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## Labeling, mutations and truncated constructs: approach to solving the structure of the CPEB3 ribozyme through NMR spectroscopy

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Ribozymes are RNA molecules capable of catalyzing specific chemical reactions. Several small ribozymes were recently discovered in mammals<sup>1</sup>. The cytoplasmic element binding protein 3 (CPEB3) ribozyme is a self-cleaving ribozyme that was found to be highly conserved in the mammalian genome<sup>1</sup>. Characterization of the CPEB3 ribozyme showed that it has similar properties as the hepatitis delta virus (HDV) ribozyme, including the fold and catalytic mechanism<sup>1,2,3</sup>. Unlike some self-cleaving ribozymes such as the hammerhead, hairpin and VS ribozymes where high concentrations of monovalent metal ions can promote catalysis, Mg<sup>2+</sup> is required by the CPEB3 and HDV ribozymes<sup>4</sup>. Both ribozymes fold in a sophisticated nested double pseudoknot motif. According our previously work<sup>3</sup>, the CPEB3 ribozyme is significantly compacted with monovalent ions alone but the active fold is only achieved after addition of millimolar amounts of Mg<sup>2+</sup>. NMR studies showed the formation of a GU wobble pair with addition of Mg<sup>2+</sup>, which may correspond to the GU wobble that is an essential part of the active site in the HDV ribozyme<sup>5</sup>.

Here, we aim to solve the solution structure of the CPEB3 ribozyme through NMR spectroscopy. The assignment of the <sup>1</sup>H-<sup>1</sup>H NOESY spectra of the full length ribozyme is a challenge due to the limited building blocks of RNA as well as the length of the CPEB3 ribozyme of 67 residues. In order to alleviate the spectral overlap, various labeled nucleotides were incorporated through *in vitro* transcription including partially deuterated, fully deuterated and <sup>13</sup>C, <sup>15</sup>N-labeled nucleotides.

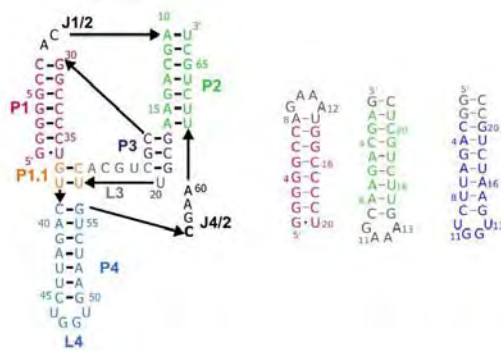


Figure 1. Secondary structure of the chimp CPEB3 ribozyme with auxiliary constructs of domains P1 (red), P2 (green) and P4 (blue)

Financial support by the Swiss National Science Foundation is gratefully acknowledged.

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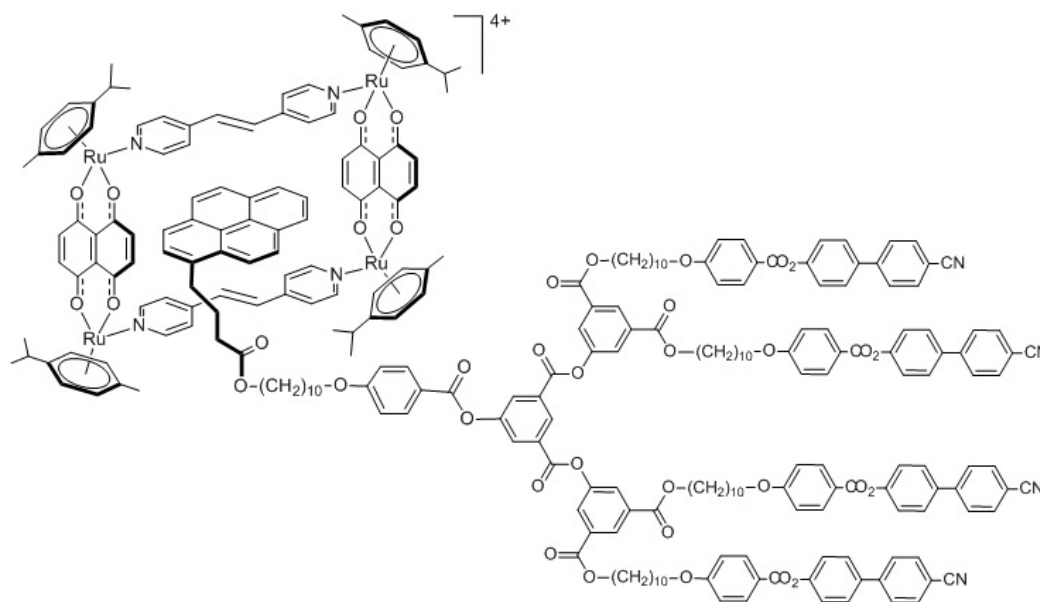
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## Designing supramolecular liquid-crystalline materials from pyrenyl-dendrimers by encapsulation in metallacycles.

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Metallacontainers have garnered great deal of attention owing to their prominent applications in different fields like molecular recognition, host-guest chemistry, crystal engineering, biomedical, and molecular devices.<sup>1</sup> Herein, arene ruthenium metallacycles containing pyrenyl-dendrimers are reported. This kind of hybrid metallogens combines the properties of metal ions and the mesogenic nature of dendrimers. These hybrid materials can generate compounds with interesting magnetic, optical or electro-optical properties. The cavity of these systems leads to the complexation of the pyrenyl moiety in the hydrophobic cavity of the cage, while the dendritic functions remain outwards.<sup>2</sup> This arrangement has allowed us to design a new supramolecular system with liquid-crystalline properties.<sup>3</sup>



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**Rational design of tetranuclear d-f complexes with ditopic Janus-type aromatic ligands**M. Asadniaye Fardjahromi<sup>1</sup><sup>1</sup>Department of Inorganic Chemistry, University of Geneva, 30 quai E. Ansermet, CH-1211 Geneva 4, Switzerland

Ditopic ligands have been recently attracted much attention since they open novel possibilities and perspective in coordination chemistry and material science [1]. Ditopic ligands containing two separate bidentate and tridentate binding units are well-suited because of their unique physicochemical properties [2]. In this study, new synthetic strategies have been exploited for the preparation of tetra nuclear complexes containing d and f block metal ions (Figure 1). The first synthetic step consists of the preparation of preorganized ditopic Janus-type ligands [3] followed by the coordination of transition metal ion with the bidentate site. Further reaction of the complex with labile nine-coordinated Ln(III) results in the formation of the targeted tetranuclear d-f complexes (Figure 1). In this contribution, chemical requirements and design favoring the formation of the tetranuclear d-f complex will be presented.

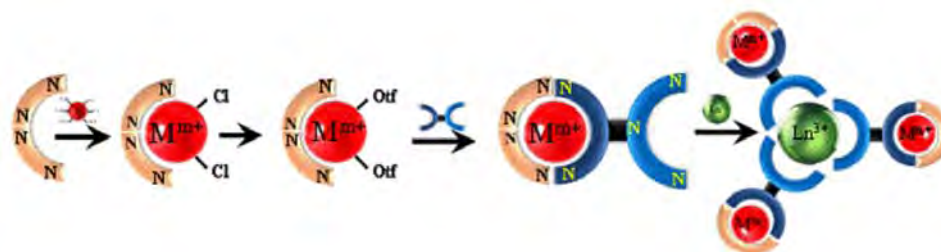


Figure1. Synthesis of tetra nuclear d-f complexes

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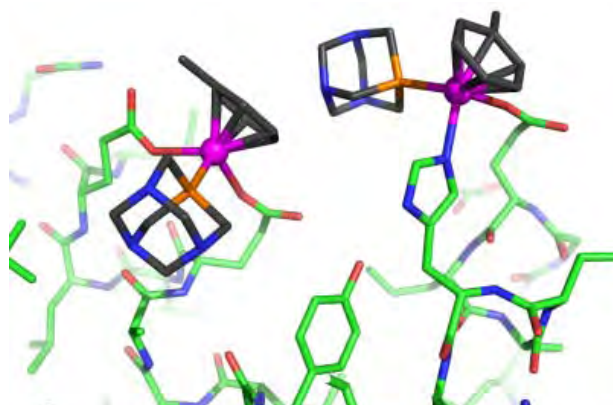
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**Exploitation of the allosteric relationship between RAPTA T and Auranofin on the Nucleosome Core Particle in the design of novel anti-cancer agents.**

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Dinuclear metal complexes have emerged as a promising class of biologically active molecules that display interesting anti-cancer activity and properties. As a consequence, both homo- and hetero-bimetallic combinations are being explored. An allosteric relationship between RAPTA-T, a ruthenium(II) anti-tumoral, and Auranofin, a gold(I) anti-rheumatic drug, is observed on nucleosome core particle (NCP). The binding of RAPTA-T to the surface of H2A-H2B dimer induces a kink in the long  $\alpha$ -helix of the H2A histone protein that enables Auranofin to bind to two previously inaccessible sites.<sup>[1],[2]</sup> This allosteric relationship has been exploited to design and synthesize two generations of hetero-ruthenium(II)-gold(I) complexes. The design is based on crystallographic and computational data with the aim of simultaneously binding to the sites of the parent drugs, Auranofin and RAPTA-T, on the NCP. Here, we demonstrate that a single hetero-bimetallic ruthenium(II)-gold(I) complex can cause the same allosteric effect as the binding of mono-nuclear RAPTA-T and Auranofin.



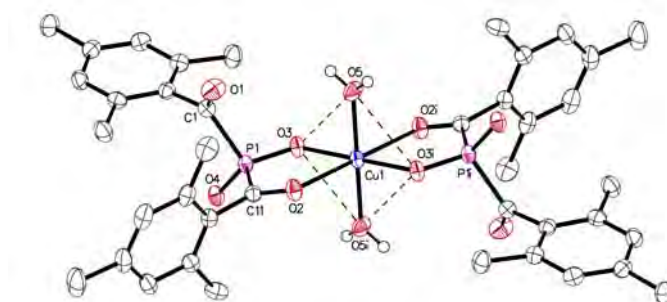
**Figure 1.** Binding sites of the RAPTA-T moiety on the histone component of the NCP.

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**Bismesitylphosphinic Acid (BAPO-OH) as 4-Electron Photoreductant for the Preparation of various Cu Nanomaterials and related Cu complexes**A. Beil<sup>1</sup>, G. Müller<sup>1</sup>, H. Grützmacher<sup>1\*</sup><sup>1</sup>ETH Zürich, Laboratorium für Anorganische Chemie, Vladimir-Prelog-Weg 1, 8093 Zürich

We present the readily available photoinitiator bismesitylphosphinic acid (BAPO-OH)<sup>[1, 2]</sup> as 4-electron photoreductant for the high yielding reduction of aqueous Cu(II) to obtain metallic copper. The diverse coordination behavior of BAPO-OH towards copper was investigated by single crystal X-ray crystallography. The described method allows access to colloidal Cu(0) and nanoscopic Cu particles of various size and morphology. This was shown by dynamic light scattering (DLS), scanning electron microscopy (SEM) and scanning transmission electron microscopy (STEM). X-ray powder diffraction confirmed the purity of the obtained Cu samples. A Cu(II) complex of BAPO-OH can be applied as both, a photoinitiator for the preparation of hydrogels and a reagent for the spatiotemporally controlled production of Cu(0) in the already cured material.<sup>[3]</sup>



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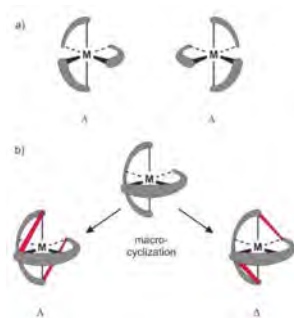
The authors are grateful to Z. Li (Sun Yat-Sen University, Guangzhou, China), F. Krumeich, D. Käser, B. Hattendorf, A. Rosenthal, M. Wörle and H. Schönberg (all ETH Zürich)

## Chiral Macrocyclic Terpyridine Complexes

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Since the pioneering work of Louis Pasteur [1], chirality is a physical chemical property in the center of interest of chemical structures and transformations. Besides chirality induced by stereogenic centers, axial chirality emerges from the helical arrangement of the molecule's subunits [2]. A prominent school book example for a helical chiral metal complex are tris(2,2'-bipyridine)-M(II) derivatives. The three ligands wrap around the central metal in a helical arrangement, resulting in a spatial arrangement which resembles a ship's screw. The two enantiomers are distinguished by the helicity of the arrangement between the left-handed (L) and right-handed (D) isomer (Figure 1a) [3]. Going from 2,2'-bipyridine to 2,2':6',2''-terpyridine an additional binding site is introduced. The two ligands are arranged perpendicular to each other and the helical chirality is lost. Two terpyridines facing each other in the periphery of macrocycles complemented by additional coordination sites resulted in chiral metal complexes. Prominent examples were only reported as racemic mixture [4,5]. Here we present our new strategy to introduce axial chirality into metal terpyridine complexes, namely by twofold interlinking of the ligands surrounding the metal ion. The concept is sketched in figure 1b) and can also be described as template supported macrocyclization reaction. The two terpyridine close a macrocycle which has been preorganized (templated) by the formation of the metal-terpyridine complex. The terpyridines are complemented by two *ortho*-ethynylphenyl moieties in 4 and 4'' positions allowing for macrocyclization by *Glaser-Hay* type oxidative acetylene coupling chemistry.



**Figure 1:** Sketch of axial chirality in metal complexes: a) axial chirality with bidentate ligands (e.g. 2,2'-bipyridine). b) Concept of introducing chirality by macrocyclization. *Top:* Achiral complex of a tridentate ligand (e.g. 2,2':6',2''-terpyridine). *Bottom:* Axial chiral metal complexes obtained by interlinking the ends of the two tridentate ligands (interlinking bridges in red).

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## Phosphine tuning for heteroleptic $[\text{Cu}(\text{N}^{\wedge}\text{N})(\text{P}^{\wedge}\text{P})][\text{PF}_6]$ in light emitting electrochemical cells

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Light emitting electrochemical cells (LEECs) are of growing importance in the field of flexible electronics and large surface lighting devices. Their simple device architecture, consisting of one emissive layer sandwiched between two electrodes (of which one has to be transparent) and the use of air stable materials make them fundamentally suitable for large area lighting as well as display applications. The emissive material usually consists of a semiconducting polymer or an emissive ion transition metal complex (iTMC) mixed with ionic liquid. Indium tin oxide (ITO) covered glass and aluminum are used readily as electrode materials. The emissive layer can be easily deposited by solution based methods such as spin coating, which makes the fabrication of a LEC fairly simple and less complex than the fabrication of e.g. an OLED (organic light emitting diode).

In the past iridium based transition metal complexes have been widely used in LECs. Their excellent colour tunability and the extremely long lifetime of the device of up to several thousand hours have led to the development of a wide range of iridium complexes for LEC applications. But the main drawback of iridium as a key compound is the low availability and the associated high costs of the material. Therefore scientists soon began to search for alternative metals for LEC applications. One very promising candidate was found to be copper. The high availability and low cost of this metal make it a suitable candidate for lighting applications.<sup>[1]</sup>

Heteroleptic copper complexes of the type  $[\text{Cu}(\text{N}^{\wedge}\text{N})(\text{P}^{\wedge}\text{P})][\text{PF}_6]$  where  $\text{N}^{\wedge}\text{N}$  is a chelating diimine and  $\text{P}^{\wedge}\text{P}$  is a chelating diphosphine ligand show strong emission upon excitation on an MLCT (metal-to-ligand charge transfer) level as well as in electroluminescence. The key aspect of these complexes is to sterically tune the copper coordination sphere to maintain the metal in a tetrahedral environment and shield it from access by small molecules such as solvents or oxygen. This preserves the copper in the oxidation state +I which is essential for the emissive nature of the compound.<sup>[2]</sup>

In this work a series of new heteroleptic copper complexes is presented in which the phosphine ligand is tuned sterically and electronically to alter the emissive properties of the compound as well as the device functionality and lifetime.

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## Combining an asymmetric acid functionalized anchoring ligands with symmetric ancillary ligands in bis(diimine)copper(I) dyes in dye-sensitized solar cells

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The development of n-type dye-sensitized solar cells (DSCs) has made significant progress incorporating copper(I)-based dyes in order to replace the highly studied ruthenium(II) sensitizers used in conventional Grätzel cells which were first reported around two decades ago. Replacing the ruthenium(II) sensitizers by copper(I) dyes is of high interest in order to use more abundant materials and shift from rare metal sources on earth. Each copper dye has the composition  $[\text{Cu}(\text{L}_{\text{anchor}})(\text{L}_{\text{ancillary}})]^+$ .

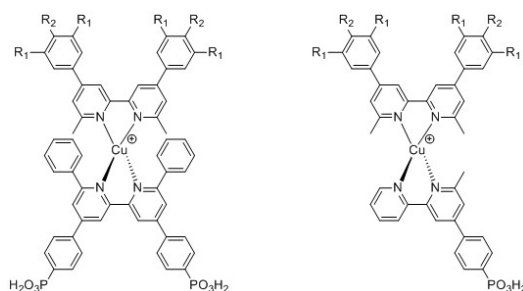
We have recently shown that by introducing phenyl substituents in the 6,6'-positions of the bipyridine anchoring moiety  $\text{L}_{\text{anchor}}$ , the light absorption can be improved towards the red-end of the visible spectra. Additionally, the bulkier substituents help to shield the copper(I) centre.

Even though we could overcome the problem of having a low spectral response in copper(I) based dyes by using our new anchoring ligand, a drawback was the bleaching of the heteroleptic dye adsorbed on the electrode surface which comes along with a low performance of the dye-sensitized solar cells. In order to overcome this problem we synthesized a series of 6-methyl-4-phenyl-2,2'-bipyridine asymmetrical ancillary ligands to remove the problem of steric crowding in the copper(I)bis(diimine) coordination sphere. Unfortunately the asymmetrical framework of the ancillary ligand in combination with the bulky anchoring ligand results in a low power conversion efficiency of the DSCs.

Following the results we achieved by combining the asymmetrical ancillary ligands with a phosphonic acid anchoring ligand we have now investigated the symmetrical analogues of these bpy-based ancillary ligands to quantify their performance within a dye-sensitized solar cell. <sup>[1]</sup>

The combination of these new ancillary ligands with the bulky anchoring ligand did not boost the solar to power conversion efficiency as expected.

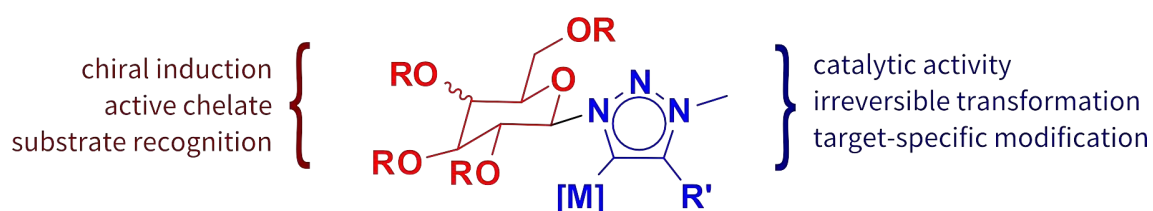
Therefore we investigated an asymmetric acid functionalized anchoring ligand to combine it with the symmetric series of ancillary ligands.



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**Carbohydrate-functionalised transition metal-NHC catalysts**J. P. Byrne<sup>1</sup>, M. Albrecht<sup>1\*</sup><sup>1</sup>University of Bern

N-Heterocyclic carbenes (NHC) have been demonstrated to be very versatile ligands in various catalytic systems[1]. We have shown the promise of 1,2,3-triazolyliidines as a class of NHC with broad applications for materials science and biochemistry[2] in addition to catalysis. Facile preparation through Cu(I)-catalysed CuAAC 'click' chemistry, and subsequent alkylation, makes these ligands very attractive. Here we report transition metal-NHC complexes with incorporated carbohydrate functionality in the ligand structure (see general structure in Figure 1).



Representing a natural pool of chirality and functionality, carbohydrates are an attractive class of substituent for providing defined stereochemistry and geometry to ligands, as well as being readily available. Their use as phosphine and phosphinite ligand scaffolds has previously shown promise in asymmetric catalysis.[3] However, similar work with NHCs is quite scarce.[4] Combining these two important classes of compound into a hybrid complex system will give rise to synergistic advantages for catalysis. Catalytic activity of these complexes is presented.

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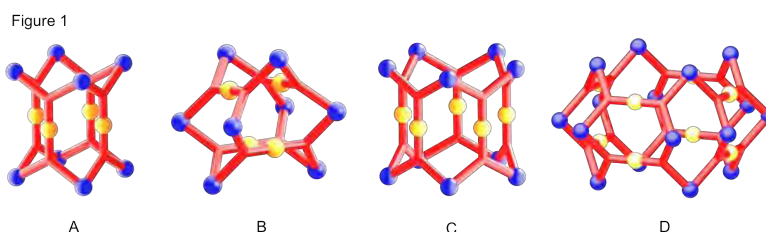
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## The Intricate Structural Chemistry of $M^{II}_{2n}L_n$ -Type Assemblies

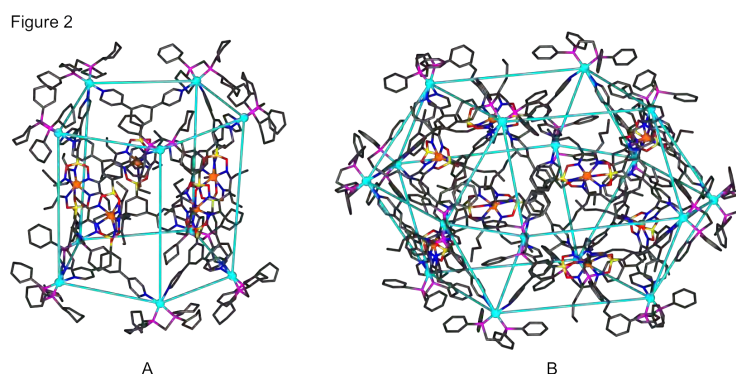
G. Cecot<sup>1</sup>, K. Severin<sup>1\*</sup>

<sup>1</sup>EPF Lausanne

By choosing an appropriate ligand, it is possible to influence the size, the geometry and the functionality of a metallasupramolecular assembly. Functionalized clathrochelate complexes have recently emerged as a promising new class of metalloligands for applications in supramolecular coordination chemistry. [1] The reaction of *cis*-blocked, square planar  $M^{II}$  complexes with tetratopic N-donor ligands is known to give metallasupramolecular assemblies of the formula  $M_{2n}L_n$ . We recently demonstrate that unusual geometries are accessible like the  $Pt_8L_4$  cage with gyrobifastigium-like geometry. [2] A geometric analysis of the ligands could explain how size and geometry influence the self-assembly process. The metalloligands used gave assemblies of type  $Pt_8L_4$ , which adopt barrel- or gyrobifastigium-like structures (Figure 1A and 1B). Larger assemblies are possible, as  $Pt_{10}L_5$  complex and a  $Pt_{16}L_8$  complex (Figure 1C and 1D). The latter has a molecular weight of more than 23 kDa and a diameter of 4.5 nm, making it the largest, structurally characterized  $M_{2n}L_n$  complex described to date.



By X-ray crystallography, we characterize both new of  $M_{2n}L_n$  complexes, namely a pentagonal  $Pt_{10}L_5$  barrel and a  $Pt_{16}L_8$  complex (Figure 2A and 2B). The latter assembly displays an unprecedented square orthobicupola geometry. Overall, we think that our study will provide an important foundation for future investigations of coordination barrels.



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## New Monometallic and Heterobimetallic Complexes of Silver(I), Zinc(II) and Copper(II) with an Amino Acid Derived Ligand as Potential Antimicrobial Agents

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<sup>1</sup>University of Fribourg

Nowadays, multiresistant bacteria are gaining more and more ground: Once very effective antibacterial drugs cannot prevail anymore over certain bacteria. Thus, scientists are bothering to invent new compounds: Some focusing to create new derivatives of famous antibiotics like Penicilline, others getting back to synthesize complexes with precious or essential metals as they are known since antiquity for their antimicrobial properties. It has not only been an old tradition to throw silver coins in fountains but rather to keep the drinking water free of microbes owing to the antimicrobial activity of this precious metal. Even the ancient Greeks and Romans drank instinctively from silver vessels to keep the liquids fresh or ate from silver plates.<sup>[1]</sup> It has been found that silver ions damage the DNA of bacteria by interfering with guanine and adenine base pairs<sup>[2]</sup> and that they induce an overproduction of reactive oxygen species (ROS) such as hydroxy radicals by disrupting the metabolic pathways of Fenton chemistry.<sup>[3,4]</sup> Furthermore, it is known that silver ions interact strongly with thiol groups and inhibit or degrade therefore the disulfide bond formation in many proteins and enzymes. This leads finally to the increase of the bacterial membrane permeability.<sup>[3]</sup>



Based on our extensive experience with antimicrobial silver compounds<sup>[f.ex.4,6]</sup>, and silver resistance of bacteria<sup>[4,5]</sup>, we now present combinations of silver ions with zinc or copper ions in bimetallic complexes with *p*-amino-L-phenylalanine to create a synergistic antimicrobial effect in order to fight more efficiently against bacteria.

