CHIMIA
CHIMIA 2015, Volume 69
ISSN 0009-4293
www. chimia.ch

SCS
Swiss Chemical
Society

Supplementa to Issue 7-8/2015

SCS Fall Meeting 2015

Poster Abstracts
Session of Inorganic & Coordination Chemistry

September 4, 2015
Ecole Polytechnique Fédérale de Lausanne (EPFL)
http://scg.ch/fallmeeting/2015

Swiss Chemical Society
Haus der Akademien
Postfach
3001 Bern
Switzerland
info@scg.ch
www.scg.ch

Homogeneous Catalytic Hydrogen Storage and Release in the Formic Acid-Carbon Dioxide Couple using Ruthenium Pre-Catalysts.

A. van Muyden, K. Sordakis[1], G. Laurenczy[1]*

[1]EPF Lausanne

The rapid increase in global energy consumption along with the depletion of fossil fuel resources require for alternative, environmentally benign and storable forms of energy to be developed. Furthermore anthropogenic greenhouse gas emissions are dramatically accelerating climate change, which has become a major concern in the last decades. In order to replace fossil fuels an attractive candidate that has gained considerable interest is hydrogen (H_2).[1] The utilization of H_2 as an energy carrier results in no direct greenhouse gas release and could provide a viable and sustainable option for meeting the world's energy requirements due to high abundance of hydrogen (e.g. in water). One of the primary challenges that needs to be overcome, besides H_2 production using renewable energy sources, is H_2 storage. Owing to the very light and inflammable nature of H_2 gas, the conventional methods, *i.e.* high pressure tanks and cryogenic storage, suffer in terms of inherent safety and energy efficiencies. Liquid chemical storage media, including methanol and formic acid (FA), are promising alternatives that have gained attention in recent years.[2] In particular formic acid, being a liquid and having low toxicity, arises as a good compromise between energy density (53 g/L) and safety.[3,4] In order for a carbon neutral hydrogen storage cycle to be envisaged, formic acid should be obtained via direct hydrogenation of carbon dioxide (CO_2)[5] (Figure 1).

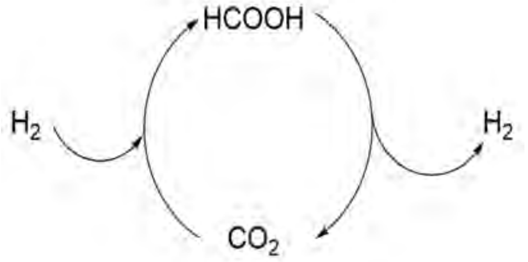


Figure 1. Hydrogen storage in the formic acid-carbon dioxide couple.

In our approach a FA-triethylamine adduct, which is well known to act as a hydrogen donor in transfer-hydrogenation reactions, was utilized as substrate in the dehydrogenation reactions. It is known that the presence of basic additives facilitates catalytic CO_2 hydrogenation viadecrease of the Gibbs free energy term. Therefore also the hydrogen storage step was realized in presence of triethylamine or with bicarbonate salt as the substrate. The activity and stability of ruthenium based catalysts for both directions in Figure 1 were evaluated in N,N-dimethylformamide as solvent. The reactions were followed by quantitative NMR spectroscopy and/or by monitoring the pressure increase due to gas formation as a function of time. The viability of this promising energy storage cycle is discussed.

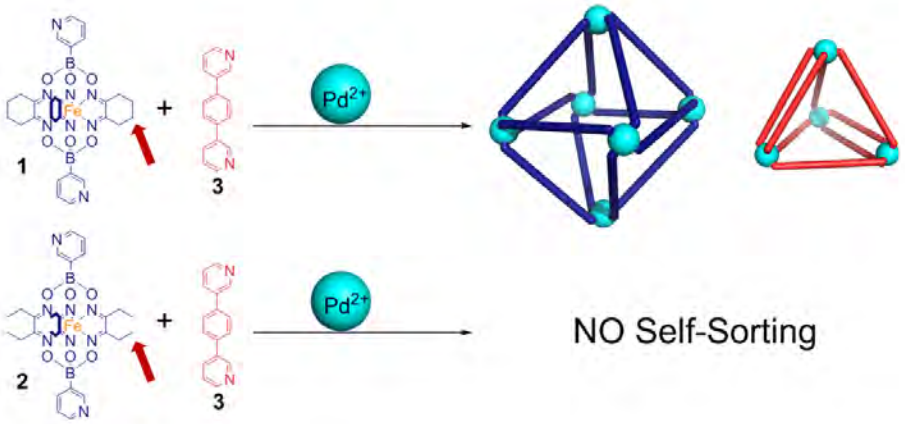
[1] David A. J. Rand, Ronald M. Dell, *Hydrogen Energy - Challenges and Prospects*, RSC, Cambridge, **2008**.
[2] Ferenc Joó, *ChemSusChem* **2008**, 1, 805–808.
[3] Céline Fellay, Paul J. Dyson, Gábor Laurenczy, *Angewandte Chemie International Edition* **2008**, 47, 3966–3968.
[4] B. Loges, A. Boddien, H. Junge, M. Beller,*Angewandte Chemie International Edition***2008**, 47, 3962–3965.
[5] Séverine Moret, Paul. J. Dyson, Gábor Laurenczy, *Nature Communications* **2014**, 5, DOI 10.1038/ncomms5017.

Self-sorting of Pd-based coordination cages: the importance of subtle steric effects

G. Cecot[1], M. Wise[1], K. Severin[1]*

[1]EPF Lausanne

Self-sorting phenomena have rapidly grown into a main theme of supramolecular chemistry in recent decades [1,2]. Highly selective narcissistic self-sorting can be obtained in the formation of metallosupramolecular cages with naked Pd^{2+} ions. The self-assembly process takes place when a clathrochelate-based 3,3'-bipyridyl ligand [1] is combined with a less bulky, isostructural oligo(phenyl) analogue and a palladium salt. Small structural changes, concerning only a few atoms on the clathrochelate ligand, are sufficient to completely change the outcome of the self-assembly process, and determine whether a complex library of products or a self-sorted mixture of just two distinct assemblies is formed. The library consists of multiple heteroleptic assemblies, the ligand ratios in which were determined by MS analysis. Furthermore, the two components of the narcissistic self-sorting mixture, which may be prepared individually from the corresponding 3,3'-bipyridyl ligand and Pd^{2+} ions, do not undergo ligand exchange when combined. These observations unveil a finely balanced state of thermodynamic equilibrium which, remarkably, may be tipped in one direction or another by a minute structural adjustment.



[1]. M. D. Wise, J. J. Holstein, P. Pattison, C. Besnard, E. Solari, R. Scopelliti, G. Bricogne and K. Severin, *Chem. Sci.* **2015**, 6, 1004-1010.

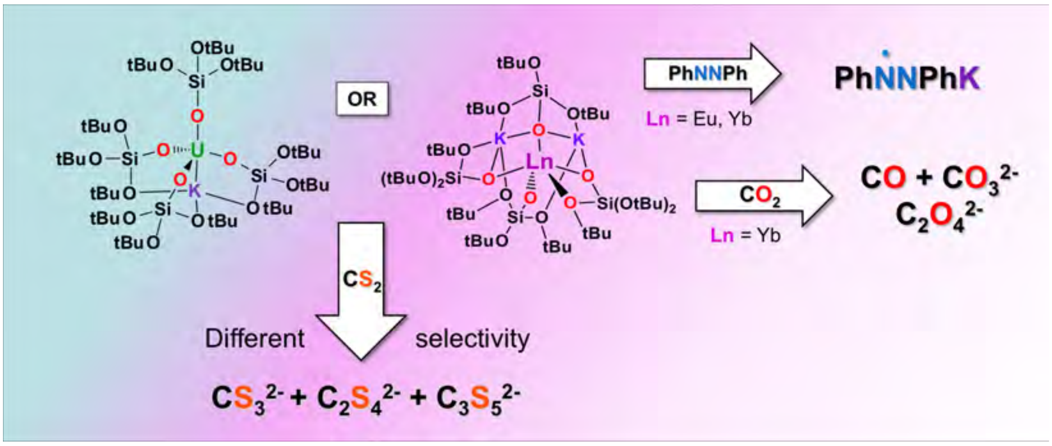
Small Molecule Activation at siloxide “ate” complexes of f elements

J. Andrez[1]

[1]Ecole Polytechnique Fédérale de Lausanne

The activation of small molecules (CO_2, CS_2, N_2...) is an important current goal in catalysis.Thanks to their oxophilicity and their Lewis acid character, divalent lanthanide complexes are good candidates for promoting small molecule activation. Yet only few examples of Ln(II) mediated CO_2 reduction have been reported and all of them involve the highly reducing Sm(II) ion.[1, 2, 3] Carbocyclic compounds have been so far the most widely used supporting ligands in reactivity studies of low valent f elements. However, recently our group has showed that commercial siloxides are effective ligands that allow the tuning of steric bulk and electronic properties at the metal center. In particular, tertbutoxy siloxide ligands can lead to stable neutral and “ate” complexes of uranium(III) enabling a rich reactivity towards small molecules such as CO_2, CS_2.[4]

We will present some recente advances in reactivity studies of U(III) and Ln(II) siloxide complexes. In particular, we will show how simple tertbutoxy siloxide ligands can turn on the reactivity of poorly reducing Eu(II) and Yb(II) ions towards heteroallens. Notably, highly reductive Eu(II) and Yb(II) “ate” complexes have been prepared that show unprecedented reactivity with azobenzene and carbon dioxide.[5] We will also compare the reactivity of 4f and U(III) siloxide ate complexes toward CS_2, and discuss the potential presence of cooperative effects in heterobimetallic complexes.[6]



[1] W. J. Evans, C. A. Seibel and J. W. Ziller, *Inorg. Chem.*, **1998**, 37, 770.
[2]W. J. Evans, J. M. Perotti, J. C. Brady and J. W. Ziller, *J. Am. Chem. Soc.*, **2003**, 125, 5204.
[3]N. W. Davies, A. S. P. Frey, M. G. Gardiner and J. Wang, *Chem. Commun.*, **2006**, 4853.
[4]V. Mougel, C. Camp, J. Pécaut, C. Copéret, L. Maron, C. E. Kefalidis and M. Mazzanti, *Angew. Chem. Int. Ed.* **2012**, 51, 12280.
[5]J. Andrez, J. Pécaut, P.-A. Bayle, and M. Mazzanti, Angew. *Chem. Int. Ed.*, **2014**, 53, 10448.
[6]C. Camp, O. Cooper, J. Andrez, J. Pécaut, and M. Mazzanti, *Dalton Trans.*, **2015**, 44, 2650-2656.

A viable hydrogen storage and release system based on formate and bicarbonate salts: mechanistic insights into the hydrogen release step.

K. Sordakis[1], A. F. Dalebrook[2], G. Laurenczy[1]*

[1]EPF Lausanne, [2]École Polytechnique Fédérale de Lausanne

In view of the rapidly declining fossil fuel resources and the accelerating global warming due to anthropogenic carbon dioxide emissions, the utilization of hydrogen as an energy vector is more than ever becoming a pole of attraction in research.[1] Key features in favor of long-term incorporation of H_2 into our energy system include its clean production and utilization pathways, attractive inherent fuel properties and its borderless availability. However in order to take advantage of its full potential, a storage method guaranteeing safe handling along with increased energy efficiency needs to be developed.[2] We studied the utilization of aqueous formate and bicarbonate solutions, which are non-toxic, non-corrosive, non-irritating and can be easily stored and transported owing to their liquid nature, as hydrogen carriers (Figure 1).[3–5]

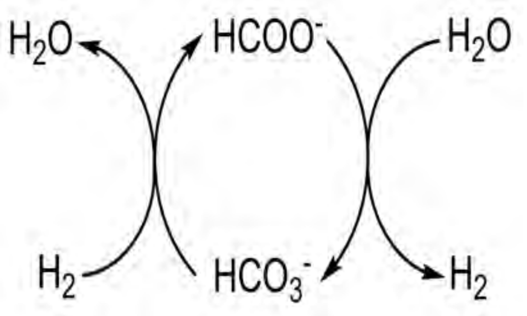


Figure 1. Hydrogen storage and release based on the formate/bicarbonate cycle.

The utilization of water as a solvent adds to the straightforward, cost-effective and “green” nature of this H_2 storage system. Its applicability strongly depends on both the maximum solubility and the conversion of the substrate substances under the specific reaction conditions. The interconnection of the bicarbonate hydrogenation and the formate decomposition reactions realized by the same *in situ* generated catalytic system, which possesses sufficient air stability and recyclability, was examined.[6] An insight into the mechanism of the formate dehydrogenation step provided valuable information about the nature of active catalytic hydride species. The absence of additives and organic solvents enhances the environmental character of the system and makes it more attractive from an economic point of view. Furthermore the formation of by-products is avoided.

The authors are grateful to the Swiss National Science Foundation and EPFL for financial support. Dr. P. Miéville is thanked for valuable support with NMR techniques.

[1] Kaveh Mazloomi, Chandima Gomes, *Renewable and Sustainable Energy Reviews,* **2012**, 16, 3024–3033.
[2] Martin Grasemann, Gábor Laurenczy, *Energy and Environmental Science,* **2012**, 5, 8171.
[3] Gábor Papp, Jenő Csorba, Gábor Laurenczy, Ferenc Joó, *Angewandte Chemie International Edition,* **2011**, 50, 10433–10435.
[4] Albert Boddien, Felix Gärtner, Christopher Federsel, Peter Sponholz, Dörthe Mellmann, Ralf Jackstell, Henrik Junge, Matthias Beller,*Angewandte Chemie International Edition,* **2011**, 50, 6411–6414.
[5] Antonella Guerriero, Hervé Bricout, Katerina Sordakis, Maurizio Peruzzini, Eric Monflier, Frédéric Hapiot, Gábor Laurenczy, Luca Gonsalvi, *ACS Catalysis,* **2014**, 3002–3012.
[6] Katerina. Sordakis, Andrew. F. Dalebrook, Gábor Laurenczy, *ChemCatChem,* **2015**, accepted manuscript.

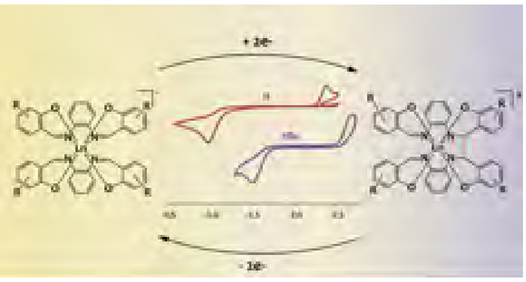
Multi-Electron Redox Reactions Promoted by f-Elements Complexes

M. Falcone[1], M. Mazzanti[1]*

[1]EPF Lausanne

Multi-electron redox reactions play a key role in many biological and synthetic catalytic processes. Multiple-electron transfer reactions can be achieved from the association of redox-active metal centers and polydentate unsaturated ligands which can store electrons in a reduced form. Alternatively several redox active metal centers can be combined in a polynuclear assembly to allow multielectron reactions; A particular high current interest arises from the ability of complexes of low-valent f-elements to promote unusual reductive chemistry through unusual reaction pathways, including attractive examples of CO, CO_2 and N_2 activation. This renders particularly attractive the development of f-elements complexes capable of performing multi-electron reductions.

Schiff bases are easy to synthesize, highly p-delocalized ligands that can stabilize metals in different oxidation states. Such redox-active ligands also provide a convenient way to store electrons in complexes of transition elements through metal assisted reversible reductive coupling of the imino groups. Surprisingly the use of such Schiff base ligands in f element chemistry has mostly been limited to the chemistry of uranyl(VI) and trivalent lanthanides. We have recently shown that the tetradentate Schiff base salophen can be used to stabilize reduced uranium and lanthanide complexes by storing electrons in C-C bonds formed by reductive coupling of the imino groups.[1]-[3] The stored electrons can become available to oxidizing agents through cleavage of the C-C bond. The reductive coupling of the Schiff base yields mono and poly-nuclear uranium complexes well suited for the study of magnetic interaction and reactivity. Here we will present the structure and reactivity of new multi-electron redox systems based on f elements.



[1] C. Camp, V. Mougel, P. Horeglad, J. Pecaut, M. Mazzanti, *J. Am. Chem. Soc.* **2010**, 132, 17374-17377.
[2] C. Camp, V. Guidal, B. Biswas, J. Pecaut, L. Dubois, M. Mazzanti, *Chem. Sci.* **2012**, *3*, 2433-2448;.
[3] C. Camp, L. Chatelain, V. Mougel, J. Pecaut, M. Mazzanti, *Inorg. Chem.* **2015**,http://dx.doi.org/10.1021/acs.inorgchem.5b00467.

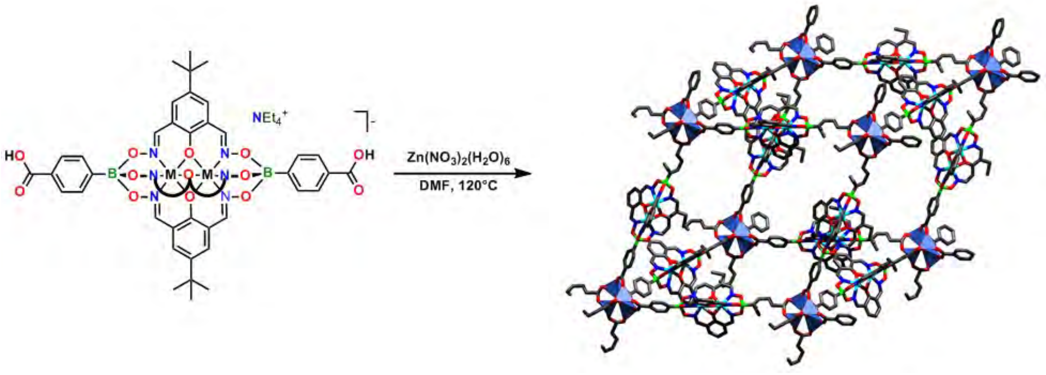
Carboxylic acid-functionalized clathrochelate complexes as scaffolds for supramolecular metalloligands

M. Marmier[1], R. Scopelliti[1], J. Holstein[2], K. Severin[1]*

[1]EPF Lausanne, [2]Global Phasing Ltd, Cambridge, UK

Metal-organic frameworks (MOFs) are a rising class of compounds that are formed from the self-assembly between organic ligands (linkers) and metal clusters known as secondary building units (SBUs). MOFs are of broad interest for their wide variety of applications such as gas storage, catalysis, sensing or separation of compounds. Among all known organic ligands that are used in this field, dicarboxylic ligands are the most extensively studied. For example, blockbuster MOF-5 is built from simple benzene-1,4-dicarboxylic acid and Zn_4O clusters and displays very large specific surface area. [1]

In this work, we present a new class of dicarboxylic acid ligands. These complexes display an interesting characteristic for applications in supramolecular chemistry: they are negatively charged. We recently showed that this anionic charge had a direct influence on the stability of supramolecular assemblies.[2] Here we demonstrate that our clathrochelates ligands can be successfully incorporated in several three-dimensional networks and could be used as new tools in metallasupramolecular chemistry.[3]



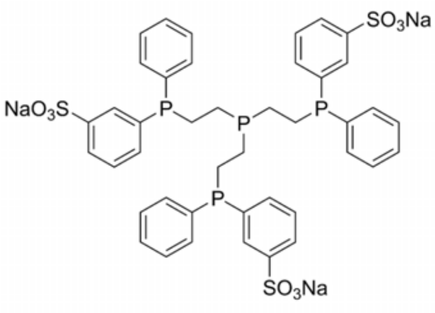
[1]. H. Li, M. Eddaoudi, M. O'Keeffe, O. M. Yaghi, *Nature*, **1999**, *402*, 276-279.
[2]. M. Pascu, M. Marmier, C. Schouwey, R. Scopelliti, J. J. Holstein, K. Severin, *Chem. Eur. J.* **2014**, *20*, 5592 –5600.
[3]. M. Marmier, R. Scopelliti, J. J. Holstein, K. Severin, *manuscript in preparation.*

Selective Hydrogen Production from Formic Acid: Development of Homogeneous Iron Catalysts in Aqueous Solution

M. Montandon-Clerc[1], A. F. Dalebrook[1], G. Laurenczy[1]*

[1]École Polytechnique Fédérale de Lausanne

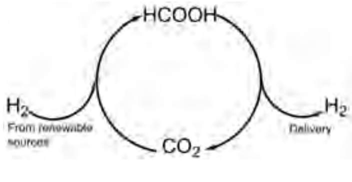
The rapid depletion of fossil fuels will require the use of new energy carriers in the near future. In this perspective, hydrogen is considered as a valid and clean alternative. Currently, hydrogen is stored in pressurized vessels that present safety hazards and are inconvenient to handle.[1–3] Therefore, an important challenge for the scientific community is the development of new hydrogen storage methods. In 2008, our group presented a novel approach for hydrogen generation from formic acid; H_2 release on demand using a robust and effective ruthenium catalyst.[4] Iron based catalysts were later proven to be active in propylene carbonate.[5] Herein we present the results concerning the development of first row transition metal based, non-noble metal catalysts for selective aqueous phase formic acid dehydrogenation. A new, water soluble phosphine ligand, namely the trisulfonated-tris[2-(diphenylphosphino)ethyl] phosphine sodium salt (**PP_3TS**) has been synthesized.



PP_3TS

New catalysts, based on iron(II), were formed *in situ* with this PP_3TS ligand and produce a mixture of H_2 and CO_2 from an aqueous FA solution, requiring no organic co-solvents or bases. Manometry, NMR and FT-IR techniques were used to follow the dehydrogenation reactions, determine kinetic parameters, and analyze the gas mixtures. These water soluble catalysts are completely selective and the gaseous products are free from CO contamination. To the best of our knowledge, these represent the first examples of common transition metal based homogeneous catalysts that selectively dehydrogenate formic acid in aqueous solution.

Acknowledgement: EPFL and SCCER are thanked for financial support.



