary. To this end we have applied a wide range of advanced spectroscopic techniques, ranging from different electron spin resonance techniques at frequencies up to the terahertz domain to optical techniques, including luminescence and magnetic circular dichroism spectroscopy. We will discuss two examples, one from the area of lanthanide MNMs,[2] one a transition metal MNM.[1]

1 Y. Rechkemmer, J. E. Fischer, R. Marx, M. Dörfel, P. Neugebauer, S. Horvath, M. Gysler, T. Brock-Nannestad, W. Frey, M. F. Reid, J. van Slageren, *J. Am. Chem. Soc.* **2015**, *137*, 13114.
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Electron Spin Relaxation of High Spin Complexes at High Field

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The spin relaxation behavior of magnetic coordination compounds, is a crucial factor for a range of applications: quantum information processing and storage, spintronics, dynamic nuclear polarization (DNP), etc. The implementation of high frequencies and fields is crucial in the study of systems with large zero-field splitting or large interactions, as for example molecular magnets and low dimensional magnetic materials. Here we will focus on the implementation of pulsed EPR at multiple frequencies of 120, 240, and 336 GHz, and the relaxation and decoherence processes as a function of magnetic field and temperature. Firstly, at higher frequencies the direct single-phonon spin-lattice relaxation (SLR) is considerably enhanced, and will more often than not be the dominant relaxation mechanism at low temperatures, and can be significantly faster than at lower fields and frequencies. In principle the measurement of the SLR rates as a function of the frequency allows to map the phonon density of states.

Secondly, the high electron spin polarization at high fields has a strong influence on the spin fluctuations in relatively concentrated spin systems, and the contribution of the electron-electron dipolar interactions to the coherence rate can be quenched at low temperatures[1]. Depending on the crystal symmetry this can lead to large orientation dependence of the spin decoherence, as will be shown for a Cr_3 compound.

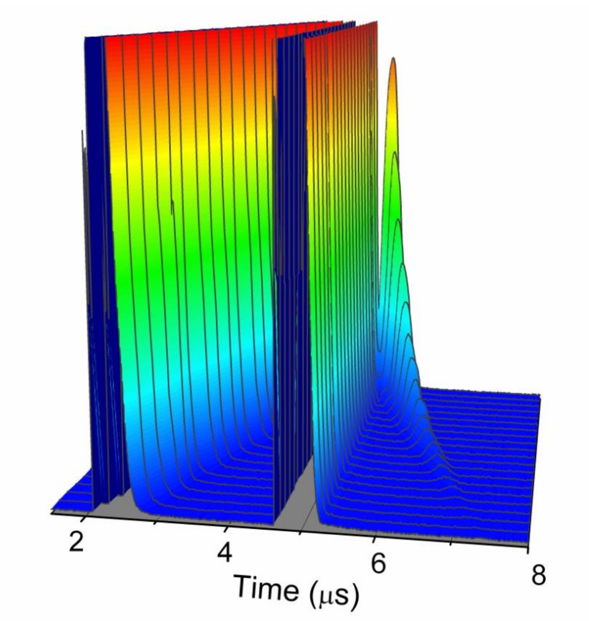

Figure 1 Echo-Detected spin decoherence in Fe_8 at 240 GHz and 1.4K

1 S. Takahashi, I.S. Tupitsyn, J. van Tol et al. *Nature,* **2011***, 476*, 76

An exceptionally wide hysteresis in a spin crossover Iron(III) complex

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Spin crossover (SCO) invokes the switching between two states: high spin (HS) and low spin (LS)[1] , thanks to stimuli like temperature, light and pressure.

This phenomenon is well-known for Fe^{II} complexes but has also been reported for Fe^{III} systems.

This bistability makes spin crossover complexes appealingly appropriated for uses in data storage devices, sensors, molecular commutators and displays.

In this communication we will present a series of SCO transition types based on Fe^{III} complexes and Schiff-base ligands (L) used to form the needed donor set. Among this wide range of compounds, we will show a staggering hysteresis around 100 K that varies with the solvation degree. As far as we know, this is one of the largest hysteresis reported in a SCO complex. We will highlight the role of the halogen group on the ligand (L-X), of the different counter-anions used and of the solvents. These compounds also exhibit rare crystallographically independent simultaneous high-spin and low-spin Fe^{III} centers.

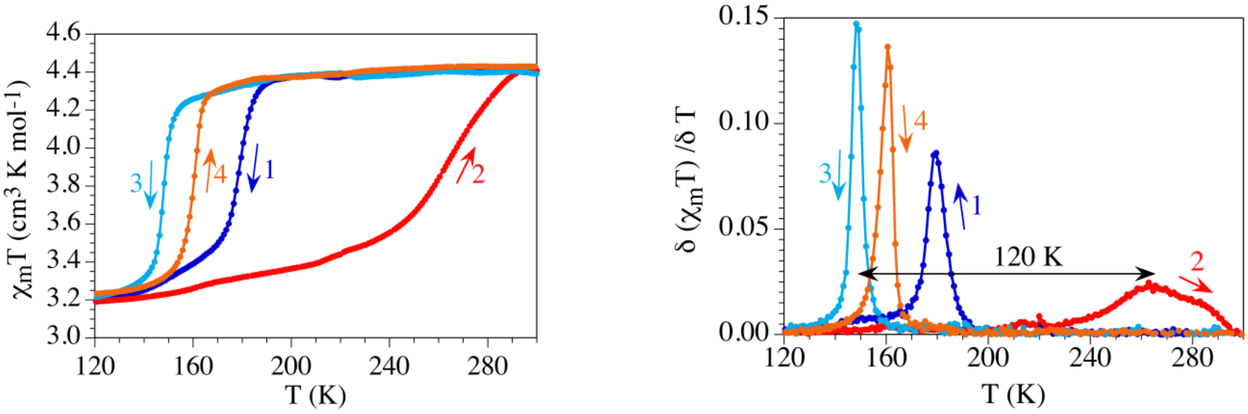

Figure 1 SCO with very large hysteresis in a Fe^{III} complex after different thermal scans

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Dispersion of spin-crossover microparticles in matrices: a way for playing with volume-dependent effects

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Spin-crossover (SCO) compounds form a class of switchable and bistable magnetic materials exhibiting changes of spin multiplicity of the metal ion under the effect of stimuli (T, P, hν). The change of volume related to SCO produces highly cooperative transformations resulting from the spreading of elastic strains. Potential technological interests, as sensor, switch or memory, mainly derive from their cooperative and hysteretic behaviors. For the high-density information storage, one key issue is the preservation of a bistable regime at nanoscale. In the last few years, developments have made possible the elaboration of SCO nano-objects and the investigation of their size-dependent properties.[1,2]

Here we focus on a prototypical SCO material $Fe(phen)_2(NCS)_2$ prepared as small particles (15-1500 nm) with the solvent-assisted approach.[2d] The particles are dispersed in matrices for avoiding aggregation, or for optimizing light penetration in photoswitching experiments. The studies conducted with the microparticles dispersed in polymers, molecular liquids or oils have revealed first a complex thermal behavior ranging from smooth, fully reversible processes to hysteretic ones.[3a,b] The investigation of the latter with the First-order reversal curves (FORC) approach and a mean-field model supports an analysis based on physisorption, volume-dependent effects between particles and matrices. Moreover, the experimental and theoretical analysis of the light-induced excited spin-state trapping (LIESST) effect indicates a matrix-assisted relaxation.[3c] These findings suggest in line with a few recent reports of hysteresis re-opening at nanoscale,[4] the possibility to tune the properties of size-reduced materials via size, interface, coating, matrix and nature of compounds.

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3. (a) A. Tissot et al *J. Mater. Chem*. **2012**, 22, 20451; (b) R. Tanasa et al *Appl. Phys. Lett*. **2014**, *104*, 031909; (c) C. Enachescu et al submitted.
4. Y. Raza et al *Chem. Commun*. **2011**, *47*, 11501; G. Félix et al *Phys. Rev. Lett*. **2014**, *110*, 235701.

Reversible control by light of the high-spin low-spin interface inside the thermal hysteresis of a robust spin transition single crystal. Experience and theory.

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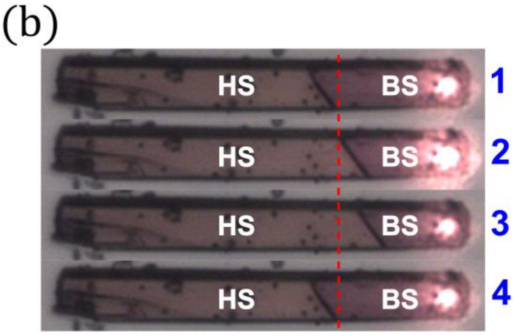

We investigated single crystals of the dinuclear iron(II) compound **$[\{Fe(NCSe)(py)_2\}_2(m\text{-}bpypz)]$,** which exhibit a thermal spin transition with hysteresis near 100 K. The robust character of the crystals made possible the investigation of both on-cooling and on-heating processes. Well-defined transformation fronts [1,2] between macroscopic high spin (HS) and low-spin (LS) phases during the thermally-induced phase transition were observed and their dynamics were controlled by a laser spot with a modulated intensity [3]. The videos of the spin transition processes and the photo-control will be shown in real (or accelerated) time. We could also study under the microscope the photo-excitation of the single crystal at 10 K [4] and recorded on time both LIEEST and relaxation processes, whose results did not show any occurrence of domain formation. Finally, we could also study the spatiotemporal features of the light-induced thermal hysteresis (LITH) at very low temperatures and recorded for the first-time the spatiotemporal features of this non-equilibrium phase transition on a single crystal.

Besides the experimental results, some microscopic models based on the description of the spatiotemporal SC behaviour by reaction diffusion equations will be introduced [5]

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Molecular Spin Crossover Phenomenon at the nanoscale Photonics, Motion and Integration

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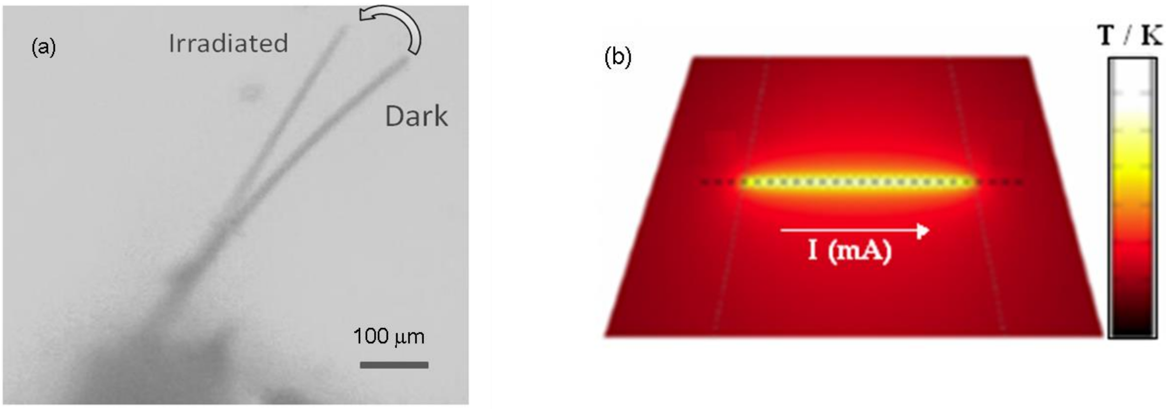
The spin crossover phenomenon in inorganic materials is one of the most spectacular examples of molecular bistability, which means that these molecules may exist in two different electronic states within a certain range of external perturbations. Most notably, the existence of a thermal hysteresis in certain complexes (in the solid state) confers a memory effect on these systems.[1-4] we are particularly interested in the synthetic elaboration of nanometric thin films[5] and nano-sized patterns[6] that we obtain by electron beam lithography and in the application of an external perturbation in the hysteresis loop of spin crossover materials leading to an irreversible switching of their physical properties.[4]

Besides generating new fundamental knowledge on size-reduction effects and the dynamics of the spin crossover phenomenon, this research aims also at the development of practical applications such as sensors, nano-electronic, photonic, motion and nano-mechanical devices,[1-12]

In this talk, I will discuss recent work in the field of molecule-based spin crossover materials with a special focus on these emerging issues, including chemical synthesis, physical properties, practical applications and theoretical aspects as well.



(a) Comparison of the cantilever bending in the photo-induced high spin (HS) and low spin (LS) states for a {Fe(3-CNpy)[Au(CN)2]2}.2/3H2O based single crystal actuator.[12,13] **(b)** Luminescence modulation by high spin, low spin optical absorptions.[9]

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[11]- Angew. Chem. Int. Ed. 52 (2013) 1185-1188.
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Spin crossover in 1,ω-di(azolyl)alkane based iron(II) coordination polymers exhibiting layered structure

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1,ω-di(tetrazol-1-yl)alkanes form 1D, 2D and 3D spin crossover (SCO) coordination polymers in which iron(II) ions are surrounded by six tetrazole rings. There is one exception found by us in which 3-(tetrazol-1-yl)-2-(tetrazol-1-ylmethyl)propene creates network in which [Fe(tetrazol-1-yl)$_3$(CH$_3$CN)$_3$] cores are present. For a change, 1,ω-di(1,2,3-triazol-1-yl)- and 1,ω-di(tetrazol-2-yl)alkanes easily form homo- as well as heteroleptic complexes. In the group of complexes containing [Fe(azolyl)$_6$]-type cores there are 2D network [Fe(ptrtz)$_3$](ClO$_4$)$_2$·CH$_3$CN and 3D networks [Fe(pbtz)$_3$](ClO$_4$)$_2$·C$_2$H$_5$OH and [Fe(qbtr)$_3$](ClO$_4$)$_2$ for which SCO is accompanied by conformational changes of bridging ligands [1-3].

Presence of axially coordinated nitriles leads to formation of crystals which have layered structure and a composition of area between layers influences on spin crossover properties. Among 1D and 2D networks [Fe(L)$_2$(RCN)$_2$]X$_2$ (L = 1,ω-di(azolyl)alkane, X = monovalent anion) there are complexes in which coordinated nitrile molecules become an another source of structural liability [4-5]. Small, coordinated nitrile molecules which remain within the layer are not engaged in formation of intermolecular contacts with neighboring layer. For a change, the larger nitrile molecules can interact with neighboring layer and SCO is accompanied by change of their orientation or conformation. In this presentation we will focus on structural liability of coordination networks triggered by change of spin state taking into account particularly a role of coordinated nitrile.

The work was partially supported by the Polish National Sciences Centre Grant No. DEC-2014/15/B/ST5/04771.

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Reversible quantitative guest sensing via spin crossover of a discrete iron(II) triazole in the solid state

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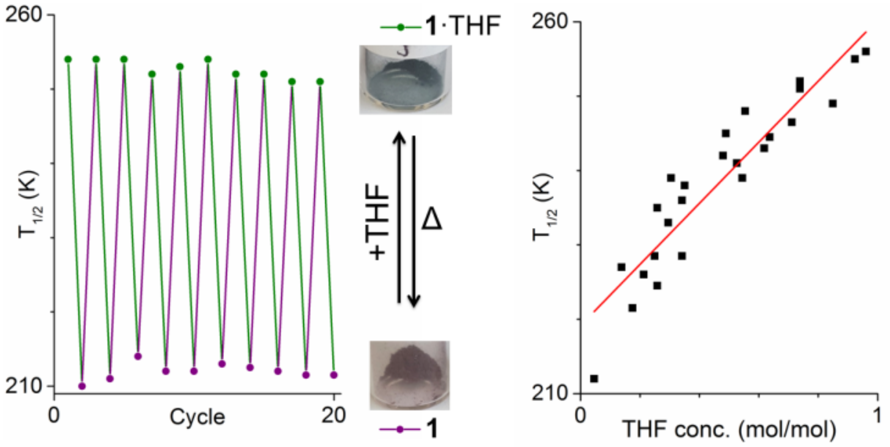
Spin crossover, switching between the high spin and low spin states, is most commonly induced by variation of the temperature, but other perturbations can also be employed, including application of a magnetic field, light irradiation, ±guest, or a change in pressure.[1,2] Due to the sensitivity of SCO-active materials to their environment, guest sensor applications are of considerable interest. Most examples to date have focused on the use of SCO as a *qualitative* on/off-sensor, in some cases showing remarkable tuning of the spin crossover $T_{½}$ by varying the type of guest molecule within the crystal lattice. Metal-organic frameworks (MOFs) with permanent porosity have been prominent in such studies. Attempts to take this further, to *quantitative sensing of a guest*, include a couple of solution iron(II) SCO-systems that have shown some promise in this regard.[3-5]

To the best of our knowledge we report herein the first demonstration of *reversible quantitative guest sensing by an SCO-active material* (Figure).



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Flexibility, multi(meta)stability and hidden phase in spin-crossover materials

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The switching process in molecular materials is widely studied, especially in Spin-Crossover compounds. In such systems, the possibility to address the spin state and subsequently the volume, the color and other properties by an external perturbation such as temperature, light, magnetic field or applied pressure, is of particular interest for potential applications.

Among the numerous Spin-Crossover systems, the extended networks are fascinating since most of them exhibit a strong thermochromism of their porous network. Hofmann clathrate phases possess such potentialities associated with a control of the pore size and of the guest molecules. However, photomagnetic effect was quite limited in these phases since the rigidity of the network prevent the propagation of the volume change consecutive of the light-induced spin change. The introduction of flexible ligands has opened the way to (i) multistep character of the thermal spin-crossover, (ii) photo-induced spin-state switching at low temperature and, (iii) the existence of hidden hysteresis.

This will be demonstrated in a new two-dimensional network that exhibits an incomplete spin-crossover allowing a bi-directional photo-switching of the spin-state and revealing a photo-induced hidden hysteresis.

Computational Modeling of the ligand tuning effect over the transition temperature in Spin-Crossover systems

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Spin-crossover (SCO) systems are the focus of intense research due to their intrinsic behavior as molecular-level switches. A key parameter in the physical characterization of SCO systems is the transition temperature ($T_{1/2}$), defined as the temperature with equal populations of both spin-states. In this communication we present our results for the application of the meta-hybrid GGA functional TPSSh for the accurate calculation of $T_{1/2}$ in SCO systems.[1,2] In particular, we will show the results on a family of tetracoordinated [PhB(MesIm)$_3$Fe–N=PR$_3$] systems, an unusual coordination number displaying SCO. Our calculations reveal the origin of the SCO behavior in this family and the interplay between the phosphine size and the changes in the $T_{1/2}$.[3] A linear relationship between the phosphine cone angle and the shift in the $T_{1/2}$ can be obtained and rationalized from the direct analysis of the underlying electronic structure in terms of the relevant molecular orbitals, results that match the experimental data.[4] Using the same methodology, we will also present the results for a series of binuclear iron(II) compounds of general formula [FeL$_1$(NCX)$_2$]$_2$L$_2$ (X = S, Se or BH$_3$), for which the stability of the different spin-states can be calculated as a function of the NCX ligand, unrevealing the origin of the experimentally observed two-step transition for some of them.[5] Using the reported methodology, quantitative information about the ligand effect on the d-based molecular orbitals and its implications on the $T_{1/2}$ can be obtained, which can be of great help in the rational design on SCO systems with tailored properties.

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Ultrafast LIESST in solid state: from coherent structural trapping to cooperative elastic switching

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Ultrafast photoswitching in bistable spin-crossover molecular crystals is associated with a complex transformation pathway, multiscale in nature, where both molecular photo-switching and macroscopic transformation of the crystal have to be considered [1-2]. We have studied the basic mechanisms allowing light to switch the molecular state, from low to high spin. Femtosecond x-ray absorption (X-FEL) and optical spectroscopy show that the stabilization of the photoinduced HS state results from self-trapping of the electronic excited state, during a two steps relaxation sequentially involving molecular stretching and torsion. The system is bobsledding across a potential energy surface along identified coordinates [4-5] during the first ps following light excitation.

In the active medium, which the crystal is, cooperative elastic effects can give rise to self-amplification. We report that because of the elastic field resulting from molecular transformation, up to 6 molecules can be transformed per photon.

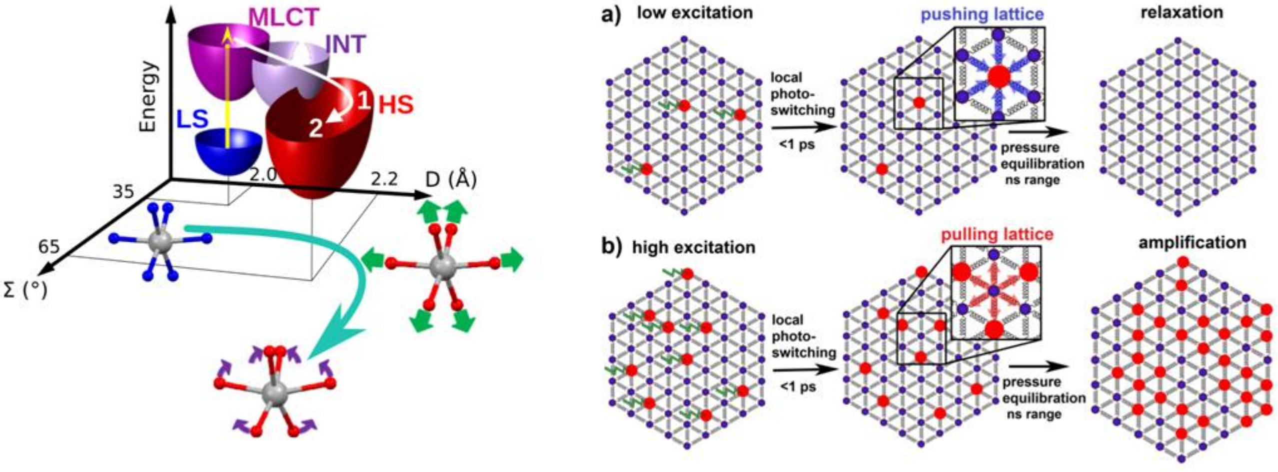

Figure 1 left: ultrafast LIESST with sequential activation of breathing and bending

right: cooperative switching after fs light excitation due to elastic field

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Thermo, piezo and photo-switchable coordination polymers

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Iron(II) spin crossover (SCO) complexes continue to attract a great deal of interest.[1,2] SCO nanomaterials have indeed emerged as an appealing class of materials considering nanostructuration processes and size reduction effects.[1] Although sophisticated techniques can be used for the preparation of SCO nanoparticles, we have introduced a biomembrane as a soft and green support for deposition of SCO micro and nanocrystals, which were used for printing on various supports.[3] More recently, we investigated the SCO properties of hybrid nanomaterials made of MCM-41 including 1D Fe(II) 1,2,4-triazole coordination polymers.[4] This later class of SCO materials, whose spin states can be switched by light,[5] afforded the first 1D chain with 1,2,4-triazole ligands displaying a two-step spin conversion.[6] This compound was discovered in the frame of our investigation of a new range of porous metal organic frameworks.[7] Indeed, using a ditopic 1,2,4-triazole-tetrazole ligand, we have isolated a mononuclear iron(II) neutral complex, with coordinated water molecules, being in the high-spin state. The situation becomes intriguing when the complex is screened for sensing abilities for a series of chemicals. Interestingly, the complex detects methanol among alcohols and hydrochloric acid among the acid series. The sensing process, which involves an unexpected spin state change for the methanol case, is visually detectable, fatigue-resistant, selective, and reusable.[8] Recent developments on the use of a new range of thermochromic and photochromic molecular switches operating in the solid state will also be highlighted.[9]

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Molecular Asymmetry in Spin-Crossover Materials

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Complete reorganization of the electronic structure in 3d-metal complexes, referred to as spin crossover, is a fascinating example of molecular bistability, associated with switchable magnetic, electric, optical and mechanical properties. Chiral spin-crossover materials attract attention as perspective photonic materials and elements of stereoselective sensors. Here we report on a homochiral coordination complex $[Fe(NH_2trz)_3](L\text{-}CSA)_2$ developed in the form of nanoparticles and gels. These nanoparticles display an abrupt switch of chiro-optical (CD) properties associated with the cooperative spin transition (Figure 1a).[1] Spin crossover in $[Fe(NH_2trz)_3](L\text{-}CSA)_2$ is sensitive to the inclusion of guest 2-butanols, and these solvates with (R)- and (S)-alcohols demonstrate different transition behaviors depending on the chirality of organic analyte (Figure 1b).[2]

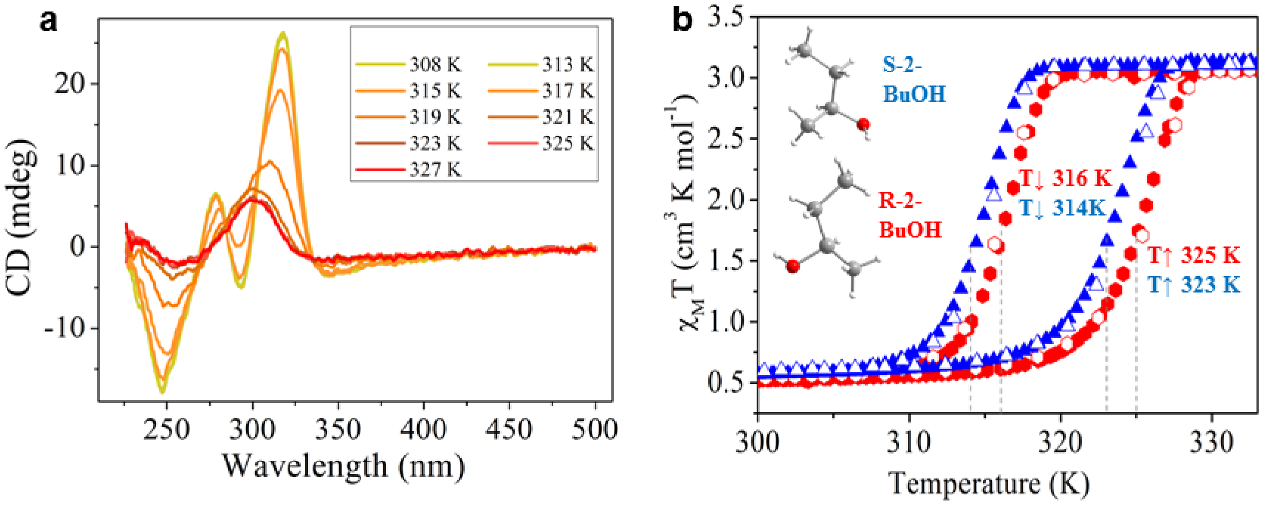

Figure 1 (a) Effect of the spin transition on CD spectra of $[Fe(NH_2trz)_3](L\text{-}CSA)_2$ chiral nanoparticles. (b) Stereoselective guest effect on spin crossover in a chiral coordination framework.

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An Unexpectedly Complicated Relationship Between Ligand Structure and Molecular Spin State in a Family of Iron(II) Complexes

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The family of complexes derived from $[Fe(bpp)_2]^{2+}$ (bpp = 2,6-di{pyrazol-1-yl}pyridine) can be derivatised at every position of the bpp ligand skeleton, and can be high-spin, low-spin or spin-crossover active depending on the ligand substituents.[1,2] Solution phase magnetochemical data from eighteen complexes substituted at the pyridyl *C*4 position ('X' in Fig. 1) show a positive linear free energy relationship[3] between the spin-crossover midpoint temperature ($T_{½}$) and the resonance-corrected Hammett parameter σ_P^+ for the ligand substituents. In contrast, data from eight complexes substituted at the pyrazolyl *C*4 sites ('Y' in Fig. 1) imply a shallower negative linear free energy correlation between $T_{½}$ and the σ_M Hammett parameter. That is, the low-spin state of the complex is stabilized by electron-withdrawing X substituents, but by electron-donating Y substituents. DF calculations reproduce these opposing trends, and show they reflect the competing influences of pyridyl and pyrazolyl ligand substituents on Fe–L σ- and π-bonding.[4]

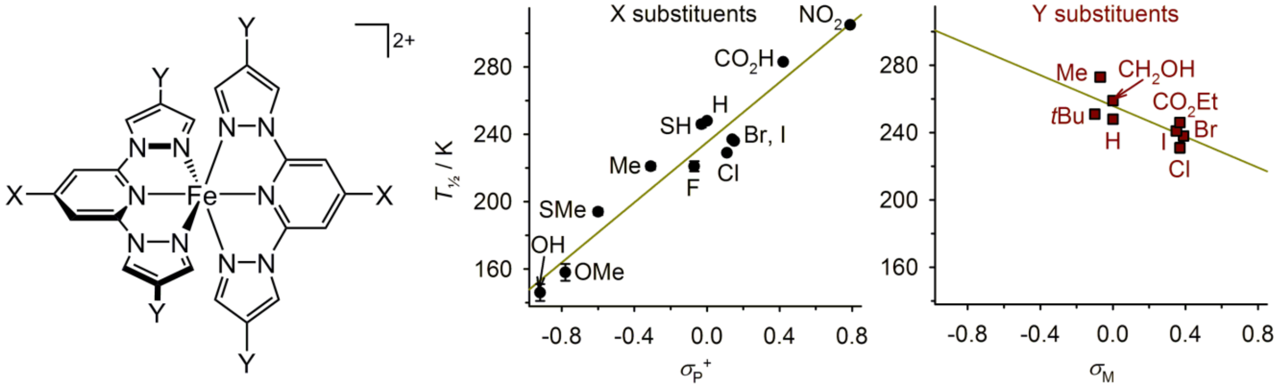

Figure 1 Dependence of spin-crossover $T_{½}$ on ligand substituents in $[Fe(bpp^{X,Y})_2]^{2+}$.

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Spin crossover in heteroleptic [Fe(qsal-Cl)(qsal-Br)]$^+$ complexes

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Spin crossover materials may be switched from a low spin (LS) to a high spin (HS) state by application of an external stimuli such as temperature, pressure and light.[1] In this research the impact of the different ligands on the magnetic behaviour of the [Fe(qsal-Cl)(qsal-Br)][anion] complexes is described. Comparisons are drawn between these mixed ligands complexes and the homoleptic [Fe(qsal-Cl)$_2$]$^+$ and [Fe(qsal-Br)$_2$]$^+$ materials.[2]

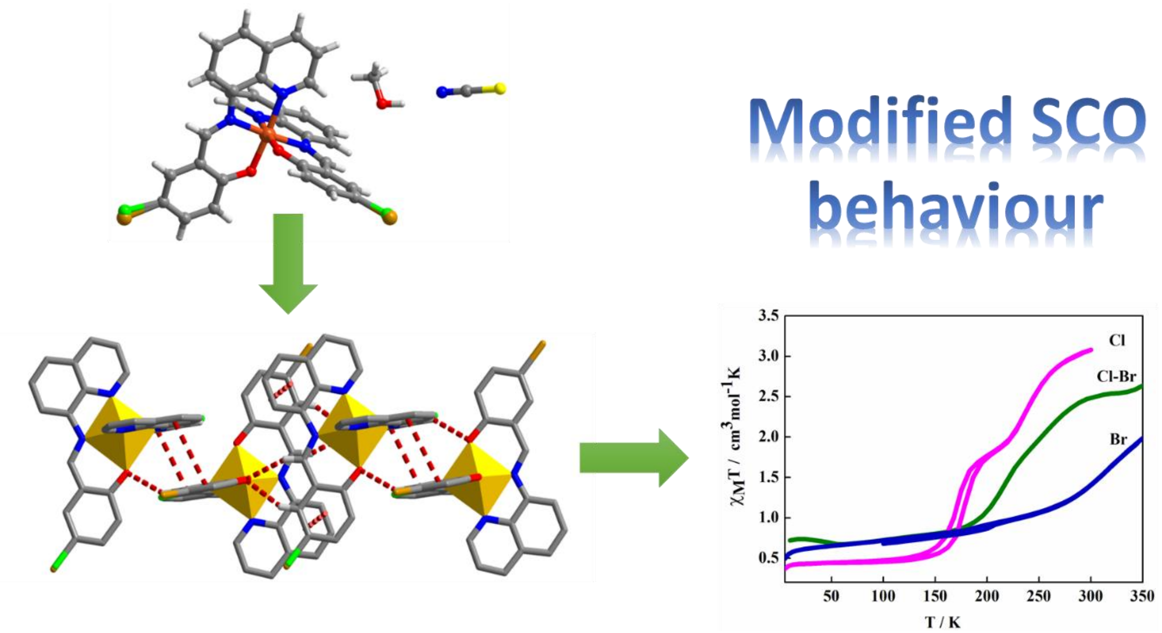

Figure 1 Structure and magnetic behaviour of some [Fe(qsal-Cl)(qsal-Br)]$^+$ complexes.

Acknowledgements

We thank the Thailand Research Fund (RSA5880048) and the Development and Promotion of Science and Technology Talents project for funding.

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Graphene Oxide and Reduced Graphene Oxide Hybrids with Spin Crossover Materials

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Graphene oxide (GO) is 2D nanosheet, and has many functionality, for example, proton conductivity.[1] The GO has negative charge because GO has many oxygen functional groups such as epoxide group, carboxyl group, hydroxyl group and so on. Therefore, GO is able to combine with positive charge cations such as proton, metal ions, complexes and so on. Furthermore the hybrids can be prepared by not only electrostatic interaction but also π-π stacking or chemical bonding between epoxy and amine groups. After reduction of GO by hydrazine, UV irradiation or annealing, reduced GO (rGO) can be produced, which shows electrical conduction. After reduction of GO hybrids, rGO hybrids also can be produced. In this study, we focus on GO and rGO hybrids with spin crossover (SCO) cation $[Fe(qnal)_2]^+$ (**1**). The complexes exhibit a unique SCO behavior depending on counter anions. GO-SCO hybrids (**1**-GO) and rGO-SCO hybrids (**1**-rGO) were synthesized (Figure 1). **1**-GO and **1**-rGO exhibited gradual SCO behavior. Moreover, a light-induced excited-spin-state trapping (LIESST) effect for **1**-rGO was observed (Figure 2). After reduction of GO hybrids, **1**-rGO also showed electrical conduction. Graphene-based materials with multi-functionality are presented here for the first time. We succeeded to control the domain size of the SCO complexes on the graphene nano sheet.

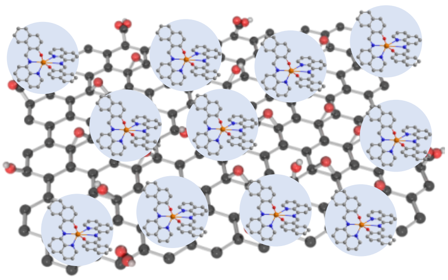

Figure 1 Structure of graphene oxide and spin crossover hybrids.

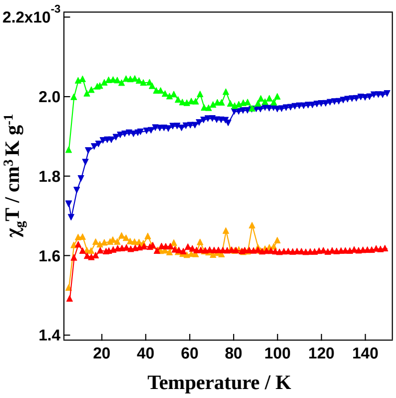

Figure 2 $\chi_g T$ vs T plots for **1**-GO and **1**-rGO before and after light irradiation at 800 nm.

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Molecular Magnetic Switches Operating at Room Temperature

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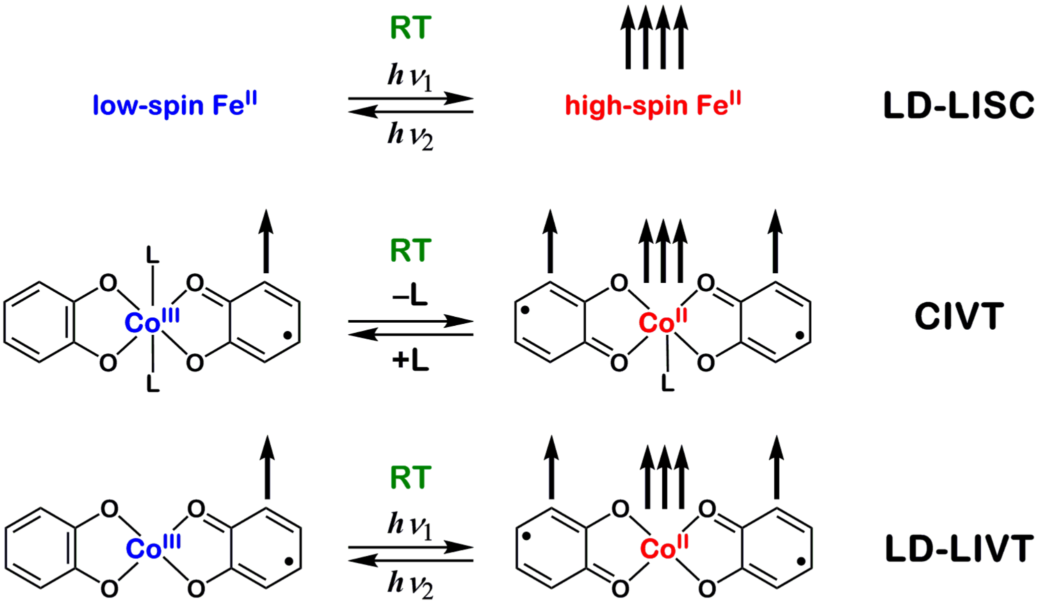
Our group develops unique molecular switches – molecular coordination compounds – whose magnetic properties can be reversibly changed at *room temperature*. To accomplish this goal, photoisomerizable ligands were introduced into bistable molecular species of two families: spin-crossover metal complexes and valence tautomers (redox-isomers).

The efficient and reversible photoswitching in spin-crossover species was achieved using the Ligand-Driven Light-Induced Spin Change (LD-LISC)[1] effect and proceeds in solution[2] and in the solid state.[3] The switching of valence-tautomeric cobalt complexes was accomplished by two novel effects: Coordination-Induced Valence Tautomerism (CIVT)[4] and Ligand-Driven Light-Induced Valence Tautomerism (LD-LIVT)[5], both developed in our group.



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Spin Crossover Behavior in Hofmann-like Coordination Polymers Containing Various Pyridine Derivatives

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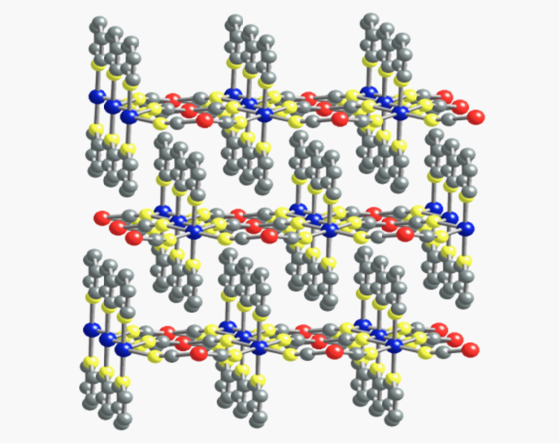

Fig. Structure of SCO coordination polymer $Fe(py)_2Ni(CN)_4$ [1]

Now, SCO coordination polymers have been important materials because they are very valuable molecule devices in the exploration of the cooperative interactions of the SCO behaviour between LS (low-spin) and HS (high-spin) states. Special attention is currently much paid to Hofmann-like coordination polymer iron(II) SCO compounds acting cooperative behaviour because they can manifest sensory and memory functions. The original Hofmann pyridine coordination polymer $Fe(py)_2Ni(CN)_4$ shows iron(II) SCO behaviour, revealed by ^{57}Fe Mössbauer spectroscopy and SQUID technique [1]. In addition, Hofmann-type SCO coordination polymer compounds, whose Fe^{II} SCO centers have bidentate cyano substituents $[M^I(CN)_2]^-$ (M^I = Cu, Ag, or Au) and $[M^{II}(CN)_4]^{2-}$ (M^{II} = Ni, Pd, or Pt), have been the subject of researches in several groups, and SCO coordination polymers with microporous frameworks have attracted the attention for many researchers because they can lead to additional functionalities between the host−guest and SCO properties[2]. Emission Mössbauer spectroscopic study for ^{57}Co-labelled analogous $^{57}Co(py)_2Ni(CN)_4$ also demonstrated the nuclear-decay-induced excited spin state trapping (NIESST). Temperature-dependent EXAFS study for $Fe(py)_2Ni(CN)_4$ was also investigated[3] . The effect on the SCO behavior of various halogen and alkyl replacements located at different positions on the pyridine ring have been also studied.

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Electrochemical properties of iron(II) complexes with 4-amino-1,2,4-triazole possessing $^1A_1 \leftrightarrow {}^5T_2$ spin cross-over

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Electrochemical properties of the series included 7 coordination compounds of iron(II) with 4-amino-1,2,4-triazole (NH_2trz) viz. $Fe(NH_2trz)_3A_n{\cdot}mH_2O$ (n = 1, 2; A = NO_3^- (I), Br^- (II), I^- (III), BF_4^- (IV), ClO_4^- (V), SO_4^{2-} (VI), SiF_6^{2-} (VII); m = 0 (I, III-VII), 1 (III)) were studied. All the complexes in exception of V possess abrupt thermal induced spin cross-over (SCO) with hysteresis on the curves μ_{eff} (T).

By the method of cyclic voltametry, the investigation was carried out in condition of complex as in water dissolved state at polycrystalline Pt-electrode and in solid state included in the mixture of spectral graphite and silicon binder of paste electrode. When using Pt-electrode, the measurements were made in solutions with background electrolyte of 0,1 M HNO_3 or HA. The measurements with paste electrodes were made in 0,1 M KNO_3. In solution and in solid state forms, the complexes were found to exhibit in the potential range of –0,200 ÷ 1,100 V (vs. silver/silver chloride electrode) the only one anodic and cathodic current peaks referred to the complex central metal transformation Fe(II) ↔ Fe(III). In the solutions of I and III, the transformations are of reversible nature ($E^{0'}$ = 0.48 B) and for others of irreversible one. For paste electrode, the transformation is quasi-reversible and $E^{0'}$ coincides with Pt-electrode data that means the independence of the complex behavior on the electrode base (Pt or graphite). For the constant concentration of complex in the paste, it was observed the dependence of peak current height on the anion of the complex ($SO_4^{2-} \sim NO_3^- > BF_4^- > Br^- > I^- > ClO_4^-$), which correlates with calculated fraction of high spin form in solid state of complex at 298 K.

By the method of conductometry, the solubility of comlexes in water was studed. The molar electroconductivity at the concentration of $1{,}0{\cdot}10^{-3}$ mole/L for the investigated series was Λ = 235 – 270 $Ohm^{-1}cm^2mole^{-1}$ except for V and VII which were partially hydrolyzed. The mobility of complex cation was estimated.

The study was partially supported by RFBR grant No 14-03-90006 and the authors acknowledge the Fund.

Ruthenium nitrosyl complexes with NO_2 and N-donor arenes: synthesis and photo-induced isomerization

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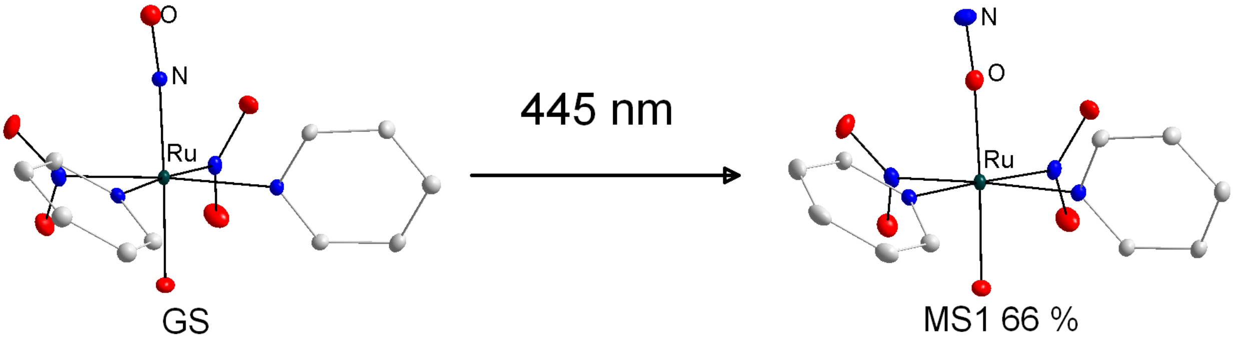
The reaction of anion $[RuNO(NO_2)_4OH]^{2-}$ with sulfamic acid was used to obtain new mixed-ligand complexes $[RuNO(NO_2)_2L_2OH]$ (L = Py, 3-MePy, 4-MePy, 1,4-diazine), $[RuNO(NO_2)_2(ONO)Py(OH)]^-$ and dimeric forms $[Ru(NO)Py_3(\eta\text{-}O)_2Ru(NO)Py_3]^{2+}$ $[Ru(NO)(2\text{-}MePy)_2(\eta\text{-}NO_2)_2(\eta\text{-}O)Ru(NO)(2\text{-}MePy)_2]$. All compounds were described by IR, CHN and single crystal X-ray analysis.

The formation of light-induced (445 nm) metastable states with Ru-ON (MS1) or $Ru<^{N}_{O}$ (η^2-coordinated NO, MS2) was detected by IR, Raman–spectroscopy and single crystal X-ray analysis. For all complexes IR spectra reveals the down-shift of the ν(NO) vibrations by 120 - 150 cm^{-1} for MS1 state and 300-350 cm^{-1} for MS2 state. Relatively high populations of MS1 (30-70 %) was achived only for complexes $[RuNO(NO_2)_2L_2OH]$ with *cis*-coordination of ligands in square. The population of isonitrosyl isomer achieved for $[RuNO(NO_2)_2Py_2OH]$ (66 - 75 %) by three techniques (X-ray, IR and Raman) agrees well. Such a high population of the isonitrosyl structure is visible in the photodifference-map. The activation parameters of the reverse transition (MS1-GS) were determined by differential scanning calorimetry (DSC) for complexes with high populations of MS1. Decay temperatures are in the range 190 – 210 K.



Coordination chemistry of nitronyl nitroxide radicals. A new molecular approach in magnetic switching materials

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Incorporation of nitronyl nitroxide free radicals into chelates has enabled the development of a rich coordination chemistry dedicated to molecular magnetism.[1,2] With imidazole type substituents (Figure 1a-b) and the Mn^{2+} ion they give lamellar structures (Figure 1c) with 2D Mn-radical coordination polymers, of formula $\{[Mn^{II}_2\ (NITR)_3]^-\}_n$ (scheme 1d) for the layers and intercalated anions (X^-) in between.[1,3,4] Some of these compounds are magnets with high Curie temperatures.[4]

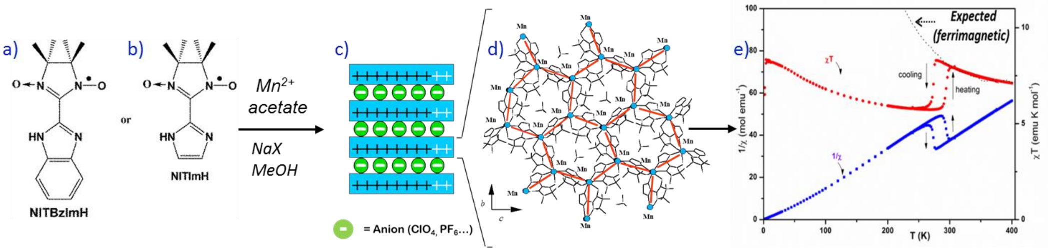

Figure 1

We recently discovered that some of these systems show a temperature-induced transition of the magnetic susceptibility, with hysteresis, in the room temperature range (Figure 1 e). This is ascribed to a valence tautomerism phenomenon (redox isomerism) through which the Mn ions, which are in their +2 oxidation state at high temperature (> 320K), are oxidized in their oxidation state +3 upon cooling (<270K) while some nitronyl nitroxide radicals are reduced. The process is reversed for heating. In this paper we present this new type of switchable materials.

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[2] G. Bussière, R. Beaulac, H. Bélisle, C. Lescop, D. Luneau, C. Reber, P. Rey *Topics Curr. Chem.* 2004, 241, 97-118.
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Light Induced Magnetism in Molybdenum Complexes

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Photomagnetic compounds attract more and more attention due to their potential interest in memory devices or optical switches.[1] In this context, complexes based on octacyanomolybdate precursors might be viewed as interesting building blocks not only for the drastic increase of their magnetization induced by visible light irradiation, but also for the design and the synthesis of multicomponent architectures. In this presentation we focus on two themes that emerge from our research:

- A spin transition centered on the molybdenum that has been evidenced on a MoZn2 complex (leading to High Spin Mo(IV), S = 1).[2]
- A family of photo switchable polynuclear molybdenum-copper complexes, from MoCux, (x = 1, 2, 4, 6) to compounds of higher nuclearity such as Mo3Cu4 and Mo6Cu14, that behave as photo-switchable high spin molecules due to a photoinduced electron transfer.[3] Most of the compounds might be used as starting material for the design of polymetallic supramolecular architectures in order to combine multi-properties.[4]

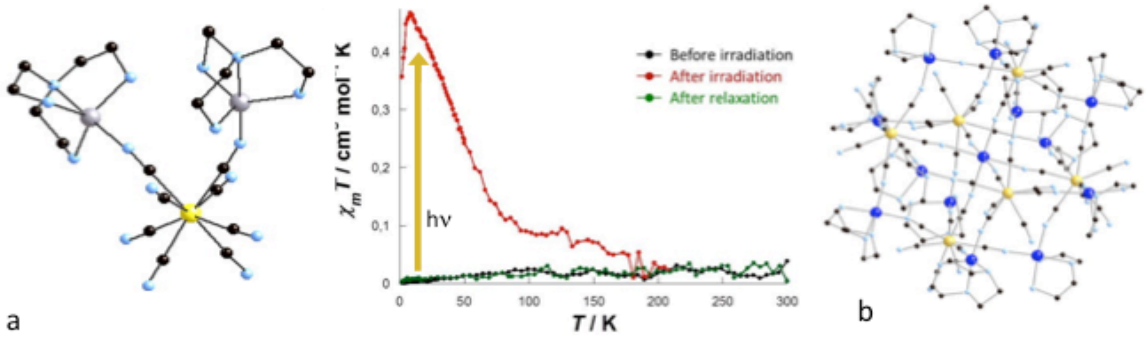

Figure 1 : a) MoZn2, spin transition on Mo(IV) b) photomagnetic cluster Mo6Cu14

[1] A. Bleuzen, V. Marvaud, B. Sieclucka, C. Mathonière, M. Verdaguer, *Inorg. Chem*, **2009**, *48 (8)* 3453
[2] N. Bridonneau, V. Marvaud *et al.* *Chem Commun,* **2015**, 51, 8229.
[3] a) V. Marvaud et al. *Angew. Chem.* 2004, 43, 5468. b) N. Bridonneau, V. Marvaud et al., *submitted*
[4] a) V. Marvaud, et al. *Inorg. Chem*, **2009**, *48 (1)* 22, b) N. Bridonneau, V. Marvaud et al.,*Chem Commun*, **2013**, 49, 9476.

Polymorphism in tridentate Fe(III) spin crossover compounds: transition temperatures and cooperativity

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The phenomenon of spin crossover (SCO) observed for d^4-d^7 first row transition metal ions is normally accompanied by drastic changes in the magnetic, optical and structural properties of molecules and materials,[1] making them very attractive for potential applications in data storage, molecular switching, molecular sensing and other molecular electronic devices.[2] Molecules exhibiting SCO may also present polymorphism which can affect dramatically their magnetic profile and their function.[3]

Here we discuss polymorphism in tridentate Fe(III) Schiff-base complexes with salEen (salEen = N-ethyl-N-(2-aminoethyl)salicylaldiminate) derived ligands. We have found that the temperature of both synthesis and crystallization highly influences the magnetic profile and transition temperatures for their perchlorate and tetrafluoroborate salts. Interesting is that very small changes in the packing of the compounds result in either abrupt spin transitions or exotic spin crossovers with stepped transition and hysteresis (Figure 1).

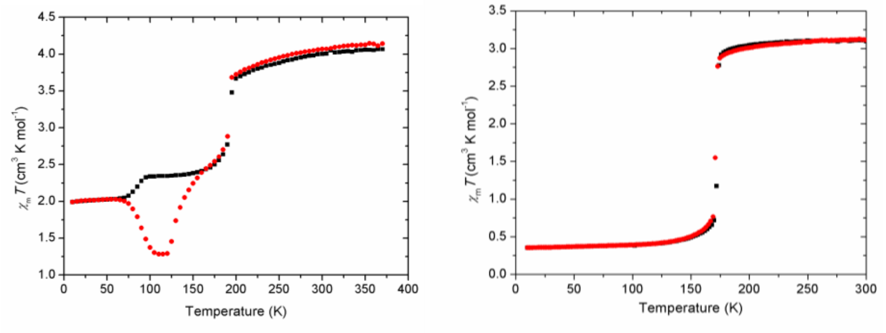

Figure 1 Magnetic profiles of two Fe(III) polymorphs.

1 P. Gamez, J. S. Costa, M. Quesada, G. Aromí, *Dalton Trans.,* **2009**, *38*, 7845.
2 J. Létard, *J. Mater. Chem.*, **2006**, *16*, 2550.
3 J. Tao, R.-J. Wei, R.-B. Huang, L.-S. Zheng, *Chem. Soc. Rev.*, **2012**, *41*, 703.

Thermal Spin State Switching in Ionic Solids, Liquids and Solutions

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Spin crossover (SCO) metal complexes which can switch the arrangement of electrons in d-orbitals from paired to unpaired are versatile molecular candidates for many electronic applications and have been extensively studied in recent years. In the last 5-7 years research in SCO has rapidly moved towards materials development and device assembly but reports on 1D SCO nanomaterials such as nanowires or tubes remain scarce. We have prepared nanowires of mononuclear spin crossover iron(III)[1] and manganese(III) complexes by a solution template method. The wires can be isolated by dissolving the alumina template in acid without decomposition of the nanorod and SEM and AFM reveal a narrow distribution of diameter widths in the range 80-100 nm. The spin transition characteristics for a collection of nanowires exactly match those of a powdered sample of the complex and electronic characterisation of a single wire is possible using Raman spectroscopy coupled to AFM (see Figure). We are currently exploring the potential for SCO nanowires in multiferroics applications and we will also present here the results of our work to prepare cooperative solution assemblies and to lower the melting point to prepare conductive SCO ionic liquids.

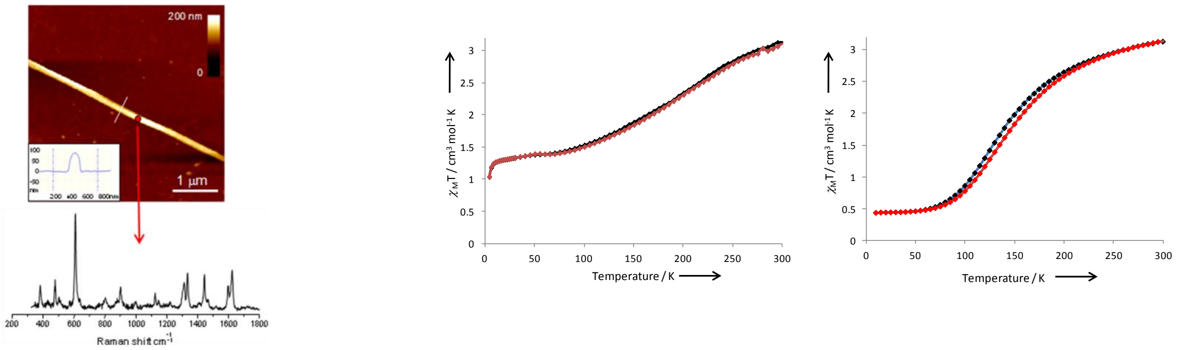

Figure AFM topography of a single nanowire of Fe(III) SCO complex with Raman (532 nm) spectrum of single wire at 293 K, confirming composition as HS (left) and plots of $\chi_M T$ vs T for templated nanowire sample and the bulk powder.

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Spin-crossover compartmentalized coordination polymers: effects of chemical stimuli

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Responsive materials for which physical or chemical properties can be tuned by applying an external stimulus are attracting considerable interest in view of their potential applications as chemical switches or molecular sensors.[1] A major source of such materials is provided by the so-called metal-organic frameworks (MOFs), in which physisorption of guest molecules, located in the pores, can cause subtle changes which affect the magnetic properties.[2] Additionally, selective sorption and separation of gases is an important issue both industrially and from an environmental point of view.

Here we present two families of Fe^{II} coordination polymers which show spin-crossover behaviour and selectively separates different mixtures of gases.[3,4] Despite the lack of permanent channels, these non-porous coordination polymers effectively trap a wide range of gas molecules into the internal cavities due to the flexible and dynamic nature of the framework. The presence of spin-crossover centres permits elucidating the strength of the interaction between the gas molecules and the framework, the strongest response being found for CO_2.

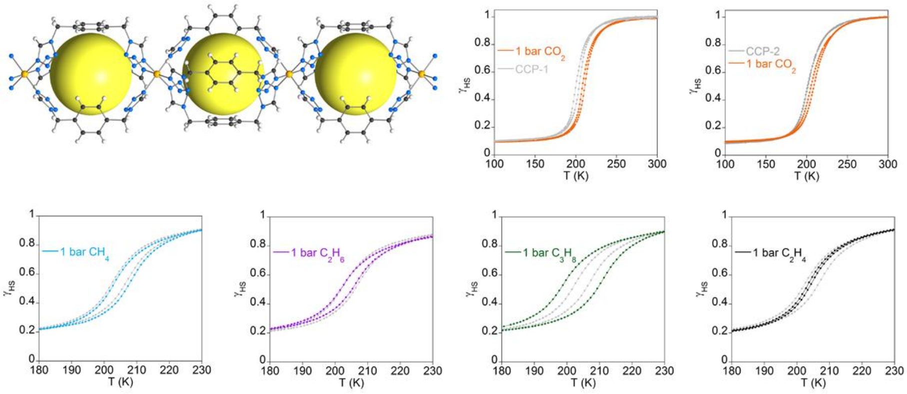

Figure 1 Crystal structure of the compartmentalized SCO coordination polymer and variation of the high spin fraction before and after sorption of different gases

1. E. Coronado, G. Mínguez Espallargas, *Chem. Soc. Rev.* **2013**, *42*, 1525
2. E. Coronado, M. Giménez-Marqués, G. Mínguez Espallargas, F. Rey and I. J. Vitórica-Yrezábal, *J. Am. Chem. Soc.* **2013**, *135,* 15986.
3. M. Giménez-Marqués *et al., submitted*.
4. N Calvo Galve, M. Giménez-Marqués, M. Palomino, S. Valencia, F. Rey, G. Mínguez Espallargas, E. Coronado, *submitted.*

The First Observation of a Spin-Crossover Phenomenon for Fe^{II}-S_6 Complexes with Zwitterionic Ligand, Bis(*N*,*N*'-diethylamino)carbeniumdithiocarboxylate

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Iron(III) complex with dithiocarbamates, $[Fe(R_2dtc^-)_3]$, led to the first recognition of the spin crossover (SCO) phenomenon with the variation in temperature.[1] Since then a large number of the iron complexes have been synthesized and studied extensively. For iron(II), many Fe^{II}–N_6 complexes are reported, although no Fe^{II}–S_6 complexes have been known yet. We prepared a new SCO complex $[Fe(EtL)_3](PF_6)_2$ (**1**), where Fe^{II} with three zwitterionic sulfur donor bidentates $(Et_2N)_2C_2S_2$ (EtL) having two oppositely charged moieties N–C–N(+) and S–C–S(–), which are perpendicular to each other in the solid state and in solution.[2]

The X-ray crystallographic analysis of **1** at 150 and 298 K disclosed that the complex has a slightly distorted triangular prismatic tris-chelate structure, and the Fe–S bond length (2.29 Å) at 150 K is fairly shorter than that (2.50 Å) at 298 K. The temperature dependence of the magnetic susceptibility (χ_M) in the solid state was measured in the warming mode after cooling for 20 h at 210 K in 100 G (Fig. 1, Solid curve **A**). The $\chi_M T$ representing the complete low spin state was almost constant up to at ca 230 K, and then a gradual spin transition to the fully high spin state established at around 280 K took place exhibiting two intermediate states at 245–260 and at 265–275 K, respectively. Without preliminary cooling at ca. 200 K, transition to the low spin state was seen on the way of warming at < 230 K (Fig. 1, Dashed curve **B**).

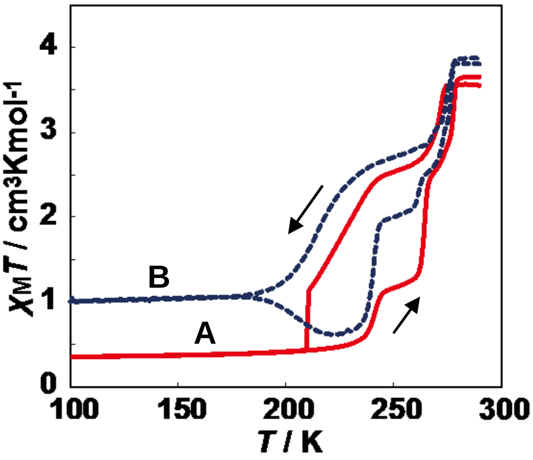

Fig. 1 Thermal variation of $\chi_M T$.

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1 L. Cambi, L. Szegö, *Ber. Deutsch. Chem. Ges.* **1931**, *64*, 167.
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Multistep Spin Crossover Transitions in Polymeric Materials

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Cameron J. Kepert[a]
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An attractive feature of the spin crossover (SCO) phenomenon is its representation of an electronic switch, whereby two distinct magnetic states (high spin (HS) and low spin (LS) are achieved by readily accessible perturbation methods, such as variable temperature, pressure and light-irradiation.[1] An intriguing characteristic of SCO is the cohort of short- and long-range lattice effects which enable solid state cooperativity, reflected by hysteretic and multi-stepped spin transitions.[2] Of multi-stepped spin transitions, those of two-step character are the most prevalent in the literature. Spin transitions proceeding *via* three or more steps are extremely uncommon and often poorly structurally characterized compared to two-step materials due to the intrinsic strain placed on the crystalline solid. We have generated a series of 2-D Hofmann-type materials which incorporate extended 1,2,4-triazole based ligands to produce one-, two-, three- and four-stepped spin transitions by tailoring host-host and host-guest interactions.[3]

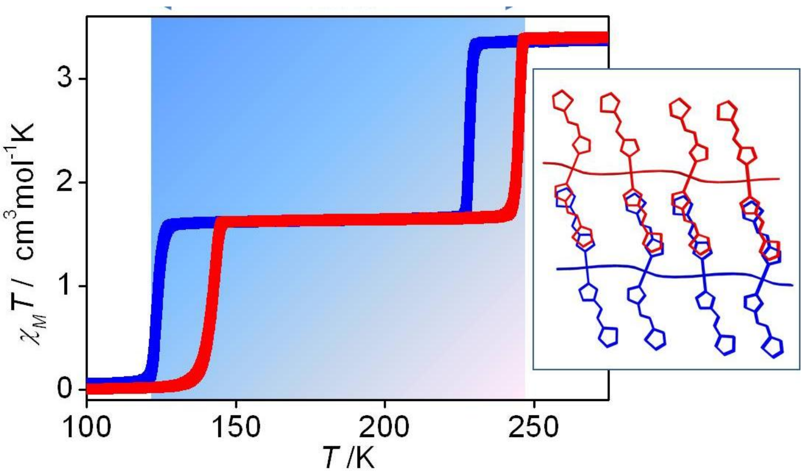

Figure 1 Example of a two-step SCO for the material $[Fe(thtrz)_2Pd(CN)_4]\cdot(EtOH)(H_2O)$ (thtrz = N-thiophenylidene-4H-1,2,4-triazol-4-amine)[3]

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Novel magneto-optical phenomena originating from phase transition in cyano-bridged bimetal assemblies

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Photomagnetic materials has been extensively studied in the field of coordination chemistry. We have reported various unique photomagnetic mateirals using cyano-bridged bimetallic assemblies.[1–5] Furthermore, we have reported a new titanium oxide, lambda-titanium oxide, which exhibits a photo-reversible metallic (Pauli paramagnetic) phase to semiconductor (non-magnetic) phase transition at room temperature.[6,7] Here, I introduce unique photomagnetic materials of iron-octacyanoniobates, $Fe_2[Nb(CN)_8](4\text{-pyridinealdoxime})_8 \cdot 2H_2O$ (1) and $Fe_2[Nb(CN)_8](4\text{-bromopyridine})_8 \cdot 2H_2O$ (**2**).[1,3]

Light-induced spin-crossover magnetic phenomenon: The long-range magnetic ordering of the Fe^{II}(HS)(S= 2) site network caused by a light-induced excited spin-state trapping (LIESST) effect. The iron-octacyanoniobate, **2**, exhibits a spin-crossover magnetic properties, in which a strong superexchange interaction between photo-produced Fe^{II}(HS) and neighbouring Nb^{IV}(S= 1/2) atoms operates through CN bridges. The photomagnetic phase showed magnetic transition at 20 K and a coercive magnetic field of 240 Oe.

90-degree optical switching of output SH light in a chiral photomagnet: A new chiral structured magnet, **3**, where Fe ions and Nb ions are three dimensionally bridged by CN ligands was developed. By alternatively irradiating with 473-nm blue light and 785-nm light, the spontaneous magnetization of the material can be reversibly switched. As a SHG nonlinear optical effects, we have observed 90-degree switching of the polarization plane of the output SH light by changing the state of the magnet with 473-nm and 785-nm lights. There have not been any other reports of chiral photomagnets. With the development of such a novel material, chirality and magnetic properties were coupled to exhibit 90-degree switching of the polarization plane of the output light.

1 S. Ohkoshi, et al., *Nature Photonics*, **2014**, *8*, 65. 2 S. Ohkoshi, et al., *Acc. Chem. Res.*, **2012**, *45*, 1749. 3 S. Ohkoshi, et al., *Nature Chemistry*, **2011**, *3*, 564. 4 S. Ohkoshi, et al., *J. Am. Chem. Soc.*, **2010**, *132*, 6620. 5 S. Ohkoshi, et al., *Nature Materials*, **2004**, *3*, 857. 6 S. Ohkoshi, et al., *Nature Chemistry*, **2010**, *2*, 539. 7 H. Tokoro, S. Ohkoshi, et al., *Nature Communications*, **2015**, *6*, 7037.

Selective state conversion in metal complexes

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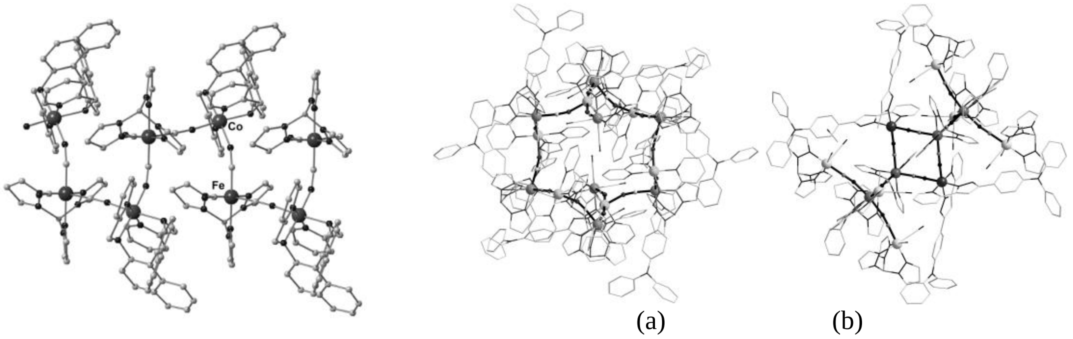
Molecules may have flexible structures with easily controlled electronic states. When molecules have several stable electronic states and their structures are flexible upon state changes, such molecular systems can be promising candidates for molecular switching devises.

Spin crossover (SCO) and mixed valence (MV) complexes rest in two spin states and two valence states, respectively. Multi-component molecules, in which each component possesses several states due to spin conversion and electron transfer, are expected to show synergistic behaviors with stepped and/or selective state conversions. In this lecture, multi-component systems showing selective spin state conversion,[1] photo-induced SCM,[2] and lability controlled cluster systheses[3] will be presented.



(a) (b)

Figure 1 Cyanide bridged 1D and discrete complexes showing photo-induced SCM (left) and clusters generated from different electronic states (right), respectively.

[1] T. Matsumoto, T; Newton, G. N. ; Shiga, T. ; Hayami, S. ; Matsui, Y. ; Okamoto, H. ; Kumai, R. ; Murakami, Y. ; Oshio, H. *Nat. Commun.* ***2014**, 5, 3865/1*.

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[3] Newton, G. N.; Mitsumoto, K.; Wei, R.-J.; Iijima, F.; Shiga, T.; Nishikawa, H.; Oshio, H.*Chem., Int. Ed.* ***2014**, 53, 2941*.

Spin Crossover Porous Metal-Organic Frameworks

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Host-guest interactions are of prime importance in the search for interesting new phenomena in the field of Spin Crossover (SCO) and, more specifically, in the area of Porous Metal-Organic Frameworks (MOFs). In this contribution we will present new results on the SCO-MOFs $[Fe(tvp)_2(NCS)_2]$ (tvp = *trans*(4,4'-vinylenedipyridine)) and $\{Fe(bpb)[M^{II}(CN)_4]\}$ (M^{II} = Ni, Pd, Pt; bpb = bis(4-pyridyl)butadiyne)), respectively (Fig. 1). The former, reported in 1995, represented a unique example of nano-porosity generated by orthogonal interpenetration of 2D SCO $[Fe(tvp)_2(NCS)_2]_n$ layers.[1] Nevertheless, systematic studies on its host-guest chemistry have been reported recently.[2] Here we will describe the crystal structures, SCO and calorimetric properties of a series of clathrates including benzonitrile, nitrobenzene, benzaldehyde, dimethylsulfoxide, dimethylacetamide, acetonitrile among others. Interestingly, simultaneous crystallographic phase transition and SCO occurs in some cases.[2]

The new $\{Fe(bpb)_2[M^{II}(CN)_4]\}$ Hofmann type MOF with enhanced loading capacity displays, a great variety of strong cooperative one-, two- and multi-step SCO behaviours. We will describe their crystal structures, magnetic and calorimetric properties.[3]

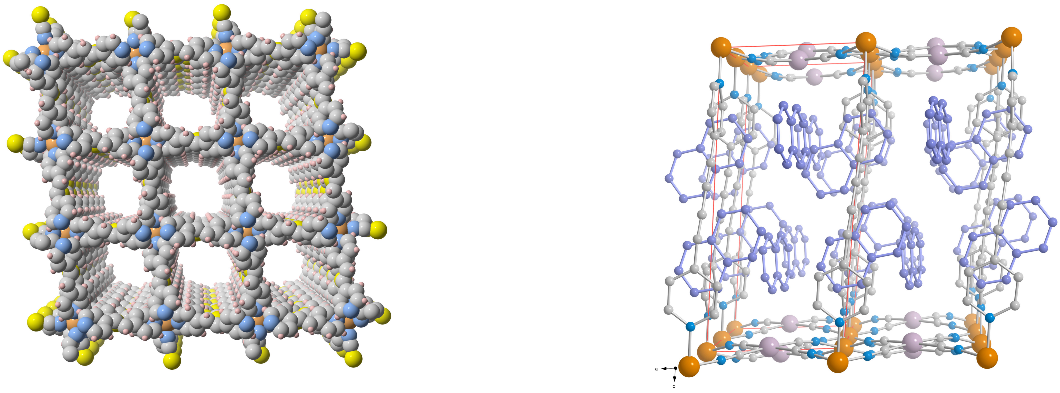

Figure 1. Porous structures of $[Fe(tvp)_2(NCS)_2]$ (left) and $\{Fe(bpb)[M(CN)_4]\}$ (right).

1 J. A. Real, E. Andrés, E.; M. C. Muñoz, M. Julve, T. Granier, A. Bousseksou, F. Varret, *Science,* **1995**, *265*, 268.

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3 L. Piñeiro-López, M. Seredyuk, M. C. Muñoz, J. A. Real, *Chem. Commun*. **2014**, *50*, 1833.

Theoretical and experimental evidence for multiple photoexcited quintet in Fe(II) spin crossover complexes

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[b] Department Chemistry and Pharmacy, Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstraße 3, 91058 Erlangen
[c] Institut de Physique de Rennes, U. Rennes 1, Campus de Beaulieu 263 avenue du General Leclerc 35042 Rennes Cedex, France
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The photophysical processes in diimine complexes have been of great interest mainly since those complexes have been used as dyes in photovoltaic cells. In this context Fe(II) complexes are of particular interest, as dyes themselves[1] or as models for those processes in Ru(II) analogues, in particular archetypal $[Fe(bipy)_3]^{2+}$ and $[Fe(terpy)_2]^{2+}$. For the latter, the splitting of the metastable $^5T_{2g}$ state due to its symmetry lower than octahedral Oh, has been recently investigated theoretically[2] and experimentally.[3] We will present recent results on a whole family of mononuclear spin-crossover complexes of *C*2 symmetry where two different metastable quintet states were evidenced experimentally and theoretically. Those two states could be addressed selectively.

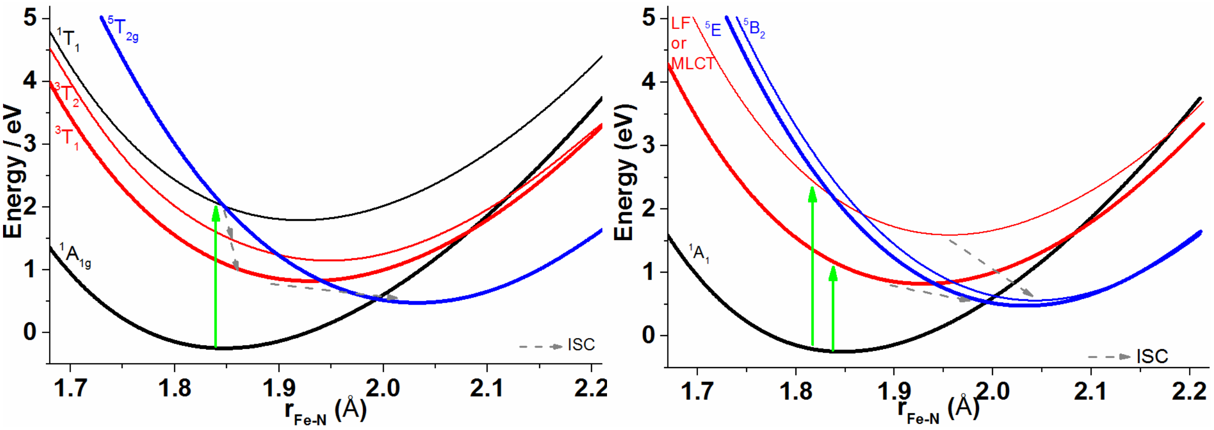

Figure 1 Schematic photophysical processes for photoinduced spin crossover for Fe(II) complexes in (left) octahedral symmetry and (right) *C*2 symmetry.

[1] J.E. Monat, J.K. McCusker, *J. Am. Chem. Soc.*, **2000**, *122*, 4092. [2] M. Pápai *et al.*, *J. Chem. Theory Comput.* **2013**, *9*, 509. [3] G. Vankó *et al.*, *J. Phys. Chem C*, **2015**, *119*, 5888.

Building Multifunctionality into Spin-Crossover Complexes via Modular Design: Opportunities and Challenges

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Spin crossover, a transition between two electronic configurations of transition metal ions, offers the possibility of reversible switching that manifests itself via pronounced changes in structural, magnetic, and optical properties of the corresponding molecular material. One can take advantage of these changes to trigger modification of other properties, such as electrical transport, dielectric permittivity, luminescence, etc., in order to achieve a synergistic combination of several useful functionalities. Our group and others have recently demonstrated the effectiveness of modular approach for the preparation of such multifunctional materials.[1,2] The underlying design principles include the assembly of compatible building blocks and incorporation of intermolecular interactions that can lead to the synergistic behavior. In this contribution, we will demonstrate the effect of thermally and light-induced spin-state on the transport and dielectric properties of such materials. The challenges to achieving the optimal multifunctional behavior also will be discussed.

1 H. Phan, S. M. Benjamin, E. Steven, J. S. Brooks, M. Shatruk, *Angew. Chem. Int. Ed.* **2015**, *54*, 823.
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Synthesis, structures, magnetic properties and oxidation reactions of Co(II) complexes with strand-type hexadentate ligands having thioether-amidato-pyridyl donor set

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The *N*-coordinated anionic amidate ligand is known as a strong σ-donor. On the other hand, the thioether has poor coordinating ability. We have interested in the coordination chemistry of ligands containing both of these donor atoms having quite different abilities (Figure 1).[1] Here, we report the synthesis, crystal structures, magnetic properties and oxidation reactions of Co(II) complexes with these ligands.

The Co(II) complexes, $[Co^{II}L^1]$ (**1**) and $[Co^{II}L^2]$ (**2**), were prepared by the 1:1 reaction of ligands and $Co(OAc)_2$ under N_2 atmosphere. Complex **1** shows bare spin-crossover (SCO) behavior whereas complex **2** shows incomplete, but more clear, SCO behavior. This is because the ligand, H_2L^2, is more flexible for the change of metal-ligand bond distances. In addition, these SCO behavior were enhanced by the introduction of an electrophilic chloro substituent on the pyridine ring.

Oxidation reaction of **1** and **2** were investigated using single crystal X-ray diffraction and UV-vis and NMR spectroscopies. For 1, the C-S bond cleavage accompanied with the oxidation of Co center was observed as reported for relating complexes.[2] On the other hand, the air oxidation of **2** gives the cyclometalated Co(III) complex.[2,3]

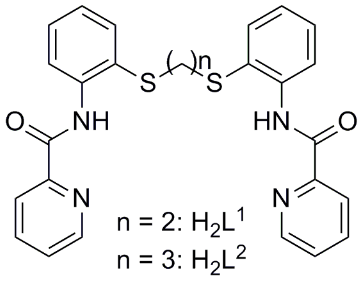

Figure 1 Structural formula of ligands

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Photoswitchable spin crossover nanoparticles

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Spin-crossover molecular materials are prototypes for photoactive and bistable solids, and thus their switching properties stimulate a lot of interest for fundamental and applicative goals, such as molecular switches and information storage. Precise control of their spin-state may be achieved by wavelength selective irradiation via the Light-Induced Excited Spin State Trapping (LIESST) effect.[1] Within the past few years, a lot of work has been dedicated to the synthesis of spin-crossover coordination-polymer-based nanoparticles in order to understand the effect of the size reduction on cooperative effects during the thermal spin transition.[2] Our aim is to elaborate switchable molecular nano-objects, particularly by focusing on the effect of size reduction on their photo-switching dynamics.[3]

With the $[Fe^{III}(3\text{-}OMeSalEen)_2]PF_6$ spin-crossover complex, nanocrystals have been prepared with a method combining fast precipitation and confinement within an organic polymer.[4] These particles, processed as a thin film, have been used to probe the Low-Spin → High-Spin photo-conversion dynamics using ultrafast optical spectroscopy.[5]

The photo-induced dynamics has also been studied on $Fe(pyrazine)Pt(CN)_4$ micro- and nano-objects. 4D electron microscopy has been used to probe individual nanocrystals, evidencing a photodriven thermal spin transition that strongly depends on the nanoparticle surroundings.[6] Moreover, the size dependence of the HS-LS relaxation dynamics has been probed with low temperature time-resolved powder X-Ray diffraction.[7]

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Zero- to three-dimensional iron(II) spin crossover coordination compounds – from ligand design to tunable spin switching behaviour

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Synthetic expertise acquired by the preparation of zero- to three-dimensional iron(II) coordination compounds based on N1-functionalized tetrazole ligands is helping to establish building principles aiming for a rational design and tunable spin switching behavior. Homologous series of halogen-substituted mononuclear complexes are evaluated with respect of electronic and steric effects on the spin transition temperature, *e.g.* the 3-halo-substituted propyltetrazole (3X-3tz) with X= F, Cl, Br and I (see Figure 1). Furthermore, a comparative study of polynuclear chain-type compounds with modified bridging ligand design is presented (see Figure 2) showing the impact of ligand rigidity on the spin transition behavior.

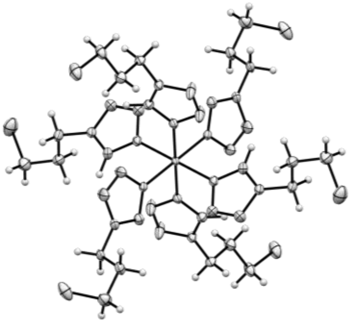

Figure 1: [Fe(*3Cl-3tz*)$_6$](BF$_4$)$_2$

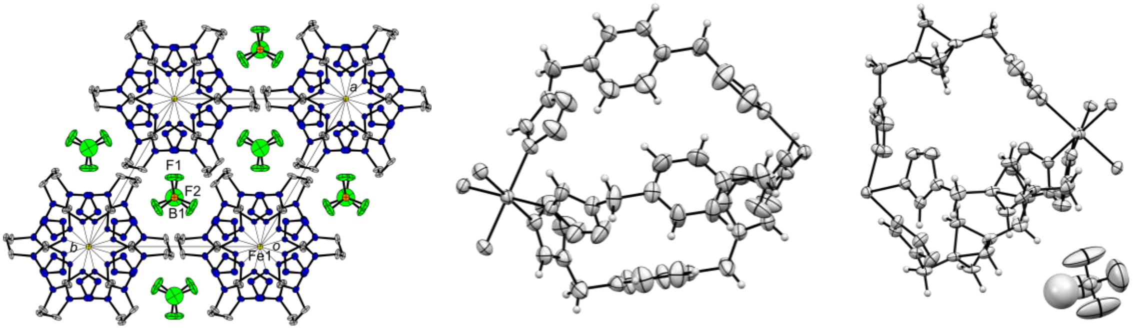

Figure 2: [Fe(*3ditz*)$_3$](BF$_4$)$_2$[1] (left), [Fe(*p-xylditz*)$_3$](BF$_4$)$_2$ (center) and [Fe(*pptz*)$_3$](BF$_4$)$_2$ (right)

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Synergy between spin crossover, magnetic coupling and fluorescence

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Both spin-crossover (SCO) complexes and molecular nanomagnets display magnetic bistable states, potentially behaving as elementary binary units (bits) used for information storage. It is a challenge to introduce SCO units into molecular nanomagnets to switch the bistable state of the nanomagnets through external stimuli-tuned SCO. In this work[1], an iron(II) SCO unit and paramagnetic iron(III) ions were incorporated into a well-isolated double-zigzag chain. The chain exhibited thermally induced reversible SCO and light-induced excited spin-state trapping (LIESST) at the Fe^{II} sites. Single-chain magnet (SCM）behavior was actuated accompanying the synergy between LIESST at the Fe^{II} sites and ferromagnetic interactions between the photoinduced high-spin Fe^{II} and low-spin Fe^{III} ions in the chain. The result provides a strategy to switch the bistable state of molecular nanomagnets using external stimuli such as light and heat, with the potential to erase and write information at a molecular level.

Moreover, the SCO unit were linked with fluorescence unit via covalent bond. The mononuclear SCO-fluorescence complex was characterized by the crystal structure, magnetic properties and variable-temperature fluorimetry. The SCO behavior can be ‘‘read out’’ by solid-fluorescence signals in a mononuclear system. The synergy mechanism was expounded at a single molecule level by the temperature dependence electric absorption spectra.

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Dynamic helicity control of helical tetranuclear complexes by chemical stimuli

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Helicity control of helical molecules by external stimuli has attracted much attention from the viewpoint of switching of chiral functions. Ion and molecular recognition is used for responsive helicity control. We have recently investigated the helicity control of helical complexes bearing a series of oligooxime ligands.[1] Here we report the dynamic helicity control of the tetranuclear complexes (Figure 1a) by coordination of chiral anions and by utilizing covalently attached chiral auxiliaries.

The helicity of helical complex $[L^1Zn_3La]^{3+}$, which was derived from achiral ligand H_6L^1, was efficiently controlled by coordination of hydroxycarboxylates and amino acids.[2,3] Acid–base triggered helicity inversion was achieved by $[L^1Zn_3La]^{3+}$ carrying cysteic acid (Figure 1b). Helical complexes that was derived from chiral ligand H_6L^1 underwent interesting successive helicity inversion upon metal exchange.[4] The helicity was changed as *P* → *M* → *P* → *M* upon the four-step conversion ($[L^2Zn_3] \rightarrow [L^2Zn_5]^{4+} \rightarrow [L^2Zn_3Ba]^{2+} \rightarrow [L^2Zn_3La]^{3+}$) (Figure 1c).

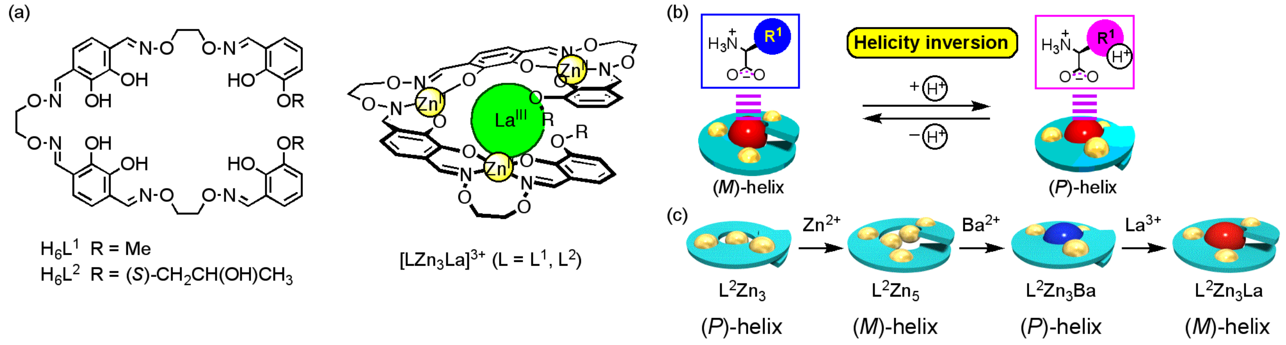

Figure 1 (a) Structural diagrams of H_6L and $[LZn_3La]^{3+}$ ($L = L^1, L^2$); (b) Concept of acid–base triggered helicity inversion using a coordinating amino acid; (c) Stepwise helicity inversion upon metal exchange.

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Molecular materials from chiral coordination compounds at the nanoscale

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The chirality of materials comprising coordination complexes in nanoscale aggregates, on surfaces and in solution, will be presented, with particular emphasis on the effects that metal ion has on the optical activity. Chirality in supramolecular multifunctional materials has been studied for a multitude of reasons,[1] ranging from the preparation of coordination chains from amino acid ligands[2], to assemblies of chromophores in which the central metal ion plays a defining role on the optical activity of the aggregates.[3] The nature of the kinetics of aggregate formation can have an influence on the chiral morphologies displayed by aggregates where intermolecular forces lead rapidly to precipitation.[4] This feature presents challenges when studying the conductivity of bulk materials. An alternative to the study of electrical conduction in materials is through the formation of coordination complexes at the interface between a mwtal surface and the tip of a scanning probe microscope.[5] While these junctions are achiral to date, the possibility of using chiral units in their construction could lead to the ready measurement of the effects of diastereoisomerism in electron tunnelling.

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Chiral Schiff bases in designing magnetic complexes and catalysts

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Schiff bases are very popular as ligands in coordination chemistry.[1] Plethora of such molecules can be easily obtained by simply varying the nature of the keto and amino precursors. An extremely rich coordination chemistry is generated by the Schiff bases derived from *o*-vanillin (Hvan).[2] Starting from Hvan and employing chiral amino precursors (amino-acids and 1,1′-binaphthyl-2,2′-diamine) chiral ligands are readily obtained. Another useful keto precursor is 3-formyl-salicylic acid (H_2fsa). In this communication, we present two families of ligands derived from these keto precursors (Hvan and H_2fsa), as well as their complexes.

First, we discuss chiral oligonuclear complexes of Co(II), Cu(II), and Mn(III), which are characterized by single crystal X-Ray diffraction, circular dichroism, and magnetic measurements. The binuclear Mn(III) complex is an efficient catalyst for enantioselective reactions.

The self-assembly process between Cu(II) ions and the anionic Schiff base resulting from the condensation reactions between Hvan and *R*-, respectively, *S*-methionine generates 1-D coordination polymers. Both enantiomers have been characterized. They exhibit unique two step single-crystal-to-single-crystal transformations (Figure 1), which are accompanied by dramatic changes of their physical properties.

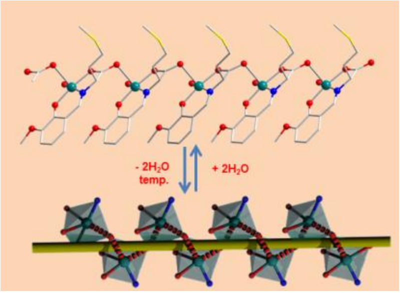

Figure 1. Single-crystal-to-single-crystal process: dimerization of chiral chains, resulting in helicoidal double chains.

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Chiral materials based on helical and methylated TTF derivatives

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Introduction of chirality into conducting systems is a topic of much current interest as it allows the preparation of multifunctional materials in which the chirality might modulate the structural disorder or expresses its influence through the electrical magneto-chiral anisotropy effect. The access to various chiral electroactive precursors for molecular conductors is therefore of paramount importance.[1]

One of the strategies we have been developing in the last couple of years consists of the use of chiral methylated TTF (tetrathiafulvalene) derivatives such as **TM-BEDT-TTF** (TM = tetramethyl, BEDT = bis(ethylenedithio), **DM-BEDT-TTF** (DM = dimethyl), and **DM-EDT-TTF** (EDT = ethylenedithio) in electrocrystallization experiments in the presence of various anions.[2-4] For example, the radical cation salts of **DMEDT-TTF** and PF_6^- show semiconducting properties in the enantiopure form and metallic conductivity for the racemic form.[4] Investigations of the structural features and conducting properties of complete series of radical cation salts (enantiopure and racemic forms) from these families of derivatives will be presented. A special attention will be given to the interplay between chirality and conductivity.[5]

A second family of chiral TTFs we will discuss present helical chirality provided by helicene units fused with the TTF moiety.[6]

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Multireversible redox processes in a self-assembled bis(triple-helical) pentanuclear iron complex

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Spontaneous self-assembly of coordination compounds is a very efficient way to synthesize functional molecules, and especially high-nuclearity metal complexes exhibiting closely spaced electronic levels. Pentanuclear bis-(triple-stranded) helical complexes have been previously isolated with the 3,5-bis(pyridin-2-yl)pyrazolate (bpp^-) ligand.[1] We will present here the redox behavior of the Fe_5 complex that strongly differs from that of the Mn_5 analogue. Remarkably, UV-visible and Mössbauer spectroscopies evidence that a single electron transfer causes the redox switch of the two axial Fe sites. The origin of this switch we will be exposed.

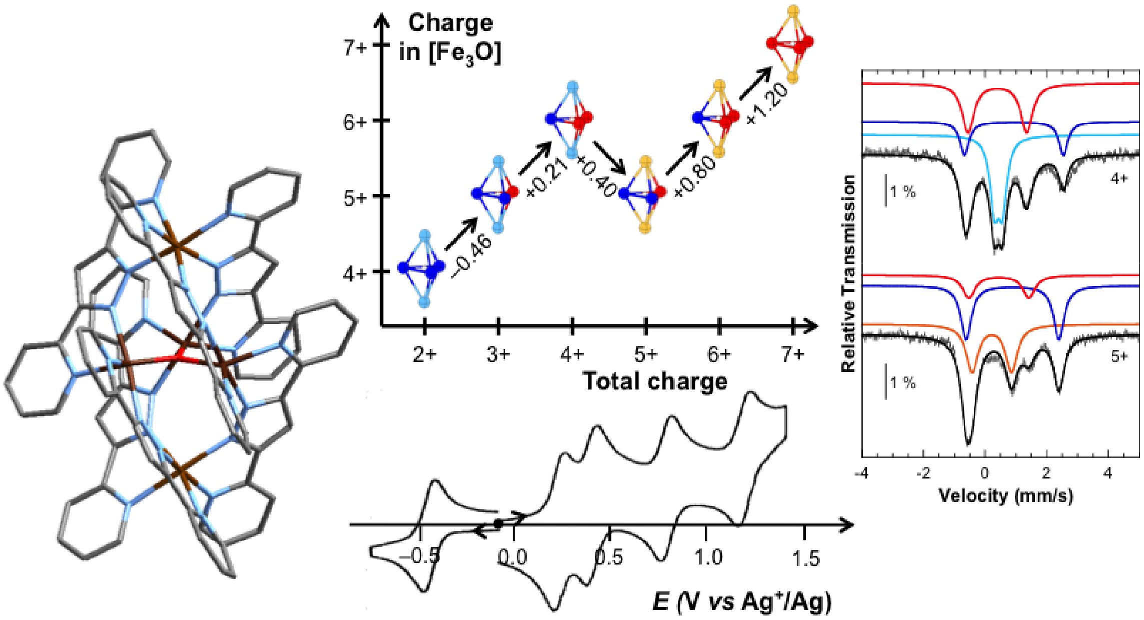

Figure 1. Left: X-Ray structure of $[\{Fe^{II}(\mu\text{-bpp})_3\}_2Fe^{III}Fe^{II}_2(\mu_3\text{-O})]^{3+}$; Middle: Cyclic voltammogram and redox changes; Right: Zero-field 80 K Mössbauer spectra of the 4^+ and 5^+ species.

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Optically-active soft nanostructures containing coordination Complexes

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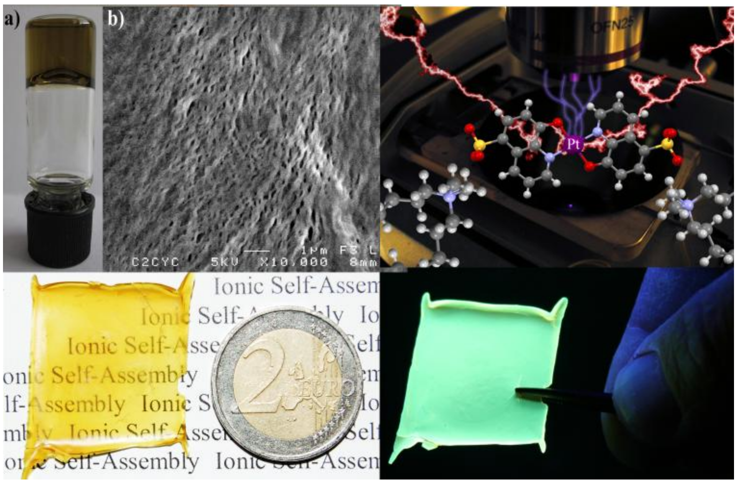
Supramolecular chemistry, in which non-covalent interactions drive the formation of elaborated and exotic superstructures, is an elegant way to organize small molecules into highly functional architectures of potential interest in life and material sciences. Among the diversity of materials able to self-assemble into organized superstructures at the micro and macroscopic scale, liquid crystalline and gel-like materials continuously emerge as attractive candidates to form active and stimuli responsive architectures, especially in the fields of optics and electronics.

We will present some covalent and electrostatic strategies which allow to easily organize optically active coordination complexes (σ-alkynyl Platinum(II) Terpyridine, Nickel-bis(dithiolene), aluminum and platinum qinolinate, Cu_4I_4 cluster…) in solid state and/or in solution into highly organized soft supramolecular architectures. We also show how original optical properties can emerge from such supramolecular architectures and how they can be modulated by external stimuli.



Patchwork of the results which will be presented

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Multifunctional compounds: spin crossover and chirality

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The synthesis of new spin crossover compounds is interesting essentially for the understanding of the physics underlying the corresponding phase transitions, as much as for the potential technological applications of those compounds. Obtaining non-centrosymmetric magnetic compounds yields interesting subjects for non-linear optical studies (study of the effect of unpaired electrons) [1], or for crystallography (see recent evidence on incommensurate spin state ordering) [2]. Various strategies are being currently pursued towards such spin crossover non-centrosymmetric molecular materials. These strategies introduce chirality by playing on the two variables components of the material, the ligands on the transition metal (typically Fe(II) or Co(II)), and the possible counteranions [3,4, 5]. We will show the results we have obtained recently using the latter approach, with various families of chiral anions. We will show that the analysis of chiral interactions in the solid state can lead to different conclusions respective to results obtained in solution (NMR, circular dichroism), and that those interactions depend heavily, as much as for the spin crossover phenomenon, on non-covalent intermolecular interactions such as hydrogen bonding.

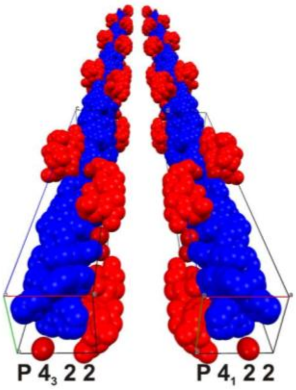

Figure Right and left handed chiral spin crossover helices based on $[Co(terpy)_2]^{2+}$ and (Δ or Λ $As_2(tartarate)_2$)(TBA) anion

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A Spin Crossover $[Fe_2]$ Supramolecular Helicate with an Encapsulated $[Cr(oxalate)_3]^{3-}$ Single Ion Magnet

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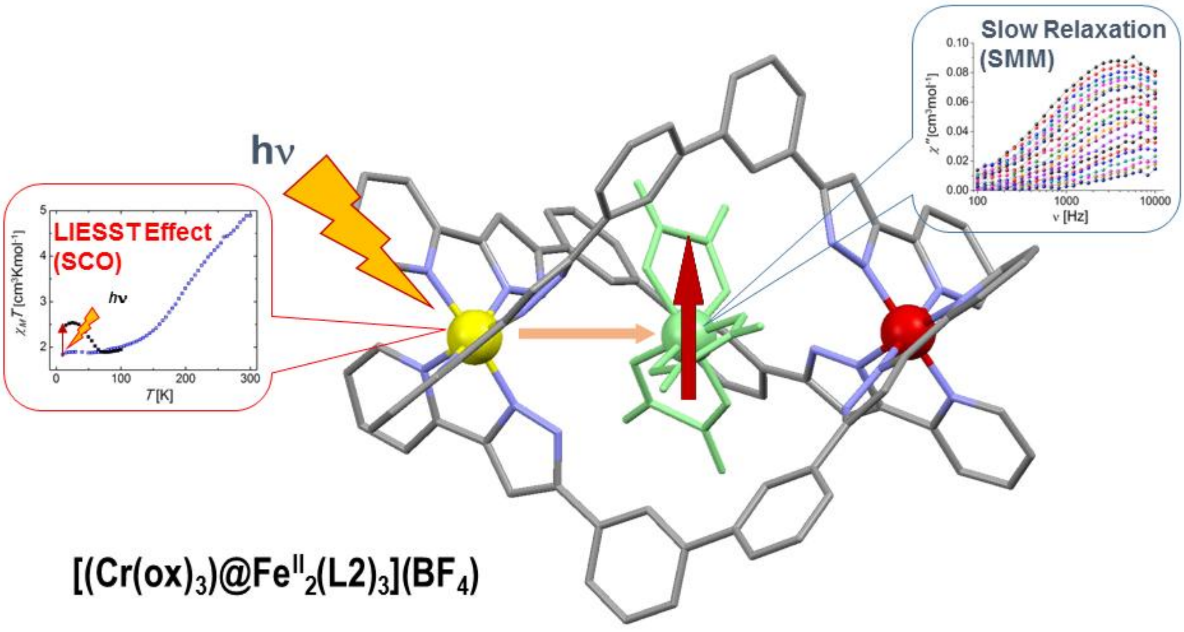
Molecular functional materials may incorporate several functions with the potential to interact synergistically and of being addressed with external stimuli. Using a new ditopic bis-(pyrazol-pyridyl) ligand, three novel metallo-supramolecular triple-stranded Fe(II) helicates were synthesized; $[M(ox)_3{\subset}Fe_2(H_2L)_3]$ and $[M(ox)_3{\subset}Fe_2(H_2L)_3]X$ (M=Cr(III) **1**; Fe(II), **2**; Fe(III), **3**; ox^{2-} =oxalate; $X=BF_4^-$). Encapsulation of $[M(ox)_3]^{3-}$ leads to a novel host-guest systems where both metals may carry different functional properties. The case of complex **1** is especially exciting; the Cr(III) guest behaves as single ion magnet (SIM) at low temperatures and the $[Fe_2]$ helicate exhibits spin crossover properties. At low temperatures, a fraction of the Fe(II) ions can be excited to the S=2 spin state *via* the LIESST effect. This opens the door to the possibility of manipulating the SIM properties of the Cr(III) center *via* the LIESST effect on the host component of the molecular assembly, since both effects may be implemented at the same temperature range.



Metallahelicenes: a favorable strategy for strong tunable chiroptical properties

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Helicenes are chiral molecules possessing a unique screw-shape and π-conjugated structure which provides them strong chiroptical properties such as huge optical rotation values.[1] Due these intrinsic properties, they have exhibited a significant potential in many applications such as in asymmetric catalysis and chiroptical materials.[1] Expanding the functionality of helicene derivatives is thus an important challenge for chemists to fully develop and explore their potential in the aforementioned domains. For this purpose, we have used organometallic and coordination chemistry to access to a variety of helicene-based frameworks.[2] The great potential of this approach will be illustrated through selected examples of metallahelicenes, exhibiting strong tunable chiroptical properties such as circular dichroism, circularly polarized phosphorescence,[3] chiroptical switching.[4]

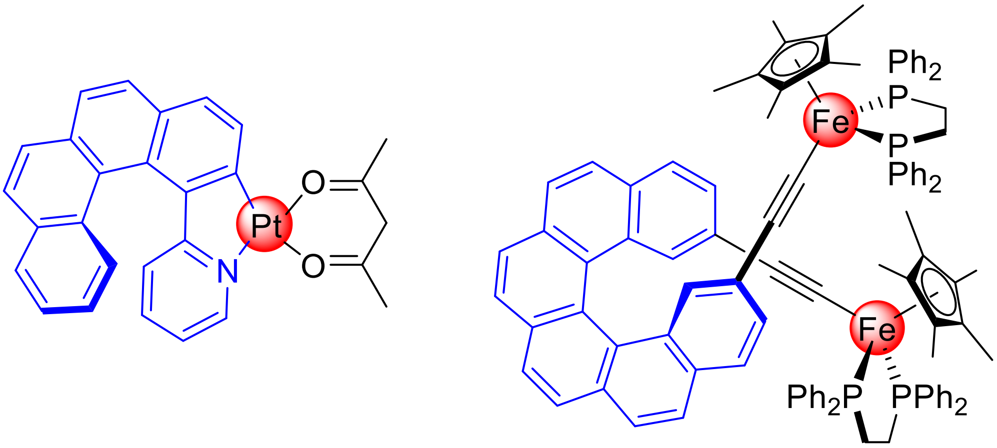

Figure 1 Structures of metallahelicenes involving platinum and iron as the metal center.

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Influence of steric effect in gold dithiolene complexes as single component molecular conductors

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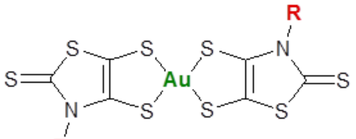
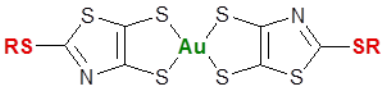
Gold bis(1,2-dithiolene) complexes have recently emerged as attractive systems for the elaboration of *single-component* molecular conductors.[1] Within this framework, it was recently reported by our group an original series of single component molecular conductors based on neutral radical gold dithiolene complexes derived from [Au(R-thiazdt)$_2$] which are pressure sensitive.[2] For instance, the [Au(Et-thiazdt)$_2$] behaves as a Mott insulator and becomes metallic under an applied pressure (1.3 GPa).[2a] In order to have a better understanding of the structure/property correlations in these materials, we focused our attention on two type of modifications of the ligand skeleton. First, we investigated the complexes, noted [Au(RS-tzdt)$_2$], where the alkyl substituents are located on the exocyclic sulfur atoms instead of the nitrogen atom of the thiazole rings.[3] Then, we also investigated the steric effect of nitrogen substituent on the organization and properties of the neutral gold dithiolene complexes. For instance we replaced the ethyl group by an isopropyl one. Here in, we will present the effect of these modifications, brought to the ligand, on the properties. Moreover, we will show that despite these modifications, these complexes, even with different organization in the solid state, present strong interactions between neighboring molecules and thus behave as single component molecular conductors.



[Au(R-thiazdt)$_2$]$^{-1,0}$
R = Et, *i*Pr



[Au(RS-tzdt)$_2$]$^{-1,0}$
R = Et, Me

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An Electrically Conductive Donor–Aceptor–Donor Aggregate with Hydrogen-bonding Lattice Based on a Dinuclear Complex

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The pair of electron donor (D) and acceptor (A) molecules gives a charge transferred state which plays important roles in several phenomena, for example, transport property in material science. Focusing on the spatial layout of pairs in solid, its segregated stacking is of advantage to the carrier transpor property due to a 1D conduction path. However, it is difficult to control the formation of segregated or mixed one. From this view point, molecules comprising both D and A moieties, especially D–A–D or A–D–A, have a potential to afford a uniformly segregated-stacking 1D column (Figure 1a). Despite this feature, there are few reports to study their transport property.

To investigate the conduction behavior of D–A–D aggregates, we give an attention to a dinuclear complex bridged by tetrathiooxalate (***tto***); (μ-tetrathiooxalato)bis[(pyrazine-2,3-dithiolato)nickel(II)], $(Bu_4N)_2$(***tto***)[Ni(**pdt**)]$_2$ (**1**). We reported that **1** is a compact, planar and low-energy gap material with D–A–D nature.[1] In addition, **1** has an ability to accept proton. The protonated **1** (**1H$_2$**) are expected to give a hydrogen-bonding lattice where 1D π-stacking columns align (Figures 1b and 1c). In this presentation, crystal structure, transport property and conduction mechanism of **1H$_2$** are discussed.

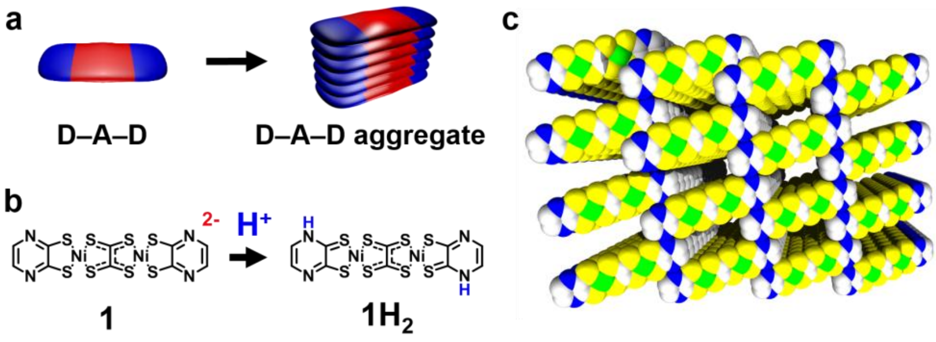

Figure 1. (a) Schematic image of aggregation of D–A–D (b) Protonation reaction of **1** (c) Crystal structure of **1H$_2$**

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One-Dimensional Organic-Inorganic Perovskite: Hybrid of $PbBr_5$ Chain and Conductive Naphthalenediimide Column

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Organic-inorganic perovskite is a mine of synergistic functions derived from metal ions and organic moieties. In particular, two-dimensional (2D) and three-dimensional (3D) lead-halide-based organic-inorganic perovskites, $(RNH_3)_2PbX_4$ and $(CH_3NH_3)PbX_3$, respectively, have been extensively studied because of their characteristic physical properties such as Wannier exciton absorption, quantum-well structure, and high power conversion efficiency for the solar cell. On the other hand, corner-sharing one-dimensional (1D) lead-halide-based perovskites have never been reported, because their expected formula, $(RNH_3)_4PbX_5$, do not match charge neutrality.

However, we recently obtained the first corner-sharing 1D lead-halide-based perovskite containing diammonium ion with naphthalenediimide (NDI) skeleton, $(NDI\text{-}enH_2)_2PbBr_5\cdot 2H_2O$ (**1**) (NDI-en = *N,N'*-bis(aminoethyl)naphthalenediimide). 1D perovskite structure is achieved because NDI skeleton is partially reduced to match charge neutrality.

The crystal structure of **1** is shown in Figure 1. Apparently, NDI-enH_2 molecules stack to form 1D column structure hybridized with $PbBr_5$ chain. Formula of **1** indicates that one electron is doped per two NDI-enH_2 molecules. ESR and UV-Vis absorption spectra support the existence of radical. The conductivity of **1** is 2.8 Ωcm^{-1} at room temperature, which is the highest of all NDI-based semiconductor.

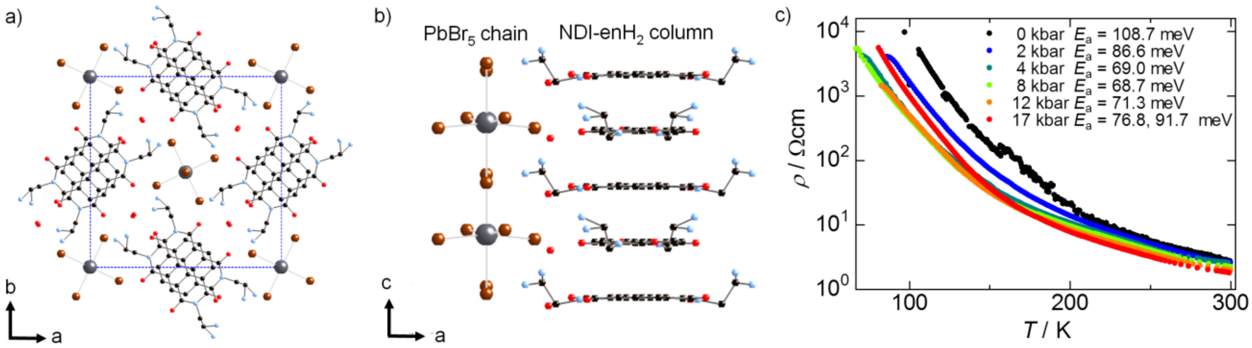

Figure 1 (a,b) Crystal structure of **1**. (c) Temperature dependence of electrical conductivity of **1**.

Multiple-band Molecular Conductors Based on Metal Dithiolene Complexes

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Molecular conductors have been characterized by simple and clear electronic structures where a conduction band originates from one frontier molecular orbital (HOMO or LUMO) and the tight-binding approximation works quite well. Recently, however, it has been reported that an increasing number of molecular conductors have more than two bands near the Fermi level and the multiple-band character provides unique physical properties. The metal dithiolene complex with the planar central core is characterized by a small HOMO-LUMO energy gap, and thus can provide various types of multiple-band molecular conductors.

One typical example is the single-component molecular conductor where an electron transfer from HOMO band to LUMO band leads them to a partially filled state. [1,2] When HOMO and LUMO bands have the opposite curvatures and intersect (crossing band structure), the HOMO-LUMO interaction generates an energy gap at the Fermi level and destroys the metallic state. But, when there are lines on which the HOMO-LUMO interaction is zero, the HOMO and LUMO bands contact at the points where these lines intersect with the Fermi line, which results in the formation of the Dirac electron system.

The small HOMO-LUMO energy gap provides another type of multiple-band system in combination with the dimerization. An isostructural series of anion radical salts $X[\mathrm{Pd(dmit)_2}]_2$ characterized by the HOMO-LUMO inversion shows a variety of ground states including quantum spin liquid when $X=\mathrm{EtMe_3Sb^+}$.[3] The isostructural Pt analogues show a strong tendency to undergo a charge order transition associated with the HOMO-LUMO inversion.[4] The spin-orbit coupling plays an important role in the $\mathrm{Pt(dmit)_2}$ salts.

This work has been done in collaboration with H.B. Cui, T. Tsumuraya, and M. Nomura (RIKEN).

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Coordination abilities of dithiolene and dioxolene sites in o-quinone annelated with dithiete.

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There are a number of promising effects such as molecular magnetism, luminescence, photo-thermomechanical effect which were observed on the o-quinone complexes. There is a problem with a manipulation of these properties via external action. A possible way to solve it is an organization of the electric contact between the coordination molecule and a metal surface. We suppose that an o-quinone **1** might serve as a such junction.[1]

An activity of sterically hindered bifacial ligand **1** towards coordination by dithiolene and dioxolene sites has been studied. The selectivity of dioxolene and dithiolene coordination sites towards different metals was of special interest. It was found that monovalent cations as well as divalent cations with strong Lewis acidity reacts towards formation of semiquinonic or catecholate complexes respectively. A number of such complexes have been characterized with the EPR spectroscopy.

At the same time a cations possessing a weak Lewis acidity such as $Pt(PPh_3)_2^{2+}$ or $Pd(PPh_3)_2^{2+}$ form dithiolate complexes. In this case an o-quinone function of the molecule in these complexes remains free for the metal coordination. EPR study of an interation of Pt and Pd dithiolate complexes with reducing agents such as K or Tl and so on reveals that corresponding semiquinonates formed. A coordination chemistry of bifacial ligand **1** will be discussed.

Acknowledgements - This scientific research was performed with financial support of the Russian Foundation for Basic Research, grants 15-43-02350 r_povolzhie_a and the Program for support of Leading Scientific Schools NSh-271.2014.3.

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Using intermetallic catalysts to grow chirality-specific single-walled carbon nanotubes

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Single-walled carbon nanotubes (SWNTs) present structure-determined outstanding properties and may find important applications in many fields. However, the chirality-controlled growth of SWNTs is always a great challenge. It is shown that the tube structure can be well controlled in a templated growth process. Carbon nanotubes and their caps or catalysts can all act as the structural templates. SWNT growth via a catalyzed chemical vapor deposition CVD process is normally more efficient. This is also true in the chirality selective growth processes. We first used intermetallic nanocrystals as the catalyst to grow SWNTs with specified chiral structures. Using W6Co7 catalysts, we realized the selective growth of (12, 6) and (16, 0). W6Co7 nanocrystals present unique structure and property, which are distinctly different from the normal alloy nanoparticles or simple metal nanocrystals, therefore can act as the template to grow SWNTs with designed (n, m) structures. Besides the catalysts, the CVD condition is also very important. The factors which can influence the chirality selectivity and the mechanism of the process will be discussed from the thermodynamic and kinetic points of view..

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Enantiopure coordination polymers containing tridentate Schiff bases ligands. Crystal structures, optical and magnetic properties

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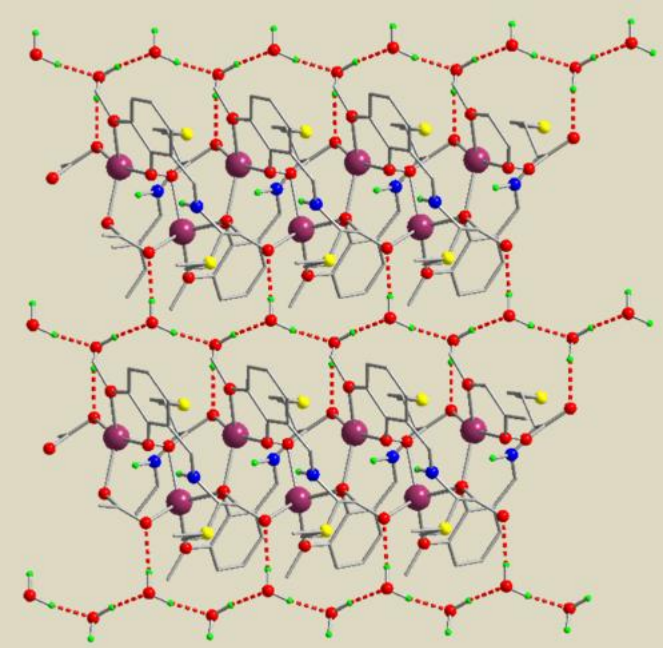
Homochirality is an intrinsic feature of the living world. The most employed strategy for introducing the chiral information into a metal-ion based network consists of choosing of an enantiomerically pure ligand [1]. In this respect, the usage of natural amino acids as chiral precursors is a simple and practical alternative. Moreover, the preservation of amino acid moieties within the resulting ligand can afford both an increased denticity and different kinds of hydrogen bonds that play a critical role in the self-assembly process.

The curent study is centred on several tridentate salicylaldimine-type ligands containing mainly methionine or arginine moieties. In this communication we present: (i) supramolecular architectures of simple organic chiral Schiff base, (ii) chiral 1-D ladder like sodium coordination polymers constructed from these ligands, (iii) chiral copper(II) chains constructed from Schiff base ligands and ancillary bridging ligands(4,4'-bipy, dca^{-}), (iv) physical properties (electronic, fluorescence, CD spectra and magnetic behavior) according to their relevance for each compound.



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Exploiting Metal-Centered Chirality for Asymmetric Catalysis

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This presentation will give an overview of recent contributions from the laboratories of the author to design novel asymmetric catalysts based on exploiting octahedral metal-centered stereochemistry.

1.) Low-loading metal-templated asymmetric "organocatalysts":[1-3] In this enzyme-like catalyst design, the central transition metal serves as a structural ankerpoint and provides metal centrochirality, while catalysis is mediated through the organic ligand sphere.

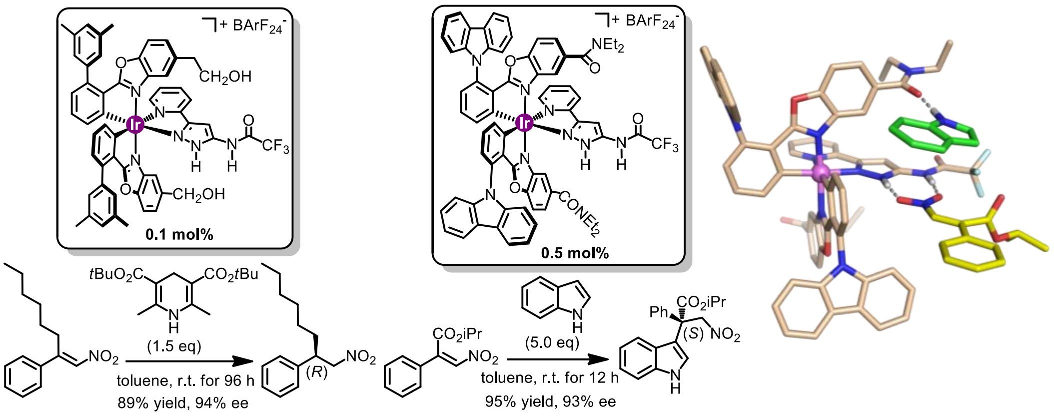

Figure 1 Asymmetric hydrogen bonding catalysis with inert Ir^{III} complexes.

2.) Visible-light-activated asymmetric catalysis with chiral transition metal complexes:[4-6] In this catalyst design, the metal center serves multiple functions at the same time: as a precursor for the photosensitizer, as a chiral Lewis acid for substrate activation, and as the exclusive chiral center.

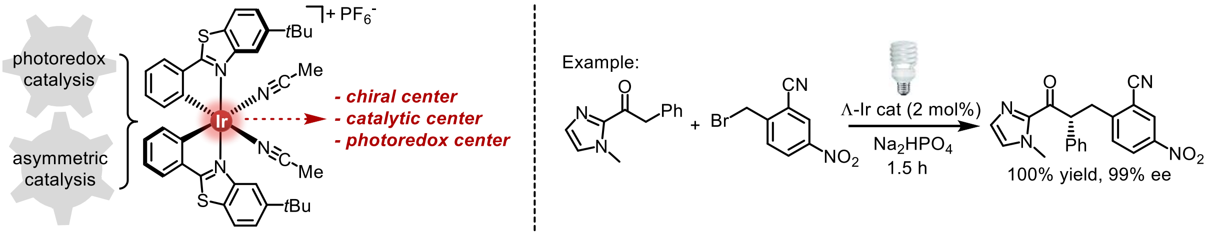

Figure 2 Chiral-at-metal Ir^{III} complex for merging asymmetric Lewis acid catalysis with photoredox catalysis.

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Shifting conformational equilibria of transition metal complexes by solvents and chiral ions

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Vibrational Circular Dichroism (VCD) spectroscopy measures the small difference in the absorption of left- and right circular polarized infrared light by a chiral sample. It allows the unambiguous assignment of absolute configurations by comparison of experimental VCD spectra with computationally predicted spectra. Besides its unique sensitivity to chirality and absolute configurations, VCD spectroscopy is highly sensitive to even very subtle differences in structures, such as conformational changes induced by solute-solvent interactions. In our work, we take advantage of this conformational sensitivity and use VCD spectroscopy to probe intermolecular interactions in solution with a special focus on understanding mechanisms of chirality transfer in asymmetric catalysis.

In this contribution, I will first briefly introduce the spectroscopic technique. For a chiral transition metal complex, I will show how VCD spectroscopy reveals an unexpected solvent dependence of the equilibrium between two diastereomeric forms.[1] We then turn to a VCD study of a chiral ion pair-based asymmeric catalyst.[2] The catalyst itself consists of a manganese(III)-salen cation which is the catalytically active component, and a chiral anion which is the „chirality donor“ and responsible for the asymmetry of the catalytic process. In particular, it will be discussed how the experimental VCD spectra can be used to explain the enantioselectivity of the catalyst in different solvents as well as the low enantioselectivity of ion pair catalysts with certain chiral anions.

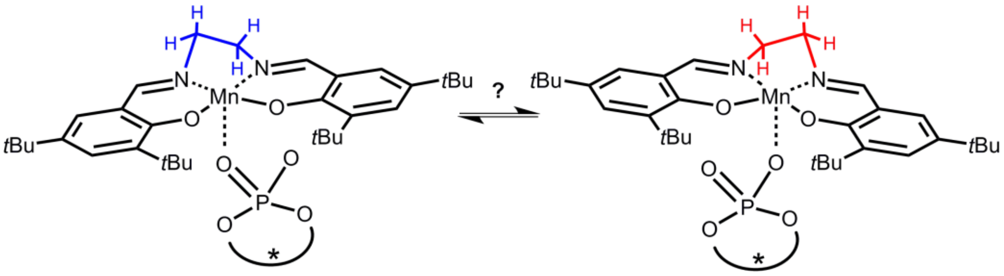

Figure 1 VCD spectroscopy reveals chiral phosphate induced equilibrium shifts

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Solid-solid Interconversion by Geometric Distortion and Magnetic Stabilization in the Hydrogen-bond-unit Based Molecular Conductors

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Novel functionalities of proton-π-electron coupling (PEC) in molecular conductors have been developed in my group. In the catechol-fused TTF system [1], the metallic state of purely organic single-unit crystal of κ-H_3(Cat-EDT-ST)$_2$ [2], the quantum spin liquid state of κ-H_3(Cat-EDT-TTF)$_2$ [3], and electronic switching induced by deuterium and charge transfer of κ-D_3(Cat-EDT-TTF)$_2$ and of κ-D_3(Cat-EDT-ST)$_2$ [4,5] have been unveiled.

In this report, the novel PEC conductors, β'-[H_3(Cat-EDO-TTF)$_2$]BF_4 [6] and related crystals, are introduced; the solid-solid interconversion from β'- to α-phase accompanying resistivity and magnetic switching of the BF_4 complex is derived from geometric distortion from planar to bent form of the composed hydrogen-bonded unit and the magnetic stabilization towards spin singlet state with dimerization of molecules (Figure 1).

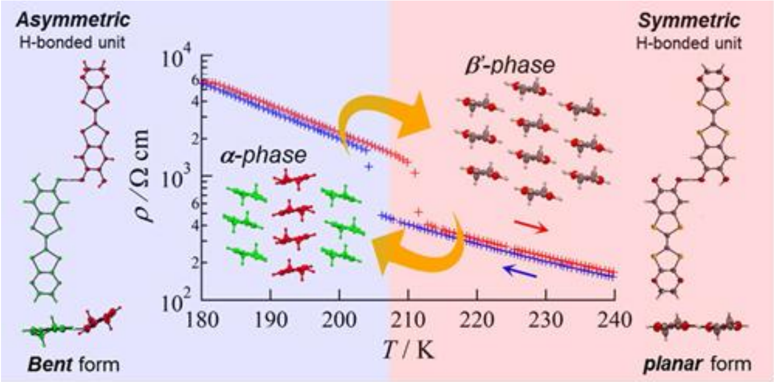

Figure 1 The solid-solid interconversion from β'- to α-[H_3(Cat-EDO-TTF)$_2$]BF_4 at 210 K is originated from the geometric distortion of the intra-hydrogen-bond-unit H_3(Cat-EDO-TTF)$_2$ and magnetic stabilization.

This research is collaborated with Mr. J. Yoshida, Drs. A. Ueda, A. Nakao, R. Kumai, H. Nakao, and Y. Murakami.

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Stereochemistry Determines Structure in Complex Assemblies

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This talk will explore different aspects of stereochemistry encountered during the use of subcomponent self-assembly, whereby complex structures are prepared through the simultaneous formation of dynamic coordinative (N→Metal) and covalent (N=C) bonds. This technique allows the study of stereochemical information transfer processes within metal-organic assemblies, which may contain different combinations of fixed (carbon) and labile (metal) stereocenters. Subcomponents with fixed stereogenic centers can be incorporated in the organic ligands of mononuclear metal complexes, and communicate stereochemical information to the metal center, resulting in diastereomeric enrichment.[1]Further work allowed control of the stereochemistry of increasingly complex architectures.[2] This strategy has allowed exploration of the degree to which stereochemical information is propagated through tetrahedral frameworks cooperatively,[3] leading to the observation of stereochemical couplings across more than 2 nm between metal centers[4] and the enantioselective synthesis of a face-capped tetrahedron containing no carbon stereocenters*via* a stereochemical memory effect.[5] Studies on the communication of stereochemistry between the configurationally flexible metal centers in tetrahedral metal-organic cages have shed light on the factors governing this process, allowing the synthesis of an cage in which all symmetry elements have been broken.[6] Finally, the use of octahedral metal templates with *facial* stereochemistry in subcomponent self-assembly, which predictably gave rise to structures of tetrahedral symmetry, was extended to *meridional* metal centers. These lower-symmetry linkages have allowed the assembly of a series of intricate and functional 3D architectures.[7]

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Study of the organization of optically active molecular materials based on chiral porphyrins

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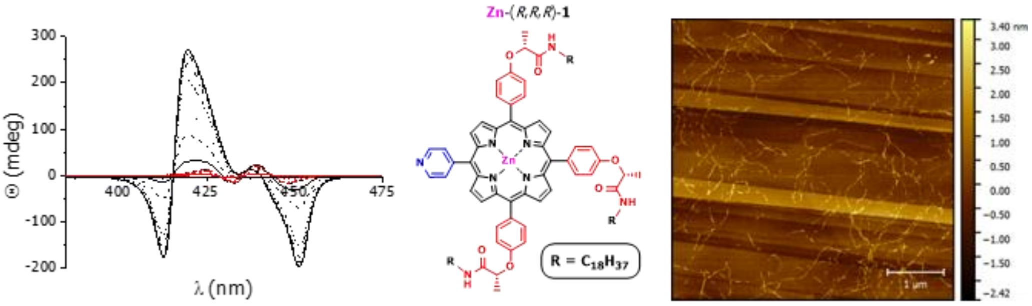
The study of the self-assembly of porphyrins and metalloporphyrins has received great attention in recent years because of their optical, electronic and magnetic properties that make these chromophores suitable for a broad range of potential applications.

In this work, the design of chiral supramolecular systems based on porphyrins has been carried out in order to determine the influence of chirality in the hierarchical morphology of the aggregates and, in consequence, the influence of the chiral organization in the properties.

The self-assembly studies in solution and in the solid state of a family of metalloporphyrins which contain in their structure chiral amide groups and pyridyl units show the influence in their optical activity and morphology of the aggregates, all of them mainly formed through coordination between the pyridyl unit and the zinc (II) metal ion (Figure 1).[1]



The self-assembly studies of C_3 symmetric molecules[2] based on chiral porphyrins have been performed by CD in different solvents and the morphology of the aggregates by AFM after deposition on HOPG and mica.

Acknowledgements: We thank the Région Pays de la Loire and the University of Angers for financial support through the LUMOMAT project.

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Chiral macrocyclic europium(III) complexes for security tagging

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Highly emissive sensitised lanthanide complexes based on macrocyclic chelating ligands have been used extensively to study biological function at a cellular level, due to their long-lived, sharp emission bands and high stability.[1] These photophysical properties also make these complexes promising candidates for security labelling and as anti-counterfeiting tools. The annual cost of counterfeiting to the global economy is estimated to be \$1.7 trillion,[2] and in the last 10 years, the Bank of England has withdrawn >5 million counterfeit banknotes from circulation with a value of nearly £100 million.[3]

Chiral europium complexes, (e.g Fig. 1), may be resolved by chiral HPLC. Each enantiomer gives mirror-image circularly polarised luminescence (CPL). This fingerprint can be exploited as a security feature for the labelling of authentic items such as banknotes and certificates. Simple methods of detection of the complexes have been developed using band pass filters attached to a commercially-available DSLR camera and flash lamp. Using this setup and introducing a time delay between excitation and capture of an image, other emitted light can be filtered out, leaving only the image produced by the labelling agent. Any counterfeit that does not possess the correct photophysical properties will not appear in the image.

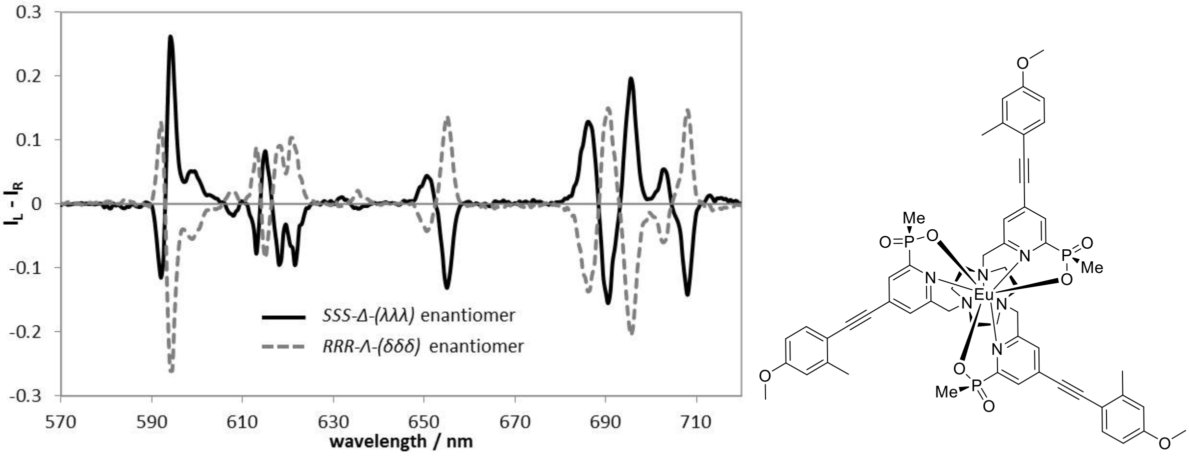

Figure 1. Structure of the *RRR*-*Λ*-(*δδδ*) enantiomer and CPL spectra of enantiomeric complexes.

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Natural circular dichroism in the x-ray range

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The detection of x-ray natural circular dichroism (XNCD) became possible with third generation synchrotron radiation sources[1]. XNCD stems from the interference terms which mix multipole transition moments of opposite parity: the Electric Dipole-Electric Quadrupole (E1.E2) and the Electric Dipole-Magnetic Dipole (E1.M1) that could be observed only in structures with broken space inversion symmetry. The pseudoscalar E1.M1 term known to be responsible for optical activity in the visible is vanishingly small for core level spectroscopies. The E1.E2 interference term, on the contrary, can be large in the x-ray region, but it is a traceless second rank tensor and therefore observable only in oriented systems.

XNCD is inherently element selective technique and could give access to the absolute configuration of chiral absorbing centers. Moreover, it is shown that the effect is closely related to the orbital anapole moment at the absorbing atom. Great potentialities of this technique in studies of chiral systems are shown and reviewed in this talk.

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Coordination Modes in Alkali Metal Doped Phenacenes: Implications for Superconductivity and Magnetism

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The manners by which molecules arrange themselves in the solid state have significant implications for the electronic and magnetic properties of the resultant material. Competition for directional intermolecular interactions, including coordination modes, controls crystallization pathways. Small energy differences between polymorphic structures can enable crystallization conditions to dictate the phase of the crystallized product. A new class of *anion* radical salts derived from alkali metal doped phenacenes have been suggested to stabilize superconductivity at temperatures above 25 K. To date, these materials have been prepared as powders, with ill-defined structures, complicating the development of structure/property relationships. We report the growth of single crystals of phenacene-based alkali metal salts and demonstrate that the choice of alkali metal cation can significantly alter the solid state structure. The various coordination modes of alkali metals with phanacenes will be described and the prospects for crystallization of new superconducting salts discussed.

This work was supported by the Independent Research and Development program while serving at the National Science Foundation and by Argonne National Laboratory, a U.S. Department of Energy Office of Science laboratory, operated under Contract No. DE-AC02-06CH11357.

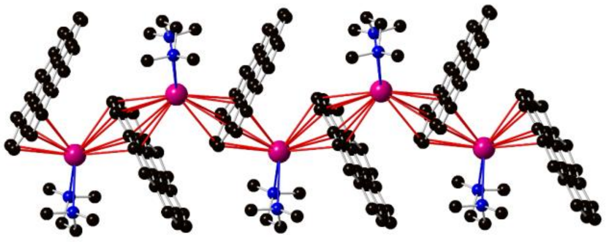

Figure 1 In the Rb(tmeda)Coronene (tmeda = tetramethyl-ethylenediamine) structure, Rb^+ cations coordinate to 'outer' rings of adjacent coronene anions to form a chain-type structure.

Interplay between magnetism and chirality: from molecules to metal-organic frameworks

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Structural chirality, also referred as the breaking of space symmetry, is an essential and fascinating aspect of many systems ranging from biology to physics. We are specifically interested by the interplay of structurally chiral systems with their own magnetic properties or with external magnetic fields.

At the molecular level, based on the use of chiral stoichiometric reagents and catalysts, chemists have proposed many solutions to synthesize enantioselectively chiral molecules. More recently, many efforts were made to transfer this knowledge to the synthesis of enantiopure metal-organic frameworks. In the case of magnetic compounds, several synergetic properties arose from the long-range magnetic ordering and the physical properties (circular dichroism, second harmonic generation, ferroelectricity) allowed by the loss of centrosymmetry.[1] Moreover, it was also the occasion to study the interplay between structural chirality and the link between structural chirality and chiral magnetic ordering.

For biologists, an important question is the origin and generalization of the homochirality of life. Based on symmetry arguments, the hability of physical influences to generate enantiomeric excess starting from achiral or racemic systems are currently under study. Several mechanisms have been proposed theoretically as soon as in 1894 by P. Curie[2] and/or demonstrated experimentally.[3]

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Chiral Coordination Polymers: Interpenetration and Enantioselective Separations

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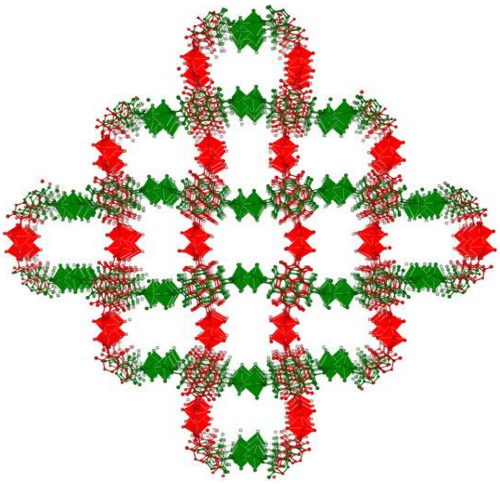
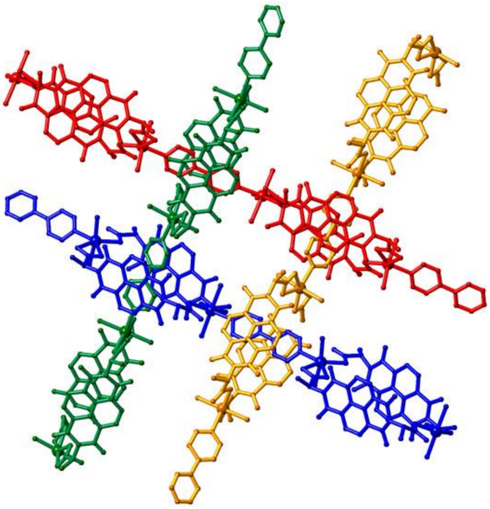
Ligands containing either naphthalenedimmide or perylenediimide core groups form coordination polymers that have a propensity to interpenetrate due to strong pi interactions and the formation of a reproducible macrocyclic motif that can host an aromatic guest, including by self-recognition. The latter feature allows a degree of control and predictability, which we have exploited to form both poly-catenane and poly-rotaxane networks by using dipyridyl co-ligands that are able to pass through the macrocycle.[1] Two 2D→3D interpenetrated networks have been used as stationary phases in liquid chromatographic separations, showing good resolution of enantiomers and selective behavior for different analytes thought to be related to the chemical nature of the ligand.[2]





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Detection of Circularly Polarized Luminescence of a Chiral Eu(III) Complex in Raman Optical Activity Experiment

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Circularly polarized luminescence (CPL) spectra are extremely sensitive to molecular structure. However, conventional CPL measurements are difficult and require expensive instrumentation. As an alternative, we explore CPL using the Raman scattering technique and Raman optical activity (ROA) spectrometer. The cesium tetrakis(3-heptafluoro-butylryl-(+)-camphorato) Eu^{III} complex was chosen as a model as it is known to exhibit very large CPL dissymmetry ratio. The fluorescent bands could be discriminated from true Raman signals by comparison of spectra acquired with different laser excitation wavelengths.[1] In addition, the ROA technique enables fluorescence identification via measurement of the degree of circularity. The CPL dissymmetry ratio was measured as the ROA circular intensity difference of 0.71, the largest one ever reported. We hope that the alternative ROA/CPL measurements will enhance applications of lanthanides in analytical chemistry and chemical imaging of biological objects.

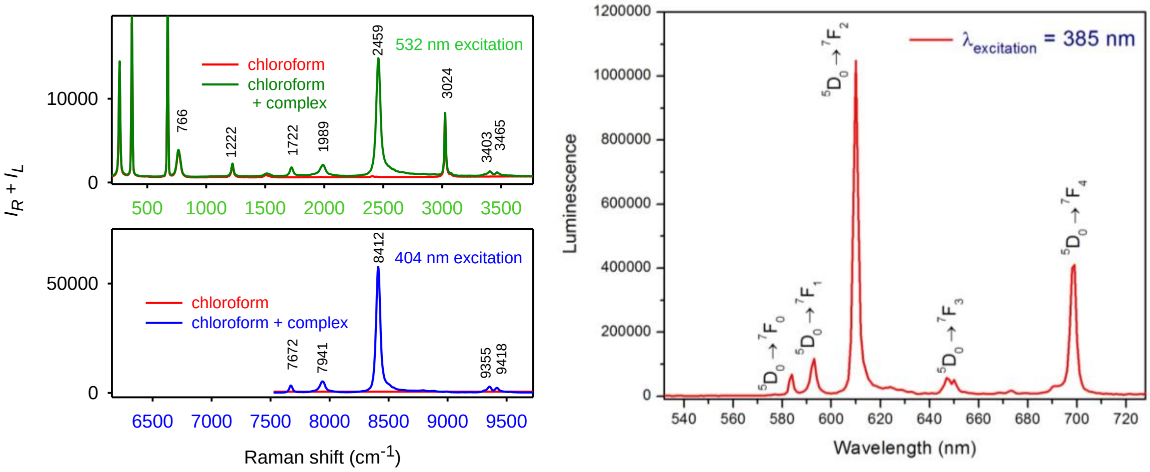

Figure 1 Raman spectra of the Δ-CsEu[(+)-hfbc]$_4$ complex in chloroform solution measured with 532 nm and 404 nm excitation wavelengths (left), in comparison with its luminescence spectrum measured with 385 nm excitation (right).

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Chiroptical properties of Ag doped $Au_{38}(SC_2H_4Ph)_{18}$ nanocluster

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Thiolate-protected gold clusters and heteroatoms doped gold clusters have attracted increased attention by their well-defined structure and size-dependent properties.[1] Among them, The $Au_{38}(SCH_2CH_2Ph)_{24}$ cluster bears intrinsically chiral features due to the arrangement of the protecting ligands on the surface of the cluster.[2] Enhanced stability and surface flexibility of gold nanoclusters have been achieved by doping two Pd atoms inside Au_{38}.[3] However, the dopant number effect on nanocluster chiral properties has not been studied. Multiple Ag atoms were doped inside Au_{38} by time-dependent metal exchange. The enantiomers of selected $Ag_xAu_{38-x}(SCH_2CH_2Ph)_{24}$ samples (average x=6.5 and 7.9) have been separated by HPLC. Doping changes the electronic structure, as is evidenced by the significantly different CD spectra (Figure 1). The temperature required for complete racemization follows Au_{38}> Ag_xAu_{38-x} (x=6.5)> Ag_xAu_{38-x} (x=7.9) (Figure 1), which shows an increased flexibility of the cluster with increasing silver content. The weaker Ag-S bonds compared to Au-S, is proposed to be at the origin of this observation.

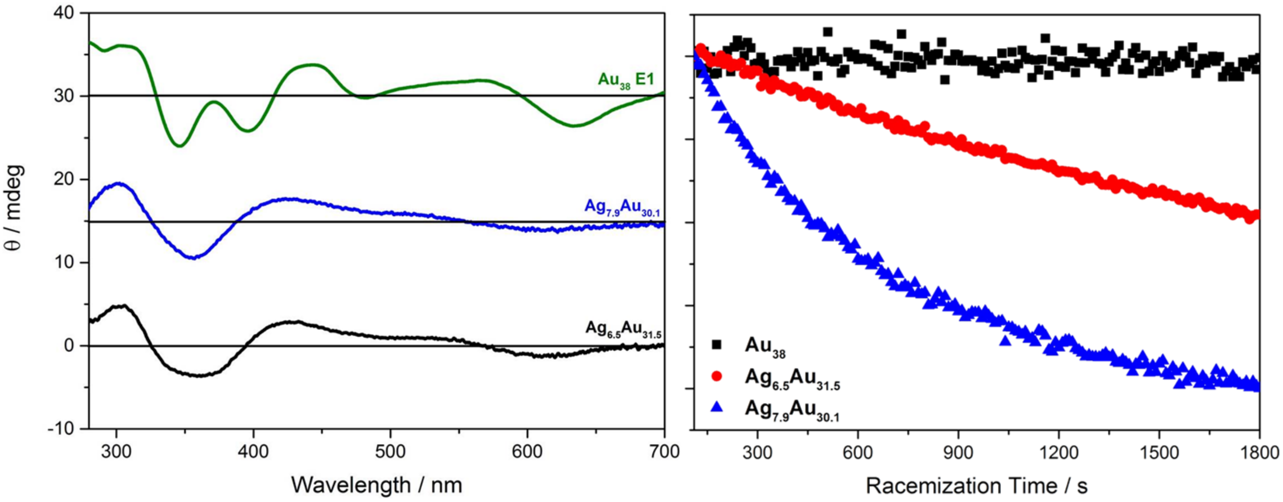

Figure 1 First enantiomer of $Ag_xAu_{38-x}(SCH_2CH_2Ph)_{24}$ nanoclusters (x=0, 6.5 and 7.9). left: CD spectra; right: CD response as a function of time at 40˚C in racemization experiment.

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Homochiral Metal Phosphonate Compounds

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Chiral coordination polymers have been of intense current interest mainly due to their potential applications in the areas of enantioselective catalysis and separation, as well as their potential applications in multifunctional materials, including chiral magnet and polar magnet. Metal phosphonates are a class of promising inorganic-organic hybrid materials, possessing higher thermal and chemical stabilities comparing with the other coordination complexes. However, only a limited number of chiral metal phosphonates have been reported so far, attributed to the synthetic challenges of such materials. In recent years, we have succeeded in isolating a series of chiral metal phosphonates by using asymmetric or homochiral phosphonic acids as starting materials, including compounds with one-dimensional nanotubular structures, two-dimensional layer structures and three-dimensional framework structures. The relationship between the structures and properties has been explored.

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Syntheses, Assembling and Properties of Multifunctional Materials Based on Tetrathiafulvalene Derivatives

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Molecular-based materials involving interplay and synergy among multiple physical properties remain the challenge for scientists. Particularly, materials possessing electrical and magnetic properties have received much attention due to the important applications in molecular spintronics.[1] To reach such multi-property system, some organic ligands are well adapted. Among them, tetrathiafulvalene (TTF) and its derivatives showing strongly electron-donating and attractive reversible redox properties have been successfully employed to the preparation of functional materials.[2]

Tricyanometalate-based clusters are widely studied magnetic systems and these well tailored cyano-bridged clusters sometimes exhibit single-molecule magnets (SMMs) behaviors. We used different π-conjugated ligands containing tetrathiafulvalene unit in the assembly of tricyanometalate-based clusters or 1D polymeric metal complexes. Some clusters show SMMs behavior and this is one of the few attempts to fabricate conductive SMMs. The new triple-decker sandwich-type lanthanide complexes with phthalocyanine and redox-active Schiff base ligand including TTF units are synthesized.[3] Interestingly, the non-centrosymmetric target Dy(III) complex displays a bias dependent selective adsorption on a solid surface, as observed by scanning tunneling microscopy at the single molecule level.

More recently, a strategy to coat Fe_3O_4 nanoparticles (NPs) with tetrathiafulvalene-fused carboxylic ligands and to control electron conduction and magnetoresistance within the NP molecular junction spin-valves assemblies is developed. The different TTF-COOH ligands are used to modify Fe_3O_4 nanoparticle surface spin polarization and to tune interparticle spacing. As a result, the electron conductivity and magnetoresistance of a TTF-COO-Fe_3O_4 nanoparticle assembly can be better controlled by TTF molecular structure and/or by iodine doping.[4]

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Tuning the physical properties in anilate-based molecular materials by substituent exchange

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In the search for new functional molecular materials whose physical properties can be easily tuned by simple changes on the molecular structures of their building units, we have designed and synthesized a family of paramagnetic metal complexes of general formula $[M^{III}(X_2An)_3]^{3-}$ (M^{III} = Cr, Fe; X = Cl, Br, I, H; An = 2,5-dihydroxy-1,4-benzoquinone).[1,2] These metal complexes are valuable building blocks for the preparation of functional materials, such as molecule-based ferrimagnets and magnetic molecular conductors, where the nature of the X substituent at the 3,6 positions of the anilate ring can play a key role in determining their physical properties.[3-5] A simple change of one chloro substituent on the chloranilate ligand with a cyano group dramatically affects the electronic properties of the anilate moiety inducing unprecedented luminescence properties in the class of anilate-based ligands and their metal complexes[6]. The crystal structures and physical properties of the most challenging anilate-based luminescent and magnetic/conducting hybrid systems will be discussed in this communication.

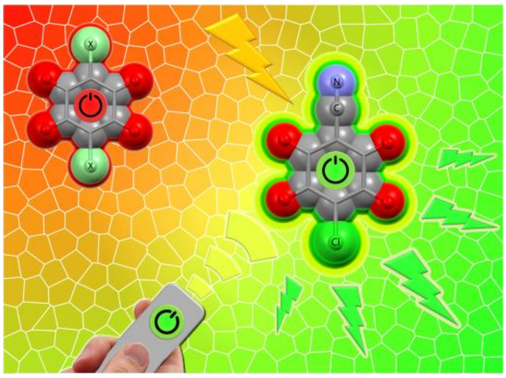

Figure 1. Switching-on luminescence by a simple change of one chloro substituent on the chloranilate ligand with a cyano group

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Molecular and Supramolecular Aspects of Guest-Infiltrated Copper Paddlewheel MOFs

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Copper "paddlewheel" Metal-Organic Frameworks (CuP-MOFs) are a large category of porous coordination polymers in which the secondary building units are metal dimers bridged by four carboxylate linkers. Recently, we showed that the paddlewheel MOF HKUST-1 becomes electrically conducting when infiltrated with the redox-active guest molecule 7,7,8,8-tetracyanoquinododimethane (TCNQ).[1] In this presentation I will discuss the mechanism of conductivity using two classes of molecular coordination complexes as analogues: copper acetate ($Cu_2(CH_3CO_2)_2$•L; L=H_2O or pyrazine) and Robin-Day donor-bridge-acceptor (DBA) complexes. Copper acetate is a Cu(II) dimer bridged by four acetate ligands and is structurally analogous to supramolecular CuP-MOFs. Copper acetate was the first transition metal dimer for which the magnetic properties were explained in terms of antiferromagnetic coupling. Its electronic structure is also well understood.[2] DBA charge transfer systems with intermediate coupling (Robin-Day Class II/III systems[3]) suggest a mechanical for electronic conductivity in TCNQ@HKUST-1 and related bridged systems.[4] Together, these molecular systems provide insight needed to design new Guest@MOF materials with tailored properties.

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Coordination chemistry to design processable cluster-based hybrid nanomaterials.

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The main challenge to take up in the design of hybrid organic-inorganic materials is to keep the added value of inorganic entities while preventing their self-aggregation within the hybrid matrix.

The term “metal atom cluster” describes a finite group of metal atoms held together by metal-metal bonds. The $[(M_6L^i_8)L^a_6]^{n-}$ unit (^{a} = apical, ^{i} = inner, M = Mo, Re; L = halogen, chalcogen, $1< n <8$)) constitutes the basic building block in the octahedral cluster chemistry and is easily obtained *via* high temperature solid state synthesis. Metallic clusters show unusual electronic, magnetic and optical properties due to the full delocalisation of valence electrons on the whole metallic scaffold. In particular, they can be highly emissive in the red-NIR area.

We will describe in this presentation the strategies we developed to coordinate luminescent octahedral transition metal atom clusters in order to be integrated into liquid crystalline (clustomesogen) and macromolecular materials. These strategies are based on either covalent grafting or using supramolecular interactions (ionic self-assembling or host-guest strategies). The optical properties of the hybrid materials will be discussed.

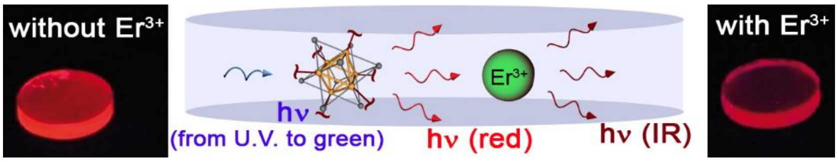

Figure 1: Polymer pellets containing Mo_6 clusters which sensitize Er^{3+} IR photoluminescence

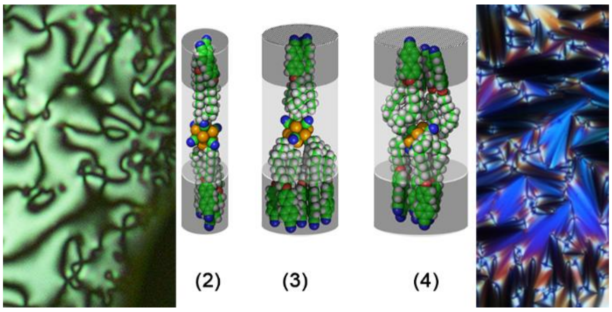

Figure 2: Polarized optical micrographs of nematogenic and smectogenic clustomesogens obtained via ionic assembling and their respective representation.

Y. Molard et al*., Angew. Chem. Int. Ed.,* **2010***, 49, 19, 3351 ;* M. Amela-Cortes et al. *Chem. Eur. J.* **2014**, *20*, 8561 ; Y. Molard et al., *Adv. Func. Mat.*, **2013**, *23*, 4821 ; M. Amela-Cortes et al. *J. Mater. Chem. C*, **2014**, *2*, 1545 ; Y. Molard, et al. *Chem. Mater.*, **2011**, 23, 5122-5130

A giant {$Mn_{26}Dy_6$} heterometallic oxo-hydroxo-carboxylate nanocluster

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The development of new synthetic pathways to assemble novel 3d-4f heterometallic nanoclusters is a considerable challenge. Starting from a simple manganese isobutyrate salt, in two steps we prepared an unusual bean-like dotriacontanuclear heterometallic nanocluster $[Mn_{26}Dy_6O_{16}(OH)_{12}(is)_{42}]$ (**1**), where His = isobutyric acid, with ca. 3.4 x 1.8 nm size (Fig. 1a). The nanocluster possesses C_2 molecular symmetry and comprises a $[Mn_{26}Dy_6]^{86+}$ core, encapsulated by fourteen μ_4-O, two μ_3-O, twelve OH^- groups and fourty-two bridging isobutyrate moieties. Interestingly, Mn atoms are either five- or six-coordinated while Dy atoms are either eight- or nine-coordinated in **1**. Charge consideration of the cluster **1** and BVS (bond valence sum) calculations indicate that 16 Mn centers are in the 3+ oxidation state, whereas the remaining 10 Mn centers are in the 2+ oxidation state. Fig. 1b shows the magnetic data as a χT vs. T plot for nanocluster **1**.

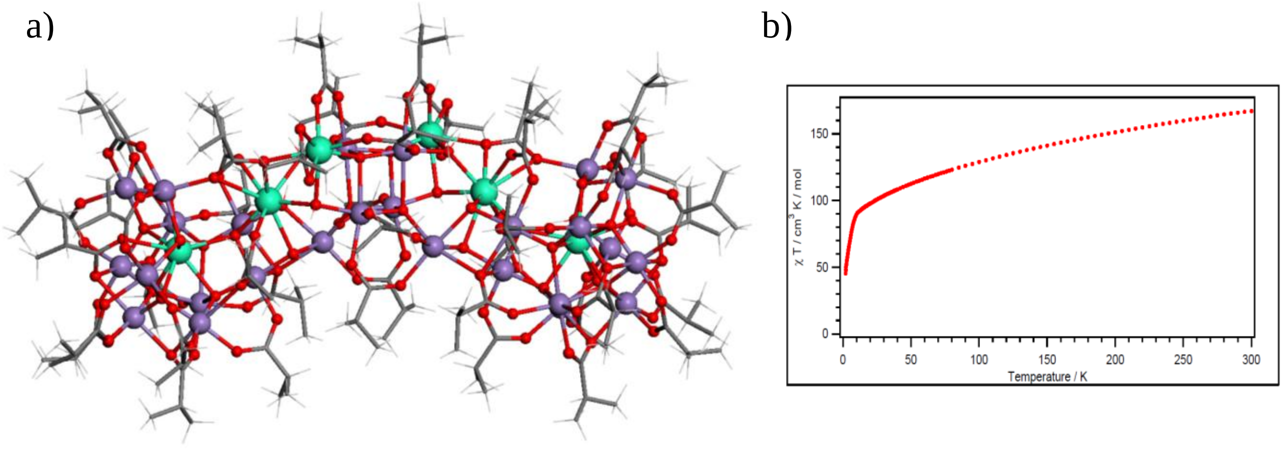

Figure 1 A view of nanocluster **1** with highlighted Dy atoms as green balls and Mn atoms as violet balls (a) and a χT vs. T plot of **1** (b).

Acknowledgement. Financial support was provided by the SNSF (project **SCOPES IZ73Z0_152404/1**).