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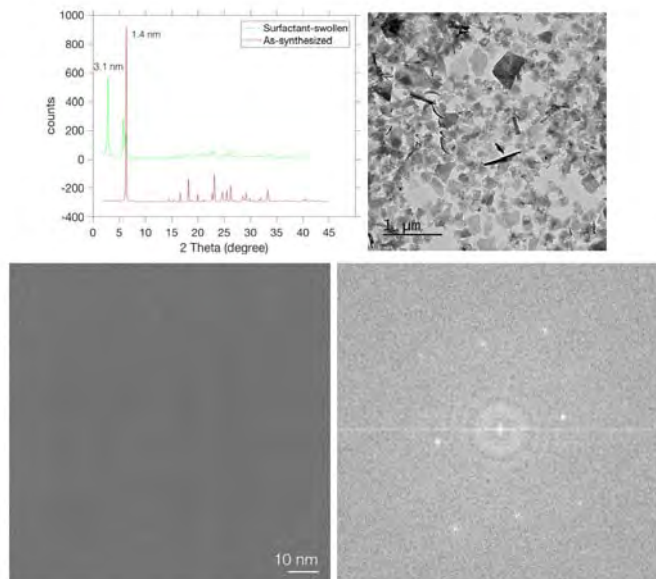
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**Two-dimensional atomically bridged nanoporous silicate**M. Dakhchoune<sup>1</sup>, K. Agrawal<sup>1\*</sup><sup>1</sup>École Polytechnique Fédérale de Lausanne

Two-dimensional nanoporous materials are highly attractive for the synthesis of the next-generation membranes, capable of delivering gigantic permeance as well as a sharp molecular cut-off for energy-efficient separations. However, synthesis of such two-dimensional nanoporous sheets with a precise array of molecular hugging nanopores is not trivial. One of the leading approaches to achieve this is the top-down synthesis involving the crystallization of a layered nanoporous material followed by exfoliation of layers. Herein, for the first time, we report a nm-thick, two-dimensional silicate, RUB15-nanosheet, consisting of atomically bridged arrays of 4 and 6-member silica rings, synthesised by exfoliation of layered RUB-15, a precursor to the sodalite zeolite.

RUB-15 layers were synthesised by the hydrothermal synthesis route using a modified method reported by Gies and co-workers [1]. The as-made material was confirmed to be RUB-15 using X-ray diffraction, Si29 MAS NMR and electron diffraction. Ion-exchange of RUB-15 with a C16-cationic surfactant was performed in order to increase the inter-layer spacing from 14.2 Å to 30 Å. Finally, the atom-thick single layer silicate (RUB-15 nanosheets) was achieved by the melt compounding technique reported before by our group [2-3]. RUB15-nanosheet crystallinity was investigated by TEM and HRTEM, which confirmed a highly crystalline orthorhombic structure. A uniform thickness-contrast in TEM along with the height profile in AFM mapping of nanosheets confirmed a successful exfoliation.



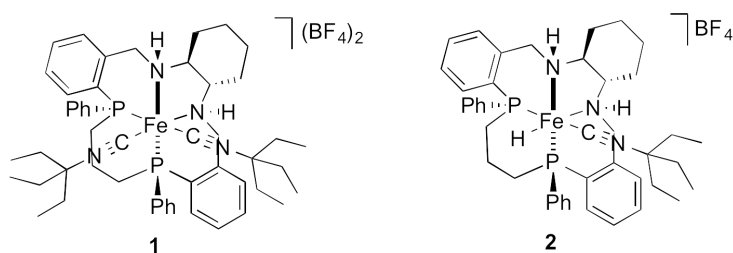
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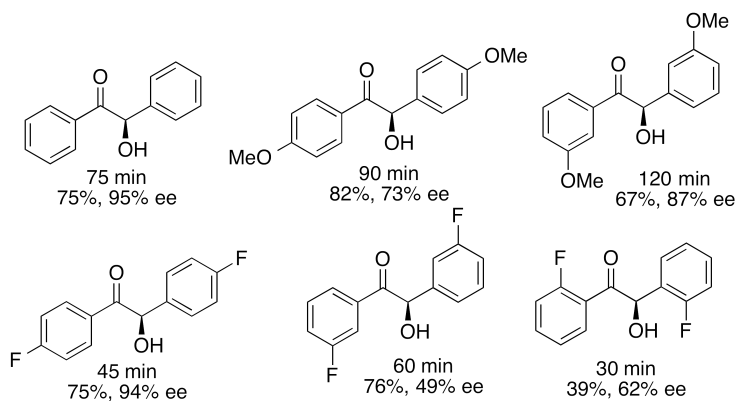
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**Base-Free Asymmetric Transfer Hydrogenation of Base-Sensitive Ketones**L. De Luca<sup>1</sup>, A. Mezzetti<sup>1\*</sup><sup>1</sup>ETH Zürich

In general, the iron(II) catalysts employed in the asymmetric transfer hydrogenation of ketones (ATH) require basic conditions, which sets severe limitations to the reaction scope. Upon base activation, the catalyst  $[\text{Fe}(\text{CNR})_2(\text{N}_2\text{P}_2)]^{2+}$  (**1**) recently reported by our group has shown high activity (up to >99.5% yield) and enantioselectivity (up to 99% ee) in the ATH of polar double bonds. [1] In order to broaden the substrate scope to base sensitive substrates, we prepared the hydrido isonitrile complex **2**, which does not require base activation as it bears the HFeNH motif responsible for hydrogen transfer.



Complex **2** catalyzes the asymmetric transfer hydrogenation of base-sensitive substrates, such as benzils, in good yield and excellent enantioselectivity without the addition of base.



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## Controlling the Selectivity in Ethenolysis of Cyclic Olefins with Ru-Based Metathesis Catalysts via Ancillary NHC Ligands: A Structure Activity Study

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Cross-metathesis reaction between cyclic olefins and ethylene (ethenolysis) yields valuable terminal dienes.<sup>1</sup> While ethenolysis of ethyl oleate with Grubbs-type Ru metathesis catalysts has been widely studied<sup>2</sup> there currently are only a few reports on ethenolysis of cyclic olefins with Ru catalysts,<sup>3</sup> presumably due to the high activity of Grubbs-type initiators in the ring opening metathesis polymerization. Supporting ligands can greatly influence the selectivity of Ru catalysts.<sup>4</sup> For instance, ruthenium metathesis catalysts with unsymmetrical N-trifluoromethyl NHC ligands display an unusually high selectivity (80–90%) for terminal olefins in ethenolysis of ethyl oleate.<sup>5</sup> In the present work we tested 28 isostructural Ru metathesis catalysts featuring various NHC ligands in ethenolysis of *cis*-cyclooctene as a model substrate. Our study identified the dissymmetry of the NHC ligand as a key structural feature for improving the chemoselectivity to the terminal diene from 12% for the benchmark second-generation Grubbs catalyst up to 53% for the catalyst containing an unconventional CF<sub>3</sub>-functionalized NHC ligand. To rationalize the experimental results, a computational study was conducted that explained the observed dependence via the univariate correlations of activity to electronic and steric properties of the ligand. The optimal catalyst compared favorably to the Grubbs 2<sup>nd</sup> generation catalyst in ethenolysis of other cyclic olefins including functionalized norbornenes.

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## Synthesis, Magnetism and Reactivity of Hetero-Polymetallic Uranyl(V) Schiff-base complexes

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Uranium is one of the most investigated actinides due to its various applications and relatively low radioactivity in comparison to the other actinides. The chemistry of uranyl(V) is particularly relevant for understanding the migration of uranium in the environment and developing depollution strategies. Uranyl(V) compounds, also possess exceptional interest for the design of exchange-coupled molecular magnets<sup>[1]</sup>. In this decade a few uranium(V) compounds were synthesized<sup>[2],[3],[4],[5]</sup>, but the chemistry of uranyl(V) complexes remains under-explored due to the inherent instability of U(V) towards disproportionation reaction in both aqueous and organic solvents to yield uranium(IV) and uranyl(VI) products.

Here we will report the synthesis and reactivity of several stable 3d-5f hetero-polymetallic coordination complexes containing uranyl(V). We will also present the effect of iron binding on the complexes structure, reactivity and magnetic properties.

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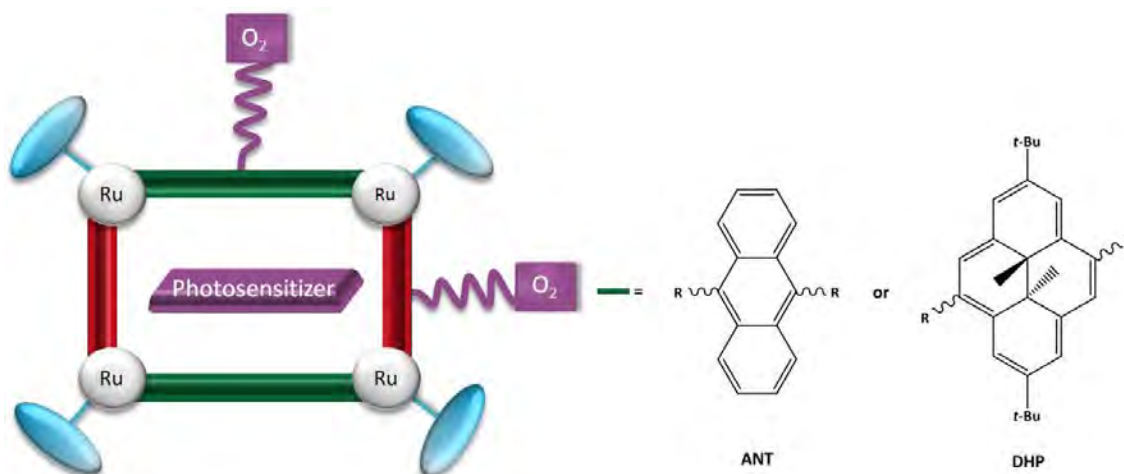


**Development of organometallic assemblies for PDT**M. Gaschard<sup>1</sup>, B. Therrien<sup>1\*</sup><sup>1</sup>Université de Neuchâtel

Photodynamic therapy (PDT) treatments represent a promising alternative to treat cancers. PDT involves the injection of a photosensitizer, which is later on activated by light at a specific wavelength. Upon an irradiation in a spatial-controlled area, the photosensitizer reaches a high-energy triplet state and, when returning to its ground state, an energy transfer toward cellular oxygen occurs. The reactive oxygen species appear in the surroundings of the irradiated zone and can later destroyed cancerous cells. Therefore, such PDT treatments need oxygen to be effective, which can be problematic when treating hypoxic cancers.[1]

Some already known compounds can be converted into their endoperoxide forms to reversibly transport singlet oxygen (<sup>1</sup>O<sub>2</sub>), such as anthracene (ANT)[2] or dimethyldihydropyrene (DHP)[3]. They offer great perspectives for biological applications, especially for PDT treatments.

The project consists of preparing metalla-assemblies to transport both the photosensitizer and <sup>1</sup>O<sub>2</sub> to cells. DHP or ANT units can be attached to the assembly as connectors between the dinuclear arene ruthenium clips or inserted as appendages on the different building blocks. The cavity of the metalla-assembly can also be used to transport a photosensitizer.[4]



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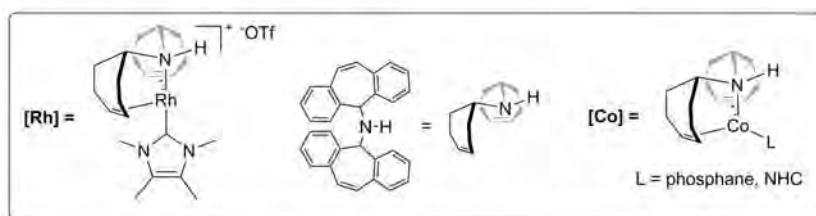
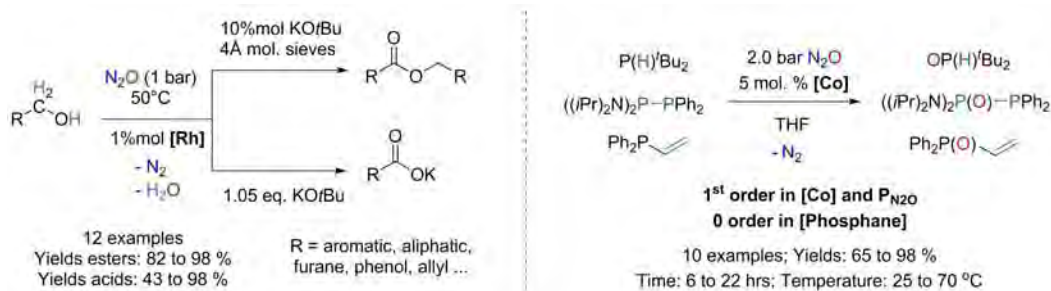
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## Toward a useful catalytic transformation of N<sub>2</sub>O using group 9 organometallic complexes

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<sup>1</sup>ETH Zürich, Department of Chemistry and Applied Biosciences, Vladimir Prelog Weg 1, 8093 Zürich, Switzerland

Nitrous oxide (N<sub>2</sub>O) gases have been recently identified as the largest global ozone depleting agents and as the 3<sup>rd</sup> largest emitted greenhouse gases worldwide and 300 times more powerful than CO<sub>2</sub>.<sup>[1]</sup> N<sub>2</sub>O is naturally produced via nitrification and denitrification of nitrate during nitrogen cycle, but is also an industrial waste. N<sub>2</sub>O emission has increased significantly during industrialization as a result of agricultural soil management, N-fertilizer use, livestock waste management, mobile & stationary fossil fuel, combustion and industrial processes. Its transformation to less harmful chemicals is of particular interest but very challenging, since even if thermodynamically unstable, nitrous oxide is kinetically inert.<sup>[2]</sup> We have successfully design low valent and reactive organometallic species containing group 9 metals (Rh<sup>[3]</sup> and Co<sup>[4]</sup>) that activate and catalytically transform, under mild conditions, this environmentally unfriendly molecules to valuable chemicals.



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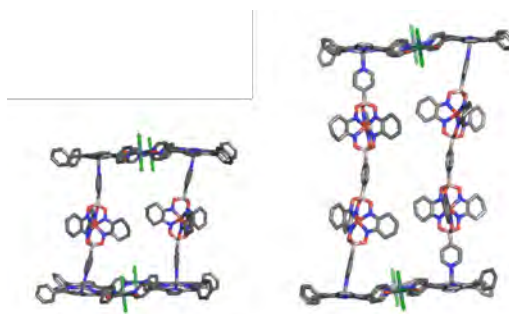
## Heterotrimetallic assemblies based on Zn(II)-porphyrin metallacycles and dipyridyl-capped Fe(II)-clathrochelate complexes.

E. Giraldi<sup>1</sup>

<sup>1</sup>EPF Lausanne

In supramolecular coordination chemistry, metalloporphyrins and dipyridyl-capped clathrochelates are suitable and versatile building blocks for the construction of a variety of increasingly complex 2D and 3D metallosupramolecular architectures.<sup>1,2</sup> Over the past few years, a modular strategy has been developed for the synthesis of multiporphyrinic discrete systems and coordination cages of different size and geometry based on pyridyl-capped clathrochelates.<sup>3,4</sup>

New multiporphyrinic discrete systems were obtained by self-assembly of Ru(II)-based metallacycles of Zn(II)-porphyrins, [*trans*, *cis*, *cis*-RuCl<sub>2</sub>(CO)<sub>2</sub>(Zn•4'-*cis*DPyP)]<sub>2</sub>, and dipyridyl Fe(II)-clathrochelates of tunable length up to 3.2 nm. These heterotrimetallic assemblies, bearing two bridging mono- and dinuclear clathrochelate ligands axially connected to the Zn(II)-metallacycles, were fully characterized by 1D and 2D NMR spectroscopy, including <sup>1</sup>H DOSY analysis, and by X-ray crystallography. A preliminary investigation on the self-sorting behaviour of mixtures of different type of Fe(II)-clathrochelate ligands and Zn(II)-porphyrin metallacycle was performed by <sup>1</sup>H NMR spectroscopy. A library of new 3D heterotrimetallic supramolecular systems with extended dimensions spanning 2.0 nm to 3.0 nm and increased number of metallic cores was assembled by separate combination of Zn(II)-metallacycles and dipyridyl Fe(II)-clathrochelate complexes. Introduction of these new discrete supramolecular assemblies looks promising for future potential application, due to their stability and the presence of metal-active centres and peripheral antenna units.



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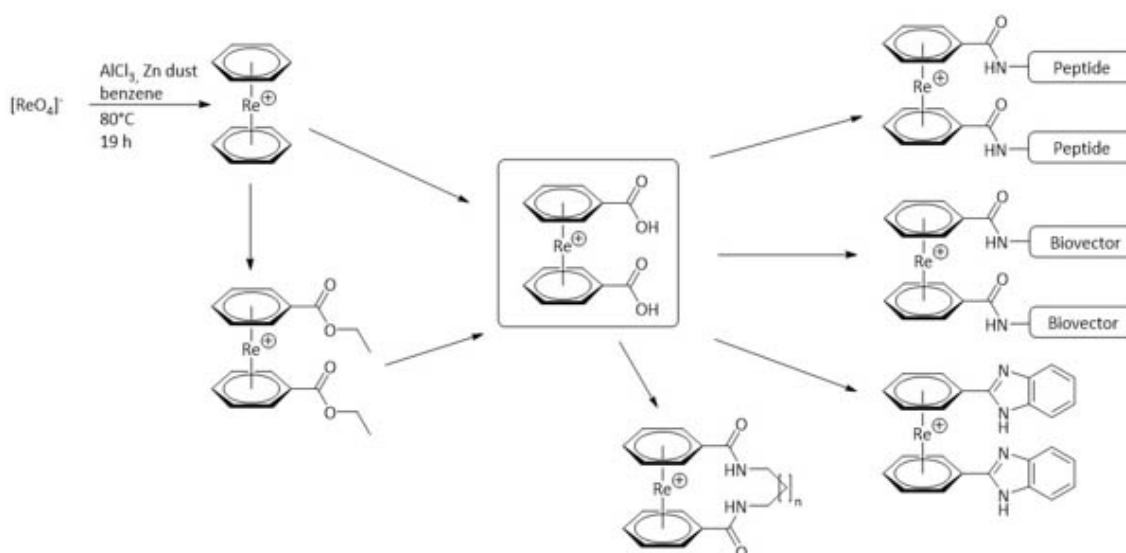
## Synthesis and Derivatisations of $[\text{Re}(\eta^6\text{-C}_6\text{H}_5\text{COOH})_2]^+$

C. Gotzmann<sup>1</sup>, H. Braband<sup>1</sup>, R. Alberto<sup>1\*</sup>

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Functionalised bis-arene complexes of transition metals are used as precursors for numerous reactions with applications in different fields, including medicinal inorganic chemistry and bioorganometallic chemistry.<sup>[1-4]</sup> Recently, functionalised  $[\text{M}(\eta^6\text{-arenes})_2]^{n+}$  sandwich complexes, containing the  $d^6\text{-}\{\text{Ru}\}^{2+}$  and  $\{\text{Os}\}^{2+}$  cores attracted attention as potential anti-cancer agents.<sup>[1,5]</sup> The introduction of functionalities in  $d^6\text{-metal}$  bis-arene complexes with chromium and molybdenum has also been described but studies with those complexes are comparably rare in bioorganometallic chemistry. Studies with group 7 bis-arene compounds (Re and Tc) are very rare in any respect, although their syntheses were already described in the 1960s.<sup>[1]</sup>

Searching for new organometallic building blocks for imaging ( $^{99\text{m}}\text{Tc}$ ) and therapy (Re) in the context of theranostics, our group introduced a new synthetic route for the synthesis of the precursor complex  $[\text{Re}(\eta^6\text{-C}_6\text{H}_6)_2]^+$  directly from  $[\text{ReO}_4]^-$ .<sup>[1,6]</sup>



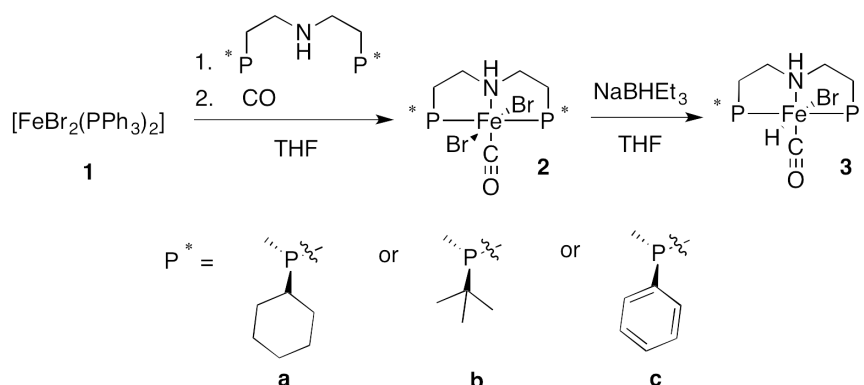
This work focuses on an improved synthetic pathway to  $[\text{Re}(\eta^6\text{-C}_6\text{H}_5\text{COOH})_2]^+$ . Beside the high chemical stability of these complexes and its inertness towards oxidation and hydrolysis, the carboxylic groups represent a core feature for derivatisations with targeting moieties via amid bond formation. Amino acids, peptides or other biomolecules can conveniently be introduced along this approach.

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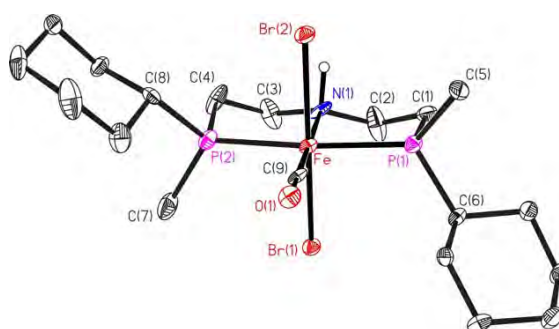
## Chiral Iron(II) PN(H)P Pincer Complexes for the Asymmetric Hydrogenation of Ketones

E. Gubler<sup>1</sup>, A. Mezzetti<sup>1\*</sup><sup>1</sup>ETH Zürich

Iron(II) complexes of PN(H)P pincer ligands are active catalysts in the direct hydrogenation of ketones,<sup>1</sup> and also enantioselective versions appeared.<sup>2,3</sup> Based on our long-term experience in the synthesis of chiral phosphine ligands, we prepared enantiopure, *P*-stereogenic, *C*<sub>2</sub>-symmetric PN(H)P pincer ligands and their iron(II) complexes, which will be tested in the asymmetric hydrogenation of ketones.



The enantiopure pincer ligand **a** bearing cyclohexyl and methyl substituents on each P atom was obtained in a 7-step synthesis from PC<sub>3</sub>. Starting from the iron(III)-free iron precursor **1** and ligand **a**, the blue precatalyst [FeBr<sub>2</sub>(CO)(**a**)] (**2a**) formed immediately upon setting the reaction mixture under CO atmosphere (1.1 bar). Complex **2a** (see X-ray structure below) was converted into the hydride **3a**, which showed good activity but low selectivity (22% ee) in the hydrogenation of acetophenone at room temperature in toluene. We are currently preparing ligands with sterically more demanding dialkylphosphine donors (such as **b**) and arylalkylphosphine donors (such as **c**) to improve the enantioselectivity.



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## Synthesis of Nanocrystalline Iron(III) trifluoride from Molecular Precursors and its Li- and Na-ion Storage Properties

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The performance demands placed on batteries for the use in electrical mobility and portable devices are enormous. Cathode materials remain a bottleneck for the further increase on energy density. A promising candidate compound featuring low cost and high natural abundance is iron trifluoride (FeF<sub>3</sub>). It has been demonstrated that FeF<sub>3</sub> intercalates lithium with near theoretical capacity of 237 mAh/g [1], also with promising rate capability [2]. However, there remains a strong need to develop low-cost synthesis methods for this material in a nanoscale form, needed for maximizing the performance. Herein, we show a new synthesis for nanocrystalline FeF<sub>3</sub> based on a thermal decomposition of an organic precursor. Such inexpensive FeF<sub>3</sub> can be charged and discharged in a lithium half-cell at a reversible capacity of 155 mAh/g within 1 min (10 A/g) or even faster. After 100 cycles, a capacity retention of 88 % has been achieved. In a sodium-ion half-cell, a capacity of 160 mAh/g at a current rate of 0.2 A/g could be measured. [3]

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**N-heterocyclic carbene complexes of Silver(I) for C-C bond activation of alkylnitriles and catalytic oxazoline synthesis**R. Heath<sup>1,2</sup>, E. Keske<sup>2</sup>, M. Albrecht<sup>1,2\*</sup><sup>1</sup>Universität Bern, <sup>2</sup>University College Dublin

N-heterocyclic carbenes (NHCs) are increasingly prevalent ligands for the synthesis of organometallic complexes and in homogeneous catalysis [1]. Reaction of azolium salts with Ag<sub>2</sub>O afford Ag-NHC complexes, which are commonly transmetallated *in situ* to different metals [2]. However, to date little attention has been paid to the Ag-NHC intermediates regarding complex formation and potential catalytic applications [3].