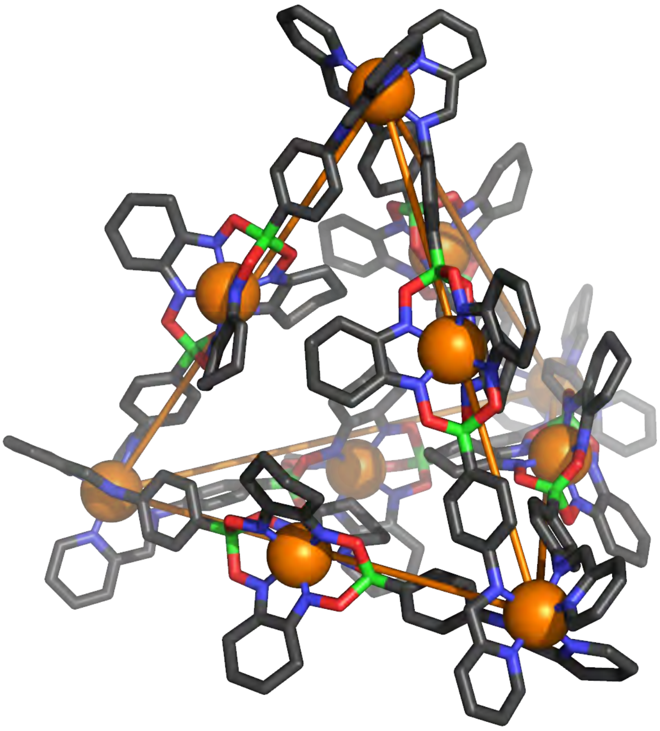
[1] Léon, A. *Hydrogen Technology in Mobile and Portable Applications*; Springer-Verlag: Berlin, Heidelberg, 2008.
[2] Dalebrook, A. F.; Gan, W.; Grasemann, M.; Moret, S.; Laurenczy, G. *Chem. Commun.* **2013**, *49*, 8735–8751.
[3] Grasemann, M.; Laurenczy, G. *Energy Environ. Sci.* **2012**, *5*, 8171–8181.
[4] Fellay, C.; Dyson, P. J.; Laurenczy, G. *Angew. Chemie - Int. Ed.* **2008**, *47*, 3966–3968.
[5] Boddien, A.; Mellmann, D.; Gartner, F.; Jackstell, R.; Junge, H.; Dyson, P. J.; Laurenczy, G.; Ludwig, R.; Beller, M. *Science* **2011**, *333*, 1733–1736.

Supramolecular cages from clathrochelates and stabilized imines

S. M. Jansze[1], K. Severin[1]*

[1]EPF Lausanne

Supramolecular cages have been obtained from simple building blocks with the help of coordination chemistry. As building blocks, we have used clathrochelates, which are constructed from a small molecule containing a boronic acid moiety, di-oximes and an chelating metal ion.[1] When these clathrochelates are functionalized with the right end-groups, they can form larger and more complex coordination structures based on the chemistry of ion-coordination stabilized imines[2]. An extensive study has been performed on the use of different clathrochelates building blocks and the effect different counter ions on the cage formation.



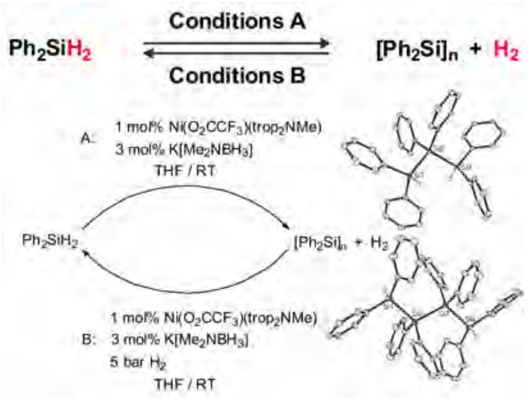
[1] M. D. Wise, A. Ruggi, M. Pascu, R. Scopelliti, K. Severin, *Chemical Science* **2013**, *4*, 1658-1662.
[2] M. M. J. Smulders, I. A. Riddell, C. Browne, J. R. Nitschke, *Chemical Society Reviews* **2013**, *42*, 1728-1754.

Nickel Complexes as Catalysts for Silane Dehydrogenation and Hydrogenative Cleavage Reactions of Oligosilanes.

B. Pribanic[1], M. Trincado[1], H. Grützmacher[1]*

[1]ETH Zurich

Ligands based on the 5*H*-dibenzo[a,d]cyclohepten-5-yl platform (tropylidene = trop) are suited for the stabilization of low-valent metal complexes. Here we report the synthesis of Ni(0) hydride complexes. The hydride species was postulated as intermediate in the dehydrogenation of amino boranes, which proceeds with very high activity[1]. It was found that these complexes can be used in the dehydrogenative coupling of silanes and in the reverse reaction, the hydrogenative cleavage of Si-Si bonds. Key intermediates have been isolated highlighting the participation of silyl metal complexes in the catalytic transformations.



[1] M. Vogt, B. de Bruin, H. Berke, M. Trincado, H. Grützmacher *Chem. Sci.*, **2011**, *2*, 723-727.

Synthesis of New Polarization Matrices for Dynamic Nuclear Polarization

D. L. Silverio[1], H. A. van Kalkeren[2], F. Bernada[3], D. Gajan[4], C. Thieuleux[2], P. Tordo[3], O. Ouari[3], A. Lesage[4], L. Emsley[4], C. Copéret[1]*

[1]ETH Zurich, [2]CPE Lyon, [3]Institut de Chimie Radicalaire, Aix-Marseille Université / CNRS, [4]Centre de RMN à très hauts champs

Our group, in collaboration with others, has shown that SBA-type materials containing a radical can be used to polarize a solution for use in dynamic nuclear polarization (DNP). [1]. Importantly, due to the solid-support controlling the distribution of the radicals, DNP can be theoretically carried out in any solvent and with any class of radical. This trait allows us to expand the types of radicals used from the simple radicals of our initial reports to some derivatives of more complex biradicals, which are known to afford higher levels of enhancement in DNP. Examination of a variety of these biradical-containing materials shows they can afford higher levels of enhancement than our original materials.

[1] (a) Gajan, D.; Schwarzwälder, M.; Conley, M. P.; Grüning, W. R.; Rossini, A. J.; Zagdoun, A.; Lelli, M.; Jeschke, G.; Sauvée, C.; Ouari, O.; Tordo, P.; Veyre, L.; Lesage, A.; Thieuleux, C.; Emsley, L.; Copéret, C. *J. Am. Chem. Soc.,* **2013**, *135*, 15459–15466. (b) Gajan, D.; Bornet, A.; Vuichoud, B.; Milani, J.; Melzi, R.; van Kalkeren, H. A.; Veyre, L.; Thieuleuz, C.; Conley, M. P.; Grüning, W. R.; Schwarzwälder, M.; Lesage, A.; Copéret, C.; Bodenhausen, G.; Emsley, L.; Jannin, S. *PNAS*, **2014**, *111*, 14693–14697.

The Mechanism of C-H activation by Transition Metal Siloxides

D. P. Estes[1], C. Copéret[1]*

[1]ETH Zurich

Transition metal ions supported on metal oxide surfaces, such as silica and alumina, catalyze a variety of reactions of hydrocarbons. These reactions often involve C-H activation as a key step in the catalytic process. However, the large distribution of sites on metal oxide surfaces makes these catalysts difficult to study. $Co_2(OSi(O\textit{t}Bu)_3)_4$ activates a variety of C-H bonds in solution. We were able to measure the rate of C-H activation by observing H/D scrambling between R-H and excess $DOSi(OtBu)_3$. The rate of activation varies with the acidity of the C-H bond (more acidic C-H bonds react faster). Our results suggest that these C-H activation occur by a heterolytic mechanism involving proton transfer.

Catalytic Dehydrogenation of Amino Boranes – Formation of Condensed Borazine Compounds

F. Müller[1], M. Trincado[1], H. Grützmacher[1]*

[1]Laboratory of Inorganic Chemistry and Applied Biosciences, ETH Zurich

Amino boranes are studied as fuels with respect to hydrogen storage and as precursors for inorganic materials. Thermal decomposition leads to polymeric BN compounds in form of nanotubes, nanoparticles or clusters.[1]

With a new Ru diazadiene diolefin complex we achieved the synthesis of condensed borazine compounds (Figure 1). Remarkably, these poly(borazines) are soluble and contain likely polycondensed rings up to $B_{50}N_{49}H_{28}$ and only little insoluble polymeric material is formed.[2]

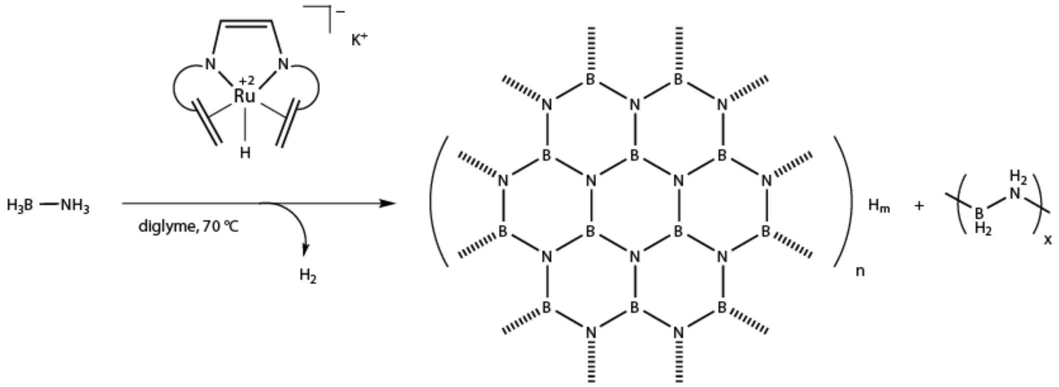


Figure 1. Reaction equation of dehydrogenation of amino boranes.

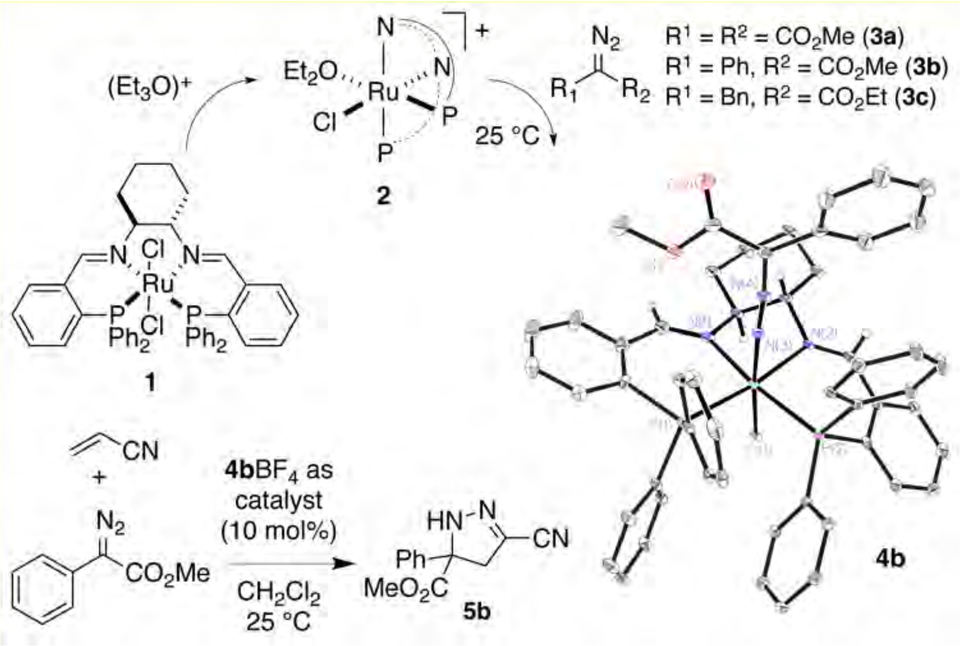
[1] U. Kusari, Z. Bao, Y. Cai, G. Ahmad, K. H. Sandhage, L. G. Sneddon, *Chem. Commun.* **2007**, 1177–1179.
[2] M. Trincado, H. Grützmacher, *Unpublished Results*, **2015**. br

Cycloaddition Reactions of Diazoalkane Ruthenium Complexes with Chiral PNNP Ligands

J. Egloff[1], A. Mezzetti[1]*

[1]ETH Zurich

We have recently reported that $[RuCl(OEt_2)(PNNP)]SbF_6$ (**2**), prepared from $[RuCl_2(PNNP)]$ (**1**) and $(Et_3O)SbF_6$, catalyzes the asymmetric aziridination of imines with ethyl diazoacetate with the intermediacy of a diazoester complex.[1]



We find now that complex **2** reacts with dimethyl 2-diazomalonate (**2a**), methyl 2-diazo-2-phenylacetate (**2b**), or methyl 2-diazo-3-phenylpropanoate (**2c**) to give the corresponding stable diazoalkane complexes *trans*-$[RuCl(NNCR^1R^2)(PNNP)]^+$ (**3a-c**). At –20 °C, *cis* addition occurs, and the resulting adducts slowly isomerize at room temperature to the trans products, which were isolated as air- and moisture-stable solids. The methyl 2-diazo-2-phenylacetate adduct **4b**BF_4 catalyzes the dipolar [3+2] cycloaddition of acrylonitrile onto diazoalkane **2b** to give methyl 3-cyano-5-phenyl-4,5-dihydro-1*H*-pyrazole-5-carboxylate (**5b**), albeit with low enantioselectivity (ca. 10% ee). An analogous stoichiometric reaction has been recently reported by Albertin.[2] More insight in the catalytic reaction will be presented.

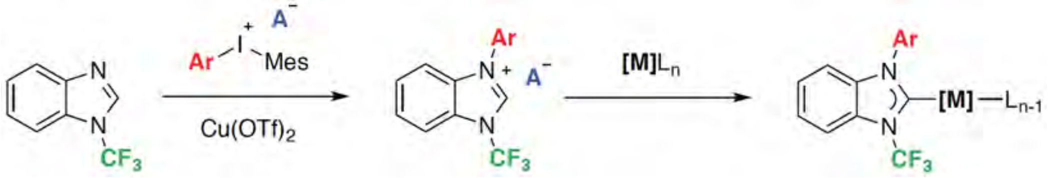
[1] J. Egloff, M. Ranocchiari, A. Schira, C. Schotes, A. Mezzetti, *Organometallics*, **2013**, 32, 4690-4701.
[2] G. Albertin, S. Antoniutti, A. Botter, J. Castro, M. Giacomello, *Organometalics*, **2014**, 33, 3570-3582.

Synthesis and Application of N-Trifluoromethyl N-Heterocyclic Carbene Ligands and Their Complexes

P. Engl[1], R. Senn[1], E. Otth[1], A. Togni[1]*

[1]ETH Zurich

A series of *N*-trifluoromethyl NHC ligand precursors have been synthesized and fully characterized starting from *N*-trifluoromethyl benzimidazole. In order to explore their electronic properties, these new ligands have been engaged in the formation of several organometallic complexes. IR analysis of $[IrCl(CO)_2(NHC)]$ complexes revealed that NHCs bearing a trifluoromethyl substituent are significantly weaker donor ligands compared to standard NHCs, as reflected by their higher TEP values. The decreased σ-donating ability of the carbene carbon is considered to be a consequence of the diminished π-overlap with the nitrogen lone pair, due to hyperconjugation into the $\sigma^*_{\text{C-F}}$ antibonding orbital of the trifluoromethyl group. On the other hand, the π-accepting property of these novel ligands is enhanced, which was verified by examining the ^{77}Se NMR resonance of [Se(NHC)] adducts and the redox potentials of [RhCl(COD)(NHC)] complexes. To further evaluate and compare the electronic properties of our *N*-trifluoromethyl NHCs to those of well established NHCs and PPh_3, the intermolecular hydroalkoxylation of cyclohexene with 2-methoxyethanol using Au(I) complexes was carried out. The gold(I) complexes bearing the N-trifluoromethyl NHC ligands compete with $[Au(PPh_3)Cl]$ in terms of catalytic activity.



Moreover, Grubbs (II) and Hoveyda-Grubbs-type ruthenium-based metathesis catalysts, containing a *N*-trifluoromethyl moiety, showed a fluorine metal interaction as revealed by short M-F distances. Such interactions between the fluorine atom and the metal center have been shown to exert a significant influence on the activity of transition-metal complexes in catalysis.[2] Hence, the efficiency of these Grubbs (II) and Grubbs-Hoveyda type ruthenium complexes was evaluated in benchmark olefin metathesis transformations.

[1] Pascal S. Engl, Remo Senn, Elisabeth Otth, Antonio Togni, *Organometallics*, **2015**, *34*, 1384-1395

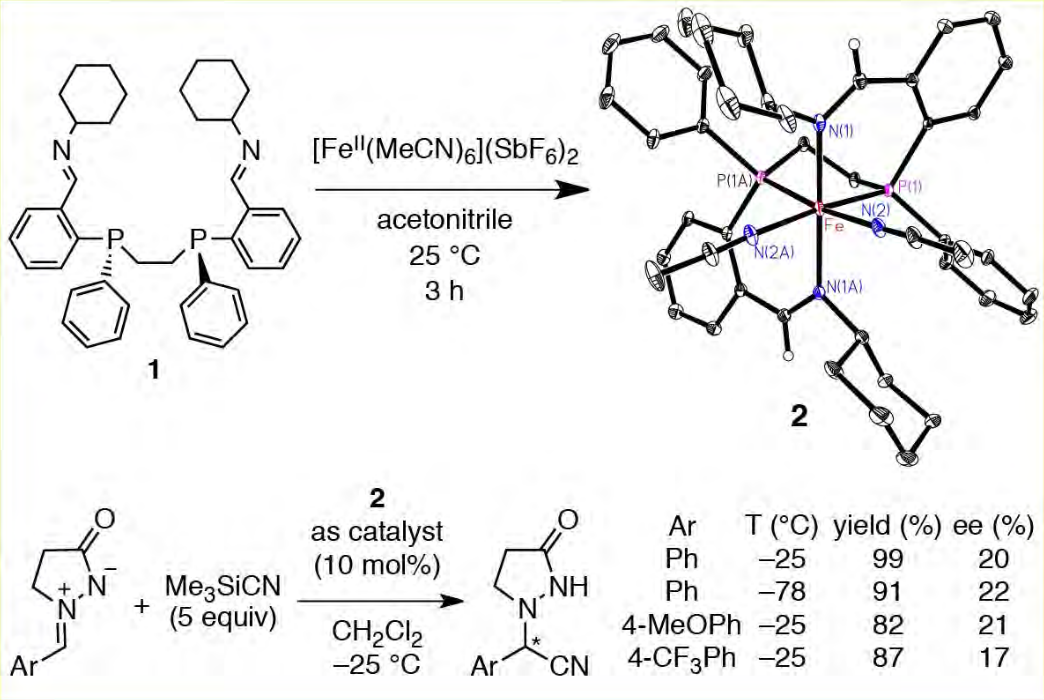
[2] (a) Tobias Ritter, Michael W. Dey, Robert H. Grubbs, *J. Am. Chem. Soc.*,**2006**, *128*, 11768-11769 (b) Jomon Mathew, Cherumuttathu H. Suresh, *Organometallics*,**2011**, *30*, 3106-3112

Iron(II) Catalysts with a P-Stereogenic NPPN Ligand for the Enantioselective Strecker Reaction of Azomethine Imines

R. Huber[1], A. Mezzetti[1]*

[1]ETH Zurich

Replacing precious metals with iron has several advantages - iron is abundant, cheap, relatively non-toxic and environmentally benign. However, iron complexes are inherently less stable than their fourth and fifth row analogues. Multidentate ligands can, at least in part, compensate for this by virtue of their chelate effect. We used the enantiomerically pure, P-stereogenic synthon (1*S*,1'*S*)-2,2'-(ethane-1,2-diylbis(phenylphosphane-diyl))dibenzaldehyde to prepare the tetradentate NPPN ligand **1** by condensation with cyclohexylamine. Ligand **1** reacts with $[Fe(MeCN)_6](SbF_6)_2$ to give $[Fe(MeCN)_2(\mathbf{1})](SbF_6)_2$ as a stable, diamagnetic complex, which can be further transformed into its carbonyl, bromocarbonyl, ^{t}Bu-isonitrile, and trimethylsilyl cyanide derivatives. All dicationic complexes analyzed by X-ray crystallography feature a Λ-*cis*-α geometry.



Ar	T (°C)	yield (%)	ee (%)
Ph	–25	99	20
Ph	–78	91	22
4-MeOPh	–25	82	21
4-CF_3Ph	–25	87	17

Complex **2** catalyzes the enantioselective Strecker reaction of azomethine imines with up to 22% ee. $^{31}P\{^1H\}$ NMR spectroscopy reveals that the product displaces the NPPN ligand from the metal, which explains the low enantioselectivity.

Low temperature synthesis of nickel silicide: from preparing colloidal nanoparticles to coating silicon

T.-H. Lin[1], T. Margossian[1], M. Thannasack[2], M. d. Marchi[2], P. Gaillardon[2], D. Baudouin[1], C. Copéret[1]*, G. De Micheli[2]*

[1]ETH Zurich, [2]EPFL Laussane

Formation of a metal silicide layer onto a semiconductor device is a crucial process to minimize contact resistivity. Nickel silicide (NixSiy)is routinely used in the industry thanks to its' low resistance, high compatibility, and good stability1.However, mono-directionalmetal sputtering technique is no longer compatible with the advanced3D-structure devices due to its poor multi-directional coverage ability.Therefore, one-pot chemical approachis used to synthesize NixSiylayer onto silicon wafer allowing a homogenous coverageof3D-structuredevice.A200nm metal rich layer was observed by electron microscopy (STEM-EDX) and the composition characterized by XPS spectroscopy showed a Si/Ni ratio of 1. Furthermore, carbon content can be decreased by different approaches: high temperature post-treatment or/and the use of specific nickel precursors. In addition to the composition and layer chemical state, the diffusional behavior of Ni-based layer on different types of Si wafer was investigated in this work.