Stabilization of Multinuclear 3*d* Metal-Oxo Cores by Lacunary Polyoxometalate Units and Phosphate Groups

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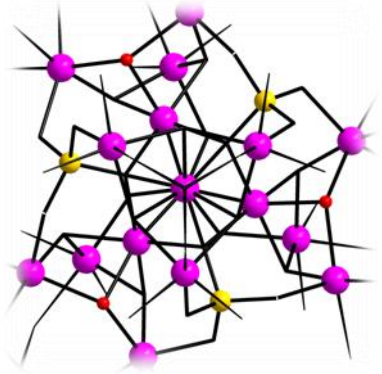
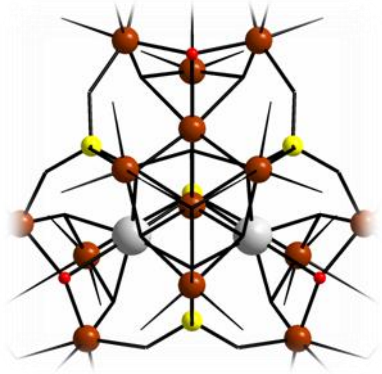
Lacunary (defect) heteropolytungstate POM precursors can act as inorganic ligands for coordination to electrophilic centers such as 3*d* transition metal ions.[1] Paramagnetic transition metal-containing POMs are of special interest for their catalytic and magnetic properties. It remains a challenge to encapsulate multi-3*d* metal-oxo cores by lacunary heteropolytungstates leading to discrete, stable assemblies.[2]

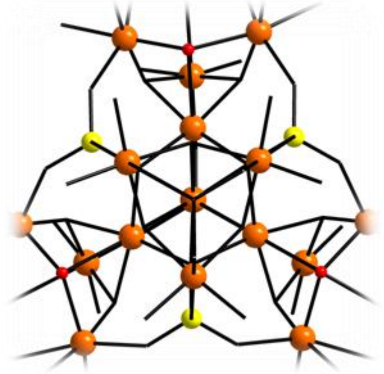
In this context, our group has prepared a family of large, tetrahedral structures with M_{16}-oxo type cores (M = Co^{II}, Fe^{III}, $Mn^{III/IV}$), stabilized by four trilacunary Keggin units $[XW_9O_{34}]^{n-}$ (X = P, n = 9; X = Si, Ge, n = 10) and four phosphate groups.[3] These compounds exhibit different physicochemical and topological properties, depending on the transition metal used.



$\{Co_{16}\}$
Single Molecule Magnet



$\{Fe_{14}Na_2\}$
Sodium Entrapment



$\{Mn_{16}\}$
Mixed-Valency

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Synergy of sesquioxane and organic ligands as an easy approach to cage compounds of Cu(II), Mn(II), Fe(III)

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Use of flexible heterochained ligands is prospective as a way to metal-containing cage compounds. For instance, examples of metal complexes containing Si-sesquioxane ligands are not very rare.[1] Our previous works revealed that compounds of this type may be regarded as unusual precatalysts[2] and molecular magnets[3]. Here we present recent results on synthesis of metallacomplexes based on simultaneous use of sesquioxane $[REO_{1.5}]_n$ (E = Si or Ge) and different organic ligands. Products of these reactions are attractive both as models of unique molecular architecture (Figure 1) and objects of cage self-assembly' study. Features of such complexes' syntheses, structures and supramolecular aggregation will be presented in detail.

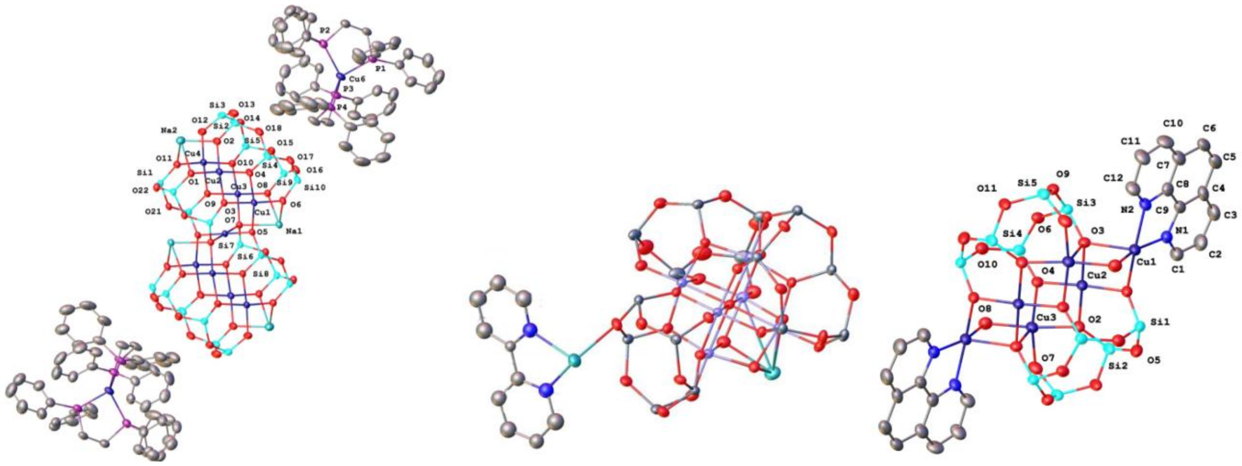

Figure 1 Complex of Cu(II)-silsesquioxane with dppe (left), complex of Fe(III)-germsesquioxane with 2,2'-bipy (center), complex of Cu(II)-silsesquioxane with 1,10-phenanthroline (right).

This work was supported by RFBR (projects 14-03-00713, 16-03-00206 and 16-03-00609)

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Octahedral cluster complexes of molybdenum and rhenium: From the synthesis to the possible applications

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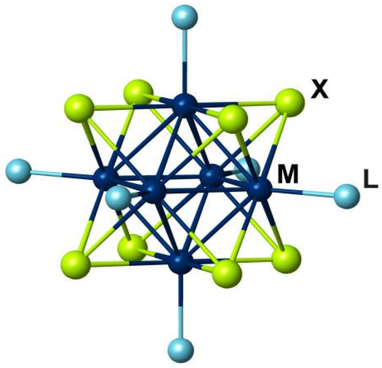

Figure 1 Representation of $[\{M_6X_8\}L_6]$ cluster complex

In the last decade, the chemistry of soluble complexes containing $\{Re_6(\mu_3\text{-}X)_8\}^{2+}$ (X = S, Se) or $\{Mo_6(\mu_3\text{-}X)_8\}^{4+}$ (X = Cl, Br, I) octahedral cluster cores has attracted much attention due to their intriguing chemical and physical properties, in particular, the remarkable photophysical properties being highly emissive in the red-NIR region with up to hundreds of microseconds excited state lifetimes. Such properties offer promising perspectives for applications of cluster containing materials to various red-NIR emitters.[1-3] The cluster luminophores can be also used as luminescent dyes for biolabelling, light-emitting diodes, or photoredox-active molecular arrays. The recent investigations of the photophysical properties of such cluster complexes also support their potential applicability in biology and medicine.[4,5]

Details on syntheses, structures, and key properties of some octahedral molybdenum and rhenium cluster complexes with inorganic and organic outer ligands (L) as well as materials based on them will be presented at the conference.

Acknowledgements: This research was supported by the Brain Pool Program of the Korean Federation of Science and Technology Societies (Grant 151-S-1-3-1190 to K. A. Brylev) and by the Grant of President of the Russian Federation (MK 4054.2015.3).

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From micro to nano: Synthesis and properties of benzotriazolate-based NMOFs

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Scaling down the size of MOF particles is a challenging but important task for extending the spectrum of potential MOF applications. Recently, an exciting new class of materials known as nanoscale MOFs (NMOFs) has been reported.[1] NMOFs offer the same rich diversity of compositions, structures and properties of bulk MOFs with the obvious advantages of nanomaterials. Their properties (chemical properties, catalytic activity, etc.) change as their size approaches the nanoscale and as the percentage of atoms at the surface of a material becomes significant.

In this work, possibilities of downsizing particles of benzobistriazolate-based MOFs, i.e. MOFs recently developed by our group,[2-4] are shown. By combining suitable parameters - such as temperature, time, solvent and usage of different additives including alkali hydroxides and various amines – a precise size-control of particles between 40 nm to 5 µm can be achieved (Figure 1). A comparison of MOF properties based on different particle sizes (including their thermal and chemical stability, and surface properties) is included as well as possibilities of MOF surface derivatization.

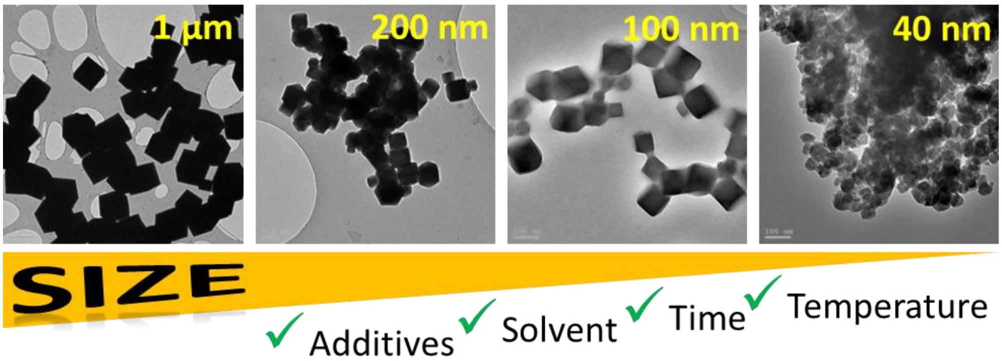

Figure 1 Scaling down the particle size of MFU-4, a benzotriazolate-based MOF,[2] by altering various synthesis parameters.

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A Manganese Metal-Organic Framework as a matrix for isolating catalytic intermediates

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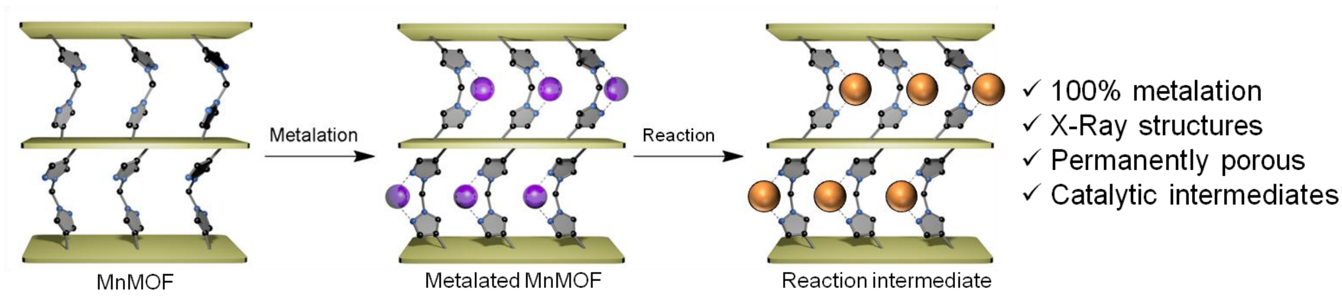
Metal-Organic Frameworks (MOFs) containing vacant metal binding sites can be used to anchor active catalytic metal centres by post-synthetic modification.[1] Anchoring catalytic moieties within these materials is expected to yield more stable and reusable heterogeneous catalysts compared to their homogeneous catalytic parents, enabling size and shape-controlled catalysis.[1,2] Despite these motivations, MOFs with catalytically active metal centres are rare[3] and suffer from a lack of characterisation regarding the precise coordination sphere of the active species.[4]



We have synthesised a unique porous 3D manganese-containing MOF (MnMOF) replete with non-coordinated pyrazole donors capable of quantitative post-synthetic metal binding.[5] The metalation step occurs in a single-crystal to single-crystal (SC-SC) manner which facilitates unequivocal elucidation of the bound metal species (coordination sphere) by X-ray crystallography. In particular, active catalytic species such as the cationic rhodium(I) biscarbonyl moiety have been site specifically grafted into the metal binding sites of MnMOF. Subsequent reactions involving the fully metalated rhodium(I) MnMOF have yielded new catalytic intermediates, revealing the critical role of the solvent and reagent sterics in this heterogeneous system.

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Multifunctional MOFs: from gas sorption to spin-crossover

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Since 1990, coordination polymers, also named MOFs (metal-organic frameworks) in their porous form, have been widely developed and have recently become one of the most studied materials. Here we will focus on magnetic MOFs,[1] particularly on those presenting spin-crossover (SCO) phenomena for their interest in combining magnetic bistability with gas sorption. The work presented here emphasizes the gas sorption capacity of a MOF with spin crossover whose transition temperature can be modified by CO_2 adsorption.

We have previously reported[2,3] two spin-crossover compounds which have a CO_2 maximum capacity of one molecule per void. Now, we have successfully enhanced these two systems by chemical design, synthesizing an isostructural MOF with a larger ligand.[4] Thus, the new compound has a similar structure with discrete voids (**figure 1**), but larger in size (257 $Å^3$ vs. 136 $Å^3$). Gas sorption studies show that two molecules of CO_2 can be physisorbed in each void, doubling the result for the original system as expected. The effects on the SCO transition temperature of the increasing number of CO_2 molecules in the voids will also be discussed.

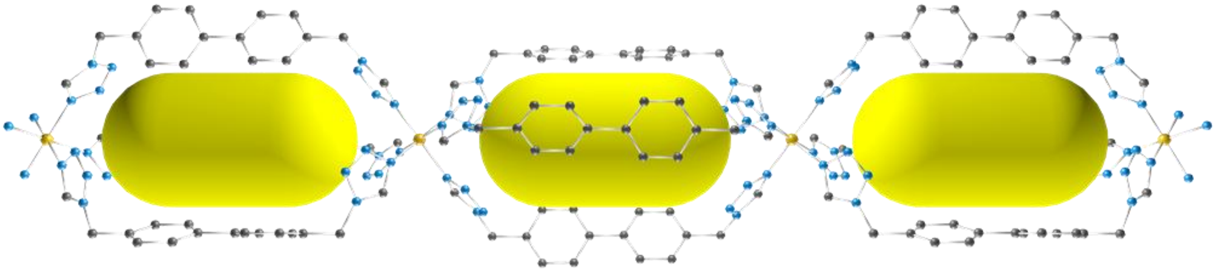

Figure 1 Crystal structure of the MOF. The yellow ellipsoids represent empty space

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Exploring Electron Transfer Reactions in Polyoxometalates

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Heteropolyoxometalates have a designable template which not only determines certain physical properties of the cluster, but increasingly has been found to control the range and connectivity of the building blocks.[1] Amongst the structural diversity of HPOMs architectures, $[M_{12}O_{36}(XO_4)]^{n-}$ and Wells-Dawson (WD) [2] anions $[M_{18}O_{54}(XO_4)_2]^{m-}$ form a basic set of extensively reviewed geometries which encapsulate tetrahedral heteroanions such as $[SO_4]^{2-}$, $[PO_4]^{3-}$, etc. In general, POMs exhibit significant stability for both the oxidized and one-electron reduced form and the electrochemistry of HPOMs has been extensively studied. In this respect, in an effort to tune the redox properties of POMs, we have been able to engineer clusters that incorporate redox-active anions and expand the classic WD family.[3-5] Building on this fundamental understanding we have been using theory, synthesis, modelling, and spectroscopy to both understand, control, and develop a range of new devices, see Scheme. In this talk I will describe our approach as well as highlighting some fundamental new aspects of these molecules[6-8].

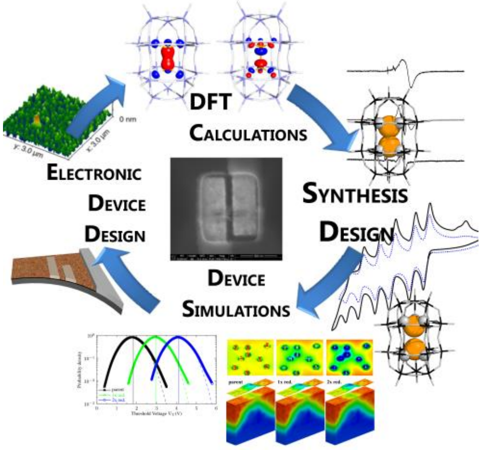

Figure 1 Our multidisciplinary approach combining the synthesis, modelling and device fabrication of nanoelectronic devices that take advantage of the intrinsic electronic properties of POMs as switchable p- or n- type molecular semiconductors. By combining our expertise we have designed and built functional circuits using molecular metal-oxides (MMOs), by connecting self-assembled MMOs into top-down, lithographically defined CMOS

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Metal Organic Framework type Materials Containing Polyoxometalates: POM@MOF versus POMOF

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Polyoxometalates (POMs) are soluble early-transition-metal clusters with a large diversity of structures and compositions. They possess redox and acid-base properties which can be exploited for (electro)catalytic applications. Their immobilization within stable and insoluble frameworks offers great advantages for their use as heterogeneous catalysts: increase number of accessible active sites, easy recovery and recycling. We have developed two strategies to synthesize new POM-based materials (Figure 1): i) the incorporation of POMs in the cavities of porous metal organic frameworks (MOFs) either by a one pot synthesis[1] or by impregnation of a preformed MOF[2] and ii) the construction of hybrid materials called POMOFS by using ε-Keggin type POMs as nodes and bi- or tridentate carboxylate linkers.[3] The high electrocatalytic activity of these systems for proton reduction will be presented. In addition, the influence of the dispersion into MOFs of Single Molecule Magnet POMs on the magnetic properties will also be discussed.

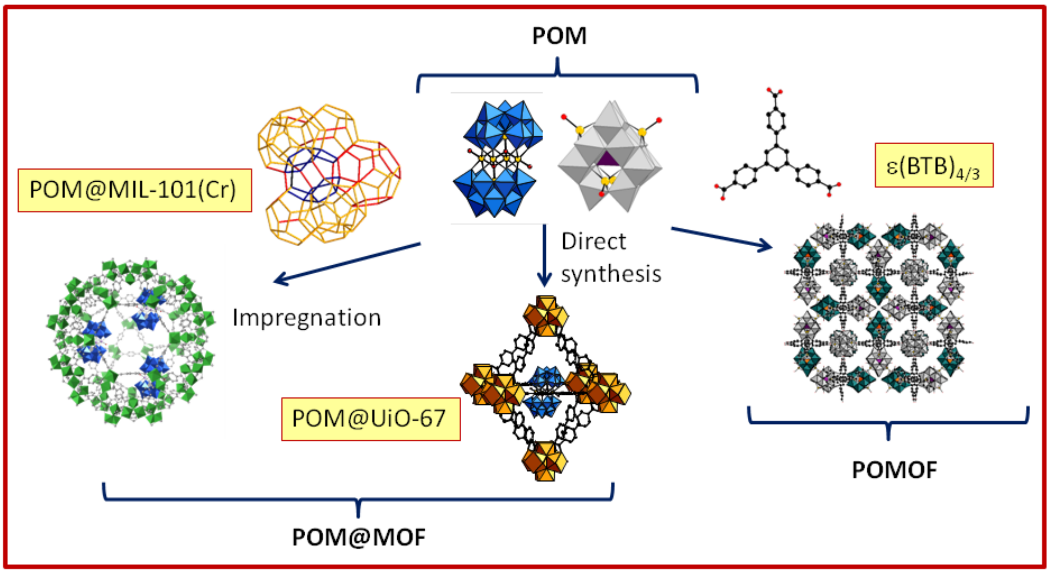

Figure 1. The various approaches used to incorporate POMs in MOF type materials

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Incorporation and stabilization of polynuclear tetravalent clusters by trivacant polyoxometalates

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Polyoxometalates (POMs) have been widely used to stabilize polynuclear transition metals or lanthanides clusters, exhibiting many properties in catalysis, magnetism and material science. Several years ago, they also found an interest in the nuclear energy field to react with radionuclides elements like uranium, plutonium, americium and curium. Thus, we are currently interested in the use of several trivacant polyanionic units for their coordination properties towards the tetravalent oxidation state of cerium, uranium and thorium. The purpose of such studies lies in the development of new strategies related to purification processes in the nuclear industry. For instance, these systems could be considered has possible molecules in actinide separation processes [1,2]. We will present our results based on the use of the $[SiW_9O_{34}]^{10-}$ and $[AsW_9O_{33}]^{9-}$ polyanionic moieties, giving rise to several new tetravalent polynuclear clusters embedded in POMs units [3,4]. In case of uranium, this association provides molecules (Figure 1) possessing unusual direct U^{VI}=O-U^{IV} bonding that was never observed before in POM chemistry.

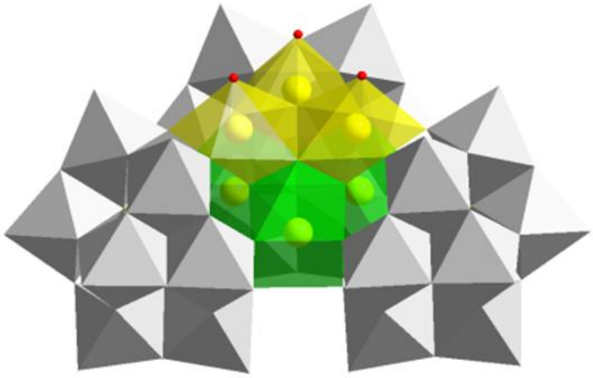

Figure 1 Polyhedral representation of the mixed valence U^{IV}/U^{VI} hexavalent uranium $\{U_6O_8\}$ cluster stabilized by $[AsW_9O_{34}]^{9-}$ unit.

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Non-aqueous chemical reduction of polyoxometalates.

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Interest in polyoxometalates (POMs) for energy storage applications is based on their acknowledged redox properties. Electrochemical studies by the Souchay group in Paris were seminal in establishing the complex relationships between the various redox states of different Keggin-type anions, and showed that more extensive reduction may result in isomerization and metal-metal bond formation.[1]

Our investigations of non-aqueous chemical reduction of $[PMo_{12}O_{40}]^{3-}$ has provided rational access to a series of capped phosphomolybdates $[PMo_{12}O_{40}\{EL_n\}_x]^{z-}$, where up to six electrons have been added to the POM core (**Fig. 1**), and this provides new opportunities for systematic studies of this family of electron-rich POMs.[2]

In extending our methodology to $[Mo_6O_{19}]^{2-}$ we have found that extensive reorganization occurs with the formation of new reduced derivatives based on the capped ε-$\{Mo_{13}\}$ framework (**Fig. 1**), in which the added electrons are localized in Mo^V–Mo^V bonds.

This talk will describe our synthetic approach, highlight features of the solution reactivity and draw comparisons with previous electrochemical and aqueous reduction studies.

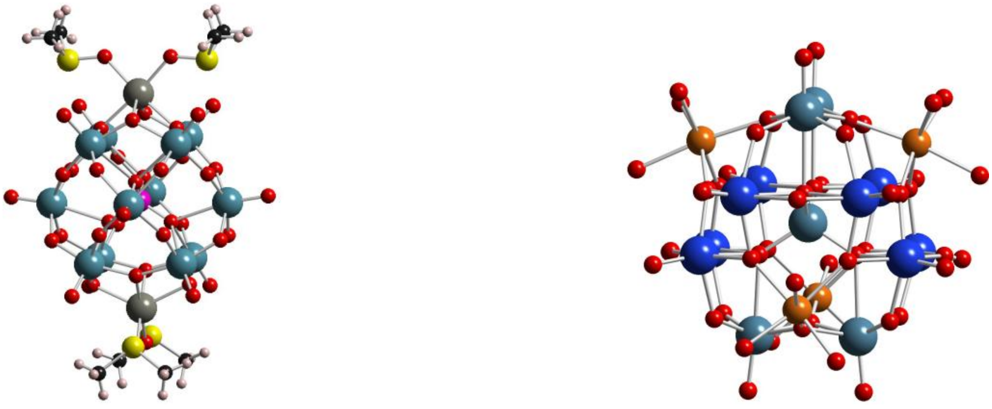
(a)
(b)

Figure 1 Structures of $[PMo_{12}O_{40}\{Zn(dmso)_2\}_2]^{3-}$ (a) and ε-$[Mo_{13}O_{40}H_4\{Mg(dmso)_3\}_4]^{2+}$ with SMe_2 groups omitted and Mo^V sites shown in darker blue (b).

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Functional Metal-Organic Frameworks (MOFs)

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Metal–organic frameworks (MOFs) are an emerging class of solid-state materials built up from metal-based nodes and organic linkers. They exhibit permanent porosity and unprecedented surface areas which can be readily tuned through coordination chemistry at the inorganic node and/or organic chemistry at the linkers. The high porosities, tunability, and stability are highly attractive in the context of catalysis. As exemplified by many catalytic enzyme assemblies in nature, site-isolation is a powerful strategy for performing catalytic reactions. MOFs provide an exciting platform for deploying catalysts in a site-isolated fashion and the cavities surrounding them can be engineered to conceptually mimic enzymes. This talk will address new advances in the syntheis and catalytic activity of MOF materials.

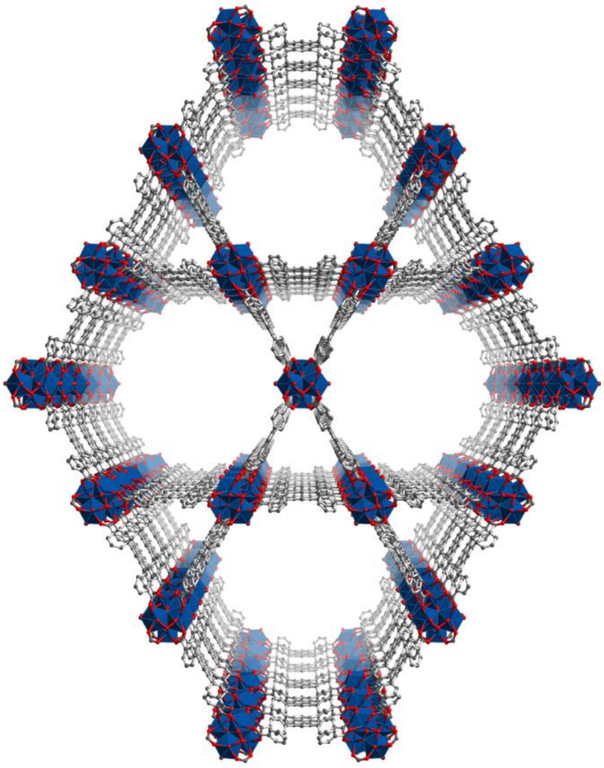

Figure 1 A representative Metal-Organic Framework structure

The octahedral iodide clusters of molybdenum and tungsten: synthesis and luminescence

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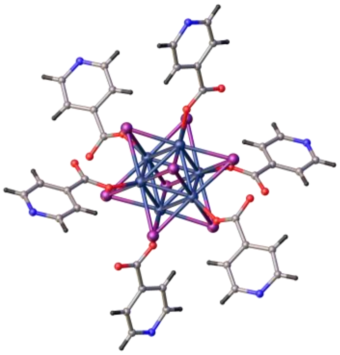
The octahedral halide bridged clusters of Mo(II) and W(II) possess remarkable photophysical properties which can be used for development of new fluorescent materials. While numerous papers describe luminescence properties of various chloride and bromide molybdenum octahedral cluster complexes, few studies on the luminescence properties of the $\{Mo_6I_8\}^{4+}$-based clusters have been reported. Only recently it was demonstrated that photoluminescence of the complexes with fluorinated carboxylates or *closo*-dicarbaborane C-carboxylates as external ligands are characterized by superior lifetime and quantum yield values and narrow and blue shifted emission spectra in comparison with those of any other member of the $\{M_6X_8\}$ cluster family (including M = Mo or W and X = Cl or Br; M = Re and X = S, Se or Te). New insights on little-studied chemistry of $[Mo_6I_{14}]^{2-}$ and $[W_6I_{14}]^{2-}$ will be presented in this contribution. Starting from $[Mo_6I_{14}]^{2-}$ or $[W_6I_{14}]^{2-}$ several types of new luminescent cluster complexes were obtained: carboxylate complexes with a general formula of $[M_6I_8(OOCR)_6]^{2-}$ (R = C_5H_3O (α-furyl), $C_{10}H_7$ (α-naphthyl), CH_3, $C(CH_3)_3$, C_6F_5, 4-C_5H_4N (pyridyl, see figure)), phenolate complexes $[Mo_6I_8(OR)_6]^{2-}$ (R = $C_6H_4NO_2$, $C_6H_3(NO_2)_2$), thiolate complexes $[M_6I_8(SR)_6]^{2-}$ (R = C_6F_4H) and acetylenide complexes $[M_6I_8(C{\equiv}CR)_6]^{2-}$ (R = CO_2CH_3) (M = Mo, W).



The acetylenides are the first example of purely organometallic ligand environement for octahedral clusters $\{M_6Q_8\}$. The triple bond is able to coordinate other metal ions such as Ag^+. The luminescence properties of the complexes were studied both in acetonitrile solutions and solid state and will be discussed in detail. Recent developments involving use of $[Mo_6I_{14}]^{2-}$ in aqueous solutions for detection of fluoroquinolones will be presented.

Coordination materials towards gas biology applications

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Gaseous molecules such as nitric oxide (NO) and carbon monoxide (CO) are recently known to be signaling molecules (gasotransmitters) working both for intercellular communications and intracellular regulations. In particular, NO is one of the most investigated gasotransmitters, having important roles in numerous signaling events as well as therapeutic potentials. However, the design of functional scaffolds or devices that can release NO with precisely controlled timing, dosage and location remains challenging, due to handling issues that arise from their high reactivity and physical state.

Here we show a synthetic strategy for developing spatiotemporally controllable NO-releasing platforms based on photoactive metal-organic frameworks (MOFs). By organizing molecules with poor reactivity into framework structures of MOFs, we observe increased photoreactivity and adjustable release using light irradiation. We further embed photoactive MOF crystals in a biocompatible matrix, leading to a functional cell culture substrate, and demonstrate precisely controlled NO delivery at the cellular level via localized two photon laser activation. The biological relevance of the exogenous NO produced by this strategy is evidenced by an intracellular change in calcium concentration, mediated by NO-responsive plasma membrane channel proteins.[1] We further shape photoactive MOF crystals at the mesoscale[2] by coordination modulation[3] and confirm its delivery inside cell and NO stimulation at the subcellular resolution..

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Heterometallic MOFs as efficient solid catalysts

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The field of metal-organic frameworks (MOFs) is currently among the most extensively studied topics in materials chemistry given the large number of fascinating potential applications associated with their regular and large porous structure and chemical versatility. Their foremost applications were originally based on storage and separations of fluid mixtures and have been recently extended to sensors, magnetic and electronic devices and biomedicine.[1]

In particular, one of the most relevant applications of MOFs appeared with their use as heterogeneous catalysts for specific chemical transformations.[2,3,4] This relies on their ideally suited architectures, which can present catalytically active sites that are generally coordinatively unsaturated metal sites (CUSs), which provide MOFs with Lewis acid properties or redox reactivity. In this sense, the appropriate rational design of MOFs may provide with ideally suited architectures with the catalytically active sites spatially arranged, which may play a role improving conversions and product selectivity in catalytic reactions of industrial interest.

With the expansion of this field, a new emergent class of heterometallic MOFs has recently been considered as improved solid catalysts.[5] Herein we present the design and preparation of heterometallic MOFs with appropriate chemical stability. Their catalytic performances will be discussed through first representative reactions.

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New aspects of the chemistry of tri- and tetrametallic molybdenum cluster sulfides

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Trimetallic $Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3$ and $Mo_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3$ clusters can be conveniently functionalized with different ligands to obtain molecular materials with a number of properties and applications. In the recent past, we have developed approaches to synthesize homoleptic cationic $[Mo_3S_4Cl_3(\text{diimine})_3]^+$ and heteroleptic neutral $[Mo_3S_7Br_4(\text{diimine})]$ complexes containing bipyridine or phenanthroline based ligands and exhibiting interesting physicochemical properties (Figure 1). Some examples include luminescence[1], nonlinear optics[2] or hydrogen evolution activity[3]. We have also used homoleptic diimino Mo_3S_4 clusters for the preparation of tetrametallic diimino $Mo_3M'S_4$ clusters (M' = Cu, Pd) that have unusual reactivity at the heterometal (M') site[4].

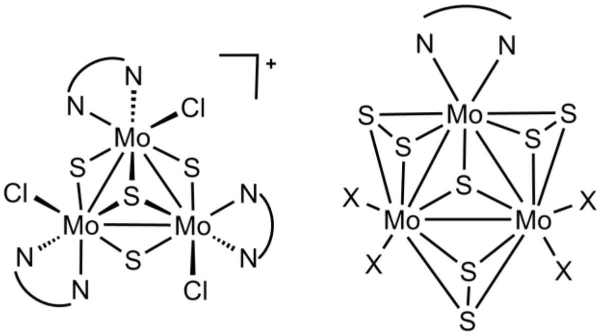

Figure 1 Schematic representation of homoleptic $[Mo_3S_4Cl_3(\text{diimine})_3]^+$ (left) and heteroleptic $[Mo_3S_7Br_4(\text{diimine})]$ (right) complexes containing heterocyclic diimine ligands

The financial support of the Russian Foundation for Basic Research (grant 15-03-02775 a) is gratefully acknowledged.

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Synthesis and Crystalline Oriented Thin Film Fabrication of Novel Three-Dimensional Accordion-Like Metal–Organic Framework

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Metal–organic frameworks (MOFs) show varied physical properties (gas separation, catalysis, switching, and so on). For future practical applications of MOFs, such as membranes, catalysts, and sensing devices, the use of oriented crystalline MOF thin films has been intensively pursued in recent years. However, to our knowledge, there are only two examples of three-dimensional (3D) MOF thin films with high crystallinities and orientations, as confirmed by X-ray diffraction along both the horizontal and vertical directions, relative to the substrate.[1–3] Moreover, these two examples are both pillared-layer-type structures. Here, we report on the synthesis and sorption properties of a novel 3D accordion-like MOF, $Fe(H_2O)_2(bpy)[Pt(CN)_4]\cdot H_2O$ (**1**; bpy = 4,4'-bipyridine). Fe^{2+} and $[Pt(CN)_4]^{2-}$ form 1D neutral accordion-like chains (Fig. 1a), and these chains are connected through bpy ligands to form an extended 3D accordion-like structure (Fig. 1b). We also demonstrate successful fabrication of the crystalline oriented thin film, despite the MOF not having a conventional layer structure, but rather a unique accordion-like structure. Synchrotron X-ray studies revealed not only the crystalline oriented nature but also anisotropic lattice expansion upon guest adsorption. Details of this study are reported.

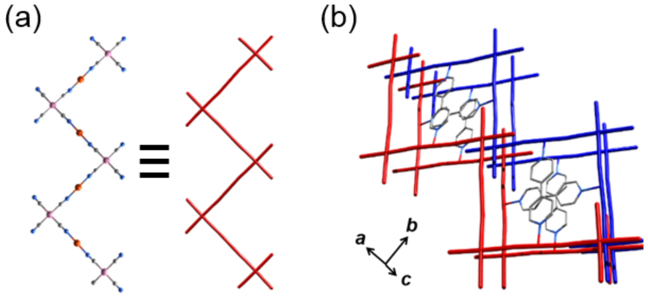

Figure 1. (a) Accordion-like chain structure composed of Fe^{2+} and $[Pt(CN)_4]^{2-}$.
(b) Schematic crystal structure of **1**.
C, N, Fe, and Pt are grey, blue, orange, and pink, respectively.

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Applications for functionalized polyoxometalates

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We have developed over the last decade several synthetic approaches for functionalizing POMs with organic molecules, and for performing organic reactions on grafted ligands. The interplay between these inorganic metal-oxide clusters and organic molecules diversifies their properties and applications. This presentation will focus on three examples of uses of organically functionalized POMs:

- The combination of POMs with polymers – either obtained by grafting polymer chains or by polymerization from grafted initiator – gives rise to smart materials.[1, 2]
- The grafting of organocatalysts onto chiral, enatiomerically pure POM, yields a chiral catalyst. The chiral information can be transferred from the inorganic framework to organic substrates in an enatioselective reaction.[3]
- A POM bio-functionalized with a DNA primer was successfully used in a PCR protocol, the POM-DNA hybrid was annealed to electrode surface bound DNA, and detected by electrochemistry. This opens the way to electrochemical DNA sequencing.[4]

For each case, the synthetic and analytical challenges that were solved are also presented.

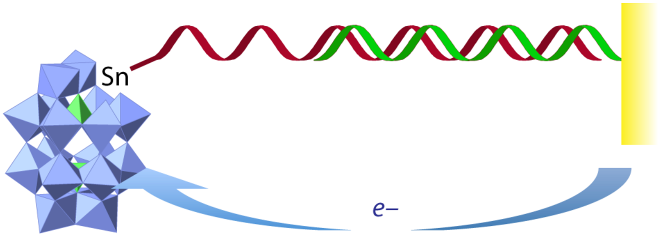

Figure 1 POM-DNA hybrid annealed to surface bound DNA as electrochemically active label for DNA detection.

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Polyoxometalate Catalysts and Systems for Solar Fuel Production

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New transition-metal-substituted POMs have been developed that catalyze the highly efficient 4-electron oxidation of water and the reduction of H_2O and CO_2 under mild conditions.[1-3] These reactions have now been coupled to visible-light sensitizer systems in both solution and on electrodes.[4] The central photoelectrochemical parameters have been studied and the rates of key processes have been measured by transient absorption spectroscopy. One important point from the latter (TAS) studies is that oxidation of the POM catalyst by the visible-light-generated hole (oxidizing center) is remarkably fast despite the fact the POM is anchored to the photosensitizer solely by electrostatic interactions.

Recently, the role of counter cations in electron transfer and proton-coupled-electron-transfer processes in POM systems, including those relating to artificial photosynthesis, have been probed by 5 independent techniques including X-ray crystallography. One new finding is that the size of the POM counter cation(s) can dictate distinct and strong binding modes with the polyanion. POMs with strongly and structurally-specific counter cation bonding exhibit significantly altered thermodynamic and dynamic processes.

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Zero-Magnetic-Field Splitting in the Excited Triplet States of Octahedral Hexanuclear Metal Clusters

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Octahedral hexanuclear metal complexes with the general formula, $[M_6E_8L_6]^{Z-}$ (M = Mo(II), W(II), Re(III); E = X (halogen), S, Se, *etc*; L = X, CN, SCN, *etc*), show relatively intense and long-lived emission in both solution and solid phases and, thus, their emissive excited triplet states are very much interested. In particular, we reported in 2005 that some Re(III) cluster complexes showed large temperature (T)-dependent emission spectra and lifetimes in the T range of 3 ~ 300 K, and demonstrated that the origin of the large T-dependent emission characteristics was large zero-magnetic-field splitting in the excited triplet states of the clusters.[1] As an example, Figure 2 shows the T-dependent emission spectra of $[Mo_6X_8(n\text{-}C_3F_7COO)_6]^{2-}$ (X = Cl, Br, I) in polymer matrices. As seen in the figure, the iodide complex showed different T-dependent emission behaviors from the Cl and Br clusters. In the present talk, the emission and excited triplet state characteristics of a series of hexanuclear metal clusters (Mo(II), Re(III), W(II)) will be presented.

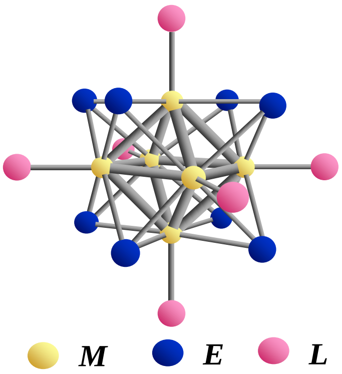

Figure 1 Structure of $[M_6E_8L_6]^{Z-}$.

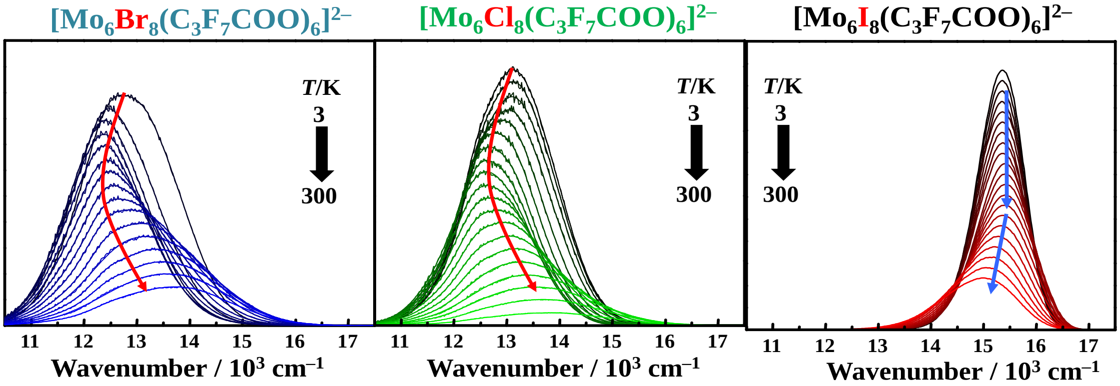

Figure 2 T-Dependent emission of $[Mo_6X_8(n\text{-}C_3F_7COO)_6]^{2-}$ (X = Cl, Br, I) in polymer matrices.

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Metal-Organic Frameworks with Ultrahigh Porosity

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Metal-Organic Frameworks have received considerable attention in recent years because they provide extremely high specific surface areas exceeding traditional adsorbents such as zeolites and activated carbon. Especially mesoporous MOFs provide a wide range of options for further functionalization and even chiral groups can be incorporated rendering such materials as potential candidates for gas storage, enantioselective separation, catalysis and sensing. In recent years, exciting developments have pushed the limits of materials performance to ever higher surface areas up to 7000 m^2/g and pore sizes unattained so far in traditional porous solids such as zeolites or activated carbons. In order to design mesoporous MOF materials with high accessible surface area the co-linker approach was applied for the synthesis of highly porous materials such as DUT-6 (DUT = Dresden University of Technology) with a surface area of 4080 m^2/g [1]. DUT-32 is a new MOF with umt-topology and ultrahigh specific surface area (6411 m^2/g). DUT-49 is a mesoporous flexible MOF composed of connected Metal-Organic Polyhedra (MOPs) to form a ccp analogue and has the highest gravimetric methane uptake among all known MOFs (308 mg/g at 298 K). Chiral mesoporous MOFs were also obtained using chiral btb- or bdc-linkers (btb = benzene tribenzoate, bdc = benzene dicarboxylate. A number of new highly mesoporous MOFs and will be presented [2].

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Dielectric properties of Preyssler-type polyoxometalate with lanthanide ion fluctuation

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Polyoxometalates (POMs) are anionic molecular metal-oxides that consist of early transition metals. Owing to their stability and high redox activity, POMs have been widely explored as oxidation catalysts. On the other hand, POMs have attracted much attention for the development of functional molecular materials such as single molecular magnets (SMMs).[1]

The Preyssler-type POM, $[M^{n+}P_5W_{30}O_{110}]^{(15-n)-}$, has a cavity including one ion inside (Figure 1), and two ion stable sites in the cavity. We recently found a possibility of ion fluctuation between two ion sites at around room temperature via X-ray single crystal structural analysis. On the POM including Tb^{3+} ion (Tb-$P_5W_{30}O_{110}$), the temperature dependence of dielectric constants showed peaks depending on the frequencies due to the ion fluctuation, and the activation energy was estimated to be 0.450 eV from the Arrhenius plot. Moreover, *P-E* hysteresis curves are observed at around room temperature, and spontaneous polarizations are held below the temperature.

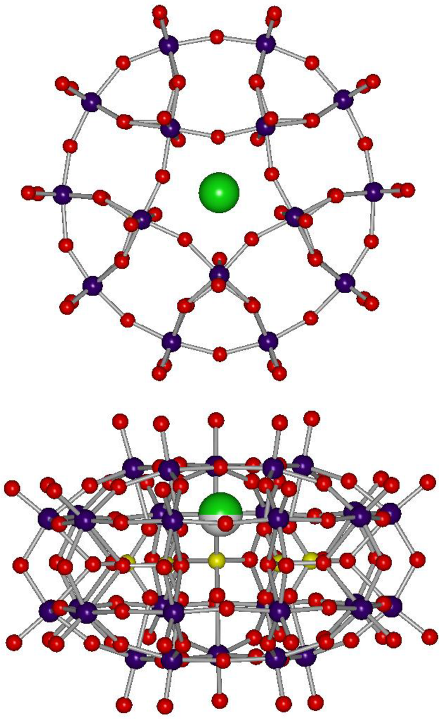

Figure 1 Preyssler-type POM (side and top view)

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Selective sorbents and catalysts based on porous coordination polymers of 3d metals

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Porous coordination polymers (PCPs) of 3d metals are considered as promising sorbents for separation of organic compounds, as well as selective catalysts of various reactions. In this work new and previously reported chiral PCPs, containing lactate, α-aminocarboxylate, camphorate and other chiral groups, were examined as sorbents or carriers for adsorption or chromatographic separation of chiral alcohols. The correlation between sorption of certain enantiomer from gaseous phase and chromatographic isolation of this isomer from racemate was found, the influence of PCP composition, preparation conditions and solvent (in chromatography) was checked. Catalytic activity of several carboxylate PCPs in reactions of aldehydes condensation with compounds, possessing active methylene group, or in electrocatalytic dehalogenation of halides, was studied; in particular, special methods for creation of redox-active PCPs, as well as for examination of their redox-properties, were developed. The relation between the rate and yield of aldehydes condensation with malonic nitrile or nitromethane, and the size of the reagent molecules, their intrinsic reactivity and kinetics of reagents diffusion in pores of PCPs was studied.[1,2] Activity of PCPs in electrocatalytic dehalogenation of organic halides correlated with sorption capacity of the catalyst in respect to the halide and with the linear size of delocalization area of "additional" electron in reduced form of the catalyst.[3-5]

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Tuning optical properties of small gold clusters through the modulation of surface organic environments

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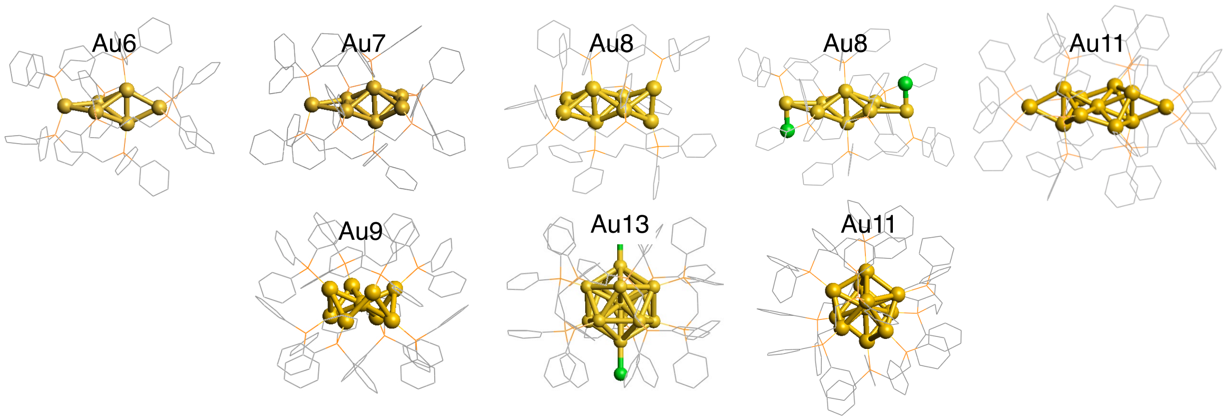
The chemistry of ligand-protected gold clusters with nuclearity less than ~50 has attracted continuing interest due to their unique optical/electronic properties. During the course of our study on diphosphine-ligated clusters, we have found a variety of novel clusters with unique geometrical structures and optical features, and demonstrated that their electronic properties depend not only on the size (nuclearity) but also on the geometrical structures of the gold core unit.[1,2] Here we show that the optical properties can be altered also by the modulation of surrounding organic environment. For example, the core+exo type non-spherical Au8 clusters bearing two pyridylethynyl ligands at the exo gold atoms showed reversible visible absorption and photoluminescence responses to protonation / deprotonation events.[3] The optical responses were highly dependent on the relative position of the nitrogen atom, implying the involvement of the attached π-systems. The pyridylthio-modified analogues also showed definite optical responses but the profiles were much different. We will also show that the π-units in the diphosphine ligands can substantially alter the optical properties of the phosphine-ligated clusters.



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Organoantimony(III)-Functionalized Heteropolytungstates: From Structural Design to Controlled Biological Activity

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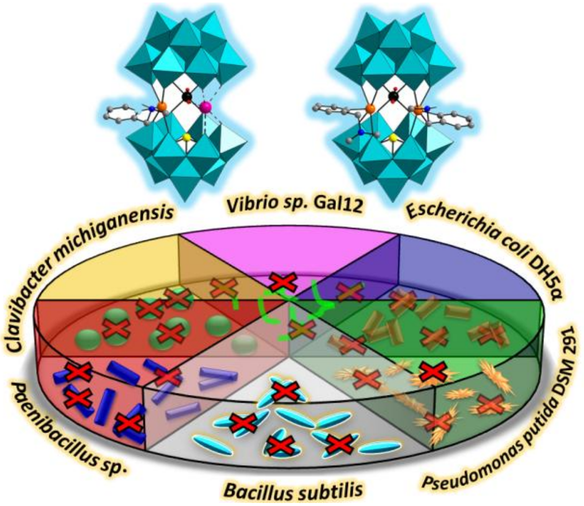
Polyoxometalates (POMs) are discrete metal-oxides with a large variety of shape, size, structure, and composition, and their functionalization by incorporation of transition metal or rare earth ions has led to many novel compounds.[1] Covalent attachment of organometallic moieties to POMs leads to organic-inorganic hybrid species, comprising features of both organic and inorganic components, resulting in potential applications as antiviral or antibacterial agents.

Our group has prepared numerous organometallic POMs over the years, mainly focusing on Sn, Ru, and very recently also Te.[2] Recently we have developed a novel family of organo-Sb^{III}-functionalized POMs, in which the exact number of incorporated organo-Sb^{III} units can be deliberately tuned by careful control of the reaction parameters.[3] In addition, the type of organic functionality can be modified, leading to control of steric and electronic features. All these species are solution-stable in physiological medium. The inhibitory activity of these POMs against different types of bacteria has been studied, revealing an interesting structure-activity relationship.



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“Bi-pyridinium carboxylate“ based MOFs for ammonia detection and storage

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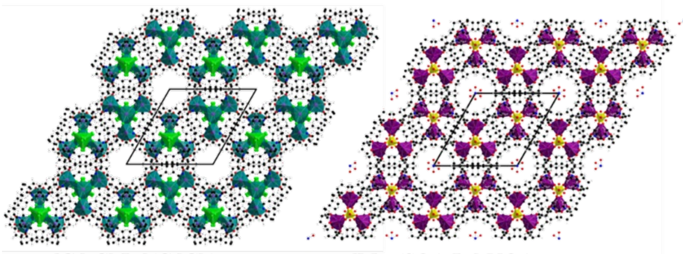
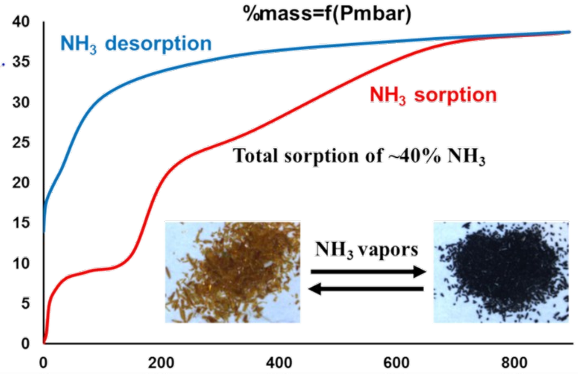
MOFs (Metal Organic Frameworks) are crystalline materials whose structures consist of metal-based nodes bridged by organic linking groups, which can have applications in gas storage (H_2, CO_2…), heterogeneous catalysis and chemical sensors.[1] Up to now the main strategy to increase the absorption properties has been to introduce coordinately unsaturated metal centers. In contrast, the incorporation of cationic organic ligands is much rarer despite a certain potential as shown by some reports[2]. Our original approach consists of mixing electro-active viologen derivatives[3] with carboxylate functions, to synthesize new MOFs for gas storage and molecular recognition. Our synthetic strategy and new results will be described, taking $[Cd_4Cl_6L_3](CdCl_4)$ and $[M_3(SO_4)_2L_3](NO_3)_2$ (with M=Mn, Zn) compounds as examples, with L=N,N’-carboxyphenyl,4,4’-bipyridinium. Those MOFs exhibits accessible channels with a large zwitterionic surface area which allow reversible sorption of gas and small molecules. The color shift in presence of ammonia vapors due to a strong donor-acceptor interaction offers a high potential for chemical sensors applications. Moreover we have shown an adsorption up to 40% in mass of ammonia for $[Cd_4Cl_6L_3](CdCl_4)$ which makes it one of the better MOF for ammonia storage[4]. On the other hand $[M_3(SO_4)_2L_3](NO_3)_2$ which have a very similar structure seems to show similar properties and a strong affinity for ammonia (investigations in progress).



$[Cd_4Cl_6L_3](CdCl_4)$ $[Mn_3(SO_4)_2L_3](NO_3)_2$



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Self-assembly and Self-recognition in Solutions of Metal-oxide Clusters and Metal-organic Nanocages – Where Simple ions, Colloids and Polyelectrolytes Meet

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In the transition area between traditional simple ions and large colloidal particles – macroionic solutions, the charged solutes have solution behavior fundamentally different from the above two categories.[1] The best model macroions are polyoxometalate (POM) macroanions and metal-organic hybrid cations – both are structurally well-defined molecular clusters with sometimes accurately tunable charge density.

Many unexpected, exciting phenomena are observed in macroionic solutions. Such macroions tend to strongly attract with each other although they carry the like charges, and reversibly self-assemble into robust, single-layered, hollow, spherical “blackberry” structures via counterion-mediated attraction, with the blackberry formation and size being accurately controlled by the solvent content, macroionic charge density or solution pH.[2]

The blackberry formation mimics some biological processes, such as the virus capsid shell formation, in many aspects, from the formation mechanism to the permeability to small cations. The macroions can be used as valuable models to understand some fundamental biological behaviors involving long-range electrostatic interaction, such as the self-recognition of biological assemblies.[3] The inorganic macroions with can achieve the level of self-recognition similar to biomolecules in dilute solution, even among highly similar macroions (identical in size, shape or change) or even among enantiomers. Amazingly, chiral recognition and chiral selection processes among enantiomers have been achieved, which might be connected to the interesting phenomenon of homochirality in the origin of lives.[4]

Course-grain simulation studies have nicely confirmed all the experimental observations.

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Molybdenum Sulfide Trimetallic Clusters as Low Cost Catalysts

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Molybdenum sulfide materials have recently emerged as low cost alternatives for the catalytic reduction of organic substrates as well as for the photo- and electrocatalytic reduction of water.[1-3] Herein we present the synthesis of new aminophosphino, diamino and diimino trimetallic molybdenum cluster sulfides, represented in Figure 1, emphasizing relevant reactivity aspects related to their catalytic applications.

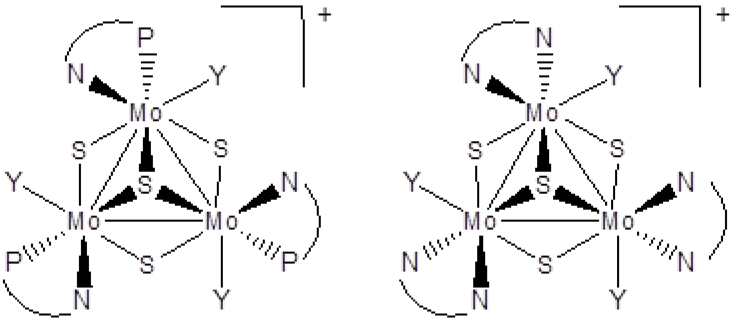

Figure 1. Structures of aminophosfino, diamino and diimino Mo_3S_4 complexes

The activity and selectivity of these new cluster complexes in the catalytic reduction of nitrocompounds directed toward the production of aniline derivatives and secondary amines will be discussed. Finally, we will show the generation of a Mo-sulfide co-catalyst starting from Mo_3S_7 diimino clusters that enhances the activity of TiO_2 for hydrogen photogeneration, in the presence of Na_2S + Na_2SO_3 as sacrificial agent.

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Nano/ Mesoscale Metal-Organic Frameworks: Interplay between Morphology and Functionality

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Recently, there has been growing interest for fabrication of nanoscale porous coordination polymers (PCPs) or metal-organic frameworks (MOFs) of different morphologies for controlling and tuning the size dependent properties.[1-6] The lesser the particle size of MOFs, the smaller is the diffusion barrier and it is expected to strongly influence the catalytic activities, separation processes, sensing and sorption properties over the respective bulk MOFs. Nanoscale MOFs also show enhanced solution processability which is useful for biological applications and also for device fabrication. But in order to understand these aspects in nanoscale, the structural periodicity of bulk MOFs should be invariant even in nanoscopic dimension. This talk would try to introduce versatile morphologies in nano/mesoscale scale MOFs and their diverse applications including changeable surface area and selective adsorption, bimodal imaging, self-cleaning behavior and tunable emission for sensing and light harvesting applications.[1-6]

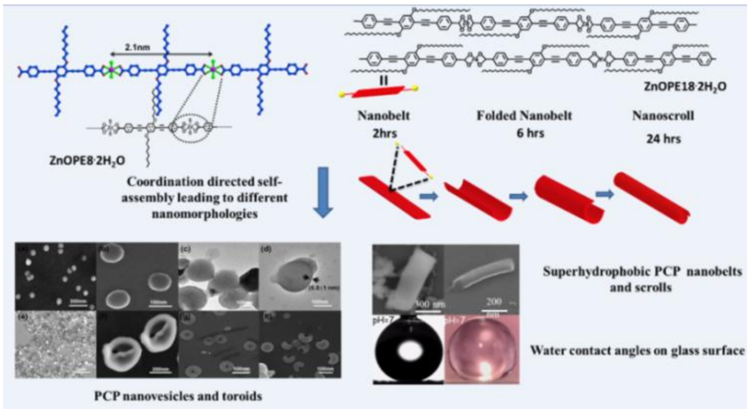

Figure 1 Time dependent change in morphologies in soft NMOFs

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Trinuclear Pt(II$_3$), Pt(II,III$_2$), and Pt(II$_2$,III) Complexes with ESR Isotropic Broadening around the Pt-Pt-Pt Bonds

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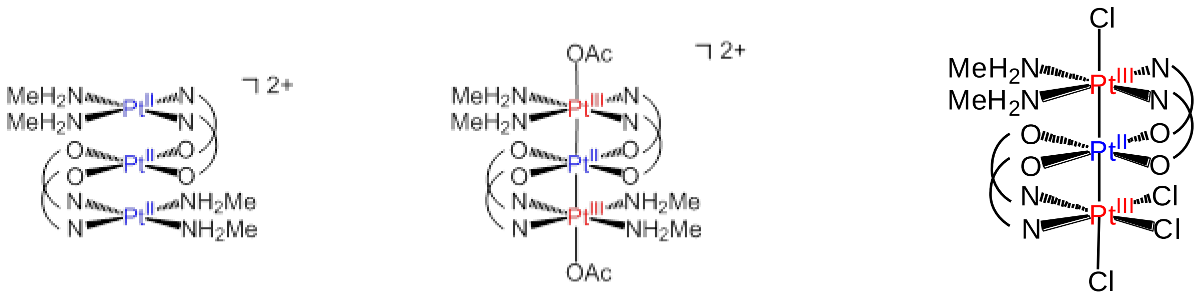
Amidate-bridged Pt-Pt-Pt metal-metal bonded complexes with different Pt oxidation states as shown in the title, have been synthesized, and their structures, CV, and ESR were studied. Several synthesized trinuclear complexes with different Pt oxidation states are shown in Figure 1. The complex of (Pt(II$_2$,III)) state (not shown in Figure 1) was especially noteworthy, since it has a spin of isotropic broad signal around g=2.0, in addition to an axial signal (g(perpendicular)= 2.403 and g(parallel)=1.986, which is familiar to other amidate-bridged Pt(II,III) mixed-valent complexes. The latter axial signal corresponds to delocalization of a spin of Pt(III) along the three Pt cores of metal-metal bond axis. The origin of the former isotropic broad signal is not known, however it suggests extensive spin delocalization on Pt cores, or to the ligands or even over the crystal lattice. Such spin behavior and tendency of the trinuclear complexes to further elongate the Pt-Pt bond by aggregation suggests that this class of complexes might be a building block to created novel materials having electro, thermal, or spin conductivity..

Figure 1 **Different oxidation states of trinuclear Pt complexes.**



1 **2** **3**

Light-harvesting hybrid devices for the Photo-production of Chemical Energy

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Metal Organic Frameworks (MOFs) have proven to be very versatile materials over the last 20 years, since it is easy to tune up either, organic linkers or metallic clusters, for a desired application. They have been tested as gas storage materials[1], separation[2], catalysts[3], chemical sensing[4], and recently they have been tested as photocatalysts[5], where they have shown very promising results[6]. MOFs, ideally, can contain a photosensitizer and a catalyzer in the same structure, and by taking advantage of the enormous surface area of the material it is possible to design novel photocatalysts by choosing different ligands and metallic clusters, obtaining materials with different responses and functionalities[6].

An UiO-type MOF is been developed to contain *Zr* as the metallic node that gives rise to the crystalline structure, Ti as a catalyzer and finally Ru tris-bipyridyl complexes that have been well characterized as photosensitizers. To achieve the synthesis of this material, a solvothermal approach has been used for the building of the Ru doped MOF, while the addition of the catalyzer has been achieved through Post-synthetic Metal Exchange.

This material has been fully characterized with ICP-MS, X-Ray Fluorescence, PXRD, TGA and UV-visible analysis; also, preliminary results as a photosensitive device are discussed.

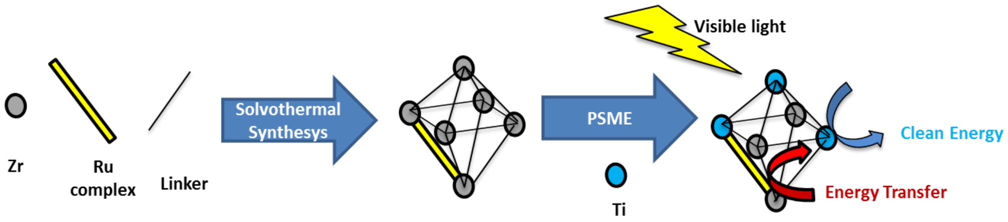

Figure 1 Post-synthetic metal exchange on Zr-UiO-MOF to generate efficient Photo-Sensitive materials

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Mixed-linker approach in designing porous zirconium based MOFs with high stability and hydrogen storage capacity

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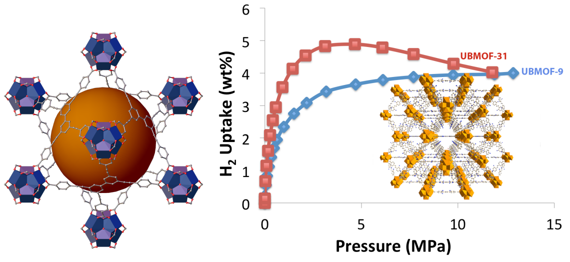
Metal-organic frameworks (MOFs) have gained progressive attention of the researcher community since late 1990s due to their potential applications in various areas, like gas storage, separation, catalysis, drug delivery, etc.[1] Despite their high potential these porous materials suffer from poor stability, which is the main barrier to integrate them for practical applications. To enhance the stability, we are using highly charged metal ions like Zr(IV) which forms stable [$Zr_6O_4(OH)_4(CO_2)_{12}$] secondary building units (SBUs) that are inter-connected by rigid carboxylate linkers.[2] Modular character of the linkers provides the flexibility to replace them by other linkers with additional functionalities, but with similar coordination modes. With some examples from our recent works this presentation will emphasize how the stability and different physical and chemical properties of highly porous Zr-based MOFs were tuned by using mixed-linker approach.[3] This work will also highlight very high hydrogen uptake (4.9 wt%) for a new Zr-based MOF, UBMOF-31.



(A) (B)

Figure 1 : (A) A Zr-based MOF synthesized using biphenyl-based extended linkers showing large void space (B) High hydrogen storage capacity (4.9 wt%) of a new mixed-linker Zr-based MOF, UBMOF-31 derived from an isostructural MOF (*inset*)

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Unsupported metal-oxo clusters from across the periodic table, contributing to a sustainable energy future

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Molecular metal-oxo clusters are best known and most easily synthesized from the polyoxometalate (POM) forming metal cations V^{5+}, Nb^{5+}, Ta^{5+}, Mo^{6+} and W^{6+}, or the Group 13 polyoxocation forming metals—Al^{3+} and Ga^{3+}. It is a grand challenge to synthesize polynuclear anionic or cationic clusters from any metal on the Periodic Table that are not supported by neither lacunary POM fragments nor organic ligands. Specifically we are interested in designing molecular cluster precursors for function metal oxide thin films of any metal on the periodic table. Polynuclear clusters, like small pieces of soluble metal oxide, provide the advantage of pre-assembly and minimization of organic ligands or counterions. In the collaborative Center for Sustainable Materials Chemistry we have made considerable progress in 1) Successful synthetic strategies of new metal-oxo clusters; 2) Understanding and controlling speciation in solution, and 3) Growing high quality thin films from aqueous solutions of said metal-oxo clusters. Functional materials obtained from simple, low energy, aqueous processes are an important part of a sustainable energy future.

I will present synthesis of rare-earth clusters, open-shell transition metal clusters, and novel Hf^{4+} clusters, and how the syntheses may be more broadly applied across the periodic table. Importantly, these syntheses and resulting cluster products do not involve ligation with coordinating organics of POM lacunary fragments. Second, I will show both self-assembly processes and cluster behavior in solution, revealed by X-ray scattering and electrospray ionization mass spectroscopy characterization. Finally, I will exemplify the utility of clusters in thin film deposition and nanopatterning.

This material is based on work in the Center for Sustainable Materials Chemistry, which is supported by the U.S. National Science

Constructing Heterometallic [$M^{III}_8M^{II}_6$] Coordination Cubes

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Supramolecular processes proffer a synthetic strategy towards the rational design of 3D metallic coordination capsules by making use of rigid ligands with predefined donor sites and metal precursors with restricted available acceptor sites. Diamagnetic capsules based on Platonic and Archimedean solids are particularly attractive within supramolecular chemistry due to their often large internal cavities which can play host to a large array of potential guests. This ability to perform host-guest chemistry has seen an increased use of these capsules in areas such as photochemistry, catalysis and drug delivery.[1] Surprisingly, there is limited use of paramagnetic metals in the construction of these capsules and their intramolecular magnetic exchange interactions have rarely been reported.[2] Herein we present the synthetic strategy and magnetic studies of a new series of cubes (Figure 1), based on [$Cr^{III}L_3$] (HL = 1-(4-pyridyl)butane-1,3-dione) as a paramagneic building block, which acts as a tritopic donor towards a "naked" M^{II} salt (Co or Cu).[3]

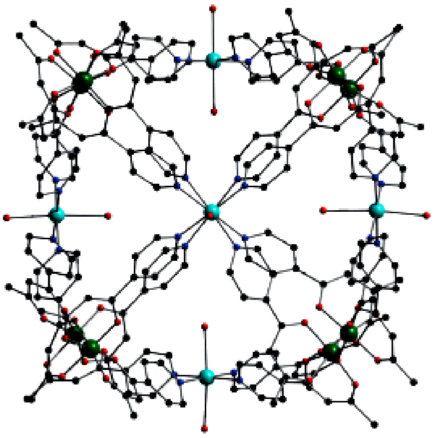

Figure 1 Molecular structure of a [$M^{III}_8M^{II}_6$] cube with hydrogen atoms removed for clarity. Atomic colour code: green = M^{III}, light blue = M^{II}, dark blue = N, red = O, black = C.

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Interconversion of Nuclear-Spin Isomers of Molecular Hydrogen in Porous Coordination Polymers

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Porous coordination polymers (PCPs) providing permanent and designable regular microporosity have attracted much attention as desirable new functional materials. The designable and controllable nano-sized space provides us an ideal stage for fascinating physical and chemical phenomena. We are systematically researching on interlocking functions with porous and magnetic properties using magnetic PCPs [1,2]. In a series of studies, we found an interconversion of nuclear-spin isomers for hydrogen molecule, ortho-H_2 (o-H_2) and para-H_2 (p-H_2), confined in a Hofmann type PCP, {Fe(pyrazine)[Pd(CN)$_4$]}, by the temperature dependence of Raman spectra [3]. The charge density study using synchrotron radiation X-ray diffraction revealed the electric field generated in the pore accelerated the o-p conversion. These results suggested that excitation of H_2 molecule by external stimuli is one of the effective methods for accelerating the o-p conversion which is a spin-forbidden process. To verify the effectiveness of PCPs and accelerate the o-p conversion more, we prepared several PCPs and porous magnets. Acceleration of the o-p conversion was confirmed by In situ measurement using microscopic Raman scattering in the temperature range of 20 – 100 K. In addition, some compounds showed improvement of conversion temperature which deviated from the Boltzmann distribution, which would be related to not only inner electric and magnetic fields and also anisotropic suppression of molecular motion. Details will be discussed based on temperature dependences of Raman spectra and X-ray diffraction using a series of compounds.

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Proton Conduction in a Hydrophobic Nanospace of Metal–Organic Nanotubes

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Ladder materials situated in a dimensional crossover region between 1D and 2D electronic systems have attracted significant attention because of their unique physical properties which depend strongly on the number of constituent legs. Among them, metal–organic halogen-bridged ladder systems are currently of particular interest. These new series of ladder materials are composed of two or four halogen-bridged transition-metal complexes, the so-called MX-chains, as legs that are connected to each other by organic rung units. To date, we have successfully synthesized a variety of two- and four-legged halogen-bridged ladder compounds, two-legged MX-ladders,[1,2] four-legged MX-tubes.[3–5] For the four-legged MX-tube, $[Pt(dach)(bpy)Br]_4(SO_4)_4 \cdot 32H_2O$ (**1**, dach: (1*R*, 2*R*)-(–)-1,2-diaminocyclohexane, bpy: 4,4'-bipyridine), a hydrogen-bonded ice nanotube composed of water tetramers and octamers was found within the hydrophobic nanochannel as confirmed by single-crystal X-ray crystallography (Figure 1). In addition, we also demonstrated that very high proton conduction up to 10^{-2} Scm^{-1} through the ice nanotube within hydrophobic nanochannel of **1**. Details are presented.

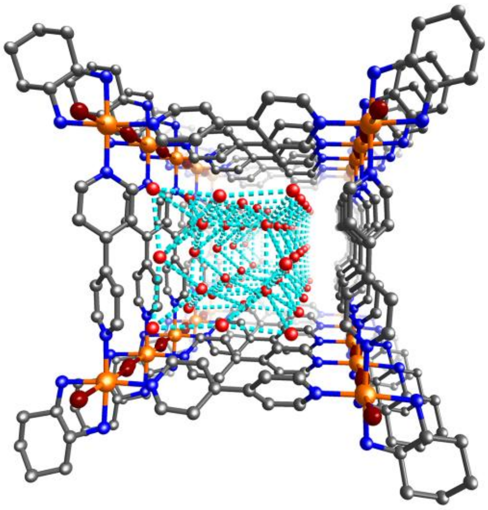

Figure 1 Crystal Structure of **1**. Ice-tube structure is shown by red spheres (waters) and light-blue dotted bonds.

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Luminescent mechanochromic and thermochromic copper iodide clusters

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Controlling or tuning the photo-luminescence properties by means of external stimuli is particularly attractive in order to obtain photofunctional materials. In this context, luminescent mechanochromic compounds whose emission wavelengths change upon mechanical solicitation, are especially appealing.[1] For the development of such pressure-sensitive materials, a deep understanding of the involved mechanism is essential.[2]

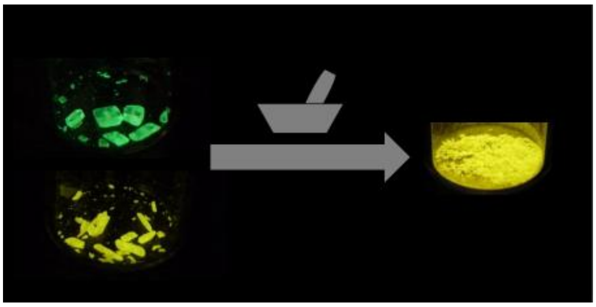

Figure 1. Two crystalline polymorphs of [$Cu_4I_4L_4$] (L = phosphine ligand) display different emission properties and only one of them exhibits luminescence mechanochromism upon grinding.

Here, we report our investigation concerning the mechanochromic luminescence properties of molecular copper(I) iodide clusters formulated [$Cu_4I_4L_4$] (L = phosphine ligand).[3] These compounds present a great reversible change of their solid state emissions and also modification of their luminescence thermochromism upon grinding. Comparative studies of different crystalline polymorphs of the clusters permit to establish correlation between molecular structures and emission properties giving important clues into the mechanochromism mechanism (Figure 1).

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Zirconium-substituted polyoxometalates as artificial proteases

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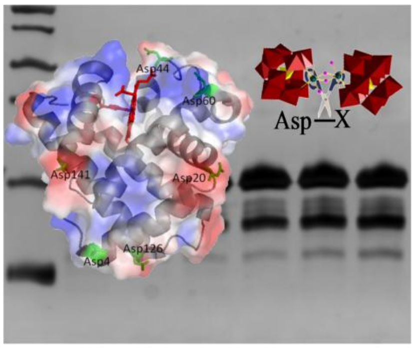
Selective hydrolysis of proteins is an important procedure in numerous biochemical applications. Based on the non-covalent, electrostatic interaction between negatively charged polyoxometalates (POMs) and positive surface domains of proteins[1], we recently introduced a conceptually new approach in the development of artificial proteases by using POMs as ligands for Lewis acid metal ions. In our approach the POM acts as a ligand for the Zr ion, and due to its three-dimensional shape and negative charge it also induces the selectivity that is necessary for a controlled fragmentation of the polyamide backbone. Zr(IV)-substituted POMs were proven to be catalytically active towards the hydrolysis of the highly inert amide bond in dipeptides and oligopeptides.[2] More importantly, these POMs were shown to display unprecedented hydrolytic activity towards insulin chain B, lysozyme, myoglobin and albumin proteins.[3] The hydrolysis occurs at peptide bonds which are located either at clearly defined positive patches that are able to accommodate the POM ligand, or on the interface of positive surface zones containing negatively charged Asp or Glu residues that allow for additional anchoring of Zr(IV).



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Electrochemical and spectroscopic investigation of a Molecular Proton Reduction Catalyst incorporated into a Metal-Organic Framework

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Incorporating organometallic catalysts into Metal-Organic Frameworks (MOFs) is a powerful strategy to heterogenize potentially labile molecular species and stabilize reactive intermediates. Previously[1], we could show that incorporation of a molecular proton reduction catalyst with structural similarities to the [FeFe]-hydrogenase active sites into a highly robust Zr(IV)-based framework could lead to enhanced photochemical hydrogen production in conjunction with a photosensitizer in aqueous buffer solution.

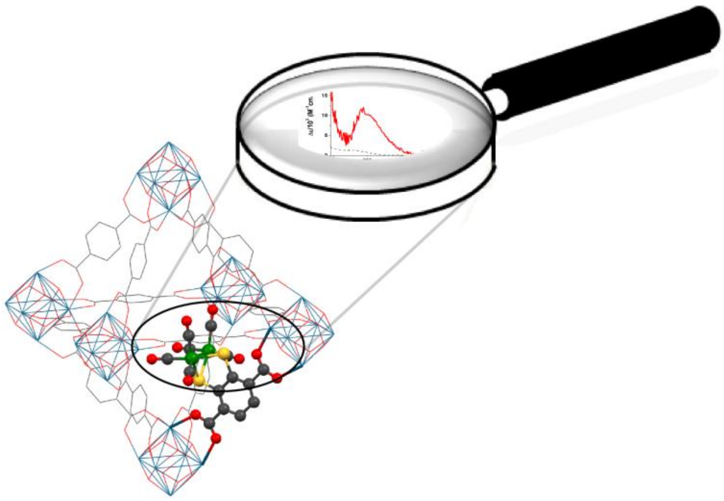

Figure 1 Spectroscopic analysis of the molecular catalyst incorporated into MOF.

Building on these initial results we investigated the MOF-catalyst with a variation of electrochemical[2] and spectroscopic methods. In this presentation, mechanistic aspects as well as improved performance of the MOF-catalyst will be discussed.

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Modulation of MOF properties by deliberate introduction of defects

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The deliberate introduction of defects is a well stablished means of controlling the electronic, catalytic and ion conductive properties of solid state materials. Nevertheless, this approach has been poorly explored in metal-organic frameworks (MOFs). In this communication, we will show some strategies for the creation of defects, on robust MOF systems, and the impact of such defects on the adsorptive (capture of environmentally relevant gases), catalytic (degradation of toxic gases) and ion conductive properties of these systems (Figure 1).[1-3]

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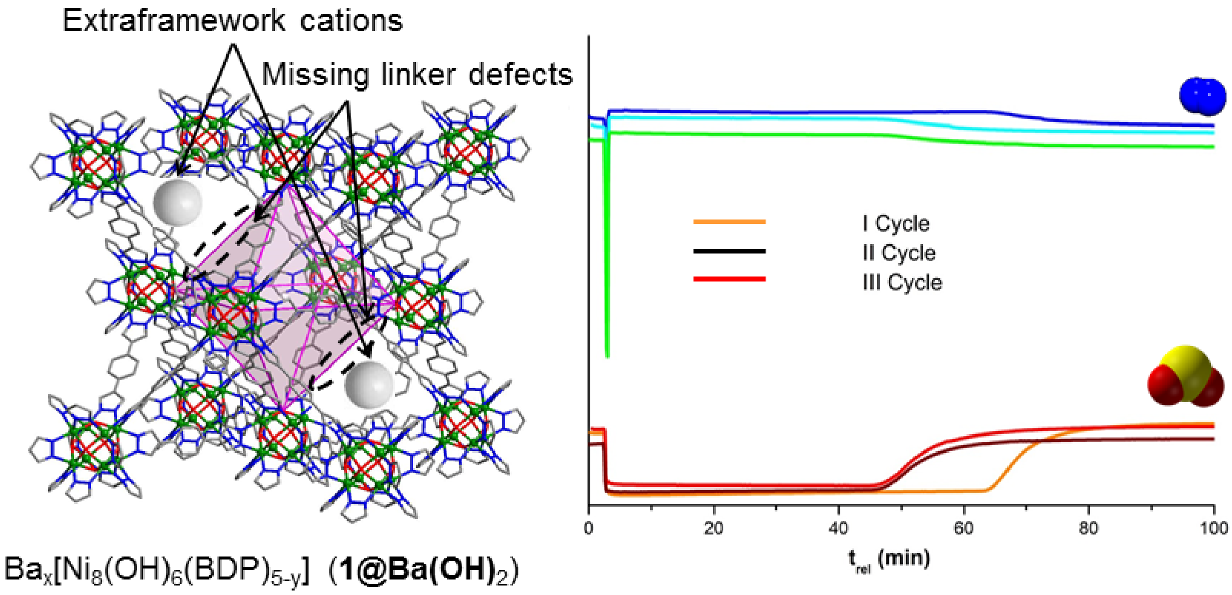

Figure 1 Sketch of the defective structure of 1@Ba(OH)$_2$ (left) and SO_2 capture properties of this system over multiple adsorption-activation cycles of a N_2:SO_2 (97.5:2.5).mixture (right).

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Soft-oxometalates (SOMs) and Light: From Synthesis to Catalytic Applications

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Synthesis of soft-state of oxometalates [1], that show soft-matter properties (like scattering, shear under soft forces, etc.) and are proposed to be called 'soft' oxometalates (SOMs) [2] will be discussed. Such SOMs can be especially useful for various catalytic applications, as in principle any shape of SOM can be envisaged, and their shapes can be directed using light. Hence, directed structure formation in mesoscopic length scale with SOMs using light will be discussed. [3] Even patterning of polyoxometalates en route SOMs using light [4,5] and directed soft structure formation using SOMs as photo-catalytic reaction templates and vessels will be discussed. [6,7] We will also show recently developed SOM based active motors exploiting their redox chemistry [8] and their application in water oxidation catalysis. [9]

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Dense Hypercoordinated *vs.* Porous ZIFs of Alkali and Alkaline Earth Metals: Single Source Precursors for Hybrid Borohydrides

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Zeolitic imidazolate frameworks (ZIFs) are an outstanding class of MOFs, constructed from tetrahedrally configured transition metal cations linked through bridging imidazolate (Im) spacers. ZIFs are structurally isiomorphic to zeolites since the metal-Im-metal angle is similar to the Si–O–Si angle (145°) in the latter compounds. This feature was exploited to produce a huge variety of porous transition metal-based ZIFs. Our initial goal was to combine Im and alkali metal borohydrides in the same structure with the formation of porous borohydride compounds, where Im serves as a structural unit of the framework, while borohydride anions provide with functionality. Surprisingly, we found that alkali and alkaline earth metal-based imidazolates are not structurally characterized so far. This might be explained both by their general unavailability and by efficient hydrolysis. Thus, the coordination chemistry of Im towards alkali and alkaline earth metal cations remains a challenge. With this in mind and inspired by the storage properties of ZIFs, we have turned our attention to Im-based coordination compounds with Li^+, Na^+, K^+ and Mg^{2+} as well as determination of their structures and properties.

The coordinative demand of the metal cation increases with an increase of the ionic radii. The Li^+ cation exhibits a strong propensity to form heteroleptic structures, while the K^+ cation allows to coordinate the Im ring through the *π*-system. While the alkali metal cations found in the CSD show preferred coordination to the nitrogen atom in the plane of Im, the alkali metal sites in this work are distributed over a larger range from 0 to 90°, and show even a wider distribution than for non-alkali metal cations found in the CSD (Figure 1).

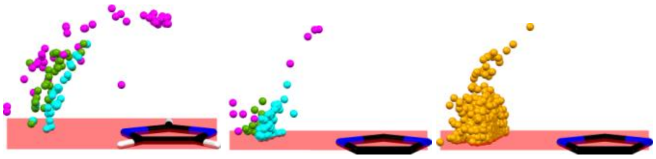

Figure 1 Distribution of the metal sites around Im for the structures reported herein (left), for the structures of substituted Im with alkali (middle) and with other metal cations (right).

Investigating the complex chemistry of high valence MOFs

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Metal-organic frameworks based on high valence transition metal ions (Fe^{3+}, Al^{3+}, Cr^{3+} and Ti^{4+}, Zr^{4+}) have been intensively developed and modified in the past few years majorly due to their good thermal, hydrothermal and chemical stabilities.[1] These MOFs showed great potential in different promising applications, such as catalysis, separation and drug delivery.[2] The high valence cations are well known for their strong binding affinities towards oxygen containing functional groups (-COOH, -OH, O2-), which result often in much better stability of their related MOFs compared to the other metal ions. Their very high chemical reactivity cations in solution is a strong limitation to the discovery of new porous architectures.[3] Herein we will report new series of porous high valence cations based MOFs as well as selected recent experimental and theoretical relevant properties in the field of energy or environment.

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INCORPORATION OF NOBLE METALS INTO POLYTUNGSTATES

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Noble metal-containing polyoxometalates (POM) represent a rapidly depeloping area. These complexes are important for catalytic water splitting and transformations of various organic substrates. Moreover, incorporation of noble metals into POM offers new structural and electronic features for the coordination environment of a noble metal ion. This incorporation also supports strong metal-metal bonding, provides unique stereochemistry around noble metal ion, allows subtle chemical softness/hardness interplay, and leads to enhanced stability of organometallic derivatives. This contribution reports new results in the field of coordination chemistry of Rh, Ir, Ru, Pt and Au with homo- and heteropolytungstates.

This contribution offers a personal view of recent advances in the field of POM complexes with noble metals, concentrating on the synthesis of new Keggin and Lindqvist structures with incorporated noble metal centres, and on their reactivity. Incorporation of Rh, Ir, Ru, Os, Pt and Au into the $\{PW_{11}O_{39}\}$ framework (and related structures) will be discussed. The synthesis of their organometallic derivatives will be addressed. Reactivity studies about CO and NO ligation to the $\{PW_{11}O_{39}Ru\}$ will be presented. Stabilization of Ir_2^{4+} and Rh_2^{4+} dimeric units within the POM framework will be reported. Examples of stabilization of Ir(V) by incorporation into POM will be given, as well as outlook for stabilization of other high oxidation states.

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Discovery of Bi- and Ce-based metal-organic frameworks

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Metal-organic frameworks (MOFs) containing polycarboxylate linker molecules have been reported with a large variety of metal ions. Most common are divalent metals like Zn, Cu, Co, Mn, Ni, etc. but tri- and tetravalent have been shown to be of special interest, since they often lead to more stable materials. Hence, the ions Al^{3+}, Cr^{3+} Fe^{3+}, and especially Zr^{4+} have been employed for the synthesis of new MOFs during the last years.

Recently, we have started to incorporate metal ions like Bi(III) and Ce(IV) into MOFs since these could be of special interest for catalytic applications. These studies led to new Bi-MOFs[1] based on tricarboxylic acids and a series of Ce-MOFs that contain the inorganic building unit $\{M_6(OH)_4(O)_4\}^{12+}$ which is well-known from Zr-MOFs.[2] Importantly, short reaction times and relatively mild reaction conditions are mandatory for the successful synthesis of Bi(III) and Ce(IV)-MOFs, which was also studied by in situ powder X-ray diffraction using synchrotron radiation. In the case of Ce-MOFs incorporation of terephthalate (BDC) as well as functionalized terephthalate ions (BDC-F, -Cl, $-CH_3$, $-NO_2$ and -COOH) was accomplished. To test the general applicability of the approach, the use of linear dicarboxylic acids of different sizes, heterocyclic dicarboxylic acid as well as tri- and tetracarboxylic acids was also studied and Ce(IV)-compounds isostructural to the previously reported Zr-MOFs DUT-67, MOF-545 and -808 were obtained.[3] The thermal stability of these MOFs can be improved by synthesizing mixed-metal compounds.

In the contribution results of our systematic synthetic studies, the structures of the various Bi-, Ce- and Zr/Ce-MOFs and properties of selected materials are presented.

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Fabrication of Metal Sulfide Nanoparticles in Metal-Organic Framework and Application in Electrocatalytic Oxygen Reduction Reaction

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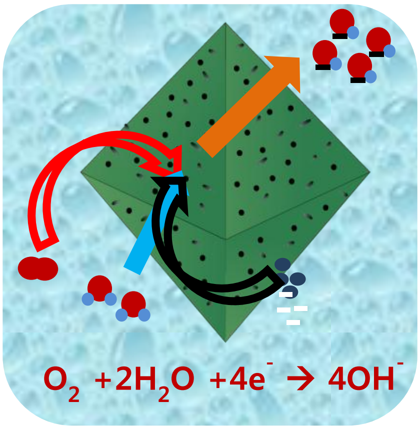
Previously, we made great efforts to apply metal-organic frameworks (MOFs) in gas storage and gas separation. Recently, we have tried to apply MOFs as electro-catalysts for oxygen reduction reaction in fuel cell batteries. MOFs contain abundant micropores, which would facilitate oxygen diffusion, and they also contain many metal sites, which can be utilized in the catalytic reactions. However, MOFs are intrinsically insulators and thus they should be modified in order to apply them in the electro-catalysis. For this purpose, we have developed very simple fabrication method of CuS NPs in a MOF since CuS has low resistivity and has shown to be active in ORR with carbon support materials. By changing the reaction conditions, the size and amounts of CuS NPs fabricated in the MOF could be varied. The composite materials showed remarkably enhanced conductivity values and highly increased onset potential as well as a quasi 4 electron oxygen reduction pathway compared to the pristine MOF or CuS NPs alone, exhibiting synergistic effect of the hybrid materials.



Stimuli-Responsive Reversible Structural Transformation of Multinuclear Metal Cores Sandwiched by Polyoxometalates

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Inorganic materials that undergo reversible structural transformations by external stimuli exhibit unique structure-dependent properties; thus, they are promising candidates for use in sensors and memory devices. Although, reversible transformations of discrete transition metal clusters would lead to functional switchable materials, the development of such materials remains a difficult task. Lacunary polyoxometalates (POMs) with bulky and highly negatively charged frameworks allow the inclusion and isolation of various metal–oxygen clusters. We have recently reported that organic-solvent-soluble lacunary POMs are useful ligands for construction and structural control of multinuclear clusters with unique catalytic, photocatalytic, and magnetic properties. In this presentation, we report the successful demonstration of the water- and temperature-triggered reversible structural transformation of tetranuclear Co(II) cores within silicotungstates (Figure 1). Specifically, a cubane-type tetranuclear Co(II) core was synthesized by the reaction of silicotungstates and Co(II) cations in an organic solvent, and demonstrated to be interconvertible with a planar-type core upon hydration and dehydration. The arrangements and coordination geometries of the Co(II) cations were interconverted via simple hydration and dehydration; moreover, their magnetic and optical properties were manipulated as a result of the structural transformation. In addition, this system exhibited unique thermochromism because of the temperature-dependent dynamic structural interconversion.

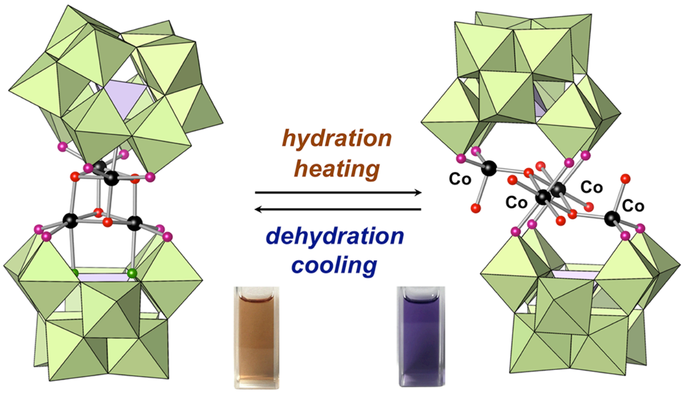

Figure 1 Outline of this study.

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Active Porous Transition towards Spatiotemporal Control of Molecular Flow in a Crystal Membrane

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Valve functionality is an essential tool for flow regulation in microfluidic systems. Here, we employ porous crystals which undergo mechanical reorientation of their internal subnanometer channels in order to manipulate spatiotemporal flow.[1] (Fig. 1a)

In previous study, we clarified the anisotropic gas permeation along 1-D channels (diameter: 0.8 nm) in a single crystal of a microporous metal-complex [Cu(II)$_2$(bza)$_4$(pyz)]$_n$ (bza: benzoate; pyz: pyrazine).[2] In this study, We have found stress-induced martensitic transition of the single crystal involving reorientation of the channels and the spontaneous reverse-transition caused by removing the stress, as an organosuperelasticity.[3] We have successfully observed switchabilities of gas-flow directions and positions in the crystal with a good reproducibility by loading/unloading the stress, which acts as a gas valve. (Fig. 1b and 1c)

Because this porous crystal is an assembrage of pore units (*porons*: pore+on(s)) in subnanometer scale, the reorientation of *porons* driven by mechanical stress can realize a digital control of molecular flow, which is quite different from an analog control of fluids in present microvalves.

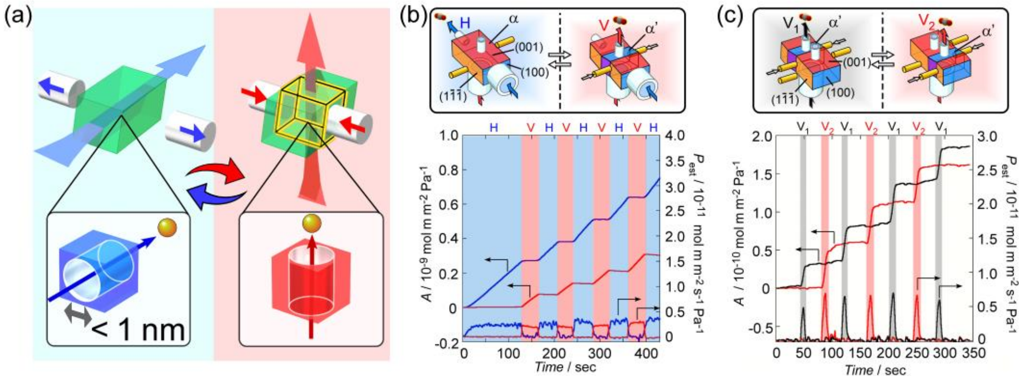

Figure 1 Reorientation of “*poron*” induced by mechanical stress (a); directional (b) and positional (c) switches of CO$_2$ gas permeation through the single crystal at room temperature and differential partial pressure of 100 kPa.

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Electric networks based on polyoxometalate clusters wired by counter cation

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Polyoxometalates (POMs) are anionic metal oxide molecules with a transition metal such as Mo, W and V. They shows the diversities of cluster morphology and composition with uniform cluster size at nano-scale and they are generally prepared by simple reaction procedures through self-assembly processes.[1-3]. We have been explored macroscopic electronic conduction in POM-based solids by hybridizing cationic π-molecules for electrically wiring each POM molecules in crystalline solids. The conducive single crystal was constructed by salting oxidized tetrathiafulvalene substituted with pyridinium ($TTFPyH^{2+}$) with $[PMo^{V}Mo^{VI}{}_{11}O40]^{4-}$. This cluster anions are packed with dimers of $TTFPyH^{2+}$ with alternative packing manner, giving $(TTFPyH)_2[PMo^{V}Mo^{VI}{}_{11}O_{40}]$. Even though $TTFPyH^{2+}$ were isolated by POMs where they did not form conductive columns as is well-seen in TTF-based molecular conductors, conductivity of the single crystals was comparable to that of Si ($\sim10^{7}$ S/cm). Electron transport characteristics were suggested to represent electron hopping through interactions between cluster and cationic π-molecules (figure 1).[4] Here, we explored other conductive crystalline salts by changing both POM cluster and wiring cations. Their electron transport properties from a view of nature of POM and cations, as well as packing manner.

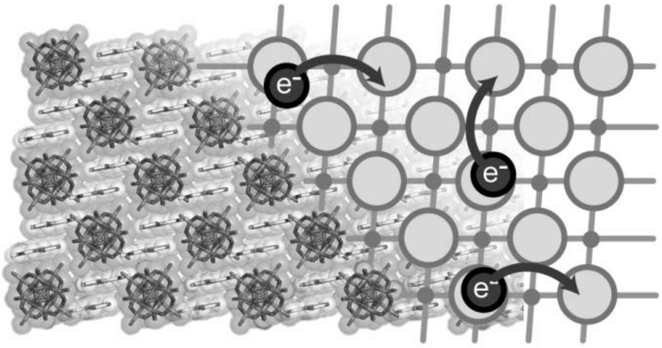

Figure 1 Schematic view of crystal structure of $(TTFPyH)_2[PMo^{V}Mo^{VI}{}_{11}O_{40}]$

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Electronic Properties of Mixed Valence Polyoxometalates

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Polyoxometalates are a family of molecular compounds which has centered the attention of researchers due to the versatility of the electronic properties they present. [1] They can be easily reduced thus giving different mixed valence species, which maintain their structural identity. These systems present super-exchange phenomena and also high delocalization between the metal centers. This delocalization affects the interpretation of the magnetic phenomena, in the sense that the latter cannot be described by the localized models. [2,3]

Our group has been dedicated to the study of different polyoxovanadates. [4–6] Among these POMs the vanadates can be classified as Class II under the Robin & Day classification presenting phase transition between localized and delocalized regime. This transition has been detected using EPR, DC magnetization and heat capacity measurements. In this work different polyoxovanadates will be presented and their physical properties discussed.

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Acknowledgements

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Functional Coordination Materials derived from Kuratowski-type Building Units

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Kuratowski-type coordination units[1] are represented by the non-planar graph $K_{3,3}$ for which until now only very few chemical compounds have been reported. These units form via self-assembly from 1,2,3-triazolate ligands and metal ions, the smallest entities being T_d-symmetrical pentanuclear complexes as shown in Fig.1 (inset). Recent investigations suggest a great potential of Kuratowski units in building up functional coordination architectures, including metal-organic frameworks (e.g. MFU-4(l), CFA-1, CFA-7). An attempt to systematize the design principles and formation mechanisms, which either lead to core-expanded clusters or polymeric 3D coordination materials, will be made.[2] Potential applications derived from photo-[3], or magnetochemical[4] properties will be high-lighted.

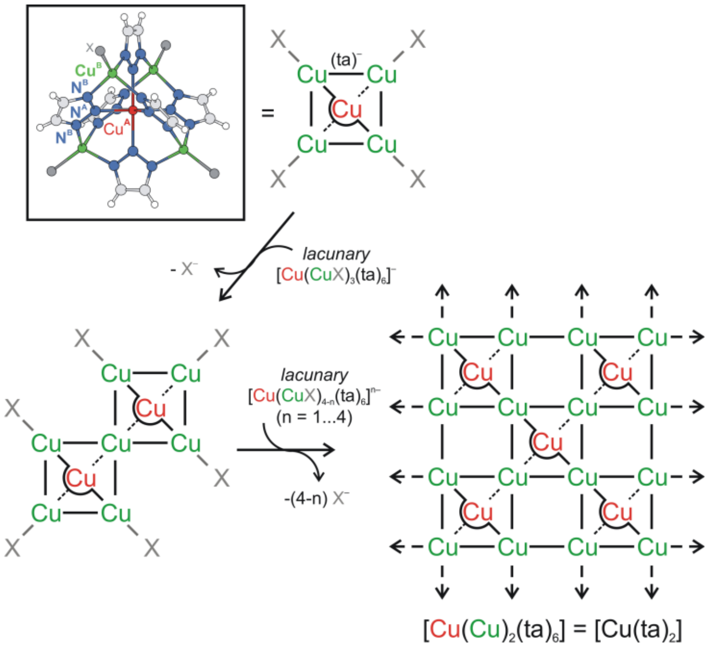

Figure 1 Reaction scheme showing the formation of a 3D coordination framework by stepwise polymerization of (lacunary) Kuratowski-type building units (inset). [from Ref. 2]

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Self-assembly of polyoxometalates toward soft ionic cluster-organic frameworks

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Nanoporous structures within two and three dimension have attracted huge interest over recent years because of their potentials as advanced materials in fundamental research and industrial applications. Among those known architectures, porous coordination supramolecular polymers and metal organic frameworks (MOFs) exhibit quite uniform pores from less than one to several nanometers. The main drawbacks for the inorganic porous structures, however, are the difficulties to mold thin film in large scale conveniently because the connections between components are normally coordination interaction and/or covalent bond. To overcome the severe challenge, flexible binding such as electrostatic force should be considered. But the issues are its non-saturation and non-preferential binding angels, leading to a key problem in precisely controlling porous structure. Fortunately, polyoxometalates (POMs) as a family of nanosized polyanionic clusters have demonstrated good merits in fabrication of hybrid self-assemblies due to their diverse composition and topology. Importantly, multi-negative charges around the surface of POMs are delocalized, making the clusters ideal candidates as the nodes for soft framework architectures through flexible intermolecular interaction.[1] In this presentation, we succeed in creating flexible single molecular layer ionic POM cluster organic frameworks with unprecedented uniform orthogonal pores in large area. The bolaform cations with azobenzene and flexible spacer are used as the stick bridging POMs via charge compensation.[2] The soft film bearing well-defined framework structure can be prepared feasibly and the pore size can be modulated for precise size-selective separation of quantum dots. Detailed characterizations and discussions support our conclusion. The present idea are illuminative in supramolecular polymers and porous materials because the obtained single layer ionic cluster-organic framework also demonstrates potentials in absorption-separation, catalysis, and bio-filtration.

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Molecular Platinum Carbonyl Nanoclusters

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Since the discovery of the so called "platinum carbonyl", $[Pt_{3n}(CO)_{6n}]^{2-}$ (n ~ 10), platinum has played a key role in the development of molecular cluster chemistry.[1,2] Metal clusters and nanoparticles are intermediate species between mononuclear complexes and bulky materials.[3] The study of molecular nanoclusters may contribute to a better understanding of metal nanoparticles, and they may be used as building-blocks and precursors of nanostructured materials. We have shown that Chini's clusters $[Pt_{3n}(CO)_{6n}]^{2-}$ (n = 4-8) self-assemble in the solid state with miscellaneous cations into 0-D, 1-D, 2-D and 3-D materials (Figure 1a), which display interesting conductivity properties.[4] Moreover, their controlled thermal degradation affords globular platinum carbonyls featuring CO/Pt ratio <2, such as $[Pt_{19}(CO)_{22}]^{4-}$, $[Pt_{24}(CO)_{30}]^{2-}$, $[Pt_{33}(CO)_{38}]^{2-}$ and $[Pt_{40}(CO)_{40}]^{6-}$ (Figure 1b) Finally, Chini's clusters react with Sn(II) and Cd(II) salts resulting in surface decorated Pt carbonyl clusters.[5] Our recent results in the field of molecular platinum nanoclusters will be herein discussed.

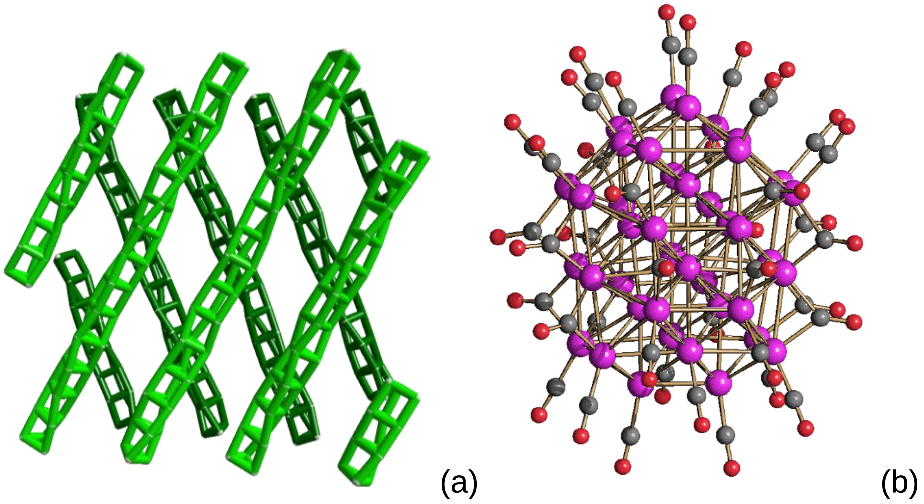
(a) (b)

Figure 1 (a) Crystal packing of $[NBu_4]_2[Pt_{24}(CO)_{48}]$; (b) molecular structure of $[Pt_{40}(CO)_{40}]^{6-}$.

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Merging Organic Dyes and Versatile Auxiliaries in Metal-organic Frameworks for Shape-controlled Photocatalysis

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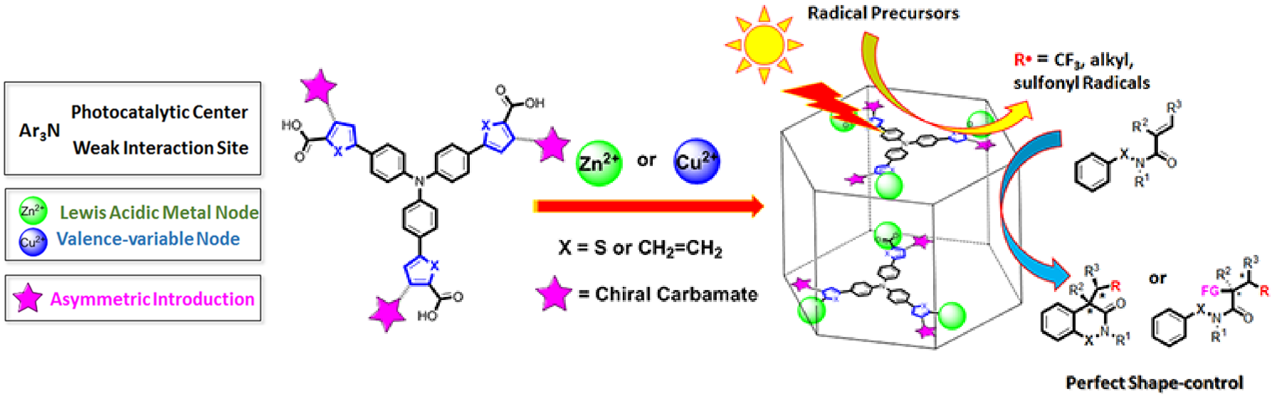
Visible-light provides the green energy to promote challenging chemical reactions, avoiding the unproductive decomposition caused by UV photons. However, the shape-control of photocatalysis has been hindered due to the dearth of effective binding strategy for substrates/intermediates. It is advantageous for recovery of photocatalysts and imposing non-covalent orientation for shape-control of photocatalysis by heterogenizing the photocatalysts within confined environments of MOFs for their practical applications.



Revising the triphenylamine-based tricarboxylic ligand by enlarging the π system, the resulting ligands were endowed with sufficient visible-light absorption ability and the π weak interaction binding sites. The Zn-MOFs with those ligands were capable of photoinduced generation of the free trifluoromethyl, alkyl, or arylsulfonyl radicals under visible-light, furnishing the tandem radical coupling-cyclization reactions of *N*-aryl acrylamides. The non-covalent interactions between MOF scaffolds and substrates enhanced the shape-control of photocatalysis. While in due Cu-MOFs, the catalytic pathway changed to yield 1,2-difunctionalized products of olefins, and also implying a promising asymmetric photocatalysis if a chiral auxiliary was introduced into the ligand to make a homochiral MOF catalyst.

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Redox Active Metal-Organic Framework Brings New Mechanism to the Lithium Batteries

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Over the last decade, the development of metal-organic frameworks (MOFs) has been a compelling research topic for coordination chemists and material scientists. In recent years, with the increasing demand for portable-sized electronic devices, the possibility of using MOFs as electrical storage materials has been widely discussed. Although quite a few examples have illustrated the application of MOFs as electrical double layer capacitors (EDLCs), very limited studies based on the intrinsic redox activity of MOFs have been conducted, which means the pseudocapacitive properties, or the application to electrochemical batteries, have rarely been investigated for MOF materials. Due to the high resistivity of MOF materials, new mechanisms must be developed to solve issues such as partial reduction and insufficient Li-ion extraction of MOF-based batteries.

By incorporating redox active sites on both metal clusters and ligands, we developed redox active MOFs. With these MOFs as the active material of the cathode of a lithium battery, we achieved a high gravimetric capacity of ~200mAh/g. To investigate the mechanism of the electrochemical process, we performed a series of *in situ* physical measurements, including XANES, powder X-ray diffraction and NMR, and discovered a new mechanism rather than the conventional Li-ion batteries, namely, not only the Li-ions but also the anions in the electrolyte were inserted into the framework of MOFs.

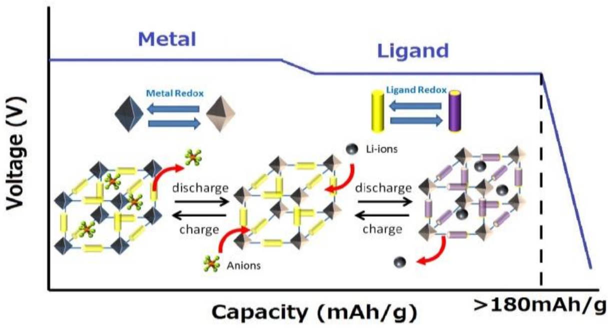

Figure 1 MOFs with redox active sites on both metal and ligands.

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Surface Coordination Chemistry of Metal Nanoclusters and Ultrathin Nanocrystals

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Surface of nanomaterials plays an important role in determining many of their physical and chemical properties.[1] The synthesis of high-quality metal nanoparticles often involves the use of organic capping agents. However, due to the lack of effective tools to characterize the surface structure of small ligands on metal nanoparticles, it is extremely challenging to deeply understand how surface ligands influence the core structure and also overall properties of metal nanoparticles. In this presentation, we will focus on the surface chemistry of two nice model metal nanoparticulate systems, atomically precise metal nanoclusters and ultrathin metal nanocrystals. The importance of small ligands in controlling the surface structure and morphology of metal nanocrystals and nanoclusters will be discussed.[2-8] Together with the unique metal nanostructures (e.g., ultrathin Pd nanosheets) made by the use of specific ligands, the structures of some giant metal nanoclusters will be presented. I will then talk about how the surface ligands influence the catalytic performance of metal nanocrystals. The presence of surface ligands on metal nanoparticles are often considered deleterious to their catalysis applications. However, in my talk, some examples including metal nanoclusters and ultrathin metal nanocrystals will be given to discuss how surface ligands promote the catalysis of metal nanoparticles.[9-10]

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Electron crystallography and electron tomography as important techniques in developing novel MOF materials

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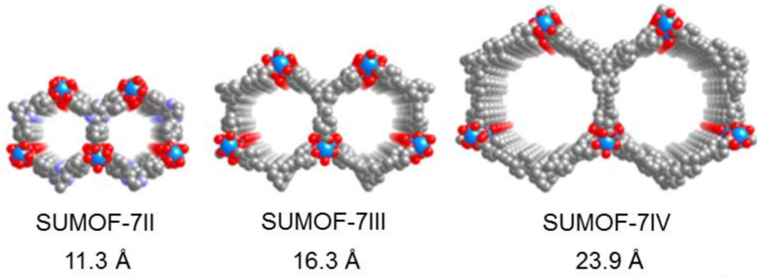
Electron crystallography (EC) is an important technique for structure determination of novel MOF crystals too small to be studied by single crystal X-ray diffraction (SXRD). We developed the Rotation Electron Diffraction (RED) method for automated collection and processing of 3D electron diffraction data[1]. Unknown structures can be solved from the RED data in a similar way as for SXRD data. Electron tomography (ET) can be used for studying MOFs with hierarchical pore structures. Here we demonstrate the solution of 3D structures of novel metal-organic frameworks (MOFs) from RED data. These include a series of highly stable porous isoreticular Ln-MOFs, SUMOF-7I to SUMOF-7IV, synthesized using tritopic carboxylates (Fig. 1)[2] and a Zr-MOF (PCN-128W) built from Zr_6 clusters and tetraphenylethylene-based ETTC linkers[3]. Electron crystallography has been used to study the pore structure of an exceptionally stable Al-MOF (PCN-333) that contains the largest mesoporous cages (5.5 nm), synthesized by Prof. H.-C. Zhou's group.[4] Electron tomography has been used for studying the size and distribution of the mesopore in DOX@ZIF-8, synthesized using a one-pot process [5]. The size of the mesopores in DOX@ZIF-8 can be tuned.



SUMOF-7II 11.3 Å

SUMOF-7III 16.3 Å

SUMOF-7IV 23.9 Å

Figure 1 A series of isoreticular Ln-MOFs built from Ln-O chains and tritopic carboxylates. The sizes of the accessible pore diameters are given.

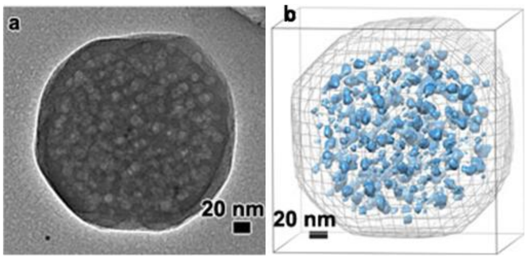


Figure 2 Mesopore distribution in DOX@ZIF-8. (a) TEM image. (b) 3D distribution of the mesopores.

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Design, Synthesis and Gas Storage-Separation Properties of Functional MOFs materials

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Over the past two decades, the research community has witnessed the prominent growth of a special class of materials, namely metal–organic frameworks (MOFs), that offers a high degree of structural tunability (e.g., use of different metals, reticular chemistry, post-synthetic modifications, etc.) that make them ideal candidate to address many enduring societal challenges pertaining to energy and environmental sustainability.

Here, we will show how the adequate selection of a platform associated with a structural control at the molecular level leads to the discovery of new MOFs with interesting potential for many gas storage or gas separation applications.

For example, the utilization of **soc**-MOF platform allowed us to fabricate an Al-based MOF that, for the first time, address the challenging Department of Energy dual target of 0.5 g/g (gravimetric) and 264 cm^3 (STP)/cm^3 (volumetric) methane storage. Furthermore, Al-**soc**-MOF exhibited the highest total gravimetric and volumetric uptake for CO_2.[1]

We also applied this strategy with another platform, i.e. RE-**fcu**-MOF, with the objective to obtain aperture with an appropriate size that allow specific gas separation. With the use of fumarate-**fcu**-MOF, we could for the first time separate paraffin from isoparaffin (molecular exclusion of isobutene from butane), an important industrial topic that is currently obtained using the intensive-energy distillation.[2]

A last example concerns the direct air capture application that can be regarded as an alternate approach to mitigate the increasing CO_2 emissions. We will show how the appropriate modification of a known fluorinated MOF can enhance the adsorption energetics and subsequently displays CO_2 uptake and selectivity at very low partial pressures relevant to air capture and trace CO_2 removal.[3,4]

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Hybrid materials from fluorene phosphonic acids derivatives

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During this last decade, we have synthesized hybrid organic-inorganic materials with magnetic [1], luminescent [2] or drug storage/release properties [3]. These materials, also known as Metal Organic Frameworks (MOF's) or coordination polymers, were obtained by hydrothermal synthesis from an inorganic salt and a rigid poly-functional organic molecule which bears at least one phosphonic acid and / or one carboxylic acid grafted on a rigid scaffold (e.g. a benzene ring or a heterocycle).[4]

To reach the targeted applications, one of the fundamental questions deals with the structure of the hybrid materials. In order to understand and control the dimensionality of the final materials (1D, 2D or 3D network) several parameters have been considered in this work: the nature of the organic precursors (bent or linear, rigidity, position, number and type of reactive functions…), the nature of the inorganic precursor (type of cations, electronic configuration, geometry of coordination…) and the influence of the experimental conditions (solvent, concentration, pH, temperature).

In this work, we will present the synthesis, single crystal structures and the properties of new hybrid materials which could present luminescence and / or magnetism properties obtained from fluorene phosphonic acid and 3d cationic salts (Mn^{2+}, Cu^{2+}, Zn^{2+}, Co^{2+}).

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About Supramolecular Chemistry with Very Large Polyoxometalates

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Synthetic approaches for the formation of the literally “polyoxo**thio**metalate” compounds (or ChalcoPOMs) with a special emphasis on the unique reactivity of the preformed sulphur-containing cationic Mo-S building block toward polyoxometalate units.[1] Such a simple chemical system based on chemical and structural complementarities between constitutive modular units has allowed producing a series of relevant very large hollow clusters with unrivalled structural arrangements, like ring, cylinder, cubic boxe or sphere (see Figure 1). [3,4] Specific reaction parameters and considerations will be discuss showing that a deliberate *pure* inorganic supramolecular chemistry based on weak interactions, flexibility and dynamic is achievable with polyoxometalates. Furthermore solution investigations revealed striking supramolecular properties involving related events such as surface adsorption, transfer processes and confined situations.[5]

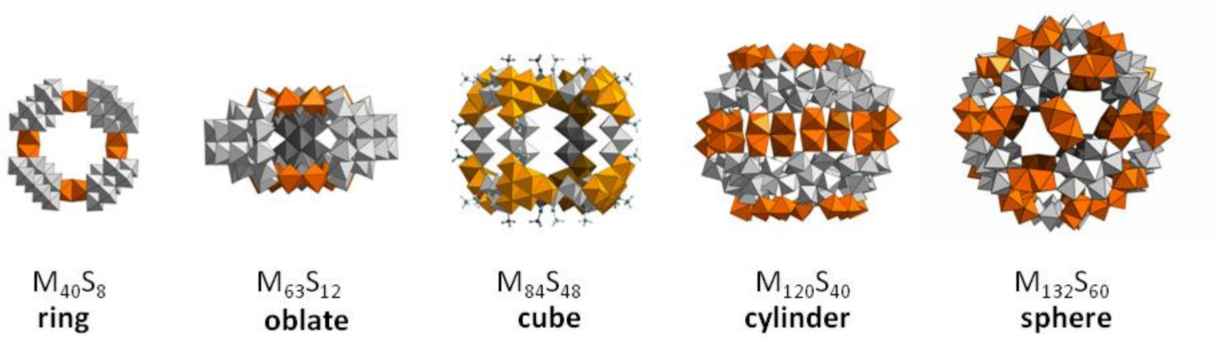

Figure 1: Molecular topologies resulting from polyoxometalate units (grey) and $\{Mo_2O_2E_2\}$ linker (orange)

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MOF visions in Catalysis: Extended molecular networks vs. Surface Science

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Because of their crystallinity and versatility, Metal-Organic Frameworks are ideal candidates for rational design of heterogeneous catalysts. Site isolation, pore size engineering, and functionalisation are the main approaches for tailoring MOF activities and selectivities.[1] Through examples, we will show that the grafting of functions onto MOF provide extremely active and selective catalysts which outperform state of the art catalysts.

It would be questionable for the material science community to regard MOF as only "extended" molecular materials and to evaluate them as “molecular” assembly. MOFs are by essence solids, where interfaces, defects, medium to long range electronic effects and heterogeneity play key catalytic roles in contrast to isolated molecular sites. We provide a comprehensive review of the nature of these defective catalytic sites.[2] Since a decade, a number of striking studies report outstanding catalytic activities and selectivity. Authors were intrigued as it was unexpected from the ideal structure.

We emphasize here that defects are at the origin of the catalytic activities. The vacancy of ligands or linkers systematically generates terminations which can possibly show Lewis and/or Brønsted features. The engineering of catalytic sites at the nodes by the creation of defects on purpose appears today as a rational approach for the design of active and selective MOFs.

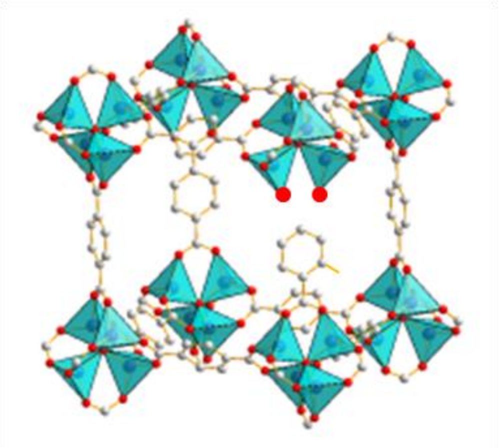

Figure 1 : MOF-5 showing Zn-OH defects created on purpose by substitution of a linker by a mono carboxylate.

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Deep Red Phosphorescent Iridium(III) Complexes with Chromophoric N-Heterocyclic Carbene (NHC) Ligands.

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N-heterocyclic carbene (NHC) ligands have been an important class of ligands in organometallic chemistry and catalysis, since the landmark paper by *Arduengo et al.* which described the isolation of a stable imidazole-2-ylidene.[1] They are strongly σ-donors and provide stable complexes. However, their application in emissive transition-metal complexes has been less investigated in comparison with bipyridyl and phenylpyridyl based ligands.[2] In this communication, we report a novel class of stable phosphorescent Ir(III) complexes with N-heterocyclic carbenes bearing a naphthalimide cyclometalating chromophore[3] (see Figure). All complexes turned out to be strong deep red emitters in the solid state with an excited state of ^{3}LC nature, centered on the naphthalimide moiety.[4]

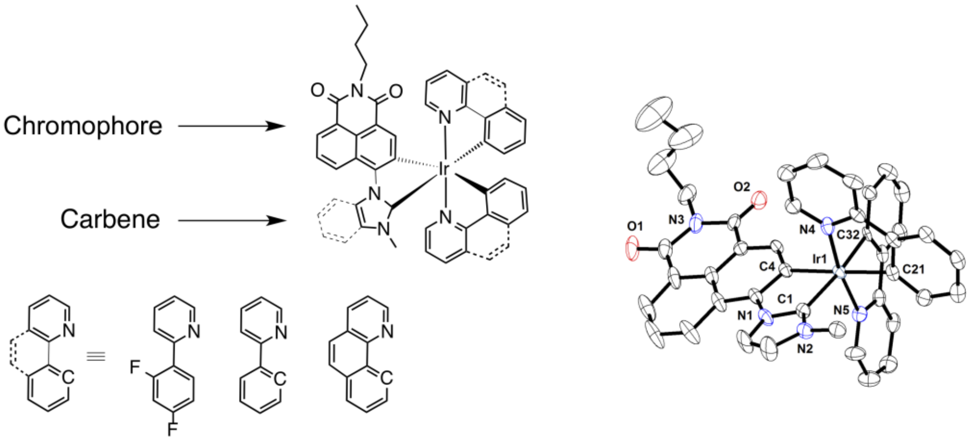

Figure. Iridium complexes with chromophoric N-heterocyclic carbenes.

The molecular structures of several complexes were determined and validated our synthetic strategy. The photophysical properties were investigated in fluid solution and solid state, and the observed luminescent properties were rationalized by TD-DFT studies.

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Molecular Sensors for Diagnostic

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We have synthesized Re organometallic complexes and further characterized by X-ray diffraction, NMR, IR, UV, Electrochemistry and relativistic DFT calculations. We explored the organometallic complexes intracellular localization by taking advantage of its revealed luminescence.

We have performed several biological applications in the field of precision agriculture and public health issues. In particular, we have developed molecular sensors for the detection of *Botrytis cinerea*, and we have synthesized a compound that inhibits the growth of this fungus. These findings have the potential for establishing a protocol in precision agriculture.

We assessed antimicrobial and antifungal activities of some of our organometallic complexes in bacteria (*Salmonella enterica*) and yeast (*Cryptococcus* spp., *Candida albicans and Candida tropicalis*). We determined their minimal inhibitory concentration (MIC). We observed that our complexes exerts antifungal effect against *Cryptococcus* spp. and has proven to be a suitable marker for bacteria and yeast sensing.

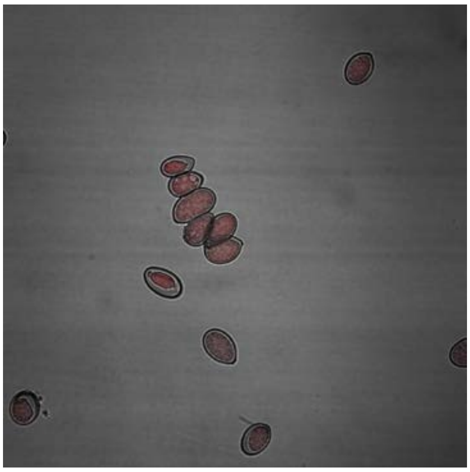

Fig. 1 Sensing *Botrytis cinerea* conidia

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Phosphorus Based Multidenate Ligands: Synthesis,Transition Metal Chemistry and Catalytic Applications

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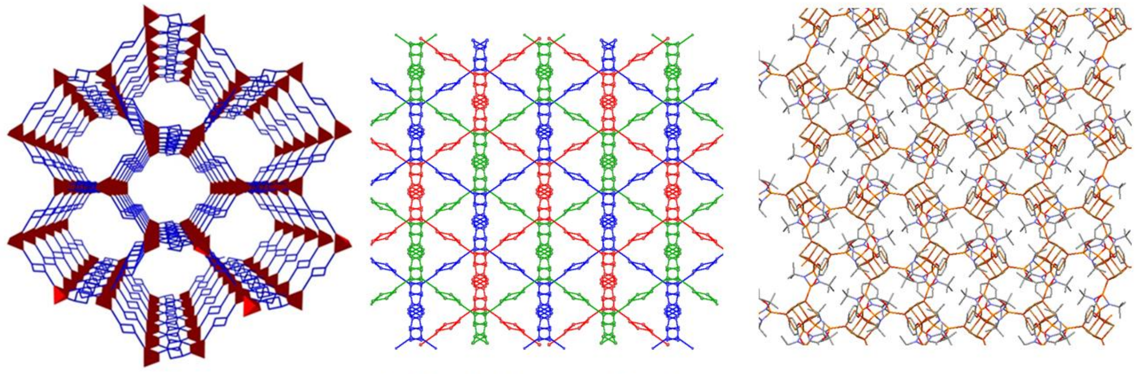
In the last several decades a large number of phosphorus based ligands have been synthesized and used in coordination chemistry and homogeneous catalysis.[1] This is essentially due to the easy synthetic methodologies available to generate a variety of phosphorus based ligands with tunable steric and electronic properties. However, the utility of phosphorus ligands in supramolecular chemistry or in homoleptic metal organic frameworks is limited due to the lack of phosphine systems with rigid framework, free rotational orientations of phosphorus substituents and the conformational flexibility of lone pairs on phosphorus atoms. In this context, we have designed bi-, tri-, tetra or polydentate phosphines having rigid backbone and static conformation and explored their coordination chemistry and catalytic applications.[2-5] The details will be presented.



$[\{Cu_4(\mu_3\text{-}I)_4\}\{\textit{trans}\text{-}(PhC{\equiv}CP)_2(\mu\text{-}N^tBu)_2\}_2]_n$ $[\{Cu_8(\mu_3\text{-}Br)_4(\mu_2\text{-}Br)_4(\textit{cis}\text{-}(PhC{\equiv}CP)_2(\mu\text{-}N^tBu)_2)_5]_n$ $[\{Cu_4(\mu_3\text{-}Br)_4(\textit{cis}\text{-}(C_6H_4O_2P)_2(\mu\text{-}N^tBu)_2)_2]_n$

Figure 1 Various coordination polymers involving phosphorus(II) ligands

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Versatile coordination modes of biological active imidazoles. Structural, chemical and electronic properties driven by their NO_2, SO_2 or CO_2 substituents

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Coordination compounds of transition metal ions with biological active ligands have shown that there is a synergistic effect, enhancing or modification of their activity, when coordinated to a metal ion. The bonding mode, structure, and weak interactions are relevant to the biological activity of coordination compounds wit imidazole derivatives. Intra molecular lone pair S=O •••π interactions play an important role in the stabilization of biologically active complexes. Intermolecular hydrogen bonding and lone pair•••π interactions, such as O-N-O•••π and Cl•••π give place to a variety of supramolecular arrangements.

The structural, electronic and magnetic properties were investigated for a series of cobalt(II), nickel(II), copper(II) coordination compounds of biological active imidazole derivatives with different substituents, as NO_2, SO_2, –OCO. Some examples are shown in Fig. 1.

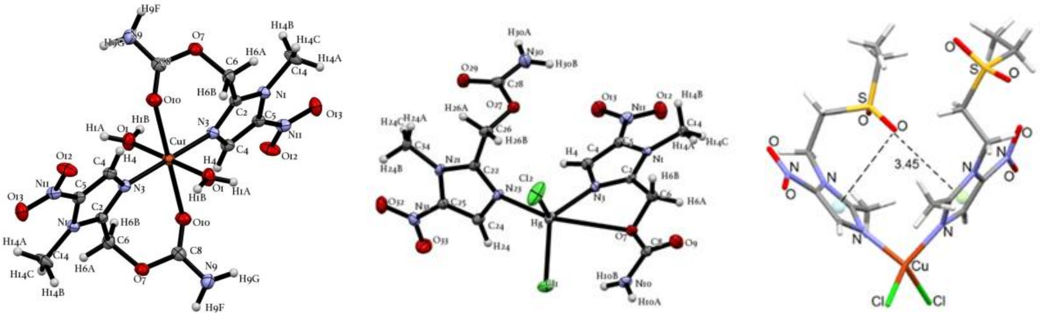

Fig. 1 Coordination compounds of biological active imidazole derivatives with different substituents –OCO, NO_2 and SO_2,

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Polynuclear oxo-hydroxocomplexes in aqueous solutions and the periodic table of elements

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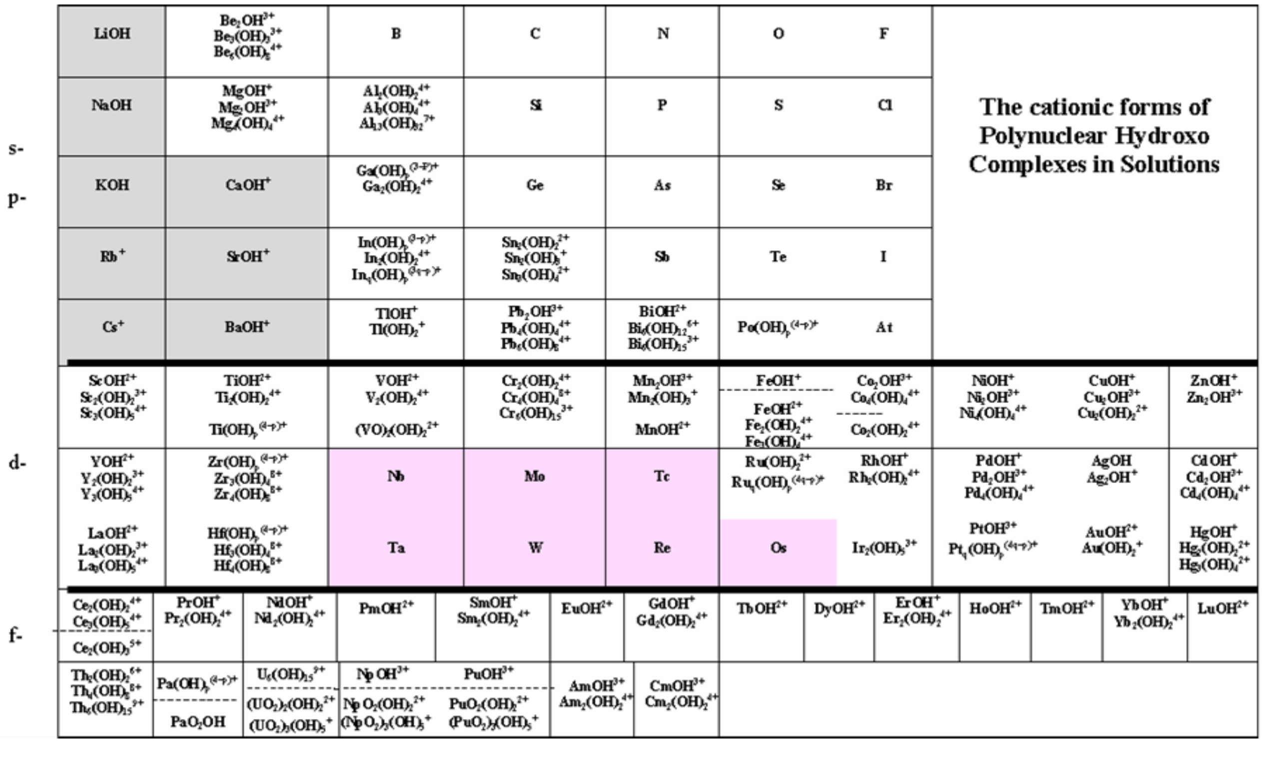
Practically all metal ions are subject to a hydrolysis reaction in aqueous solution. We have conducted a large number of experiments and elaborated a broad empirical data on this subject. As well we have collected the existing data in the literature. To understand the nature of formation and the diversity of forms of complexes we conducted a comparative analysis of these data for all metals ions. All these results are presented in the table below. Three groups of oxo-hydroxocomplexes have been defined based on their different forms: $M(OH)aq^{0,+(z-1)}$; $M_q (OH)_p aq^{+(zq-p)}$ and $M_q O_m(OH)_p aq^{-(2q-2m-p)}$. For first two groups all main forms of complexes are shown in the table. For anionic complexes for metal ions such as Mo, W the results are not presented in this table. We analyzed the forms of complexes in these three groups in the context of the periodic table and revealed that the different forms of complexes and the existence of the three groups are connected with the type of their respective Metal-Oxygen chemical bond (ionic, covalent or their combination).



	LiOH	Be_2OH^{3+} $Be_3(OH)_3^{3+}$ $Be_6(OH)_8^{4+}$	B	C	N	O	F	**The cationic forms of Polynuclear Hydroxo Complexes in Solutions**
	NaOH	$MgOH^+$ Mg_2OH^{3+} $Mg_4(OH)_4^{4+}$	$Al_2(OH)_2^{4+}$ $Al_3(OH)_4^{4+}$ $Al_{13}(OH)_{32}^{7+}$	Si	P	S	Cl	
s- p-	KOH	$CaOH^+$	$Ga(OH)_p^{(3-p)+}$ $Ga_2(OH)_2^{4+}$	Ge	As	Se	Br	
	Rb^+	$SrOH^+$	$In(OH)_p^{(3-p)+}$ $In_2(OH)_2^{4+}$ $In_q(OH)_p^{(3q-p)+}$	$Sn_2(OH)_2^{2+}$ $Sn_2(OH)_3^+$ $Sn_3(OH)_4^{2+}$	Sb	Te	I	
	Cs^+	$BaOH^+$	$TlOH^+$ $Tl(OH)_2^+$	Pb_2OH^{3+} $Pb_4(OH)_4^{4+}$ $Pb_6(OH)_8^{4+}$	$BiOH^{2+}$ $Bi_6(OH)_{12}^{6+}$ $Bi_6(OH)_{15}^{3+}$	$Po(OH)_p^{(4-p)+}$	At	

	$ScOH^{2+}$ $Sc_2(OH)_2^{3+}$ $Sc_3(OH)_5^{4+}$	$TiOH^{2+}$ $Ti_2(OH)_2^{4+}$ $Ti(OH)_p^{(4-p)+}$	VOH^{2+} $V_2(OH)_2^{4+}$ $(VO)_2(OH)_2^{2+}$	$Cr_2(OH)_2^{4+}$ $Cr_4(OH)_4^{8+}$ $Cr_6(OH)_{15}^{3+}$	Mn_2OH^{3+} $Mn_2(OH)_3^+$ $MnOH^{2+}$	$FeOH^+$ $FeOH^{2+}$ $Fe_2(OH)_2^{4+}$ $Fe_3(OH)_4^{4+}$	Co_2OH^{3+} $Co_4(OH)_4^{4+}$ $Co_2(OH)_2^{4+}$	$NiOH^+$ Ni_2OH^{3+} $Ni_4(OH)_4^{4+}$	$CuOH^+$ Cu_2OH^{3+} $Cu_2(OH)_2^{2+}$	$ZnOH^+$ Zn_2OH^{3+}
d-	YOH^{2+} $Y_2(OH)_2^{3+}$ $Y_3(OH)_5^{4+}$	$Zr(OH)_p^{(4-p)+}$ $Zr_3(OH)_4^{8+}$ $Zr_4(OH)_8^{8+}$	Nb	Mo	Tc	$Ru(OH)_2^{2+}$ $Ru_q(OH)_p^{(4q-p)+}$	$RhOH^+$ $Rh_2(OH)_2^{4+}$	$PdOH^+$ Pd_2OH^{3+} $Pd_4(OH)_4^{4+}$	$AgOH$ Ag_2OH^+	$CdOH^+$ Cd_2OH^{3+} $Cd_4(OH)_4^{4+}$
	$LaOH^{2+}$ $La_2(OH)_2^{3+}$ $La_3(OH)_5^{4+}$	$Hf(OH)_p^{(4-p)+}$ $Hf_3(OH)_4^{8+}$ $Hf_4(OH)_8^{8+}$	Ta	W	Re	Os	$Ir_2(OH)_5^{3+}$	$PtOH^{3+}$ $Pt_q(OH)_p^{(4q-p)+}$	$AuOH^{2+}$ $Au(OH)_2^+$	$HgOH^+$ $Hg_2(OH)_2^{2+}$ $Hg_3(OH)_4^{2+}$

f-	$Ce_2(OH)_2^{4+}$ $Ce_3(OH)_5^{4+}$ $Ce_2(OH)_3^{5+}$	$PrOH^+$ $Pr_2(OH)_2^{4+}$	$NdOH^+$ $Nd_2(OH)_2^{4+}$	$PmOH^{2+}$	$SmOH^+$ $Sm_2(OH)_2^{4+}$	$EuOH^{2+}$	$GdOH^+$ $Gd_2(OH)_2^{4+}$	$TbOH^{2+}$	$DyOH^{2+}$	$ErOH^+$ $Er_2(OH)_2^{4+}$	$HoOH^{2+}$	$TmOH^{2+}$	$YbOH^+$ $Yb_2(OH)_2^{4+}$	$LuOH^{2+}$
	$Th_2(OH)_2^{6+}$ $Th_4(OH)_8^{8+}$ $Th_6(OH)_{15}^{9+}$	$Pa(OH)_p^{(4-p)+}$ PaO_2OH	$U_6(OH)_{15}^{9+}$ $(UO_2)_2(OH)_2^{2+}$ $(UO_2)_3(OH)_5^+$	$NpOH^{3+}$ $NpO_2(OH)_2^{2+}$ $(NpO_2)_3(OH)_5^+$	$PuOH^{3+}$ $PuO_2(OH)_2^{2+}$ $(PuO_2)_3(OH)_5^+$	$AmOH^{3+}$ $Am_2(OH)_2^{4+}$	$CmOH^{3+}$ $Cm_2(OH)_2^{4+}$							

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Betaine Adducts of Imidazolidenes and Carbodiimides, Promising Electroneutral Amidinate-Type Ligands

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Betaines are zwitterionic compounds that are usually generated reacting electroneutral nucleophilic and electrophilic reagents. A number of interesting betaines can be readily accessed from the reaction of heterocyclic carbenes with heterocumulenes X=C=Y, such as CO_2, CS_2, etc. [1] These betaines can act as ligands towards transition metal centres, but this potential remains largely unexplored. Specifically, the interaction of imidazolium carbenes with carbodiimides gives rise to betaines that can be regarded as neutral analogues of the well-known imidinate ligands. However, no complexes containing this cabene-carbodiimide betaines have been reported so far.

A simple one-pot procedure has been developed for the synthesis of carbodiimide adducts of imidazolium-based carbenes. The new molecules have been fully characterized, and a series of Cu(I) complexes have been prepared.[2] Both terminal (κ^{i}-*N*) and bridging (□-*N,N'*) coordination modes of the betaine ligand have been identified.

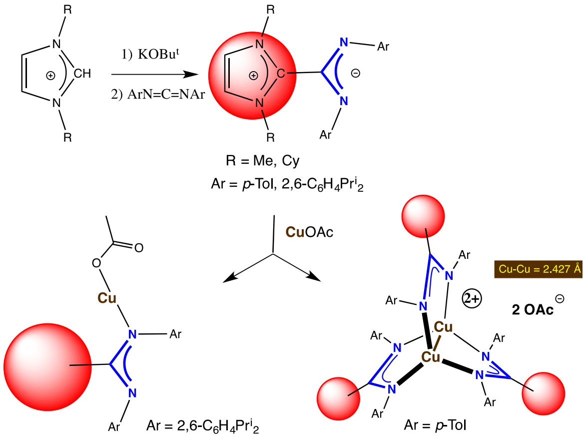

Figure 1

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Luminescence of hybrid coordination compounds with Schiff base ligands

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Lanthanide ions (Ln^{3+}) show weak luminescence in aqueous solution due to the *f-f* transitions, which can be improved by using appropriate chromophores that act as sensitizers. Near-infrared (NIR) emitting lanthanide ions such as Nd^{III}, Er^{III} and Yb^{III} are of interest, due to their numerous potential applications which range from biomolecular labelling in luminescence bioassays to functional materials [1]. Herein we present the synthesis, characterization and spectroscopic study of mononuclear (f), heterodinuclear (d–f) and heterotrinuclear (d–f–d) coordination compounds containing Nd^{III}, Sm^{III}, Eu^{III}, Gd^{III}, Tb^{III} and Dy^{III}, and Zn^{II}, Cu^{II} and Ni^{II} and two symmetric Schiff Bases. Solid state luminescence studies are discussed.

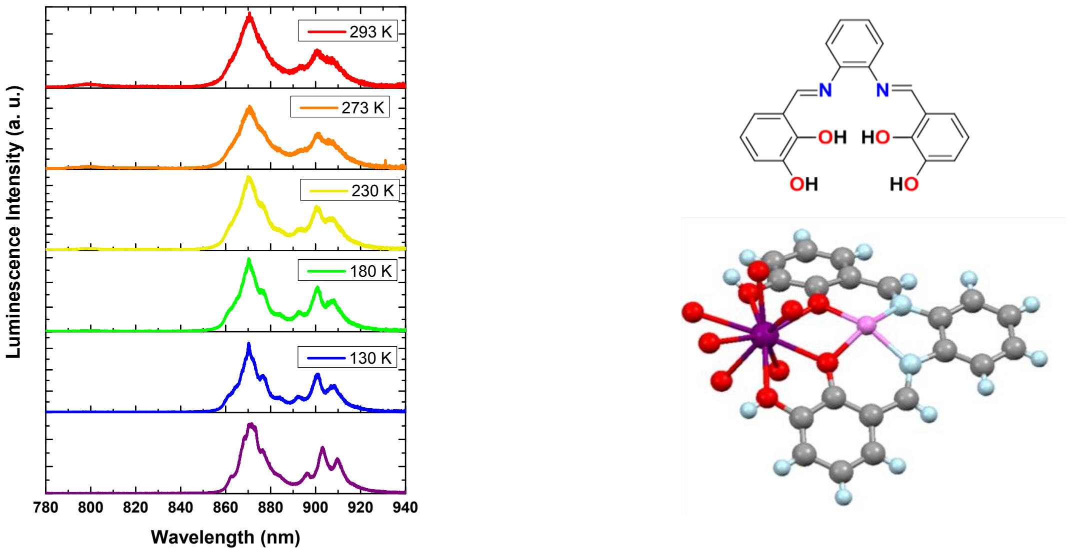

Fig. 1 Luminescence of $[NdCu(O_2NO)_3(L^a)]\cdot(H_2O)$ as function of temperature (left), between 293 (red) and 80 K violet; Ligand a (L^a) and proposed structure for $[NdCu(O_2NO)_3(L^a)]\cdot(H_2O)$ (right).

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Hybrid organic-inorganic light-harvesting antennae based on metal complexes

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For multiple institutions use a b (centered, arial, 12)
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An antenna for light harvesting is an organized multicomponent system in which many chromophoric molecular units absorb the incident light and then channel the excitation energy to a common acceptor component. Two different approaches will be discussed in the following: (i) a multiterpyridine system coupled to a hexathiobenzene benzene core exhibiting aggregation induced phosphorescence and (ii) Silicon nanocrystals (SiNCs) functionalised by metal complexes.

In the first system, Mg^{2+} complexation turns on phosphorescence of the hexathiobenzene core. [1] Metal ion coordination yields the formation of a supramolecular polymer which hinders intramolecular rotations and motions of the core chromophore, thus favoring radiative deactivation of the luminescent excited state. Upon excitation of the $[Mg(tpy)_2]^{2+}$ units of the polymeric structure, sensitization of the core phosphorescence takes place with >90% efficiency. The light-harvesting polymeric antenna can be disassembled upon fluoride ions addition, thereby switching off luminescence and offering a new tool for fluoride ion sensing.

The second approach is based on Silicon nanocrystals that, in the quantum size range (2-12 nm), can be made as viable light emitters with emission wavelength that can be tuned from the near-infrared (NIR) into the visible by decreasing their size. Covalent Si-to-carbon bonding also offers the possibility of integrating inorganic and organic components into robust structures. In the present work, the H-terminated nanocrystals were used as a platform for co-passivation with dodecene and Zn(II) tetraphenylpporphyrins by thermal hydrosilylation.[2] To the best of our knowledge this is the first time in which highly efficient light harvesting from photoactive units to the silicon core have been demonstrated.

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Stabilization and coordination properties of dearomatized PN ligands

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During the course of our research program aimed at exploring the behavior of non-innocent ligands in transition metal (TM) catalysis,[1] we became particularly interested in the use of (phosphinomethyl)pyridine (PN) ligands.[2] These are known to facilitate the activation of E-H bonds (N-H, S-H, B-H, C-H) thanks to reversible dearomatization process.[3] With the objective to replace TM by abundant and cheap elements, we have recently extended the coordination chemistry of these ligands to group 13 Lewis acids. Thanks to this platform, we were able to prepare and isolate dearomatized compounds that are usually considered as high energy intermediates (Figure 1).

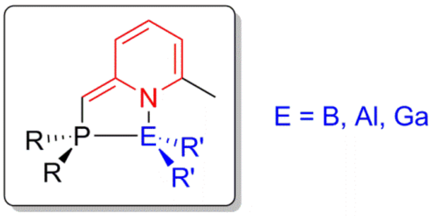

Figure 1. Group 13 for the stabilization of dearomatized PN ligands

Structurally related rhodium complexes could also be obtained starting from silyl-substituted compounds (Figure 2). The unusual bonding situations, as well as the similarities of these two types of coordination compounds will be discussed.

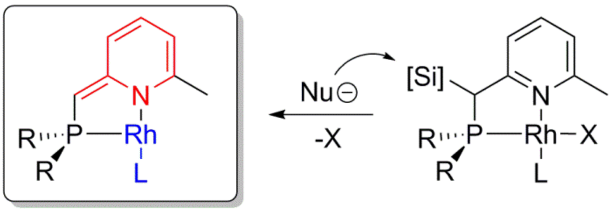

Figure 2. Dearomatization induced by an external attack on a silyl-substituted Rh complex

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Single-Source Precursors for the Synthesis of Energy Related Materials

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The presentation will describe recent advances in a design of heterometallic coordination compounds that can be used as single-source precursors for the low-temperature synthesis of energy-related materials. The ultimate goal of this research is to create heterometallic precursor with discrete molecular structure and with a proper metal:metal ratio for the target material. Several new strategies for a rational design of heterometallic compounds such as mixed-valent, mixed-ligand, and asymmetric ligand approaches will be discussed. These techniques were demonstrated to effectively bring about changes in the connectivity pattern within heterometallic assembly and to yield molecular precursors with required stoichiometry, while avoiding the formation of coordination polymers. Heterometallic precursors obtained in the course of this work were shown to be highly volatile and soluble compounds that are capable to provide the target oxide materials upon low-temperature decomposition. The applicability of the above approaches to the synthesis of single-source precursors for multiferroic oxides,[1] oxygen evolution reaction catalysts,[2] and prospective cathode materials of rechargeable batteries[3] will be presented.

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Conjugated Light-emitting Materials: New Strides on aSynthetic Polyaromatic Journey

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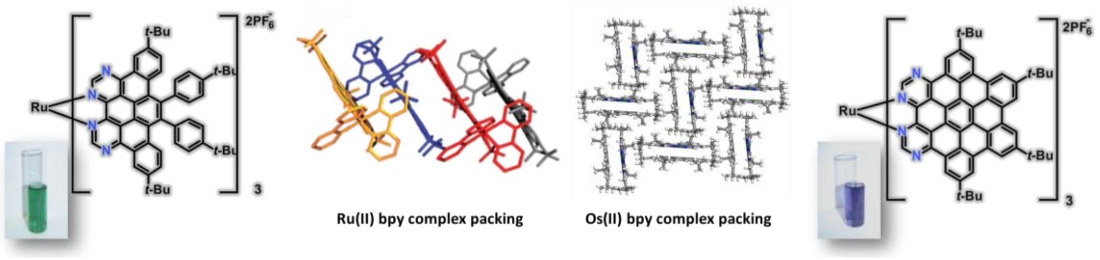
Over the last two decades great strides have been made in the development of new materials and device architectures which tap into the superior electronic and optical properties of heavy transition metal complexes e.g. as the phosphors in OLEDs where they offer 100% electro-harvesting of their singlet and triplet excitons (via spin-orbit coupling). To date the organic ligands at the forefront of literature investigations comprise polyimines (bipyridine, phenanthroline, terpyridine and quaterpyridine with/without anchoring groups), long-range electron transfer motifs such alkenyl and alkynyl linkers, polyaromatic donor functionalities such as anthracene and pyrene and hole and electron transporting units that include triphenylamine, bodipy and napthalamide.This paper will illustrate the valuable addition made to this field through the rare, extended, ligand motifs generated within the Draper team[1,2] (Figure 1). In particular it will look at the synthetic challenges that must be overcome in order to tap into the notable potential of these materials as photosensitisers and NIR emitters in new emerging technologies.[3]



Ru(II) bpy complex packing

Os(II) bpy complex packing

Figure 1(left and right) The dramatic effect of reduced aromaticity on the absorption properties of trishomoleptic Ru(II) complexes of N-HSB; (centre) the dimeric "paved" lattice-packing for the $[(bipy)_2Os(NHSB)]^{2+}$ complex, and the off-set stack of its Ru(II) analogue.

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Complexes of divalent transition metal chlorides with the tetradentate Schiff base ligand

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ABSTRACT

The transition metal (II) chlororides complexes of Shiff base ligand 1.2-bis(4-pyridylcarboxaldehydeethylenediimine) (L1) and 1.2-bis(4-pyridylcarboxaldehyde-hexamethylenediimine) (L2) derived from 4-pyridinecarboxaldehyde and ethylediamine, hexamethylenediamine respectively. The compound of $[Cu_2L_1Cl_4]2H_2O$, $[Fe_2L_1Cl_4]2H_2O$, $[Cu_2L_2Cl_4]2H_2O$, $[Co_2L_1Cl_4]2H_2O$, $[Fe_2L_2Cl_4]2H_2O$, were prepared.

The complexes were characterized by elemental analyses, conductivity mesurements, magnetic susceptibilities and spectroscopic (IR and ^{1}H-NMR for ligand) studies.

The complexes of Schiff base found applications in fields as diverse such as the catalysis [1-4], the molecular magnets [5], artificial photosynthesis [6] and the biomimetic chemistry [7-12].

Keywords : divalent transition metal, Schiff Base, complexes,4-pyridinecarboxaldehyde.

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Synthesis of a novel terpyridine based from carbazole and its approach to NO (nitric oxide) release.

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In the last decades nitric oxide (NO) has been recognized to possess a variety of physiological and pathological functions, which has stimulated the need for efficient NO donors. Among them, Ruthenium nitrosyls are the most promising candidates due to (i) their inherent stability in aqueous media compared to other metal complexes, (ii) their relatively low toxicity and (iii) the fact that they release NO only when exposed to light, making them ideal candidates for photodynamic therapy.

Our team has recently reported on a $[Ru^{II}(FT)Cl_2(NO)]^+$ complex[1] (FT = fluorenyl-terpyridine, stable in the dark, but able to release NO by a "push-pull" charge transfer mechanism induced under irradiation at 405 nm.

Seeking to increase the NO release efficiency, we are now targeting ligands that can act as better electron donors in order to increase the charge transfer capabilities and hence the amount of NO released. After a general introduction of our strategies and first achievements, the effect of the introduction of a carbazole fragment will be presented and discussed in relation to its "push-pull" or quadratic geometries in a perspective of application through a two photon absorption excitation.

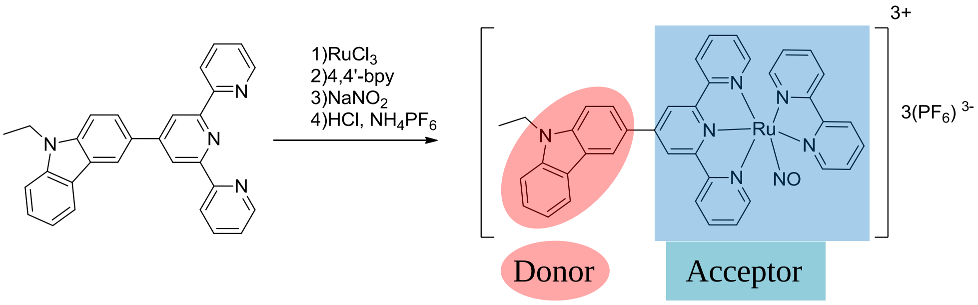

Figure 1 Synthesis of "push-pull" carbazole-terpyridine metal complex

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New entries in borabenzene chemistry: exploring novel coordination modes on reactivity

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Since the first synthesis of a borabenzene complex by Herberich in 1970, these heterocyclic species have been coordinated in a η^6 fashion to most transition metals, either as an analogue of benzene or as anionic analogues of the ubiquitous cyclopentadienyl ligands.[1] We have been interested in the past few years in looking at unusual coordination modes for borabenzene ligands where the exocyclic moiety of the boratabenzene ring, namely a chloride[2] or a phosphide functional group[3], interacts with the metal center (Figure 1). This presentation will focus on the synthesis and on the reactivity of these organometallic boratabenzene complexes.

Figure 1 Cl-boratabenzene of platinum(II) (A) and *t*Bu$_2$P-boratabenzene species of late transition metals (M = Pt, Ni, Rh, Cu, Fe).

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Blue thiohydrazide coordination compounds of platinum(II): synthesis, characterization and biological activity against some cancer cell lines

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The blue platinum complexes including classical “platinblau” that has been reported only a few was characterized. They were shown to be tetranuclear complexes containing three platinum(II) and one platinum(III) bridged through N,O- donor ligand like α-pyridonate or α-pyrrolidonate ion. The blue color originates from inter-valence electron transfer and Pt – Pt distance is around 3 Å in these compounds. A new class of “platinum blue” complexes[1] of some substituted thiosemicarbazide ligands has been characterized by a combination of spectroscopic methods.

Blue diamagnetic platinum complexes of four aromatic thiohydrazide ligands, namely, thiobenzhydrazide, 2-hydroxytiobenzhydrazide, furan-2-thiohyazide and thiophene-2-thiohrazide have been synthesized and characterized by spectroscopic methods. The structure of one compound, bis2-hydroxythiobenzhydrazidoplatinum has been determined by X-ray crystallography. The complex has planar structure and the metal bound nitrogen and sulfur atoms are in trans position. The nearest distance between two platinum atoms is 7.386 Å. The blue color of the complexes is due to metal to ligand charge transfer.

The biological activity of bis2-hydroxythiobenzhydrazidoplatinum(II) was evaluated in a prostate cancer PC3 and a lung adenocarcinoma cell lineA549. The compound induces apoptosis to both of them. Cells incubated overnight with the compound showed signs of membrane blebbing and condensed DNA, suggesting apoptotic cell death. The IC50 value of in PC3 cell line was 0.5 microgram/ml and A549 was 1.2 microgram/ml. Another feature of this compound was the formation of numerous micronuclei formation and an increase in the number of multinucleated cells.

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The reaction of Re(V) precursors and orotic acid: Re^{IV}-Re^{IV} dimers, Re^{III}/Re^{V} monomers and decarboxylation

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As a result of its position in the Periodic Table, rhenium displays a wide variation in its coordination chemistry and structures in oxidation states from -1 to +7. The reaction therefore of rhenium(V) with versatile ligands may lead to interesting and unexpected coordination compounds, and to this end we have focussed on orotic acid (H_2or) as a possible ligand.

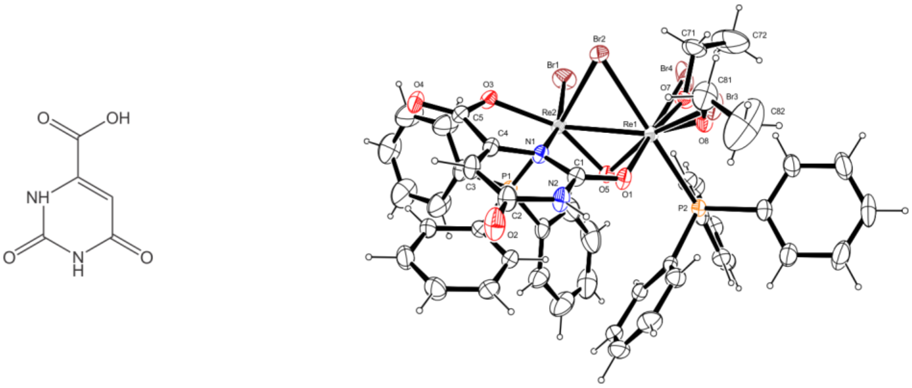

Figure 1. Line structure of orotic acid and crystal structure of 1.