We describe that generation of Ag-NHC complexes from azolium salts in refluxing CH<sub>3</sub>CN results in a selective C-C bond cleavage and formation of [(NHC)Ag(CN)] complexes; which can also be extended to other alkyl nitrile reagents [4].

Additionally, we will present the catalytic performances of a series of Ag-NHC complexes for the synthesis of oxazolines *via* aldol condensation. These highly active systems reveal relatively unexplored applications of easily accessible silver carbene complexes.

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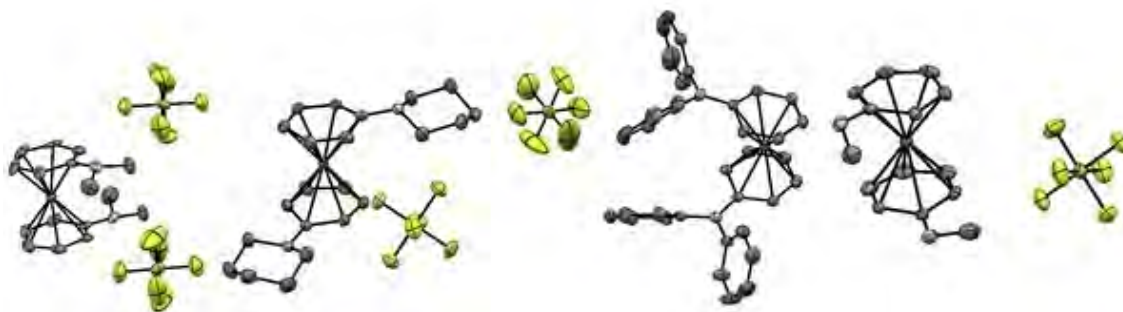
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**Towards the direct synthesis of nitrogen functionalized bis arene complexes of Re and  $^{99(m)}\text{Tc}$** D. Hernández Valdés<sup>1</sup>, G. Meola<sup>1</sup>, H. Braband<sup>1</sup>, B. Spingler<sup>1</sup>, R. Alberto<sup>1\*</sup><sup>1</sup>University of Zurich, Winterthurerstrasse 190, CH-8057 Zurich, Switzerland

Functionalized sandwich complexes of transition metals are used as precursors for numerous reactions with applications in different fields, including medicinal inorganic chemistry and catalysis<sup>1-3</sup>. Re(I) and  $^{99(m)}\text{Tc(I)}$  bis arene complexes represent a new promising route to low valent, nonpolar, and inert compounds<sup>1</sup> and could represent building blocks for the development of new potential pharmaceuticals and catalyst. The synthesis of technetium and rhenium bis arene complexes was first established by Fischer and Hafner in the 1950s and 1960s using  $\text{AlCl}_3$  as an activation agent. More recently, some modification to the synthesis have been done by Kudinov<sup>3</sup> and in our group<sup>1</sup> but still  $\text{AlCl}_3$  is needed in the reaction. The high reactivity of  $\text{AlCl}_3$  limits the synthesis of Re(I) and  $^{99(m)}\text{Tc(I)}$  bis arene complexes to only alkyl arene substituents. Here, we present the first direct synthesis of nitrogen functionalized bis arene complexes of rhenium(I). Different ligands presenting  $\text{sp}^3$  and  $\text{sp}^2$  nitrogen were evaluated. Whereas the presence of  $\text{sp}^2$  nitrogen in the ligand hampers the formation of sandwich complexes, promising results have been obtained for ligands containing  $\text{sp}^3$  nitrogen. The synthesis of  $[\text{Re}(\text{N,N-dimethylaniline})_2]^+$  analogue was performed following Benz procedure<sup>1</sup> as a proof of applicability in technetium chemistry. Optimization of reaction conditions and purification procedures, as well as the search for other suitable ligands are currently on going.

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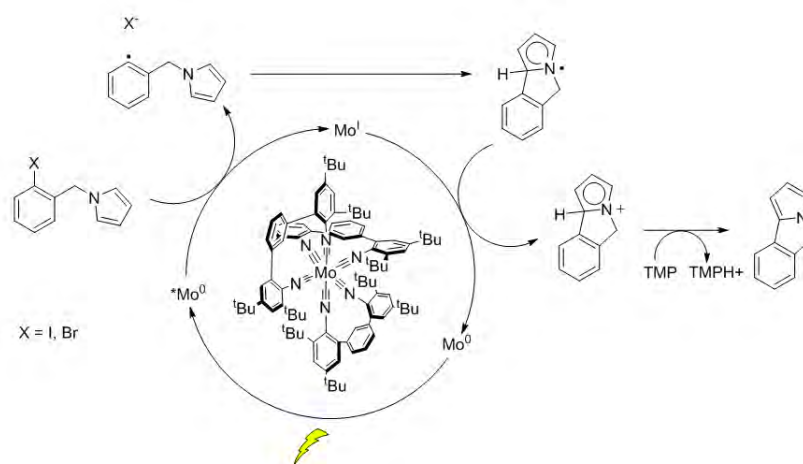


**A Bidentate Mo(0) Isocyanide Complex is a Powerful Photoredox Catalyst**P. Herr<sup>1</sup>, L. A. Büldt<sup>1</sup>, C. B. Larsen<sup>1</sup>, O. S. Wenger<sup>1\*</sup><sup>1</sup>University of Basel

Photoredox catalysis has received significant attention in recent years, providing mild reaction conditions for a wide range of photoreactions in organic syntheses.[1] However, this class of reactions is often limited by the reducing power of the photocatalysts. To further improve the substrate scope, the development of stable photocatalysts capable of performing more demanding chemical transformations is desirable.

We demonstrated that bidentate isocyanide complexes of molybdenum(0) can act as strong photoreductants.[2,3] With an excited state oxidation potential of -1.9 V vs. SCE, the Mo(0) complex in Scheme 1 is 0.2 V more reducing than the widely used [Ir(ppy)<sub>3</sub>] complex.

We present the photophysical properties of this Mo(0) complex and demonstrate its application in photoredox catalysis. A specific example is the photocatalytic base-promoted homolytic aromatic substitution (BHAS) reaction shown in Scheme 1.



**Scheme 1:** Catalytic cycle for the photocatalysed base-promoted homolytic aromatic substitution (BHAS) reaction using a Mo(0) isocyanide complex.

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**Boc( $\beta$ ala) $_2$ N $_2$ H $_3$  and its interaction with silver**A. Holzheu<sup>1</sup>, A. Crochet<sup>1</sup>, K. M. Fromm<sup>1\*</sup><sup>1</sup>University of Fribourg

**INTRODUCTION:** For centuries it is known that silver possesses antimicrobial properties. It was regularly used for the treatment of burns, wounds and several bacterial infections, but with the emergence of antibiotics it was nearly forgotten for almost 50 years<sup>1,2</sup>. Nowadays, due to the rising concern regarding infectious diseases induced by multidrug-resistant bacteria, silver has made a remarkable comeback as a potential antimicrobial agent<sup>2</sup>. Therefore, we study the antimicrobial effects of a dipeptide, Boc( $\beta$ ala) $_2$ N $_2$ H $_3$ , that has four potential silver coordination sites and the capability, due to the hydrazine end group, to reduce silver ions to silver nanoparticles (AgNPs). **METHODS:** To obtain the Boc( $\beta$ ala) $_2$ N $_2$ H $_3$  dipeptide, a standard liquid phase synthesis was used<sup>3</sup>. The dipeptide was characterized by <sup>1</sup>H- and <sup>13</sup>C-NMR, MS-ESI, thermal analysis (TGA, DSC), FT-IR and XRD measurements. Crystals were obtained in DMSO. <sup>1</sup>H-NMR and MS-ESI titrations were performed with Boc( $\beta$ ala) $_2$ N $_2$ H $_3$  and AgNO $_3$  in DMSO d $_6$  or D $_2$ O. AgNP formation with Boc( $\beta$ ala) $_2$ N $_2$ H $_3$  and AgNO $_3$  were recorded overnight by UV-Vis spectroscopy and analysed with TEM, MS-ESI and FT-IR. Different temperature conditions were hereby investigated. Antimicrobial tests were performed with *E.coli* (ATCC 25922) and Boc( $\beta$ ala) $_2$ N $_2$ H $_3$ . The OD $_{600}$  was taken over a time period of 24 h at 37 °C. **RESULTS:** Figure 1a represents the time-resolved formation of AgNP at pH 7 and 60 °C, while 1b depicts the obtained AgNPs. Figure 1c shows the crystal structure of Boc( $\beta$ ala) $_2$ N $_2$ H $_3$ . A first trial of silver complexation with Boc( $\beta$ ala) $_2$ N $_2$ H $_3$  by NMR titration gave a high-field shift for the hydrazine end group of 1.026 (NH $_2$ ) and 0.591 ppm (NH). Antimicrobial tests revealed an OD $_{600}$  of 0.7 for just *E.coli*, 0.68 for *E.coli* with 1 mg/ml Boc( $\beta$ ala) $_2$ N $_2$ H $_3$ , and 0.55 for *E.coli* with 2 mg/ml Boc( $\beta$ ala) $_2$ N $_2$ H $_3$  after 24 h of growth. **DISCUSSION & CONCLUSIONS:** The peptide crystallizes in the orthorhombic space group  $P2_12_12_1$ . The packing reveals three H-bonds of 2.03–2.13 Å, which connect the peptide molecules into 1D-ribbons, which are themselves connected in an anti-parallel fashion via H-bonds between the hydrazine groups to form dimers of ribbons. These dimers of ribbons are arranged in zigzag into layers, which are themselves assembled through short interactions into a 3D structure with a mean distance of  $\sim 2.3$  Å. First tests showed that Boc( $\beta$ ala) $_2$ N $_2$ H $_3$  is capable to form AgNPs at 40, 50 and 60 °C but not at RT. For 60 °C the highest absorbance was observed meaning that the reaction is temperature dependent. AgNP formation occurred over several hours, reaching in case of 60 °C sizes of 30 to 90 nm. The NMR titration showed that the interaction with silver takes place mainly at the hydrazine end group. The antimicrobial tests indicated a slight decrease in bacterial growth for 2 mg/ml of Boc( $\beta$ ala) $_2$ N $_2$ H $_3$ .



Figure 1: a) UV-VIS of AgNP formation with 1.25 mM Boc( $\beta$ ala) $_2$ N $_2$ H $_3$  and 1.25 mM AgNO $_3$  at pH 7 and 60 °C; b) TEM of 30-90 nm big AgNP formed, scale 2  $\mu$ m; c) Crystal structure of Boc( $\beta$ ala) $_2$ N $_2$ H $_3$ , R = 3.61 %

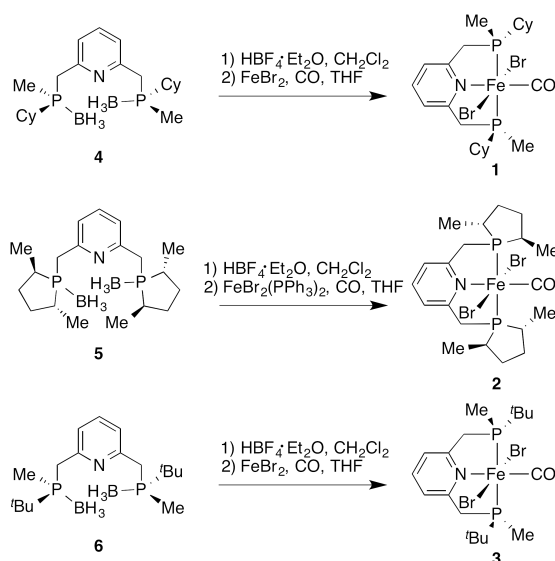
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## Iron(II) Complexes of Chiral, C<sub>2</sub>-Symmetric, P- or C-Stereogenic PNP Pincer Ligands and their Application in the H<sub>2</sub> Hydrogenation of Ketones

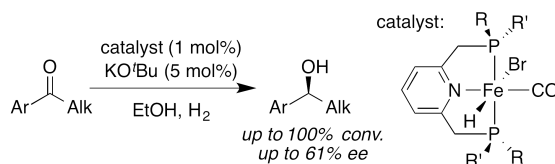
R. Huber<sup>1</sup>, A. Passera<sup>1</sup>, A. Mezzetti<sup>1\*</sup>

<sup>1</sup>ETH Zürich

Chiral pincer ligands for iron(II) have been recently developed and applied in the direct H<sub>2</sub> hydrogenation of ketones.<sup>1,2</sup> We report here the preparation and characterization of iron(II) dibromocarbonyl complexes **1**, **2**, and **3** of the type [FeBr<sub>2</sub>(CO)(L)], where L is one of the tridentate, P- or C-stereogenic, C<sub>2</sub>-symmetric PNP pincer ligands (*S*<sub>P</sub>,*S*<sub>P</sub>)-2,6-bis((cyclohexyl(methyl)phosphanyl)methyl)pyridine (**4**), 2,6-bis(((2*R*,5*R*)-2,5-dimethylphospholan-1-yl)methyl)pyridine (**5**), or (*S*<sub>P</sub>,*S*<sub>P</sub>)-2,6-bis(*tert*-butyl(methyl)phosphanyl)methyl)pyridine (**6**).



The corresponding bromocarbonylhydride complexes were prepared by addition of NaBHET<sub>3</sub> (1 equiv.) and either isolated or directly used in catalysis. They were active in the direct H<sub>2</sub> hydrogenation of a variety of arylalkyl ketones under 50 bar of H<sub>2</sub> pressure and in the presence of KO<sup>t</sup>Bu as base. The enantioselectivity reached 61% ee with (*S*)-1-(2-naphthyl)ethanol. The origin of enantioselectivity was investigated using DFT calculations.



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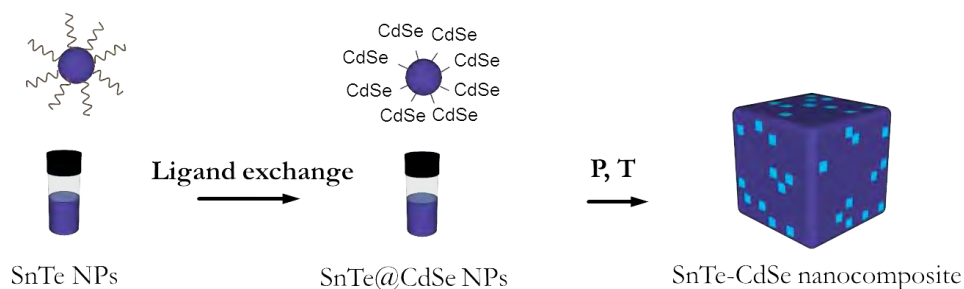
## High thermoelectric performance of p-type solution processed SnTe nanocomposite through band engineering

M. Ibáñez<sup>1,3</sup>, R. Hasler<sup>1</sup>, B. Kuster<sup>1</sup>, A. Cabot<sup>2,4</sup>, M. V. Kovalenko<sup>1,3\*</sup>

<sup>1</sup>ETH Zürich, <sup>2</sup>IREC, <sup>3</sup>EMPA, <sup>4</sup>ICREA

The bottom-up assembly of semiconductor colloidal nanoparticles into macroscopic multi-compound materials is a particularly versatile methodology to precisely design thermoelectric materials. Beyond the control over crystal domain size, shape, crystal phase and composition during nanoparticle synthesis, solution-processed nanoparticles allow an exquisite surface engineering, which provides additional means to modulate transport properties. The exchange of native surface organic ligands by short inorganic molecules can be envisioned as carriers of foreign ions, which may diffuse to the nanoparticle lattice to tune the type and concentration of majority carriers or to modify the electronic band structure.

Herein, we report the thermoelectric performance of consolidated surface modify SnTe nanoparticles. CdSe complexes were selected as ligands to suppress the excess of holes arising from the intrinsically large number of Sn vacancies, to converge the light- and heavy- bands, and to generate nanoinclusions of a secondary phase to further reduce the lattice thermal conductivity. The SnTe-CdSe nanocomposites produced allowed us to obtain figures of merit up to 1.3 at 850 K, which is, to the best of our knowledge, the highest thermoelectric figure of merit reported for Sn-based solution processed chalcogenides, and comparable to the highest figure of merit stated for SnTe.

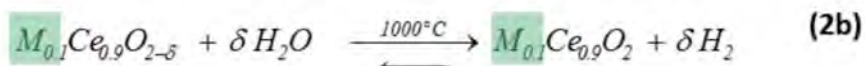
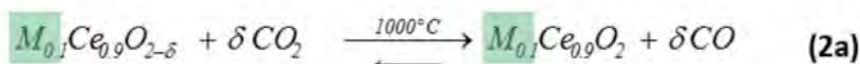
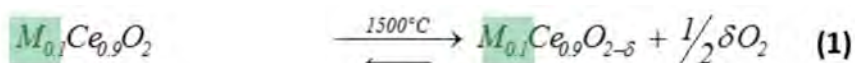


## Dopant Screening of Ceria-Based Materials for Solar Thermochemical Two-Step CO<sub>2</sub>-Splitting

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We consider the solar-driven 2-step thermochemical cycle for splitting H<sub>2</sub>O and CO<sub>2</sub> via CeO<sub>2</sub>-based redox reactions<sup>[1]</sup>. In the first endothermic step, ceria is thermally reduced using concentrated solar energy by releasing O<sub>2</sub> (Eq. 1). In the second exothermic step (Eq. 2a and 2b), reduced ceria reacts with H<sub>2</sub>O and/or CO<sub>2</sub> to generate H<sub>2</sub> and/or CO, respectively. The fuel yield is proportional to the oxygen exchange capacity (OEC), which can be improved with cationic doping.



Starting from our earlier work,<sup>[2]</sup> we investigate all possible tetravalent dopants of the periodic table because of their potential to yield higher OEC values due to flexible vacancy formation processes. The doped ceria samples were analyzed with a wide range of analytical techniques (e.g. PXRD, TG, ICP-MS, SEM-EDX, XAS). We found a correlation between the effective ionic radius and the OEC that was supported by DFT calculations. The tetravalent dopants with best redox performance were tested for their high temperature long-term stability in thermogravimetric cycling experiments.

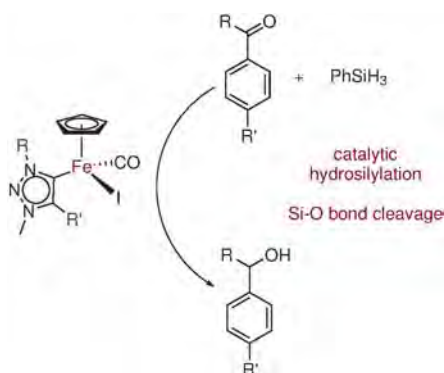
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**Triazolylidene iron(II) piano-stool complexes: synthesis and catalytic hydrosilylation of carbonyl compounds**C. J. Johnson<sup>1</sup>, M. Albrecht<sup>1\*</sup><sup>1</sup>Universität Bern

1,2,3-Triazolylidenes are a recently developed sub-class of NHC ligands which have tremendous versatility due to the synthetic flexibility of the copper catalysed cycloaddition of alkynes with azides (CuAAC).<sup>1,2</sup> These ligands are strong  $\sigma$ -donors, exhibiting stronger donor properties than classic Arduengo-type imidazole-2-ylidenes.<sup>2</sup> This property, coupled with the electronic flexibility of the mesoionic ligands makes them a powerful class of ligands for a large variety of catalytic transformations.

Iron is inexpensive, earth-abundant, non-toxic, biologically relevant, and environmentally benign. Thus, iron catalysts offer an attractive alternative to the systems based on rare and precious platinum group and coinage metals which dominate current literature.<sup>3</sup> Herein we present a new class of triazolylidene iron(II) piano stool complexes and their activity in catalytic hydrosilylation reactions.



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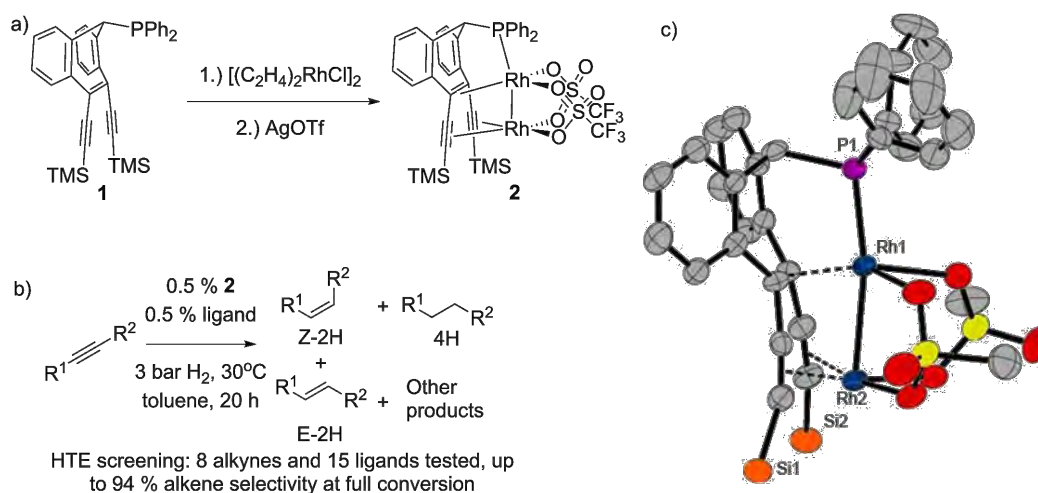
## Semi hydrogenation of alkynes by a novel bimetallic rhodium(I) complex

P. Jurt<sup>1</sup>, T. L. Gianetti<sup>1</sup>, A. Fedorov<sup>1</sup>, S. Gauthier<sup>2</sup>, H. Grützmacher<sup>1\*</sup>

<sup>1</sup>ETH Zurich, <sup>2</sup>Universite Rennes 1

Catalytic semi hydrogenation of alkynes to alkenes is an important process in both academia and industry. Developed in the 50's, Lindlar's catalyst (Pd/CaCO<sub>3</sub>/Pb(OAc)<sub>2</sub>/quinoline) still remains a privileged system for Z-selective semi hydrogenation reactions. However, the system utilizes a toxic lead additive. Further drawbacks are narrow substrate scope, over hydrogenation to alkenes, Z/E isomerization and double bond migration reactions.<sup>[1]</sup>

Herein, we report a new bimetallic complex **2** bearing a [Rh(I)]<sub>2</sub>-moiety. The stabilization of the rhodium-rhodium bond, while leaving two reactive rhodium centers, was achieved by a tailored ligand with olefin/alkyne sites to anchor the two metal centers. The complex **2** was shown to be active in semi hydrogenation of alkynes under very mild conditions. In order to optimize the stability and activity of the complex, high throughput ligand- and substrate screening was performed, leading to a catalyst system able to perform semi hydrogenation reactions with up to 94 % alkene selectivity.



**Figure 1.** a) Synthesis of a dirhodium complex **2**, b) Conditions for semi hydrogenation reactions, c) crystal structure of **2**. Methyl groups and fluorine atoms omitted for clarity.

[1] A. Fedorov, H. Liu, H. Lo, C. Copéret, *J. Am. Chem. Soc.* **2016**, *138*, 16502.

## Selective Semihydrogenation of Alkynes with Copper Nanoparticles Supported on Passivated Silica

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<sup>1</sup>Department of Chemistry and Applied Biosciences, ETH Zurich

Semihydrogenation of alkynes to Z-alkenes is an important industrial process catalyzed by noble-metal-based systems, in particularly Pd.<sup>1</sup> The scarcity and high price of such catalysts spur the development of alternative earth-abundant semihydrogenation catalysts. For instance, supported Cu nanoparticles were found to catalyze the semihydrogenation of propyne under flow conditions.<sup>2</sup> Surface organometallic chemistry offers a general approach to small narrowly-dispersed supported metallic nanoparticles using molecular organometallic precursors.<sup>3</sup> With this methodology, our group has prepared silica-supported Cu particles and utilized high-throughput screening to identify PCy<sub>3</sub> as a ligand for the highly chemo- and stereoselective semihydrogenation of alkynes into Z-olefins.<sup>4</sup> Here, we explore the modification of the support through passivation<sup>5</sup> of the OH group to modify the adsorption properties of the supports and to enable the use of broader ligand libraries.