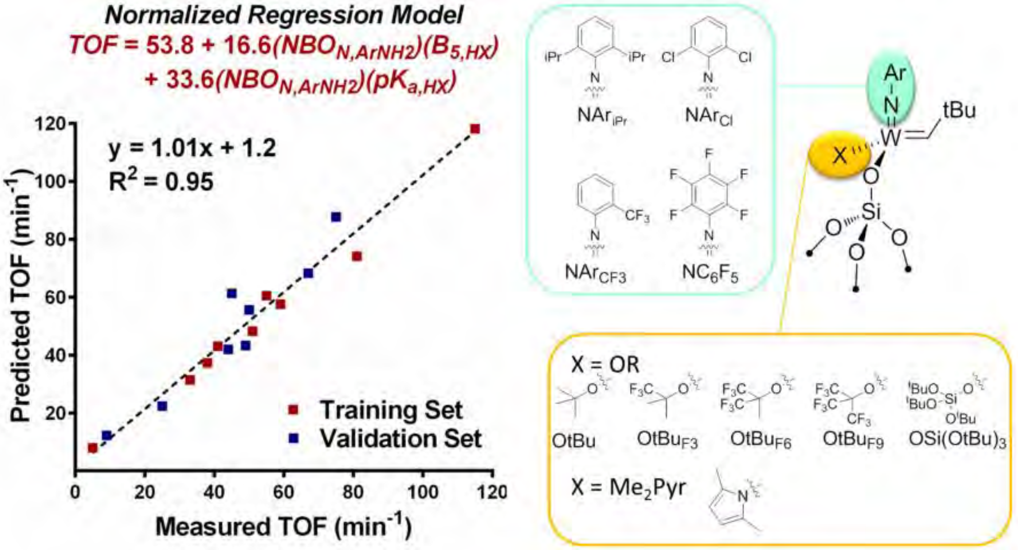
[1] J. Chen, J. Colinge, D. Flandre, R. Gillon, J. P. Raskin, D. Vanhoenacker, J. Electrochem. Soc., 1997, 144, 2437.

Quantitatively Analyzing Metathesis Catalyst Activity and Structural Features in Silica-Supported Tungsten Imido–Alkylidene Complexes

V. Mougel[1], C. B. Santiago[2], P. Zhizhko[1], E. N. Bess[2], J. Varga[3], G. Fráter[3], M. S. Sigman[2], C. Copéret[1]*

[1]ETH Zurich, [2]University of Utah, [3]XiMo AG

Over the past years, experimental and computational investigations of d0group 6–7 homogeneous and heterogeneous catalysts have provided insights allowing for tremendous advances in the understanding of active site structure and reactivity of metathesis catalysts.1, 2However, the ligand effects and structural factors that influence the catalytic activity of these catalysts still remain unclear. We have here synthesized a broad series of fully characterized well-defined silica-supported W metathesis catalysts with the general formula [(≡SiO)W(=NAr)(=CHCMe2R)(X)] by grafting bis-X substituted complexes [W(NAr)(=CHCMe2R)(X)2] on silica partially dehydroxylated at 700 °C, and evaluated their activity with the goal to obtain detailed structure–activity relationship (Figure 1). Quantitative influence of the ligand set on the turnover frequency (TOF) in self-metathesis of*cis*-4-nonene was investigated using multivariate linear regression analysis tools. We will describe here how the TOF of these catalysts can be predicted from simple steric and electronic parameters of the parent protonated ligands.



1 Solans-Monfort, X.; Copéret, C.; Eisenstein, O. *Organometallics* **2012**, *31*, 6812.
2 Mougel, V.; Copéret, C. *Chem. Sci.* **2014**, *5*, 2475.
3 Mougel, V.; Santiago, C. B.; Zhizhko, P.; Bess, E. N.; Varga, J.; Frater, G.;Sigman, M. S.; Copéret, C., *J. Am.Chem. Soc.,* **2015**, DOI: 10.1021/jacs.5b03344

Amorphous Cobalt Silicate Nanobelts@Carbon Composites as Stable Anode Material for Lithium Ion Batteries

W. Cheng[1]

[1]ETH Zurich

Metal silicates such as M_2SiO_4 (M=Co, Fe, Mn) have rarely been studied as electrode materials for lithium ion batteries. Only very recently, Franziska Mueller et al. reported that cobalt silicate can be used as anode, undergoing a conversion reaction during lithiation and delithiation.[1] However, this bulky cobalt silicate exhibited limited capacity and poor cycling stability. Nanostructure engineering and carbon coating represent two promising strategies to improve the electrochemical performance of the electrode materials.[2-3]

Herein, we report the synthesis of a highly anisotropic and amorphous silicate nanostructure with a carbon coating and its lithium storage properties. Amorphous cobalt silicate nanobelts are synthesized by a template-assisted method. The carbon coating is realized by the deposition of phenol formaldehyde resin on the nanobelts, followed by annealing under N_2 atmosphere. As an anode material in lithium ion batteries, the amorphous cobalt silicate nanobelts@carbon composite can deliver a reversible high capacity of about 745 mA h g^{-1} at a current density of 100 mA g^{-1}. At a higher current density of 500 mA g^{-1}, the composite exhibits an extraordinary long life of 1000 cycles with a stable capacity retention of about 480 mA h g^{-1}, which is much higher than the theoretical capacity of the commercialized graphite anode. It is the first time to demonstrate that such a high capacity and long term cycling stability can be accomplished for metal silicates M_2SiO_4 (M=Co, Fe, Mn et.al) as anode materials. These results are expected to stimulate further research on transition metal silicate nanostructures for lithium ion battery applications.

[1] F. Mueller, D. Bresser, N. Minderjahn, J. Kalhoff, S. Menne, S. Krueger, M. Winter, S. Passerini, *Dalton Trans.* **2014**, 43, 15013-15021.
[2] P. G. Bruce, B. Scrosati, J. M. Tarascon, *Angew. Chem. Int. Ed.***2008**, 47, 2930- 2946.
[3] H. Li, H. Zhou, *Chem. Commun.* **2012**, 48, 1201-1217.

High Resolution Powder X-ray Diffraction on Functional Metal-Organic Frameworks with UiO-66 Topology

M. Taddei[1], N. Casati[1], M. Ranocchiari[1], J. A. van Bokhoven[2,1]*

[1]Paul Scherrer Institute, Villigen, [2]ETH Zurich

Metal-organic frameworks (MOFs) are a class of highly porous materials based on the connection of metal atoms and organic ligands. They can be employed in a wide range of applications, including gas sorption/separation, heterogeneous catalysis, and drug delivery.[1,2] UiO-66, based on zirconium-oxo clusters and terephthalic acid (H_2bdc), is one of the most-studied MOFs, thanks to its chemical and thermal stability and to the easy functionalization of the framework, which make it very attractive for practical application.[3] Functionalization can be accomplished in various ways: direct synthesis using modified H_2bdc ligands as starting reagents, post synthetic exchange (PSE), and post-synthetic modification (PSM).[4]

We show a high resolution powder X-ray diffraction study at the MS beamline at SLS on a series of amino- and bromo-functionalized UiO-66 samples, prepared both by direct synthesis and PSE, to elucidate the structural changes and defects of the material.[5]. The MYTHEN detector allows to observe fine features of the diffraction patterns and consequently to gain deep insight into the crystal structure. The framework dynamically responds to the presence of increasing amounts of functional groups and different methods of functionalization lead to different effects on the lattice parameters and on the defectivity, and as a consequence different materials properties.

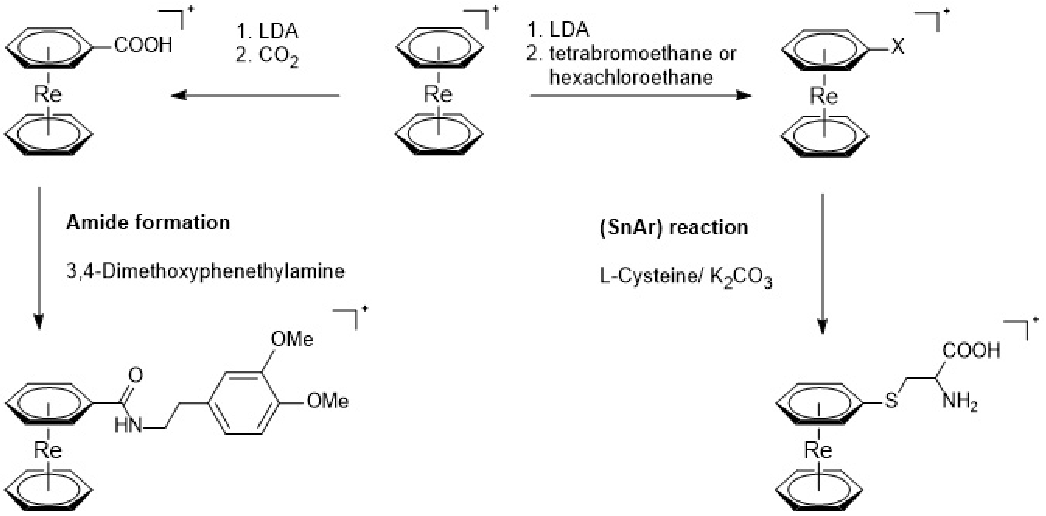
[1] J.-R. Li, R. J. Kuppler, H.-C. Zhou, *Chem Soc. Rev.* **2009**, *38*, 1477-1504.
[2] M.Ranocchiari, J. A.van Bokhoven, *Phys. Chem. Chem. Phys.,* **2011**, *13*, 6388-6396.
[3] J. H.Cavka,S.Jakobsen, U.Olsbye, N.Guillou, C.Lamberti, S.Bordiga, K. P.Lillerud,*J. Am. Chem. Soc.,***2008**, *130*, 13850-13851.
[4] M.Kim, S. M.Cohen,*CrystEngComm,***2012**,***14***, 4096-4104.
[5] M. J. Cliffe, W. Wan, X. Zou, P. A. Chater, A. K. Kleppe, M. G. Tucker, H Wilhelm, N. P. Funnell, F.-X. Coudert, A. L. Goodwin *Nat. Commun.* **2014***, 5,* 4176.

Synthesizing Functionalized $[M(\eta^6\text{-arene})_2]^+$ (Re,$^{99(m)}$Tc) Complexes for Receptor Targeting

G. Meola[1], H. Braband[1], R. Alberto[1]*

[1]University of Zurich

Ruthenium-arene complexes play an important role in the field of medicinal inorganic chemistry.[1] Especially, bis-arene complexes are of particular interest, since they represent fundamental precursors for numerous reactions.[2] Recently, $[M(\text{arene})_2]^+$type complexes (M = Re,$^{99(m)}$Tc) came into the focus of our research, because these type of complexes has a high potential for 'theranostic' applications in (nuclear) medicine. Therefore we optimized the synthesis of $[Re(\text{arene})_2]^+$type complexes (arene = benzene, toluene, mesitylene, *o*-xylene, *p* -xylene and naphtalene) and developed an efficient and practical one-step synthesis for $[^{99(m)}Tc(\text{arene})_2]^+$ compounds.[3],[4] Furthermore, novel synthetic pathways for the functionalization of this basic class of coordination compounds have been developed, which led to a variety of mono- and bi-functionalized $[Re(C_6H_5R)(C_6H_{6-n}R_n)]^+$compounds (R = -COOH, -Br, -Cl, -F, $-COC_2H_5$, -CH(OH)Ph, $-C(OH)Ph_2$). These introduced functional groups enable the rational design of metal modified biomolecules via amide bond formation or nucleophilic aromatic substitution (SnAr). Following this strategy, new classes of organometallic compounds were synthesized with high potential for therapeutic and diagnostic applications (inorganic drugs), in the future.



[1] Yaw K. Yan, Michael Melchart, Abraha Habtemariam, Peter J. Sadler, *Chemical Communication*, **2005**, 38, 4764-4776.
[2] Guido Pampaloni, C*oordination Chemical Review*s, **2010**, 254, 402-419.
[3] Eveniya A. Trifonova, Dmitry S. Perekalin, Konstantin A. Lyssenko, Al-exander R, Kudinova, *Journal Organometallic Chemistry*,**2013**, 727, 60-63.
[4] Michael Benz , Henrik Braband, Paul Schmutz, Jonathan Halter, Roger Alberto, *Chemical Science*,**2015***,* 6*,* 165-169.

Target Specific Multimodality Nanoparticles for (Nano)Medical Applications

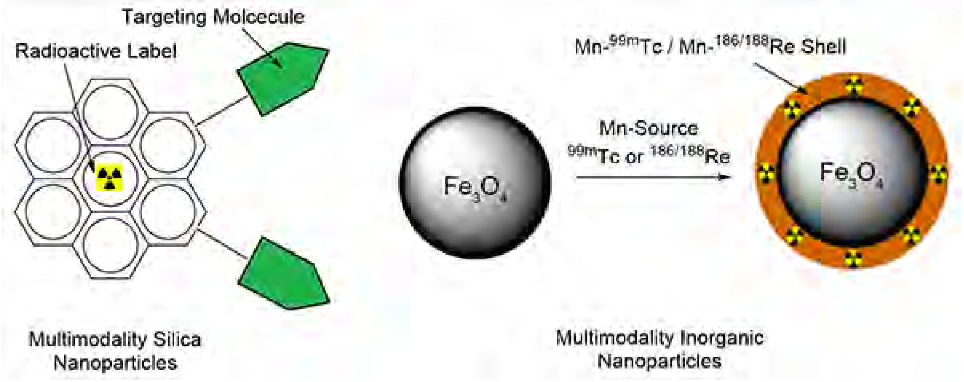
M. Wuillemin[1], H. Braband[1]*, R. Alberto[1]*

[1]University of Zurich

Nanoparticles, such as silica or superparamagnetic nanoparticles, are currently under intense exploration in nanomedicine. In this context we are aiming at the development of novel synthetic pathways for the synthesis of ^{99m}Tc- and/or $^{186/188}$Re-containing multimodality probes.

Mesoporous silica nanoparticles enable the combination of targeting moieties, imaging functions (radiolabels), and drug loading. This creates a promising multifunctional nanoplatform for the combination of therapy and diagnostic applications (theranostics). Recently we established a novel labelling procedure for silica based particles which proceeds via the reaction of high-valent *fac*-$\{^{99m}TcO_3\}^+$ complexes with alkenes ((3 + 2)-cycloaddition)[1]. Currently, our research is focused on determining the most suitable type of silica particles to optimize the labelling procedure. Based on these results, these silica particles will be selectively labelled by radio nuclides at the inner pore surface. The desired targeting functions will exclusively be attached onto the outer surface of the particles.

Metal containing inorganic nanoparticles represent another interesting type of material with high potential as multifunctional nanoplatform. Therefore, we are developing procedures for the synthesis of Mn-oxide shells which contain incorporated radio isotopes, such as ^{99m}Tc and/or $^{186/188}$Re, in a specific bound fashion. Thereby, a general method for the synthesis of multimodality inorganic nanoparticles (quantum dots, magnetic nanoparticles, etc.) will be generated. In this way the bioprofile of the modified particles is not altered by the introduced modality and can be tailored depending on needs and biological restrictions. This approach enables the combination of different imaging techniques such as MRI and SPECT.



[1] Michel Wuillemin, Wanda Stuber, Thomas Fox, Michael Reber, Dominik Brühwiler, Roger Alberto, Henrik Braband, *Dalton Trans.*, **2014**, 43, 4260-4263.

Structural and magnetic investigations of a mononuclear 4f polyoxometalate family with single molecule magnet behaviour

R. Güttinger[1], O. Blacque[1], R. Westerström[2], A. Kostanyan[2], G. R. Patzke[1], P.-E. Car[1]*

[1]Department of Chemistry, University of Zurich, [2]Department of Physics, University of Zurich

Polyoxometalates (POMs) are a fascinating class of metal-oxo clusters containing transition metal ions, mainly W and Mo, in their high oxidation states. POMs have been widely explored over the last 50 years for various applications in catalysis, for bio-medical and biological features. Indeed, these metal-oxo clusters offer undeniable qualities for future applied devices such as a wide structural and compositional diversity (possible tuning of their electronic structure). The story of molecular magnetism begins with the reports by *Sessoli* et *al.*[1] on the $[Mn_{12}O_{12}(O_2CMe)_{16}(H_2O)_4]$, $\{Mn_{12}\}$, and the observation of its slow magnetic relaxation process in a molecular material. With the evolution of devices for magnetic investigations and the knowledge-increase on the physical properties based on theoretical calculations, a lot of research groups still investigate the $\{Mn_{12}\}$. Over the last two decades the number of reported SMM did not cease to grow. A single molecule magnet (SMM) can be seen as a molecule which is magnetized in a magnetic field and still remains magnetized even after switching off the magnetic field. Its main characteristic is the presence of a high energy barrier (U) that prevents the spins from re-orientation to the ground state. This can be defined in terms of large ground spin state (S) combined with a large magnetic anisotropy of the "easy axis" with a negative zero-field splitting parameter (D).[2] After the discovery of $\{M_{12}\}$ as SMM several examples of 3d, 4f and even mixed 3d-4f complexes were discovered.[3]

Up to now, only 3d and 4f substituted POMs exhibiting single molecule magnet behaviour have been reported to date. The first mononuclear lanthanide complex $[Ln(W_5O_{18})_2]^{9-}$ (Ln = Ho, Er) with SMM behaviour was published by *Coronado* et *al.* in 2008.[4] After this breakthrough, similar approaches were extended to the mononuclear family with the Preyssler-type series $[Ln(P_5W_{30}O_{110}]^{12-}$ (Ln = Tb, Dy, Ho, Er, Tm, Yb) and the Keggin-type structure $[Ln(\beta\text{-}SiW_{11}O_{39})_2]^{13-}$ (Ln = Dy, Ho, Er, Yb). Up to now, only three types of mononuclear 4f POM complexes exhibiting SMM behaviour are observed and join the very short list of published polyoxometalates showing this magnetic property.

Here, we highlight a new isostructural family of 4f mononuclear "sandwich" Keggin POMs with a large variety of lanthanide ions (Ln = Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb). The crystal structure of all new POMs was successfully solved and the full magnetic measurements with alternating current (ac) and direct current (dc) are under investigation. Preliminary results on the $[Dy(\beta_2\text{-}GeW_{11}O_{39})_2]^{13-}$ derivative revealed the presence of SMM behaviour. Moreover, careful studies of the Dysprosium coordination geometry show that the Dy^{3+} ion is embedded in a favourable antiprismatic geometry for SMM behaviour. Furthermore, the new POM family was characterized with ATR-FTIR and photoluminescence spectroscopy techniques.

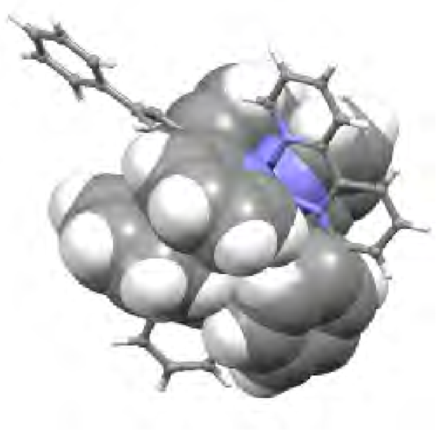
[1] (a) A. Caneschi, D. Gatteschi, R. Sessoli, A. L. Barra, L. C. Brunel, M. Guillot, *J. Am. Chem. Soc.* **1991**, 113, 5873. (b) R. Sessoli, D. Gatteschi, A. Caneschi, M. A. Novak, *Nature* **1993**, 365, 141.
[2] H. L. C. Feltham, S. Brooker, *Coord. Chem. Rev.*, **2014**, 276, 1.
[3] For example: (a)S. Accorsi, A. L. Barra, A. Caneschi, G. Chastanet, A. Corina, A. C. Fabretti, D. Gatteschi, C. Mortalo, E. Olivieri, F. Parenti, P. Rosa, R, Sessoli, L. Sorace, W. Wernsdorfer, L. Zobbi, *J. Am. Chem. Soc.* **2006**, 128, 4742. (b) M. H. Zeng, M. X. Yao, H. Liang, W. X. Zhang, X. M. Chen, *Angew. Chem. Int. Ed.* **2007**, 46, 1832. (c) L. Lisnard, F. Tuna, A. Candini, M. Affronte, R. E. P. Winpenny, E. J. L. McInnes, *Angew. Chem. Int. Ed.* **2008**, 47, 9695.
[4] M. A. Aldamen, J. M. Clemente-Juan, E. Coronado, C. Marti-Gastaldo, A. Gaita-Arino, *J. Am. Chem. Soc.* **2008**, 130, 8874.

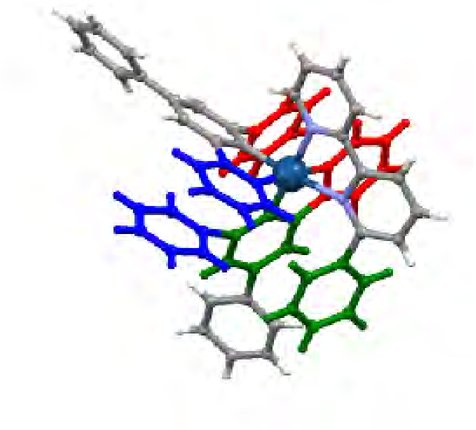
Exceptionally long-lived light-emitting electrochemical cells: multiple intra-cation π-stacking interactions in $[Ir(C^\wedge N)_2(N^\wedge N)][PF_6]$ emitters [1]

A. M. Bünzli[1], E. C. Constable[1], C. E. Housecroft[1], A. Prescimone[1], H. J. Bolink[2], G. Longo[2], L. Gil-Escrig[2], A. Pertegás[2], E. Ortí[2]

[1]University of Basel, [2]Universidad de Valencia

Light-emitting electrochemical cells (LEECs) consisting of an iridium(III) based ionic transition metal complex (iTMC), sandwiched between two electrodes show promising properties for highly efficient and low-cost applications in ultra-thin flexible lighting. iTMCs support all the required processes of charge injection, charge transport, emissive recombination and can be deposited by spin coating or printing casts at ambient temperature.





To obtain long-lived luminance outputs, highly stable iTMCs are required for the use in LEECs. Herein two series of cyclometallated iridium(III) complexes of the type $[Ir(Phppy)_2(N^\wedge N)][PF_6]$ and $[Ir(Ph_2ppy)_2(N^\wedge N)][PF_6]$ (HPhppy = 2-(3-phenyl)phenylpyridine, HPh_2ppy = 2-(3,5-diphenyl)phenylpyridine, N^N = 2,2'-bipyridine backbone) are presented. Various pendant phenyl rings on the C^N and N^N ligands lead to the formation of multiple intra-cation π-stacking interactions, whose effect on the stability and the emission color was investigated. The most stable LEEC device achieved an extrapolated lifetime exceeding 2800 hours under accelerated testing conditions.