The reaction of H_2or with *trans*-$[ReOBr_3(PPh_3)_2]$ in ethanol produced the triply-bridged $Re^{IV}{\equiv}Re^{IV}$ dimer $[Re_2(\mu\text{-}Br)(\mu\text{-}O)(\mu\text{-}or)Br(OEt)_2(PPh_3)_2]$ (**1**). In order to eliminate the oxo group as a bridging ligand, the imido-coordinated $[Re^{V}\{=NC_6H_4(2\text{-}NH_2)\}Br_3(PPh_3)_2]$ was used as starting material, giving the monomer $[Re\{NC_6H_4(NH_2)\}Br(or)(PPh_3)_2]$. By utilizing the *trans*-dioxo cation $[Re^{V}O_2(py)_4]^+$ as starting complex, in order to remove PPh_3 as a possible ligand, the monomer $[ReO(OEt)(or)(py)_2]$ was isolated. Surprisingly, the reaction of *5-amino*-orotic acid (H_2aor) with $[ReOBr_3(PPh_3)_2]$ produced the complex $[Re^{V}(apd)Br(aor)(PPh_3)_2]$ (apd^{2-} = 5-imidopyrimidine-2,4-dione). The ligand apd^{2-} is formed by the decarboxylation of H_2aor, and it is coordinated *via* the dinegative imido nitrogen only. This study has also been extended to the related 6-hydroxypicolinic acid as ligand.

The syntheses, spectroscopic results and X-ray crystal structures of these and related compounds will be presented.

Coordination Chemistry-Derived Scaffolds for Developing Anticancer Agents

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Coordination chemistry provides key advantages over traditional organic synthesis in the development of anticancer agents. Not only can the three-dimensional structure of a molecule be changed in a rapid manner, but multiple physiochemical features can be "tuned" through the choice of the metal center, oxidation state, coordinated ligands, or counter ions. In parallel, inorganic compounds possess features that can be exploited for use as pro-drugs to be activated by light, electrons, or nucleophiles. Furthermore, their properties often facilitate biological evaluation by tracking within tissues or cells. We have explored the potential of ruthenium-based coordination compounds as anticancer agents by developing scaffolds that can be activated by light to transform into potent chemotherapeutics with sub-micromolar activity.[1-3] We are assessing how charge,[4] choice of co-ligands,[5] and complex geometry affect subcellular localization, affinities for specific biomolecules, and biological properties within cancer cells. We are also learning how the reactivity with biological nucleophiles can be modulated by adjusting structure and distortion in the coordination sphere.[6] These ruthenium compounds can be designed to target different nucleic acid structures, such as G-quadruplexes and triplexes,[7-9] or proteins within the cell, providing the ability to regulate the mechanism of action. The potential to develop ruthenium agents that target various essential cellular processes such as transcription, translation, and protein degradation will be presented.

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Thermodynamics and kinetics in self-assembled supramolecular systems with lanthanides

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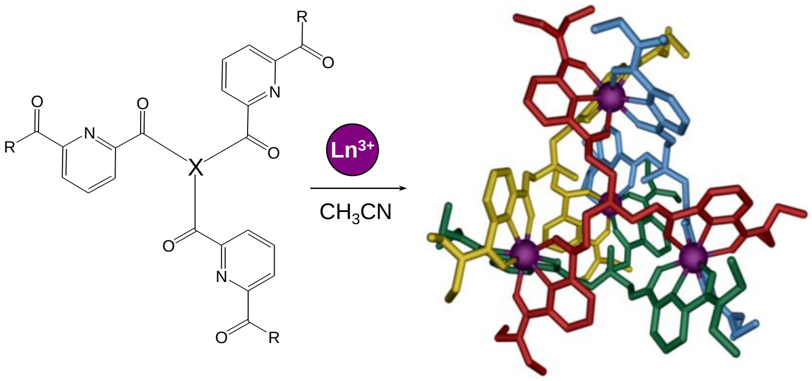
After a strong development of structural supramolecular chemistry in 1990s, people started to be more interested in thermodynamics and kinetics of self-assembly processes. These studies were particularly rare for lanthanide-containing systems and the first self-assembly process with lanthanides, a dinuclear triple-stranded helicate, was characterized from the mechanistic point of view only in 2003 by us.

In this contribution we focus on thermodynamics and kinetics in the self-assembly of different polynuclear lanthanide helicates. We present the mechanistic study of dinuclear systems and the key reaction steps in details. When the system complexity increases, the kinetic evolution slows down due to an increased number of self-repairing steps. This behaviour is shown for lanthanide assemblies derived from tripodal polytopic ligands.[1,2,3] In addition, the metal exchange and the size discrimination along the series are discussed.

Figure 1 Self-assembly process leading to polynuclear tetrahedral edifices.



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New Roles for Classic Cobalt Chemistry

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Cobalt(III) is an ion with a venerable and distinguished history in coordination chemistry. It was one of the key ions for Werner and Jørgensen, as they set about preparing the compounds on which coordination theory was based, and was central to many of the mechanistic studies of the ‘50s, ‘60s, and ‘70s. Now we are exploring its potential use in medicine, as part of dinuclear Ru(II)-Co(III) assemblies, and, in passing, we have developed some classic Werner-type chemistry as well as functional group chemistry on coordinated ligands.

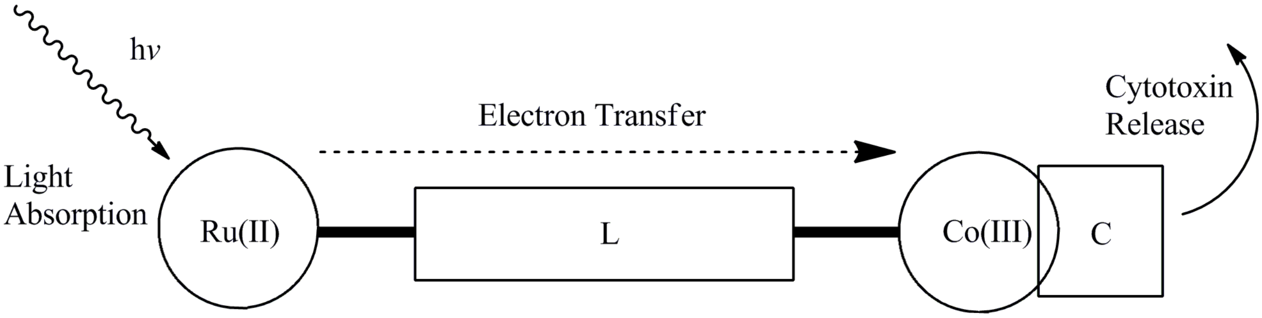

Figure 1 Schematic of a photoactivated cytotoxin

Photoinduced electron transfer from Ru(II) to Co(III), through a bridging ligand (L), has been shown to result in ligand release from the Co centre.[1] The synthetic challenges are to put the metal centres in the right places and to prepare systems containing cytotoxic ligands without having to handle the free cytotoxin. The cytotoxin is much less reactive when bound to the inert Co(III) centre and can be prepared late in the synthesis, on the metal ion, after coordination of a precursor molecule

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Reactive Metal-Carbon Bonds in Three-Coordinate Iron and Cobalt NHC Complexes.

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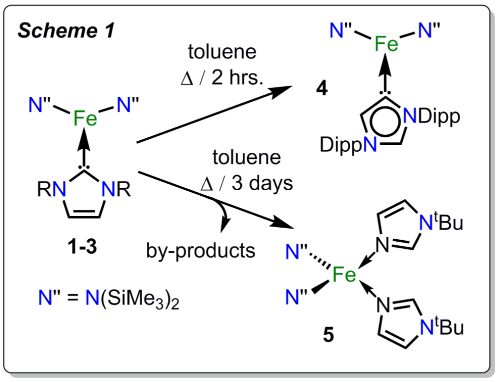
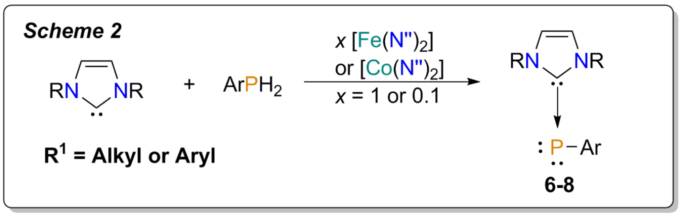
The use of NHC ligands in iron chemistry is a growing topic with applications in the stabilization of novel coordination environments and unusual oxidation states, biomimetic chemistry, and homogeneous catalysis.[1]


Scheme 1

We recently reported the three-coordinate iron-NHC complexes [(IPr)Fe(N′′)$_2$] (**1**), [(IMes)Fe(N′′)$_2$] (**2**),[2] and [(I^{t}Bu)Fe(N′′)$_2$] (**3**) (Scheme 1), and our initial studies of the reactivity of **1-3** have produced some unexpected results. Refluxing **1** in toluene results in a normal-to-abnormal rearrangement of the NHC, giving [(*a*IPr)Fe(N′′)$_2$] (**4**) (Scheme 1). Refluxing **3** in toluene affords a C–H/C–N activation reaction, in which a ^{t}Bu substituent is eliminated from the NHC ligand as isobutene. The same outcomes were observed with the cobalt analogues of **1-3**.[3]


Scheme 2

We have recently reported the reactivity of [(NHC)M(N’’)$_2$] (M = Fe, Co) towards primary phosphines. Reacting [(IMe$_4$)M(N’’)$_2$] with mesityl phosphine produced the phosphinidene-bridged dimers [(IMe$_4$)$_2$Co(PMes)]$_2$. In an attempt to form a terminal phosphinidene complex bulkier NHCs were utilised. Unexpectedly, these reactions yielded carbene-phosphinidene adducts (**6-8**) (Scheme 2). Remarkably, **6-8** can be formed using a stoichiometric or catalytic amount of [M(N’’)$_2$]. Overall, the observations depicted in Scheme 2 provide evidence for metal-catalyzed phosphinidene transfer.[4]

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Unusual Coordination Chemistry with Flexible Bis-phospholane-Based Ligands: Macrocycles, Chains and Nanotubes

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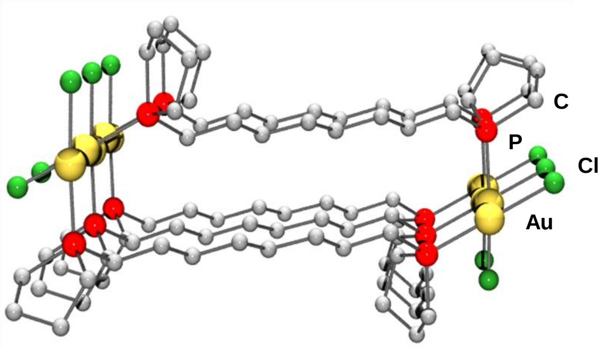
Since the development of the chiral bis-phosphine ligand DuPHOS by Burk *et al.* at DuPont, phospholane chemistry has been in the focus of interest.[1] Phospholanes are five-membered rings containing phosphorus and belong to the so-called "privileged structures".[2] Due to the rigidity of the phospholane moiety, their corresponding transition metal complexes have found a wide range of applications in asymmetric catalysis, e.g., in hydroformylation. However, bis-phospholane ligands with long flexible or rigid spacers are scarce. These ligands are expected to combine the excellent properties of phospholanes with a backbone which allows them to be used as bridging ligands between metal-complex fragments. Selective formation of macrocycles ("nanoframes", up to 28-membered rings), cages or chains is observed, without using high-dilution techniques, depending on the number of carbon atoms in the ligand backbone of highly flexible bis-phospholane ligands. For gold(I), additionally polymeric chains or nanotubes (see Figure) are formed via aurophilic interactions.

First examples of the fascinating coordination chemistry of highly flexible bis-phospholane ligands having five to eleven methylene groups in the backbone with transition metals (e.g., Rh, Ni, Pd, Pt, Cu, Ag, Au) will be presented.



Financial support from the VCI (doctoral grant for A.S.), the European Union and the Free State of Saxony (M.S., R.H.), the Marie Curie ITN SusPhos, Grant Agreement No. 317404 (P.C.B.) and the Graduate School BuildMoNa is gratefully acknowledged.

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Luminescent Copper(I) Complexes Exhibiting Chromic Phenomena

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Recent developments of luminescent copper(I) complexes are remarkable and some copper(I) complexes exhibit interesting chromic behaviors of luminescence in response to outer stimuli such as temperature, vapor, and mechanical force. The copper(I) complexes are also intriguing for their versatile structures: Mononuclear complexes with relatively low coordination numbers, various types of multinuclear clusters, and infinite chains or coordination polymers. This presentation focuses on mono- and multi-nuclear copper(I) complexes with $\{Cu_nX_n\}$ cores (X = halide, n = 1, 2, 4)[1-3] and $\{Cu_nS_n\}$ cores (n = 2, 4, 6) which show strong luminescence and the color changes in the solid-state.

Mononuclear copper(I)-halide complexes, $[CuX(PPh_3)_2(L)]$ (L = *N*-heteroaromatics) (Fig. 1a) exhibiting very intense luminescence can be prepared by easy procedures such as simple manual grinding.[1] A dinuclear copper(I) complex bearing dimethyl sulfoxide (dmso), $[Cu_2(\mu\text{-}I)_2(dmso)_2(PPh_3)_2]$ (Fig. 1b) exhibits unique photochromic luminescence on the basis of the flip and release of the dmso molecules.[2] We also succeeded in the fabrication of luminescent porous coordination polymers (PCPs) containing $\{Cu_2I_2\}$ and $\{Cu_4I_4\}$ cores.[3] Interestingly, the $\{Cu_4I_4\}$ PCP only exhibits vapochromic luminescence. Thiolato-bridged hexanuclear cluster with a flexible core (Fig.1c) shows thermochromic luminescence. The characteristic luminescence properties of these complexes will be discussed.

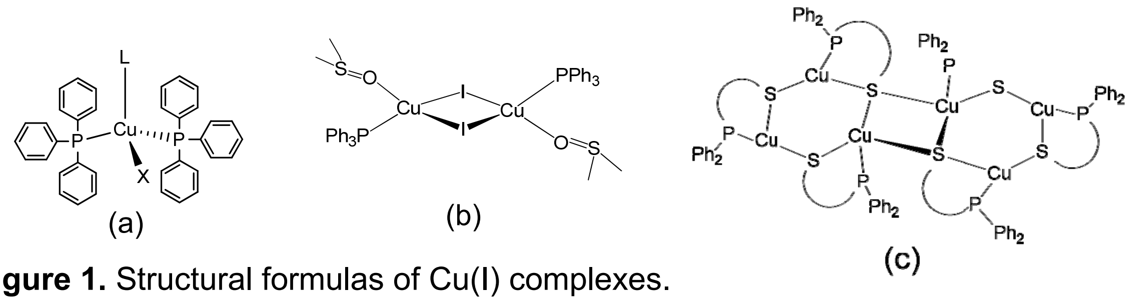

Figure 1. Structural formulas of Cu(I) complexes.

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New complexes of Pd(II) and Pt(II) with 1-phenyl-1,4-dihydrophosphinoline ligands

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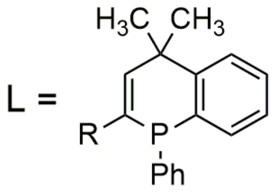
Complexes of platinum and related metals such as Pd, Ir, Rh, Ru contained phosphine ligands are widely employed in homogeneous catalysis as well as getting used to being attractive candidates for a theoretical study. A few examples *viz.* 1,4-dihydrophosphinolines **1** and **2** of a new class of heterocyclic phosphines have been obtained and fully characterized in our laboratory recently. Here we report the synthesis of Pd(II) and Pt(II) complexes contained these phosphine ligands and full account study of their structure in solid state as well as in the solution.

Reaction between nitrile complexes $[PdCl_2(NCCH_3)_2]$ (**3**) or $[PtCl_2(NCCH_2CH_3)_2]$ (**4**) with phosphines **1** or **2** proceeds in CH_2Cl_2 at r.t. for *ca*. 1 d giving$[MCl_2L_2]$ species **5**–**8**in good (82–94 %) isolated yields.



1: R = H
2: R = Br

$$\underset{\mathbf{3},\ \mathbf{4}}{[MCl_2(NCR)_2]} + \underset{\mathbf{1},\ \mathbf{2}}{2\ L} \xrightarrow[-2\ NCR]{} \underset{\mathbf{5}\text{–}\mathbf{8}\ (82\text{–}94\%)}{[MCl_2(L)_2]}$$

3: M = Pd, R = CH_3
4: M = Pt, R = C_2H_5

***trans*-5**: M = Pd, L = **1**
***cis*-6**: M = Pt, L = **1**
***trans*-7**: M = Pd, L = **2**
***trans/cis*-8**: M = Pt, L = **2**

Complexes **5**–**8**were characterized by high resolution ESI$^+$-MS, ^{1}H, ^{13}C{^{1}H, ^{31}P}, ^{31}P{^{1}H} and ^{195}Pt NMR spectroscopies. In addition, the structures of all complexes were elucidated by a single-crystal X-ray diffraction.The configuration of the complexes was investigated via comparing of ^{31}P NMR data in $CDCl_3$solution and solid state.

This work has been supported by Russian Foundation for Basic Research (grants16-33-60123 мол_а_дк and 14-03-00297 а). The authors acknowledge the financial support from Saint Petersburg State University.Physicochemical studies were performed at the Center for Magnetic Resonance, Center for X-ray Diffraction Studies, and Center for Chemical Analysis and Materials Research of Saint Petersburg State University.

Photochemical property and reactivity of NAD$^+$/NADH Functionalized Ru complexes

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Ru complex bearing pbn as an NAD functionalized ligand (Figure 1 left) can store photoenergy through the pbn localized two-electron reduction producing pbnHH (pbnHH, Figure 1 right) as an NADH mode.[1,2] The treatment of Ru-pbnHH with strong base created the hydride donor ability of the complex, since the complex reduced CO_2 to produce $HCOO^-$.[3] From the viewpoint of the importance of renewable organic hydride donor, we newly designed NAD/NADH functionalized 1,10-phenanthroline ligand (bpp), and investigated the photochemical property and reactivity of the Ru complex, $[Ru(bpp)(bpy)_2]^{2+}$ (**1**, Figure 2 left).[3]

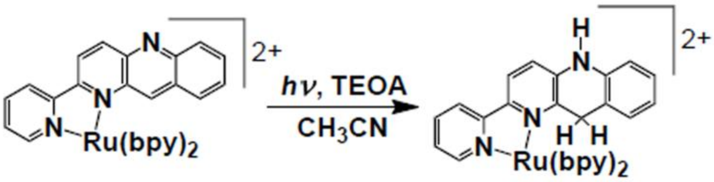
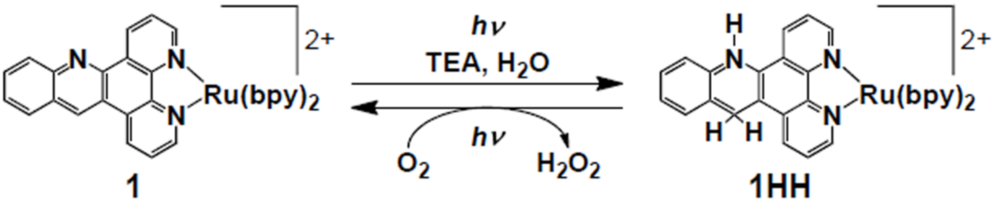


Figure 1 Photo chemical reduction of Ru-pbn complex.

Complex **1** (Figure 2 left) underwent photochemical reduction by the visible light irradiation in $CH_3CN/TEA/H_2O$ (8/1/1, TEA: trimethylamine) to form Ru-bppHH (**1HH**, Figure 2 right) as an NADH form. Both **1** and **1HH** showed two emission bands around 600 nm with good quantum yields. Visible right irradiation of **1HH** under air regenerated **1** with producing H_2O_2.[4]



1 **1HH**

Figure 2 Photo reduction and oxidation of Ru-bpp (**1**) and Ru-bppHH (**1HH**)

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Redox-Noninnocent Behavior of Tris(2-Pyridylmethyl)amine in a Lewis-Acidic Rh(III) Coordination Sphere

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Kazunari Yoshizawa,[b,c] Takahiko Kojima[a,*]
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[b] Institute for Materials Chemistry and Engineering, Kyushu University, Motooka, Nishi-Ku, Fukuoka 819-0395, Japan
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Metal-ligand cooperation has gathered much attention as a new strategy to produce new functionality of metal complexes. Tris(2-pyridylmethyl)amine (TPA) and its derivatives have served as useful spectator ligands to provide functional coordination spheres and to perform various catalytic reactions including substrate oxidations. However, redox-noninnocent behavior of versatile TPA ligands has yet to be reported.

In this study, we revealed that TPA (L_1-H6) and its derivative having methoxycarbonyl groups at the 5-positions of pyridine rings of TPA (L_2-H6) bound to a Lewis-acidic Rh(III) ion could undergo reversible and site-selective deprotonation of the axial methylene proton. The deprotonated species, [$RhCl_2(L_1$-H5)] and [$RhCl_2(L_2$-H5)], can be oxidized to afford carbon-centered ligand radicals formed in the axial pyridylmethyl moieties in both cases (Figure 1).[1] This is the first example to demonstrate redox-noninnocent characteristics of TPA induced by C-H deprotonation of the methylene moiety.

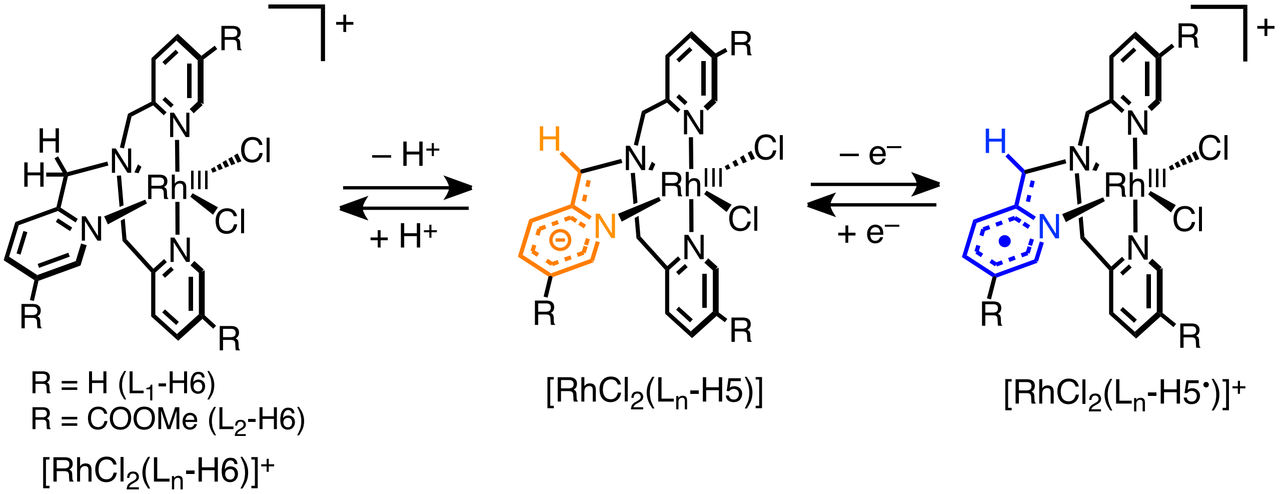

Figure 1 Deprotonation of [$RhCl_2(L_n$-H6)]$^+$ and subsequent oxidation to form Rh(III)-bound TPA radicals.

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Heterometallic Nitrido and Oxo Complexes Supported by Kläui's Tripodal Ligand

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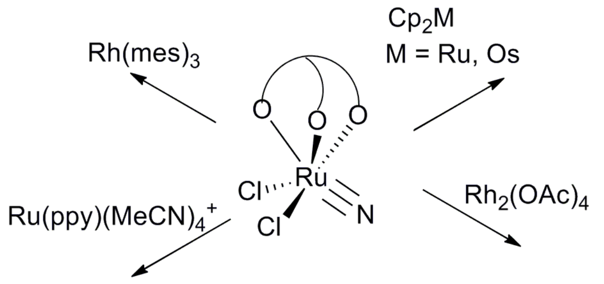
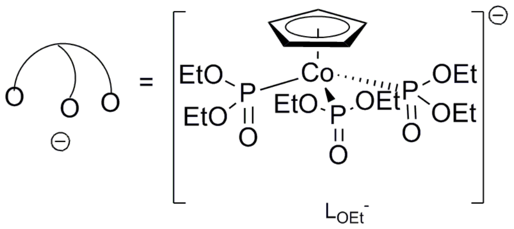
Nitrido- and oxo-bridged bimetallic complexes have attracted attention due to their interesting redox and magnetic properties and their potential applications in catalysis. The dinuclear M-O-M systems play key roles in catalytic oxidations in chemistry and biology. Recent work has shown that the μ-nitrido ligand can stabilize highly active dimetal oxo species that can oxidize alkane C-H bonds.[1] Herein, we report the synthesis and structures of heterobimetallic nitrido and oxo complexes supported by the Kläui's tripodal ligand $[CpCo\{P(O)(OEt)_2\}_3]$- (L_{OEt}^-). Heterometallic Ru-N-M complexes have been synthesized from reactions of the Ru(VI) nitride $[(L_{OEt})Ru(\equiv N)Cl_2]$ with organo-ruthenium and rhodium complexes[2] and metalloporphyrins. Also, heterometallic Ce-O-M complexes and clusters have been synthesized from $[Ce(L_{OEt})_2X_2]/[Ce(L_{OEt})Cl_3]$ and oxo-metal complexes. The catalytic activity of Ce-O-M complexes in organic oxidations will be reported.





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Acknowledgement. This work was supported by the Hong Kong Research Grants Council (16301815).

Tuning the Electronic Effects of Phosphinines: From π-Acceptor to π-Donor Ligands

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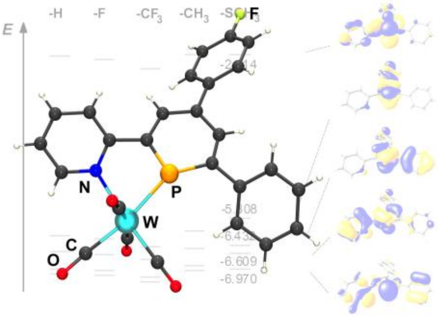
Even though 2,4,6-triphenylphosphinine was first synthesized in 1966 by Märkl,[1] these aromatic heterocycles are less well-researched than their lighter analogues, the pyridines, for which a broad range of applications is known. Since phosphinines are structurally related, but show differences in electronic, steric and coordination properties, they are interesting for future applications. In contrast to pyridines phosphinines are poor σ-donors and good π-acceptors.[2] With 2-(2-pyridyl)-4,6-diphenylphosphinine our group developed a P,N-hybrid ligand.[3] It was used in the preparation of various transition metal complexes and compared to the corresponding bipyridine based coordination compounds.[4] In a next step we are now aiming for controlled modification of the electronic- and coordination properties *via* introduction of substituents in *para*-position on the 4- or 6-phenyl ring. A MeS-, a MeO- and a CF_3-group as well as a fluorine atom were chosen as substituent.

The new ligand systems have been successfully synthesized and characterized. Subsequently, they have been converted into the corresponding $[(P,N)W(CO)_4]$ and $[(N,N)W(CO)_4]$ complexes, as such compounds allow an facile analysis of the bonding situation. In order to compare the electronic properties of the different ligands, the CO stretching frequencies of the heteroleptic tungsten carbonyl complexes were investigated *via* IR spectroscopy. Strikingly, we could prepare for the first time a phosphinine derivative, which shows significant π-donor properties, in contrast to previous assumption. The influence of the substituents was demonstrated through changes in the $\tilde{\nu}$(CO) band in the IR spectra and confirmed by DFT calculations.[5]



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Synthesis of bisarylamine ligands with Schiff base arms and their reaction with first row transition metal ions

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First row transition complexes with macrocyclic ligands that feature 2,2'-diimine-diphenylamine ligands have been shown to have interesting spin state and electrochemical properties.[1] Initial work into related non-cyclic Schiff base diphenylamine ligands unexpectedly resulted in the spontaneous formation of an acridine moiety when the amine and cobalt(II) salt were added to the dialdehyde head unit (Figure 1), with the resulting acridine-based ligand isolated as a four coordinate cobalt(II) complex (**1**). Subsequently the intended complex (**2**) was obtained by instead isolating the ligand first, then complexing it (Figure 1).[2] Recent results from investigations into a wider range of coordination complexes with acyclic and macrocyclic ligands, featuring diphenylamine and related head units, will be presented.

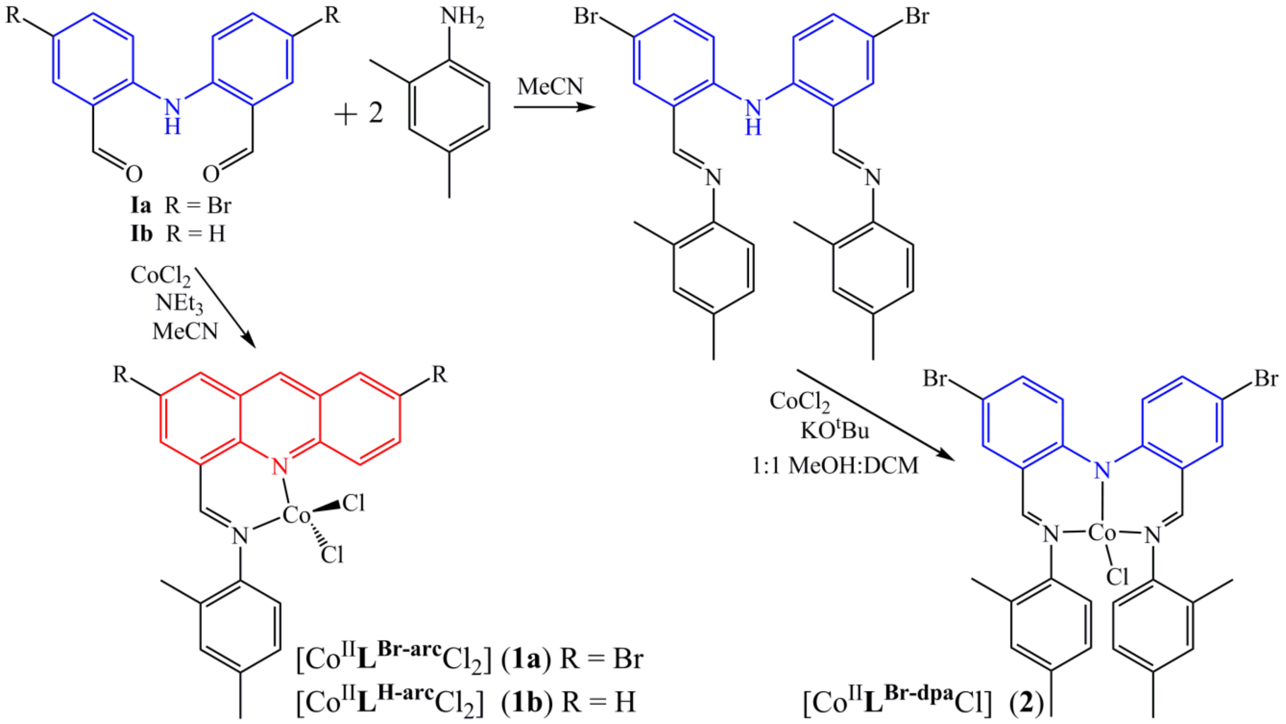

Figure 1: Formation of cobalt(II) complexes (**1**) and (**2**) featuring acridine or diphenylamine ligands respectively, starting from 2,2'-iminobisbenzaldehyde.

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Dinuclear zinc disalphen complexes: syntheses, properties and photophysical behaviour

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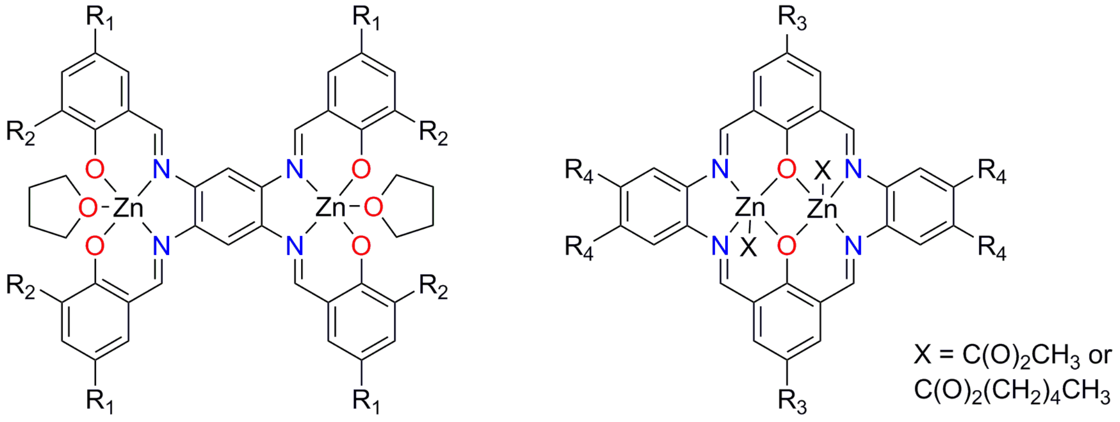
A series of dinuclear zinc complexes which are coordinated by derivatives of the 'salphen' ligand are reported, including 'open' and macrocyclic ligands, as illustrated in the figure below. The complexes have been characterized by ^{1}H NMR spectroscopy, mass spectrometry, and elemental analysis. In addition, their photophysical properties and stabilities have been investigated in order to determine their suitability as new emitting materials for organic light emitting diodes (OLEDs) and other light emitting applications. The investigation has so far found that the solution and solid state emission from these complexes varies significantly between the open and macrocyclic structures, as does their stabilities. The open structures tend to be highly emissive in solution and the solid state, although their stabilities were found to be significantly lower than the macrocyclic structures. Whereas the highly stable macrocyclic structures were found to have significantly higher emission in the solid state compared to solution. The syntheses of the zinc complexes, along with the preliminary results on their emission in solution and the solid state are to be presented.



Dinuclear zinc salphen complexes

Dinuclear zinc salphen macrocyclic complexes

Figure 1 Generic structures of the dinuclear zinc disalphen complexes investigated.

Facile Ring Expansion Reactions of N-Heterocyclic Carbenes with Zinc and Diboron(4) Compounds

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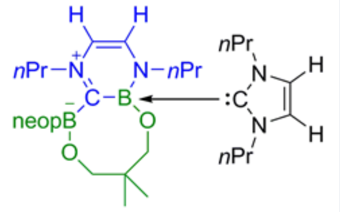
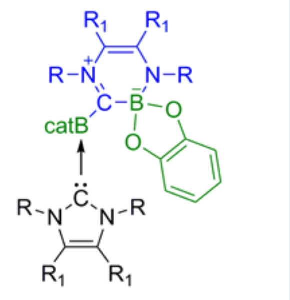


RER 4



RER 1 and **RER 2**

The use of NHC's[1] as ligands in homogeneous catalysis and directly in organocatalysis, including recently developed borylation reactions, is widespread.[2] Recently, several examples[3] of ring expansion reactions (RER) involving NHCs were reported to take place at elevated temperatures, with Be, B, and Si. We report NHC ring-expansions upon reaction with diboron (4) giving products of types RER 1 and RER 2 under very mild conditions demonstrating that ring expansion and B–B bond cleavage can be a very facile processes.[3b] We have also observed both B and Zn insertion into NHC's as a catalyst deactivation pathway in a Zn-catalyzed C-X borylation process.[3d]

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Harnessing Reversible Electronic Energy Transfer : From Molecular Dyads to Molecular Machines

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Reversible electronic energy transfer (REET) may be instilled in bi-/multichromophoric molecule-based systems, following photoexcitation, upon judicious structural integration of matched chromophores.[1] This leads to a new set of photophysical properties for the ensemble, which can be fully characterized by steady-state and time-resolved spectroscopic methods. Combining transition metal complexes with matched organic chromophores has proven a reliable strategy to instil this process, taking into account specific kinetic and energetic considerations. Herein, we show some examples of this type of supermolecule, which has seen systems evolve from covalently-tethered dyads[2] to synthetic molecular machines, exemplified by two different pseudorotaxanes.[3,4] Indeed, REET holds promise in the control of movement in molecular machines or assembly / disassembly as well as photosensitizers for charge separation.

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Coordination chemistry of a Diphosphine-Ketone Ligand with Mid-to-Late First-Row Transition Metals

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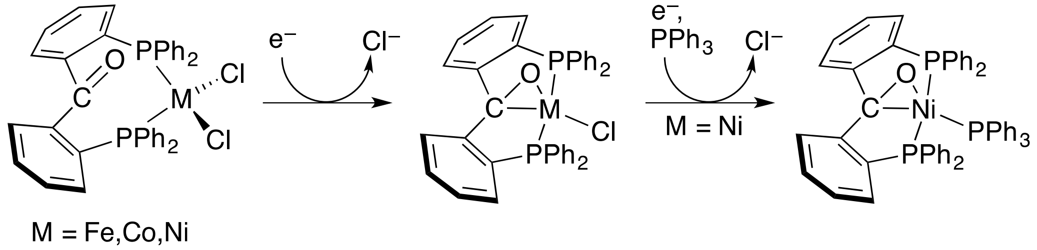
The development of greener and cheaper chemical processes motivates a widespread investigation of complexes of first-row transition metals as potential homogeneous catalysts to replace or, better, improve on traditional systems that are widely based on noble metals.[1] Progress in this area has been intimately related to the development of tailored ligands: cooperative ligands that actively participate in chemical reactions and hemilabile ligands that facilitate reaction steps by adapting their coordination mode to the electronic structure of the metal center along the reaction coordinate.[2]



In this contribution, we investigate the chemistry of a diphosphine-ketone ligand[3,4] (dpbp, Scheme 1) with mid-to-late transition metals (Ni, Co, Fe). The dpbp ligand acts as a wide bite angle for MCl_2 fragments; moving to more reduced states (Fe(I), Ni(I), Ni(0)) results in coordination of the ketone moiety in an η^2(C,O) fashion, forming pincer-like structures. Possible implications for small-molecule activation and catalysis are discussed.

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Coordination complexes of aminophenol-based redox-active ligands. Ligand-radical-driven bond-forming reactions

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Generation of ligand-radicals can lead to interesting ligand-centered reactivity, with the mechanism of galactose oxidase serving as an inspiration for synthetic inorganic chemists. The design of metal complexes to catalyze multielectron reactions usually relies on one or more transition-metal ions capable of two-electron changes in a formal oxidation state. An alternative strategy to multielectron chemistry employs redox-active ligands, as reservoirs of electrons to supply oxidizing or reducing equivalents for bond-breaking and bond-making reactions at coordinatively unsaturated metal complexes.[1]

In this presentation, an account of detailed molecular (X-ray), spectroscopic and magnetic, and reactivity (redox) aspects of a number of ligand radical-coordinated metal complexes involving a group of redox-active ligands to correctly assign the spin-state of the metal and oxidation level of the coordinated ligands will be discussed. Our designed chelating ligands provide bis-phenolate(2−) and phenoxyl(1−) radical, *o*-amidophenolate(2−), *o*-iminobenzosemiquinonate(1−) π radical and *o*-benzoquinone forms of the coordinating ligands. The electronic structure of the complexes is then rationalized by the Density Functional Theory (DFT) and Time-Dependent (TD)-DFT calculations, which successfully rationalize the observed properties of the complexes. Radical-driven reactivity aspects (N–N, –C–N– and –O–C–O– bond formation) will be discussed.

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Oxygen Responsive Emission in the Solid State Based on Copper(I) Complexes Bearing Fluorinated Diphosphine Ligand

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Copper complexes are important for photofunctional materials and bioinorganic chemistry.[1,2] On the other hand, luminescence in the solution state due to long-lived excited state is well-known to be quenched by oxygen through energy transfer. However, reports for oxygen responsive luminescence in the solid state are limited, because oxygen is difficult to diffuse inside of the solid.[3]

Oxygen quenching in the solid state of our several highly emissive metal complexes with long-lived excited state is found to be negligible.[4,5] In contrast, the copper(I) complex bearing 6,6'-dimethyl-2,2-bipyridine and 1,2-bis(bis(pentafluorophenyl)phosphino)ethane ligands (**1**) shows drastic oxygen responsive abilities in the solid state.[6] For example, emission under the vacuum is very strong, while that under the air is negligible (Figure 1). The emission lifetime under the argon is more than 100 μs, which is much larger than those of typical copper(I) complexes bearing a diimine ligand. X-ray structural analysis reveals that the voids are found in the single crystal. These factors play a key role in oxygen responsive emission in the solid state. The oxygen responsive abilities are observed even at 423 K, because the thermally activated delayed fluorescence significantly contributes to the emission.

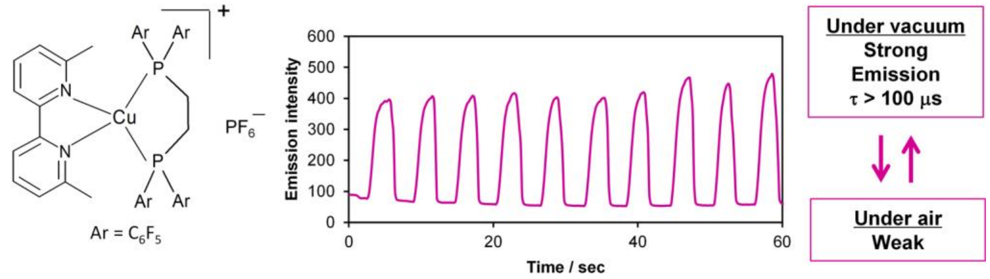

Figure 1 Chemical structure of **1** (left) and time course of the emission intensities in the solid state upon repeated operations of exposing the sample to vacuum and to air (right).

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The good without the bad: selective chelators for beryllium encapsulation

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Beryllium is an indispensable metal. Its unmatched combination of unique properties such as extreme strength, low density and high machinability has made it vital in the automotive, nuclear, space, medical, defence sectors and other consumer industries. However, beryllium is considered the most toxic non-radioactive element on the planet. It is also a class one carcinogen and the cause of chronic beryllium disease (CBD).[1] Surprisingly, this fact has not deterred its use in manufacturing. Therefore it is imperative that chemical agents be developed for better detection and remediation of beryllium in the environment and as therapies for individuals exposed to this element.

The goal of this research is to develop strong, selective chelating agents for the encapsulation of beryllium. The main ligand motif will be based on a di-pyridyl scaffold with selected chelating pendant groups (R), allowing the formation of tetradentate complexes which can form the desired six-membered chelate rings with Be^{II} cations (figure 1). Preliminary complexation studies will use boron and aluminium ions as safe analogues. ESI-MS will be used for the study of the Be-ligand complexes, allowing their synthesis on a small scale and minimising exposure to beryllium. The final successful chelators should provide selectivity which will allow us to harness the good, while minimising the bad, of this indispensable metal.

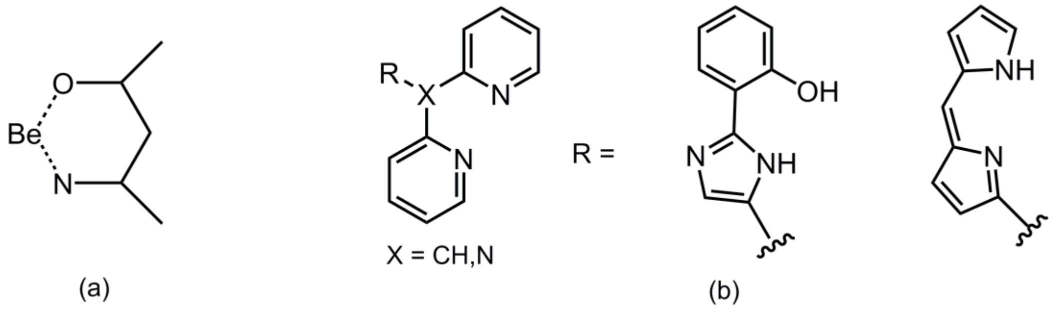

Figure 1 (a) six-membered chelate ring (b) di-pyridyl scaffold and chelating R groups

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Effect of intermolecular interaction on luminescence spectra of d^8 square-planar complexes at variable pressure

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Luminescence properties of square-planar complexes of nickel(II), palladium(II) and platinum(II) with a d^8 electron configuration are investigated at variable pressure. Increasing pressure from 0 to 40 kbar usually causes a blue shift of luminescence maxima for square-planar complexes in crystals.[1] Intermolecular interactions with the d_{z^2} orbital of the metal have an important effect on the maxima shift. A series of dimethyldithiocarbamate (MeDTC) complexes with nickel(II), palladium(II) and platinum(II) metal centers are presented, which show greater blue shifts than previously published square-planar dithiocarbamate (DTC) complexes. This is due to a weakening of an M···H-C intermolecular interaction with increasing pressure. The influence of the nature of the metal on the intermolecular interaction is investigated, also for deuterated complexes. Such interactions are usually stronger at high pressure, leading to red shifts of the maxima. This is documented for several platinum(II) compounds and a first example for palladium(II) is presented.

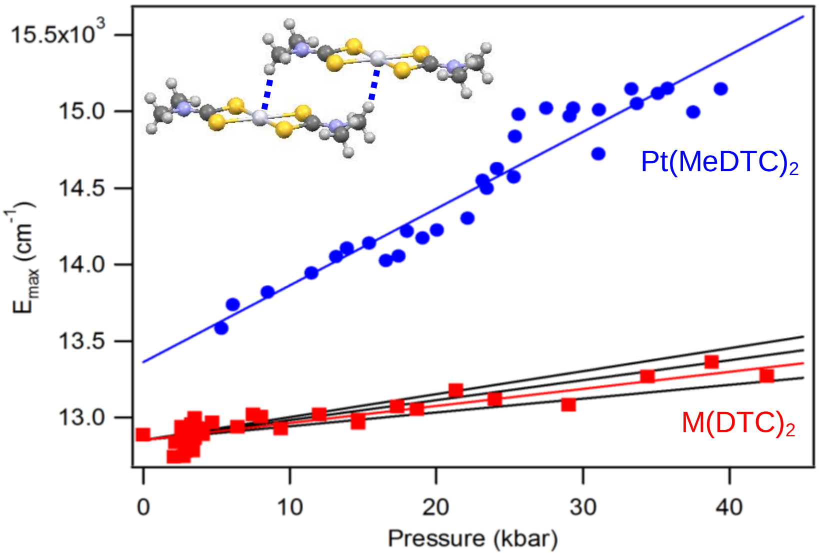

Figure 1 **E_{max} evolution with pressure for a complex with M···H-C interactions ($Pt(MeDTC)_2$, blue) and dithiocarbamate complexes with no intermolecular interaction ($M(DTC)_2$, red and black).**

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Nitrogen-rich complexes of *p*-block elements: Highly endothermic polytetrazolates and polyazides

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Our aim is to stabilise and control the reactivity of N-rich coordination compounds. Upon decomposition, N-rich compounds generate mainly N_2 - ideal for smokeless, CO_2-free, “green” energetic materials as replacement for conventional propellants, explosives & pyrotechnics.[1] Low barriers toward decomposition pose major challenges in their preparation and characterisation. Here, we discuss $E(Y)_n$, n = 2-6, Y = N-rich ligand, E = *p*-block coordination centre in low or high oxidation state. We apply synthetic methodology novel to energetic chemistry, which involves a combination of hypercoordination, bulky counterions, and ligand exchanges, to achieve the preparation and isolation of new classes of complexes as candidates for efficient & controllable energy storage.[4] These include Lewis base adducts,[3,6] homoleptic azido complexes,[2,5] covalent, binary azides $E(N_3)_n$,[3] the first homoleptic *p*-block element tetrazolates $E(T)_6^{2-}$ and $E(T)_3^{-}$ (E = Si - Sn, T = CHN_4, Fig. 1). The new complexes have a unique chemistry – reactions with nitriles and phosphines afford unusual *poly*(tetrazolato) and *poly*(phosphiniminato) complexes. Syntheses, reactivity, structures, and thermal and spectroscopic properties of the new species, including the application of fast time-resolved IR spectroscopy to study photoreactivity, will be described.

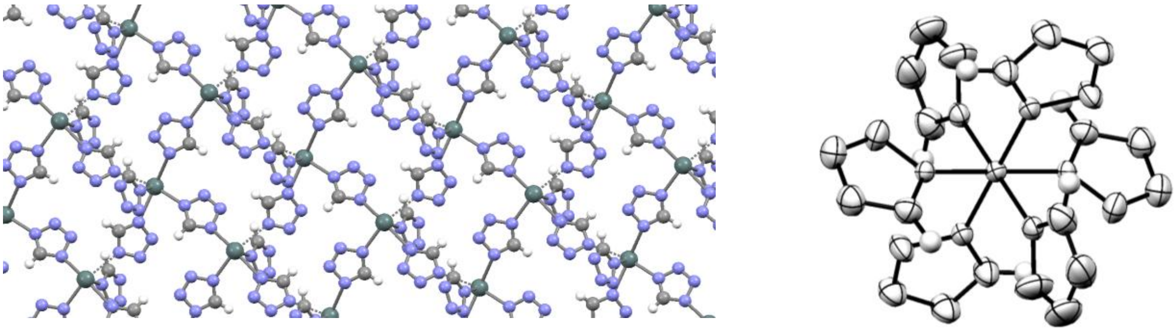

Figure 1 Tetrazole-based N-rich coordination networks and complexes: $\{Sn(CHN_4)_3^{-}\}_\infty$ (left, blue, N; turquois Sn, white H), $[Si(\kappa\text{-}N\text{-}CHN_4)_6]^{2-}$ (right, ellipsoid plot, 50%).

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An unprecedented 5-phosphasemibullvalene derivative

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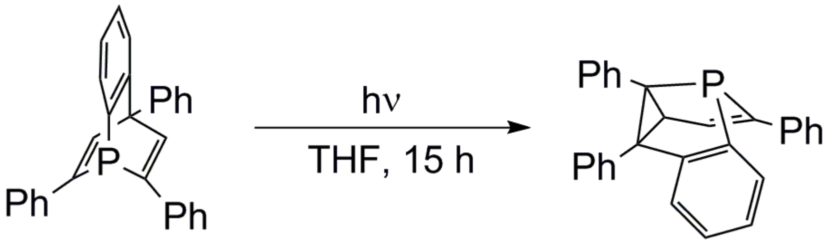
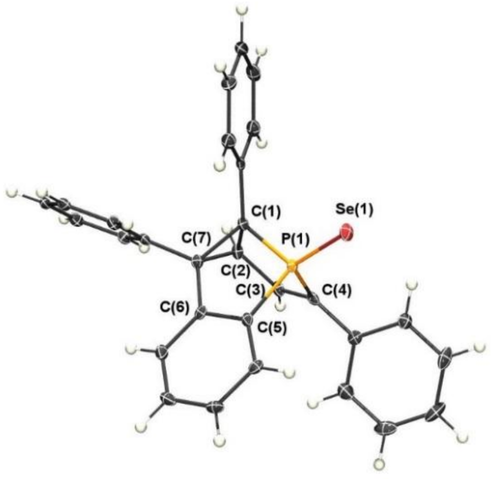


Figure 1. Photorearrangement of a phosphabarrelene to a phosphasemibullvalene.

During our extensive research on phosphabarrelenes, we started to investigate a new class of phosphorus ligands with interesting properties. We could demonstrate for the first time that phosphabarrelenes can undergo a quantitative and even more selective photochemical di-π-methane rearrangement towards 5-phosphasemibullvalenes, as shown for barrelene derivatives before. This hitherto unknown conversion of unsaturated phosphorus cage compounds leads to stable, chiral products as proved by means of HPLC analysis.[1]



Moreover, the molecular structure of a 5-phosphasemibullvalene-selenide derivative in the crystal was unambiguously verified by means of X-ray crystallography. First results on the investigating the ligand properties of these novel compounds show that they are stronger net donors compared to the phosphabarrelene-precursors. These preliminary investigations pave the way for their use as (chiral) ligands in (asymmetric) homogeneous catalysis.

Figure 2. Molecular structure of a 5-phosphasemibullvalene-selenide.

[1] M. Rigo, M. Weber, C. Müller; *Submitted for publication.*

Functionalized corroles as electro-catalysts for oxygen evolution and oxygen reduction reactions in water

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Oxygen reduction and water oxidation are two key processes in fuel cell application.[1] Water oxidation to dioxygen is a $4H^+/4e^-$ process whereas oxygen can be fully reduced to water by $4e^-/4H^+$ or partially reduced by fewer electrons to reactive oxygen species like H_2O_2 and O_2^-. During the talk we will demonstrate that a novel manganese corrole complex behaves as bi-functional catalyst for, both, the electrocatalytic generation of dioxygen as well as the reduction of dioxygen in aqueous medium. Furthermore, our combined kinetic, spectroscopic, and electrochemical study of manganese corroles adsorbed on different electrode materials – down to a submolecular level – reveals mechanistic details of the respective oxygen evolution and -reduction processes.[2-4]

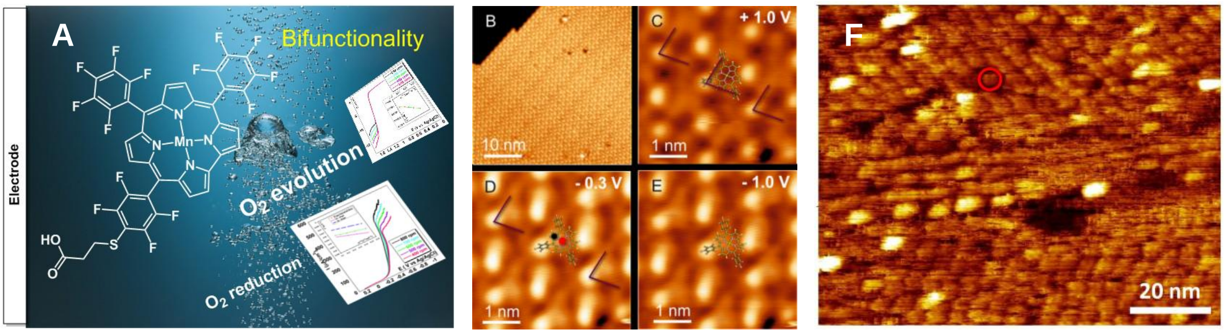

Figure 1 A) The bifunctional nature of manganese corroles**.** B-E) Low-temperature STM images of ordered manganese molecules on Ag(111) at 5 K. F) STM image of a self-assembled monolayer of manganese corroles at a solid-liquid interface on highly ordered pyrolytic graphite (HOPG) and 1-phenyloctane.

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Thyminato-bridged cyclic tetranuclear rhodium(III) complexes containing a calcium ion as a template metal core

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Reactions of $[(\mathrm{Cp^*Rh})_2(\mu\text{-OH})_3]\mathrm{OH}$ (Cp* = η^5-$\mathrm{C_5Me_5}^-$) and thymine (= $\mathrm{H_2thym}$) in methanol in the presence of a certain metal salt MX_n {= $\mathrm{NaPF_6}$, $\mathrm{NaBF_4}$, $\mathrm{NaNO_3}$, $\mathrm{Ca(NO_3)_2}$, $\mathrm{Ca(ClO_4)_2}$, $\mathrm{La(NO_3)_3}$, $\mathrm{Eu(NO_3)_3}$, $\mathrm{Dy(NO_3)_3}$ or $\mathrm{Er(NO_3)_3}$} were examined.[1] Orange crystals of the thyminato(2–)-bridged tetranuclear Cp*Rh complexes incorporating a M^{n+} cation, $[(\mathrm{Cp^*Rh})_4(\mu\text{-thym})_4\mathrm{M}]\mathrm{X}_n$, were obtained. All complexes were characterized by the single-crystal X-ray diffraction method, which revealed that homochiral aggregations of four $\mathrm{Rh^{III}}$ centers were achieved to form metallacalix[4]arene-type clusters. It is also observed that the bridging modes of thym^{2-} ligands are dependent on the template metal ion. In the Na^+ complexes a thym^{2-} ligand bridged two $\mathrm{Rh^{III}}$ and the third Na^+ ion with a μ_3-$1\kappa N^1{:}2\kappa^2N^3,O^2{:}3\kappa O^2$ mode, while in the Ln^{3+} analogues it exhibited a different bridging mode, μ_3-$1\kappa N^1{:}2\kappa^2N^3,O^4{:}3\kappa O^2$. In the cases of Ca^{2+} ion, the bridging mode is further dependent on the anion; only the μ_3-$1\kappa N^1{:}2\kappa^2N^3,O^2{:}3\kappa O^2$ complex resulted in the $\mathrm{NO_3}^-$ salts, but the $\mathrm{ClO_4}^-$ salts afforded both bridging complexes aggregated alternatively in the crystals. The tetranuclear $(\mathrm{Cp^*Rh})_4(\mu\text{-thym})_4$ structures with a template metal cation (M^{n+}) of the complexes are maintained in solution.

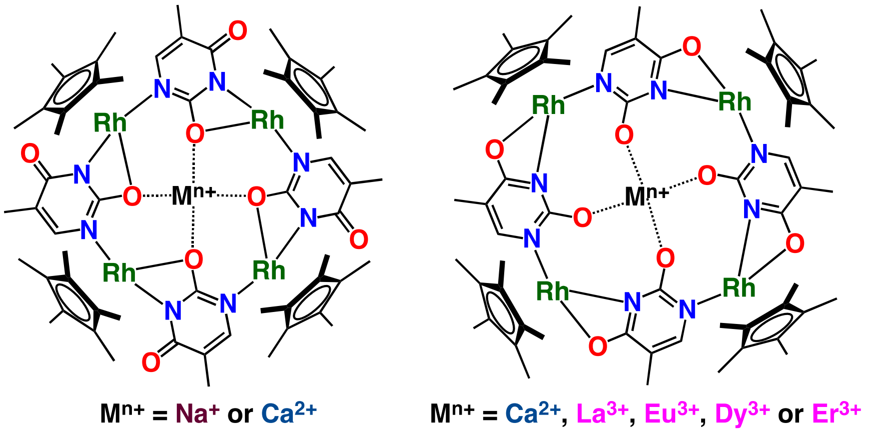

Figure 1 Two bridging modes of thym^{2-} in the tetranuclear Cp*Rh clusters.

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Transition-Metal Complexes with Amidinato- and Guanidinatosilylene Ligands

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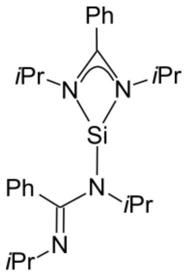
The donor-stabilized bis(amidinato)silylene **1**,[1,2] bis(guanidinato)silylene **2**,[3,4] and mono-(guanidinato)silylene **3**[3] were studied for their reacitivity towards transition-metal complexes. In continuation of earlier investigations,[5,6] both nucleophilic substitution reactions and Lewis acid/base reactions were studied. Compounds **4**–**12** are examples of the transition-metal silylene complexes obtained in these studies.



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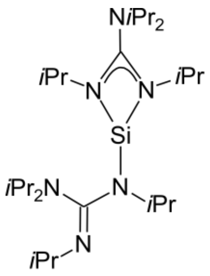

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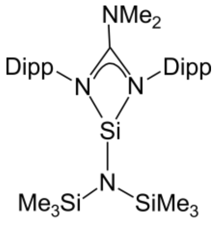

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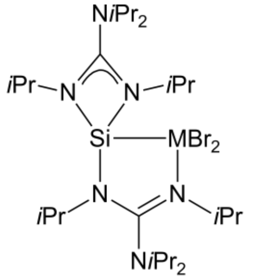
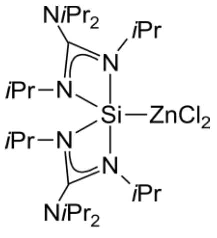


M = Fe (**4**), Co (**5**), Ni (**6**)



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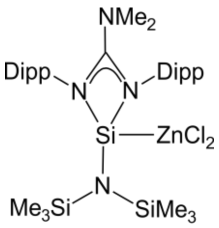

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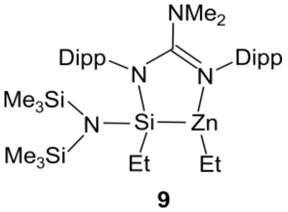

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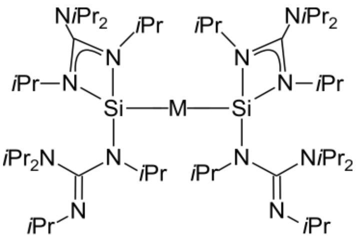
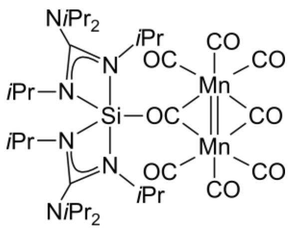


M = Pd (**10**), Pt (**11**)



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Structural investigations and reactivity of related Rh(O,O′-bidentate) complexes

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This study forms part of current research on the manipulation of structure and reactivity relationships of metal complexes for catalytic, radiopharmaceutical and separation importance. Different O,O′-, O,N-, O,S- and P,P′- bidentate ligands are utilized.[1-5] The importance of the choice of ligands in the design of complexes cannot be overestimated. In the process of obtaining the optimum complex, a fundamental approach is so often bypassed, reverting to a trial and error evaluation of complexes synthesized for a particular purpose. The key to fundamental research is the greater understanding of the relationships between activity and structure, as well as ways to better predict, understand and control molecular architecture. Oxidative addition is one type of reaction that features prominently in the mechanistic representation of many catalytic reactions. The extent to which the oxidative step is affected by, for instance, the electronic and steric modifications to the phosphine ligand, can lead to more effective modelling of catalysts. Phoshine ligands are exceptionally well suited to manipulate the electron density and/or steric accessibility of the metal centre and in combination with the systematic variation of the bidentate ligand, a better control of reactivity emerge.

Various [Rh(Cupf)(CO)(PX_3)],[1] [Rh(Cupf)(CO)(AsX_3)], [Rh(Neocupf)(CO)(PX_3)] complexes as well as a range of substituted cupferrate complexes like [Rh(MeCupf)(CO)(PX_3)][5], [Rh(Cl_2Cupf)(CO)(PX_3)] and [Rh(Cl_2Cupf)(CO)(AsX_3)] have been studied with an extensive structural and kinetic effort to yield a detailed reaction mechanism (Cupf = cupferrate; Neocupf = neocupferrate bidentate ligand, MeCupf = *o*- and *p*-methyl cupferrate; PX_3 = PPh_3, PCy_3, P(*o*-Tol)$_3$, P(*p*-Tol)$_3$, $PPh_2C_6F_5$, P(*o*-ClC_6H_4)$_3$ and P(*p*-$MeOC_6H_4$)$_3$; AsX_3 = $AsPh_3$, As(*p*-Tol)$_3$). Oxidative addition of iodomethane to these Rh(I) complexes form Rh(III) alkyl compounds. Structures of a number of the starting complexes and their Rh(III) alkyl products were solved crystallographically.

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Luminescent copper(I) complexes with pyrimidines

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Synthesis of luminescent metal complexes is currently a hot topic of coordination chemistry. Copper(I) compounds are one of the main classes of luminescent materials. These compounds attracted significant attention due to their interesting photophysic properties. In present study we used pyrimidine-based ligands to synthesize copper(I) complexes. π-conjugated pyrimidine-based organic compounds are reported as materials showing liquid crystalline properties, light-emitting and non-linear optical properties and tendency toward self-assembling. The aim of this study is to synthesize effective copper(I) emitters. We synthesized a series copper(I) halide complexes with 4-(1*H*-pyrazol-1-yl)pyrimidines[1], $[CuL^nX]$ (n = 1, X = Cl, Br; n = 2, X = Cl, Br, I), $[CuL^nPPh_3X]$ (n = 1, 2 , X = Cl, Br, I; n = 4, 5, X = I), $[Cu_2(L^n)_2I_2]$ (n = 1-5) and $[Cu_2L^4X_2]$ (X = Cl, Br), and copper(I) iodide complexes with 2-aminopyrimidines, $[Cu(Pym^I)I]_n$, $[Cu(Pym^{II})I]_n$, $[Cu_2(Pym^I)_2(PPh_3)_2I_2]$ and $[Cu_2(Pym^{III})_2I_2]$ (Figure 1).

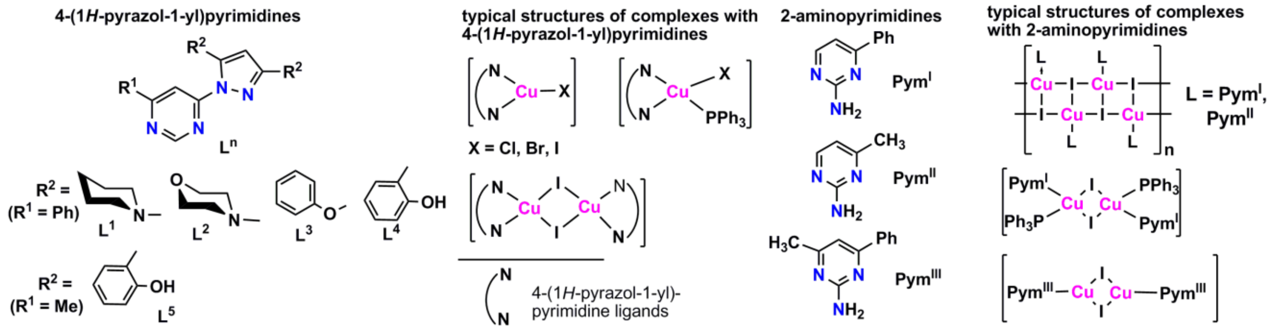

Figure 1 Structures of pyrimidine ligands and copper(I) halide complexes

The complexes exhibit phosphorescence, emission bands are found in the range of green to red. The compounds show high quantum yields up to 48%.

1 K. A. Vinogradova, V. F. Plyusnin, A. S. Kupryakov, M. I. Rakhmanova, N. V. Pervukhina, D. Y. Naumov, L. A. Sheludyakova, E. B. Nikolaenkova, V. P. Krivopalov, M. B. Bushuev, *Dalton Trans.*, **2014**, *43*, 2953.

A highly active oxovanadium(IV) macrocycle catalyst for the selective liquid-phase oxidation of various substrates

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The field of macrocyclic complexes of different transition metals is gaining considerable interest over the years due to their various applications and importance in coordination chemistry.[1] Schiff base metal complexes find wide applications for a number of interdisciplinary areas that include bioinorganic chemistry, catalysis and magnetochemistry.[2] Vanadium compounds promising catalytic activity have induced a growing significance in the coordination chemistry of vanadium. Especially, oxovanadium(IV) complexes have been extensively researched over the last decades due to their outstanding catalytic performance for oxidation reactions using aqueous H_2O_2 as oxidant.[3] Herein, the selective oxidation of phenol, cyclohexene and benzene catalyzed by a oxovanadium(IV)macrocycle complex, $VO[Me_4(Et)_2tetraneN_4]$ is demonstrated. The complex was synthesized via a metal template condensation approach. The structure of $VO[Me_4(Et)_2tetraneN_4]$ were characterized by spectroscopic methods (FTIR, UV-Vis, ESR and ^{51}V, ^{1}H and ^{13}C NMR), thermogravimetric analysis (TGA) and cyclic voltammetry (CV). After reaction conditions were optimized, the formed products were achieved in good yields with exceptional selectivity for most reactions. Kinetic studies suggest the mechanism is promoted via a oxoperoxo(V) intermediary species that encourage the formation of the C-O bond. ^{51}V NMR supports the perceived mechanism.

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Coexistence of Metal and Ligand Redox Activities in a One-Dimensional Coordination Compound

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We reported herein a coordination material with independent redox active sites on both metal and ligands as electrode material. During the charge-discharge process, both metal ions and ligands were involved in the redox reaction, which were revealed by Co 2p, C 1s and O 1s XPS spectra and cyclic voltammetry. Highly stable capacities and high coulombic efficiency were obtained via the coordination between metal centers and ligands. It is the first example using a one-dimensional coordination polymer as energy storage active substances instead of using the classic porous three-dimensional materials that subject to the size of the channel for lithium-ion diffusion and blocking the windows of the framework by organic solvents during the charging and discharging process.

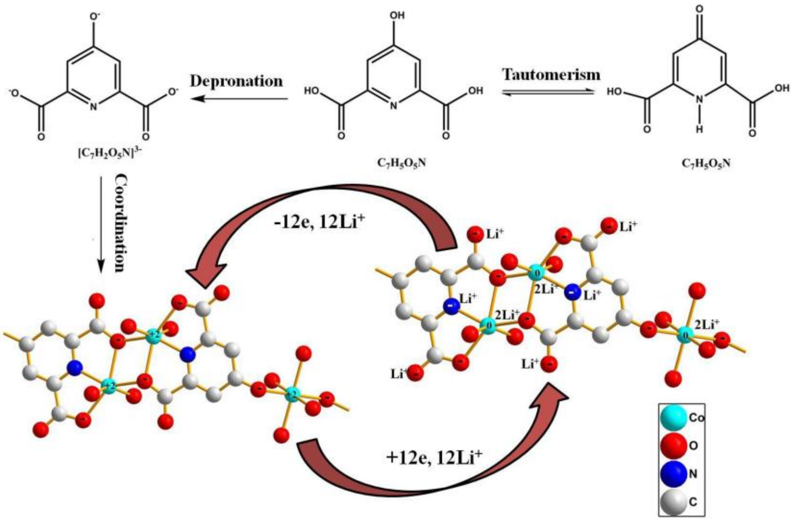

Figure 1 Electrochemical redox reaction mechanism.

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Protean Ligands: Heavy Pnictogens with L/X/Z-Ligand Properties in the Coordination Spheres of Pd and Rh

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The diverse Lewis-acid *vs.* -base reactivity of heavy trivalent pnictogen (E^5) compounds is reflected in their transition metal (TM) complexes: The E^5 atom is found to act as L- (E^5→TM), Z- (E^5←TM) or the intermediate X-type (E^5–TM) ligand. Because of the interesting catalytic[1] or photophysical properties[2] of E^5/TM complexes, there is a need to deeper understand the intermetallic E^5–TM bonds, which are often crucial for the unique behavior of these bimetallic compounds. In this context, fundamental studies on E^5/TM compounds are reported herein. The E^5(III) compounds $E^5(pyS)_3$ (pyS^-: pyridine-2-thiolate, E^5 = As, Sb, Bi) react with $[Pd(PPh_3)_4]$ with formation of $[(\kappa S\text{-pyS})E^5(\mu\text{-pyS})_2Pd(PPh_3)]$ (**A**, Figure 1). The reactions of $E^5(pyS)_3$ (E^5 = Sb, Bi) with $[Rh(pyS)(cod)]_2$ afforded the dimeric complexes $[Sb(\mu\text{-pyS})_4Rh]_2$ (**1**) and $[(\kappa^2\text{-pyS})Bi(\mu\text{-pyS})_3Rh]_2$. Complexes of type **A**, **1** and its Bi derivative reveal Z-type ligand characteristics of E^5 (E^5←TM). Whereas complexes of type **A** fail to maintain the E^5–TM bond upon oxidation, treatment of **1** with $ONMe_3$ results in the formation of $[OSb(\mu\text{-pyS})_3Rh(\kappa^2\text{-pyS})]_2$ (**2**) featuring a Sb–Rh bond. Unexpectedly, the Sb ligand atom switches from Z-type (in **1**) to L-type (in **2**) ligand characteristics which is in strict contrast to previously reported oxidation processes of similar binuclear complexes. For all complexes, the results of X-ray diffraction analyses, NLMO calculations and ^{121}Sb Mössbauer spectroscopic investigations (for E^5 = Sb) are discussed with special emphasis on the nature of the E^5–TM bond.

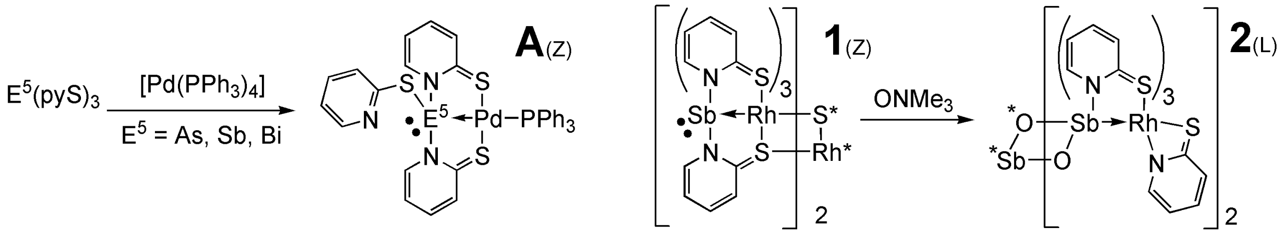

Figure 1 Synthesis of complexes of type **A** and oxidation induced Z- to L-ligand switch.

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Synthesis and Structural Characterization of Coumarilate Complexes with Co(II), Ni(II) and Zn(II) Cations

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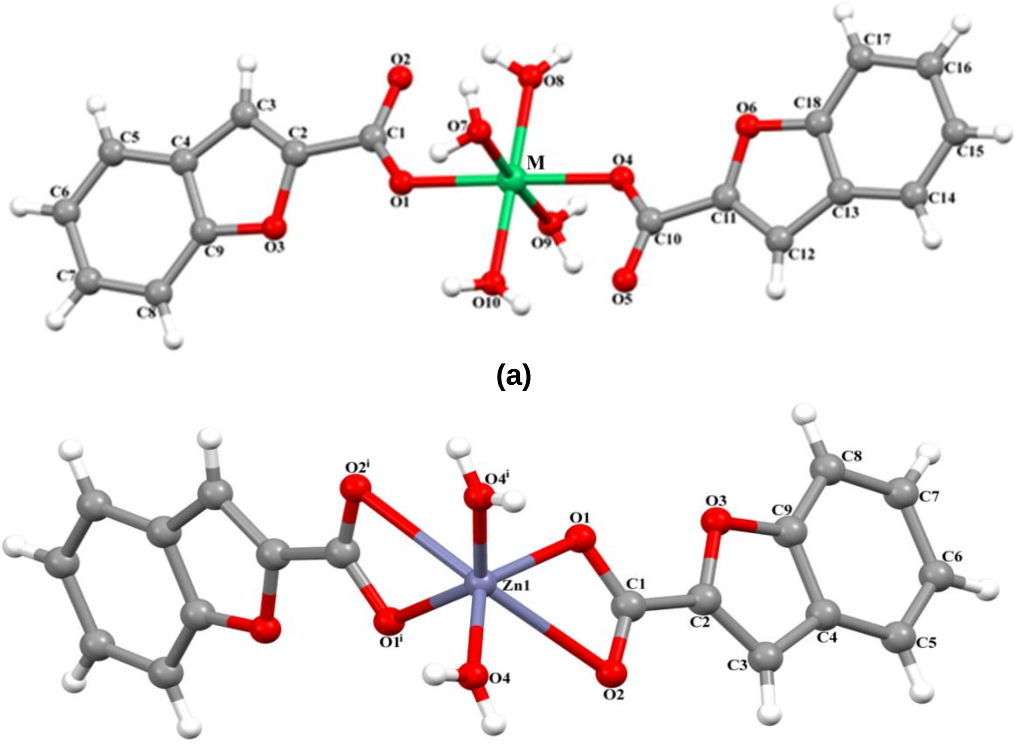
This study include that the synthesis and structural characterization of Co^{II}, Ni^{II} and Zn^{II} metal cation complexes with coumarilic acid. The molecular structure of the products were dissolved using FT-IR, UV-Vis spectroscopy, elemental analysis and single crystal XRD methods and thermal properties were investigated with TG/DrTG-DTA curves. While, in the Co^{II} and Ni^{II} complexes, coumarilic acid ligands bind to metal center as monoanionic – monodentate, in the Zn^{II} complex, the binding of the coumarilic acid monoanionic – bidentate. The Co^{II} and Ni^{II} cations complete to octahedral geometry with two moles coumarilate and four moles aqua ligands. The Zn^{II} metal cation has octahedral geometry that centered of two moles bidendate coumarilate and two mole aqua ligands. Also, the presence of coordinated aqua molecules was confirmed by thermal characterization.



(a)

(b)

Figure 1. The molecular structure of the complexes **(a)** Co^{II} and Ni^{II}, **(b)** Zn^{II} metal cations.

Cyclometalated ruthenium-triarylamine conjugated complexes: electronic coupling studies and applications

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Materials with well-defined multiple redox states are of interest for electrochromism, information storage, and molecular electronics. Thin films that display distinctly different absorptions in the NIR region at different redox states are of great importance in many military and civilian uses. Cyclometalated ruthenium complexes contain a characteristic Ru-C bond, which significantly decreases the Ru(III/II) redox potential and enhances the metal-metal electronic coupling in bridged diruthenium system.[1] These complexes have been examined in term of mixed-valence chemistry, long-range electronic coupling, and NIR electrochromism.[2] We recently found that the combination of cyclometalated ruthenium and triarylamine gave rise to strongly-coupled systems with multiple redox processes at low potentials (Figure 1).[3] Thin films of these materials can be prepared either in the form of self-assembled monolayer[4] or by electropolymerization.[5] The resulting thin films are useful in NIR electrochromism and molecular logic gates.

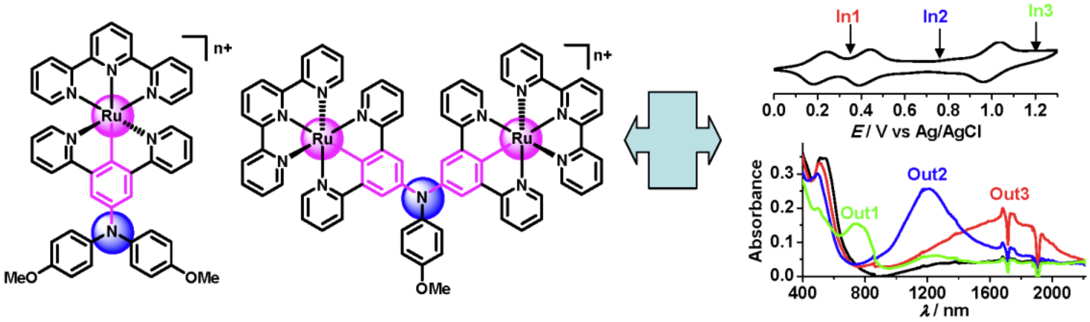

Figure 1 Electronic coupling studies (left) and applications in NIR electrochromism and molecular logic gates (right) of ruthenium-amine conjugated complexes.

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Assessment of non-covalent intramolecular interactions within transition metal complexes by high-resolution XRD analysis

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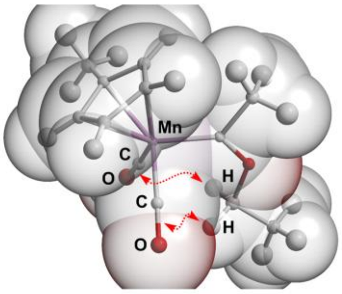
Far beyond geometrical features, high-resolution X-ray diffraction analysis (S > 0.9 Å^{-1}) can provide an experimental model of the electron density (ED) of molecules embedded in the condensed phase.[1a] Complemented by a subsequent analysis of the topology of the ED according to Bader's Quantum Theory of Atoms in Molecules,[1b] this methodology has emerged as a powerful tool for the experimental assessment of all sort of bonding features, including supramolecular non-covalent interactions.[1c]

We have used such an approach for assessing non-covalent intramolecular secondary interactions within chosen transition metal complexes, including piano-stool Mn(I) Fischer carbenes, and Mn(I), Mn(II) and Fe(II) N-Heterocyclic carbene complexes. The topological analysis of the experimental electron density in combination with DFT calculations clearly revealed the occurrence of hitherto unsuspected weak intramolecular C…H or C…C inter ligand interactions, which are likely to play a key role regarding the conformational stability and/or spectroscopic properties of the given complexes.



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Designs of Gas Sorption, Dielectric Response, and SHG Activity for Cu(II) Complexes bearing Benzoate Ligands

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Paddle-wheel type copper (II) binuclear coordination polymers with bridging *m*-substituted benzoate (BA) and axial pyrazine (pz) ligands showed a variety of physical functions such as dielectric responses coupled with gas sorption properties and SHG responses.[1-3] The gas adsorption-desorption properties of these polymers were affected by the interchain interactions between the BA ligands of the polymers. In addition, the dielectric properties were also affected by the CO_2 gas adsorption into the polymer crystals.[1, 2] Herein, we report the preparations, crystal structures, dielectric properties and gas adsorption-desorption properties of Cu(II)-binuclear coordination polymers of $[Cu_2(X\text{-BA})_4(pz)]_\infty$ and $[Cu(p\text{-XBA})_2(py)_2(H_2O)]$ complexes, here X in X-BA ligand was systematically modified at F, Cl, Br, I, CH_3, and CH_3O. These one-dimensional coordination polymers have the bulky BA ligands to control the interchain interactions.

Figure 1 showed the crystal structure of $[Cu(p\text{-BrBA})_2(py)_2(H_2O)]$ (**1**), which was constructed by the one-dimensional $[Cu_2(p\text{-BrBA})_4(pz)]_\infty$ chains and the puddle-wheel $Cu_2(p\text{-BrBA})_4$ units were bridged by the axial pz ligand. One of the two *p*-BrBA ligands within the asymmetric unit showed the orientational disorder, where the π-planes of the two disordered phenyl rings were almost the orthogonal to each other. The solvent accessible void space was not observed between polymer chains. Although the crystal structures of $[Cu(p\text{-ClBA})_2(py)_2(H_2O)]$ (**2**) and $[Cu(p\text{-IBA})_2(py)_2(H_2O)]$ (**3**) were isostructural to each other, the gas sorption properties of these three salts were different to each other. To analyze the interchain interactions in detail, Hirshfeld surface analyses were examined. The gas adsorption-desorption properties and interchain interaction of these compounds will be discussed.

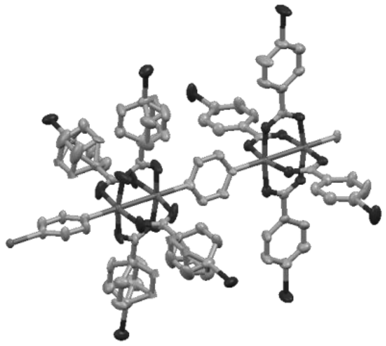

Figure 1
Crystal structure of 1. Half of the *p*-BrBA ligands showed the orientational disorder.

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LUMINESCENT CORE/SHELL CRYSTALS BASED ON LANTHANIDE COMPLEXES, BIO-INSPIRED AND RECYCLABLE

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Taking inspiration from natural systems,[1] guanidium is an excellent counter-cation for lanthanide complexes since it facilitates the crystallization of this water soluble molecules and improves their luminescent properties in the solid state.[2] Control of crystallization is a very delicate issue, hence only a few examples can be found in the literature.[3] Using the guanidinium counter-cation, we studied the entire lanthanide series of $[Ln(DPA)_3]^{3-}$ complexes (DPA = pyridine-2,6-dicarboxylate) and found interesting changes of the lattice parameters, the complexes not being isostructural throughout the series. Applying this new information, we could successfully control the growth during crystallization, obtaining epitaxial core/shell crystals. A non-emissive Ln complex surrounding a Tb or Eu core led to the interesting phenomenon of shielding effect induced by the outer layer which blocks the excitation wavelength. Furthermore, a more interactive effect can be observed using dual Tb/Eu core/shell systems by specifically choosing the excitation wavelength.

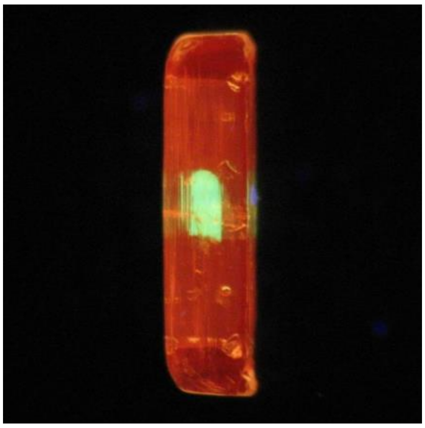

Figure 1. Tb@Eu core/shell crystal under UV (λ_{ex}=365nm).

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Luminescent lanthanide complexes and their application

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As luminescent materials, lanthanide complexes exhibit unique properties, such as high luminescence quantum yields, sharp emission bands, large Stokes shifts (>200 nm), and long luminescence lifetimes (~ms). Although the parity-forbidden transition of lanthanide ions results in very low molar absorption coefficients (typically < 3 M^{-1} cm^{-1}), using of organic ligands is found to be effective in light harvesting and sensitizing the lanthanide emission through "antenna effect"[1-3]. Bright luminescence can be detected even if the luminescent lanthanide complexes are diluted into extremely low concentration. Therefore, the luminescent lanthanide complexes are very promising for a wide range of applications, such as organic light emitting diodes (OLEDs), functional light conversion films, sensors and bio-imaging and so on. Large quantities of luminescent lanthanide complexes have been synthesized and tremendous progress have been made to improve their properties for practical applications. However, there are still many challenges ahead in developing lanthanide luminescent materials with high emission quantum yield (> 0.5 under near UV/blue excitation), enhanced absorption cross-section (5-6 orders of magnitude larger than the intrinsic *f-f* transition), broadened excitation range (>100 nm) and excellent photostability (no degradation under >20 h UV/blue excitation). Moreover, new electroluminescent materials are required for the application in OLEDs to realize >100 cd m^{-2} brightness at <10 V applied voltage [4].

In this talk, we will present our recent progress in lanthanide complexes based luminophores, especially, Eu and Tb complexes which are being developed for improving the color properties of electroluminescent displays [5-8] and other applications.

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Lanthanide Coordination and Self-Assembled Luminescent Edifices

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Photonics is the second most important category of rare-earth applications with respect to the commercial value of the elements entering in the end-products. The main characteristic of the latter is that only minute quantities of these elements are needed: the screen of a smart phone contains 7 of them, totalling 100-200 mg; an optical quartz fibre doped with less than 0.1% of erbium is an efficient amplifier for optical telecommunications; highly sensitive immunoassays use much less than 1 µg of luminescent lanthanide(s) [1].

After a brief introduction on lanthanide photonics [2] and on the design of highly luminescent coordination compounds [3], the presentation focuses on a special class of lanthanide luminescent compound: self-assembled mutinuclear edifices. Coordination-directed self-assembly of supramolecular compounds allows one to program weak interactions between ligand strands so as to create a cavity well adapted for hosting specific metal ions. A family of such edifices is built from hexadentate ditopic ligands based on the benzimidazole-pyridine framework and yielding $[Ln_2(L)_3]$ dinuclear helicates. These entities are thermodynamically stable, kinetically inert and they can be conjugated to monoclonal antibodies for the purpose of selectively detecting breast cancer cells [4]. Extension to heterometallic and higher nuclearity f-f or f-d entities permits the tailoring of specific metal-metal interactions [5].

Stereocontrol of the self-assembly processes is another fascinating tool and chiral tetrahedral cages can be obtained in this way; the systems display fascinating self-sorting properties in addition to luminescence [6].

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Design and Properties of Redox-active Metallomesogens

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In recent decades, significant progress has been made in the fabrication of functional columnar liquid crystals (LCs) based on pure organic and metal-containing mesogenic skeletons (metallomesogens). The research has been accelerated because of their great potential in next-generation optoelectronic devices (such as light-emitting-diodes, field-effect transistors and photovoltaic-diodes) manufactured by cost-effective processes based on the self-assembling nature of LC molecules.

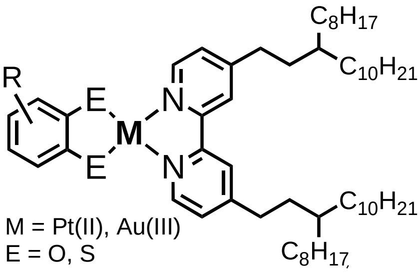

Figure 1. Structure of redox-active metallomesogen

In 2007, our group reported the first hexagonal columnar ordered phase (Col$_{ho}$) comprising a mesogenic skeleton made from by redox-active catecholato and 4,4'-di-(3-octyl tridecyl)-2,2'-bipyridine (C8,10bpy) bound with a Pt(II) centre (Figure 1).[1] The Col$_{ho}$ phase appears at ambient temperature and survives up to around 200 ˚C. Our design was further extended to the fabrication of [Pt(Bdt)(C8,10bpy)] (Bdt = 1,2-benzenedithiolato) with S-coordinating atoms and [Pt(Htp)(C8,10bpy)] (Htp = 1,2-thiophenolato) with S,O-mixed-coordinating atoms[2] and [Au(Bdt)(C10,8bpy)]PF$_6$ with a cationic mesogen, in keeping with the Col$_{ho}$ phases.[3] In this paper, the design and physicochemical properties[4,5] of the series of redox-active metallomesogens together with the related materials will be presented and discussed.

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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, $\mathrm{Pt^{II}}$ 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.[1]

As a second strategy, we have explored the formation of covalent links between the two functional subunits by preparing $\mathrm{Fe^{II}}$ 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.[2]

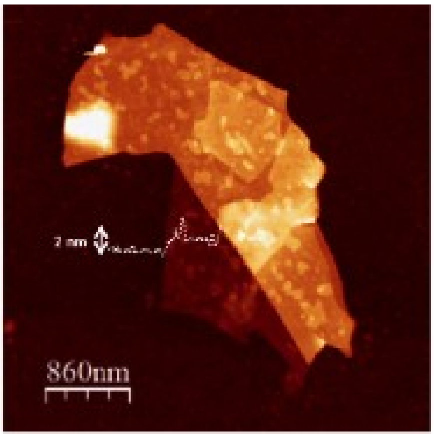

Figure 1 AFM image of a flake of $[\mathrm{Fe^{III}(acac_2\text{-}trien)}][\mathrm{Mn^{II}Cr^{III}(Br_2An)_3}]$

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Multifunctional hybrid coordination networks based on imidazolium dicarboxylate salts and lanthanides.

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Hybrid coordination networks have been the subject of considerable research in recent years. This interest comes from the versatility and flexibility of their architecture as well as their potential application in many areas such as gas storage, catalysis, drug delivery, and information storage…[1-7]

They are often obtained by solvothermal reaction between metal salts and neutral ligand bearing coordination functions. In our group, we have focused on the synthesis of coordination networks from imidazolium salts bearing carboxylate coordination functions to monitor the structural building process. This strategy has been successfully applied to transition metals giving rise to different coordination networks[8] and has been extended to lanthanides since they show a large variety of coordination spheres (unlike transition metal ions showing mainly tetrahedral or octahedral coordination).

We will present our recent results concerning the synthesis and the characterization of new hybrid coordination networks based on achiral and chiral imidazolium dicarboxylate salts and lanthanides (see Figure 1). We will focus particularly on the study of their magnetic and luminescent properties. Beyond the interest to explore new families of compounds, the incorporation of imidazolium salts with special functionalities into the coordination networks let glimpse the possibility to obtain new multiferroic materials.

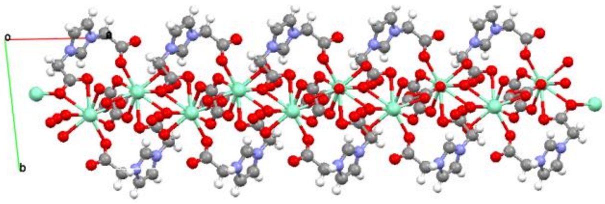

Figure 1. Crystal structure of $[((MimCO_2)_2)Sm(C_2O_4)(H_2O)].H_2O$.

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MULTIFUNCTIONAL NANOLANTHANIDE COMPLEXES: CONTROLLABLE NUCLEARITY AND MOLECULAR DOPING, LUMINESCENCE AND MAGNETIC DEPENDENCE

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A large number of 3*d* metal complexes have been studied using β-diketone compounds these last decades[1] and several researches show their considerable importance in analytical and inorganic chemistry. More recently, lanthanide-based complexes based on this type of ligands have been also intensively studied. Ln^{3+} ions are well known for their unique luminescent properties such as a broad spectral range from ultraviolet to infrared region, efficient narrow-width emission band in the visible region, and a long decay lifetime for various applications.[2] Besides lanthanide systems are materials with fascinating magnetic properties as they exhibit ferromagnetism and antiferromagnetism phases, and have the largest atomic magnetic moments of all elements. Multifunctional molecular materials combining at least two different physical properties (luminescence and magnetism) have been the subject of our research. These systems are subjected to deep investigation because they exhibit promising combined magnetic and optical properties as a consequence of the unique spectroscopic and electronic characteristics associated with their $4f^n$ electronic configuration.[3] Using simple or functionalized acetyl acetone, we have synthesized and fully characterized three families of polynuclear lanthanide clusters. According to the synthesis conditions, the nuclearity of the complexes can be finely controlled from [Ln_2] to [Ln_{14}]. We also studied the magnetic and luminescence properties and some of these complexes can behave as bifunctional materials, combining SMM and luminescent properties.

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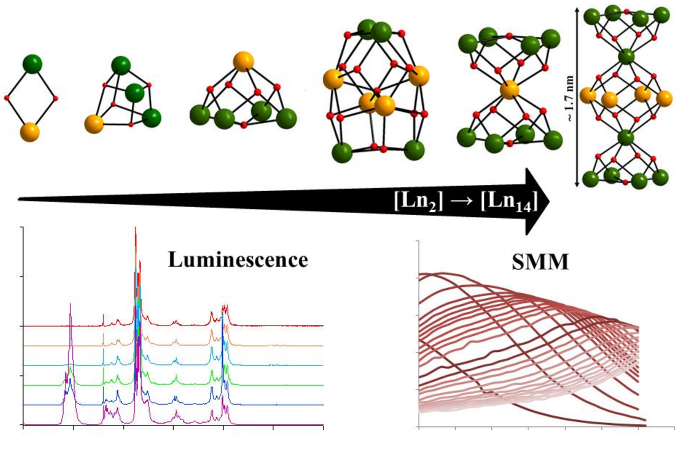

Figure 1: Schematic summary of lanthanide cluster studies.

Conferring memory effect to organic conductors via spin crossover probes

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Spin-crossover (SCO) materials have been extensively studied for their potential applications in various areas, such as data storage and sensing.[1] These materials are typically bistable molecular inorganic complexes of transition-metals ions with ligands that allow for the presence of a low lying metastable high spin (HS) excited state that can be populated through external stimuli. In the solid state, cooperativity may arise when this electronic transition triggers a crystallographic transition, and hysteretic behavior has been observed in some examples.

Beyond the different electronic properties of the low spin (LS) ground state and the HS excited state, these SCO materials can also be used as probes to promote a switch in an additional physical property when incorporated into a multifunctional composite hybrid. Here we will present our results showing the influence of the spin transition on the conducting properties of hybrid materials from organic conductors, with appearance of a temperature-dependent transport transition with memory effect.[2] The conductivity behavior can be described by the pressure dependence density of states at the energy band structure in the semiconducting polymer and variable range-hopping model.

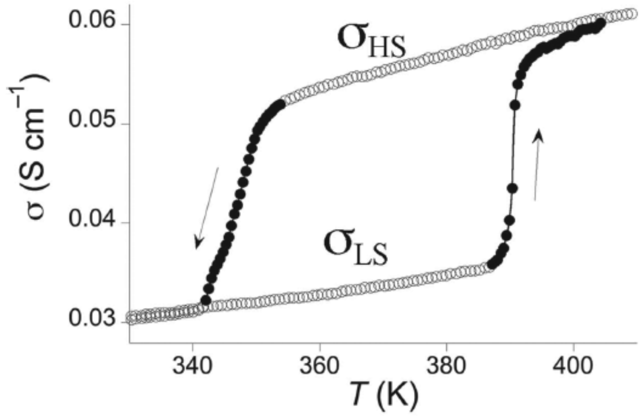

Figure 1 Bistability in a SCO/polypyrrole film.

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Multifunctionality in anilato-based materials: magnetic order, luminescence, porosity, electrical conductivity, chirality, solvent exchange, gas absorption, easy delamination,...

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The search of multifunctional molecular materials has been one of the main challenges in Materials Science in the last twenty five years. The main approach has been the combination of different molecular blocks able to furnish in the solid state the desired properties as magnetic order, electrical conductivity or even superconductivity, chirality, porosity, luminescence,...

In this communication we will show the ability of anilato-based ligands to construct coordination polymers of different dimensionalities presenting simultaneously several interesting properties as magnetic order (including tuning of the critical temperature), luminescence, porosity, electrical conductivity, chirality, solvent exchange, gas absorption, easy delamination,...

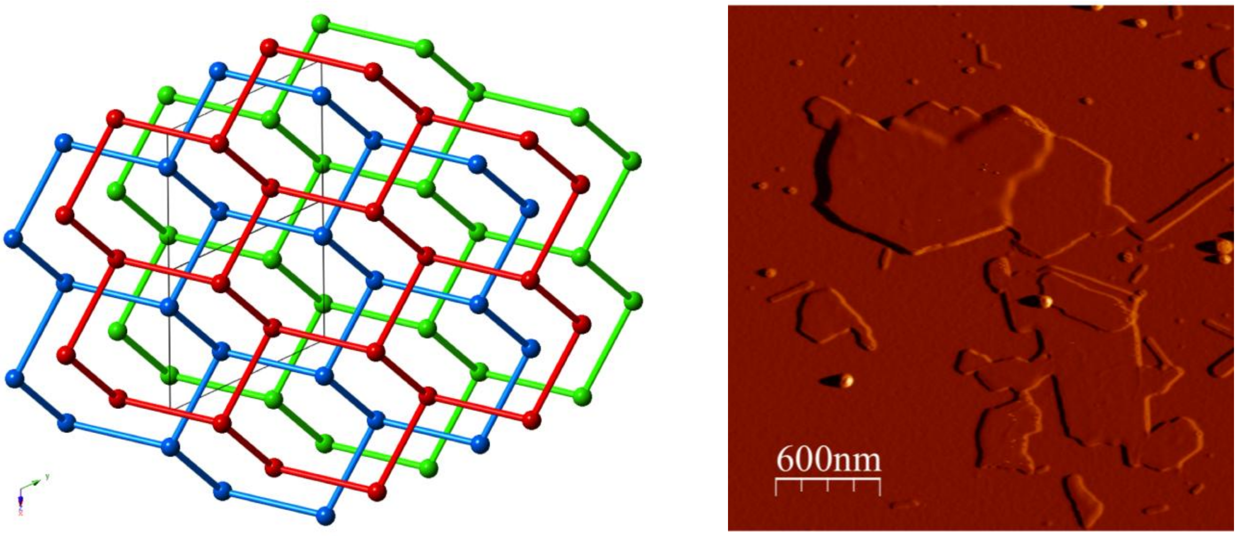

Figure 1 (left) Structure of three consecutive layers of a 2D honey comb anilato-based multifunctional coordination polymers and an example of solvent-assisted exfoliation

Coordination Chemistry Approach for Chiral Magnets

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By quantum mechanics, particles behave as linear waves with quantum phase. The quantum phase control is one of the key issues to create for new stage of materials. It is difficult to control discrete quantum phase, but the coherent quantum phase control is relatively easy. Then the first step of this issue is how to establish coherent quantum phases. The coherence quantum phase of photon, charge are achieved in the laser lights and conductive electrons in superconductors, respectively. There are no report before our studies[1] the coherence quantum phase order in spin system. The quantum phase coherence easily lost in centrosymmetric crystal, but protected in non-centrosymmetric crystal. Chirality is commonly found in nature, from particle physics to molecular chemistry, and one of the non-centrosymmetric systems. It is characterized by a reflection asymmetry that we are most familiar with in terms of our left hand being the mirror opposite of our right hand. When this kind of handedness appears in the structure of atoms or molecules in a solid, it affects the way that the magnetic moments of unpaired electrons organize themselves through the Dzyaloshinskii-Moriya (DM) interactions[2-4]. In a symmetric structure, these interactions cancel out, but in a chiral lattice they do not. The DM interactions stabilize a screwlike helical arrangement of the magnetic moments, but they must compete with ferromagnetic exchange, which tries to align all the magnetic moments in the same direction.[5] The result is a helical magnetic arrangement with a winding period of several tens or hundreds of nanometers, which is much longer than the lattice constant. Therefore, even though the chiral properties depend on the symmetry of the lattice, they can be understood and manipulated at the mesoscopic level, independently of the structural details. The properties of these magnetic arrangements are similar to that of electronic dipole moments of chiral liquid crystals. Both materials have helical structures, and they both contain extremely stable excitations called solitons. Solitons are nonlinear excitations that behave like particles, maintaining their shape and energy as they propagate, as exemplified by tsunamis that travel across entire oceans. In chiral magnets, solitons take the form of one-dimensional kinks, two-dimensional and three dimensional vortices called skyrmions[6] and hopfions[7] respectively. These solitonic excitations are stabilized by temperature and magnetic fields. They are extremely robust and can be manipulated by electric currents or even condense to form a regular lattice, such as the lattice of skyrmions found in MnSi and other related systems[6]. In this paper, we would like to discuss how can synthesize chiral magnetic materials using coordination chemistry[8].

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Solid-state Protonics in Coordination Polymers

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Solid-state protonics is a new research field attracting much current attention. One of the most urgent subjects in this field is to create a novel proton conductor, from the viewpoint of developing new energy and energy conservation technologies, including photovoltaic, hydrogen storage and fuel cell technologies. In this work, we report on a proton-conductive organic-inorganic hybrid system, which is a coordination polymer. Such a metal-dimer system with multi-redox property has a large potentiality for the creation of new-functional and high-performance materials in metal-complex solids[1].

We have developed several kinds of proton conductors, which are 0-D, 1-D, 2-D and 3-D coordination polymers. From the complex-plane impedance measurements, all the coordination polymers were found to be highly proton-conductive at room temperature. Among them, H_2dtoaCu exhibits highest proton conduction (~ 10^{-2} S cm^{-1}). This value is comparable to that of Nafion, which is famous for a solid electrolyte of fuel cell. The mechanism of proton conduction is discussed in detail. New highly proton-conductive coordination materials, conductive mixed-valent nanotube-MOFs and highly-concentrated hydrogen-storage nano-materials are also presented.

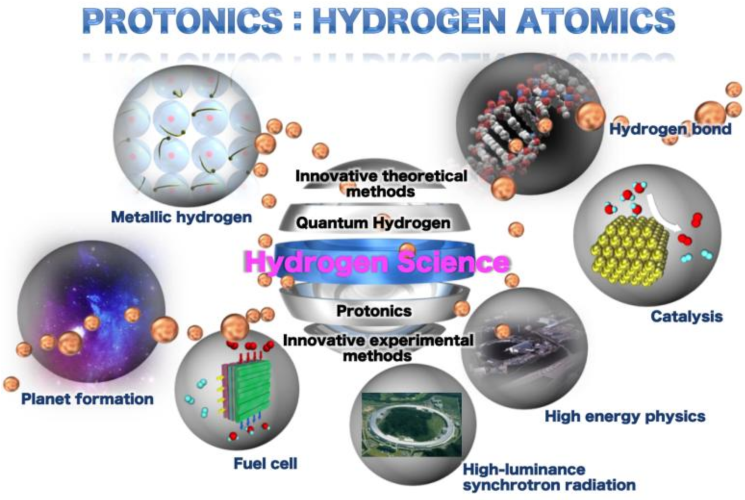

Figure 1 Solid-state protonics

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Luminescent Open-Shell Organic Radicals and the Metal Complexes

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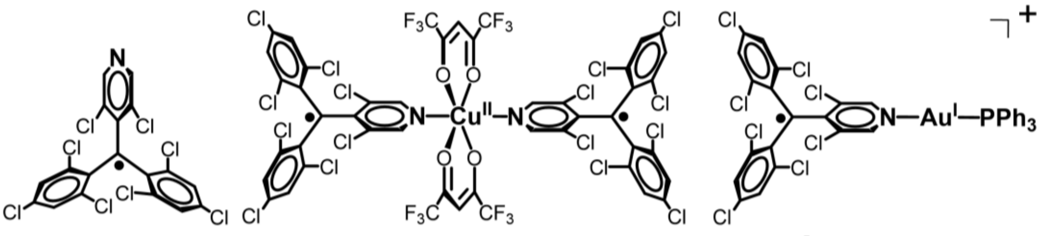
The luminescence of open-shell radicals has attracted growing interest owing to the unique characteristics such as high efficiency and long emission wavelength, based on the unusual spin-multiplicity. However, the photofunctions of luminescent organic radicals are much less investigated due to two main problems: few examples of luminescent organic radicals and low chemical stability upon photoirradiation.

We prepared a novel luminescent radical, PyBTM (Figure 1).[1] PyBTM displayed fluorescence in CH_2Cl_2 with the emission peak wavelength (λ_{em}) of 585 nm and the quantum yield (ϕ_{em}) of 0.02. The excellent ϕ_{em} of 0.81 was obtained in EPA (diethyl ether : isopentane : ethanol = 5:5:2) at 77 K. Importantly, PyBTM exhibited superior stability upon photoirradiation in solution; the stability was up to 115 times higher than that of chlorinated triphenylmethyl radical TTM, a previously reported luminescent radical.

PyBTM can coordinate to metal ions through the nitrogen atom. We revealed that a PyBTM-ligated Au^I complex $[Au^I(PyBTM)PPh_3](BF_4)$ is the first example of luminescent metal complexes with luminescent organic radicals.[2] ϕ_{em}, λ_{em}, and the stability in the photoexcited state all increased upon the coordination to Au^I.

$Cu^{II}(hfac)_2(PyBTM)_2$ has elongated octahedral geometry, in which the two PyBTM molecules coordinate at the equatorial positions.[3] The magnetic measurements revealed a ferromagnetic PyBTM−Cu^{II} exchange interaction with J/k_B = 47 K, owing to the orthogonality of the two spin orbitals.



PyBTM $Cu^{II}(hfac)_2(PyBTM)_2$ $[Au^I(PyBTM)PPh_3]^+$

Figure 1. Molecular structures of PyBTM and metal complexes.

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Multifunctional Molecular Magnetic Materials

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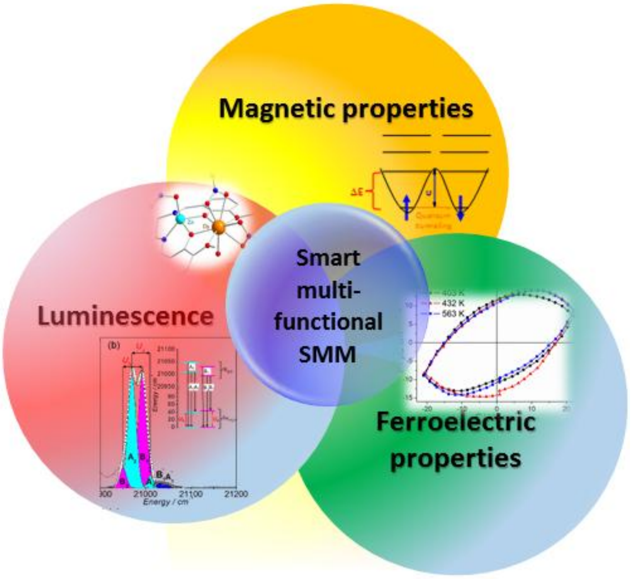
Multifunctional molecular magnets are emerging class of materials synthesized using molecular chemistry concepts, in which the targeted compounds may exhibit different physical features when subjected to various external stimuli. Such systems may combine magnetism with other physical properties displayed independently or in synergy. This lecture gives an overview on recent advances in this field focalising on lanthanide-based molecular systems presenting long range magnetic ordering (molecule-based magnets) or exhibiting slow relaxation of the magnetization (Single Molecular Magnets) associated with luminescence and/or ferroelectricity.



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Design and synthesis of new open-shell polytopic ligands and redox non-innocence in multifunctional materials

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It has long been recognized that strong exchange coupling is one key design element in molecule-based magnets with enhanced properties, such as higher blocking and hysteresis temperatures in *single molecule magnets* (SMMs) as one example [1,2]. Strong magnetic coupling serves to isolate the spin ground state from excited states, which feature inferior magnetic properties. This can be achieved by coordinating paramagnetic transition metal or lanthanide ions with stable, open-shell ligands. However, most reported paramagnetic ligands can bind one or at most two metal ions and the synthesis of radical ligands that can assemble into larger polynuclear clusters in a rational manner (e.g. large grid-type complexes) is challenging.

In this two-part presentation we will first describe our recent efforts [3] to synthesize polytopic open-shell ligands {Figure 1, left) that we are confident will self-assemble into large coordination grids in the presence of metal ions. Next, we will report on redox-active transition metal (Fe, Co [4] and Cu [5]) (Figure 1, right) and lanthanide ion (Gd, Tb, and Dy) complexes of redox active arylazo ligands, which exhibit interesting magnetic and luminescent properties and offer strong potential as multifunctional materials.

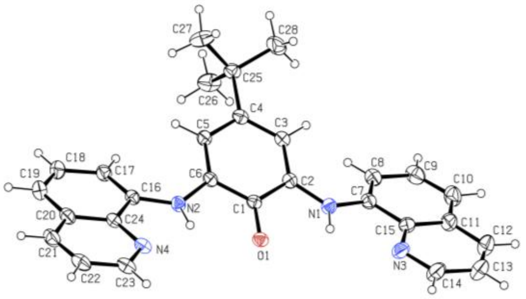

Figure 1 Structure of ditopic radical BAQP.

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Proton Order−Disorder Phenomena in a Hydrogen-Bonded Rhodium−η^5-Semiquinone Complex: A Possible Dielectric Response Mechanism

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A newly synthesized one-dimensional (1D) hydrogen-bonded (H-bonded) rhodium(II)–η^5-semiquinone complex, [Cp*Rh(η^5-*p*-HSQ-Me$_4$)]PF$_6$ ([**1**]PF$_6$), exhibits a paraelectric–antiferroelectric second-order phase transition at 237.1 K. Neutron and X-ray crystal structure analyses reveal that the H-bonded proton is disordered over two sites in the room-temperature (RT) phase. The phase transition would arise from this proton disorder together with rotation or libration of the Cp* ring and PF_6^- ion. The relative permittivity ε_b' along the H-bonded chains reaches relatively high values (ca. 130) in the RT phase. Temperature dependence of ^{13}C CP/MAS NMR spectra demonstrates that the proton is dynamically disordered in the RT phase and that the proton exchange has already occurred in the low-temperature (LT) phase. Rate constants for the proton exchange are estimated to be 10^{-4}–10^{-6} s in the temperature range of 240–270 K. DFT calculations predict that the protonation/deprotonation of [**1**]$^+$ leads to interesting hapticity changes of the semiquinone ligand accompanied by reduction/oxidation by the π-bonded rhodium fragment, producing stable η^6-hydroquinone complex, [Cp*Rh^{3+}(η^6-*p*-H$_2$Q-Me$_4$)]$^{2+}$ ([**2**]$^{2+}$), and η^4-benzoquinone complex, [Cp*Rh$^+$(η^4-*p*-BQ-Me$_4$)] ([**3**]), respectively. Possible mechanisms leading to the dielectric response are discussed on the basis of the migration of the protonic solitons comprising of [**2**]$^{2+}$ and [**3**], which would be generated in the H-bonded chain.

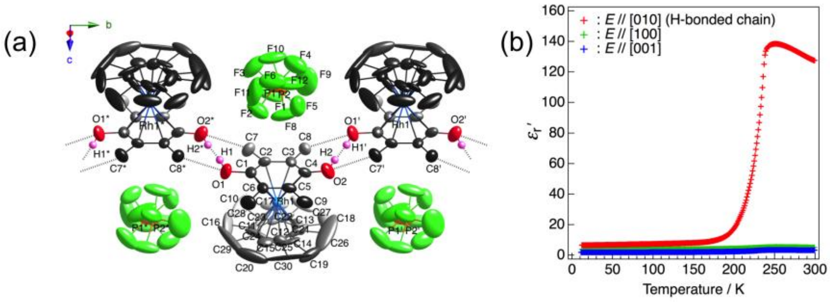

Figure 1 Crystal structure of RT phase (a) and ε_r' vs *T* plot (b) of [**1**]PF$_6$.

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Novel dinuclear cyanido-bridged molecular complexes exhibiting Single Molecule Magnet, photo- and thermo-induced Electron Transfer and Spin Crossover properties

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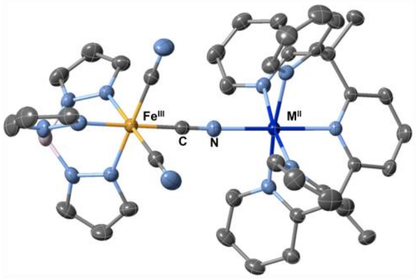
The design of molecule based magnetic materials is an emerging area in material sciences.[1] Molecules exhibiting tunable optical and magnetic properties through the application of external stimuli (temperature, pressure, light irradiation, magnetic field *etc*) have become an important research area in the field of material sciences, offering appealing future applications for electronic devices, information storage/processing, molecular switch, high-density recording media and molecular sensors.[2]

The cyanido-based chemistry has been particularly fruitful and, for more than twenty years, a large number of cyanide-bridged polymetallic systems have been synthesized through rational choices of cyanido-based building blocks. These systems exhibit interesting properties, such as single-molecule magnets (SMMs) and single-chain magnets (SCMs) behaviours,[3] spin crossover (SCO),[4] electron-transfer process,[5] and photoinduced magnetism.[6] In 2013, we have reported a dinuclear complex,[7] which exhibits switchable optical and magnetic properties depending on its physical state. Very recently we have successfully design a new dinuclear [Fe/Co] complexes exhibiting both thermally and light induced electron transfer in solid state.[8]

In this presentation, we will report different novel dinuclear complexes $[(L)Fe^{III}(CN)_3M^{II}(L')]^+$ (L' = pentadentate N-donor ligand; L = tridentate N- donor ligand, M(II) = Co, Ni, Mn), designed by rational building-block approach. Combined structural, magnetic and photomagnetic studies reveal that SMM, SCO and metal-to-metal electron transfer properties could be triggered by application of magnetic field, light and temperature.



Acknowledgements. We thank, the Centre Franco-Indien pour la Promotion de la Recherche Avancée (CEFIPRA), the Centre National de la Recherche Scientifique (CNRS), the Conseil Regional d'Aquitaine, the University of Bordeaux and the Agence Nationale de la Recherche (ANR) for financial support.

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Tetranuclear heterometallic {Zn_2Eu_2} complexes with 1-naphtoate and 1-naphthylacetate anions: synthesis, structure and luminescence properties

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It is well known that complexes with rear earth (RE) atoms possess unique photoluminescent (PL) properties, while the presence of certain coordinated organic ligands enhances PL since RE ions themselves are characterized by low probabilities of the radiative transitions. This phenomenon is called the “antenna” effect, or sensitized luminescence. Studies for the synthesis of coordination compounds with so-called “organic antennas”, *i.e.*, ligands comprising various organic moieties, are in progress.

A series of new tetranuclear Zn^{II}-Eu^{III} heterometallic complexes $[(bpy)_2Zn_2Eu_2(naph)_{10}]$ (**1**), $[(bpy)_2Zn_2Eu_2(naph)_8(NO_3)_2]$ (**2**), $[(phen)_2Zn_2Eu_2(naph)_8(NO_3)_2]$ (**3**), $[(Py)_2Zn_2Eu_2(naphac)_{10}]$ (**4**), $[(dtb\text{-}bpy)_2Zn_2Eu_2(NO_3)_2(naphac)_8]$ (**5**) and $[(diMe\text{-}bpy)_2Zn_2Eu_2(NO_3)_4(naphac)_6]$ (**6**) have been synthesized, where $naph^-$ and $naphac^-$ are the 1-naphthoate or 1-naphthylacetate anion, respectively, bpy = 2,2′-dipyridyl, phen = 1,10-phenanthroline, Py = pyridine, dtb-bpy = 4,4′-di-*tert*-butyl-2,2′-dipyridyl and diMe-bpy = 4,4′-Dimethyl-2,2′-dipyridyl. The solid-phase complexes consist of large supramolecular ensembles due to inter and intramolecular stacking interactions between the aromatic ligands. PL measurements were carried out for synthesized complexes at the room and cryogenic temperature and life times and external quantum yields were determined as well. It has been shown that partial replacement of naphthoate ligands in the coordination environment of Eu^{3+} by NO_3^- anions influences the PL properties. The external quantum yield for the solid phases of complexes **1**–**3** exceeds 20% [1].

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Implementation of chirality and luminescence into octacyanido-based magnetic coordination polymers

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The incorporation of chirality and luminescence into magnetic octacyanido-based material may be exploited in future molecule-based materials for molecular electronics or spintronics.[1-3]To address this challenge, we have explored the potential of bimetallic chains constructed of Ln(III) (Eu^{III}, Nd^{III} and Gd^{III}) complexes with chiral Pybox derivatives and $[W^V(CN)_8]^{3-}$ ions. The enantiopure pair of $Eu^{III}-W^V$ chains combine chiral helicity with paramagnetism and thermally switchable luminescence.[4] A remarkable series of eight enantiopurechiral helices of $Nd^{III}-W^V$ and $Gd^{III}-W^V$ exhibit ferromagneticcoupling with Nd^{III}-based near-infrared emission and antiferromagnetic coupling with red ligand phosphorescence, respectively.[5]The luminescent organic bis(oxazoline) molecules, Tb^{3+} and $[W^V(CN)_8]^{3-}$ ions give rise to an unprecedented 2-D$Tb^{III}-W^V$layered ferromagnet (T_c = 2.4 K) showing a switchability between Tb^{III}-centered green and ligand-based red emission by using a different wavelength of excitation light.[6]The series of Ln^{III}-Mo^V (Ln = Ce−Yb) layered materials combineLn-dependent diversity of luminescent and magnetic phenomena,as well as unusual two-step sliding of cyanido-bridged layers.[7]

The presented molecular systems open a new perspective in the area of magneto-optical molecular materials revealing tunable optical properties and magnetism, as both results from the property of a single coordination networks.

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Synergetic effects between spin state change and fluorescent properties of Schiff base-like 3d metal complexes.

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Spin crossover (SCO) complexes belong to a type of molecules whose spin state can be switched by physical stimuli such as pressure or temperature change, or light irradiation.[1] Structural and electronic changes associated with this transition can be exploited for numerical data storage,[2] temperature and pressure sensors,[3] or display devices.[2] Fe(II) is the most widely used metal center for the synthesis of SCO complexes, however, the phenomenon itself is not limited to iron(II) or other $3d^{4-7}$ metal centers with an octahedral coordination sphere. The coordination induced spin state change of Ni(II) complexes from diamagnetic ($S = 0$) square planar to paramagnetic ($S = 1$) square pyramidal or octahedral coordination sphere shifted recently back into focus.[4]

A new ligand system based on a Schiff base-like ligand bearing a phenazine fluorophore was synthesized, as well as the corresponding Fe(II), Ni(II), Cu(II), and Zn(II) complexes. The fluorescence properties of the $S = 0 \leftrightarrow S = 1$ switchable Ni(II) complexes were investigated with steady-state extinction and fluorescence spectroscopy as well as time-resolved fluorescence spectroscopy.[5] The SCO Fe(II) complexes were investigated with respect to thermally induced synergetic effects.

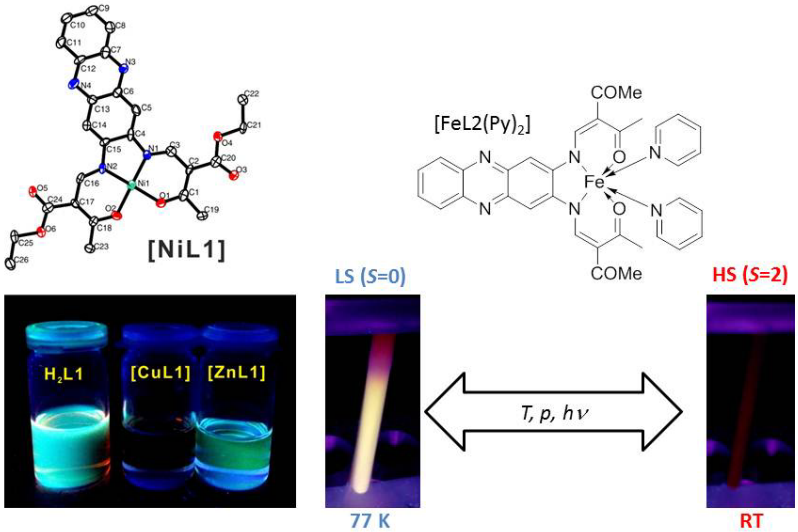

Figure 1 Molecule structure and fluorescence properties of the complexes discussed in this work.

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Shrinking Crystals: extreme thermomechanical properties through a molecular materials approach

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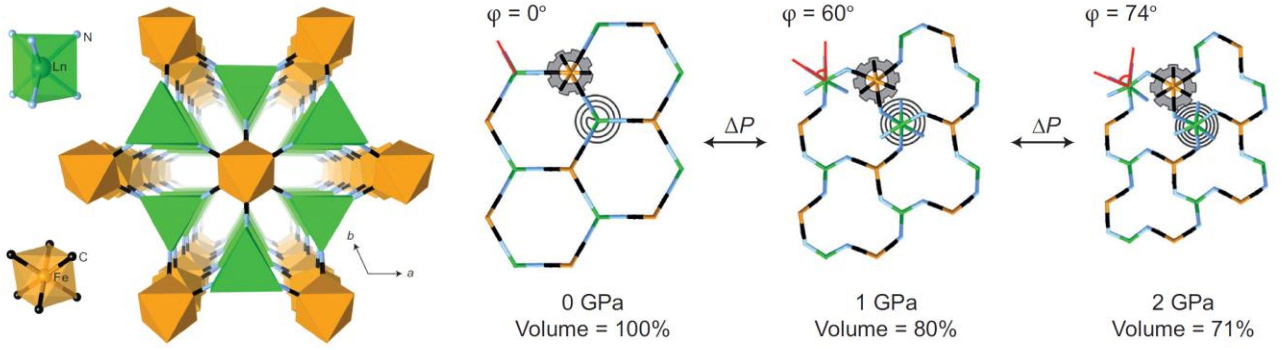
Coordination frameworks have recently gained prominence as a highly versatile class of materials with interesting structural and chemical features that distinguish them from other families of solids. One such feature is the comparatively low energies associated with the deformation of their lattices, a property that emerges both from the flexibility of their molecular building units and from the underconstrained, open topologies of their framework lattices. This feature has recently been found to lead to a very rich array of dynamic lattice properties, as seen for example in the often extreme flexibility of porous framework systems in response to the adsorption and desorption of guest molecules. Less explored has been their flexibility in response to other stimuli such as temperature and pressure. Our efforts in this area have led to the finding that the thermal excitation of transverse molecular vibrations within open coordination frameworks commonly yields unprecedented negative thermal expansion (NTE; i.e., contraction upon warming) – an interesting and potentially useful property that can be moderated through control of both the framework and host-guest chemistry. More recently we have found that the low energy deformation of these lattices can also occur under high pressure to yield extreme mechanical behaviours, as seen in the achievement of unprecedented compressibilities (see Figure).



Cleavage and Coupling of CO with Molybdenum Complexes

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Molybdenum complexes supported by multidentate ligands displaying terphenyl linkers have been employed for small molecule activation. The central arene of the terphenyl unit acts as a labile donor and coordinates in a variety of modes as a function of metal oxidation state and the nature of the other ligands. Molybdenum-CO complexes can be reduced by multiple electron equivalents. The most reduced species show significant distortion of the arene donor, indicating partial localization of reducing equivalents at this moiety. Treatment with electrophiles results in C-O bond cleavage and C-C bond formation. The mechanism of conversion of CO to C_2 products will be discussed.

Water oxidation at iridium centers containing mesoionic and related ligands: concepts to enhance catalytic activity

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Water oxidation is a key process en route to developing an efficient system for artificial photosynthesis. Amongst the various precursors for this thermodynamically uphill and highly complex reaction, iridium(III) complexes of the type [IrCp*(L,L')X] stand out as they provide relatively high turnover numbers and frequencies (L,L' = chelating neutral or anionic ligand). In this context, we have explored chelating ligands derived from mesoionic 1,2,3-triazolylidenes,[1] a subclass of N-heterocyclic carbenes which impart efficient water oxidation activity (Figure).[2] We will discuss strategies that enable the rational optimization of catalytic activity through ligand tailoring and will focus in particular on ligand design aspects and the relevance of dipolar meso- or zwitterionic ligand sites. These efforts have led to some of the most active catalysts known to date.[3]

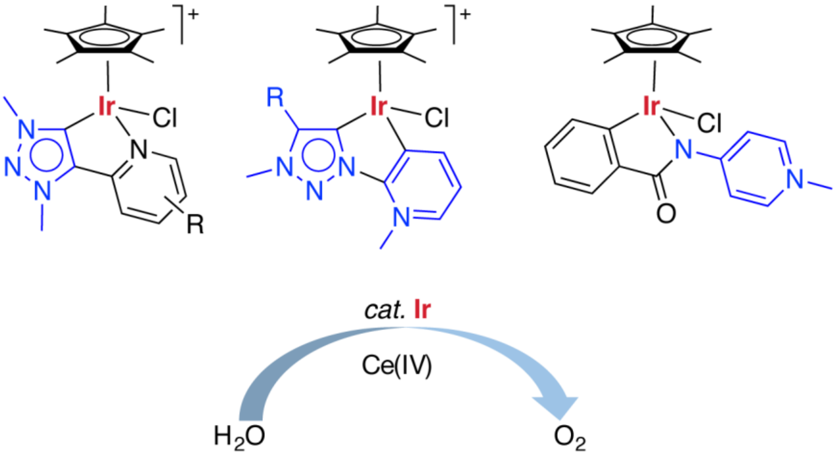

Figure Iridium complexes with tunable mesoionic ligands for efficient water oxidation.

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Electrochemical O_2 reductive activation with Fe complexes

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Iron-(hydro)peroxo and oxo species are key intermediates in the catalytic cycle of Fe containing enzymes (*eg.* CytP450, Rieske Dioxygenases) capable of cleaving the O-O bond and of oxygen atom insertion into organic substrates. Numerous studies of the catalytic activity of bioinspired Fe complexes using chemical oxidants have been published already.[1] We have reported on the electrochemical formation and reactivity of Mn-peroxo intermediates resulting from the interactions between Mn(II) complexes, O_2 and electrons.[2] Here we describe an analogous approach to study O_2 reductive activation with Fe(II) complexes. The non-heme $[(TPEN)Fe^{II}]^{2+}$ complex is used as a prototype in the cyclic voltammetry (CV) study of O_2 activation (Figure 1). CV analysis allows to propose an O_2 activation mechanism involving several iron intermediates similar to those found to be involved in CytP450 mechanism.[3] Furthurmore new results concerning porphyrinic Fe(II) catalysts will be presented.[4] These results may pave the way for the development of performant oxidation catalysts using the benign O_2 instead of chemical oxidants.

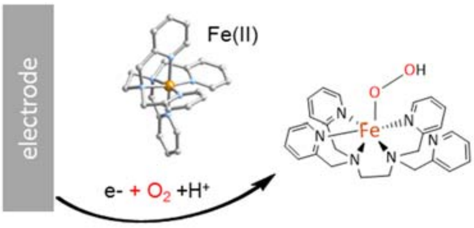

Figure 1 Electrochemical activation of O_2 using $[(TPEN)Fe^{II}]^{2+}$ complexes

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The reaction between the peroxide VO(η^2-O_2)(pyridine-2-carboxylate) and Fe^{II}_{aq} is not a Fenton like reaction

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The reduction of VO(η^2-O_2)(pyridine-2-carboxylate) by $Fe(H_2O)_6^{2+}$ proceeds via the formation of the transient complex (pyridine-2-carboxylate)(O)$V^V(\mu-\eta^2:\eta^2\text{-}O_2)Fe^{II}(H_2O)_3^{2+}$ that is transformed via intra-molecular electron transfer into (pyridine-2-carboxylate)(O)$V^{IV}(\mu-\eta^2:\eta^2\text{-}O_2)Fe^{III}(H_2O)_3^{2+}$. The latter transient reacts with another $Fe(H_2O)_6^{2+}$ to yield $2Fe(H_2O)_6^{3+}$ + $V^VO(OH)$(pyridine-2-carboxylate)$^+$. These results point out that:

1. V^V does not activate the η^2 bound peroxide towards the Fenton like reaction. In this aspect V^V differs from Fe^{III} in $(H_2O)_5Fe\text{-}OOH^{2+}$.
2. Transients of the type $L_mM^n(\eta\mu-\eta^2:\eta^2\text{-}O_2)M'L_l$" have to be considered in the reductions of complexes of η^2 bound peroxides.

New reactions and new reaction channels of nonheme iron oxidation catalysts

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Bispidine ligands are extremely rigid, easy to synthesize and available in a large variety. They enforce coordination geometries derived from cis-octahedral, and the two vacant coordination sites with the tetradentate ligand systems are sterically and electronically distinct; with the isomeric pentadentate ligands, the site of the oxo group is enforced by the ligand. Coligands coordinated trans to N3 generally have strong and short bonds, those trans to N7 are more labile. Reasons are thoroughly analyzed on the basis of computational work as well as experimental structural data, thermodynamics, spectroscopy and reactivities. Implications with respect to the mechanism of formation and the structure and spin state of high valent iron oxidants are analyzed, and possibilities to tune the spin state, structure and reactivity of high valent iron complexes are discussed.

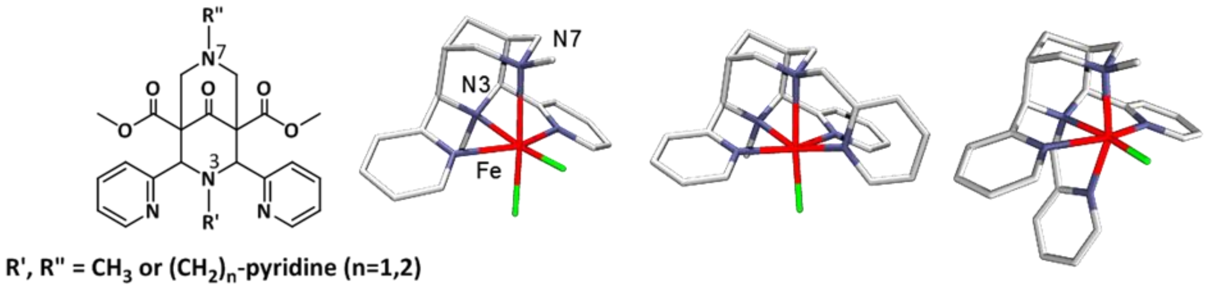

Figure 1 Bispidine ligands and structures of the Fe^{II} complexes with the tetradentate and the two isomeric pentadentate bispidine ligands.

Special emphasis will be on the question why different families of supporting ligands and the variation of the metal center (e.g. Fe^{IV} vs. Mn^{IV}) may lead to subtle changes in the reaction mechanism and a novel environmentally important reaction, the anaerobic formation of methane from methionine.

CO_2 Reduction by Iron Porphyrin Complexes

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An iron porphyrin complex with a proton transfer motif in its distal side is found to reduce CO_2 to CO as well as formic acid selectively under different experimental conditions. The selectivity is governed by relative binding affinity of the reduced Fe center towards CO2 and H+ which in turn can be tuned by utilizing the distal functional groups. Resonance Raman spectroscopy, electrochemical techniques and Density Functional Theory calculation are used to elucidate the reaction mechanism. In particular, the role of hydrogen bonding in governing the stability of different intermediates will be discussed.

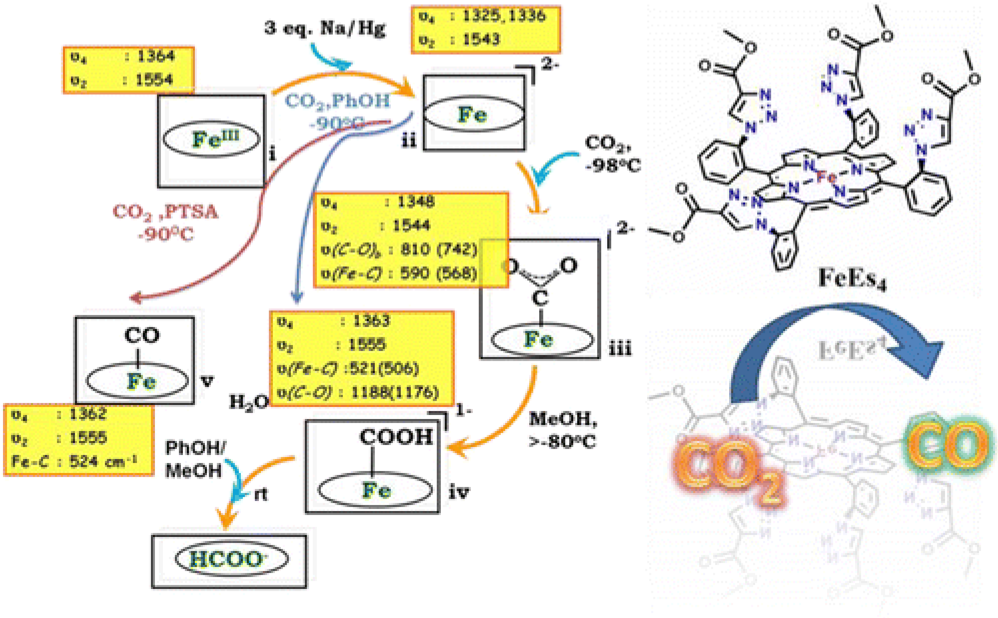

Figure 1 Reaction mechanism of CO_2 reduction by Iron(0)porphyrins

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1 B. Mondal, A. Rana, P. Sen, and A. Dey J. Am. Chem. Soc., 2015, 137, 11214

Activation and Functionalization of Molecular Nitrogen by Coordination Complexes

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While the field of coordination chemistry has been centrally involved in the discovery and elucidation of numerous new homogeneous catalytic processes, the one area that has defied efforts is in the use of molecular nitrogen as a feedstock. While the Haber-Bosch process for the production of ammonia from N_2 and H_2 over heterogeneous catalysts has been known for more than a 100 years, discovery of a homogeneous catalyst that can use N_2 productively to generate higher-value, nitrogen-containing products still eludes the efforts of coordination chemists all over the world.[1] The reasons for this are many but the most obvious is that the dinitrogen molecule is incredibly inert, which makes it difficult to use as a feedstock despite the fact that it is abundant and easily manipulated.

We have been examining the activation of functionalization of this simple, small molecule for over two decades. This keynote lecture will describe our efforts to synthesize new coordination complexes that contain ligated N_2, and to develop reactions that functionalize the dinitrogen unit in the coordination sphere of the complex. A key problem that must be addressed is the aforementioned inertness of N_2, which translates to dinitrogen being a very poor ligand. If one is going to examine new reactions for coordinated N_2, displacement of the dinitrogen moiety versus functionalization of coordinated N_2 will always be an issue. One of the themes that we will develop is trying to discover dinitrogen-containing metal complexes that have strong enough M-N_2 interactions that facilitate N-E bond formation in lieu of N_2 displacement.[2]

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Mössbauer studies of trinuclear iron complexes supported by a *tris*(β-diketiminate) cyclophane

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The same cyclophane ligand serves as backbone for trinuclear iron complexes with approximate trigonal symmetry. Here we present several of those complexes, with μ-sulfide or μ-hydride as bridging ligands, and various iron oxidation states. As the versatility of this ligand framework continues to yield new unprecedented complexes, their electronic structures are analyzed in light of the reactions that they are able to effect[1,2]. The triferrous μ-hydride complex[2] is expected to be highly reactive, as it contains several μ_2-hydride ligands, similar to the proposed E_4 reaction intermediate of FeMoco. However, reactivity toward N_2 was not detected, although the complex is able to transform CO_2 into formate. Sulfide ligands, on the other hand, yield complexes that contain planar (Fe_3S_x) clusters[3] with various iron oxidation states, some of which show the ability to bind a solvent molecule and bear some similarities with the proposed reaction site of FeMoco.

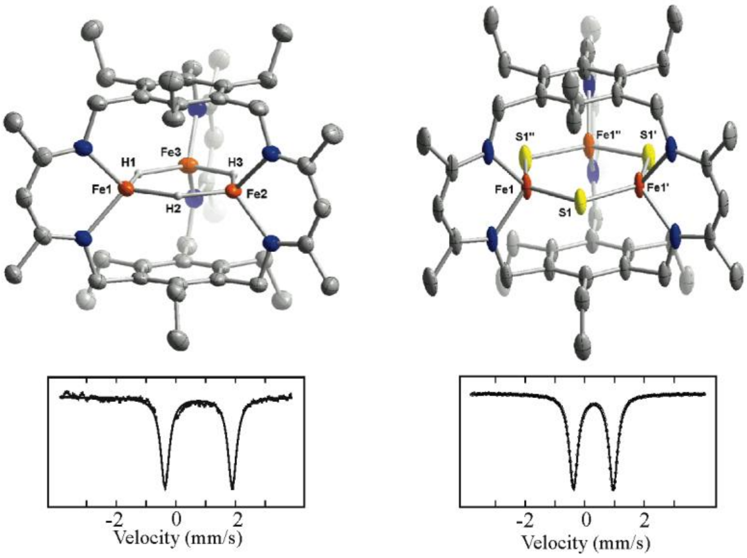

Figure 1 Solid-state structures and Mössbauer spectra of Fe_3H_3L (left) and Fe_3S_3L (right)

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Activation and cleavage of dihydrogen at a single sulphur and other non-metal centres

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The activation of dihydrogen, its cleavage and next the reuniting of the molecular hydrogen are very important since they are strongly connected with the industrial modes of its use as the source of energy. The H_2 activation at transition metal centres analyzed most often is not convenient for industrial processes where light and small volume materials are preferred for the storage and transportation of dihydrogen. Hence the non-metal centres to activate dihydrogen seem to be promising materials for the potential use in industry. The studies on the role of non-metals for the molecular hydrogen cleavage are very rare; for example; H_2 may be activated if it acts as the Lewis base in the A-H...σ hydrogen bond interactions [1]; the theoretical study on the splitting of dihydrogen by nucleophilic activation at a single carbon centre of singlet carbenes [2] is another one of only few examples.

Non-metal centres such as sulphur, phosphorus, arsenic, selenium and bromine in simple species were considered recently [3] as possible active sites to split the dihydrogen. Since the most promising results were obtained for sulphur thus the more detailed studies were performed on numerous sulphur species. The reactions of the activation of dihydrogen, its cleavage and next its reuniting are analyzed, in the gas phase and in different solvents. The MP2/aug-cc-pVTZ calculations, supported by the Quantum Theory of Atoms in Molecules [4] and the Natural Bond Orbitals [5] methods, were performed here and it was found that solvents (especially polar ones) strongly decrease the potential barrier heights for the mentioned processes; few of species considered are promising ones to be considered as potential materials for hydrogen storage.

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Electronic structure and small molecule reactivity of metal-Mabiq complexes

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Studies pertaining to the characterization and reactivity of late, first-row, transition metal complexes coordinated by the macrocyclic biquinazoline ligand, Mabiq, will be presented. The Mabiq ligand offers two distinct metal coordination sites, and both mono- and bi-metallic compounds have been isolated. Low-valent forms of the mono-metallic Fe, Co and Ni compounds were generated and characterized using a range of spectroscopic methods and magnetic susceptibility studies. The redox activity of the Mabiq ligand adds complexity to the electronic structures of these species. The reactivity of the metal-Mabiq complexes with respect to H_2 production and CO_2 activation will be discussed. The studies are highly relevant to current efforts to develop catalysts for renewable energy related processes.

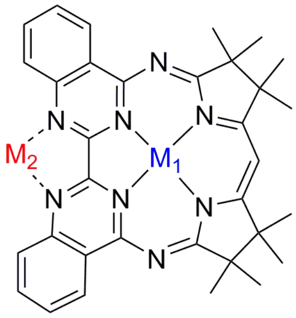

Figure 1. The Mabiq ligand provides two metal coordination sites.

Hydrogen Production by Dehydrogenation of Formic Acid using Azole and Azoline-Type Catalysts

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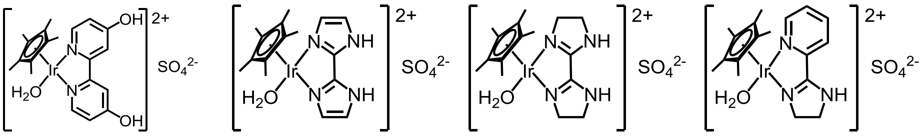
The combination of hydrogenation of CO_2 and dehydrogenation of formic acid (FA) has received great attention for hydrogen storage.[1] We have reported highly efficient Iridium-based catalysts with proton-responsive ligands (e.g., 4,4',6,6'-tetrahydroxy-2,2'-bipyrimidine) for both reactions.[2] In this presentation, we describe Ir catalysts with electron-rich azole- and azoline-type ligands for FA dehydrogenation in water without any organic additives.



1 **2** **3** **4**

Figure 1. Iridium Catalysts for FA Dehydrogenation

We investigated FA dehydrogenation using the series of iridium catalysts **1-4** in 1 M FA aqueous solution at 60 °C. The catalysts **2-4** showed higher activities (TOF/h^{-1}; **2**: 4000, **3**: 54,700, **4**: 13,300) than the conventional catalyst **1** (TOF 2400 h^{-1}). The evolved gas was composed of CO_2/H_2 (1/1) without CO contamination. Unfortunately, the most active catalyst **3** was easily degraded in a highly concentrated FA solution or elevated reaction temperature. Catalyst **4** with a robust pyridine moiety incorporated into the bidentate ligand showed high activity and durability in highly concentrated FA solution, and as a consequence, 1.02 m^3 of gas (TON of 2,000,000) was produced from 20 mol of FA using 10 μmol of **4**. These results promise to contribute to the realization of a viable hydrogen storage system in the future.

Y. H. thanks the Japan Science and Technology Agency (JST), CREST for financial support. The work at BNL was carried out under contract DE-SC00112704 with the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences.

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N_2 Binding and Functionalization by Iron Complexes

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The predominant heterogeneous catalyst for the iron/potassium Haber-Bosch catalyst is composed of iron metal, but there is not atomic-level understanding of how the surface iron atoms weaken, cleave and protonate N_2.[1] In order to provide soluble analogues with precisely defined structures and mechanisms, we have synthesized a number of high-spin iron complexes with multiple iron and alkali metal centers, characterized them using crystallography and spectroscopy, and studied their N-H bond forming reactions.[2] Formally iron(I) and iron(0) complexes with several three- and four-coordinate metal atoms can weaken and break the triple bond of N_2 below room temperature, showing that cooperative reactivity of the metals is a reasonable hypothesis for surface reactions as well.

While cooperation of two iron atoms can lengthen and weaken the N-N bond, three working together enables iron atoms to completely cleave the N-N bond to nitrides.[3] Alkali metals (typically introduced into the reaction as part of the reducing agent) stabilize highly reduced complexes, pull electron density into the N_2 unit, and make reduced nitride products more stable. Alkali metals can also play a kinetic role, because cation-π interactions with the supporting ligands can organize the approach of multiple iron atoms.[4] This presentation will describe new details on the trends in reactivity based on the alkali metal cation, and also new details on N-H and N-C bond forming reactions. Overall, multi-iron systems have great promise for using N_2 as a raw material for commodity and fine chemical products.

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Bioinspired Reactivity of Iron Complexes on a *tris*(thiolato)phosphine platform

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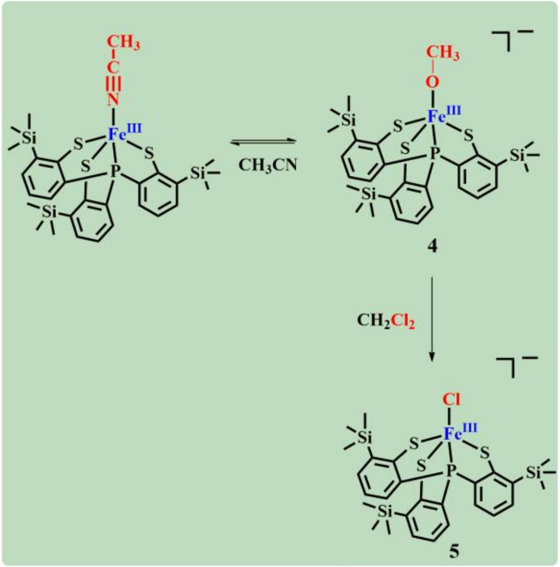
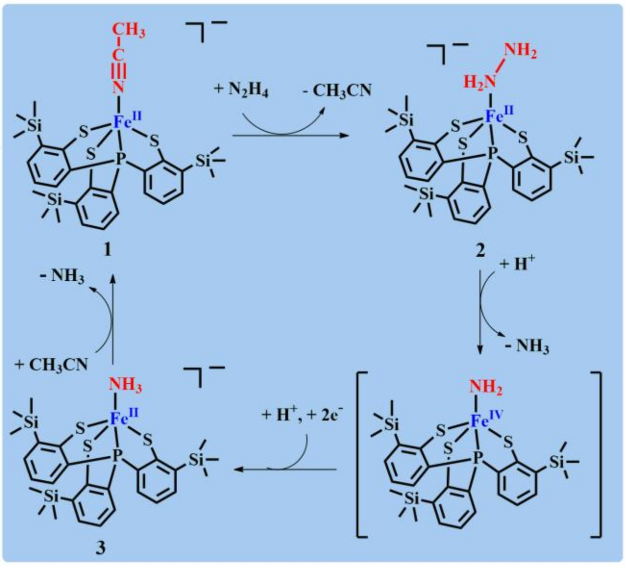
In this presentation, we report an Fe^{II} complex binding with a *tris*(thiolato)phosphine ligand, $[P(Ph)_4][Fe^{II}(PS3")(CH_3CN)]$ (**1**) (PS3" = $P(C_6H_3\text{-}3\text{-}Me_3Si\text{-}2\text{-}S)_3^{3-}$) that catalyzes the reduction of hydrazine, an intermediate and a substrate of nitrogenase. The substrate- and product- bound adducts, $[N(Bu)_4][Fe^{II}(PS3")(N_2H_4)]$ (**2**) and $[N(Et)_4][Fe^{II}(PS3")(NH_3)]$ (**3**), respectively, are also synthesized. The work provides the feasibility that the late stage of biological nitrogen fixation can be conducted at a single iron site with a S-rich ligation environment. In addition, complex **1** is oxidized by dioxygen to yield a Fe^{III} methoxide bound complex, $[P(Ph)_4][Fe^{III}(PS3")(OCH_3)]$ (**4**). The bound methoxide group is labile in CH_3CN and replaced by CH_3CN solvent molecule. Importantly, the Fe^{III} bound methoxide has a strong nucleophilic character that reacts with a weak electrophile, dichloromethane, to produce a Fe^{III}-Cl species, $[P(Ph)_4][Fe^{III}(PS3")(Cl)]$ (**5**). The strong nucleophilic nature of a Fe^{III} bound base provides a mechanistic implication for the role of Fe^{III}-OH site in nitrile hydratase.





Nucleophilic reactivity of a Fe^{III} bound alkoxide

Ctalytic reduction of hydrazine to ammonia by a defined monuclear Fe^{II} thiolate complex

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Mononuclear Copper Reaction Center for Oxygen Activation

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Mononuclear copper(II) active-oxygen complexes are receiving much recent attention as the key reactive intermediate of copper monooxygenases such as dopamine *β*-monooxygenase (D*β*M), tyramine *β*-monooxygenase (T*β*M), and peptidylglycine-*α*-hydroxylating monooxygenase (PHM).[1] These enzymes catalyze the stereo-selective hydroxylation at the benzylic position of dopamine and tyramine, the biologically important hormone and monoamine neurotransmitter (for D*β*M and T*β*M), and the initial step of amidation of *C*-terminus of peptide hormones and neuropeptides (for PHM).[2] Amzel and coworkers succeeded to determined the crystal structure of the oxy-form of PHM using a slow substrate (inhibitor), to demonstrate existence of a mononuclear copper active center having an end-on bound O_2 having a distorted tetrahedral geometry (Figure 1).[3] Recently, polysaccharide monooxygenases (PMO) have also been shown to have a simple mononuclear copper reaction center for the oxidative degradation of stable polysaccharides such as cellulose and chitin,[4, 5] for which a mononuclear copper(II) active-oxygen superoxide species is also suggested to be involved as a key intermeidtae.[6]

To get insights into the physicochemical properties and reactivity of such reactive intermediates involved in the enzymatic reactions, we have investigated the structure and reactivity of the series of mononuclear copper active-oxygen species such as superoxide, alkyl- or hydro-peroxide, and oxide by using a variety of N3- and N4-supporting ligands.[7] In this presentation, I will introduce our recent studies of the mononuclear copper complexes that are developed for oxygen activation chemistry.

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A DFT mechanistic journey into the world of CO_2 activation.

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Metal-mediated redox transformation of small molecules, under mild conditions, is an area of great current interest. Of utmost importance is the fixation of the “inert” CO_2 molecule, which constitutes a highly attractive low cost, abundant and renewable C1 source for fine chemicals and fuel production. To this moment, this transformation can be mediated by numerous systems containing *s*-, *p*-, and more often *d*-transition metals.[1-3] Nowadays, complexes containing low-valent *f*-block elements have attracted remarkable attention, due to their easiness to activate and functionalize this greenhouse gas.[4,5]

Mechanistically such transformations are difficult to be fully elucidated by experimental techniques. Herein, we present our recent advances, based on DFT calculations, and involving elements coming from different parts of the periodic table.[6-9] One of the most significant outcomes is the disclosure of novel bimetallic pathway that is likely to operate when carbonate complexes are forming as final products. This original route is operating in a concerted fashion, by reducing two molecules of CO_2, and involves a transient six-membered ring metallacycle-intermediate, presumably in competition with the formation of oxo-intermediate. Likewise, the formation of highly stable bimetallic bridged $(CO_2)^{2-}$ complexes which are denoted as “key intermediates” in the beginning of the reaction will be highlighted, being a common feature for the aforementioned reactivity and independent of the metal is used or the ligand environment. Finally, an intriguing case of cooperativity found between a reduced uranium center and a Lewis acid will be presented as well.[10]

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Formation and high reactivity of anti-dioxo form of high-spin μ-oxodioxodiiron(IV) that cleaves a strong C-H bond

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Recently, we have reported that upon reaction of a μ-oxodiaquadiiron(III) (**1**) with H_2O_2, high-spin μ-oxodioxodiiron(IV) (**3**) is formed via O-O bond scission of μ-oxo-μ-peroxodiiron(III) (**2**).[2] The dinuclear structures of **1-3** are stabilized by a bis-tpa type dinucleating ligand, 1,2-bis[2-[bis(2-pyridylmethyl)aminomethyl]-6-pyridyl]ethane (6-hpa).[1] Chemical structures of **1-3** are shown in Figure 1. Since **3** is the first example of high-spin diiron(IV) mimicking spin state of the active species Q in sMMO, and expected to be highly reactive to the C-H bond cleavage. Here, formation and reactivity of the active species is shown on the basis of resonance Raman spectra, detailed kinetic studies for the reaction of **3** with substrate, activation parameters, tunneling effect, DFT studies, large KIE values, and catalytic alkane oxidation with H_2O_2.

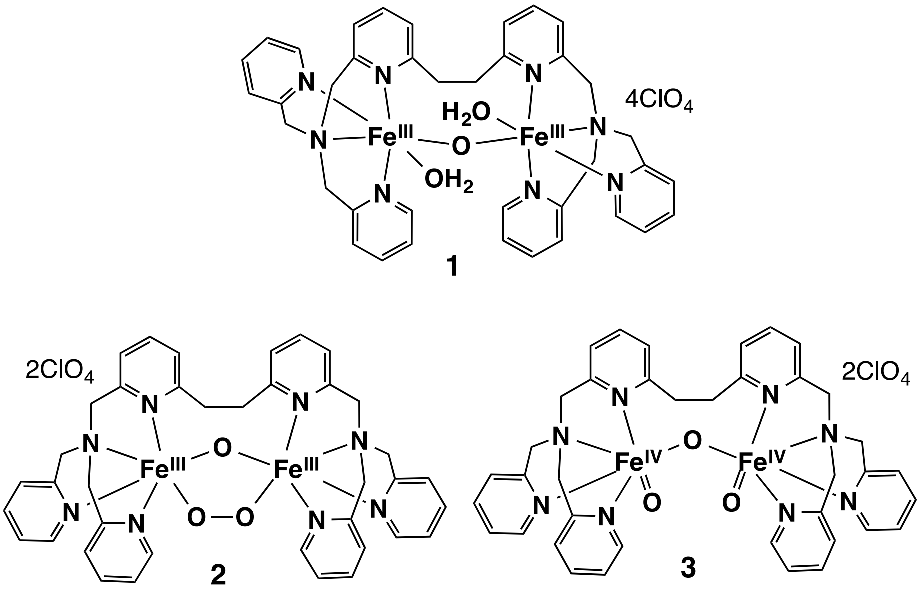

Figure 1 Chemical structures of **1-3**

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Mechanistic Insights into NO to N_2O Transformation at a Mononuclear Nickel Site

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Nitrous oxide (N_2O) is a long-lived (~114 years) greenhouse gas with 298 times global warming potential per molecule as compared to that of CO_2. Global emission of N_2O is mainly attributed to biological denitrification and fossil fuel combustion. The most critical step in microbial denitrification route for N_2O formation is the transition metal mediated reductive coupling of two nitric oxide (NO) molecules.[1] During denitrification, either iron or copper containing nitrite reductase (NiR) enzymes catalyze the reduction of nitrite (NO_2^-) to NO. Surprisingly, Cu-NiR exhibits dual-activity and can also participate in reductive N-N coupling of two NO moieties leading to N_2O under high NO flux.[2] The X-ray crystal structure[3] of Cu-NiR active site shows a side-on $\{CuNO\}^{11}$ complex; however, the previously reported model[4] Cu-nitrosyl complexes are found to be end-on.

To demonstrate the role of non-covalent interactions in governing the transition-metal nitrosyl binding modes, we employ an electron-poor β-diketiminato-Ni core that allows to synthetically access a $\{NiNO\}^{10}/[\{NiNO\}^{11}]^-$ redox-couple. Specifically, one-electron reductions of the neutral $\{NiNO\}^{10}$ species by potassium-graphite in presence of different cryptands, such as 18-crown-6, [2.2.2]-cryptand afford anionic $\{NiNO\}^{11}$ cores with corresponding $[K^+]$ counter-cations ($[K^+] = K^+$[cryptand]). X-ray diffraction analyses on these $[K^+]\{NiNO\}^{11}$ complexes exhibit the involvement of both side-on and end-on anionic $\{NiNO\}^{11}$ cores depending on the solvation of the potassium cation by 18-crown-6, [2.2.2]-cryptand, respectively. Addition of one equivalent of NO to these well defined anionic $\{NiNO\}^{11}$ complexes result immediate formation of anionic $[Ni](k^2\text{-}O_2N_2)$ species, thereby demonstrating that $\{MNO\}^{11}$ cores are prone to undergo N-N reductive coupling with NO and form *cis*-hyponitrite complexes $[M](k^2\text{-}O_2N_2)$. Finally, protonation of the anionic $[Ni](k^2\text{-}O_2N_2)$ species results in a quantitative N_2O evolution.

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Dioxygen Activation via Two-Electron Transfer from Hydroxide to Dioxygen Mediated by a Manganese(III) Salen Complex

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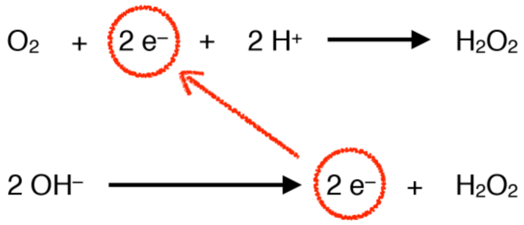
O_2 activation for use in oxygenation reactions intrinsically requires a costly sacrificial reductant. The present study investigated the possibility to use aqueous alkaline solution for O_2 activation (Scheme 1). The OH^- ion in aqueous alkaline solution is an electron-rich species, which is expected to serve as an electron source material. A great advantage of using OH^- is that the electron release from OH^- is expected to generate H_2O_2. In contrast to unwanted byproducts from usual electron source materials, H_2O_2 from OH^- could be utilized as an oxidant.