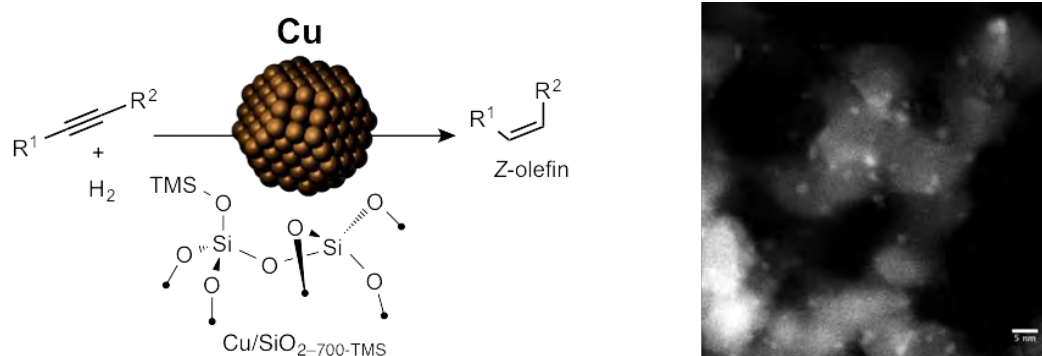


Fig.1. General scheme of selective alkyne semihydrogenation (left) and high-angle annular dark field transmission electron microscopy image of Cu nanoparticles on passivated silica (right).

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## Heteroleptic light-emitting copper(I) complexes with applications in light-emitting electrochemical cells

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<sup>1</sup>University of Basel, <sup>2</sup>Universidad de Valencia

The access to artificial light sources is one of the basic human needs and crucial for our modern society. As the energy to light conversion with "classic" lighting systems is relatively inefficient, the development of new lighting devices such as LECs (Light-Emitting Electrochemical Cells) and OLEDs (Organic Light-Emitting Diodes) promises considerable savings in terms of both energy and resources. The main advantage of this technology lies in the conversion of energy into visible light as main product instead of heat with light only as a by-product. Furthermore, the straightforward production of especially the LECs allows the cost-efficient production of light-emitting devices for miscellaneous application types. We present new results on the synthesis and investigation of light-emitting copper(I) complexes, which are a low-priced alternative to materials based on less abundant elements such as ruthenium or iridium. In order to stabilize the  $d^{10}$  state of copper(I) and protect it from being oxidized, the ligands should be coordinated in a tetrahedral geometry. Encouraging results have been obtained with P<sup>^</sup>P chelating bisphosphanes such as POP (bis[(2-diphenylphosphino)phenyl] ether) and xantphos (4,5-Bis(diphenylphosphino)-9,9'-dimethylxanthene), in combination with 2,2'-bipyridines, 2,2':6',2''-terpyridines and other chelating N<sup>^</sup>N-donors.<sup>[1,2]</sup> The copper(I) systems are very susceptible to the steric demand of the ligands. Due to sensible ligand tuning involving for example alkyl or aryl groups at the N<sup>^</sup>N ligands, we successfully prepared yellow emitting Cu(I) complexes with quantum yields of 37% and improving, with the respective LECs exceeding device lifetimes of 80 hours.<sup>[3]</sup>

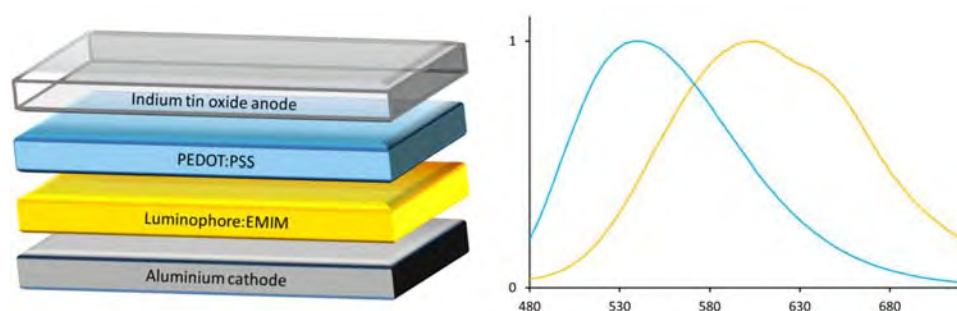


Figure 1. Left: Schematic buildup of a light-emitting electrochemical cell. Right: Normalized powder (blue) and solution (yellow) emission spectra of  $[\text{Cu}(\text{xantphos})(6,6'\text{-Me}_2\text{bpy})][\text{PF}_6]$ .

The research on emissive Cu(I) compounds is very promising and still relatively new, leaving the field open for innovative ideas. Further alteration of the ligands will provide much needed insights into their influence on the important complex properties such as electroluminescence, lifetime of the excited state, quantum yield and ion mobility, thus allowing the fabrication of even more efficient light-emitting devices.

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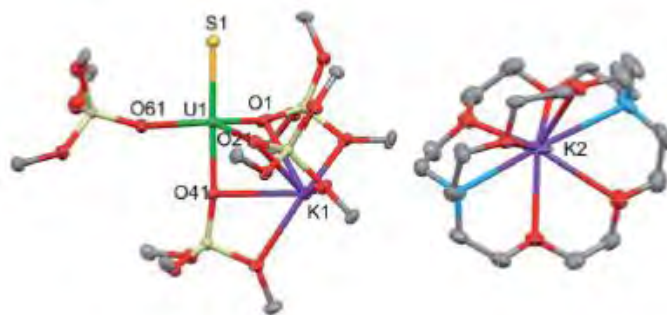
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**In search of uranium terminal sulfide complexes**R. P. Kelly<sup>1</sup>, M. Falcone<sup>1</sup>, J. Andrez<sup>1</sup>, R. Scopelliti<sup>1</sup>, C. A. Lamsfus<sup>2</sup>, L. Maron<sup>1</sup>, M. Mazzanti<sup>1\*</sup><sup>1</sup>EPFL, <sup>2</sup>INSA, Toulouse

There has been renewed interest in uranium complexes with uranium-ligand multiple bonds (e.g. N, O, S), since such complexes could open up new reactivity and catalytic applications due to the large size of uranium ions and the involvement of *f* orbitals in uranium-ligand bonding. Also, they are of fundamental interest because they can be used to probe the nature of the bonding in actinide complexes. The list of well-characterised uranium terminal oxo complexes is growing but there are only a few uranium complexes bearing terminal sulfide ligands.[1-4] Sulfur-containing ligands are used in the selective extraction of actinides from nuclear waste, and this necessitates further studies into the nature of An-S bonds.

Different approaches have been used to prepare uranium(IV) terminal sulfide complexes. Hayton and co-workers treated a uranium(III) ylide adduct with 0.125 eq. of S<sub>8</sub>,[1] while Meyer and coworkers deprotonated a uranium(IV) hydrosulfide complex.[3] Reductive cleavage of a uranium(IV) thiolate complex after treatment with Na(Hg) also yielded a uranium(IV) terminal sulfide complex.[2] Our group recently prepared a uranium(IV) terminal sulfide complex supported by bulky tris(tertbutoxy)siloxide ligands (L = OSi(OtBu)<sub>3</sub>) (Fig. 1). This complex was prepared by first treating [KUL<sub>4</sub>] with 0.5 eq. of Ph<sub>3</sub>P=S. Then, 2.2.2-cryptand was added to abstract two of the potassium ions from the complex that is formed, [SUL<sub>4</sub>K<sub>2</sub>]<sub>2</sub>, affording a new uranium(IV) terminal sulfide complex. [4]

The synthesis of uranium(V) terminal sulfide complexes more complicated than that of analogous uranium(IV) complexes, but our preparation of a uranium(IV) terminal sulfide complex supported by tris(tertbutoxy)siloxide ligands suggests that they could be suitable supporting ligands for a uranium(V) terminal sulfide complex.



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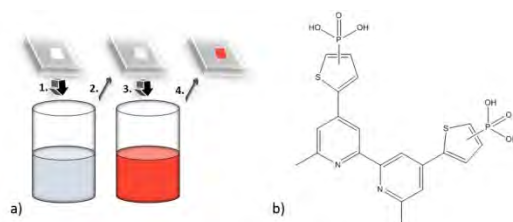
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## Modifying spacers and anchoring groups for heteroleptic Cu(I) - 6,6'-dimethyl-2,2'-bipyridine based DSSCs

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Heteroleptic  $[\text{Cu}(6,6'\text{-dimethyl-2,2'\text{-bipyridine}})_A(6,6'\text{-dimethyl-2,2'\text{-bipyridine}})_C]^+$  (A: anchoring ligand, C: capping ligand) complexes in which the bpy units are functionalized in the 4- and 4'-positions are known to be good light harvesting materials in dye-sensitized solar cells (DSSCs). When the formation of isolated heteroleptic  $[\text{Cu}(\text{bpy})_A(\text{bpy})_C]^+$  complexes is attempted, equilibration occurs giving mixtures of homo- and heteroleptic complexes; separation is very difficult. Therefore our group has developed a stepwise build-up of DSSCs (Figure 1a): a 'surface-as-ligand, surface-as-complex' approach. For the first step a 6,6'-dimethyl-2,2'-bipyridine ligand, which is modified in the 4 and 4'-positions by a spacer bearing an anchoring group (e.g. 4-phenylphosphonic acid, Figure 1b) is bound to a  $\text{TiO}_2$  surface. Afterwards Cu(I) and a capping ligand are introduced by a ligand exchange reaction between the anchored  $\text{bpy}_A$  and a  $\text{bpy}_C$  of the homoleptic  $[\text{Cu}(\text{bpy})_2]^+$  complex. In previous work done by our group, much focus was put on the modification of the capping ligand to enhance photo to current efficiencies. The standard anchoring ligand with the best performance, which is currently used in our group is shown below. Changing the anchoring group from phosphonic acid to alternative groups<sup>1</sup>, as well as modifying the phenyl spacer to a thiophene spacer has been investigated<sup>2</sup> with a goal of enhancing solar cell performance for  $[\text{Cu}(\text{bpy})_2]^+$  complexes. Targets are to gain better affinity of the anchoring group to  $\text{TiO}_2$ , better electron transport through the spacer, less electron recombination between dye and electrolyte and an overall longer electron lifetime within the complex.



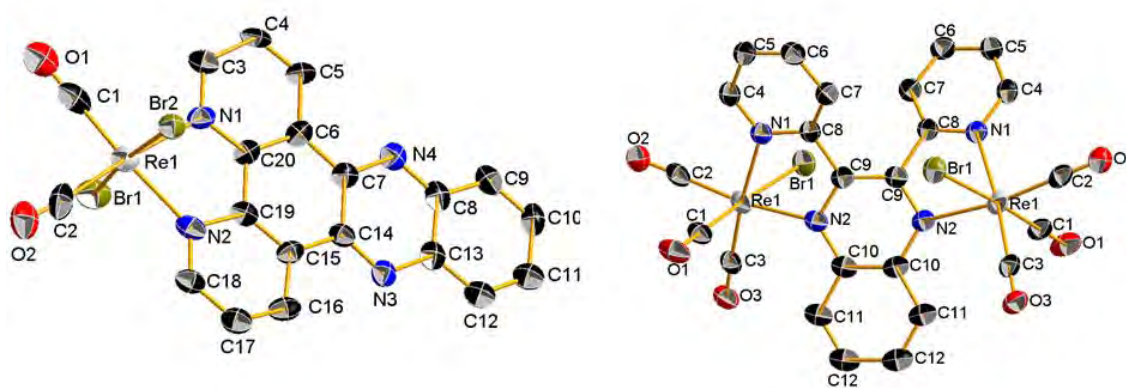
**Figure 1:** a) Stepwise build of heteroleptic Cu(I) - DSSCs. b) Anchoring ligand for Cu(I) - DSSCs.

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**Structural Cytotoxicity studies of  $\{\text{Mn}(\text{CO})_3\text{Br}\}^+$ ,  $\{\text{Mn}(\text{CO})_3\text{Br}\}^+$  and  $\{\text{Mn}(\text{CO})_3\text{Br}\}^+$  bearing bipyrimidine derivatives or isocyanides as ligands**E. Kottelat<sup>1</sup>, F. Zobi<sup>\*1\*</sup><sup>1</sup>University of Fribourg

Carbon monoxide (CO) is known as fundamental gaseous neurotransmitter in humans and there is a growing interest in its pharmacological or medical applications. CO is acknowledged to be involved in several cellular, physiological and pathological pathways, such as endothelial injuries, vasodilatation, inflammation. Organometallic carbonyl complexes are best suited to play the role of CO carriers. Targeting of the molecules to local injuries can thus be achieved by modifying the coordination sphere of the metal ion via a proper selection of ligands or by appending CO releasing molecules (CORMs) to biomolecules.



There exist, however, a delicate balance between cytoprotective and cytotoxic effects of CO releasing molecules. Various studies have reported promising cytoprotective effects of Mn- and Re-based CORMs in different preclinical models, while other studies have focused on the toxicity of the same molecules on cancer cells or their bactericidal activity. Nevertheless, there is no structure-activity known for CORMs, nor is it understood how the metallic center, its oxidation state and ligand framework impact on the relative cytoprotective and cytotoxic of CORMs.

In order to attempt a predictive correlation between the cytotoxicity and the structure of CORMs, we report the effects on mouse cancer cells of 18 different complexes. Three metallic carbonyl cores, Mn(I), Re(I) bis-CO, Re(I) tris-CO, with two series of three similar ligands (isocyanide and bipyrimidine-type) were tested. Seven crystal structures were determined by X-ray diffraction. The kinetics of the degradation of Mn(I) and Re(I) bis-CO complexes as their CO delivery capabilities were also investigated.

## Aluminum Chloride-Natural Graphite Battery and its Energy Density

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Non-aqueous, ionic liquid-based aluminum chloride-graphite batteries emerge as a highly promising post-Li-ion technology for low-cost and large-scale storage of electricity, because it features exclusively highly abundant chemical elements and simple fabrication methods. In this work, we examined the recently proposed aluminum-ionic liquid-graphite architecture.<sup>1</sup> Although previous studies have focused on graphitic cathodes, we analyzed the practicality of achievable energy densities and found that the  $\text{AlCl}_3$ -based ionic liquid is a capacity-limiting anode material. By focusing on both the graphitic cathode and the  $\text{AlCl}_3$ -based anode, we improved the overall energy density.<sup>3,4</sup> First, high cathodic capacities of  $\leq 150 \text{ mAh g}^{-1}$  and energy efficiencies of 90% at high electrode loadings of at least  $10 \text{ mg cm}^{-2}$  were obtained with highly crystalline natural graphite flakes or with synthetic kish graphite flakes, which were subjected to minimal mechanical processing. Second, the  $\text{AlCl}_3$  content in the ionic liquid was increased to its maximal value, which essentially doubled the energy density of the battery, resulting in a cell-level energy density of  $\leq 65 \text{ Wh kg}^{-1}$ .

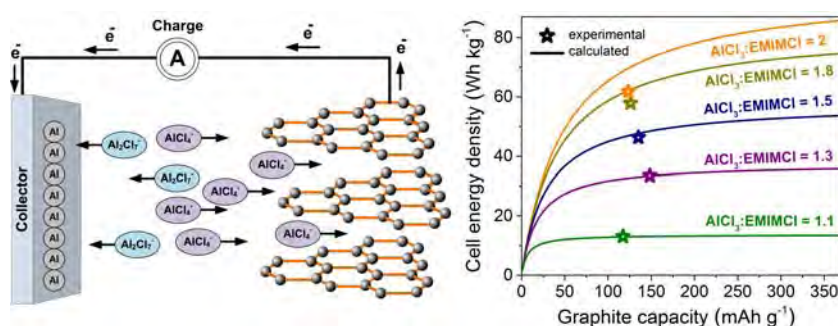


Figure 1. An aluminum chloride-graphite battery. (a) Schematics of the charging process. (b) Comparison of the calculated (curves) and experimental (data points) cell-level energy densities.

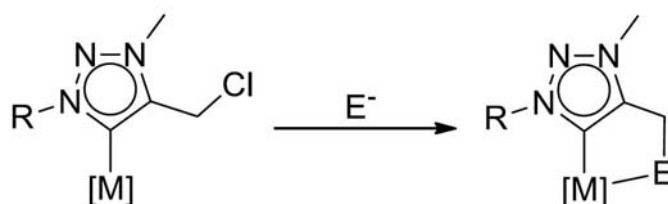
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**Efficient modulation of the donor sites of triazolylidene metal complexes for enhancing catalytic activity**K. Lenzen<sup>1</sup>, M. Albrecht<sup>1</sup><sup>1</sup>Departement für Chemie und Biochemie, Universität Bern, CH-3012 Bern, Switzerland

N-heterocyclic carbene (NHC) metal complexes have shown versatile applicability in a wide variety of catalytic transformations.[1] Mesoionic NHCs, such as 1,2,3-triazolylidenes, are an interesting sub-class of NHCs, exhibiting even stronger  $\sigma$ -donation and additional beneficial properties in, for instance, redox catalysis.[2] Introducing specific functional groups into NHC ligands is often highly beneficial for enhancing catalytic performance of the complexes, though generally such functionalization requires a challenging multi-step synthetic procedure. Such multi-step ligand by ligand synthesis can be simplified by a post-modification procedure.[3,4] We have developed a system that is based on a chloro-functionalized triazolylidene ligand (see Figure). Chloride substitution on the complex allows for postmodification of the ligand and the formation of novel chelating systems, some of which are hard to make by any other route. Here we demonstrate the potential of this approach by the synthesis and catalytic screening of a variety of donor-functionalized Ir and Ru complexes. The rapid access to a wide range of functionalized triazolylidene metal complexexs gives immediate information on the best systems for a specific catalytic reaction. The versatility of the method will be discussed as well as the effect of the functional donor sites on different types of catalysis.



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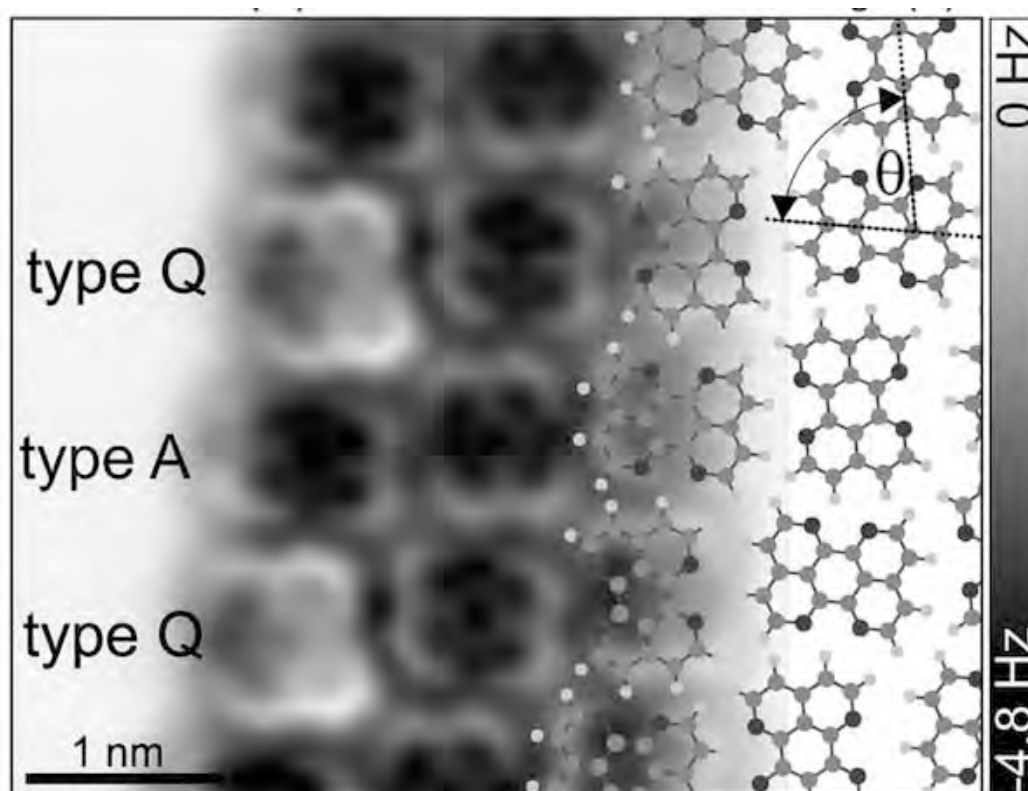
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## Periodic charging of individual molecules and charge patterns of an assembly of aromatic heterocyclic molecules on the surface

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Single-electron charging is critical for many areas of nanoscience. Charging and discharging events can be detected, i.e. in the force and in the frequency shift in atomic force microscopy. In a combined STM/FM-AFM study, the periodic charging of individual molecules assembled on a Ag(111) substrate was investigated [1]. The molecule under investigation, 1,6,7,12-tetraazaperylene (**tape**), is a planar heterocyclic compound (Figure 1). The incorporated hydrogen bonding capacity stabilizes on surface a two-dimensional molecular assembly. Interestingly, different charge patterns on the 1 nm scale can be created and addressed in a controlled way on the Ag(111) substrate.



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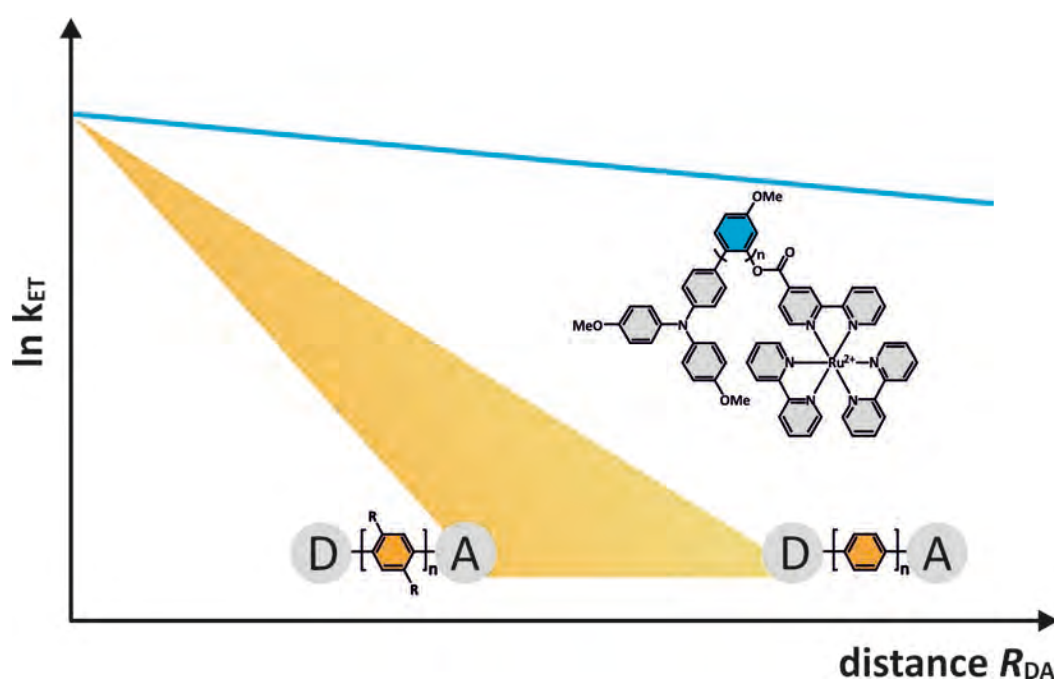
## Electron transfer across oligo-ortho-phenylenes

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<sup>1</sup>University of Basel

In photosynthesis electron transfer over long distances plays a crucial role and has been studied in many molecular donor-acceptor compounds. Especially *para*-substituted oligo-phenylenes as molecular bridges have received much attention.<sup>1</sup> For electron transfer across *para*-phenylenes and *para*-xylenes, time-resolved measurements revealed a significant distance dependence with  $\beta$  parameters of  $0.2 \text{ \AA}^{-1}$  to  $0.8 \text{ \AA}^{-1}$ , respectively.<sup>2</sup>

For the first time we investigated photoinduced electron transfer through a molecular bridge consisting of oligo-*ortho*-phenylenes. Compared to their *para* connected congeners, these molecules show a much weaker distance dependence for electron transfer.



Comparison of electron transfer rates ( $k_{ET}$ ) vs. donor-acceptor-distances ( $R_{DA}$ ) in *para*-phenylenes, *para*-xylenes, and oligo-*ortho*-phenylenes.