[1] Andreas M. Bünzli, Edwin C. Constable, Catherine E. Housecroft, Alessandro Prescimone, Jennifer A. Zampese, Giulia Longo, Lidón Gil-Escrig, Antonio Pertegás, Enrique Ortí, Henk J. Bolink, *Chemical Science.* **2015**, 6, 2843-2852.

Porphyrin-decorated polypyridines for dye sensitized solar cells

A. Lanzilotto[1], A. Wiesler[1], F. Malzner[1], E. C. Constable[1]*, C. E. Housecroft[1]*

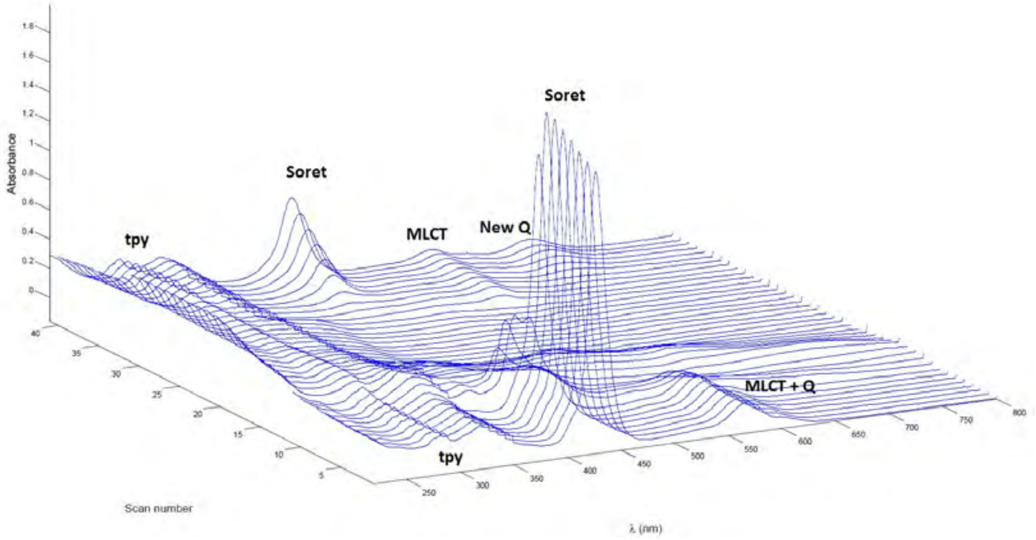
[1]Department of Chemistry, University of Basel, Spitalstrasse 51, 4056 Basel

The presented work focuses on the synthesis of new organic ligands and their metal complexes for application as sensitizers in dye-sensitized solar cells (DSCs). Although a wide range of such complexes exists, a major problem still has to be overcome: the inefficient absorption in the range covered by sunlight. Most dyes can only partially absorb the visible light, depending on their structure. In general they mostly absorb in the UV region with high extinction coefficients and absorb less effectively in the visible range. Aromatic rings, unsaturated substituents and conjugated structures provide ligand centred transitions in the UV, while complexation to a metal ion adds, for example, a metal-to-ligand charge transfer band (MLCT), typically in the visible.

Our group focuses on the application of copper(I) polypyridine complexes as dyes. My research fits in this context as I am developing porphyrin-based polypyridine dyes. With the aim of expanding the porphyrin absorption over the largest energy range possible, derivatives of the commercially available tetraphenylporphyrin (TPP) were synthesized. The well-known light-harvesting ability of TPP has been coupled with the MLCT of transition metal ions to which it complexes and with the UV absorption arising from the polypyridine domain.

The spectroelectrochemical characterization of **L** (**L** = [ZnTPP-phtpy]), (phtpy = 4’-phenyl-2,2’:6’,2’’-terpyridine), [Zn$\mathbf{L}_2$]$^{2+}$ and [Fe$\mathbf{L}_2$]$^{2+}$ was performed. TPP and ZnTPP were used as model compounds to investigate how the presence of an octahedral metal domain influences the absorption spectrum upon oxidative/reductive cycle. The simple ligand **L** shows features which are characteristic of a ZnTPP derivative. Examining the [Zn$\mathbf{L}_2$]$^{2+}$ complex, it displays very similar spectral features with respect to the ligand. It is reasonable since the zinc(II) centre cannot exist in more than one oxidation state, and so does not display an MLCT band upon complexation. Considering the [Fe$\mathbf{L}_2$]$^{2+}$ complex, the presence of an oxidizable metal centre allows an MLCT band to appear in the same spectral region of the porphyrin Q band. The MLCT band is reversible upon oxidative cycle as it would be expected for a redox couple as Fe^{II}/Fe^{III}.

Figure: oxidative spectroelectrochemistry of the [Fe$\mathbf{L}_2$]$^{2+}$ complex.



Asymmetric copper(I)-based dyes to combine with sterically demanding anchoring ligands for dye-sensitized solar cells.

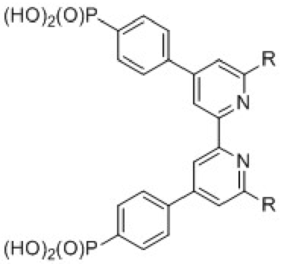
A. Büttner[1], S. Brauchli[1], R. Vogt[1], E. C. Constable[1]*, C. E. Housecroft[1]*

[1]University of Basel

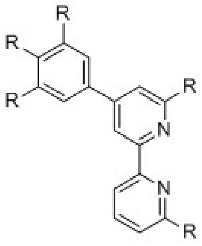
Most of the world's energy is obtained from fossil fuels. The emissions generated in the production of this energy are associated with climate change and leads to pollution of the environment. In order to decrease environmental effects renewable energy sources are essential. Therefore our group is interested in exchanging these old energy sources with novel, clean technology, using cutting-edge energy generation such as dye-sensitized solar cells (DSC). [1]

The development of n-type DCSs using copper(I)-based dyes for sensitizing solar cells has advanced considerably during the last few years. Replacing the ruthenium(II) sensitizer by copper(I) dyes is of high interest in order to use more abundant metals and shift from rare metal sources on earth. [2]

To improve the efficiency of copper(I)-based DSCs our group recently reported a new anchoring ligand to functionalize the TiO_2 surface towards the preparation of a heteroleptic copper(I) complex absorbed on the electrode surface.



R= Me or Ph



R= various

A series of new asymmetric ancillary ligands was synthesized and their beneficial properties in combination with the sterically demanding anchoring ligands on the stability of the heteroleptic copper(I) complexes are presented herein.

[1] Kalyanasundaram K., "Dye-Sensitized Solar Cells", 1st edition, CRC Press and EPFL Press, (2010).
[2] S. Y. Brauchli, F. J. Malzner, E. C. Constable and C. E. Housecroft, *RSC Advances*, **2015**, submitted. br

Going to Extremes: From Fluorine-Free Blue to Stable Red Emitting Iridium Complexes for LEECs

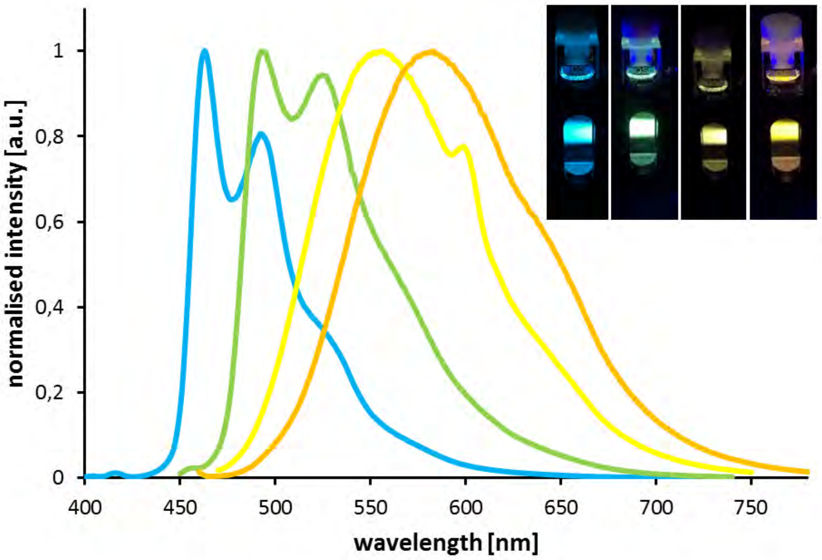
C. D. Ertl[1], A. Pertegás[2], H. J. Bolink[2], E. Ortí[2], E. C. Constable[1]*, C. E. Housecroft[1]*

[1]University of Basel, [2]Universidad de Valencia

Cationic iridium(III) complexes of the type $[Ir(C\^N)_2(N\^N)]^+$ are the most intensely studied emissive compounds for light emitting electrochemical cells (LEECs). In addition to their good photophysical and chemical properties and ionic nature, emission colour tuning is straightforward due to spatial separation of the frontier orbitals, making these complexes well suited for LEEC applications.

Nonetheless, there is still a lack of stable blue and red emitters. We have introduced a series of thioether and sulfone groups on the cyclometallating ligands to investigate the influence on the emission colour.[1] Electron-withdrawing sulfone groups yielded a large blue-shift in the emission maximum and were combined with electron-rich pyrazolylpyridine ancillary ligands[2] to further blue-shift the emission without the need of fluorine groups, which have been reported to have a detrimental effect on device stability both in OLEDs[3] and LEECs.[4]

Emission red-shifts on the other hand were achieved by the introduction of benzothiazolylpyridine ancillary ligands, leading to extremely stable LEECs with the longest reported lifetimes for red-emitting iridium complexes.



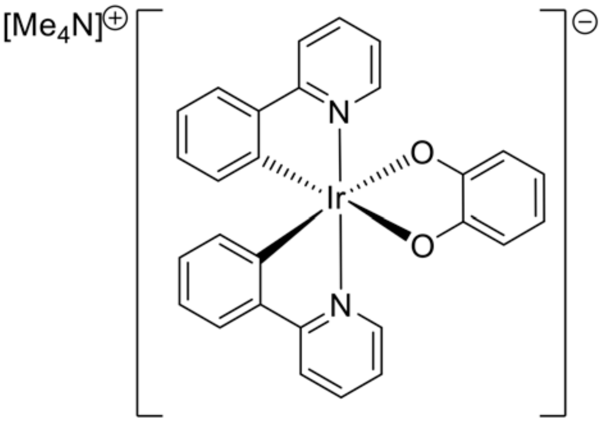
[1] E. C. Constable, C. D. Ertl, C. E. Housecroft and J. A. Zampese, *Dalton Trans.*, **2014**, 43, 5343.
[2] C. D. Ertl, J. Cerdá, J. M. Junquera-Hernández, A. Pertegás, H. J. Bolink, E. C. Constable, M. Neuburger, E. Ortí, C. E. Housecroft, *RSC Adv.*, **2015**, accepted.
[3] S. Schmidbauer, A. Hohenleutner, B. König, *Adv. Mater.*, **2013**, 25, 2114.
[4] D. Tordera, J. J. Serrano-Pérez, A. Pertegás, E. Ortí, H. J. Bolink, E. Baranoff, Md. K. Nazeeruddin, J. Frey, *Chem. Mater.*, **2013**, 25, 3391.

Anionic Ir(III) Complexes for Light-Emitting Electrochemical Cells

C. D. Morris[1], E. C. Constable[1], M. Spulber[1], C. G. Palivan[1], C. E. Housecroft[1]*

[1]University of Basel

With roughly 20% of the world's total energy consumption attributed to lighting, more efficient devices are highly sought after and the subject of intense research efforts [1]. Significant progress has been made in the area of solid-state lighting with advances in light-emitting diodes (LEDs) and organic light-emitting diodes (OLEDs), however the high cost currently associated with producing multilayer OLED devices imposes limits on their widespread use. Light-emitting electrochemical cells (LECs) have emerged as an attractive option for solid-state lighting [2]. The simple design and ability to solution deposit the emissive layer of LEC devices without strict requirements on their encapsulation are highly advantageous in large-scale fabrication. Inorganic transition metal complex LECs are comprised primarily of cationic bis-cyclometallated Ir(III) complexes with a neutral N^N ancillary ligand. Anionic Ir complexes have been investigated to a much lesser degree but the few reported examples containing monodentate cyanide and thiocyanate ligands have shown promising photophysical properties [3,4]. We have investigated the use of catechol as a bidentate ligand for an anionic Ir(III) complex. The synthesis and characterization of the complex along with a detailed study of its redox behavior using EPR spectroscopy and spectroelectrochemistry are presented.



[1] International Energy Agency, *"Light's Labour's Lost-Policies for Energy-efficient Lighting",* http://www.iea.org/, **2006**.
[2] Ruben D. Costa, Enrique Orti, Henk J. Bolink, Filippo Monti, Gianluca Accorsi, Nicola Armaroli, *Angew. Chem. Int. Ed.*, **2012**, 51, 8178-8211.
[3] Md. K. Nazeeruddin, R. Humphry-Baker, D. Berner, S. Rivier, L. Zuppiroli, M. Graetzel, *J. Am. Chem. Soc*, **2003,** 125, 8790-8797.
[4] Hsiao-Fan Chen, Chao Wu, Ming-Cheng Kuo, Mark E. Thompson, Ken-Tsung Wong, *J. Mater. Chem.*,**2012**, 22, 9556-9561.

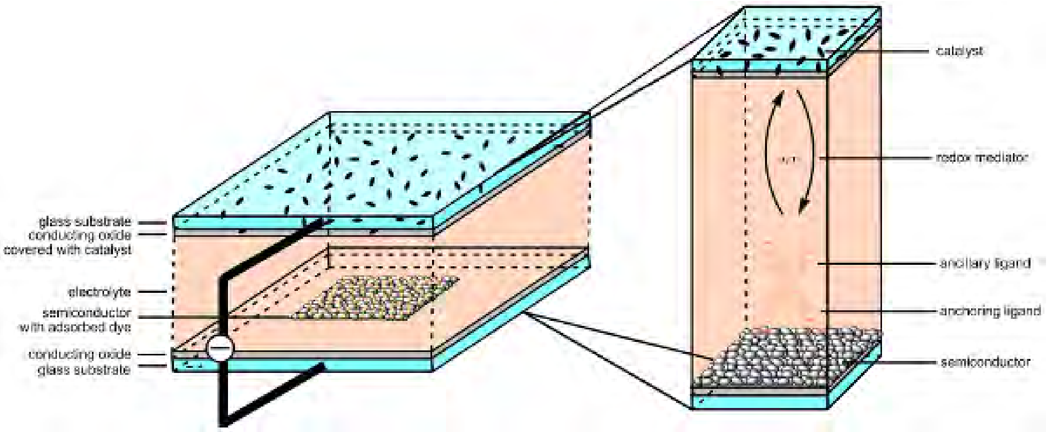
Influence of a co-adsorbent on the performance of copper(I)-based dye-sensitized solar cells

F. J. Malzner[1], S. Brauchli[1], E. C. Constable[1]*, C. E. Housecroft[1]*

[1]University of Basel

Renewable energy sources are the answer to maintain an energy supply to a growing population. Photovoltaics play a key role. Today, the most ubiquitous photovoltaic modules are based on silicon, but a very good alternative is the dye-sensitized solar cell which had its breakthrough in 1991 [1]. The most efficient cells contain ruthenium-based or organic dyes, but a disadvantage of ruthenium is its rarity on earth and its cost.

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.



The most important part of a dye-sensitized solar cell is the dye. In our case, the dye is a heteroleptic copper(I) complex containing the anchoring and the ancillary ligand. A lot of research has been done to optimize the dye [2]. The effect of the co-adsorbent chenodeoxycholic acid on the efficiency of optimized copper(I) dyes is examined [3].

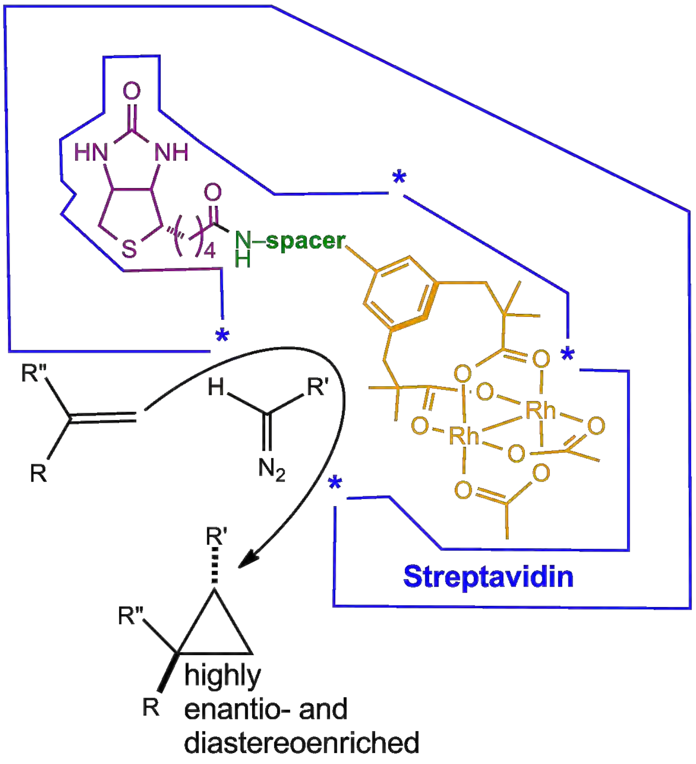
[1] B. O’Regan, M. Grätzel, *Nature*, **1991**, **353**, 737-740.
[2] F. J. Malzner, S. Y. Brauchli, E. C. Constable, C. E. Housecroft, M. Neuburger, *RSC Adv.*, **2014**, 4, 48712-48723.
[3] S. Y. Brauchli, F. J. Malzner, E. C. Constable, C. E. Housecroft, *RSC Adv.*, **2014**, 4, 62728-62736.

Rhodium-catalyzed Olefin Cyclopropanation by Engineered Streptavidin

J. Zhao[1], T. R. Ward[1]*

[1]University of Basel

Artificial metalloenzymes (ArMs) result from the incorporation of an abiotic cofactor within a protein environment.[1] Such systems combine attractive features of both organometallic and enzymatic catalysis and can be optimized with chemogenetic means.[2] Thus far however, most ArMs have relied on the use of purified proteins as the abiotic cofactor is inhibited in the presence of cell components.



Indeed, it has been demonstrated that the dirhodium tetracarboxylate system, efficient catalysts for asymmetric olefin cyclopropanation,[4] is tolerant towards cellular extracts.[5] Herein, we incorporate this moiety within streptavidin to afford an artificial metalloenzyme for enantioselective olefin cyclopropanation (Scheme 1). The optimization of the catalytic performance is achieved upon combining both chemical and genetic means.

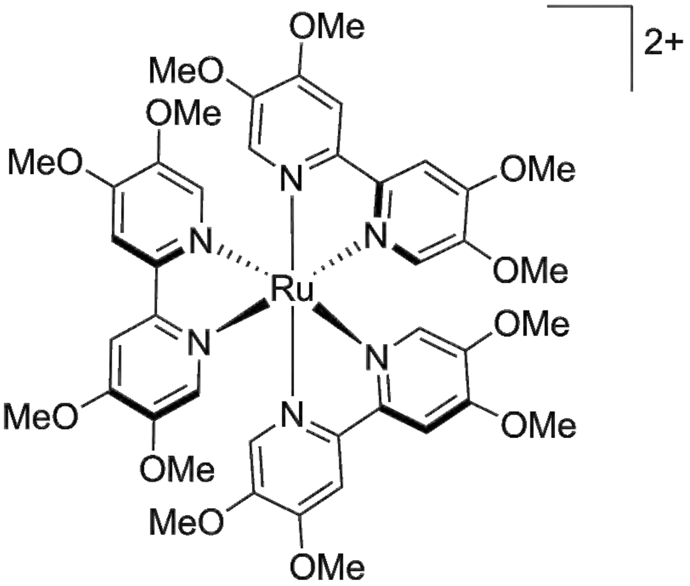
[1] F. Yu, V. Cangelosi, M. Zastrow, M. Tegoni, J. Plegaria, A. Tebo, C. Mocny, L. Ruckthong, H. Qayyum and V. L. Pecoraro, *Chem. Rev.*, **2014**, *114*, 3495.
[2] T. R. Ward, *Acc. Chem. Res.*, **2011**, *44*, 47.
[3] (a) P. Sasmal, C. Streu and E. Meggers, *Chem. Commun.*, **2013**,*49*, 1581; (b) Y. Wilson , M. Dürrenberger , E. Nogueira and T. R. Ward, *J. Am. Chem. Soc.*, **2014**, *136*, 8928; (c) P. Coelho, E. Brustad, A. Kannan and F. H. Arnold, *science* **2013**, *339*, 307.
[4] (a) M. P. Doyle and D. Forbes, *Chem. Rev.*, **1998**, 98, 911; (b) I. Nicolas, P. Maux and G. Simonneaux, *Coor. Chem. Rev,.* **2008**, *252*, 727.
[5] Z. T. Ball, *Acc. Chem. Res.*, **2013**, *46*, 560.

Strong, Chemically Robust Photoreductants

L. A. Büldt[1], O. S. Wenger[1]*

[1]University of Basel

In recent years photoredox catalysis developed into an important method in organic synthesis[1, 2]. More and more light-driven reactions are employed to get access to products which are difficult to prepare under mild conditions. Ruthenium-(II) diamine complexes are in the center of attention in this field, since they are comparatively robust and their excited state redox properties are easily tuned by the nature of the ligands. While there are several ligands known which enable ruthenium complexes to act as strong photooxidants, the number of strong photoreductants is more limited. One of the strongest ruthenium-based photoreductants is the $[\mathrm{Ru}(4,4'\text{-di}(N,N'\text{-dimethyl})\text{amino-}2,2'\text{-bipyridine})_3]^{2+}$. The electron-rich ligands enable a facile oxidation of the system[3]. On the other hand the dimethylamino groups are easy to protonate, which makes them unsuitable for reactions in acidic media.