Scheme 1. Aqueous alkaline solution (OH^-) as an electron source material.

Very recently, I reported that a manganese(III) salen complex, a well-known oxidation catalyst, mediates this attractive O_2 activating reaction.[1] Upon the reaction with aqueous KOH solution under air, a manganese(III) salen complex is immediately converted to a di-μ-oxo dimanganese(IV) salen complex, which is also obtained by the reaction with H_2O_2 (Figure 1). ^{18}O isotope experiments revealed that the half of the O atoms of the μ-oxo bridges comes from O_2, while the other half comes from OH^-, which is exactly consistent with Scheme 1.

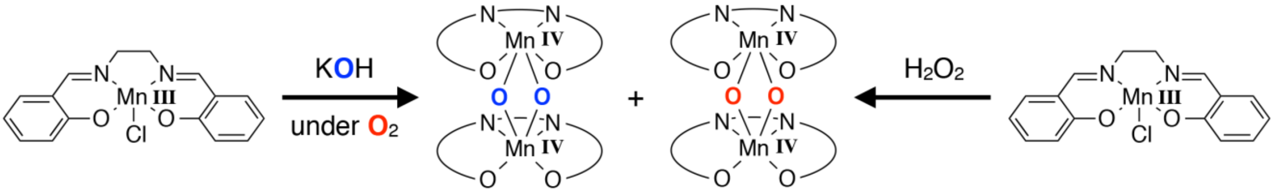


Figure 1. O_2 / KOH is equivalent to H_2O_2 in the reaction with Mn(III)(salen)(Cl).

To achieve O_2 activation under less demanding conditions, I am now investigating details of this reaction. The reaction of a manganese(III) salen complex with Bu_4NOH at –80 °C gave a distinct species with unique spectroscopic and redox properties. I want to discuss key properties of this species that enable the present O_2 activation.

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N-Heterocyclic Carbenes (NHCs): New Platform for Novel Chemistry

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N-heterocyclic carbenes (NHCs) are well-known in catalysis and main group chemistry. There have been numerous reports on NHC based organocatalysts or on transition metal catalysts for novel and efficient organic transformations. More interestingly, NHCs have been intensively explored for stabilizing unstable species such as radicals and zerovalent nonmetal species, and for activating small molecules such as CO, H_2, NH_3, N_2O, etc.[1] We found that NHCs stabilize nitric oxide (NO) radical in a solution phase to form stable NHC NO radicals.[2] Full characterization of the compounds including X-ray crystallography, EPR, and cyclic voltammetry will be discussed in addition to the mechanistic studies and NO transfer experiments. Inspired by this work, we have explored NHC chemistry further as new platforms for novel chemistry such as redox functionalization of small molecules and triazenyl chemistry, which will be discussed in detail.

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Outer-Sphere Control in Redox Reactions Catalysed by Perrhenate

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The exploitation of supramolecular interactions to assemble and define catalysts and their active sites has the potential to provide the required complexity for catalytic control using the spontaneous assembly of simple components.[1]

We have been exploiting this approach in metal recovery by solvent extraction, in particular designing receptors for the selective recovery of metalate anions,[2] and report here their application as new redox catalysts. We have used lipophilic pyrdinium receptors to transfer perrhenate (ReO_4^-) from its aqueous environment into an organic phase, upon which it becomes an active alkene epoxidation catalyst under biphasic conditions.[3] We have extended this concept to include single-phase, perrhenate-catalysed deoxydehydration (DODH) of diols to alkenes, and the reduction of carbon dioxide to methanol equivalents (Figure 1).[4] Experimental observations are underpinned by DFT calculations and show that the cation can be implicated in the catalytic mechanism.

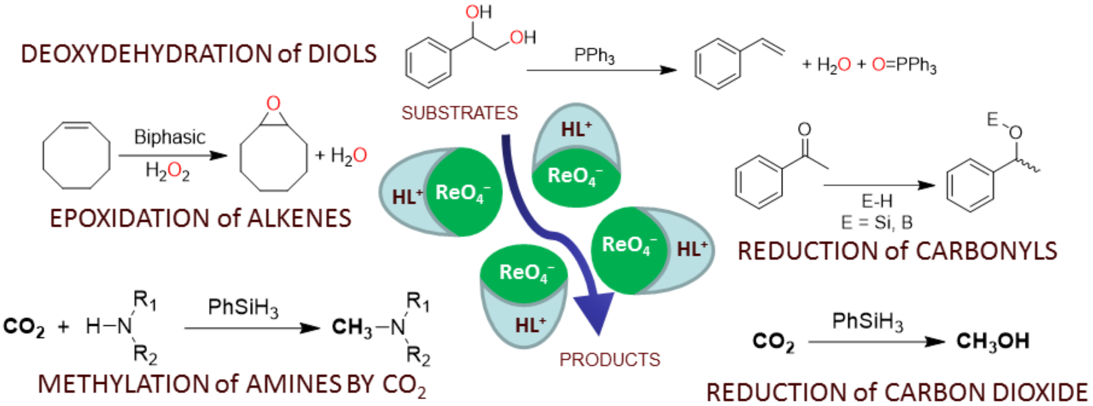

Figure 1 Redox reactions catalysed by simple, lipophilic perrhenate compounds

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Hydrogenase and its Mimics for Fuel Cell Electrodes

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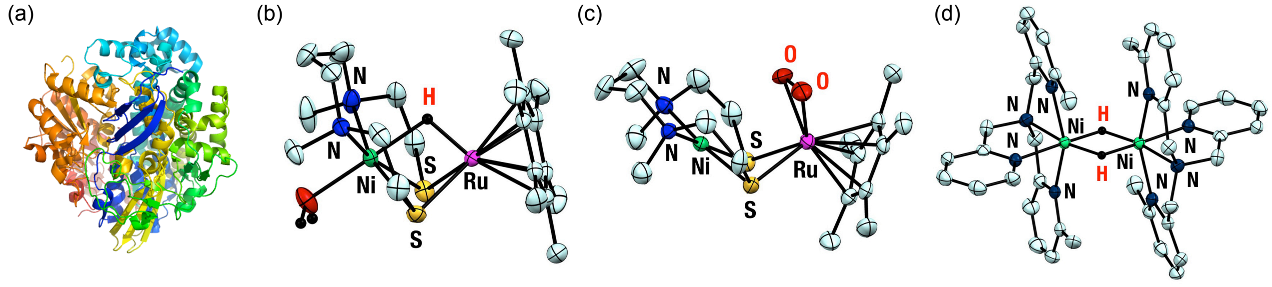
H_2-O_2 fuel cells are one of the most promising energy conversion systems, but they are in desperate need of an alternative to the scarce and expensive Pt catalyst. O_2-tolerant [NiFe]hydrogenases ([NiFe]H_2ases) are bifunctional enzymes that are capable of acting as both H_2ases and oxidases, whose function is the same as Pt catalyst in the fuel cells. Thus, we have applied [NiFe]H_2ase from *Citrobacter* S-77 and its mimics, $Ni^{II}(\mu\text{-}H)Ru^{II}$, $Ni^{II}Ru^{II}(\eta^2\text{-}O_2)$, and $Ni^{II}_2(\mu\text{-}H)_2$ complexes (Figure 1), for electrode catalysts of polymer electrolyte fuel cells (PEFCs).[1–5] These catalysts were mixed with carbon black and loaded on a waterproof carbon cloth to make a gas-diffusion electrode. A piece of proton exchange membrane was sandwiched between two gas-diffusion to afford a membrane electrolyte assembly (MEA). The MEA was assembled in fuel-cell hardware. Such bio- and biomimetic PEFCs were able to generate electricity. We analyzed the detailed electrochemical aspects of these catalysts by Tafel plots, impedance spectra, Koutecky-Levich plots, and rotating ring disk voltammetry experiments.



[NiFe]H_2ase — $Ni^{II}Ru^{II}$ hydride complex — $Ni^{II}Ru^{II}$ peroxo complex — Ni^{II} dihydride complex

Figure 1 Hydrogenase and its mimics for fuel cell electrodes.[1–5]

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Nickel(III)-Oxygen Adducts That Oxidize Inert Hydrocarbons

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High-valent terminal metal-oxygen adducts are hypothesized to be the potent oxidising reactants in late transition metal oxidation catalysis. In particular, examples of high-valent terminal nickel-oxygen adducts are sparse, meaning there is a dearth in the understanding of such oxidants. Herein we describe the preparation of a family of Ni(III)-oxygen adducts. Electronic absorption, electronic paramagnetic resonance, and X-ray absorption spectroscopies, and density functional theory calculations have been used to probe the electronic and structural properties of these compounds. Structure function relationships in a series of complexes have been elucidated, providing us with critical insight into the reactivity properties of high-valent nickel oxidants.

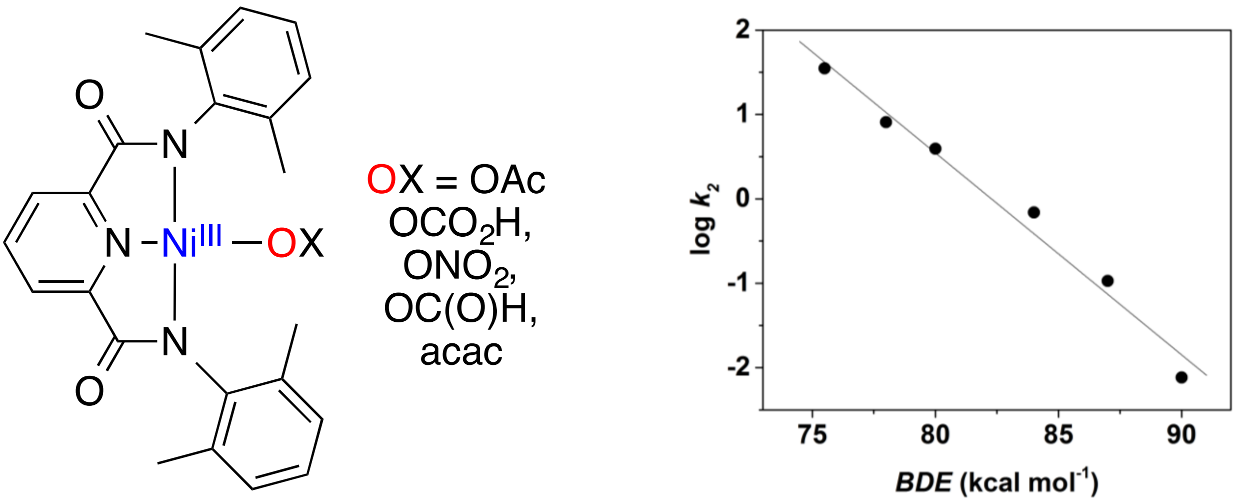

Figure 1. Nickel(III)-oxygen adducts (left) and a plot (right) of log(k_2) versus C–H BDE for the reactions between a nickel(III)-oxygen adduct and various hydrocarbons.

P. Pirovano, E. R. Farquhar, M. Swart, A. J. Fitzpatrick, G. G. Morgan, A. R. McDonald *Chem. Eur. J.* **2015**, *21*, 3785-3790.

New Turns in Biomimetic Dioxygen Activation at Dicopper Sites

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In order to achieve the activation and transformation of small molecules, numerous enzymes take advantage of the cooperative action of two (or even more) proximate metal ions hosted within the protein active site. Understanding the functional principles of these biological systems offers great inspiration for the development of novel bioinspired catalysts, most importantly for catalysts relevant to the global energy challenge. Work in our group has exploited the use of compartmental pyrazolate-based ligand scaffolds for preorganizing two metal ions in proper spatial arrangement (Figure 1).[1] In this presentation, recent results will be discussed for bioinspired copper-mediated dioxygen activation, including novel intermediates that represent snapshots of the O_2 binding trajectory at biological type 3 dicopper sites,[2,3] unusual interactions of such intermediates with Lewis acids,[2] and proton- and redox-mediated interconversions between, and equilibria of, different Cu_2/O_2 species.[4]

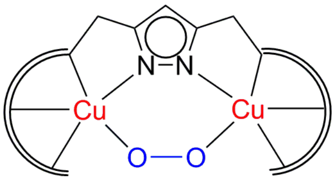

Figure 1 Pyrazolate-based dicopper peroxo complex

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Synthesis, Characterization and Reactivity of Bio-inspired Metal Complexes for Small Molecule Activation

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Many biological transformations are performed by enzymes that incorporate a red-ox active first-row transition metal in the active site. Many of these biochemical transformations require selective oxidation of hydrocarbons and this is accomplished by activating dioxygen, a kinetically inert species.[1] Dioxygen activation leads to formation of many reactive oxygen species (ROS) such as superoxide, peroxides. Metal-center at the active site in the enzymes plays a critical role controlling the formation of these ROS's so that substrate oxidation can be accomplished avoiding detrimental effects of auto-oxidation.[2] Understanding the mechanism of metal supported formation and reactivity of the reactive oxygen species can provide valuable information that would have impact in synthesis of new pharmaceuticals or other commodities.[2] Developing catalysts that include inexpensive first-row transition metals and can oxidize wide array of organic molecules under relatively mild conditions is one of the goals of bio-inorganic chemists. In the last 25 years many different metal complexes were synthesized and their catalytic potentials were investigated. One of the activated species of dioxygen activation is metal-hydropperoxo intermediate, but reactivity of this metal-oxygen adduct was less explored. Particularly studying reactivity of mono-nuclear metal-hydroperoxo intermediate was challenging owing to their fleeting nature. In our lab we are focusing on synthesizing coordination compounds of Ni and Cu and studying their reactivity toward hydrogen peroxide. The main focus of the research is to stabilize and study reactivity of early metal-oxygen adducts like metal-superoxo, metal-hydroperoxo intermediates toward hydrocarbon oxidation. In our knowledge very few reports were known of early metal oxygen adducts supported by Ni and Cu.[3] Only two reports show direct reactivity of mono-nuclear copper-hydroperoxo intermediate toward hydrocarbon oxidation.[4] In this presentation I will discuss initial efforts in my lab to stabilize metal-oxygen adducts supported coordination compounds of Cu and Ni. Preliminary data on reactivity of the metal-oxygen adducts toward substrates will also be discussed.

N_2 Activation by Triiron Complexes

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The iron-molybdenum cofactor (FeMoco or Fe_7S_9MoC) in molybdenum-dependent nitrogenases catalyzes the reduction of N_2 under ambient temperature and pressure using biological reducing agents. The proposed mechanism relies on cooperative interactions between the metal centers within the cluster, which allow for formation of a transient low valent iron center. In principle then, a detailed understanding of the design criteria to harness redox cooperativity and multimetallic complexes can allow access to similar reactivity in synthetic systems. We employ cyclophanes ligands to template the assembly of triiron complexes, and have used these complexes for the reductive activation of dinitrogen. Our recent work towards understanding the mechanism of this reaction as well as that of other related triiron compounds will be presented. The relevance of our results to the biological system will be discussed.

Mechanism of Cu-Catalyzed Aerobic Oxygenation of Phenols

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The copper-catalyzed aerobic oxygenation of phenols is an attractive green method for the conversion of abundant phenols into reactive and synthetically useful *ortho*-quinones. This method is reminiscent of the copper-containing enzyme tyrosinase that oxygenates tyrosine to dopaquinone in the first step of the ubiquitous biosynthesis of melanin pigments.[1] A reaction developed in the Lumb group reproduces fully catalytic tyrosinase-like conditions (Scheme).[2] This reaction employs catalytic amounts of both copper(I) and a diamine ligand and proceeds with unsurpassed yields and efficiency. Our mechanistic study of this reaction reveals the intermediacy of a tyrosine-like side-on peroxodicopper(II) intermediate, as well as a copper(II)-semiquinone intermediate, **SQ**, that remains at steady-state concentration during the reaction.[3] Subsequent oxidative coupling of **SQ** with another equivalent of phenol provides the final product, which can be further functionalized through the addition of nucleophiles. We hereby present the details of this mechanistic study, using in-situ UV-Vis spectroscopy and low-temperature stopped-flow techniques, and demonstrate that the oxidative coupling of the phenol to the quinone **2** is necessary for the nucleophilic substitution and formation of **3**.[4]

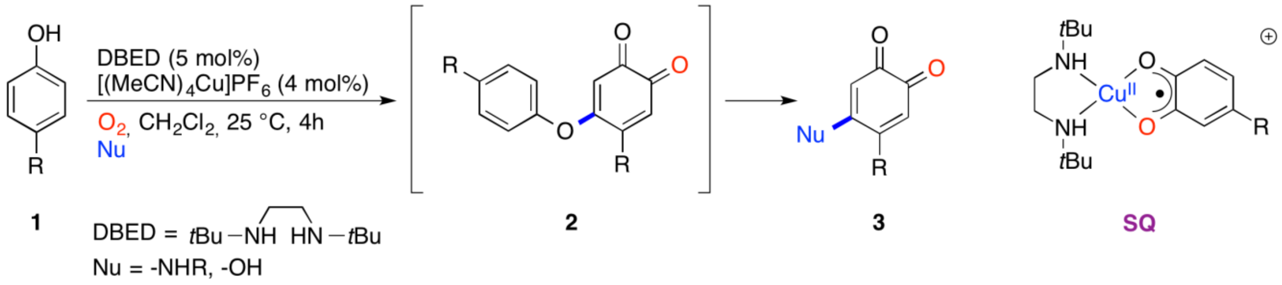

Figure 1 Typical conditions for the fully catalytic oxygenation of phenols under O_2.

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Hydrides and [FeFe]-Hydrogenases: Models vs Reality

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Hydrogenases are enzymes that catalyze the redox of H_2:

$$H_2 \rightleftharpoons 2\,H^+ + 2e^- \qquad (1)$$

There is much interest in how these enzymes operate since the production and oxidation of H_2 are of both fundamental and practical interest. For the [FeFe]-hydrogenases, equation 1 has been assumed to be mediated by iron hydrides, and my group has discussed the likely intermediacy of terminal iron hydrides.[1] *Biophysical studies have however consistently failed to identify hydrides for any redox state of the enzyme.*[2]

The lecture will attempt to reconcile the biophysical and organometallic modeling results. New data obtained in collaboration with the Cramer and Lubitz groups will be presented on proteins labeled via new synthetic methodology (Figure 1). These results appear to give direct evidence for hydride states and explain why hydrides have remained so elusive.[3,4]

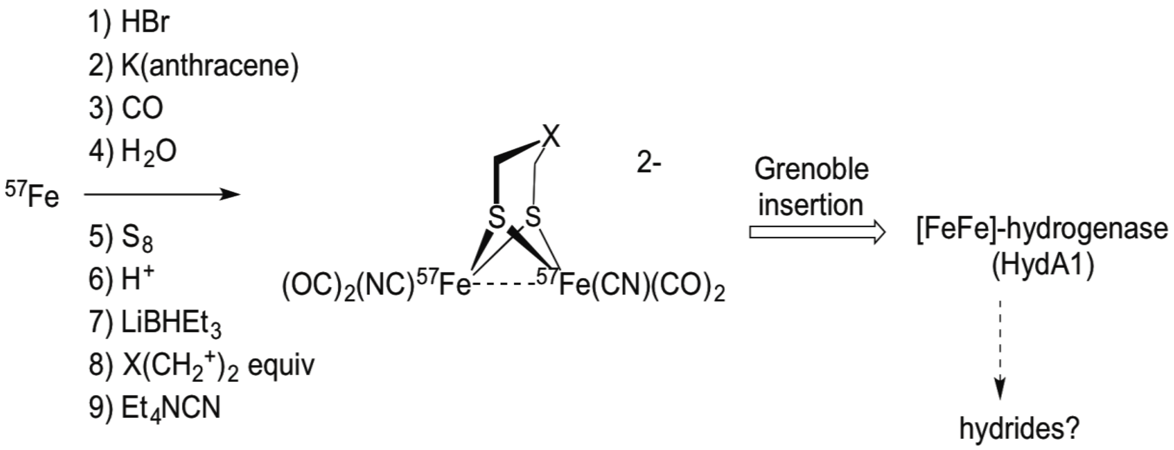

Figure 1. Synthetic route to ^{57}Fe-labeled [FeFe]-hydrogenase HydA1.

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Molecular carbide complexes: chemical and physical properties of Ru≡C ligands

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The simplest conceivable organometallic fragments are arguably two-atom metal-carbon units such as terminal carbide complexes. These units influence natural and artificial small molecule activations, being present in nitrogenases and on Fischer-Tropsch process catalyst surfaces.[1,2] Moreover, carbide is a simple though relatively rare ligand with clear relevance to coordination chemistry.

Our work concerns systems derived from the terminal ruthenium carbide, $Ru(C)Cl_2(PCy_3)_2$ (**RuC**) (Cy = cyclohexyl). With this as a synthetic entry, we report new terminal carbide complexes and their elaboration to polynuclear carbide-bridged complexes.[3,4] Computational and spectroscopic studies indicate **RuC** to act as a π-accepting ligand towards other metal fragments. This contradicts earlier experimental claims that **RuC** acts as a σ-donating ligand towards metal centres.[5]

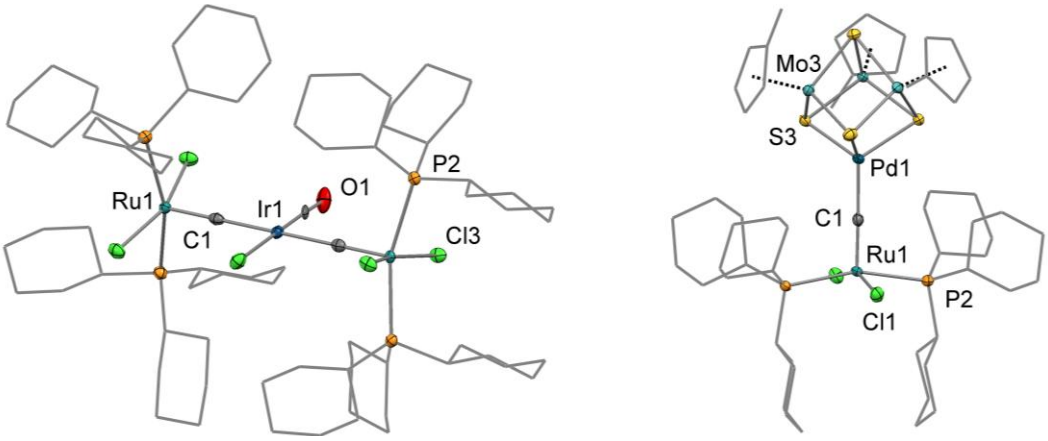

Figure 1. Representative molecular carbides: *trans*-$(\textbf{RuC})_2IrCl(CO)$ (left), an analogue of Vaska's complex and **RuC**-$PdS_4(MoCp')_3^+$ (right), a cubane-like carbide-sulfide cluster.

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Transformation of N_2 to Nitriles

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Synthetic nitrogen functionalization at ambient conditions remains as one of the most challenging tasks in homogeneous catalysis. In recent years, we examined elementary reactions relevant to nitrogen fixation such as nitride hydrogenolysis,[1] nitride coupling to N_2,[2] and N_2 splitting to terminal nitrides.[3] In this contribution, the use of rhenium pincer complexes for the catalytic conversion of N_2 to nitriles is presented. The mechanism is discussed based on a synthetic cycle (Figure 1).

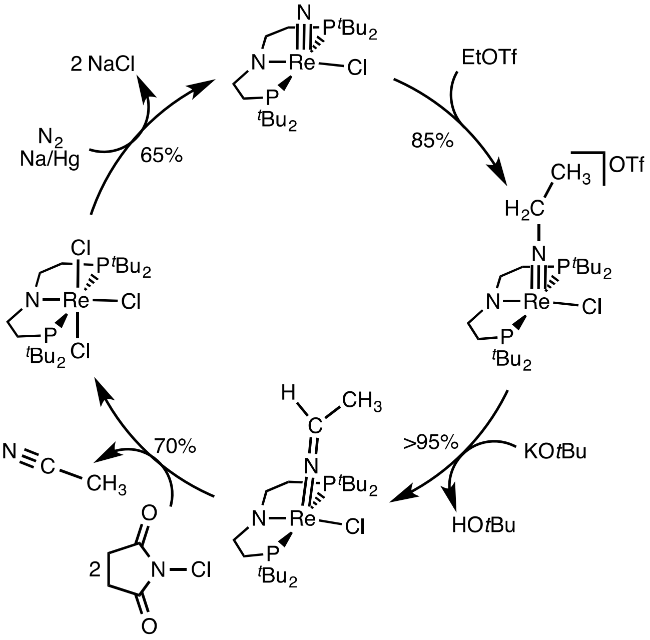

Figure 1 Conversion of dinitrogen to acetonitrile.

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NO splitting by an alkyne complex based bisphos moiety

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Alkynes with proximate donor substitution are electronically flexible linkers with a high conjugation potential which allow the assembly of supramolecular complexes in different coordination modes.[1,2] Alternatively, mononuclear alkyne complexes bearing α-donor substituents raise the question, if metal based paramagnetism of the alkyne complex involve radical activity at these terminal heteroatoms.

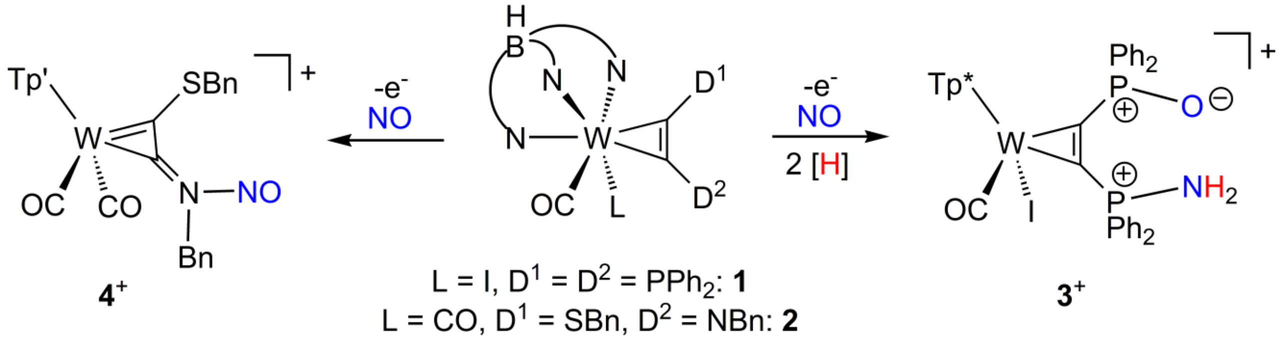

Figure 1 Proof of radical reactivity by NO trapping and splitting (Tp' = hydridotris(3,5-dimethylpyrazolyl)borate, Tp* = hydridotris(3,4,5-trimethylpyrazolyl)borate, Bn = benzyl)

In this contribution we present the novel *P*,*P*- and *S*,*N*-ligand systems **1** and **2** governed by a W(II) alkyne complex scaffold. Basing on an excellent electrochemical reversibility for the redox couple **1**/**1**$^+$, the cation shows radical reactivity at the P atoms. Addition of NO gas led to a remarkable NO splitting reaction, which finally yields complex **3**-BF_4 with one terminal amino phosphonium and one phosphine oxide group by H atom transfer (HAT) (Fig. 1). According to EPR spectroscopic evidence the radical reactivity at the phosphine moiety is only weakly interrelated with the experimentally derived spin density at the P centres. The related *S*,*N*-substituted alkyne complex **2** shows upon oxidation HAT at ambient and radical combination with NO at low temperature leading either to a terminal amino or a nitrosamine group delivering a rational for the first step of the NO splitting at **1**$^+$.

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Stable *N*-Heterocyclic Carbenes with a 1,1'-Ferrocenediyl Backbone and Their Heavier Homologues

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N-Heterocyclic carbenes (NHCs)[1] are extremely valuable as nucleophilic organocatalysts. They are widely applied as ligands in transition-metal catalyzed reactions, where they are known as particularly potent σ-donors. They are commonly viewed as workhorses exhibiting reliable, but undramatic, chemical behavior. We recently demonstrated that a stable ferrocene-based NHC (Fig. 1, left) is able to add ammonia, dichloromethane, methyl acrylate, *tert*-butyl isocyanide, and carbon monoxide under mild conditions.[2] Such small-molecule activation reactions are typical of (alkyl)(amino)carbenes, but were completely unprecedented for diaminocarbenes.[3] In view of the surprising reactivity of this ferrocene-based NHC, which is due to its ambiphilic nature,[4] we surmised that its heavier homologues (Fig. 1, right), too, can be expected to show unconventional chemical behavior.

While the synthesis and isolation of corresponding germylenes and stannylenes turned out to be easily possible, we are still hot on the heels of stable or persistent silylenes. We have obtained a reactive plumbylene, which forms stable adducts with suitable donors such as, for example, NHCs or 4-(dimethylamino)pyridine. Its reaction with $PbCl_2$ affords an unusual lead(II) cluster by a process involving a C–H activation.

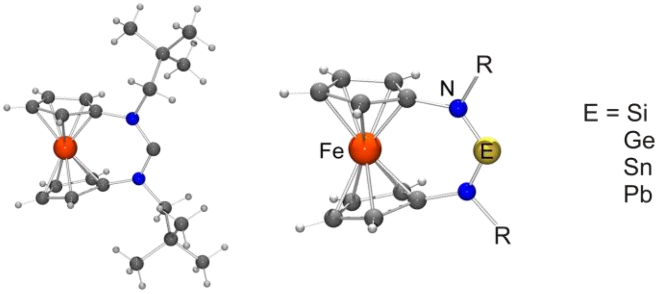

Figure 1 A stable ferrocene-based NHC (XRD result, left) and its heavier homologues.

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NN bond splitting by silica supported tantalum hydrides in N_2 and N_2H_4: Differences and similarities

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The monometallic silica supported tantalum hydrides $[(\equiv SiO)_2Ta\text{-}H_X]$ (X = 1 or 3) are able to split the NN bond in N_2 in presence of H_2. The final product is the silica supported imido amido tantalum complex $[(\equiv SiO)_2Ta(NH_2)(NH)]$.[1] On the basis of spectroscopic and DFT calculations, we proposed a reaction mechanism that implies successive proton and hydride transfers to the two nitrogen ends of the N-based ligands before the final NN splitting occurs.[2] The H^+ transfers arise from H_2 heterolytic splitting and increase the electrophilicity of the ligand receptor of H^+ favoring the subsequent hydride transfer. In addition, the calculations show that this process occurs one time more than required by the stoichiometry of the reaction. Indeed, H_2 was shown to act as a co-catalyst since in a set of consecutive steps, H_2 adds and is eliminated. This rationalizes some experimental particularities of the reaction.

It is currently accepted that metal mediated decomposition of hydrazine gives insights on unraveling the mechanism of N-N splitting in N_2. Noteworthy, reaction between N_2H_4 and $[(\equiv SiO)_2Ta\text{-}H_X]$ (X = 1 or 3) leads to the same final product $[(\equiv SiO)_2Ta(NH_2)(NH)]$.[3] In the present contribution, we will use both spectroscopic evidences and DFT calculations to propose a reaction mechanism for the NN splitting in N_2H_4 that shows that the reaction pathways for NN splitting of N_2 and N_2H_4 share some intermediates and steps. However, N_2H_4 is not formed during N_2 dissociation, which is an illustrative “cautionary tale” in the use of N_2H_4 in N_2 splitting.

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Molybdenum Dinitrogen Complexes Supported by Pentadentate Tetrapodal (pentaPod) Ligands: Structure, Synthesis, and Reactivity

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The conversion of dinitrogen into ammonia is one of the most important reactions in nature. In the context of synthetic nitrogen fixation our workgroup developed Chatt-like systems[1,2] with a pentaphosphine environment consisting of a tripod ligand and a bidentate coligand.[3-5] In order to further increase the stability of these systems, molybdenum complexes have been synthesized which are supported by novel pentadentate tetrapodal (pentaPod) ligands like $P_2^{R}PP_2^{Ph}$, R = Ph (**1**) or Me (**2**) (Figure 1). Reaction of **2** with $[MoCl_3(thf)_3]$ followed by Na_x/Hg reduction affords the complex $[MoN_2(P_2^{Me}PP_2^{Ph})]$ (**3**), which is the first example for a Chatt-like system supported by a pentadentate phosphine ligand (Figure 2).[6] It shows the highest activation of N_2 ever found for a molybdenum dinitrogen complex with a phosphine environment (ν(NN) = 1929 cm^{-1}). Reaction with HOTf leads to the NNH_2 complex $[MoNNH_2(P_2^{Me}PP_2^{Ph})](OTf)_2$ under full retention of the pentaphosphine ligation. Reactivity studies regarding the formation of ammonia and hydrazine from N_2, mediated by **3**, are presented and discussed.

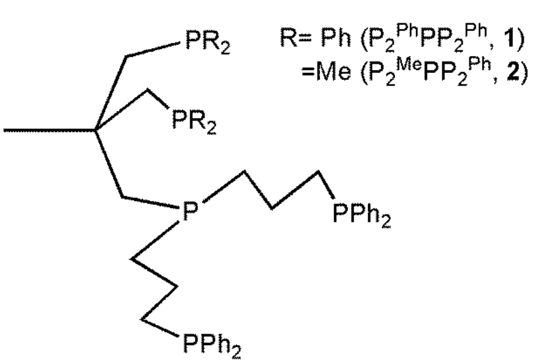

Figure 1 Constitution of pentaPod ligands

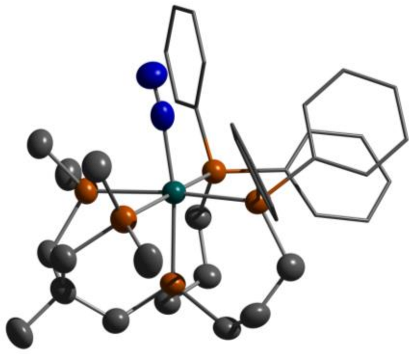

Figure 2 Single crystal x-ray structure of **3**

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FeNi Sulfides as Highly Efficient, Sustainable and Stable Electrocatalysts for H_2 Generation

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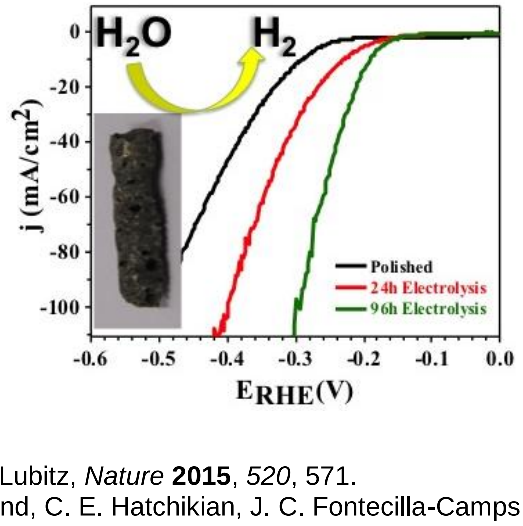
The efficient reduction of protons under mild conditions and catalysis by non-noble metals is a current challenge and a need of modern society. Nature utilizes sophisticated enzymatic machineries – the hydrogenases – that comprise iron- and nickel- containing active sites to perform this transformation.[1,2]

In order to gain similar cooperative metal-metal interactions we aimed at establishing a well-defined and simple iron-nickel compound as potential electrocatalyst. We found that $Fe_{4.5}Ni_{4.5}S_9$ as simple inorganic platform allows for an efficient reduction of protons. Remarkably, the 'rock' electrode acts as a highly efficient and durable catalyst for hydrogen evolution under aqueous conditions at low overpotentials without the need of further processing, e.g. laborious surface structuring. It reaches an overpotential as low as 190 mV and is stable for more than 180 h at high current densities. The superior hydrogen evolution reaction performance of $Fe_{4.5}Ni_{4.5}S_9$ qualifies this material as a promising electrocatalyst for a future hydrogen-based economy.



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Control of Proton Delivery by Changing Molecular Dynamics in Nickel Electrocatalysts for H_2 Production

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Electrocatalysts that efficiently convert between electrical energy and chemical energy are needed for sustainable energy in the future. We are developing nickel(II) complexes for the electrocatalytic production of H_2 by reduction of protons. These biologically inspired synthetic complexes incorporate pendant amines that function as proton relays in the second coordination sphere of metal complexes. A series of $[Ni(P^{Ph}{}_2N^{C6H4\text{-}R}{}_2)_2]^{2+}$ complexes, including R = *n*-hexyl, *n*-decyl, *n*-tetradecyl, and *n*-octadecyl, were studied as electrocatalysts for H_2 production. The turnover frequency of H_2 production inversely correlated with the rates of ring inversion (chair-boat isomerization) of the six-membered ring of the Ni-P_2N_2 group, which is essential to catalysis because this isomerization process controls the positioning of the proton relays relative to the metal center. The complex with the C_{18} hydrocarbon chain gives slower chair-boat isomerization and faster catalysis compared to the C_6, C_{10} or C_{14} analogs (Figure 1). Turnover frequencies observed at 25 °C are up to 10^6 s^{-1} in acetonitrile-water, and 10^7 s^{-1} in protic ionic liquid-water media. This research was supported as part of the Center for Molecular Electrocatalysis, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences.

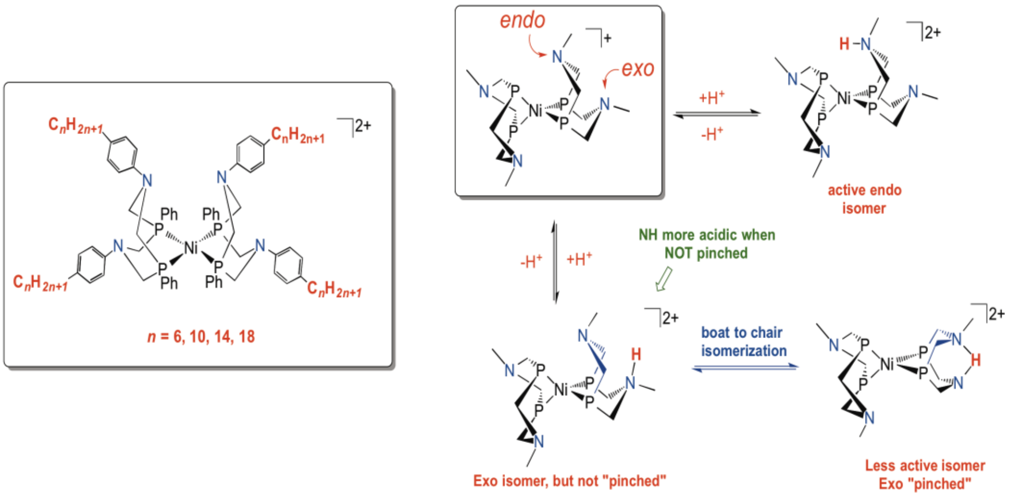

Figure 1. Endo protonation leads to the more active catalyst, while protonation exo leads to less active isomers. Slower boat-chair isomerization gives faster catalysis.

Electrochemical Reduction of CO_2 by Intact Organometallic Catalysts Chemically Bonded on GCE Surface

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Photoelectrochemical conversion of CO_2 into valuable chemicals, i.e. "Solar Fuels", is one of the most active and key topic in the contemporary research.[1] The "homogenenous" approach make easier the design, synthesis, characterization and study of mechanistic aspects (i.e. also by computational approaches) of a molecular organometallic complex involved in the CO_2 conversion. The combination with an "heterogeneous" approach is desirable, because it could make the CO_2 conversion by green-renewable energy more industrially feasible and appealing.[3]

The surface electrode modification by different approaches, namely by electropolymerization, reduction and oxidation of thiophene-, diazonium salt- and amino-containing complexes, respectively, gave surface-modified Glassy Carbon Electrodes (GCE) suitable for electrocatalytic reduction of CO_2. The complexes Re(bpy-R)$(CO)_3Cl$, Mn(bpy-R)$(CO)_4Br$, where bpy-R is an appropriate bipyridine substitute with R (i.e. thiophene, diazonium salt and amino) group, were tested. For example, Figure 1 shows the catalytic current enhancement over GCE after electropolymerization of Re(2,2':5',2''-terthiophene)$(CO)_3Cl$.[2]

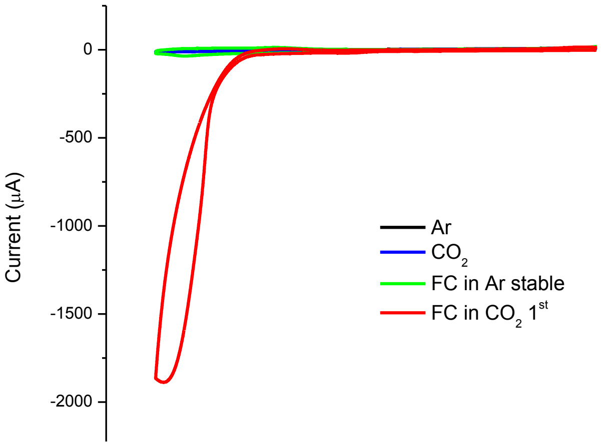

Figure 1 CV in MeCN of the modified GCE by Re(terthiophene)$(CO)_3Cl$ ($\Gamma = 35.3\times10^{-10}$ mol/cm^2) at scan rate 0.2 V/s under CO_2.

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Ruthenium complexes bearing extended poly-*N*-heterocyclic ligands: deciphering properties for charge photoaccumulation

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The design of molecular devices for direct solar fuel production has been the subject of intensive research in the last decade.[1] To optimize their efficiency, it is crucial to adjust the timescale and the monoelectronic nature of the light-induced charge separation step with the targeted multielectronic redox catalysis, reduction of water into hydrogen or of carbon dioxide into valuable carbon-based fuels, typically. One promising strategy relies on the introduction of photoaccumulation functions in the molecular design.[2,3] For instance, charge photoaccumulation has been smartly achieved by the group of F. MacDonnell with ruthenium polypyridine photosensitizers,[4-6] and favorable energetics were obtained with a dinuclear Ru complex displaying a bent geometry.[5]

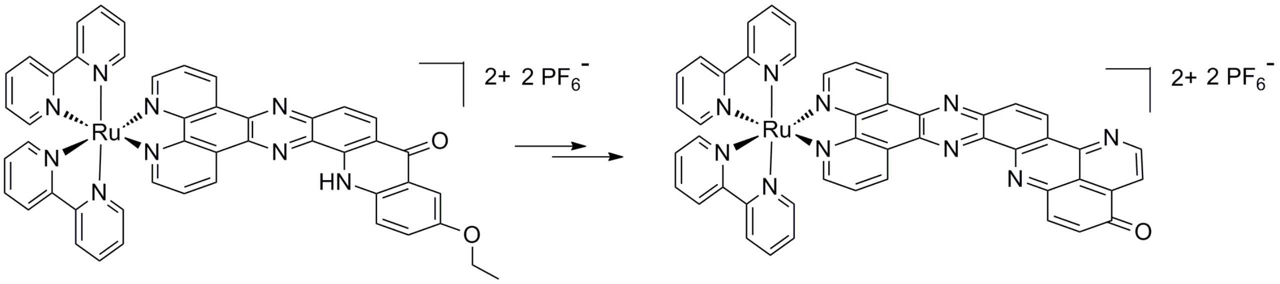

Figure 1 Structure of two Ru complexes based on hepta- and octacyclic ligands.

New mononuclear Ru(II) complexes bearing bent poly-*N*-heterocyclic ligands (Figure 1) have been prepared by a high-yielding procedure, relying on a “chemistry-on-the-complex” approach. A spectroscopic and theoretical investigation of their electronic properties will be discussed in the context of charge photoaccumulation.[7]

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Light-driven hydrogen generation: from efficient molecular catalysts to the development of a functional photocathode

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Solar driven water-splitting into hydrogen and oxygen, also referred as artificial photosynthesis, has emerged as a very attractive sustainable approach to produce the fuel H_2, as promising energy carrier for the future.[1,2] Water-splitting can be achieved *via* the construction of photoelectrochemical cells combining a photoanode for water oxidation to a photocathode for water reduction (protons) into H_2 based on the association of metal-oxide semi-conductors and molecular compounds.[3] Considerable efforts have been made for the development of homogeneous molecular photocatalytic systems for H_2 evolution, involving a light-harvesting antenna (photosensitizer), a H_2-evolving catalyst (HEC), and a sacrificial electron donor (DS). By contrast, examples of molecular based-photocathodes for protons reduction, using a *p*-type semi-conductor in place of the DS start only to emerge.[3] This lecture will present our recent results on homogeneous systems for visible-light driven H_2 production in fully aqueous solution using rhodium and cobalt as HECs (Fig. 1).[4-8] The advantages of coupling by a covalent bond HEC and sensitizer will be also presented,[7] as well as the results obtained toward the development of a functional photocathode combining these molecular systems and a NiO semi-conductor electrode.[9]

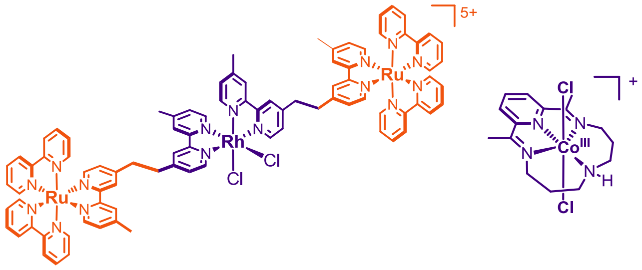

Figure 1. Chemical structures of a ruthenium-rhodium photocatalyst and a cobalt catalyst**.**

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Hydrogen storage and release by bicarbonate-formic acid hydrogenation-dehydrogenation cycle catalysed by novel Fe and Ru complexes

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Selective dehydrogenation of formic acid (FA, 4.4 %wt) affords H_2 + CO_2 in an “atom efficient” process, and CO_2 (or $NaHCO_3$) can be re-hydrogenated back to FA or $NaHCO_2$, affording a zero-carbon footprint cycle for hydrogen storage and release.[1] We have used the linear tetraphosphine 1,1,4,7,10,10-hexaphenyl-1,4,7,10-tetraphosphadecane (tetraphos-1, P4)[2] in its *rac*-isomer as ligand for Fe(II) and tested the properties of molecularly defined complexes and *in situ* precatalysts for sodium bicarbonate hydrogenation to formate and formic acid dehydrogenation to H_2 and CO_2, obtaining high yields and selectivities under moderate reaction conditions. The mechanisms were studied by NMR and HPNMR techniques showing complex $[FeH(rac\text{-}P4)]^+$ as the key intermediate (Figure 1).[3] Ru(II) complexes of *meso*-P4 and catalytic systems made *in situ* were also tested for FA dehydrogenation and preliminary results will be presented.

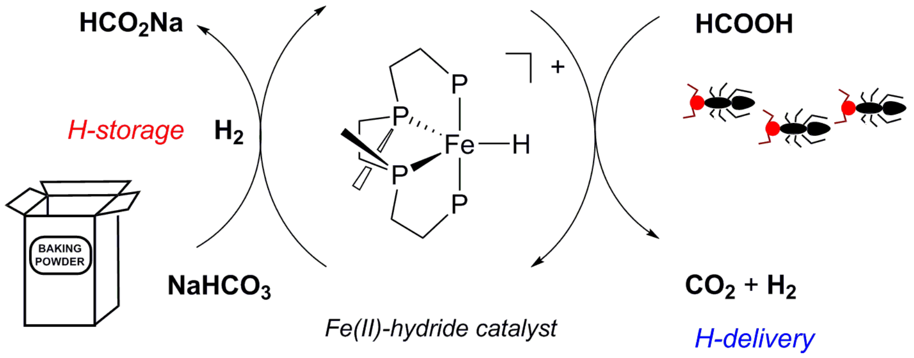

Figure 1 Fe(II)-hydride catalyst for FA dehydrogenation / $NaHCO_3$ hydrogenation

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Prussian-blue-based catalysts for water oxidation

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Prussian-Blue (PB), $Fe^{III}_4[Fe^{II}(CN)_6]_3\cdot xH_2O$, and its derivatives (Figure 1a) present a wide variety of practical applications. Due to their rich redox and electron transfer properties, these compounds have been used, for instance, in lithium-ion batteries[1] and electrosensors[2]. They have also shown to be active catalysts for the hydrogen evolution reaction[3] and, very recently, for the water oxidation[4]. The latter is of particular interest in search of cost-effective water electrolysis devices driven by renewable energy sources. One of the biggest challenges in this field is the development of efficient, robust and inexpensive WOCs. In this sense, we have developed nanostructured PB derivatives such as that shown in Figure 1b that present excellent catalytic activity in both hydrogen and oxygen evolution reactions, at neutral pH and ambient conditions, being possible to work even with natural waters without any pre-conditioning. Furthermore, these compounds present the typical advantages of molecule-based materials, i.e., well-defined crystal structure, easy processing from solution, light-weight or transparency to visible light. In this communication we will report our latest results in this research line, including the incorporation of PB derivatives onto high surface area supports.

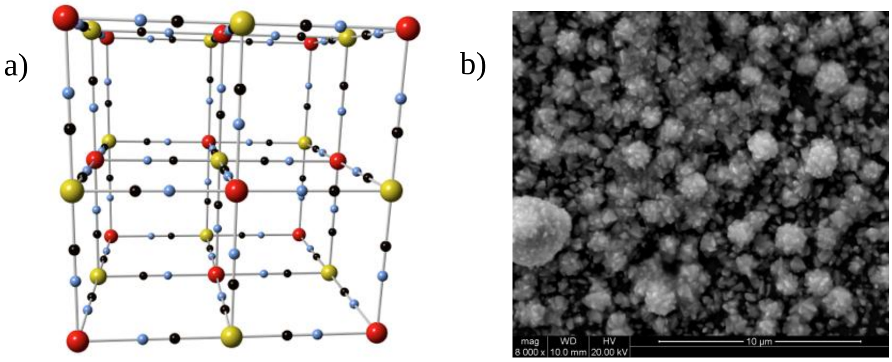

Figure 1: *(a) Face-centered cubic struture of a PB derivatives (metal centers = red and yellow; carbon = black; nitrogen = blue). (b) SEM image of a PB derivative-based electrode.*

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In operando studies of iron based electro-catalysts for the oxygen evolution reaction.

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In operando studies are crucial to accurately pinpoint the design criteria of molecular water oxidation catalysts. It is important to carry out such studies under well-defined reaction conditions, meaning in absence of sacrificial reagents that are often employed in combination with homogeneous catalysts. In my group we study molecular redox catalysts by electrochemical techniques coupled to in situ spectroscopic techniques (IR, Raman, UV-vis).[1] In addition we use on-line mass spectroscopy to detect gaseous products at the electrode interface and rely on electrochemical quartz crystal microbalance techniques to follow deposition of inorganic materials on the electrode.

Using these techniques we were able to show that **1** and **2** are active catalysts for the water oxidation reaction, whereas complex **3** is not active. We showed that deposition of inorganic materials on the electrode only occurs in cas/e of **3** after prolonged electrolysis. For the other catalysts we confirmed by recording the current and by on-line monitoring the O_2 levels simultaneously that the maximum oxygen evolution rates are already obtained in the very first seconds of the catalytic reaction. This clearly points to a molecular catalyst as the true active species. The highest catalytic activity was observed in case of **1**, which is in line with a water nucleophilic attack mechanism assisted by a hydroxide in *cis*-position acting as an internal base as speculated earlier by Costas *et al*.[2]

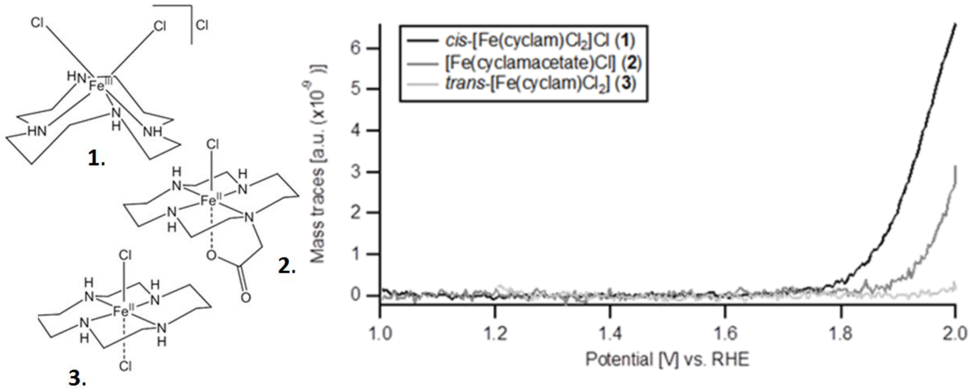

Figure 1 Oxygen evolution rates of **1**, **2** and **3** as a function of applied potential.

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High-pressure hydrogen evolution from formic acid catalyzed by iridium complex

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Recently,producing high-pressure H_2 gas is one of the enthusiastic targets because of the feeding H_2 into fuel cell vehicles (FCVs). Current H_2 system is composed of mechanical H_2 compressor, cryogenic liquidizedH_2 and a heating system to feed the high-pressure H_2 gas, which requires large amount of energy and tends to be expensive. To overcome this problem, we used the decomposition of formic acid catalyzed by Iridium (Ir) complexes.1)Even though it has a possibility to apply formic acid as a H_2 generator, equal amount of CO_2 was produced. Therefore, a separation system is necessary to purify H_2 from the generated gas. In this presentation, we would like to report a simple and continuous method to generate the high-pressure gas over 100 MPa from formic acid and the system with a gas-liquid phase separation related to purification of H_2gas. Our method has many advantages such as continuous feeding of high-pressure H_2 gas without any compressors, and an associated separation system to feed without using any additional filter or absorbents.2)

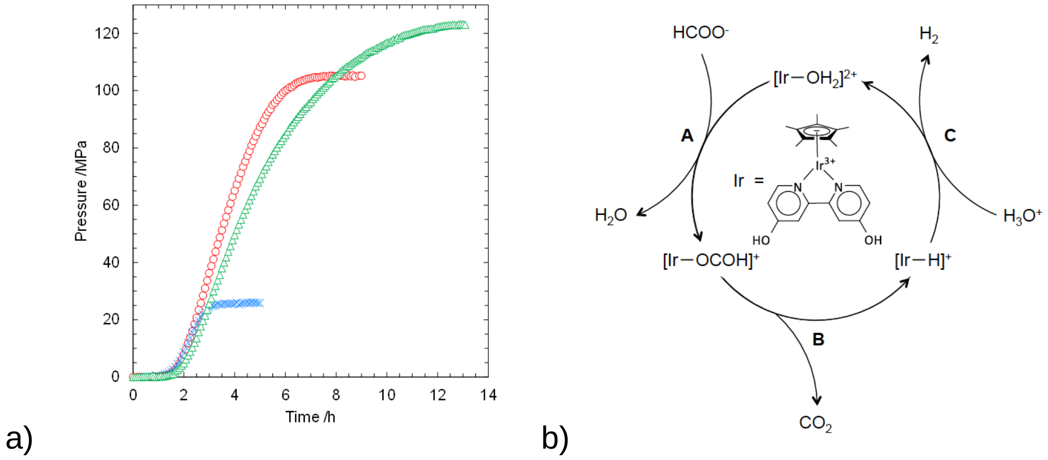

Figure 1 a) Production of high-pressure gas from formic acid and b) Ir catalyst.

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Catalytic water oxidation based on seven-coordinate metal oxo and d^0 metal nitrido oxo active intermediates

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The search for efficient and robust catalysts for the oxidation of water is a grand challenge for chemists. We present here two approaches for the development of active molecular water oxidation catalysts. The first approach involves the design of catalysts that can go through seven-coordinate metal oxo active intermediates. Recently seven-coordinate ruthenium(V) oxo species have been proposed as active intermediates in catalytic water oxidation. We will describe the synthesis and catalytic water oxidation by a series of ruthenium(II) complexes $[Ru(qpy)(L)_2]$ (qpy = 2,2':6',2'':6'',2'''-quaterpyridine; L = substituted pyridine). Qpy is known to form metal complexes in *trans* configuration with a relatively large N-M-N bite angle, hence it may be possible to form a seven-coordinate M=O species. We will also describe the synthesis, structure and reactivity of a seven-coordinate osmium oxo species, $[Os^V(O)(qpy)(pic)Cl]^{2+}$ (qpy = 2,2':6',2'':6'',2'''-quaterpyridine; pic = 4-picoline). Although this species does not oxidize water, it undergoes facile O-atom and H-atom transfer reactions with various organic substrates.

Our second approach in the development of active water oxidation catalysts involves the use of d^2 metal nitrido species that can undergo oxidation to generate d^0 metal nitrido oxo species as the active oxidant. We will describe catalytic water oxidation by a Mn(V) nitrido complex, $[Mn^V(N)(CN)_4]^{2-}$ using this approach.

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Benchmarking Molecular Water Oxidation Catalysts

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The replacement of fossil fuels by a clean and renewable energy source is one of the most urgent and challenging issues our society is facing today, which is why intense research is devoted to this topic recently. Nature has been using sunlight as the primary energy input to oxidize water and generate carbohydrates (a solar fuel) for over a billion years. Inspired, but not constrained, by nature, artificial systems[1] can be designed to capture light and oxidize water and reduce protons or other organic compounds to generate useful chemical fuels. In this context this contribution will present a variety of molecular water oxidation catalysts based on first row and second row transition metal complexes, and their relative performance will be analysed and discussed.[2]

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Electrochemical and spectroelectrochemical evaluation of copper-oxygen adducts relevant to energy conversion strategies

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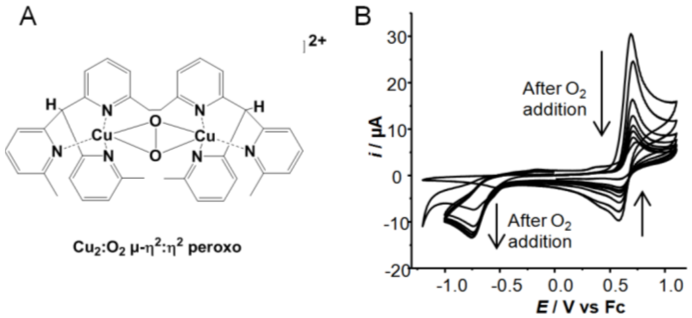
Copper-oxygen adducts have been invoked as pivotal intermediates in energy conversion schemes such as the developing of commercially viable fuel cells[1] or the enzymatic oxidation of methane in methanol[2] which in turn could work as an energy carrier. Thus the catalytic reduction of oxygen by copper complexes is thought to occur through the formation of a peroxo copper compound[1] and a bis(μ-oxo) copper species has been postulated as the key intermediate in the oxidation of methane to methanol in the enzyme pMMO (Particulate Methane Monooxygenase).[3]

In this context, we have studied at room and low temperature (-80 °C) the electrochemical and spectroelectrochemical properties of the (μ-η^2:η^2-peroxo)dicopper(II) complex produced after the reaction of the dinuclear copper(I) complex $[Cu_2(H6M4h)(CH_3CN)_2]^{2+}$ with O_2. Experiments at low temperature were made possible by the design and construction of new cryo-electrochemical and spectroelectrochemical cells, paving the way to the study of other interesting biomimetic $Cu\text{-}O_2$ species only stables at low temperature.



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The investigations on water oxidation catalysts

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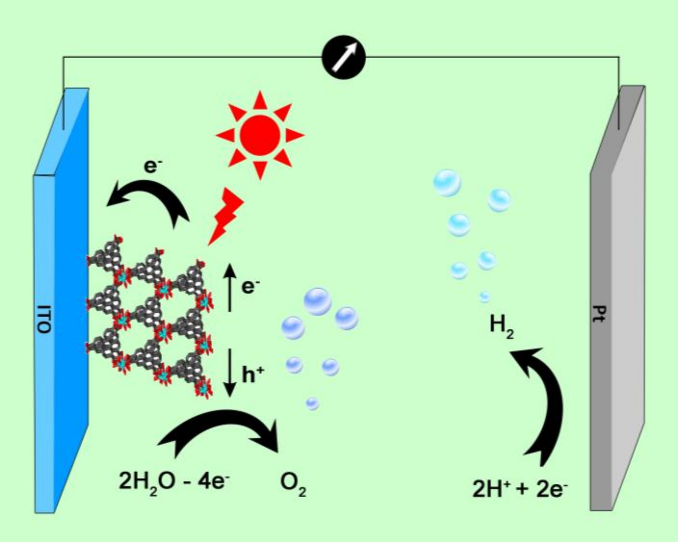
Water splitting continues to attract much attention for the purpose of hydrogen production, which is regarded as the most promising alternative energy source. While the development of efficient water oxidation catalysts (WOCs) based on nonprecious materials remains the major obstacle in water splitting device. In this presentation, we will give a few examples of WOCs based on the first-row nonprecious catalysts [1-3].



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Cobalt Dithiolene Metal-Organic Surfaces (MOS) for Solar Energy Conversion

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Hydrogen production through the reduction of water has emerged as an important strategy for the storage of renewable energy in chemical bonds. One attractive scenario for the construction of efficient devices for electrochemical splitting of water requires the attachment of stable and active hydrogen evolving catalysts to electrode surfaces, which remains a significant challenge. Molecular catalysts are attractive because the ligand environment allows for tuning of their reduction potentials and chemical properties. However, the reported methods for the immobilization of molecular catalysts onto electrodes are scarce and suffer from low catalyst loadings. Metal-organic frameworks have received huge attention in the last years as promising porous materials for a wide range of applications, including electrocatalysis. We demonstrate here the successful integration of cobalt dithiolene catalysts into metal-organic surfaces to generate very active modified cathodes for hydrogen generation from water.[1] These materials display low overpotential and remarkable activity and stability under acidic conditions, much higher than those of the molecular complex, suggesting that immobilization as MOS provides a significant increase in efficiency and thus paves the way towards development of practical devices. Moreover, these materials can be integrated with planar *p*-type Si to generate very efficient photocathode materials for solar-driven hydrogen production from water.[2]

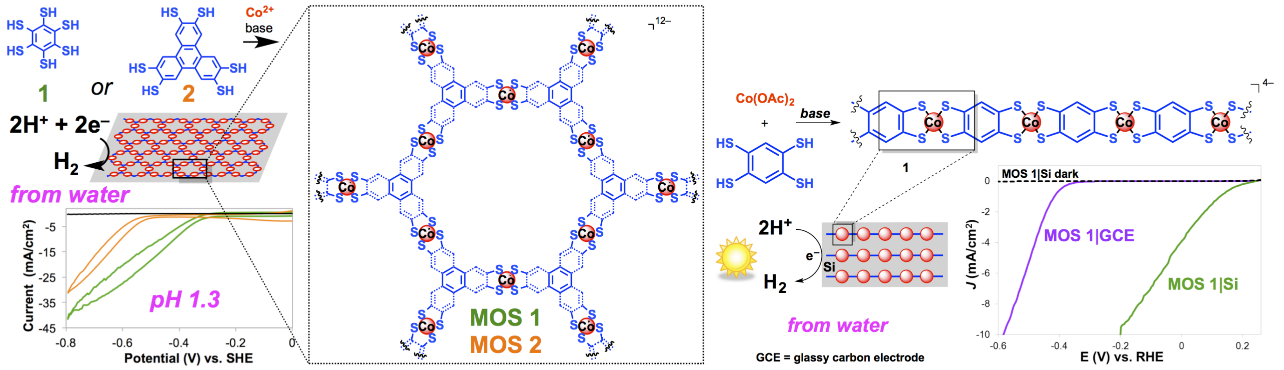

Figure 1 1D and 2D Cobalt dithiolene MOS for efficient hydrogen evolution from water.

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$[Fe\{C_5(C_6H_4Br)_5\}(CO)_2Br]$ as a catalyst precursor for the hydrogen evolution reaction

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The undoubtedly finite reserves of fossil fuels, the concomitant generation of CO_2 when they are combusted to release energy, and humankind's increasing thirst for energy, lead inescapably to the imperative that alternative and renewable energy sources and energy carriers become commercial realities relatively quickly. The generation of hydrogen as an energy carrier from renewable sources is an attractive and, importantly, scalable, proposition. This commonly involves the hydrogen evolution reaction (HER), promoted by an electron transfer catalyst. We report here the synthesis, structure and electrochemical characterization of $[Fe\{C_5(C_6H_4Br)_5\}(CO)_2Br]$ (Fig.1) as a precursor for an electron transfer catalyst for the HER (Figure 2). This complex outperforms cyclopentadienyl analogues.

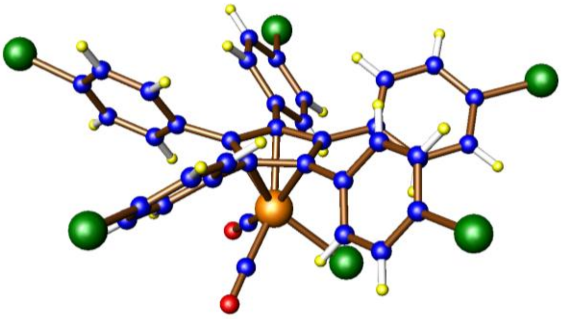

Figure 1. Structure of $[Fe\{C_5(C_6H_4Br)_5\}(CO)_2Br]$

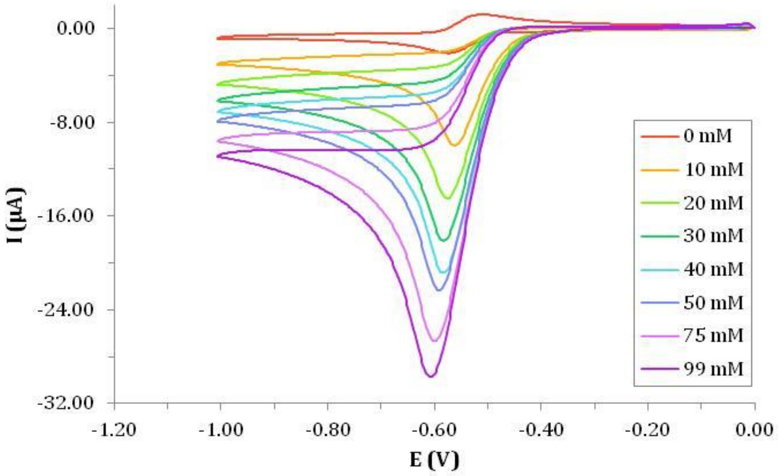

Figure 2. Cyclic voltammograms of of $[Fe\{C_5(C_6H_4Br)_5\}(CO)_2Br]$ *vs.* Fc/Fc^+ with the addition of Cl_3CCO_2H (0–99 mM), in 0.1 M $TBAPF_6$ in DMF at a scan rate of 100 mV s^{-1}.

Plausible roles of carbonate in catalytic oxidations.

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The reactions:

$OH^{\cdot} + HCO_3^{-} \rightarrow H_2O + CO_3^{\cdot -}$ $k = 1.0x10^{7}\ M^{-1}s^{-1}$

$OH^{\cdot} + CO_3^{2-} \rightarrow OH^{-} + CO_3^{\cdot -}$ $k = 4.0x10^{8}\ M^{-1}s^{-1}$

are fast and clearly exothermic. However, the radical anion is still a powerful oxidizing agent, E° = 1.57V *vs.* NHE. Therefore, it is of interest to check whether the carbonate radical anion is not formed directly in a variety of catalytic processes. Indeed recent results suggest that in the AOP based on the reaction of H_2O_2 with Co^{II}_{aq} in the presence of bi-carbonate $CO_3^{\cdot -}$ is formed directly without the formation of hydroxyl radicals. Also the Fenton reaction between Fe^{II}_{aq} and H_2O_2 in the presence of bi-carbonate $CO_3^{\cdot -}$ is formed directly without the formation of hydroxyl radicals.

In the electrocatalytic water oxidation in the presence of Cu^{II}_{aq} and carbonate/bi-carbonate the oxidizing agent $Cu^{III}(CO_3)_2^{-}$ decomposes *via* a second order reaction independent on the concentration of $[CO_3^{2-}/HCO_3^{-}]$ and of $[Cu^{II}_{aq}]$a result that indicates that two ligated $CO_3^{\cdot -}$ react to yiel a peroxide without the involvement of free or ligated hydroxyl radicals.

DFT calculations indicate that the photo-catalyzed oxidation of water by GaN is facilitated by carbonate.

The results indicate that carbonate is a non-innocent ligand.

Towards photoelectrosynthesis of ammonia

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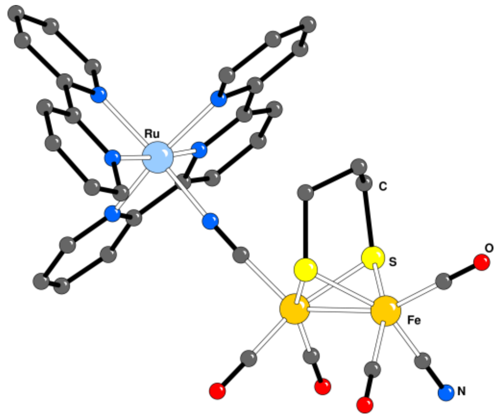
Some thirty years ago Jean Talarmin, who has very recently retired from the Universite de Bretagne Occidental at Brest, and I described a stepwise pathway for the electrosynthesis of ammonia from molecular nitrogen[1,2]. This was based on transformations at a robust tungsten bis(diphospine) molecular platform. The talk will outline some exploratory work on driving nitrogen fixation photoelectrochemically at this same platform - and why me might wish to do this. Some other (photo)electrochemical excursions[3] into solar fuel generation by small molecule activation using molybdenum (bis)diphosphine,[4,5] iron porpyrin[6] and diiron dithiolate assemblies (Figure 1), will also be discussed.[7]

Figure 1



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Towards H_2 generation from C_1-molecules and water at ambient conditions

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Our research focus on hydrogen generation at low temperature. We showed that C_1-entities like hydrated formaldehyde (8.4 wt% H_2) is suitable for molecular H_2-storage as these molecules can be easily and selectively dehydrogenated forming pure H_2 and CO_2.[1] The reaction runs on air using a novel water-stable molecular catalyst which is generated in situ using a commercial precursor under base-free conditions. This catalytic decomposition of H_2CO can be envisioned as novel approach for simultaneous H_2 production and decontamination treatment of wastewater with formaldehyde impurities a waste to value approach.[2] Moreover, we achieved the first room temperature reforming of methanol following a bio-inspired approach using multi-catalytic system consisting of enzymes and a biomimetic formaldehyde dehydrogenase (Figure 1).[3] These studies include also coupled conversion of the *in situ* generated H_2 and CO_2 towards a full/extended hydrogenation/dehydrogenation cycle.

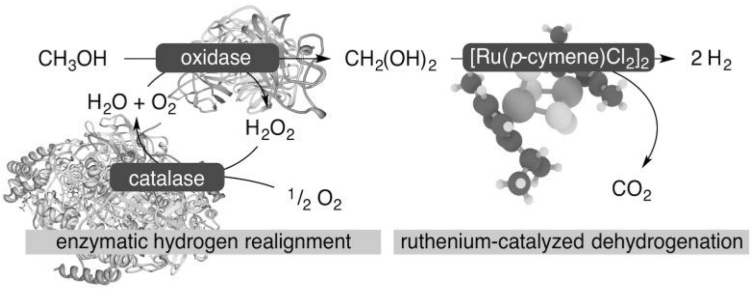

Figure 1 Methanol oxygenation with air and subsequent H_2 generation at room-temperature.[3]

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Closed redox cycles in artificial photosynthesis without sacrificial agents and noble metals

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Solar fuel synthesis requires the finely tuned combination of solar light absorption, charge separation and the coupling of multi-electron half-reactions. This demanding task is highly controlled in natural photosynthesis but much less so in artificial systems. A drawback in many synthetic approaches is the reliance on sacrificial redox reagents, which does not only prevent truly energy-storing chemistry to proceed but also introduces deceptive free radical chemistry. Another limitation in most artificial systems is their reliance on expensive materials, which prevents the development of ultimately scalable devices. This presentation will give an overview about our recent progress to perform controlled full redox cycle solar fuel catalysis with enzymatic and synthetic 3d transition metal catalysts.

Photoelectrochemical (PEC) full water splitting was achieved through three different approaches. In a semi-artificial system through the wiring of the water oxidation enzyme Photosystem II to a H_2 producing enzyme known as hydrogenase,[1] in a molecular PEC cell based on a H_2-evolving Ni catalyst[2] and a water-oxidising Fe catalyst,[3] and an all-solid-state tandem PEC water splitting cell, which was constructed through single-source precursor chemistry.[4] PEC approaches are ideally suited for the separation of individual half reactions on different electrodes and compartments, but are rather difficult and expensive to assemble and scale. Progress in the assembly of photocatalytic molecule-nanoparticle hybrid systems, which operate in a single compartment will also be discussed.[5,6] This work was supported by the Christian Doppler Research Association and the OMV Group.

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Molecular catalysis of the reduction of CO_2 with Fe complexes in pure water. From highly selective catalysts to efficient, low cell voltage electrolizer for CO_2 splitting into CO and O_2

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Recent attention aroused by the reduction of carbon dioxide has as main objective the production of useful products – the "solar fuels" – in which solar energy would be stored. One route to this goal consists in first converting sunlight energy into electricity, then used to reduce CO_2 electrochemically. Conversion of carbon dioxide into carbon monoxide is thus a key-step through the classical dihydrogen-reductive Fischer-Tropsch chemistry. We have shown that various substituted iron tetraphenylporphyrin derivatives prove to be remarkable catalysts of the reduction of CO_2 to CO when generated electrochemically[1-3] (or photochemically[4]) at the Fe(0) oxidation state, both in terms of selectivity, durability, overpotential and turnover frequency in DMF-water mixtures. Benchmarking with other catalysts, through catalytic Tafel plots, shows that they are the most efficient homogeneous molecular catalysts of the CO_2-to-CO conversion at present.[3]

We have recently discovered that it was possible to catalyze the electrochemical conversion of carbon dioxide into CO in pure water[5] with a water-soluble Fe porphyrin, as well as with a grafted molecular catalyst onto the electrode surface.[6] A further step has been achieved with the successful splitting of CO_2 into CO + O_2 within an efficient, low cell voltage electrolyzer in pH neutral water.[7]

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Hybrid Molecular Systems for Photocatalytic Water Oxidation and Reduction

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Solar driven water oxidation and reduction are considered as promising chemical conversion processes that enable practical application of hydrogen energy in our future society. Importantly, natural photosynthesis has a great relevance to these processes. The key issues involve development of efficient method of generating photo-driven charge separated states and effective man-made catalysts accelerating both water oxidation and reduction. Our group has been focusing on both photochemical water oxidation and reduction by use of transition metal complexes as photosensitizing and catalytically active centers. Some of our works involve development of photosensitizer-catalyst dyads [1]. Homogeneous catalysis of water reduction by Pt, Co, and Ni complexes together with water oxidation by Ru, Co, and Cu complexes will be discussed. Complexes having a Pt(tpy)Cl or Pt(bpy)Cl_2 units with covalent linkage to multiple viologen acceptors have been shown to exhibit intriguing behaviors as photo-hydrogen-evolving molecular devices [2-6]. Co NHC complexes have been shown to exhibit low overpotentials for water reduction [7]. Ni thiolates catalyze electrochemical hydrogen evolution by use of PCET paths, the mechanism for which has been studied in detail by DFT method [8]. Co porphyrins are found to be active catalysts for water oxidation, and its robustness during photocatalysis could be improved by introducing halide substituents in the arryl group of tetrapheynylporphyrin motifs [9,10].

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Artificial Photosynthesis—Transition metal complexes as highly efficient catalysts for water splitting

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A series of molecular catalysts for water splitting have been developed in our groups during the past years, inspired by the active sites of OEC in Photosystem II and [FeFe]- or [NiFe]-Hydrogenases. These molecular catalysts are based on transition metal complexes, such as Ru, Fe, Co and Cu. We found that these catalysts are highly active towards water oxidation or hydrogen generation in homogeneous systems driven by chemical, electrochemical and photochemical methods. The reaction mechanisms of O-O bond formation and H-H bond formation have been successfully illustrated by experiments and DFT calculations. Some exciting results in photochemical driven water splitting in supramolecular systems have been achieved recently with high quantum efficiency. Photoelectrochemical devices for water splitting using molecular catalysts will be presented in this talk as well during the conference.

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Iron based photosensitizers for sustainable reductive water splitting

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Photocatalytic water splitting using sunlight allows to produce hydrogen and oxygen in a sustainable way. Herein we focus on the molecular reductive water splitting generating hydrogen as an alternative fuel and as an important reactant for the chemical industry.

A typical system for this task consists of a molecular photosensitizer (PS) and a catalytic center (Figure 1). By harvesting light with the PS an electron is transferred to a MLCT state, promoting the electron transfer to the catalytic center (Cat.). Here protons of water are reduced to hydrogen. For the reduction of the photosensitizer a sacrificial electron donor like EDTA or TEA is used (Donor).

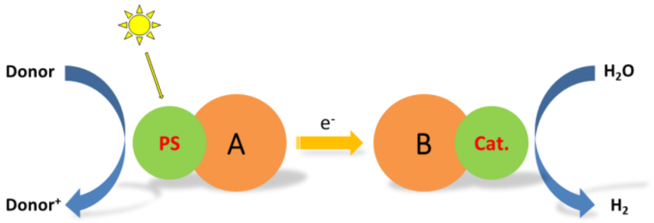

Figure 1 Model System for reductive water splitting

To replace noble metal (Ruthenium or Iridium) based PS by cheap iron based complexes both their stability under irradiation and the lifetimes of the excited states have to be improved. Based on first attempts using NHC-Ligands[1,2] a series of new photosensitizers with iron is introduced (Figure 2). Strongly coordinating NHC-Ligands enlarge the lifetime of the MLCT-state, whereas the terpyridine ligand improves light absorption in the visible range.

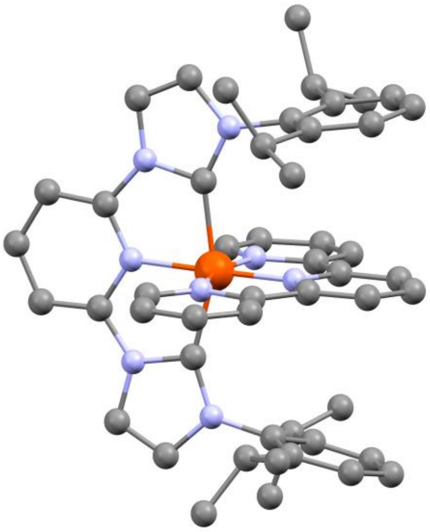

Figure 2 Iron based photosensitizer

The new complexes have been characterized by spectroscopical and electrochemical methods, in addition physicochemical methods supported by DFT-calculations were applied to determine the character and lifetime of the excited states. Finally the complexes have been tested as Photosensitizers in the photocatalytic water splitting. Their catalytic activity has been compared to established iridium complexes to get insights into structure-activity relationships of the new systems.

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Photochemical Hydrogen Evolution Based on the Nonprecious Metal Complexes with Redox-active Ligands

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Molecular hydrogen is one of candidates as clean energy carrier.[1] Because of the difficulty in the storage of hydrogen, the development of hydrogen storage materials is desired. Among a several materials, organic compounds, known as organic hydrides, are fascinating candidate. Recently, quinoline/1,2,3,4-tetrahydroquinoline system was reported as efficient hydrogen production/storage material that can evolve hydrogen at relatively low temperatures (*ca.* 110-140 °C), under the presence of Ir catalyst.[2] However, even in the excellent example, the operating temperature in the hydrogen-evolution reaction (HER) is still high. Therefore, the creation of a HER that can be driven at moderate temperature with use of nonprecious-metal catalysts is an important issue.

Recently, we reported interesting and important reactions of transition metal complexes with redox-active ligands.[3] For example, Fe(II) complex with *o*-phenylenediamine (opda), e.g., $[Fe^{II}(opda)_3](ClO_4)_2$, was reported to show the photochemical HER at room temperature (Figure 1).[4] In this reaction, the protons and electrons in opda ligand skeleton were found to be the source of photochemically evolved hydrogen. It was suggested that the oxidized complexes with *semi*-benzoquinoimine (s-bqdi) or *o*-benzoquinodiimine (bqdi) is formed after the HER. These results indicate the possibility for creation of novel hydrogen storage materials operable under room temperature based on the nonprecious metal-based complexes with redox-active ligands. We herein report the detailed HER from $[Fe^{II}(opda)_3](ClO_4)_2$ and other related complexes together with mechanistic investigations and photocatalytic HER under the coexisting of electron and proton donor.

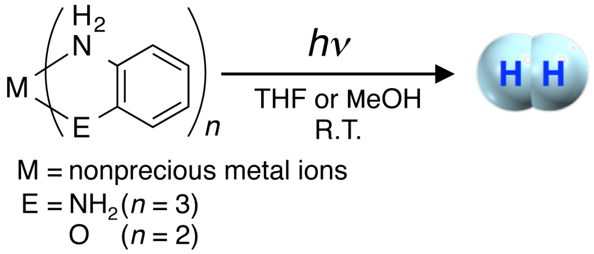

Figure 1. Photochemical hydrogen evolution reaction from nonprecious metal complexes with redox-active ligands.

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Metalloporphyrin Nanorings

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Recent advances in the supramolecular chemistry and photophysics of macrocycles consisting of up to 50 covalently linked metalloporphyrin units[1,2] will be presented, including ring-in-ring assemblies such as that shown below.[3] Results from a variety of techniques provide insights into the flow of charge and electronic excitation in these nanostructures.

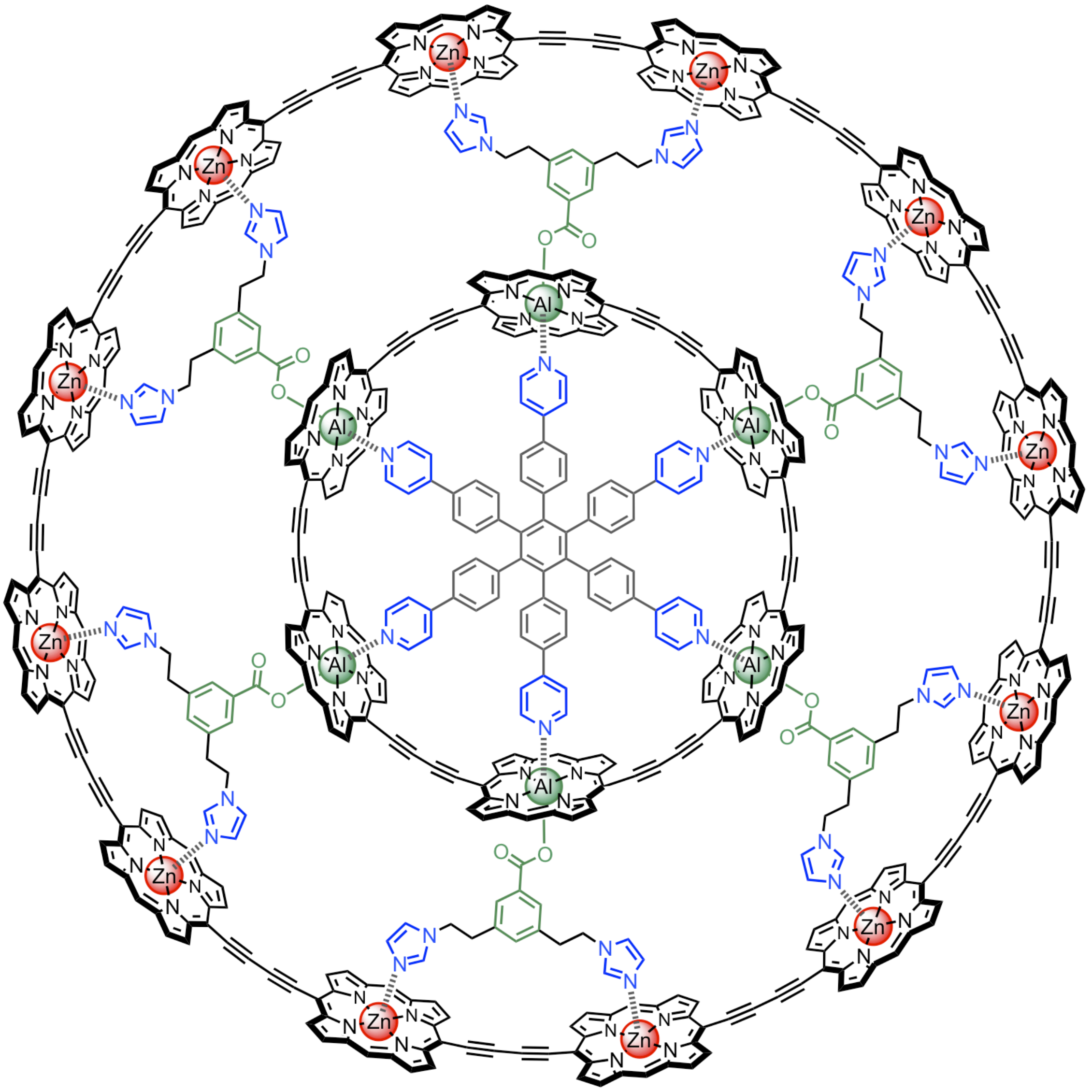

Figure 1 Structure od a Russian doll complex assembled using aluminium coordination.

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A deeper insight into allosteric cooperativity factors

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Affinities for the complexation of bisbenzimidazolpyridine ligands with lanthanide carriers have been widely studied.[1-3] For polymers (N≥2), the *Ising* model expresses the binding isotherms with the help of two microscopic thermodynamic parameters: (i) the non-cooperative intermolecular intrinsic affinity $f_{\mathrm{N3}}^{\mathrm{Ln}}$ of one lanthanide for a tridentate binding unit and (ii) the intramolecular intermetallic interactions $\Delta E_{1\text{-}2}^{\mathrm{Ln,Ln}}$ which operates between two occupied neighboring sites. Those parameters were determined with [Ln(hfac)$_3$dig] (hfac = hexafluoroacetylacetonate, dig = diglyme) on tridentate ligands of variable lengths.[2-3] The titrations were conducted in deuterated dichloromethane and monitored by ^{1}H and ^{19}F NMR in order to assess the successive metal loading. The value of the allosteric cooperativity factor is influenced by the number of sites of the ligand, a surprising phenomenon, which can be explained with solvation energies.

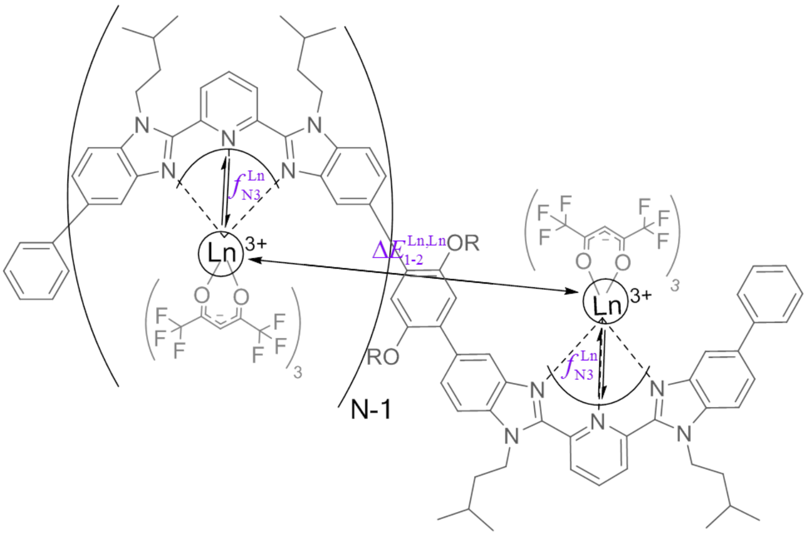

Figure 1. Schematic representation of the lanthanidopolymers [Ln$_N$(hfac)$_{3N}$**L**] highlighting the two microscopic parameters used in the thermodynamic model.

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Supramolecular Catalysis within Metal-organic Architectures

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Metal-organic supramolecular systems that constructed through the coordination of metal ions and organic linkers, represent a unique class of functional molecular containers that display interesting recognition properties and fascinating reactivity reminiscent of the natural enzymes. These architectures generating well-defined cavities provided specific inner environments for selective bonding of guest molecules and catalyzing their reactions. The great flexibility in terms of the molecular design and the potential benefits of integrating inorganic and organic components within a single composite make them interesting candidates for supramolecular catalytic chemical transformation. Yet only few "artificial enzymes" achieved the magnificent catalysis of natural enzymes. Through incorporating amide-containing multidentate chelators or the chiral organocatalyst within the ligand backbone or the cavities of the architectures, we described herein the syntheses and catalytic properties of several metal-organic architecture to investigate the possibility in the application of molecular flasks and heterogeneous catalysts.

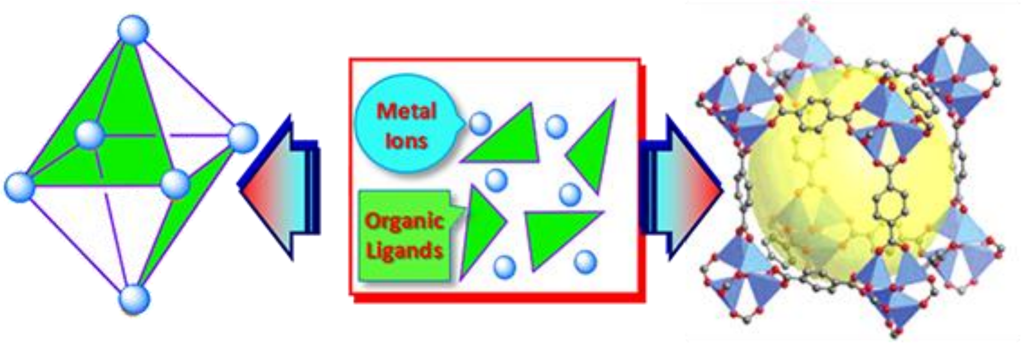

Figure 1 Controlled Constructions of Metal-organic Architectures for Catalysis

1 X. Jing, C. He, Y. Yang, C. Duan*, *J. Am. Chem. Soc.*, **2015**, *137*, 3967.
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Stimuli-Responsive Cages with a Size-Controlled Cavity

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Molecular cages with a three dimensional active cavity able to stabilize guest molecules for sensor or transport applications, for drug delivery or to perform a chemical reaction in a confined environment are especially attractive.[1] Porphyrins as constituents of a cage framework offer several ways to be active partners in the cage activity due to their coordination, redox, electronic and photophysical properties.[2]

Porphyrin coordination cages are formed quantitatively by coordination of silver(I) ions to pyridyl[3] or triazolyl–pyridine[4] units of ligand-appended porphyrins.

The synthesis of covalent cages consisting of two porphyrins connected by four flexible spacers each incorporating two 1,2,3- triazolyl ligands (Figure 1) is also reported.[5]

Binding of four silver(I) to the peripheral ligands induces conformational changes in solution and locks the porphyrins of the covalent cages in a face-to-face disposition.[5] Such behavior offers interesting perspectives for an allosteric control of the 3D porphyrinic cages reactivity.

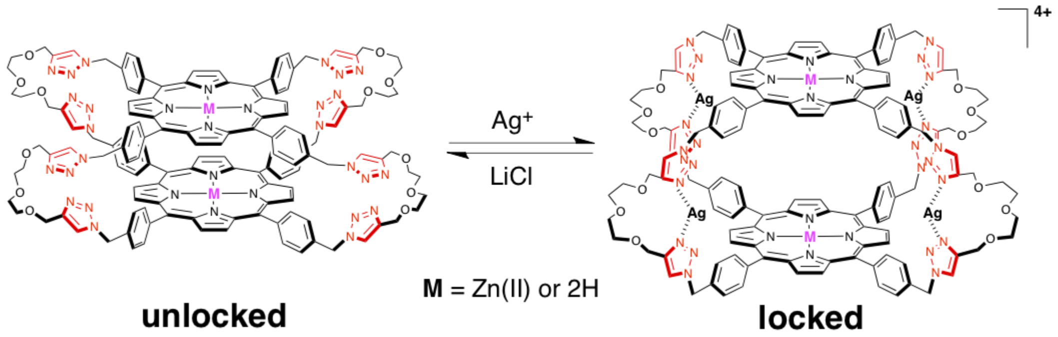

Figure 1 Control of the conformation of the covalent cages.

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Assembling Molecular H-bonded crystals

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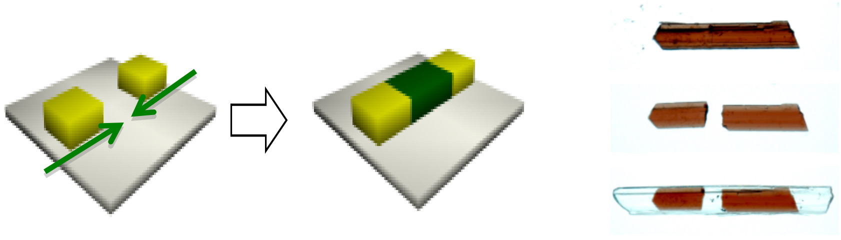
The understanding and design of complex molecular systems in the crystalline phase with the control of the short- and long-range orders at the microscopic and macroscopic levels is important for both fundamental and applied sciences. Mastering molecular organization in the solid state is crucial for the development of new materials and devices. For this purpose, the use of a powerful strategy like *molecular tectonics*,[1] allows to obtain a large variety of molecular networks, in particular H-bonded infinite assemblies.[2] Among many challenges in the area solid state supramolecular chemistry, the hierarchical interconnection of single crystals into supercrystals like "crystals of crystals" (core shell crystals)[3] or "networks of crystals", for which specific subsections are interconnected with the continuation of the crystalline order, may be a powerful tool for generating new hierarchically organized crystalline materials. This strategy allowed us to obtain and study new crystalline species called "welded crystals", a networking of single crystalline isostructral phases, obtained through three-dimensional epitaxial growth (figure 1).[4]



a **b**

Figure 1 a) *Schematic representation of the welding ofmolecular crystals by epitaxial growth of oriented crystals; b) Pictures of welding of isostructural H bonded crystals.*

1 a) M. W. Hosseini, *Acc. Chem. Res.*, **2005**, *38,* 313; b) M. W. Hosseini, *Cryst. Eng. Comm.*, **2004***, 6*, 318; c) M. W. Hosseini, *Coord. Chem. Rev.* **2003**, 240, 157; d) M. W. Hosseini, *J. C. S. Chem. Commun.* **1998**, 727.

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Crystalline Sponge Method Updated

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Single crystal X-ray diffraction (SCX) analysis has the intrinsic limitation that the target molecules must be obtained as single crystals. We recently reported a new protocol for SCX analysis that does not require the crystallization of the sample.[1-5] In our method, tiny crystals of porous complexes are soaked in the solution of a target, where the complexes can absorb and orient the target molecules in the pores. The crystallographic analysis clearly determines the absorbed guest structures along with the host frameworks. As the SCX analysis is carried out with only one tiny crystal, the required sample amount is of the nano-to-microgram order. With chiral guests, the space group of the crystal turned into chiral ($C2$ or $P2_1$), enabling the determination of absolute configuration of the guests by anomalous scattering effect from the host ZnI_2 component. When combined with high performance liquid chromatography (HPLC), multiple fractions were directly characterized, establishing a prototypical LC-SCD analysis. In this talk, improved protocols, x-ray details,[6] and recent examples of the applications[7,8] of the method will be discussed.

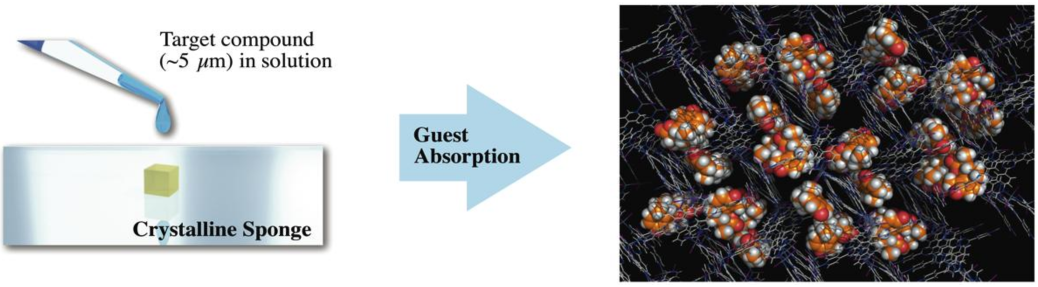

Figure 1 Cartoon presentation of the crystalline sponge method.

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Molecularly Designed Architectures: Selective Binding of Cations and Anions

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Utilization of coordination complexes as the building blocks to generate extended networks is an attractive synthetic approach for the design of new materials with multi-dimensional topologies and applications.[1] Considerable efforts have been devoted for the assembly of such materials from the molecular building blocks to reach the initial stage of rational design with predictable architectures.[1] We have developed a strategy that uses a transition metal ion to assemble simple amide–based ligands into a coordination complex that can serve as the molecular building block, i.e., *metalloligand*. Such metalloligands, appended with assorted functional groups, could be utilized to either coordinate a secondary metal ion or be involved in the hydrogen bonding based self-assembly. Such metalloligands have been utilized for the synthesis of discrete trinuclear complexes,[2] two–(2D) as well as three–dimensional (3D) heterometallic coordination networks;[3] and hydrogen–bonded self–assembled architectures.[4] These examples illustrate the significance of coordination complexes based building blocks for the construction of ordered architectures.[2-4] The judicious selection of Lewis acidic and/or redox-sensitive metals in such materials has been utilized by displaying heterogeneous catalysis including regio-selective, chemo-selective and size-selective reactions.[2,3] This work will discuss the genesis of metalloligands as the molecular building blocks for the construction of designed architectures and their application in catalysis[2,3] and sensing.[5]

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Diamondoid and Lonsdaleite Networks from the same Ag(I)-ligand combination with Lonsdaleite the softer network

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The combination of tetrahedral ligands (black lines) with tetrahedral metal centres (pink spheres) often results in networks with a diamondoid (**dia**) topology. A Lonsdaleite (**lon**) topology, although rare, is another possible outcome but comprises only 0.4% of this combination. When all centres are C-atoms, **lon** is found to be 58% harder than **dia**.[1] Lonsdaleite is an attractive, if challenging target, for network synthesis. In MOF chemistry, reticulations based on the **lon** network using simple tetrahedral building blocks are rare because the network obtained is usually the simpler, higher symmetry **dia** network. The work presented will describe the use of the tetrakis(4-cyanophenyl) adamantane ligand to form either **dia** or **lon** networks when combined with various Ag(I) salts. The effect of counteranion and solvent on the formation of these networks will be discussed. In some cases depending on the solvent, 2D honeycomb networks reminiscent of sections through the **dia** or **lon** network can be isolated. Results of the nanoindentation studies, the thermogravimetric and the puckering analyses on these **dia** and **lon** networks will be described.

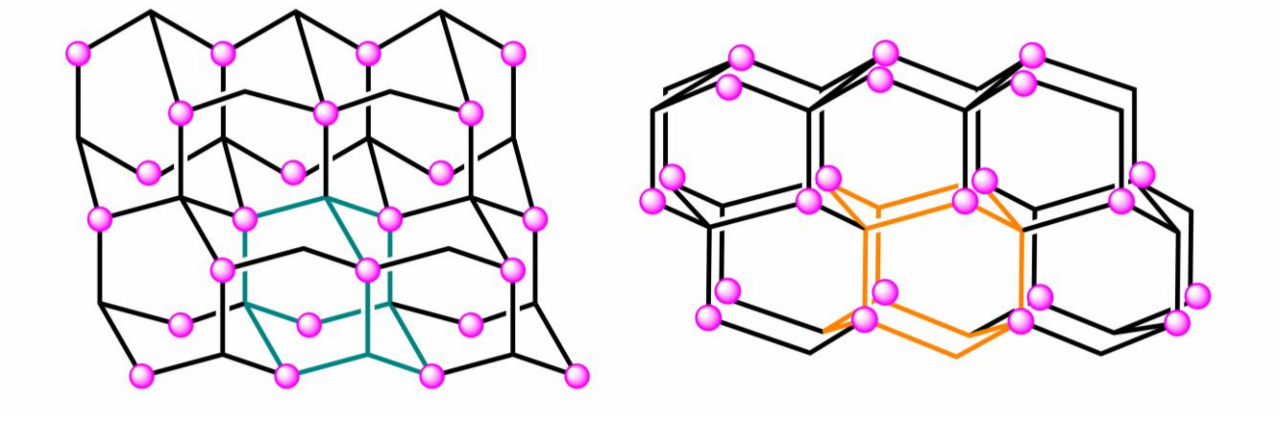

Figure 1 Schematic representation of **dia** net (left) constructed by connecting 10 node building blocks with four fused rings in chair conformations (in red) and **lon** net (right) constructed by connecting 12 node building blocks with 3 rings in boat and 2 in chair conformations (in green).

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Functional Materials from Hybrid Ligands

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Our laboratory is interested in hybrid ligands that are represented by small molecules that have di- or poly-donating sites with different donor characteristics but could function in cooperation.[1] Their complexation behaviors determine the materials potential especially towards properties, functions and activities. Given in Fig. 1 is an example of a supramolecular material formed from self-assembly of the ligand and metal substrates. In this presentation, we shall present some latest advances in our adventure in hybrid ligands and illustrate how the end-applications of the materials influence the basic design of these ligands, especially through the use of spacers and linkers. We shall also draw reference to our related work in catalysis in oxygen reduction in electrode[2] and ligand-free catalysis.

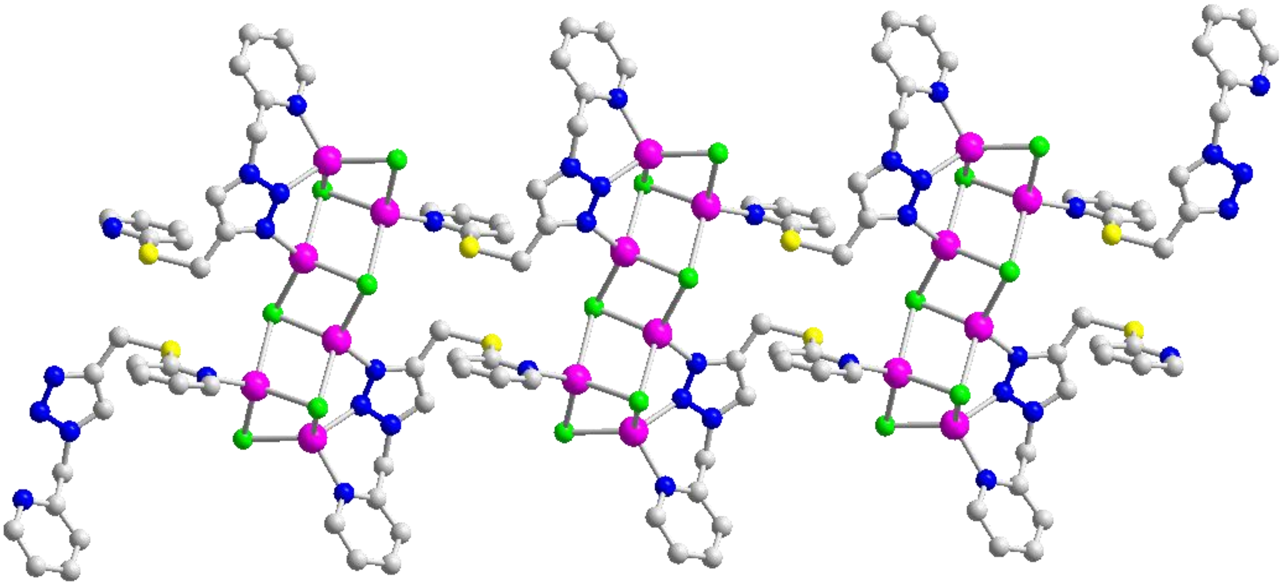

Figure 1 A typical “intelligent” multi-functional hybrid ligand in a polymer of oligomers

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Covalent polyoxometalate hybrids as versatile platforms for the elaboration of self-assembled nano-architectures

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The formation and characterization of self-assembled architectures integrating polyoxometalates (POMs), as nanosized molecular building blocks is particularly attracting owing to their various properties and potential applications.[1] In this context, we recently elaborated various self-assembled nano-architectures from POM-based covalent hybrids bearing organic remote sites prone to self-assemble via different interactions (ππ, hydrophobic or metal coordination). We herein describe the formation and characterization of different self-assembled POM-based architectures (POM@SWCNT,[2] POM@cyclodextrin[3] and discrete POM-based coordination oligomers[4]) as well as their resulting properties.

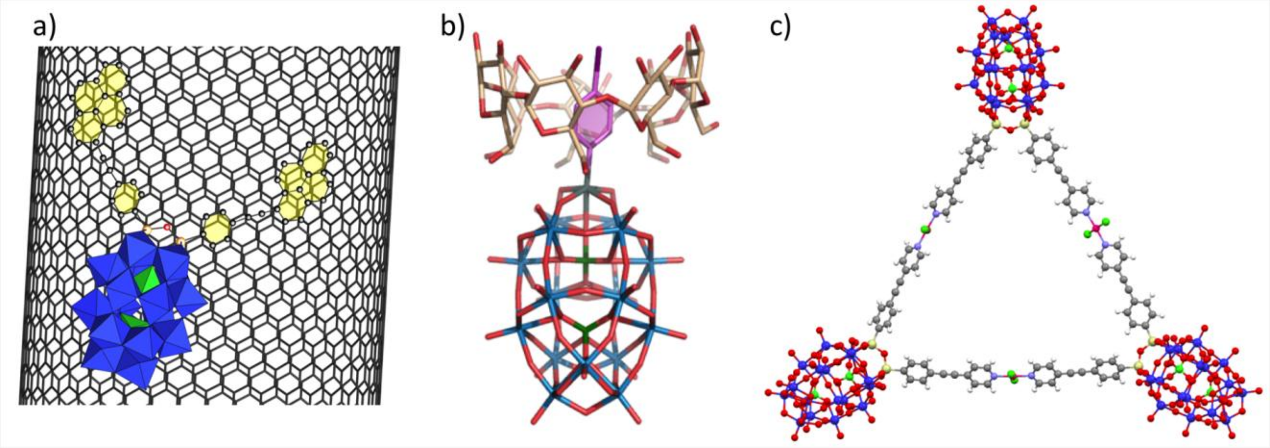

Figure 1 Self-assembled POM-based nano-architectures. a) POM@SWCNT, b) POM@cyclodextrin, c) POM-based molecular triangle.

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Sulfonamides and analogs in separations and sensing: Combining metallo-supramolecular chemistry and solvent extraction for separation and sensing of metals and ion pairs

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Designing selective and practical sensors for larger and relatively "softer" targets, with lower charge density, such as the toxic metals Pb(II) and Cd(II) and the anions ClO_4^- and NO_3^- still presents significant challenges, despite their environmental and health importance. Solvent extraction from water into less polar organic solvents via formation of complexes with distinct optical or electrochemical properties presents opportunities for improving selectivity by combining ligand design targeted to the unique coordination properties of each target species, with more favorable dehydration-resolvation energetics as compared to harder more charge-dense species (such as Ca^{2+}), which are naturally present in high concentrations and often compete for the same ligand binding sites. Sulfonamides with incorporated fluorophores have been shown previously to be effective ion-exchange extractants and sensors.[1] Herein we are expanding this approach with a variety of ligands and targets and demonstrate the combined effects of coordination and solvent extraction principles in sensor design.

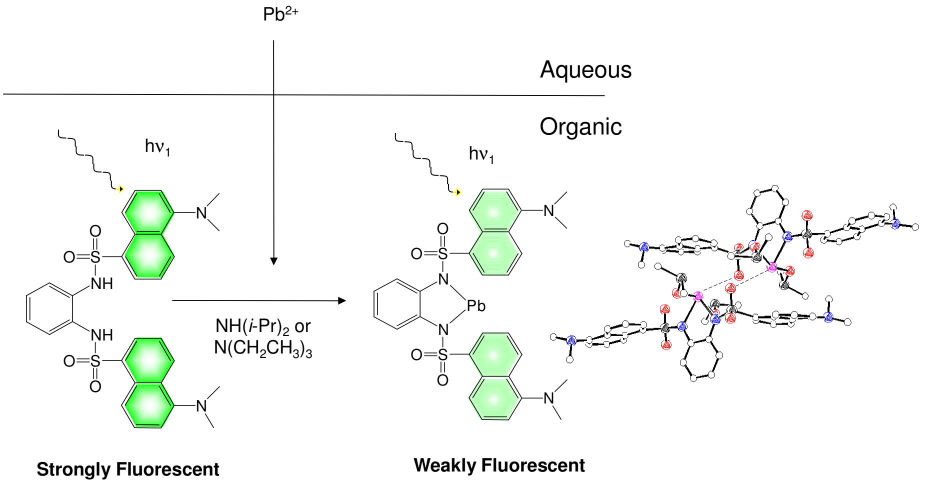

Figure 1 An extraction-based sulfonamide sensor based on the dansyl fluorophore.[1]

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Rotaxanes in the Solid State and in Solution

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Assembled macrocyclic and axle component molecules form (pseudo)rotaxanes, which show unique properties of independent motion of the components. Previously, we prepared a pseudo-rotaxane containing ferrocenyl and 4-methylphenyl groups as the end groups of the axle component and reported the phase transition between the two crystalline phases at 128 °C (on heating).[1,2] The structural change of the cationic rotaxane shown in Figure 1 as well as a large shift of PF_6^- anions occur during the process. The two aryl planes of the axle and macrocyclic components are parallel in the low temperature phase, and becomes non-parallel due to C-H···π interaction via rotation of the aryl plane.[3]

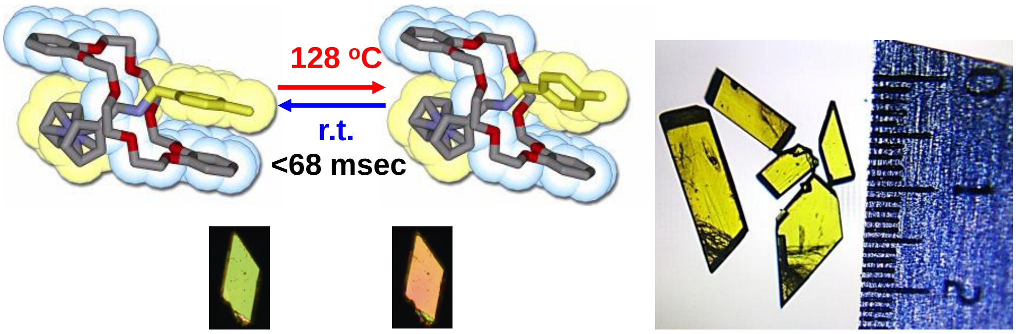

Figure 1. Phase Transition of the Rotaxane Crystal

This paper includes further details of the change of the conformation of the compounds caused by the temperature change. Also, structural change in solutions is discussed..

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Perchlorate removals from aqueous solutions by M_2L_4 type cage complexes

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Bis-imidzole and bis-benzimidazole type ligands, which are designated as L^B, have been used for syntheses of many metal complexes with various self-assembly structures.[1] We have focused on anion removals from aqueous solutions by using coordination compounds constructed by L^B. This paper describes syntheses and perchlorate (ClO_4^-) removals by using the self-assembly $M_2L^B_4$ type complexes.

Additions of $CuSO_4{\cdot}5H_2O$ and bitb into an aqueous solution, containing various inorganic anions (F^-, Cl^-, Br^-, NO_2^-, NO_3^-, SO_4^{2-}, ClO_4^-), removed ClO_4^- selectively because of the formation of water-insoluble complex $[ClO_4 \subset Cu_2(\text{bitb})_4(ClO_4)_2]ClO_4$ (**1**).[2,3] On the other hand, water-insoluble $M_2L^B_4$ complex $[SO_4 \subset Cu_2(m\text{-bbitrb})_4]\ SO_4$ (**2**) removed ClO_4^- with high efficiency from an aqueous solution by anion-exchange reaction, indicating that the cationic $M_2L^B_4$ cages are useful units for ClO_4^- removals.[4] We have also succeeded in synthesis of 2D coordination polymer $[Cu(p\text{-bbiteb})_2(\text{-}\mu\text{-Cl-}[Cl{\cdot}(H_2O)_2 \subset Cu_2(p\text{-bbiteb})_4])]Cl_4$ (**3**) that bears $M_2L^B_4$ cages on the sheet framework, which has channel-like cavities between the cationic cages.[5] Although ClO_4^- removal activity of **2** was remarkably dependent on the particle size, **3** removed ClO_4^- from aqueous solutions with less dependency on the particle size. The ClO_4^- removals by various self-assembled metal complexes are described.

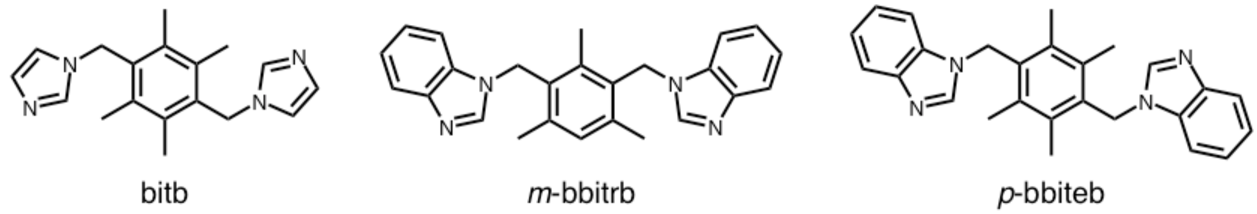

Figure 1 Structures of the L^B ligands.

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Metal β-diketonate derivatives as versatile building units to prepare volatile heterometallic complexes

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We proposed to create volatile supramolecular structures based on metal-organic (MO) complexes which form coordination polymers based on weak intermolecular interactions. Cu and Pb β-diketonates were shown to produce heterocomplex compounds of different composition through the incorporation of Cu complexes between the molecules of the Pb complex, forming chains of coordination polymers by means of bridging donor atoms [1]. As the initial complexes, these heterocomplexes are volatile and sublimate on heating in vacuum. By varying the substituents in the ligand we prepared coordination oligomers consisting of tetra- and binuclear structural units which are endowed with interesting properties. Analogous range of complexes has been prepared for the less labile Pd diketonate derivatives. The coordination behavior of MO complexes under cocrystallization is quite distinct in comparison with Cu based complexes. The unique structure of the Pd-based heterometallic complexes is due to some noncovalent metal-metal interactions in the crystals [2]. It was additionally confirmed by DFT calculations of intermolecular interaction energy and the gradients of the residual electron density between atoms of neighboring molecules. A variety of observed structures is enhanced by such phenomena as a ligand exchange and isomerization of the metal complexes engaged. It has been found that the *cis*-complexes of transition metal tend to form tetranuclear species and *trans*-complexes allow polymeric structures, i.e. recognition and selectivity related to supramolecular chemistry are implemented. We invented a new type of volatile bimetallic Cu/Pd complexes using bridging function of terminal substituents of the ligand. Such compounds appeared to be promising precursors to prepare Cu/Pd alloy films with floating stoichiometry which is apt to prepare membrane materials for hydrogen separation [3].

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Self-assembly formation of functional supramolecular architectures incorporating various guest metal ions and the development of healable luminescent metallogels from triazole- based heterocyclic ligands

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Nitrogen containing heterocycles, such as triazoles, are ideal for template-directed generation of discrete polynuclear assemblies,[1] coordination polymers and novel functional nanomaterials such as gels[2] and various other intriguing architectures. Interest has grown in the development of this relatively recent family of ligands for their potential application in materials science,[2] catalysis[3] and other highly topical areas of chemistry.[4] Utilising host-guest chemistry in the design of diverse functional structures using appropriate organic ligands by changing metal centres has always been a keen aim in the Gunnlaugsson Group. We have combined the 'guest' ability of *d*- and *f*- block metal ions[5] with various versatile triazole derivative 'hosts' in the investigation of the self-assembly behaviour, and the design of healable luminescent soft matter.[6]

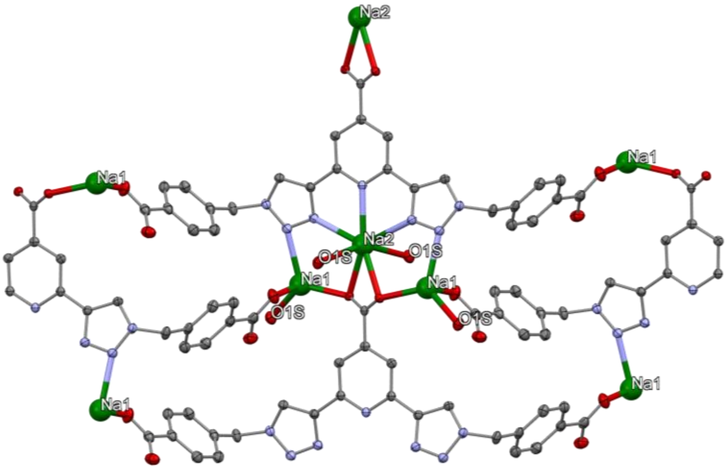

Figure 1 2,6-bis(1,2,3-triazol-4-yl)pyridine coordination polymer towards healable gels.

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Metalation and Dynamic Structural Changes of Multinuclear Sandwich Frameworks

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The extended π-conjugated sp^2-carbon frameworks, such as polycyclic aromatic hydrocarbons (PAHs) and π-conjugated polyenes, are of great interest as a new class of polydentate ligands for homogeneous metal clusters. These unsaturated frameworks could serve as a "slippery" carbon plate on which metal atoms can change their positions with a low barrier due to the labile nature of metal-carbon(sp^2) bonds, as represented by facile metal atom slippage on a small carbocyclic ligand. If such high mobility of each metal atom on the sp^2-carbon plate is coupled with inherently labile nature of metal–metal interaction in metal clusters, a metal assembly laid on the sp^2-carbon plate may show unique two-dimensional multiatomic dynamic behavior.

Our group has shown that the multinuclear sandwich complexes containing a metal chain or a metal sheet exist as the isolable compounds.[1] This new class of organometallic clusters show unique structural changes. For example, metalation and demetalation of bis-polyene metal chain sandwich clusters took place.[2] Furthermore, a metal chain in a sandwich framework showed interesting redox-induced reversible structural changes.[3]

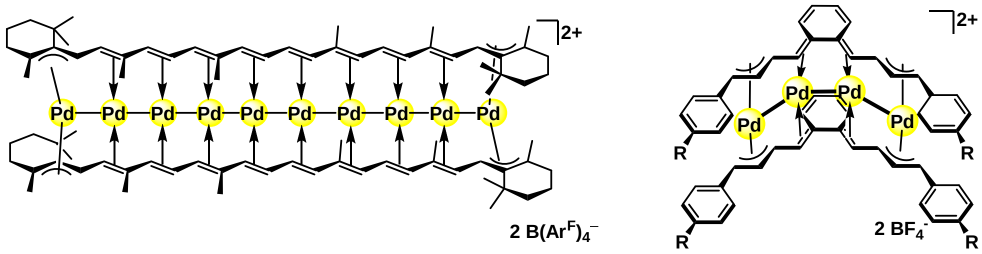

Figure 1. Sandwich clusters which showed unique structural changes such as demetalation/metalation reactivity or redox-induced metal assembly/disassembly behavior.

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Inorganic and Organometallic Chemistry of Caffeine

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Caffeine, a well-known xanthine alkaloid and central nervous system stimulant, has been used as a ligand to prepare a number of transition metal complexes.[1,2] It can also be functionalized to generate the corresponding N-heterocyclic carbenes (NHCs) and metal complexes thereof.[3,4] This presentation outlines the syntheses, structures, and reactivity of N-heterocyclic thione (NHT) and selone (NHSe) derivatives of caffeine (Fig. 1) and their first metal compounds. More specifically, these novel soft donor ligands have been used to prepare a number of complexes of mercury(II), copper(I), and gold(I), including $(\mathrm{CaffE^{Me}})_n\mathrm{HgX_2}$ (E = S, Se; n = 1, 2; X = Cl, Br, I) and $(\mathrm{CaffE^{Me}})\mathrm{MX}$ (E = S, Se; M = Cu, Au; X = Cl, Br), several of which have been structurally characterized. A combination of ^{1}H NMR spectroscopy and electrospray ionization mass spectrometry (ESI-MS) has been used to evaluate the selenophilicity of mercury and the results of these experiments will also be described in this presentation.

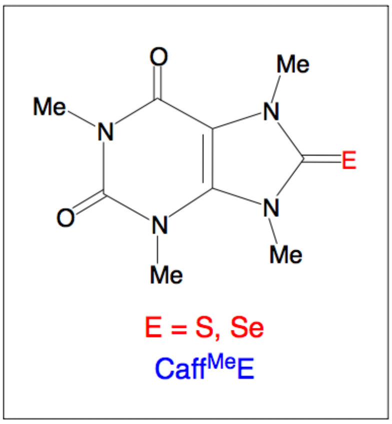

Figure 1 N-heterocyclic thione (NHT) and selone (NHSe) derivatives of caffeine.

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A coordination-driven triangle as nanoreactor and nanovessel

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Metallo-supramolecular architectures generated from metal centers and well designed polytopic ligands are an excellent bench test for supramolecular and self-organization concepts and a wide source of new functional materials. In particular, coordination driven discrete boxes and capsules have drawn increasing attention due to their hollow superstructure.[1] Such architectures provide space confined cavities for a variety of applications including storing, sensing, and nanoreactors. In this context, we studied the self-assembly of a metallo-supramolecular triangle $[Cu(o–L)]_3$ generated by self-assembly between Cu(II) ions and a bis-acetylacetone ligand (o-L).[2] $[Cu(o–L)]_3$ is a metallo-macrocycle with a triangular cavity in equilibrium with a dimeric species[3] $[Cu(o–L)]_2$ and endowed with host-guest properties.[4] This dynamic system adapts in response at both chemical and physical stimuli. We show that the triangle can act as nanoreactors to modulate the guest reactivity and as nanovessels to access guest degradation products.[5]

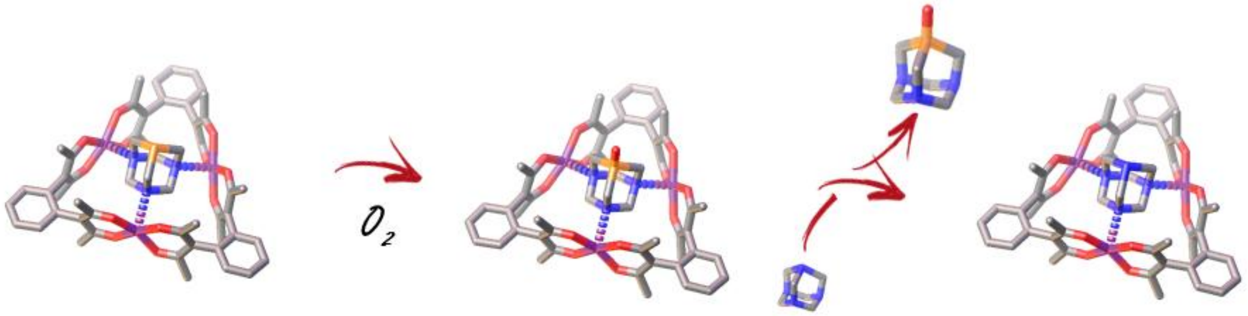

Figure 1 Guest oxidation in the $[Cu(o–L)]_3$ metallo-supramolecular pocket and product recovering by guest exchange.

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Stimuli-Responsive Coordination Polymers

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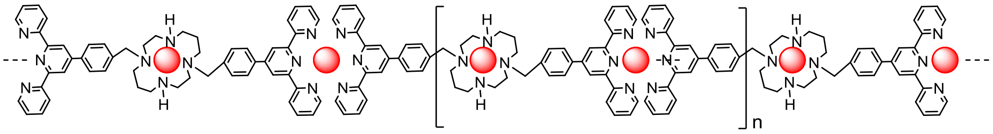
One of the greatest challenges today facing physics, chemistry, and materials science is to find a way to structure molecules so as to build functional superlattices, molecular devices or responsive materials at mesoscale. For these purposes, soluble coordination polymers are of particular interest. These 1D to 3D architectures are obtained spontaneously from self-assembly of metal ions and polytopic bridging coordinating units (ligands). In these systems, the relation between concentrations, binding constants, and chain trajectory of the polymers can be exploited to elaborate materials with specific behaviours. An important point is that these structures may exhibit the properties of classical organic polymers (viscosity, processability…) but the incorporation of metal species in the polymer chain opens new perspectives since they give access to magnetic, redox, optical, electrochromic or mechanical properties and may also provide dynamic features relevant for the construction of novel materials that can respond to their environment, i.e. stimuli-responsive and intelligent materials.

In this context, different classes of responsive coordination polymers will be presented. In particular, remarkable electrochromic systems and redox responsive metallogels will be described.[1-4]



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Polyphosphorus Complexes for Supramolecular Aggregations

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Polyphosphorus complexes are an important class of compounds useful for many applications. Due to the lone pairs at the phosphorus atoms they are able to self-assembly with Lewis acidic transition metal and main group moieties. Here, two different directions have been discovered; (i) the generation of organometallic-organic hybrid compounds as 2D and 3D materials[1,2] and (ii) the creation of molecular giant spheres.[3]

Within the first area of research the use of the dynamic equilibria between the P_n ligand complexes and Lewis acidic cations in the presence of multitopic organic linkers is applied to construct 3D materials. The cations are accompanied by coordinating or weekly coordinating anions. In the second field, the advantages of the five-fold symmetric building block of the pentaphosphaferrocenes are used to create with Cu(I) and Ag(I) units unprecedented giant spheres which exhibit a fullerene-like topology constructed by non-carbon atoms (Figure 1). Although usually template controlled encapsulation occur, novel strategies are also successful in the absence of appropriate templates.[4,5]

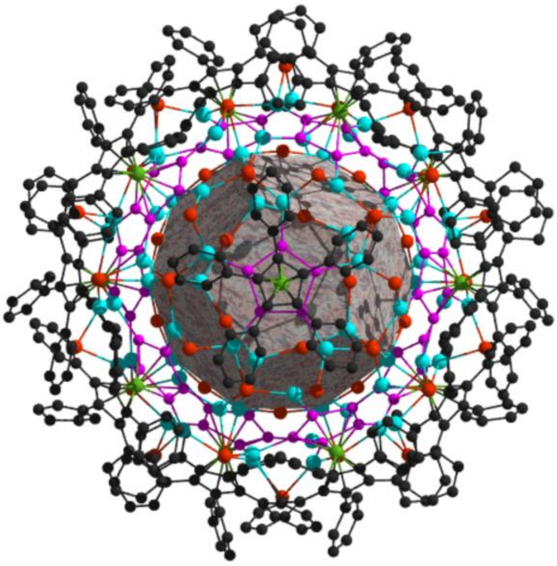

Figure 1 Molecular structure of a supersphere

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Boronic Acids in Structural Supramolecular Chemistry

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The lecture summarizes efforts to construct molecular and polymeric nanostructures using boronic acids as key building blocks. Among other things, I will describe the synthesis of macrocycles and cages by polycondensation reactions,[1,2] the synthesis of crystalline[3] and soft networks[4] based on dative boron-nitrogen bonds, and novel metalloligands containing boronate ester caps.[5] These metalloligands can be used to construct polynuclear coordination cages (Fig. 1).[6]

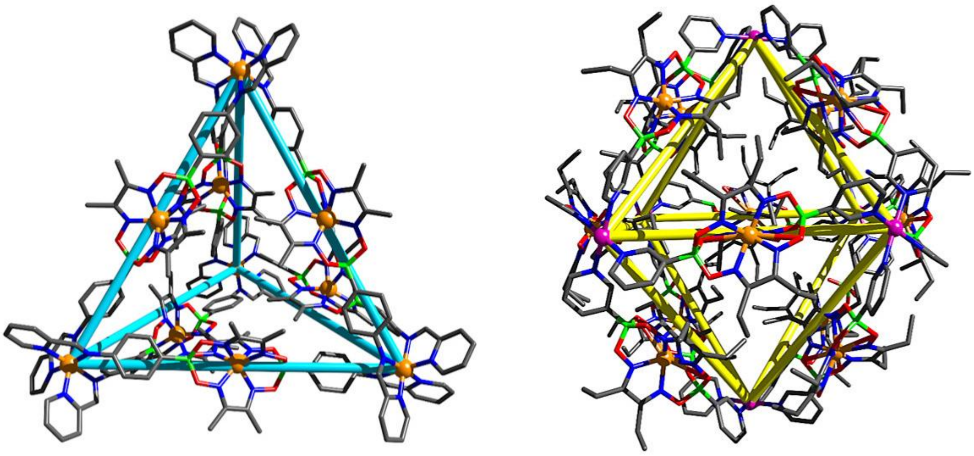

Figure 1 Coordination cages based on boronate ester-capped metalloligands.

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Neutral Electroactive Metallacages: Towards the control of reversible guest encapsulation

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The fundamental understanding of host-guest interactions lies within the heart of modern supramolecular chemistry. Applications in molecular recognition, substrate delivery or signal processing have provided the main driving force to research aiming to control these interactions. On the other hand, coordination-driven self-assembly has allowed the preparation of a large number of molecular polygons (e.g. triangle, square) and polyhedrons (e.g. cubes, prisms) with remarkable host properties.

In this context we recently described the first electron-rich self-assembled discrete octacationic cages based on the extended tetrathiafulvalene (exTTF) unit[1] and showed that one of these metallacages undergo electrochemically induced reversible anionic guest release/uptake (**Figure 1**).[2]

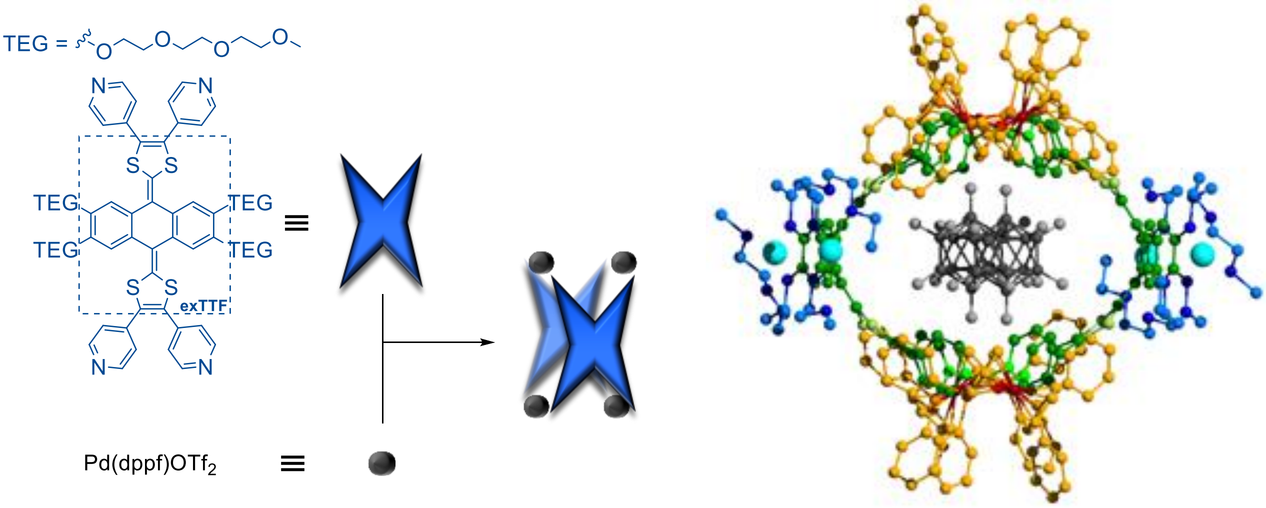

Fig. 1 *An exTTF based electron-rich metallacage and the X-ray structure of a corresponding host-guest complex.*

In this communication, we present our recent results in this field, focusing on neutral analogous metallacages by addressing: 1) their synthesis; 2) the differences in host-guest properties compared to those of the isostructural cationic cages marked by a remarkable higher affinity for neutral guests in the case of the neutral cages (K_a up to 10^5 M^{-1}).

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Columnar Liquid Crystalline Metallomacrocycles

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Designer molecular nanospaces are promising systems for promoting multiple chemical processes such as specific recognition, storage, the construction of arrays, transportation, and the reactions of accommodated molecules. Herein, we report nanospaces in flowable media composed of thermotropic columnar liquid crystalline macrocyclic molecules to add flexibilities and stimuli-responsive properties to the systems (Figure 1).[1] The macrocycle **1** has a highly symmetric mesogen with an inner vacant cavity of 14 Å diameter enclosed by a planar ring composed of four bis(salicylidene)-*o*-phenylenediamine (salphen) moieties alternating with four carbazoles. It was revealed that the macrocyclic ligand and their metal complexes self-assembled into columnar liquid-crystalline phases depending on the temperature, and displayed a highly fluid character over a wide range of temperatures. We are currently investigating the inclusion of guest molecules into the nanospaces as well as the metal insertion into the four salphen ligands.

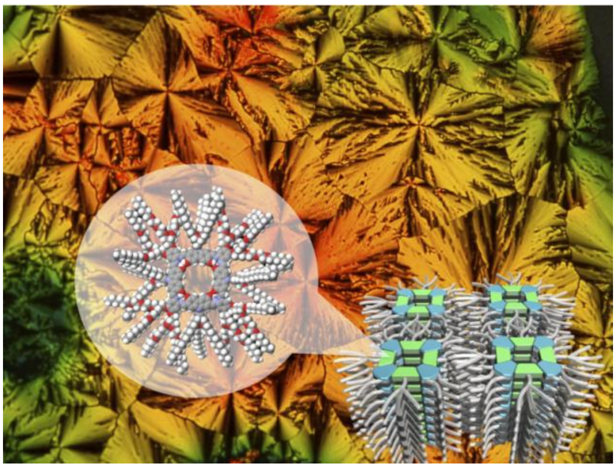

Figure 1 Columnar liquid crystalline macrocycle 1

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Inner/Outer Sphere Ligand Design for Metal recovery Processes

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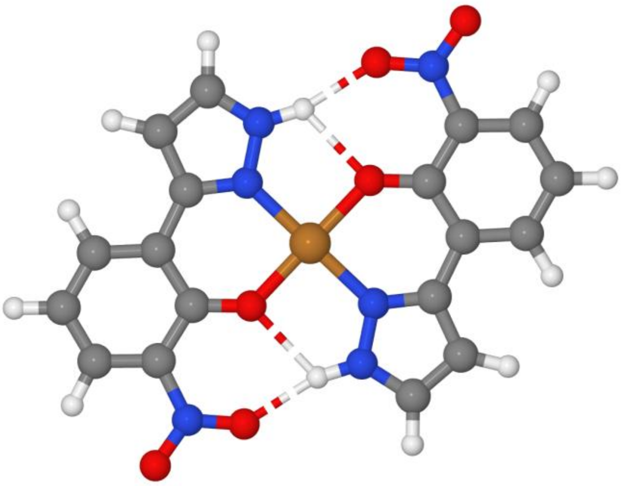
We have shown that equilibrium constants for solvent extraction of metals can be increased by orders of magnitude by introducing substituents which create H-bonds in the outer coordination spheres of the metal ions.[1] An example is copper extraction, $Cu^{2+} + 2LH_{org} = [CuL_2]_{org} + 2H^+$, by phenolic pyrazoles:[2]

$X = NO_2$



In the current paper we extend this concept to extractions that involve synergistic combinations[3] of reagents, $M^{2+} + 2LH_{org} + 2L'_{org} = [ML_2L'_2]_{org} + 2H^+$, where the charge-balancing anions, L^-, can be present in the inner or the outer coordination sphere, or both. A combination of computational and experimental techniques has been used to define the speciation and the bonding *in solution* and to evaluate whether substituent effects operate by changing bonding in the outer or inner coordination shells or by changing the acidities of the extractants. In many cases there is a remarkable correlation between calculated *gas phase* formation energies and the observed strengths of reagents *in solution* in solvent extraction experiments.[1b,2]

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Self-assembled copper and manganese metallacrowns as porous and magnetic materials

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Metallacrowns (MC) are the inorganic analogs of crown ethers, capable to encapsulate transition metal ions or lanthanides (Fig. 1 left).[1] Metallacrowns can be assembled using transition metal ions (*e.g.* Cu^{II}, Zn^{II}, Mn^{III}) and aminohydroxamic acids. MCs are investigated as luminescent probes for bioimaging, as single-molecule magnets (SMMs), as hosts for anions and cations, and as building blocks of large MOF-like assemblies.[2]

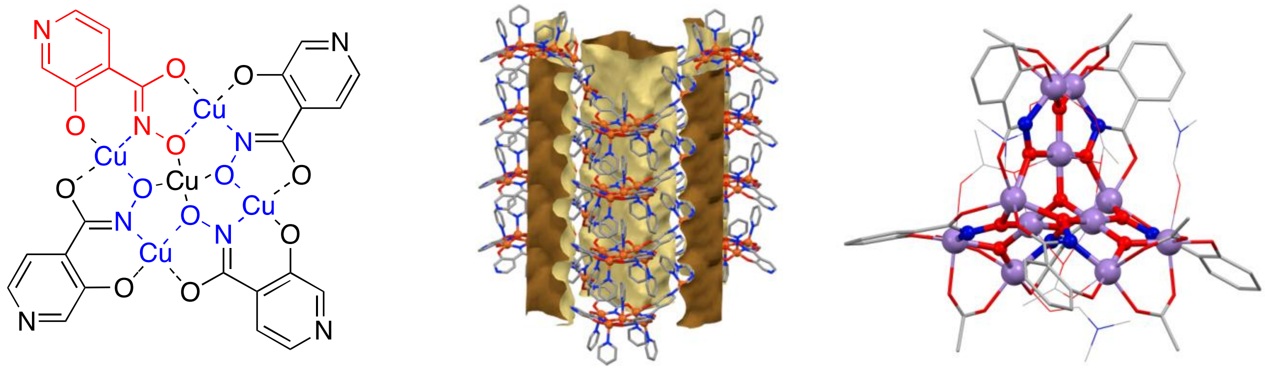

Figure 1 Left: Scheme of the 12-metallacrown-4 complex of H_3HinHA (total 2- charge omitted); center: channels in the crystal architecture of the 12-MC-4 of $HinHA^{3-}$; right: $Mn_{11}L_6$ metallacryptate of Mn(II/III) and salicylhydroxamate.

In this contribution we report the design and the isolation of the first permanently porous metallacrown architecture, which can be obtained by direct self-assembly from copper(II) acetate and a pyridinic analog of salicylhydroxamic acid (H_3HinHA, Fig. 1). The material presents infinite channels into which N_2 and CO_2 are absorbed (Fig. 1, center). We also report the characterization of self-assembled Mn(II/III) MCs with single-molecule magnetic properties, including a $Mn_{11}L_6$ metallacryptate which bears a $Mn_3(\mu_3\text{-}O)$ core (Fig. 3 right).

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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Heterometallic rotaxanes and their supramoleculal assembly

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We are working to make supramolecular assemblies of hybrid organic-inorganic [n]-rotaxanes. The components of hybrid organic-inorganic rotaxane are the heterometallic octanuclear $[Cr_7NiF_8(O_2C^tBu)_{16}]^-$ rings and the axle is an organic thread which act also as a template for formation of the heterometallic ring about this axle[1]. This route has allowed us to make hybrid organic–inorganic [2]- and [3]-rotaxanes [2]. Using functionalised 'stoppers' on the axles we can produce hybrid organic–inorganic [2]- and [3]-rotaxanes that can act as ligands [3,4]. Then these polymetallic rotaxane-ligands can be used as building blocks (modules) for construction of various supramoleculal assemblies[5]. Here we present the designed modular supramolecular architectures by linking hybrid organic–inorganic [2]- and [3]-rotaxanes into various [n]-rotaxanes (where n= 4 - 24). As the rings have been proposed as qubits for QIP, the strategy provides a possible route towards scalable molecular electron spin devices for QIP.

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Controlling the Structure and Properties of Halobismuthates

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Inorganic-organic hybrid materials containing halobismuthates have been recently demonstrated to exhibit important physical properties like NLO,[1] thermochromism,[2] piezo-electricity,[3] ferro-electricity[4] and semiconductivity[2]. Halobismuthates are known to exist in a wide range of nuclearity as zero-dimensional (e.g., $[BiCl_6]^{-3}$, $[Bi_2Br_9]^{-3}$, $[Bi_2Cl_{11}]^{-5}$, $[Bi_3Cl_{12}]^{-3}$, $[Bi_4Cl_{18}]^{-6}$, $[Bi_5I_{18}]^{-3}$, $[Bi_6Cl_{26}]^{-8}$, $[Bi_7I_{24}]^{-3}$, $[Bi_8I_{30}]^{-6}$) and one-dimensional networks (eg. $[BiI_4]^{-1}$, $[BiI_5]^{-2}$, $[Bi_2I_7]^{-1}$ and $[Bi_3I_{11}]^{-2}$).[5] We have shown, for the first time, that the halobismuthates with specific bismuth:halide ratio stabilized by anilinium cations can be prepared in a controlled manner.[6] Both one and two dimensional polymeric halobismuthate compounds with new structural motifs have been isolated (Figure 1). Organic substituents on the anilinium cations have significant role in directing the dimensionality and structure of the halobismuthate polymers and hence their properties. Many of the newly obtained halobismuthates exhibit optical, thermochromic and piezo-electric properties.

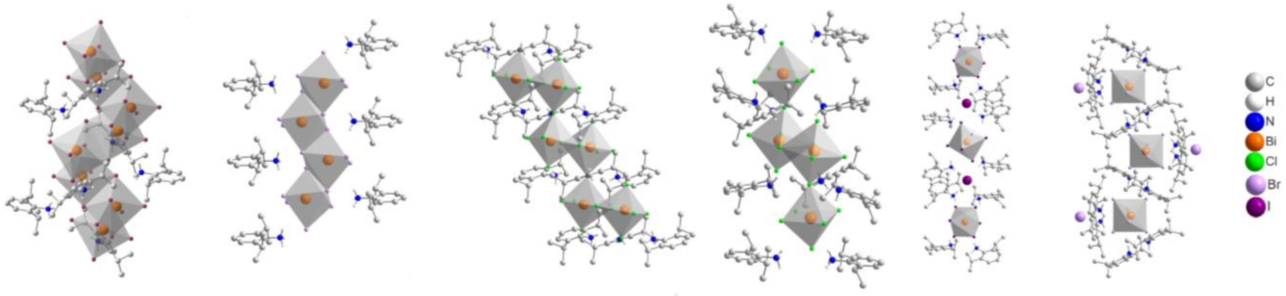

Figure 1 Crystal structures of 1-dimensional halobismuthates stabilized by 2,6-diisopropylanilinium cations via hydrogen bonding.

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Functionalized Tetrahedral Helicates: Toward Luminescent Bioprobes

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Among different applications, lanthanides complexes have already found their place in the domain of medical diagnostic and imaging (i.e., MRI). However, due to their unique luminescence properties (long luminescence lifetimes, sharp emission bands from visible to near-infrared (NIR)), lanthanide-mediated polynuclear compounds can also be advantageously used for optical bioimaging, especially in the NIR. This specific application requires a good sensitisation of lanthanide luminescence via an organic chromophore ("antenna") in proximity. The development of such molecular probes suitable for aqueous media is a challenging task and different constraints must be considered in their design.

In our laboratory, we focus on designing and exploiting different types of multimetallic lanthanide-containing systems in order to collect a high visible/NIR light intensity. We hereby present our supramolecular approach, which consists in the incorporation of several lanthanide cations in well-defined discrete tridimensional self-assemblies.[1] The required tripodal ligands are synthesised by coupling an aromatic amine with tridentate binding moieties, which possess additional functional vectors. The self-assembled tetrahedral edifices are characterised with different structural and physico-chemical methods (NMR, HRMS). In addition, the luminescence properties of those supramolecular complexes with lanthanide cations emitting in the visible and NIR are evaluated in terms of potential interest in optical imaging.

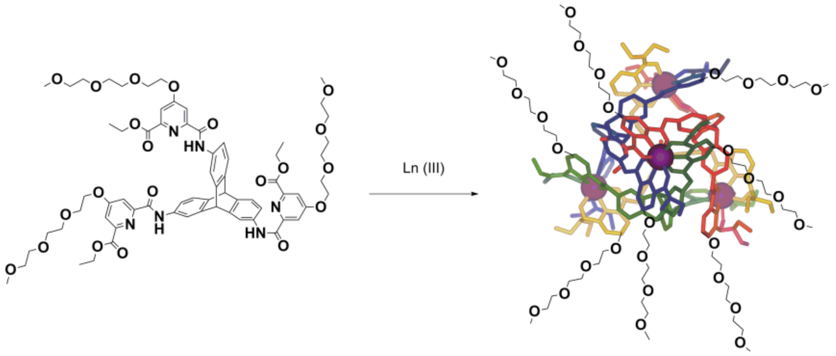

Figure 1 Self-assembly of lanthanide-containing tetrahedral helicates.

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Efficient catalysis of a bimolecular reaction in a coordination cage arising from orthogonal binding of both reactants

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A water-soluble M_8L_{12} cubic coordination cage, with a metal ion at each vertex and a bridging ligand spanning every edge, shows strong binding of hydrophobic guests in water (K up to 10^8 M^{-1}) into its central cavity.[1] In addition to a good shape / size match, guest binding is dominated by the hydrophobic effect,[2] which means that ionisable guests (*e.g.* amines and carboxylic acids) bind strongly in their neutral forms but are released in their charged forms (protonated ammonium cations or deprotonated carboxylate anions).[3] The neutral molecule benzisoxazole is a competent guest with $K \approx 10^4$ M^{-1}, and when bound undergoes extremely efficient catalysis of its reaction with hydroxide to give 2-cyanophenolate (the Kemp elimination) with k_{cat}/k_{uncat} of >> 10^5.[4] The catalysis is based on two independent recognition events: (i) binding of the substrate in the central cavity due to the hydrophobic effect, and (ii) accumulation of hydroxide ions around the surface of the cationic cage due to ion-pairing effects which gives a very high local concentration of HO^- around the bound guest. Multiple turnovers are assured by the fact that the product is an anion and therefore hydrophilic.

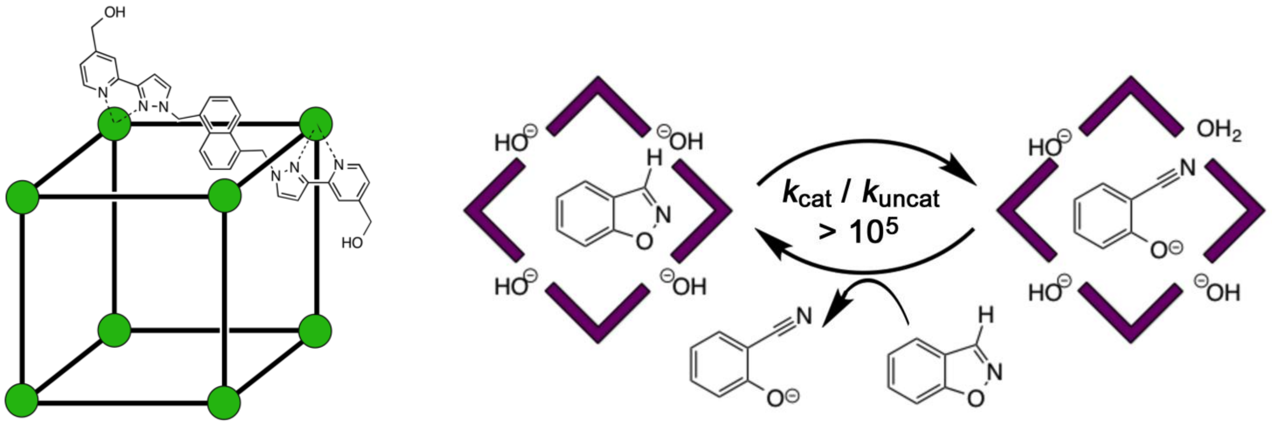

Figure 1. Left: sketch of the host M_8L_{12} cage. Right: schematic outline of the catalysed Kemp elimination reaction in the cage cavity.

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The coordination flexibility which Ni(II) provides within Metal Organic Frameworks containing the 1,2,4,5-benzenetetracarboxylic acid ligand

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Metal-organic molecular frameworks (MOFs) may be formed in the crystalline phase by the self-assembly of structurally defined molecular modules possessing translational symmetry of one or more dimensionality. Such open framed network materials have a wide variety of structural diversity and are expected to exhibit novel properties such as inclusion behaviour. The MOF's are a systematic modular complex which resembles a scaffold-like structure. The energetic levels between Ni coordination geometries are close enough to allow an ease of transition between these geometries, which can result in a structural shift in response to physical stimuli. Ni(II) complexes have been synthesised and their thermal natures have been studied and characterised. Acetic acid and water coordinated species were compared, as well as the inclusion of Ni(II) into a Zn(II) framework. The results showed that the water coordinated species exhibited thermo-geometry shifts while the acetic acid coordinated molecules showed glass-like thermal behaviour. The inclusion of Ni(II) within the Zn(II) framework showed the physical reaction to the unfavourable dehydration environment, hence a thermo-geometry shift was achieved. The shifting in geometry reacts to thermal stress and thereby avoiding dehydration voids within the complex.

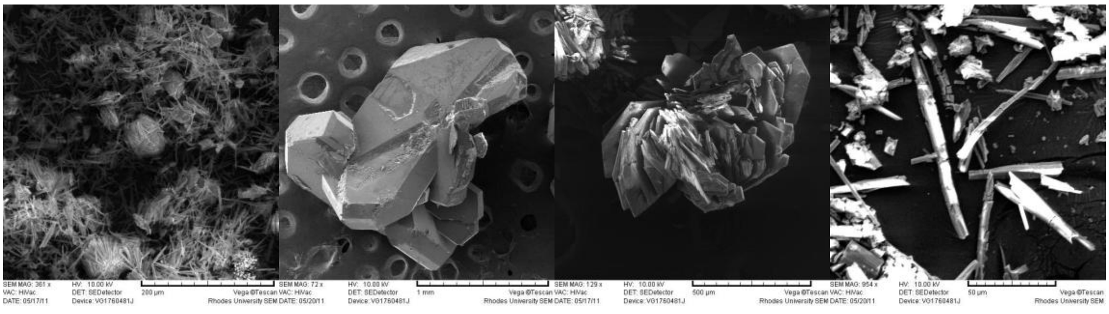

Figure 1 Ni(II) & Zn(II) based metal organic frameworks. 1st LEFT: $[Ni_2B4C(H_2O)_4]\cdot 4H_2O$. 2nd LEFT:: $[NiB4C(AcOH)_2]\cdot 9H_2O$. 1st RIGHT:: $[Zn_2B4C(H_2O)_5]\cdot 2H_2O$. 2nd RIGHT: $[ZnNi_4B4C(H_2O)_4(OH)_2]\cdot 10H_2O$.

Stimulus Responsive Rolling/Unrolling Structural Deformation Based on A Common Coordination Skeleton

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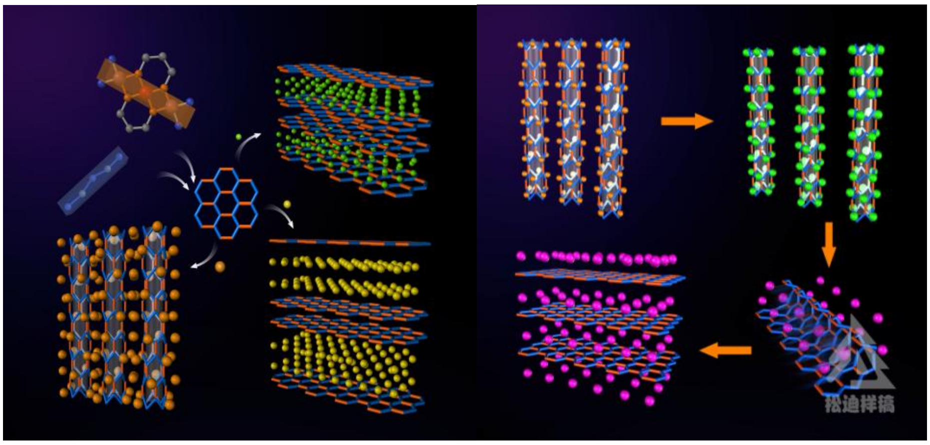
Stimulus-responsive structural transformation is a general feature of living system and synthetic assemblies based on amphiphilic building blocks. In MOF chemistry, similar dynamic deformation is defined as "Supramolecular Isomerism". In most cases, such structural deformation processes are guest-induced and are exclusive features for flexible coordination frameworks. Herein, we describe a series of coordination frameworks based on a common honeycomb skeleton, which represent a gradually rolling/unrolling deformation process in response to internal and external stimulus. This sheet/tube structural transformation is redolent of self-assembly process in peptide, amphiphilic molecules and block copolymer systems and provides potential for targeted synthesis of Metal-Organic Nanotubes. [1]



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Syntheses, Inclusion Behavior, and Sensitizing Ability of Macrocyclic Tetranuclear Ruthenium Complexes: Light-harvesting Host

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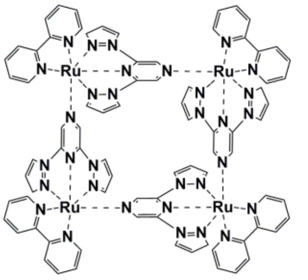
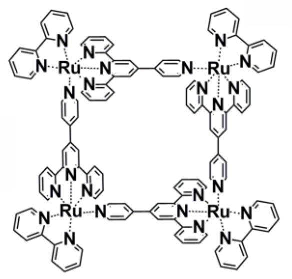
Macrocyclic multinuclear metal complexes draw much attention, since they show not only inclusion behavior, but also have catalytic activity. Fujita has reported the formation of macrocyclic or cage-shaped multinuclear palladium complexes by self-assembly, and their inclusion behaviors accompanying catalytic activity in the cavity.[1] Ruthenium complexes have distinguishing abillities on their photochemistry such as photodissociation of the ligand under visible light irradiation and sensitization of photoreaction.[2]

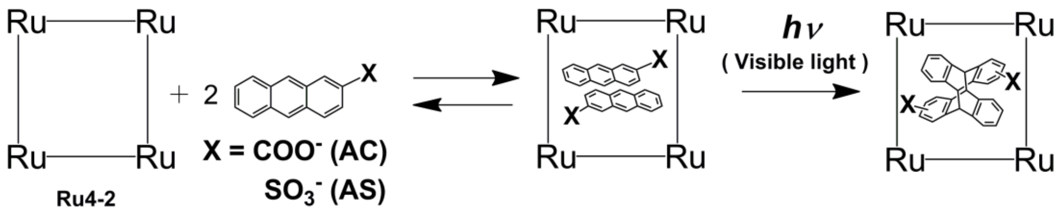
We have prepared macrocyclic tetranuclear ruthenium complexes bridged by a pyrazine (Ru4-1) or a 4,4'-bipyridine (Ru4-2) moiety by self-assembly. It was found that Ru4-1 included a thiocyanate ion and Ru4-2 included two aromatic molecules in water. Ru4-2 in water was stable under visible light irradiation and did not dissociate.

We have examined the photodimerization of anthracene derivatives in the presence of Ru4-2. Anthracene derivatives and Ru4-2 produce a 1:2 host-guest complex quantitatively in water. Photodimerization of anthracene derivatives proceeded by irradiation of visible light (> 455 nm) in the presence of Ru4-2.[3] We concluded that Ru4-2 acted as a host and a photosensitizer for the photochemical reaction of the guest molecules: light-harvesting host for photodimerization of anthracene derivatives.