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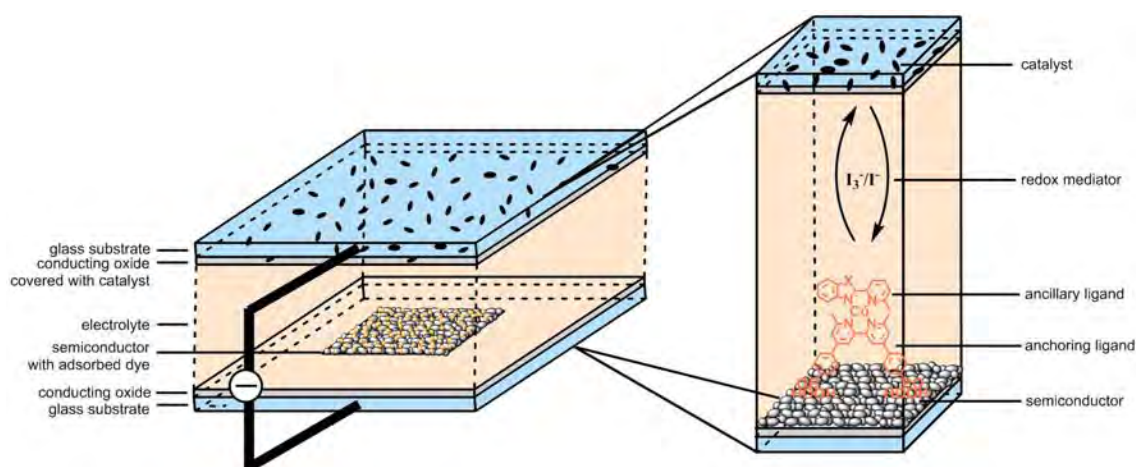
## The History of “BLORANGE”: Co-Sensitized Copper(I) Dye-Sensitized Solar Cells

F. J. Malzner<sup>1</sup>, C. E. Housecroft<sup>1</sup>, E. C. Constable<sup>1</sup>

<sup>1</sup>University of Basel

Renewable energy sources are the answer to save the world from drastic climate changes. The most promising one is photovoltaics. Today, photovoltaic modules are based on silicon but also consist rare elements. A very good alternative are dye-sensitized solar cells, which had its breakthrough in 1991 [1]. The most efficient cells contain ruthenium which is also rare on earth.

Our group focuses its research on the application of copper(I) complexes in dye-sensitized solar cells [2]. A dye-sensitized solar cells consists of different components, which can be optimized to yield higher efficiencies.



**Figure 1:** Structure of a dye-sensitized solar cell with zoom-in example for investigated copper(I) dye-sensitized solar cells.

The most important part of a dye-sensitized solar cell is the dye. It consists of two parts – the anchoring and the ancillary ligand [3]. In case of a copper(I) dye-sensitized solar cell the absorption maximum is at about 480 nm and the photon-to-electricity conversion efficiency between 600 and 700 nm is rather low. To reach a panchromatic absorption, co-sensitization with another dye is sufficient. The relatively high efficiencies show the huge potential of co-sensitized copper(I) dye-sensitized solar cells.

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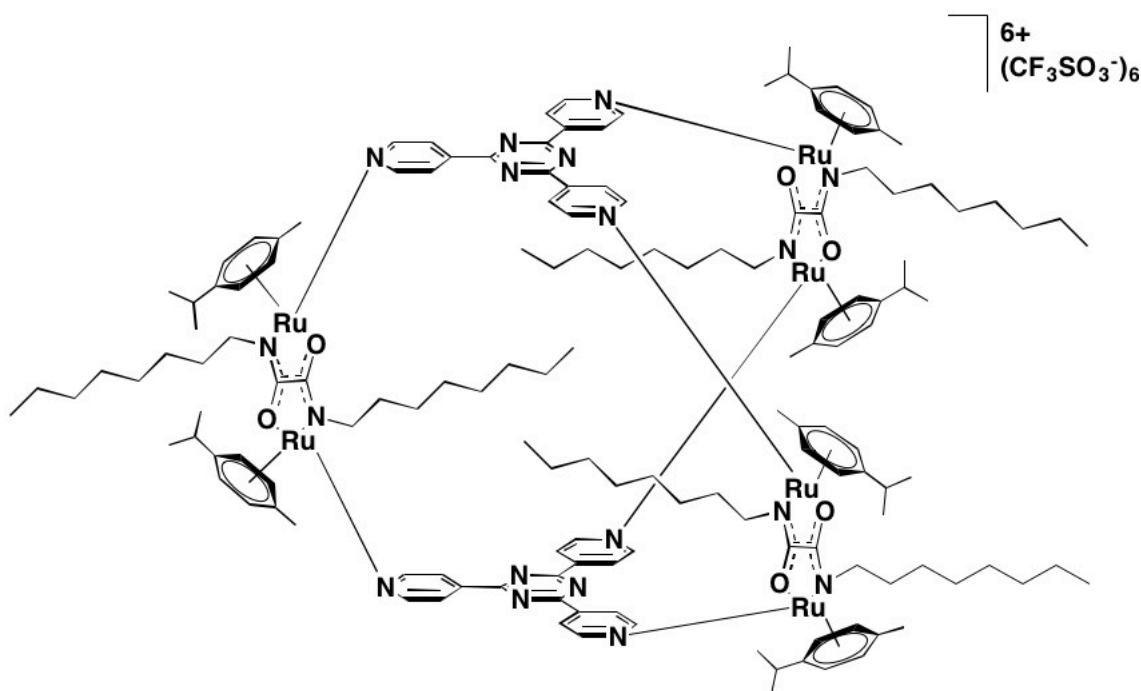
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## Fighting Cancer with the Next Generation of Organometallic Assemblies

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Due to defective vascular architectures, tumor blood vessels are better in extravasating large molecules from the blood. Tumors show a poor lymphatic drainage which causes retention of high-molecular weight substances.<sup>1</sup> These two features are the bases for the EPR (Enhanced Permeability and Retention) effect. Due to this enhanced permeability, large molecules are able to enter into the tumor tissue and accumulate locally due to the poor lymphatic drainage, thus increasing the selectivity and reducing side effects.<sup>2</sup> Our research uses organometallic assemblies that taken up by cancer cells.<sup>3</sup> Therefore, to better exploit the EPR effect, we have designed larger arene-ruthenium metalla-assemblies.



These large compounds are composed of three metalla-clips that are connected by two tridentate panels forming a hollow which might transport guests (drugs). Functional groups can be anchored on the building blocks to enhance the size, activity and physiological property. For example, octyl chains can be anchored on the clip, thus increasing significantly the volume of the assembly (Figure 1). In the future, the influence of introducing longer and/or shorter, alkyl- and/or PEGylated chains, will be evaluated.

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**Characterization and improvement of p-type dye sensitized solar cells.**

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<sup>1</sup>University of Basel

We present recent research that has been done in our group detailing the mechanism of a p-type cell. A p-type electrode will eventually be used as the cathode electrode in a tandem cell, in order to achieve that the performance of the cell has to be improved.

In our group we working with NiO as a p-type semiconductor the properties of which has yet to fully understand. The surface chemistry studies which consist of solid state UV, electrochemistry and sun simulation measurements will reveal the reason why a p-type cell is not achieving his theoretical values and what are the change that has to be made to in order to do so.

Design and synthesis of the dye is a strong asset, as well, in the performance of the solar cell. When designing a dye for a p-type solar cell it should be taken into account that the HOMO of the dye should be situated at his anchoring ligand. Cyclometalated Ru dyes have been developed in our group a long time now. Those dyes consist of Ru-metal center bipyridine as ancillary ligand and a phosphoric or carboxylic acid as an anchoring ligand. A dye with these characteristics has been synthesized in our group. The performance of which, in a solar cell exceeds most of the known p-type dyes.

Moreover, the electrolyte used as an ion carrier in the solar cells should be examined closely. The redox potential of the electrolyte should conform with the valence band of the semiconductor in order to achieve the highest open circuit voltage.

Until recently iodine triiodide electrolyte has been used in p-type regardless the fact that is an n-type optimized electrolyte. Cobalt dimethylamine electrolyte has been found to be much more suitable for p-type solar cells according to their redox potential. In our group research to improve the electrolyte performance by changing the ancillary ligands is been held.

## Pincer-type Pyridylidene Amide (PYA) Ruthenium Complexes in Transfer Hydrogenation Catalysis

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Ligand systems that offer flexibility and assist the metal in catalytic bond making and breaking have received much attention recently.<sup>1</sup> Pyridylidene amide (PYA) ligands have been shown to be electronically flexible N-donor sites and have successfully been used for several applications in homogeneous catalysis, such as in challenging water oxidation and transfer hydrogenation.<sup>2,3</sup> Here we will present new pincer-type ligands based on the well-known pyridine-2,6-dicarboxamide scaffold,<sup>4</sup> now containing two PYA moieties. The N<sub>3</sub>-pincer cavity allows for a facile synthesis of different ruthenium(II) complexes which can be further modified in an easy one step reaction (Fig. 1). We will discuss the influence of different PYA ligand systems and the variation of spectator ligands on the electrochemical and photochemical properties of the complexes and on their catalytic activity.

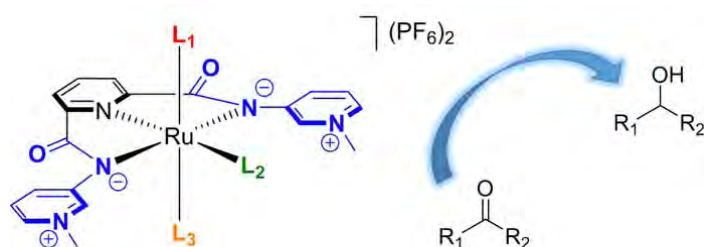


Figure 1. General structure for ruthenium PYA complexes

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**Induced-circular dichroism resulting from the interaction between a chromophoric calix[6]arene and a chiral non-chromophoric amine**N. Ménard<sup>1</sup>, B. Colasson<sup>1</sup>, O. Reinaud<sup>1</sup>, Y. Jacquot<sup>2\*</sup><sup>1</sup>Laboratoire de Chimie et Biochimie Pharmacologiques et Toxicologiques, CNRS UMR 8601, 75006 Paris, France, <sup>2</sup>Laboratoire des Biomolécules, CNRS UMR7203, 75005 Paris, France

Like resorcinarenes, cucurbiturils and cyclodextrins, calixarenes are supramolecular cyclooligomers. They are synthesized through the condensation of *p*-substituted phenols and formaldehyde. These macrocyclic molecules share a hydrophobic cage-like cavity (host) with the ability to complex a variety of organic derivatives (guests) such as cationic amines. They can be used as ion channel mimics, enzyme models, surface agents for protein recognition, or gene transfection vectors.

To study asymmetric host-guest interactions, we have used circular dichroism (CD) spectroscopy, and more specifically induced-circular dichroism (ICD). ICD is recorded when a non-chiral molecule interacts with a chiral molecule. Towards this aim, we have explored the effects of different parameters on the formation and the stability of an inclusion complex composed of a chiral amine, *i.e.*, (*S*)-(-)-2-methylbutylamine (chiral guest) and a calixarene, *i.e.*, [Zn.X<sub>6</sub>tBu<sub>6</sub>] (chromophoric host), where the small rim is functionalized by three imidazoles which are coordinated to a zinc atom. We have studied the effects mediated by amine concentration enhancement, solvents (dichloromethane and acetonitrile) and by temperature changes.

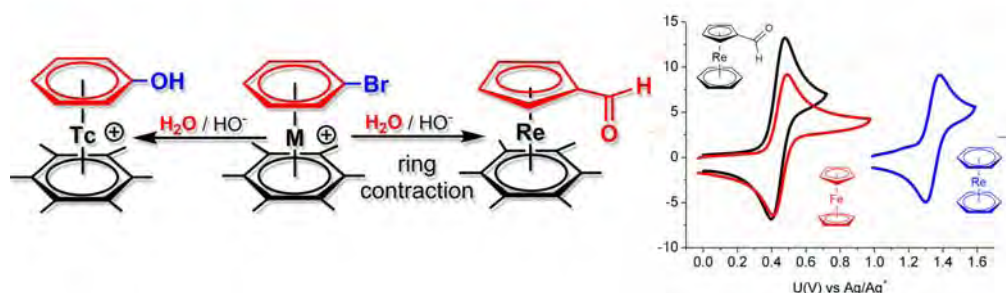
Whereas [Zn.X<sub>6</sub>tBu<sub>6</sub>], alone, exerts a negative Cotton effect with a negative maximum at 240 nm, a positive Cotton effect at the same wavelength is recorded when the complex is formed. Whereas the 1:1 complex is obtained with 1 eq. of (*S*)-(-)-2-methylbutylamine in DCM, it is formed in ACN with 5 eq. of the amine. Temperature effects show that the complex is more stable in DCM when compared to ACN. In conclusion, DCM appears as the most appropriate solvent to stabilize the complex resulting from [Zn.X<sub>6</sub>tBu<sub>6</sub>] and (*S*)-(-)-2-methylbutylamine.

## A Mixed-Ring Sandwich Complex from Unexpected Ring Contraction in [Re( $\eta^6$ -C<sub>6</sub>H<sub>5</sub>Br)( $\eta^6$ -C<sub>6</sub>R<sub>6</sub>)](PF<sub>6</sub>)

G. Meola<sup>1</sup>, H. Braband<sup>1</sup>, D. Hernández Valdés<sup>1</sup>, C. Gotzmann<sup>1</sup>, T. Fox<sup>1</sup>, B. Spingler<sup>1</sup>, R. Alberto<sup>1\*</sup>

<sup>1</sup>University of Zurich

[M(arene)<sub>2</sub>]<sup>+</sup>-type complexes (M = Re, <sup>99(m)</sup>Tc) of rhenium and technetium came recently into the focus of our attention since their homologous metal complexes are an established matched-pair for radio diagnosis and (radio)therapy. Hence, the synthesis of [Re(arene)<sub>2</sub>]<sup>+</sup> type complexes was optimized and an efficient and applicable one-step synthesis for [<sup>99(m)</sup>Tc(arene)<sub>2</sub>]<sup>+</sup> compounds was developed.<sup>1,2</sup> Furthermore, novel synthetic pathways for the functionalization of this basic class of organometallic complexes was developed, which led to a variety of mono- and di-functionalized [Re(C<sub>6</sub>H<sub>5</sub>R)(C<sub>6</sub>H<sub>6-n</sub>R<sub>n</sub>)]<sup>+</sup> compounds (R = -COOH, -Br, -Cl, -F, -COC<sub>2</sub>H<sub>5</sub>, -CH(OH)Ph, -C(OH)Ph<sub>2</sub>). This type of complexes can be used as scaffolds in medicinal chemistry.<sup>3</sup> In contrast, the synthesis of mixed-ring sandwich complexes of Re<sup>I</sup> or Tc<sup>I</sup> is poorly reported in the literature. We report here on the conversion of a bromo-benzene, coordinated to a Re(I) center, into a cyclopentadienyl aldehyde [Re( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>CHO)( $\eta^6$ -C<sub>6</sub>R<sub>6</sub>)] (R = -H, -CH<sub>3</sub>) under strong alkaline condition and in quantitative yield whereas the phenol complex of Re and <sup>99</sup>Tc was achieved under mild alkaline condition.<sup>4</sup> Such a ring contraction is unprecedented so far. We elucidated the mechanism of this reaction with <sup>1</sup>H and <sup>2</sup>H NMR and support the reaction path with DFT calculations. Following this strategy, new classes of organometallic compounds can be synthesized with high potential for therapeutic and diagnostic applications (inorganic drugs), in the future.



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**Structural investigation of silica-supported copper (I) surface sites by IR spectroscopy**J. Meyet<sup>1</sup>, K. Searles<sup>1</sup>, J. A. van Bokhoven<sup>1,2\*</sup>, C. Copéret<sup>1\*</sup><sup>1</sup>ETH Zurich, <sup>2</sup>Paul Scherrer Institute

The rational design of heterogeneous catalysts requires detailed structural understanding of surface sites for the development of structure reactivity relationships. One approach for developing well-defined heterogeneous catalysts is Surface Organometallic Chemistry (SOMC). SOMC relies on selectively anchoring metal complexes to the surface of oxide-supports via grafting.[1] This ultimately allows for the generation and subsequent study of well-defined metal sites on surface. Here will be described the synthesis of well-defined silica-supported copper (I) site(s) and their characterization by infrared spectroscopy using CO as probe molecule.

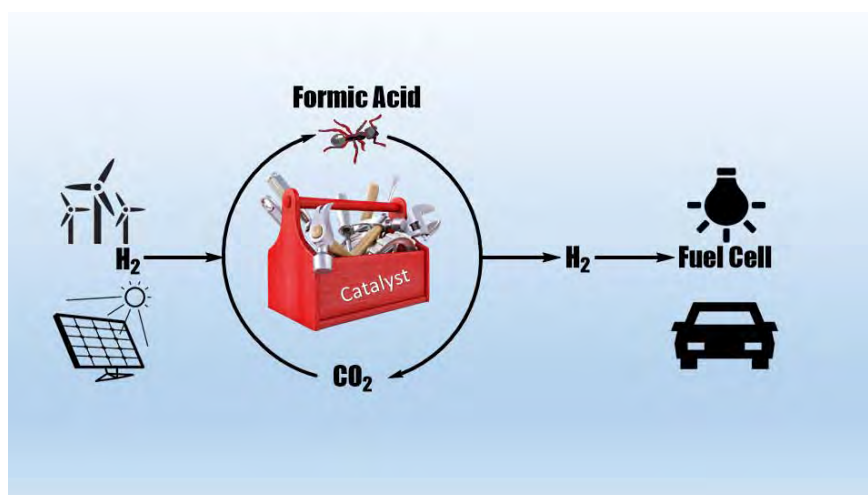
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## Formic Acid: A Promising Hydrogen Storage Material

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Hydrogen is, among others, widely known as a renewable and clean energy source, more precisely an energy vector. However, it is less known that the storage of hydrogen is not so evident. Indeed, the current methods to store hydrogen habitually involve high pressure (stainless steel) cylinder, having weight and safety issues,<sup>[1]</sup> not easy to handle, having obvious hazards. In order to imagine a general use of hydrogen as an energy carrier, other storage methods should be developed.<sup>[2]</sup> The principle idea would be to use renewable energy sources such as solar or wind to produce hydrogen, store it chemically bounded in small organic molecules such as formic acid, deliver it on demand and then start the cycle again, thus being CO<sub>2</sub> neutral if one can reuse the CO<sub>2</sub> released in the process.



To store and to deliver hydrogen chemically, one needs catalysts. Our group developed in 2006 a ruthenium based catalyst for the dehydrogenation of formic acid and later came up with the reduction of CO<sub>2</sub> to formic acid in acidic aqueous media.<sup>[3-4]</sup> In our recent work we presented a catalyst based on a non-noble metal, iron, for the dehydrogenation of formic acid in aqueous solutions.<sup>[5]</sup> In the perspective of a wide usage of formic acid as a hydrogen storage material, it would be of high interest to use a non-scarce metal, leading in lower cost of production and no risk of shortage in supply. We are now investigating the reduction of CO<sub>2</sub> in formic acid using similar catalysts.

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## Quinones as Reversible Electron Relays in Artificial Photosynthesis

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The ultimate source of electrons for photocatalytic hydrogen production is water. The four-electron oxidation of two H<sub>2</sub>O to O<sub>2</sub> involves several steps associated with a high kinetic overpotential. So far, this prevented its widespread use as an electron donor in full, molecular water splitting systems. Therefore, the two half-reactions in artificial photosynthesis are commonly studied using sacrificial agents. On the reductive side, irreversible or semi-reversible electron donors such as tertiary amines or ascorbic acid were applied.<sup>[1,2]</sup> This practice was established to study the half-reaction individually, without interference of the oxidative side. However, this concept has little practical significance.

In contrast, nature uses a completely reversible electron relay in the form of the hydroquinone/quinone system to shuttle electrons between PSII and PSI.<sup>[3]</sup> Compared to the oxidized form of tertiary amines and ascorbate, oxidized hydroquinones are excellent electron acceptors, thus efficiently inhibiting any productive electron transfer reactions in the reductive half-reaction to H<sub>2</sub>. A photocatalytic proton reduction system featuring a reversible hydroquinone/quinone shuttle system that overcomes this limitation will be presented along with a kinetic analysis of the system elucidating the fate of the quinone species as well as the bottle neck of the system.<sup>[4]</sup>

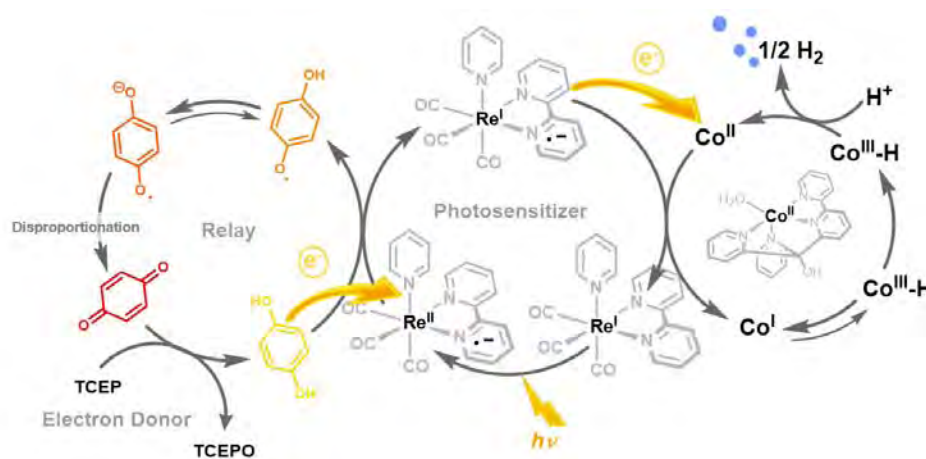


Fig. 1: Reductive half reaction of artificial photosynthesis with TCEP as sacrificial electron donor, a quinone-based relay, a Ru-photosensitizer and a Co-based water reduction catalyst (WRC).

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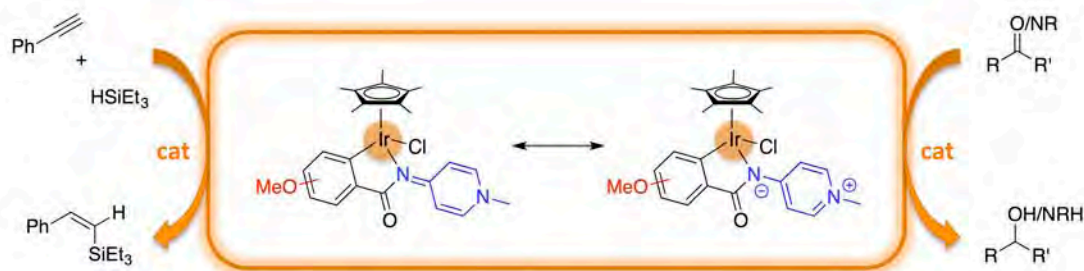
## Enhanced Catalytic Activity of Iridium(III) Complexes by Facile Modification of C,N-bidentate Chelating Pyridylideneamide Ligands

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Non-innocent ligands that can significantly modulate their donor properties have become increasingly popular as a powerful class of ligands for a variety of homogenous catalytic applications, since they can stabilize different metal configurations.<sup>1</sup> Pyridylideneamines (PYEs) and pyridylideneamides (PYAs) are electronically highly flexible N-donor sites that can coordinate to the metal center as a  $\pi$ -acidic imine or as a  $\pi$ -basic pyridinium amide. Their flexibility is represented by the two limiting resonance forms comprised of a diene heterocycle and a neutral imine donor site with minimal charge separation and a zwitterionic form, which features an anionic amide donor site and aromatic stabilization of the pyridinium residue.<sup>2</sup>

Here, we applied this concept for facile catalyst tailoring by incorporating donor substituents in different positions of the phenyl ring of the C,N-bidentate chelating PYA ligand (Fig. 1). These modifications greatly enhance the catalytic activity of the coordinated iridium center.



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## Synthesis of iridium complexes containing both hydride and functionalized triazolylidene ligands

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Iridium complexes with functionalized triazolylidene ligands have shown attractive performance in catalyzing oxidation reactions such as water oxidation and in mediating C–H bond activation.<sup>1,2</sup> On the other hand, hydride systems are considered to be the key species for enhancing such bond activation.

Here we will discuss the synthetic aspects of a new family of iridium(III) complexes containing both a hydride and a mesoionic carbene ligand as potential catalyst precursors for application in bond activation catalysis.



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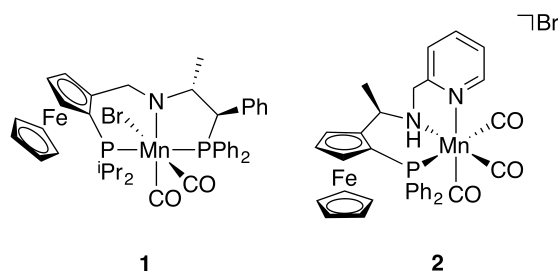
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## Mn(I) complexes with chiral pincer ligands in the asymmetric hydrogenation of ketones

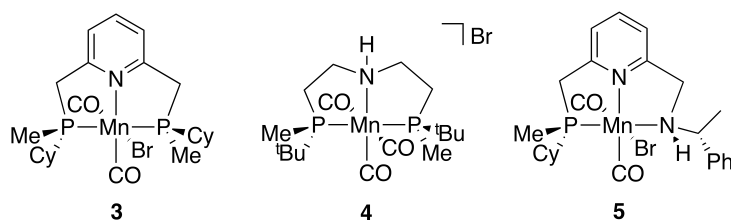
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In 2017, two Mn(I) complexes with chiral pincer ligands were reported as catalysts in the asymmetric hydrogenation of ketones, which is an appealing reaction for industrial application due to the low-toxicity, earth-abundance, and low cost of manganese. Complex **1** is active in ATH and complex **2** in AH [1,2].