More and more systems submitted to photoredox catalysis employ the principle of proton-coupled electron transfer (PCET) to avoid high energy reaction intermediates, e.g. in the photoreduction of ketones to ketyls[4]. The 4,4',5,5'-tetra(methoxy)-2,2'-bipyridine serves in this study as an electron-rich, but chemically robust, ligand for iron(II), ruthenium(II) and osmium(II). We demonstrate that the ruthenium(II) complex can be used as a strong photoreductant in acidic media.

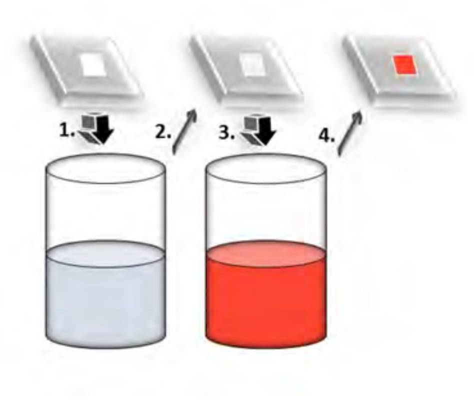
[1] Prier, C. K.; Rankic, D. A.; MacMillan, D. W. C., *Chem. Rev.* **2013,** 113, 5322.
[2] Narayanam, J. M.R.; Stephenson, C. R. J., *Chem. Soc. Rev.* **2011,** 40, 102.
[3] Slattery, S. J.; Gokaldas, N.; Mick, T.; Goldsby, K. A., *Inorg. Chem.* **1994,** 33, 3621.
[4] Tarantino, K. T.; Liu, P.; Knowles, R. R., *J. Am. Chem. Soc.* **2013,** 135, 10022.

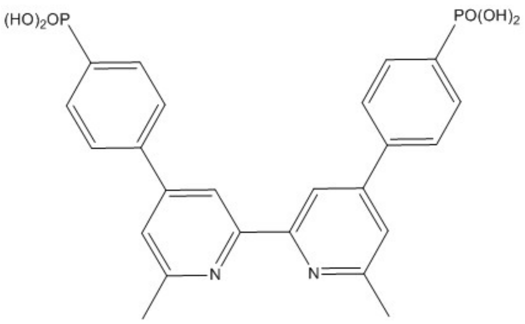
Modifying spacers and anchoring groups for heteroleptic Cu(I) - 6,6'-dimethyl-2,2'-bipyridine based DSSCs

M. Klein[1], E. C. Constable[1]*, C. E. Housecroft[1]*

[1]University of Basel

Heteroleptic [Cu(6,6'-dimethyl-2,2'-bipyridine)$_A$(6,6'-dimethyl-2,2'-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 [Cu(bpy)$_A$(bpy)$_C$]$^+$ complexes is attempted, equilibiation occurs giving mixures 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.[1] 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 TiO_2 surface. Afterwards Cu(I) and a capping ligand are introduced by a ligand exchange reaction between the anchored bpy$_A$ and a bpy$_C$ of the homoleptic [Cu(bpy$_C$)$_2$]$^+$ 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, as well as modifying the phenyl spacer has been investigated with a goal of enhancing solar cell performance for [Cu(bpy)$_2$]$^+$ complexes. Targets are to gain better affinity of the anchoring group to TiO_2, better electron transport through the spacer, less electron recombination between dye and electrolyte and an overall longer electron lifetime within the complex.





E. Schönhofer, B. Bozic-Weber, C. J. Martin, E. C. Constable, C. E. Housecroft and J. A. Zampese, *Dyes and Pigments,* 2015, **115**, 154.

Heteroleptic light-emitting copper(I) complexes for possible applications in LECs and OLEDs

S. Keller[1], C. E. Housecroft[1]*, E. C. Constable[1]*

[1]University of Basel

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 generation of visible light as main product instead of heat with light only as a by-product.
Based on the encouraging results of the Cu(I) complexes with heteroleptic N^N and P^P chelating ligands in our group [1], the strategy is to further modify and fine tune these ligands. Improving the features of the Cu(I) compounds will make them a low-priced alternative to the materials which are based on less abundant elements such as ruthenium or iridium. In order to stabilize the d^{10} state of Cu(I) and protect it from being oxidized, the ligands should be coordinated in a tetrahedral geometry. Promising ligands are 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-donors. We recently demonstrated that simple structural modification of the bpy ligand leads to improved luminance and efficiency of LECs containing $[Cu(POP)(6\text{-}Mebpy)][PF_6]$ and $[Cu(POP)(6,6'\text{-}Me_2bpy)][PF_6]$ (6-Mebpy = 6-methyl-2,2′-bipyridine, 6,6′-Me2bpy = 6,6′- dimethyl-2,2′-bipyridine) [2]. Further alteration of the ligands will provide new insights into their influence on the important complex properties such as electroluminescence, lifetime of the excited state, quantum yield and ion mobility.

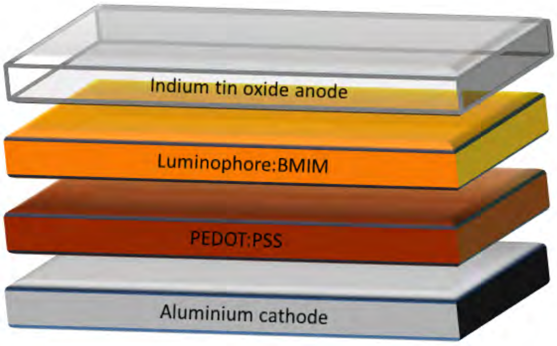


Figure. Schematic layout of the LECs applied for testing of our compounds.

Acknowledgements
M. Neuburger, A. Prescimone, G. Longo, A. Pertegás, M. Sessolo, H. J. Bolink, European Research Council (Advanced Grant 267816 LiLo), Swiss National Science Foundation.

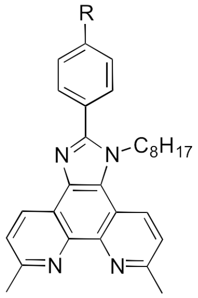
[1] R. D. Costa, D. Tordera, E. Orti, H. J. Bolink, J. Schönle, S. Graber, C. E. Housecroft, E. C. Constable, J. Zampese, *J. Mater. Chem.*, **2011**, *21*, 16108 - 16118.
[2] S. Keller, E. C. Constable, C. E. Housecroft, M. Neuburger, A. Prescimone, G. Longo, A. Pertegás, M. Sessolo, H. J. Bolink, *Dalton Trans.* **2014**, *43*, 16593-16596.b

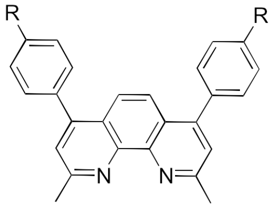
The Performance of a Series of Copper(I) Phenanthroline Dyes in DSCs

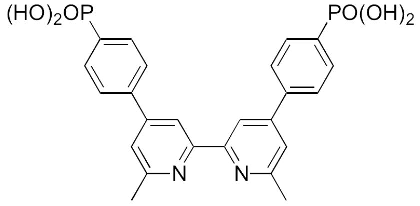
S. O. Fürer[1], C. E. Housecroft[1]*, E. C. Constable[1]*

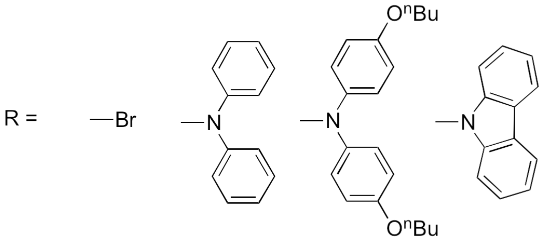
[1]University of Basel

Recently, dye sensitized solar cells (DSCs) have gained a lot of interest as a promising low-cost alternative to conventional silicon solar cells. To date the best performing dyes in DSCs are based on ruthenium [1]or zinc-porphyrines [2]and are hence either expensive or difficult to synthesize on a large-scale for commercial applications. Here we present a series of dyes from of earth-abundant copper for the production of low-cost DSCs. 4,7- and 5,6-disubstituted phenanthroline ligands of the type **L1** and **L2** with a series of different donor groups were synthesized. Following our established *on-surface* method,[3-5]heteroleptic copper(I) dyes were synthesized from **L3** anchored to a mesoporous TiO_2 surface through ligand exchange with homoleptic Cu(I) dyes of ligands **L1** and **L2**. The performance of these dyes in DSCs was studied and the different behaviour of the substituents investigated in DSCs containing either I^-/I_3^- or $[Co(bpy)_3][PF_6]_{2/3}$ electrolytes.









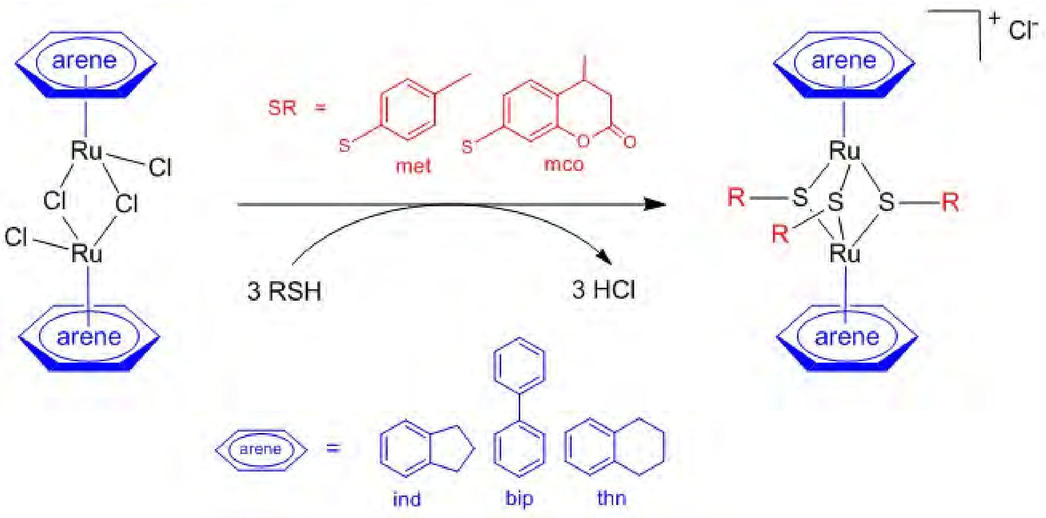
[1] Abbotto, A.; Manfredi, *Dalton Trans.*, **2011**, 40, 12421.
[2] Yella, A.; Lee, H.-W.; Tsao, H. N.; Yi, C.; Chandiran, A. K.; Nazeeruddin, M. K.; Diau, E. W.-G.; Yeh, C.-Y.; Zakeeruddin, S. M.; Gratzel, M. *Science* **2011**, 334, 629.
[3] Bessho, T.; Constable, E. C.; Graetzel, M.; Hernandez Redondo, A.; Housecroft, C. E.; Kylberg, W.; Nazeeruddin, M. K.; Neuburger, M.; Schaffner, S. *Chem. Commun.* **2008**, 3717.
[4] Bozic-Weber, B.; Constable, E. C.; Fürer, S. O.; Housecroft, C. E.; Troxler, L. J.; Zampese, J. A. *Chem. Commun.* **2013**, 49, 7222.
[5] Bozic-Weber, B.; Brauchli, S. Y.; Constable, E. C.; Fürer, S. O.; Housecroft, C. E.; Wright, I. A. *Phys. Chem. Chem. Phys.* **2013**, 15, 4500.b

Tuning the in vitro cell cytotoxicity of dinuclear arene ruthenium trithiolato complexes: Influence of the arene ligand

L. Geiser[1], F. Giannini[1], L. Paul[1], G. Süss-Fink[2], J. Furrer[1]

[1]University of Bern, [2]University of Neuchatel

A new series of cationic dinuclear arene ruthenium complexes bridged by three thiophenolato ligands, $[(\eta^6\text{-arene})_2Ru_2(\mu_2\text{-SR})_3]^+$ with arene = indane, R = met : 1 (met = 4-methylphenyl); R = mco: 4 (mco = 4-methylcoumarin-7-yl); arene = biphenyl, R = met : 2; R = mco: 5; arene = 1,2,3,4-tetrahydronaphthalene, R = met : 3; R = mco: 6, have been prepared from the reaction of the neutral precursor $[(\eta^6\text{-arene})Ru(\mu_2\text{-Cl})Cl]_2$ and the corresponding thiophenol RSH.



Interestingly, the 4-methylphenylthiolato complexes (R = met) are highly cytotoxic towards human ovarian cancer cells, the IC_{50} values being in the sub-micromolar range, while the 4-methylcoumarin-7-yl thiolato complexes (R = mco) are only slightly cytotoxic [1].
From our results, it appears possible to compensate the effect of the rather hydrophilic Smco thiolato bridge by a more lipophilic arene, resulting in complexes with a gradually increased lipophilic character from indane to biphenyl. Such compensation effects were also observed in the series of mixed complexes $[(\eta^6\text{-p-cymene})Ru_2(\mu_2\text{-SR}^1)(\mu_2\text{-SR}^2)_2]^+$ [2], where it is possible to compensate the effect of one thiolato bridge by the other one. The results demonstrate that the arene ligand is an important parameter that should be more systematically evaluated when designing new half-sandwich organometallic complexes.

[1] Federico Giannini, Lennart Geiser, Lydia E.H. Paul, Thomas Roder, Bruno Therrien, Georg Süss-Fink, Julien Furrer, *J. Organomet. Chem.* **2015**, 783, 40-45.
[2] Federico Giannini, Julien Furrer, Georg Süss-Fink, Catherine M. Clavel, Paul J. Dyson, *J. Organomet. Chem.* **2013**, 744, 41-48.

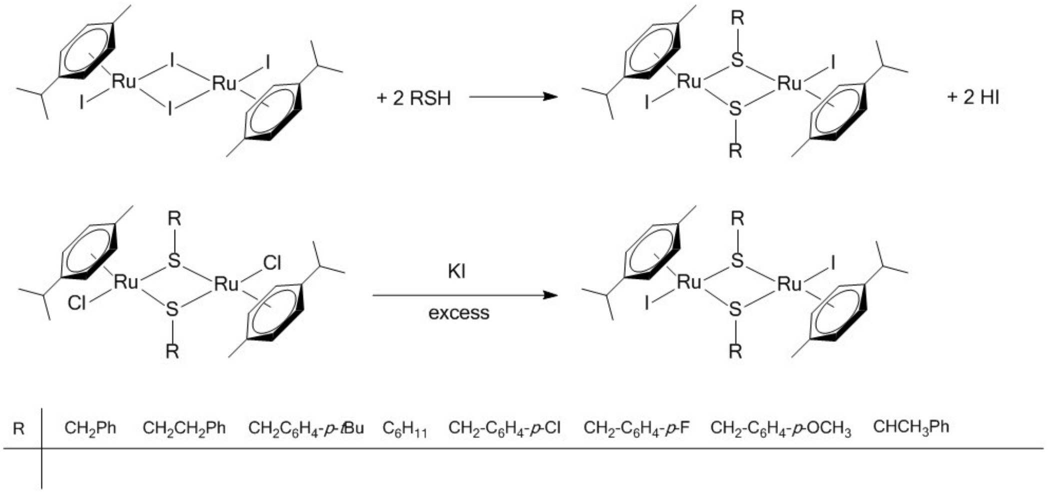
Synthesis, reactivity and cytotoxicity of dithiolato diruthenium complexes $[(\eta^6\text{-p-cymene})_2Ru_2(\mu_2\text{-SR})_2X_2]$, X = Cl, I

L. Geiser[1], J. Furrer[1]

[1]University of Bern

There have been few studies of the effects of Cl−I substitutions on the activity of transition metal complexes. Halide switch from chloride to iodide was shown to increase the polarization of positive charge on the chelated face of Ru- and Os-pseudo-octahedral complexes. This results in iodido complexes which are more potent and more selective toward cancer cell lines, and are not cross-resistant with platinum drugs used in the clinic [1].

Dithiolato diruthenium complexes $[(\eta^6\text{-}p\text{-cymene})_2Ru_2(\mu_2\text{-SR})_2Cl_2]$ complexes were shown to be cytotoxic against human ovarian cancer cells, with IC_{50} values as low as 0.20 µM [2]. However, dithiolato complexes are much less cytotoxic than the corresponding trithiolato ruthenium complexes $[(\eta^6\text{-}p\text{-cymene})_2Ru_2(\mu_2\text{-SR})_3]^+$ (IC_{50} values of 0.03 µM) [3], presumably because of the presence of reactive Ru-Cl bonds. In this work, we set out to synthesize new dithiolato diruthenium complexes $[(\eta^6\text{-}p\text{-cymene})_2Ru_2(\mu_2\text{-SR})_2X_2]$, X = Cl, I, and to evaluate their cytotoxicity, the aim being to rationalize the effect of the halide switch from chloride to iodide. To this end, the cytotoxicity is compared to properties such as the rate of aquation and the reactivity towards biomolecules (amino acids, nucleotides).



The iodido complexes are synthesized using two different strategies: starting from the ruthenium dimer precursor $[(\eta^6\text{-}p\text{-cymene})Ru(\mu_2\text{-I})I]_2$ and from the neutral dithiolato diruthenium complexes $[(\eta^6\text{-}p\text{-cymene})_2Ru_2(\mu_2\text{-SR})_2Cl_2]$ upon addition of KI using the Finkelstein reaction.

[1] Isolda Romero-Canelón, Luca Salassa, Peter J. Sadler, *J. Med. Chem.* **2013**, 56, 1291−1300.
[2] A.-F. Ibao, M. Gras, B. Therrien, G. Süss-Fink, O. Zava, P. J. Dyson, *Eur. J. Inorg. Chem.* **2012**, 1531-1535.
[3] F. Giannini, J. Furrer, A.-F. Ibao, G. Süss-Fink, B. Therrien, O. Zava, M. Baquie, P. J. Dyson, P. Štěpnička, *J. Biol. Inorg. Chem.* **2012**, 17, 951-960.

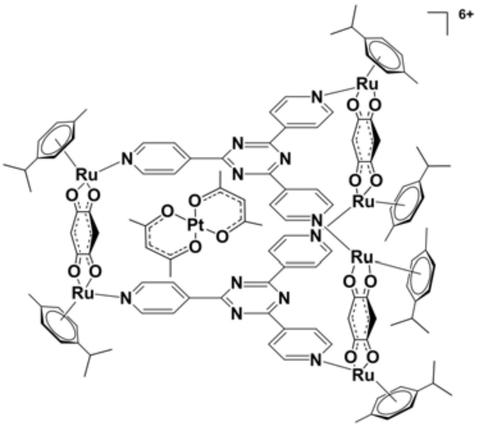
Did the presence of a guest in the cavity of an arene ruthenium metallaprism modify its reactivity towards biomolecules?

L. Paul[1], B. Therrien[2], J. Furrer[1]*

[1]University of Bern, [2]University of Neuchatel

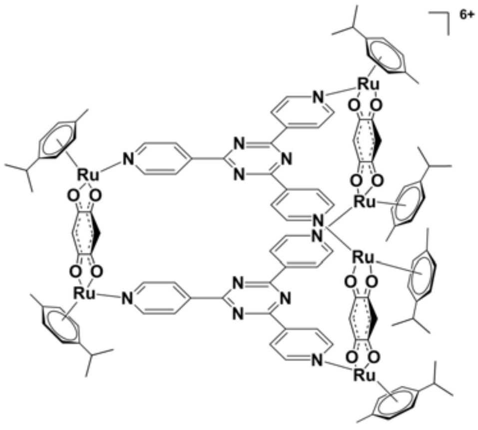
Over the past decades, ruthenium-based anticancer drugs received much attention due to their favourable properties compared to platinum-based drugs. [1,2] In recent years, we have designed several hexacationic hexaruthenium assemblies that can encapsulate planar platinum complexes and therefore act as drug delivery vectors. [3] For those host-guest systems, the rate of dismantling of the metallaprism represents a crucial parameter. Indeed, the guest molecule is expected to remain encapsulated in the metallaprism until the host-guest system enters cells.

We therefore set out to compare the reactivity and rate of dismantling of the complex-in-a-complex cation $[Pt(acac)_2\subset(p\text{-}cym)_6Ru_6(tpt)_2(dhbq)_3]^{6+}$ ($[Pt(acac)_2\subset\mathbf{1}]^{6+}$) towards amino acids, proteins, nucleotides and DNA with the empty metallaprism $[\mathbf{1}]^{6+}$. [4]



$[Pt(acac)_2\subset 1]^{6+}$

vs.



$[1]^{6+}$

[1] M. J. Clarke, *Met. Ions Biol. Syst.* **1980**, *11*, 231.
[2] G. Süss-Fink, *Dalton Trans.* **2010**, *39*, 1673.
[3] B. Therrien et al., *Angew.Chem. Int. Ed.* **2008**, *47*, 3773.
[4] L.E.H. Paul, et al., *J. Organomet. Chem.* **2015**, http://dx.doi.org/10.1016/j.jorganchem.2015.02.042

Synthesis of metal oxide precursors for the generation of oxides or similar nanomaterials for Na-ion battery cathode production

B. Baichette[1], K. Fromm[1]*

[1]Department of Chemistry, University of Fribourg, Chemin du Musée 9, 1700 Fribourg

The current growing need of energy storage is an issue that can be solved at least partially by electrochemical storage, like batteries. Nowadays, most of the Li-ion battery cathodes are made of lithium cobalt oxide, $LiCoO_2$, prepared by highly energy consuming solid state processes, involving solid state method at high temperature and for long reaction times (600-900°C, 36hours [1]). Aurelien Crochet and Jean-Pierre Brog of the Fromm group developed a way of producing the high-temperature phase of $LiCoO_2$ (HT-$LiCoO_2$) [2] at low temperature using heterometallic Li-Co alkoxides complexes as molecular precursors, following the general equation 1.

$$[Li_2Co(OR)_4(L)_4] \xrightarrow[\text{Air, 2h}]{\text{350-450°C}} \text{HT-}LiCoO_2 + Li_2Co_3 + CO_2 + H_2O$$

Despite lower performances, Na-ion batteries are good candidates in an effort to produce cheaper and more environmentally friendly batteries compared to Li-ion batteries. Complexes of $[Na_xM_y(OR)_z(L)_a]$, where M is a transition metal, OR an alkyl or aryl oxide group and L a ligand, can be synthesized in analogy to the lithium precursors in order to use them for the generation of sodium metal oxides. Those oxides will be characterized and tested as cathode materials. We will present our first efforts and results on this kind of synthesis.