Ru4-1


Ru4-2

Scheme 1



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Functional Materials *via* Coordination and Hierarchical Self-Assembly

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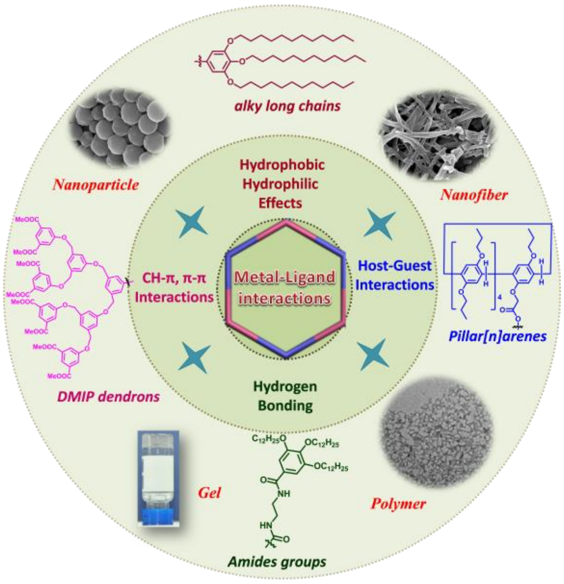
Hierarchical self-assembly is omnipresent in many biological systems and has been widely explored in construction of artificial functional supramolecular systems. Based on our previous research on coordination-driven self-assembly of functional metallacycles[1], recently, we have expanded our research towards the construction of functional materials via hierarchical self-sssembly. The judicious combination of reversible coordination in metallacycles with other non-covalent interactions allows for the fabrication of a variety of nanoscale supramolecular structures and functional materials (Figure). For example, various nanostructures[2,3], metallohydrogels[4], and stimuli-responsive supramolecular polymers[5], have been successfully prepared by this strategy with the tailored chemical and physical properties.



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Supramolecular Chemistry with Metal-Carbene Complexes

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Recently, based on the successful construction of organometallic molecular assemblies[1,2] using polydentate ligands with N-heterocyclic carbene donor functions, we have recently been able to perform photochemical modification (PCM) reactions on rectangular metalacycles built from bridging dicarbene ligands and featuring internal olefin groups (A) via a photochemical [2+2] cycloaddition reaction (Scheme 1).[3] These results indicate the suitability of the $[M_2(\text{dicarbene})_2]^{2+}$ (M = Ag, Au) metalacycles as scaffolds for the photodimerization of the olefinic bonds to yield cyclobutane units within the molecular rectangles. While complexes of type B feature an internal cyclobutane unit obtained by [2+2] cycloaddition of internal olefinic bonds, we also became interested in utilizing $[M_2(\text{dicarbene})_2]^{2+}$ (M = Ag, Au) complexes with terminal double bonds (C), which upon [2+2] cycloaddition would lead to complexes featuring a macrocyclic ligand as in D (Figure). Removal of the metal atoms from such assemblies leads to interesting new macrocycles. The desired molecular size of the tetraimidazolium macrocycle can be tuned easily by changing the length and breadth of the internal bridging groups of ligands. This system presents an excellent starting point for a new method to multipurpose receptors.

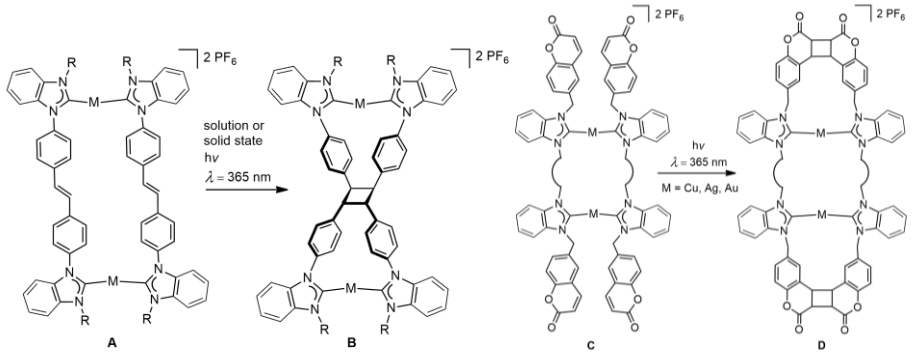

Figure 1

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Multi-Layered Tripalladium(II)cyclophanes: Construction and Properties

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Nano-dimensional (23(2) × 21(1) × 16(1) Å^3) hetero four-layered trimetallacyclophanes via the proof-of-concept experiments that utilize a suitable combination of π···π interactions between the central aromatic rings, tailor-made short/long spacer tridentate donors, and the combined helicity are constructed. In a previous research, the reaction of K_2PdX_4 with *N,N',N"*-tris(2-pyridinylethyl)-1,3,5-benzenetricarboxamide (L^{SA})[1] produces discrete C_3-symmteric racemic helical tripalladium(II)cyclophanes, (P,M)-[$Pd_3X_6(L^{SA})_2$]. Consecutive reaction of (P,M)-[$Pd_3X_6(L^{SA})_2$] with L_2 or direct reaction of K_2PdX_4 with L^{SA} and L^{LE} yields a ball-joint-type aggregate consisting of unprecedented helical metallacyclophanes conglomerate crystals, chiral isomer (P)-[$Pd_3X_6(L^{SA})_2$]@(M)-[$Pd_3X_6(L^{SA})(L^{LE})$] and its enantiomer (M)-[$Pd_3X_6(L^{SA})_2$]@(P)-[$Pd_3X_6(L^{SA})(L^{LE})$].[2] The host-guest aggregation can be ascribed to one π···π interaction and three –NH···O=C– hydrogen-bonds along with the combined helicity. A synthetic strategy for hetero four-layered tripalladium(II)cyclophanes via direct, stepwise, or substitution procedures utilize a suitable combination of π···π interactions between the central aromatic rings, tailor-made short/long spacer tridentate donors, and the combined helicity (Figure 1). Further investigation of this system will help to realize potential supramolecular host-guest system applications such as molecule-accommodating recognition, DNA binding, electronic transition, dynamic catalysis, and metal-graphene interaction.

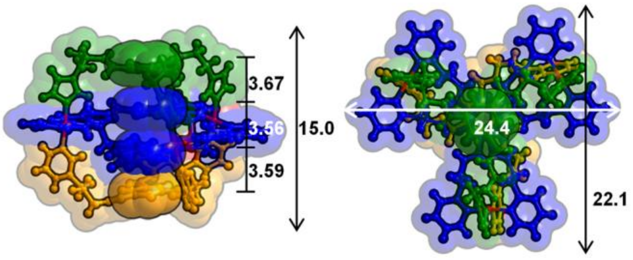

Figure 1 Side and top views of [$(L^{LA})(L^{SE})Pd_3(L^{SE})(L^{LE})$]$(NO_3)_6$ in space-filling/ball-and-stick representations along with the relevant molecular dimensions (Å) (Pd^{2+}, red; L^{SA}, blue; L^{LE}, yellow; L^{LA}, green).

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Association of a non-heme biomimetic iron complex to a Calix[6]arene receptor: towards supramolecular biomimetic reactivity.

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Metalloenzymes are natural catalysts performing a wide range of reactions in mild conditions with exquisite regio- and stereo-selectivities using readily available metals (Zn, Fe, Cu…) and reagents (O_2, H_2O_2…).[1] These remarkable reactivities are the result of the association of an efficient active complex to a substrate binding site which selects and preorganizes the substrate in the vicinity of active site the by weak interactions (Fig. 1, left). Such supramolecular patterns are absent in classical biomimetic models. We thus decided to design a supramolecular model of non-heme mononuclear iron enzymes by associating a mononuclear iron model to a calix[6]arene receptor complex (Fig. 1, right).[2,3] The synthesis of the scaffold and its heterodinuclear Fe^{II}/Zn^{II} complex will presented, as well as its host-guest properties and reactivity towards oxidizing agents (H_2O_2, PhIO).

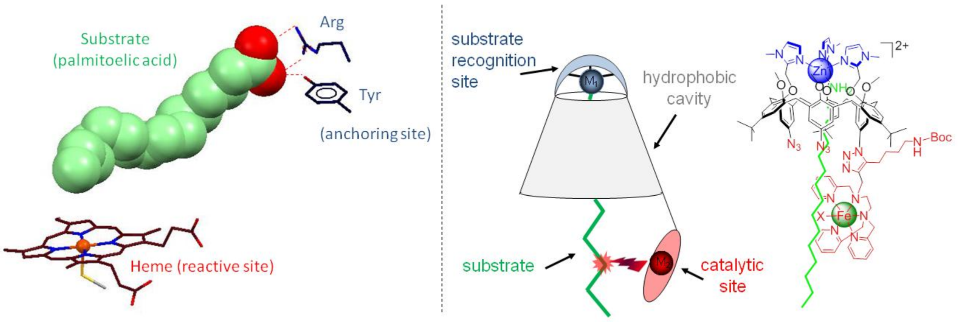

Figure 1. Association of substrate binding site and a reactive site in metalloenzymes (left, structure the active site of P450-BM3) and a supramolecular model (right, non-heme iron mononuclear complex appended to a calix[6]arene metal receptor)

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Silicon analogues of crown ethers and cryptands: Synthesis and coordination

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Siloxanes and cyclosiloxanes are known as very weak coordination ligands and there is an ongoing debate on the reasons for the low Lewis basicity of such compounds in the literature.[1-3] In this talk the synthesis of different new ligands containing Si-O-Si or Si-O-C units will be presented and the coordination chemistry of these new ligands will be discussed. Our results show that these compounds have a very different ability to coordinate alkali and alkali earth metal ions, depending on the chain length of the Si_n units between the oxygen atoms.[4-7]

Figure 1 Different silicon containing ligands whose synthesis and coordination ability will be presented in the talk

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Bioresponsive MRI Agents: Insights from Coordination Chemistry

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Bioresponsive or smart contrast agents (SCAs) can substantially improve the specificity of magnetic resonance imaging (MRI) in studying processes on molecular and cellular level. These probes can alternate their MR signals upon change in the local environment, thus reporting the occurrence of a particular physiological or pathological process.

Monitoring changes in concentration of ions or molecules that are involved in neuronal signaling with SCAs could be extremely valuable for MR neuroimaging and allow investigation of brain activity in unprecedented fashion. To this end, we developed a series of cyclen-based paramagnetic complexes that strongly respond to calcium ions and amino-acid neurotransmitters. They possess a common chelator of the paramagnetic ion covalently linked to EGTA-derived moiety or aza-crown ether to achieve an interaction with calcium ions or neurotransmitters, respectively.[1-2] The high-resolution NMR and DFT studies revealed dramatic calcium-induced changes in the coordination of the paramagnetic ion and its chelator, which result in the altered hydration of the complex and its extraordinary relaxometric response.[1] This response remains strong upon various synthetic modifications of these SCAs and can be detected *ex vivo* and *in vivo*.[2,3]

The obtained results indicate development of a robust macrocyclic chelator that responds to various types of analytes. It is suitable for further structural optimizations which improve the physico-chemical and biokinetic properties of the resulting SCA. Ultimately, it leads to potent sensor molecules that can serve as MRI markers in functional imaging studies for monitoring important biological processes.

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Coordination Chemistry From SPECT to PET: New Tracers for Old Targets

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The last decade has seen increased emphasis on PET rather than SPECT in development of radionuclide tracers for clinical translation and basic research. While this trend may slow down in the next few years as new SPECT instrumentation becomes available and supplies of Tc-99m recover from recent setbacks, it has led to development of PET replacement for long-established SPECT and gamma camera imaging methods, aiming for improved sensitivity, quantification and image quality. This presentation will summarise three developments of this type based on coordination chemistry of gallium, boron and sulfur, and zirconium. It will cover new chelator chemistry for gallium-68, using tripodal tris(hydroxypyridinone) ligands with fast chelation under mild conditions, that places radiopharmaceutical synthesis on a simple “kit” basis analogous to technetium-99m chemistry (i.e. Gallium-68 as the “new technetium-99m”); fluorine-18-labelled substrates for the sodium/iodide symporter: tetrafluoroborate and fluorosulfate, for PET imaging of thyroid disease and reporter gene imaging (replacing SPECT imaging with Tc-99m-pertechnetate and I- 123/131/iodide); and cell labelling with zirconium-89, using hydroxyquinolinate ionophores to transport zirconium across the cell membrane, providing a long half-life tracer for in vivo cell tracking (replacing cell labelling with indium-111).

Light-induced apoptosis in cancer cells by a tetrapyridyl ruthenium prodrug offering two *trans* coordination sites

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Photopharmacology consists in activating medicinal compounds *in vivo* with light in order to circumvent the biological action of the drug in space and time. In cancer research light activation of chemotherapeutic prodrugs is regarded as a promising alternative to chemotherapy as it might limit side effects and increase treatment efficacy. In this presentation two new photopharmacological ruthenium prodrugs [1]Cl and [2](PF_6) will be described. In these complexes the tetrapyridyl biqbpy ligand (6,6'-bis[N-(isoquinolyl)-1-amino]-2,2'-bipyridine) coordinates in the basal plane of the metal center, leaving two *trans* coordination sites for the binding of monodentate sulfur-based ligands. Due to the distortion of the coordination sphere these *trans* ligands are photosubstituted by water upon visible light irradiation in aqueous solution. *In vitro* cytotoxicity data on A431 and A549 cancer cell lines shows a 20-fold increased cytotoxicity after green light irradiation (520 nm, 75 J.cm^{-2}), compared to the dark control. Optical microscopy cell imaging and fluorescence-activated-cell-sorting indicate that the cancer cells die *via* apoptosis, while low to very low singlet oxygen quantum yields (1.3-2.3%) conclude that light-induced cell death is not caused by singlet oxygen generation).

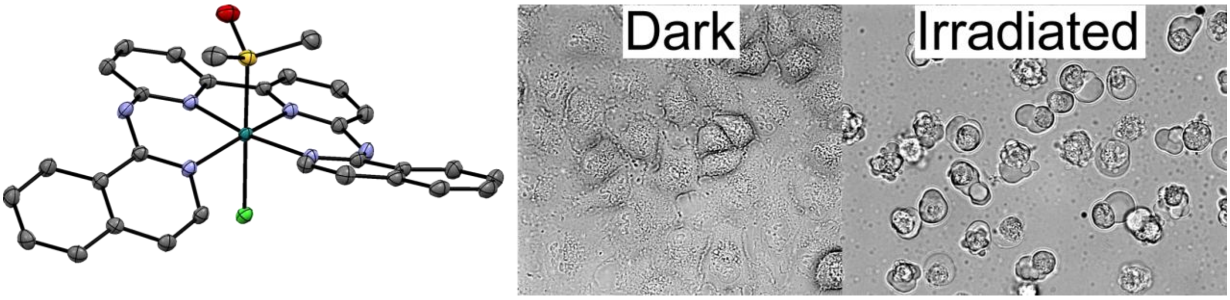

Figure 1 Left: X-ray structure of compound [1]Cl. Middle and right: Bright field microscopic images (40× magnification) of A549 cells treated with [1]Cl (1.5 μM) for 6+1 h in the dark (middle), and for 6 h in the dark, followed by 1 h green light irradiation (520 nm, 75 J.cm^{-2}, right).

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Novel Metal-Containing Reagents for Single-Cell Imaging by Mass Cytometry

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Imaging mass cytometry (IMC) is a new technology that simultaneously detects multiple biomarkers on a histological section with single-cell spatial resolution. IMC combines laser ablation of single cells within tissue sections with the mass cytometry platform[1]. Tissue imaging typically uses microscopy, where much of the information is qualitative; the technique faces limitations in the number of targets that can be visualized simultaneously. IMC is projected to enable quantitative measurement of multiple analytes. IMC uses FFPE or cryosections stained with a cocktail of more than 40 biomarkers detected with metal-tag antibodies and other metal-containing reagents, for example Ruthenium Red for mucinous stroma, Trichroma stain for collagen fibers, iodine in IdU for S-phase cell cycle, Rh-intercalator bound to dead cells in cell smear samples, Indium within a lipophilic complex for cell membrane staining. To carry out multiplexed immunoassays by mass cytometry, we developed metal-chelating polymer (MCPs) as antibody-tagging reagents.[2] The immunostained and dried samples are inserted into an ablation chamber where a small-spot-size pulsed laser scans the tissue. Metal isotopes associated with each spot are measured and indexed against the source location, yielding an intensity map of the target proteins throughout the tissue or the region of interest. We will validate the application of this advanced technology to human tissues and cells cultured or affixed to glass slides to investigate the highly multiparametric biomarker expression. We will show as well the intrinsic distribution of elements present in cells within tissues treated with chemotherapy drugs (cisplatin), hormones (iodine), and histological stains used to identify stroma (collagen, mucin, etc). Imaging mass cytometry enables single-cell heterogeneity and functional studies in complex tissue sections and cultured cells.

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Bridging the optimization of two-photon lanthanide luminescent complexes and functional bio-imaging

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Lanthanide ions exhibit peculiar photophysical properties that stem from their 4*f* electrons, thus attracting substantial attention in the development of luminescent bioprobes. The advantages of their sharp and characteristic emissions, as well as their long luminescence lifetimes, enable various applications in bio-imaging.[1]

Our group has designed and characterized several luminescent Ln^{3+} complexes, which optimized luminescence is sensitized by two-photon antennae.[2-4] From the elaboration of such bioprobes, taking a further step towards application in biological conditions is a necessary endeavour. In this contribution, we will discuss the modulation of cell internalization by changing the charge of the complex, thanks to modifications of the macrocyclic platform. On the other hand, in addition to the light-collecting role of the antenna, this moiety can be sensitive to the environment, and an example of two-photon functional imaging will be shown.

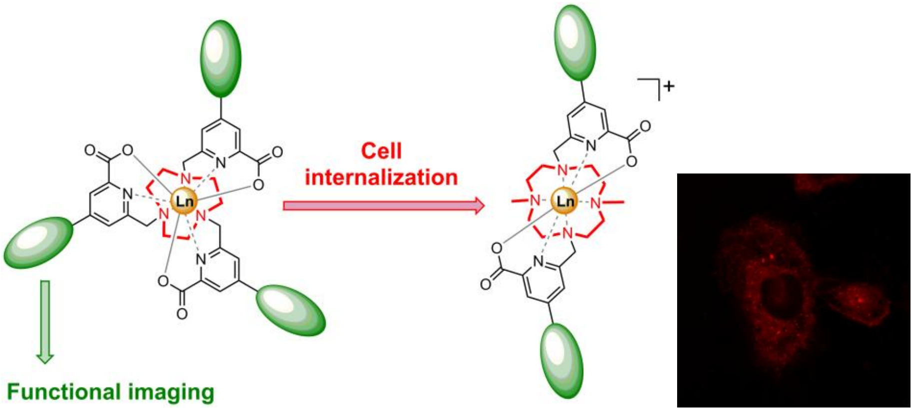

Figure 1 Schematic representation of discussed strategies for the development of Ln^{3+} bioprobes.

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Mn(II) complexes as molecular probes for MR imaging

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The high spin Mn(II) aqua ion is a potent nuclear relaxation agent that rivals Gd(III) in its ability to shorten the T_1 relaxation time of solvent water. For in vivo applications, the Mn(II) ion must be chelated to limit the exposure of the potentially toxic Mn(II) ion. However, the development of stable Mn(II) probes is challenging. High spin Mn(II) has no ligand field stabilization energy to reduce metal ion lability, and Mn(II) is at the low end of the Irving-Williams series with respect to thermodynamic stability. For MR applications, an inner-sphere water ligand is required and this results in sacrificing a donor group in the multidentate ligand designed to chelate the Mn ion.

The ability to access other oxidation states like Mn(III) offers the opportunity to develop molecular probes sensitive to the local redox environment. For instance Mn(III) is generally a poorer relaxation agent than Mn(II) and reduction results in a “turn-on” of the MR signal. Development of redox-sensitive Mn probes must overcome several coordination chemistry challenges. The multidentate ligand must stabilize both oxidation states, the redox process should be reversible and biologically accessible, and the Mn(II) complex should possess a water co-ligand. Here we describe our efforts in the design, synthesis, characaterization, and application of Mn probes for MR imaging.

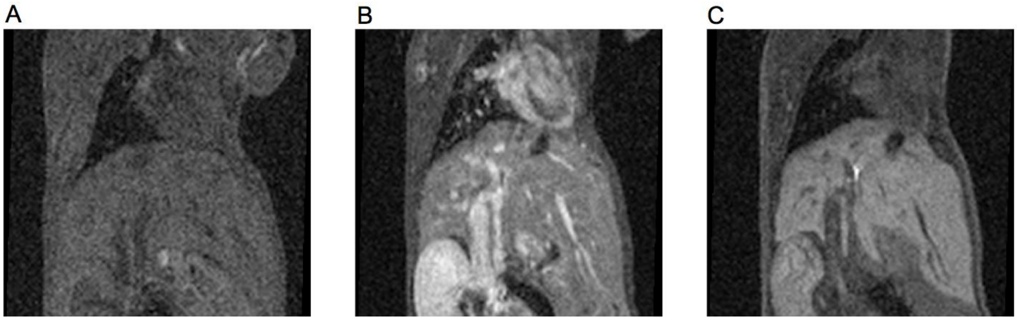

Figure. Coronal T_1-weighted MR images of a balb/C mouse acquired prior to (A), 3 min (B), and 25 min (C) following i.v. administration of 60 µmol/kg Na[Mn(PyC3A)(H_2O)] showing strong enhancement of the blood, liver, and kidneys that clears with time.[1]

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"Gold-finger" domains formation: implications for the use of gold compounds in therapy

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Gold-based compounds have raised attention in recent years as new promising experimental anticancer agents.[1] Among the possible pharmacological targets for cytotoxic gold complexes, zinc finger (ZF) proteins occupy an important place, being involved in a wide range of functions in DNA repairing, recognition, transcription, replication, apoptosis and metabolism. All of these processes are essential for cell growth and development, having direct implications in health and disease. Therefore, ZFs are frequently recognized as possible medicinal targets.[2]

Determining the structural changes induced by the substitution of Zn^{2+} ions with Au^{+}/Au^{3+} ions in ZFs, and correlating them to possible inhibition properties is fundamental to the understanding of the mechanism of action of gold-based cytotoxic agents at a molecular level. Thus, we investigated the reactivity of gold complexes with different ZF domains via different techniques, including high-resolution mass spectrometry, UV-vis absorption spectroscopy and quantum mechanics/molecular mechanics among others.[3,4]

The obtained results support a model whereby displacement of zinc from the ZF peptide by gold ions leads to decreased protein activity, and to formation of the so-called ''gold-finger'' (GF) domain. The influence of both the gold oxidation state and the ZF coordination sphere in GF formation provided useful insights into the possible design of new gold complexes targeting specific ZF motifs.

Financial support by EU COST Action CM1105 is gratefully acknowledged.

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Curcumin-based gallium-68 radiotracers for early diagnosis of Alzheimer's Disease.

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The accumulation of amyloid-beta (Aβ) aggregates as soluble oligomers and senile plaques in brain are key landmarks for Alzheimer's disease (AD) and their presence can be exploited as a selective target for diagnostic and therapeutic drugs[1]. Recently, several studies revealed that curcumin has high affinity for Aβ-amyloid plaques *in vitro* and *in vivo* and anti-AD properties due to its ability to bind and subsequently disrupt the aggregation of amyloid peptide and fibrils. Therefore, radio-labelled curcumin derivatives could be potential biomarkers for imaging of Alzheimer's disease by means of nuclear medicine imaging techniques. In this study, new curcuminoids are used as chelating agents to bind radiometals suitable for nuclear medicine applications. If compared with fluorine-18 and technectium-99m, gallium-68 exhibits advantageous features, being a generator produced positron emitter radionuclide with characteristics suitable for diagnostic nuclear medicine and direct labelling of biomolecules (89% β^+, maximum energy = 1.92 MeV; $T_{1/2}$ = 67.7 min), hence it was selected to label curcumin derivatives. Our aim is to investigate the biological properties *in vitro* of $^{nat/68}$Ga-curcuminoids complexes exploiting both the intrinsic fluorescence of these derivatives and the radioactive properties of gallium-68. The results will give insight into the possibility to employ these compounds as radiotracer for monitoring the presence of Aβ-amyloid plaques *in vivo* by positron emission tomography.

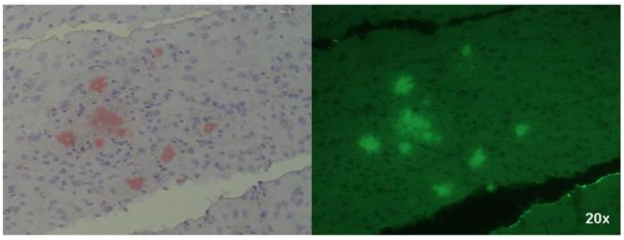

Figure 1. Micrographs of hippocampal sections showing Aβ-amyloid plaques stained with Ga-curcuminoids complexes (right panel) and Congo-Red (left panel).

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Cobalt picolinamide complexes as potential anti-cancer agents

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Cobalt complexes have recently shown great promise as anti-cancer agents with cobalt(III) nitrogen mustard complexes[1] and Co-ASS[2] (a dicobalt hexacarbonyl aspirin derivative). Much of this interest stems from the easily accessible oxidation states. Due to the reducing nature of hypoxic cancer cells, a drug can be administered in the cobalt(III) form and potentially reduced *in vivo* to a more potent cobalt(II) analogue.[1, 3]

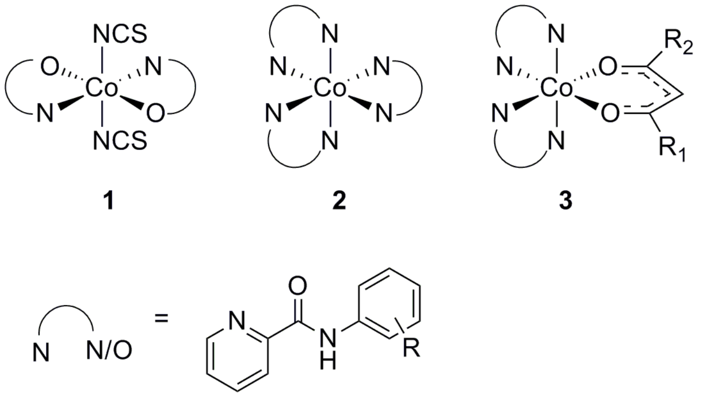

Figure 1 Cobalt picolinamide complex classes

This project is concerned with the synthesis and characterisation of a series of novel *N*,*N*- and *N*,*O*- cobalt(III) and cobalt (II) compounds (Figure 1). The project is based on previous work carried out within the McGowan group, in which a range of hypoxia sensitive ruthenium(II) arene complexes were prepared.[4] Three classes of compounds have been prepared: *bis*-picolinamide cobalt(II) complexes (**1**), *tris*-picolinamide cobalt(III) complexes (**2**) and mixed ligand cobalt(III) complexes (**3**). The data presented will include cell cytotoxicity studies against a range of cancer cell lines with comparison to a non-cancerous cell line, under both normoxic and hypoxic conditions. Hydrolysis and hydrophobicity studies will also be discussed.

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DNA-binding ruthenium(II) polypyridyl complexes for targeted cancer therapy

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Molecular targeted therapy employing cytostatic agents aims to inhibit the growth and spread of cancer by modulating molecular components specific to cancer cells.[1] Kinetically inert ruthenium(II) polypyridyl complexes are an emerging class of dual imaging/therapeutic agent and several systems demonstrate reasonable *in vitro* anti-cancer activity in addition to their DNA imaging properties.[2] Important in the development of these systems towards biomedical application is mechanistic understanding in cell line models, including biological pathway activation and regulation. We will describe the isolation and development of several candidates, discussing how anti-cancer activity may be influenced by chemical attributes and DNA binding modes. Examples include VR54, a cytostatic Ru(II)-Pt(II) bis(terpyridyl) derivative which inhibits cell growth in cisplatin-resistant ovarian cancer by up-regulating the cyclin-dependent kinase inhibitor p27KIP1 via a DNA-damage independent pathway (Fig. 1).[3] Results will be placed in context of achieving specific cancer cell-targeting and compatibility with existing clinical regimens.

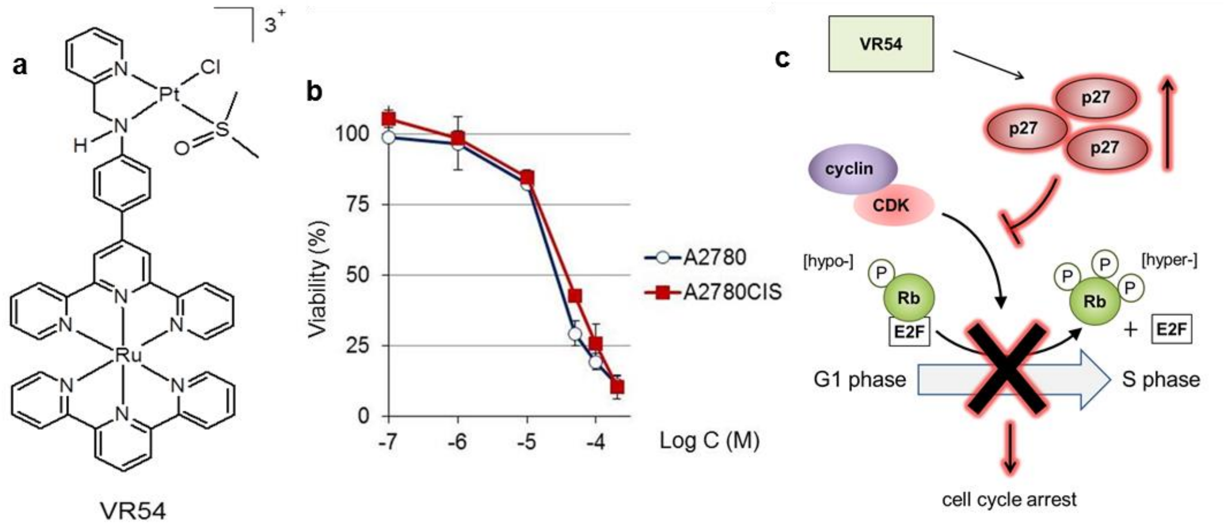

Figure 1 VR54 (a), impact on ovarian cancer cell proliferation (b) and mechanism of action in cisplatin-resistant A2780CIS ovarian cancer cells (c).

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How Zn can impede Cu detoxification by chelating agents in Alzheimer's Disease: a proof-of-concept study

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The aetiology of Alzheimer's disease is linked to the aggregation of the amyloid-β (Aβ) peptide, a central event of the so-called amyloid cascade. The intervention of Cu and Zn ions in the amyloid cascade is widely acknowledged and directly linked to the consequences of their coordination to the Aβ peptide, i.e. to the modulation of the Aβ aggregation and to the production of Reactive Oxygen Species (ROS). This will be first described and commented on.[1] The role of both ions in the Aβ aggregation process is still controversial. Conversely the higher toxicity of the redox competent Cu ions (compared to the redox inert Zn ions) in ROS production is acknowledged.[2] Thus the Cu ions can be considered as the therapeutic target. Because Zn ions are present in higher quantity than Cu ions in the synaptic cleft, they can interfere and even preclude detoxification of Cu by chelators unless they have an unusually high Cu over Zn selectivity. Here, we describe a proof-of-concept study where the role of Zn on the metal swap reaction between two prototypical ligands and the Cu(Aβ) species has been probed using XANES, EPR and UV-Vis. How Zn impacts the effect of the ligands on ROS production by Cu(Aβ) and on Cu-modulated Aβ aggregation will also be shown.[3]

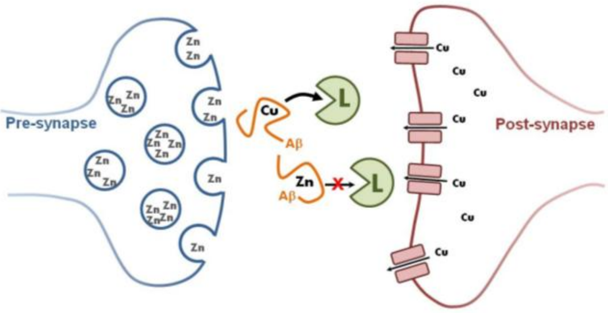

Figure 1. Scheme of the PoC study.

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Bifunctional systems for MRI detection and two-photon PDT

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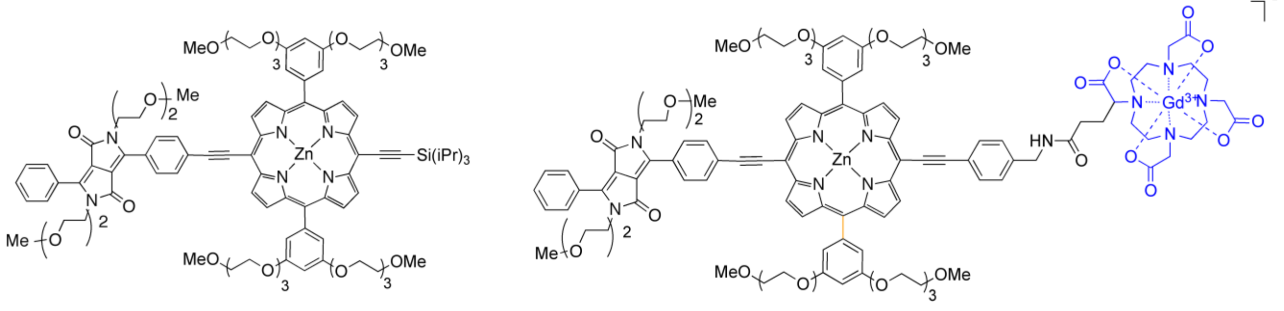
The design of non invasive theranostic agents based on bifunctional molecular systems gathering components able to diagnose, to cure and to follow the therapy outcome is a challenge in the development of personalized treatment.[1] Combining two-photon absorbing photosensitizer for photodynamic therapy [2] (PDT) with contrast agent for magnetic resonance imaging [3] (MRI) should increase the potential of applications of PDT with a better localization of the drug, a higher spatial control and an increase in the depth of the treatment.[4] We have developed new photosensitizers absorbing in the near infrared with high two-photon cross sections. The **DPP-ZnP** conjugate (Figure 1a) demonstrated high phototoxicity in cancer cells and is a promising sensitizer for two-photon PDT. [5]



DPP-ZnP **DPP-ZnP-GdDOTA$^-$**

Figure 1. (a) A dicetopyrrolopyrrole-porphyrin conjugate as two-photon sensitizer for PDT (b) a bifunctional agent for theranostic applications.

For theranostic applications, a molecular system consisting of a **DPP-ZnP** photosensitizer associated to a **GdDOTA$^-$** complex as MRI probe was synthesized and its physicochemical properties and in cell studies will be discussed (Figure 1b).[6]

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Paramagnetic complexes of macrocyclic ligands as contrast agents for ^{19}F MRI

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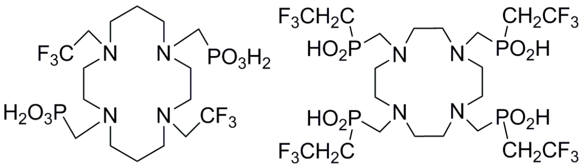
The ^{19}F MRI is very attractive imaging modality as there is no fluorine present in body and, thus, ^{19}F presence is seen as a "hot spot" and can be used in responsive MRI probes, to trace drug delivery or label cells, etc.[1] To improve sensitivity, a number of ^{19}F nuclei should be high and a rather long ^{19}F T_1-relaxation time should be shortened. This relaxation enhancement can be achieved with paramagnetic metal ions as Ln(III) [2,3] or transition metal ions which have not been used in contrast agents for ^{19}F MRI till now.

Here for the first time, it will be shown that transition metal complexes of cyclams modified with CH_2CF_3 groups (e.g. in Figure 1) surprisingly produce ^{19}F NMR signals exhibiting suitable relaxation times.[4] The short NMR T_1-relaxation (~100-times shorter in complexes than in the free ligands) with NMR T^*_2/T_1 relaxation times ratio enables fast MRI acquisition leading to a better image quality. Due to coordinating pendants, the complexes are, surprisingly, reasonably kinetically inert to be used *in vivo*. A number of ^{19}F nuclei in Ln(III) complexes of a cyclen derivative (Figure 1) is high and only one ^{19}F NMR signal is observed. Their ^{19}F NMR T_1-relaxations and chemical shifts can be tuned by Ln(III) ions. It leads to "colour" MRI images according to the Ln(III) ion used. As other Ln(III) complexes of DOTA-like ligands, they are thermodynamically and kinetically stable; it leads to a high *in vivo* stability. The first *in vivo* results will be presented.

Figure 1 Ligand examples



Support by the Grant Agency of the Czech Republic is gratefully acknowledged.

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Bioinspired Mononuclear Nonheme Iron Complexes for Detection of Hydrogen Peroxide inside Living Cells

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Hydrogen peroxide is produced as an oxidative stress or signaling molecule [1]. To elucidate the distinct roles of hydrogen peroxide, various types of small molecular probes have been developed to specifically visualize hydrogen peroxide in living systems [2,3]. A number of hydrogen peroxide probes with unique hydrogen peroxide -responsive components have been reported, but very few can be applied to live cell imaging. You and Nam and co-workers described the intracellular hydrogen peroxide imaging using a fluorescent probe bearing two mononuclear nonheme iron centers [4]. Metal-complex-based hydrogen peroxide fluorescent probes are characterized by rapid responses to hydrogen peroxide, when compared with other probes having organic molecules-based responsive components. We have developed three iron-complexes as fluorescent probes for H_2O_2: MBFh1 [5], MBFh2 [6], and MBFh3 [7] (Figure 1). The former two probes release the red-emitting fluorophore resorufin within seconds upon addition of hydrogen peroxide. This rapid response to hydrogen peroxide is an advantage of using a metal complex as the reactive site for hydrogen peroxide, because it generally takes longer to turn on fluorescence with conventional nonmetal-based hydrogen peroxide probes. Moreover, MBFh2 is applicable for intracellular imaging of not only exogenous hydrogen peroxide but also hydrogen peroxide endogenously produced by growth factor stimulation.

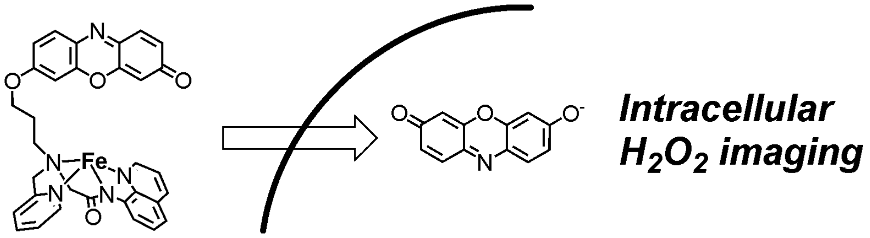

Figure 1 Detection of intracellular hydrogen peroxide by MBFh2.

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Are we getting closer to the Mn(II)-MRI Contrast Agents?

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Over the past decades, research and development of novel Magnetic Resonance Imaging (MRI) contrast agents produces structurally diverse ligands and complexes with a variety of metals. Although the majority of approved MRI contrast agents are still based on gadolinium complexes, manganese has gained certain attention due to its ability to form high spin complexes with five unpaired electrons. An appropriate ligand would form a redox- and thermodynamically stabile, kinetically inert Mn^{2+} complex with high relaxivity. All of these, often contradictory, requirements are needed for in vivo applications. Mn is an essential trace element in the human body with likely less toxic effect compared to the highly toxic Gd, however the knowledge collected for gadolinium based CAs can not be directly translated to Mn^{2+}. Our attempt to find a suitable ligand for Mn^{2+} complexation started from equilibrium, kinetic and relaxometric characterization of Mn^{2+} complexes with known open-chain (OCh)[1] and macrocyclic (MC) amino-polycarboxylates in order to collect data for structure – function relations, than we synthesized some new ligands. One of the key finding is, that the kinetic inertness of the Mn^{2+} complexes plays very important role. Suitable structural changes to increase the inertness involve the rigidifying of the ligand backbone, or the pendant arms, changing the protonation properties and charge of the ligands etc., exemplified on Figure 1.

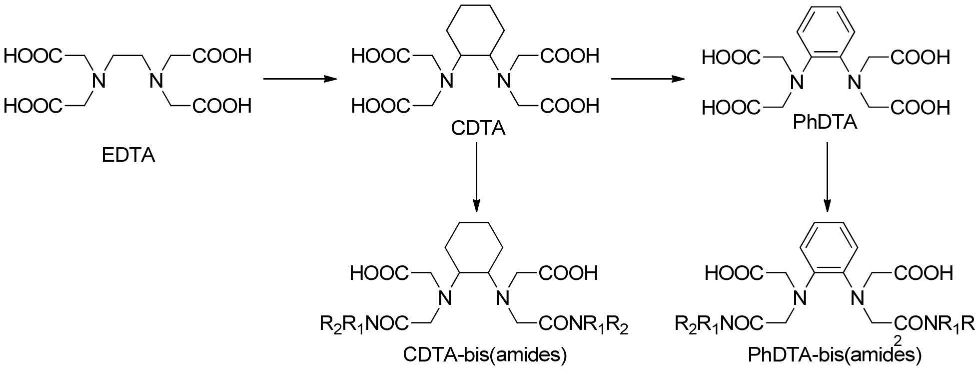

Figure 1. Open-chain ligands for complexation of Mn^{2+}

The authors thank the Hungarian OTKA (K-84291 and K-109029) for financial support.

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Luminescent Rhenium(I), Ruthenium(II), and Iridium(III) Complexes as Intracellular Sensors, Cytotoxic Agents, and Bioorthogonal Probes

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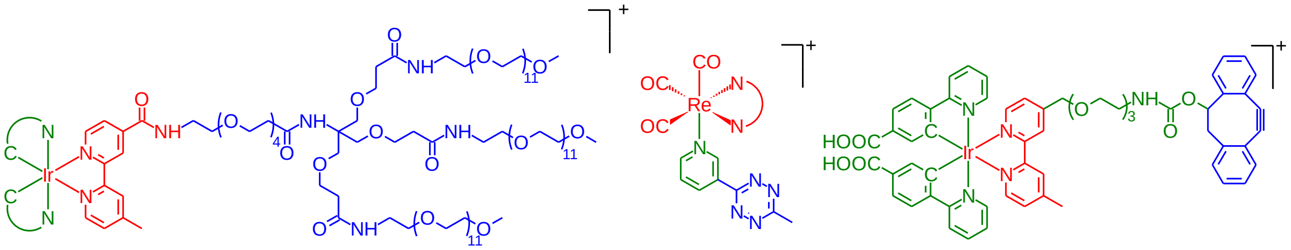
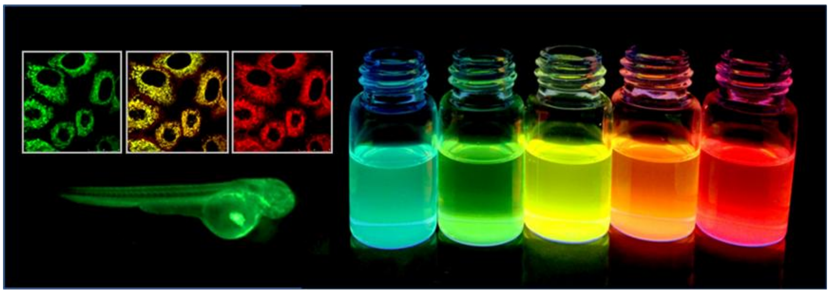
The covalent and noncovalent interactions of transition metal complexes with biomolecules have been of long-standing interest. In the past few years, there is an emerging area of research that focuses on the use of luminescent transition metal complexes as intracellular sensors and bioimaging reagents. This interest is mainly attributed to the highly environment-sensitive and long-lived phosphorescence of luminescent transition metal complexes. In particular, the interesting luminescence properties of rhenium(I), ruthenium(II), and iridium(III) complexes have prompted us to develop new cellular reagents. In this presentation, we will describe our design of these complexes as intracellular sensors for small molecules, photofunctional cytotoxic agents, and phosphorogenic bioorthogonal probes. We will focus on the photophysical properties, cytotoxic activity, cellular uptake behavior, and intracellular functions of these complexes.





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Zinc responsive MR Contrast Agents for in vivo imaging

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Zn(II) is an essential mineral in the organism, responsible for the secretory function of several tissues including the pancreas, mammary glands, and prostate (1). The healthy human prostate has been reported to have the highest levels of free zinc while malignant prostate cells undergo a metabolic transformation that results in a reduced accumulation of Zn(II). Here, we report several gadolinium-based contrast agents capable of detecting free Zn(II) ions by MRI at physiological concentrations. In the absence of Zn(II), GdDOTA-BPEN derivatives have little to no affinity for albumin but after binding to 1 equivalent of free Zn(II), the resulting complexes then bind to human serum albumin (HSA) which in turn results in an increase in r_1 relaxivity as high as 57 mM^{-1}s^{-1} (860% increase) (2). The rate of water exchange was optimized and analyzed by NMR in a series of BPEN derivatives by introduction of different functional groups as spacers (phosphinate groups, extra methylene carbons, piperazine units, one single BPEN arm) and interesting binding properties were observed for the new derivatives. Depending on the individual structure, these new agents demonstrate significantly improved longitudinal relaxivities (r_1) and exhibit highly sensitive MRI detection of Zn(II) and nicely enhance the mouse prostate *in vivo* by MRI only after co-injection of glucose, similar to that observed previously for the pancreas. These results demonstrate that it is possible to design and optimize functional MRI contrast agents that respond to alterations of important biological ions *in vivo* at an acceptable dose relevant for translation to human imaging.

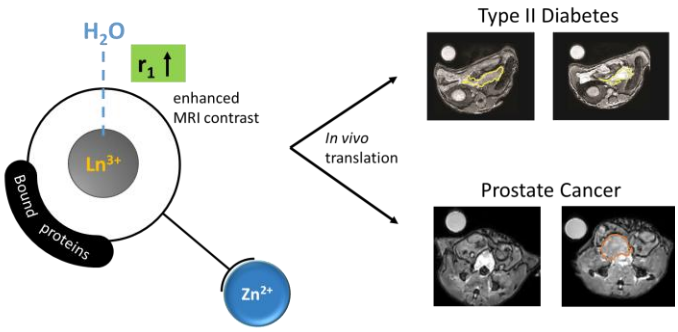

Figure 1 Illustration of a zinc responsive gadolinium based responsive agent translated in high quality MR images *in vivo* (pancreas and prostate).

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2 J. Yu, A.F. Martins et al.**,** *JACS*, **2015**, *137*, 14173

Coordination Polymer Particles as Contrast Agents for Medical Imaging

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In this study, we propose new nanomaterials based on coordination polymers[1] that can integrate different contrast agents for medical imaging such as fluorescent probes, or contrast agents for MRI. These preliminary studies are aimed to explore the possibilities of the coordination polymer particles (CPPs) to be used as multifunctional, robust and biocompatible contrast agents to be used in different imaging techniques [2]. The nanoconstructs consist on iron, zinc, manganese or gadolinium based CPPs that can exhibit fluorescence or can act as T1/T2 contrast agent for MRI. The integration of different contrast agent in the same nanoparticles would afford multifunctional contract agents for using in different imaging techniques.

The results of these studies indicate the easy, low cost and reproducible synthesis of different CPPs with potential use as contrast agents in diverse medical imaging techniques. The integration of different contrast agents in the same nanoparticles, their low toxicity, and stability in physiological media allow to design multifunctional nanoprobes with potential use for medical imaging. The properties and versatility of novel coordination polymer nanoparticles opens a wide range of possibilities for these multifunctional nanoconstructs to be used as contrast agents and for imaging-guide drug delivery.

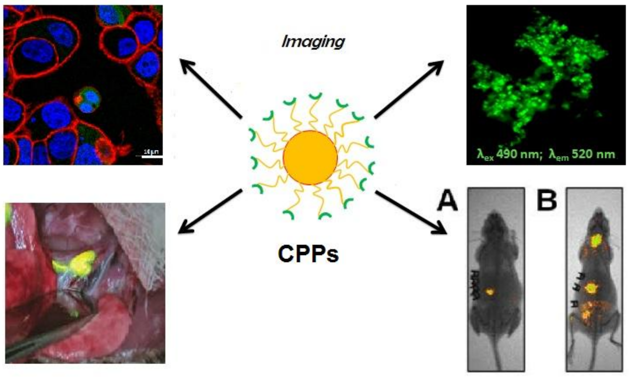

Figure 1 The multifunctionality and versatility of CPPs open a wide range of applications for medical imaging in vitro and in vivo.

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Elaborating the “pa” Ligand Family for Radiopharmaceutical Applications

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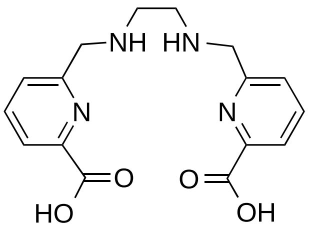
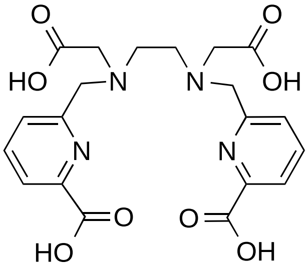
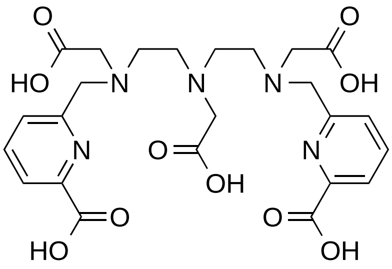
In radiopharmaceutical research, significant research effort has led to bifunctional chelates of the aminocarboxylate macrocycles NOTA or DOTA for the isotopes $^{66,67,68}Ga$; NOTA and DOTA have become the “gold standard”. We report our findings concerning the di- and triamine picolinic acid N_xO_y chelating ligands H_2dedpa, H_4octapa, H_5decapa and related analogues for application with a wide variety of radiometal ions useful for imaging, diagnosis and therapy. For instance, bifunctional versions of H_2dedpa all label ^{67}Ga at RT within 10 minutes. The stabilities of these building blocks and their modular family of easily accessible ligands are comparable to, or higher than, that of DOTA; the “pa” family of ligands is under intense current investigation, as are the biodistribution profiles of these platform chelate candidates, with a variety of radiometal ions (e.g. $^{64}Cu^{2+}$, $^{111}In^{3+}$, $^{89}Zr^{4+}$, $^{86,90}Y^{3+}$, $^{177}Lu^{3+}$) in a variety of applications (such as labelling of hypoxia and tumours).



H_2dedpa



H_4octapa



H_5decapa

Hexadentate Bis(thiosemicarbazones) for Radiolabeling Biomolecules with ^{99m}Tc and ^{188}Re

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Molecular imaging with metallic radionuclides is mainly achieved with the use of bifunctional chelators (BFCs) that couple the radiometal indirectly to a biologically-active targeting molecule. Although technetium-99m (^{99m}Tc) radiopharmaceuticals are the most frequently used radioactive tracers in medical diagnostic procedures, the development of new ^{99m}Tc BFCs, suitable for use with sensitive biologically active molecules such as antibodies, is still required. In addition, rhenium-188 (^{188}Re), an emitter of high-energy β^- particles that can be used for radiotherapy, shares important similarities with the coordination chemistry of technetium, leading to the potential for imaging and therapy 'matched pairs'. A hexadentate bis(thiosemicarbazonato) complex [Re(**L^1**)]$^+$ (Fig 1a) is a rare example of a distorted trigonal prismatic Re(V) complex.[1] We now report the synthesis and characterization of the ^{99m}Tc(V) and ^{99}Tc(V) (Fig 1b) bis(thiosemicarbazonato) complexes. Radiolabeling was fast (< 30 min) and easily performed under mild conditions suitable for use in the presence of antibodies and peptides.

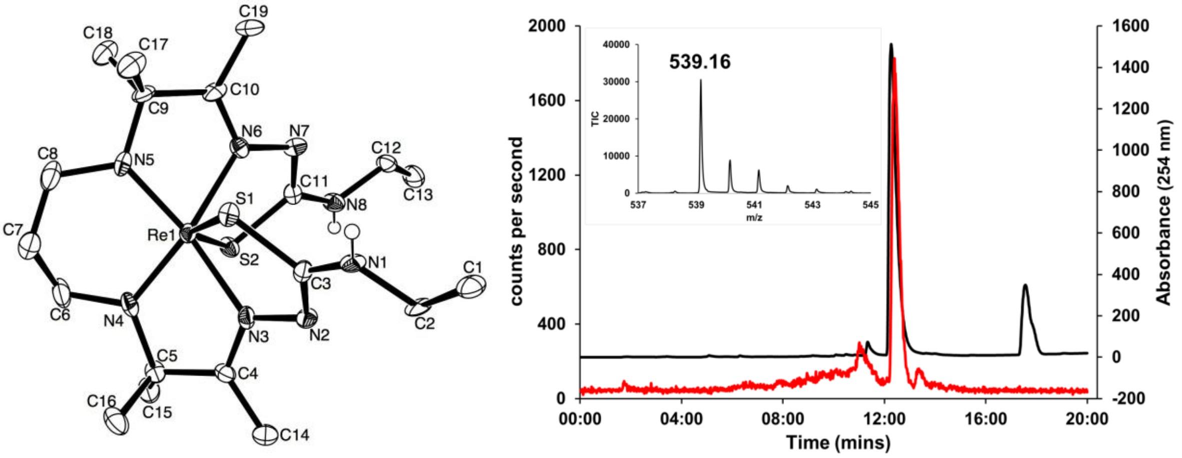

Figure 1 (a) X-ray crystal structure of [Re(**L^1**)]$^+$ and **(b)** RP-HPLC chromatograms of [^{99m}Tc(**L^1**)]$^+$ (red, R_T = 12:24 min), [Re(**L^1**)]$^+$ (black, R_T = 12:15 min) and $B(C_6H_5)_4^-$ (black, R_T = 17:24 min). Inset: mass spectrum of [^{99}Tc(**L^1**)]$^+$.

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Coiled coils as new ligands for lanthanide ions – exploring their use in MRI and beyond…

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De novo designed miniature protein scaffolds, such as the coiled coil, offer exciting opportunities for metal ion coordination.[1] Not surprisingly due to the protein like nature of the scaffold, the large majority of *de novo* metallocoiled coil examples have focussed their efforts on mimicking the active sites of native metalloenzymes. Our approach is to instead to use these artificial proteins as novel ligands for the coordination of xeno metals, with no known biological role, with the view to developing functional systems for valuable applications beyond the scope of nature.

We recently reported the design of the first gadolinium coiled coil, which displayed promise as a potential MRI contrast agent, despite no evidence of inner sphere water (see Figure 1).[2] We have since interrogated the coordination of various lanthanide ions to different coiled coil designs, and demonstrate for the first time the profound impact binding site location can have on lanthanide coordination chemistry and in turn MRI relaxivity. Recent results will be reported, and include studies into the impact of coiled coil length (and thereby the complexes tumbling rate) on MRI relaxivity, as well as changes to its exterior and altered interaction with water molecules.

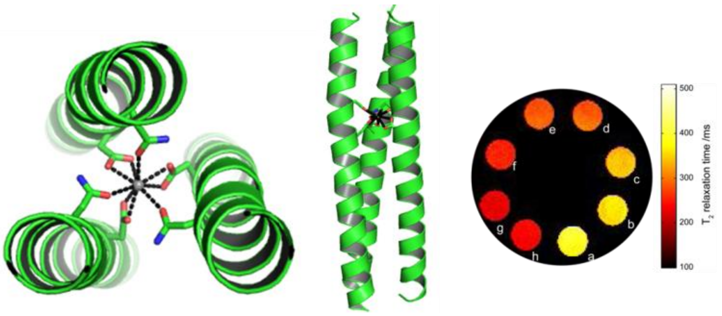

Figure 1 Designed first generation gadolinium coiled coil.[2]

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2 M. R. Berwick, D. J. Lewis, A. W. Jones, R. A. Parslow, T. R. Dafforn, H. J. Cooper, J. Wilkie, Z. Pikramenou, M. M. Britton, A. F. A. Peacock, *J. Am. Chem. Soc.*, **2014**, *136*, 1166.

Developing Ln Based Metallacrowns for Luminescent Imaging

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Lanthanide compounds possess fascinating luminescent properties that have led to numerous applications and technologies. Luminescent lanthanide-based molecular scaffolds hold great promise for applications in biological imaging as their unique photophysical properties allow for spectral and time discrimination of their emission bands, which range from visible to near infrared (NIR) regions. The synthetic challenge for lanthanide complexes is the employment of appropriate “antenna” chromophores to sensitize the whole series of lanthanide ions with high quantum yields. In this presentation both mixed Zn^{2+}/Ln^{3+} and mixed Ga^{3+}/Ln^{3+} metallacrown complexes are reported. These molecules are among the brightest Near IR luminescent agents and the Ga complexes provide a broad range of spectral colors. The work also describes the first example of quantitative NIR luminescence reported for a Dy^{3+} complex in solution and demonstrates the sensitization of less common NIR luminescent lanthanide ions (Tm^{3+} and Ho^{3+}) in the solid state. We will describe the interaction of some of these compounds with HeLa and mesenchymal cells, discuss the ability to stain and image cells simultaneously and distinguish necrotic cell death. We will also discuss how the molecules may be modified to enhance solubility, brightness and couple molecules for biological recognition.

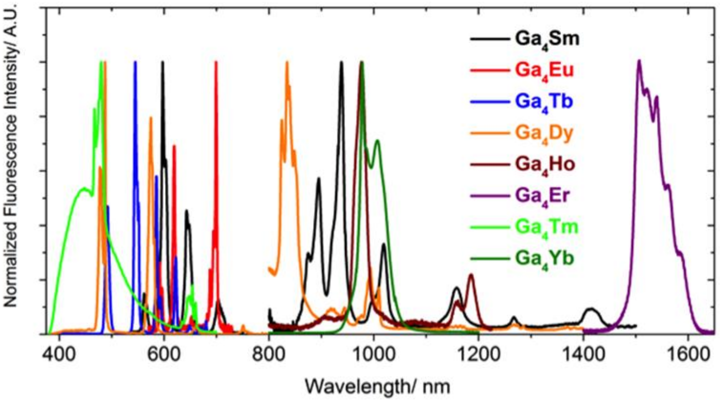

Figure 1 Solid State Emission Spectra for Ga_4Ln

Understanding Water Exchange Rates in Gd^{3+}-Based MRI Contrast Agents. Definition of the Labile Capping Bond Effect

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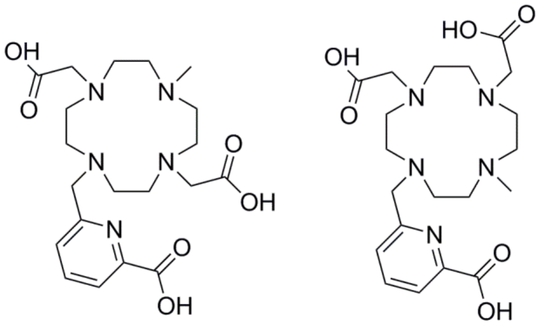
Complexes of trivalent lanthanide ions are of interest due to their application as contrast agents (CAs) in magnetic resonance imaging (MRI).[1] CAs are paramagnetic compounds, often Gd^{3+} complexes, which accelerate the relaxation rates of water molecules in the surrounding tissue. The most important factors that affect the efficiency of the CA are the rotation dynamics of the complex, the water exchange rate of the inner-sphere water molecule and the electron spin relaxation. Herein, we report two new cyclen-based ligands containing two acetate groups in either *cis* or*trans* position of the cyclen unit and a picolinate pendant arm (Figure 1). The different topology of the ligands results in Gd^{3+} complexes having a coordinated water molecule either occupying a position in one of the squares faces of the square antiprismatic coordination polyhedron (1,7-Medo2ampa), or capping that square face (1,4-Medo2ampa). We will show that this subtle structural change provokes a drastic effect in the exchange rate of the coordinated water molecule.



1,7-H_3Medo2ampa 1,4-H_3Medo2ampa

Figure 1 Ligands presented in this work.

[1] The Chemistry of Contrast Agents in Medical Magnetic Resonance Imaging (Eds: A. E. Merbach, L. Helm, E. Tóth), Second Edition, Wiley, New York, **2013**.

Insight Into Aluminium-based Immune-Potentiators and Vaccine Formulations

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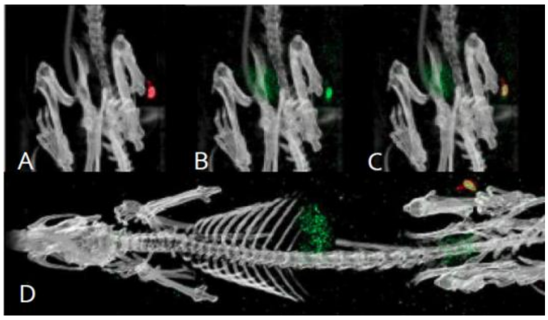
Knowing more about one of the world's oldest adjuvants can help in the design of next-generation immune-potentiators and vaccine formulation strategies. Alum is a broad term that encompasses aluminum-containing vaccine adjuvants, such as aluminum oxyhydroxide (AlO(OH)). Commercially known as Alhydrogel®, this adjuvant consists of 1-12 µm aggregated clusters of nanoparticles. Alum adjuvants enhance antibody-mediated immune responses in a Th2-dependent manner and have an extensive safety record. Many human vaccines, such as HAVARIX® against hepatitis A, include alum. Despite being used clinically since the 1930s, the biodistribution of AlO(OH) is poorly understood and there is evidence to suggest that the long-standing theory that this adjuvant remains at the site of injection is incorrect. In order to investigate if the nanoparticles distribute to distant sites following injection, a novel traceable form of AlO(OH) was synthesized by doping the adjuvant with different metal ions (Ga, In, Ln). Various characterizations including PXRD ensured the new structure matched the commercial Alhydrogel®. InAlO(OH) was used to assess the cellular distribution of alum in the draining lymph node over time using mass cytometry by time of flight (CyTOF). Our first pilot imaging scan showed the drainage of ovalbumin (OVA, antigen) was slowed when adsorbed to Alhydrogel® and injected subcutaneously; these scans confirmed also that the adjuvant forms an antigen depot at the site of injection. The Figure shows SPECT/CT images of OVA adsorbed on AlO(OH). The distribution of radiolabeled AlO(OH) is shown in red (A), radioactive OVA in green (B) and the merged signal in (C-D). Our recent study investigates the biodistribution in a mouse model by quantitative serial dual isotope SPECT/CT imaging over a period of 2 weeks with ^{111}In-AlO(OH) adjuvant and ^{67}Ga-OVA antigen. These results show that AlO(OH) moves from the site of injection and drain through the lymph nodes. The mechanism of action and side effect profile of the adjuvant are currently undergoing further investigation. Complete results will be presented.



Metal-Ligand Complex-Based Nanomaterials for Multifunctional Biological Imaging

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Bárbara Rodríguez,[d] José-Ramón Galán-Mascarós,[d,e] and Harry B. Gray[c]

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Over the past few decades, molecular imaging (MI) has become central to today's medical diagnosis and disease intervention through the advancement of modern technologies in science, engineering, and medicine. MI also plays a crucial role in non-clinical and pre-clinical settings, namely, drug development as well as research in disease mechanisms and pathways. Magnetic resonance (MR), X-ray computed tomography (CT), nuclear, fluorescence optical, and ultrasound imaging techniques are among the most common approaches used in biomedical research. As a result, chemical development of MI probes appropriate for multiple imaging modalities is of essence to modern healthcare.

Here, we present our work on two families of inorganic nanomaterials (Figure 1), namely, conjugated metal oxide nanoparticles (MONPs)[1,2] and nanoscale hexacyanometallate coordination polymers or Prussian blue analogs (PBAs), developed for MI as potential multimodal and multifunctional platforms. These biocompatible nanoscale materials based on metal-ligand coordination complexes have been studied by optical, micro-CT, and MR imaging techniques in our laboratories. The results revealed that selected MONPs and PBAs are promising candidates as probes for dual modality, including optical/CT and CT/MR imaging. Designs, syntheses, characterizations, and MI applications of these versatile coordination complex-based nanomaterials will be discussed in this presentation.

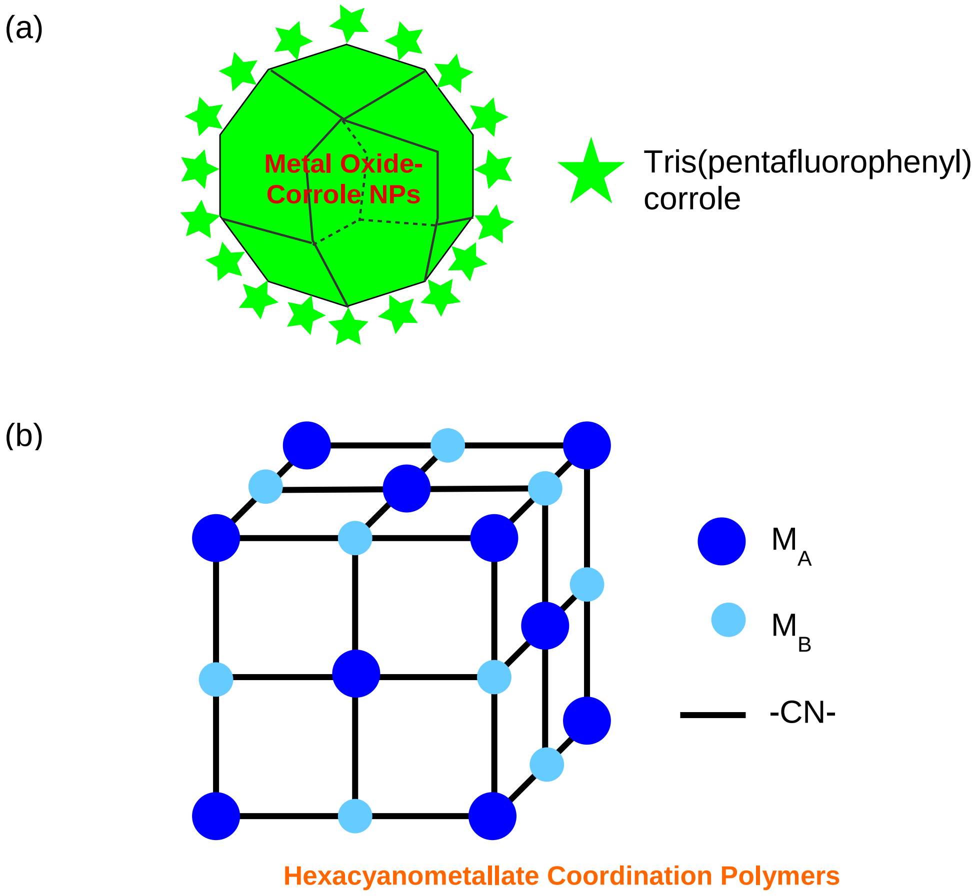

Figure 1 (a) Metal-oxide nanoconjugates (b) Prussian blue analogs

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Optical imaging using lanthanide centered emission, going beyond the visible spectrum

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Using optical imaging in biological research relies on the ability to identify the origin of the photons used to generate images. So far, this has been achieved almost exclusively by ensuring that the vast majority of photons originate from the dye(s) used to stain the sample. This is highly invasive. To follow natural processes a much lower concentration of dye has to be used. Thus, different means of identifying photons are needed. The narrow emission lines and distinct emission lifetimes of lanthanide centered emission may offer the tools needed to do so, se figure 1.[1] By combining kinetically stable complexes and the 'antenna principle' lanthanide based probes for optical imaging has seen huge advances the last decade.[2] In our work with NIR emitting lanthanide ions, we have developed two approaches[1] that work using simple and responsive lanthanide probes.[3] In this talk the coordination chemistry and photophysics of the lanthanide based probes will be covered, and the pitfalls of the imaging techniques will be detailed.

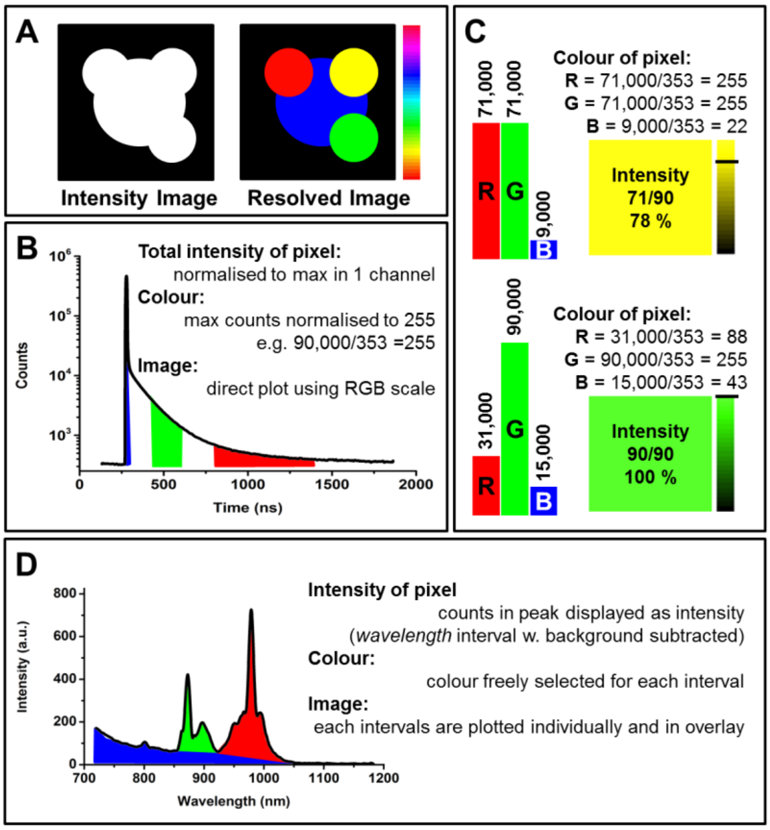

Figure 1 Optical imaging using lanthanide centred emission. **A** shows the difference between an intensity image and a resolved image, **B** shows how photon arrival time can be used to resolved an image, **C** shows the details, and **D** shows how an image is resolved using photon energy.

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[3] a) A. Watkis et al., *Chem. Comm.*, **2015**, *51*, 15633. b) T. J. Sørensen *et al., Chem. Sci.* **2015**, *6*, 2054.

Ligand rigidity as a key tool in design of kinetically inert Gd^{3+} complexes: open-chain and macrocyclic examples

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Gd^{3+} complexes formed with open-chain (OC) and macrocyclic (MC) ligands are widely used as contrast agents (CA's) in Magnetic Resonance Imaging (MRI). A rare but potentially fatal disease associated with the release of toxic Gd^{3+} from certain Gd^{3+}-based CA's in patients with insufficient renal function known as Nephrogenic Systemic Fibrosis (NSF) shook the ground under the CA's since early 2000's. As a result of administration guidelines the occurrence of NSF was believed to be eradicated since then. However, a shocking recent review of E. Kanal and M. F. Tweedle[1] that summarizes the findings of T. Kanda, Y. Errante, R. J. McDonald and A. Radbruch indicates that certain OC ligand based Contrast Agents (CA's) in MRI may cause problems for patients even with normal renal function. These results are raising new questions about the safety of Gd^{3+}-based CA's and trigger new research in order to design safer CA's for MRI. We believe that this can be achieved either by replacing the highly toxic Gd^{3+} ion with metal ions showing better toxicity profiles in vivo (Mn^{2+}, Fe^{2+}, etc.), or by improving the dissociation kinetic parameters of the Gd^{3+}-based CA's. The given talk intends to focus on the results of equilibrium and kinetic studies performed with Gd^{3+} complexes of two octadentate ligands CDDADPA and DOTMA. Our results indicate that the rates of acid catalyzed dissociation of the complexes can be tuned (1-3 orders of magnitude) by applying modifications either to the ligand backbone (CDDADPA) or at the side arm (DOTMA) of the chelator yielding ligands with very favorable features for further development of safer MRI contrast agents.

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Lanthanide Containing Liponanoparticles in Theranostic Approaches

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Liponanoparticles have gained an important place in drug delivery and biological imaging. In both imaging and drug delivery, the control of the in vivo integrity of the liponanoparticles and the monitoring of the release of the drug at the site of interest remains a challenge. Recently we have demonstrated that the integrity of liposomes or lipoproteins could be monitored by lanthanide-luminescence via sensitization by a non-covalently bound chromophore cargo in the particle. This strategy has been extended to the use of a drug molecule, incorporated into nanolipoparticles, as antenna for lanthanide luminescence which allows for monitoring of drug release by optical means.

Lanthanide containing liponanoparticles also revealed promising for application in photodynamic therapy (PDT). Micelles constituted of amphiphilic lanthanide complexes and hypericin (Hyp) as photosensitizer have been used to demonstrate the concept of X-ray triggered PDT. Lanthanide luminescence is induced by X-ray irradiation and excites the photosensitizer, which leads to the generation of singlet oxygen. This versatile approach can be extended to a variety of photosensitizers and liponanoparticles and can allow for simultaneous MRI guidance.

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A correlative approach for the imaging of a cell-penetrating peptide in skin slices

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Fluorescence microscopy is a well-spread and well-established technique to image labeled molecules in cells. This technique allows reaching high resolution (< 100 nm) and good signal-to-noise ratio. However, it also possesses drawbacks, such as photo-bleaching and low tissue penetration. On the contrary, infrared (IR) imaging techniques do not induce photo damage, can deeply penetrate tissues but the resolution is limited due to the Rayleigh criterion. We have recently shown that metal-carbonyl compounds ($M(CO)_n$) can be mapped inside cells using their IR-signature.[1,2] Interestingly $(L)M(CO)_n$ bearing specific ligands (L) are luminescent,[3] leading to a probe with two modalities called SCoMPI (Single Core Mutimodal Probe for Imaging).[4] We have demonstrated that such probes allowed performing correlative imaging at the cellular level, and we have implemented this approach at the tissues scale. We have labelled a cell penetrating peptide (CPP) with a $(L)M(CO)_n$ probe. After a 6-hour skin-permeation experiment, the labelled CPP was found mainly in the *stratum corneum* and was not detected in the deeper layers of the epidermis. After a 24-hour exposure, it was found by fluorescence microscopy and by synchrotron-based infrared microscopy in the whole epidermis and not detected in the dermis (Figure 1). These proof-of-principle experiments lead to promising results and highlighted the fact that SCoMPI are useful tools for tissues imaging by IR and fluorescence microscopies.

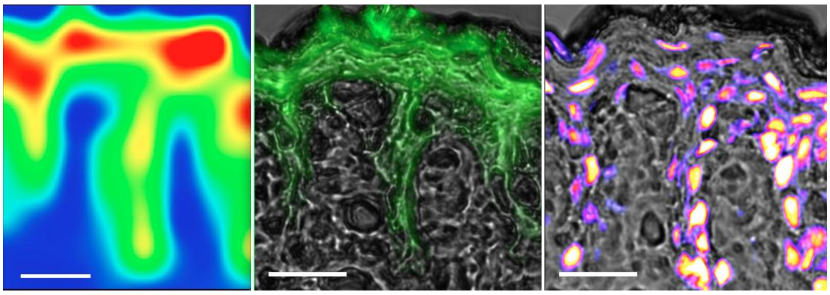

Figure 1. Skin slice after a 24-h exposure to a solution of the labelled CPP in water (0.02 M). ***Left***: mapping of the A_1-band (2040-2000 cm^{-1}). ***Middle***: bright field image merged with the luminescence signal of **1**. ***Right***: bright field image merged with the nuclei staining by DAPI that shows the limits of the epidermis. Scale bar 20 µm.

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Novel Cu(II) complexes; crystal structure, DNA/BSA interaction ability and cytotoxicity evaluation

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Copper is one of the metals that are essential for body in a way that some significant biochemical compounds such as cytochromes have this metal ion, so its complexities are under serious studies. As a result, small amount of copper compounds is not considered toxic. So we expect that these compounds would be less toxic than cisplatin, with platinum heavy metal. In this research, we considered bithiazole as the ligands, where this ligand and its derivatives have been observed in many natural compounds like antibiotics. In addition, they have several usages in various fields such as biochemistry and pharmaceuticals, polymers, sensors, photography, color preparation, and analysis of cations.[1]

We synthesized [Cu(dmbt)Br_2(DMSO)] and [Cu(bt)Br_2(DMSO)], where dmbt is 2,2'-dimethyl-4,4'-bithiazole and bt is 4,4'-bithiazole. The DNA interaction of mentioned compounds along with [Cu$(dmbt)_2NO_3$](NO_3) and [CuCl(dmbt)(μ-Cl)$]_2$ has been explored by using absorption, emission and thermal denaturation, as they illustrate high interaction ability with CT-DNA, at 298 K. Also the intermolecular interaction between Cu complexes and bovine serum albumin (BSA) under imitated physiological conditions was investigated using UV-Vis. and fluorescence. Tryptophan quenching experiment showed that the complexes bind BSA strongly. All complexes were also used for in vitro cytotoxicity evaluation against four cultures, NIH-3T3, Caco-2, HT-29 and T47D by MTT assay. Interestingly, one complex illustrated no toxicity on normal cell line (NIH-3T3), with high antitumor activity against cancer cell lines, comparing with cisplatin.

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An artificial enzyme made by the covalent grafting of an Fe^{II} complex into β-lactoglobulin : molecular chemistry, oxidation catalysis and monitoring of reaction intermediates in a protein

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The development of artificial metalloenzymes has received much attention in the last decade as these hybrid systems are expected to combine the complementary characteristics of homogenous catalysts and enzymes.[1] If the rational design of a biohybrid system is *a priori* easy from known proteins and catalysts, interpretation of its reactivity may be more difficult, especially in the absence of X-ray structures.

We have prepared an artificial metalloenzyme by grafting a nonheme Fe^{II} polyazadentate complex, known to stabilize high oxidation state intermediates (Fe^{III}-(hydro)peroxo, Fe^{IV}-oxo), into bovine β-lactoglobulin. This biohybrid has been thoroughly characterized using various spectroscopic techniques to determine the location of the complex and its structure. This biohybrid catalyst activates hydrogen peroxide to oxidize thioanisole into phenylmethylsulfoxide with a significant enantiomeric excess. Investigation of the reaction reveals the generation of a high spin (S=5/2) $Fe^{III}(\eta^2\text{-}O_2)$ intermediate, proposed to be responsible for the substrate's oxidation.[2] This Fe-peroxo is one of the scarce examples of Fe oxidizing species identified in artificial metalloenzymes.[3]

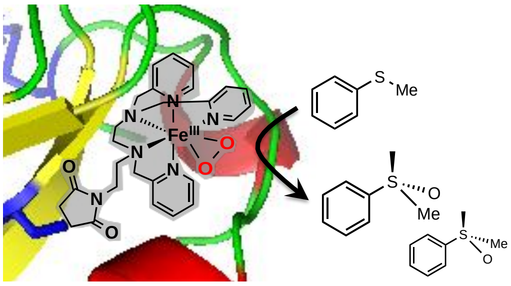

Figure 1 Sulfoxidation of thioanisole by a Fe-peroxo grafted into β-lactoglobulin.

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Preparation and bio-properties of precious metal carborane polymer nanoparticles

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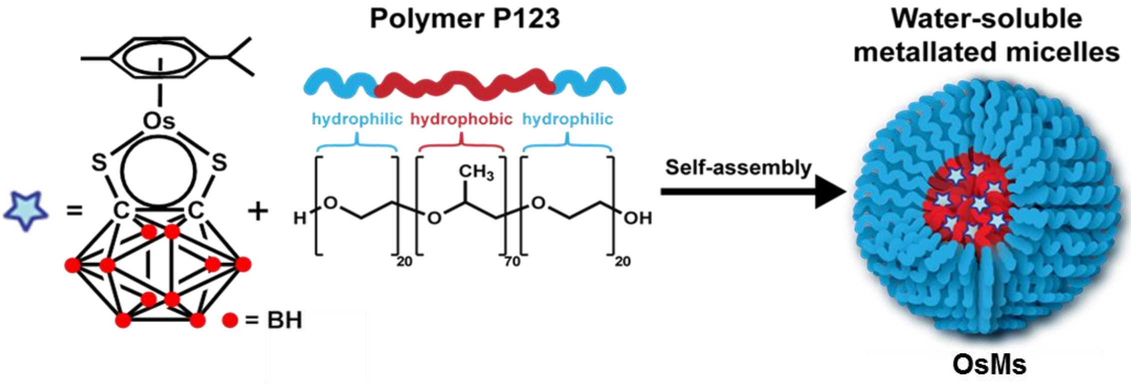
Organometallic precious metal complexes containing unusual boron-rich carborane ligands have potential as anticancer drugs, as Boron Neutron Capture Therapy agents,[1] and as bio-sensors.[2] The utilization of tools from nanotechnology, such as large drug delivery systems made of polymers, might offer control of solubility and biodistribution of these organometallic complexes.[3]



We show that the size distribution, morphology, and stability of nanoparticles made of water-soluble poloxamer polymer[4] and highly hydrophobic Ru^{II} and Os^{II} arene carborane complexes are highly dependent on the assembly conditions (*e.g.* temperature, complex loading). The formation and characterisation of metallated core-shell micelles, their *in vitro* anticancer activity[5] and neutron capture properties[6] will be discussed.

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New insights in Tyrosinase enzyme inhibition from a coordination chemistry approach

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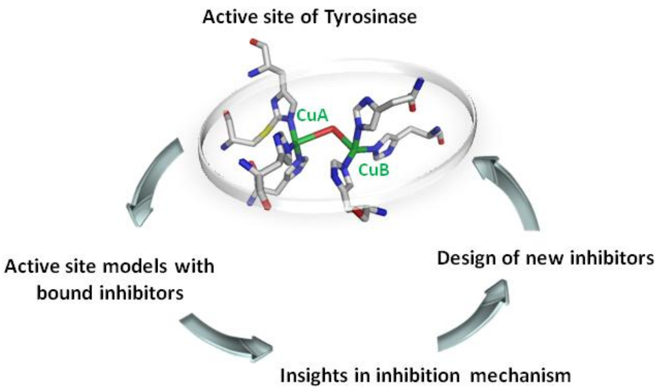
Tyrosinase(Ty)is a copper-containing metalloenzymesinvolved in mammals in the two-step oxidation of *L*-tyrosine into dopaquinone, which is the key product for melanin (protective pigments) biosynthesis. Melanin-related disorders are known to cause serious lesions and Ty inhibition is a well-known approach against increased production of melanin. In relation with Ty inhibition mechanism, the molecules targeting binuclear copper sites represent a relevant strategy to achieve Ty inhibition specificity. In this regard, the detailed studies of binding on dicoppercenterin relation with the inhibition behavior are fundamental to established binding properties/inhibition activity relationship.[2]In this communication, we will describe from structural and advancedspectroscopic studiesassociated with theoretical modeling, our efforts to understand the binding of copper chelators using functional models of the Ty active site. The implications of these findings in relation with the source of tyrosinase enzyme and development of new inhibitors will be presented.



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Structural and functional model systems for the [2Fe-2S] cluster in mitoNEET proteins

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Iron-sulfur clusters are ubiquitous cofactors which exist in a variety of forms and serve a multitude of functions including electron transport, redox reactions and sensing. While the majority of iron-sulfur clusters are ligated by four cysteine residues of the surrounding protein, it has been found that a subset of [2Fe-2S] clusters features different terminal ligands. The most commonly observed of those alternative ligands is histidine but in most cases the role of this alternative ligand is not yet fully understood.[1]

First structural model systems for the special $\{Cys_2\}\{His_2\}$ coordinated [2Fe-2S] cluster of the Rieske protein have recently been reported by our group.[2,3] Proton coupled electron transfer (PCET) was studied in those and related functional model systems, highlighting the importance of the distal nitrogen of the ligand as protonation site.[3,4]

MitoNEET is an outer membrane protein whose exact function remains unclear to date, though a role of this protein in redox and iron sensing as well as in controlling maximum mitochondrial respiratory rates has been discussed.[5] It was shown to contain a redox active and acid labile [2Fe-2S] cluster, which is ligated by one histidine and three cysteine residues.[6] The first structural and functional model complex for this special cluster and its properties in different oxidation and protonation states are presented here. The ability of this cluster and of a related homoleptic system to undergo PCET has been studied, and the corresponding square schemes have been established and compared with the Rieske models.

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What do we know about the redox reactivity of copper bound to neuronal peptides

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Growing evidence supports the view that disruption of copper homeostasis in the brain is linked to neurodegenerative diseases such as Alzheimer's and Parkinson's diseases.[1,2] Toxic effects of copper may be directly associated with its capacity to promote and stabilize oligomers of neuronal peptides, but most probably depend on its redox properties and production of reactive oxygen species (ROS). In particular, the interaction of copper with neuronal peptides influences: (i) the redox potential of the Cu^{II}/Cu^{I} couple, and hence, the reactivity of copper(I) towards dioxygen and/or hydrogen peroxide, which leads to the formation of ROS, (ii) the ability to promote copper-mediated oxidation of external substrates present in the cell, and (iii) the induction of endogenous post-translational modifications in the peptides. It is therefore of extreme importance to clarify to which extent the interaction of copper with neuronal peptides has pro-oxidant effects.

We have carried out a comparative investigation of the reactivity of copper(II) bound to four peptide fragments of β-amyloid ($A\beta_{16}$), α-synuclein (αSyn_{15}), tau protein (R1τ), and prion protein ($PrP_{84\text{-}114}$), respectively, containing the residues which act as binding sites for the metal ion. The first important target of the oxidative reactivity of copper-peptide complexes is dopamine, because of the importance of this and related neurotransmitters in several brain areas. The behaviour of copper bound to the various peptides is very different, as we found that $A\beta_{16}$ and $PrP_{84\text{-}114}$ strongly promote, R1τ slightly enhances, and αSyn_{15} depresses dopamine oxidation by copper(II). In all cases, concomitant oxidation of the peptides is observed, but this effect is particularly marked for the prion peptide. On the other hand, the copper-peptide complexes do not exhibit any significant pseudo-enzymatic monooxygenase activity,[3,4] because the characteristics of the Cu binding environments in these complexes are far from those of copper enzymes.[5]

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Biologically inspired approaches to the cleavage and formation of the O-O bond with coordination complexes

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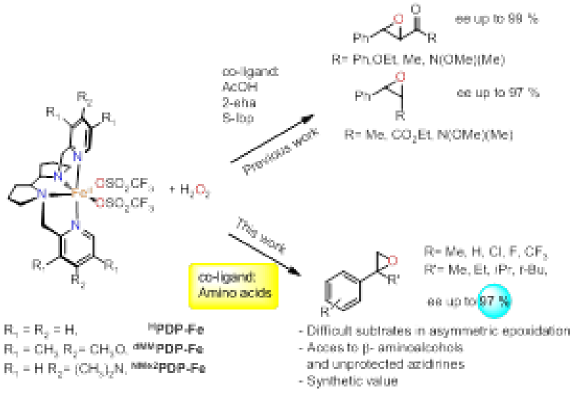
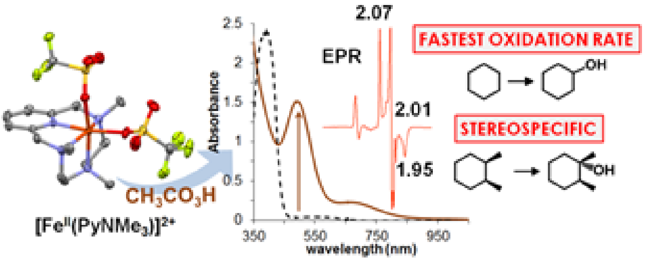
Biologically inspired catalysts are currently explored with the aim to produce selective oxidation reactions. The quest for catalytic methodologies that provide novel reactivities and selectivities that could complement those attained with traditional oxidants, or that could represent a more efficient alternative constitute major reasons of interest for this approach.[1-3] Towards this end, iron coordination complexes ligated to amine and oxygen containing functionalities, and that could be viewed as a minimalistic model of iron coordination sites in non heme iron dependent oxygenases, are employed as catalysts for the oxidation of organic substrates. By control of their structure and electronic properties, catalysts have been designed by our research team that engage in controlled O-O lysis of H_2O_2 to form highly electrophilic high valent metal-oxo species that are finally responsible for enzyme-like selective oxidation chemistry.[4] Principles of catalyst design and use of these catalysts in selective C-H and C=C oxidation reactions, and reaction intermediates involved in these reactions[5] will be discussed in this contribution.





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Cytotoxicity of Oxindolimine Metal Complexes Immobilized on Beidellite Clays towards HeLa cells

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During the last years, copper(II) and zinc(II) complexes with oxindolimine ligands have been investigated as potential antitumor agents.[1,2] These complexes are able to induce apoptosis, acting as multifunctional compounds. They can bind to DNA, and in the case of copper, cause oxidative damage. In the mitochondria, they decrease the membrane potential, acting as discoupling agents. Additionally, they significantly inhibit human topoisomerase IB and cyclin-dependent kinase (CDK1 and CDK2). In all cases, the observed biological activity is modulated by the metal, and by the ligand. Herein, these complexes were immobilized on a synthetic beidellite clay, capable of entering the cell, and the supported species were tested against HeLa cells, in comparison to the corresponding complexes in solution. The beidellite $[Na_{0.85}(Si_{3.10}Al_{0.91})Al_2][O_{10}(OH,F)_2]$ (BD) was synthesized according to procedure already described, and characterized by XRD, showing interlayer space 12.49Å. The composites were obtained by mixing clay and complex (at ratio 1:0.25), in water:DMF solution (90:10 v/v), at pH 5.5. After 3h under stirring at RT, the composites were centrifuged, washed with water, and dried overnight at 70°C. In the isolated composites, this interlayer space varied very little, up to 12.90Å. These composites showed to be very stable, with zeta potential in the range -30.8 to -35.9 mV, and surface charge around -220 μeq/g. The pure clay shows corresponding values of -(33.3±0.70)mV, and -612μeq/g, respectively. As shown in Table 1, copper species were more active than the zinc ones, both in solution or supported in BD clay.

Compound	IC_{50}, μM	Composite	$IC_{50,}$ mg/mL (μM)
Free ligand (isapn)	>150	BD	no toxic
[Cu(isapn)]	81,9	BD-[Cu(isapn)]	0.41 (207)
[Zn(isapn)]	>150	BD-[Zn(isapn)]	>0.5
Free ligand (isaepy)	>150		
Cu(isaepy)(H_2O)	19.2	BD-[Cu(isaepy)]	0.22 (119)
Zn(isaepy)$_2$	101	BD-[Zn(isaepy)]	>0.5

Table 1. HeLa cell viability in the presence of metal complexes or BD-composites.

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Siderophore scavenging in bacterial iron uptake: a binding protein with preference for enterobactin hydrolysis product

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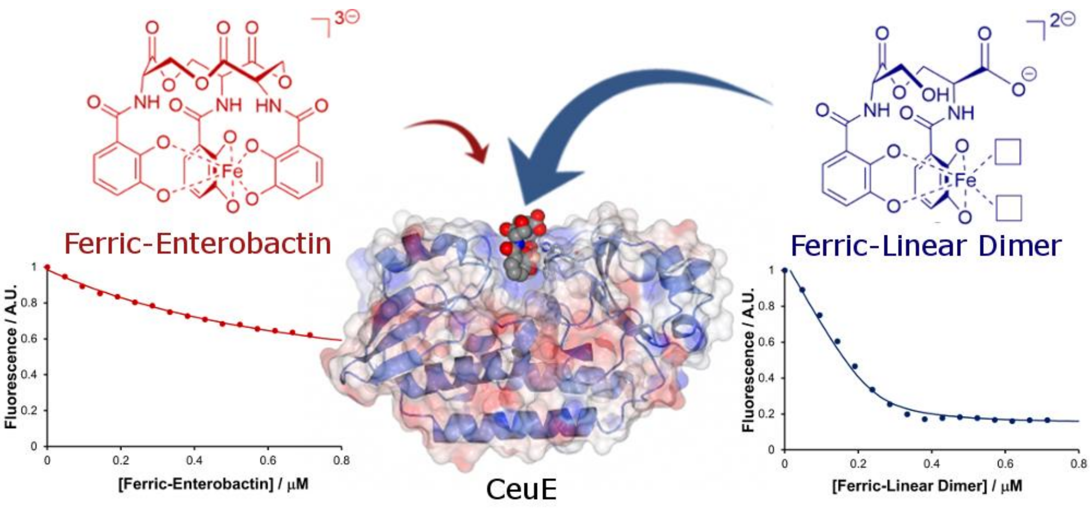
Almost all bacteria require Fe(III) for growth. To compete successfully for the essential nutrient, bacteria produce and secrete siderophores with high affinity for iron(III) to mediate its uptake into the cell. To gain a competitive advantage, many bacteria have evolved to scavenge siderophores from other species. We show that CeuE, a key protein involved in Fe(III) uptake in the food-borne pathogen *Campylobacter jejuni* is adapted to scavenge enterobactin hydrolysis products,[1] a strategy that may enable the pathogen to efficiently exploit enterobactin produced by other bacteria and hence their resources.

CeuE binds the ferric complex of the enterobactin hydrolysis product (ferric-linear dimer) with much higher affinity (K_d=10.1±3.8 nM) than ferric-enterobactin (K_d=0.4±0.1 μM). Co-crystal structures show that in addition to electrostatic interactions and hydrogen bonding, the $[Fe(linear\ dimer)]^{2-}$ binds through co-ordination of His227 and Tyr288 to the iron center. These results suggest a new role for CeuE within the iron(III) uptake system of *C. jejuni*, provide a molecular level understanding of the underlying binding pocket adaptations and rationalize reports on the use of enterobactin hydrolysis products by *C. jejuni*, *Vibrio cholerae* and other bacteria with homologous periplasmic binding proteins.



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Mn-SiO_2 hybrid material with catalase-like activity: stabilization of Mn^{III}_2 complexes in water solution.

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Reactive oxygen species such H_2O_2, $O_2^{\bullet -}$ and $HO^{\bullet}$ (ROS) are endogenously produced during the metabolism and, they may perform undesirable oxidations if their concentration is uncontrolled. Hence, cells are loaded with high amounts of very efficient ROS scavengers.[1,2] Mn-catalase (Mn-CAT) is one of the enzymes that protects cells from damage caused by H_2O_2, catalyzing its decomposition into H_2O and O_2.[3,4]

In our group, we synthesized a series of binuclear Mn(III) compounds (Figure 1) that are able to effectively decompose H_2O_2. However, their low stability in water does not allow to use them as antioxidant agents.[3,5] In order to overcome this limitation, we inserted the aforementioned compounds in mesoporous silica (MCM-41) previously functionalized with pyridine functions.

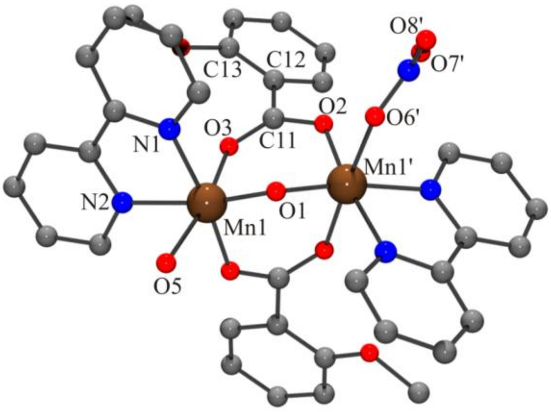

Figure 1. Binuclear manganese complex.

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The Functional Role of the Dioxo-isobacteriochlorin Structure of the Catalytic Site of Cytochrome cd$_1$ in Nitrite Reduction

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Denitrification is an important component of the global nitrogen cycle that is responsible for regulating the amount of fixed nitrogen available for plant growth. In denitrification process, the reduction of NO_2^- to NO is catalyzed by nitrite reductase (NiR), containing either heme *cd$_1$* or copper. The copper-containing NiR (Cu-NiR) catalyzes the nitrite reduction at the type-2 Cu site, which consists of three-histidine ligand, while the heme-containing NiR (*cd$_1$*-NiR) catalyzes at the unique heme *d$_1$* site, iron dioxoisobacteriochlorin cofacter. Previously, we reported role of the three-histidine ligand of the type-2 Cu site in the nitrite reduction with synthetic model complexes. The three-histidine ligand of Cu-NiR donates electrons into copper-bound nitrite *via* copper(I) ion and enhances reactivity of the copper-bound nitrite to form nitric oxide. To compare functional role of the ligand environment in Cu-NiR with *cd$_1$*-NiR, we studied reactions of heme *d$_1$* with nitrite with synthetic model complexes. We prepared iron complexes of dioxo-octaethyl isobacteriochlorin (**1**), mono-oxo-octaethylchlorin (**2**) and octaethylporphyrin (**3**) as models for *cd$_1$*-NiR and compared catalytic activity of these complexes in each step of catalytic cycle of *cd$_1$*-NiR. We found that the reduction potential for the transition from the ferric state to the ferrous state and the binding constant for binding of NO_2^- to the ferrous complex increases with a trend of **3** < **2** < **1,** but the reactivity of the ferrous nitrite complex with protons increases in the reversed order, **1** < **2** < **3**. Based on these experimental results, as well as DFT calculations, we discuss the functional role of heme *d$_1$* in nitrite reduction by *cd$_1$*-NiR.

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Myoglobin Reconstituted with Cobalt Corrin Derivatives: A Functional Model of Methionine Synthase

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Methionine synthase, a methyltransferase, contains cobalamin (vitamin B12 derivative) as a cofactor and the holoprotein is still difficult to characterize in entirety. Recently, we have designed and prepared an enzyme model using a unique conjugate between apomyoglobin and a tetradehydrocorrin cobalt complex.[1] X-ray crystal structure of the reconstituted protein reveals that the Co(II) complex is stabilized in the heme pocket with ligation of His93 in a penta-coordinate form. Reduction of the protein yields a Co(I) complex and the crystal structure clearly indicates the tetra-coordinate species which forms due to the cleavage of the axial ligation. This is the first example of the crystal structure of Co(I) species in the protein. Next, the addition of methyl iodide to the Co(I) species causes formation of a photo-labile CH_3–Co bond in the heme pocket and the methyl group is then transferred to the Nε2 atom of the His64 imidazole ring quantitatively within 24 hours.[2] The methyl transfer was monitored by mass spectroscopy and trypsin-dialysis experiment. The stability of the organometallic species and the following methyl transfer to the imidazole ring will be regulated by the axial ligation of His93, which is supported by theoretical studies. Thus, the present system represents a new cobalt corrinoid-dependent methyltransferase model.

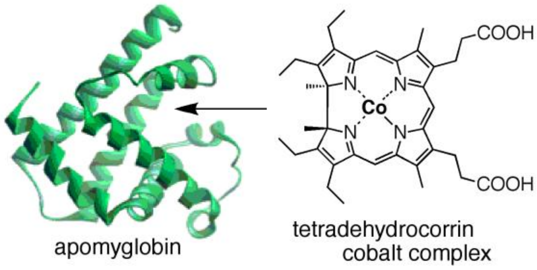

Figure 1 Insertion of tetradehydrocorrin Co(II) complex into apomyoglobin to yield a methionine synthase model.

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Reactivity and Electronic Structure of Mononuclear Manganese(III)-Hydroxo Complexes

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Redox-active manganese enzymes participate in vital biological processes, including defense against free radicals by Mn superoxide dismutase and the dioxygenation of polyunsaturated fatty acids by Mn lipoxygenase (MnLOX). Mononuclear Mn(III)-hydroxo species play important roles for each enzyme. For MnLOX, the Mn(III)-hydroxo unit is proposed to initiate substrate oxidation by abstracting a hydrogen-atom from a weak C-H bond. In synthetic chemistry, mononuclear Mn(III)-hydroxo units are rare, and only a limited number of these are known to perform substrate oxidation.[1-3] We have recently described a Mn(III)-hydroxo species supported by an amide-containing N5 ligand, $[\mathrm{Mn^{III}(OH)(dpaq)}]^+$ (Figure 1), which is capable of oxidizing weak O-H and C-H bonds.[3] To define the factors governing H-atom abstraction reactivity of Mn(III)-hydroxo units, we are modifying the dpaq ligand to perturb geometric and electronic structure. For example, a Mn(III)-hydroxo complex featuring the $\mathrm{dpaq^{2\text{-}Me}}$ ligand (Figure 1) reacts with substrates 300-times faster than the parent $[\mathrm{Mn^{III}(OH)(dpaq)}]^+$ complex. Spectroscopic methods, such as magnetic circular dichroism and Mn K-edge X-ray absorption spectroscopies, are being used in conjunction with density functional theory (DFT) computations to define geometric and electronic structure perturbations, and relate these to the observed H-atom abstraction reactivity.

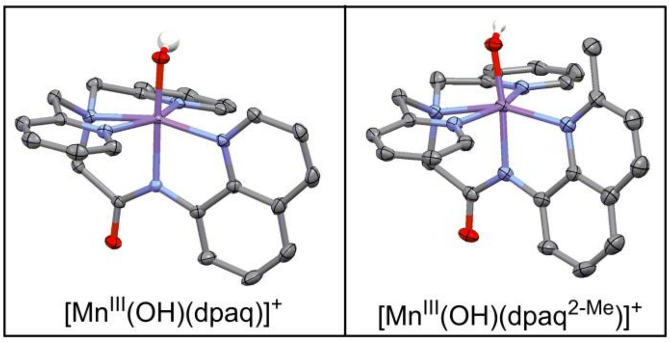

Figure 1 X-ray diffraction structures of $[\mathrm{Mn^{III}(OH)(dpaq)}]^+$ (left) and $[\mathrm{Mn^{III}(OH)(dpaq^{2\text{-}Me})}]^+$ (right).

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Regulation of redox enzymes activity by cytotoxic ruthenium and osmium complexes

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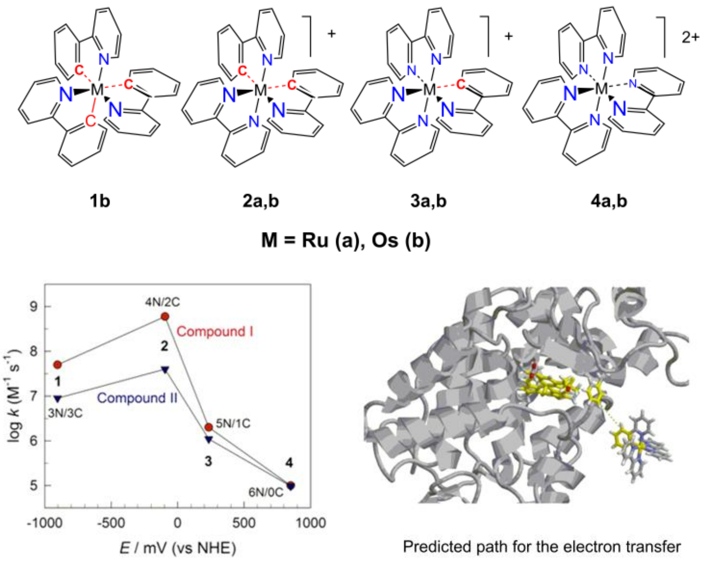
Ruthenium compounds have displayed interesting anticancer properties, and usually the side effects and resistance mechanisms are reduced compared to platinum drugs. However, their exact modes of action remain mostly unknown. Series of structurally similar cyclometalated ruthenium and osmium complexes, $[M(C\sim N)_x(N\sim N)_{3-x}]^{m+}$ (Fig. 1), have displayed important cytotoxicity and have also been studied as regulators of redox proteins.[1-3] The redox potentials, charges, lipophilicities, as well as their antitumour activity, change drastically as nitrogen atoms are successively replaced by σ-bound sp^2 carbon atoms. As oxidoreductases have been closely associated with the development of cancers, their route of action could be linked to the interaction with such enzymes. In order to shed light on how the complexes can interact with redox enzymes, the effects of the complexes on the *in vitro* activity of enzymes such as peroxidase, glucose oxidase and lactate dehydrogenase were evaluated. Kinetic parameters, theoretical docking simulations and influence of the redox potential and oxidation state will be discussed.



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Combining electrochemistry and theoretical chemistry to study the catalytic mechanism of hydrogenases

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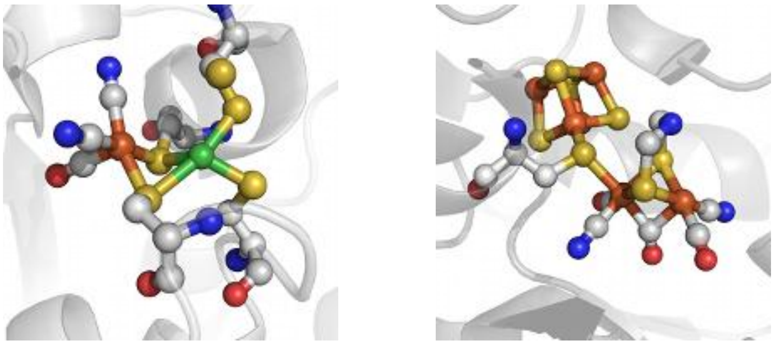
After enzymes were first discovered in the late XIX century, and for the first seventy years of enzymology, kinetic experiments were the only source of information about enzyme mechanisms. Over the following fifty years, these studies were taken over by approaches that give information at the molecular level, such as crystallography, spectroscopy and theoretical chemistry. We have shown that combining theoretical chemistry (DFT, MD, QM/MM) and detailed experimental investigations that make use of modern kinetic methods, such as protein film voltammetry, is a novel way of learning about individual steps and/or complex reactions that are part of the catalytic cycles of metalloenzymes. We illustrate this approach with recent results from our lab, including studies of gas transport along substrate channels and mechanisms of catalysis, inhibition or inactivation. Emphasis will be on hydrogenases, the enzymes that oxidise and produce H_2.



The active sites of NiFe (left) and FeFe (right) hydrogenases

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The role of metal ions in memory gene expression induced by Nerve Growth Factor and its mimicking peptides.

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Neurotrophins (NTs) are secreted proteins essential for development, maintenance and survival of central and peripheral nervous systems. The nerve growth factor (NGF), the first neurotrophin discovered, drives cell signalling through the interaction with receptor TrkA (pro-survival signalling) and the p75 receptor (pro-apoptic signalling). NGF has been indicated as therapeutic agents in different brain disorders, in particular Alzheimer disease (AD), due to its ability to prevent or reverse neuronal degeneration. However, its use as therapeutic is hampered by low serum stability, poor oral bioavailability and different serious side effects due to the activation of p75. To overcome these limitations we have synthesized a peptide, NGF(1-14), encompassing the 1-14 sequence of the human NGF N-terminal domain, able to bind to TrkA.[1] NGF(1-14) partly exerts an effective and specific NGF-like action on some crucial NGF intracellular targets such as cAMP-response element binding protein (CREB), able to induce dendritic spine growth, morphology change, synaptic plasticity, and long-term memory. Metal ions dyshomeostasis affects AD and a direct link with NGF and biometals has not been taken into account. Here we report that copper and zinc ions affects NGF and NGF(1-14) activity on PC12 cells. Live cell imaging experiments of PC12 treatment with fluorescent labelled peptide NGF(1-14)FAM, show that the peptide is able to pass cellular membrane and acts as a ionophore, increasing the intracellular amount of copper. Such activity is not observed with the acetylated form of the peptide, which bind metal weekly, confirming the biological relevance of metal coordination environment.

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Metal Sequestration by Human Calprotectin

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Human calprotectin is a metal-sequestering host-defense protein that exhibits unusual biological coordination chemistry. This protein is produced by neutrophils and, at sites of infection, is released into the extracellular space where it competes with microbial invaders for first-row transition metal ions that are essential nutrients. Here we describe the iron-binding properties of human calprotectin.[1] Iron is an essential nutrient for almost all organisms, and our studies establish that human calprotectin chelates Fe(II) at an unprecedented hexahistidine metal-binding site that expands the known biological coordination chemistry of non-heme iron. We also show that human calprotectin blocks microbial iron uptake. These studies indicate that human calprotectin is an unappreciated contributor to mammalian iron homeostasis.

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High valent iron oxo complexes as catalysts for the oxidation of alkanes and alkenes

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This lecture will describe a number of mononuclear Fe(II), Fe(IV)=O (ferryl) and Fe(V)=O (perferryl) complexes,[1,2] as well as dinuclear Fe(III)-O-Fe(III) complexes,[3,4] that function as catalysts or precatalysts for (*i*) hydroxylation of alkanes and alkenes via hydrogen atom transfer (HAT) and oxygen atom transfer (OAT) mechanisms (*ii*) oxidation of substrates via OAT (*iii*) (asymmetric) epoxidation of prochiral alkenes. Reactivity studies on the various complexes that aid the elucidation of mechanistic aspects of the oxidation reactions will be described.

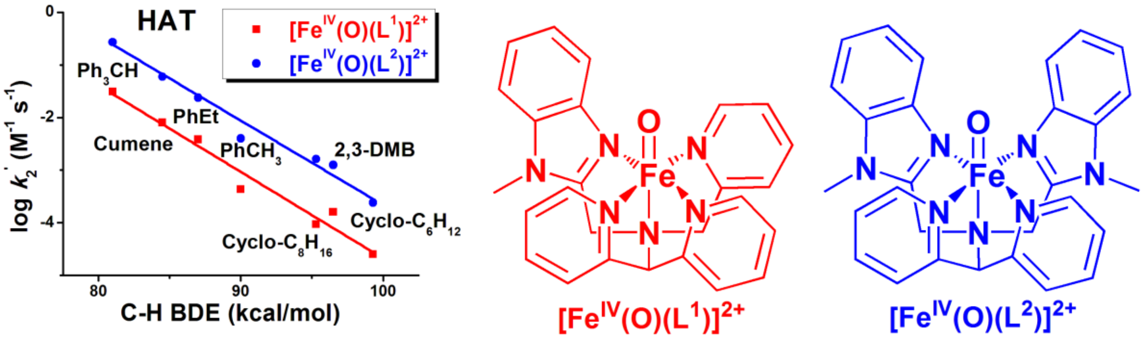

Figure 1 Rates of hydrogen atom transfer reactions vs substrate C-H bond dissociation energies for reactions effected by two Fe(IV)=O complexes.

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Designing and syntheses of some novel Ru(II), Rh(III), and Ir(III) complexes and their anticancer activity

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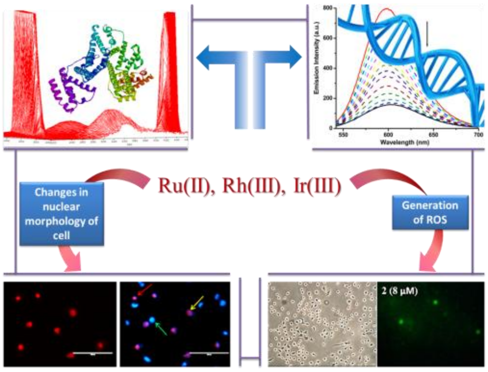
Enormous current interest has arisen in the synthesis and characterization of metal based anticancer agents after the success of cisplatin and other platinum based drugs in the treatment of cancer. Despite having beneficial antitumour properties these are also associated with severe side effects, toxicity, and ineffectiveness against certain types of cancer. To overcome the drawbacks of cisplatin and other platinum based drugs, scientific community is looking for drugs based on other metal complexes. In this direction, ruthenium has drawn particular attention because of its diverse characteristics and prominent role in biological systems. Lately, half-sandwich organometallic Rh(III) and Ir(III) complexes have also been shown to display high versatility and promising anticancer activity. In this quest, our group have also been active in developing non-toxic but effective novel Ru(II), Rh(III), and Ir(III) based anticancer drugs. Water soluble Ru(II) and Rh(III) complexes have been used as a topoisomerase II inhibitor.[1] DNA, and protein binding, molecular docking, and in vitro anticancer activity of some heteroleptic Ru(II), Rh(III), and Ir(III) complexes containing dipyrromethenes have also been successfully studied.[2] Recently, the DNA, protein binding, and anticancer activity of some half-sandwich cyclometalated Rh(III) and Ir(III) complexes has been studied in human lung cancer cell line (A549).[4] In this talk I would like to discuss some of our recent results in this direction.



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Redox Active Inorganic Complexes and Control of the Properties: Entasis from Geometrical Constraints and Other Parameters

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Controlling properties of metal complexes is important for the design of inorganic-based derivatives. The possible control of metal properties by the coordination geometry was an idea introduced by Vallee and Williams[1] with the concept of "entatic state"[2] and refers to proteins in which metal cations are in an unusual energized state.[3] Entatic states can be achieved using ligands enabling the coordination but with some constraints leading to a geometry that does not match the geometrical intrinsic requirements of the metal ion.[2a, 3] In this talk we will present the development of metal complexes with a constraint coordination sphere associated to a control of the redox potential using sugar-based central platforms.[4]

Other physico-chemical parameters can also be used to control redox potential and reactivity. The application to the design of catalytic SOD mimics will be presented, [5] Several physico-chemical parameters can be tuned to improve the an anti-superoxide catalytic activity, including redox potential and overall charge.[5-6]

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Copper-containing monooxygenases: the union of two coppers does the strength?

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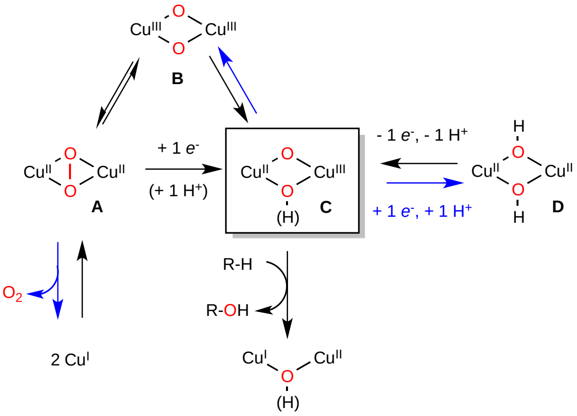
Methane has the strongest C—H bond of any hydrocarbon (104 kcal/mol), thus its selective oxidation to methanol without further oxidation is extremely challenging. In nature, methane monooxygenases (MMO) accomplish the direct conversion of methane into methanol at ambient temperature and atmospheric pressure allowing the harnessing of methane as an energy source and for the synthesis of the life required molecules. MMO exists as soluble and particulate forms. The soluble enzyme (sMMO) which contains a (μ-oxo)$Fe^{II}Fe^{II}$ active site has been the subject of a lot of investigations that suggests that a (μ-oxo)$Fe^{IV}Fe^{IV}$ is the active species in methane hydroxylation. Compared to sMMO, the knowledge on the particulate form (pMMO) is recent and pMMO has been the subject of a controversy about the metal content and the structure of its active site. Nevertheless, the most recent results propose a dinuclear copper center, which reacts with dioxygen to produce a Cu2/O2 as active species in methane oxidation such as (μ-η2:η2-peroxo)$Cu^{II}Cu^{II}$ or bis(μ-oxo)$Cu^{III}Cu^{III}$. However, DFT calculations suggest that a 1-electron reduced mixed-valent bis(μ-oxo)$Cu^{II}Cu^{III}$ species has greater oxidizing power to cleave the methane C-H bond rather than either the symmetric (μ-η2:η2-peroxo)$Cu^{II}Cu^{II}$ or bis(μ-oxo)$Cu^{III}Cu^{III}$.



With a bioinspired chemical approach that has allowed to identify the (μ-oxo)$Fe^{IV}Fe^{IV}$ as the active species in methane hydroxylation by sMMO, we will report recent results on the study of (μ-η2:η2-peroxo)$Cu^{II}Cu^{II}$ (**A**), bis(μ-oxo)$Cu^{III}Cu^{III}$ (**B**) as well as the 1-electron reduced mixed-valent bis(μ-oxo)$Cu^{II}Cu^{III}$ species (**C**).

Lanthanide complexes, new agents for structural biology: protein crystallization and structure determination

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Introduction of lanthanide complexes in proteins crystals is an efficient approach for the determination of protein structures with high resolution using anomalous-based X-ray diffraction techniques.[1] Moreover, our first results using tris-dipicolinate lanthanide complexes have shown that such complex can also play an active role in the organization of the proteins at the solid state through a non-covalent binding mode, especially with arginine residues.[2]

We will present the new generation of luminescent lanthanide complexes, based on a triazacyclononane (TACN) platform, that present remarkable properties as nucleating and crystallizing agents for biological macromolecules.[3] Such entities are able to induce new crystallization conditions and to greatly improve the crystal quality. Studies of these phenomenon and the possible mechanisms implied will be discuss. In particular, we will focus on the studies of the supramolecular interactions of these lanthanide complexes with proteins in solution and at the solid state.

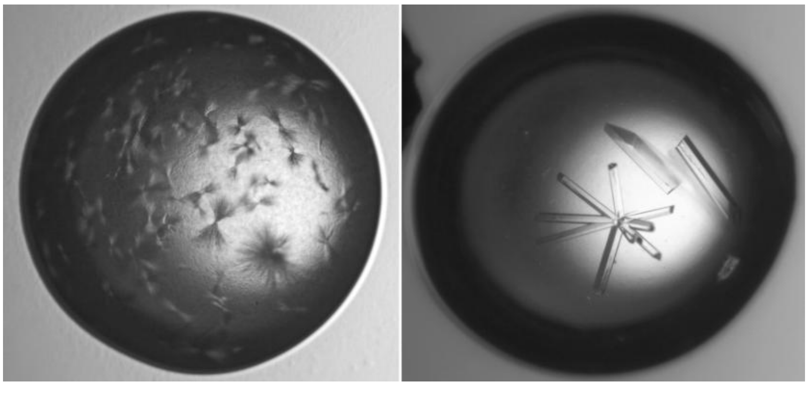

Figure Crystals of PB6 protein: classical conditions (*on left*); with Ln-complex (*on right*).

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Design of new silver-based hybrid materials with potential bactericidal properties.

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Silver metal, nanoparticles or salts, presents bactericidal properties due to its interaction with biomolecules. Our previous work in this field has shown that a silver-based hybrid material obtained from méta phosphonic acid was able to release silver ions in aqueous solution thus exhibiting a bactericidal effect against six bacterial strains and, especially, on Gram-negative strains[1].

The dimensionality and the structure of a hybrid material, for a selected metal, are easily controlled *via* the nature of the organic precursor or the synthesis conditions. We aimed to study the influence of the dimensionality and structure of the final material, on their capacity to release silver ions in aqueous solution. To this end, we have synthesized hybrid materials with original architectures from: silver salt and a) rigid polyfunctional ligands possessing at least one phosphonic acid and/or one carboxylic acid bonded to a rigid ring or b) n-alkylphosphonates. For the synthesis of the hybrid materials, different experimental conditions were explored (e.g. pH, temperature). Several materials were obtained and their structure was solved by X-ray diffraction on single crystals. The synthesis, structure, thermal stability and the quantification of silver release in aqueous solution will be presented. The influence of the rigidity, polarity and the number and type of reactive functions of the organic building block involved in the synthesis will be also discussed.

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Potential transition metal complexes: Chemical reactivity and biological applications

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Transition metal complexes are appealing candidates in the search for new diagnostic and therapeutic agents. In order to change the characteristics of the complex in either subtle or dramatic fashion, the ligand environments can be varied with ease. Hence, transition metal complexes with different O-N and/or N-S donor ligand scaffolds open a new era of pharmaceutical research since their presence can moderate physicochemical properties as well as can enhance the medicinal properties. The study of complexes of hydrazone ligands is of unabated interest to inorganic chemists because of their relevance to apparently dissimilar fields, like bioinorganic chemistry and catalysis.[1-5] Additionally, thiosemicarbazones (TSCs) are a class of Schiff bases which are considered as one of the most important scaffolds and are embedded in many biologically active compounds. Transition metal complexes with TSCs as ligands continue to be the subject of many studies, especially as anticancer chemotherapeutic and as DNA–binding and cleaving agents. [6] In the similar manner, metal complexes with azo-derivatives have the potential to photoregulate the biofunctions, such as gene-expression and enzymatic action. Recently, it has been recognized that the photoinduced isomerisation of azobenzene can regulate biological processes that have important applications in pharmacology, nanotechnology, and cell biology. [7] Our most recent achievements in this area of research will be presented in my lecture.

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Metal Ion-Coordinating Properties of 2-Thiocytidine

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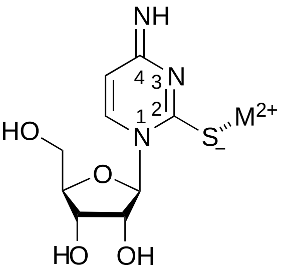
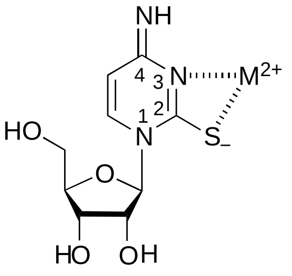
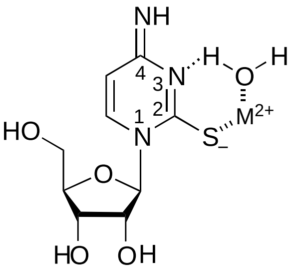
More than 100 different modified derivatives of the four major nucleosides, i.e., adenosine, guanosine, uridine, and cytidine have been found in nucleic acids,[1,2] especially in tRNAs, 2-thiocytidine (C2S) being very prominent. The joining of forces by several groups[3] has provided interesting results:[3,4] Replacement of the (C2)O unit in cytidine (Cyd) by (C2)S facilitated somewhat the release of the proton from $(N3)H^+$ in $H(C2S)^+$ (pK_a = 3.44) compared with $H(Cyd)^+$ (pK_a = 4.24) (aq. solution; 25°C; I = 0.5 M). However, the deprotonation of the $(C4)NH_2$ group is much more affected, its acidity increases from pK_a ca. 16.7 in Cyd to pK_a = 12.65 in C2S. The reason is that the neutral amino-thione tautomer (which forms via (C2)S relatively stable $M(C2S)^{2+}$ complexes) tranfers upon deprotonation into the imino-thioate form, with the charge largely localized on the $(C2)S^-$ site, and this species forms with Zn^{2+} or Cd^{2+} very stable $M(C2S - H)^+$ complexes already at a pH slightly above 3, that is, we observe an acidification of more than 9 pK units. Remarkably, even Mg^{2+} with a much smaller thiophilicity is expected to achieve deprotonation in the physiological pH range; this is of relevance[5] regarding C2S-containing tRNAs. The structures of the more important isomers of $M(C2S - H)^+$, which are in equilibrium with each other, are shown below, where also information from X-ray crystallographic studies was taken into account.







Supported by the Department of Chemistry of the University of Basel, Switzerland.

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Integrated Heme and non-Heme Manganese Environments for a Dual Catalytic Strategy Against Oxidative Stress

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As a by-product of respiration, oxidative stress in living systems is a major source of irreversible cell damage and severe pathologies. In mitochondrial respiratory chain, any failure of the multi-electron transfer mechanism for oxygen processing is associated to the release of Reactive Oxygen Species (ROS), including the superoxide anion ($O_2^{\bullet-}$), hydrogen peroxide (H_2O_2), and hydroxyl radical species (HO•). The natural defence against ROS-induced cell damage is provided by the combined action of superoxide dismutases (SOD), and catalase (CAT) enzymes that give rise to a cascade detoxification effect. Herein, we present the design of a novel anti-oxidant “catalytic strategy” that can emerge by the engineering of a synzyme with integrated SOD/CAT domino mechanisms arising from the joining of the two catalytic subunits, a manganese non-heme core and a manganese heme environment, in one dual synzyme.[1,2,3] This concept sets a new anti-ROS paradigm with respect to conventional systemic antioxidant scavengers, ruling out single electron transfers pathways and radical intermediates.

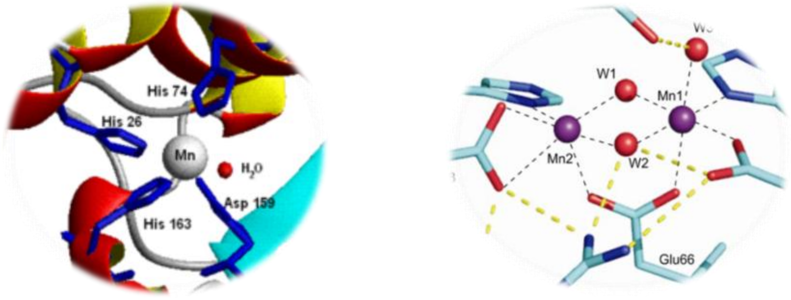

Figure 1 A view of the catalytic cores of the natural born enzymes SOD (left) and CAT (right) mimed by the dual SOD/CAT synzyme.

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Second Coordination Sphere interactions in Catalysis: Artificial metalloenzymes based on biotin-streptavidin

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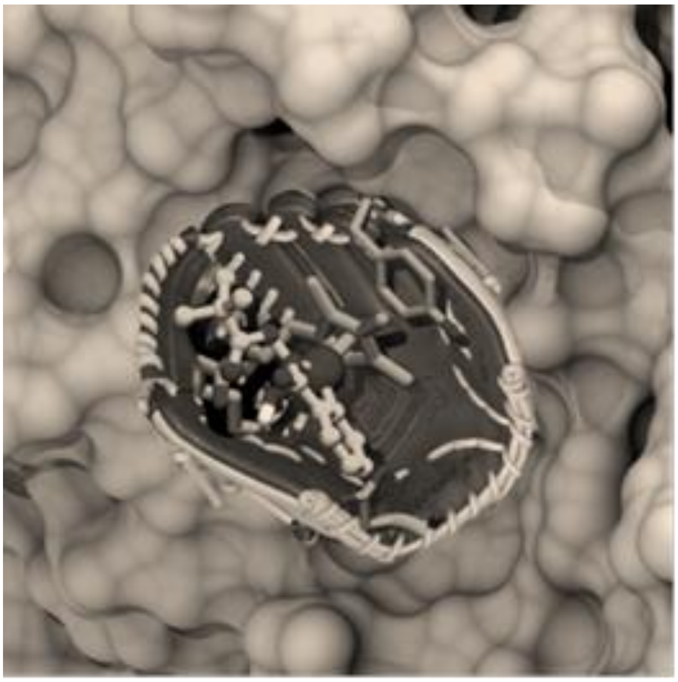
In stark contrast to enzymes, predictably exploiting second coordination sphere interactions remains challenging in homogeneous catalysis. To overcome this challenge, artificial metalloenzymes offer an attractive means to engineer proteins as host for coordination complexes. In this context, the biotin-streptavidin technology has proven versatile in the past decade.

Such artificial metalloenzymes can be improved either by chemical (varying the spacer between the biotin and the metal moiety) or genetic- (mutation of (strept)avidin) means. These chemogenetic schemes were applied to optimize the performance for eight different catalyzed transformations as well as reaction cascades in the presence of natural enzymes. This talk will summarize our efforts to complement both homogenous and enzymatic catalysis with artificial metalloenzymes. Particular emphasis will be set on controlling second coordination sphere interactions to improve catalytic performance in a biological environment.



Reactions implemented thus far:
Hydrogenation (up to 96 % ee)
Transfer Hydrogenation of
ketones (up to 98 % ee)
imines (up to 96 % ee, 3’000’000 TON)
enones (up to 1000 TONs)
Allylic Alkylation (up to 95% ee)
C-H Activation (up to 86 % ee)
Olefin Metathesis (up to 140 TONs)
Alcohol Oxidation (up to 250 TONs)
Sulfoxidation (up to 93 % ee)
Dihydroxylation (up to 98 % ee)
NAD+ regeneration (up to 20’000 TONs)

Design of the geometry of antidiabetic vanadium compounds using phosphatase active site complementarity

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Vanadate, and vanadium compounds are insulin enhancing agents and representative compounds have been tested in animal systems and human beings.[1-3] One mode of action of these compounds is believed to be inhibition of phosphatases.[1-7] In the following we examine the active sites of the 29 known X-ray structures binding vanadium and analyze the coordination chemistry of the vanadium atoms and characterize them with regard to trigonal bipyramidal or square pyramidal character. We will compare the vanadium systems with small molecule vanadium complexes.[8-10] These considerations demonstrate that a trigonal bipyramidal geometry is observed in the vanadium-phosphatase complexes even though the square pyramidal geometry is more stable for the small molecule complexes themselves. These observations were compared to the biochemical data available measuring K_i values for vanadium compounds.[9] However, a peptide-vanadate complex reported previously is found to be a particularly potent inhibitor of protein tyrosine phosphatase 1B (PTP1B).[11] The PTP1B undergoes hydrolysis by a concerted mechanism and it is thus consistent with the observed potent inhibition by a five coordinate vanadium geometry however additional stability is provided by the ligand.[11,12] Because the vanadium complex is readily hydrolyzed we suggest that approaches to overcome this problem and the potential degradation of the peptide is likely to involve new formulation strategies.Please check the graphical quality of the pdf file of your abstract automatically generated before final submission (step 4 overview).

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Metal Ions in Biomimetic Cavities

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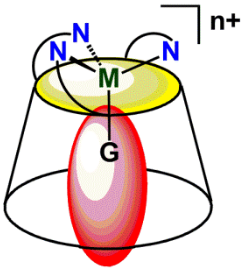
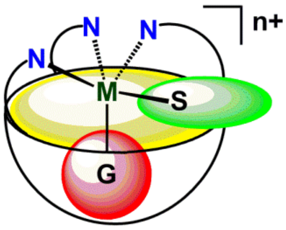
The aim of our work is to design supramolecular systems that mimic both the coordination core and the hydrophobic pocket of a metallo-enzyme active site. Our strategy relies on the synthesis of cavity-based ligands allowing the control of the coordination sphere of the metal ion together with the approach and the binding of an external molecule.[1] Since many years, we have been developing systems based on the calix[6]arene scaffold.[2] Our last developments concerned various aspects such as the guest covalent capture by a host,[3] the supramolecular control of hetero-multinuclear binding of metal ions,[4] and water-soluble receptors[5] and dioxygen activation.[6]



Funnel complexes



Bowl complexes

Recently, we started to explore metal complexes based on the resorcin[4]arene scaffold, which provides a supramolecular environment different in shape, rigidity and binding properties.[7] Hence, Bowl vs. Funnel supramolecular concepts for biomimetic metal complexes will be discussed.

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Molybdenum enzymes in Drug Metabolism and Biotransformations

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Mononuclear molybdenum is found in the active site of a diverse group of enzymes that, in general, catalyze oxygen atom transfer reactions[1]. Enzymes of the xanthine oxidase (XO) family are the best-characterized Mo-containing enzymes. They catalyze the hydroxylation of a wide variety of compounds, especially those containing N-heterocycles, and are known to have importance in a number of fields related to medicine, environment and industry. These enzymes contain Mo bound to an organic molybdopterin cofactor (Moco), [2Fe-2S] centres and often flavin. Reactivity appears to be conferred solely by the Mo centre, while specificity is controlled by the amino acid residues in the substrate binding pocket and the other cofactors are responsible for electron transfer.

Aldehyde Oxidase (AOX) is a Moco enzyme, belonging to the XO family, and has great toxicological importance since, along with cytochrome P450, it metabolizes different classes of xenobiotics being one of the principal drug-metabolizing enzymes in the liver[2]. In addition to the increasing role of AOX in drug metabolism, its true physiological significance is still largely unknown. An important contribution to clarify these aspects has been through the determination of several crystal structures. In 2012 we solved the first mammalian AOX structure, the mouse liver AOX3 isoform[3] and more recently the human AOX1 structure, free and in complex with a substrate and an inhibitor[4]. The ensemble of these crystal structures has provided valuable insights into the protein active site and on the catalytic specificities between AOX and XO. Several variants were prepared and, kinetic studies in combination with computational and structural studies, allowed identifying the structural determinants for the specific of hAOX1.

The new structural insights into the catalytic and inhibition mechanisms of AOX1 will be of great value for the rational analysis of clinical drug interactions involving inhibition of AOX1 and for the prediction and design of AOX-stable putative drugs.

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Cationic Phosphines, Arsines and Sulfides: Synthesis and Applications

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Our research focuses in two main areas, the synthesis of cationic ligands and their applications in catalysis and natural product synthesis, and the design of more selective and atom economical reagents for organic synthesis. In this regard, we have successfully prepared a series of cationic phosphines and arsines in which the positively charged group is directly attached to the phosphorus center renders the corresponding phosphines as poor α-donor and strong π-acceptor ligands (Figure 1a). [1]

In addition, we have also reported recently the syntheses of imidazolium thiocianates and imidazolium thioalkynes from dihalo(imidazolium) sulfuranes. These compounds react with nucleophiles of diverse nature acting as very efficient CN^+ and $R\text{-}CC^+$ synthons (Figure 1b). [2]

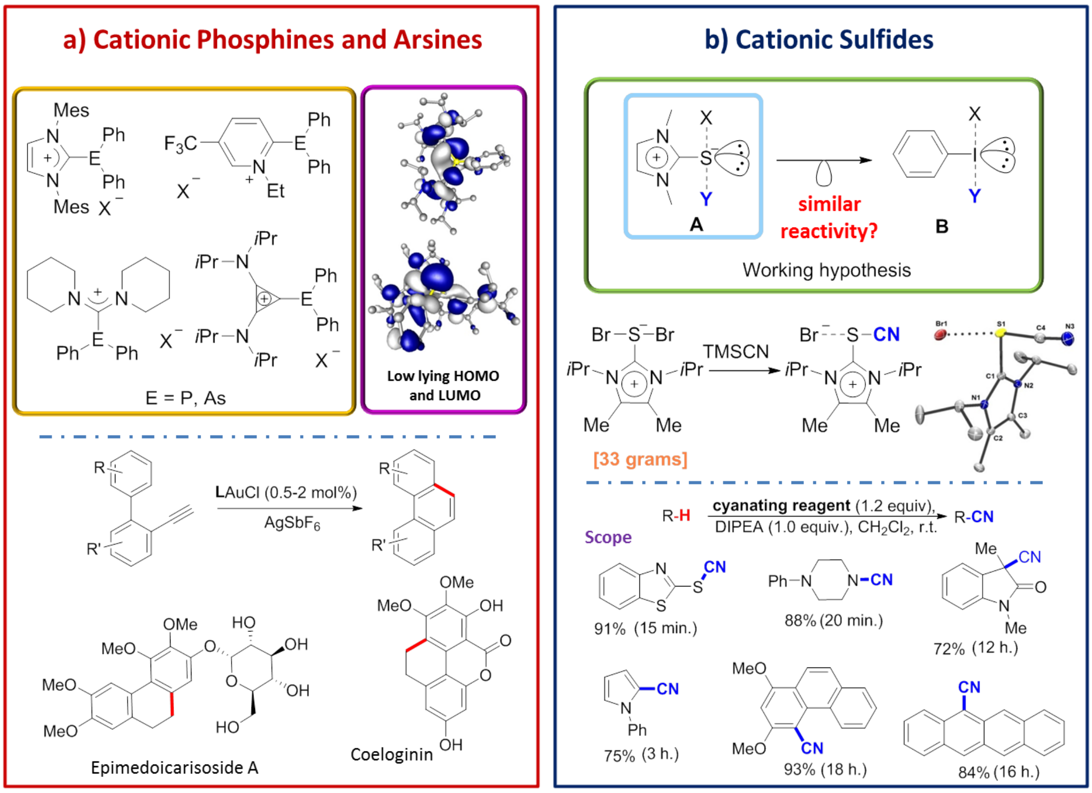

Figure 1: An overview of our research.

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“Cocktail” of catalysts in homogeneous and heterogeneous catalytic systems

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Fascinating development of transition metal catalysis created a new paradigm in organic synthesis towards preparation of functionalized molecules with atomic precision [1]. Detailed mechanistic studies have shown that homogeneous catalytic reactions, traditionally considered with monometallic active species, are in fact carried out in multicomponent reaction mixtures, which contain a number of metal species in solution. Participation of different metal species in the catalytic transformation initiates formation of “cocktail”-like systems [2]. Tuning of “cocktail” of catalysts provides outstanding opportunity to create dynamic and adaptive catalytic systems [3]. Heterogeneous catalysis may also involve formation of a number of active species that possess dynamic properties and interconversions on the surface [4].

The topics related to construction of efficient and selective catalytic systems based on easily available transition metal catalysts [5] will be presented and discussed.

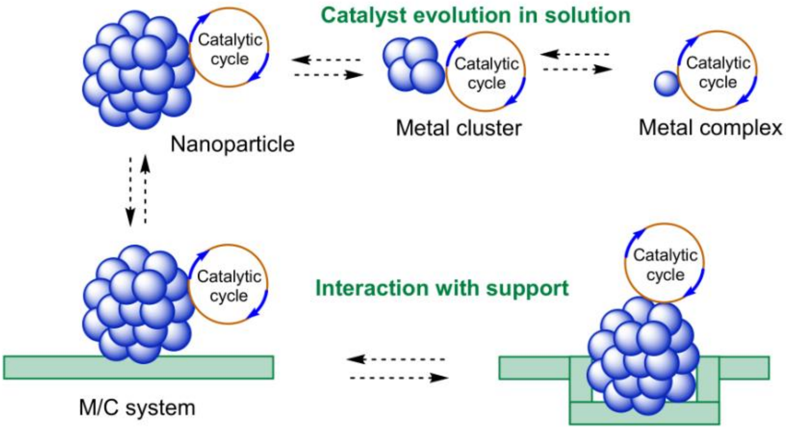

Figure 1 Catalyst dynamics in solution and on the surface of supported systems.

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Coordination Chemistry of PCP Pincer Iridium Hydrides

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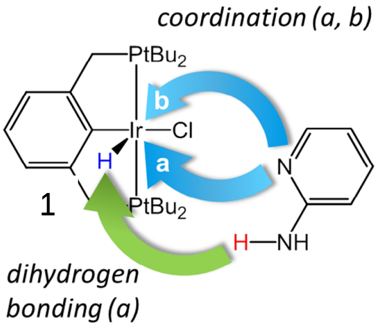
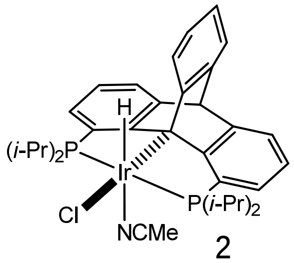
The transition metal complexes bearing pincer-type ligands have been extensively studied over the last decades.[1] Among them, (κ^3-PCP-pincer)-ligated iridium systems turned out being preferred for transfer dehydrogenation and acceptorless dehydrogenation catalysis.[2] So far, the most popular scaffold used to design pincer ligands relies on an aromatic moiety (PC(sp^2)P). The reports on the chemistry and practical applications of the aliphatic C(sp^3)-metalated pincer complexes are far less common.[3,4] We have studied the interaction of (^{tBu}PCP)IrH(Cl) (**1**) and (^{R}PC$_{sp3}$P)IrH(Cl) (**2**, **3**) with Et$_3$N, (amino)pyridines, CH$_3$CN, DMSO, CO in order to establish the nature of the interaction, the accessibility of the metal, preferred stereochemistry of the six-coordinated products and factors ruling such reactivity.[5,6] Our study unveiled the flexibility of the dibenzobarrelene-based scaffold **3** unprecedented for conventional "coordinatively rigid" carbometalated pincer ligands, as e.g. **1**. The results obtained allow discussing the fundamental aspects of the coordination chemistry of this class of compounds.





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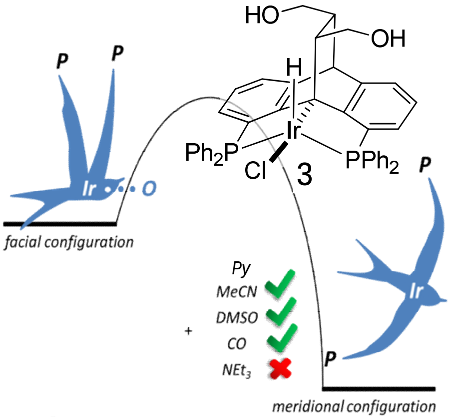

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Annulated and Abnormal: NHC Ligands in Oxidation Chemistry

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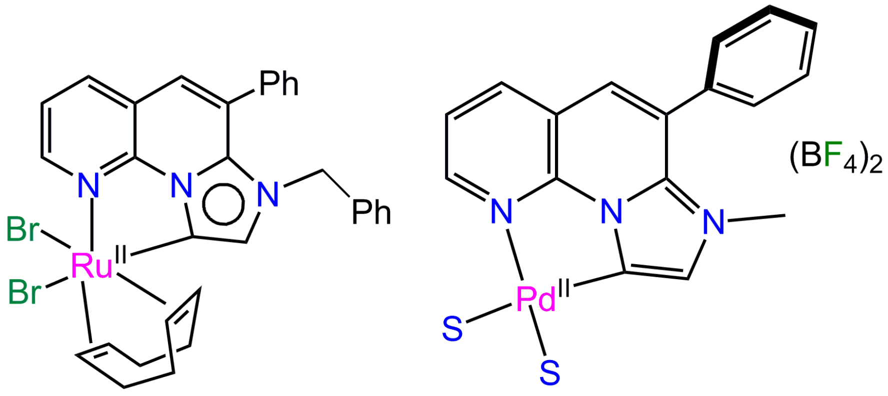
Metal-N-Heterocyclic carbene (NHC) compounds are less susceptible to decomposition under oxidative conditions and therefore considered suitable for oxidation chemistry. The C4/C5-bound mesoionic or abnormal NHCs (aNHCs) have superior σ-donating ability compared to C2-bound (normal) counterparts. Further, π delocalization in annulated systems provides higher conjugational stability compared to their non-annulated analogues. Combining both these traits, an annulated and abnormal NHC ligand based on imidazo[1,2-a][1,8]naphthyridine is designed and its Ru(II) and Pd(II) compounds are synthesized.[1,2] The Ru(II) complex is shown to be an a highly efficient catalyst for selective oxidative scission of olefins to aldehydes.[3] The Pd(II) complex is employed in copper-free Wacker type selective oxidation of alkenes to ketones. The scope of these compounds for oxidation chemistry is evaluated and the mechanism of action is ascertained. This talk will examine the utility of metal-NHC compounds for catalytic oxidation reactions.



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Efficient Rh-catalyzed C–H borylation of arenes under photochemical conditions

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Photocatalysis allows innovations in organic synthesis. Among the various catalytic reactions, CH-functionalizations offer valuable possibilities for the refinement of easily available building blocks. Especially the “waste-free” functionalization of arenes constitutes highly ambitious goals for synthetic methodologies. In fact, more and more researchers from academia and industry consider light as sustainable and “green reagent” in organic chemistry. In this respect, catalytic borylation is of interest, too for direct access to useful reagents for C-C cross-couplings. Here, we describe a new efficient synthetic route to aryl-boron derivatives using *trans*- $RhCl(CO)(PMe_3)_2$ as active photocatalyst. This novel approach allows the synthesis of a broad variety of borylated arenes and heteroarenes under mild conditions. Interestingly, we achieved high TON at low catalyst loading with improved turnover frequencies by simply using inexpensive pinacolborane (HBPin) as boron reagent and *trans*-$RhCl(CO)(PMe_3)_2$ as the photocatalyst. A catalytic cycle that relies on a Rh(I)–Rh(III) interconversion can be proposed.[1]

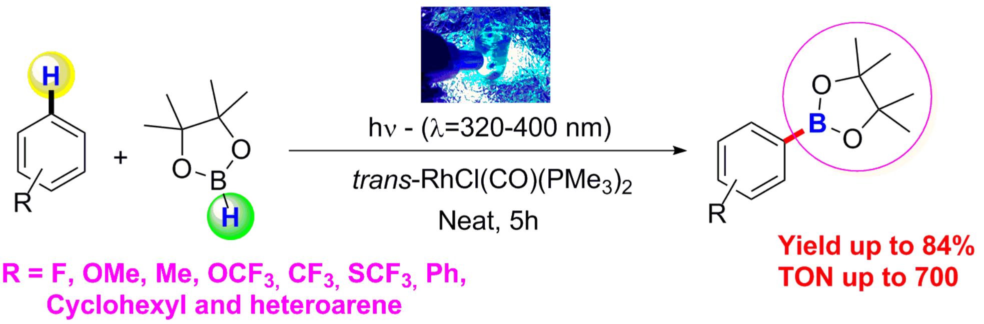

Figure 1 Photocatalytic C-H borylation

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Phosphane Diene (Arene)ruthenium Complexes: Synthesis & Catalysis

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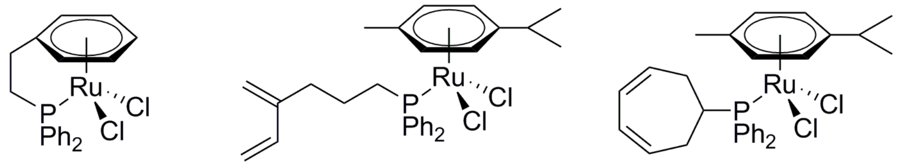
Arene-ruthenium complexes are known to be catalytically active for a wide range of reactions.[1] In some cases, these complexes are believed to release the arene ligand in situ, thus leading to highly reactive coordinatively unsaturated species.[2] This key intermediates may allow the coordination of the substrate and therefore the reaction to take place. One inconvenient is the low stability of these 12-electron species. Several groups have developed phosphane systems bearing a pendant arene complex leading to the corresponding chelating complexes (Figure 1; complex 1).[3] The main drawback of this strategy is the generation of over-stabilized complexes resulting in lower activity.



1 **2** **3**

Figure 1 Ruthenium complexes with phosphane arene and phosphane diene ligands

In view of these results, we decided to replace the pendant arene group with a potentially more labile function. We designed phosphane ligands with a diene group and synthesized the corresponding complexes (Figure 1; complexes 2-3).[4] We assessed their catalytic activity in atom-transfer radical addition (ATRA) and polymerization (ATRP), olefin cyclopropanation, ring-opening metathesis polymerization (ROMP), and enol ester synthesis.

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Copper(I) Catalyzed C-N Coupling: Mechanistic Insights

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There is a growing interest in copper based catalysis driven by the sustainability, low cost, and low environmental impact of this metal. This contribution focuses upon the role and function of copper(I) catalysts in C-N bond forming protocols. The structures and solution behavior of copper(I) amides are little reported in the literature despite their often cited role as intermediaries in the copper-catalyzed modified-Ullmann reaction. By preparing these complexes and identifying them as competent intermediates on the catalytic cycle we have been able to gain key additional insights into mechanism of the coupling reaction (Figure 1a).[1] These studies have been further augmented by additional Reaction Progress Kinetic Analysis (RPKA) experiments on the overall catalytic process, leading to a refined understanding of the catalytic cycle (Figures 1b,1c). Suggested improvements to the reaction protocols based upon this new understanding will also be presented.

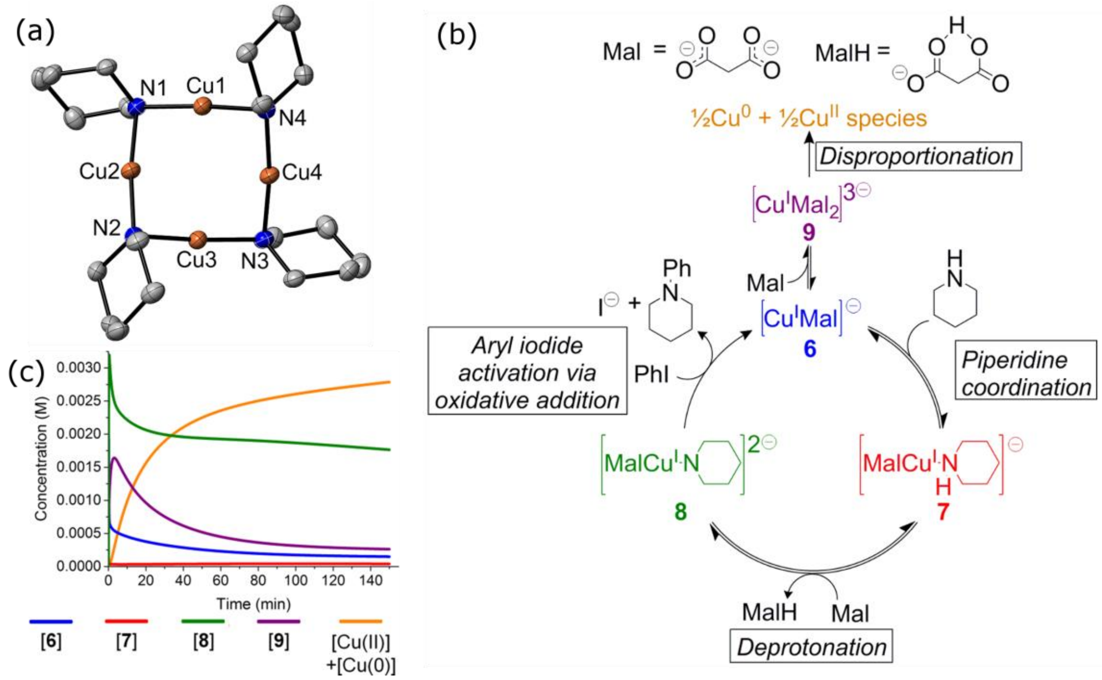

Figure 1. a) Solid-state structure of $[CuNC_5H_{10}]_4$; b) proposed catalytic cycle for Cu(I)-coupling of piperidine and iodobenzene based upon Reaction Progress Kinetic Analysis (RPKA) and NMR experiments; c) modelled concentration of copper species over time

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Low-Coordinate Iron and Cobalt Complexes with NHC Ligation: Synthesis, Reactivity, and Catalytic Application

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The knowledge on the formation, structure, and reactivity of low-coordinate transition-metal species lays the basis for modern organometallic chemistry. While the conventional wisdom of organometallic chemistry has been focusing on the noble metal complexes, the renaissance of base metal catalysis in the recent years urges a deeper understanding on low-coordinate 3d metal chemistry. This presentation will introduce our studies on low-coordinate iron and cobalt complexes with N-heterocyclic carbene (NHC) ligation. NHCs are found excellent ancillary ligands to stabilize iron(IV, III, II, I, 0) /cobalt(V, IV, III, II, I, 0) complexes with their coordination numbers ranging from 4 to 2 (Fig. 1).[1-3] The reactivity pattern of the low-coordinate species of oxidative addition, group-transfer, sigma-bond metathesis, and metal-carbon bond homoleptic scission will be discussed.

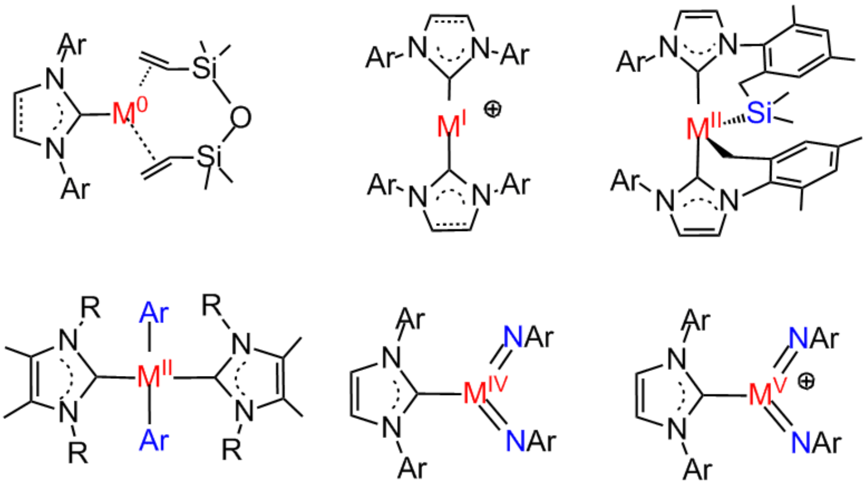

Figure 1 Representative Low-Coordinate Iron- and Cobalt-NHC Complexes

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Cooperative catalysis with redox non-innocent ligands

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Increasing concerns regarding sustainability and cost-related issues of noble metals are driving chemists to revisit the chemistry of first-row early transition metals (Fe, Co, Ni, Cu). Although widely used, these metals tend to be limited by their electronic structure, which makes them prone to mono-electronic transfers and limits their efficiency and selectivity.

An emerging area in catalysis is the use of redox non-innocent ligands, which can act as a storage and supply unit of electrons, allowing the metal to perform reactions once forbidden, thus imparting noble metal character and broadening the scope of their synthetic applications.[1] Catalytic relevance of these ligands is promising and new applications are being increasingly developed. Progress made in iron-catalyzed tandem catalytic C–H activation/arylation of unactivated arenes[3] and copper-catalyzed trifluoromethylation[4] will be presented.

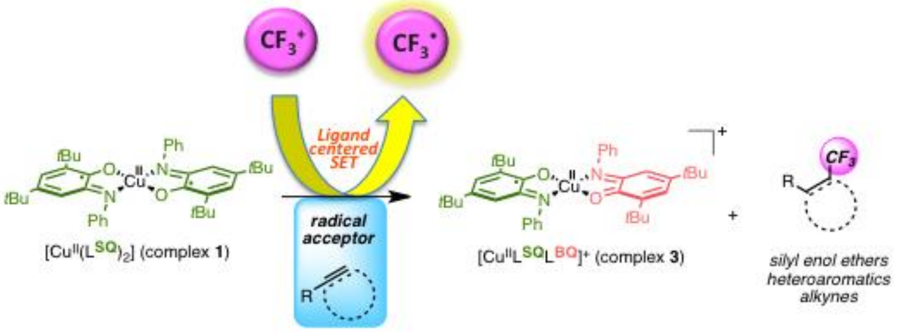

Figure 1 Copper-catalyzed radical trifluoromethylation sustained by redox ligand

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Reverse Alchemy: Turning Gold into a Transition Metal

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Gold catalysis is currently experiencing huge growth, and gold complexes have shown remarkable selectivity and conversion in a variety of complex transformations. Classical gold(I) cationic complexes almost exclusively adopt linear 2-coordinate environments. We have sought to develop ligands which force gold to adopt higher coordinations and/or 'unusual' coordination geometries, eliciting novel electronic and steric properties. We have developed a rapid and efficient synthesis of cationic bipyridine gold(I) alkene complexes from commercially available materials. Using this synthesis, we have been able to characterise a variety of derivatives of this type (figure 1).

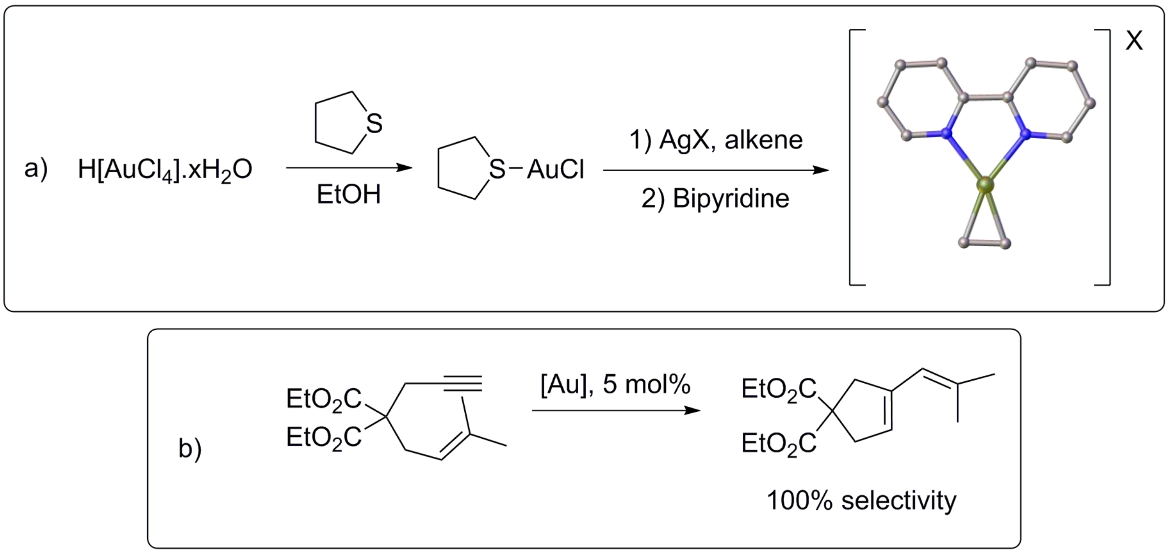

Figure 1. (a) Synthesis of bipyridine-gold(I)-alkene complexes; (b) Ene-yne cycloisomerisation

Gold(I) typically acts as a soft lewis acid, though in this complex significant back-donation occurs.[1] The NMR spectroscopy and bond lengthening in this class of compound is more akin to homoleptic platinum(0) alkene.[2] Herein, we report on a new synthesis and reactivity of these compounds, as well as some initial results of ene-yne cycloisomerisation catalysis.