We have prepared novel Mn(I) complexes with chiral PNP (**3,4**) and PNN pincer ligands (**5**) based on stereogenic phosphorus. We are testing these complexes as catalysts in the AH and ATH of ketones. The hydrogenation of acetophenone with complex **4** as catalyst (1 mol% catalyst, 50 bar H<sub>2</sub>, toluene, 100 °C) gives 99% of yield and 48% of ee after 16 h. With the aim of enhancing the enantioselectivity, a more rigid linker will be introduced between the N and P atoms.



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**Potentiometry as a tool to study metal ion coordination to metallothioneins**M. Perinelli<sup>1</sup>, M. Tegoni<sup>2</sup>, E. Freisinger<sup>3\*</sup>

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The aquatic fungus *Heliscus lugdunensis* was found to be able to survive in a polluted spring on a former mining area in Germany, which shows high metal ion concentrations. The fungus produces a number of different thiolate-containing molecules, among them the metallothionein Neclu\_MT1<sup>1</sup>.

MTs are a large super-family of small metalloproteins (10 electron configuration. Neclu\_MT1 is with only 24 amino acids one of the smallest MTs, but features with eight Cys residues the same high Cys content as the vertebrate forms. In addition, Neclu\_MT1 contains a single C-terminal His residue, which is one of its most interesting features since it was shown to be a Cd(II)-specific MT, both on the protein and on the gene transcription level.<sup>2</sup> Based on the available ligands two types of clusters can be envisioned, Cys<sub>8</sub>M<sup>II</sup><sub>3</sub> or Cys<sub>8</sub>HisM<sup>II</sup><sub>3</sub>, which both would be of great interest, since none of them has been found in MTs before.

In order to better understand the role of the His residue, an arginine mutant was produced (Neclu\_H24R\_MT1). The binding capacity of Neclu\_H24R\_MT1 is comparable to the wild-type: both are able to complex three Cd(II) or Zn(II) ions. With potentiometric measurements we were able to calculate the pK<sub>a</sub> values of all titratable residues of wild-type and mutant apo-Neclu\_MT1. Furthermore, complexation studies are being carried out on the two systems with both Cd(II) and Zn(II).

The obtained data is intended to provide information about the binding ligand pattern and the specific role of the His residue. UV-visible, circular dichroism and mass spectrometry experiments complement the potentiometric data.

*Project funding by the Swiss National Science Foundation (SNSF) to EF is gratefully acknowledged.*

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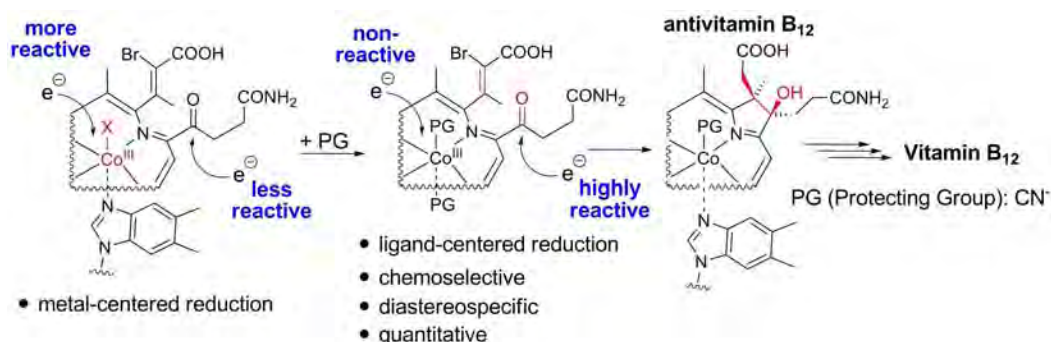
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## A Reversible Route for the Stereospecific Reconstitution of Vitamin B<sub>12</sub> Using Cyanide as Inorganic Protecting Group

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Vitamin B<sub>12</sub> is one of the most complex natural products and acts as an essential cofactor in many forms of life, including humans.<sup>1</sup> The enzymatic activity of this nutrient is dominated by cobalt-dependent organometallic reactions and the electronic and kinetic properties of the metal centre are strongly influenced by the equatorial corrin ligand. Therefore, stereospecific and reversible modifications of this sophisticated macrocycle show huge potential for the development of new B<sub>12</sub>-based therapeutic agents.<sup>2</sup>



We present the 4-step stereospecific reconstitution of vitamin B<sub>12</sub> from a B ring modified secocorrinoid.<sup>3,4</sup> The key step of the route is a quantitative and rapid ring closure reaction that leads to a new B<sub>12</sub> derivative with antivitamin activity. Chemoselectivity in this reaction is achieved by introducing inorganic cyanide as protecting group. Synthetic aspects and biological properties of these compounds will be described.

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## Interaction of thiolato-bridged dinuclear arene ruthenium complexes with phospholipids and model membranes

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Thiolato-bridged dinuclear arene ruthenium complexes are highly cytotoxic against various cancer cell lines with IC<sub>50</sub> values of up to 30 nM [1]. A recent *in vivo* study has demonstrated that these complexes have potential as anticancer drugs, as one complex significantly prolongs the survival of tumor-bearing mice [2]. Interestingly, these complexes are very stable under physiological conditions as well as acidic and basic conditions, and they are particularly inert toward substitution. Only sulfur containing biomolecules such as cysteine and glutathione undergo catalytic oxidation in their presence [3].

Since many aspects of cellular uptake and of the tumor-inhibiting action displayed by these complexes are still largely unknown, we have studied the interactions of three trithiolato complexes with different degrees of lipophilicity  $[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{Pr}^i)_2\text{Ru}_2(\text{R}^1)_2(\text{R}^2)]^+$  ( $\text{R}^1 = \text{SC}_6\text{H}_4\text{-}m\text{-Pr}^i$  :**1**;  $\text{R}^2 = \text{SC}_6\text{H}_4\text{-}m\text{-Pr}^i$  :**1**;  $\text{R}^1 = \text{SC}_6\text{H}_4\text{-}p\text{-OMe}$  :**2**;  $\text{R}^2 = \text{SC}_6\text{H}_4\text{-}p\text{-OH}$  :**2**;  $\text{R}^1 = \text{SCH}_2\text{C}_6\text{H}_4\text{-OMe}$  :**3**;  $\text{R}^2 = \text{SC}_6\text{H}_4\text{-}p\text{-OH}$  :**3**) and of one dithiolato complex  $[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{Pr}^i)_2\text{Ru}_2(\text{SCH}_2\text{C}_6\text{H}_5)_2\text{Cl}_2]$  :**4** with lipid membrane models in form of 1,2-dioleoyl-sn-glycero-3-phosphocholine (DOPC) vesicles, 1,2-dihexanoyl-sn-glycero-3-phosphocholine (DHPC) micelles and sodium dodecyl sulfate (SDS) micelles by nuclear magnetic resonance (NMR) spectroscopy and other techniques. 1D <sup>1</sup>H NMR spectra, 2D <sup>1</sup>H diffusion ordered spectroscopy (DOSY) spectra and T2 (spin-spin) relaxation time measurements together with electrospray ionization mass spectrometry (ESI-MS) suggest noncovalent interaction between the vesicles and the three trithiolato complexes. As expected, the strength of the interaction with the vesicles parallels the lipophilicity of the complexes. The results with the dithiolato complex **4**, on the other hand, suggest that none or only very weak interaction takes place. **1** was further studied with DOPC in presence of the lanthanide shift reagent PrCl<sub>3</sub> for estimating if the complex remains at the vesicle surface, is inserted between the fatty acid chains or is localized inside the DOPC vesicle.

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**Synthesis and isolation of previously infeasible dithiolato bridged dinuclear ruthenium complexes  $[(p\text{-MeC}_6\text{H}_4i\text{Pr})_2\text{Ru}_2\text{SR}_2\text{Cl}_2]$  using optimized reaction conditions**H. Primasova<sup>1</sup>, M. De Capitani<sup>1</sup>, I. Gjuroski<sup>1</sup>, J. Furrer<sup>1\*</sup><sup>1</sup>Departement für Chemie und Biochemie, Universität Bern, Freiestrasse 3, CH-3012 Bern, Switzerland

It is well known that the dimer *p*-cymene-ruthenium dichloride  $[(p\text{-MeC}_6\text{H}_4i\text{Pr})_2\text{Ru}_2(\text{m-Cl})_2\text{Cl}_2]$  reacts with aromatic thiols to give cationic trithiolato complexes  $[(p\text{-MeC}_6\text{H}_4i\text{Pr})_2\text{Ru}_2(\text{SR})_3]^+$  [1]. The reaction proceeds through neutral dithiolato intermediates  $[(p\text{-MeC}_6\text{H}_4i\text{Pr})_2\text{Ru}_2(\text{SR})_2\text{Cl}_2]$ , some of which could be isolated in good yields [2]. From our previous studies, a prerequisite for the successful isolation of dithiolato intermediates was that the thiol must be aliphatic, otherwise the reaction cannot be controlled and leads immediately to the corresponding cationic trithiolato complexes [3].

Herein, we report the synthesis of new dithiolato complexes  $[(p\text{-MeC}_6\text{H}_4i\text{Pr})_2\text{Ru}_2(\text{SR})_2\text{Cl}_2]$  with aromatic thiols (R=*p*-*t*-Bu-Ph: **1**; *p*-MeO-Ph: **2**; *p*-Br-Ph: **3**) in good to excellent yields and sufficient level of purity for **1** and **2**. The complexes could be obtained using optimized conditions (DCM, 4h, 0-25°C).

Despite being generally biologically less active than their corresponding trithiolato counterparts, dithiolato intermediates can be further functionalized with a different thiol, R<sup>2</sup>, giving a mixed trithiolato complexes  $[(p\text{-MeC}_6\text{H}_4i\text{Pr})_2\text{Ru}_2(\text{SR}^2)(\text{SR})_2]^+$  which are known to be highly cytotoxic against cancer cells [4]. Depending on the nature of R<sup>2</sup>, the complexes can be further functionalized with bioactive molecules, thus strongly increasing the chemical variability and the bioactivity of the complexes [5]. As such, the present work represents the first step of our general goal which is to synthesize numerous new ruthenium conjugates with different properties.

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**Optimized reaction conditions for the synthesis of trithiolato-bridged dinuclear arene ruthenium complexes: reducing the reaction time and synthesis of new complexes**H. Primasova<sup>1</sup>, J. Daepf<sup>1</sup>, I. Gjuroski<sup>1</sup>, J. Furrer<sup>1\*</sup><sup>1</sup>Departement für Chemie und Biochemie, Universität Bern, Freiestrasse 3, CH-3012 Bern, Switzerland

Trithiolato-bridged dinuclear arene ruthenium complexes  $[(\text{arene})_2\text{Ru}_2(\text{SR})_3]^+$  can be obtained using a very simple and efficient method (complexes are obtained in yields larger than 80%), using a refluxed solution of thiols dissolved in ethanol taking advantage of the remarkable preference for the SH function versus the OH function of the solvent by the dinuclear ruthenium unit [1]. Depending on the reactivity of the thiol, very good yields are typically obtained within 12 to 48 h [2]. We have however noticed that some of those trithiolato-bridged dinuclear arene ruthenium complexes were difficult to obtain.

In this contribution, our idea is to use organic bases to increase the reactivity of the thiols in order to reduce the overall reaction time and to synthesize trithiolato-bridged dinuclear arene ruthenium complexes that were difficult to obtain by the classical method. For this, three known diruthenium trithiolato complexes  $[(p\text{-MeC}_6\text{H}_4^i\text{Pr})_2\text{Ru}_2(\text{SR})_3]^+$  ( $\text{R} = p\text{-}^t\text{BuPh}$  :**1**,  $p\text{-MeOPh}$  :**2**;  $p\text{-BrPh}$  :**3**) were synthesized using various reaction conditions. Under optimized conditions (dichloromethane in presence of N,N-diisopropylamine under reflux) **1** could be obtained in as short as two hours with quantitative yield. These optimized reaction conditions were implemented for **2** and **3**, with 96% and 87% yield, respectively, in as less as 2 h as [well](#), compared to 24 h using the classical method. [2] Finally, using the optimized reaction conditions applied for 70 h, complex with  $\text{R} = \text{CH}_3(\text{CH}_2)_5$  :**4**, related to the previously reported complex with  $\text{R} = (\text{CH}_2)_7\text{CH}_3$  obtained in 7 days in yield of 28% [3], could be prepared and isolated in good yield of 68%.

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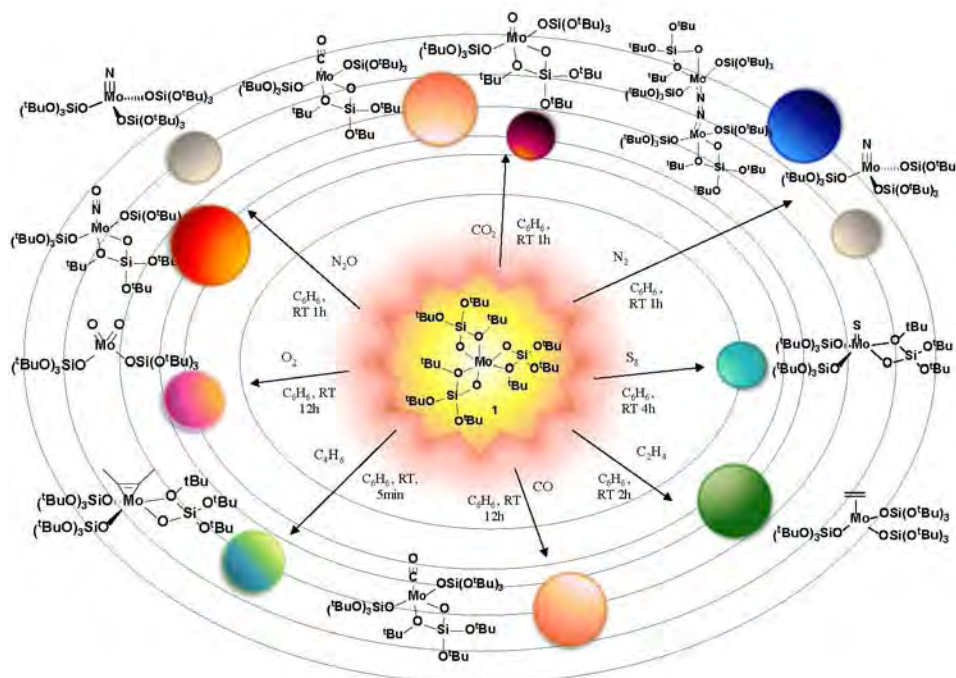
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## Mo(OSi(tBu)<sub>3</sub>)<sub>3</sub>: Structure and Reactivity

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Cr(III) surface species, prepared from Cr(III) siloxide molecular precursor, are highly active catalysts for olefin polymerization and alkane dehydrogenation.<sup>1,2</sup> We have thus become interested in generating low coordinated isoelectronic Mo(III) surface to investigate their corresponding reactivity. To date, low coordinate Mo(III) compounds are rare; they typically require large somewhat rigid ligands like in Mo[N(R)Ar]<sub>3</sub> (R= tBu, Ar= 3,5-C<sub>6</sub>H<sub>5</sub>Me<sub>2</sub>)<sup>2</sup> and Mo(OSi<sup>t</sup>Bu)<sub>3</sub>.<sup>3</sup> Here, we have developed the synthesis of Mo(OSi(OtBu)<sub>3</sub>)<sub>3</sub> (**1**) and investigated its reactivity towards a broad range of small molecules (CO<sub>x</sub>, N<sub>2</sub>O, O<sub>2</sub>, S<sub>8</sub>, ethylene and N<sub>2</sub>). The complex **1** has three siloxy ligands adopting a k<sup>2</sup>-coordination, yielding an overall distorted octahedral geometry. This complex reacts at room temperature with N<sub>2</sub> to give the corresponding Mo(VI)-nitrido compound by dinitrogen splitting *via* [Mo=N=N=Mo] intermediate, which was isolated at low temperature and fully characterized. This complex also reacts with N<sub>2</sub>O, but does not lead to the splitting of N-O bond as expected from metal mediated decomposition of nitrous oxide<sup>4</sup>, but rather of N-N bond, leading to [Mo-h<sup>1</sup>-NO] with NO in linear fashion and Mo(VI)-N. Similarly, reaction with CO<sub>2</sub> yields Mo(III)-CO and Mo(V)-O. The former can also be obtained from the reaction of **1** with CO. Reaction of **1** with S<sub>8</sub> yields Mo(V)-S complex. Finally, the reaction of **1** and ethylene generates the corresponding p-complex as it does by reaction with 2-butyne.



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**Self-Assembly of Chiral Alleno-Acetylinic Coordination Complexes**B. L. Quigley<sup>1</sup>, O. Gidron<sup>1</sup>, M. Jirásek<sup>1</sup>, N. Trapp<sup>1</sup>, M. Ebert<sup>1</sup>, F. Diederich<sup>1\*</sup><sup>1</sup>ETH Zürich

Previous work in our group has established the utility of chiral phenanthroline-based alleno-acetylenic ligands in the formation of supramolecular assemblies, including double-stranded helicates,<sup>1</sup> triple-stranded helicates<sup>2,3</sup> and catenanes.<sup>1</sup> In order to elucidate the factors governing selectivity in the formation of these complexes, a systematic study was undertaken on the self-assembly of alleno-acetylinic ligands bearing substituted phenanthrolines with various metal ions. These results demonstrate that the self-assembly of these supramolecular complexes is responsive to subtle changes in the structure of the phenanthroline-based ligands, the identity of the metal ion and the conditions under which self-assembly is conducted. This allows the selectivity of the system to be tuned for formation of double- or triple-stranded complexes, helicates or mesocates, and for catenation. The transfer of chirality from the alleno-acetylinic ligands to the metal ions is also highly dependent on the ligand structure, resulting in a strong influence on the enantio-/diastereoselectivity of complex formation.

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**Defect chemistry as a route to engineer oxide materials with new functionalities**C. Ricca<sup>1</sup>, U. Aschauer<sup>1\*</sup><sup>1</sup>University of Bern

Defect chemistry is an emerging parameter to take into account in the design and/or discovery of new functionalities in transition metal oxides. Defects, like oxygen vacancies or substitutional cations, can indeed tune the properties of these materials and even more importantly, new functionalities may arise because of defects. For example, in transition metal perovskite oxides, paraelectric to ferroelectric and antiferromagnetic to ferromagnetic transitions can be observed as a function of defect type and concentration.

It would thus be interesting to be able to screen, at the theoretical level, the effect of different types of defects, in different charge states, on the properties of these materials. In this way, general trends can be deduced and new material/defect combinations, together with the required experimental synthesis conditions, can be suggested to be used as guidelines by experimentalists. To reach this goal, we designed a computational strategy that will allow a systematic and automated exploration of the defect chemistry of oxide materials and which should be able to provide accurate results for experimental synthesis conditions.

The computation of reliable defect formation energies is complicated by the need for an accurate description of the electronic properties of the bulk and defective system, which can be obtained by the application of advanced density functional methods or application of appropriate corrections schemes. To adequately describe the electronic structure of strongly correlated materials containing transition metals within a reasonable computational time, we suggest to apply the DFT+U approximation, by determining the value of the U parameter from first principles and as a function of the distance from the defect sites. Accurate formation energies are then computed by applying adequate *a posteriori* corrections, like elastic, band filling, and more importantly electrostatic correction in the case of charged defects.

In order to manage this sequence of calculations for a variety of material/defect combinations we use the AiiDA (Automated Interactive Infrastructure and Database for Computational Science)[1] informatics platform to chain the various calculation steps, allowing to obtain the formation energy for several defect types in an automated way based solely on the bulk structure of a given material. All the aspects relative to the theoretical and computational foundation for this systematic exploration of functional defects in materials are here described in detail. Furthermore, results on selected perovskite materials are also reported to demonstrate the validity and efficiency of the suggested computational strategy.

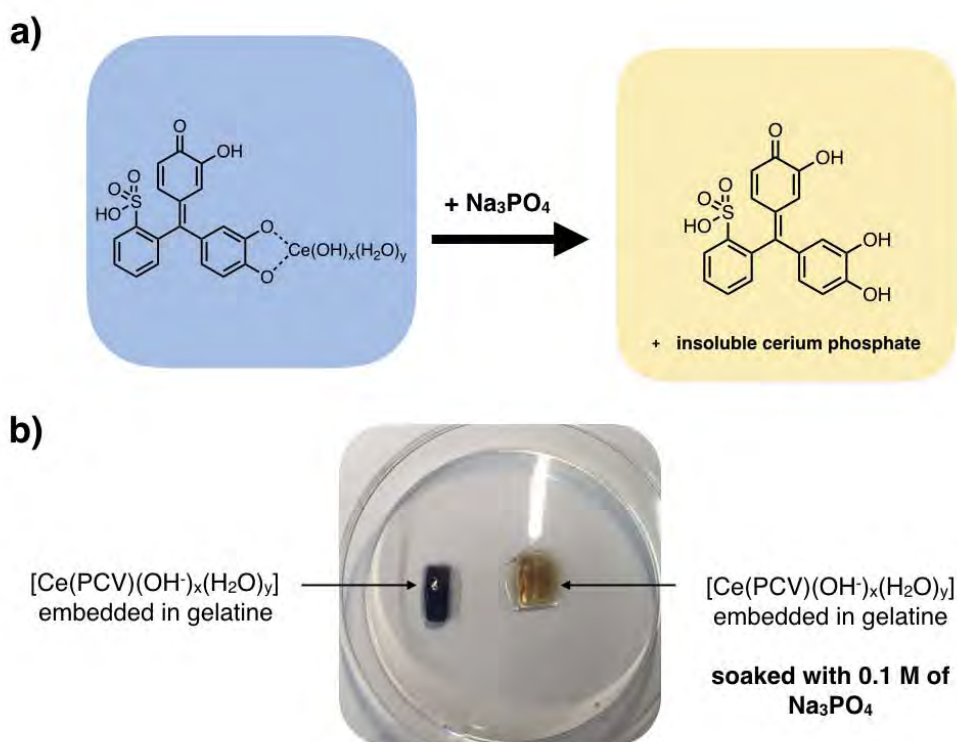
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## Smart and simple bioinorganic polymers to detect and absorb phosphates out of water

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High concentrations of phosphates in water are characteristic of eutrophication of fresh water systems, causing grave negative ecological impact in our lakes and rivers. Therefore, simple systems able to detect phosphates selectively and to extract them out of water are urgently needed. In this spirit, we embedded an inorganic complex consisting of Ce(IV) bound to a pyrocatechol violet (PCV) ligand<sup>1</sup> into gelatine (an easily accessed, inexpensive commercial polymer) to yield a Polymeric Indicator Displacement Assay (**PIDA**). The polymer changes colour from blue to yellow once exposed to a solution of phosphates, indicating their absorption, effectively soaking the phosphate out of solution. The polymer is extremely easy and inexpensive to assemble in high yield, is stable at room temperature and allows naked-eye detection of phosphate.

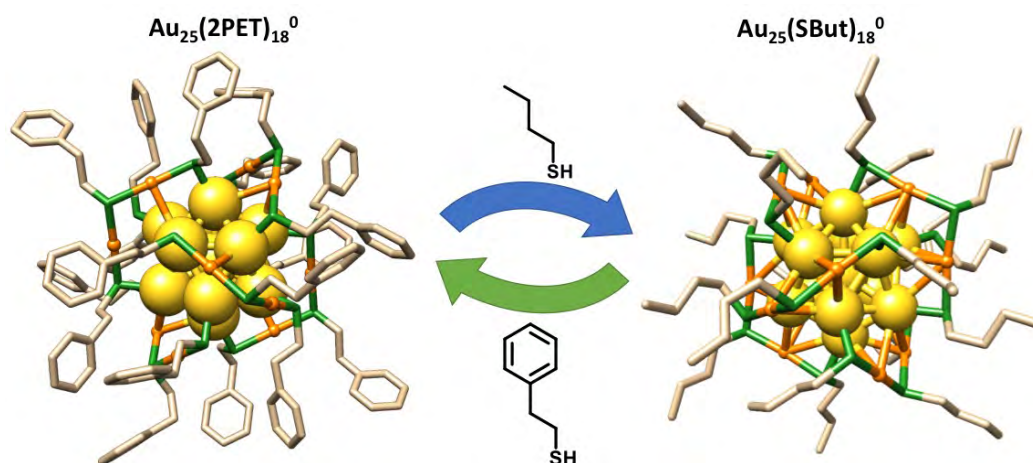


**Fig:** Principle of the PIDA. a)  $[\text{Ce(IV)(PCV)(OH)}_x(\text{H}_2\text{O})_y]$  embedded in gelatine forms  $[\text{Ce(IV)(PCV)(OH)}_x(\text{H}_2\text{O})_y] \subset$  gelatine, a blue polymer, which once exposed to phosphate changes colour from blue to yellow forming cerium phosphate embedded in gelatine. b) Macroscopic view of the blue  $[\text{Ce(IV)(PCV)(OH)}_x(\text{H}_2\text{O})_y] \subset$  gelatine and the yellow product after soaking in 0.1 M of sodium phosphate in a 100 mM HEPES pH=7.4.