[1] Y. Shao-Horn, L. Croguennec, C. Delmas, E. C. Nelson, and M. A. O'Keefe, "Atomic resolution of lithium ions in LiCoO2," *Nat. Mater.*, vol. 2, no. 7, pp. 464–7, Jul. 2003.
[2] J.-P. Brog, A. Crochet, and K. Fromm, "Lithium metal aryloxide clusters as starting products for oxide materials," WO/2012/000123, 05-Jan-2012.

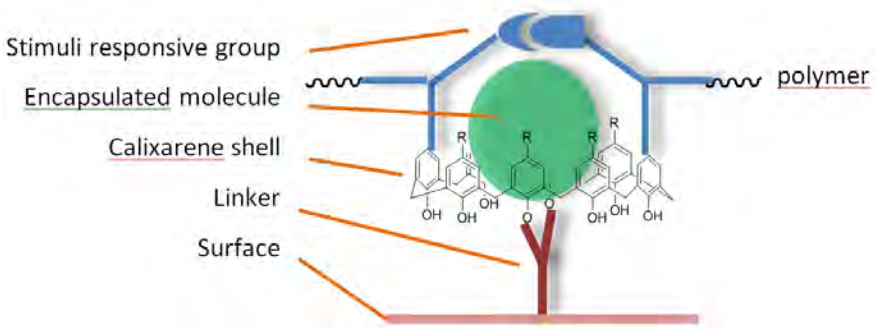
Stimuli responsive cavitands for triggered release of antimicrobial drugs

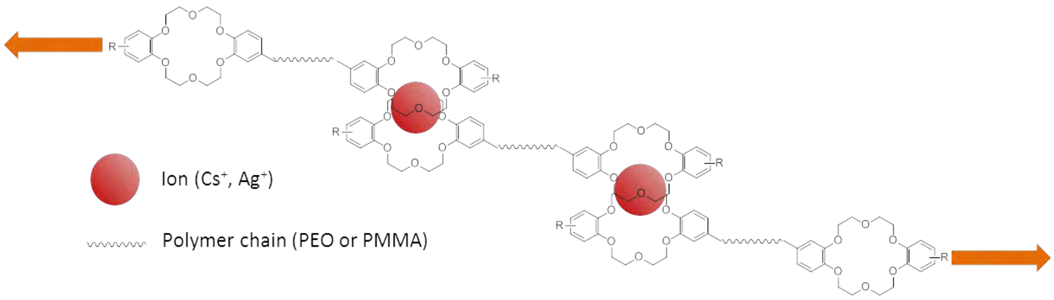
N. Voutier[1], K. Fromm[2]*

[1]Université de Fribourg, [2]University of Fribourg

Cavitands[1] like calixarenes and crown-ethers find a broad range of applications nowadays in various domains: for ion-transport[2,3], ionic channels[4], as carriers in liquid membrane transport[5], or even as catalysts[6]. These container-shaped molecules are able to encapsulate guests of various but complementary forms and sizes, via coordination or cation-π interactions[7]. It is interesting to use this kind of molecules for drug delivery.

The use of implants in medicine encounters one major issue, which is biofilm formation by bacteria[8]: one solution could then be to have a targeted triggered release of an antimicrobial drug, in order to have an efficient action against bacteria, thus enabling the use of smaller amounts of the medicine and consequently reduced side effects.
This project aims to combine the cavitands' properties with a stimuli-responsive unit and then insert the system into a polymer that can be coated on the implant's surface. We are herein focusing on the syntheses of such systems: firstly, a dibenzo-18-crown-6 ether-based organometallic polymer, and secondly, a calixarene based mechano-responsive sensor for bacterial detection. Later on, these molecules will be tested *in vitro* for cytotoxicity and bactericidal properties.





[1] D. J. Cram, *Science*, **1983**, 219, 1177-1183
[2] S. Ayata and M. Merdivan, *J. Radioanal. Nucl. Chem.*, **2010**, 283, 603-607
[3] N. P. Clague, *Chem. Commun.*, **1999**, 379-380
[4] K. M. Fromm, R. D. Bergougnant and A. Y. Robin, *Z. Anorg. Allg. Chem.*, **2006**, 828-836
[5] L. Mutihac, H. J. Buschmannb, Elena Diacuc, *Desalination,* **2002**, 148, 253-256
[6] A. Soriente et al. *Adv. Synth. Catal.*, **2005**, 347, 816–824
[7] E. Makrlı´k, P. Toman and P. Vanura, *J. Radioanal. Nucl. Chem.,* **2013,** 298, 429-434
[8] S. Veerachamy1, T. Yarlagadda, G. Manivasagam and P. KDV Yarlagadda, *J. Engineering in Medicine,* **2014**, 228, 1083-1099

Sn/C composite anode material for lithium ion batteries

S. Maharajan[1], N. H. Kwon[1], K. Fromm[1]*

[1]University of Fribourg

Introduction: Alloy-type anodes (Si, Ge, Sn, Al, Sb, etc.) have much higher Li storage capacity than the intercalation-type graphite anode that is currently commercially used in Li-ion batteries [1]. Metallic Tin (Sn) is one of the most promising anode materials for next-generation LIBs due to its high theoretical capacity of 991 mAhg^{-1} or 7313 mAhcm^{-3}, multiple times that of commercialized graphite anode material (372 mAhg^{-1} or 833 mAhcm^{-3}). However, the huge volume expansion (up to 360%) consequently leading to the dramatic mechanical stress of Sn during cycling causes cracking and pulverization of the active material. This also leads to the loss of conductivity at the electrode, resulting in quick capacity fading, which greatly hinders the practical application of Sn as an anode material and thereby letting down its application in LIBs[2]. Another impactful problem is the rupture of the SEI layer ending up in low Coulombic efficiency, ionic and electronic resistivity[3]. It is therefore essential to control the volume expansion and thereby preventing the loss of active materials. The idea of a composite electrode which could facilitate a buffer volume to survive the volume expansion will be the call of the moment. We have adopted a novel synthesis method to control the volume expansion by engineering a composite Sn/C electrode which serves as a buffer volume to the volume expansion.

Reverse micelle micro emulsion synthesis: A reverse micelle micro emulsion technique has been developed which can synthesize Tin nanoparticles into Carbon shell with a void in between to accommodate the volume expansion[4]. We have achieved tiny Sn nanoparticles within the Silica shell in 20- 30 nm range. The EDX spectrum (Fig. 1b) proves the existence of Sn^0 and SiO$_2$shell.

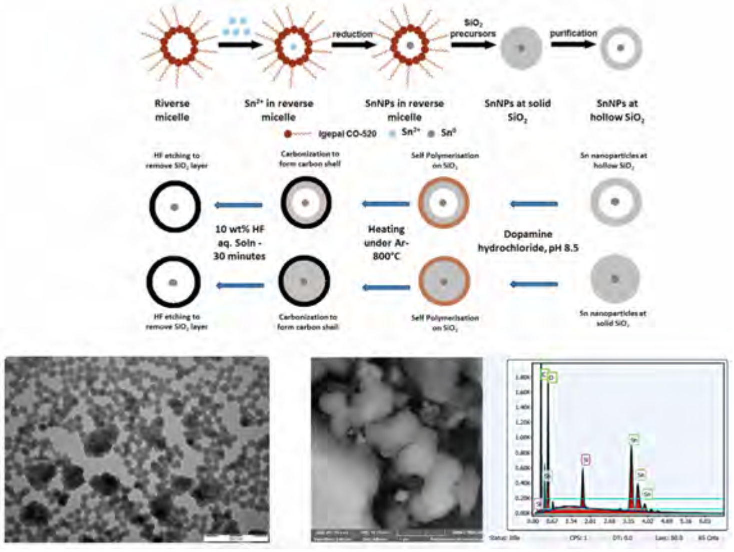


Figure 1: a) TEM image showing Sn nanoparticles b) EDX spectrum with SEM image

Conclusion:A composite anode material is proposed and synthesized by reverse micelle micro emulsion technique. The sequential steps of cycling the composite electrode and electrochemical testing will be done after further quantification analysis in near future.

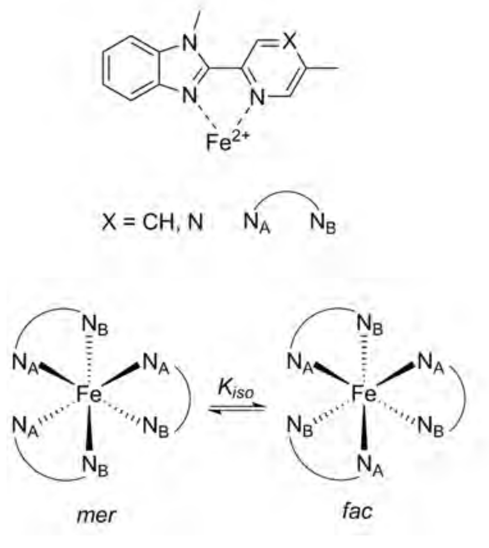
[1] W.-J. Zhang, *Journal of Power Sources* **2011**, 196, 13-24.
[2] J. O. Besenhard, J. Yang and M. Winter, *Journal of Power Sources* **1997**, 68, 87-90.
[3] D. Aurbach, *Journal of Power Sources* **2000**, 89, 206-218.
[4] M. Priebe and K. M. Fromm, *Particle Particle Systems Characterization* **2014**, 31, 645-651.

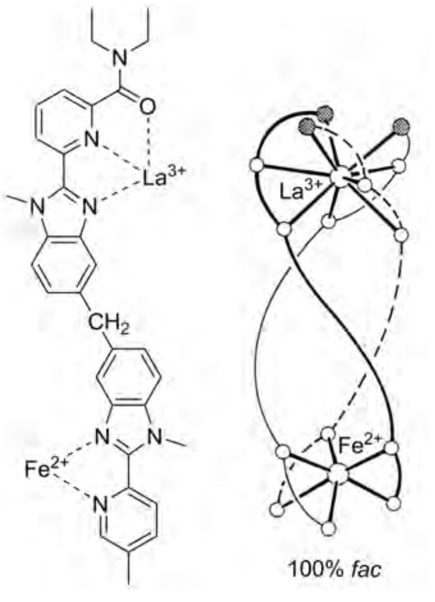
Pyridine versus pyrazine in asymmetric didentate ligands: unexpected behaviour in Fe^{II} spin crossover complexes

T. Lathion[1], E. Rivara-Minten[1], L. Guénée[1], C. Piguet[1]*

[1]University of Geneva

Paramagnetic measurements, carried out in solution using Evan's method for spin crossover complexes of Fe^{II} with asymmetric tris-diimine ligands, reveal unusual nonlinear van't Hoff isotherms for the spin transition. In these complexes, the thermodynamic equilibrium involves *mer* and *fac* isomers, for which different paramagnetic properties can be expected (Figure, left). Based on statistics, a 1:3 ratio of *fac* and *mer* isomers is expected, but significant deviations have been observed and recently reported.[1] Thermodynamic studies of the *mer* to *fac* isomerization reveal that about 20% of the complex undergoes isomerization to the entropically favoured *mer* isomer upon heating, hence the detection of a non-standard spin crossover transition. By using a lanthanide cation as a template in heterometallic dinuclear complexes, we are able to induce the formation of 100% of the *fac* arrangement of the diimine ligands around Fe^{II} (Figure, right). This restores spin crossover transitions characterized by linear van't Hoff plots and standard thermodynamic interpretations.[2]





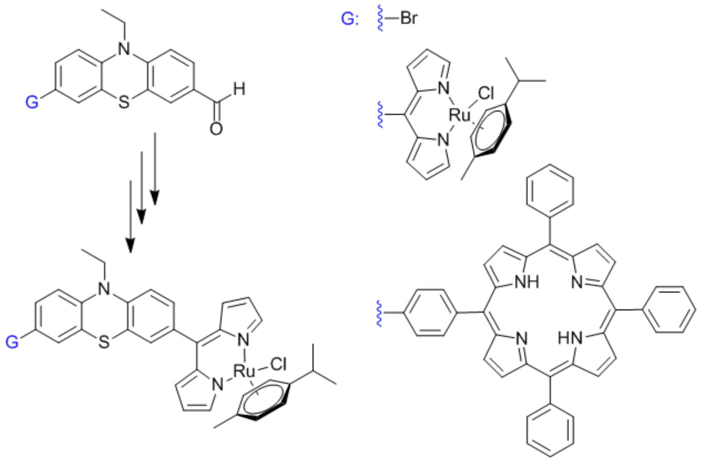
[1] Aboshyan-Sorgho, L.; Lathion, T.; Guenee, L.; Besnard, C.; Piguet, C. *Inorg. Chem.* **2014**, *53*, 13093.
[2] Piguet, C.; Rivara-Minten, E.; Bernardinelli, G.; Bünzli, J.-C. G.; Hopfgartner, G. *J. Chem. Soc., Dalton Trans.* **1997**, 421.

Synthesis of heteroaryl meso substituted porphyrins, and their coordination with ruthenium complexes

B. Brem[1,2], L. Silaghi-Dumitrescu[2]*, B. Therrien[1]*

[1]Institute of Chemistry, University of Neuchâtel, Neuchâtel, Switzerland , [2]Faculty of Chemistry and Chemical Engineering, Babes-Bolyai University, Cluj-Napoca, Romania

Ruthenium complexes have a potential affinity to cancer tissues because they can bind readily to transferrin molecules[1]. The properties of the very potent pharmacophore phenothiazine have been largely exploited in medicinal applications[2], while recent literature reports demonstrated progress in the identification of promising new biological applications[3,4].The porphine macrocycle is hydrophobic, with a tendency to aggregate in body fluids and tissues, leading to suboptimal concentration in target tissues and poor photodynamic activity[5]. These reasons explain the continuous interest for the design of new porphyrin derivatives with improved biocompatibility[6], reduced toxicity[7] and enhanced photodynamic effect on target cells[8]. Our goal is to combine the photodynamic action of porphyrins and the cytotoxic properties of ruthenium complexes and the pharmacophore phenothiazine unit. To generate such multifunctional molecules, arene ruthenium moieties have been coordinated to phenothiazinyl-dipyrrin and phenothiazinyl-porphyrin-dipyrrin derivatives.



Acknowledgements: *This work was possible with the financial support of the* Sciex-NMS^{ch} *programe*.

[1] Y. N. Vashisht Gopal, D. Jayaraju, A. K. Kondapi, *Biochemisry*, **1999**, 38(14), 4382-4388.
[2] K. Pluta, B. Morak-Mlodawsca, M. Jelen, *Eur. J. Med. Chem.*, **2011**, 46(8), 3179-3189.
[3] G. Sudeshna, K. Parimal, *Eur. J. Pharmacol.*, **2010**, 648(1-3), 6-14.
[4] E. Gal, B. Brem, I. Pereteanu, L. Gaina, T. Lovasz, M. Perde-Schrepler, L. Silaghi-Dumitrescu, C. Cristea, L. Silaghi-Dumitrescu, *Dyes and Pigments*, **2013**, 99, 144-153.
[5] J. Kralova, *Photochem Photobiol*, **2006**, 82(2), 432-438.
[6] B. Therrien, *Chem. Eur. J.*, **2013**, 19, 8378-8386.
[7] F. Schmitt, P. Govindaswamy, G. Süss-Fink, W. H. Ang, P. J. Dyson, L. Juillerat-Jeanneret, B. Therrien, *J. Med. Chem.*, **2008**, 51, 1811-1816.
[8] F. Schmitt, P. Govindaswamy, O. Zava, G. Süss-Fink, L. Juillerat-Jeanneret, B. Therrien, *J. Biol. Inorg. Chem.*, **2009**, 14, 101-109.

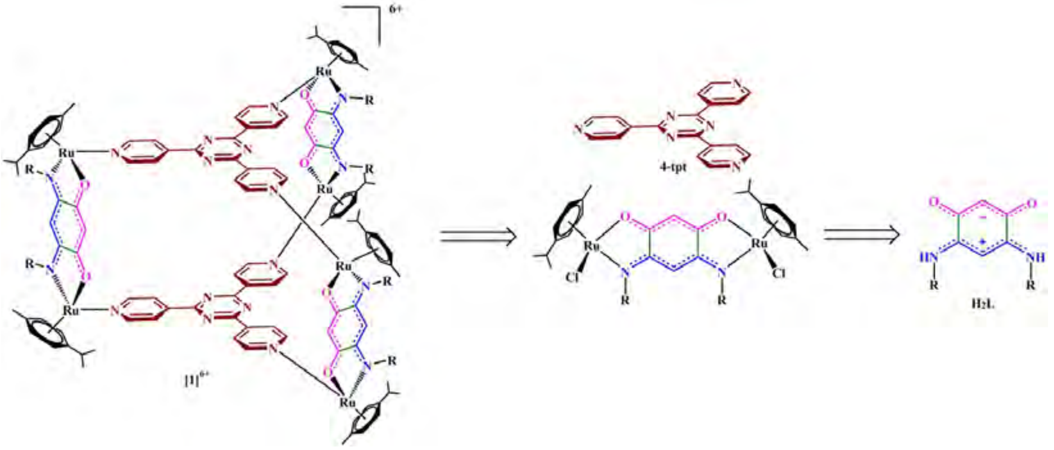
Anti-Cancer Activities of Zwitterion-Bridged Arene Ruthenium Metalla-Assemblies

M. Yuan[1,2], L. Routaboul[2], B. Therrien[1]*, P. Braunstein[2]*

[1]Institute of Chemistry, University of Neuchâtel, Switzerland, [2]Coordination Chemistry Laboratory (UMR 7177 CNRS), University of Strasbourg, France

e-mail: minghui.yuan@unine.ch; m.yuan@unistra.fr

Hexaruthenium metalla-prisms have been shown to possess anti-cancer properties and able to transport therapeutic compounds into cells.[1] New zwitterion-bridged arene ruthenium metalla-assemblies of the general formula $[(p\text{-cymene})_6Ru_6L_3(4\text{-tpt})_2](CF_3SO_3)_6$ ($[\mathbf{1}](CF_3SO_3)_6$) incorporating (*p*-cymene) ruthenium building blocks, bridged by zwitterionic quinonoid linkers (H_2L = *N,N′*-R,R-2-amino-5- lcoholate-1,4-benzoquinonemonoiminium),[2] and connected by two 2,4,6-tri(pyridin-4-yl)-1,3,5-triazine (4-tpt) have been isolated as their triflate salts.[3] The zwitterionic quinonoid linkers possess two functional groups, adding functionality to the supramolecular systems and enhancing the biological activity of the metalla-assemblies by modifying their physical and/or chemical properties. Several metalla-assemblies were evaluated as anticancer agents against cancerous (A2780) and noncancerous (HEK293) cell lines, showing an excellent selectivity for cancer cells.



[1] a) Therrien, B.; Süss-Fink, G.; Govindaswamy, P.; Renfrew, A.-K.; Dyson, P.-J., *Angew. Chem. Int. Ed.* **2008**, *47*, 3773–3776; b) Mattsson, J.; Govindaswamy, P.; Furrer, J.; Sei, Y.; Yamaguchi, K.; Süss-Fink, G.; Therrien, B., *Organometallics* **2008**, *27*, 4346-4356.
[2] a) Siri, O.; Braunstein, P., *Chem. Commun*, **2002**, 208-209; b) Yang, Q.-Z.; Siri, O.; Braunstein, P., *Chem. Commun.*, **2005**, 2660-2662.
[3]Yuan, M.; Weisser, F.; Sarkar, B.; Garci, A.; Braunstein, P.; Routaboul, L.; Therrien, B., *Organometallics*, **2014**, *33*, 5043–5045.

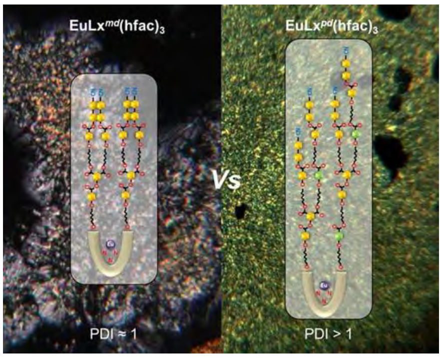
Acknowledgements: Financial supports by the CNRS, the Région Alsace and the University of Neuchâtel.

Poly versus Mono-Disperse Rodlike Lipophilic Fluoroacetylacetonate Eu(III) Complexes: Mesomorphic and Thermodynamic Consequences

S. Guerra[1], E. Terazzi[1], L. Guénée[1], C. Piguet[1]*

[1]University of Geneva

A series of three different mesomorphic dendritic-like tridentate ligands **L0-L2** decorated with terminal cyanobiphenyl units have been synthesized. Upon reaction with [Eu(hfac)$_3$ · diglyme], the central 2,6-bis(*N*-ethyl-benzimidazol-2-yl)pyridine scaffold is tri-coordinated to the Eu(III) in order to lead to “U” shape complexes. The detection of additional sets of doublets on the ^{1}H-NMR spectra of the final complexes results from self-condensation leading to polydispersity index larger than 1.0 (PDI › 1). Two key steps during the synthesis were responsible of these defects in the ligand structures. In order to restore the formation of monodisperse receptors, a novel synthetic strategy based on protected C10 spacers has been implemented. Following this approach, monodisperse (PDI = 1) Eu(III) complexes have been synthesized. The mesomorphism and thermodynamics of melting of these complexes have been studied in order to explore the influence of polydispersity on the liquid-crystalline behaviours.



[1] Thomas Binderup Jensen, Emmanuel Terazzi, Bertrand Donnio, Daniel Guillon, and Claude Piguet, *Chem. Commun.*, **2008**, 181-183.