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Propeller Catalysts - Asymmetric Chiral Induction

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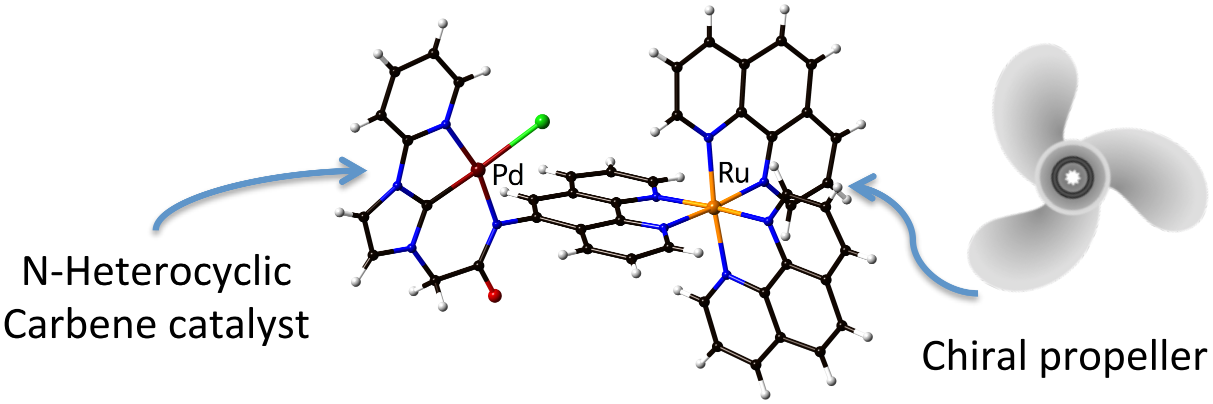
The requirement for the stereochemical purity of products in both small and large scale reactions has been a persistent challenge in the synthesis of organic molecules for the last 30 years, and remains an on-going problem for chemists. One common approach is to construct enantiometically pure catalytically active molecules that can control the steric environment around an active site to give only one enantiomer as the product from achiral starting materials. Typically control is exerted by use of a small organic molecule derived either from the chiral pool, or an atropisomeric fragment (eg BINOL), as part of a coordinating ligand, creating an enantiomerically pure metal complex.[1] We are interested in the potential of the propeller-based chirality of tris-chelated octahedral metal complexes a new source of chiral molecules for the formation of metal-based and organocatalysts. These helical fragments have been curiously underutilised for the formation of chiral catalysts despite their long history in the formation of chrial supramolecular aggregates.[2] To this end we have synthesised a series of phenanthroline based metal complexes (see figure 1) with pendant N-heterocyclic carbene functionality and investigated the potential for these complexes to catalyse a series of reactions to produce enantiometically pure products. A comparison of this approach to catalysts derived from camphor will be discussed.



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Iron Catalyzed Hydrophosphination: A comparative study of two highly active μ-oxo species

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Phosphines are important ligands for transition metal catalysis. Hydrophosphination can be used to access secondary and tertiary phosphines through a, potentially, 100% atom economic pathway. These reactions are most commonly catalyzed by Group 10 (Ni, Pd, Pt), Group 3 (Y) and lanthanide (La, Sm, Yb) metal salt reactions.[1]

However, seminal work from Gaumont *et al.* showed that iron salts can be used for hydrophosphination; we have subsequently shown that a simple iron(salen)-μ-oxo compound is able to catalyze the hydrophosphination of a variety of activated alkenes at room temperature and loading of 0.5 mol%.[2,3] We will further describe the catalytically active iron(porphyrin)-μ-oxo complex which, under similar conditions, shows a greater level of reactivity with more challenging alkene substrates. By increasing the loading to 5 mol% we have also demonstrated the hydrophosphination with phenylphosphine, a reaction mediated by only a handful of metals, can take place with relative ease.[4,5,6]

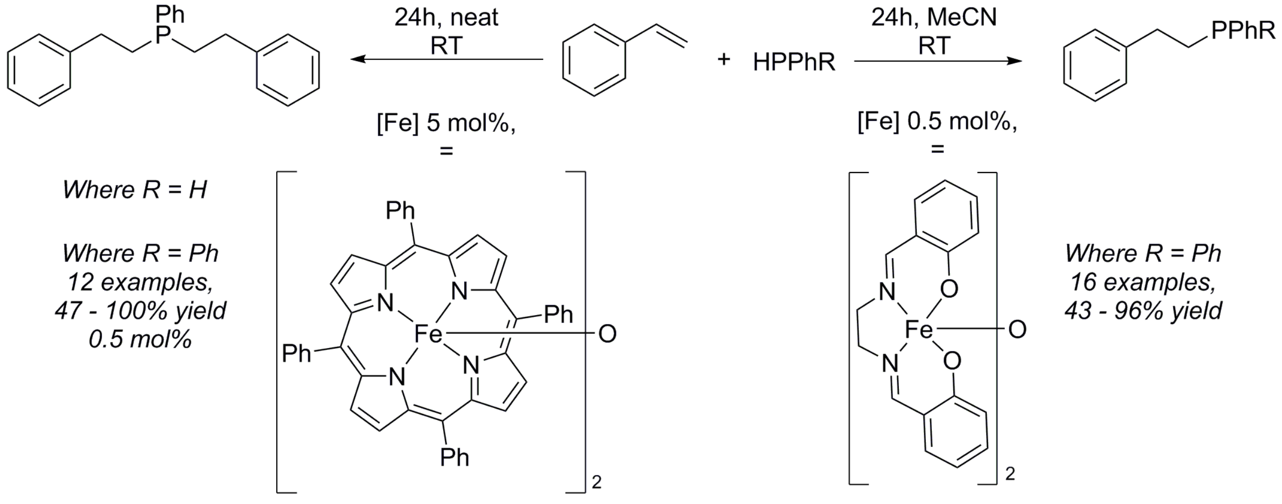

Figure 1 Hydrophosphination reactions with Fe-μ-oxo species

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C–X Bond Cleavage and Formation with Pd (*X = Br, Cl, S, F*): Oxidative Addition, Reductive Elimination, and Fluorination

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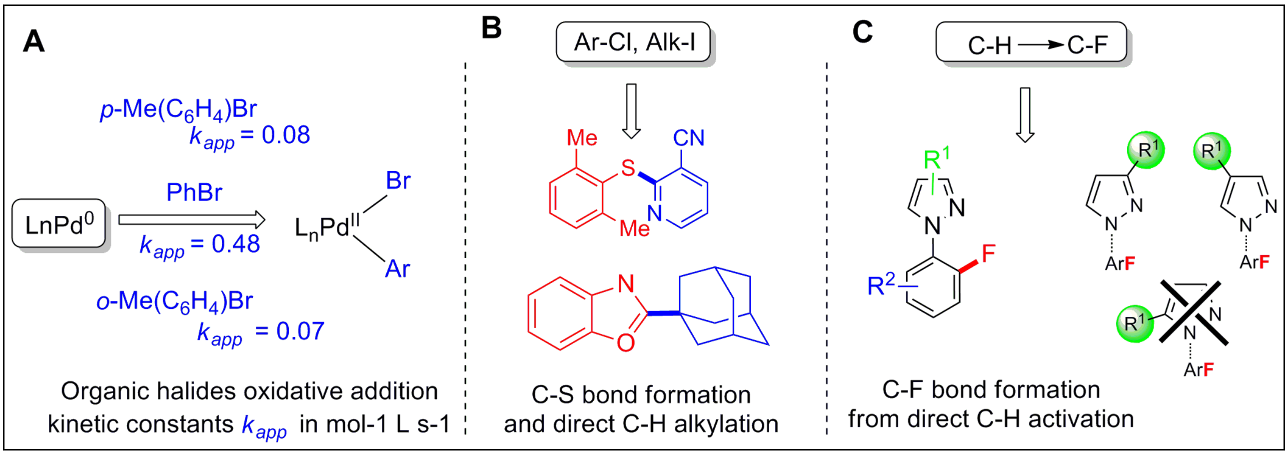
Oxidative addition (OA) of *sp*^{2}-C–X bonds (X = Br, Cl) to palladium is a ubiquitous fundamental step of metal catalysis directed towards organic synthesis. However, quantitative and comparative data (rates, kinetics) on these reactions are infrequent in the literature due to the lack of well-defined metal/ligand systems. *Ferrocenyl polyphosphines can give a powerful solution for measuring intrinsic data on bromo- and chloroarenes activation* (**A**).[1] These ligands are also useful for promoting efficient C–S bond formation and *sp*^{2}-C–H alkylation (**B**).[2,3] In the C–S bond formation *reductive elimination* (RE) from Pd was long-believed to be a decisive step, this is not always the case.[2] Finally, the C–F bond formation is one of the most challenging carbon-heteroatom construction at metal due to very demanding RE, yet new opportunities are developed from ligand-directed C–H functionalization, with however unrevealed limitations that can be elucidated by DFT (**C**).[4]



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NHC Effects on NiH Catalyzed Hydroalkenylation

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Catalytic unsymmetric preparation of synthetically valuable gem-olefins directly from simple olefins is a persistent challenge & interesting topic in chemistry. This is because the substrate pairs differentiation are difficult in terms of both chemo- & regio-selectivity, and the products are thermodynamically less stable. For those employ M-H as catalysts,[1,2,3] the isomerization & oligomerization problems are additional complications. Here we report our recent progress and solutions in the area by using NHC, and also the other interesting findings related to NHC-Ni bond and π-systems coordination.[4,5]

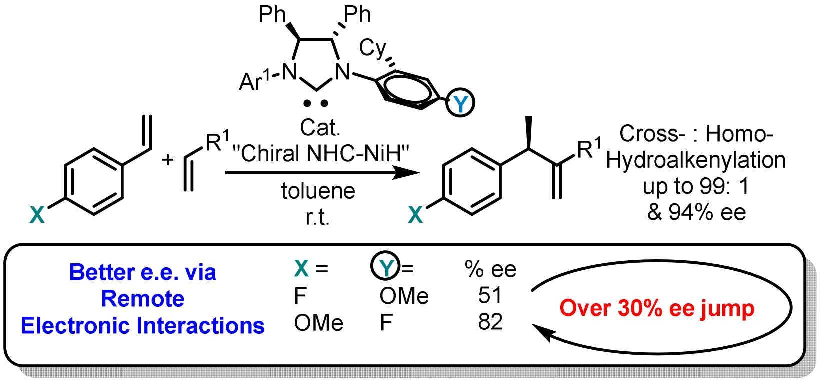

Figure 1 Synergistic Electronic Effect on NHC-NiH Cat. Asymmetric Hydroalkenylation

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Synthesis and catalytic activity of oxo-functionalised triazolylidene ruthenium(II) complexes

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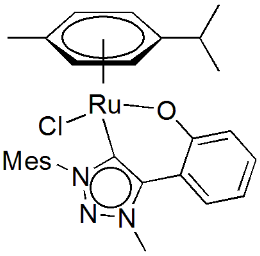
In recent years, mesoionic 1,2,3-triazolylidenes have emerged as a highly versatile subclass of N-heterocyclic carbene (NHC) ligands.[1] This NHC scaffold can be effectively tailored to specific functions as a consequence of the flexibility of the [3 + 2] cycloaddition of alkynes with azides. This feature, coupled with the ligands' stong σ-donor abilities have led to their diverse application in catalytic transformations.[2]

Here we present the synthesis of a range of oxo-functionalised triazolylidene ruthenium(II) complexes. The implications of this *C,O*-bidentate motif is discussed in terms of catalytic activity.



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A highly nucleophilic rhodium(I) pincer-catalyst for the selective isomerization of terminal epoxides to methylketones

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The chemistry of epoxides is of high relevance due to the good availability of synthetic methods for their synthesis.[1] The isomerization of epoxides, the so called *Meinwald*-rearrangement, is usually carried out by Lewis acids and leads to the respective aldehyde. However, [$Co_2(CO)_8$] was found to catalyze the rearrangement of terminal epoxides in methanol leading exclusively to the methylketone.[2] This can be explained by *in situ* formation of a Lewis acidic Co(+I) and nucleophilic Co(-I) carbonyl species.

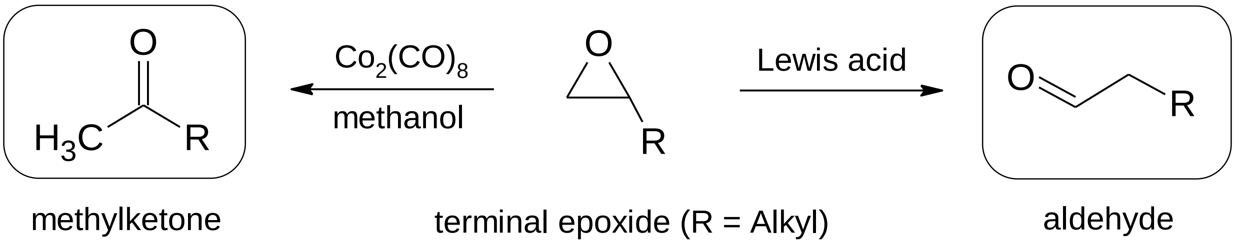
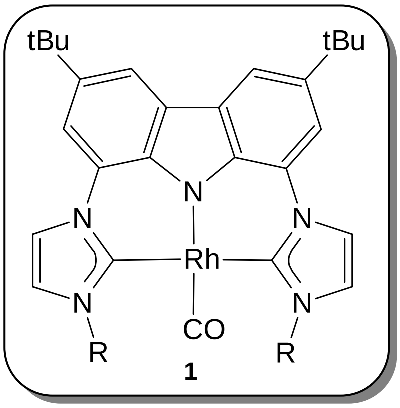


Figure 1 The *Meinwald*-reaction: catalyzed by $Co_2(CO)_8$ in methanol and Lewis acids.

We tested our [Rh(bimca^R)CO] complexes (**1**) in the *Meinwald*-reaction and found that they are highly active catalysts for the selective isomerization to the methylketones.[3] The reaction requires Lewis acids like Li^+ or Na^+ ions as cocatalysts as well as a non-polar solvent. We will also present our findings on the mechanism.



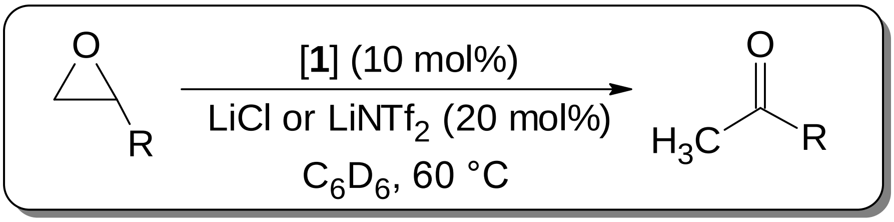


Figure 2: Formation of methylketones by catalyst **1** in benzene.

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Ruthenium Tethered Transfer Hydrogenation Catalysts

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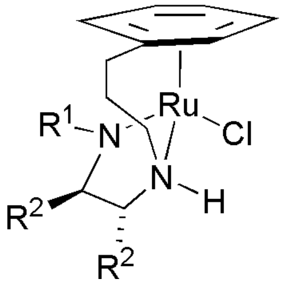
Noyori type catalysts with their bi functional mechanism have revolutionised homogeneous asymmetric catalysis by making possible the highly enantio- and chemo-selective reduction of so-called 'non functionalized' ketones. Wills 'tethered' catalysts, first described a decade ago, belong to the new generation of catalysts that work along the same mechanistic principle[1].



These catalysts provide a significant increased activity and robustness, which allow a facile application to the poly functionalized substrates of the life science industry. These catalysts can be used under both hydrogenation and transfer hydrogenation conditions and their use have been demonstrated in innovative reactions such as reductive amination of ketones to chiral primary amines. Johnson Matthey has developed these catalysts all the way from academic small scale demonstration to multi Kg synthesis and industrial commercial applications[2].

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Multinuclear Rh and Ru Complexes Based On Low Generation Dendritic Ligands As Catalyst Precursors In The Hydroformylation Of Alkenes

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Metal complexes based on dendritic ligands have in the last decade or so emerged as feasible alternatives to traditional catalysts derived mononuclear complexes[1]. The application of these metallodendrimers as catalyst precursors in a range of organic transformations has thus received increasing attention over the past few years[2]. In this paper we report on the development of novel multinuclear complexes of rhodium and ruthenium based on new low generation dendritic ligands and their application as catalyst precursors in the hydroformylation of alkenes. Examples of the multinuclear complexes employed in this study are shown in Figure 1.

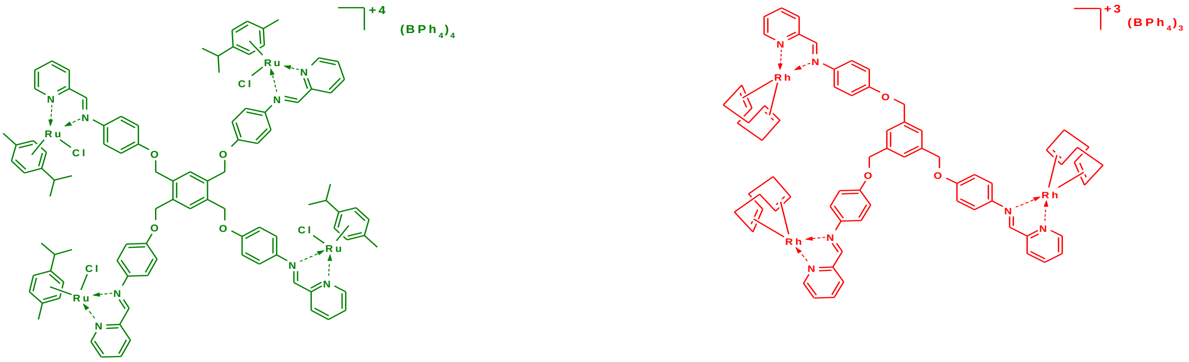

Figure 1: Some metallodendrimeric catalysts employed in alkene hydroformylation

Both the Rh and Ru dendrimeric complexes were found to be active hydroformylation catalysts with the dendrimeric catalysts outperforming simple model mononuclear analogues both in terms of selectivity and activity. It was however observed that under similar reaction conditions the Rh complexes were substantially more active than their Ru counterparts. Under mild reaction conditions it was found that alkene isomerization initially prevailed over the hydroformylation reaction leading to the detection of high levels of internal alkenes. The latter undergoes subsequent hydroformylation to form branched aldehydes. The impact of a range of reaction conditions on the overall outcome of the hydroformylation reaction was systematically investigated and the results in this regard are discussed here.

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Stable “anti-Bredt” diaminocarbenes: synthetic approaches and applications in organometallic catalysis

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N-heterocyclic diaminocarbenes (NHCs) have found widespread applications in homogeneous catalysis. However, they still suffer from low modularity, which confines them to a narrow range of strong σ-donor ligands, with little π-accepting character. Recently, we described a new stable NHC (see figure below), in which one of the two nitrogen atoms is placed in a strained bridgehead position.[1-2] This very simple topological modification prevents the donation of the nitrogen lone pair and results in significantly enhanced π-accepting properties, while the σ-donation of classical NHCs is preserved.

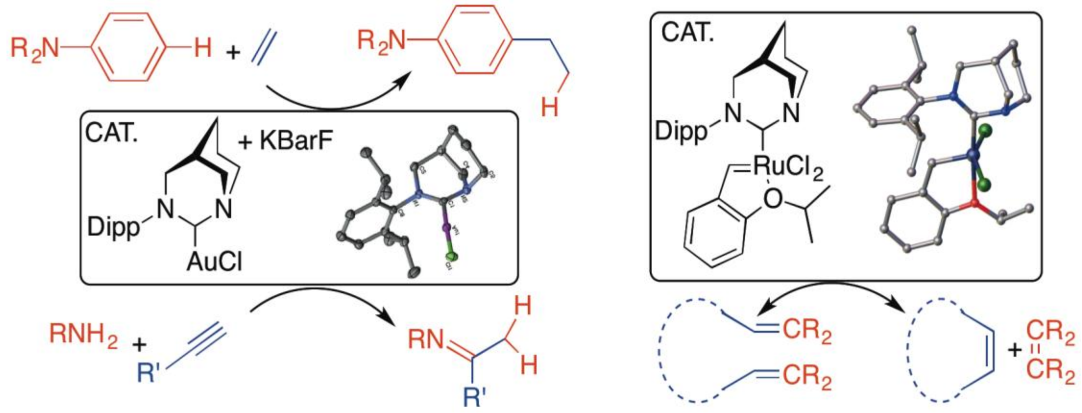

Figure 1: Gold an Ruthenium complexes of anti-Bredt NHC as catalysts

We will present the originality and the potential of this new family of ancilliary L ligands, but also some of their intrinsic limitations. We will showcase the use of anti-Bredt diaminocarbenes for gold(I)-based catalysts, especially for challenging intermolecular hydroaminations of alkynes and hydroarylation of alkenes with di(alkyl)anilines.[3,4] The added value of these ligands in Ru-catalyzed olefin metathesis will be also discussed.[5]

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Asymmetric hydroamination of alkenes: effects of silver, anion and solvent on Gold(I) catalysts.

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Achieving highly selective gold catalysed hydroamination of alkenes, activated or not, remain challenging[1] and we would like to report herein our last results.[2] Following our researches on activated alkenes[2a] and allenes,[2b] the intramolecular gold(I) catalysed asymmetric hydroamination of alkenes was studied screening a wide range of phosphines (Figure 1). Specially designed phosphoramidite ligands proved to lead to active mononuclear gold(I) catalysts when combined with silver salts.[2c] Regarding binuclear gold(I) catalysts, a specific gold(I) complex proved to perform efficiently the intramolecular hydroamination of alkenes at mild temperatures with high yields and enantioselectivities.

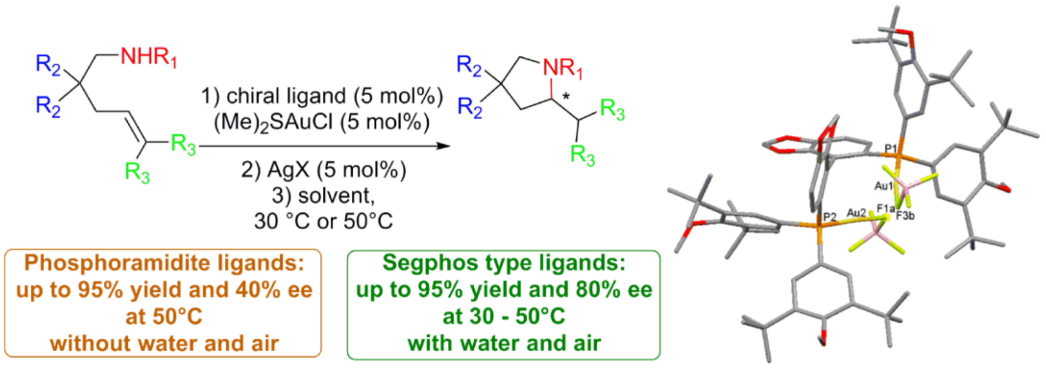

Figure 1. **Asymmetric hydroamination of alkenes catalysed by Gold(I) complexes.**

Interestingly, the stereochemical outcome of the hydroamination reaction appeared to depend on the polarity of the solvent used. Moreover, due to a Hofmeister effect of the catalyst's anion, the presence of water proved to enhance reaction yields. The effect of parameters like solvents, silver salts and anions on the catalysis was studied by X-ray diffraction analyses, diffusion ^{1}H NMR, mass spectrometry and DFT calculations.[2d-f]

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Diastereotopic Complexes of $HP(OC_6H_4NMe)_2$ with Pd(II), Pt(II) and Rh(I) with Applications as a Hydrosilylation Catalyst

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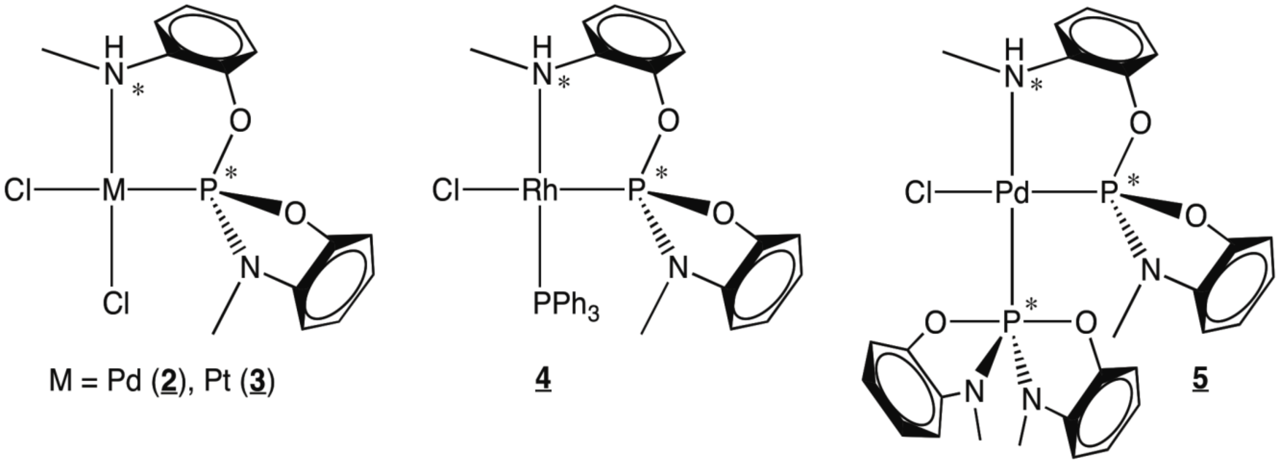
Reaction of the hydrophosphorane $HP(OC_6H_4NMe)_2$ (**1**) with $[MCl_2(NCPh)_2]$ gives the diastereotopic complex *cis*-$[MCl_2\{P(OC_6H_4NMe)(OC_6H_4NHMe)\}]$ where M=Pd (**2**), Pt (**3**). Likewise **1** reacts with $[RhCl(PPh_3)_3]$ to give $[RhCl(PPh_3)\{P(OC_6H_4NMe)(OC_6H_4NHMe)\}]$ (**4**) (Figure 1), that has been characterized by X-ray crystallography. In **2**-**4**, the hydrophosphorane coordinates in its tautomeric form, as a bidentate, neutral phosphoamidite-amine ligand. In addition, **2** reacts with $LiP(OC_6H_4NMe)_2$, to give $[PdCl\{P(OC_6H_4NMe)_2\}\{P(OC_6H_4NMe)(OC_6H_4NHMe)\}]$ (**5**), that is observed to undergo Berry pseudorotation about the P(V) centre. Compound **4** is found to be an effective catalyst for the hydrosilylation of 1-octene and 1-hexyne with $HSiMe_2Et$, $HSiMe_2Ph$, $HSiEt_3$, $HSiOEt_3$.



M = Pd (**2**), Pt (**3**)

4

5

Figure 1. Diastereotopic Complexes **2**–**5**.

Structure, Bonding and Mechanism in Iron-Catalyzed Cross-Coupling

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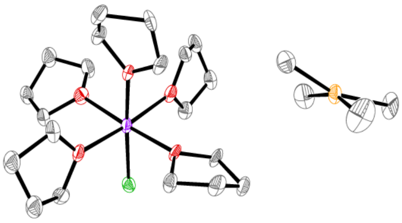
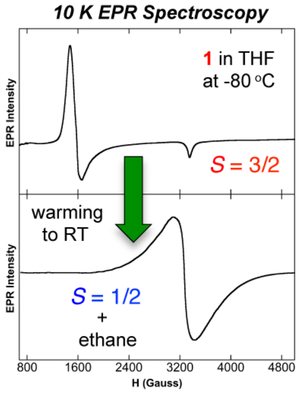
Despite the success of iron-based catalysts for cross-coupling, a detailed molecular level understanding of these systems has remained elusive. This limitation is in stark contrast to palladium chemistry, where detailed studies of active catalyst structure and mechanism have provided the foundation for the continued design and development of catalysts with novel and/or improved catalytic performance. The use of an experimental approach combining advanced inorganic spectroscopies (Mössbauer, magnetic circular dichroism, electron paramagnetic resonance), density functional theory studies, synthesis and kinetic analyses enables the direct evaluation of the active iron species and insight into the mechanisms of catalysis in iron cross-coupling. Previous studies from our group using this approach have established the active iron species in iron-bisphosphine catalysed cross-coupling of mesityl Grignard and primary alkyl halides[1] as well as phenyl nucleophiles and secondary alkyl halides.[2] Of particular interest are iron-catalyzed cross-couplings with simple ferric salts where we have previously reported the isolation and characterization of $[MgCl(THF)_5][FeMe_4]$, an intermediate in the reduction pathway of simple ferric salts with methylmagnesium bromide.[3] This presentation focuses on recent results from our group on the isolation, characterization and reactivity of iron-ate species of relevance to cross-coupling.



$[MgCl(THF)_5][FeMe_4]$ (**1**)



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Ruthenium catalyzed transfer hydrogenation of nitriles, N-heterocycles and olefins

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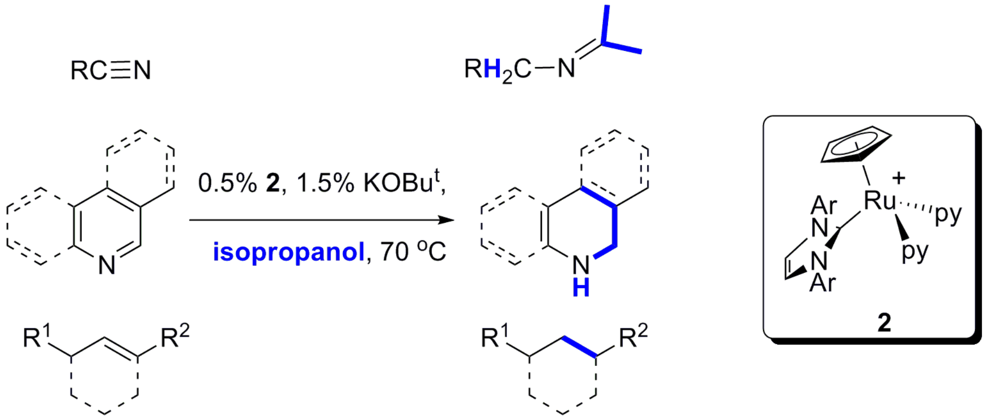
Transfer hydrogenation (TH) from alcohols and formates has emerged as a powerful method for the conversion of unsaturated organic molecules into value added products. The prevailing substrates for catalytic TH are ketones and imines, whereas applications to other unsaturated systems are much less known. The Beller group[1] and our group[2] have recently reported the application of ruthenium complexes to the TH of nitriles to amine and imines, respectively. In this presentation we report new ruthenium complexes which are more efficient catalysts for the transfer hydrogenation of nitriles, and can be also used for the reduction of heterocycles and olefins.



Scheme 1 Transfer hydrogenation catalysed by **2**

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Reaction of $Fe(acac)_3$ and ArMgBr: Competing precatalysts in iron-catalyzed cross-coupling reactions?

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Cross-coupling of an alkyl or aryl halide with an aryl Grignard commonly employs palladium catalysts. More recently, iron catalyzed reactions employing FeX_3 or $Fe(acac)_3$ have recently attracted significant attention because of possible improvements in efficiency, economy and environmental benefits.[1,2] Despite the importance of this reaction, obtaining mechanistic information has proven challenging, in part due to the sensitivity of the iron species formed *in situ*.[3] Suggested catalytically active species include low-valent mononuclear iron species or “inorganic Grignards” of form $[Fe(MgX)_n]$ (n = 1 or 2), although there is little experimental evidence for these species.[4,5,6]

In this talk we will discuss our recent work examining the products generated by the stoichiometric reaction of $Fe(acac)_3$ with ArMgBr. A complex product mixture is generated, with two distinct iron(II) species formed; $Fe(acac)_2$ and an iron-magnesium complex (see figure 1). The iron products have been isolated, and characterized by ^1H NMR and IR spectroscopies and X-ray crystallography. Importantly, the same product mixture is generated for all aryl Grignards we have used, suggesting that two different iron precatalysts are formed in the initial mechanistic step for cross-coupling. In order to probe whether the formation of two iron(II) species results in competing catalytic cycles, their performance as catalysts in cross-coupling reactions has been evaluated.

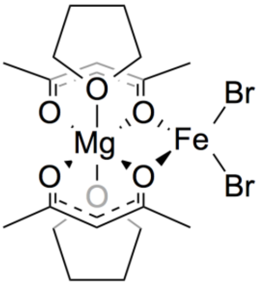

Figure 1 Structure of $(THF)_2Mg(acac)_2FeBr_2$.

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Homogeneous catalysts with Polyaromatic ligands. Effects of π-stacking

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The choice of a ligand to build a metal complex is often considered to be restricted to its well-defined stereoelectronic properties, and this is why great attention has been paid to the study of the steric and electronic properties of the ubiquitous N-heterocyclic carbenes (NHCs).[1] However, little has been made in order to design homogeneous catalysts with multifunctional NHC-based ligands. Exploring the addition of organic additives that may enhance the reactivity is also important, because some organic molecules added to the homogeneously catalysed reaction may facilitate the stabilization of transition states or modify the reactivity pattern of the substrates.

The use of NHC ligands with extended polyaromatic systems has given rise to families of metal complexes whose properties are influenced by the π-stacking affinities of the substrates with the ligands.[2a,2b] We tried to rationalize the effects of π-stacking on the catalytic properties of a series of catalysts decorated with extended polyaromatic systems, and proved that the addition of π-stacking additives, such as pyrene, had important influences on their catalytic performances.[3]

In this presentation we will try to unveil the reasons governing the influence of π-stacking in some homogeneous and heterogeneously catalysed reactions, and will demonstrate that π-stacking should be taken into account when using catalyst with extended polyaromatic systems.

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Ammonia-borane dehydrogenation mediated by transition metal complexes for H_2 storage and production

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Chemical hydrogen storage with small lightweight and hydrogen-rich molecules like ammonia-borane ($NH_3{\cdot}BH_3$, AB, 19.3 wt.% H_2) or amino boranes of general formula $RNH_2{\cdot}BH_3$ (R = alifatic chain or cycle) is a topic of great interest, as witnessed by the exponential growth of the number of papers published in the recent literature.[1] Transition metal complexes can catalyze H_2 release from these species under mild conditions and offer great potential as H-storage materials. The reactions of assorted Ir(I), Pd(II) and Ru(II) polyphosphine (Figure 1) and *pincer* type complexes with AB and amine boranes have been analyzed experimentally through variable-temperaure multinuclear (^{11}B, ^{31}P, ^{1}H) NMR spectroscopy, kinetic rate measurements and kinetic isotope effect (KIE) determination with deuterated isotopologues. At the same time, a DFT modeling of the reaction mechanisms has been carried out, starting from the experimental data available. The results will be presented.[2]

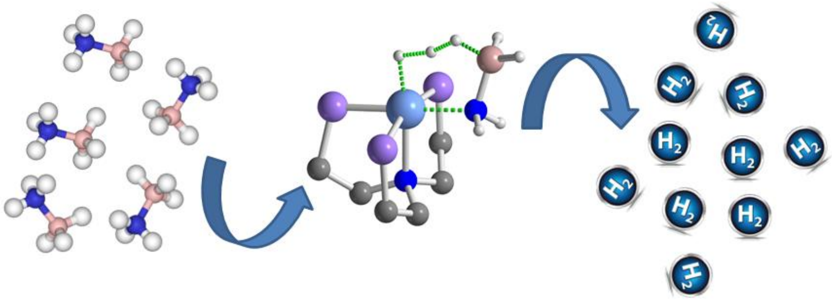

Figure 1 Homogeneous AB dehydrogenation with the classical hydride $(NP_3)Ru(H)_2$.

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Iron N-heterocyclic carbene complexes containing N- and S-based ligands

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The field of iron N-heterocyclic carbene (NHC) chemistry has attracted increasing interest during the last decade.[1,2] The low price, high abundant, and non-toxicity of iron, along with the great popularity of NHC ligands in catalysis have motivated the growing interest in this area of research. During the last few years, our research group has developed Fe(II) and Fe(III) complexes bearing chelating cyclopentadienyl-NHCs, and Fe(0)-NHC carbonyl complexes as catalysts for hydrosilylation and hydrogen transfer reactions.[3-6]

In this contribution, results from our recent works on the synthesis and characterisation of iron NHC complexes containing N- and S-based ligands will be reported. These include the preparation of (bis-NHC)FeI_2(bipy) and (bis-NHC)FeI_2(phen) (bipy = 2,2´-bipyridine; phen = 1,10-phenanthroline) and pincer-type thiophene-functionalised bis-NHC complexes of iron (Figure 1), and their application in the catalytic oxidation of alcohols. Stability of the new iron complexes in different solvents, and their reactivity with oxidants such as H_2O_2 and TBHP (*tert*-butylhydroperoxide) will be discussed.

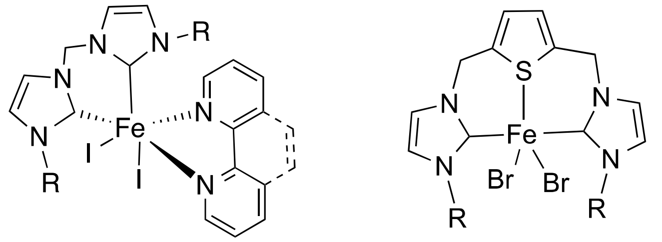

Figure 1 Iron-NHC complexes

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Assessing the redox non-innocent character of 4,5-bis(dimethylamino) imidazol-2-ylidene ligand

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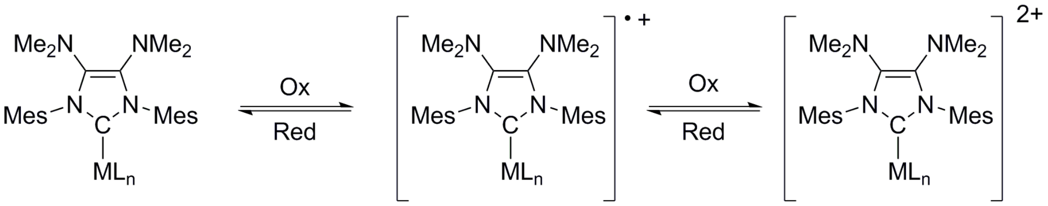
Redox non-innocent ligands have gained considerable significance in homogeneous catalysis due to their ability to act as electron reservoirs across the catalytic cycle.[1] However, even if N-Heterocyclic Carbenes (NHCs) were shown to feature such a property,[2] only few examples of redox non-innocent NHCs exist in literature.[3]

Continuing our research effort on backbone-functionalized NHCs,[4] we disclosed in 2014 a new type of NHC with improved catalytic efficiency in Pd-catalyzed amination, namely the 4,5-bis(dimethylamino)imidazol-2-ylidene IAr$^{(NMe_2)_2}$.[5] We now present our progress towards the assessment of the redox properties of this NHC.



A complete study was carried out on the archetypal 1,3-dimesityl-4,5-(bis(dimethylamino)imidazol-2-ylidene, IMes$^{(NMe_2)_2}$. Several organic compounds as well as transition-metal complexes based on this NHC were synthesized and characterized, and their redox properties were thoroughly evaluated by electrochemistry and EPR spectroscopy, complemented by DFT calculations.

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Metal-induced Cavitand Cracking

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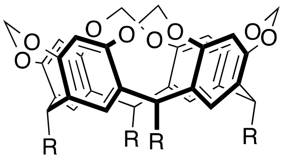
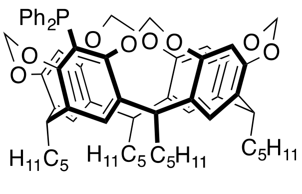
Resorcinarene-derived cavitands having all pairs of neighbouring resorcinol units linked through methylene bridges are frequently employed as rigid building blocks for the construction of functionalised, bowl-shaped molecules suitable for applications in supramolecular and coordination chemistry.[1]



rigidified cavitand



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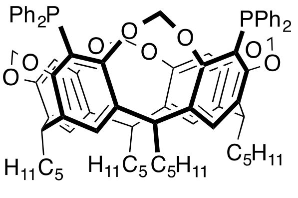

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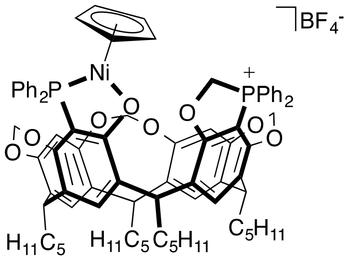

3

Cavities of this type are generally regarded as structurally very robust. However, we have now found that phosphino-cavitands **1** and **2**, when reacted with coordinatively unsaturated metal ions (ruthenium, palladium, nickel) resulted in phosphino-phenolato chelate complexes in which the macrocyclic core had undergone breaking of one of the two C–OCH_2 bonds adjacent to the P-substituted resorcinol unit(s).[2] A nickel complex containing such a ligand was found to catalyse the oligomerisation of ethylene into short α-olefins, thus strongly contrasting with the behaviour of Keim's ethylene oligomerisation catalyst [Ni($Ph_2PCHC(O)Ph$)Ph(PPh_3)], which leads to longer chains.[3]

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Di-zinc Lactide Polymerization Catalysts: Hyper-Activity by Control of Ligand Conformation and Metallic Cooperativity

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Developing new catalysts for racemic lactide (rac-LA) ring opening polymerization (ROP) is important to understand the key features controlling the production of the biodegradable polymer and to improve its physical and chemical properties. Our focus has been to investigate zinc catalysts and recently, we reported dizinc bis(ethyl) macrocycle pre-catalysts which showed good rates in rac-LA ROP.[1] One limitation was that an induction period was observed due to the slow reaction of the Zn-Et with alcohol sources to generate the active alkoxide initiator. Here, new di-zinc bis(amido) pre-catalysts are synthesized, and are shown to rapidly form alkoxide complexes upon addition of alcohol. The structure-activity relationships of two di-Zn bis(amido) macrocycles, differing in ring sizes, and their corresponding alkoxides are explored.

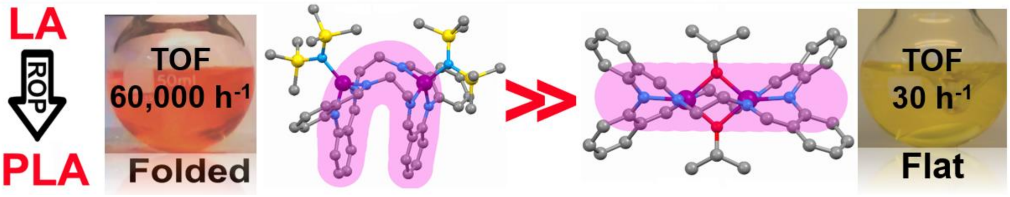

Figure 1 Dependence of the catalytic performance on the catalyst structure

The activity of the series is remarkably high, being more than an order of magnitude higher than the other known zinc catalyst under comparable conditions (Fig. 1).[2] The catalysts are highly tolerant and maintain high activity even at very low catalyst loading (≥ 0.002 mol %). The catalysts show high levels of control affording aliphatic polyesters with controlled molecular weights and narrow dispersities. Catalyst comparisons reveal that the structure of the complex exerts a strong effect on the rate of the polymerization (Fig. 1). There is a positive effect of two metal centres being in close proximity; the dinuclear macrocyclic catalysts are significantly better than their mononuclear acyclic analogues.

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Metal Complexes Based on Polydentate Ligands: Synthesis, Structure, Application in Catalysis

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In this work the synthesis of various polydentate ligands (*O*,*N*,*O*-, *N*,*N*,*O*-, *N*,*N*,*N*-, *O*,*N*,*N*,*O*-type), the complexes[1,2] of Zn, Al, Ti, Si, Ge(II), Sn(II), Pb(II) with these ligands (Figure 1, a) is described. The structures of the compounds obtained (NMR, XRD) and their catalytic activity in the polymerization of lactones was investigated. New strategy for polymerization and synthesis of macromonomers is developed[3] (Figure 1, b).

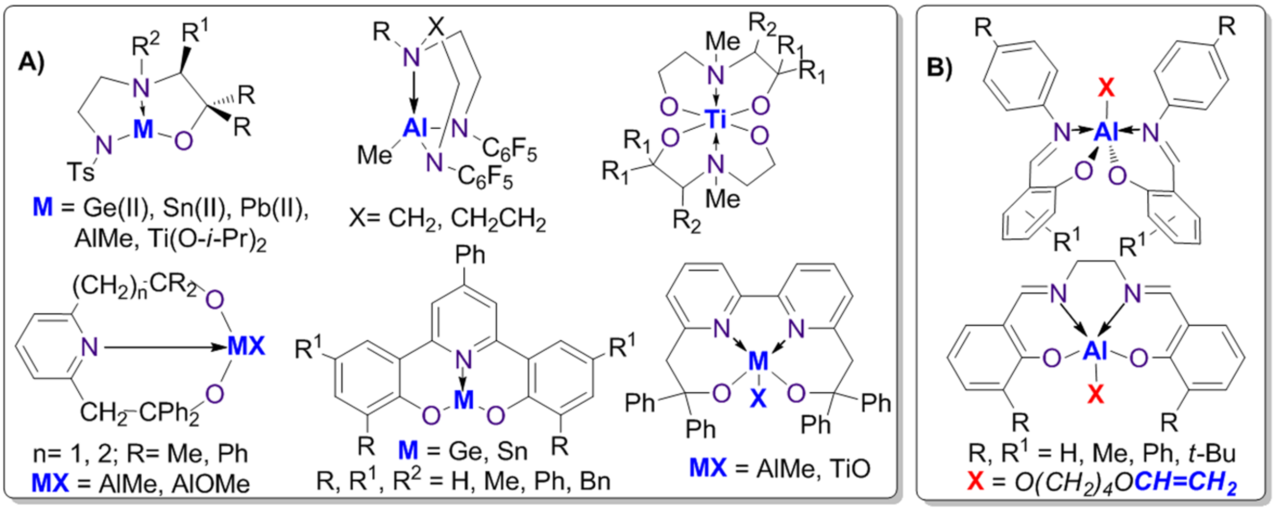

Figure 1 A) Structures of complexes studied; B) Precursors for the macromonomers.

Acknowledgement to the R.S.F. (project № 14-13-01456) for partial financial support.

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Iron-catalyzed CO_2 reduction to bis(boryl)acetal and subsequent functionalization

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CO_2 is an attractive source of carbon because it is abundant and rather non-toxic. Despite its high thermodynamic stability, CO_2 has been reduced to HCOOH, CO, CH_3OH and CH_4 under mild conditions.[1] We recently completed this C1 list with the characterization and selective trapping of CH_2O by using ruthenium polyhydride catalysts.[2] The next challenge is now to transform CO_2 into more complex and thus more valuable molecules while using earth abundant catalysts.

In this presentation, we will disclose the selective hydroboration of CO_2 into bis(boryl)acetal compound. This controlled 4-electron reduction is very efficiently catalyzed by an iron dihydride complex under mild conditions (25°C, 1 atm of CO_2, t < 1h). The subsequent transformation of the generated bis(boryl)acetal in the same pot affords a large variety of products featuring C-N, C-O and even C-C bonds.[3]

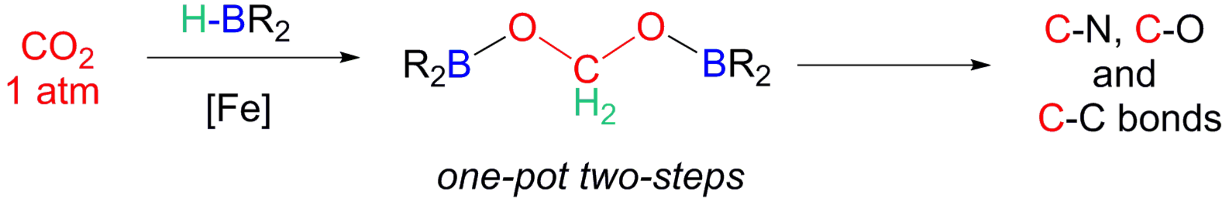

Figure 1: One-pot two step strategy

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The Chelated-Assisted Functionalization of C-H Bonds

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The transition-metal-catalyzed functionalization of C-H bonds is emerging as a powerful method for C-C bond formation and has received a great deal of attention in recent years. The regioselective functionalization of C-H bonds can be achieved by chelation-directed metalation with directing groups. The role of the directing group is to accelerate the reaction by bringing the catalyst in close proximity to the C-H bond. In addition, the directing group can also have an effect on the reaction mechanism. In this sense, the design of new types of directing groups still continues to be an important issue for the development of new types of functionalizations of C-H bonds, although a wide variety of functional groups has already been developed so far. Herein, I describe some nickel- and rhodium-catalyzed functionalization reactions of C-H bonds,[1,2] in which the reaction mechanism changes depending on the nature of the *N,N'*-bidentate directing group used such as a 2-pyridynylmethylamine and 8-aminoquinoline.[3]

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Dinuclear Chemistry and Catalysis with Redox-Active Ligands

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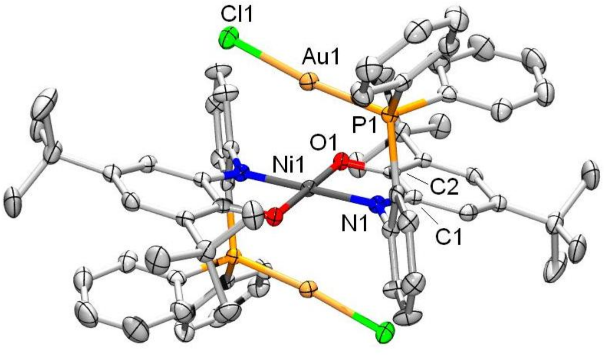
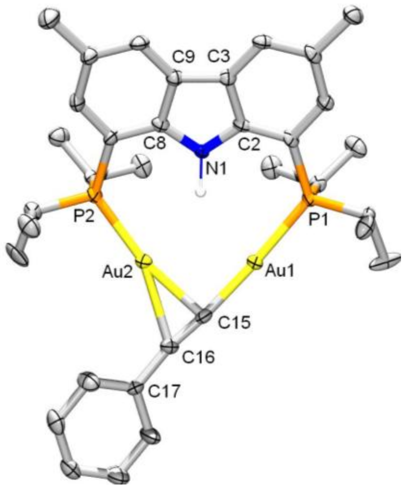
Redox-active ligands are emerging as a versatile strategy to infer e.g. base metal reactivity onto closed-shell noble metals by acting as an electron reservoir.1 We introduced novel redox-active tridentate ligand designs, with NNO and PNO donor sets, that show fascinating reactivity in the coordination sphere of mononuclear palladium(II).2 However, the coordination chemistry of redox-active ligands with di- or trinuclear transition metal architectures is nascent. This is even more true when considering ligand- or metal mixed valent situations. This contribution will discuss two lines of research within our group: i) homo- and heterobimetallic constructs with amidophenolate based scaffolds, and ii) dinuclear gold complexes with dinucleating redox-active PNP scaffolds. The former are ideal platforms to study ligand-to-ligand or metal-through-ligand-to-metal electron transfer processes, e.g. for catalytic C-X activation of alkyl halides. The latter are amenable to selective hydroaddition reactions by virtue of specific σ,π-acetylide coordination. The intricate reactivity of these heterobimetallic species, their electronic structure and spectroscopic features will be highlighted, as well as exciting results from catalytic studies.





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Inorganic Photoredox Catalysis Applied to Organic Synthesis: Trifluoromethylation of Unsaturated Hydrocarbons

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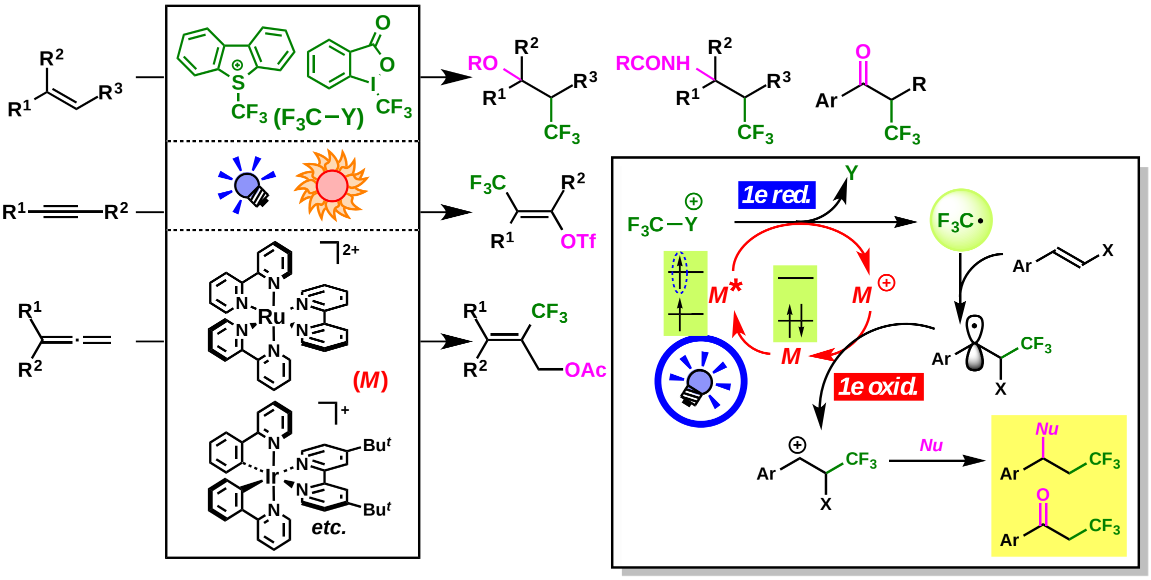
The sun provides huge and inexhaustible energy and has been regarded as a source of clean energy. While much effort has been devoted to development of transformations of small inorganic molecules promoted by visible light (sunlight) (e.g. water splitting and CO_2 reduction), little attention has been paid to application to organic transformations. During the last decade several research groups including us have developed organic "photoredox catalysis" using the photo-harnessing $[Ru(bipy)_3]^{2+}$ and related Ir species (denoted as ***M***), which is based on the unique redox properties of their photo-excited species.[1]

Visible light irradiation of ***M*** generates the excited species ***M**** with two SOMOs, which can promote oxidation and reduction of external substrates via SET processes in one catalytic cycle (reductive and oxidative quenching cycles) with no need of addition of any sacrificial reagent (*redox-neutral*) to generate two types of radical species, ***D***$^{+\cdot}$ and ***A***$^{-\cdot}$, regarded as versatile synthetic intermediates.

We have developed a series of catalytic *green* transformations of unsaturated hydrocarbons via oxidative quench cycle, in particular, *trifluoromethylation*,.



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Homogenously Catalyzed Functionalizations of Renewables: New Developments in Oleo- & Terpene Chemistry

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Homogeneous transition metal catalysis plays a major role in the valorization of renewable substrates, particularly in the transformation of oleochemicals and terpenes. Numerous methods do exist for the functionalization of those, tailored for the functional group to be attached and the moiety to be converted.

This contribution will give a survey of recent developments in our research group in the context of both laboratory investigations and their scale-up in continuously operated miniplants. This comprehensive evaluation from the chemists' and the engineers' side is a special characteristic, and features decisive advantages, as will be pointed out in this talk. Special emphasis will be payed to potential catalyst recycling *via* different physicochemical methods and the implementation of alternative reactor concepts. Two typical representatives of terpenes and fatty acid methyl ester will exemplify the discussed reactions: β-myrcene and methyl oleate (Figure 1).

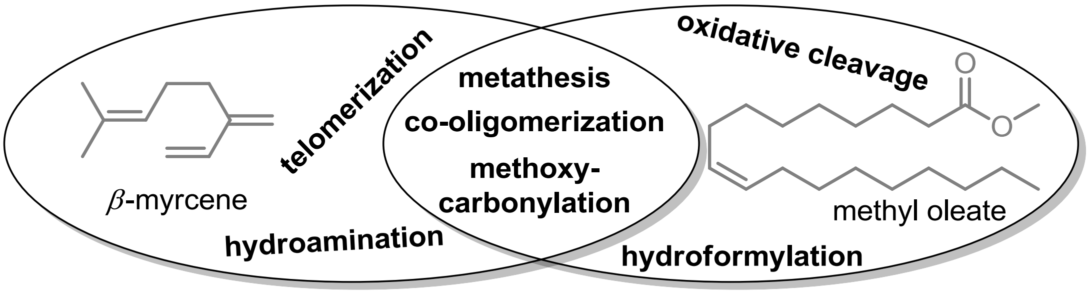

Figure 1 Homogeneously catalysed functionalizations of renewables to be presented

Our developed chemistry of renewables will be discussed in the context of relevant literature and potential applications as well as remaining challenges will be presented.

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Be Green! Sustainable Catalysis for Making Bulk and Fine Chemicals

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Abstract:

Despite numerous important methodological advancements in all areas of chemistry, still most organic synthesis as well as the industrial production of chemicals can be improved. Currently, more than 80% of all products of the chemical industry are made via catalysis. In this regard, the development of new and more efficient catalysts constitutes a key factor for achieving a sustainable production of all kinds of chemicals today and in the future. Here, several major challenges will be presented in the talk; e.g. the benign reduction of carboxylic acid derivatives. Furthermore, it will be shown that recently developed molecular-defined as well as nano-structured base metal catalysts enable us to perform catalytic hydrogenation and dehydrogenation processes in high yields and with unprecedented selectivity. Specific examples which demonstrate the potential of sustainable catalytic processes will also include examples from energy technology.

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Phosphinous acids: Key ligands for the catalytic hydration of nitriles under mild conditions

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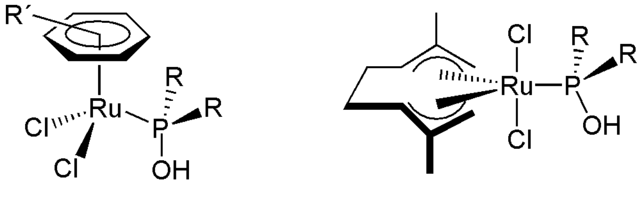
Amide bond forming reactions are among the most important and widely studied transformations in organic chemistry, but they also present a contemporary challenge because of the industrial need for cleaner and more atom-economical protocols. Nitrile hydration ideally represents the simplest method for the sustainable preparation of primary amides. However, strong acids and bases combined with harsh reaction conditions have been traditionally employed to promote the process, lowering its selectivity and applicability. In this context, significant efforts have been devoted in recent years to the search for homogeneous catalysts able to promote the selective conversion of nitriles to amides employing directly water as solvent under neutral conditions.[1]

Ruthenium complexes are particularly effective nitrile hydration catalysts, and promising results in water have been described with the help of hydrophilic phosphine ligands.[2] However, high temperature regimes (≥ 100 ºC) and metal loadings (5 mol%) are usually needed to achieve good conversions. As a significant improvement, herein we present the synthesis and characterization of a series of Ru(II) and Ru(IV) complexes (see figure) able to catalyze the selective hydration of organonitriles in water under remarkably milder conditions (≤ 60 ºC), and featuring a high activity at a low metal loading (1 mol%). The key role played by the phosphinous acid ligands PR_2OH in the catalytic reactions will be also discussed.[3]



R = aryl or alkyl group

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C−O Bond Cleavage in CO_2 and Biomass Products Using Organometallic Molecular Catalysts

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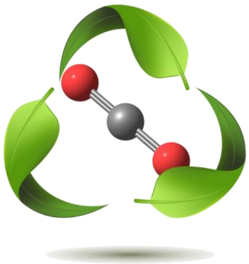

With 95 % of organic chemical commodities deriving from fossil resources, the chemical industry is currently exploring novel and renewable carbon feedstocks for the production of both bulk and fine chemicals. In this context, the utilization of CO_2 or products derived from biomass wastes is an attractive strategy to access value-added products. Because these carbon sources feature carbon atoms in an oxidized state, the development of reduction methods is needed and they call for the design of efficient catalysts able to break strong C−O and C=O bonds.

Over the last years, our group has developed novel catalytic reactions for the conversion of CO_2 to formamides, N-heterocycles, methylamines and methanol, using hydroboranes, hydrosilanes or formic acid as reductants.[1-8] In parallel, we have developed an unprecedented strategy to isolate simple aromatics, in a pure form, from natural lignin in 15 different wood species.[8-9] These new catalytic transformations rely on the use of simple organocatalysts or Zn, Fe and Ru organometallic complexes. The mechanisms at play in these transformations will be presented, based on DFT calculations and isolation of reactive catalytic intermediates.

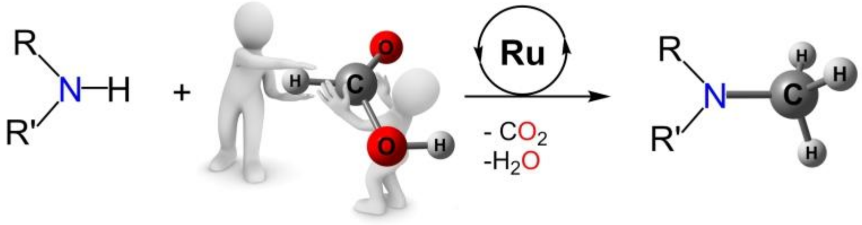

Figure 1 Methylation of amines with formic acid as carbon and hydrogen source

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Cobalt complexes as catalysts in biomass and water oxidations

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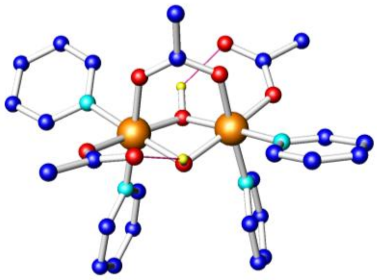
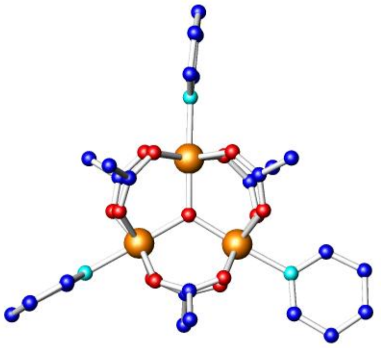
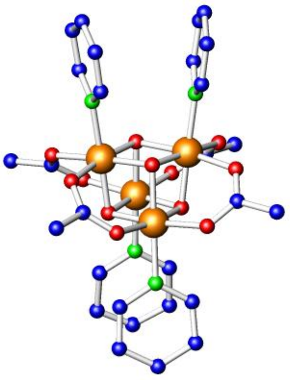
Cobalt acetate is perhaps the most widely used homogeneous catalyst in industry.[1] Complexes of putative cobalt(III) acetate have long been known as hydrocarbon oxidation catalysts and, more recently, as water oxidation catalysts.[2,3] We report the use of a range of dimers, trimers, and tetramers we have isolated from cobalt acetate (e.g., below)[4] as catalysts in oxidations of models of linkages in lignin biomass and in the electrochemical and photoelectrochemical oxidation of water.



$[Co_2(OAc)_3(OH)_2(py)_4]^+$



$[Co_3(\mu_3\text{-}O)(OAc)_6(py)_3]^+$



$[Co_4(\mu_3\text{-}O)_4(OAc)_4(py)_4]$

Lignin oxidation is exemplified by the oxidation of syringol, guaiacol, dimeric lignin model compounds representing the reactive α–O–4 linkages and dimeric β–O–4 model compounds, covering the most common lignin linkages. Additionally, the utility of these cobalt cluster species in electrochemical and photoelectrochemical water oxidation will be discussed. The cobalt cubane and dimer were inactive for the electrochemical water oxidation reaction, and the heterogeneous species derived from the trimer was found to be the active species. In the photoelectrochemical system with $BiVO_4$ as photoanode, the real active species for the observed catalytic behaviors of the three complexes were determined to be heterogeneous cobalt phosphate species.

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Merging host-guest chemistry and organocatalysis for the valorization of CO_2

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Carbon dioxide is an abundant, easy available and renewable carbon source which also has the advantage of being environmentally benign. However, its use as a C1 building block has been limited due to its high stability and low reactivity. One of the promising route for CO_2 fixation is the coupling with epoxides to generate cyclic carbonates owing to the high atom economy of the reaction and for the many applications of these compounds as building blocks or additives. Many catalysts were found to be active but, in most cases, they required fairly drastic reaction conditions and often a co-catalyst to achieve high conversions. Some systems also have the environmental drawback of the use of toxic metals. Therefore, the design of novel **metal-free** catalysts with enhanced properties still remains to be developed as a step towards effective CO_2 conversion.

Herein, we wish to report on the use of host-guest chemistry as a novel approach to this goal. By combining ammonium halide salts and specifically designed ammonium cavitand receptors, efficient incorporation of CO_2 into cyclic carbonates was successfully achieved under mild conditions, at atmospheric pressure of CO_2 and moderate temperature.[1] In this approach, enhancement is obtained by increasing the nucleophilicity of the halide rather than epoxide activation and relies on the strong binding properties of tetraphosphonate cavitand hosts towards ammonium cations.

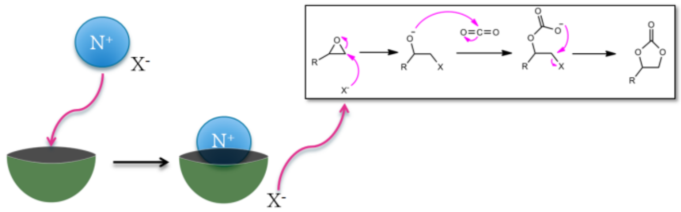

Figure 1 Principle of a dual catalytic system for the cycloaddition of epoxide with CO_2.

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Reductive Cleavage of CO_2 by Metal-Ligand-Cooperation Mediated by an Iridium Pincer Complex

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A unique mode of stoichiometric CO_2 activation and reductive splitting based on metal ligand cooperation is described. The novel Ir hydride complexes [(^{t}Bu-PNP)Ir(H)] (**1**) and [(^{t}Bu-PNP*)Ir(H)$_2$] (**2**) react with CO_2 to give the dearomatized complex [(^{t}Bu-PNP*)Ir(CO)] (**3**) and water. Mechanistic studies have identified an adduct in which CO_2 is bound to the ligand and metal, [(^{t}Bu-PNP-COO)Ir(H)$_2$] (**4**), and an η^1-CO_2 intermediate [(^{t}Bu-PNP)Ir(H)(CO_2)] (**5**). DFT calculations confirm the formation of **4** as a reversibly formed kinetic side-product, and of **5** as an intermediate leading to the thermodynamic product **4**. The calculations support a metal-ligand cooperation pathway in which an internal deprotonation of the benzylic position by the η^1-CO_2 ligand of **5** leads to a carboxylate intermediate, which further reacts with the hydride ligand to give complex **3** and water.

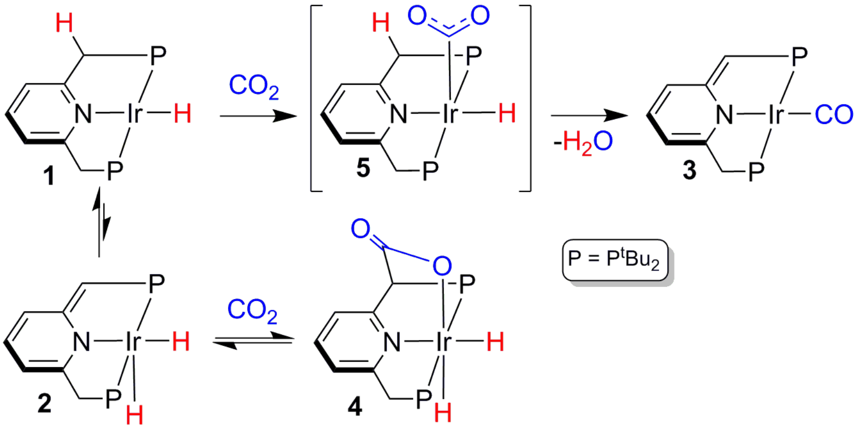

Figure 1. Reaction pathway of complexes **1** and **2** with CO_2 to give complex **4** as a kinetic product and complex **5** as an intermediate in the formation of **3**.

Giving IMes the Chop: Insights from Use of a Stumpy Carbene in Olefin Metathesis

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With the recent advent of molecular metathesis catalysts in industrial applications,[1] issues of catalyst productivity take on new importance. Studies of catalyst deactivation processes in "second-generation" ruthenium catalysts point toward C-H activation of the *N*-heterocyclic carbene (NHC) ligand as a potentially key event. Here we examined the impact of replacing the mesityl group of the IMes ligand with a methyl group: that is, incorporation of the IMe4 ligand into both mono- and dinuclear structures. We will describe new insights into Ru–NHC bonding revealed by the associated synthetic chemistry, the impact of NHC donicity on other ligands present on the metal centre, and the implications for catalytic performance and deactivation.

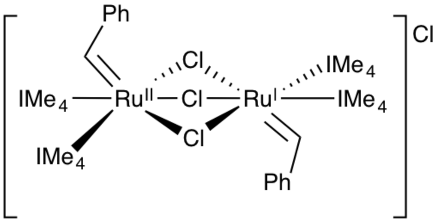

Figure 1 Structure of the dinuclear benzylidene complex formed on installation of the IMe4 ligand.

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Metal Amides as Active Sites

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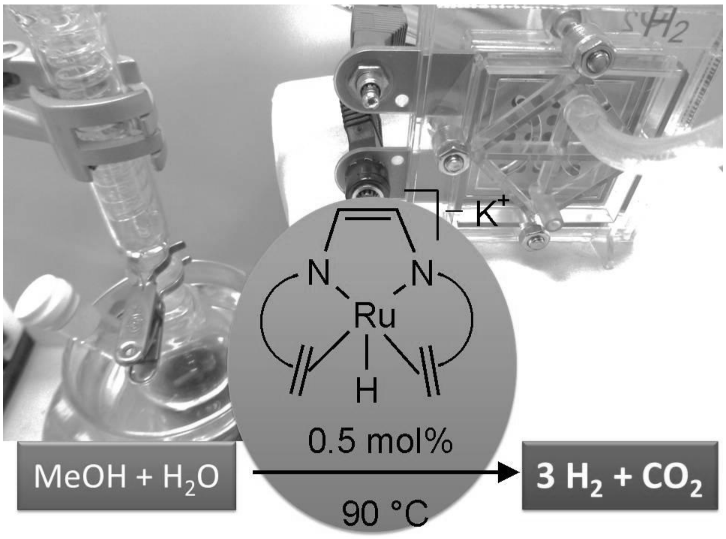
The development of an efficient catalytic process that mimics the enzymatic function of alcohol dehydrogenase is critical for using biomass alcohols for the production of H_2 as chemical energy carrier and fine chemicals under waste-free conditions.[1] Our own research efforts focus on dehydrogenative coupling reactions (DHC) which is an atom economic and efficient way to obtain carbonic acids, ester, and amides from alcohols according to: R^1-CH_2-OH + R_2-XH + 2 A □ R^1-CO-XR^2 + 2 "H_2" (X = O, NH).[1] Transition metal complexes with olefins as steering ligands and amido functions as cooperating ligands are remarkable efficient catalysts promoting the DHC of substrates from renewable feedstock with a high turnover frequency and high chemoselectivity.[2] Possible mechanisms will be discussed which inspired the development of an Organometallic Fuel Cell (OMFC),[1] efficient catalyst for the conversion of methanol water mixtures into H_2 and CO2,[3] and efficient routes to main group element compounds as precursors to materials.[4]

Figure 1 Caption



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η^5-Oxocyclohexadienyl Ruthenium(II) Complexes : A New Class of Shvo-type Catalysts ?

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Since the pioneering work in the field of transition metal catalysis, a wide span of stable ruthenium-based catalysts have been prepared. A relevant example is the cyclopentadienyl 5-membered ring Shvo's catalyst.[1] Within the family of 6-membered rings coordinated in an η^n-hapto mode to a transition metal, Shvo-type complexes incorporating η^5-oxocyclohexadienyl ligands have been little studied.[2] To the best of our knowledge, before our investigations, there was no example of a catalytically active half-sandwich ruthenium complex with an η^5-oxocyclohexadienyl as ligand (Figure 1).[2] Moreover, their corresponding tethered complexes were unknown.[3]

The straightforward synthesis of tethered η^5-oxocyclohexadienyl Ru(II)-complexes is presented (Figure 1).[3] Pioneering results in catalysis show that these unprecedented half-sandwich Ru(II) complexes allow the effective isomerization of allylic alcohols[3] and the hydration of nitriles under mild conditions without further additives. Our preliminary results illustrate that η^5-oxocyclohexadienyl ruthenium complexes may be considered as a new class of Shvo-type catalysts. The sterical and electronical properties of the ring and the Z/Y ligands can be easily tunes and the synthesis of their chiral version are envisaged.

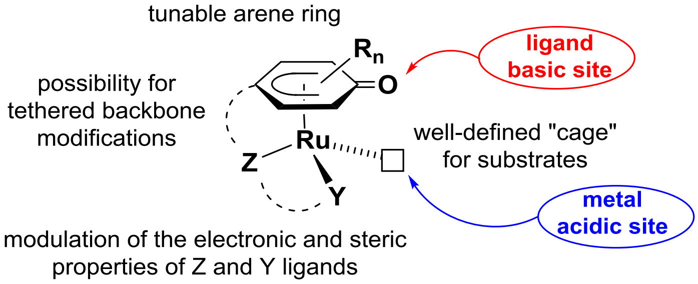

Figure 1 Schematic representation of bifunctional η^5-oxocyclohexadienyl ruthenium complexes.

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Parallel Synthesis and Screening of Polymer-supported Catalysts

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In the last decades (chiral) phosphorus ligands have proven their superiority in numerous transition-metal catalyzed asymmetric transformations. Subtle changes in ligand structure can have a decisive influence on the stability, activity and selectivity of a catalyst. The quest for efficient catalysts still relies heavily on the synthesis of ligand libraries. Several groups have successfully applied solid-phase techniques for the parallel and combinatorial synthesis of (supported) ligands.[1,2] The major advantage of this approach is the easy purification, which can be achieved by a simple washing procedure.

Scheme 1 Modular solid-phase synthesis of supported bidentate phosphorus ligands.

We developed a combinatorial solid-phase method for the synthesis of diphosphine and phosphine-phosphite ligands. This method provides access to supported diphosphines requiring minimal work-up, facilitating the generation and screening of large ligand libraries. The supported ligands were successfully employed in the rhodium-catalyzed asymmetric hydrogenation of several benchmark substrates. Small changes in ligand structure had a significant influence on the outcome of the catalysis showing the importance of trial-and-error in catalyst screening and the necessity of efficient methods for the generation of large ligand libraries. Lastly these supported ligands showed promising results in immobilized homogeneous catalyst recycling. One ligand could be used 6 times in asymmetric hydrogenation without drop in conversion and up to 11 times without loss of selectivity exhibiting minimal rhodium leaching.

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Ruthenium Catalyzed Utilization of Carbon Dioxide as Renewable C1 Resource

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In the last two decades, the utilization of renewable resources as chemical building block, solvent, or additive has emerged as important research area for the development of sustainable chemical processes. In this respect, carbon dioxide (CO_2) is an important, but challenging renewable C1 resource, which is already used as raw material for the production of industrial chemicals in certain cases and intensively researched for novel transformations.[1] Although the hydrogenation of CO_2 is broadly investigated, the direct alkylation of amines by construction of the methyl group from CO_2 and H_2 remained elusive. Traditional pathways for *N*-methylation include alkylation with methyl iodide, orthoesters, or dimethyl carbonate or reductive alkylation such as the Eschweiler-Clark method using formaldehyde and formic acid as C1 source. A CO_2-based route has the potential to be significantly more environmentally friendly and opens the possibility for new or complementary selectivity.

Herein, the homogenously catalysed direct *N*-methylation of a broad variety of amines using CO_2 and H_2 as the only sources for the construction of the methyl group is disclosed.[2-4] The starting point for the investigation represents the well-established triphos-based ruthenium system, which provides an excellent homogeneous catalyst for the hydrogenation of numerous functionalities and could be further tailored towards the envisaged transformations.[5-7]

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Non-heme Iron Catalysts for the Oxidative Cleavage of Biobased Olefins

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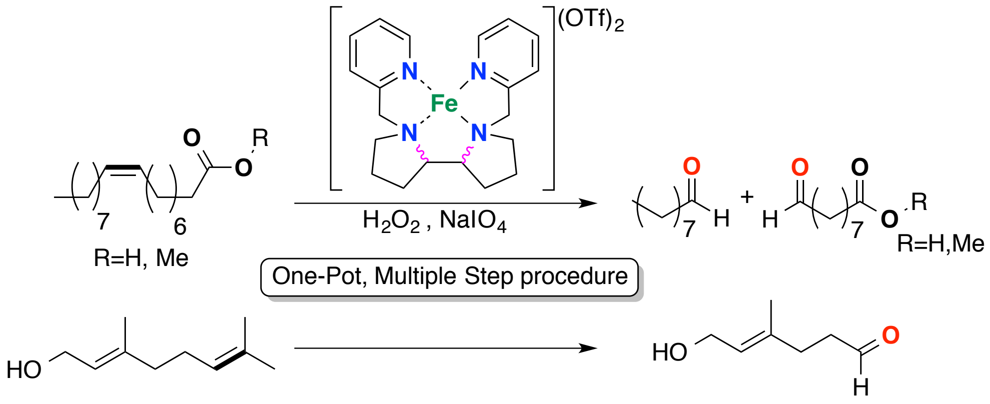
In the quest for the use of biomass in the manufacturing of chemical building blocks, the development of catalytic technologies is considered as one of the prime enabling tools. Plant oils and terpenes are natural sources of olefins and represent versatile platforms for the synthesis of bio-based chemicals through chemistries that address the olefin moiety. As part of our interest in the production of (bio-based) oxygenates, we are interested in the use of benign, iron-based catalysts for the selective oxidation of olefins. The oxidative cleavage of bio-based olefins such as terpenes and unsaturated fatty acids provides access to a wealth of mono- and dicarbonyl compounds that are of interest for the production of polymers, plasticizers, and stabilizers (see scheme).[1]

This talk provides an overview of our studies on the use of non-heme iron catalysts for the oxidative cleavage of internal olefins, and describes the use of the racemic [Fe(OTf)$_2$(*mix*-BPBP)] catalyst for the chemo-selective cleavage of unsaturated fatty acids to either aldehydes[2] and the regio-selective cleavage of terpenes.[3] Advances in catalyst design in order to arrive at more active catalysts and to the formation of carboxylic acids[4] will also be discussed.



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Mechanistic Studies on the Palladium-Catalyzed Direct C5 Arylation of Imidazoles

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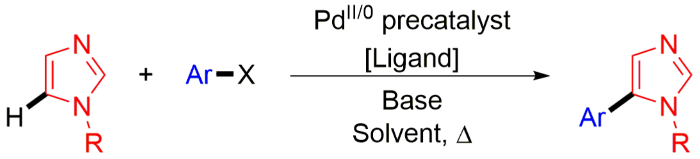
In the last decade several sets of experimental conditions have been shown to be effective for the regioselective C5 arylation of imidazole derivatives (Scheme 1).[1,2] Despite the synthetic utility of this transformation, its mechanistic understanding is far from complete and experimental findings are still hard to rationalize.



Scheme 1 Pd-catalyzed direct arylation of imidazoles at C5.

We undertook an in-depth mechanistic study of this reaction taking into account the whole catalytic cycle. Our results point out that phosphine-ligated aryl-Pd species are not able to effect the C-H functionalization of imidazoles, in contrast with previous results. The reaction, indeed, proceeds through imidazole-ligated organo-Pd intermediates. The kinetics of the oxidative addition of aryl halides with dmim-ligated Pd^0 species (dmim=1,2-dimethyl-1*H*-imidazole) has been studied in a $Pd(dba)_2$/dmim model system. An extensive characterization of the equilibria involving $[ArPd(dmim)_2X]$ complexes (X=I, OAc) and the unexpected cationic $[ArPd(dmim)_3]^+$ was performed. These novel species have the unprecedented ability to effect the C-H bond activation at room temperature.[3]

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Green and sustainable chemistry at ICCOM-CNR

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This communication highlights the most recent results obtained in four different research lines active in the group of the presenting author at ICCOM-CNR in Florence.

These will include:

1. The more recent results on the chemistry of **water soluble transition-metal complexes** based on PTA ligand (PTA = 1-phospha,3,5,7-triaza-adamantane) with emphasis on some catalytic applications in water or biphasic systems.[1]
2. The **HCOOH dehydrogenation**, which, if combined with its reverse reaction (CO_2 or $NaHCO_3$ hydrogenation), can bring about a carbon-neutral hydrogen release and storage cycle. In a Green Chemistry context, we studied these reactions in neat water phase, using monodentate and bidentate sulfonated phosphines as stabilizers for *in situ* catalytic systems based on $RuCl_3$ x $3H_2O$ and $[Ru(\eta^6-C_6H_6)Cl_2]_2$ as metal precursors.[2]
3. The utilization of Ir(I), Pd(II) and Ru(II) complexes stabilized by polyphosphine and *pincer* type ligands for H_2 storage and production based on **ammonia-borane dehydrogenation**.[3]
4. The most recent achievements in the area of **elemental phosphorus' reactivity** including: i) the unusual hydrolytic behaviour of the P_4 molecule following its η^1-coordination to a metal centre;[4] ii) the high pressure reactivity of red phosphorus towards water and other small molecules[5] and, iii) our preliminary results aimed at exploring the chemistry of the less reactive allotrope of the element, *i.e.* black phosphorus.[6] In all cases the non-innocent role of water will be highlighted.

Acknowledgments: Thanks are given to the European Research Council for funding the project PHOS*FUN* "*Phosphorene functionalization: a new platform for advanced multifunctional materials*" (Grant Agreement No. 670173) through an ERC Advanced Grant. Thanks are given also to ECRF (project Hydrolab-2), CNR (project EFOR) and EC (RFP7 ITN-SUSPHOS project).

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Iron Catalyzed C-H Borylation

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Selective carbon-hydrogen bond activation and functionalization is highly attractive to provide more complex molecules by building C-C and C-heteroatom bonds in an eco-friendly manner. Of particular interest is the borylation of C_{sp2}-H bond of arenes, heteroarenes and alkenes which represents one of the most elegant way to obtain (hetero)-aryl- and vinyl-boronate esters, versatile synthons for Suzuki-Miyaura reactions.

Very efficient catalytic borylation processes have been developed using noble metal-based catalysts such as iridium and rhodium complexes. In the case of iron which has become a valuable alternative to precious transition metals in homogeneous catalysis, achieving such a transformation remains challenging.[1] We have found recently that well-defined iron bis(diphosphine) complexes are active catalysts for the dehydrogenative C-H borylation of aromatic and heteroaromatic derivatives with pinacolborane (HBpin) (**Figure 1**).[2] The corresponding borylated compounds were isolated in moderate to good yields (25-73%). Stoichiometric reactivity studies allowed us to isolate of an original *trans*-hydrido(boryl) iron complex, $Fe(H)(Bpin)(dmpe)_2$. This methodology has been further improved to achieve the borylation of the C_{sp2}-H bond of alkenes under mild conditions.[3]

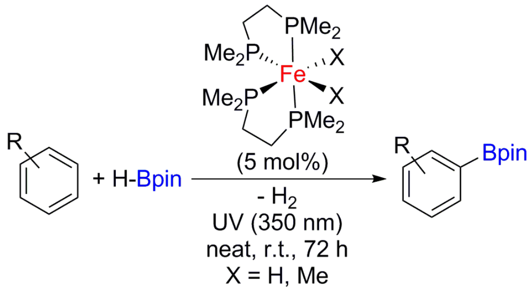

Figure 1 Iron catalyzed borylation of arenes

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Cobalt catalyzed C-H bond functionalization

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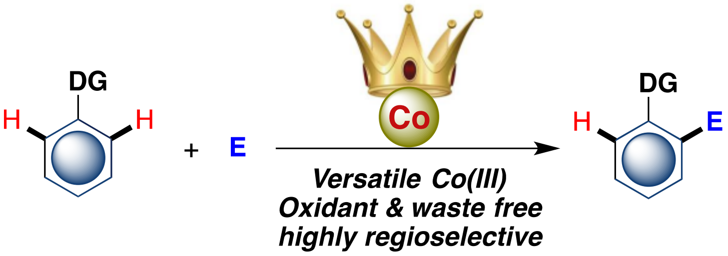
Transition-metal-catalyzed C−H functionalizations has greatly complimented to traditional organic synthesis that involves atom and step saving processes with high functional group compatibility.[1] Yet most of the known C-H functionalization was carried out using noble late transition metals, which are very expensive and hence transformation from academia to industry is very unlikely. Due to fast depletion of noble metals and cost efficiency, we need an alternative catalyst that are low cost, earth abundant and match or surpass the activity of noble metals. Certainly cobalt be the first choice, due to above mentioned factors and in addition, it possess variable oxidation state and hence it may have unique reactivity than its second row and third row counter parts.[2]



Versatile Co(III)
Oxidant & waste free
highly regioselective

Figure 1: Co(III)–catalyzed C-H bond functionalization

In this lecture we disclose some of our recent results on C-H bond functionalization using air stable, low cost, versatile cobalt (III) catalyst for C-H bond functionalization. We will discuss in detail C-H bond annulation, sequential C-H activation / oxygen atom transfer, and C-H bond allylation, etc. Our preliminary experiments on mechanistic investigation and DFT calculations suggest that C-H activation proceed through an inner sphere mechanism and oxygen atom transfer will be the rate determining step.[3]

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ONE-POT OLEFIN HYDROFUNCTIONALIZATION VIA TANDEM CATALYSTS

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One-pot olefin hydration and hydroamination is a useful tool to convert abundant low-cost feedstocks such as olefins into value-added products such as alcohols and amines. By using a tandem catalyst system, we avoid multi-stepped reactions that require isolation of reaction intermediates leading to waste generation. The hydration of terminal olefins to primary and secondary alcohols have been achieved using a Pd(II)/Ru(II) catalyst combination with high regioselectivity and yields. By varying reaction conditions, the regioselectivity can be adjusted to anti-Markovnikov or Markovnikov, to yield either primary or secondary alcohols selectively. For anti-Markovnikov olefin hydration, high primary alcohol yields of > 70 % at > 95% selectivity can be obtained from vinyl arenes. For Markovnikov olefin hydration, up to 85 % yield at > 99 % selectivity may be obtained for the secondary alcohol, from linear olefins such as 1-dodecene. Using Pd(II)/Ir(III) catalyst combination, we are able to obtain branched amines from linear olefins at yields > 85 % using just 1 mol% catalyst. Herein, we present our efforts in both anti-Markovnikov and Markovnikov olefin hydration and hydroamination to obtain linear or branched alcohols and amines respectively[1-4].

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Preparation of well-defined supported metallo N-heterocyclic carbene complexes by a combined approach of material chemistry and surface organometallic chemistry

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The rational development of functional material with a molecular comprehension of the surface sites is usefull to access materials with predictable properties that can be further optimized using reliable structure–property relationships. In this context, we have developed an original methodology to prepare well-defined heterogeneous catalysts containing highly active surface metallo-*N*-heterocyclic carbene complexes (M-NHC, M = Ru, Ir, Pd, Au…).[1] The materials were fully characterized using several techniques and particularly by advanced solid state NMR techniques using Dynamic Nuclear Polarization which allowed us to have a molecular description of the surface Metallo-NHC sites.[2,3] Their catalytic performances were found remarkable: for example, the performances of the supported Ir(I)NHC complex in hydrogenation reactions overpassed that of homologous complex in solution by one or two orders of magnitude (in term of rate and TON). This remarkable performance was attributed to surface site isolation, that suppresses bimolecular deactivation processes, and to beneficial interactions between the silica surface and the Ir-NHC sites.[3]

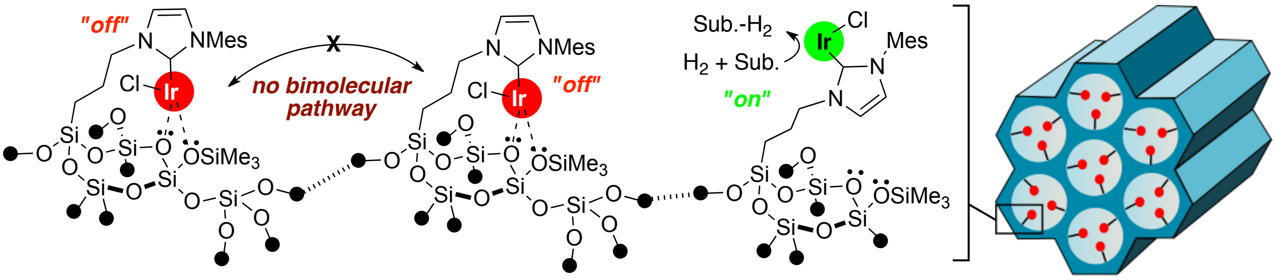

Figure 1 Illustrative representation of Ir-NHC surface sites

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Iridium carbene complexes. Formation, reactivity and dehydrogenation catalysis

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Controlled electrochemical tuning of PCP pincer complexes is an area of increasing interest, and several literature examples underpin how the nature of the coordinating carbon atom can alter the reactivity and catalytic activity. The more electron rich environment of a PC(sp^3)P coordinated metal centre relative the PC(sp^2)P counterpart, has proven particularly beneficial in the activation of unreactive bonds and in coupling reactions.[1]

The use of a cyclohexyl based pincer framework also opens up for non-innocent behaviour not the least because of the presence of a hydrogen atom in the α-position of the pincer ligand. The phosphine based cyclohexyl ligands thus form iridium carbene complexes at elevated temperatures. These carbene complexes undergo unusual reactions such as oxidative C-C couplings and they can also be formed through an unprecedented α-alkyl elimination reaction (Figure 1, left).[2] Using phosphinite pincer arms stabilises the carbene and it can now be isolated (Figure 1, right). Details about the reversible addition of e.g. dihydrogen over the carbene double bond and the application of compound **1** in acceptorless dehydrogenation of primary alcohols will be discussed. In the catalysis the non-innocent nature of the pincer ligand plays a prominent role.

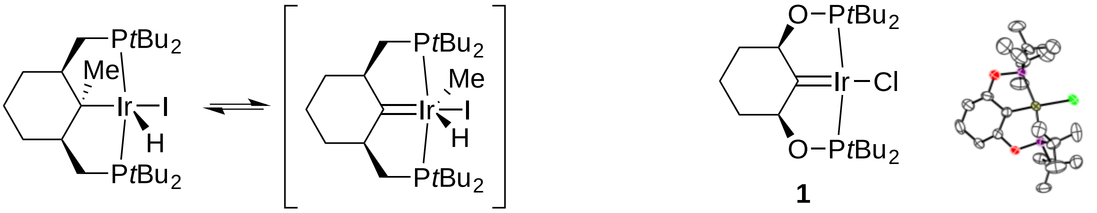

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Figure 1 Iridium carbene complexes can be formed through an α-alkyl elimination reaction (left). With phosphinite ligands the carbene complex can be isolated (right)

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A Sustainable, Regio- and Stereo-Selective Formation of Highly Substituted (*Z*)-Allylic Amines

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Allylic amines, representing a sub-class of (substituted) alkenes, are fundamental building blocks in natural product and heterocyclic synthesis.[1] Traditional and modern synthetic methodologies for the formation of allylic amines involve the nucleophilic attack of a compound containing an activated allylic C–X bond (X = leaving group), transition metal catalyzed allylic C–H bond functionalization or hydroamination of dienes/alkynes. In this latter context, Beller and co-workers have recently developed useful new methodology towards hydroamination/amidation of dienes with excellent selectivity for the *anti*-Markovnikov.[2,3]

Figure 1 Conceptual approach towards allylic amines using cyclic carbonates.

Here we report a versatile, highly mild and selective methodology towards anti-Markovnikov type allylic amines controlling to high extend the chemo-, regio- and stereo-selective features of these allylic amine scaffolds by using post-converting cyclic vinyl-carbonates.[4] Their use as intermediates for 1,4-diamines will be highlighted.

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Metal catalyzed synthesis of ethers from alcohols and butadiene

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Ethers are commonly prepared by the Williamson reaction with stoichiometric amounts of salts as by-products. Their significance requires the development of new convenient and more atom-economic synthetic pathways.[1] In this context, catalytic synthesis of ethers from an alcohol and 1,3-dienes promoted by organometallic based catalysts are advantageous. The palladium catalyzed telomerization and nickel catalyzed hydroalkoxylation reactions are atom-economic and respectively allow the synthesis of unsaturated OC8 and OC4 ethers (Figure 1) that can be further hydrogenated or chemically modified. If the palladium catalyzed telomerization reaction[2] is now well established leading to up to 95% selectivity into octadienyl telomers (OC8), investigations conducted in our group have shown that the association of simple nickel based precursors with bidentate phosphine ligands allows the highly selective hydroalkoxylation reaction of 1,3-butadiene (OC4 ethers, up to 95 %).[3]

Figure 1. Metal catalyzed telomerization and hydroalkoxylation

We will describe the catalytic optimization (catalyst, reaction parameters) as well as the scope of the reaction that encompasses the valorization of agro-based alcohols. Mechanistic insights obtained on the basis of catalytic results and the synthesis of organometallic pro-catalysts associated with theoretical molecular modeling studies will be also presented.[4]

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Mixed allyl-borohydride lanthanide complexes: synthesis of $Ln(BH_4)_2(C_3H_5)(THF)_x$, characterization and reactivity towards polymerization

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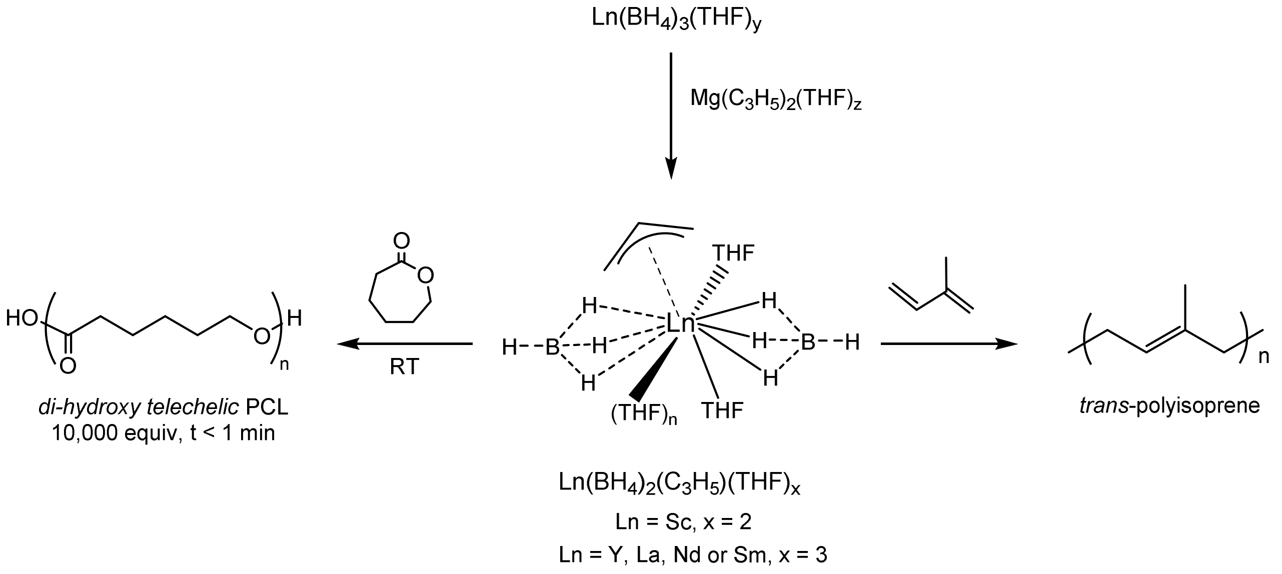
Lanthanide complexes bearing allyl ligands are of both fundamental and applied interest, notably due to their catalytic performances toward the stereospecific conjugated dienes polymerization.[1] This field was highlighted in particular by the work of Taube and co-workers on neutral trisallyl or anionic tetraallyl lanthanide complexes.[1d]

Herein, we report the synthesis and X-Ray structures of new mixed allyl-borohydrido lanthanide complexes $Ln(BH_4)_2(C_3H_5)(THF)_x$ (Ln = Y, Sc, La, Nd, Sm), isolated in high yield by reacting $Ln(BH_4)_3(THF)_y$ with half an equivalent of $Mg(C_3H_5)_2(THF)_z$. These complexes afford highly *trans*-1,4-polyisoprene, as single components or combined with Mg co-catalyst. They also display particularly high activities towards L-lactide and ε-caprolactone polymerizations, with up to 7 x 10^7 g.(mol Ln)$^{-1}$.h^{-1} in the latter case.[2]



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Beryllium phosphine complexes

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The coordination chemistry of beryllium has seen a little renaissance[1] in the last years, after decades of neglect due to its assumed high “toxicity”. While the interaction of beryllium with carbenes is relatively well investigated,[2-5] there are no studies on the coordination ability of phosphines towards beryllium. There were only two known beryllium phosphines, of which no reactivity was explored, prior to this study.[6-7]

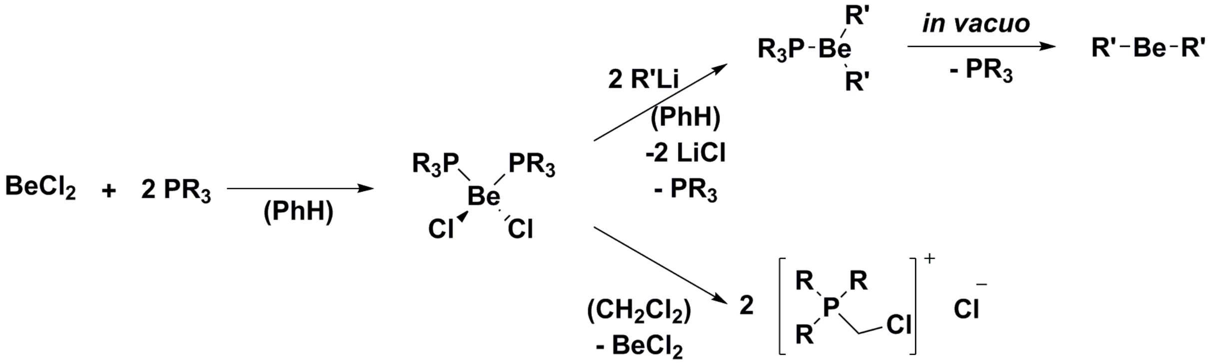

Figure 1 Synthesis of beryllium phosphines and their subsequent reactivity.

Various beryllium diphosphine complexes could be synthesized and characterized. These are readily alkylated, using standard lithium organyles. The phosphine can be removed conveniently, yielding ether free beryllium dialkyls. The beryllium phosphines also act as extremely strong Lewis acids, which are capable of C-Cl-bond activation in chlorinated solvents. In both cases the phosphines are extremely good solubilizers for beryllium chloride in aromatic and chlorinated solvents. Due to the HSAB mismatch of the very hard Be^{2+}-cation and the soft phosphorus, the phosphines – in contrast to the generally used ethers – can be removed readily. These routes now give easy access to pure, non oxygen-atom-contaminated, beryllium organyles as well as to Lewis acid chemistry in non etheral solutions, of one of the hardest known cations.

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Heterobimetallic Mg---Zr and Zn---Zr Hydrides: application to alkene and diene isomerisation

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The development of new heterobimetallic complexes has, in part, stemmed from the promise they hold in catalysis and synthesis. Co-location of two, or more, metals offers the opportunity not only to develop new fundamental reactivity but also fine tune selection events in known reactions.[1] Here we describe the preparation of **Mg•Zr** and **Zn•Zr**: well-defined heterobimetallic hydrides of M(II) and Zr(IV) (M = Mg, Zr).[2]

The **Mg•Zr** analogue is an active catalyst for the isomerisation of terminal alkenes to internal alkenes across one position with a strong bias for (*E*)-stereochemistry in the products. Control reactions with a series of heterobimetallic complexes under identical conditions demonstrate a pronounced heterobimetallic effect. At very low loadings, the parent Zr hydride, $[Cp_2ZrH(\mu\text{-}H)]_2$, will also isomerise alkenes efficiently. While **Mg•Zr** also isomerises cycloocta-1,5-diene to cycloocta-1,3-diene, the reaction of **Zn•Zr** with this substrate occurred with concomitant production of complex **1** (**Figure 1b**), an alkyne-bridged heterobimetallic with little precedent.[3] Calculations demonstrate that the contrathermodynamic isomerisation of the organic fragment is aptly compensated for by the large binding energy of the alkyne to the heterobimetallic, the reaction is again sensitive to the nature of the heterobimetallic and has only been observed for the zinc analogue of the series.

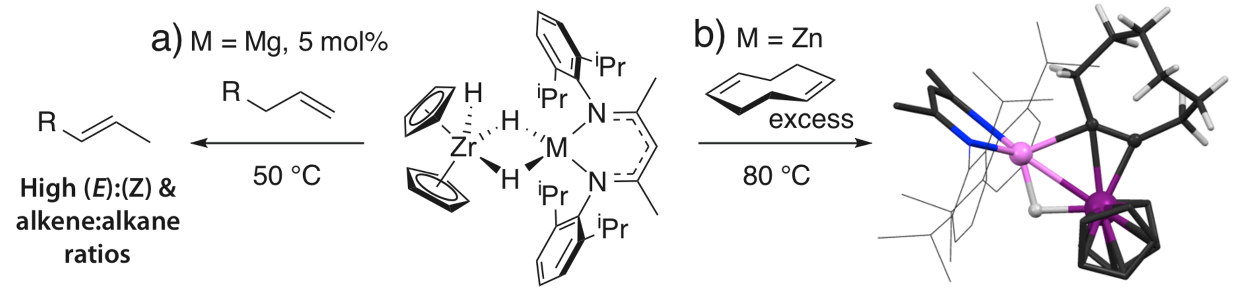

Figure 1 a) Isomerisation of terminal alkenes by **Mg•Zr** in benzene-d_6 b) synthesis from **Zn•Zr** and 1,5-COD and crystal structure of **1** (alkyne protons and hydride shown).

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Stereoselective Polymerization of Polar Vinyl Monomers by Group 4 Metallocenes

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The regularity of stereocenters in a macromolecule can profoundly affect the macroscopic material properties. This is illustrated most impressively by isotactic polypropylene, produced on the 10^6 tons/year scale. The development of well defined homogeneous catalysts for non-polar olefins polymerization has dominated the last 20 years, and has allowed to develop a highly detailed knowledge of the key parameters leading to polymers with the desired macromolecular architecture, in terms of molecular mass and stereoregularity. In the last years, the challenge has been shifted to develop a similar control over the polymerization of polar monomers to highly stereoregular polymers with high molecular mass.[1,2]

In this contribution we will present the current mechanistic understanding in the stereoselective polymerization of monomers of the methacrylate family. Starting from the successful polymerization of methylmethacrylate to iso and syndiotactic polymers by early transition metal cataysts,[3,4] we will arrive to the rationalization of stereoselectivity in the polymerization of polar divinyl monomers by zirconocenes.[5]

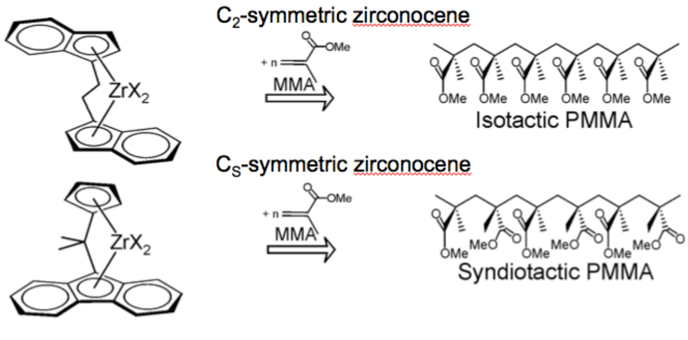

Figure 1. Examples of methylmethacrylate polymerization by zirconocenes

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Scandium Terminal Imido Complexes: Synthesis, Structure and Reactivity

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Over the last three decades, terminal imido complexes of early-transition metals, which contain the M=N double bond, have attracted intensive interests and been extensively studied. The research on such complexes has revealed rich reactivity and applications in the group transfer and catalytic reactions.[1] In contrast, the chemistry of rare-earth metal (Sc, Y and lanthanide metal) terminal imido complexes is far behind developed. The rare-earth metal terminal imido species once formed can easily assemble into more stable μ or μ_n (n = 3, 4) bridged bimetallic or multi-metallic species, or undergo reactions with solvents via C–H bond activation.[2] Meanwhile, the chemistry of the rare-earth metal terminal imido complexes is of great interest as the highly polar and reactive Ln=N double bonds should lead to rich reactivity. Recently, we obtained and characterized the first rare-earth metal terminal imido complexes, the scandium terminal imido complexes (Figure 1). The scandium terminal imido complexes are capable of activating elemental selenium, undergoing cycloaddition with CO_2 and a series of unsaturated organic small molecules, activating the Si–H bond of phenylsilane and the C–H bond of terminal alkenes, and reacting with metal halides.[3]

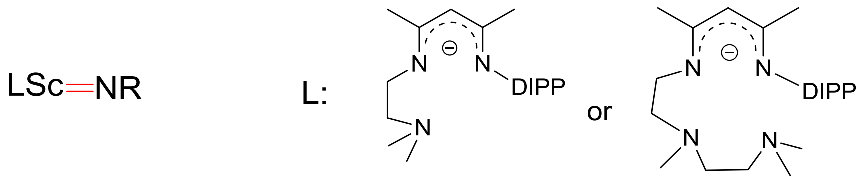

Figure 1 Scandium terminal imido complexes.

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Yttrium Phosphasalen Initiators for *rac*-Lactide Polymerization: Effect of Ligand Variation on Activity and Stereocontrol

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Polylactide (PLA) is an important class of polymer produced by the ring-opening polymerization (ROP) of lactide (LA), which is derived from high starch content biomass. The ROP of LA is initiated by Lewis acidic metal alkoxide complexes, which infer control over the rate of polymerization and polymer properties (molecular weight and stereochemistry). The tacticity of the resultant PLA plays a highly important role as it can influence the material's thermal and mechanical properties.

Recently our group has reported a highly active and selective yttrium phosphasalen complex **1** for ROP of *rac*-LA that exhibited very high rates, tolerance to low catalyst loadings and high iso-selectivities (P_i = 0.86).[1,2] In this presentation, we describe the synthesis, characterization (X-ray crystallography and multinuclear NMR spectroscopy) and polymerization catalysis of yttrium phosphasalen complexes **2** - **4** (Figure 1). By examining the effect of changes in the sterics, electronics and rigidity of the diimine bridge, we are able to provide insight into new structure-activity relationships for this particular system, but in specific, the concomitant effect that these changes have on the tacticitiy of the resultant polymer.

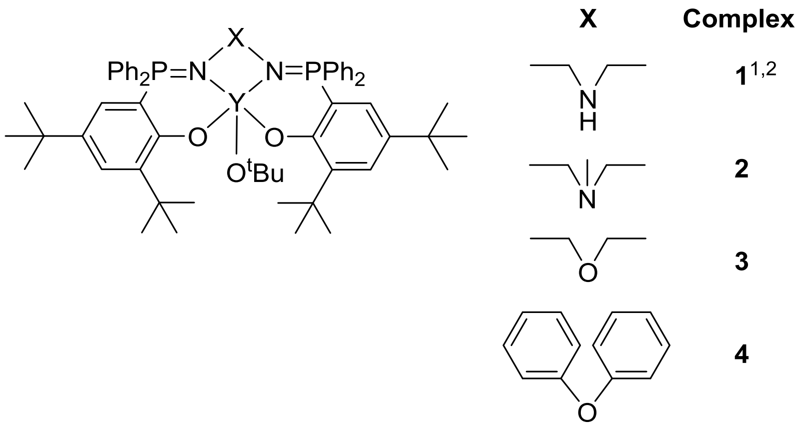

Figure 1. General structure of the phosphasalen yttrium initiators.

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Supported lanthanide catalysts: Role of the grafting on the stereochemical outcome of different polymerization reactions.

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In the context of the research of low cost and environmentally benign catalytic systems, development of highly active and selective catalysts is of prime importance. From an industrial point of view, heterogeneous processes are advantageous because of the facile separation of the final products from the catalysts and the easy recycling of these catalysts. Moreover, the easier solid–liquid separation reduces the solvent consumption, which is in agreement with the constant demand for greener chemical processes. In the case of homogeneous catalysts, every entity can act as a single active site. This makes homogeneous catalysts more active and selective compared to heterogeneous catalysts. Therefore, a catalytic system, which takes the advantages of both homogeneous and heterogeneous catalysis, would greatly enhance the interest for industrial applications. One possibility to achieve this type of catalytic system is the use of supported catalysts.

Among the metals applied within the field of supported catalysis, rare-earth systems have been the subject of constant interest due to their high activity in several fields, such as in polymerization[1] and fine chemistry[2]. In this oral presentation we would like demonstrated through a theoretical/experimental approach that support effects can be used to change the stereochemical outcome of different polymerization reactions. Thus, we will try to shed light on the origin of the influence of catalyst grafting in different selective processes such as the β-butyrolactone ring opening polymerization or Methyl methacrylate polymerization mediated by supported lanthanide catalysts.

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Investigations into the Reactivity and Physical Properties of Thorium(III) Complexes

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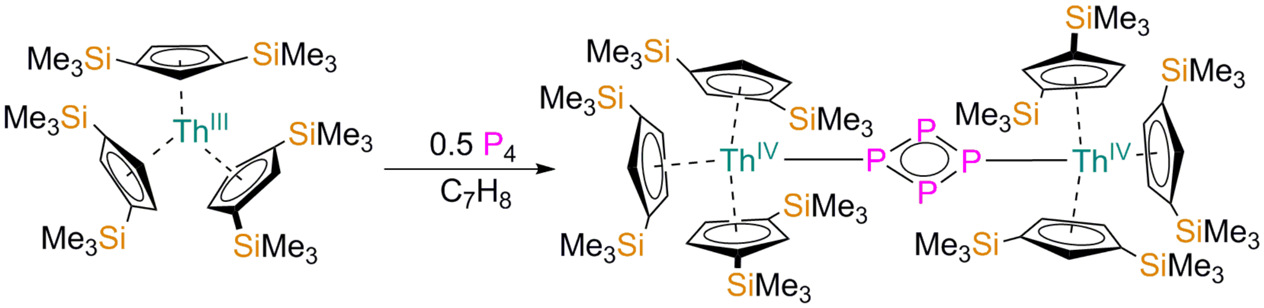
The small molecule activation chemistry of U(III) complexes has flourished in recent years,[1] whilst the corresponding Th(III) chemistry is underdeveloped.[2] This is surprising given that the calculated Th(IV) → Th(III) standard reduction potential ($E^{\ominus}$ –3.7 V) is far greater than its U(IV) → U(III) counterpart ($E^{\ominus}$ –0.6 V);[3] therefore a rich small molecule activation chemistry of Th(III) complexes can be anticipated.

We have started our investigation by studying the reactivity of Lappert's Th(III) complex, $[Th(Cp'')_3]$ (**1**, Cp″ = $\{C_5H_3(SiMe_3)_2\text{-}1,3\}^{-}$)[4] towards selected substrates. We found that **1** reacts with white phosphorus to give $[\{Th(Cp'')_3\}_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-}P_4)]$ (**2**), which exhibits a novel cyclo-P_4 binding mode (Scheme 1).[5] The U(III) homologue of **1**, $[U(Cp'')_3]$, does not activate P_4, and we have observed such divergent reactivity profiles for a wide range of substrates. Our current progress in these studies will be presented here, along with our investigations into the physical properties of the Th(III) oxidation state.

We thank The University of Manchester, the EPSRC and Nuclear FiRST DTC for project funding, and the RSC Radiochemistry Marie Curie Award for conference funding.



Scheme 1. Preparation of the cyclo-P_4 complex, **2**, from **1** and P_4.

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A Molecular Approach to Silica-Supported Metal Catalysts

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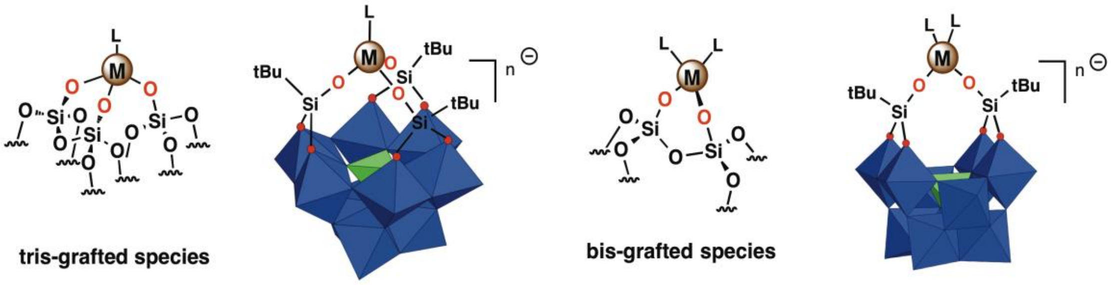
A molecular approach to a heterogeneous surface active in driving the transformations of organic substrates should fulfill the following criteria: (i) a geometrically and chemically environment similar to the active site, (ii) a single isolated site, and (iii) the successful achievement of the same kind of transformations through a close chemical pathway. More, a relevant molecular model should help to bring insights on the structure/activity relationships. The silanol-decorated polyoxotungstates[1] that are depicted in Figure 1 prove to be capable of mimicking surface vicinal silanols of dehydroxylated silica.[2] First, they display a rigid and geometrically pre-organized set of silanol moieties and, second, the bulky *tert*-butyl groups at the silicon atoms create a sterical protection around the metal coordination site. The combination of both aspects prevents the formation of oligomers and allows the metal ion to fit in a well-defined single site.



tris-grafted species

bis-grafted species

Figure 1 Tris-grafted and bis-grafted species on a siloxide surface and on POM hybrids.

In this context, oxidovanadium(V) derivatives were prepared, characterized and used as precatalysts for the epoxidation of olefins with *tert*-butyl hydroperoxide.[3] Reaction progress kinetic analysis by monitoring the epoxidation reactions by nuclear magnetic resonance clearly confirmed that the confined tris-grafted species does not act as an efficient catalyst whereas a more labile bis-grafted does. These studies and other applications of these systems will be presented in this communication.

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Metal-Ligand Synergies on Y^{III} Heteroaryl-Containing Amidopyridinate Complexes

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Highly electrophilic lanthanide metal ions in combination with pyridylamido ligands are the basis of nonconventional, highly efficient and selective catalyst precursors of great promise for polyolefin production[1] and hydroamination reactions.[2] Recent studies from our group have unveiled the wealthy organometallic chemistry of these nitrogen-based systems, highlighting at the same time their unique structure-activity relationship.[2a,3]

Herein, we describe the synthesis and characterization of a series of Y^{III} alkyl complexes stabilized by tridentate mono- or di-anionic heteroaryl-containing amidopyridinate ligands. A careful study of their reactivity in the presence of selected protic reagents along with the investigation of their ability to undergo unexpected intramolecular reactivity paths, have allowed the isolation and full characterization of unique organolanthanides (Figure 1). A detailed discussion on the mechanistic paths underpinning the observed rearrangements will be tackled from an experimental and theoretical perspective.

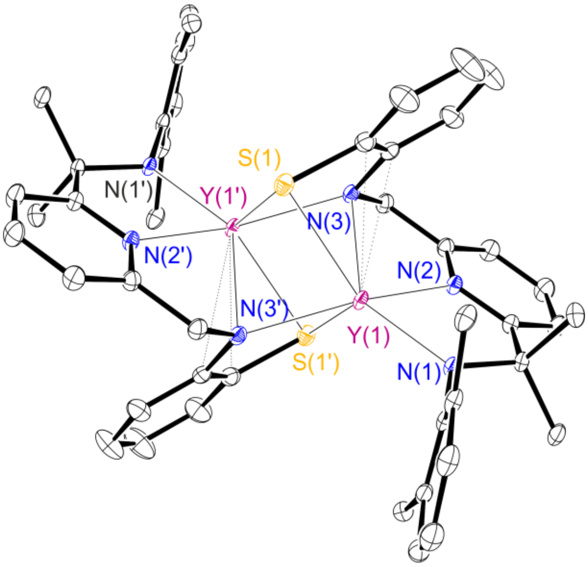

Figure 1 X-ray structure of a rare dimeric Yttrium complex stabilized by two bridging trianionic tetradentate $\{N^{-},N,N^{-},S^{-}\}$ ligands.

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Ca-talysis: Development and Working Principles

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The rapid growth of the field of early main group metal catalysis is partially driven by the non-toxicity and low prices of the metals but also strongly stimulated by academical interest.[1] In this context, organocalcium compounds have been reported as efficient catalysts for various alkene conversions normally catalyzed by transition metals: *e.g.* polymerization, hydroamination, hydrosilylation, hydrogenation or hydrophosphination. In contrast to transition metal catalysis, the alkenes are not activated by metal-alkene ($d \rightarrow \pi^*$) orbital interactions. Instead, it is suggested that alkene activation proceeds through an electrostatic interaction with a Lewis-acidic Ca^{2+}. This leads to vertical and horizontal polarization of the π-electron density thus giving an incentive for nucleophilic attack.

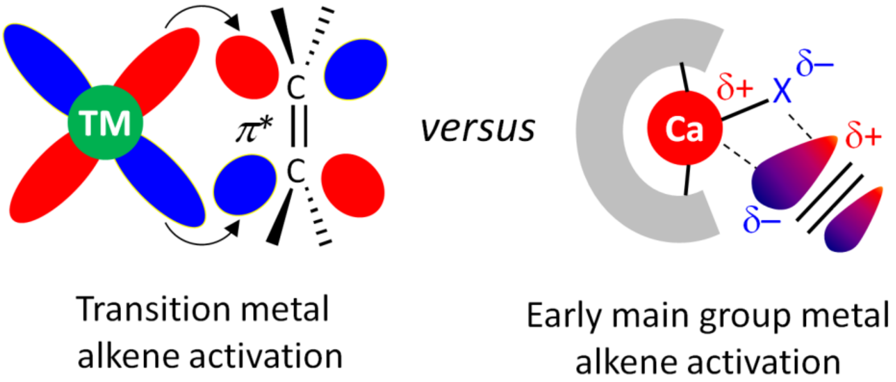

Figure 1 Alkene activation by transition metals or early main group metals

This discusses the development and working principles giving an overview of selected examples and presents our latest results in the area.

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How to switch stereoselectivity in the polymerization of *rac*-LA - a curious case of dialkylgallium and dialkylindium alkoxides

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Despite constantly appearing new reports on the stereoselective ring-opening polymerization (ROP) of *rac*-lactide (*rac*-LA) with metal alkoxides, there is still a need for tools enabling controlled and stereoselective polymerization leading to new PLA microstructures. Recently, both stereocontrol and switchable catalysis has been named important aspects in the field of ROP.[1] In this regard, gallium and indium alkoxides have been shown to polymerize *rac*-LA and other heterocyclic monomers in controlled and stereoselective fashion.[2] In our pioneering studies on gallium catalysts for the ROP of *rac*-LA, we reported stereoselective gallium alkoxides which allowed for easy switch of stereoselectivity from heteroselective to isoselective mode,[3] and the synthesis of the first example of (heterotactically enriched PLA)-*b*-(isotactically enriched PLA).[4]

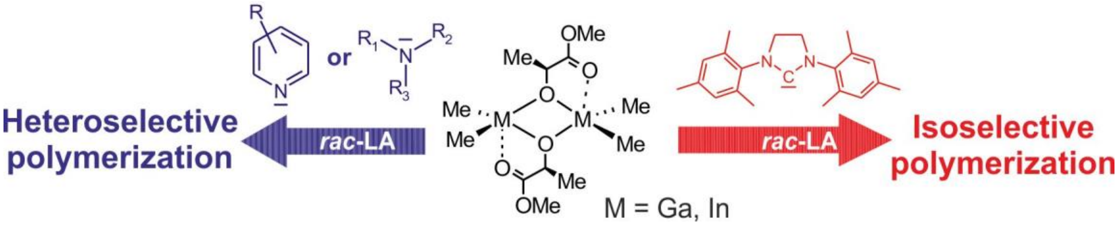

Figure 1 Stereoselectivity of $[Me_2M(\mu\text{-}OCH(Me)CO_2Me)]_2$/Lewis base system (M = Ga, In)

Recently, in order to develop this type of catalysts and understand the origin of stereoselectivity, we have focused on the role of Lewis base in the polymerization of *rac*-LA with dialkylgallium and dialkylindium alkoxides. Noteworthy, the studies on heteroselective complexes (Figure 1) led us to striking finding, that stereoselectivity of *rac*-LA polymerization can be controlled by chiral recognition induced formation of homochiral dimeric dialkylgallium and dialkylindium alkoxides.[5] This finding could be of importance for the rational design of catalysts for the stereoselective polymerization of heterocyclic monomers and is going to be emphasized during presentation.

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Organo Rare Earth Catalysts for Novel Chemical Transformations

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The search for new catalysts for more efficient, selective chemical transformations and for the synthesis of new functional materials has been a long-standing research subject in both academia and industry. We have previously reported that cationic half-sandwich rare earth alkyls generated by treatment of the dialkyl precursors with a borate compound can serve as excellent catalysts for the polymerization and copolymerization of a wide range of olefins as well as for the *ortho*-selective C−H bond alkylation of some aromatic compounds such as anisoles and pyridines with alkenes.[1,2] In this lecture, I will describe our recent studies on the step-growth copolymerization of 1,4-dialkoxybenzenes with non-conjugated dienes such as 2,5-norbornadiene and 1,4-divinylbenzene through C−H polyaddition to dienes catalyzed by the half-sandwich rare-earth catalysts. These reactions constitute an atom-economical route for the synthesis of a new family of polymer materials with perfect alternating sequences of different units linked by C−C bonds. A proper combination of the rare earth metals and the supporting ligands is required to achieve high catalytic activity.

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Cationic Zicrconocene Isoselective Polymerization Catalysts

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Single-site group 4 metallocene systems are intensely used for the production of isotactic polypropylene (iPP) (and iPP-based olefinic copolymers),[1] which is one of the landmarks of the plastics market with a global annual production of ca. 45 MT.

In this study, solution and in the solid state of mono- and heterobimetallic ion-pairs of isoselective zirconocenes incorporating different counteranions ($[MeB(C_6F_5)_3]^-$, $[B(C_6F_5)_4]^-$, [“Me–MAO”]$^-$) have been investigated (Figure 1).[2] Details of the stability, dynamics and interconversion of ion pairs, as well as their behavior in isoselective polymerization of propylene and structure-activity relationship will be discussed.

The authors are grateful to Total Raffinage-Chimie for the financial support of this work.

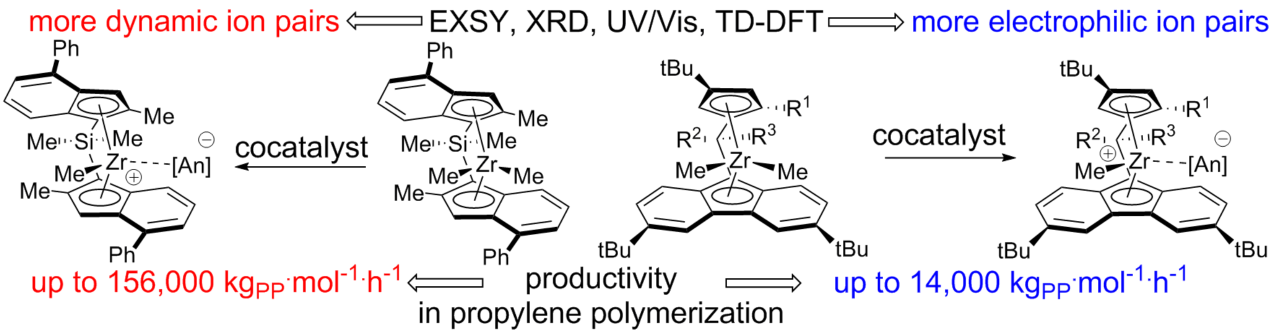

Figure 1 Ion-pairs of isoselective zirconocenes

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N-Heterocyclic Carbene Complexes of Group 4 as a New Class of Catalyst for Copolymerization of Epoxide with CO_2

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The synthesis of alternated polycarbonates via metal-catalyzed coupling reactions of CO_2 with epoxides has attracted a great deal of attention over the past several decades and is among the most promising processes for CO_2 utilization.[1] Since the seminal reports of Inoue in 1969 using a mixture of $ZnEt_2/H_2O$, a plethora of catalysts based on divalent (Zn, Co) and trivalent (Al, Co, Cr) metal centers with a wide variety of ligands (mostly with porphyrin, salen and β-diiminate type ligands) have been studied for various epoxides copolymerizing with CO_2.[2] The only examples of tetravalent metals complexes (with Ti, Zr, Ge and Sn) were recently investigated by Nozaki's group showing moderate activities and high selectivities towards epoxides/CO_2 copolymerization.[3] Inspired by this work, we investigated the potential of a new family of catalyst based on the use of tridentate *N*-heterocyclic carbene (NHC) pincer ligand combined with group 4 metals as catalyst component for the copolymerization of cyclohexene oxide (CHO) with CO_2 (Fig. 1).[4]

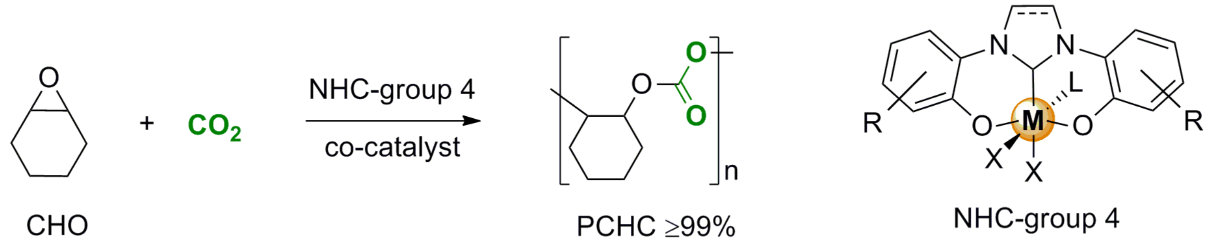

Figure 1 NHC group 4 complexes catalyzing CO_2/CHO copolymerization

The influence of different catalytic conditions applied to NHC group 4 complexes leading to the selective formation of poly(cyclohexene oxide-*alt*-carbon dioxide) (PCHC) will be discussed.

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Phosphorus-Stabilised Rare Earth(III) and (IV) Methanediides: Structure, Bonding, and Magnetism

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In contrast to well-studied and -understood transition metal carbene and alkylidene complexes, rare earth analogues that do not derive from stable, free carbenes are relatively limited. In recent years, however, various advances have been made, principally by using pincer methanediides to stabilize the formal M=C linkage.[1] We will describe the synthesis and characterization of methanediide complexes of rare earth metal complexes in formal oxidation states III and IV,[2-4] and describe their structure, bonding, and magnetism. For the latter formal oxidation state we will compare our observations to related uranium(IV) and thorium(IV) complexes.[5-8]

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Small Molecule Activation by Complexes of Low-valent f Elements

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Complexes of low-valent f-elements and of uranium in particular are excellent candidates for small molecule activation. Differing sterical and electronic environments at the U(III) and Ln(II) centers have a critical impact on the nature, structure, stability and reactivity of the reduction products. Careful tuning of the ligand is also essential to promote multi-electron transfer which is rare in U(III) chemistry. Notably, bulky siloxide ligands can be used to isolate stable U(III) complexes which act as multi-electron reducing agents in the reaction with a variety of small molecules such as CS_2, CO_2 and azides,[1] chalcogenides. Reduction of azides leads to highly reactive nitride-bridged diuranium complexes that can functionalize small molecules such as CO_2 and CS_2. Moreover, the sterical demand and electron-rich coordination environment of homoleptic siloxide complexes of Eu(II) and Yb(II) leads to the reduction of azobenzene, carbon disulphide and carbon dioxide and the ready release of the reduction products, a prerequisite for the implementation of catalytic cycles.[2] Finally, siloxide ligands lead to the formation of heterobimetallic complexes enabling the multimetallic cooperativity in uranium mediated reduction of carbon dioxide.[3] The redox chemistry of f element complexes with siloxides and other bulky ligands[4] will be presented together with the structure and properties of original compounds.

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Low nuclearity aluminum and aluminate derivatives with unusual structures: reactivity and catalytic activity.

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Aluminium chemistry awakens a broad interest due to its reactivity and structural behavior.[1] In our group we are interested in species containing Al-O bonds since often show interesting catalytic properties.[2] In particular we are focused in the preparation of low nuclearity species of well defined structures that can be active in catalytic polymerization processes. In order to achieve the formation of these species we have used as ligand precursors either functionalized or highly bulky phenols.[3]

Our studies have led to new homometallic aluminium species that show a high activity in ROP processes of functionalized monomers. As well the reaction of alkali metal phenolates and $(AlMe_3)_2$ allowed us to prepare heterometallic derivatives where the $AlMe_3$ moieties remained intact, coordinated to the alkali metal by the oxygen atom of the phenolate (see Figure 1). These species have a very interesting reactivity in activation reactions of C-H bond and small molecules such as CO_2. As well they are active in catalytic polymerization processes of functionalized monomers, *via* a different path than the one observed for the homometallic counterparts.

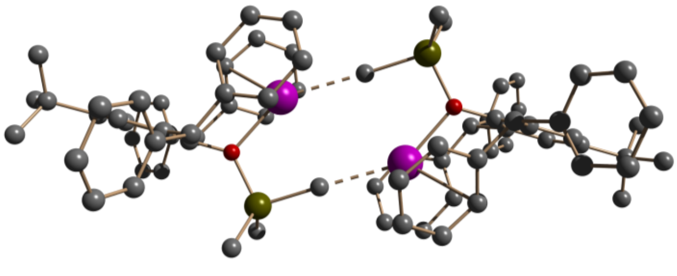

Figure 1. Structure of $[AlNa(Me)_3(OR)]$ in the solid state.

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Solvent dependent β-SiH vs. silazide abstractions by BPh_3 from alkali metal tetramethyldisilazides and catalysis.

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Tetramethyldisilazide [$–N(SiHMe_2)_2$] is an interesting amide functionality as the corresponding metal complexes often show unexpected reactivity through those β-SiH moieties.[1] Alkyl and hydride group abstractions by strong Lewis acidic $B(C_6F_5)_3$ are well-known routes to generate cationic or zwitterionic metal complexes.[2] Whereas, the weaker BPh_3 mediated group abstractions are rare in literature.[2c] Polydentate tris[2-(dimethylamino)ethyl]amine Me_6-TREN (L4) has recently become popular as an ancillary ligand to s-block metal complexes, enabling their isolation in monomeric form.[3] Solvent dependent β-SiH vs. silazide abstractions from $L_4MN(SiHMe_2)_2$ [L_4 = Me_6-TREN, M = Li, K] are observed in the presence of BPh_3 (Fig. 1). Whereas, $B(C_6F_5)_3$ prefers the β-SiH abstraction irrespective of solvents. The resulting $[L_4M][HBPh_3]$ complexes readily insert CO_2, and are also active for its catalytic reduction. whereas, the $[L_4M][HB(C_6F_5)_3]$ species are inert under similar conditions.

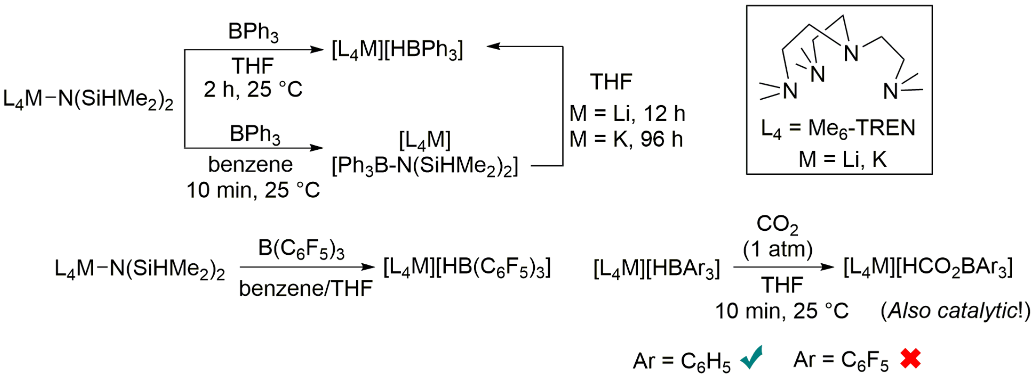

Figure 1. Solvent dependent β-SiH vs. silazide abstractions mediated by borane Lewis acids. Subsequent CO_2 insertion and catalysis are also observed.

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Coordination Chemistry and Reactions of Oxo-Titanium Polymers

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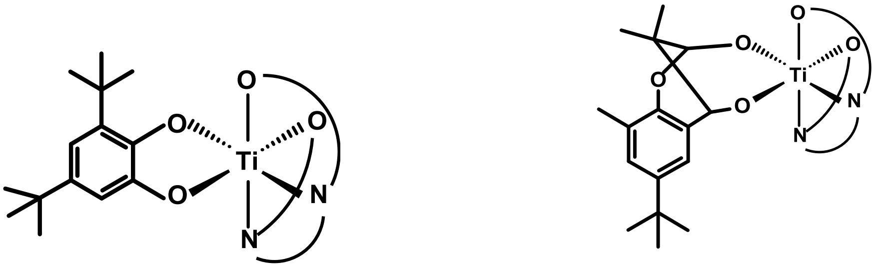
Polymeric titanium-oxo complexes containing salicylidene ligands are prepared in near quantitative yield and on a large scale by reacting a salicylidene ligand with $[Ti(OCHMe_2)_4]$ in ethanol containing water.[1] The polymeric complexes prepared were $[TiO(salen1)]_n$ (**1**) [salen1-H_2 = N,N'-bis(salicylidene)-2,2-dimethyl-1,3 diaminopropane], $[TiO(salen2)]_n$ (**2**), [salen2-H_2 = N,N'-bis(3,5-di-*tert*-butylsalicylidene)-2,2-dimethyl-1,3-diaminopropane] and $[TiO(salen3)]_n$ (**3**) [salen3-H_2, N,N'-bis(5-*tert*-butyl-3-methylsalicylidene)-2,2-dimethyl-1,3-diaminopropane]. Complexes (**1**)-(**3**) are highly insoluble in organic solvents and do not react with coordinating ligands such as pyridine to give lower polymers or monomeric complexes. The complexes do dissolve in hot solutions of aldehydes or ketones in which polymer deconstruction takes place but the solutions usually give back the original polymer on cooling. Potent reactivity is observed for some solutions whereby unprecedented carbon based chemistry is demonstrated by the formation of new complexes containing catecholato and diolato ligands (fig 1). The solubilised polymers are efficient catalysts for some aldol type C-C bond formations, various oxidations of organic compounds, an epimerisation reaction and the addition of CN^- to aldehydes. Catalyst deactivation takes place in the presence of organic acids forming $[(RCO_2)(salen)Ti\text{-}O\text{-}Ti(salen)(O_2CR)]$ complexes. The polymers have potential as 'smart catalysts' which revert to the insoluble poymeric form after reaction.

Figure 1 Catecholato and diolato complexes



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Reactivity of Organolanthanides Complexes with Redox Non-Innocent Ligands

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Redox non-innocent ligands are a matter of much recent interest in the development of catalytic species and the seminal work of Wieghardt and Chirik lead to the fast development of such catalysts capable of allowing important chemical reactions at lower economic and environmental costs.[1] The use of delocalized substituted pyridyl fragments is a typical strategy for the design of such redox non-innocent ligands and the extent of delocalization and the shape of the symmetry orbital that accept the electron(s) is of crucial importance because if significant spin density is built up at a specific site of the ligand, chemistry will occur and the stored electron(s) may be lost.

In our group, we use organolanthanides fragments in order to study the electron transfer from a metal complex to redox non-innocent ligands such as N- or P- aromatic heterocycles.[2,3] Recently, we have been able to show that when a single electron is transferred to a phenanthroline, a reversible sigma C-C bond formation occurs.[4] This strategy was also adapted to other organolanthanide fragments containing samarium and thulium and we whish to report the preparation of several phenanthroline adducts with divalent lanthanide fragments having different redox potential and different steric hindrance.[5] Despite their very different electronic nature, these complexes feature a C-C reversible coupling between the phenanthroline moieties in all cases albeit they show different thermodynamics in solution. We will also discuss the continuing story of these lanthanides complexes containing redox non-innocent ligands and its expansion to heterometallic complexes with lanthanides and transitions metal ions.

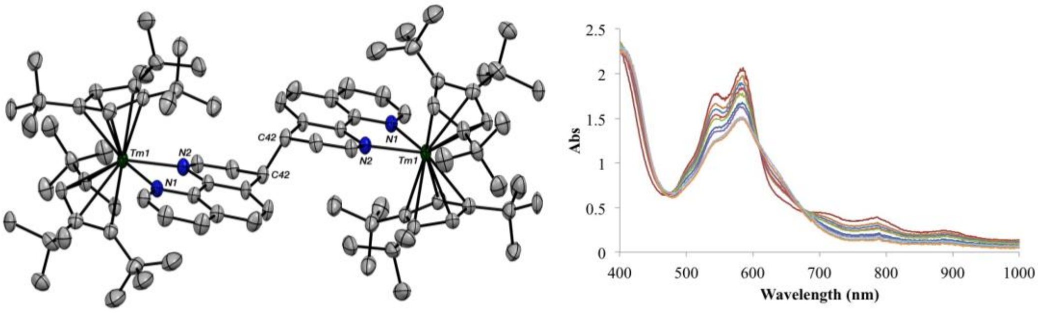

Figure 1 Crystal Structure of a Tm dimer exhibiting C-C reversible coupling and Visible spectra of the complex at different temperature.

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The butterfly effect from Mg to Ca in organometallic complexes

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The organometallic chemistry of magnesium has been widely developed for common Grignard reagents.[1] By contrast, calcium organometallic chemistry remains a permanent challenge.[2] Although Mg and Ca are adjacent group 2 metals in the Periodic Table, Ca–C bonds have a much stronger ionic character compared to Mg–C ones. Heteroleptic Ca and Mg amido and alkyl complexes show better activity than homoleptic compounds for catalytic purposes.[2,3] However, the Schlenk equilibrium, i.e. the redistribution of ligands that gives two homoleptic complexes: $(L_nX)AeX' = (LnX)_2Ae + AeX'_2$, often plagues the chemistry of heteroleptic alkaline-earth metal complexes. To prevent it, several monoanionic ancillary ligands of the type $(L_nX)^-$ have been devised .[2,3,4]

In this paper, we will present Ca and Mg heteroleptic complexes containing ancillary electron-withdrawing highly fluorinated tris(pyrazolyl)borate ligands $(F_{12}\text{-}Tp^{4Bo,Ph})^-$, which render these complexes more reactive.[3] Two kinds of heteroleptic complexes $[(F_{12}\text{-}Tp^{4Bo,Ph})AeX']$ (Ae = Mg, Ca) have been obtained for both metals, corresponding to two different labile co-ligands X': $-N(SiMe_2H)_2$ and $-C{\equiv}CPh$. Drastic changes in the X-ray structures and the agostic bonding patterns are caused by the different size of the two metals (Mg^{2+} = 0.72 Å and Ca^{2+} = 1.00 Å). The syntheses, structures and reactivity of these complexes will be discussed.

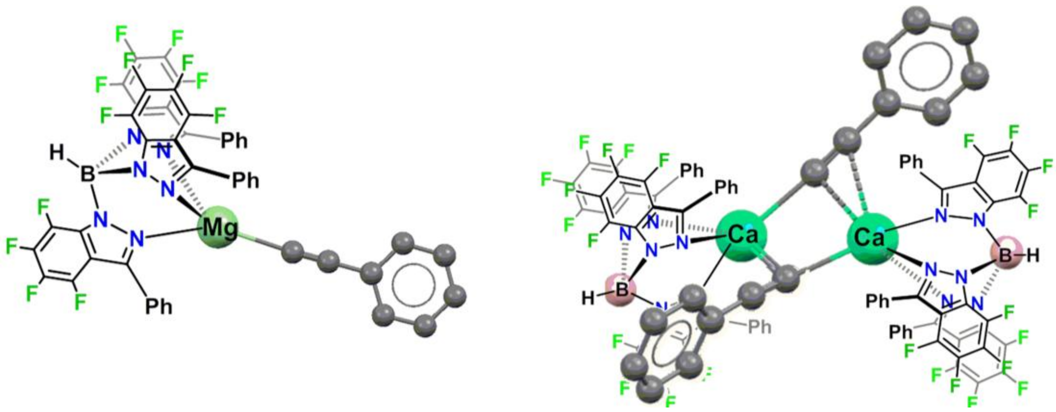

Figure 1 A monomer $[(F_{12}\text{-}Tp^{4Bo,Ph})Mg\{C{\equiv}CPh\}]$ and a dimer $[(F_{12}\text{-}Tp^{4Bo,Ph})Ca\{C{\equiv}CPh\}]_2$.

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Asymmetric Hydroamination with Piano-stool Compounds

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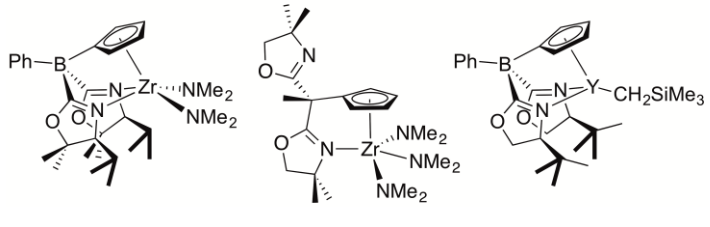
The hydroamination reaction offers a direct, waste-free, single-step route to chiral amines from olefins and less-substituted amines, but requires a catalyst. Low temperature hydroamination reactions are important because thermodynamics of N-H addition are less favorable at high temperature. We have prepared a series of mixed cyclopentadienyl-bis(oxazolinyl)borate-coordinated zirconium compounds $\{PhB(Ox^R)_2Cp\}Zr(NMe_2)_2$ that cyclize aminoalkenes at temperatures even down to -30 °C and give highly enantioenriched amine products.[1] Mechanistic features of these and related catalysts may provide design principles that allow challenging intermolecular additions.

Interestingly, the valence of the metal site affects the absolute configuration. Tetravalent zirconium and trivalent yttrium catalysts, with the identical chiral ligands, give chiral amines with ee > 90%, but opposite absolute configuration. Remarkably, charged Zr and neutral yttrium catalysts give products with identical configurations. The enantioselectivity in these systems is subjected to isotopic perturbation resulting from amine deuteration. Surprisingly room temperature reactivity is observed with even $CpZr(NMe_2)_3$, and oxazoline substitution also enhances cyclization rates in the zirconium system.[2]

$\{PhB(Ox^R)_2Cp\}Zr(NMe_2)_2$ cyclizes dialkene amines to give stereocenters from C-N bond formation and desymmetrization.[3] While the α-stereocenter is controlled by the chiral ancillary ligand, the peripheral stereocenter, as probed by diastereoselectivity, is influenced by reaction conditions including concentration, temperature, and isotopic substitution.



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Advances in Group 4 Hydroamination Catalysis. Intermolecular Alkene Hydroamination with Zirconium

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Group 4 catalyzed hydroamination has been intensively investigated for decades. Regioselective hydroamination of terminal alkynes has been realized using a Ti(amidate) complex (**1**).[1] The selective synthesis of reactive aldimine and more recently enamine intermediates has resulted in tandem sequential approaches to prepare amine and N-heterocyclic products. Advances in the one-pot synthesis of primary amines and selectively substituted pyridines from alkynes and silylated amines will be presented. This same catalyst promotes intramolecular reactivity resulting in tandem sequential routes for the enantioselective synthesis of morpholines and piperazines. A tethered Zr(ureate) complex (**2**)[2] that is effective for aminoalkene cyclohydroamination can also be used for intermolecular, alkene hydroamination with select substrates. Mechanistic insights into the anti-Markovnikov hydroamination of activated and unactivated alkenes will be presented.

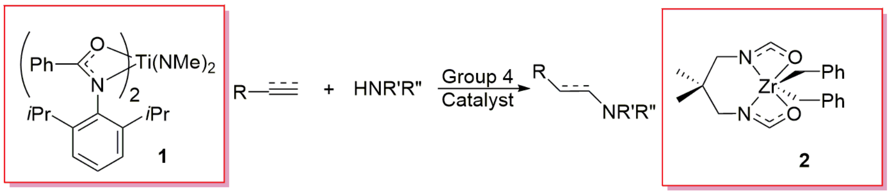

Figure 1 Amidate and ureate group 4 catalysts for advances in alkyne and alkene hydroamination catalysis.

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Alkene (asymmetric) hydroamination promoted by alkali- and rare earth-based complexes

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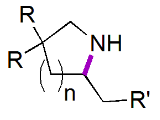
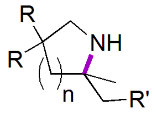
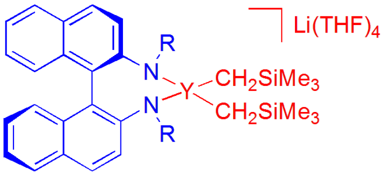
The metal-catalysed (asymmetric) hydroamination of olefins, formally the addition of a NH unit on a C=C double bond, perfectly meets the criteria of atom economic reaction.[1] The fine tuning of catalysts to perform this transformation with high selectivities remains at present a real challenge to take up, considering the importance of these compounds in medicinal and natural products chemistry. In recent years, numerous lanthanide and group III based catalysts proved successful for promoting this reaction. Our contribution in this field deals with the synthesis of well-defined new lanthanide amido alkyl ate and neutral complexes based on the binaphthylamido ligand. These catalysts promoted efficiently various intramolecular hydroamination reactions of amines tethered to simple[2] or polysubstituted alkenes[3] delivering the targeted nitrogen-containing heterocycles in high yields and selectivities. Easy routes towards (chiral) lithium binaphthylamido catalysts have also been discovered for the asymmetric hydroamination of amino-1,3-dienes[4] as well as for the *anti*-Markovnikov addition of amines on vinylarenes.[5]

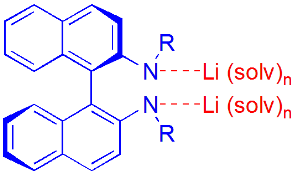


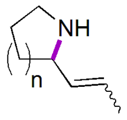
up to 77% ee



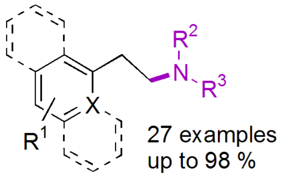
up to 55% ee







up to 72% ee (*E*)
E:*Z* up to 92:8



27 examples
up to 98 %

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Organolanthanides for catalytic olefin hydrophosphination

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Lanthanide complexes proved to be efficient catalysts for a wide range of transformations of unsaturated substrates (polymerization, hydroamination, hydrosilylation, hydroboration etc).

The synthesis and characterization of heteroleptic alkyl, hydrido, amido rare-earth (+2 and +3) and alkaline-earth complexes supported by various N,N-, N,N,N,N-, N,N,O-, N_2,O_4-, N,N,P(O)-ligands as well as their catalytic activity in intermolecular olefin hydrophosphination and hydroamination will be reported. The new complexes afford highly active, chemoselective and, in the case of monoadditions, 100% *anti*-Markovnikov regiospecific catalysts (down to 0.04 mol-% loading) for the hydrophosphination of styrene with $PhPH_2$ under mild conditions. The highest TOF 330 h^{-1} at 60 °C was observed for Yb(II) amido complex. These complexes also turned out to be efficient precatalysts for the intermolecular hydroamination of styrene and pyrrolidine.

Steric Control of Redox Events in Organo-Uranium Chemistry

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The use of well-defined molecular complexes of uranium has heralded new examples of chemical reactivity, especially in the topical field of small molecule activation.[1] For instance, in our laboratory we have shown the efficacy of organo-uranium complexes in promoting the reductive activation of CO and CO_2, and in particular the importance of the steric environment around the U(III) centre in controlling C-C bond formation.[2] Here we present further work underlining the influence of sterics in manipulating the oxidation state of the uranium centre, and resulting to the isolation of terminal oxo and nitride U(V) complexes (Figure 1).

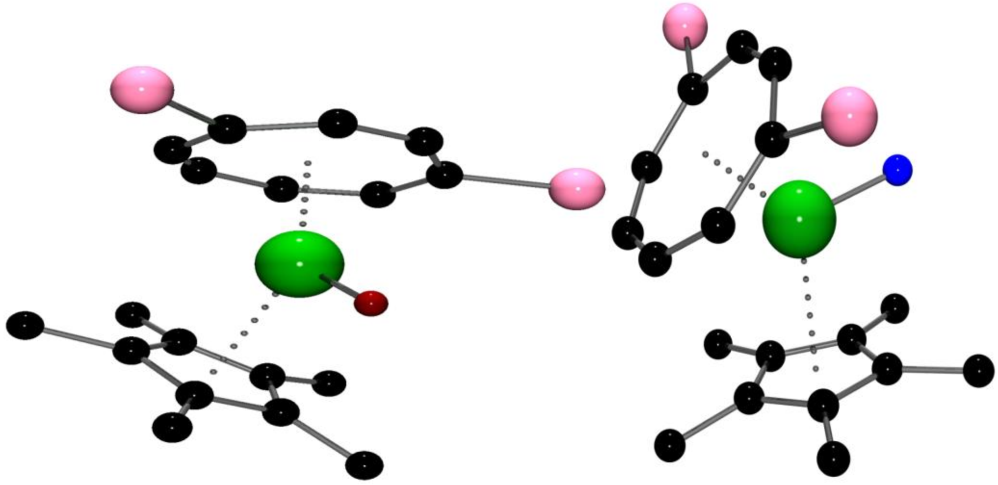

Figure 1 Mixed sandwich U(V) terminal oxo (left) and terminal nitride (right; Na counter-cation omitted for clarity) complexes

[1] a) Stephen T. Liddle, *Angew. Chem. Int. Ed.,* **2015,** *54,* 8604. b) P. L. Arnold, *Chem. Commun.*, **2011,** *47,* 9005. c) M. Ephritikhine, *Organometallics,* **2013,** *32,* 2464. d) H. S. La Pierre and K. Meyer, *Prog. Inorg. Chem.,* **2014,** *58,* 303.

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Switchable Catalysis: From Mixed Metals to Sequence Controlled Polymers

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The ring-opening copolymerization (ROCOP) of carbon dioxide and epoxides is an attractive means to add-value to waste CO_2 and to make useful polymers.[1] The process depends on the catalyst, with homogeneous dinuclear metal complexes showing significant potential. So far, these have all been homodinuclear complexes, however, the first example of a heterodinuclear Zn/Mg complex which significantly out-performs either the di-zinc or d-magnesium analogues was recently reported (Fig. 1).[2] The synthesis, catalysis, kinetic data and mechanistic hypotheses will be presented.

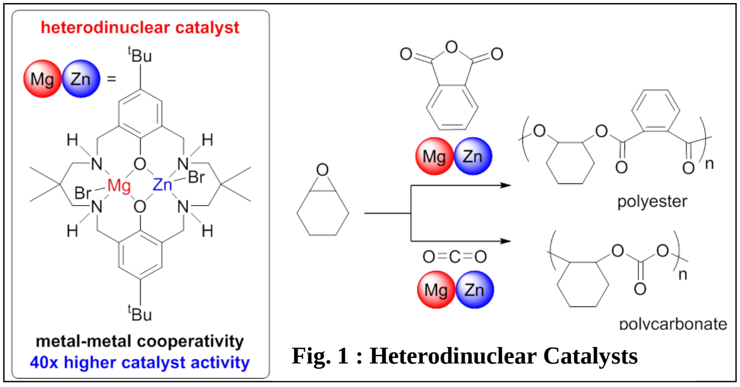

Fig. 1 : Heterodinuclear Catalysts

The same type of dinuclear catalysts can also be made to 'switch' between different polymerization cycles.[3] This allows a single catalyst, in one-pot, to selectively enchain mixtures of monomers to prepare sequence selective block polyesters/carbonates (Fig. 2). This novel 'switch' catalysis has been studied in detail, by a combination of spectroscopic, kinetic and theoretical (DFT) methods. This revealed the importance of the chemistry of the metal-polymer chain end group as a means to control the monomer selectivity.

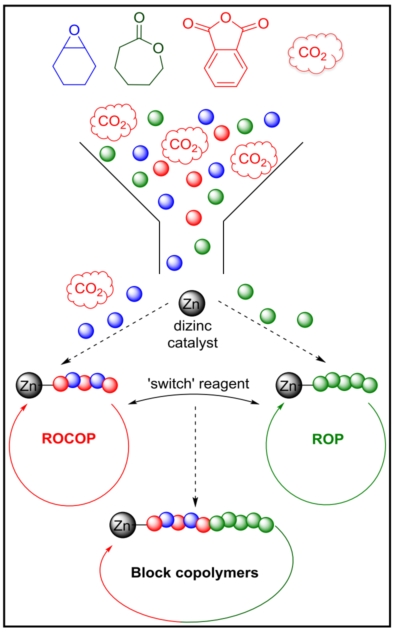

Fig. 2 : Switch Catalysis

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3. (a) Zhu, Y.; Romain, C.; Williams, C. K. *J. Am. Chem.Soc.* **2015**, *137*, 12179-12182; (b) Romain, C.; Williams, C. K. *Angew.Chem.Int. Ed.* **2014**, *53*, 1607-1610.

Triscyclopentadienyl-lanthanides/actinides and some derivatives: structural investigations

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Triscyclopentadienylactinide$^{(iii)}$ complexes ($Cp_3An^{(iii)}$) are among the first in the literature described organometallic actinide compounds. Their properties have been investigated extensively and reported since the 1965 [1, 2]. Nevertheless until present there has been a substantial lack of structural investigation of these compounds.

In the presentation the structural features of $Cp_3An^{(iii)}$ will be compared to those of their isosteric $Ln^{(iii)}$-complexes. Results from NMR spectroscopic investigations as well as some selected Lewis base adducts will be presented as well.

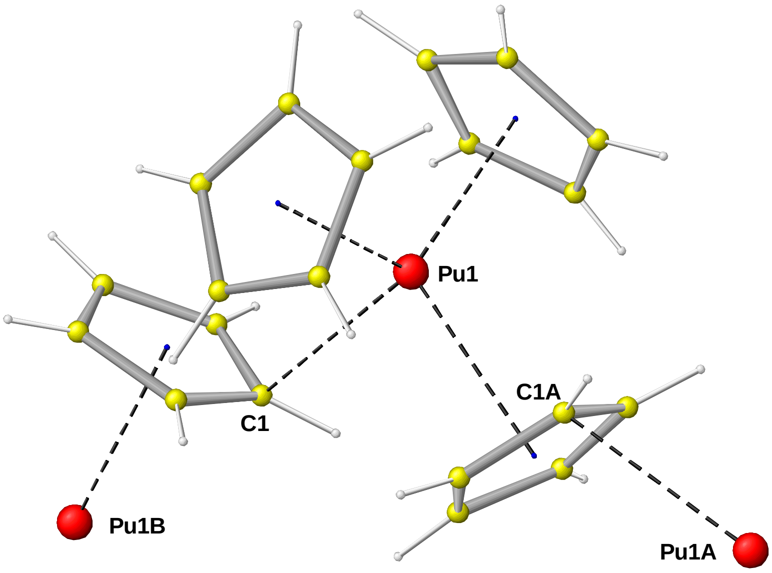

Figure 1 View to a representative part of the polymeric molecular structure of $Cp_3Pu^{(iii)}$ in the crystal, symmetry generated atom names are indexed with A or B.