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**$^1\text{H-NMR}$  and MALDI investigation of thiol-exchange reaction in  $\text{Au}_{25}(\text{SR})_{18}$  cluster**G. Salassa<sup>1</sup><sup>1</sup>University of Geneva, <sup>2</sup>Univeristá di Padova, <sup>3</sup>Université de Gêneve

Small thiol protected gold nanoparticles (< 2nm), also known as gold cluster, are self-assembled systems formed by Au(0) core and a thiol protecting monolayer. The latter is fundamental not only for stabilization and solubility of the clusters themselves, but also is the principal responsible for their reactivity.[1] One of the most frequent reactions used to functionalized the monolayer are the thiol-exchange reactions.[2]. These reactions usually present difficulties in controlling the number of substitutions and the reaction time can vary from minutes to days. In this study we investigated the thiol-exchange reaction using nuclear magnetic resonance (NMR) spectroscopy and MALDI analysis.[3] Kinetic studies were performed on  $\text{Au}_{25}(\text{SC}_2\text{H}_4\text{Ph})_{18}$  exchange with butane thiol and vice versa ( $\text{Au}_{25}(\text{SBut})_{18}$  exchange with  $\text{HSC}_2\text{H}_4\text{Ph}$ , Figure 1). By these studies, were possible to understand: 1) the affinity of different thiol ligands towards the  $\text{Au}_{25}$  cluster, 2) calculating the number of thiols exchange, 3) the position of exchange and 4) obtaining the relative binding constants. From this information was possible to gain a clearer picture on the mechanism of this reaction that can help in fine-tuning the functionality of the monolayer.



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**Plant metallothionein 2 protein - following the metalation process**A. Salim<sup>1</sup>, E. Freisinger<sup>1\*</sup><sup>1</sup>University of Zurich

Metallothioneins (MTs) are low molecular weight (~8kDa), mostly cytosolic proteins involved in both essential metal homeostasis and a variety of stress responses. The MT2 protein from the plant *Cicer arietinum* (cicMT2) features two cysteine-rich regions with eight and six cysteine residues, respectively, which are separated by a 41 amino acids long, Cys-free linker region. It can coordinate five divalent metal ions *in vitro*. Previous results strongly suggest that the coordinated metal ions are arranged in a single metal-thiolate cluster leading to a hairpin-like protein fold.<sup>1,2</sup> However, so far, the metalation pathway has never been investigated for any plant MT. In the presented study we focus on the identification of the binding region for each metal ion. Cluster formation upon stepwise metal ion reconstitution is monitored by changes in the ESI-MS profiles aided by limited proteolytic digestion with *Tritirachium album* proteinase K, which cleaves the protein backbone mainly in the Cys-free region. Identification of the binding region for each metal ion is complemented and corroborated by investigations with size exclusion chromatography, atomic absorption spectroscopy, and dynamic light scattering.



Figure 1. Schematic presentation of the hairpin-like backbone arrangement of Cd<sub>5</sub>cicMT<sub>2</sub>. (adapted from 2)

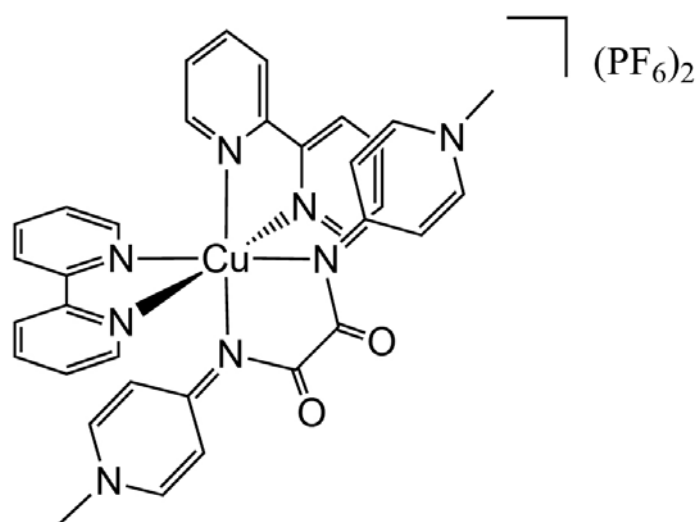
Project funding by the Swiss National Science Foundation (SNSF) to EF is gratefully acknowledged.

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**Bis-Pyridylidene Amide Ligands for Copper(ii) Photocatalysts**K. Salzmann<sup>1</sup>, M. Albrecht<sup>1\*</sup><sup>1</sup>Universität Bern

Redox-active ligands play a crucial role for photophysical and catalytic applications. Such noninnocent ligands can display varying degrees of donor ability and may stabilize several intermediates of the catalytic cycle. Pyridylideneamides (PYAs) are an innovative class of flexible ligands who show either a higher contribution of a neutral or a mesoionic resonance structure depending on its environment and are suitable for metal coordination.[1] Recent findings of our group have shown that ligands with two PYA moieties (bis-PYA) may be beneficial over 2,2'-bipyridine (bpy) and its analogues in photophysical and electrochemical applications.[2] Successful coordination of such bis-PYA ligands to second and third row transition metals has already been achieved and we were therefore interested to expand to first row transition metals. Here we introduce a novel analogue of  $[\text{Cu}(\text{bpy})_3]^{2+}$  with one bipyridine ligand site substituted by chelating bis-PYA. Photo- and electrochemical measurements and show that the presence of PYA moiety facilitates oxidation processes.



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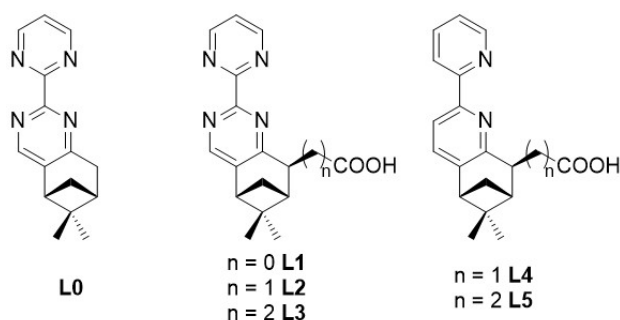
## Enantiopure ligands and their luminescent lanthanide complexes

A. B. Solea<sup>1,3</sup>, L. Yang<sup>2</sup>, C. Allemann<sup>1</sup>, K. M. Fromm<sup>3</sup>, O. Mamula Steiner<sup>1\*</sup>

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One of the possible ways for predetermining the stereochemistry of a metal centre is through diastereoselective synthesis: the chiral information is transferred from the chiral ligand to the metal ion, enabling the preferential formation of one stereoisomer. Ligands containing a chiral pinene moiety are one type of such molecules and they have been used extensively to control the configuration in complexes of transition metals.[1] If a carboxylic unit is also attached to this backbone these ligands form complexes with interesting luminescent and supramolecular features when reacted with lanthanide(III) ions.[2]

We have synthesized and fully characterized a series of chiral ligands with a bipyrimidine (**L0-L3**) or bipyridine backbone (**L4, L5**). These ligands were further employed in complexations with Eu(III) and Tb(III) ions. The characterization of the obtained complexes will be presented herein.



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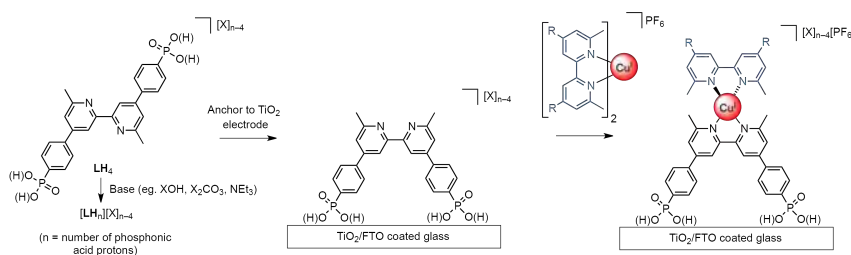
## The Influence of Phosphonic Acid Protonation State on the Efficiency of Bis(diimine)copper(I)-based Dye Sensitized Solar Cells

A. J. Stephens<sup>1</sup>, F. J. Malzner<sup>1</sup>, E. C. Constable<sup>1</sup>, C. E. Housecroft<sup>1</sup>

<sup>1</sup>University of Basel

The photoactive component of a Dye-Sensitized Solar Cell (DSC) consists of a dye molecule bound (either electrostatically or covalently) to a mesoporous TiO<sub>2</sub> surface through functional groups such as phosphonic acids.<sup>[1]</sup> Here, we investigate how the protonation state of such phosphonic acids affects their ability to anchor to TiO<sub>2</sub> substrates, and how the operational parameters of the resultant DSCs are influenced in turn.

Stepwise titration of bases into a solution of LH<sub>4</sub> alters the ligands protonation state and the nature of its associated cations to give [LH<sub>n</sub>][X]<sup>n-4</sup> (Fig. 1). The formation of Cu(I) dye molecules is achieved by sequentially exposing TiO<sub>2</sub> electrodes to [LH<sub>n</sub>][X]<sup>n-4</sup>, followed by the homoleptic Cu(I) complex of the ancillary ligand. Our results demonstrate that the addition of a small amount of base to LH<sub>4</sub> (~1 eq) can afford up to a 30% increase in DSC efficiency. These results are rationalized through consideration of proton / cation transfer from the ligand to the surface, deprotonation of surface hydroxides, and changes in the photochemical and electrochemical properties of ligand LH<sub>4</sub> upon deprotonation.



**Figure 1.** The sequential formation of a bis(diimine)copper(I) dye on a TiO<sub>2</sub> electrode using phosphonic acids in different protonation states.

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## Highly Stable Platinum(II) Triplet Emitters Displaying High Photoluminescent Quantum Efficiencies

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New efficient light-emitting materials have attracted a broad range of potential applications in the fields of sensors, storage, photoelectronic devices, and optical devices.<sup>[1-4]</sup> Extensive investigations on transition metal complexes as triplet emitters for application in phosphorescent organic light emitting devices (PhOLEDs) have been carried out.<sup>[5-10]</sup> Transition metal complexes with suitable ligands allow tailoring the properties for a specific application as luminescent compounds. Achieving high stability, powerful quantum efficiency and specific chromaticity of such organoplatinum(II) complexes present a major challenge in this field. Recently, our group has demonstrated a series of highly emissive platinum(II) complexes bearing N-heterocyclic carbene ligands with promising photophysical properties.<sup>[11]</sup> The thermal stability of such complexes was improved by the use of more rigid chelating ligands which are less prone to undergo reductive elimination. The complexes were fully characterized and the photophysical properties were investigated.

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## Improved upconversion luminescence in $\beta$ -NaGdF<sub>4</sub>: Er<sup>3+</sup>, Yb<sup>3+</sup> nanoparticles: A new microwave-assisted synthesis in anhydrous ionic liquids

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A new microwave assisted synthesis of  $\beta$ -NaGdF<sub>4</sub>: Er<sup>3+</sup>, Yb<sup>3+</sup> nanoparticles was investigated in ethylene glycol (EG) and ionic liquids (IL). Sub-10 nm nanoparticles with an intense green upconversion (UC) luminescence were synthesized. The UC intensity was strongly enhanced by changing the solvent from EG/IL mixture to pure IL, as well as the design from core to core/shell nanoparticles. The reaction in hydroxyl-free conditions reduces the number of oxygen impurities in the fluoride material. Protecting the particle surface by an undoped shell limits surface defects and shields the active core from contact with surface ligands which are required for solubility. Both decrease non-radiative losses and concomitantly yield a stronger UC emission. The UC emission is visible by eye already for low excitation power in sub-5 nm  $\beta$ -NaGdF<sub>4</sub>: 2%Er<sup>3+</sup>, 18%Yb<sup>3+</sup> nanoparticles, see the Fig. below. These results are unique for such small particle size. The new synthesis is robust, scalable, and economically favourable, involving low temperatures and well accessible chemicals.

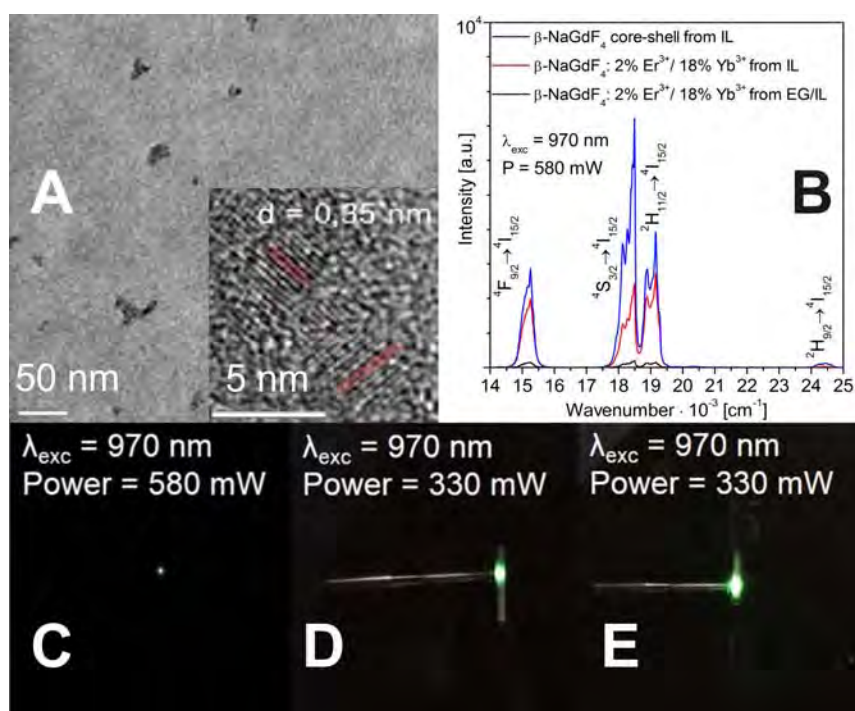


Figure: (A) HR-TEM picture of sub-5 nm nanoparticles. (B) Upconversion luminescence spectra of nanoparticles from ethylene glycol / ionic liquid (IL) synthesis (black trace), from IL synthesis (red trace), and core-shell nanoparticles from IL synthesis (blue trace). (C-E) Photos of the green upconversion luminescence from the samples in Fig. (B) under 580 mW (C) and 330 mW (D,E) excitation at 970 nm.

**Molecular and physical aspects of dye sensitization of photoelectrodes with copper-based sensitizer molecules**

J. Top<sup>1,3</sup>, B. S. Mun<sup>2</sup>, A. Stephens<sup>3</sup>, C. E. Housecroft<sup>3\*</sup>, A. Braun<sup>1\*</sup>

<sup>1</sup>Empa, <sup>2</sup>GIST, <sup>3</sup>University of Basel

Early work on dye sensitization dates back almost a hundred years and became a field of energy conversion in the late 1960s<sup>1</sup> and early 1970s<sup>2</sup>. Dye sensitized solar cells (DSSC) are basically a technology of artificial photosynthesis. Ruthenium is a favourite component in high performance dye molecules.<sup>3,4</sup>

Because of the low abundance and high cost of Ruthenium, our research focusses on Copper based dye molecules.

For DSSCs, the charge transfer between dye molecules and metal oxide semiconductor photoelectrode is very important. We show how we determine the electronic structure of the metal oxide - dye interface<sup>4</sup> operando with ambient pressure photoelectron spectroscopy for electronic structure determination, and electroanalytical methods for determination of the charge carrier dynamics.<sup>5,6</sup>

Furthermore, ab initio calculations are employed to aid in the interpretation of these results.

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**Enhanced Ethylene Polymerization Activity in Union Carbide Catalysts**D. Trummer<sup>1</sup>, A. Fedorov<sup>1</sup>, C. Serba<sup>1\*</sup><sup>1</sup>ETH Zürich

Chromocene on silica was discovered in the early 1970's as commercial ethylene polymerization catalyst.[1] The Union Carbide Catalyst displays high activity in ethylene polymerization at low pressure and temperature in absence of co-catalysts and activators.[2] Linear, high density polyethylene featuring narrow molecular weight distribution is characteristic for metallocene based systems. Substituted cyclopentadienyl (Cp) rings as well as mixed silica/alumina supports are known to diminish catalytic activity. However, preparation of silica surface itself seems crucial in controlling both activity and stability. For example, OH-groups in closed proximity to active sites are believed to act as catalyst inhibitors.

The predominant proportion of chromium on silica surface is present in the divalent state. Due to remarkably high transfer respond to hydrogen it is believed that active sites contain one Cp ligand during polymerization. Moreover, solid state NMR based studies have assigned half sandwich Cr(II) dimers to be the predominant surface sites.[3] However, in homogeneous phase only few half sandwich Cr(III) complexes show activity in ethylene polymerization.[4]

Greater insight in molecular level understanding is appropriate to evaluate actives sites and polymerization mechanism. The enhanced catalytic performance of chromocene on silica prepared by applying principles of surface organometallic chemistry will be discussed.

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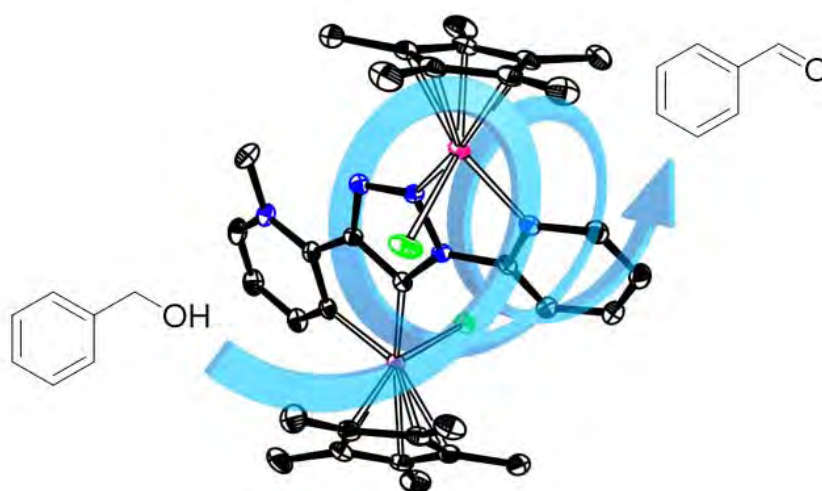
## Synthesis and Catalytic Behavior of a New Family of Dinuclear Iridium Carbene Complexes

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Iridium Cp\* complexes containing mesoionic carbene ligands have shown high activity in a variety of catalytic applications such as water oxidation, transfer hydrogenation or amine dehydrogenation.<sup>1</sup> In extension of this work, we have now synthesized a set of mono- and bimetallic complexes featuring a functional pyridine-containing triazolylidene ligand, and have characterized the new complexes by NMR spectroscopy, microanalysis, and by X-ray diffraction. These complexes have been evaluated as potential alcohol oxidation catalysts without the need of an oxidant or base as additive as well as in the hydrosilylation of carbonyl substrates.<sup>2</sup> Comparison of those bimetallic systems with monometallic analogues reveals a strongly enhanced selectivity of the bimetallic complexes.

We will discuss the spectroscopic and electrochemical similarities and differences of mono and di-iridium systems to rationalize the synergy between the two iridium centers.



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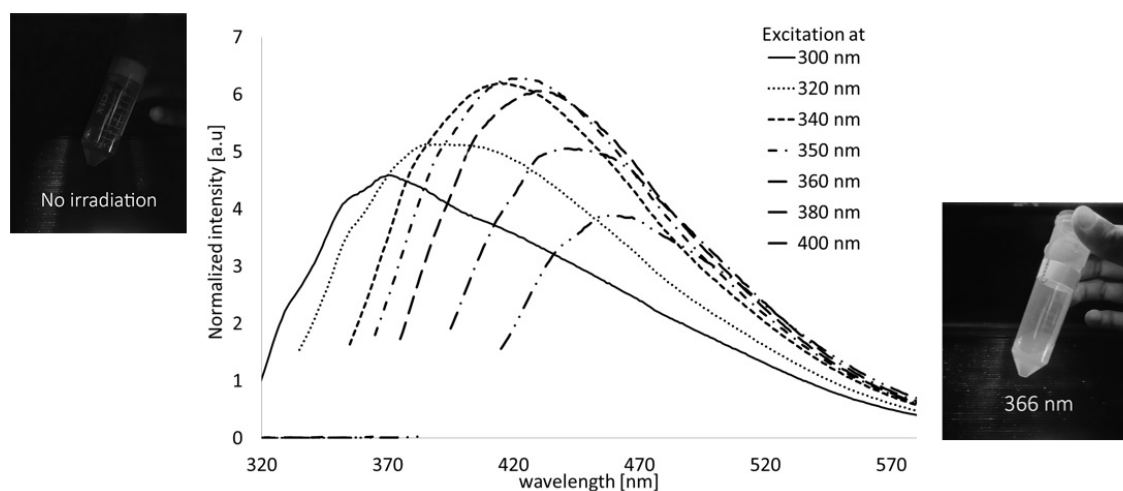
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**Different types of carbon quantum dots obtained from wastes of fermentation**M. Varisco<sup>1</sup>, D. Zufferey<sup>1</sup>, O. Mamula Steiner<sup>1\*</sup><sup>1</sup>University of Applied Sciences of Western Switzerland, HEIA-FR

CQDs are a multifunctional material which knew a rapid growth of interest from its discovery in 2004,<sup>1</sup> because of their multiples applications: catalysis agents, bio-imaging chromophores, photoluminescent or electroluminescent materials, metal ions detectors and electron-acceptors for photovoltaics.<sup>2, 3</sup>

Many starting materials have been used to obtain the CQDs. Here we present a new material source which is the wine lees, an expensive-to-treat, phytotoxic waste resulting in vast amounts from the wine fermentation.<sup>4</sup>

We will present here the procedure leading to an easy, scalable synthetic process for CQDs as well as their characterisation (e.g. photoluminescence, fig.1).



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## Porous MOFs and molecular capsules for gas absorption based on anthracene derivatives.

S. Vasylevskiy<sup>1</sup>, K. M. Fromm<sup>1\*</sup>

<sup>1</sup>University of Fribourg

The synthesis and study of new functional materials for the adsorption of potentially valuable energetic gases is an extremely demanding area in modern chemistry, since we have global warming issues causing climate change and natural disasters as a result. Therefore, reduction of the amount of CO<sub>2</sub> and CH<sub>4</sub> in the atmosphere is crucial for the “green” future of our globe.<sup>[1-2]</sup> Secondly, the high partial pressure of hydrogen can be decreased upon adsorption processes by porous materials which gives the possibility of sorption, storage and transportation of molecular hydrogen.<sup>[3]</sup> Then the absorbed hydrogen can be easily used as a fuel for industry and for cars due to its green product upon combustion with oxygen.<sup>[4]</sup> Thus, the synthesis of new materials for such purposes, especially metal organic frameworks (MOFs) is one of the key directions.

At this SCS meeting we will present new MOFs and coordination compounds of Ni(II), Cu(II) and Zn(II) which have been synthesized with anthracene derived ligands. Their crystal structure (Fig. 1a-b) was determined by single crystal x-ray diffraction. The complexes show different types of voids: open infinite 1-D channels with diameters ranging from 8 to 20 Å, as well as 0-D capsules. Estimating the porosity by calculation with the crystallographic program PLATON, the complexes show 37-50% of porosity. The determination of the sorption capacity by BET for CO<sub>2</sub>, CH<sub>4</sub> and H<sub>2</sub> for the Ni-MOF and the capsule compounds of Cu(II) and Zn(II) will complete the study.

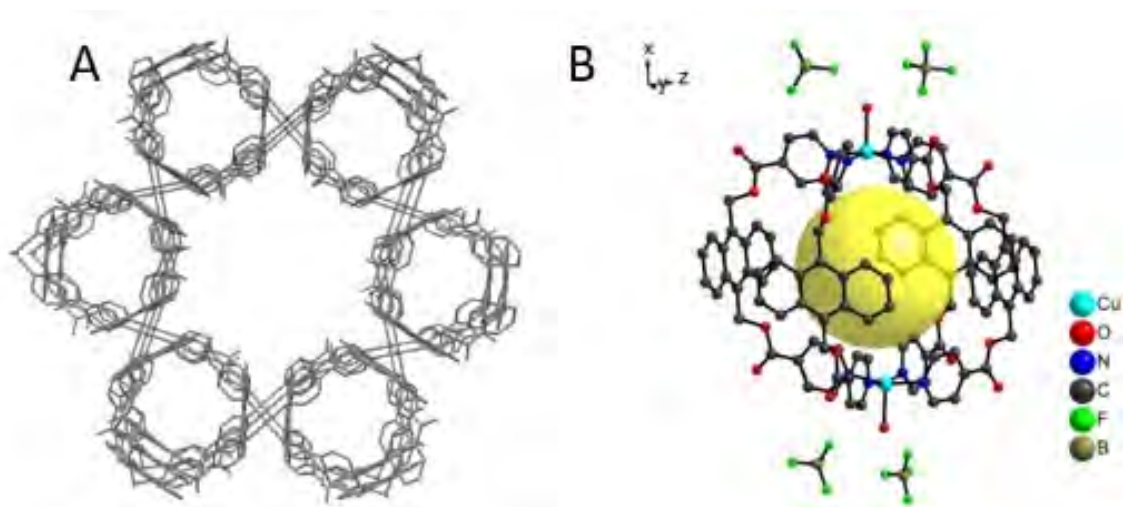


Fig 1. A) Hexagonal structure of Ni-MOF  $\{[\text{Ni}(\text{L})_4\text{Cl}_2]\}_n$  with pore size  $8 \times 8$  Å and  $20 \times 20$  Å. B) Structure of Cu-capsule  $\{[\text{Cu}_2(\text{L})_4(\text{H}_2\text{O})_2](\text{BF}_4)_4\}_n$ .