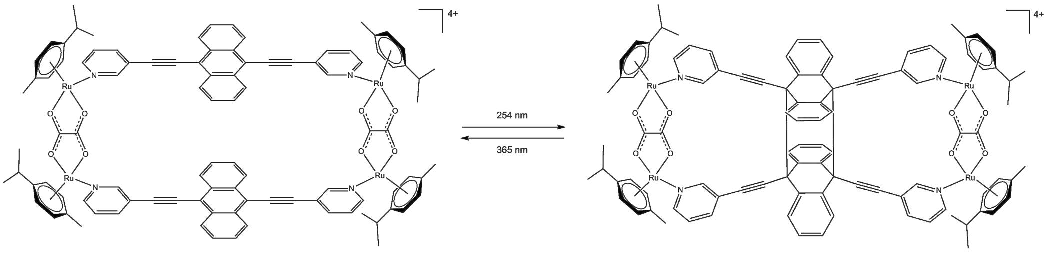
[2] Thomas Binderup Jensen, Emmanuel Terazzi, Kerry-Lee Buchwalder, Laure Guénée, Homayoun Nozary, Kurt Schenk, Benoît Heinrich, Bertrand Donnio, Daniel Guillon, and Claude Piguet, *Inorg. Chem.*, **2010**, 49, 8601-8619.

Water-soluble organometallic assemblies containing photo-switchable ligands

T. Cheminel[1], B. Therrien[1]*

[1]University of Neuchatel

Research in our group is focused on the synthesis of organometallic cages for biological applications. These cages are able to encapsulate and deliver various molecules such as drugs[1] or photosensitizers[2] to cells. Herein, anthracene derivatives are used to synthesize ruthenium metalla-cages similar to those already prepared in our group. The interesting feature of these molecules is the photo-dimerization of the anthracene unit which occurs under ultraviolet irradiation[3], making possible changes in the conformation of the assembly by “blocking” the cavity of the cage, and thus facilitating the releasing control of the guest molecule *via* an opened-closed switchable system – indeed, so far, the release of the guests molecules has been regulated by changing the size and shape of the aperture of the organometallic cages[4], or by uncontrolled breakage of the assembly[5].



1. Therrien, B.; Süss-Fink, G.; Govindaswamy, P.; Renfrew, A. K.; Dyson, P. J. *Angew. Chem. Int. Ed*. **2008**, *47*, 3773-3776.
2. Schmitt, F.; Freudenreich, J.; Barry, N.; Juillerat-Jeanneret, L.; Süss-Fink, G.; Therrien, B. *J. Am. Chem. Soc.* **2012**, *134*, 754-757.
3. Greene, F. D.; Misrock, S. L.; Wolfe, J. R. *J. Am. Chem. Soc*. **1955**, *77*, 3852-3855.
4. Barry, N.; Zava, O.; Dyson, P. J.; Therrien, B. *Chem. Eur. J*. **2011**, *17*, 9669-9677.
5. Paul, L. E. H.; Therrien, B.; Furrer, J. *Inorg. Chem*. **2012**, *51*, 1057-1067.b

Efficient Triplet Blue Emitters Based on Neutral Gold(III) Complexes

A. Szentkuti[1], T. von Arx[1], K. Venkatesan[1]*

[1]University of Zurich

Luminescent late transition metal complexes have gained a wide spread interest in the past decades due to their unique photophysical properties and their applications in the field of optoelectronic materials, such as organic light emitting diodes (OLEDs). The phenomenon of "triplet-harvesting", where both singlet and triplet excitons can be harvested, makes them ideal candidates for a number of photoluminescent applications.[1] Triplet emitters with iridium(III) and platinum(II) as metal centers are extensively explored in contrast to gold(III) complexes, which is mainly attributed to their latter's low stability due to the often observed reductive elimination when carbon based ligands are bound to the metal center.[2] One other problem with gold(III) concerns their low lying d-d ligand field (LF) states and its strong electrophilic character that quenches the luminescence excited states significantly at room temperature. To enhance the phosphorescence properties of such organogold(III) complexes, we have employed a design strategy that involves the utilization of appropriate ligand scaffolds that not only raise the d-d levels of the resulting gold complexes and make them highly emissive but also renders them immense stability. Following several conceptual approaches, we have successfully achieved an array of compounds that are robust and show efficient triplet blue emission. Fabrication of OLEDs in order to evaluate their efficiency is currently on-going.[3]

[1](a) Baldo, M. A.; O'Brien, D. F.; You, Y.; Shoustikov, A.; Sibley, S.; Thompson, M. E.; Forrest, S. R. *Nature*, **1998**, *395*, 151. (b) Yersin, H.; Finkenzeller, W. J. *Highly Efficient OLEDs with Phosphorescent Materials*; Yersin, H., Ed.; Wiley-VCH: Weinheim, 2007; pp 1-89.
[2](a) Au, V. K.-M.; Wong, K. M.-C.; Zhu, W.; Yam, V. W.-W. *Chem. Eur. J.*, **2011**, *17*, 130-142. (b) Garg, J. A.; Blacque, O.; Fox, T.; Venkatesan, K. *Inorg. Chem.* **2010**, *49*, 11463-11472.
[3] (a) Szentkuti, A.; Bachmann, M.; Garg, J. A.; Blacque, O.; Venkatesan, K. *Chem. Eur. J.* **2014**, *20*, 2585-2596. (b) Szentkuti, A.; Von Arx, T.; Blacque, O.; Venkatesan, K. **2015** Manuscript to be submitted.

Investigating the structure of the metallothionein 2 protein from the plant Cicer arietinum

A. Salim[1], E. Freisinger[1]*

[1]University of Zurich

Metallothioneins (MTs) are low molecular mass, cysteine-rich proteins with a variety of functions including involvement in metal homeostasis, protection against heavy metal damage, and direct scavenging of cell damaging reactive oxygen species (ROS). MTs typically bind metal ions in characteristic metal-thiolate clusters that provide high thermodynamic stability coupled with kinetic lability.

The MT2 form from *C. arietinum* (chickpea), cicMT2, features two Cys-rich domains with 8 and 6 Cys residues, respectively, which are separated by a Cys-free 41 amino acids long linker. Initial investigations suggest that cicMT2 coordinates up to five divalent metal ions such as Zn^{II} and Cd^{II} in form of a single cluster (1).

Apart from wheat E_c-1, no three-dimensional structure information about plant MTs is available, probably due to the dynamic behaviour of these proteins. Hence, a number of different approaches will be tested to obtain three-dimensional structural information for cicMT2 with NMR spectroscopy. One approach is the separate investigation of the Cys-free linker region, which was suggested to contain a high amount of β-sheets (2). In addition, the backbone-cyclized form of the full-length cicMT2 protein will be produced with the modified IMPACT-CN vector system (3) to reduce the flexibility.

Financial support from the Swiss National Science Foundation, the Institute of Chemistry, and the Faculty of Sciences of the University of Zurich is gratefully acknowledged.

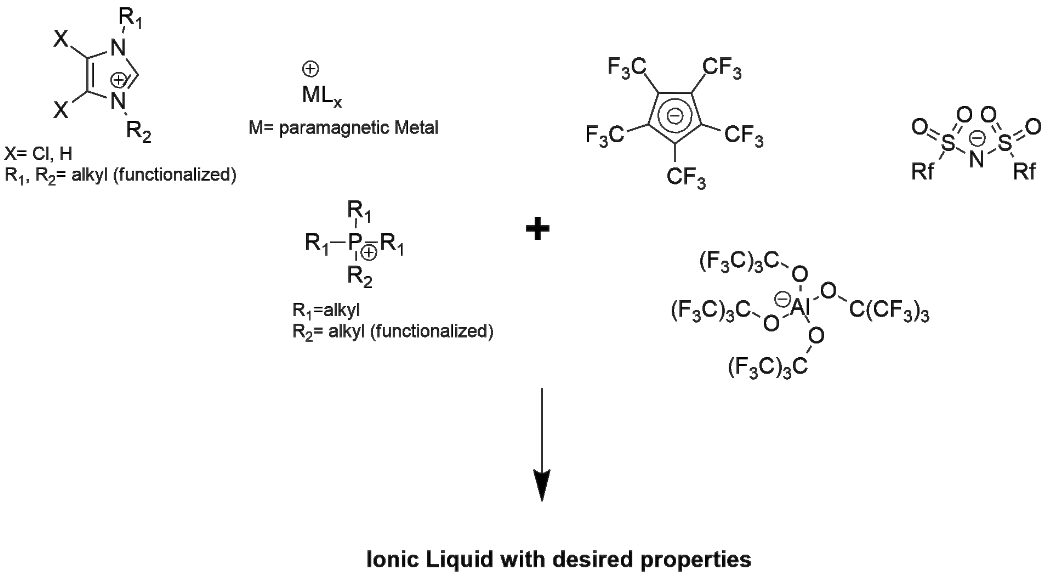
1. X. Wan and E. Freisinger, *Metallomics*, 2009, 1, 489-500.
2. E. Freisinger, *J. Biol. Inorg. Chem.*, 2011, 16, 1035-1045.
3. K. Tarasava and E. Freisinger, *PEDS*, 2014, 12, 481-488.

Highly Homoperfluorinated Ionic Liquids for NMR Field Probes for Magnetic Field Monitoring in MRI

A. C. Looser[1], S. Gross[1], C. Barmet[1,2], R. Alberto[1]*, K. P. Prüssmann[1,3]*

[1]University of Zurich, [2]Skope Magnetic Resonance Technologies LLC Zurich, [3]ETH Zurich

Magnetic resonance imaging (MRI) methods rely on observing nuclear magnetic resonance (NMR) during complex choreographies of time-varying magnetic fields. These field evolutions are subject to hardware imperfections and numerous external perturbances limiting image quality and the feasibility of high-performance methods. Continuous concurrent magnetic field monitoring[1] is a method for probing the spatiotemporal magnetic field evolution in an MR system with a set of NMR field sensors. For these sensors highly homoperfluorinated liquid compounds with short fluorine NMR relaxation time (‹ 1 ms) are required. Herein we present different ionic liquids (ILs) containing the Pentakis(trifluoromethyl) cyclopentadienyl (CpF*) anion[2] (Scheme 1) and other magnetically equivalent fluorinated anions or cations (Scheme 1), in combination with paramagnetic additives as promising candidates for NMR field sensors. Furthermore we show an improved synthesis for CpF* as well as new compounds which demonstrate its feature as a highly non coordinating anion.



Scheme 1:Chemical construction kit for probe fillings.

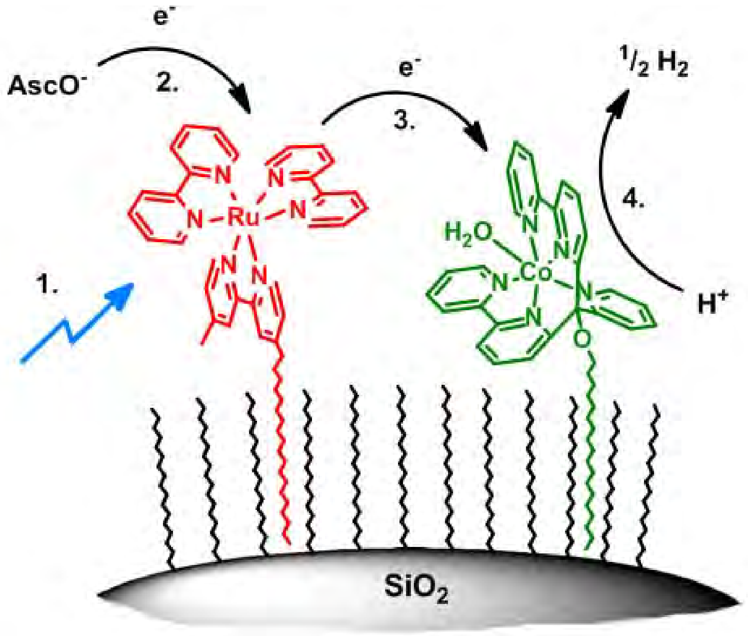
[1] C. Barmet, N. De Zanche, B. J. Wilm and K. P. Pruessmann, *Magnetic Resonance in Medicine*, **2009**, 62, 269.
[2] R. D. Chambers, S. J. Mullins, A. J. Roche and J. F. S. Vaughan, *Journal of the Chemical Society, Chemical Communications*, **1995**, 841.

Photocatalytic Proton Reduction with Molecular Ru and Co Complexes Immobilized on Hydrophobic Silica

C. Bachmann[1], B. Probst[1], M. Oberholzer[1], R. Alberto[1]*

[1]University of Zurich

Photocatalytic water splitting (artificial photosynthesis) is considered to be a promising way to store solar energy in chemical bonds.[1] However, a fully homogeneous molecular water splitting architecture will most likely not work since numerous back electron transfers (shortcuts) between the O_2 and H_2 evolving half reactions (OER, HER) lead to self inhibition.[2] Immobilizing molecular catalysts on suitable supports and physically separated OER and HER is therefore a promising approach. We present the straightforward immobilization of a highly active molecular Co based water reduction catalyst[3] and Ru based photosensitizer on hydrophobic silica. The loaded particles exhibited excellent properties in heterogeneous photocatalytic hydrogen production from water (scheme 1) and clearly exceeded the performance of their homogeneous analogues.[4]



Scheme 1: Proposed mechanism of photocatalytic hydrogen production on support surface.

[1] Styring, S., *Faraday Discuss.* **2012,** *155*, 357-376.
[2] Berardi, S. et al., *Chem. Soc. Rev.* **2014,** *43*, 7501-7519
[3] Bachmann, C.; Probst, B.; Guttentag, M.; Alberto, R., *Chem. Commun.* **2014,** *50*.
[4] Bachmann, C.; Probst, B.; Oberholzer, M.; Alberto, R., *in preparation*

Unique histidine-rich metallothioneins – “cracking the code”

J. Habjanic[1], E. Freisinger[1]*

[1]University of Zurich

Metallothioneins (MTs) are a superfamily of cysteine-rich proteins with low molecular weight found in all phyla. They are able to coordinate various transition metal ions with a d^{10} electron configuration, including the essential metal ions Zn^{II} and Cu^{I}, but also the toxic metal ions Cd^{II} and Hg^{II}. The precise function of MTs is still a matter of debate, but it is assumed that they have a role in metal homeostasis, provide protection against metal toxicity, and have redox capabilities, hence can act against oxidative stress. The most widely studied MTs are the mammalian forms. In bacteria, only the three-dimensional structure of the SmtA MT from *Synechococcus elongatus* has been explored.[1]The structure of SmtA is unique as it shows several unexpected features for MTs like a high percentage of secondary structural elements, the presence of aromatic residues, and for the first time it was revealed that also histidine residues can contribute to metal ion coordination in MTs.

Pseudomonas fluorescens is a species of ubiquitous gram negative bacteria. Genomic sequencing of a number of strains revealed the presence of MT sequences unusually rich in histidine residues. These sequences can be divided into three groups distinctive by the length of the sequence, overall charge of the respective protein, and number of His residues. At the same time they show rather conserved Cys distribution patterns consisting of an N-terminal CxCxxCxC motif, a central YCC/SxxCA stretch as well as an C-terminal Cxxxx(x)CxC part.

We are focusing on the investigation of the metal ion binding abilities by optical spectroscopy (CD, UV-Vis) and other analytical methods (MS, AAS, 2-PDS assay) as well as on the elucidation of the 3D structure by solution NMR of one representative of each group of these novel MTs.

Financial support by the Alfred Werner Foundation (JH) and the Swiss National Science Foundation (EF) is gratefully acknowledged.

[1]C. A. Blindauer, M. D. Harrison, J. A. Parkinson, A. K. Robinson, J. Cavet, N. J. Robinson, P. J. Sadler, Proc. Natl. Acad. Sci. **2001**, 98, 9593-9598.

Tackling the structure of the metal binding domains of a plant metallothionein 3

J. Jakovleska[1], E. Freisinger[1]*

[1]University of Zurich

Metallothioneins (MTs) are low molecular weight, cysteine-rich metal-binding proteins. Due to the softness of the cysteine thiolate ligands, MTs form very stable complexes with soft metal ions, such as Zn^{II}, Cd^{II}, and Cu^{I}. In plants, MTs are involved in essential metal ion homeostasis and detoxification of toxic metal ions, as well as in the scavenging of reactive oxygen species.

Based on the cysteine distribution pattern in their primary amino acid sequences, the plant MTs are divided into four subtypes. We are focusing on the MT3 form from banana (*Musa acuminata*). Like the plant MT1 and MT2 forms also the MT3 proteins feature a N- and a C-terminal Cys-rich region, which are separated by a long Cys-free linker region. As shown previously by our group the full length MT3 form has the ability to coordinate three divalent metal ions in two separate domains [1].

As a continuation of this work, we analyse in the present study the structures and metal ion binding abilities of the two separate metal binding domains in presence of Zn^{II} and Cd^{II} with NMR spectroscopy and eliminate in this way the difficulties brought about by the flexibility of the linker region.

In addition, results obtained with a mutant form of the C-terminal domain, in which the potentially also metal ion coordinating amino acid histidine is mutated to a cysteine residue, will be presented in order to study the relevance of non-cysteine residues for the metal ion binding properties of MTs.

Financial support from the Swiss National Science Foundation (EF) and the CMSZH Graduate School is gratefully acknowledged.

[1] Eva Freisinger,*Inorg Chim Acta*, **2007**,360, 369-380.

Characterization of Mg^{2+} binding sites in the CPEB3 ribozyme studied by NMR spectroscopy.

K. Adea[1], M. Skilandat[1], M. Rowinska-Zyrek[1,2], R. K. O. Sigel[1]*

[1]University of Zurich, [2]University of Wroclaw

Ribozymes have been thought to only occur in prokaryotes and lower eukaryotes, but recently several small ribozymes were also discovered in mammals. The cytoplasmic element binding protein 3 (CPEB3) ribozyme was initially discovered through an in vitro approach searching for self-cleaving ribozymes in the human genome. It was observed that the CPEB3 ribozyme shared biochemical properties with the hepatitis delta virus (HDV) ribozyme and, most likely also its structure[1]. In this work, the secondary structure of the CPEB3 ribozyme was confirmed with NMR to be similar to that of the HDV ribozyme[2].

Metal ions play important roles in the folding of ribozymes. Interestingly, the fold of the CPEB3 ribozyme occurs mainly in the presence of monovalent ions, however low millimolar concentrations of Mg^{2+} promote compaction to the active fold. The location of important Mg^{2+} binding sites in corresponding areas in the human CPEB3 ribozyme and HDV ribozyme were discovered, highlighting the importance of Mg^{2+} in the folding of the nested-double pseudoknot structure[2].

Financial support by the Swiss National Science Foundation (to RKOS), a Marie Curie Fellowship (to MRZ), the European Research Council (ERC Starting Grant to RKOS) and the University of Zurich are gratefully acknowledged.

1. Salehi-Ashtiani, K., Lupták, A., Litovchick, A. and J.W. Szostak. Science, 2006. **313**(5794): p. 1788-1792.
2. Skilandat, M., Rowinska-Zyrek, M. and R.K.O. Sigel. J Biol Inorg Chem, 2014. **19**(6): p. 903-12.

Polyoxometalate catalysts for artificial photosynthesis

K. D. von Allmen[1], R. Moré[1], G. R. Patzke[1]*

[1]University of Zurich, Department of Chemistry B, Winterthurerestrasse 190, CH-8057 Zürich

Polyoxometalates (POMs) represent a class of negatively charged metal oxo clusters, mainly formed from tungsten, molybdenum and vanadium in their highest oxidation states. They are used in various fields of application such as catalysis and for bio-medical materials. They have attracted particular attention as highly active water oxidation catalysts (WOC) and water reduction catalysts (WRC). [1]

For the more detailed understanding of the earlier reported WOC $[\{Co(H_2O)_3\}_2\{CoBi_2W_{19}O_{66}(OH)_4\}]^{10-}$ [2] copper substituted structural analogues have been prepared by the reaction of the lacunary precursor material $Na_9[BiW_9O_{33}]\cdot 19.5\ H_2O$ with Cu(II) ions. New 2D Cu-bridged POM structures could be isolated and characterized by X-ray crystallography. The counter cation has been found to have an important influence of the coordination mode of the lacunary ligand to the Cu(II) ions. Selected structures have been tested for water oxidation.

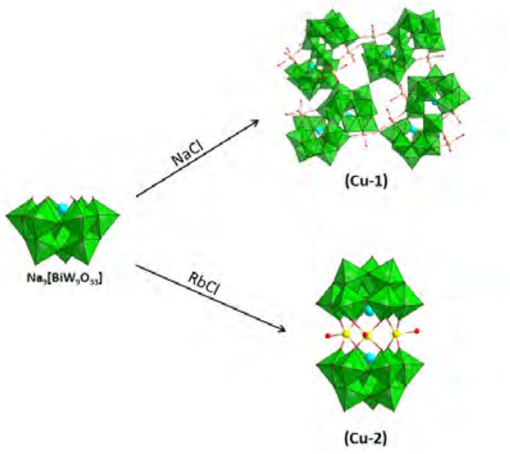


Fig. 1. Reaction scheme of $[BiW_9O_{33}]^{9-}$ with Cu(II); tungstobismutate network with a Cu_2W_2 core (**Cu-1**) Cu_3 core (**Cu-2**).