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2 C. Name, P. Name, *Journal*, **year**, *vol*, first page (arial 10).

Bis- and Tris(pyrazolyl)methanides of Calcium

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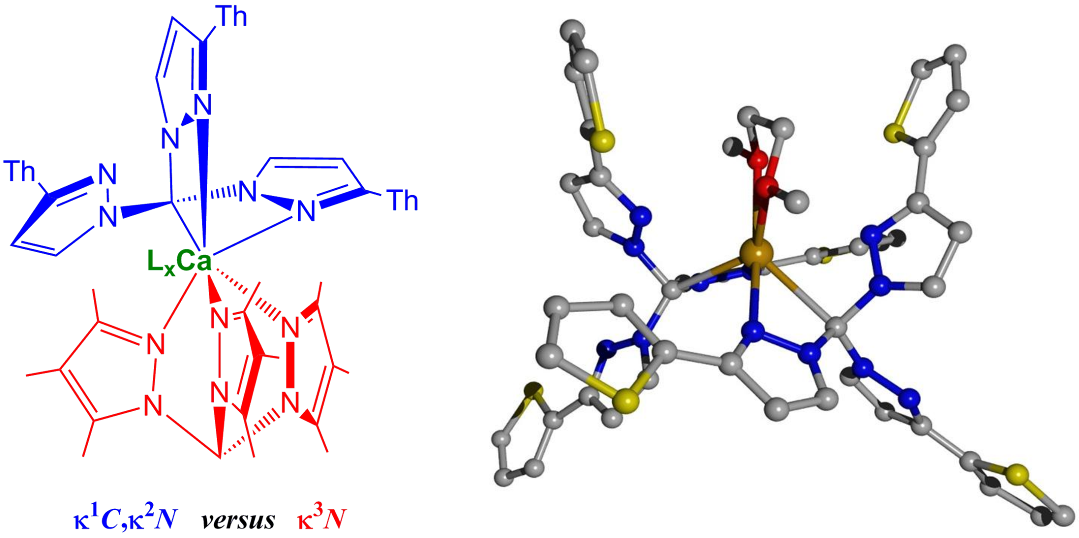
Tris(pyrazolyl)boranate complexes of main group and transition metals commonly exhibit an enormous stability and are able to facially shielding the central metal ions. Isoelectronic tris(pyrazolyl)methanes and -methanides are common in d-block metal chemistry but are quite rare in s-block metal coordination chemistry. In principle, the tris(pyrazolyl)methanide ligands can show the common κ^3N coordination mode (Figure 1, red) or the rare $\kappa^2N,\kappa C$ binding mode (Figure 1, blue).[1]

Figure 1: Coordination modes of tris(pyrazolyl)methanide ligands at calcium (Th = thienyl) (left) and molecular structure of $[(dme)Ca\{\kappa^2N,\kappa C\text{-}C(Pz^{Th})_3\}_2]$ (right, Pz^{Th} = 3-thienyl-pyrazolyl, C gray, Ca brown, N blue, O red, S yellow).[2]



Formation of a calcium-carbon bond ($\kappa^2N,\kappa C$ coordination mode) initiates decomposition, finally yielding calcium bis(pyrazolates) and tetrakis(pyrazolyl)ethene.[2,3] A degradation mechanism is discussed and stabilization strategies are presented.

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Synthesis of new cationic amino Group IV metallocenes: Toward Organometallic Frustrated Lewis Pairs

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In 2006, D. W. Stephan introduced the concept of "Frustrated Lewis Pairs".[1] The main characteristic of these compounds is their ability to activate cooperatively small molecules such as H_2, CO_2, alkene alkyne… Initially based on P/B combination, the concept has been extended to several other main groups elements (N/B, P/Al, N/Al …).[2,3,4,5] Recently the groups of Wass,[6] Stephan[7] and Erker[8] have revived the idea that transition metal complexes can also be involved as one of the two FLP partners and they independently reported a series of zirconocene and titanocene -phosphine complexes which feature FLP properties. These organometallic FLP (omFLP) are obviously non-metal free systems but they extend significantly the scope of FLP applications. Seeking to develop such systems, we initiated a research toward new FLP combinations (N/Ti, N/Zr) and focused on the synthesis of titanocene and zirconocene complexes bearing pendant bulky amine with C1 spacer between cyclopentadienyl ring and the amine function. Herein we present the synthesis of these new omFLPs and the study of their reactivity (Figure 1).

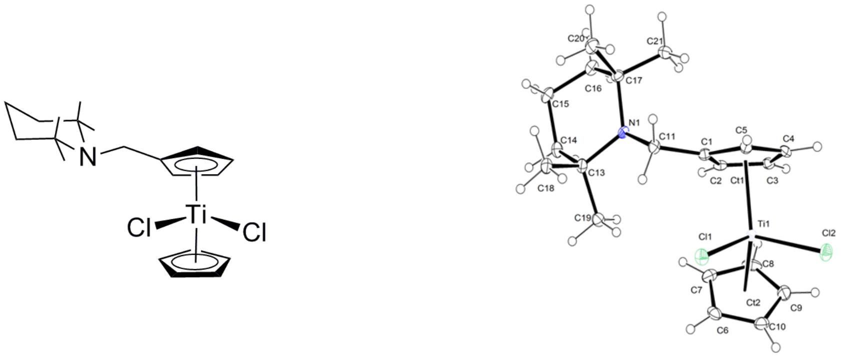

Figure 1 Titanocene tetramethylpiperidine as intermediate toward om-FLP

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Optical and electrochemical properties of chiral salen-type transition metal(II) complexes for dye-sensitized solar cell

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Recently dye for dye-sensitized solar cells (DSSC) are studied to absorb vis-NIR light with high efficiency.[1] Previously certain chiral salen-type Cu(II) complexes as DSSC with electron withdrawing gruops absorbes wide wavelengths of sunlight.[2] Herein, to tune CT bands and redox potential by a substituent effects, we have systematically prepared chiral salen-type Fe(II), Co(II), Ni(II), Cu(II), and Zn(II) complexes **1-25** (Figure 1) and compared their electronic properties. Diffuse reflectance UV-vis-NIR spectra for Co(II) ones (Figure 2) exhibited long-wavelength shift of CT bands accompanying with gradual changes of their redox potentials. Among other metals, short-wavelength shifts of the corresponding bands and changes of redox potentials (TiO_2 / I_3^-) could also observed except for Zn(II) ones. Adsorption of Cu(II) ones with XPS and fluorescence spectra of Zn(II) ones were also measured. Performance as DSSC cells will be reported at the conference.

X-	Y-	M				
		Cu	Fe	Co	Ni	Zn
H-	H-	**1**	**6**	**11**	**16**	**21**
Br-	H-	**2**	**7**	**12**	**17**	**22**
Br-	Br-	**3**	**8**	**13**	**18**	**23**
Cl-	H-	**4**	**9**	**14**	**19**	**24**
Cl-	Cl-	**5**	**10**	**15**	**20**	**25**

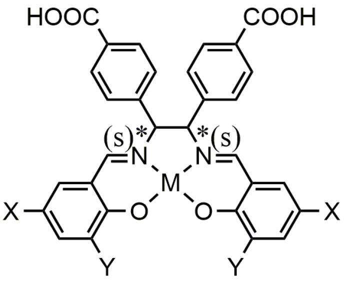

Figure 1 structures of complexes **1-25**.

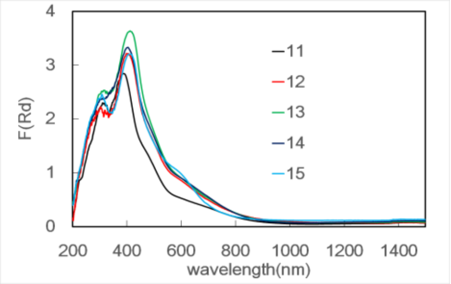

Figure 2 UV-VIS-NIR spectra of Co(II) complexes **11-15**

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[1] H. Kim *et al*., *J. Am. Chem. Soc.*, **2008**, *130*, 12184.

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New trends in the design of transition-metal based OLED phosphors

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Luminescent third-row transition metal Os(II), Ir(III) and Pt(II) based complexes, particularly those with cyclometalating chelates and equivalents, play a key role in the recent development of optoelectronic technologies such as organic light emitting diode (OLED), light emitting electrochemical cells, and solid-state organic lighting applications. Their attractiveness comes from their higher chemical stability due to the strong metal-ligand bonding interaction, as well as the longer excitation lifetimes and higher emission quantum yields. Furthermore, the strong spin-orbit coupling induced by the central metal ion promotes an efficient intersystem crossing from the singlet to the triplet excited state manifold, which then facilitates strong electroluminescence by harnessing both singlet and triplet excitons of the as-fabricated optoelectronic devices. As a result, syntheses of these metal complexes were extensively examined. In this presentation, the recently development of new OLED phosphors, particularly those constructed with tridentate chromophores, with functional diimine, NHC carbene, azolate and even biazolate chelates, as well as those have showed bright blue phosphorescence, will be elaborated in a systematic manner.

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Photochemical Upconversion and New Frontiers in Triplet Sensitization

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One focus of our research program involves the study of sensitized triplet fusion (TF) processes that convert low energy photons to higher energy light. Selective excitation of long-wavelength absorbing triplet sensitizers in the presence of appropriate molecular acceptors enables TF, resulting in either frequency upconverted light or the formation of desired chemical products. Various combinations of donor and acceptor have been explored and data will be presented on a number of these compositions spanning light conversions ranging from the near-UV to the near-IR. This presentation will also describe recent examples of upconversion phenomena realized in solid-state and fluidic polymeric materials along with emerging classes of sensitizers and acceptor/annihilator chromophores. Semiconductor (SC) nanocrystals are demonstrated to sensitize interfacial triplet-triplet energy transfer with molecular acceptors, providing a general paradigm for extracting triplet exciton energy from SC nanomaterials while extending their reactivity time by six orders-of-magnitude. The concept of SC nanocrystals serving as effective surrogates for molecular triplets suggests myriad of possible chemical and redox transformations relevant for fields as diverse as optoelectronics, solar energy conversion, and photobiology.

Molecular and Supramolecular devices for room temperature upconversion in heavy water.

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Upconversion (UC) is an Anti-Stokes luminescent process by which photons of low energy are piled up to generate light at a higher energy. For a long time restricted to solid state materials or polymers,[1] very recent examples have paved the way to the observation of UC in solutions,[2-4] in organic solvents or at low temperatures.

We have recently observed that lanthanide complexes of ligand L self-assemble in aqueous solution in the presence of fluoride anions to generate supramolecular dimers stabilized by fluoride bridging, hydrogen bonds and aromatic stacking interactions.[5]

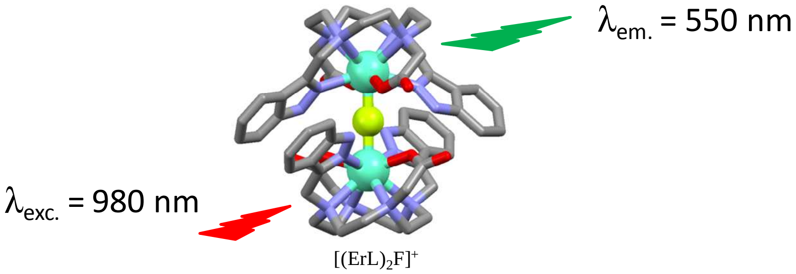

Figure 1 Fluoride templated formation of supramolecular Ln dimers of Er.

We here show that the formation of the Er dimer is accompanied by the unique observation of UC with green Er emission being observed upon excitation in the NIR domain (980 nm) at room temperature in D_2O,[6] the dimerization improved UC pleading in favor of an intramolecular energy transfer UC process.

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High Structural and Optical Diversities in Gold(I) Thiolate Coordination Polymers

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[b] ILV, CNRS / Université de Versailles St-Quentin, Versailles, France.
[c] Departamento de Quimica, Universidad de La Rioja, Logroño, Spain
[d] ILM, CNRS / Université Lyon 1 - Villeurbanne, France.
[e] LMI, CNRS / Université Lyon 1 - Villeurbanne, France.
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Polynuclear hybrid Au(I) compounds exhibit a very large domain of applications such as electronic devices, contrast agents, sensors or photocatalysts. All these applications are related to the ability of gold(I) to give luminescent materials.[1] Among hybrid gold species, gold(I) thiolate compounds are an important class of materials due to the high affinity of gold for sulfur atoms that can generate molecular complexes, extended polymers, stabilized gold nanoparticles or self-assembled monolayers. However relatively little is known about the relationship between the structure of the Au(I)-thiolate and their photophysical properties. So to understand their luminescence, we present syntheses and crystallographic structure, solved from powder X-Ray diffraction, of series of $[Au(I)(SR)]_n$ coordination polymers. Their photophysical properties are studied in solid-state with the temperature and present various luminescence behaviors. Thus, one displays a high quantum yield of around 75 % and another shows a dual emission with a strong potential as ratiometric thermometer (Fig. 1).[2] DFT calculations lead to explain the origin of these emissions that is not only due to the aurophilic interactions. In addition $[Au(SPh)]_n$ compound exhibits a rare solid-state amorphous-to-crystalline phase transition upon heating which is also associated with the apparition of luminescence.[3]

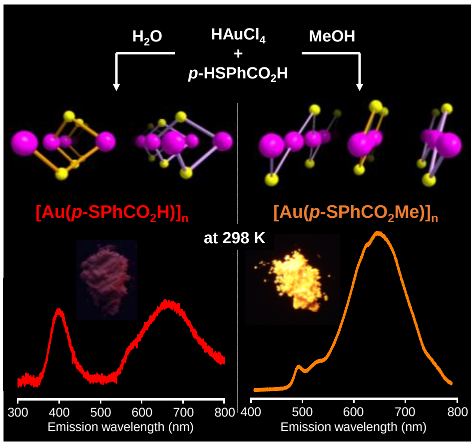

Figure 1 Examples of $[Au(SR)]_n$ coordination polymers.

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Red-absorbing, near-infrared-emitting lanthanide complexes

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Luminescence imaging is an attractive technique for the investigation of complex biological samples due to its non-invasiveness, high spatiotemporal resolution and the relatively low cost of the required instrumentation. Lanthanide-based emitters, in particular Eu- and Tb-complexes, have long been employed in biochemical assays, and recently have become popular for live cell imaging.[1] This is due to their long-lived emissions, which enables essentially background-free data acquisition with time-resolved techniques, and their narrow emission bands, the positions of which are characteristic of the metal, and are quite insensitive to the environment.

In order to achieve deep sample penetration, and to minimize damage to biomolecules, long-wavelength excitation light is desirable. Eu and Tb emit in the visible, which necessitates their excitation through light-harvesting antennae that absorb in the UV. Nd and Yb are near infrared emitters, and can be sensitized with antennae that absorb in the visible. However, Yb- and Nd-complexes usually have very low quantum yields, especially in aqueous systems (such as biological samples), and few successful examples of near infrared-emissive lanthanide complexes for biological imaging exist.[2]

We have been exploring the utility of a class of hydroporphyrins (chlorins) for the sensitization of Yb and Nd.[3,4] Chlorins have intense and narrow absorption bands in the red. The absorption band is tunable by judiciously chosen peripheral substituents. The combination of chlorins with either Yb or Nd in principle opens the door to red-absorbing, near infrared-emitting complexes with readily adjustable absorption bands. The synthesis and photophysical characterization of several chlorin-appended lanthanide complexes will be presented, and their utility as imaging agents evaluated.

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From Ruthenium to Iron Complexes: The Challenging Chemical Tuning of Photophysical Properties

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The interest in organometallic complexes for optical applications is growing continuously. Ruthenium polypyridine complexes have long been considered as lead compounds due to their ideal photophysical and geometrical properties and used with success in Dye-sensitized Solar Cells (DSSCs) with efficiencies in the 9-12 % range. While ruthenium-based complexes have been widely investigated and used in many different lab scale applications,[1] it is a scarce metal. In contrast, iron is naturally abundant, of low cost and low toxicity and thus appears as an ideal substitute.

However, the replacement of ruthenium by iron is extremely challenging since in Fe-pyridine complexes an ultrafast non-radiative deactivation of the ^{1,3}MLCT states into the low-energy metal-centered quintuplet $^5T_2$ make Fe-pyridine unsuitable for applications requiring higher free energies.

Our group has reported new carbene-based ligands for the stabilization of the ^{3}MLCT state in iron complexes, clearly demonstrated by means of ultrafast photophysics, together with a concomitant destabilization of the MC state. We have obtained the longest ^{3}MLCT state ever reported for iron(II) complexes. We have shown that several of our iron complexes can sensitize the TiO_2 semiconductor in a laboratory DSSC, leading to measurable photocurrent and power conversion efficiency.[2]

The conference will present our works on the preparation of iron complexes with focus on the chemical tuning of electronic and photophysical properties as well as their applications in DSSCs.

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DEVELOPMENT OF PHOSPHORESCENT IRIDIUM CYCLOMETALATED COMPLEXES WITH BIS(BENZIMIDAZOLYL)BENZENE OR PYRIDINE

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New direction to future functional luminescent materials of phosphorescent cyclometalated Ir complexes is clearly emerging since the applications of the Ir complexes as OLED devices have only been highlighted for two decades. We have studied synthetic studies of cyclometalated Ir complexes bearing tridentate N-heteroaromatic ligand such as bis(benzimidazolyl)-benzene or –pyridine, 1,3-bis(3-methylpyrazolyl)benzene, and found the mixed-ligand Ir complexes [Ir(N^C^N)(N^C)X] had highly phosphorescent materials and the emission color was tuned to blue by the change of tridentate N^C^N ligand from benzimidazole to imidazole or pyrazole group. Considering from the potential flexibility for these Ir complexes, our study is now engaged in the design of new photo-functional materials having (1) external stimuli response by pH and metal ion, and (2) luminescent network structure on surface, which will present in this talk.

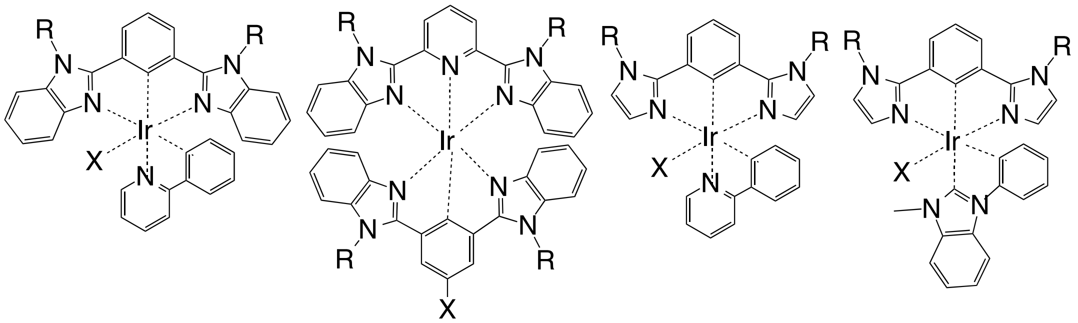

Figure 1 Chemical structures of Ir complexes bearing tridentate ligand

References

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Luminescence Properties of Praseodymium Complexes with a Series of Hexadentate N$_6$-Ligands

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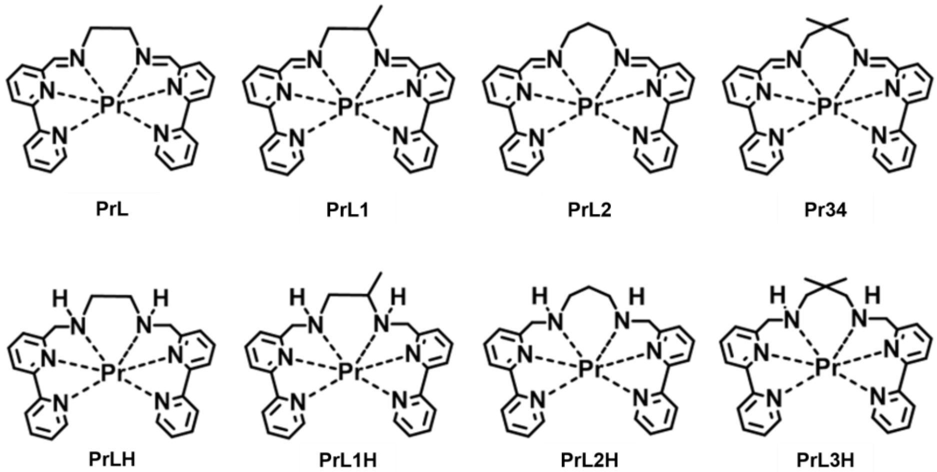
Trivalent praseodymium ion has useful luminescent levels in triplet or singlet spin multiplicity, supporting to understand the luminescence mechanism through intramolecular energy transfer[1]. We succeeded to realize helicate rare earth complexes with Eu^{III}, Gd^{III}, Tb^{III}, Nd^{III} and Ho^{III}.[2] Here, luminescence and structural properties of eight Pr^{III} complexes with hexadentate ligands (**Figure 1**) were examined. The helicate structure of each complex was determined by a single crystal X-ray structural analysis. The molecular distortion of Pr**L1** is larger than that of Pr**L** due to the different lengths of the bridging site. Pr**L** shows luminescence bands originated from ff transitions by UV excitation, and especially the 600 nm band significantly appears. Since the ligand of Pr**L** was reduced as Pr**LH**, ff emission bands in Pr**LH** appearing at higher energy are strengthened more than those in Pr**LH**. Thus, the conjugation length of series of **LH** becomes shorter than those of **L**, which clearly influences the energy donor levels. In this presentation, we will introduce their characterizing system based on the luminescence and structural properties[3].



PrL **PrL1** **PrL2** **Pr34**

PrLH **PrL1H** **PrL2H** **PrL3H**

Figure 1 Pr^{III} complexes with hexadentate ligands to evaluate their structural effect on luminescence properties.

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Understanding and Tuning of Excited States of NIR-Luminescent Transition Metal Complexes

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Near-IR emissive ruthenium(II) and chromium(III) complexes based on tridentate ligands with large bite angles and on tridentate cyclometalated ligands will be presented.[1-6] Their differing excited state properties will be discussed based on ligand field effects, orbital symmetry and electronic push-pull effects of the ligands. The luminescence quantum yields and excited state lifetimes correlate to the effects of close-lying ligand field states (Ru: $^3T_1$, Cr: $^4T_2$), ligand-to-ligand charge transfer (^{3}LL'CT) excited states or high-energy oscillators, as will be shown by steady-state and time-resolved emission spectroscopy, variable temperature emission spectroscopy, transient absorption spectroscopy, as well as density functional theory calculations.

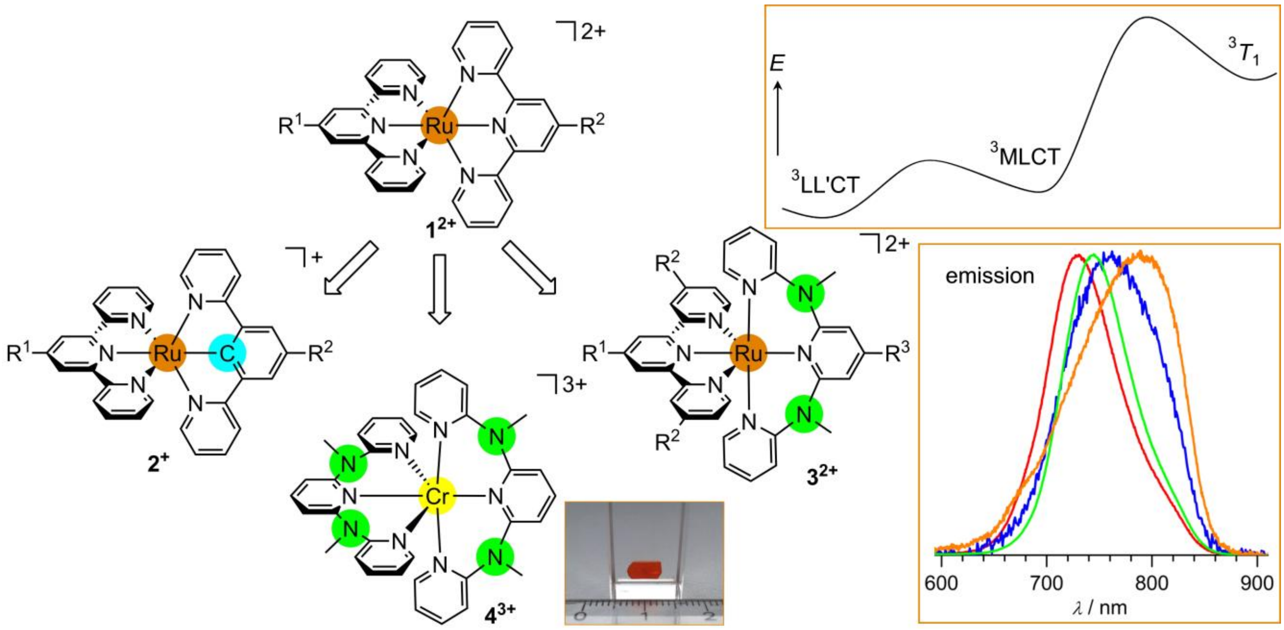

Figure 1 Luminescent transition metal complexes **1**$^{2+}$, **2**$^{+}$, **3**$^{2+}$, and **4**$^{3+}$.

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Angew. Chem. Int. Ed. **2015**, *54*, 11572.

Luminescent Rhenium(I) Diimine and Carbene Complexes – Photophysics, Photocatalysis and Anion-Sensing

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Transition metal complexes with N-heterocyclic carbene (NHC) ligands have been rapidly developed over the past two decades. The unique properties of the NHC complexes can be explained by the excellent σ-donating ability, stability and the ease of functionalization of the NHC ligands, which allow for the tuning of their electronic and steric properties. In recent years, we have designed and synthesized serval new classes of readily tunable luminescent isocyano Re(I) diimine complexes, $[Re(CNR)_4(N–N)]^+$, $[Re(CO)(CNR)_3(N–N)]^+$, and $[Re(CO)_2(CNR)_2(N–N)]^+$.[1a] Inspired by the excellent emission properties of these complexes, we have also developed a new series of charge-neutral strongly phosphorescent isocyanoborato Re(I) complexes for the electroluminescent device application.[1b,1c] As isocyano metal complexes are good synthetic precursor for the preparation of metal NHC complexes, we have extended our work to develop new classes of luminescent Re(I) NHC complexes.[2,3] Some of these Re(I) NHC complexes not only show photophysical properties different from that of the Re(I) diimine complexes, they also exhibit interesting anion-binding and CO_2 capturing properties.[4] To elucidate the electronic structures and transitions of these complexes, DFT and TD-DFT calculations have also been performed.

On the other hand, the uses of the ^{3}MLCT excited states of these complexes and that of the cyclometalated Ir(III) complexes as photocatalysts for catalyzing the amide formations will also be described.[4]

---

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4 The work described in this paper was supported by the RGC GRF grants from the Research Grants Council of the Hong Kong (Project Nos. CityU 101212 and CityU 11303515)

Luminescent polynuclear copper group metal complexes based on heterocyclic phosphines

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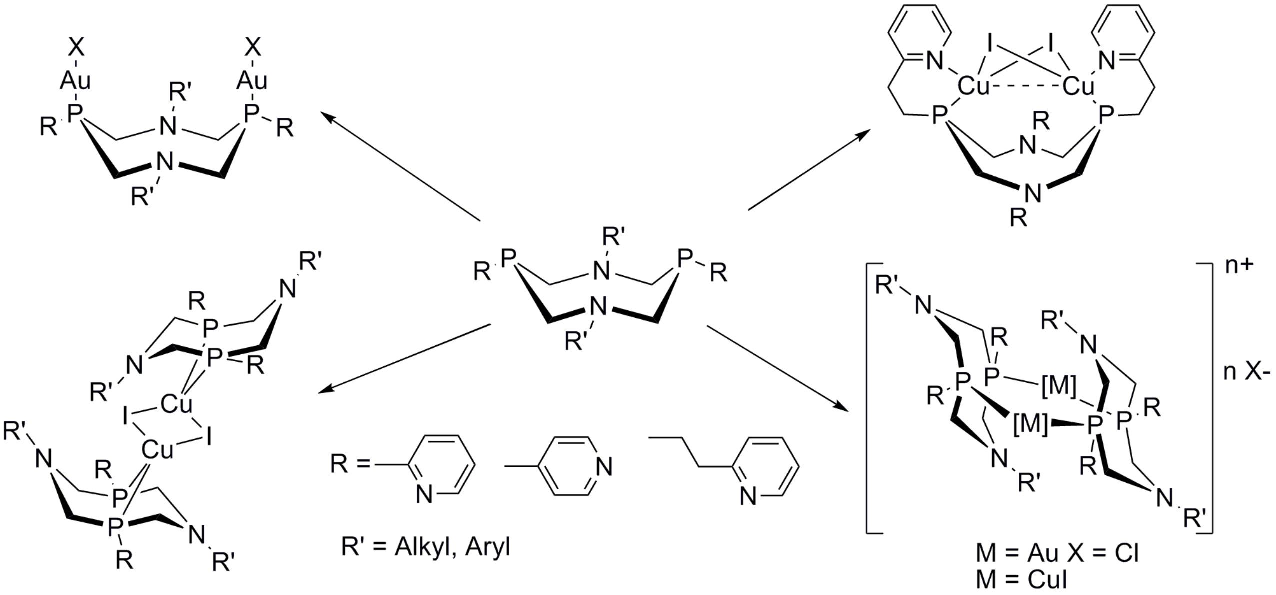
Cyclic aminomethylphosphines are compounds with phosphorus and nitrogen atoms incorporated into one cyclic system so that these atoms influence on each other. Despite the presence of two different heteroatoms this system is not a hybrid ligand because usually nitrogen atom is non-coordinated. In the present work we are representing the new pyridylphosphines [1,2] on the cyclic aminomethylphosphine platform and their polynuclear cupper group metal complexes with luminescent properties.



All complexes obtained show solid state luminescence in the green range of spectra. Moreover, gold complexes demonstrate the distinct vapochromic behavior. An emission band shifting from green to red range of spectra after contact with solvent has been found.

This work was supported by the Russian Scientific Foundation (grant no. 15-13-30031)

1. E.I. Musina, V.V. Khrizanforova, I.D. Strelnik, M.I. Valitov, Yu.S. Spiridonova, D.B. Krivolapov, I.A. Litvinov, M.K. Kadirov, P. Lönnecke, E. Hey-Hawkins,Yu.H. Budnikova, A.A. Karasik, O.G. *Chem. Eur. J.l*, **2014**, 20, 3169
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Electronic excited states of transition metal sandwich complexes: From DFT calculations to experimental gas-phase optical properties

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Metallocenes and related sandwich systems reveal unique gas-phase optical properties due to Rydberg transitions appearing in the absorption and ionization spectra. Rydberg parameters of sandwich molecules reflect the molecular symmetry, electron density distribution, excitation energies and configuration interactions. Rydberg spectroscopy represents, therefore, a powerful instrument to verify the results of quantum chemical calculations. In this work, the nature and energies of the (Arene)$_2$M (M = Ti, Ti$^+$, V, V$^+$, Cr, Cr$^+$, Arene = benzene and its methylated derivatives) and $(C_7H_7)(C_5H_5)M$ electronic excited states have been determined on the basis of the time-dependent density functional theory (TD DFT) approach and experimental photoabsorption/photoionization spectra. Both valence-shell and Rydberg electronic excitations were taken into account. The TD DFT results appear to describe correctly the influence of the metal atom and the ligand on the band positions and intensities in the UV-visible absorption spectra as well as the mixing of Rydberg and intravalency states. The TD DFT calculations suggest new assignments for long-wavelength absorption bands in the spectra of (Arene)$_2$V and (Arene)$_2$Cr$^+$. To get precise experimental data on the energies of the lowest Rydberg excitations in sandwich systems the resonance-enhanced multiphoton ionization (REMPI) and multiphoton dissociation/multiphoton ionization (MPD/MPI) spectroscopic techniques were adjusted for measuring ion signals from sandwich molecules cooled in a supersonic jet. The MPD/MPI spectra of $(C_6H_6)_2Cr$ in the region of the first Rydberg 4p transition have been obtained for the first time. The spectra appeared to reproduce exactly the features observed in the REMPI spectrum. This provides new opportunities for high resolution studies of sandwich excited states.

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 14-13-00832 supported by the Russian Science Foundation.

Phosphorescent *N*-Heterocyclic Allenylidene Complexes

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Our recent studies focus on the cumulenic homologues of *N*-heterocyclic carbenes and pyridylidenes. The heteroatoms are mandatory for the stabilization of the allenylidene structures through π-interactions. The resonance between the zwitterionic acetylide and the neutral allenylidene forms have been argued to contribute to the ground-state stabilities. The pyridylium acetylide is structurally similar and isoelectronic to the widely used arylisocyanide, such as 2,6-dimethylphenylisocyanide, implying that the *N*-heterocyclic allenylidene (NHA) chemistry could be as rich as that of the arylisocyanides and *N*-heterocyclic carbene (Figure 1). We report here that many NHA complexes (Figure 2) are stable and exhibit intriguing properties, such as phosphorescence, metallophilicity, chromonic self-organization and cytotoxicity.

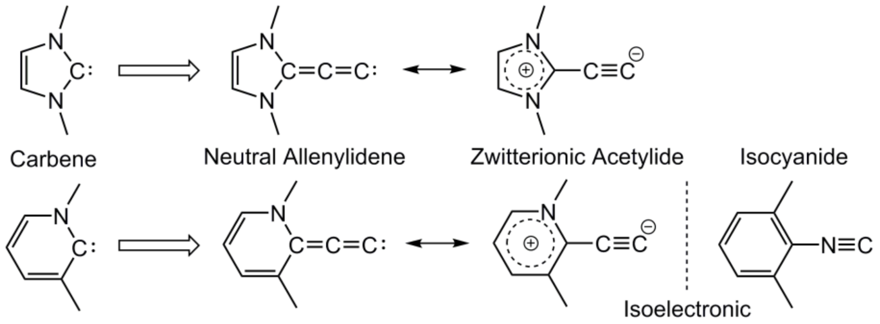

Figure 1 Extension from NHC to NHA and mesomerism between allenylidene and zwitterionic acetylide

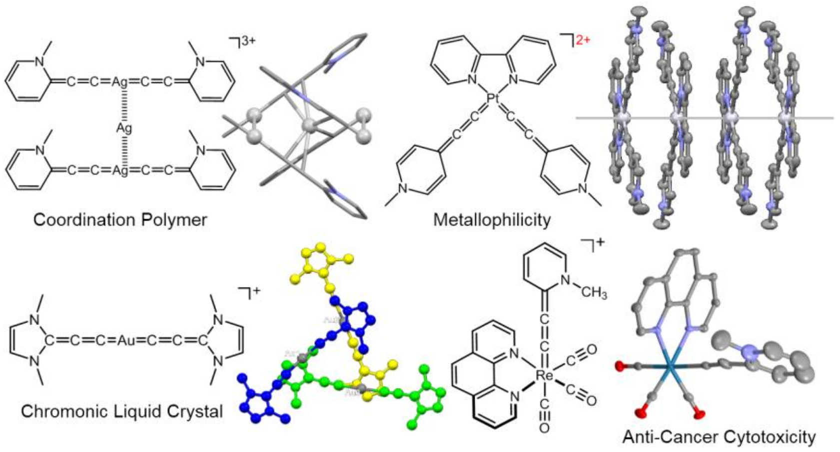

Figure 2 Chemical and crystalline structures of NHA complexes under study.

Lanthanide Complexes Enabling Spectral and Temporal resolution in biphotonic imaging microscopy

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The sensitization of lanthanide luminescence by nonlinear two-photon (2P) absorption process allows *a priori* to combine the intrinsic advantages of rare earth spectroscopy (line shape emission with large Stokes shift, long lifetime) and those of biphotonic microscopy (NIR excitation, 3D resolution,…) for bio imaging purpose.[1] In this context we reported a family functionalized triazacyclononane ligands leading to the formation of ultra-bright Eu, Tb, Yb, Sm(III) complexes featuring optimized brightness.[2] We also developed original microscopy set-up enabling two-photon imaging in the NIR-to-NIR configuration,[2a] multiplexing experiments,[3] time resolved imaging (PSLIM) and temporal Sampling Lifetime Imaging Microscopy (TSLIM).[4]

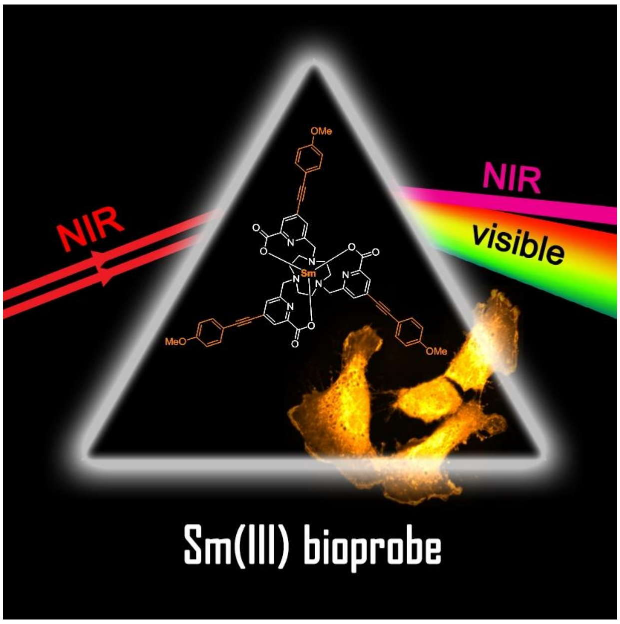

Figure 1. Biphotonic bioimaging using Sm(III) bioprobe.

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Sensitised Ln(III) Emission and Excited-State Dynamics of Cofacial 'Pacman' Porphyrin Terpyridine Complexes

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Lanthanide luminescence has received significant literature interest due to the sharp emission bands and long-lived excited states of these metals.[1] However, since direct *f-f* transitions are Laporte forbidden, a strongly absorbing chromophore is typically required to absorb incident light and transfer this energy to the metal centered 4*f* excited states.

Highly emissive Ln(III) complexes with Near-Infra-Red (NIR) emitting cations such as Yb(III) and Nd(III) have diverse applications in telecommunications and biological imaging, and the use of porphyrin derivatives as sensitisers for these metals is well documented,[2,3] since their excited state energies are particularly well matched to NIR emitting cations.

We have recently prepared[4] a cofacial Zn(II) porphyrin anchored to a terpyridine chelate using a rigid xanthene moiety, [Zn(PXT)], and its interactions with several Ln(III) cations (Ln = Nd, Yb and Lu) have been examined herein. The resulting [Zn(PXT)Ln(NO_3)$_3$] complexes with Ln = Yb and Nd demonstrate characteristic Ln(III) centered emission in the NIR. Moreover, the kinetics for the energy transfer processes from the Zn(II) porphyrin donor to Ln(III) acceptor have also been investigated using ultrafast transient absorption techniques, allowing an insight into the mechanism and efficiency of the antennae effect.

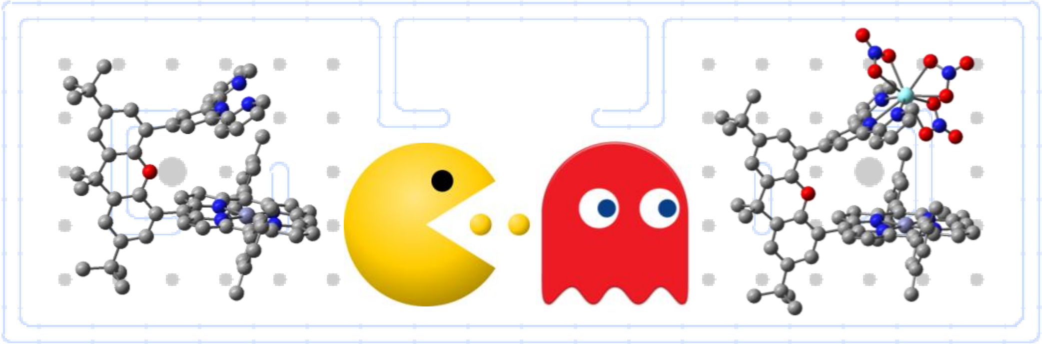

Figure 1 Cartoon showing $Ln^{III}(NO_3)_3$ complexation by the cofacial [Zn(PXT)] complex.

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A novel class of luminescent phosphinine and pyridylidene metal complexes: Towards white-light emitters

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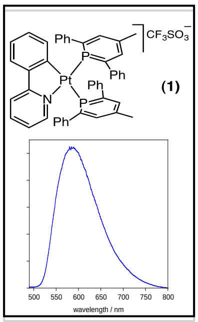
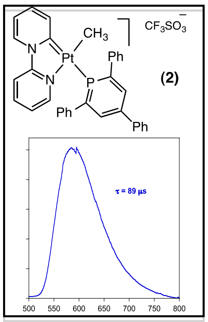
[a] *UPMC Université Paris 06, Institut Parisien de Chimie Moléculaire, Paris, France*
[b] *Department of Chemistry, Durham University, Durham, DH1 3LE, U.K.*

We describe the syntheses and photoluminescent properties of original cyclometallated transition-metal complexes incorporating phosphinines and pyridylidene ligands. In stark contrast to the extensive reports and applications of transition metal complexes with imidazolylidene-based ligands,[1] 2- and 4-pyridylidenes remain scarcely investigated for obvious synthetic challenges yet to be overcome.[2]

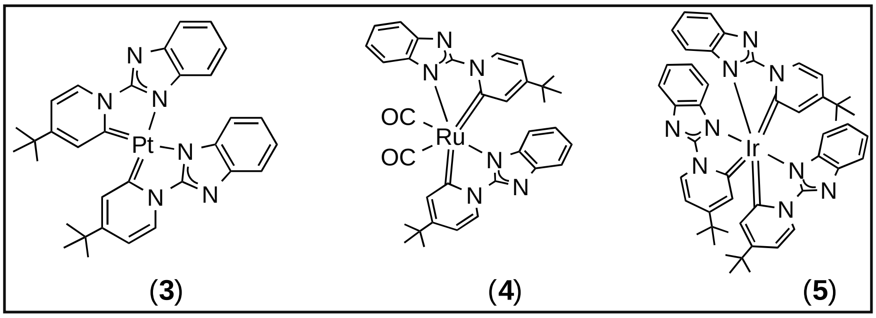


(1)



(2)

On the other hand there are surprisingly very few reports about coordination chemistry of phosphinines with Pt(II),[3] and no studies into the electronic excited states of such compounds. In this context, we have recently reported some Pt(II) complexes with phosphinine and pyridylidene ligands (**1** and **2**) in which the phosphinines exhibited strong phosphorescence at low temperature.[4] More recently we have extended our approach to related C^N cyclometalating pyridylidene ligands and prepared their ruthenium(II), platinum(II) and iridium(III) complexes (**3-5**).



(3) **(4)** **(5)**

These novel compounds are highly emissive in solution and in the solid state and some of them exhibit very peculiar white-light emission, which hold promise to the design of impressive luminescent materials.

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Optical Imaging of Uranyl in the Environment; From First Principles to Applications

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The world currently holds a substantial nuclear legacy arising from fission activities, with a large proportion of high activity wastes that pose a radiological threat to natural and engineered environments. The decision to dispose of these high level wastes (following separation) in a suitable geological disposal facility (GDF) has provided some of the most demanding technical, and environmental challenges facing the world in the coming century. In order to address these issues, we have begun a programme of work to establish a comprehensive understanding of the electronic properties and physical and chemical properties of the radioactive actinide metals using state of the art emission spectroscopic techniques[1] in order to probe actinide speciation at sub micron resolution over a given time period.

We will discuss the potential to use the inherent fluorescent properties of the uranyl cation to study redox speciation in uranium-containing environmental samples by one and two-photon confocal fluorescence and phosphorescence microscopy and lifetime image mapping. Previous studies carried out on crystalline samples have shown that uranyl species are capable of experiencing two-photon excitation. Here we study uranyl species in solution at room temperature and report fundamental properties such as quantum yield, two-photon excitation and emission spectra and two-photon cross sections. These capabilities are then applied to confocal fluorescence microscopy of uranyl in a range of bacterial and mineral samples, to study and map potentially useful process in (bio)remediation strategies including incorporation, biosorption and the *in situ* enzymatic reduction of uranyl.[2]

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Molecular systems for artificial photosynthesis: charge photoaccumulation and photosynthetic Z-scheme functions

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The storage of sunlight into chemical bonds is an appealing strategy to practically exploit solar energy. The reaction centers of natural photosynthesis have inspired numerous efforts to mimic their working principles with the aim to develop our fundamental understanding as well as to explore possibilities for future renewable fuels technologies. To efficiently accomplish useful chemical transformations with sunlight, such as water splitting, the photocatalyst must accumulate multiple redox equivalents to perform multi-electronic redox reactions with a high energy charge separated state. The production of such a state with a single photon of the visible spectrum represents a difficult endeavor.[1] In this presentation, charge photoaccumulating systems along with molecular mimic of the Z-scheme will be presented. These systems absorb several visible light photons leading to the formation of either several redox equivalents on a molecular reservoir or a highly energetic charge separated state that cannot be reached by one single photon absorption (Figure). Our proof-of-principle results demonstrate the capability to translate a crucial photosynthetic energy conversion principles into man-made molecular systems for solar fuel formation.

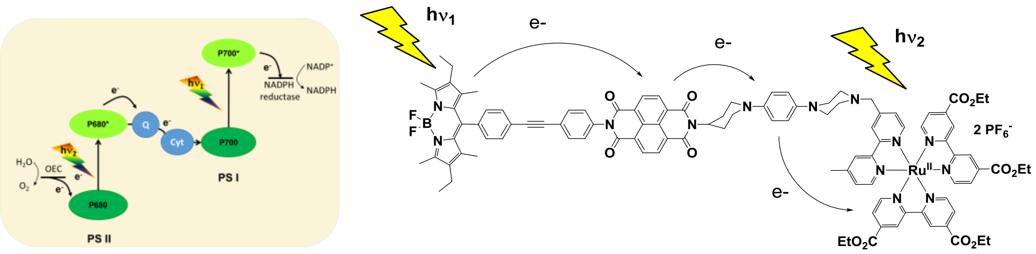

Figure 1 Schematic representation of the Z-Scheme principle and structure of a molecular system mimicking the Z-Scheme function

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Trivalent Chromium: a Rich Optical Partner for Linear Lanthanide Photophysics

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Trivalent chromium is famous in coordination chemistry for its extreme kinetic inertness toward ligand exchange processes and for its forbidden spin-flip $^2E \leftrightarrow {}^4A_2$ electronic transition, which is responsible for the red color of ruby, and for the building of the first successful coherent laser in 1960. The lack of identified strategy for incorporating Cr^{3+} into thermodynamic self-assembling processes has drastically limited its exploitation in metallosupramolecular chemistry, with only scarce reports on the design of discrete chromium-lanthanide complexes, despite their potential unprecedented optical properties.[1] However, recent efforts showed that (i) labile Cr^{2+} analogues react with multidentate segmental ligands to give thermodynamically-driven Cr^{3+}-Ln^{3+} self-assemblies (Ln is a trivalent lanthanide, Figure 1)[2] and (ii) constrained tridentate ligands increase the lability of Cr^{3+} leading to the formation of heteroleptic complexes.[3] We report here on (supra)molecular polynuclear complexes, in which Cr^{3+} is used as linear optical relay for sensitizing adjacent luminescent lanthanide cations displaying light-downshifting and light-upconversion processes. Hence, unprecedented Ln-centered near-infrared emission extending in the millisecond range can be programmed for molecular complexes possessing high-energy oscillators, while green Er-centred emission is detected upon near-infrared irradiation of two Cr^{3+} cations.

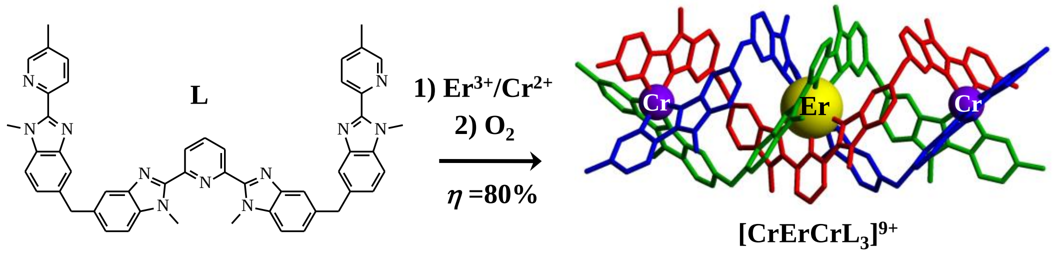

Figure 1 Recent synthetic strategy for incorporating inert Cr^{3+} into optically-active supramolecular entities

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Inorganic noncentrosymmetric building block for the construction of new NLO materials: a new perspective

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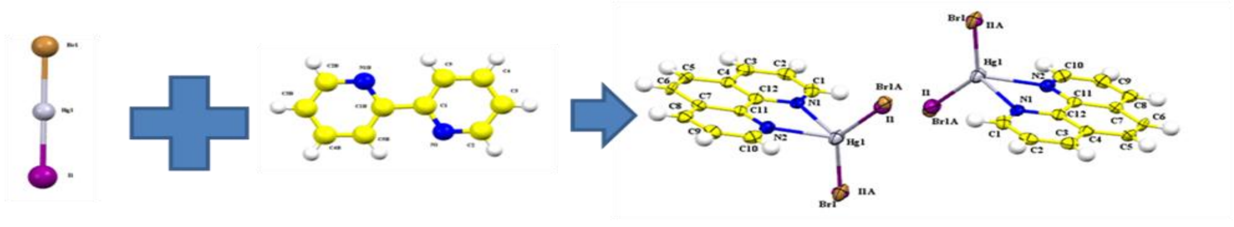
The recent success in the design and synthesis of novel materials based on metal-organic coordination networks has prompted the scientific attention to the supramolecular engineering of non-centrosymmetric solids by exploiting the strong and highly directional metal-ligand coordination bonds. The organometallic approach in this field however consists usually in the use of versatile organic molecules associated with stable and inorganic part with electronic peculiarities. The asymmetric center that generates the noncentrosymmetric structure usually is the organic ligand. We tried to reverse this perspective, using an inorganic noncentrosymmetric building block to control the space group symmetry of the crystalline compounds, and the organic part to modulate the electronic properties. This different approach has been applied in the synthesis of a series molecular materials based on organic ligands with different symmetries 2,2'-bipyridine, 2,2';6',2''-terpyridine, 1,10-phenanthroline and 2-pyridilnaphtiridine) with the asymmetric HgBrI unit. This inorganic salts is well known to be a good material for SHG in the solid state [1]. The obtained materials have been analyzed through SHG microscopy [2] in powder and single crystal form, in order to obtain the different tensor components of the emission, and the results show thatthe use of different ligand and a rational control of substitutional disorder allow a new way of modulating NLO properties.



Molecular point group: $C_{\infty v}$
Space Group: $Cmc2_1$

Molecular point group: C_i

Figure 1: Molecular complex obtained with HgBrI (noncentrosymmetric) and 2,2'-bipy (centrosymmetric)

[1] Q. Wu, Y. Li, H. Chen, K. Jiang, H. Li, C. Zhong, X. Chen, J. Qin, *Inorg. Chem. Commun.*, **2013**, *34*, 1
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Novel Cu(I) emitters showing thermally activated delayed fluorescence and short-lived phosphorescence

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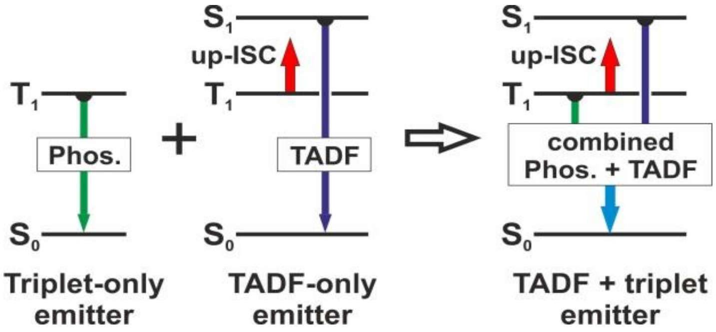
Luminescent materials that exhibit thermally activated delayed fluorescence (TADF) have gained high attractiveness as emitters for OLEDs.[1-3] Nevertheless, even utilization of TADF can be further improved, introducing a novel concept.[4,5] This is demonstrated by new brightly luminescent Cu(I) compounds, for which the ambient-temperature emission stems from both the lowest excited singlet S_1 *and* the triplet T_1 state. Both states are of MLCT character showing a small energy separation of $\Delta E(S_1\text{-}T_1) \approx 0.1$ eV or less. For a specific example, the emission quantum yield is higher than 90 %. About 60 % of this intensity represents TADF and importantly ≈ 40 % stems from the lower lying triplet state T_1. Effective spin-orbit coupling induces this efficient radiative $T_1 \rightarrow S_0$ emission path. Thus, the overall emission decay time is distinctly reduced with respect to a TADF-only situation. Combined use of both decay paths allows for distinct improvement of OLED emitter materials.



Two radiative decay paths for novel TADF Cu(I) complexes with high SOC for an effective decrease of the overall radiative decay time.

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Variable-pressure luminescence spectroscopy of square-planar d^8 complexes: characteristics of transitions and interactions

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Luminescence transitions of square-planar platinum(II) and palladium(II) complexes are often observed in the yellow to red spectral region. Different types of transitions can occur, and variations of temperature and in particular pressure lead to characteristic trends. Transition characteristics can be determined from the shifts of luminescence maxima, with ligand-centered (LC) transitions showing the smallest shifts, followed by charge-transfer transitions and metal-centered bands.[1] Intermolecular interactions can strongly affect these trends. The characteristic shifts of band maxima vary between -100 cm^{-1}/kbar and +47 cm^{-1}/kbar, a surprising variation in view of the often weak intermolecular effects.[2]

The origins of such variations reveal subtly different electronic structures and are explored through comparisons with structural data, vibrational spectra and model calculations. The resulting information can be used either to tune emission energies or to characterize the structural environment of the luminophores.

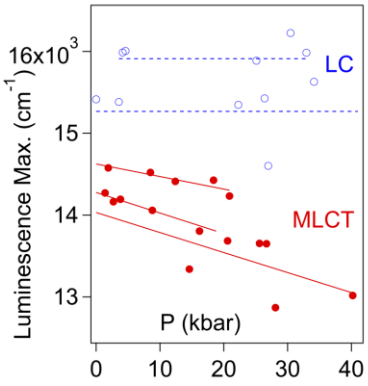

Figure 1 Variable-pressure luminescence maxima of ligand-centered (LC) and charge-transfer (MLCT) luminescence bands of platinum(II) complexes.

1 A. Rodrigue-Witchel, D. L. Rochester, S.-B. Zhao, K. B. Lavelle, J. A. G. Williams, S. Wang, W. B. Connick, C. Reber, *Polyhedron (Modern Inorg. Chem. in Canada),* **2016**, doi:10.1016/j.poly.2015.12.011.
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Design of copper and gold carbene complexes for fabrication of highly efficient organic light-emitting diods

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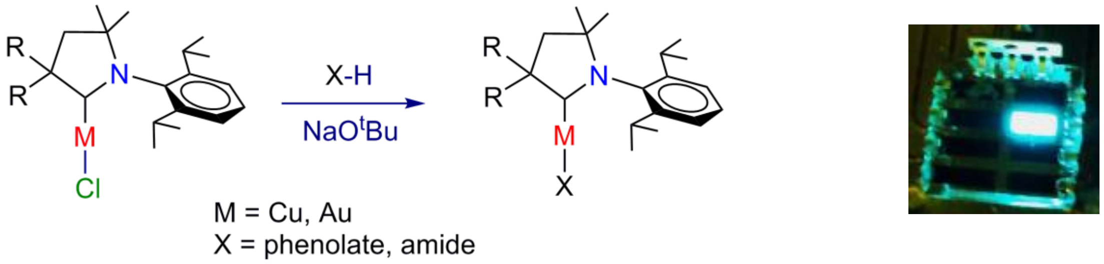
A number of coinage metal carbene complexes have been shown to give rise to photoluminescent compounds, especially copper based complexes which are particularly attractive since copper is inexpensive and abundant. At the same time one of the most modern type of carbene ligands is Cyclic (alkyl)(amino)carbenes (CAACs) have proved to be remarkably versatile in transition metal chemistry with a multitude of applications.

We report here highly efficient synthesis of CAAC copper and gold complexes with phenolate and amide ligands (Scheme 1). All complexes are stable (up to 260°C) and display intense photoluminescence which is important for fabrication of OLEDs. Electrochemistry allowed us to probe the energies of the frontier orbitals for all complexes and identify the promising candidates for use in OLED. We developed very bright OLED based on (CAAC)M(amide) complexes with brightness (up to 12500 cd/m^2) at maximum efficiency which far exceeds that necessary for display and lighting applications.



Scheme 1 General synthetic scheme for preparation of amide and phenolate complexes. Inset shows operation of OLED based on (CAAC)Au(carbazolate).

We synthesized a full spectrum of the compounds emitting from blue to near-infrared by modifying the amide ligands. Investigation of the structure-property relationship for numerous complexes allowed us to elaborate a reliable prediction rule for the emission color depending on the starting amide ligand. The TD DFT calculations and cryogenic photoluminescence studies support the Thermally Activated Delayed Fluorescence emission mechanism for our complexes.

Phosphorus chemistry as new tool for tuning ground and excited states properties of ruthenium polypyridyl complexes

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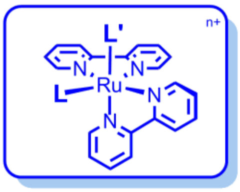
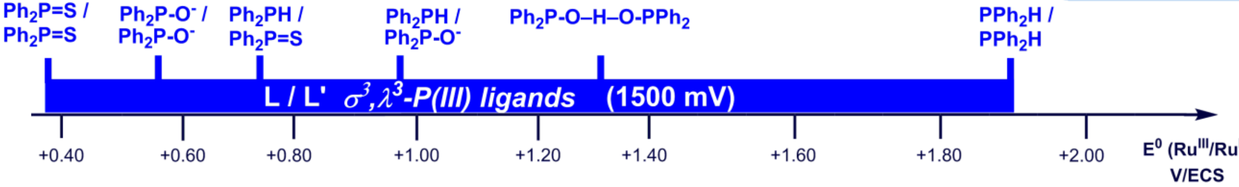
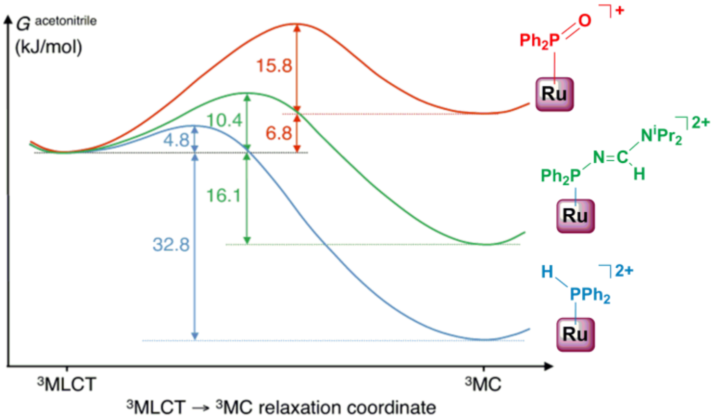
Ruthenium polypyridyl complexes constitute a model class of compounds for molecular optic applications. Complexes incorporating *N*-, *O*- and *S*-coordinated ligands have been widely studied but organophosphorus *P*-ligands – which are the most widely applied ligands in the field of catalysis – were surprisingly ignored in this domain.

Lately, we demonstrated that functionalized phosphorus ligands can promote room temperature emission of [Ru(tpy)(bpy)L]$^{2+}$ complexes.[1] We will present the major effect of anionic phosphoryl and thiophosphoryl ligands in tuning the ground state redox properties of [Ru(bpy)$_2$LL']$^{n+}$ complexes in an unprecedented range of 1500 mV.





Excited states are also highly affected as a function of the organophosphorus *P*-ligands promoting the room temperature luminescence of the complexes. Our experimental results are supported by DFT ground state calculations and highly challenging theoretical TD-DFT studies of the excited states of the complexes.



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Development of Bis(arylimino)acenaphthene (BIAN) Copper and Indium Complexes as Visible Light Harvesters for Photovoltaic and Artificial Photosynthetic Applications

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Artificial photosynthesis has been recognized as a sustainable approach to utilize solar energy for chemical reactions and energy storage. One of the unsolved challenges is the development of an affordable, robust, panchromatic light harvester for the desired photochemistry. The most common molecular photosensitizers include the noble metal-based Ru and Ir complexes, synthetically laborious porphyrin derivatives, and expensive, functionalized polypyridine compounds. Herein, I will describe my team's efforts in the development of Cu(I) and In dyes supported by bis(arylimino)acenaphthene (Ar-BIAN) ligands. The In complexes have been prepared through solvent-free, mechanochemical methods.[1] Structural studies, electrochemical measurements, and optical absorption spectroscopy will be reported.[1] The diamagnetic, homoleptic Cu(I) complexes exhibit panchromatic light absorption extending to the near infrared (NIR) region.[2] Remarkably, the crystal structure of the complex bearing an *ortho*-iodoarylimino substituent displays a unique, almost-planar, rhomboid geometry around the copper(I) center.[2] Density functional theory (DFT) calculations were performed to provide insights into the spectroscopic features and the unusual coordination sphere.[2] Preliminary studies were conducted to explore the application of these copper photosensitizers in dye-sensitized solar cells.[2]

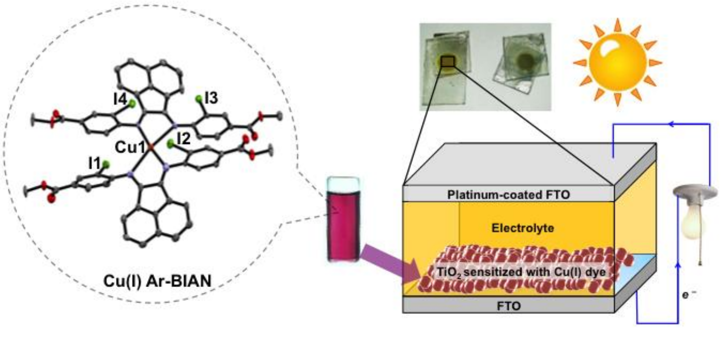

Figure 1 Incorporation of panchromatic Cu(I) chromophores in dye-sensitized solar cells.

Luminous Gold Complexes Exhibiting Color Sensitivity to the Structure of Molecular Aggregates

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Gold(I) complexes show strong luminescence via Au(I)–Au(I) interaction (aurophilic interaction). Their quantum yields (Φ) of photoluminescence, therefore, are enhanced in the condensed phases, and one can expect the gold complexes are possible candidate for materials for light-emitting devices. It has been reported that luminescent properties of those complexes depend on the aggregated structure in the condensed phases, thus the aggregated structure should be controlled to be suitable for luminescence.[1-4] In this work, in order to control the aggregated structure, we designed and synthesized several types of liquid-crystalline (LC) gold(I) complexes. Molecular structures of LC gold complexes are shown in Fig. 1. All materials showed intense photoluminescence (*e.g.* Φ > 50 % for **R6** in crystal).[4] Deep-blue photoluminescence was observed from the complex **R6** both in the crystalline and LC phases. Very interestingly, when the complexes were introduced in side-chains of polymers as a mesogen of polymer LCs, white-color photoluminescence was observed from a single material (Fig. 1).

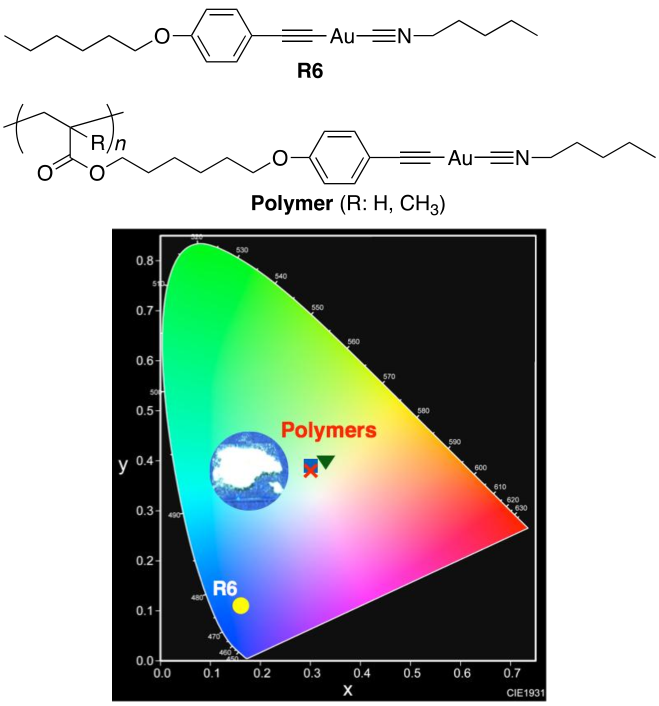

Figure 1 Molecular structures of gold complexes used in this study and CIE chromaticity diagram for the photoluminescence in the crystals of **R6** and in amorphous solids of the polymers.

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Selective Ion-Binding Properties of Rhodamine-Transition Metal Bichromophoric Hybrid and Novel Rhodamine Derivatives

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Herein we report various bichromophoric sensory assemblies, from the combination of a rhodamine sensing derivatives and luminescent transition metal complexes.[1-3] The nature of the rhodamine derivative, ligating group, transition metal ion as well as the linker were found to affect the sensing properties and luminescence behaviors. In some cases, energy transfer process could be modulated by the ring-opening of the rhodamine through the selective binding of Hg(II) ion. Another novel class of rhodamine derivatives, in which there are two spirolactam groups with five fused six-membered rings will also be discussed.[4] Mercury(II) ion was found to selectively induce ring-opening of the spirolactam groups. In view of the different extent of π-conjugation upon successive ring-opening processes, different solution color, electronic absorption, and emission responses were found to exhibit in the presence of various concentrations of mercury(II) ions.

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Designing brightly luminescent metal complexes

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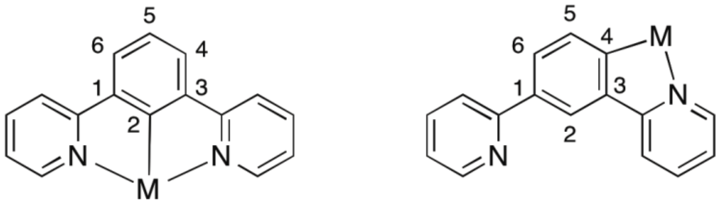
In optimizing the luminescence of platinum(II) complexes, the use of tridentate ligands is shown to offer advantages over more commonly used bidentate analogues, owing to greater rigidity reducing excited-state distortion.[1] N^C^N-coordinating ligands in particular, as in Fig. 1, lead to rigid complexes in which non-radiative decay is minimized. Strategies for the synthesis of such ligands and their Pt(II) complexes will be discussed. The performance of the complexes as phosphors in organic light-emitting diodes will be presented, focusing on the generation of NIR and white light.[2]

In some instances, direct comparison is possible with iridium(III) complexes featuring the same class of ligands.[3] Our results show that spin-orbit coupling (SOC) pathways are more efficient for Ir(III) than for Pt(II), in line with contemporary theories about SOC. However, despite having smaller triplet radiative rate constants, Pt(II) complexes may be able to compete with Ir(III) systems in terms of overall luminescence quantum efficiency, owing to the suppression of non-radiative decay pathways.

Examples of new phosphors based on rhodium(III) and palladium(II) will also be presented.[4] Although the radiative rate constants of such complexes of second-row metal ions are necessarily lower than for their third-row analogues {Ir(III) and Pt(II) respectively}, relatively bright luminescence can be achieved if rigid systems are employed.



N^C^N binding mode

N^C binding mode

Figure 1 The tridentate N^C^N and bidentate N^C binding modes of 1,3-di(2-pyridyl)benzene

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Controlling Optical Properties of Conjugated Oligomers Using Metal and Main Group Chemistry

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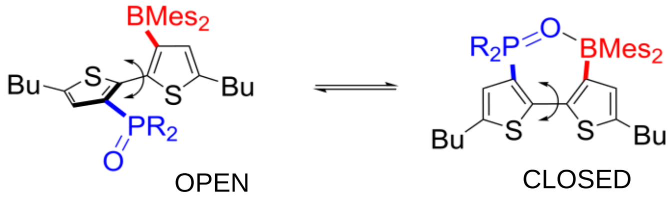
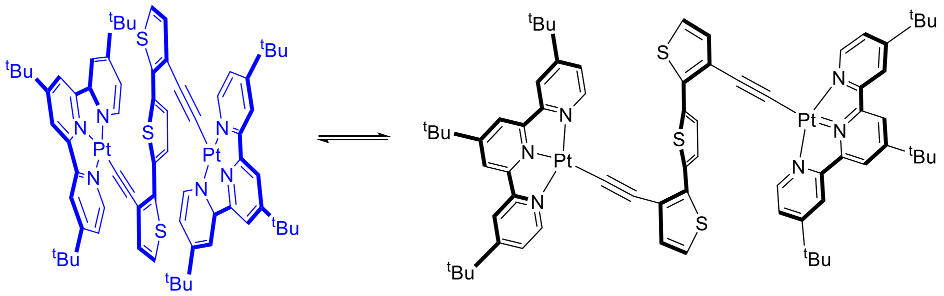
Conjugated oligomers are of interest for a broad range of applications including solar cells, chemical sensors, molecular switching and catalysis. Many of these applications are dependent on the optical properties of the materials, including absorption and emission properties, excited state charge separation and energy transfer. Thiophene-based conjugated materials in which conjugated oligomers are combined with light-absorbing metal-complexes and main-group elements, that give rise to enhanced photofunctional behavior will be described. The photophysical properties of these novel compounds will be discussed, along with possible applications in optics.





New Strategies Towards Design of Metal-Ligand Chromophores and Luminophores

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The major focus of our research is on the molecular design and synthesis of novel inorganic/ organometallic metal complexes that may find potential applications as functional metal-based molecular materials. Recent works have shown that novel luminescent metal-based molecular materials could be assembled through the use of various metal-ligand chromophoric building blocks. In this presentation, various design and synthetic strategies together with the successful isolation of new classes of complexes of selected metals will be described. A systematic study of the electronic spectroscopy of the newly synthesized metal complex systems has provided fundamental understanding on the spectroscopic and luminescence origin as well as the structure-property relationship of these complexes. Through a fine control of the interplay amongst various coordination motifs, electrostatic assembly, and non-covalent metal-metal, hydrophobic-hydrophobic and π-π interactions, together with the modulation of various photo-induced electron and energy transfer processes, new strategies towards the rational design of metal-ligand chromophores and luminophores and their assembly into various ensembles, conjugates and nanostructures that would lead to interesting optical properties and functions, have been made.

Strategies for Bright Charged Iridium(III) Emitters for Solid-State Lighting

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One of the longstanding challenges in the design of electroluminescent devices such as organic light-emitting diodes (OLEDs) and light-emitting electrochemical cells (LEECs) is the development of emissive materials exhibiting very high photoluminescence quantum yields in the solid state, a parameter that defines the potential maximum EQE of the device. Herein, I will present our recent efforts to rationally design very bright cationic iridium(III) complexes in both the deep blue and red parts of the visible spectrum. I will then present OLED and LEEC device data to show how these materials perform in solution-processed electroluminescent devices.

Coordination Compounds based on Porphyrins & Curcuminoids as appliances in Molecular Electronics

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The implementation of the bottom-up approach in Nanoscience and Nanotechnology requires the use of well-developed equipment and molecules with tailored properties suitable for such studies. My group integrates straightforward organic molecules and coordination compounds into the fields of bulk heterojunction (BHJ) organic solar cells (OSCs), molecular magnetism and molecular electronics.

Here, we introduce a family of organic species of curcuminoid or porphyrinic nature and mononuclear 3d/4f coordination compounds[1] which have been used as molecular components in mechanically controllable break junctions and electromigration break junctions with their electronic properties analyzed.[2] Finally, functionalized surfaces are being developed in the group toward the control on deposition and luminescent studies of final coordination compounds.

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Molecular control of the magnetic exchange between self-assembled metal-complexes and ferromagnetic surfaces: towards molecular spintronics

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Controlling the interface poses a challenge when constructing molecular spintronic devices. This study shows that it is possible to modulate the magnetic response of a system with a molecule and control the interaction between the molecule and the surface *via* the interface. A family of lanthanide complexes was synthesized by the subcomponent self-assembly methodology. Molecular architectures, which were stable in solution and in ambient conditions, were designed by the in-situ formation of ligands around metal ion templates (**1**: Co(II) and **2**: Ni(II)). These molecules display magnetic anisotropy and can be chemically tethered onto ferromagnetic surfaces. Anchoring induced, in the paramagnetic cobalt(II)-containing complex, a magnetic ordering and hysteresis that was studied by X-ray absorption spectroscopy (XAS), X-ray magnetic circular dichroism (XMCD) and time-of-flight secondary ion mass spectroscopy (Tof-SIMs). While, we do not observe any coupling with the ferromagnetic electrode for the isostructural nickel(II)-containing complex. This result highlights the fundamental effect that the electronic structure of the metal ion in conjunction with the nature of the organic spacer has on the resulting molecule/electrode interaction.

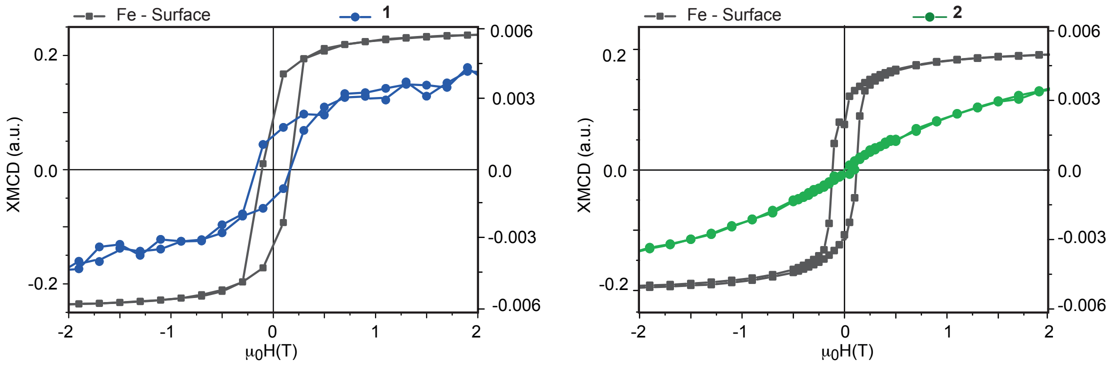

Figure 1. Element-specific field dependence of the magnetization of the Co atoms of 1, the Ni atoms of 2 and of the ferromagnetic substrate (Fe). Hysteresis curves of the Co atoms (blue), Ni atoms (green) and Fe atoms (grey) obtained at the $L_{2,3}$ edge XMCD maxima. (Monochromatized X-rays are set at the energy of the maximum absolute value of the XMCD signal (i.e. hn = 787.5 eV for Co and hn = 851 eV for Ni) then the external magnetic field is switched step by step from +6T down to -6T and back to +6T. At each step the magnetic field is switched from left to right circular polarization to yield the element specific magnetization curves).

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The Conductance Studies on Metal-inserted π-Conjugated Molecules

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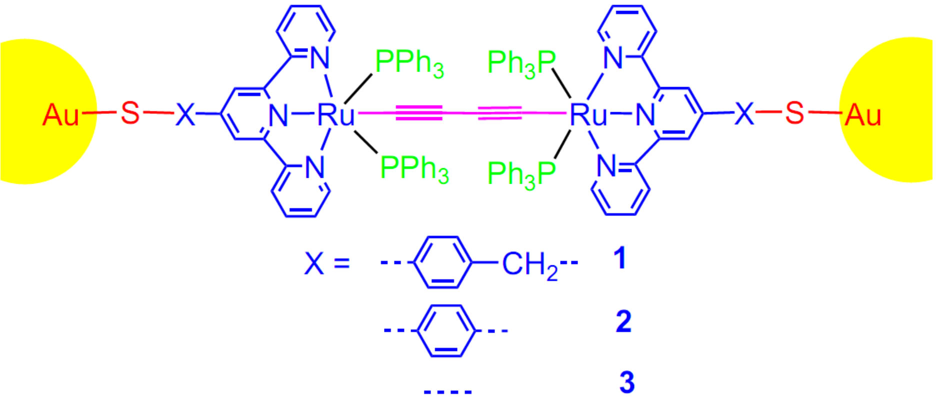
Molecular wires behave as connectors that permit charge transport from one element of electronic devices to another one through charge delocalization along conjugated molecular backbones. We present herein the preparation and conductance studies on a series of metal-inserted π-conjugated molecules through STM-break junction or mechanically controllable break junction (MCBJ) approach.

In comparison with π-conjugated organic molecules without metal insertion, whether mononuclear or dinuclear ruthenium(II) inserted molecules exhibit higher molecular conductance and weaker length dependence than that of OPE or OPV with comparable length. Modulation of molecular conductance is achieved by changing the length and π-conjugated system of both bridging and ancillary ligands. The conductance improvement in these ruthenium-inserted molecules is ascribed to the better energy match of the Femi level of gold electrodes with the HOMO that mainly focuses on C≡C–Ru–C≡C or Ru–C≡C–C≡C–Ru backbone.



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A Redox- & Photo-Responsive Quadri-State Switch Based On Dimethyldihydropyrene-Appended Cobalt Complexes

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The use of photochromic couples as key component in light-powered molecular switches has been shown to be one of the most attractive and straightforward strategy towards the development of useful molecules or materials in molecular electronics.[1,2]

In this context, the development of multi-addressable molecular switches able to display multiple functionalities in response to different stimuli represents a new challenge for chemists. An appealing strategy consists in combining photo-responsive derivatives with electron-responsive transition metal complexes displaying at least two well-defined and accessible redox states.[3] For this purpose a new dimethyldihydropyrene-appended cobalt complex has been synthetized and characterized: combining the two distinguishable forms of the photo-chemically addressable photochromic core and the two distinct redox states of the electrochemically addressable complexed metal centre affords a quadri-state switch from which a molecular logic circuit with NOR and AND gates can be constructed.[4]

Figure 1 Multi-addressable switches: the four states for dimethyldihydropyrene-appended cobalt complex complex modulated by photo or thermal and electrochemical redox processes.

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In situ synthesis of single-molecule electronic components

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Typical studies in single-molecule electronics involve surface self-assembled components first synthesized elsewhere (*ex situ*). Yet surface-based (*in situ*) preparations (e.g. utilizing “click” chemistry[1]), offer distinct advantages including: (i) control of the orientation of the molecular species with respect to the substrate surface; (ii) rapid purification of components; and (iii) combinatorial approaches. If such approaches are commonly used for large scale surface modifications, to date only two reports have described *in situ* modifications which were subsequently probed at the single-molecule level (using the scanning tunneling microscopy break-junction (STM-BJ)).[2,3] Whereas these employed single-step reactions, there is great potential in exploiting reversible (Figure 1), and/or multi-step schemes. Such efforts could ultimately be applied to construct surface-based molecular circuitry, by considering the latter as if it was a ‘total synthesis’ problem.

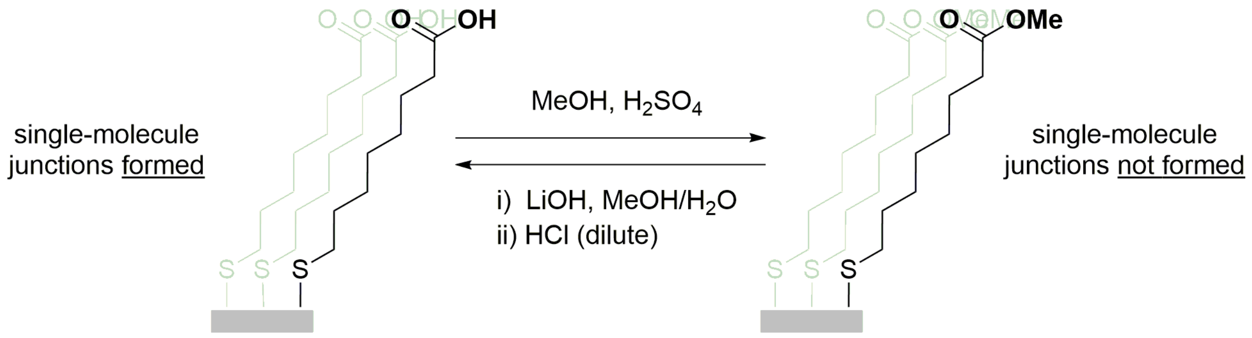

Figure 1 Example *in situ*, synthetic modification of a functionalized monolayer on Au. Previous studies[4] have shown that –COOH groups bind to Au, whereas –COOMe do not.

We will discuss the suitability of surface-binding groups in this context, and report the results of preliminary *in situ* reactions. The latter will be characterized at the single-molecule level using STM-BJ experiments, as well as in bulk, for example, using surface electrochemistry, contact angle measurements and X-ray photoelectron spectroscopy.

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Spin Observation and Control of Magnetic Molecules with Scanning Tunnelling Microscopy

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A research field of molecular spintronics attracts attentions. One of advantages of organic molecules for the use in spintronics devices is that the spin and electronic states are strongly correlated with their structures. By using 'molecule switching' with outer simulations like as current and light, a single spin of a single molecule could be controlled. Special attentions were paid for single molecule magnet (SMM) which can store spin information in the molecule. These molecules include double decker phthalocyanine (Pc) or porphyrin molecules, which sandwich lanthanide metal atom. The blocking temperature of these molecules, below which a single SMM molecule works as an quantum magnet, reaches ~ 40 K and are regarded as promising material for quantum information process devices. Recent developments enabled STM to access to spin properties of the surface with the atomic scale resolution. Here, we demonstrate the investigation of the spin state of magnetic molecules through the detection of the Kondo resonance, which occurs due to interactions between conduction electrons and the spin of the molecule, for the molecule of fused copper corrole and 2,3,7,8,12,13,17,18-octaethylporphyrin (OEP)-TbIII double-decker complex. Further, spin manipulations were executed by changing the configurations of the molecules by injecting tunneling electrons to the molecules. The manipulations include the rotation of the azimuthal angle of the two Pc planes of the $TbPc_2$ molecule, and dehydrogenations from the protonated porphyrin double-decker molecules. As the results of the chemical change of these molecules, the spin state can be switched on/off in a controlled manner[1].

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Metallo-organic Assemblies as Electrochromic Materials: Switching Stability, Coloration Efficiencies and Devices

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Stepwise deposition from solution, combined with metal-ligand coordination, has served as a powerful tool for generating functional architectures on surfaces.[1,2] Such systems might find many applications in molecular electronics, sensor, and solar cells. More significantly, owing to their interesting electrochromic (EC) behavior, redox-active metallo-organic assemblies are promising candidates for use in smart windows. In this study, we used a dip-coating process to generate EC molecular assemblies (MA) from metal polypyridyl complexes cross-linked with a palladium salt. These complexes are considered ideal chromophores for fabricating EC materials, due to their excellent stability and light absorption that significantly depends on their oxidation state. Varying the number of pyridine moieties was used to control (i) the materials' stability, (ii) color, (iii) redox-chemistry, and (iv) the film growth (i.e., linear vs. exponential). Our observations also demonstrated that minor structural differences (i.e., the pyridine-bipyridine bond order, X) at the molecular level become apparent in stability and EC properties, (Figure 1). The MAs exhibit very high coloration efficiencies (CEs) and are extremely stable. Furthermore, we demonstrate solid-state devices.

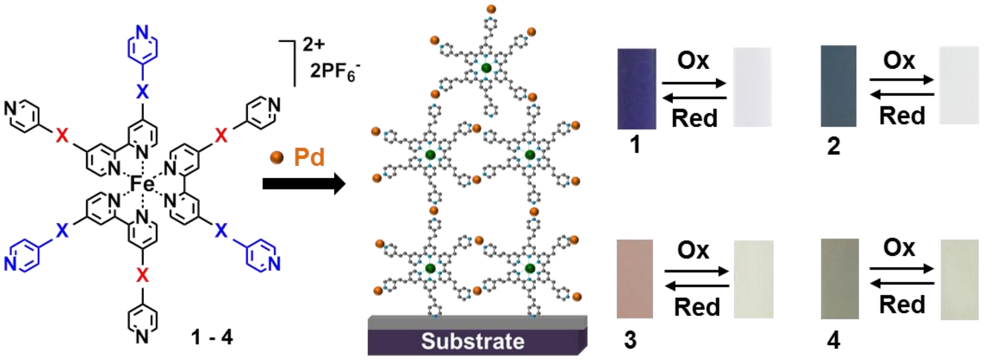

Figure 1 Left: Formation of the surface-confined molecular assemblies (MA). Right: photographs of MA1-4 showing the colored (Fe^{2+}) and the bleached (Fe^{3+}) states.

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Ferrocene ringtronics – new macrocycles for molecular electronics

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The capability of single molecules as mediators of electron transfer has led to great interest in their development as analogues of known solid-state electronic components such as wires, switches or diodes.[1] In recent years however, it has become widely recognized that molecules can exhibit functionality beyond that of existing macrocyclic circuitry e.g. examining the impact of quantum effects on through-molecule conductance.[2] To understand this and so allow development of the field, the study of unique molecular structures is essential. To this end, we are pursuing the synthesis and characterization of various new, fixed-shape, redox-active macrocycles (and other branched materials),[3, 4] some of which feature surface-binding groups to allow a 'wiring up' between electrodes (see examples below). The presentation will detail the latest synthetic methodologies towards these ferrocene-containing macrocyclic and branched compounds and the investigation of their interference properties, transport mechanisms and redox-activity.

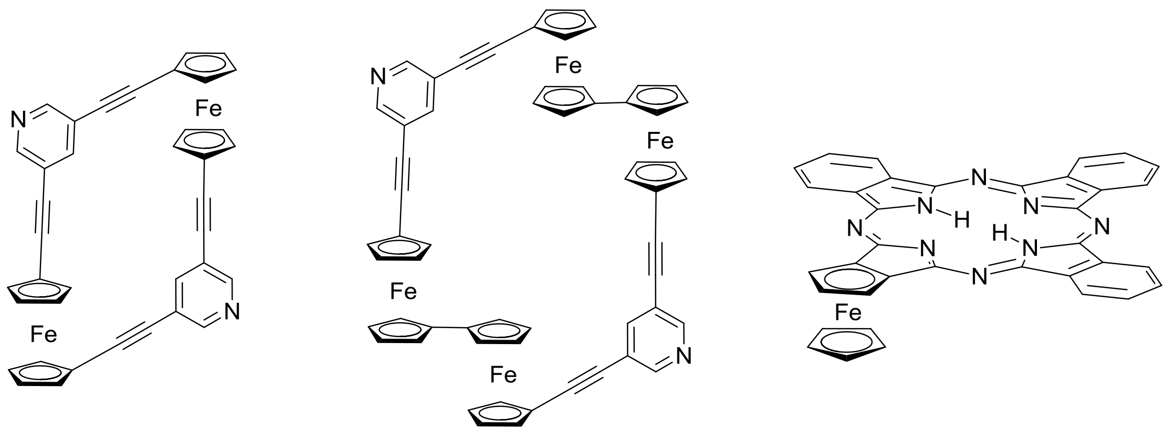

Figure 1 Novel ferrocene-containing macrocycles synthesised within this work.

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Metal complexes and Moore

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Molecular electronics is now considered a viable future technology base for the enhancement of existing silicon-based microelectronics. By incorporating electronically active molecular units into solid-state platforms, ‘hybrid’ systems with higher component density, lower energy demand, lower cost and potentially new function compared with conventional devices may become possible. The rational development of molecular electronics is critically dependent on the coupling of the molecule to (semi)conducting surfaces and interfaces, and the ability to fabricate these contacts into device structures. In this presentation, the nature of some of these problems will be outlined, and progress towards some solutions described. Examples will include the use of coordination complexes and organometallic molecules as components in molecular electronics,[1] the use of electrochemical STM based platforms in the assessment of molecular wire- and transistor-like behaviour,[2] and the use of organogold complexes as precursors to scaleable metal|molecule|metal devices.[3]

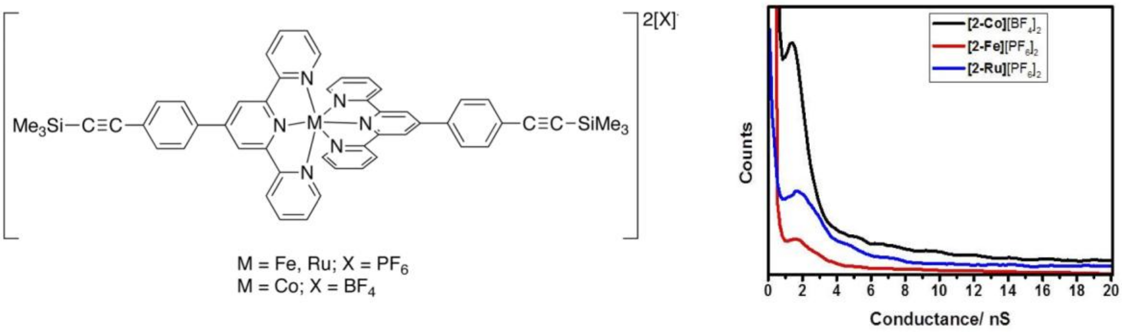

Figure 1 An example of a family of ‘wire-like’ coordination complexes and conductance histograms.

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Rotary Motors Driven by Tunneling Electrons

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In the macroscopic world, the movement of rotation is at the source of many examples of machines and motors. Advances in the imaging and manipulation of single molecules has stimulated much interest in the synthesis of molecules exhibiting unique mechanical properties such as unidirectional molecular motors.[1]

In this presentation will be presented the design and synthesis of two molecular motor built around a ruthenium[2] or an europium center.[3] The synthesis of the motor will be presented as well as variable temperature NMR experiments, electrochemistry and STM study showing the control of the unidirectional rotation.[4-5] The motor adsorbed on a gold surface can be made to rotate in a clockwise or counterclockwise direction by selective electron tunnelling through different sub-units of the molecule. The directional rotation originates from saw-tooth-like rotational potentials, which are solely determined by the internal molecular structure and are independent of the surface adsorption site. This is the first exemple of a molecular motor working reversibly.

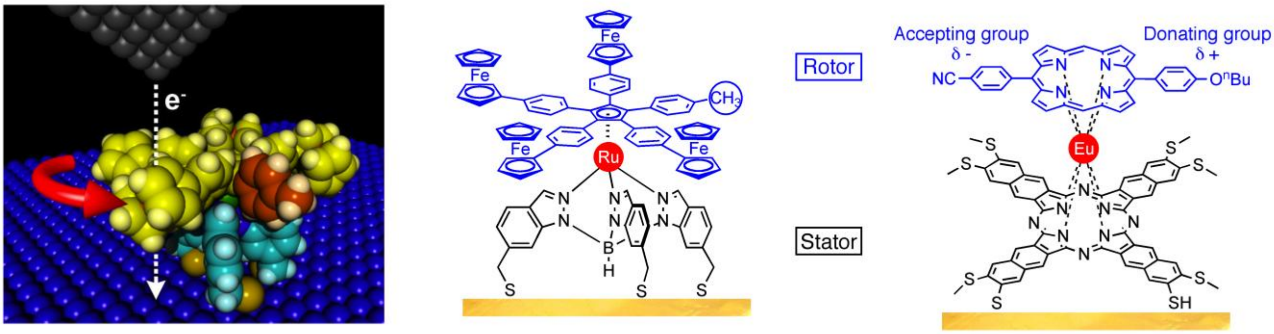

Figure Ruthenium-based (left and center) and Europium based molecular motors.

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Coordination Chemistry meets Quantum Physics: Metal Complexes as Qubits

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Magnetic metal complexes have been proposed as Quantum Bits (Qubits) candidates units for Quantum Computing (QC) and Quantum Information Processing (QIP).[1] Herein, we report on the implementation of metal complexes into nanometre-sized (single-) molecular spintronic devices by a combination of bottom-up self-assembly and top-down lithography techniques. The controlled generation of magnetic molecular nanostructures on conducting surfaces and electrodes will be shown, self-assembled on sp^2-carbon nano-structures (SW-CNTs, graphene, etc.), or inside nano-gap gold junctions. The quantum properties of the metal complexes inside of the obtained supramolecular Quantum Devices (SMQD) are addressed at the single molecule level in view of their I-V-characteristics by means of UHV- and solution-based scanning probe and electromigration techniques.[2-9]

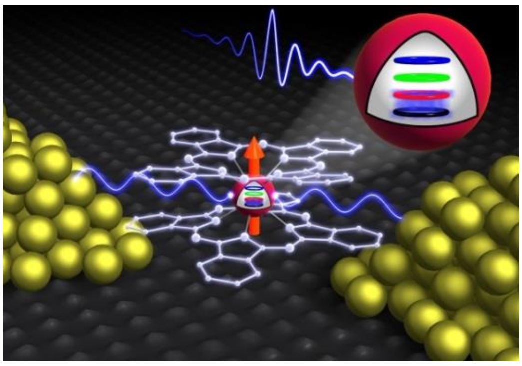

Figure 1 Artistic representation of a Molecular Spin Transistor based on a TbPc$_2$ Single Molecule Magnet (SMM) acting as a molecular Qubit.[9]

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Use of Non-Innocent Ligands for Generating Polyelectrochromic Molecular Materials

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Systems that display switchable optical absorptions as a function of an applied redox potential are highly sought after as electrochromic materials, and find use for example as smart optical windows.[1] The combination of redox non-innocent ligands with redox-active metal centers is a sound strategy for generating such electrochromic materials.[2]

In this contribution, we will present molecules that contain a redox-active iminoquinone bridge and other redox-active stopper ligands. We will show that such molecular platforms are capable of displaying polyelectrochromism with the optical absorptions being tunable over the entire visible and NIR regions of the spectrum. Additionally, the presence of multiple reversible redox processes in these molecules allow us to perform optical switching as a function of a variety of applied redox potentials.[3]

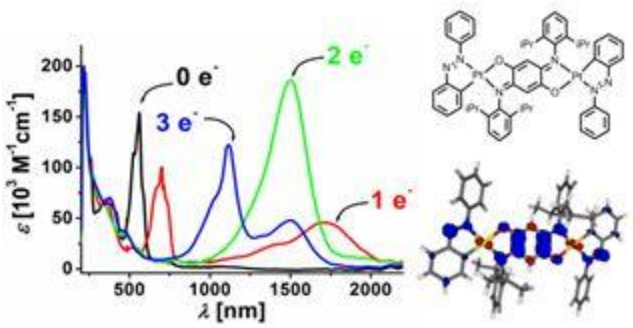

Figure 1. A redox-active complex containing multiple non-innocent ligands (right, top), spin density distribution (right, bottom), electrochromic behaviour (left).[3a]

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Tailoring Organometallic Complexes for Switching and Conductance Properties

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Redox-active molecules have been pursued for their interesting electronic properties and their potential applications in the field of molecular electronics.[1] In this context metal-alkynyl complexes with various suitable ligands ancillary ligands have been investigated.[2] We have explored the switching properties of a number of mononuclear complexes with appropriately chosen metal centers and ligand environment through synthetic, theoretical and electrical transport studies. The systematic investigations reveal insights into the interplay of different electronic aspects of the metal and the ligands that strongly impacts the switching property in these molecules.[3] In a complementary study, electrical transport studies on a series of dinuclear complexes with tailored designed ligand environment and different terminal groups that are able to bind to the gold electrodes were investigated. The results pinpoint to a significantly enhanced conductance of the dinuclear complex bearing a covalent binding terminal group versus the coordinatively bound end groups.[4] The outcomes of these studies serve to enhance the understanding in the design of molecules with effective switching and high conductance properties for applications in molecular electronics.

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Proton-Coupled Mixed Valency in Hydrogen Bonded Dimers

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The study of organometallic mixed valence systems has achieved much attention over recent decades with potential applications in photochromic systems[1]and as components in future molecular electronics technology.[2] Such systems are of the archetypal donor-bridge-acceptor (D-B-A) architecture bearing redox active metal units linked through covalently bonded bridging units, often organic in nature, including many reports of dimetal redox moieties.[3] In contrast to this we present here a novel class of systems where metal-bridge-metal systems are prepared by exploiting self-complimentary hydrogen bonding functionality of the ligand to form dimeric species.[4] Electrochemical analyses of these hydrogen bonded dimers show that in weakly / non-coordinating solvents thermodynamic stability of the cation is observed by cyclic voltammetry to show two consecutive reversible one-electron oxidations. The requirement for the hydrogen bond is then observed by the addition of DMSO, which serves to cleave the dimergiving rise to a single redox event. Further results from EPR spectroscopy and IR spectroelectrochemistry have shown that timescale for this process is slower than slower than 10^9 s^{-1}. Further evidence to support the requirement for the hydrogen bond is observed in UV-vis NIR spectroelectrochemistry of the mixed valence state where no IVCT band is observed, as would be expected in classic mixed valence systems. In trying to understand the mechanism for PCMV we have probed the possible mechanisms by DFT and results show that ET is directly related to the proton coordinate in what can be considered a dipole induced electron self-exchange mechanism (see, Figure 1).

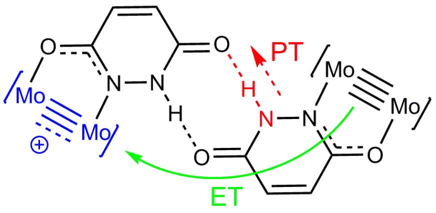

Figure 1: Proposed mechanism for proton-coupled mixed-valency

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Photoinduced electron transfer across anion-responsive molecular wires in donor-bridge-acceptor compounds

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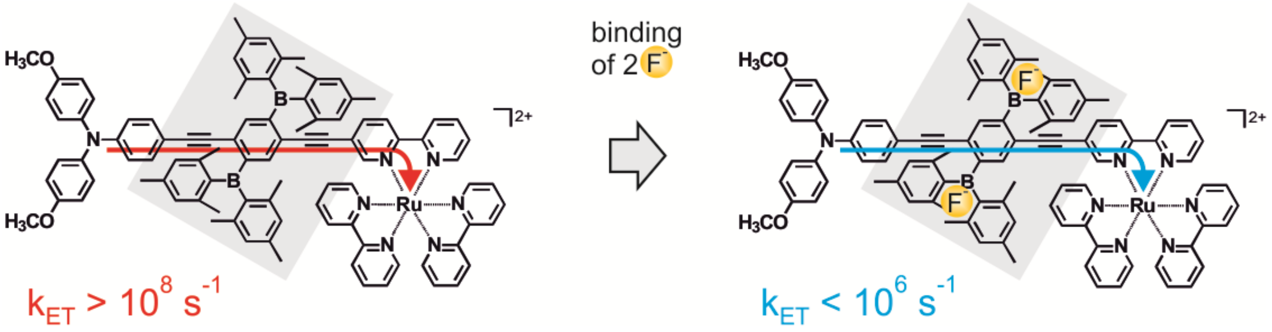
In a recent study we have found that the rate for long-range electron transfer across a conjugated organoboron wire can be controlled by anion binding to the wire.[1] In a covalent donor-bridge-acceptor compound, intramolecular electron transfer from a triarylamine unit across an organoboron bridge occurred to a photoexcited Ru(2,2'-bipyridine)$_3^{2+}$ complex. In CH_2Cl_2, this intramolecular electron transfer took place with a rate constant (k_{ET}) exceeding 10^8 s^{-1} (left part of figure).



In apolar solution, fluoride anions bind with high affinity to the organoboron bridge, and this slows down photoinduced electron transfer by more than two orders of magnitude. Thus, when two F^- anions are bound to the wire (right part of the figure), the rate constant for electron transfer from the triarylamine to the photoexcited Ru(2,2'-bipyridine)$_3^{2+}$ complex is lower than 10^6 s^{-1}. This study illustrates the broader principle of anion-responsive molecular wires.

This talk will focus on a series of chemically related donor-bridge-acceptor compounds,[2] including the example illustrated above. Results from these studies are relevant in the greater context of a possible future molecular electronics technology.

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Hydrogen-bonded dimetallic dimers that show reversible proton-coupled electron transfer.

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Proton-coupled electron transport is a frequently observed phenomenon in transition metal chemistry.[1] The need to displace an electron and the much heavier proton leads to slow kinetics and irreversible cyclic voltammograms. We report here a series of hydrogen-bonded dimers showing reversible CVs for proton coupled electron transfer.

With divalent metals Ligand L (Fig. 1) forms complexes $[ML_2]^{2+}$. One alcohol proton of the complex may be removed at neutral pH; the resulting species $[ML(L\text{-}H)]^+$ then dimerises to give the species $\{[ML(L\text{-}H)]_2\}^{2+}$ held together by the hydrogen bonds shown in Fig. 2a. Trivalent ions form complexes $[M(L\text{-}H)_2]^+$ which are fully deprotonated even at pH 3. The complexes $[M^{III}(L\text{-}H)_2]^+$ react with divalent complexes $[M^{II}L_2]^{2+}$ to form dimers *via* the hydrogen bonds shown in Fig. 2b. A number of $M^{II}M^{II}$ and $M^{II}M^{III}$ dimers have been characterized by X-ray crystallography and the $Mn^{II}Mn^{III}$ complex is shown in Fig. 3.

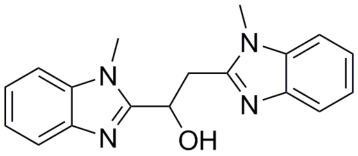
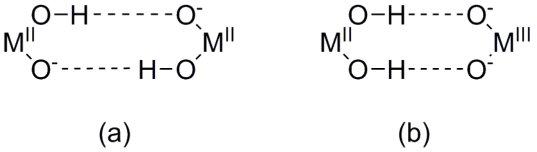


Figure 1 Ligand L



(a) (b)

Figure 2 H-bond motifs for (a) $M^{II}M^{II}$ and (b) $M^{II}M^{III}$ complexes

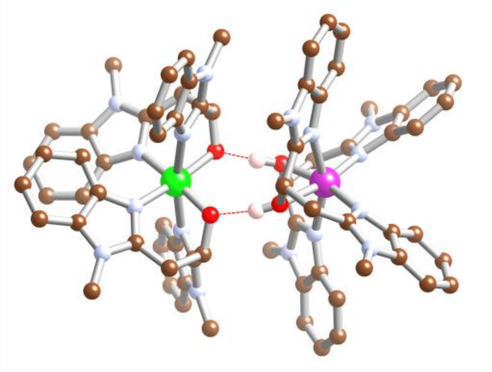


Figure 3 The complex $[Mn(L\text{-}H)_2ML_2]^{3+}$; Mn^{III} green, Mn^{II} violet

Oxidation of the $M^{II}M^{II}$ complex does not require proton loss but simply a proton shift from the oxidized metal to the reduced one by a distance of roughly 0.5 Å. This rearrangement will have a small barrier, and in contrast to the mononuclear complexes where the CVs show irreversible character, the dimers show reversible $M^{III}M^{II}/M^{II}M^{II}$ couples.

[1] M.H.V Huynh,T.J. Meyer, *Chem. Rev.*, **2007**, *107*, 5004.

Linear, branched and cyclic $Ru(dppe)_2(-C{\equiv}C-)_2$ systems for molecular electronics

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Complex geometries for molecular wires may hold the key to advancing the capabilities of single molecular electronics. Theoretical and physical studies have shown that branched systems can increase the conductance of a molecular electronics system by a factor greater than 2, due to conductive interference. Our work aims to test this experimentally using large complex systems.[1, 2]

Building on our previous work,[3] we have produced robust and repeatable routes to a series of linear, branched and cyclic organometallic molecular wires with several binding groups(Figure 1).*Trans*-$Ru(-C{\equiv}C-R)_2(dppe)_2$ centres are incorporated into these designs aseffective HOMO conductors that allow redox control.[4]Thorough investigation of these molecules through cyclic voltammetry and scanning tunnelling microscopy (STM)have probed the effects of interference, metal connectivity and redox properties on the conductance of these systems. The presentation will feature these results and latest data.

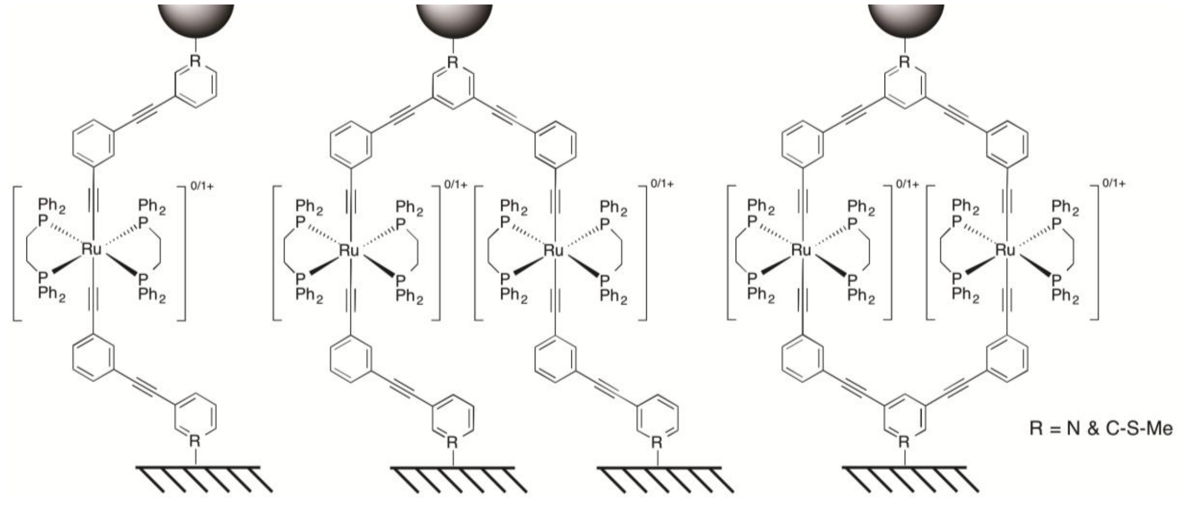

Figure 1: Organometallic molecular wires synthesised and studied within this work.

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Metallamacrocycles from Divinylphenylene-Bridged Diruthenium Precursors

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Treatment of diarylvinylene-bridged diruthenium complexes $\{Ru(CO)Cl(P^{i}Pr_3)_2\}_2(\mu\text{-}CH{=}CH\text{-}Aryl\text{-}CH{=}CH)$ with various isophthalic acid derivatives provides access to metallamacrocylic tetra- or hexaruthenium complexes (Figure 1). These undergo up to six consecutive one-electron oxidations that come as pairs of closely spaced one-electron steps. IR spectroscopy evidences complete charge delocalization in the mixed-valent states over the π-conjugated sides but not across the dicarboxylate linkers. The polyelectrochromism of the divinylarylene-bridged constituents[1,2] is even amplified in the metallacycles, which leads to intense absorptions in the Vis and the NIR for the dications or at the Vis/NIR borderline for the tetracations. The di- and tetracations are EPR active and have paramagnetic ground states as shown by EPR spectroscopy at variable T. Experimental studies are augmented by quantum chemical calculations.

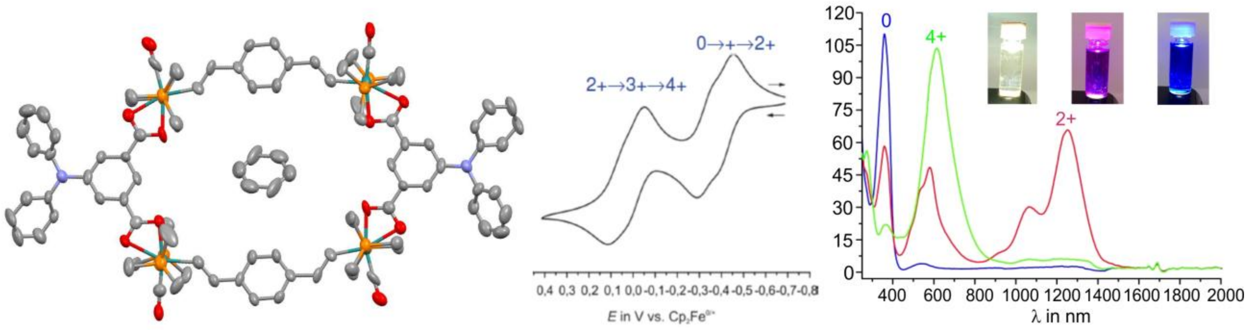

Figure 1 Expemplary structure (left) and cyclic voltammogram (middle) of tetraruthenium macrocycles and comparison of the electronic spectra in their different charge states (right)

1 J. Maurer, B. Sarkar, B. Schwederski, W. Kaim, R. F. Winter, S. Záliš, *Organometallics*, **2006**, *25*, 3701.
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Near room-temperature memory devices based on hybrid spin-crossover@SiO_2 nanoparticles coupled to single-layer graphene nanoelectrodes

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Here, we report the charge transport properties of SCO $[Fe(Htrz)_2(trz)(H_2O)](BF_4)$ nanoparticles covered with a robust silica shell placed in between single-layer graphene electrodes. We evidence a reproducible thermal hysteresis loop in the conductance above room-temperature. Importantly, the low-spin state possesses a higher conductance, consistent with previous studies on small assembles of SCO-based nanoparticles based on the same compound $[Fe(Htrz)_2(trz)(H_2O)](BF_4)$. Such bistability combined with the versatility of graphene and a silica shell represent a promising scenario for a variety of technological applications but also for future sophisticated fundamental studies.

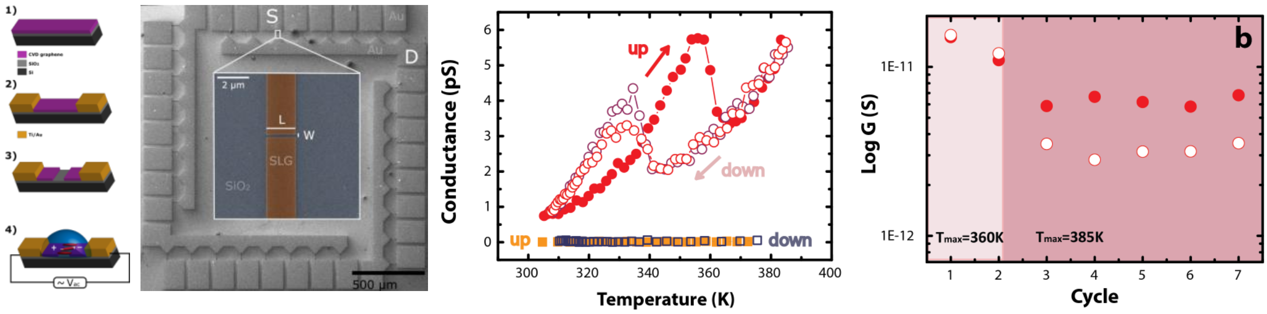

Figure 1 (Left) Schematic for the fabrication process flow. Scanning-Electron Micrograph of a chip before nanoparticle deposition (*Step 3*). Inset: Single-layer graphene electrodes of length L = 1.7 µm and width W = 300 nm on a Si/SiO_2 substrate. **(Middle)** Conductance as a function of temperature for the sample A before nanoparticle deposition (orange and navy/white squares) and after (filled red/empty red and purple dots) for both heating and cooling modes, respectively. **(Right)** Conductance of Sample A at T = 355 K and V = 20 V in the heating (red circles) and cooling (white circles) modes for several cycles. Cycle 1-2: Maximum sweeping temperature (heating mode) T_{max} = 360 K. Cycle 3-7: T_{max} = 385K.

Electrografting of diazotized Ruthenium complex: from self-organized monolayer to molecular junctions

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[b] Univ. Reims Champagne-Ardenne, Institut Chimie Moléculaire Reims, UMR 7312 CNRS, BP1039, 56187 Reims Cedex 2, France
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The research efforts devoted to the design and the incorporation of ruthenium complexes onto ordered arrays systems are driven by their potential use as building blocks in molecular electronics, especially in the elaboration of photoactive surfaces. The long-lived excited state lifetimes of the ^{3}MLCT excited state is especially of interest for a multitude application such in, e.g., heterogeneous catalysis, chemical and biological sensors, electrical and optical thin-film devices, and optics. Electrodeposition of an aryl diazonium salt has been used as an alternative efficient method to functionalize surfaces with a strong covalent bond between the reagent and the electrode. On one hand, molecular junctions using classical trisbipyridine diazoted ruthenium complex have been fully characterized *vs* thickness and temperature dependence. On the other hand, designing a novel fluorene substituted bipyridine ligand and its corresponding ruthenium complex, unexpected self-organized monolayer has been obtained and fully characterized by AFM, XPS, electrochemistry and STM (Figure). Such organization suggests a strong cooperative process during the electrochemical grafting.

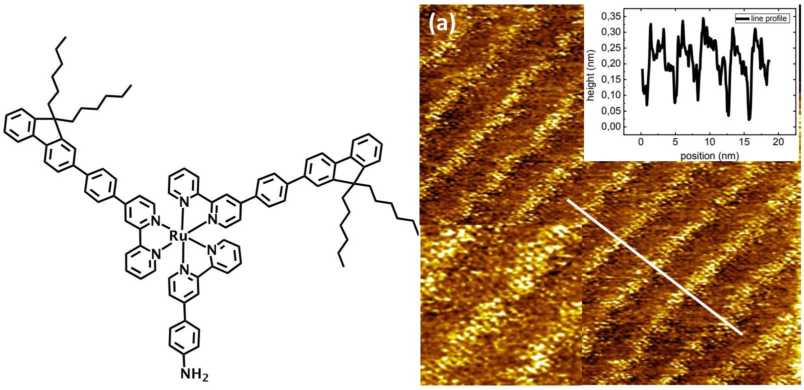

Figure 1 Molecular structure of grafted Ru(II) complex and STM images on HOPG.

Electronic communication between tetrathiafulvalene electrophores through metal bisalkynyl bridge (Hg, Pt, Ru)

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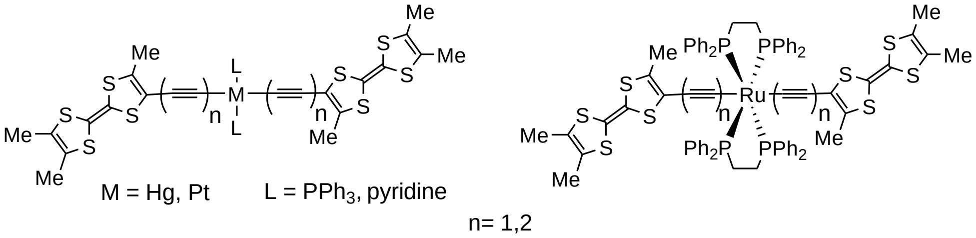
Tetrathiafulvalenes (TTFs) have been extensively studied in the search for molecular conductors. Within these materials the presence of mixed valence species is one of the key points for obtaining such properties. The formation of such species is not easy to control unless two electro-active units interact either through space or through bond in a dimeric structure. Accordingly, a range of TTF dimers linked by various organic linkers have been synthesized.[1] The interplay between two redox active TTF generates a multistage redox behaviour affected by the type of linker rather than the two reversible oxidation steps expected for an isolated TTF. Most of the interactions detected through organic linkers are weak and in order to increase these interactions the elaboration of transition metal complexes containing two TTF ligands has been developed.[2] In this context we recently investigated the synthesis and the electronic properties of mononuclear Hg, Pt and Ru complexes where two TTF are linked to the metal through an ethynyl or a butadiyne linker.[3] Herein we present the various electrochemical and spectroelectrochemical investigations which have evidenced, depending on the metal and the length of the linker between the metal and the electrophores, electronic communication between the two TTFs.



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Electron Transfer in Coordination-based Molecular Assemblies

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Directional electron-transfer events are the basis of many technologically important systems and biological processes. In this study, we demonstrate how the distance over which electron transfer occurs through organic materials can be controlled and extended. Coating of conductive surfaces with nanoscale layers of redox-active metal complexes allows the electrochemical addressing of additional but distant layers that are otherwise electrochemically silent. We also show that our composite materials can pass electrons selectively in directions that are determined by the positioning of redox-active metal complexes and the distances between them. These electron-transfer processes can be made dominantly uni- or bidirectional. Our design strategy involves 1) a set of isostructurally well-defined metal complexes with different electron affinities, 2) a scalable metal-organic spacer, and 3) a versatile assembly approach that allows systematic variation of material composition, structure, and electron transfer properties. We control the electrochemical communication between interfaces by the deposition sequence of the components and the length of the spacer, and therefore we are able to program the bulk properties of the assemblies.

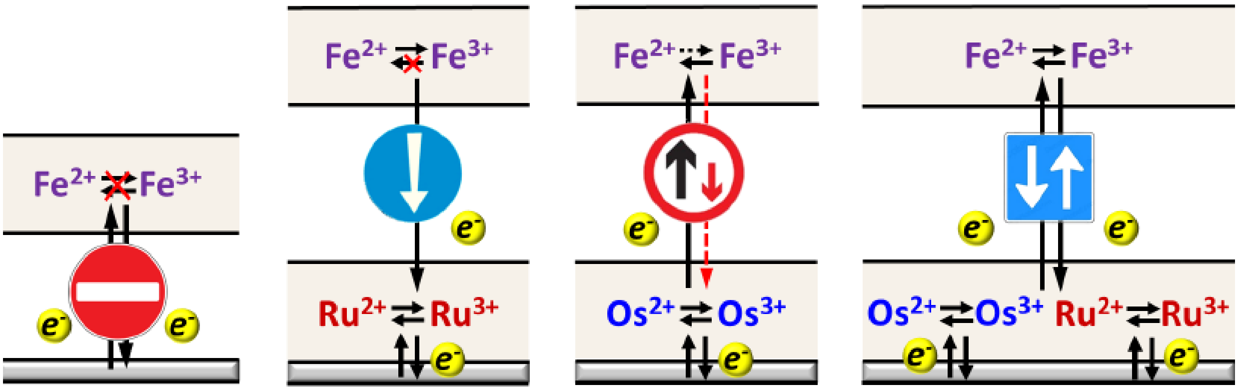

Figure 1 Examples of Rerouting Electron Transfer by Composite Molecular Materials

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Bottom-up Nanopatterning of Coordination Polymers.

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The development of methods to design large nanopatterned surfaces is one challenging aspect of nanotechnology. Surface nanopatterning is currently achieved by 'top-down' approaches generally implementing optical or electron beam lithography. Nevertheless, their replacement by simpler and cheaper methods is highly desired.

In order to organize coordination polymer nanoparticles on surfaces, we develop a strategy based on the use of ordered nanostructured oxides elaborated by sol-gel chemistry as hard templates.[1,2] We will present our last works on the controlled formation of coordination polymers nanoparticles within the porosity of nanoperforated thin oxide layers exhibiting a 2D hexagonal organization. The localized formation of Prussian blue analogue particles within the nanoperforations is achieved by a sequential growth method, leading to a 2D hexagonal organization of PBA islands isolated from each other by TiO_2 walls (Figure 1). Furthermore, their thermal treatment under controlled atmosphere results in the localized transformation of the PBA particles into corresponding oxide or metallic particles. Thus, by adjusting the chemical composition of the coordination polymer and the thermal treatment, periodically organized photomagnetic and ferromagnetic islands were elaborated.

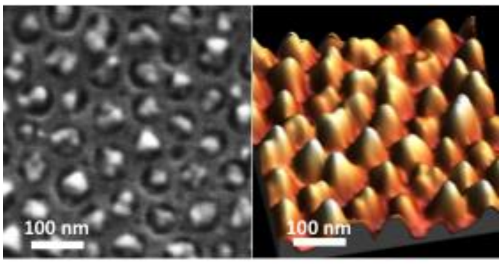

Figure 1 SEM and 3D AFM images of an ordered nanoperforated TiO_2 film filled with CoFe PBA particles.

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Magnetic Properties of Compounds with Different Spin Carriers: An Electronic Structure Insight.

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The combination of three different spin carriers within the same molecular entity (three different paramagnetic metal ions molecules containing at least one 3*d* and one 4*f* paramagnetic ions plus an organic radical) represents a valuable synthetic strategy leading to SMMs[1]. Here we present an *ab inito* characterization of SMMs containing lanthanide ions along with organic radicals or transition metals ions by DFT and CASSCF methods. Our approach has been applied to binuclear lanthanide (Dy and Tb) complexes, with non-equivalent metal centers, which are designed using as a ligand the TEMPO molecule[2]. Calculations have been also performed on compounds of block-*f* metal ions (Gd, Dy, Tb) using bis(iminoyl-nitroxide) biradical[3]. For every compound, the exchange coupling constants between the different magnetic centers and the single ion anisotropy have been computed. Calculations gave insights of how electronic structure can influence magnetic behaviour, optical properties and relaxation mechanisms. The first-principles calculations allowed to give insights in the electronic and magnetic properties of this new class of systems and to suggest new synthetic routes for their enhancements.

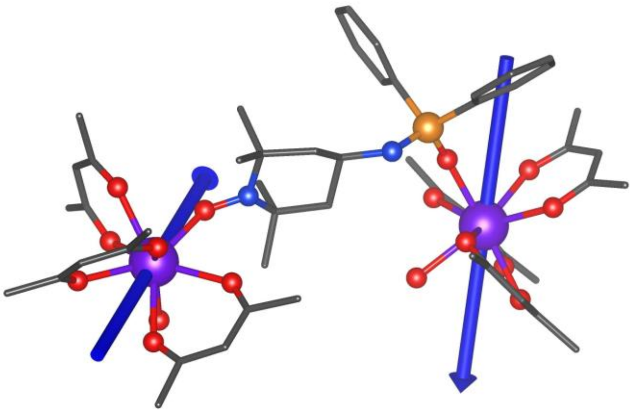

Figure Molecular structure of [$Tb_2(hfac)_6(H_2O)_2$(dppnTEMPO)] and the directions of the main anisotropy axis.

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Tailorable magnetic coordination nanoparticles: from information storage to biomedical applications

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Coordination chemistry offers the possibility to tailor in metal-based coordination networks designed for multiple goals in the field of information storage, sensing and biomedical applications. In this context, we have developed efficient routes to controlled nanoparticles and core-shells based on bimetallic cyanide-bridged coordination networks that display magnetic/optical properties triggered by several stimuli such as light, temperature, pressure, guest inclusion or magnetic field. The fine control over size, composition and architecture of these heterostructures allows reaching new synergies between core and shell's (photo)magnetic properties, and their assembly as individual particles or extended monolayers is achievable on various substrates. Besides, highly efficient T_1 contrast agents for MRI are obtained using Mn^{II} and Gd^{III}-containing nanoparticles through a one-step green process, while theranostics issues are pursued using Prussian blue's photothermal properties. This communication will illustrate some of the wide possibilities offered by these nano-objects in the context of the recent litterature.

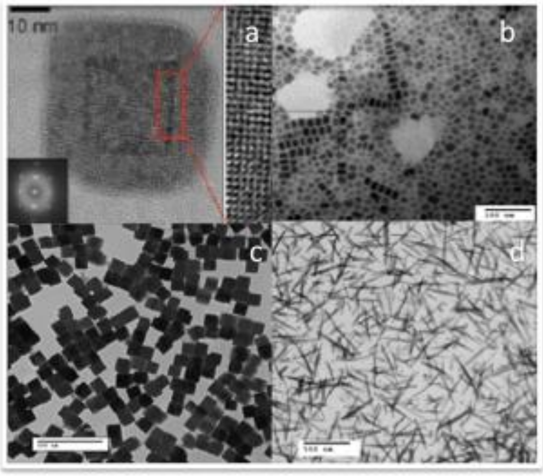

Figure 1 High resolution TEM (a) and TEM (b to d) micrographs of nanoparticles and core shells of Prussian blue analogues (a, c) and octacyanometallate-based networks (b, d)

Artificial Photosynthesis, Biosensors, and Drug Delivery Using Layered Structured Nanomaterials

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We are studying new applications of layered inorganic nanomaterials such as the zirconium phosphates (ZrP). The θ phase of ZrP can be directly ion-exchanged with large metal complexes, producing intercalated phases useful for artificial photosynthesis schemes, water decontamination, amperometric biosensors, and vapochromic materials' applications. Recently, we have demonstrated that the hormone insulin and the anticancer drugs cisplatin and doxorubicin, as well as several metallocenes, can be intercalated in ZrP. The intercalation reaction results in nanoparticles with an expanded interlayer distance. UV-vis spectrophotometry, XPS and ^{31}P-NMR spectroscopies, and molecular modeling studies indicate that for cisplatin the drug's chloride ligands have been substituted by phosphate groups of the ZrP material. Results of in-vitro drug release as well as cytotoxicity studies with breast-cancer cell lines for both anticancer agents indicate that the use of these materials for cancer treatment could prove to represent a new strategy for nanotherapeutics. Nanoparticles of these materials can specifically target tumor cells by the Enhanced Permeability and Retention Effect. We have recently intercalated neurological agents: carbamazepine and dopamine.

Enhancement of Transition Metal Photocatalysts using Plasmonic Nanoparticles

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Industrial scale chemical processes often require high temperature and pressure to proceed whilst also generating large amounts of waste. Sunlight is an abundant and economical resource that provides an attractive 'clean' alternative for driving chemical reactions. When irradiated with visible light, transition metal photoredox catalysts including $Ir(ppy)_3$and $[Ru(bpy)_3]Cl_2$ facilitate a number of synthetic transformations.[1]However, the diffuse nature of sunlight is often not sufficient to power these processes and typically require external light sources (ie. LEDs).

Coinage metal (Cu, Ag and Au) nanoparticles exhibit localised surface plasmon resonance in the visible spectrum that can affect molecules adsorbed, covalently bound or in close proximity to the nanoparticle via a number of pathways (thermal effects, hole or electron transfer, antenna effects).[2,3] Antenna effects in particular generate a transmitter-receiver pair which enhances Raman scattering, triplet formation, fluorescence and absorption of the receiver molecules.

The aim of this work is the preparation of coinage metal nanoparticles decorated with transition metal photoredoxcatalysts. The nanoparticle acts a transmitter to enhance the excited state properties of the receiver transition metal complex, which can then be exploited in photocatalytic mediated organic synthesis.

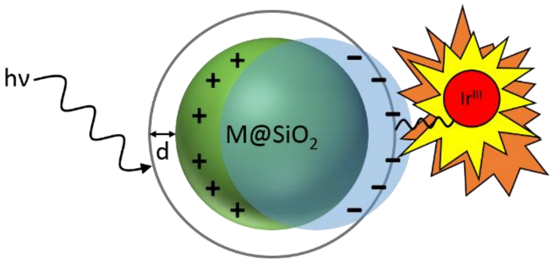

Figure 1 Diagram of transition metal (TM) complex undergoing plasmonic enhancement when tethered to a core/shell M@SiO_2 nanoparticle (M=Cu, Ag or Au).

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Luminescent metal complexes and their assemblies

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Luminescent molecules that can undergo self-assembly are of great interest for the development of new materials, sensors, biolabels…. The talk will illustrate some of the recent results on soft structures based on metal complexes able to aggregate in fibers, gels and soft mechanochromic materials [1]. The use of platinum complexes as building block for luminescent reversible piezochromic and mechanochromic materials will be illustrated. The emission of the compounds can be tuned by an appropriate choice of the coordinated ligands as well as of their aggregation in different structures. The formation of soft assemblies allows the tuning of the emission color, by pressure and temperature leading to a new class of materials possessing reversible properties. We demonstrate how even small changes in molecular design can completely inhibit or enhance the formation of organized supramolecular architectures, leading to a deep understanding of the key factor affecting the whole self-assembly process.

For some of the compounds we have indeed unraveled a highly complex supramolecular landscape comprising two kinetic assemblies and the thermodynamic isoform. We have not only characterized all the assemblies, but also the full chemical management is successfully achieved by the proper use of supramolecular and photochemical approaches. The monitoring of the different emission properties, used as fingerprint for each of the assembled species, allowed an unprecedented real-time visualization of the evolving self-assemblies [2]. We have been able to control the assemblies and obtain uniform size of the aggregate that can even be converted in a thermodynamic unstable species by light. The full control of multiple pathways opens the way to design complex systems in and out of their thermodynamic equilibrium.

The assembly processes can also be studied in confined spaces. The use of zeolites and mesoporous silica able to entrap precursor for the formation of product with defined conformation and properties is shortly illustrated.

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Ligands in Flatland: Recent Advances in the Study of Small Molecules/Ligands in Confined Environments

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There is more than a century of progress in "classical coordination chemistry" and one may ask which direction will future research on coordination compounds take? One of the next growing edges could be to explore ligand systems in a confined environment and to learn about their chemical and physical properties, for instance in an on-surface adsorbed state. Figure 1 addresses such a ligand system, a tetraazaperylene molecule with its characteristic N^N bis-chelating structural motif. This ligand clearly differs from its parent perylene molecule. Importantly, single-molecule characterization techniques allow identifying and imaging individual molecules on diverse surfaces. Different molecules/ligands were explored in various confined environments, being either adsorbed on surfaces or anchored between electrodes [1-4], all a topical issue in the field of molecular electronics.

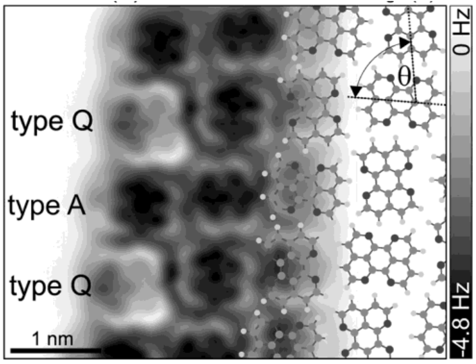

Figure 1 AFM image at the edge of a monolayer island on Ag(111) which is constructed by a typical bridging ligand with an N^N bis-chelating motif; Q and A refer to different charge states [1].

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Ru nanospecies as promising catalysts for selective C-H activation reactions in neat water

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Selective C-H bond activation reactions, through oxidation processes, constitute an attractive synthetic methodology with high impact on fine chemistry, transforming relatively cheap precursors into value-added products (alcohols, ketones...).[1] However, in the drive towards eco-responsible chemistry, the development of cleaner and milder conditions through the use of selective and active catalysts, alongside with greener oxidants, is still needed.[2] For that purpose, metal nanoparticles could offer original surface reactivities, owing to their original properties such as large surface area-to-volume ratio and a high number of potential active sites, and recyclabilities under adapted conditions.

In that context, we report the use of metallic nanospecies as active, selective and reusable catalysts for oxidation reactions, using t-BHP as oxidant, in neat water. These catalytic systems have been investigated on various substrates, such as cycloalkanes[3] and terpenes, leading respectively to the corresponding ketones and enones, with high selectivity (up to 90%).

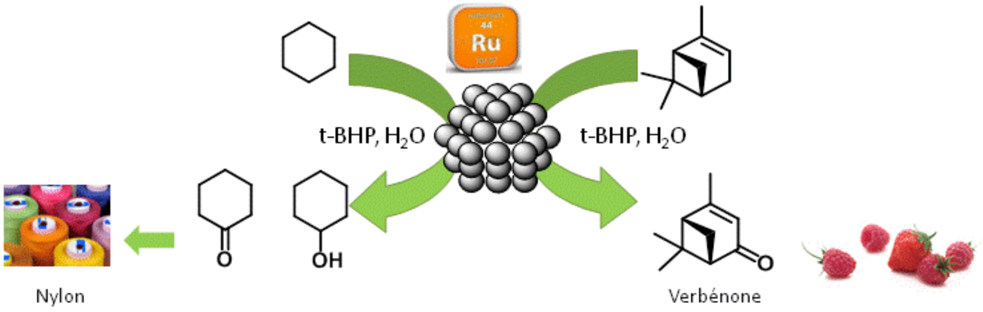

Figure 1. Ru nanocatalysts for selective oxidation in neat water

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Bimetallic Phosphorus-Based Complexs as Building Blocks for multi-dimensional Organometallic-Organic Hybrid Material.

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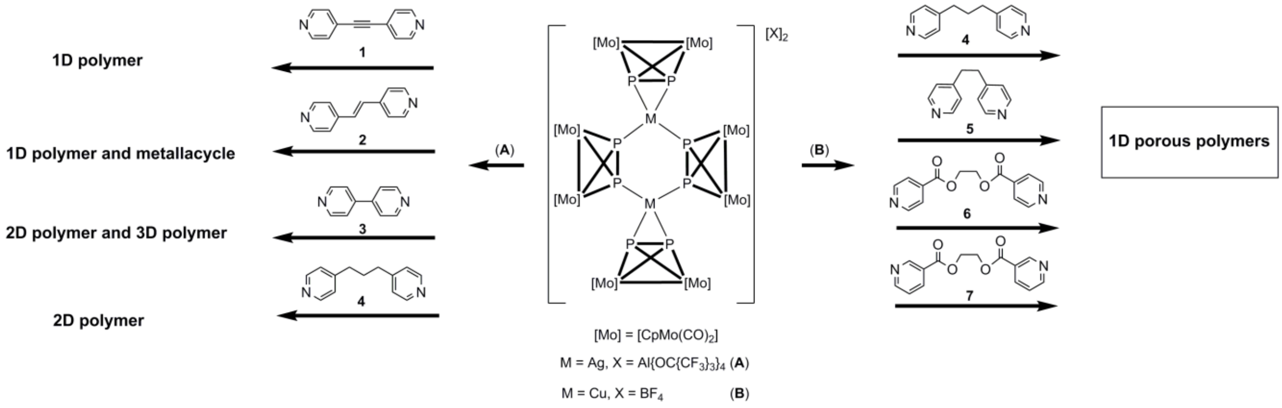
In the past decades, synthesis and development of porous materials have attracted considerable attention resulting in a number of important technological applications [1]. In this field our group study extensively the potential of organometallic complexes based on polyphosphorus ligands as bridging units between metal centers [2]. These complexes show a versatile coordination behavior and allow the formation of one- and two-dimensional coordination polymers [3] as well as giant spherical molecules [4]. In one approach the dimeric compounds **A** and **B** were synthesized from the reaction of the tetrahedrane complex [$Cp_2Mo_2(CO)_4(\eta^2\text{-}P_2)$] with the silver (Ag[Al{$OC(CF_3)_3$}$_4$]) or copper ($Cu(CH_3CN)_4BF_4$) salts respectively [5]. The reactions of **A** with the ditopic linkers **1-4** lead to the formation of multi-dimensional organometallic-organic hybrid polymers depending on the organic linker used [6]. The reactions of **B** with the flexible ditopic linkers **4-7** lead to the selective formation of porous one-dimensional ladder-like polymers regardless of the organic linker used. This novel synthetic method opened up a new opportunity to use multitopic linkers in order to synthesis a new class of porous three-dimensional material.



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A Reflection of Gold Nanoparticles Capped with Novel Thiazolidine Polymer in Dye Reduction

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Abstract

Gold nanoparticles (AuNPs) are useful [1]especially when they are used to improve the quality of lifehence its synthesis and applications are highly sought after. A small number of compounds, including the citrates, can stabilize AuNPs thereby influencing their morphology in the process. However, more recent investigations report the advantage of using polymeric stabilizers; it reduces the degree of aggregation of AuNPs primarily due to the steric repulsion between AuNPs and the polymer.Also stabilizedpolymer- AuNPs can be stored and used for longer periods compared to stabilizedsmall molecules -AuNPs.

In this study, the synthesis of a novel water-soluble polymer containing thioether moieties is reportedand characterization by traditional spectroscopic techniques is elucidated. Furthermore the polymer is utilized to cap AuNPsvia green protocols: its characterization by SEM/EDX, TEM, DLS and FT-IR and NMR follows and finally their efficacy as a catalytic system to reduce dyes such as Methylene blue, Congo red and Allura red is presented.

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Nanoconcentrator: Pre-organization of catalysts and substrates in nanospheres

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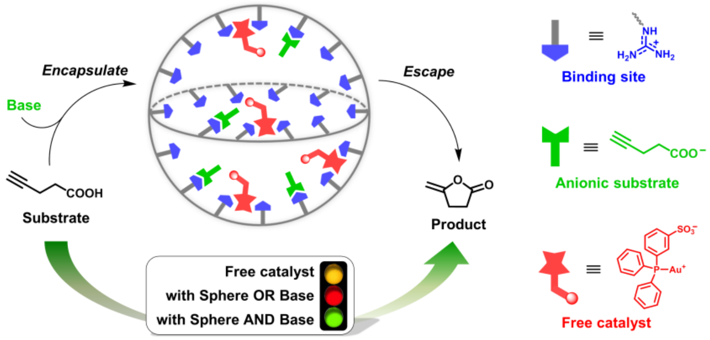
Advances in the field of transition metal catalysis have been dominated by ligand design strategies in which catalyst's properties are controlled by the ligands attached to the metal center. The design of well-defined second coordination spheres around transition metal complexes provides a novel manner of controlling those properties. A recent example of such a strategy comprises the pre-organization of 24 gold-complexes in a nanosphere leading to extreme high local concentration of gold (1.1 M), resulting in more efficient catalytic transformations.[1] Along these lines, we now report a system that is able to co-encapsulate the catalyst and substrates within a confined space, leading to high local catalyst/substrate concentrations. It consists of a nanosphere endohedrally functionalized with 24 guanidinium moieties, which by means of multiple hydrogen bond interactions strongly binds the catalyst inside the sphere. The remaining guanidinium functionalities can be used to preorganize the substrates by weaker interactions. This strategy leads to improved reaction rates in the gold catalyzed cyclization of acetylenic acid to enol lactone (Scheme 1).[2]



Scheme 1

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Syntheses and Optical Limiting Studies of Mixed-Metal Clusters

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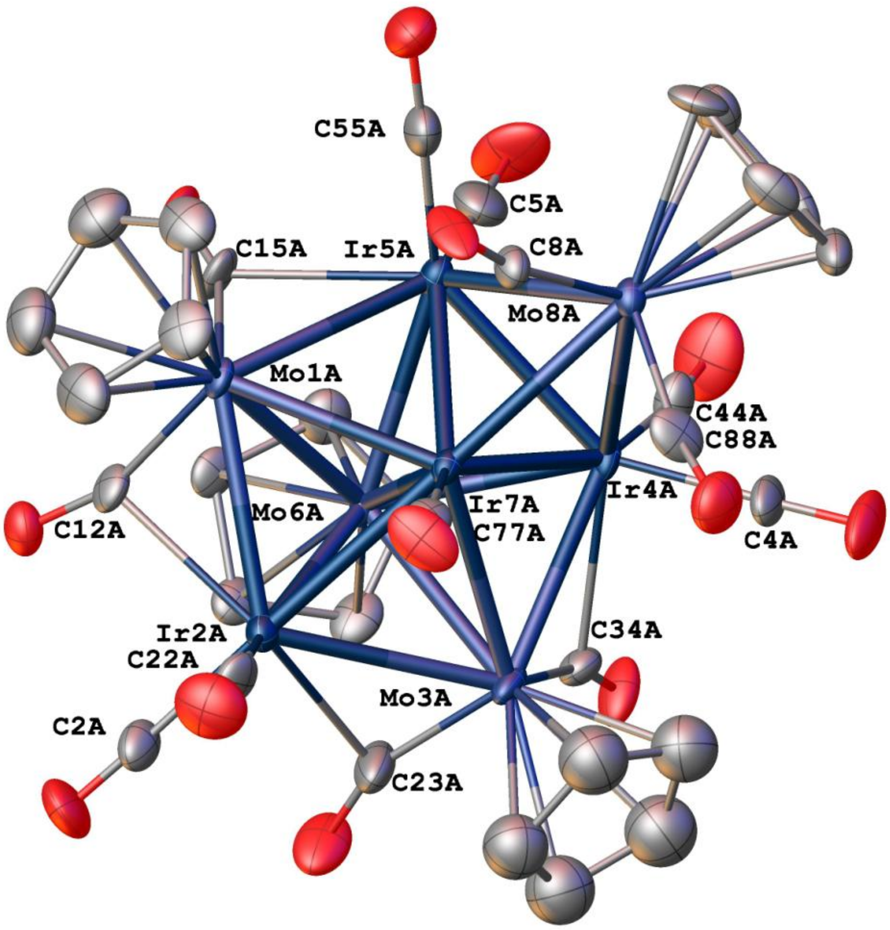
Metal clusters have been studied for many years as interesting synthetic targets and as catalyst models/precursors, but a comparatively recent trend is the detailed and systematic investigation of specific physical properties, including optical power limiting. Optical power limiters are materials that have good linear transparency and transmittance below a threshold light intensity, but above a threshold value, they can block intense laser light over a broad frequency range. We have been interested in developing metal carbonyl cluster chemistry and structure-optical limiting property relationships for mixed group 6 - group 9 clusters. Recent highlights from our synthetic/optical limiting research programme will be presented.



Photoinduced deposition of platinum mirrors from simple Pt(II) precursor complexes in aqueous solutions at room temperature

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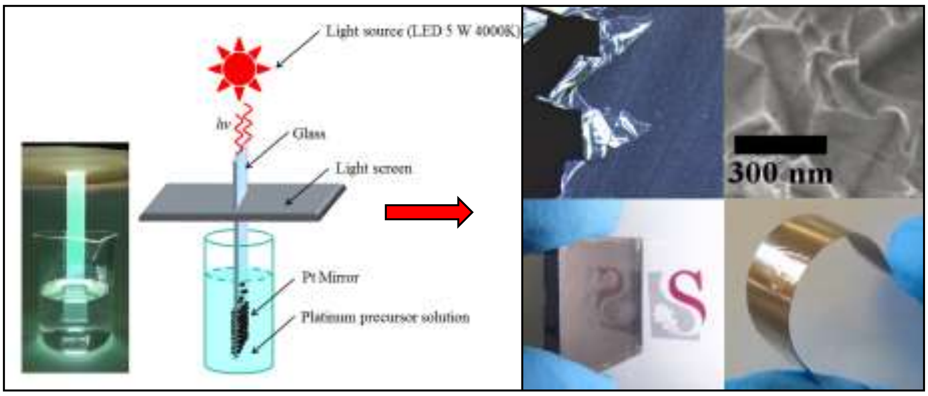
Excellent quality pure platinum mirrors can readily be deposited directly at room temperature (20 ± 3^{o}C) onto a variety of substrates such as FTO glass, borosilicate glass, polypropylene and other substrates such as cellulose by means a controlled photoinduced reductive deposition of Pt from low concentrations (1-5 mM) of $[PtCl_4]^{2-}$ anions in water containing a water miscible sacrificial organic reducing agent, under irradiation with visible polychromatic light form a simple LED light source (λ in the range 329- 475 nm). The highly reflective, relatively non-porous Pt-mirrors of variable thicknesses (200-600 nm) deposited onto FTO glass can be removed to give the ultrathin “platinum foils” which are catalytically active. These ultrathin platinum foils display a shiny reflective side mimicking the micromorphology of the FTO glass template, while the relatively matt reverse side (exposed to the precursor solution) consists of densely packed platinum nanoparticles. The these Pt-mirrors have been characterized by optical microscopy, SEM and EDS, X-ray diffraction, and laser-ablation inductively coupled plasma mass spectrometry (LA-ICP-MS).Significantly ^{195}Pt NMR spectroscopy of the precursor solutions shows that the *chemical speciation* of the precursor Pt(II) complexes plays a critical role in the successful fabrication of photoinduced Pt-nanolayers.



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Photochromic Ruthenium Alkynyl Complexes as Molecular Switches

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Molecular switches can be broadly defined as molecular species that undergo reversible changes between two or more distinct structures in response to some thermal, chemical, electronic or, most commonly, photochemical stimulus. These elementary molecular machines and photochromes attract considerable attention arising from their potential applications in sensing, molecular-scale data storage and processing, and for optical or electronic signal modulation.[1-4] The inclusion of a ligated ruthenium moiety to ethynyl spiropyran (SP), 5'-ethynyl-1',3',3'-trimethyl-6-nitrospiro[chromene-2,2'-indoline], has been shown to increase the lifetime of the ring-opened merocyanine (MC) form twentyfold. Calculations suggest that the higher barrier to thermal reversion of the merocyanine form of the metal alkynyl complex arises from the capacity for greater delocalisation of charge consequent of the presence of the ruthenium moiety. These complexes provide a different switching mechanism to the 5,5'-dithienylperfluorocyclopentene electrode decoupling seen previously.[5] Our most recent results in this area will be presented.

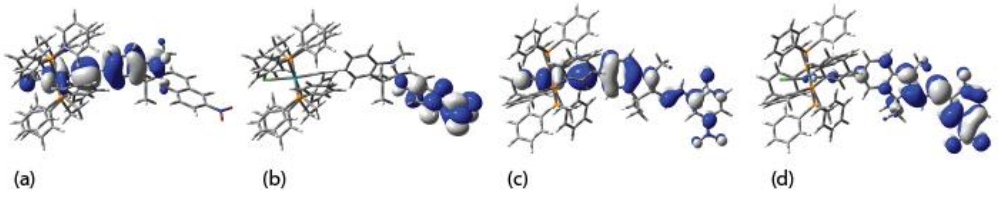

Figure 1. Plots of the (a) HOMO and (b) LUMO of the SP form and (c) HOMO and (d) LUMO of MC form(±0.02 $(e/bohr^3)^{1/2}$).

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Core-shell Au@Prussian Blue Analogue Nano-heterostructures: Towards Multifunctionality at the Nanoscale

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Comparatively to metal/metal oxides nanoparticles, the synthesis and study of Prussian Blue Analogues (PBA) nanoparticles is a recent field of study in coordination chemistry. These systems are the ideal candidates to study the evolution of magnetism upon size reduction. On the other hand, gold nanoparticules present remarkable properties arising from the surface Plasmon resonance phenomena. Combining the properties of both systems paves the way towards multifunctional systems. We present here a new synthetic strategy to design core-shell Au@PBA nanoheterostructures based on a coordination chemistry approach.[1] The obtained core-shell nanoparticles show optical properties resulting from the surface Plasmon band and magnetic properties relative to the PBA shell. Additionally, these nanoparticles can be used to either *i*) remove the gold core to obtain hollow PBA nanoparticles or *ii)* subsequently grow a second PBA shell of different composition with tunable thickness in order to modulate the magnetic properties. We show here that the peculiar architecture of these nanoparticles modify greatly influence the magnetic behavior, leading to a spin-glass behavior for small magnetic shell thickness.

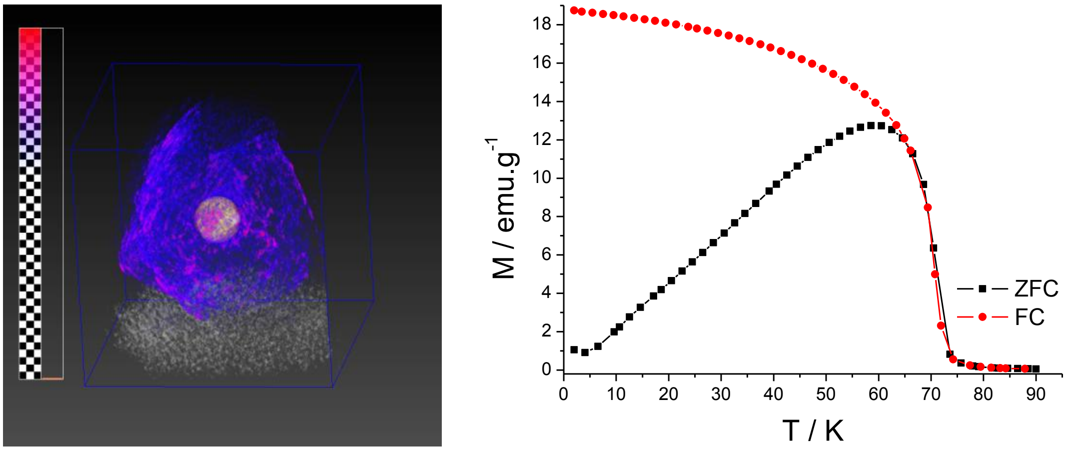

Figure 1 3D HRTEM reconstruction of a Au@KNi^{II}[Fe^{II}(CN)$_6$] nanoparticle and ZFC/FC magnetization curves for double layered Au@KNi^{II}[Fe^{II}(CN)$_6$]@ KNi^{II}[Cr^{III}(CN)$_6$] system.

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Single Source Molecules and Ethylene Glycol-Functionalized Dendrimers for Metal- and Metal-Oxide Nanoparticle Formation

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The synthesis of type **A** – **C** molecules will be discussed, as well as their use for spherical and aspherical metal- and metal-oxide nanoparticle (NP) formation and stabilization without addition of any reducing agent or stabilizing components.[1,2] The thermal decomposition behavior of **A** and **B** to give the respective NPs will be discussed. Depending on the precursor concentration and decomposition temperature particle sizes of 4 to 80 nm in narrow size distributions are obtained.

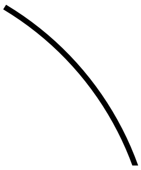

Figure 1 Molecules **A** – **C** and their use in the formation and stabilization of metal- and metal-oxide NPs (M = Cu^{I}, Cu^{II}, Ag^{I}, Au^{I}, Au^{III}, Ru^{II}, Pd^{II}, Pt^{II}, Rh^{III}, ...).[1,2]

The usage of the above described NPs in inkjet printing, spray-coating and combustion chemical vapor deposition processes for the formation of conductive (Cu, Ag, Au) and semi-conductive (Cu_2O, Ag_2S, ZnO, ...) thin layers will be discussed. In addition, their use for the generation of magnetic NPs (Fe_2O_3, Fe_3O_4, Mn_2O_3, Co_2O_3, ...) and as catalysts (*C,C* cross-coupling reactions; Pd, Ru, ...) is envisaged.

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Photophysical properties of 1,10-phenanthroline ligand-based Ru(II) complexes and related nanoparticles

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Our research concerns either fundamental aspects than potential applications of the photophysical properties of new molecular and supramolecular edifices.[1] Will be described (*i*) the huge solvatochromism of 5-substituted-1,10-phenanthroline derivatives and related materials[2] which give them interesting properties for applications as optical sensors. One compound is the siege of a solvent-tuned dual emission[3] (*ii*) related fluorenyl Ru(II) complexes-based ^{3}MLCT excited-states and their absorption, and lifetime (τ) properties for several applications such as two-photon excited luminescence or photodynamic therapy (2PE-PDT),[4] and optical power limiting[5] (*iii*) multifunctional nano-edifices[6] with novel properties; a switch from 2P absorption of Ru(II) coordination complexes to saturable absorption for the related decorated-gold nano-particles was recently highlighted.[7]

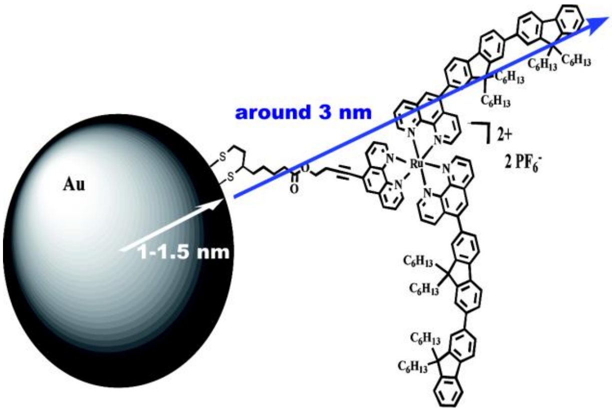

Figure 1 Schematic representation of [Ru(II)] complexes confinement around small gold nanoparticles

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Bio-hierarchical architectures of N-La codoped TiO_2 nano-materials and enhanced photocatalytic activity

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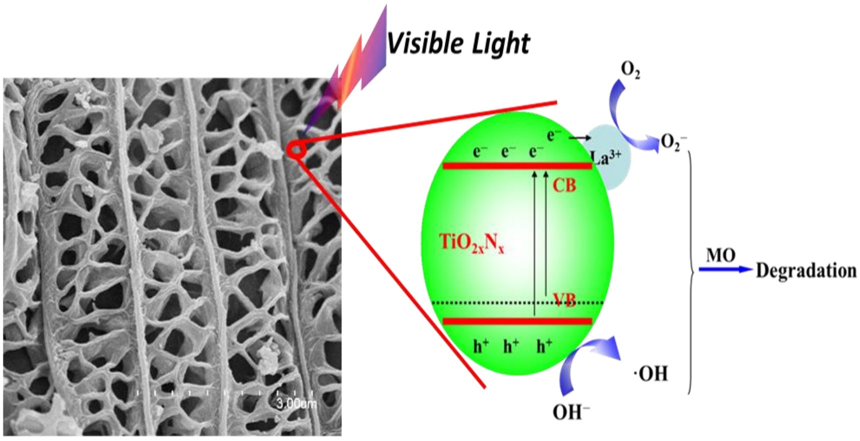
Bio-hierarchical TiO_2-based porous structures with N and La co-doping (denoted as N-La-morph-TiO_2) are successfully synthesized via a facile one-pot reaction by using butterfly wings as bio-template and surfactant as co-template[1-3]. Due to the novel dual-template strategy, the well-aligned 3D bio-hierarchical porous structures in combination with N-La codoped not only modify the band structure of TiO_2 to make it more responsive to visible light, but also increase the surface area and lead TiO_2 to have enhanced photocatalytic activity for methyl orange (MO) degeneration under UV and/or visible light illumination as compared with P25 and TiO_2 without bio-hierarchical architectures. The optimized N-La-morph-TiO_2 nanostructures present a narrow pore size distribution with an average pore diameter of 8.7 nm and a high specific surface area (196 m^2 g^{-1}), which is nearly 5 times that of P25 TiO_2. The enhanced photocatalytic activity is attributed to the combination of the functionality from the doped inorganic oxide, the fine hierarchical biological structures and well-aligned porous nanostructures. The promotional mechanisms and principles reported here would have great significance in heterogeneous photocatalysis.

Figure 1 FE-SEM images and photocatalytic mechanism of N-La-morph-TiO_2.



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Polyoxometalates-Based Hybrid Magnetic Nanocatalysts

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Magnetic nanospheres with magnetically responsive cores and functionalized shells have attracted increasing attention, especially in the field of catalysis due to their unique size and physical properties. The challenge of switching towards processes that avoid the use of wasteful separations but in the same time demand environmental friendly and efficient technologies is becoming one of the main concerns. Thus, heterogenization of catalytically active species onto the surface of magnetic core@shell nanoparticles constitutes an elegant solution, since it may allow the combination of the activity and selectivity of the homogeneous catalyst with the ease of recovery of the heterogeneous one.

As a result, we developed a project based on the elaboration of catalytic materials functionalized with polyoxometalates hybrids (POMs, *i.e.* transition metal oxoanion nanosized clusters).

In the chosen strategy, lacunary POM hybrids[2] (also able to bind transition metal active centers) and their supporting nanoparticles partners present complementary organic functions in order to favor their covalent association with an adequate coupling agent. The nanostructuration of POMs in these materials has been evaluated by HR-TEM and correlated to their catalytic activity in the frame of mild oxidation processes[3].