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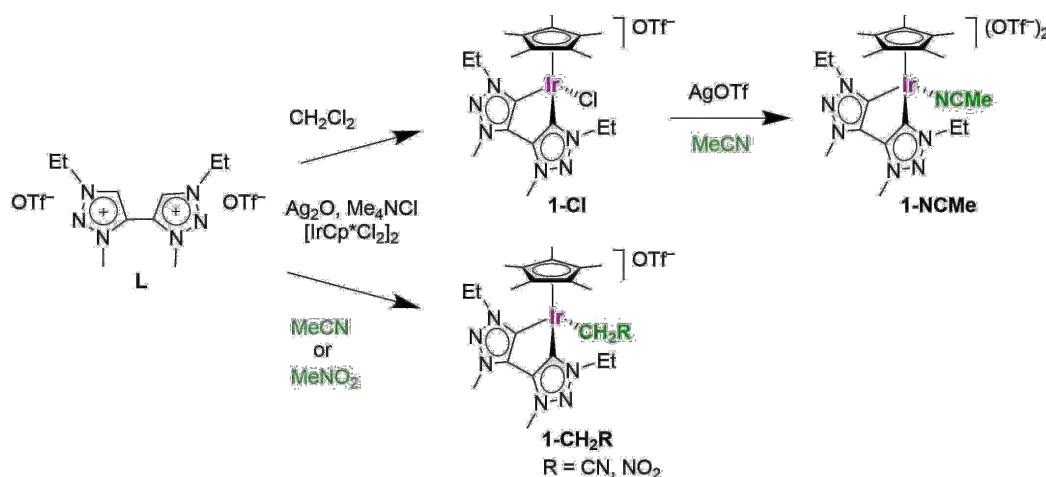
## Activation of $sp^3$ Carbon-Hydrogen Bonds Mediated by Bis(NHC) Iridium Complexes

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The activation and functionalization of C-H bonds remains a significant challenge for organometallic chemistry, with wide implications for organic synthesis. Many transition-metal systems that initiate stoichiometric C-H activation are known, but complexes capable of both C-H activation and subsequent transformations of the substrate are relative rare,<sup>1</sup> especially for substrates with  $sp^3$  C-H bonds.<sup>2</sup> Considering the high activity of iridium complexes in mediating C-H bond activation, in particular when bound to triazolylidene ligands,<sup>3</sup> we became interested in investigating a range of iridium complexes containing bis(carbene) ligands for facilitating alkyl C-H bond activation.<sup>4</sup>

Herein, we describe the C-H bond cleavage of acetonitrile and nitromethane by iridium(III) complexes bearing bis(triazolylidene) ligands. Metal hydroxide species formed during the metalation step have been demonstrated to be responsible of the bond scission.<sup>5</sup> Moreover, we will discuss opportunities to couple this alkyl fragment to substrates, potentially providing a new method for alkyl functionalization.



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**From Frustrated Ligands Towards Thermally Activated Delayed Fluorescence**T. von Arx<sup>1</sup>, K. Venkatesan<sup>1,2\*</sup>

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Intramolecular frustrated Lewis pairs (FLP) recently gained an intense interest due to their ability to activate small molecules (e.g. CO, NO, SO<sub>2</sub> etc.)<sup>[1]</sup>. Especially the reversible activation of H<sub>2</sub> had raised the number of metal-free protocols for catalytic hydrogenations using FLPs<sup>[2]</sup>. Since they bear a donor center (Lewis base) and an acceptor center (Lewis acid) which are spatially separated, intramolecular FLPs could be utilized as a suitable ligand-framework for metal centers<sup>[3]</sup>. With such a new class of transition-metal complexes we target thermally activated delayed fluorescence (TADF) – as a donor/acceptor interplay in the emitter molecules is known to decrease the T<sub>1</sub> - S<sub>1</sub> energy difference and therefore enhance the reverse intersystem crossing (RISC)<sup>[4]</sup>.

Hence, our group synthesized and photophysically investigated a series of Au(I) complexes bearing a P/B-FLP and an aryl or an alkyne as ancillary ligand. By altering the donor/acceptor ability of the ancillary ligand we tend to tune the ratio between prompt (prompt fluorescence or phosphorescence) and delayed (TADF) emissions.

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## The Unexpected Role of Ligand Moieties on the Catalytic Activity of Cobalt-Tetra-pyridyl Complexes

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The catalytic properties of Co(II)-tetra-pyridyl (CoTPY) complexes for hydrogen production have been examined for a long time. Despite the fact that more effective WRCs are known, CoTPY and its derivatives offer ideal subjects to study mechanistic aspects of water reduction. The understanding of this 2-electron-2-proton transfer is of crucial importance to improve catalytic systems in terms of efficiency and stability and finally to drive photo catalysis towards being a sustainably applicable energy source.

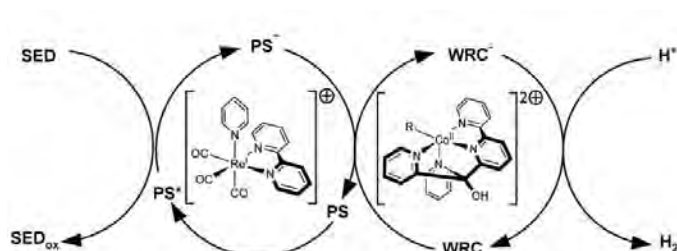


Figure 1: General mechanism of a molecular photocatalytic system including photosensitizer (PS), water reduction catalyst (WRC) and sacrificial electron donor (SED). R = H<sub>2</sub>O

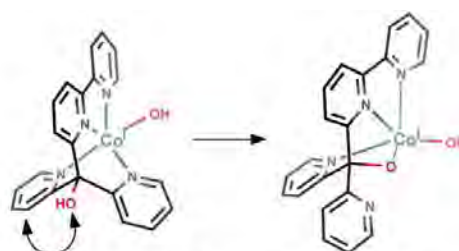


Figure 2: Ligand switch reaction from the pyridine-coordinated to the active, oxygen-coordinated form of Co(II)-tetra-pyridyl WRC

Following on the work of P. Hamm et al.<sup>[1]</sup>, we investigated the catalytic mechanism of a cobalt(II)-tetra-pyridyl complex at pH 8.5. For a photocatalytic system including a rhenium(I)-based photosensitizer (PS) and triethanolamine as sacrificial electron donor (SED, see Fig.1), P. Hamm suggested successive reduction-protonation-reduction-protonation steps, leading to the release of H<sub>2</sub> and back to the initial Co(II) state of the catalyst. However, our time resolved NEXAFS measurements in a new experimental setup on the very same system brought up so far not observed mechanistic steps, precisely, an irreversible initial reaction, leading to the actual catalytic cycle. More specifically, irreversible changes of the X-ray fluorescence spectra of the cobalt upon illumination of the sample, combined with the unchanged catalytic activity of the solution implied that the catalyst undergoes an irreversible structural change during the initial phase. Most probably, the low-spin configuration of the reduced Co(I) intermediate, which is required for the following protonation (see Fig. 2) is stabilized by a “ligand-switch”, upon which the oxygen at the bridge-position coordinates the cobalt center instead of one pyridine moiety. This in situ formed cobalt complex is catalytically active and retains its configuration even after switching of the light source. Such a mechanistic approach has not been considered so far and might have a large influence on the development of new, more active and stable WRCs.

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**Cobalt Complexes as Electrolytes in Combination with Copper(I) Dyes in Dye Sensitized Solar Cells**

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<sup>1</sup>University of Basel

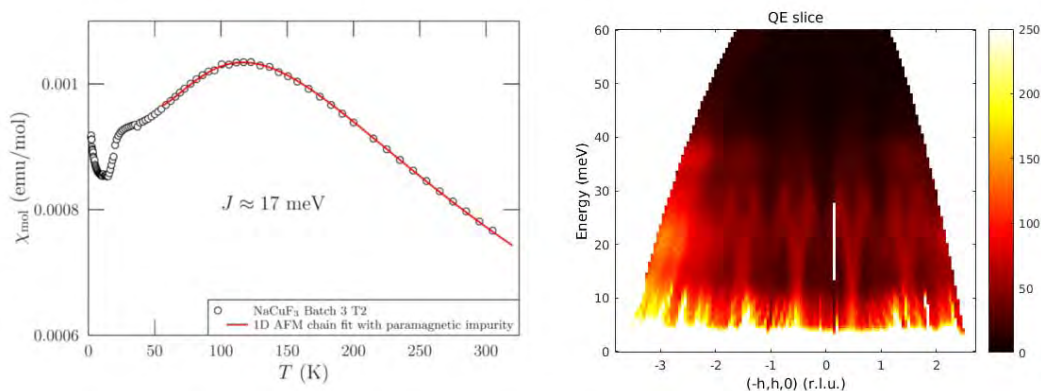
In order to achieve higher efficiencies and prolong long-term stability in dye sensitized solar cells (DSCs) the widely-used iodine/triiodide electrolyte is replaced by various cobalt(II)/cobalt(III) polypyridyl complexes. In our research we use heteroleptic copper(I) complexes as dye sensitizers. The complexes consist of an ancillary and an anchoring ligand, both of which are bidentate polypyridyl containing units. The ancillary ligand harvests the incident photons and the anchoring ligand binds the complex to the semiconductor surface of the photoanode.

Since the most commonly used iodine/triiodide electrolyte has a number of major downsides such as its corrosive nature, absorption of visible light and its not-tunable energy level. Cobalt electrolytes address all these major drawbacks as they absorb less visible light, they are not corrosive and their energy level can be altered by modifying or exchanging the ligands.

In our research we test the combination of different copper(I) dyes with cobalt electrolytes whilst optimizing the concentration, solvent and changing the additives of the electrolyte

**An experimental approach to solve the single-band Hubbard model in new fluorides**F. Xiao<sup>1,2</sup>, K. W. Krämer<sup>2\*</sup>, C. Rüegg<sup>1\*</sup><sup>1</sup>Paul Scherrer Institut, <sup>2</sup>University of Bern

A strongly correlated electron system may be described by the single-band Hubbard model[1]. Despite the simple form, the richness of the Hubbard model's phase diagram has attracted much current research interests. In this project, experimental work on a physical realization of the Hubbard model NaCuF<sub>3</sub> has been carried out inspired by recent theoretical calculation[2], aiming to solve the Hubbard model with a more practical approach. Large quantities of NaCuF<sub>3</sub> single crystals have been successfully synthesized using solid state chemistry methods. The samples were characterized by means of x-ray powder diffraction and magnetic susceptibility measurements. This fluoride compound forms a low-dimensional quantum Heisenberg system with the superexchange pathway going through corner-sharing CuF<sub>6</sub> octahedra. The excitation spectra revealed by recent inelastic neutron scattering experiment, has shown a two-spinon continuum at low temperature, characteristic of a well-isolated antiferromagnetic Heisenberg spin chain.



(Left) The magnetic susceptibility of NaCuF<sub>3</sub>. Red solid lines correspond to a linear antiferromagnetic chain fit above 50 K. The extracted intra-chain coupling  $J$  is 17 meV. A phase transition is also observed below 20 K. (Right) Extracted from the inelastic neutron scattering results, the neutron intensity is displayed as a function of momentum and energy along the spin chain  $(-110)$  direction. Two spinon continuum spectra was observed, characteristic of 1D antiferromagnetic chain.

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## A Disassembly Approach for Imaging Endogenous Pyrophosphate in Living Cells using Metal-Salen Complexes

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In this poster, a stimulus-induced disassembly approach in water is presented<sup>1</sup>. In this approach, an analyte sequesters selectively a metal ion from a metal-chelate complex, leaving behind the “unlocked” ligand. This metal free ligand then hydrolyses into its molecular subunits. This hydrolysis reaction induced by the analyte binding to the metal is detectable as the optical properties of the free ligand and the hydrolysed species are distinguishable.

The focus is on the fluorometric detection of pyrophosphate which is an important diagnostic marker in many diseases like cancer, with metal salen complexes in water and biological media.<sup>1-3</sup> Initially, the intrinsic fluorescence of the salicylaldehyde is quenched in the metal complex, but reverts back during the disassembly of the salen ligand.



Unprecedented applications of this strategy for endogenous pyrophosphate detection in the mitochondria of bacterial cells are presented.<sup>4</sup>

Ongoing research focuses on synthesizing optimized probes for targeting various cell organelles.

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## Orbital Analysis of Carbon-13 Chemical Shift Tensors Reveals Patterns to Distinguish Fischer and Schrock Carbenes

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Fischer and Schrock carbenes have M=C bonds that display highly deshielded carbon chemical shifts (greater than 250 ppm), in particular Fischer carbenes (greater than 300 ppm). They are typically described according to the electrophilic and nucleophilic nature of their metal-carbon double bonds. Recently, we have shown that the analysis of <sup>13</sup>C NMR chemical shift anisotropy (CSA), defined by its principal components  $\delta_{ii}$  ( $\delta_{11}$ ,  $\delta_{22}$ ,  $\delta_{33}$ ), and the corresponding chemical shielding  $\delta_{ii}$ , is a powerful tool to understand the nature of M=C bonds in Schrock alkylidenes (**1**).<sup>1</sup> Here, we show how this approach, which combines solid-state NMR spectroscopy and DFT calculations supplemented by localized MO analysis (called NCS analysis), can provide characteristic information about Fischer carbenes (**2**) and Ru-based carbenes (**3**) in comparison with Schrock alkylidenes (**1**) (Figure 1). The highly deshielded <sup>13</sup>C isotropic chemical shifts observed for Fischer carbenes result from the particularly low-lying  $\pi^*(M=C)$  associated with the CO ligand. The same analysis on Ru-based metathesis catalyst show that they are similar to Schrock alkylidenes, albeit with a high-lying Ru=C  $\sigma$  orbital associated with the  $d^6$  configuration of Ru.

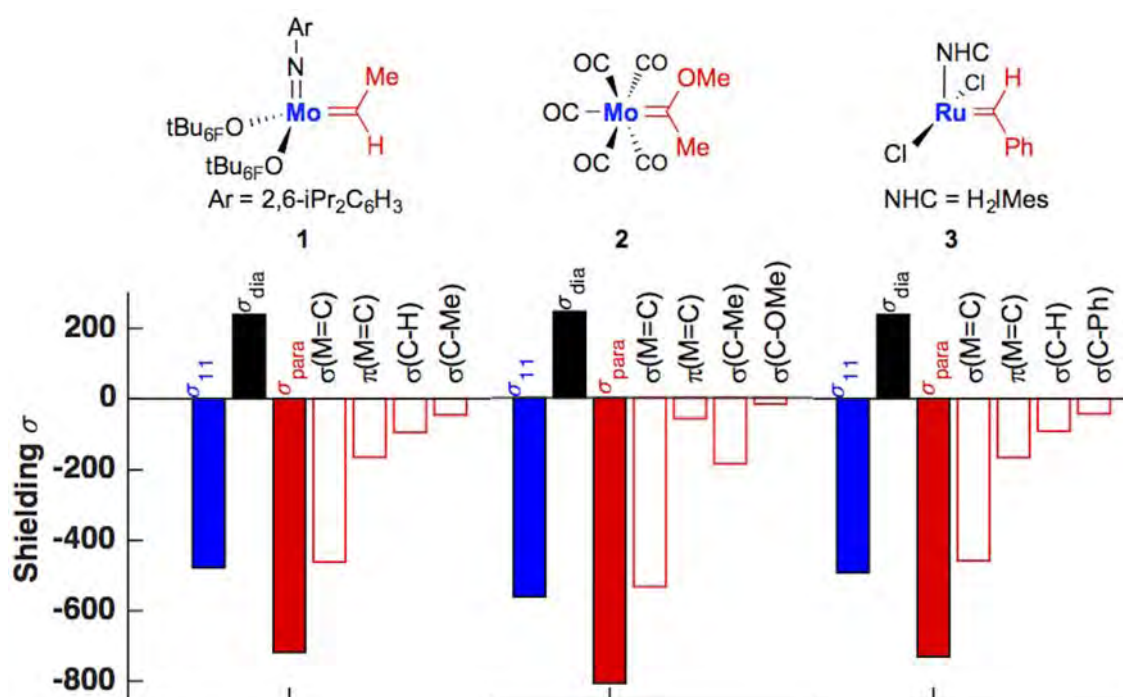


Figure 1. Histograms of orbital contributions to  $\sigma_{11}$  of M=C complexes based on NCS analysis.

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## Upscaling Colloidal Nanocrystal Hot-Injection Syntheses via Reactor Underpressure

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Hot-injection technique approaches are convenient and fast one-pot processes, which are capable of providing colloidal nanocrystals with ultra-narrow size distributions. Effective time separation between nucleation and growth processes is facilitated by fast addition (*i.e.*, injection) of an elemental precursor or reducing agent to the hot reaction mixture. However, it is this fast addition of large volumes that presents a serious challenge for upscaling hot-injection protocols.

Here we focus on the possibility to upscale injection-based syntheses of colloidal nanocrystals without modifying the original protocol or using specially designed jet equipment. This work presents an easy and universal solution for linear upscaling of hot-injection synthesis (**Fig. 1**). [1] Applying a mild vacuum to the reaction mixture prior the injection enables an injection rate of  $100\text{-}150\text{ mL}\cdot\text{s}^{-1}$  such that large volumes of 200-500 mL can be introduced into the reaction flask within few seconds. We apply this underpressure-assisted approach to successfully upscale synthetic protocols for metallic (Sn) and semiconductor (PbS, CsPbBr<sub>3</sub> and Cu<sub>3</sub>In<sub>2</sub>Se<sub>9</sub>) nanocrystals by one-to-two orders of magnitude to obtain tens of grams of nanocrystals per synthesis. We provide the technical details of how to carry out underpressure-assisted upscaling and demonstrate that nanocrystal quality is maintained for the large-batch syntheses by characterizing the size, size distribution, composition, optical properties, and ligand coverage of the nanocrystals for both small- and large-scale syntheses.

This work shows that fast addition of large injection volumes does not intrinsically limit upscaling of hot injection-based colloidal syntheses. An underpressure-governed hot-injection method enables a systematic optimization of nanocrystals and nanocrystal-based devices from a single source batch for research and development purposes and reinforce the commercial viability of electronic, photonic, and electrochemical devices that use large numbers of colloidal nanocrystals (*e.g.*, solar cells, lithium-ion batteries, thermoelectrics, phase-change memories, etc.).

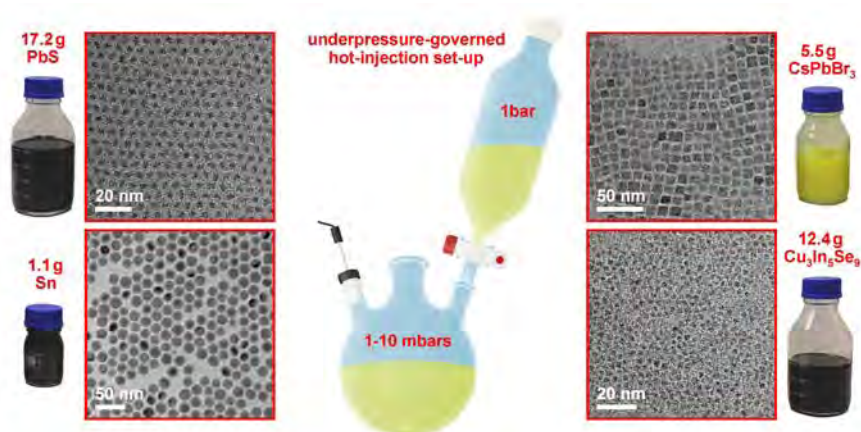


Fig. 1. Schematic illustration of underpressure-governed hot-injection set-up and various colloidal nanocrystals, obtained from single-batch large-scale syntheses

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## Hydrogen Bonded Arene Ruthenium Metalla-Assemblies

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Hydrogen bonds are the most utilized non-covalent interactions in biological systems, due to their directionality, stability, reversibility and diversity. The weak strength of hydrogen bonds can be modified by combining several hydrogen bonds in the same unit like in the melamine-cyanuric/barbituric acid rosette-type system.<sup>1</sup>

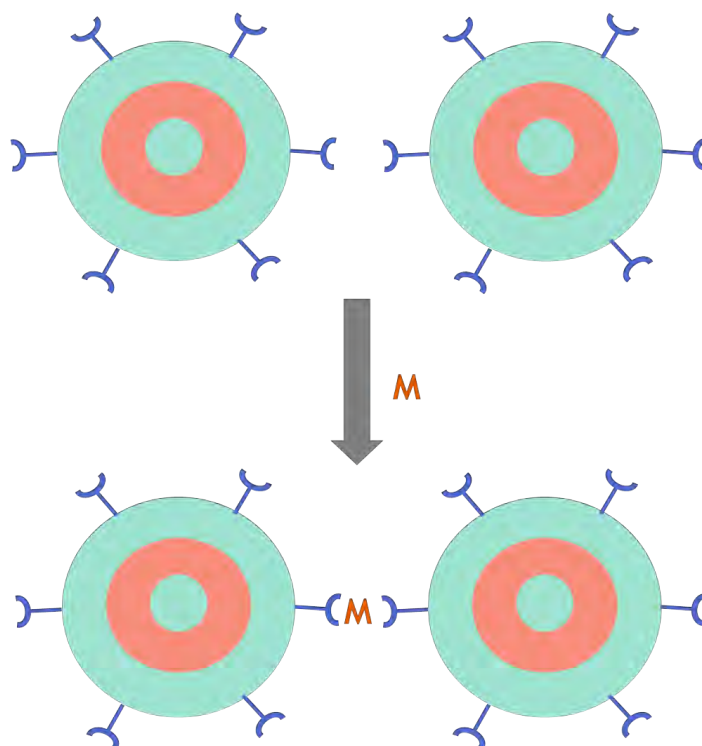
Arene ruthenium metalla-assemblies have showed great biological potential.<sup>2,3</sup> Inspired by the combination of Hbonding and metal complexation from the group of de Mendoza,<sup>4</sup> we have recently prepared a series of hydrogen bonded metalla-assemblies.<sup>5</sup> Therefore, to further investigate hydrogen bonded metalla-assemblies, we used the melamine-barbituric rosette-type system with piano-stool complexes. The introduction of a pyridyl group on the barbituric acid moiety allows coordination of metals at the periphery of the rosette. New rosette-type metalla-assemblies have been prepared and fully characterized.



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**Molecular factories based on  $\{M(2,2':6',2''\text{-terpyridine})_2\}^{2+}$ -zipped co-block polymer vesicles**A. Wiesler<sup>1</sup>, C. G. Palivan<sup>2</sup>, A. I. Dinu<sup>2</sup>, E. C. Constable<sup>1\*</sup>, C. E. Housecroft<sup>1\*</sup><sup>1</sup>Department of Chemistry, University of Basel, Spitalstrasse 51, 4056 Basel, Switzerland, <sup>2</sup>Department of Chemistry, University of Basel, Klingelbergstrasse 80, 4056 Basel, Switzerland

We show how the chelating power of bis(2,2':6',2''-terpyridine)metal(II) complexes can be applied to 'zip' together co-block polymer vesicles to give pre-organized assemblies.<sup>1</sup> Different approaches have been used to functionalize polymer vesicles which condense with appropriately functionalized 2,2':6',2''-terpyridine (tpy) domains; sequential reaction with metal ions e.g. Fe<sup>2+</sup> leads to an organized assembly. All reactions are carried out under ambient conditions and in aqueous media. The principle of the procedure is shown in the scheme below:



**Figure 1:** Strategy for assembly of arrays of coupled polymer vesicles.

The characteristic MLCT absorption associated with the  $\{Fe(tpy)_2\}^{2+}$  chromophore is a powerful probe with which to assess the degree of vesicle aggregation. This along with AFM and TEM studies will be discussed.

The ordered structure of the polymer vesicle assembly provides a platform for an array of artificial compartments for a molecular factory. Surface modification is particularly attractive.<sup>2</sup> Future directions of the work will be discussed, e.g. encapsulation of components of the 'factory' within hollow vesicles and communication between the compartments.

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