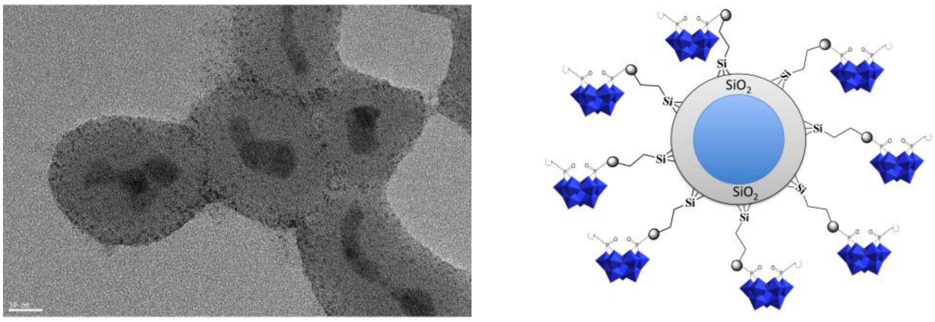

Figure 1 HR-TEM image of magnetic nanoparticles with POMs

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Core-shell Functionalized Polymers as Nanoreactors for Biphasic Catalysis: Coordination Chemistry inside the Core.

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We have recently used new nanoreactors to carry out the efficient hydroformylation of higher olefins under biphasic conditions. The catalytic reaction occurred within the particle core and that the catalyst could be recycled several times by simple decantation with low Rh leaching. These nanoreactors are tailor-made macromolecules obtained in a straightforward method by controlled radical polymerization and are composed of two parts: a hydrophobic shell and a cross-linked hydrophobic core containing covalently bound phosphines.[1-6]

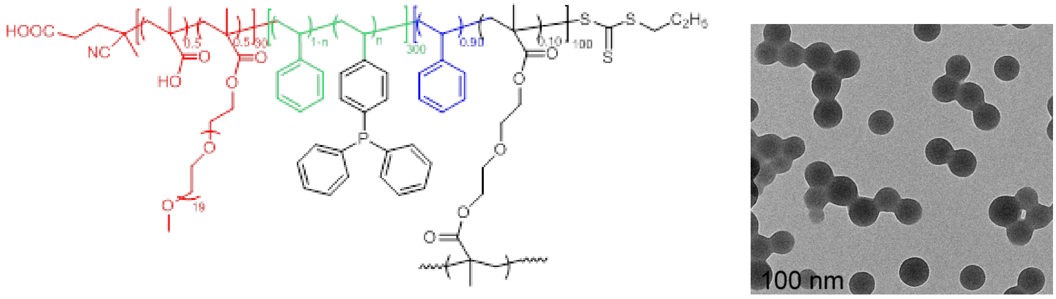

Figure 1 (Left) Structure of nanoreactors; (Right) TEM images of nanoreactors

We studied the water/hydrophobic core interface structuring, the coordination chemistry of the rhodium pre-catalysts inside the swollen hydrophobic cores[2] and the interparticle metal migration,[6] allowing us to make hypotheses on the mechanisms of mass transport to and from these nanoreactors and of rhodium leaching to the organic phase.

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Cellulose Nanocrystals as Catalysts Supports and Chiral Inducers

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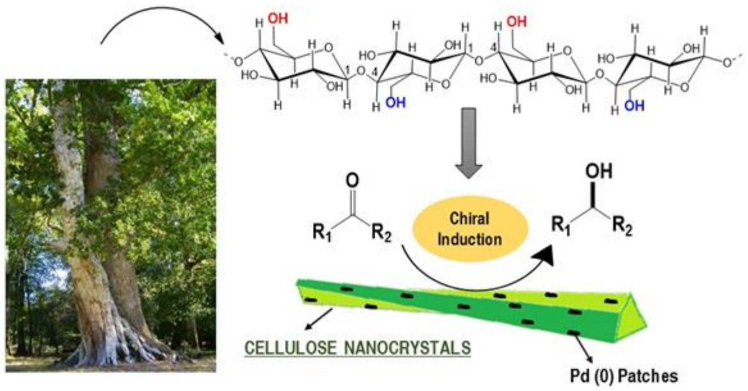
Cellulose nanocrystals (CNCs) are rod-shaped nanomaterials readily obtained from cellulose *via* sulphuric acid hydrolysis and now commercially available. CNCs have well-defined size and morphology, high aspect ratio, high crystalline order, chirality, and form stable suspensions in water. We have explored the possibility of using these CNCs as supports for Pd, Ru and Ag nanocatalysts. Using Pd nanoparticles (NPs) deposited onto CNCs,[1] the hydrogenation of prochiral ketones at room temperature and 4 bars H_2 was performed and afforded unprecedently high ees for a system relying only on cellulose as chiral inducer.[2] High resolution transmission electron microscopy and tomography were used to better characterize the catalyst and shed light onto the chiral transfer mechanism. Ru NPs were also deposited onto CNCs, and successfully used as a biphasic and recyclable arene hydrogenation catalyst under 4 bar of H_2 and room temperature.[3] At last, a CNC suspension was used to synthetically harvest Ag NPs directly from silver metal rods, which were used as catalysts for the hydrogenation of aldehydes.[4] These new CNC/metal hybrid species call for fine imaging techniques, which we recently reviewed.[5]



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Pt(IV) Prodrug Cocktailed Coordination Polymer Nanoparticles: Towards Anti-neuroblastoma Drug Delivery

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In this work, we present novel platinum-based coordination polymer nanoparticles (CPPs)[1,2] as promising nanoconstructs for neuroblastoma therapy. In this system, a Pt(IV) prodrug, with intriguing property towards anti-neuroblastoma, is used as buiding-block of the coordination polymer. The synthesized **CPP1** namely [{Zn(Bix)(Pt^{IV}-prodrug)(H_2O)$_2$}.EtOH]$_{\propto}$ was chemically and nano-structurally characterized by various techniques. In the proposed system, a cisplatin prodrug is coordinated to another metal node (Zn) and assisted by secondary ligands (Bix) (Figure1). Using the prodrug as part of the nanoparticle we can increase the payload of the therapeutic agent, its control release and the properties of the metal nodes (such as fluorescence or pH sensitivity) can be used to achieve multifunctional nanodevices. Scanning electron microscopy revealed the presence of nanoparticles with average size of 116 nm which showed good colloidal stability in physiological conditions. The study of Pt(IV) prodrug release was carried out using a dialysis method and ICP-MS technique was used for Pt quantification confirming a controlled and stable release of Pt^{IV} prodrug over a period of 3 days. Current in vitro assays using neuroblastoma cell lines are addressed to determine the cytotoxicity and the therapeutic effect of these nanoconstructs.

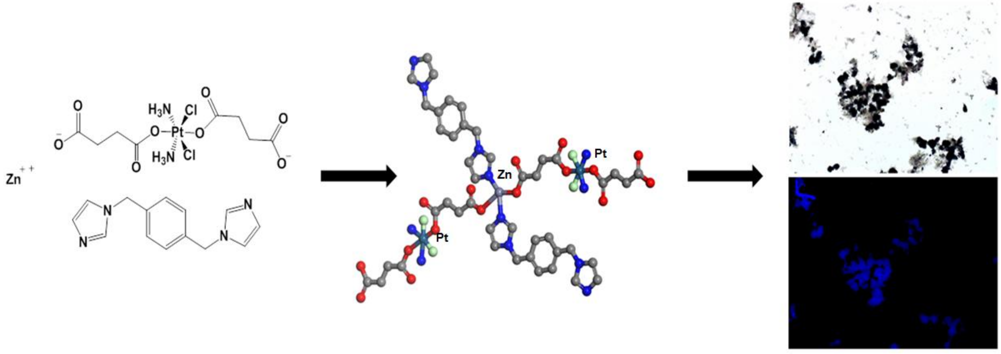

Figure 1: Schematic representation of the synthesis of Pt^{IV}-based CPPs using Zn as metal node and the Bix ligand as coligand. The resulting nanoparticles showed fluorescent properties afforded by the Zn-Bix polymer as observed by fluorescence microscopy.

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Synthesis of well-controlled nanocatalysts using coordination chemistry concepts

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Nowadays, many efforts are devoted to the synthesis of metal or metal oxide nanomaterials given their attractive properties that can find applications in various areas such as catalysis.[1]

The synthesis of well-defined metal nanostructures with a narrow size distribution and a controlled composition can be performed applying the concepts of coordination and organometallic chemistry.[2] The decomposition of metal organic complexes in solution may lead to nanoparticles of tunable characteristics the control of which is possible by an adequate choice of the reaction parameters. Among others, the metal precursor and the ligand used as a stabilizer are of prime importance as they can influence strongly the size, shape or surface chemistry of the obtained nanoparticles and consequently, their properties. This methodology can be applied to prepare various monometallic nanostructures or bimetallic ones (alloy, core-shell or surface-decorated) that have shown their interest in catalysis.[3] Moreover, supported-nanoparticles can be also produced by impregnation of a support (silica, carbonaceous…) or by direct synthesis of the nanoparticles in the presence of the support. The functionalization of the support can be the driving force to get supported nanoparticles that are well-dispersed and more stable against leaching. This will be illustrated through examples of Pd[4], NiPd[5] or Rh nanocatalysts.[6]

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Real-time imaging and characterisation of precious metals nanocrystallisation

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Tailoring nanoscopic objects is of importance for the production of the materials of the future, for example in medicine, industrial manufacturing, construction, and space exploration.[1] However, the direct observation of resolved single atoms, atom-by-atom crystal formation, and crystallization process is still an experimental frontier.[2]

We discuss the atom-by-atom synthesis of 3D-metal nanocrystals using transmission electron microscopy.[3] This technology allows experimental observation of crystal assembly from single metal atoms and captures the dynamics of nucleation in real space with atomic precision. The fabrication and characterisation of various precious nanocrystals (Ru, Os, Ir, or Au) is reported by various techniques, both *in situ* and after air exposure.[4]

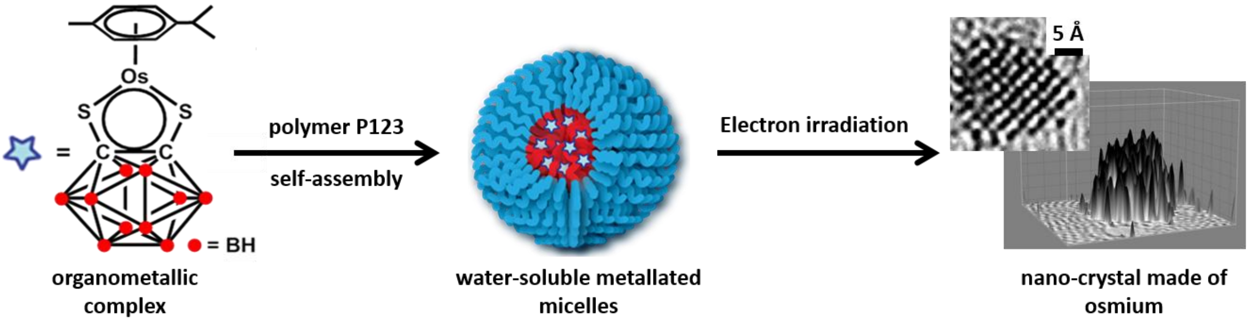

Figure 1 Synthesis of nanocrystals of osmium from organometallic complexes encapsulated in polymeric micelles.

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Acknowledments
We thank the Leverhulme Trust (Early Career Fellowship No. ECF-2013-414 to NPEB), the University of Warwick RDF Strategic Award (Grant No. RD14102 to NPEB) and the Science City: Creating and Characterising Next Generation Advanced Materials, with support from Advantage West Midlands and part funded by the European Regional Development Fund.

Adsorption studies of divalent, dinuclear coordination complexes as molecular spacers on SWCNTs: Applications toward energy storage

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In order to enhance the electrical energy storage capabilities of nanostructured carbon materials, inter-particle spacer strategies are needed to maintain ion-accessible surface area between the nanoparticles. This paper presents a comparison between different classes of divalent, dinuclear coordination complexes which both show strong adsorption to single-walled carbon nanotubes (SWCNTs) and have molecular spacer properties that maintain electrochemical activity. We find that a novel, dinuclear zinc hydrazone complex binds as an ion-pair at very high loading while not inducing significant aggregation as compared to our previously studies of dinuclear ruthenium complexes. These conclusions are supported by conductivity and dispersion stability data. Moreover, since zinc is an earth abundant metal, these complexes can be used as components in sustainable energy storage materials. Binding kinetics and binding equilibrium data are presented. Modeling of the adsorption isotherm is best fit with the BET model. Kinetics data support an independent binding model. Capacitance, energy storage, power dissipation, electrochemical impedance spectroscopy, and membrane resistance data are consistent with the complexes acting as molecular spacers between the SWCNTs in a condensed thin film. Enhanced pseudocapacitance from novel functionalized complexes with a series of metal centers will be presented.

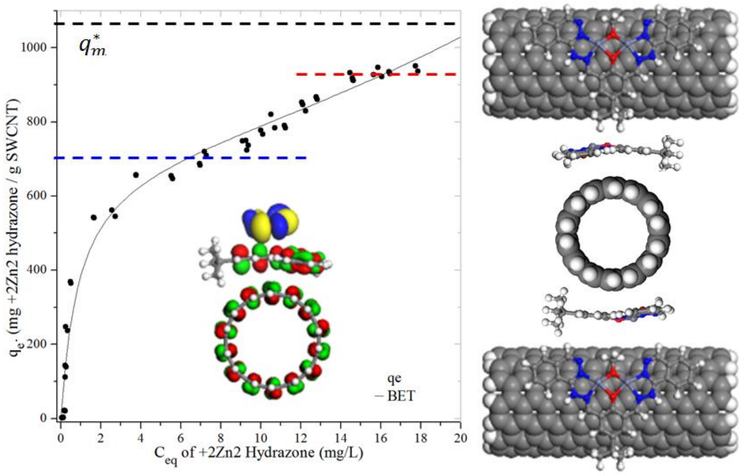

Figure 1: Adsorption Isotherm and Molecular Spacer Model

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Fibrous Nano-Silica (KCC-1) based Hybrid Nanomaterials for Catalysis, Photocatalysis, CO2 Capture and Conversion

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We recently reported the synthesis of a new class of fibrous nano-silica (KCC-1).[1-9] Such fibrous morphology observed in these nanospheres has not been seen before in silica materials. KCC-1 exhibits excellent physical properties, including high surface area, a fibrous morphology, good thermal/hydrothermal, and high mechanical stability. Uniqueness of KCC-1 is, its high surface area is by virtue of its fibrous structure instead of pores (unlike MCM-41 and SBA-15 silicas), and hence easily accessible. We also showed successful utilization of nano-silica (KCC-1) for range of important catalytic applications such as metathesis, hydrogenolysis, C-C coupling reactions etc.[2-9] KCC-1 based oxynitrides showed multifold enhancement in activity as a solid base.[6] This enhancement in activity was explained on the basis of excellent accessibility of active sites due to the open and flexible fibrous structure of KCC-1,[6] as well as due to different types of amine groups present on the surface.[7] We also showed how KCC-1 oxynitrides are better than SBA-15 oxynitrides.[8] KCC-1 oxynitrides were also used to capture CO_2 with improved sorbent stability.[9] We also synthesised high surface area photocatalysts by coating TiO_2 on the fiber of KCC-1 using atomic layer deposition (ALD). It showed extraordinary photo-catalytic activity, far better than well-known MCM-41 and SBA-15 supported catalysts as well as other silica supported catalysts reported in the literature till date.[10] Thus, we observed that it is the fibrous morphology of KCC-1 which provides better accessibility of active sites for enhanced catalytic activities and capture efficiencies.

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Atomically-Thin MoS_2 Layers on 2D SiO_2/Si Support by Surface Coordination Chemistry for ALD.

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2D materials of group VI transition metal dichalcogenides (TMD) have attracted considerable attention in microelectronics.[1] Thus far, several synthetic methods have been developed aiming at atomically-thin uniform deposits, but these methods suffer from bottlenecks such as lack of reproducibility, presence of contaminants, or non-ideal temperature and annealing conditions.[2]

We report here an ALD/MLD method based on coordination chemistry applied to the solid surface of the silicon wafer, for the growth 2D MoS_2 crystals (see Figure 1). We will present the method, the characterization of the 2D layers (among which the first in-plane micrographs of ALD-grown MoS_2 samples) and the proposed surface coordination chemistry mechanism at hand obtained through modelling studies on the silica beads.

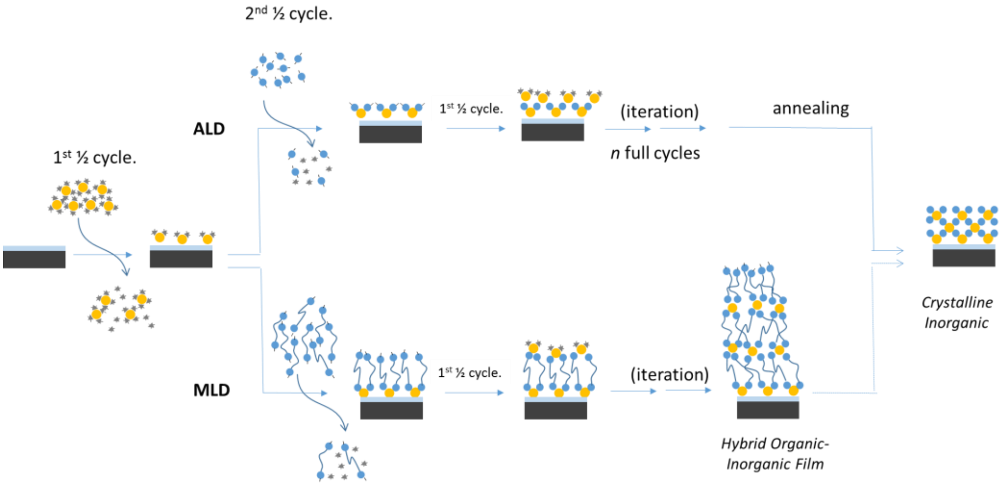

Figure 1 Schematic representation of an ALD (Atomic Layer deposition) and MLD (Molecular Layer Deposition) process on 2D support

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Photofunctional "bottom-up" metal complex nanosheets

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Although molecule-based bottom-up nanosheets manufactured directly from molecular components can exhibit greater structural diversity than top-down nanosheets, the bottom-up nanosheets reported thus far lack useful functionalities. In this five years, we have created “functional” bottom-up metal complex nanosheets. One such example includes a bottom-up nanosheet featuring a photoactive bis(dipyrrinato)zinc(II) complex motif (Fig. 1).[1] A liquid/liquid interfacial synthesis between a three-way dipyrrin ligand and zinc(II) ions results in a multi-layer nanosheet, whereas an air/liquid interfacial reaction produces a single-layer or few-layer nanosheet with domain sizes of >10 μm on one side. The bis(dipyrrinato)zinc(II) metal complex nanosheet is easy to deposit on various substrates using the Langmuir-Schäfer process. The nanosheet deposited on a transparent SnO_2 electrode functions as a photoanode in a photoelectric conversion system and is thus the first photofunctional bottom-up nanosheet.

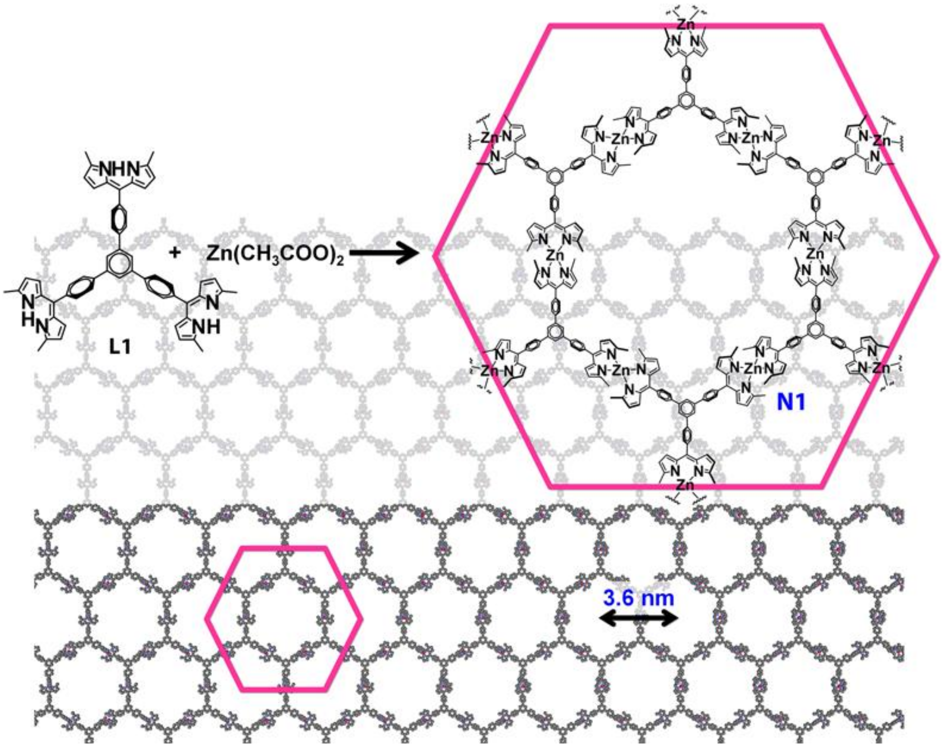

Figure 1 Bis(dipyrrinato)zinc(II) complex nanosheet.

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Coordination polymers as nonlinear optical materials

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Nonlinear optical (NLO) effects are often studied as manifestations of certain properties of electron distributions in various materials involving the symmetry properties and the delocalization of electrons. However, real life applications of NLO materials in areas such as frequency conversion, electrooptic modulation and nonlinear refraction are limited to just a few classes of materials available as good optical quality single crystals or glasses. On the other hand, the NLO phenomenon of nonlinear absorption can be employed in various types of materials, including those in the form of liquid and solid solutions, composites and nanoparticles.

Among the materials that may be potentially considered for NLO applications a special interest has emerged in specially crafted coordination polymers including metal-organic frameworks. Such materials offer a number of potentially useful features including those of aggregation induced emission and aggregation enhanced nonlinear effects. At the present time the NLO studies of such materials have included second-order NLO effects such as second-harmonic generation[1], which is of limited potential practical usefulness, but first indications exist[2] that it is obtaining highly efficient nonlinear absorption (two-photon and multi-photon) in such systems that may become the primary target of investigations.

Preliminary results of our NLO studies on several systems of coordination polymers type will be presented in the talk and the issues of quantitative determination of their NLO properties will be discussed.

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On the modification of nanoscopic SnO_2 for applications in photocatalysis

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Metal oxide semiconducting nanoparticles show promise in photocatalysis with research into the properties of nanostructured SnO_2 having focused on increasing sensitivity and selectivity towards targets and improving photocatalytic activity.[1] To this end, we have developed different routes to modified SnO_2. The facile synthesis of SnO_2-based nanocomposites and heterostructures in which the modulation of photocatalyst structure and composition improves the separation of photogenerated electron-hole pairs has been explored. Photocatalytic activity and good catalyst recyclability is demonstrated in photochemical dye degradation under visible light irradiation.[2] We are now preparing materials in which SnO_2 immobilization using a filtering membrane delivers substrate separation before the target interacts with the nanoparticle, suggesting applications in flow chemistry.[3] Work on the fabrication of SnO_2-doped ZIF-8 monoliths points to the molecular sieving performance of ZIF-8 delivering separated targets to photocatalytic detection.

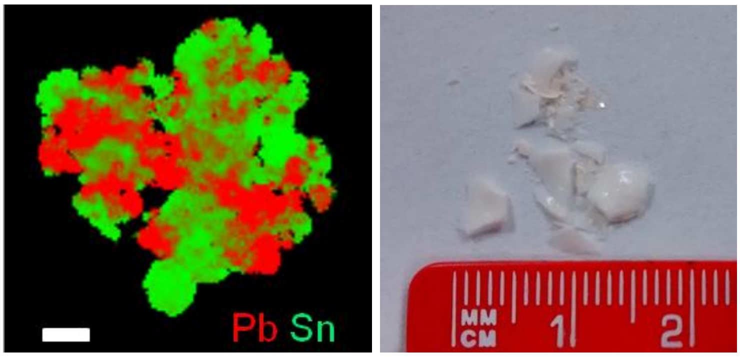

Figure 1 Modified SnO_2: HADDF-STEM analysis of a SnO_2-PbS nanocomposite (scale bar 200 nm; left) and monolithic SnO_2-impregnated ZIF-8 (right).

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Enhanced Optical Nonlinearities of Porphyrin Covalently Functionalized Graphene and Carbon Nanotube Nanohybrids

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The rapid development of nanoscience and nanotechnology provides many unique opportunities for nonlinear optics. A growing number of nanomaterials, including graphene, carbon nanotubes and their derivatives have been shown to possess remarkable nonlinear optical properties, which promotes the design and fabrication of nano-scale optoelectronic and photonic materials. It is thus of critical importance to explore innovative NLO materials required for the practical applications.

Porphyrin covalently functionalized graphene and multi-walled carbon nanotube (MWCNT) nanohybrids have been synthesized via various facile approaches for potential NLO materials. The axial ligands dihydroxotin(IV) tetraphenylporphyrin and the phosphorus-cored porphyrin were covalently linked to the surface of graphene oxide (GO), resulting in the enhanced optical limiting.[1,2] The fabrication of MWCNT-porphyrin conjugates by using 1,3-dipolar cycloaddition reactions was investigated, which significantly improves the solubility and dispersion stability of MWCNT-based materials in organic solvents;[3] while the porphyrin covalently functionalized reduced-GO was also prepared through 1,3-dipolar cycloaddition for the first time. The conjugated polymers with porphyrin units were introduced onto the surface of MWCNTs through radical polymerization, which may help to improve the solubility of the nanotubes in various solvents.[4] All these nanohybrids exhibit enhanced optical nonlinearities compared to their precursors and the physical blended systems, due to a combination of different nonlinear mechanisms, such as nonlinear scattering, excited-state absorption and photoinduced energy/electron transfer. Porphyrin covalently functionalized graphene and MWCNTs represent a key branch in the field of nano-scale materials and devices for nonlinear optics. Particularly, it is being attached significant importance to the electron/energy transfer from porphyrin moieties to graphene or MWCNTs, which is considered to play an important role in improving optical limiting effect.

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The effects of electron correlation and relativity on the mechanisms of spin crossover in Fe(II) complexes

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The inclusion of the effects of electron correlation and relativity may complicate accurate quantum chemical study of molecules and materials, but on the other hand these effects also allow for the design and synthesis of materials with fine-tuned physical properties. This contribution discusses a number of recent quantum theoretical studies of the mechanisms of spin crossover in Fe(II) complexes. In these studies cost-effective approaches based on density functional theory, DFT, are combined with wave function based quantum chemical methods.

Spin crossover occurs in complexes of transition metals with organic groups that induce a weak ligand field. Spin crossover compounds have two low-energy states, with minimum spin and maximum spin, respectively, and a transition between them can be induced by changing temperature, pressure or by light. Especially light induced excited spin-state trapping (LIESST) is of technological importance. The crossover mechanisms may involve various processes, such as intersystem crossings via intermediate states and internal conversion. Conventional and time-dependent DFT give us access to the equilibrium geometries and vibrational frequencies of the spin crossover complexes, while complete active space second order perturbation theory, CASPT2, reasonably describes the relative energies of the relevant spin states. This quantum chemical approach is combined with a time-dependent formalism [1] for calculating intersystem crossing transition rates in order to estimate the transition rates between the relevant states and to elucidate the mechanism of the LIESST process. Our method, applied to $[Fe(bpy)_3]^{2+}$ system [2], not only reproduced the experimental time-frame of the whole LIESST process, but also shed the light on the intermediate steps, in good agreement with more recent experiments [3]. In addition we discuss thermal spin crossover of a series of Fe(II) based spin crossover compounds [4].

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Molecular Dynamics Study of the Structure and Reactivity of Ruthenium Polypyridine Complexes in Aqueous Solution

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Ruthenium polypyridine complexes have been the subject of intense studies due to their physico-chemical properties, in particular their photosubstitution, photoisomerisation abilities and their potential biomedical applications.[1] Computational studies have provided a theoretical understanding of these properties,[2] however, they have mostly been achieved in the framework of static DFT which prevents a full understanding of these systems.

We present an *ab initio* molecular dynamics study of the $[Ru(terpy)(bpy)(Hmte)]^{2+}$ complex (see Figure 1) in aqueous solution. After describing the hydration shell of this complex, we discuss its dissociation mechanism as obtained by the metadynamics approach (Figure 1) and the formation and the structure of the $[Ru(terpy)(bpy)(H_2O)]^{2+}$ complex. Similar simulations on the substituted $[Ru(terpy)(dmbpy)(Hmte)]^{2+}$ complex are also presented and discussed. Our results suggest a two-step mechanism where the departure of the Hmte ligand is the rate-limiting step.[3]

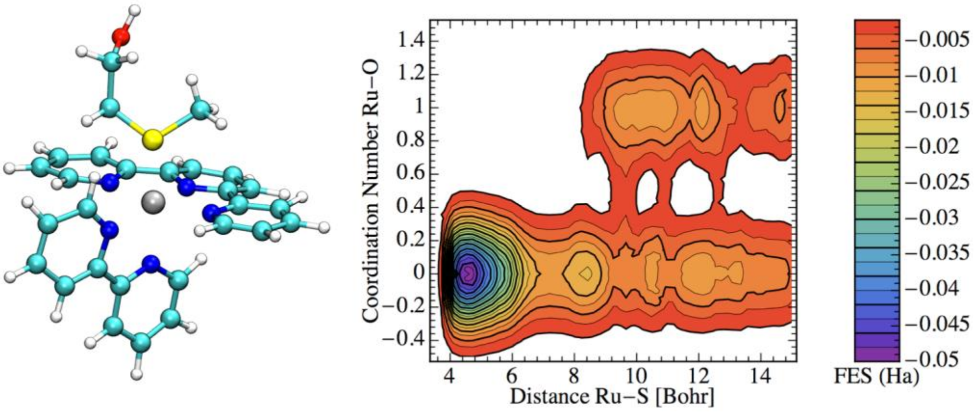

Figure 1 Structure of the $[Ru(tpy)(bpy)(Hmte)]^{2+}$ complex (left) and free energy surface obtained for the substitution of the thioether Hmte ligand by H_2O (right).

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Non-adiabatic quantum dynamics for ultra-fast processes in transition metal complexes

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This lecture will illustrate the progress made in the past few years in our understanding of ultrafast events underlying photophysical and photochemical processes in transition metal complexes taking into account spin-orbit and vibronic couplings. Related experiments, based on ultrafast picosecond (ps) and femtosecond (fs) transient absorption or luminescence spectroscopies, and optical laser pump/X-ray probe techniques using ps and fs X-ray pulses, are still subject to unresolved questions.

The multimode molecular dynamics beyond the Born-Oppenheimer approximation has been successfully applied to many small polyatomic systems. Its application to large molecules containing a transition metal atom is still a challenge because of the nuclear dimensionality of the problem, the high density of electronic excited states and the spin-orbit coupling (SOC) effects. Here we emphasize on the role of spin-vibronic coupling on the mechanism of ultrafast intersystem crossing (ISC) put in evidence in [Re (X)$(CO)_3$(bpy)] (X= Cl, Br, I).[1] For this purpose we have developed a model Hamiltonian for solving a four electronic excited states multi-mode problem including vibronic and SOC within the linear vibronic coupling (LVC) approximation.[2] The simulation of the ultrafast dynamics by wavepacket propagations using the multi-configuration time-dependent Hartree (MCTDH) method[3] is based on electronic structure data characterizing the low-lying excited states.[4] We believe that the interplay between time-resolved experiments and these pioneering simulations will promote a number of quantum dynamical studies that will contribute to a better understanding of ultrafast processes in a wide range of organic and inorganic chromophores easily incorporated in bio-systems or supramolecular devices for specific functions.

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Disentangling a long lasting issue: which is the magnetic dimensionality of the Cu_2(1,4-diazacycloheptane)$_2Cl_4$ crystal?

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The Cu_2(1,4-diazacycloheptane)$_2Cl_4$ (CuHpCl) crystal is a molecular transition metal antiferromagnetic complex, whose magnetism has been an issue for several experimental groups.[1] The outcome of this variety of experimental studies provided many different fitting J values depending on the fitting ladder model. From all the available experimental data, one can infer that CuHpCl is a very complex structure with many competing microscopic magnetic J_{AB} interactions leading to its overall antiferromagnetic behavior. Here we incorporate data from *ab initio* computations providing the magnitude of the microscopic magnetic J_{AB} interactions to re-study the microscopic magnetic coupling in CuHpCl to understand the macroscopic magnetic behavior of this crystal. Surprisingly the resulting magnetic topology is three-dimensional 3D consisting of antiferromagnetically (-1.1/-1.4 cm^{-1}) interacting spin-ladders whose rails (-0.4/-3.9 cm^{-1}) alternate with ferromagnetic and antiferromagnetic rungs (2.3/-0.3 cm^{-1}). This 3D magnetic topology does not agree with the suggested ladder motif (with uniform rails) that arises from direct observation of the crystal packing of CuHpCl radicals. Magnetic susceptibility and heat capacity versus temperature computed data using 3D magnetic models show good agreement with the experimental data. A first-principles bottom-up study of the CuHpCl crystal is thus necessary in order to fully disentangle its magnetism.

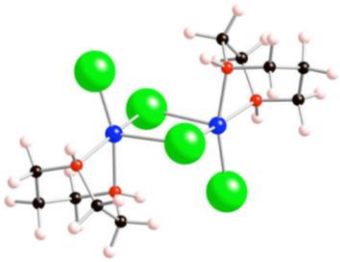

Figure 1 Chemical formula of Cu_2(1,4-diazacycloheptane)$_2Cl_4$ (CuHpCl) unit

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Spin-State Energetics and Oxyl Character of Mn-Oxo Porphyrins by Multiconfigurational ab initio Calculations: Implications on Reactivity

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The role of electromeric states in the multi-state catalytic reactivity of Mn-oxo heme systems in oxygen atom transfer (OAT) reactions depends on two key properties, the spin state energetics and the oxyl radical character of the Mn-oxo bond. We evaluate these two properties in two Mn-oxo porphyrin model systems, $MnO(P)^+$ and $MnO(PF_4)^+$ (P=porphyrinato, PF_4=*meso*-tetrafluoroporphyrinato) with second-order perturbation theory based methods (CASPT2, RASPT2). The ground state of both complexes is a Mn^V singlet state ($^1A_1$) with a very weak oxyl character that renders this state to be unreactive. Nonetheless, OAT reactions can proceed through thermally accessible triplet and quintet states with a more pronounced oxyl character. Two possible candidates are the Mn^V triplet state ($^3B_1$) and the porphyrin radical $Mn^{IV}O(L^{\bullet}a_{2u})^+$ quintet state ($^5A_2$). The latter is high-lying in $MnO(P)^+$ but becomes stabilized by the fluorination of the porphyrin *meso* carbons. The analysis of the CASSCF spin density distribution along the Mn–O bond reveals that the oxyl character emerges from either (a) a positive oxygen spin density resulting from the occupation of Mn–O antibonding orbitals or (b) a negative oxygen spin density resulting from diradical contributions of the Mn–O bonds with empty antibonding orbitals (Fig. 1). Furthermore, we use the RASPT2 results to benchmark a wide range of DFT functionals on the description of spin state energetics and the oxyl character of Mn-oxo porphyrins.

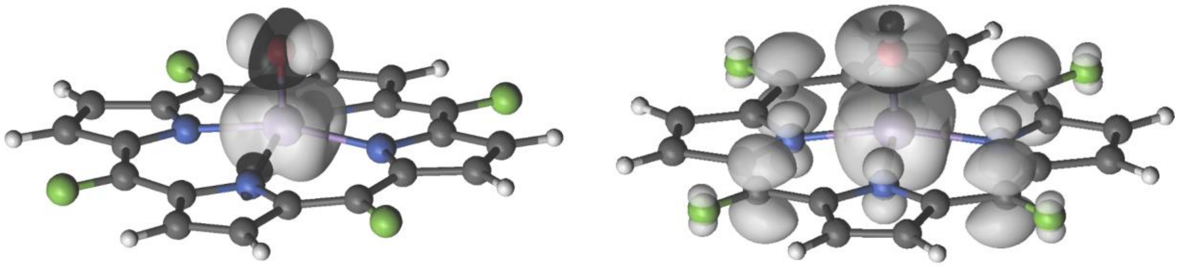

Figure 1 Spin density distributions of the Mn^V $^3B_1$ state (left) and the Mn^{IV} $^5A_2$ state (right) of $MnO(PF_4)^+$ obtained from CASSCF.

Quantitative prediction of the photoluminescence quantum yields of Ir(III) complexes from first principles

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Ir(III) complexes are often used as triplet emitter dopants in phosphorescent organic light-emitting diodes (PhOLEDs). Optimizing their photoluminescence quantum yields (PLQY) at room temperature is one of the keys to attain highly performant PhOLEDs.[1] This work demonstrates for the first time that quantitative predictions of the PLQY of blue-to-green Ir(III) complexes can be derived exclusively from electronic structure calculations and the use of simplified kinetic models.[2] Within these models, only a few calculations are needed to obtain the PLQY; i.e., computing the radiative rate from the emissive state and characterizing the potential energy surfaces of the temperature-dependent non-radiative deactivation channels. This approach is extremely beneficial for the *in silico* prescreening of promising deep blue PhOLED emissive materials.

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[2] **Quantitative prediction of photoluminescence quantum yields of phosphors from first principles**. D. Escudero, *Chem. Sci.,* **2015,** 44, DOI: 10.1039/C5SC03153B

Mechanistic Investigations on the Copper-Catalyzed Arylation of N-Heterocycles from Anilines

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The arylation of pyrazole and its derivatives can be achieved by coupling arenediazonium species (formed in situ from anilines) using a catalytic system that employs low-toxicity and inexpensive copper metal under very mild and ligand-free conditions[1] (see Figure 1).

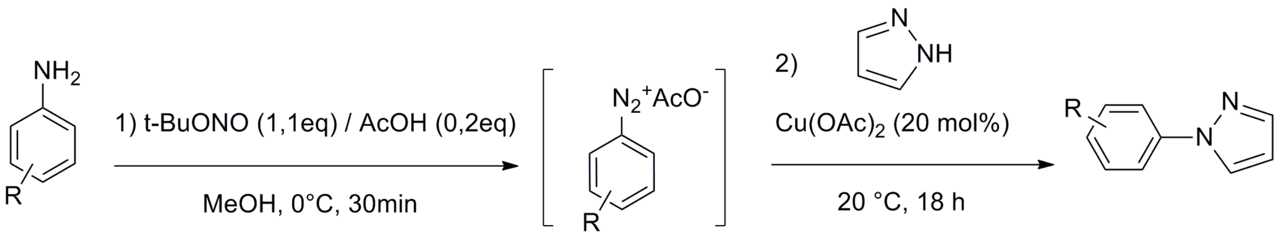

Figure 1 Optimized reaction conditions

Our study combines theoretical outcomes from Density Functional Theory (DFT) calculations and experimental data to investigate the mechanism of this reaction. It is supported by a preliminary evaluation of the DFT performance *via* comparison with wavefunction-based methodology that allowed us to choose the most relevant functional. We find explanation for the different reactivity observed between imidazole and pyrazole substrates, and rationalize the oxidation state, geometry and stoichiometry of active copper species.

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Theoretical study of (hetero)aromatic fluorination catalyzed by Palladium

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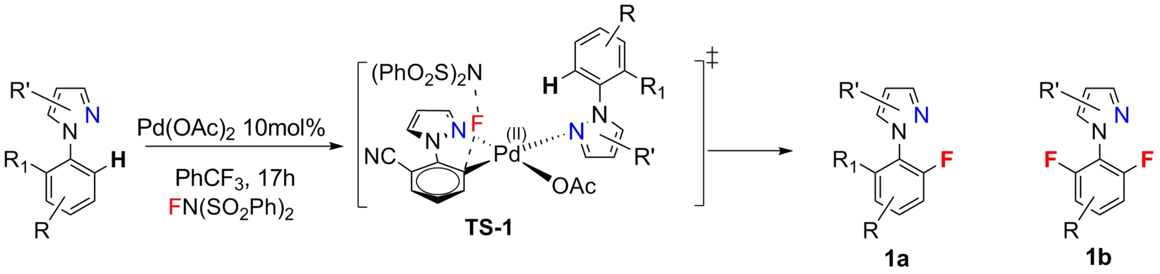
Fluorinated molecules are widely present in pharmaceuticals and medical imaging radiotracers.[1] However, synthetic methods to efficiently form carbon–fluorine bonds under mild conditions remain limited.[2] Therefore, directed C–H bond fluorination catalyzed by palladium has appeared to be a very attractive approach.[3]

We will present here a detailed mechanistic investigation combining experiments and theoretical calculations. We focused on the electrophilic fluorination of substituted arylpyrazole, where the pyrazole moiety is used as a directing group for the fluorination of the aryl (Scheme 1). In a first study of a model reactant (R=R'=H, R_1=CN), we have proposed that this mechanism proceeds with an outer-sphere oxidative addition of NFSI and not through a Pd(IV) complex.[4]



Scheme 1

In this communication, we will detail the influence of the substituents on the experimental yields such as: R'=H, 3-Me, 4-Me, 5-Me, 3-CF3 and R_1=H, CN, OMe, Cl or R=p-Cl, p-OMe. Three pathways will be discussed: the standard Pd(IV)/Pd(II) route involving complex II-1, the outer-sphere mechanism (Scheme 1) and the formation of Pd(III) dimers.

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Calculating magnetic properties of actinide complexes from first principles

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Actinide complexes with unpaired electrons exhibit fascinating magnetic properties. An ongoing research project in our group is devoted to first-principles calculations of magnetic resonance parameters (NMR, EPR), magnetic susceptibilities, and other spectroscopic parameters of actinide complexes. We will present results from recent computational studies of magnetic resonance parameters and the magnetic susceptibility of f-element complexes utilizing relativistic quantum chemical methods. Calculations and the analysis of magnetic resonance parameters of actinyl nitrate and carbonate complexes and of magnetic susceptibilities of selected U(IV) organo-metallic complexes will be discussed in detail. Ab-initio results will be compared with crystal field models.

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Spin state of iron complexes: The case for OPBE, SSB-D and S12g

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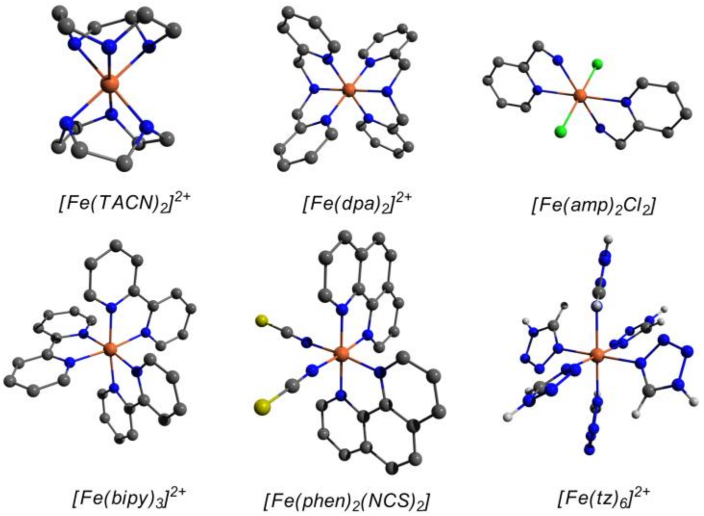
Elucidating the role and effect of different spin states on the properties of a system is presently one of the most challenging endeavors both from an experimental and theoretical point-of-view. Computational studies, including Density functional theory (DFT) have shown that a correct description of the spin state is not trivial, and it is not always straightforward to predict the orbital occupation pattern. Although the DFT, in principle, gives an exact energy, a universal functional is still unknown, leading to density functional approximations (DFAs). These DFAs are parameterized for different properties and, noteworthy, spin-state energies were not included in the development for most of nowadays available DFAs. For the reliable prediction of the correct spin ground state from a number of close lying states, OPBE and SSB-D have emerged to be one of the best DFAs for the task. Recently, Swart constructed a new density functional that combines the best of OPBE (spin states, reaction barriers) with the best of PBE (weak interactions) into the S12g[1]. Some of our recent validation studies[2] with the OPBE, SSB-D and S12g functionals, on number of iron complexes will be presented.



$[Fe(TACN)_2]^{2+}$ $[Fe(dpa)_2]^{2+}$ $[Fe(amp)_2Cl_2]$

$[Fe(bipy)_3]^{2+}$ $[Fe(phen)_2(NCS)_2]$ $[Fe(tz)_6]^{2+}$

Figure 1 Structures of some challenging Fe(II) complexes

Part of this work was supported by COST Action CM1305 (ECOSTBio).

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Targeting the reactive intermediates in [Fe]-hydrogenase with combined classical mechanics / quantum mechanical methods

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The [Fe] hydrogenase is distinct from the two other classes of hydrogenases by its monometallic active site, contrasted by the bimetallic [NiFe]- and [FeFe]-hydrogenases. Further, [Fe]-hydrogenase is only active in presence of a [CH-H_4MPT]$^+$ substrate. This talk will give an overview of the latest findings with respect to reaction mechanism of [Fe]-hydrogenase. In particular we compare two recent studies[1,2] that use a multiscale modelling (QM/MM) approach. The studies focus apart from the water bound (**1**) resting state on two of the postulated intermediates, namely a iron dihydrogen (**2**) complex and an iron hydride complex (**3**), see Figure 1. The hydride intermediate was suggested based on vacuum calculations[3] where it was favored over the di-hydrogen intermediate.

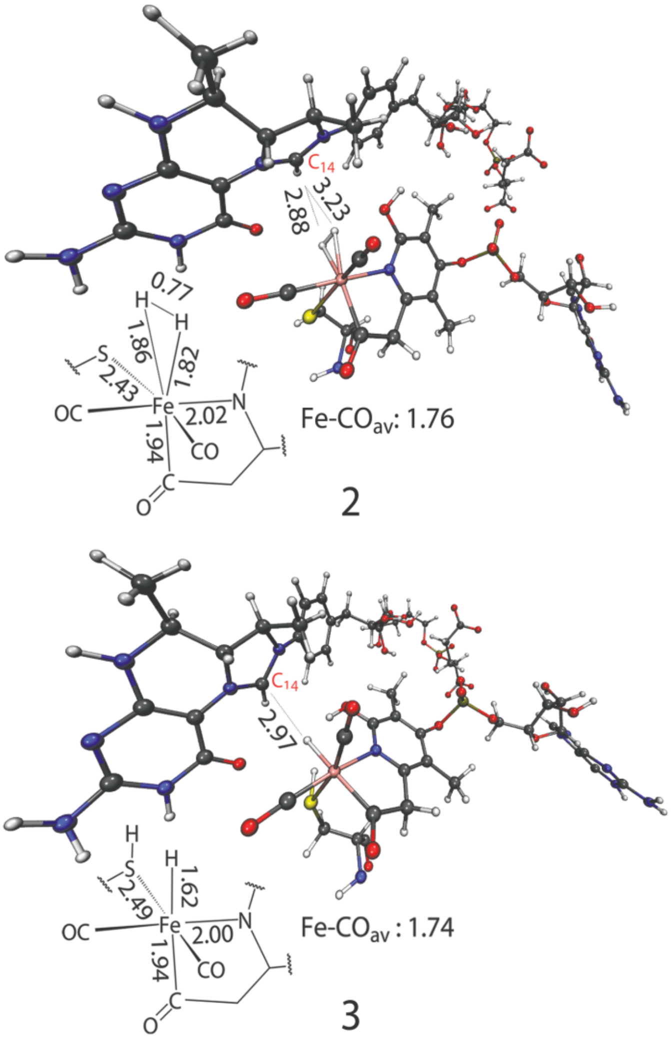

Figure 1

By addressing the (non-negligible) influence of the surrounding protein on the coordination chemistry of the iron active site, a more accurate discrimination between the two intermediates is now possible.

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Electron transfer reactivity in lanthanide complexes

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Lanthanide complexes have been used in the last decades for an increasing number of reactions from the reduction of small molecules[1,2] to C-H bonds activation[3], and they have also been studied extensively for their electronic structures – often complex – and their magnetic properties that allowed the report of highly interesting single molecules magnets[4].

Our group has been focused in developing electron transfer reactivity from a lanthanide center towards different types of molecules and analyzing them by both experimental and theoretical techniques[5]. Reduction of radical molecules, such as TEMPO, as well as organic molecules (phenanthroline), or metallic complexes ($PdMe_2TMEDA$) and their further reactivity will be discussed from the theoretical point of view.

Quantum chemistry calculations are able to give a better insight into the electronic structure of these complexes and into the mechanism associated with all their reactivity. The role of dispersion forces and the role of the methods to take into account the relativistic effects in lanthanide complexes will be discussed. DFT results, supported by CASSCF calculations, will be presented combined with the use of analysis tools such as topology (ELF and NCI) and energetic decomposition.

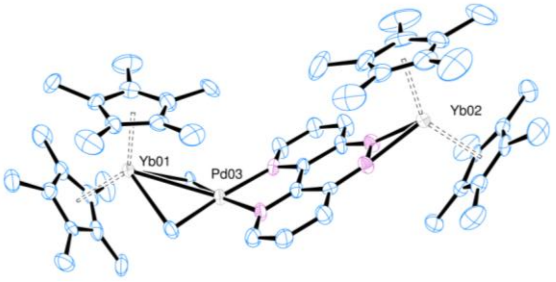

Figure 1 X-Ray crystal structure of ($YbCp^*_2$)($TAFENPdMe_2$)($YbCp^*_2$) *1*

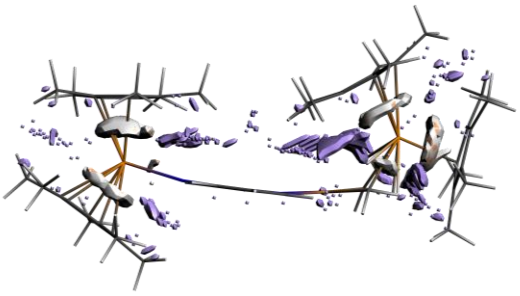

Figure 2 NCI calculation of *1* with ZORA PBE0-D3/TZVP//PBE-D3/SVP

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Effect of structure on the reaction mechanism of transition metal complexes

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Structural variation exhibits effect on the properties of transition metal complexes, more specifically, reduction potential and reactivity patterns. A change in the reactivity pattern may lead to alter the redox mechanism and biochemical application of compounds. This study reveals the mechanistic pathways of the reduction of dicyanobis(phenanathroline)iron(III) by 1-ferrocenylethanone, 1-ferrocenylethanol, and hexacyanoferrate(II), and draws a comparative profile to surface the effect of structural variation. The reactions were observed to undergo a complex kinetics. The kinetic data suggests that the reaction(s) while undergoing completion passed through three stages. The first stage was noted soon after starting the reaction(s) and that the reaction(s) followed an overall zeroth order in the first stage. The reaction(s) was found to follow overall second order in the second phase. The third phase may be termed as the competition phase. The reactions are although following same kinetic patterns and orders, but, the rate-controlling species are specific to each case. The solvent system and protonation play a vital role during the reactions. Protonation of 1-ferrocenylethanone, 1-ferrocenylethanol, and hexacyanoferrate(II) yields $FcC^{+}OHMe$, $FcCHO^{+}H_2Me$, $[HFe^{II}(CN)_6]^{3-}$, and $[H_2Fe^{II}(CN)_6]^{2-}$, which donate electrons and lead reactions mechanisms. A rise in the rate upon increasing concentration of protons highlighted protonated 1-ferrocenylethanone, a leading character of the rate-determining step in the reduction of $[Fe^{III}(phen)_2(CN)_2]^{+}$ by FcCOMe. A reverse phenomenon during reduction of $[Fe^{III}(phen)_2(CN)_2]^{+}$ by FcCHOHMe and $[Fe^{II}(CN)_6]^{4-}$, however, helped to demonstrate participation of $FcCHO^{+}H_2Me$, and, $[HFe^{II}(CN)_6]^{3-}$ and $[H_2Fe^{II}(CN)_6]^{2-}$ as the rate retarding entities, whilst FcCHOHMe and $[Fe^{II}(CN)_6]^{4-}$ as the rate motivating and rate controlling species. The influence of ionic strength, dielectric constant, and thermodynamic parameters of activation justify the consequences by providing authentic clues. The rate law has been proposed for each reaction in the view of the results and considering literature.

Theoretical study on f-π magnetic interaction in neutral terbium(III) phthalocyanine (Pc) double-decker complex.

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A single molecular magnet (SMM) is considered to be a good candidate for future ultra-high-density memory devices. About a decade ago, Ishikawa et al. have found that lanthanide phthalocyanine (Pc) double-decker complexes ($LnPc_2^-$; Ln=Tb(III), Y(III)) exhibit the SMM behavior.[1] Recently, neutral lanthanide double- and multiple-decker SMMs with Tb(III) and Y(III) ions have also been reported.[2] Our group has investigated a relationship between molecular structure and electronic structure on the Tb(III) complex.[3] In the previous paper, we pointed out that a π-π dispersion interaction plays an important role in the molecular geometry and the frontier orbitals. On the other hand, the neutral complex includes a f-π magnetic interaction between f-electrons of Tb(III) and π radical of the Pc. Usually, the f-π magnetic interaction is considered to be negligible. However, there are no reports on the quantitative analysis of f-π interaction in this complex.

In this study, therefore, we examine the f-π magnetic interaction in the neutral $TbPc_2$ complex with the use of DFT calculations. The magnetic exchange interaction was calculated by the energy gap between ferromagnetic and antiferromagnetic spin states (ΔE) as illustrated in Figure 1. The calculated energy gap indicates that the f-π interaction is ferromagnetic but is strongly affected by the complex structure.

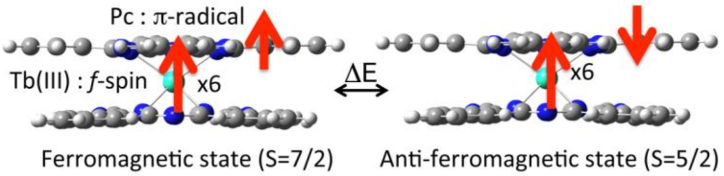

Figure 1. Ferromagnetic and anti-ferromagnetic spin states of the neutral $TbPc_2$ complex.

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Complexation of Metal Cations to Alginates: a Computational Approach

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We will present a theoretical study on the coordination of di- and trivalent metal cations to alginate biopolymers, phenomenon that is at the core of the alginate gelation and its applications. The DFT study of a large panel of alginate/M^{n+} models (M^{n+}= Mg^{2+}, Ca^{2+}, Sr^{2+}, Mn^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+}, Al^{3+}, Sc^{3+}, Cr^{3+}, Fe^{3+}, Ga^{3+} and La^{3+}) has evidenced that the unidentate binding mode is in general the most favored one. The molecular orbital composition analysis confirmed that the alkaline earth cations form ionic bonds, whereas the transition metal (TM) cations form strong covalent-coordination bonds. The good correlation obtained between the calculated binding energies and the experimental alginate affinity trend toward TM cations suggests that this affinity is related to the chemical interaction strength of TM cations−alginate complexes.[1] The size of an alginate chain model, the number of chains and the presence of water in the first coordination shell do not affect the trends of the coordination bond distances and the binding energies (see Figure 1).

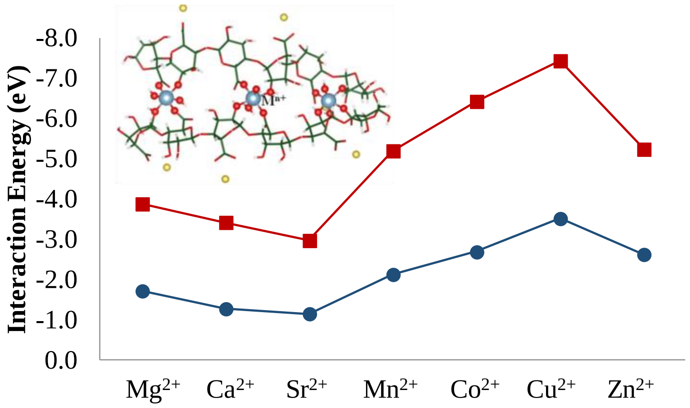

Figure 1. Binding energies of M^{2+} in complexes with two disaccharides (squares) and hexasaccharides (circles) chains. In the inset a complex with hexasaccharides is shown.

QM/MM dynamics results will be also presented and the effect of temperature and water solvent will be discussed.

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The structure and properties of endohedral clusters: a coordination chemist's perspective.

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The structures and electronic properties of endohedral clusters of the tetrel elements Si, Ge, Sn, Pb, $M@E_n$, are of great interest to both the physics and chemistry communities. To a physicist, clusters such as $Cr@Si_{12}$ represent the smallest conceivable models for metal impurities in bulk silicon, and designing systems which retain the characteristic magnetic properties of the encapsulated metal is an important target. From a chemical perspective, the Wade-Mingos rules provide an important framework for understanding the structure of clusters, although the emphasis is firmly on the bonding within the cluster rather than between the cluster and the metal. A coordination chemist might, in contrast, regard the cluster as a pseudo ligand, donating and potentially accepting electron density from the metal. In this presentation I will review our recent attempts to understand the structural diversity of these systems in this context.[1] The complex structural chemistry can be understood if the E_n cluster is viewed as an electron deficient ligand, withdrawing electron density from the metal. Most remarkably, we also present evidence that in combination with first row transition elements (in $[Mn@Si_{12}]^+$, for example), the E_n cluster can itself exhibit radical characteristics, mirroring the behaviour of redox non-innocent ligands like bipy.

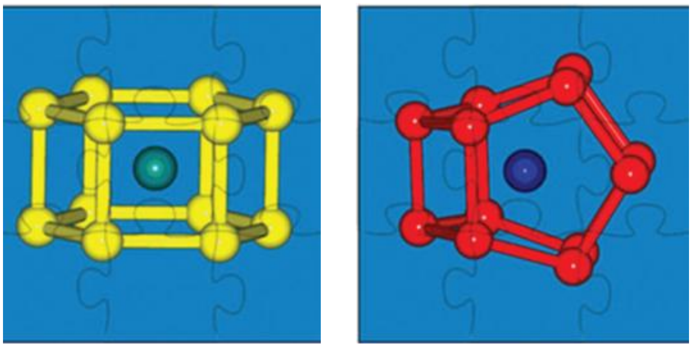

Figure 1 Jigsaw model of the electron structure in $Cr@Si_{12}$ and $[Ru@Ge_{12}]^{3-}$.

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Ab initio Ligand Field Theory for d- and f-elements. A powerful link between theory and experiment

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Rational design of molecules with taylored magnetic properties can presumably not be achieved without a thorough understanding of magnetostructural correlations. Such correlations can be established by theoretical or experimental means and must be formulated in a language that is accesible to synthetic chemists. Quantum chemistry can be of tremendous help in this context. In fact, modern first principles quantum chemical calculations can be of predictive accuracy for magnetic properties, can be used to understand actual experimental data and can be used to establish magnetostructural rules and trends. However, the method of density functional theory (DFT) that is dominating both molecular quantum chemistry and solid state physics has been found to be of rather limited accuracy in this context, in particular for the calculation of the all-important zero-field splitting (magnetic anisotropy). In our work, we have focused on multiconfiguration wavefunction based approaches that offer a more systematic and general theoretical approach for the calculation of magnetic properties. The lecture will discuss some methodological aspects and will then focus on recent examples to illustrate the fruitful interplay between theory and experiment.

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Supersized Metal-Rich Sandwiches: Combining Theory and Experiment

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The novel family of bowl-shaped polyaromatic hydrocarbons or carbon bowls having built-in curvature and extended surfaces has been rapidly expanding in recent years. The ability of carbon bowls to readily acquire multiple electrons as well as to use both concave and convex faces for metal binding makes them a unique class of curved redox-active polyaromatic ligands. The multi-electron charging of π-bowls of different symmetry yields electron-rich carbanions with variable negative charge distribution patterns, as revealed by theoretical modelling. The resulting carbanions are able to form novel supramolecular products with the highly positively charged metal belts comprised of four, five, or six metal ions sandwiched in between the curved π-decks, as revealed by X-ray crystallography. The electronic structures and bonding of these unprecedented supersized organometallic sandwiches have been systematically investigated using the DFT level of theory. A direct comparison of bowl-shaped ligands with different size and symmetry has allowed for unique structural and metal intercalation trends to be uncovered for the first time, demonstrating the record coordination abilities of highly charged carbon-rich bowls.[1-3]

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Learning on the Electronic Structure of Schrock Alkylidene Metathesis Catalysts from NMR Chemical Shift Analysis

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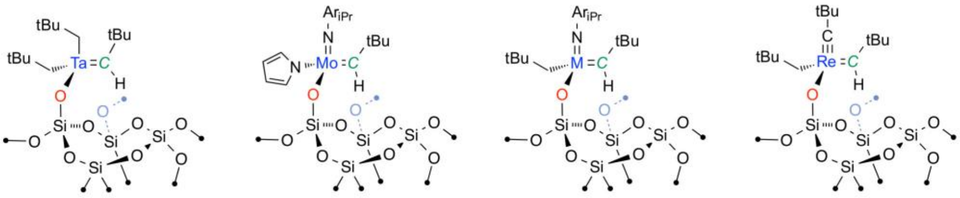
Metal alkylidene complexes have been an intense area of research in the past fifty years, because they are key reactants and/or intermediates in alkene metathesis, cyclopropanation and pseudo-Wittig reactions as well as in alkane homologation reactions such as alkane metathesis and hydrogenolysis. Of special interest for the present work, all alkylidene carbons are associated with highly de-shielded carbon chemical shifts, typically found between 200 and 300 ppm, and very large “span” (400-500 ppm). The highly de-shielded carbon, similar to what is observed for carbocation, is very surprising since d^0 metal alkylidenes are highly nucleophilic groups and usually described with a carbanionic resonance structure.



[TaCH$_2$tBu] **[MoPy]** **[MCH$_2$tBu]** M = Mo or W **[ReCH$_2$tBu]**

Figure 1 Well-defined silica-supported alkylidene metal complexes

In this work, we provide molecular insight onto the origin of the highly de-shielded chemical shift by analyzing the values and the orientations of the principal components of the chemical shift tensor of the alkylidene ligand on a series of silica-supported alkylidene catalysts (fig. 1). State-of-the-art four-component relativistic calculations of the chemical shift tensors combined with Natural Chemical Shift (NCS) analysis allow a molecular-level understanding of their orientations, the magnitude of their principal components (δ_{11}, δ_{22}, δ_{33}) and associated δ_{iso}.

New quantum chemical methods for transition metal chemistry

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In recent years, we have developed new theoretical tools to study complex reactions involving transition metal complexes and clusters. Our toolbox comprises new developments in density functional theory for open-shell systems as well as the development of new multireference approaches for validation purposes. Moreover, we have extended our possibilities to explore complex reaction mechanisms by automated-screening approaches based on heuristic rules and by interactive reactivity explorations within the framework of haptic and real-time quantum chemistry.

In this talk, I will present an overview of our recent work on theoretical coordination chemistry.

For references see: www.reiher.ethz.ch

Transport Properties of Single-Molecule Devices showing Room Temperature Magnetoresistance

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The novelty of our approach is to present a well-defined experimental/theoretical route map to reach single-molecule devices showing magnetoresistance at room temperature. STM measurements of deposited metal complexes on heavy metal surfaces that have large spin-orbit contributions allows to detect magnetoresistance effect similar to that reported by Fert and Grünberg in magnetic metal layers used in hard disk heads. Inside the device, metal complexes (such as those of Fig. 1 or porphyrin systems) deposited on a gold substrate are in contact with magnetic Ni STM tip. Our results provide a proof of concept strongly indicating that the STM conductance through the magnetic metal complex changes one order of magnitude with the direction of the Ni tip magnetic field (see Figure 1). Our study shows a theoretical analysis and the practical implementation through two-terminal devices using STM equipment to achieve the room temperature molecular-based spintronic nanodevices.

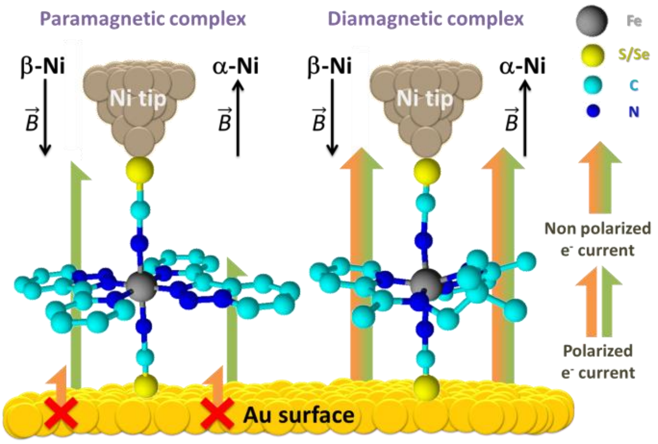

Figure 1 Schematic representation of the single-molecule junctions studied under two opposite Ni magnetic polarisations (labelled α and β). The paramagnetic $[Fe(tzpy)_2(NCS)_2]$ complex shows high tunnelling magnetoresistance against one of the Ni tip spin polarisations (see arrows), while transport in the diamagnetic $[FeL^A(NCS)_2]$ complex remains invariable

Structure and Reactivity of Phosphoranimide Tetramers of Cu, Ni, Co and Fe: A Density Functional Theory Investigation

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Phosphoranimide complexes of Cu(I), Ni(I), Co(I) and Fe(I) form saddle-shaped or planar tetramers with linear N-M-N coordination and those of the metals in oxidation state 2 form cubanes. The electron-rich metal centres make these complexes attractive as hydrotreatment catalysts. We present a computational procedure to predict the effect of the electron-donating and steric characteristics of the phosphoranimide ligands on the geometry, electronic properties and reactivity of the tetramers towards H_2 activation. In this procedure, relativistic density functional theory at the ZORA-PBE/TZP level is employed to study the effect of ligand functional groups on the structure, spin states and reactivity of the complexes. The $[Co(\mu_2\text{-}NP(tert\text{-}Bu_3)]_4$, $[Ni(\mu_2\text{-}NP(tert\text{-}Bu)_3)]_4$ and $[c\text{-}\{Cu[\mu\text{-}NPPh_3]\}_4]$ complexes previously synthesized and characterized[1,2] serve for validation of our computational method. In the reaction mechanism study, we also investigate pathways for structural rearrangements of the catalyst framework. Understanding the effect of ligand and metal selection on the structure, stability and catalytic reactivity of these complexes, as well as rational design of new complexes based on our insights, are aimed to guide the synthesis of series of electronically and sterically optimized catalysts.

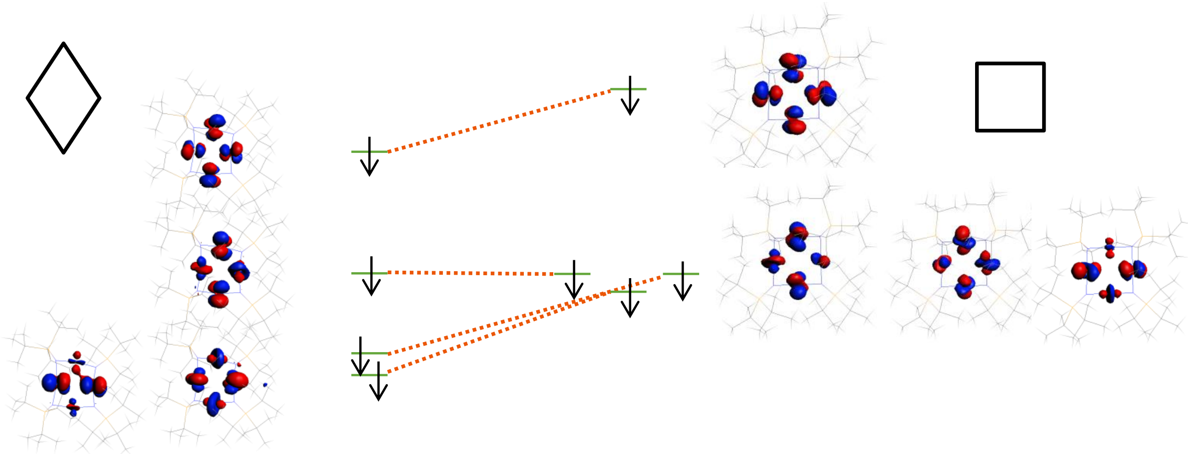

Figure 1: Walsh diagram shows stabilization of the diamond configuration of $\{Co_4\text{-}N_4\}$.

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Computational modeling of transition metal complexes possessing both spin crossover and valence tautomerism

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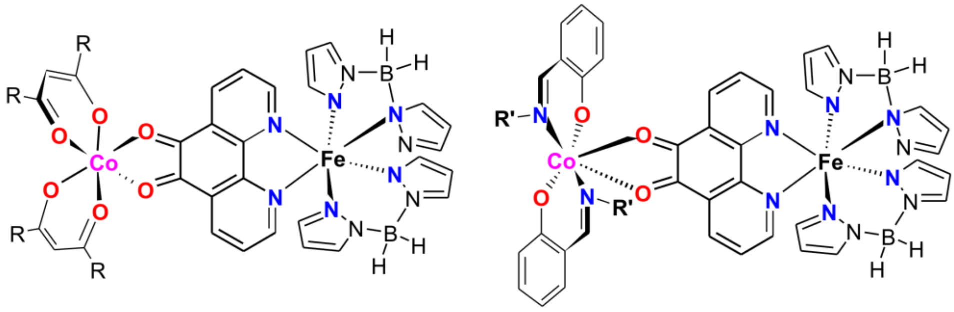
The possibility of controlling magnetic characteristics of transition metal coordination compounds *via* external stimuli makes them suitable for the development of molecular switches, molecular magnets and spin qubits [1]. The most thoroughly studied effects resulting in the change of the spin states of such compounds are spin crossover (SCO) and valence tautomerism (VT). The first one is more often reached in hexacoordinate ferrous iron complexes, while VT is realized in cobalt compounds with redox-active *o*-quinone ligands [2]. So far complexes capable to exhibit both SCO and VT have not been reported.

With the aim at search for compounds, magnetic properties of which are driven by the above mentioned effects, quantum chemical calculations of a series of heterometallic complexes (Fe + Co) on the basis of 1,10-phenanthroline-5,6-dione have been performed using density functional theory method (UB3LYP*/6-311++G(d,p)).



R=H, CH_3,CF_3, R'=Ph, Ph-NO_2

It was shown that thermally controlled transition of iron ions from the low-spin to the high-spin state (SCO) is possible in all the considered compounds. By varying the substituents in the diketone and azomethine ligands, the complexes capable to undergo a reversible electron transfer from the Co(II) atom to the redox-active ligand (VT) have been revealed.

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2 T. Tezgerevska, K.G. Alley, C. Boskovic, *Coord. Chem. Rev.*, **2014**, *268*, 23.

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Electron transport through spin crossover molecules. Inspections from wave-function theory

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Generally, the conductance through molecular junctions is computationally evaluated using the shapes and energies of the frontier molecular orbitals. To go beyond this one-electron picture, a theoretical approach has been recently developed by some of us to describe the electron transport using N-electron states.[1,2] The proposed methodological framework allows for the multi-configurational representation of the junction states, and has been designed to describe uncoherent, sequential transport within the weak-coupling regime. With a molecular spintronic goal in mind, we will discuss on the application of this perspective to study the electron transport through the spin crossover compound Fe(bapbpy)$(NCS)_2$ (see Figure). To this purpose, we have used CASPT2 calculations to obtain the wavefunctions and energies of the low-lying states of the compound, required in the description of the transfer rates. We will discuss on the resulting I/V curves (see Figure), and on the importance of the proper description of the spectroscopy of the junction by including all MS states and the excited states that lie within the bias window. Finally, we will comment on the approximations involved on this methodology, and on the perspectives that are now open in its application of for different transport regimes.

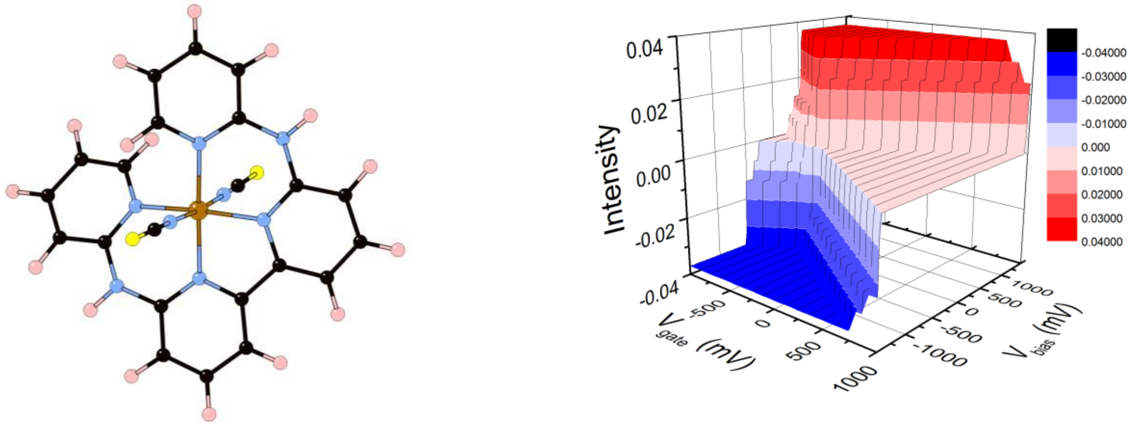

Figure 1. LS molecular structure of **1** and the I/V characteristics of its HS state.

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Polydentate CCC and CCCC Ligands as Coordination Elements to Construct Novel Aromatic Metallacycles

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Polydentate ligands have attracted considerable interest of chemists because of its important rule in the construction of various metal complexes. However, the binding atoms are mainly heteroatoms (e.g. N, P, O, S, etc). Examples of polydentate ligands with all-carbon atoms as the coordination elements are particularly rare. Recently, Xia group reported a series novel metallacycles where three and four carbons could be coordinated to a metal (Figure 1).[1-4] Interestingly, our density functional theory calculations reveal that different coordination modes lead to different aromaticity in these metallacycles. Specifically, complexes with CCC pincer ligands (**M+7C**) are Mobius aromatic whereas the unsaturated three-membered ring in complex **M+8C** is σ-aroamtic. In addition, the antiaromaticity in the four-membered ring of complex **M+9C** is significantly reduced, in sharp contrast to that in the parent cyclobutadiene. Last but not least, unexpected higher stabilisation of two classical antiaromatic frameworks with a ruthenium fragment compared to the osmium counterpart is reported in complex **M+9C**.[5] Our findings could be helpful for chemists to design and realize more metallacycles with different (anti)aromaticity.

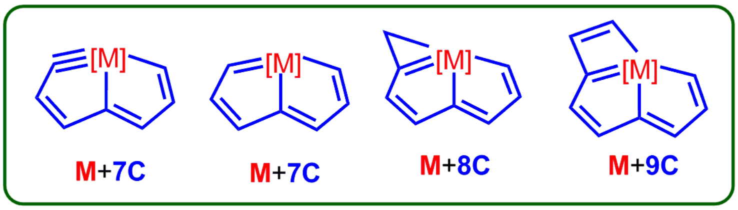

Figure 1 Aromatic metallacycles with CCC and CCCC polydentate ligands

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5 J. Wu, Y. Hao, K. An, J Zhu*, *Chem. Commun.* **2015**, DOI: 10.1039/C5CC08291A.

Reactions of Aromatic C-Au and C-H bonds with Polynuclear Metal Carbonyl Cluster Complexes

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Unsaturated metal cluster complexes containing bridging aryl ligands have been synthesized by cleavage of C - Au bonds in reactions with ArylAuL compounds, Aryl = Ph, Np, Py; L = phosphine or N-heterocyclic carbene, and by the oxidative addition of certain arene CH bonds to reactive metal carbonyl cluster complexes. The new compounds have been characterized structurally by X-ray crystallographic methods. The solution structures and the dynamical activity of the bridging aryl ligands have been studied by variable temperature NMR methods. DFT analyses have revealed the importance of π–electron donation from the aryl ligands in their bonding to the metal atoms. Facile oxidative addition and reductive elimination of aryl-CH bonds in unsaturated dirhenium complexes have been observed and their mechanisms have been studied by DFT analyses, see Scheme below.

Figure 1. A schematic with structures of the reaction of the compound $Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}\eta^1\text{-}C_6H_5)$ with N,N-diethylaniline.

1 R. D. Adams, V. Rassolov, Q. Zhang, *Organometallics*, **2013**, *32*, 1587.
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Isolation of catalytically active species of the CuAAC reaction and consequences

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The copper-catalyzed 1,3-dipolar cycloaddition of an organic azide to a terminal alkyne (CuAAC) is a highly versatile and efficient reaction, which has been applied in multiple fields of chemistry. Its attractiveness is in part due to the cheap pre-catalysts used, but also to its tolerance for a wide range of functional groups. However, despite many mechanistic studies, direct observation of key components of the catalytic cycle was still missing. We will discuss the isolation of both a previously postulated π,σ-bis(copper) acetylide and a hitherto never mentioned bis(metallated) triazole complex. We will also show that although mono- and bis-copper complexes promote the CuAAC reaction, the dinuclear species are involved in the kinetically favored pathway.[1]

The influence of the anion (X) on the successive steps of the catalytic cycle will also be discussed using copper complexes LCuX with L being a cyclic (alkyl)(amino)carbene (CAAC) ligand and X = OTf, Cl, OAc, OPh, O*t*Bu.[2]

We will show that the understanding of the nature of the active catalytic species and role of the anion in the CuAAC reaction, allows for the discovery of novel copper catalyzed reactions.[3]

1 L. Jin, D. R. Tolentino, M. Melaimi, G. Bertrand, *Science Adv.*, **2015**, *1*, e1500304.
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DITHIENYLETHENE-BASED CYCLOMETALATED PLATINUM COMPLEXES: EFFICIENT PHOTO-SWITCHES

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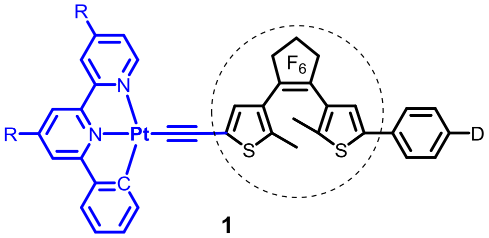
Organometallic systems with commutable optical response (luminescence, nonlinear optic (NLO)) are of growing interest due to their potential application in photonics technologies. In the course of finding new strategies for molecular photo-switches, our group has been investigating dithienylethene-based cyclometalated platinum complexes with the aim of combining the optical properties of (N^N^C)Pt(II) acetylide complexes[1] with the well-known photochromic performances of dithienylethenes (DTE)[2]. We have designed and synthetized *classical* (**1**) and *non-classical* (**2**) mono-nuclear DTE-based Pt(II) complexes, and their related di-nuclear complexes (**3**).



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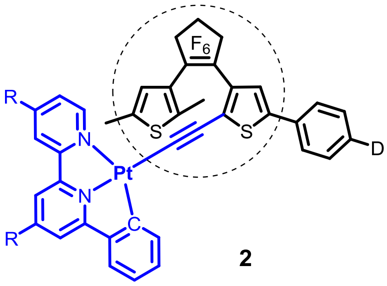

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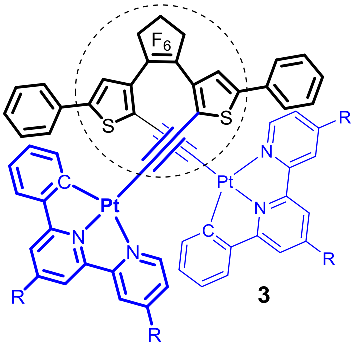

3

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.[3,4]

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2 M. Irie, T. Fukaminato, K. Matsuda, S. Kobatake, *Chem. Rev.*, **2014**, *114*, 12174.

3 J. Boixel, V. Guerchais, H. Le Bozec, D. Jacquemin, A. Amar, A. Boucekkine, A. Colombo, C. Dragonetti, D. Marinotto, D. Roberto, S. Righetto, R. De Angelis, *J. Am. Chem. Soc.*, **2014**, *136*, 5367.

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NEW LIGAND BACKBONE IN PINCER CHEMISTRY: ORIGINAL STRUCTURES AND REACTIVITIES BASED ON THE 2-INDENEDIIDE MOTIF

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Thanks to their unique properties, pincer complexes have found applications in many fields, ranging from homogeneous catalysis to material science. Tridentate meridional coordination is clearly playing a major role in all these developments: it provides a rigid and robust environment around the metal, and at the same time it offers the possibility to finely tune its steric and electronic properties by varying the nature and substitution pattern of the involved ligand. The ability of some ligand platforms to directly participate in chemical transformations (so-called non-innocent character) further extends the potential of pincer complexes.

Aiming at developing new pincer structures featuring original bonding situation and peculiar behavior, we have been studying over the last few years tridentate ligands based on the 2-indenediide motif.[1] This presentation will summarize our recent results in this area. The formation, structure and reactivity of pincer complexes of type **A** will be discussed (Chart 1).

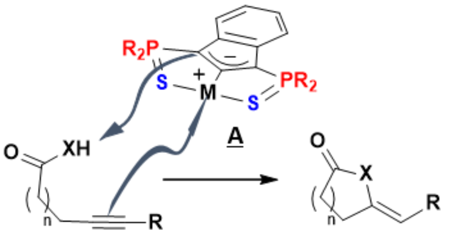

Chart 1 General structure of indenediide-based pincer complexes **A** and their application in cooperative catalysis.

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N-Heterocyclic Silylenes as Powerful Steering Ligands in Catalysis

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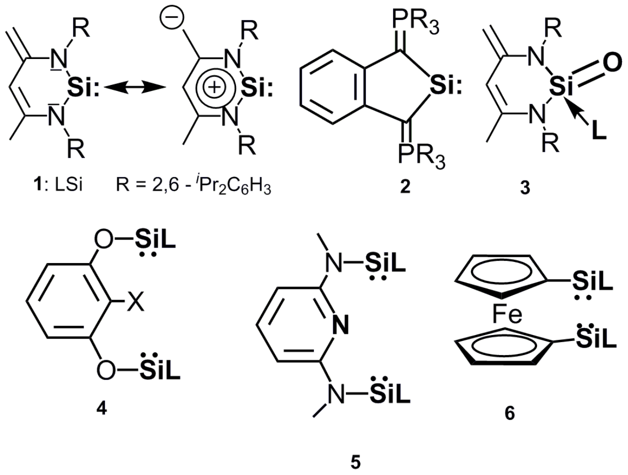
Activation of small molecules by using non- and semi-metals instead of precious metals is a contemporary challenge in molecular science. Recently, we developed two new types of zwitterionic silylenes **1** and **2** (Scheme 1) which show an unprecedented reactivity pattern with respect to small molecule activation based on silicon. [1,2] The facile oxygenation of **1** with N_2O or CO_2 in the presence of donor ligands coordinated to the divalent silicon led to isolable silanone complexes **3** which are also capable for facile activation of small molecules including ammonia, water, and hydrogen sulfide. Furthermore, the remarkable rich reactivity pattern of **1** and the first silicon(II)-based pincer arene ligands **4**, **5** and **6** (Scheme 1) can be employed as a new generation of powerful steering ligands in homogeneous catalysis. [3-6]. I wish to discuss selected features on the reactivity of **1-6** and in particular their advantageous use in catalytic transformations.



Scheme 1. Stable N-heterocyclic silylenes for small molecule activation.

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Mixed-Valence Tetrametallic Species for Potential Utilization as Quantum Cellular Automata

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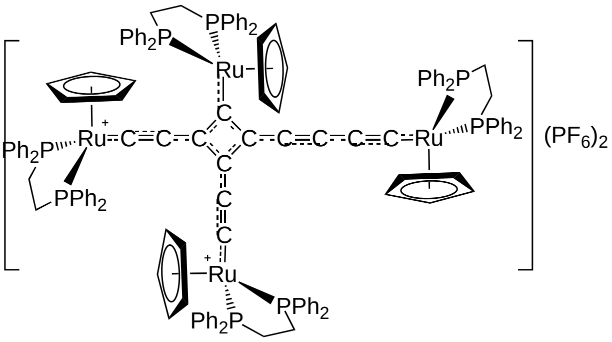
The chemistry of mixed-valence complexes[1] joins that of molecular electronics in the quantum cellular automata (QCA) paradigm,[2] a concept which has been demonstrated to be a possible alternative to the transistor-based technology, in which binary information is encoded in the configuration of charge among redox-active molecular sites.[3] Indeed, the simplest molecular QCA cell is a symmetric mixed-valence system in which the binary states are represented by the location of a mobile electron at one center or the other. Experimental and theoretical efforts have recently been devoted to molecular mixed-valence organometallic systems containing four metal centers as candidates for QCAs.[4] Properties of specific examples based on recently synthesized[5] (Scheme 1) and hypothetical tetrametallic molecules will theoretically be analyzed and discussed with the aid of DFT calculations.



***Scheme 1.** An example of a mixed-valence [Ru(II)$_2$Ru(III)$_2$] organometallic complex.*[5]

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Homogeneous Gold Catalysis – The Next Level

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In the last 15 years homogeneous gold catalysis has been a hot spot of organometallic catalysis.[1,2] The catalytic cycles involve different types of organometallic intermediates, which in some cases could be isolated.

Such examples, like vinylgold(I) and arylgold(I) intermediates (Figure 1),[3] σ,π-digold alkynes (Figure 1)[4] or gold(I) vinylidenes and gold allenylidenes[5] will be discussed. This will involve structural details from NMR spectroscopy as well as computational results.

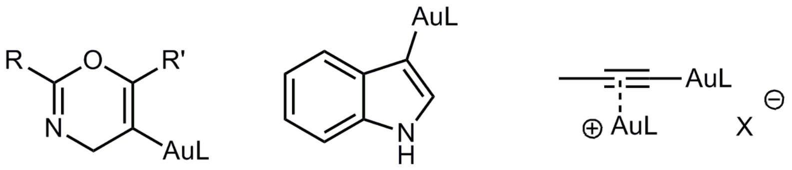

Figure 1 Vinyl-, aryl- and σ,π-digold(I) species.

Furthermore, also new types of organometallic intermediates will be covered.

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Synthesis and Reactivity of Parent Methylidyne Complexes

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Whilst parent terminal methylidene complexes $L_nM{=}CH_2$ are the key intermediates in alkene metathesis processes, comparatively few isolable examples have been reported. Far fewer examples of terminal methylidyne complexes $L_nM{\equiv}CH$ are known[1,2] and accordingly, comparatively little is known about their reactivity, or indeed generalizable synthetic routes.

We have previously shown that lithium/halogen exchange reactions involving the halocarbyne complexes $[M(\equiv CX)(CO)_2(Tp^*)]$ (M = Mo, W; X = Cl, Br; Tp* = hydrotris(dimethylpyrazolyl)borato) afford convenient access to the carbido complexes $Li[M(\equiv C)(CO)_2(Tp^*)]$ which serve as useful intermediates for the construction of novel carbyne complexes, in particular those containing unconventional hetero-atom substituents.[3] The approach is however limited by the lack of alternative halocarbyne complexes.

We have therefore turned our attention to the synthesis of new parent methylidyne complexes,[2] primarily via fluoride mediated protodesilylation of silylcarbynes, that might serve *via* deprotonation as entry points into new carbido intermediates. We will report the synthesis and reactivity of a range of parent terminal methylidyne complexes with respect to deprotonation, nucleophilic attack and metal-metal bond forming processes.

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Effects of Intramolecular Pd···S Interactions in Pseudo Five-Coordinate Thiacrown d^8 Complexes

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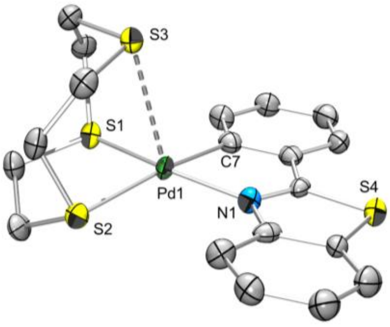
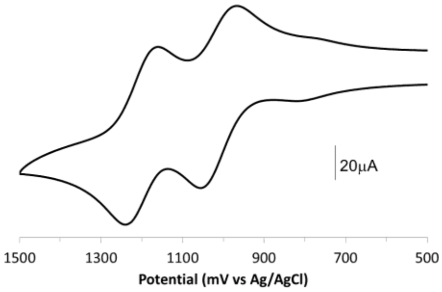
While the importance of the Pd$^{II/IV}$ redox couple has been demonstrated in palladium catalysts for C-H bond activation, growing evidence suggests the Pd$^{II/III}$ couple is implicated in related binuclear palladium systems. Our recent work on Pd(II) complexes with cyclometallated ligands and the trithiacrown macrocycle 9[ane]S_3 (1,4,7-trithiacyclononane) has shown unusual sequential one-electron reversible oxidative Pd$^{II/III}$ and Pd$^{III/IV}$ electrochemistry.[1] When complexed with d^8 metals, [9]aneS_3 provides two genuine M−S bonds as well as a M···S interaction significantly shorter than the sum of van der Waals radii. The mismatch between the endodentate preference of the [9]aneS_3 ligand and the electronic preferences of d^8 ions paired with the strongly electron-donating cyclometallating ligand allows for this unusual stabilization of Pd(III). As these stable pseudo five-coordinate Pd(II) complexes resemble postulated Pd(III) intermediates in catalysts, we have focused our work on elucidating fundamental relationships between ligand donor/acceptor properties, oxidation potentials, and intramolecular Pd···S structural features. X-ray structures of a series of cyclometallated Pd(II) [9]aneS_3 complexes clearly demonstrate tuning of the axial Pd···S interactions. Cyclic voltammetry experiments demonstrate cyclometallated ligand and solvent effects on oxidation potential and reversibility of observed electrochemistry. Furthermore, we carried out TD-DFT calculations and spectroelectrochemical studies of [Pd(pbt)(9[ane]S_3)](PF_6) (pbt = 2-phenylbenzothiazole) to characterize the Pd(II), Pd(III), and Pd(IV) oxidation states.





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Molecular Catalysts for Oxidation Reactions

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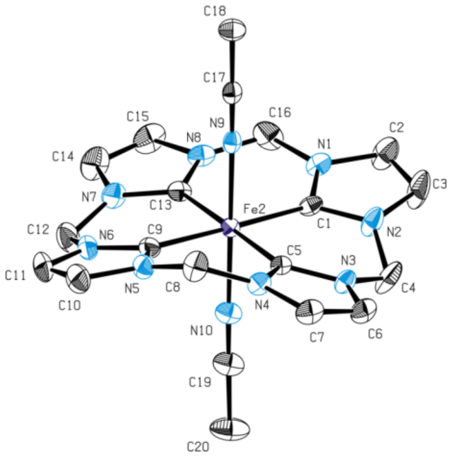
Iron compounds, ligated by tetradentate, N-heterocyclic carbene containing ligands have been synthesized and examined as oxidation catalysts. They show surprisingly high activities in epoxidation reactions,[1,2] but are also applicable for C-H oxidations and other related reactions.[3] A large variety of such compounds is obtained by variation of the ligand synthesis. The resulting complexes also vary considerably in their coordination geometry, reaction behavior and catalytic activity. Mechanistic examinations have been executed to get a clearer picture of the reasons of activity differences and selectivity variations. Furthermore, the Fe based complexes will be compared with related compounds, based on other (transition) metals.[4] Figure 1 shows the structure of one of the Fe-NHC compounds.

Figure 1: An ORTEP-style presentation of Fe-tetra(NHC) complex.



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Metal- and Ligand-Centered Reactivity of *meta*-Carboranyl-Backbone Pincer Complexes

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We report the synthesis of the chelating phosphinite-arm carboranyl POBOP-H (POBOP = 1,7-OP(*i*-Pr)$_2$-*m*-$C_2B_{10}H_{12}$) ligand precursor, preparation of its rhodium, nickel, and cobalt complexes, and their reactivity in oxidative addition/reductive elimination reactions. The unique three-dimensional geometry of icosahedral *closo*-$C_2B_{12}H_{12}$ carborane clusters, in addition to steric shielding, imposes a significant strain on the supported metal-boron bond and induces an additional reactivity centered on the boron atom that is vicinal to the metalated cage boron. The formation of the first examples of stable intermediates in B–C coupling reactions of carboranyl clusters by a direct B–H activation is reported. The unprecedented cascade reductive elimination of the aryl-, alkyl-, and halogen-*B*-carboranyl moiety followed by the oxidative addition of the vicinal B–H bond of the boron cluster to the metal center, resulting in the re-formation of the metal-boron bond will be discussed.

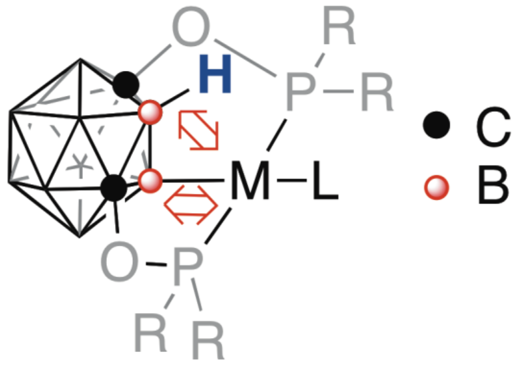

Figure 1. Metal-cluster interactions in B-carboranyl pincer complexes.

Phosphorescent Platinum(II) Complexes with C^C* Cyclometalated NHC Ligands

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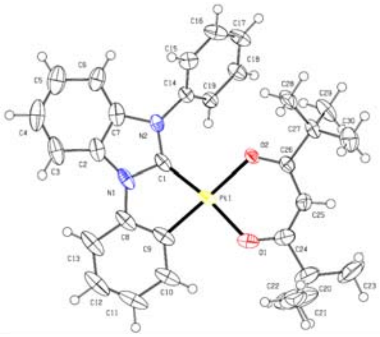
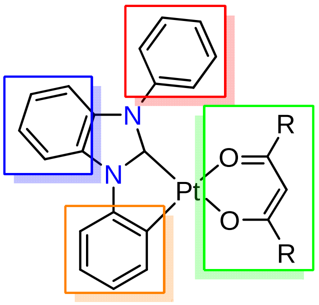
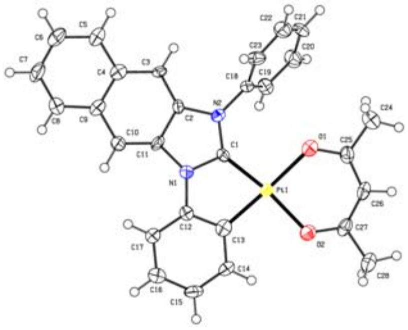
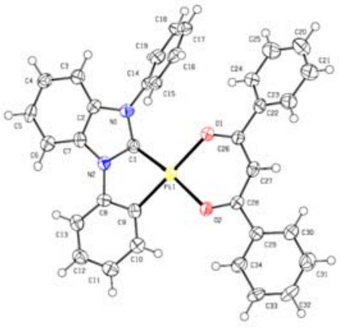
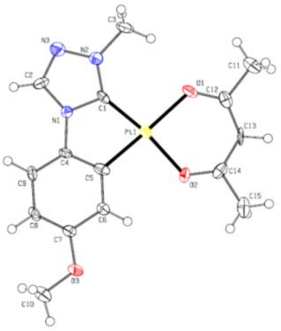
New mono- and bimetallic *N*-heterocyclic C^C* cyclometalated platinum(II) complexes are reported, which have been found to be efficient blue phosphorescent emitters with high quantum yield and short decay times. By different substitution patterns the electronic nature of the emitting state can be changed, which allows to tune the emission behaviour. The synthesis, solid-state structures and photophysical properties are presented together with results of quantum chemical DFT calculations.

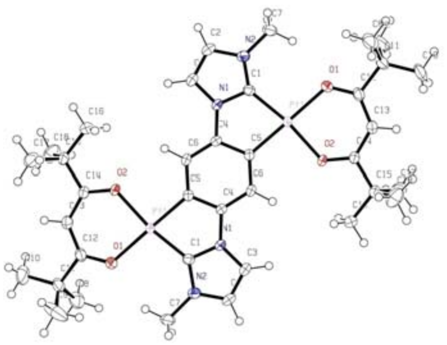












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Intrinsically Chiral Cyclopentadienide Ligands: Synthesis and Coordination Chemistry

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The discovery of ferrocene in 1951 is one of the central milestones in organometallic chemistry. During the last 60 years a multitude of cyclopentadienide (Cp^{-1}) compounds have been synthesized and characterized. We here present the first transition metal complexes of dibenzo[c,g]fluorene (H-Dbf, **1**)[1] and 5*H*-Dibenzo[*e,h*]dibenzo[3,4:6,7]cyclohept-[1,2-a]azulene (H-Cp^{C}, **2**)[2] two easily accessible H-Cp analogues possessing axial chirality with the axis of chirality included in the Cp fragment (Figure 1). The barriers of racemisation of these molecules and their transition metal complexes as well as their electronic structures have been studied in detail.

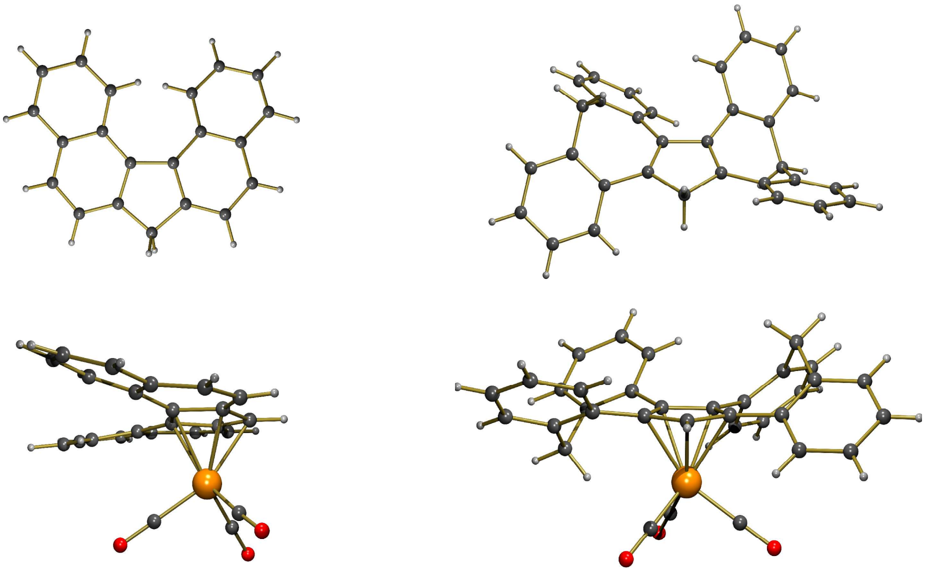

Figure 1 Solid state structures of the ligands H-Dbf (**1**, top-left) and H-Cp^{C} (**2**, top-right) and of their manganese tricarbonyl complexes (bottom).

[1] a) F. Pammer, Y. Sun, C. May, G. Wolmershäuser, H. Kelm, H.-J. Krüger, W. R. Thiel, *Angew. Chem. Int. Ed.* **2007**, *46*, 1270. b) F. Pammer, Y. Sun, W. R. Thiel, *Organometallics* **2008**, *27*, 1015. c) F. Pammer, Y. Sun, M. Pagels, D. Weismann, H. Sitzmann, W. R. Thiel, *Angew. Chem. Int. Ed.* **2008**, *47*, 3271. d) F. Pammer, Y. Sun, D. Weismann, H. Sitzmann, W. R. Thiel, *Chem. Eur. J.* **2010**, *16*, 1265. e) F. Pammer, Y. Sun, M. Sieger, J. Fiedler, B. Sarkar, W. R. Thiel, *Organometallics* **2010**, *29*, 6165.

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Homoleptic gold(III) complexes with di(N-heterocyclic carbene) ligands: different approaches for the selective synthesis of mononuclear vs dinuclear species

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Gold complexes bearing N-heterocyclic carbene ligands (NHC) are actually one of the most recent and appealing topics of organometallic chemistry, in view of their wide range of applications.[1] The synthesis of gold(I) NHC complexes is quite straightforward and can involve i) transmetalation of the carbene ligand from the corresponding silver(I) complex or ii) deprotonation of an azolium salt in the presence of a base and a gold(I) precursor.[2] Both approaches are effective also in the case of di(N-heterocyclic carbene) ligands (diNHC), affording in most cases dinuclear dicationic species with two diNHC ligands bridging two metal centers.

By contrast, due to the high instability of gold(III) towards reduction, deprotonation of an azolium salt in the presence of gold(III) precursors generally gives the corresponding gold(I) complex, so that transmetalation of the diNHC ligand remains the only viable synthetic procedure for diNHC-gold(III) species from gold(III) precursors.[3] In this way mononuclear complexes are generally obtained with the diNHC ligands coordinated in a chelating fashion. Alternatively, dinuclear gold(III) complexes can be isolated via oxidative addition of halogen X_2 (X=Cl, Br, I) to the pristine dinuclear gold(I) complexes.[4]

In this contribution, we intend to illustrate and critically evaluate the different synthetic strategies for the synthesis of mononuclear or dinuclear gold(III) complexes with diNHC ligands; particular attention will be given to the steric and electronic factors governing the output of the reaction.

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Functional Metallopolymers as Precursors to Magnetic Metal Nanoparticles: Synthesis, Lithographic Patterning and Applications

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Organometallic polymers represent an important research field due to their combination of unique and intriguing redox, electronic, magnetic, optical, and catalytic properties and their ability to be easily processed and fabricated into thin films, fibers, and other forms. Modern technology depends on fast, reliable data processing and storage. Hard ferromagnetic ($L1_0$-phase) FePt alloy nanoparticles (NPs) with extremely high magnetocrystalline anisotropy are considered to be one of the most promising candidates for the next generation of ultrahigh-density data storage systems. The question of how to generate ordered patterns of $L1_0$-FePt NPs and how to transform the technology to the practical application is challenging. As these metallopolymers can be readily shaped and patterned using various lithographic techniques, they offer a convenient synthetic access to patterned arrays of metal NPs with control of their composition and density per unit area, which are crucial factors for many magnetic and electronic device applications. However, many of the most desirable properties are exhibited by metal alloy NPs rather than single-component metal NPs. In this talk, the recent advance in developing new functional organometallic polymers (including bimetallic metallopolymers or blends of Fe and Pt homopolymers) as precursors to magnetic metal alloy nanoparticles and their lithographic patterning studies will be presented. These metallated polymers are promising as building blocks in high-density magnetic data storage media where the convenient and rapid patterning of magnetic NPs is highly desirable.

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Coordination Chemistry of N-Phosphanyl Carbenes

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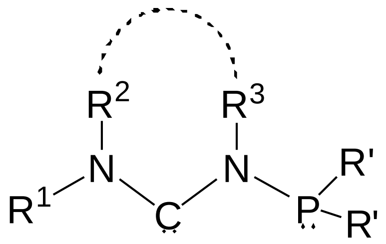

N-Phosphanyl, N-heterocyclic carbenes (NHCPs) and acyclic diaminocarbenes (ADCPs) are recently reported, stable molecules featuring a direct N-P bond between one nitrogen next to the carbene carbon and a phosphorus-containing group. Such compounds serve *inter alia* as tunable ditopic ligands in transition metal complexes with a broad spectrum of potential applications.[1,2] In the present contribution, we report on our continuing research efforts towards the synthesis, characterization and application of such complexes. In particular, we have prepared polynuclear group 11 metal complexes featuring NHCPs as bridging ligands,[1a-c] characterized by different stoichiometries and potentially amenable to technological application as catalysts, luminescent molecules or bioactive compounds. We have also prepared palladium(II) complexes in which NHCPs or ADCPs[1d] behave as chelating ligands, and have investigated on their structure-activity relationships when they are employed as catalysts in several cross-coupling reactions as well as in redox-neutral reactions, an effort that paves the way to the rational catalytic application of these compounds.

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Synthesis and coordination chemistry of 1,2-diphospholide derivatives.

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The 1,2-diphosphacyclopentadienide anion, an isolobal analogue of the Cp$^-$ and pyrazolate anion, has an significant interest as ligand in coordination chemistry due to the possibility of realizing various coordination modes with metal atoms[1]. We have found a new convenient synthesis of sodium 3,4,5-triaryl-1,2-diphosphacyclopentadienide and studied their coordination properties. Nature of substituents in obtained complexes determine the coordination mode of 1,2-diphosphacyclopenatdienide to metal and their magnetic properties.

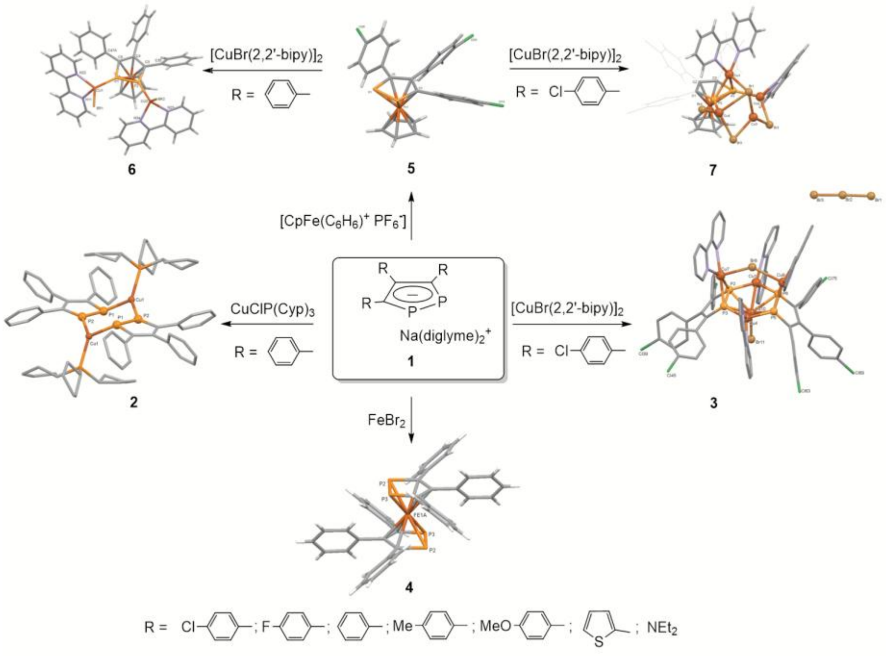

Figure 1 Coordination properties of 1,2-diphopholide anion toward transition metal complexes

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P-containing Polycyclic Aromatic Hydrocarbons: coordination chemistry and opto-electronic applications

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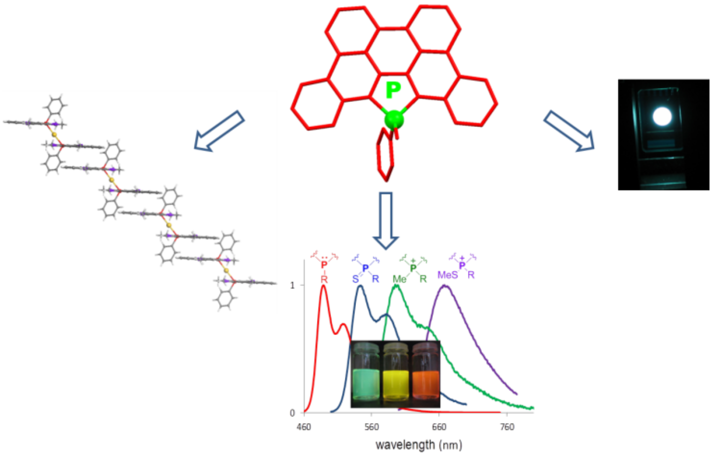
Polycyclic aromatic hydrocarbons (PAHs) are of great potential in molecular materials for opto-electronic devices. Their bandgap and supramolecular organization is tunable through modification of the π-system and lateral aliphatic substituents. An alternative original approach uses the versatility of heterochemistry with the successfull incorporation of N, O, S or B within the π -conjugated framework of PAHs.[1]

Here, we report that this strategy can be extended to P-modified PAHs.[2] A synthetic route to a family of P-modified PAHs is described. The reactivity of the P-center allows a straightforward HOMO-LUMO gap tuning. The impact of successive addition of fused aromatic rings around the P-ring was also studied. DFT calculations corroborate these studies. Furthermore, the coordination ability of the P-center allows unprecedented coordination-driven assembly of PAHs onto transition metals. The incorporation of these molecules in White emitting OLEDs shows the potential of this new family of compound for opto-electronic applications. [3]



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Luminescent Gold(I) Complexes with Phosphanyl- and Arsanylborane Ligands

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Gold(I) complexes are of interest because of their possible applications in materials science,[1] providing intense, long-living luminescence in the solid state with a wide range of emission energies.[2] We investigated the structural and photophysical properties of a series of new synthesised neutral and cationic gold(I) complexes of phosphanyl- and arsanylboranes $ERR'BH_2NMe_3$ (E = P, As; R/R' = H, Ph, ${}^tBu$),[3] which form molecular as well as polymeric structures. $[AuCl(PH_2BH_2NMe_3)]$ aggregates through closed-shell aurophilic interactions to form dimers with unsupported Au-Au distances of 3.103 Å. $[AuCl(AsH_2BH_2NMe_3)]$, the first example of a primary arsine binding to gold, aggregates in the solid state to form linear coordination polymers with Au-Au distances of 3.251 Å.

Further investigations comprise the synthesis and characterisation of monocationic complexes such as $[Au(EH_2BH_2NMe_3)_2]X$ (X = $AlCl_4$, ClO_4, CF_3SO_3). The cationic complexes represent coordination polymers in the solid state, with Au-Au contacts ranging from 2.983 Å to 3.208 Å. When irradiated with UV light, these complexes show a bright blue luminescence. After exposure to vacuum, the luminescence changes to green, indicating a vapochromic luminescent behaviour. Moreover, the emitted light exhibits a redshift with decreasing temperature. The further understanding of the relationship between molecular structures, crystal packing and switchable properties can assist in the construction of useful stimuli-responsive materials.[4]

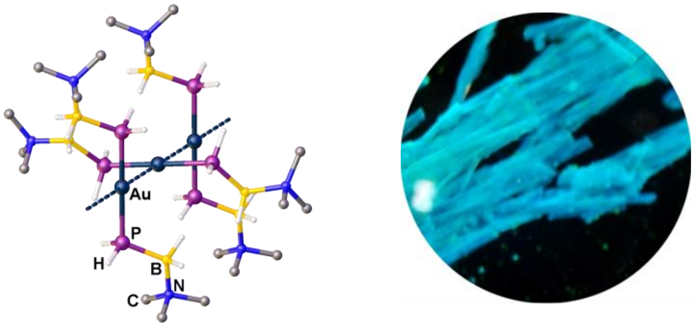

Figure 1 Solid state structure of $[Au(PH_2BH_2NMe_3)_2]AlCl_4$, crystals under UV light

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Phosphorus dendrimers decorated with copper complexes of N,N ligands, used as catalysts and as anti-tumor agents.

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Dendrimers are hyperbranched macromolecules having a perfectly defined and multifunctionalized structure, constituted of branches emanating radially from a central core. The structure of dendrimers is particularly modular, and can incorporate in different parts coordination complexes.[1]

We will focus on phosphorhydrazone dendrimers having nitrogen ligands as terminal groups (Figure 1) able to complex copper, and used either as catalysts or as anti-tumor agents. Cu-complexes of phosphorus dendrimers ended by bis(oxazoline) ligands (**A**) were used in asymmetric benzoylations,[2] and those ended by N-(pyridin-2-ylmethylene)ethanamine (**B**) in O- and N- arylation and vinylation of phenol and pyrazole.[3] Surprisingly, the same dendrimer (**B**) but also the dendrimers ended by N-(di(pyridin-2-yl)methylene)ethanamine (**C**) and 2-(2-methylenehydrazinyl)pyridine (**D**) have anti-tumor activities (both the free ligand and copper complex).[4] The interaction mode of the Cu(II) ions with these dendrimers in a biological medium has been determined by EPR.[5]

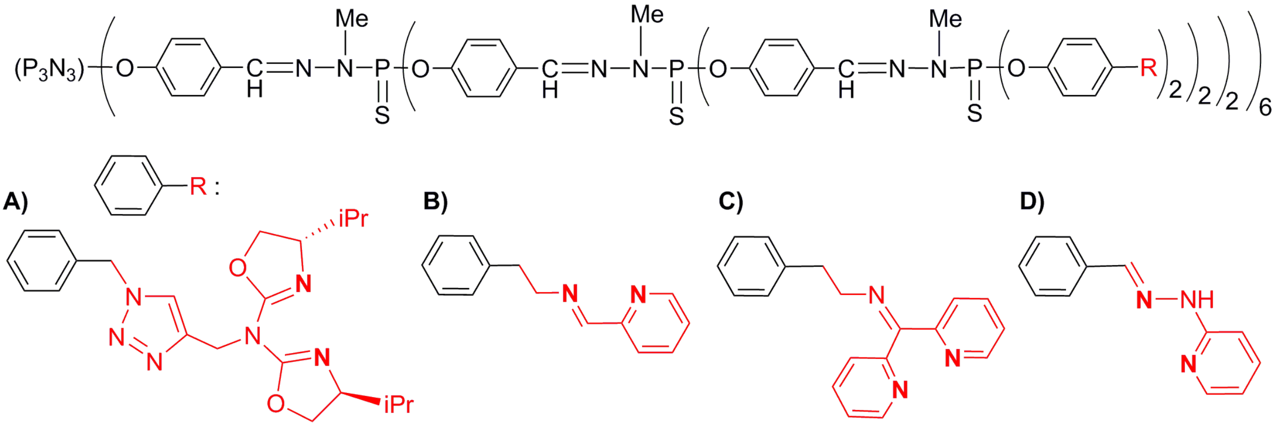

Figure 1 Linear representation of a dendrimer with different diaza ligands as end groups.

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Coordination polymers based on copper(II) and pyrazole

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Metal-azolates (simple imidazolates or pyrazolates, bis-, tris- and tetra-azolates) are a very promising class of coordination polymers (CPs), both in crystal engineering and functional materials synthesis. We have previously reported the bis(pyrazolato)copper(II) species **[Cu(pz)$_2$]$_n$**[1-3] (Hpz = pyrazole). In its β-form, the metal centre exhibits a square-planar geometry and a Lewis acidic character, allowing it to react with vapors of small Lewis bases (H_2O, MeCN, NH_3, MeOH). It is worth noting that weaker Lewis bases, such as H_2O and MeOH, interact symmetrically with the Cu(II) ions, generating a highly distorted (4 + 2) octahedral stereochemistry, whereas stronger Lewis bases (NH_3), prefer to bind to one Cu(II) ion, which adopts a 5-fold square pyramidal coordination.[6] Here we report some recent results about the reactivity of **[Cu(pz)$_2$]·H$_2$O**: when simply refluxed in water, it yields the new CP **[Cu(pz)(OH)]** (Figure 1), also obtained by refluxing in water $[Cu_3(\mu_3\text{-}OH)(\mu\text{-}pz)_3(RCOO)_2L_x]$ (L = solvent or neutral azole) or by treating, in hydrothermal conditions, copper acetate with an excess of Hpz.

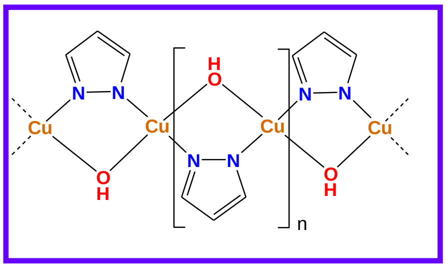

Figure 1

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About *P*-TEMPO phosphane(s), their complexes and radicals

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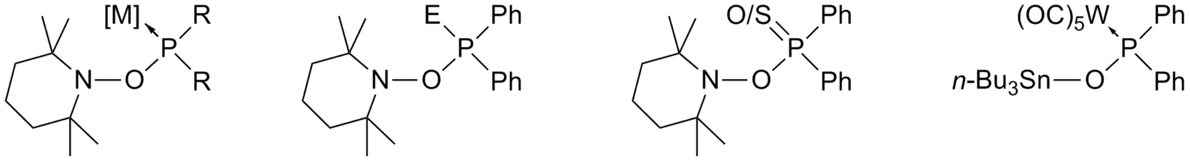
Over the last years the stable nitroxyls[1] such as TEMPO (2,2,6,6-tetramethylpiperidin-1-oxyl) obtained interest in molecular and in polymer synthesis. In contrast, the chemistry of phosphorus radicals is far less explored.[2] Our research strives to find accesses to phosphane derivatives with a *P*-bound TEMPO to study homolytic bond cleavage processes. This specific substituent enabled thermal decomposition of *P*-nitroxyl tungsten complexes **I** ([M] = $W(CO)_5$) to generate different radicals which are formed preferably *via* O–N bond cleavage; previous results were analyzed and supported by DFT calculations.[3]



I II III IV

Figure 1 Different P(III/V) phosphanes and complexes having a *P*-bound nitroxyl unit

Herein, we present synthesis of different *P*-nitroxyl derivatives with diverse bonding situations at phosphorus, *i.e.* **IIa-c** with a P(III) center (E = $M(CO)_5$, BH_3, l.p.) and P(V) derivatives **IIIa,b**. DFT calculations clearly demonstrated that after O–N bond homolysis of **I** a hydrogen atom can be abstracted from R_3SnH by the aminyl radical. The stannyl radical then reacts with the so called phosphanoxyl complex to give **IV** as final product.[4] First polymerization studies of styrene using complexes **I** were also successful. Attempts to synthesize P(III) phosphane **IIc** (E = l.p.) led to decomposition with **IIIa** (O) as main product. DFT calculations revealed complicated pathways based on an initial homolytic O–N bond cleavage and radicals thus formed being responsible for the set of final products.[5]

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Coordination modes of σ^2-phosphorus compounds

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Phosphine ligands are of high interest in coordination chemistry, combined especially with late transition metals, forming homogenous catalysts of highly important chemical transformations. Likewise phosphines, which contain σ^3-phosphorus, low valent phosphorus compounds (containing σ2-phosphorus, thus a –P=C< bond) coordinate usually also by the lone pair, which is situated in the molecular plane. Recently, several complexes were reported by the Heinicke group formed between the electron rich 1,3-azaphosphole with group 11[1] and 12[1,2] elements, exhibiting side-on coordination, with the involvement of the P=C bond. As an extension of these combined synthetic and computational studies we present here a comprehensive computational investigation on the complexing ability of differently polarized P=C bonded compounds, with a series of d-elements. Apart from structure optimization the molecular orbitals, electron densities and the interaction between the ligands and the d-elements will be discussed.

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Different facets of coinage metal-coordination chemistry: From mononuclear complexes to d^{10}-metal clusters and gold nanoparticles

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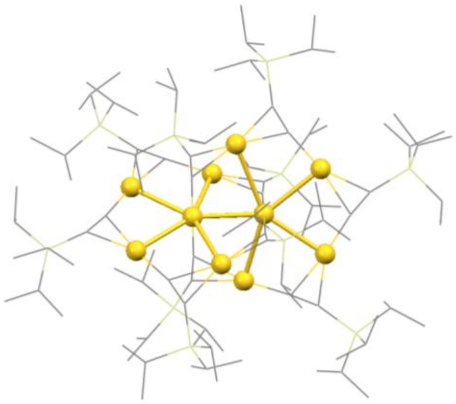
Over the last years, we have explored the coordination chemistry of various coinage metals using different ligand frameworks. We discuss the formation and properties of mono-and dinuclear gold complexes using various phosphine (and phosphaalkene) ligands.[1] Reduction of gold precursors such as AuCl(tht) or $HAuCl_4$ with triethyl silane in the presence of acetylenic phospaalkenes can lead to the dynamic and cooperative stabilization of gold nanoparticles, which can be used for facile ligand exchange reactions using other phosphine based ligands.[2] In contrast the reaction of AuCl(tht) with terminal acetylenes in the presence of a base affords discrete Au10-clusters. Similar clusters are also obtained using Cu(I)-salts. Resulting gold and copper clusters show strong emission in the yellow and orange, respectively.[3]



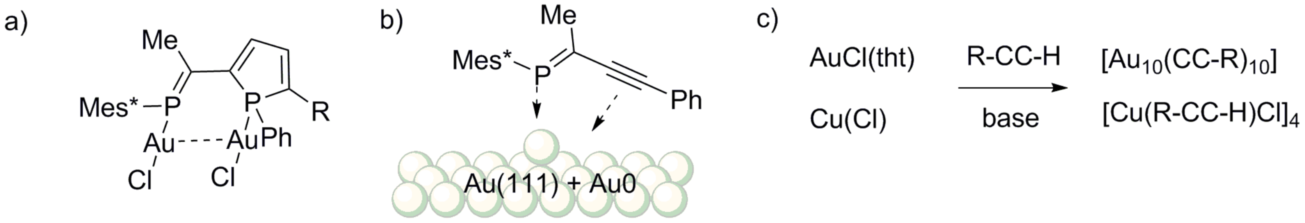


Figure 1 Coordination compounds and clusters of coinage metals using phosphane and acetylenic ligands.

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Stereocontrol in Functional [n]Ferrocenophanes

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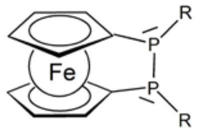
[n]Ferrocenophanes with an n-atomic chain bridging the rings of a ferrocene unit are attractive synthetic targets owing to their potential in the synthesis of metal containing polymers.[1] We are aiming at [n]ferrocenophanes (n = 2, 3) with two or more phosphorus atoms involved in the tethering unit in order to study the electronic interaction between the electrons of the metal and the bridging atoms. Ferrocenophanes tethered with more than two carbon atoms or other main group atoms are known for quite a while,[2,3] however, only few examples of diphospha-[2]ferrocenophanes have been described so far.[4]

We investigated different coupling reactions starting from low valent $\sigma^2\lambda^3$ phosphanes but also from regular $\sigma^3\lambda^3$ phosphanes to gain access to [n]ferrocenophanes of the types **I-III** incorporating trivalent or mixed tri-/penta-valent phosphorus atoms in such ring systems.[5] Moreover the inclusion of other hetero atoms such as in [3]-ferrocenophane **IV** may offer synthetic potential as a suitable precursor for phosphano substituted tetrylenes.[6] Since the phosphorus atoms behave as stereocenters, a special focus will be set on their stereochemical alignment with the aim to achieve stereocontrol.



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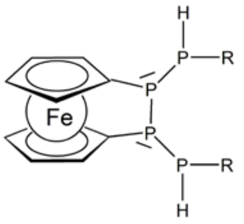

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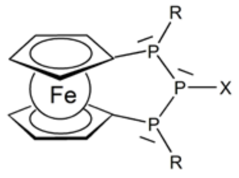

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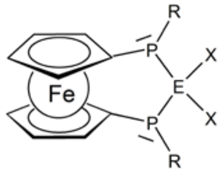

(E = group 14 element)

IV

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Functionalized and responsive nanostructures by the self-assembly of polyphosphazene-based block copolymers.

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Our group has been recently studying the self-assembly of polyphosphazene block copolymers. Such versatile materials allowed us the synthesis of block copolymers having a chosen property located in the core-forming block and, therefore, assess the influence of this property over the self-assembly in solution and in thin films.[1] Thus, we prepared polyphosphazene-based block copolymers having chiral[1a] and functional blocks[1b-c] able to direct the self-assembly to pores, helix, or nanostructures functionalised with gold nanoparticles (AuNPs). Motivated by the idea to combine the potentiality of the crystallization-driven living self-assembly (CSDA) processes with a highly dynamic system able to be responsive to an external stimuli, herein we study the self-assembly of a family of crystalline-*b*-coil block copolyphosphazenes of general formula $[N{=}P(OCH_2CF_3)_2]_n$-*b*-$[N{=}PMePh]_m$ (Figure 1) linking crystalline and highly flexible $[N{=}P(OCH_2CF_3)_2]_n$ segments, with amorphous [N=PMePh] blocks. The self-assembly of these crystalline-*b*-coil block copolyphosphazenes leads to the unexpected formation of giant unilamellar vesicles (GUVs) in non-aqueous solvent (THF). Those GUVs show a reversible response to protonation leading to small spherical micelles in which the core-corona roles are inverted.

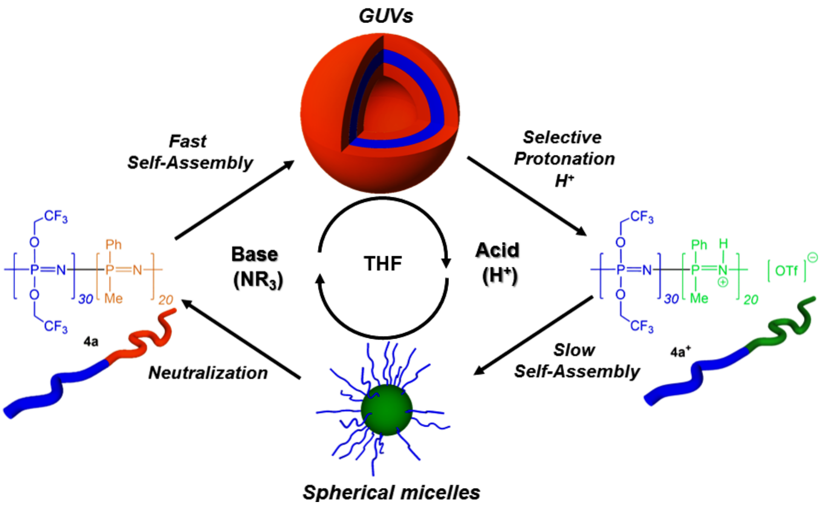

Figure 1. Schematic representation of the reversible morphological evolution

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Back-bone organometallic polymer {[(PTA)$_2$CpRu-μ-CN–RuCp(PTA)$_2$-μ-CdCl$_3$]}$_n$: a new amorphous matherial.

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Back-bone organometallic polymers is a new family of metal-compounds with new and amazing properties. The first examples of this family were the water soluble organometallic polymer {[(PTA)$_2$CpRuDMSO]-μ-AgCl$_2$-}$_n$,[1] and {[{(PTA)$_2$CpRu-μ-CN-RuCp(PTA)$_2$}-μ-Au(CN)$_4$-]}$_n$,[2] which maintain their polymeric structure in aqueous media, and the latter was the first example of an organometallic polymer thermogel in water (PTA = adamantanephosphine). In the last years, we have made an great effort to find a systematic and reproducible method to obtain new heterometallic polymers. The first success was the reproducible and robust synthesis of {[(PTA)$_2$CpRu-μ-CN–RuCp(PTA)$_2$-μ-NiCl$_3$]}$_n$,[3] which is paramagnetic and displays also gel properties in water. Herein, we present the a new member of the family, the polymer {[(PTA)$_2$CpRu-μ-CN–RuCp(PTA)$_2$-μ-CdCl$_3$]}$_n$ (**1**) that is water soluble but also amorphizes under low pressure. This finding opens up possibilities for liquid casting and shaping heterometal inorganic polymers into a variety of different solid forms, promising to be an extremely exciting step forward in producing chemically functionalizable hybrid glass materials.[4]

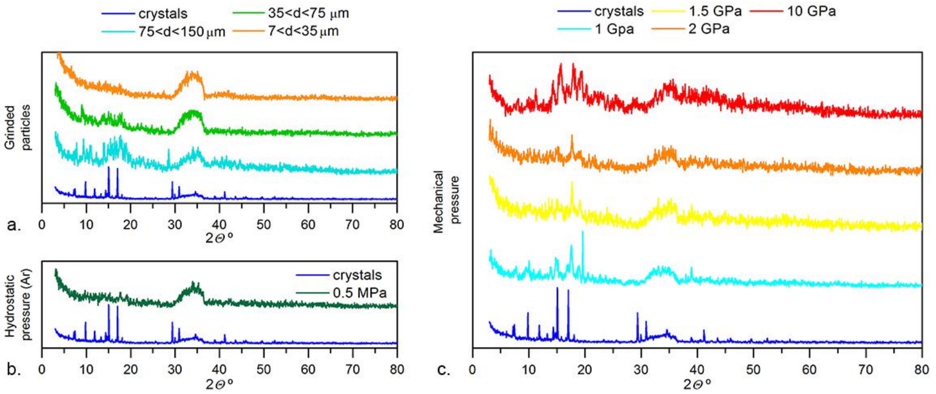

Figure 1 Amorphization and lattice transitions of **1**: PXRD of milled fractions (a); PXRD after exposition at increasing hydrostatic (b) and mechanical pressure (c).

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Functionalisation and Stepwise Expansion of Stable Unsaturated Silicon Clusters (Siliconoids)

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The understanding and the manipulation of silicon surfaces[1] are key aspects of silicon-based technologies. Stable molecular siliconoids are unsaturated neutral silicon clusters that exhibit typical features of silicon nanoparticles and surfaces,[2] in particular the presence of one or more unsubstituted vertices.[3] Evidently, functionalised vertices are a prerequisite for the embedding of siliconoids in extended supramolecular assemblies. However, only unfunctionalized siliconoids have been reported so far, severely limiting further developments in this regard.

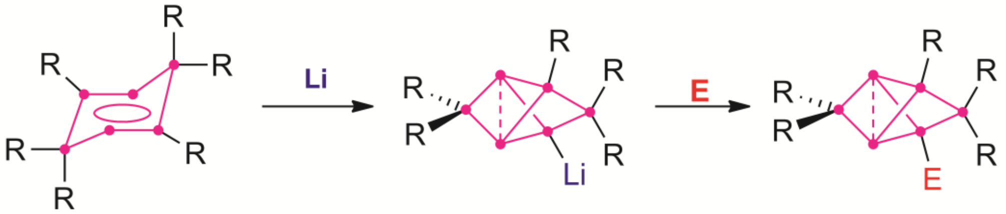

Figure 1 Synthesis of lithiated siliconoids from dismutational hexasilabenzene isomer and functionalization with common electrophiles (• = Si; R = 2,4,6-triisopropylphenyl; E = electrophile).

Here we report the site-selective reductive cleavage of aryl groups of cluster-like hexasilabenzene isomers (Figure 1). As demonstrated by reactions with representative electrophiles of Groups 13 to 15, these anionic siliconoids efficiently transfer the Si_6 motif to various substrates, while maintaining the integrity of the unsaturated cluster scaffold in most cases. On the other hand, with suitable substrates a targeted stepwise expansion of the cluster scaffold can be achieved.

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Synthesis and photophysical properties of isoxazolidine-fused *meso*-tetraarylchlorins and their metal complexes.

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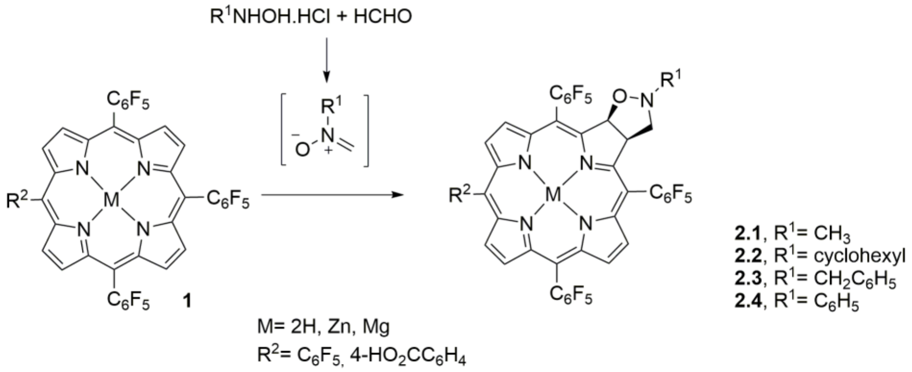
A family of isoxazolidine-fused *meso*-tetraarylchlorins **2** was synthesized *via* 1,3-dipolar cycloaddition (DC) of *meso*-tetraarylporphyrins **1** with different *N*-alkyl and *N*-aryl nitrones.[1] The corresponding metal (Zn^{II} and Mg^{II}) complexes were prepared by performing the 1,3-DC using the previously synthesized porphyrin complexes **1** (M= Zn and Mg). We intended to achieve a new series of dyes with high absorption spectra in the visible region and strong emission sensing properties, in order to apply them in a wide range of applications, including the construction of an optical sensor for monitoring harmful gases and chemical vapors[2] and also in photodynamic therapy (PDT) and diagnosis.[1] Furthermore, one of the porphyrins carries a carboxylic acid group to be conveniently attached to a polymer. The optical properties of obtained compounds will be presented and discussed.



Acknowledgments: The authors gratefully acknowledge the COST action CM1302 (SIPs). This work was supported by Fundação para a Ciência e a Tecnologia (FCT, Portugal), European Union, QREN, FEDER and COMPETE, projects M-ERA-NET/0005/2014, NORTE-07-0162-FEDER-000048, NORTE-07-0124-FEDER-000066/67, UID/QUI/50006/2013 (LAQV/REQUIMTE) and UID/Multi/04378/2013 (UCIBIO/REQUIMTE). A.L. also thanks FCT her grant (SFRH/BPD/85793/2012).

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Design of Purely Inorganic Water-Soluble Polymers: The Role of Carborane Clusters and Producing Large Structural Adjustments from Minor Molecular Changes.

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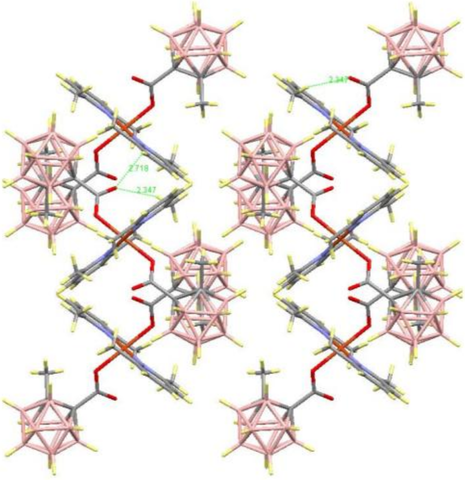
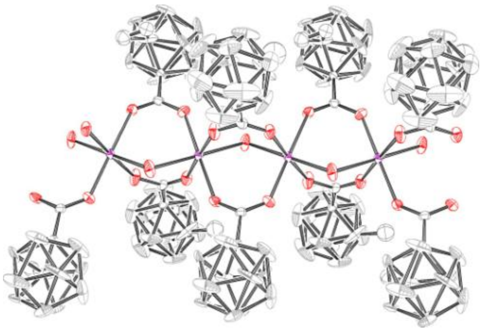
Coordination polymers are currently of great interest and represent an active area of coordination chemistry because of their special roles in fields such as ion exchange, gas storage, chemical separation, sensor technology, magnets, optoelectronics, energy conversion and storage and catalysis. Also, polynuclear metal complexes attract great interest owing to their relevance to many important naturally occurring processes. The cooperative action of closely coupled dinuclear or multinuclear centers is required for several manganese enzymes to carry out their biological functions as for example in the photosystem II. The successful behavior of these structures consists in the use of adequate building blocks that allow the synthesis of 1D linear / twisted chains, 2D squares / polygons and 3D cubes / polyhedra. A family of new carboranylcarboxylate-bridged dinuclear Cu (II) compounds with paddle-wheel structure and Mn(II) polymers with aqua bridges have been synthesized and their physical and chemical properties studied.[1] Recently, carboranylphosphinic acids have also been synthesized, and the influence of the cluster on the reactivity of coordinating group studied.[2]





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O_2 Activation and Double C-H Oxidation by a Mononuclear Manganese(II) Complex

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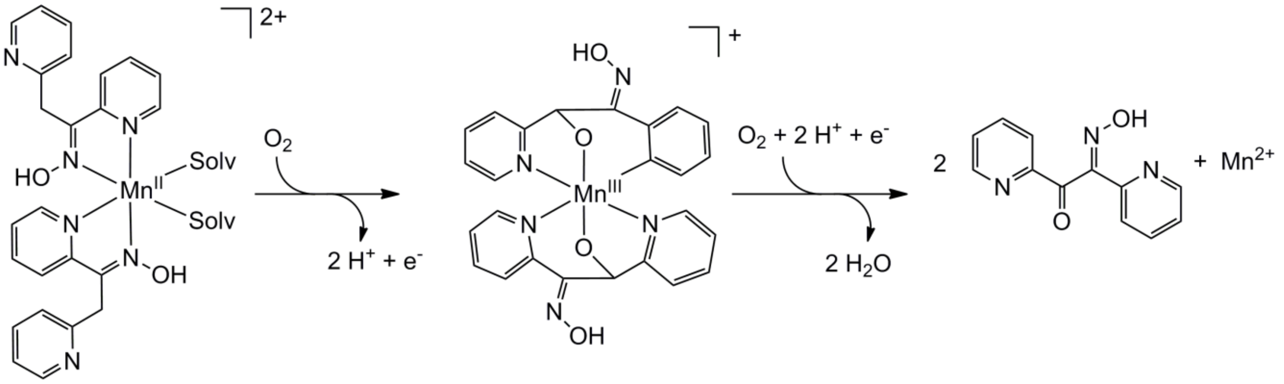
Manganese plays crucial roles in the biological formation of O_2 at the Oxygen Evolving Center (photosynthesis), catalases (H_2O_2 disproportionation) and superoxide dismutases (destruction of reactive oxygen species). These processes involve O_2 release from high valent Mn species. An example of the opposite reaction was caught here; O_2 activation by a Mn(II) species.[1] Molecular oxygen was found to be the source of the oxygen inserted into a C-H bond to form an alcohol in a first step and then a ketone derivative of the dipyridyloxime starting ligand.



Scheme 1 Stepwise oxidation of the dipyridyloxime ligand by O_2

The reaction was followed by UV-visible and Raman spectroscopy and the provenance of the oxygen atoms was demonstrated by mass spectrometry (^{18}O-labelling). By playing with the experimental conditions, relatives of the unoxidized starting material and final ketone containing complex as well as the reactive alcohol intermediate could be characterized by X-ray crystallography.

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Photoactive Spin-crossover Iron(II) Complexes 2,6-Bis(pyrazol-1-yl)pyridine Ligands

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The Spin-Crossover (SCO) phenomenon between low-spin (LS) and high-spin (HS) state presents one of the most spectacular examples of molecular bistability. The outstanding position of SCO materials is based on the number of external stimuli, by which change of the spin can be performed. Until now, the most investigated is thermally activated transition of spin, which can be influenced also by other triggers like pressure, magnetic orelectric field. Moreover, in the last three decades, the light induced LS↔HS photoconversion (LIESST and reverse LIESST effect) attracts the research interest. The iron(II)-bis(pyrazolyl)pyridine compounds represents class of materials which fulfill all technological requirements for the utilization of SCO in the nanotechnology.[1-5] The room temperature, abrupt and hysteretic transition of spin accompanied by intense thermochromism can be found in this family of materials very often. Herein we present thermal and light-induced SCO investigation in iron(II)-bis(pyrazolyl)pyridine complexes. In the case of mononuclear compounds, their thermal and photoinduced transition of spin was investigated by magnetic measurements as well as by various spectroscopic techniques (temperature variable Far-IR, Vis and Mössbauer spectroscopy). In addition to the mononuclear compounds, new photoactive anthracene-contained bis(pyrazolyl)pyridine ligand moieties were synthesized. The consecutive iron(II) complexation resulted in the formation of oligomeric polynuclear complexes with grid-like or hexagone-like molecular architecture.

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Rigidity in iron (II) tetrazole spin crossover chains

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An important feature of SCO compounds for a technological application based on their spin switching behavior is cooperativity between the metal centers, enabling an abrupt spin transition. Therefore, different iron(II) spin crossover chains based on bridging tetrazole ligands were synthesized. Main objective is an improved cooperativity through an enhancement of the ligand rigidity. The influence of several weak coordinating anions and different solvents on the molecular arrangement, and therefore the switching behavior has been investigated. Quantum chemical calculations, as well as elaborated diffractive studies provided relevant insights into the solvents' and anions' influence on the spin transition.

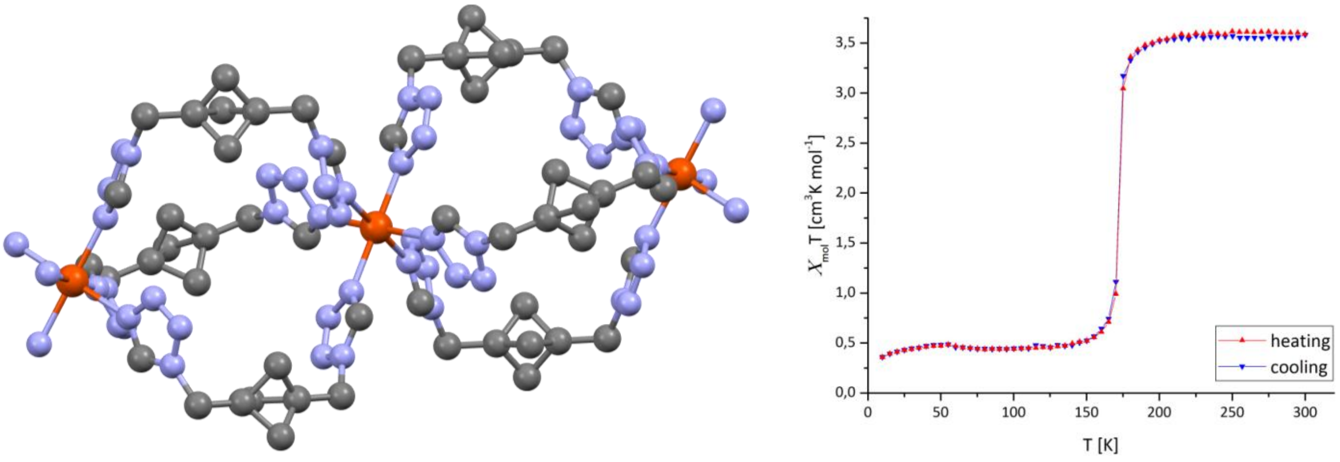

Figure 1 Molecular structure of a one dimensional SCO chain connected via tetrazole-propellane linkers (left), temperature dependent magnetic susceptibility (right)

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pH-Responsive Magnetism of Iron(II) Complexes in Solution and Under Small Confinement

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So far, a reversible spin state change between a paramagnetic high spin (HS, $S = 2$) and a diamagnetic low spin state (LS, $S = 0$) could be triggered by temperature, pressure or light irradiation.[1] We present a composite material where octahedral iron(II) complexes have been incorporated inside the supercages of Y-type zeolite. Those complexes transit from a diamagnetic to a paramagnetic state when the surrounding pH is lowered. This fully reversible mechanism is caused by a proton-driven coordination-induced spin-state-switch (*PD-CISSS*) between a MRI-silent LS and MRI-active HS state. Consequently, an on-off-like pH-response of the molar relaxivity Δr_1 is observed in field-cycling ^{1}H-NMR for the bulk complexes. Since a coordination site becomes vacant they are potential prototypes for the visualization of tissue pH in functional Magnetic Resonance Imaging (*f*MRI).[2]

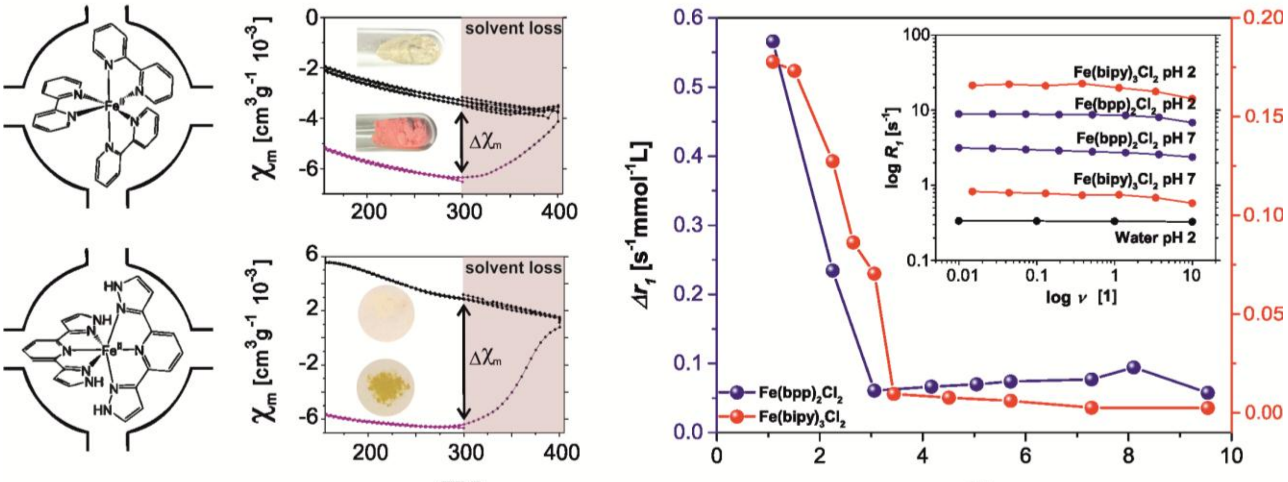

Figure 1 Left: The diamagnetic iron(II) complexes Fe(bipy)$_3$@NaY (bipy = 2,2'-bipyridine) and Fe(bpp)$_2$@NaY (bpp = 2,6-bis(1H-pyrazol-3-yl)pyridine) become paramagnetic upon interaction with zeolite protons followed via SQUID-magnetometer; right: Since thereby a free coordination site is opened pH-dependent relaxation properties are also found for the bulk complexes in ^{1}H field-cycling NMR.

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DFT Approach to spin crossover in embedded systems

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The spin state energetics, structural properties and guest-host interactions of the benchmark spin crossover systems $[Fe(bipy)_3]^{2+}$ and $[Co(bipy)_3]^{2+}$ (*bipy* = 2,2'-bipyridine) embedded into the zeolite Y cavity were studied theoretically. The PBE functional was employed within the STO 3-ζ or STO 2-ζ basis sets, respectively, for all atoms. On top of our previous study[1] the performance of the recently defined dispersion correction by Grimme et all.[2] was examined here as well.

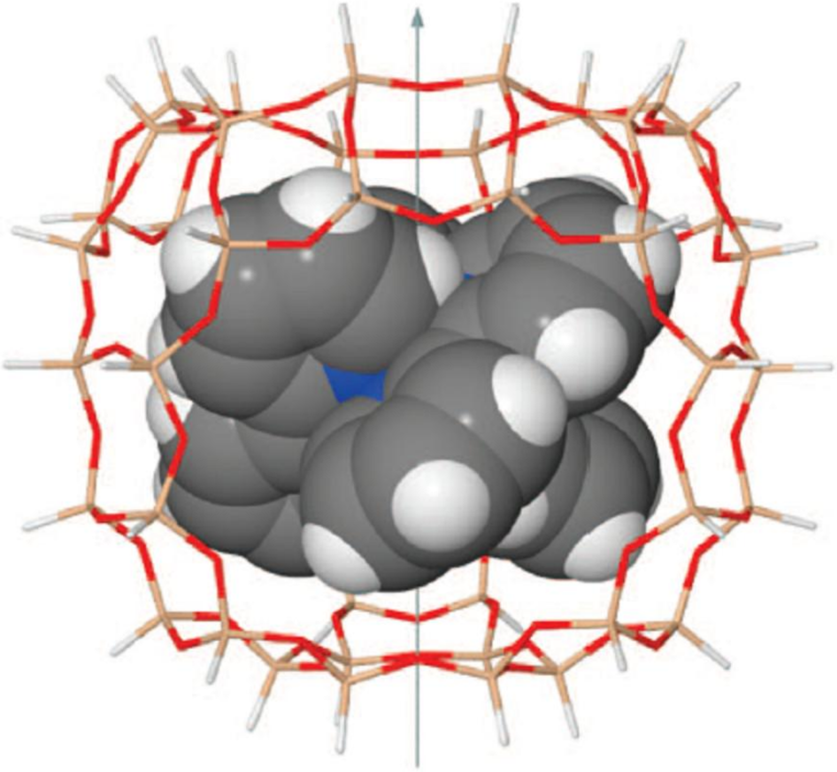

Figure 1 Schematic representation of $[Fe(bipy)_3]^{2+}$ in the zeolite Y cavity.

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Oxidation reactivity of nickel(III) carboxylate complexes

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Metastable, high-valent transition metal complexes are important intermediates in a multitude of biological and synthetic oxidations. Nickel compounds have been shown to catalysetransformations such as epoxidations and the hydroxylation of alkanes;[1] however,reactive intermediatescapable of these reactions have been observed only in a few cases.[2]

We recently reported the synthesis and characterisation of a nickel(III) bicarbonate complex,[3] which is competent in oxidations which include hydrogen atom abstraction (HAA) from phenols. In this work, we extended the study to a family of related nickel(IIII)-X complexes, supported by the same NNN pincer ligand (Figure 1, left). Amongst these, a nickel(III)-acetate species proved remarkably stable ($t_{½}$ = 800 s at 25 °C). Investigations showed accelerated decay in the presence of a series of compounds, including hydrocarbons (Figure 1, right). This observation evidenced the capability for HAA from C-H bonds of various strengths. The comparison of different substrates and intermediates offers insights in the reactivity of nickel(III)-OX species.

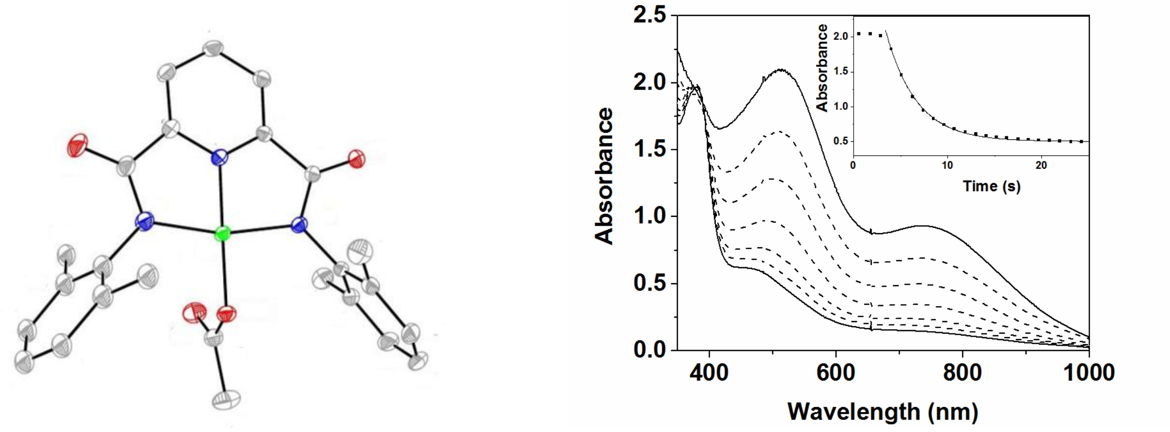

Figure 1 Left: structure of a nickel(II)-acetate precursor complex; right: decay of the UV-vis spectral features of Ni(III)-acetate in the presence of xanthene (10 eq.).

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Propargyl-*1H*-tetrazole as promising ligand for post-functionalization of spin switchable iron(II) complexes

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Spin crossover complexes with ligands suitable for a further functionalization after coordination could allow for an easy access to various multifunctional switchable materials. Within this context we recently characterized Fe(II) SCO complexes of propargyl-*1H*-tetrazole.[1] The carbon-carbon triple bond provides a well-known motif for a possible post-functionalization via standard protocols like alkyne-metathesis or click reaction. Although the design of the ligand shows similarities to the well-known propyl-*1H*-tetrazole,[2,3] the spin transition behaviour is notably different.

Due to the potential instability of those complexes, especially of the perchlorate complex, further investigations regarding their sensitivity towards thermal and mechanical stress were made. These experiments led to the conclusion that upon proper handling no enhanced risk of an explosive decomposition has been found.

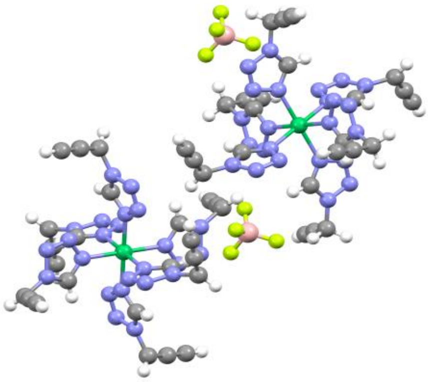

Figure 1 Molecular structure of the isotypic $[Ni(prgTz)_6](BF_4)_2$ complex

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Water activation by new molecular catalysts

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Splitting water is a good way to cleanly provide protons and electrons as starting materials for the synthesis of alternative energy carriers like H_2 or MeOH. Developing efficient and cheap catalysts are prerequisite to the achievement of such technologies. Ideally, these catalysts should operate at low overpotentials and be coupled to a photoactive unit to achieve light-driven processes. The interest of molecular chemists in this area has been mostly focusing on mimicking enzymatic systems, performing a plethora of oxidative transformations under mild conditions and sometimes with the help of solar energy.[1,2]

$$2\,H_2O \longrightarrow 1/2\,O_2 + 4\,H^+ + 4\,e^- \qquad (1)$$

$$H_2O + S \longrightarrow SO + 2\,H^+ + 2\,e^- \qquad (2)$$

In this context, our efforts have recently been directed at the development of new ligands platforms that could favor the formation of highly oxidized metal-oxo species by activation of a water bound molecule in order to perform energetically demanding and mechanistically complex water splitting reactions or clean oxidative transformations as alternatives to most pollutant industrial processes.[3,4]

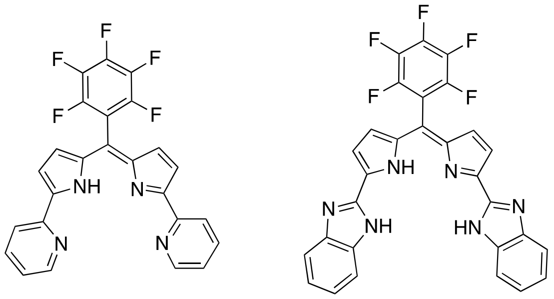

Figure 1 Examples of ligand platforms presented in this study

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Facile hydration of two nitrile groups into carboxamides in mild conditions by temporary interaction with a ferrous center: a textbook case.

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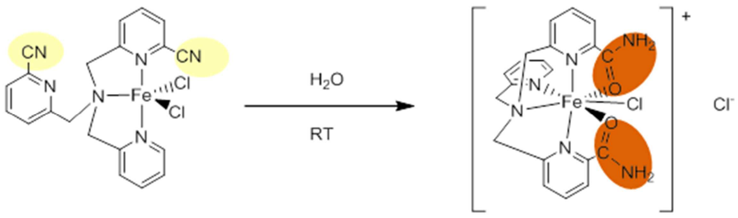
Conversion of nitrile-containing compounds into amides in ecologically friendly conditions is a particularly challenging area in our current economical context.[1-5] Here, we describe the hydration of two nitrile functions into carboxamides by a ferrous [Fe(II)] center in particularly mild conditions and very efficiently, and demonstrate that these unusual conditions result of anchimer assistance at the reaction site. Two bis(cyano-substituted) (tris 2-pyridyl methyl amine) ligands have been prepared and the structures of the corresponding $FeCl_2$ complexes are reported. These two ligands only differ by the position of the nitrile group on the tripod, respectively in α- and β- position with respect to the pyridine nitrogen. In any case, intramolecular coordination is impossible. Upon action of water, the nitrile groups are sequentially hydrated, however only if they are located in the α- position. Because of its proximity with the coordination center, a nitrile is in turn activated and ready to undergo hydration in unexpected conditions, i.e. by an Fe(II) center at room temperature, with no need for its coordination. At a preparative scale, this reaction allows the one-pot conversion of the bis(cyano-substituted) tripod into a bis(amido-substituted) one in particularly mild conditions with a very good yield.



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