In order to establish structure-activity relationships (SAR), Ni-based Keggin-type POMs of the general type $[Ni(H_2O)XW_{11}O_{39}]^{n-}$ (X = P, Ge, Si) have been synthesized. Their structure was characterized by X-ray crystallographic methods. An established photochemical assay was used to determine their activity as H_2 evolution catalyst. The heteroatom was found to play a major role and allows tuning of H_2 evolution activity. Attempts have been made to explain the observed trends with electrochemical experiments and DFT calculations. [3]

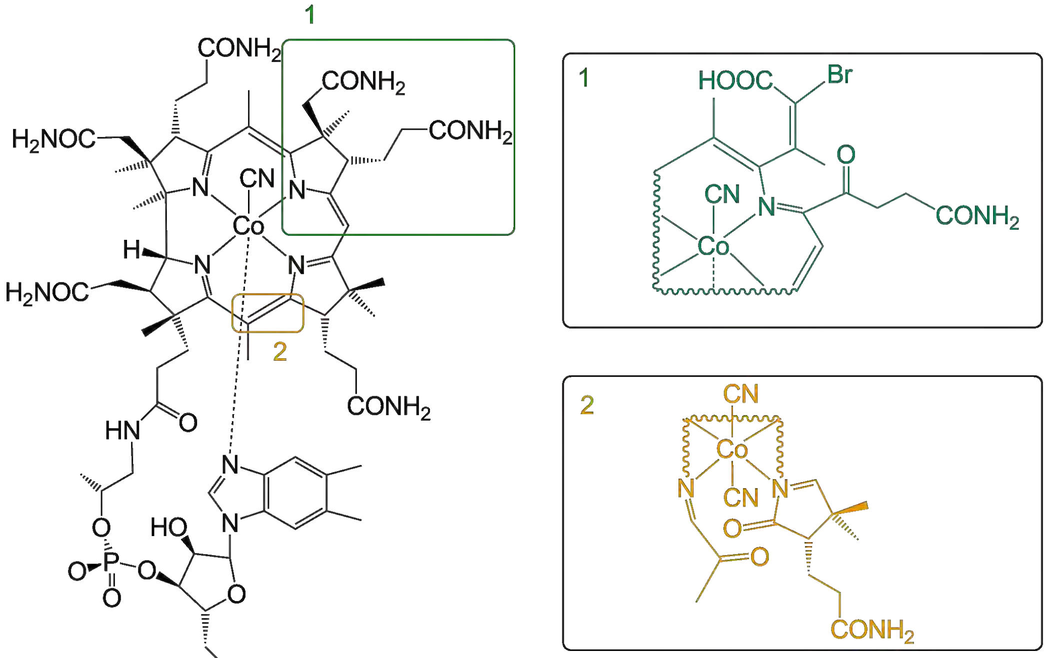
[1] Jan Reedijk, Kenneth. Poeppelmeier, *Comprehensive Inorganic Chemistry II vol. 2,* 2nd Edition, Elsevier, **2013**.
[2] Fabio Evangelisti, Pierre-Emmanuel Car, Olivier Blacque, Greta R. Patzke, *Catal. Sci. Technol.,* **2013**, *3*, 3117.
[3] Kim von Allmen, Rene. Moré, Raffael Müller, Joaquín Soriano-López, Anthony. Linden, G. R. Patzke, *ChemPlusChem*, in print.br

B_{12} derivatives with a modified corrin structure

L. Prieto[1], R. Oetterli[1], H. Brandl[1], L. Rangasamy [1], B. Spingler[1], G. Gasser[1], F. Zelder[1]*

[1]University of Zurich

Vitamin B_{12} is a biomolecule involved in human metabolic reactions.[1] Cell growth processes depend on the availability of this essential nutrient and accordingly, fast proliferating tumor cells require larger amounts of this natural product. Therefore the development of B_{12} antivitamins, structural B_{12} surrogates with modified reactivity, represents a highly interesting approach to obtain original antiproliferative agents in cancer treatment with new modes of action.[2]



Cyanocobalamin
(Vitamin B_{12})

Ring-modified cobalamins
(Antivitamin B_{12})

Figure 1. Small structural modifications of vitamin B_{12}'s corrin macrocycle lead to potential antivitamin B_{12} derivatives.

The synthesis of potential B_{12} antagonists starting from the natural product will be presented with special focus on modification of the corrin macrocycle.[3,4] The kinetic and electronic properties at the cobalt center are strongly affected by small structural changes of the equatorial ring (1,2). The bioactivity of these potential B_{12} antimetabolites is investigated.

[1] B. Kräutler, D. Arigoni, B.T. Golding, *Vitamin B_{12} and B_{12} proteins*, Wiley VCH, Weinheim, **1998**.
[2] F. Zelder, M. Sonnay, L. Prieto, *ChemBioChem.*, **2015**, DOI: 10.1002/cbic.201500072.
[3] R. Oetterli, L. Prieto, B. Spingler, F. Zelder, *Organic Letters*, **2013**, 15 (18), 4630-4633.
[4] B. Kräutler, R. Stepánek, *Angew. Chem. Int. Ed. Engl.*, **1985**, 24 (1), 62-64.

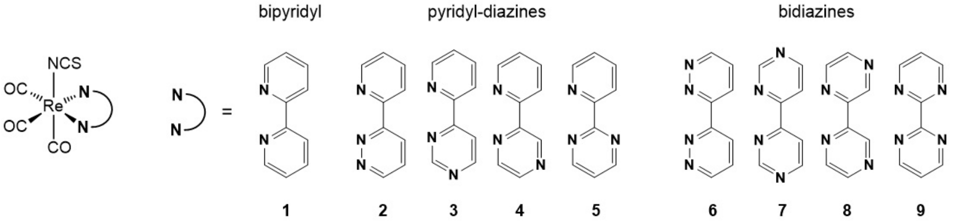
Influence of hetero-biaryl-ligands on the photophysical properties of [Re^{I}NCS(CO)$_3$diimine]-type photosensitizers.

M. L. Mosberger[1], B. Probst[1], R. Alberto[1]*

[1]University of Zurich

Metalorganic photosensitizers (PS) such as Ir^{III}-, Ru^{II}-, Re^{I}- or Pt^{II}- based complexes have found application in various fields, e.g. as OLEDs, O_2-detectors, in photocatalysis (CO_2-reduction, artificial photosynthesis) and many more.[1–4] The key-feature of these compounds is a diimine, on which the LUMO is situated. Therefore, the electronic properties can easily be tuned by altering the hetero-biaryl ligand.

In this study, we chose [Re^{I}NCS(CO)$_3$diimine] as model-PS due to its photostability and efficient charge separation. We present two series of tricarbonylrhenium diimine PS (diimine = pyridyl-diazines and bidiazines) (*Figure 1*), which showed red-shifted absorption compared to the parent complex (**1**). The photophysical properties (UV-Vis, triplet lifetime, quantum yield, etc.) of PS **1**–**9** were investigated and will be carefully compared with respect to 1) the energy level of the LUMO and 2) the effect of the position of the heteroatom in the diimine. Conclusions regarding the design of new PS featuring a redshift of absorption as compared to the parent bipy acceptor will be drawn.



Scheme 1: Investigated Re^{I}NCS(CO)$_3$diimine-type PS.

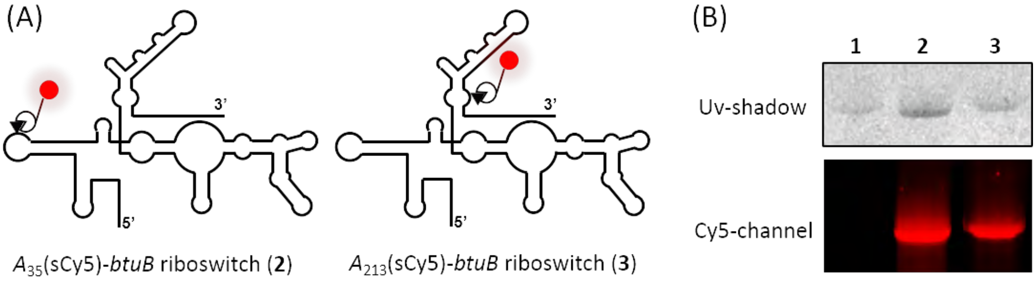
[1] M. Mauro, E. Q. Procopio, Y. Sun, C.-H. Chien, D. Donghi, M. Panigati, P. Mercandelli, P. Mussini, G. D’Alfonso, L. De Cola, *Adv. Funct. Mater.* **2009**, *19*, 2607–2614.
[2] G. Xu, M. Lu, C. Huang, Y. Wang, S. Ge, *Spectrochim. Acta. A. Mol. Biomol. Spectrosc.* **2014**, *123*, 369–75.
[3] P. Kurz, B. Probst, B. Spingler, R. Alberto, *Eur. J. Inorg. Chem.* **2006**, *2006*, 2966–2974.
[4] B. Probst, M. Guttentag, A. Rodenberg, P. Hamm, R. Alberto, *Inorg. Chem.* **2011**, *50*, 3404–3412.

Covalently labeling of the btuB riboswitch with fluorophores for the studies at the single molecule level

M. Zhao[1], R. Börner[1], R. K. O. Sigel[1]*, E. Freisinger[1]*

[1]University of Zurich

While solid phase synthesis can be used for RNA sequences shorter than 60 nucleotides, a reliable method for the covalent labeling of large RNAs at specific sites is still unavailable. The demand for such a method is high since non-coding RNAs were found to have important functions as those of proteins.[1] In this project, we developed a post-transcriptional labeling method that introduces a functional group at a specific sites in a large RNA molecule, the *E. coli btuB* riboswitch featuring more than 200 nucleotides.[2-4] The coupling with fluorophores, e.g. sulfo-Cyanine5 (sCy5), was achieved through certain high yield reactions. The sCy5-labeled *btuB* riboswitch was characterized with denaturing PAGE gels, and the labeling at different sites was successful (Fig. 1). The photo-physical properties of the sCy5-labeled *btuB* riboswitch and the single molecule studies of the dynamics in response to metal ions and metabolites are ongoing. Financial support from the Swiss National Science Foundation (EF), the UZH Forschungskredit (RB), the European Research Council (RKOS), the University of Zurich (EF, RKOS), and the SBFI (COST Action CM1105; EF, RKOS) is gratefully acknowledged.



A_{35}(sCy5)-*btuB* riboswitch (**2**) A_{213}(sCy5)-*btuB* riboswitch (**3**)

Fig. 1 Schematic illustration of different sCy5 labeling positions in the *btuB* riboswitch (A); 10% denaturing PAGE of the *btuB* riboswitch (B). Bands were either visualized with UV light (254 nm) or in the Cy5 emission channel (lane 1: unlabeled *btuB* riboswitch, lane 2: the *btuB* riboswitch labeled with sCy5 at Adenine_{35}, lane 3: the *btuB* riboswitch labeled with sCy5 at Adenine_{213}).

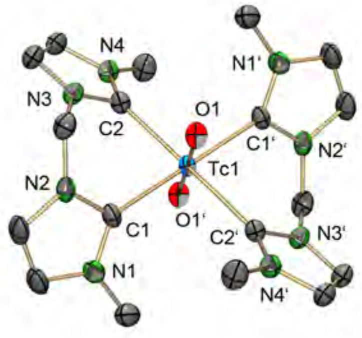
[1] T. R. Cech, J. A. Steitz, *Cell*, **2014**, 157, 77-94.
[2]D. Egloff, I. A. Oleinich, E. Freisinger, *ACS Chem. Biol.,* **2015***,* 10*,* 547-553.
[3]D. Egloff, I. A. Oleinich, S. L. B. König, R. K. O. Sigel, E. Freisinger, submitted.
[4] P. K. Choudhary, R. K. O. Sigel, *RNA*, **2014**, 20, 36-45.

N-Heterocyclic Carbenes - Stabilizing Ligands for Various Oxidation States of Rhenium and Technetium

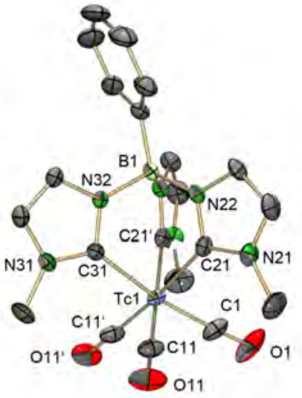
M. Benz[1], H. Braband[1]*, R. Alberto[1]*

[1]University of Zurich

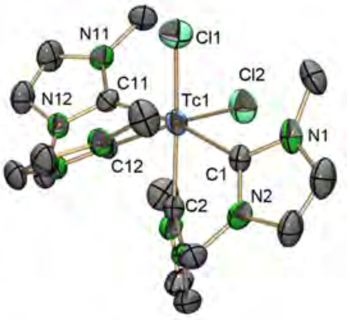
Recently, N-heterocyclic carbenes (NHCs) have gained increasing importance in the fields of *bioinorganic chemistry* and *metals in medicine*. In this context, the NHC chemistry of technetium came into our research focus. ^{99}Tc-NHC complexes are scarce, which can mostly be attributed to their tendency to hydrolyze in the presence of H_2O.[1],[2] We present novel synthetic pathways for the synthesis of water stable $\{M^{(V)}O_2\}^+$-NHC complexes (M = ^{99}Tc, Re).[3] The water stability and pH-tolerance of the products allow conversion of the $\{M^{(V)}O_2\}^+$ core into $\{M^{(V)}OCl\}^{2+}$ using HCl, which acts as the H^+ and Cl^- source. This reaction further enables derivatization of the *trans*-position in these complexes. In addition, the water stability of the presented $\{^{99}Tc^{(V)}O_2\}^+$-NHC complexes led to the synthesis of the first $^{99m}Tc^{(V)}$-NHC complex. Besides the oxidation state +V, NHCs are capable of stabilizing the oxidation states +I and +IV, therefore, *fac*-$\{M^{(I)}(CO)_3\}^+$- and $\{Tc^{(IV)}Cl_2\}^{2+}$-NHC complexes will be presented. The remarkable stability of the new complexes underlines the potential of NHCs as stabilizing ligands for $^{99(m)}$Tc and Re in various oxidation states.



$\{Tc^{(V)}O_2\}^+$



$\{Tc^{(I)}(CO)_3\}^+$



$\{Tc^{(IV)}Cl_2\}^{2+}$

[1] Sebastian J. Hock, Lars-Arne Schaper, Wolfgang A. Herrmann, Fritz E. Kühn, *Chemical Society Reviews*, **2013**, 42, 5073-5089.
[2] Henrik Braband, Theresa I. Kückmann, Ulrich Abram, *Journal of Organometallic Chemistry*, **2005**, 690, 5421-5429.
[3] Michael Benz, Bernhard Spingler, Roger Alberto, Henrik Braband, *Journal of the American Chemical Society,* **2013**, 135, 17566-17572.b

Pyrphyrin and Phenphyrin Scaffold Revisited: Physico-Chemical Properties and Photocatalysis

S. Schnidrig[1], C. Bünzli[1], B. Probst[1], R. Alberto[1]*

[1]University of Zurich

Whereas porphyrin[1] and polypyridine[2] complexes are intensely investigated in photo(electro)catalysis, purely pyridine or phenanthroline based macrocyclic ligands are not studied in this context. Such ligand systems were described as early as 1972 by Ogawa et al., but have been studied only superficially.[3], [4]

We prepared macrocycles in which two 2,2'-bipyridine or two phenanthroline units are linked by two cyano-methylene groups or nitrogen atoms. (Figure 1) This ligand frameworks were named pyrphyrin and phenphyrin due to the resemblance to porphyrins and the comprisal of pyridine and phenanthroline subunits. Derivatisation of the ligand framework at the bridging atoms leads to increased solubility and allows tunability of the ligand framework. Very stable complexes from the unsubstituted and derivatised ligands were formed with Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}. The complexes feature very interesting physico-chemical properties such as shifts in electrochemical potentials, IR and UV-Vis absorption. Further on the complexes were tested for their catalytic activity as water reduction catalysts in homogenous photocatalytic water splitting. Complex [CoBr(butylpyr)MeOH] (**1**) and [Co(OTf)$_2$(azaphen)] (**2**) are highly efficient water reduction catalysts (WRC). In presence of [Ru(bipy)$_3$]Cl$_2$ as photosensitiser, ascorbic acid as electron relay and tris(2-carboxyethyl)phosphine (TCEP) as sacrificial electron donor in water, turnover numbers (TON H_2/Co) over 20'000 could be achieved.

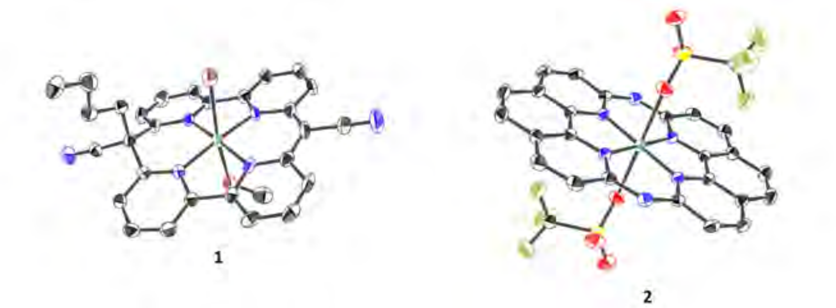


Figure 1) Single crystal structure of [CoBr(butylpyr)MeOH] **1** and [Co(OTf)$_2$(azaphen)] **2** at 50% probability level; Hydrogen atoms were omitted for clarity; Black = Carbon, Blue = Nitrogen, Red= Oxygen, Green = Co^{2+}, Brown = Bromine, Yellow = Sulfur, Lime = Fluorine.

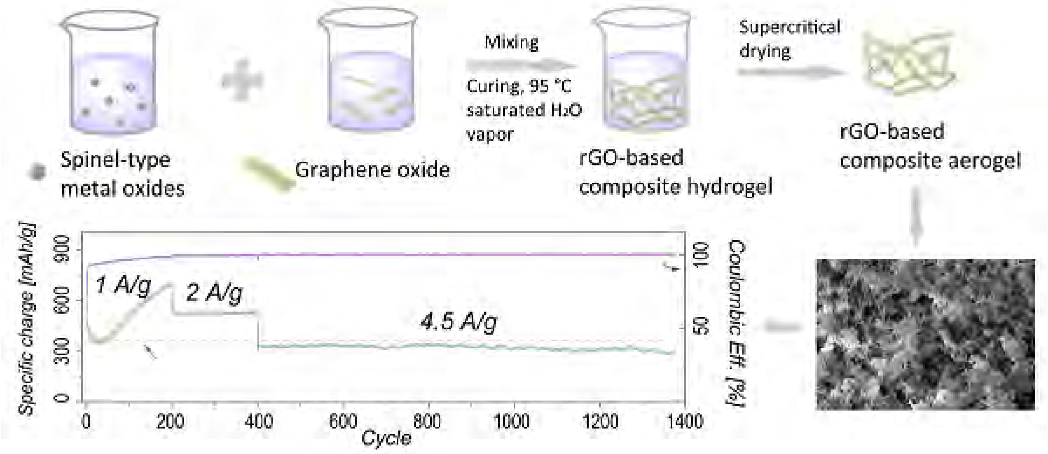
[1] Cyril Bachmann, Miguel Guttentag, Bernhard Spingler, Roger Alberto, *Inorganic Chemistry*, **2013**, 52, 6055-6061.
[2] Anne-Marie Manke, Karen Geisel, Anne Fetzer, Phillipp Kurz, *Physical Chemistry Chemical Physics*, **2014**, 16 12029-12042.
[3] Shojiro Ogawa, Ryoichi Narushima, Yoshie Arai, *Journal of the American Chemical Society*, **1984**, 106, 5760-5762.
[4] Shojiro Ogawa, Tomonobu Yamaguchi, Nobuyuki Gotoh, Journal of the Chemical Society, *Journal of the Chemical Society, Chemical Communications*, **1972**, 577-578.

A General Approach of Reduced Graphene Oxide Nanocomposite Aerogels with Multifunctional Electrode Materials towards Advanced Lithium-ion Batteries

G. Zeng[1], M. Niederberger[1]*

[1]ETH Zurich

Technological improvements in lithium-ion batteries (LIBs) are being driven by an ever-increasing demand for portable electronic devices and electric vehicles applications. The main challenge remains developing electrode materials with high capacity, excellent rate performance and longer lifespan. The conversion-type materials, e.g. spinel Co_3O_4, and alloying-type electrodes, e.g. Ge have long been exploited as high capacity anodes for LIBs; however, their huge volume change upon cycling and/or poor Li^+ and e^- conductivity impede the high-rate and cyclability performance towards their practical application in high-performance LIBs. Here we present a general and facile approach to fabricating flexible reduced graphene oxide (rGO) composite aerogel with various multifunctional electrode materials as a binder-free high-performance anode. In the composite aerogel, the electrode materials, either in the form of bare nanocrystals or in an additional protective hollow carbon shell, are homogenously integrated within an interconnected rGO network by simple electrostatic attraction and π-π interactions between rGO sheets. Benefitting from the hierarchical porosity of rGO aerogel and its mechanical stability, the hybrid system synergistically enhances the intrinsic properties of each component, yet robust and flexible. As a result, the composite aerogels demonstrate outstanding electrochemical performance and long-term stability. For instance, the $CoFe_2O_4$/rGO composite aerogel displays greatly enhanced rate capability and long-term stability without obvious capacity fading for 1000 cycles at high rates of up to 4.5 A g^{-1}. We also believe that the versatile strategy developed here can be easily extended to the co-assembly of rGO with other functional metal oxides/sulfides for diverse applications as e.g. supercapacitors or in catalysis.



Zeng, G.; Shi, N.; Hess, M.; Chen, X.; Cheng, W.; Fan, T.; Niederberger, M. *Acs Nano,* **2015**, ASAP

Phosphine oxidation catalyzed by zerovalent cobalt complexes using nitrous oxide as oxidant

T. L. Gianetti[1], R. E. Rodriguez-Lugo[1], J. Harmer[2], C. Copéret[1], H. Grützmacher[1]*

[1]ETH Zurich, [2]University of Queensland

Phosphine oxides are an important class of compounds with several industrial applications.[1]Traditional routes to their preparation from phosphines, *e. g.* aerobic oxidation or treatment with peroxides,are useful but present problems such as selectivity, functional group tolerance, complicated work-up protocols and generation of chemical waste, and arenot suitable for highly reactive or sensitive phosphines. Additionally, nitrous oxide (N_2O), industrially obtained as a by-product of chemical processes involving nitric acid, has been recently identified as one of the largest global ozone depleting agents.[2] It is a greenhouse gas 300 times more powerful than CO_2.[3] Thereby, its transformation in less harmful chemicals is of particular interest, especially if it can be applied to generate useful/added value products.

The present work illustrates the use ofzerovalent amino-olefin cobalt complexes in the selective oxidation of highly reactive phosphines using nitrous oxide as oxidant under mild reaction conditions.

[1] T.M. Shaikh, C. Weng, F. Hong, *Coord. Chem. Rev.*, **2012**, *256*, 771.[2] M. A. K. Khalil, *Annu. Rev. Energ. Env.*, **1999**, *24*, 645.[3] A. R. Ravishankara, J. S. Daniel, R. W. Portmann,*Science*, **2009**, *326*, 123.

Multitopic precursors for oxide materials' synthesis

A. Finelli[1], A. Crochet[1], K. M. Fromm[1]*

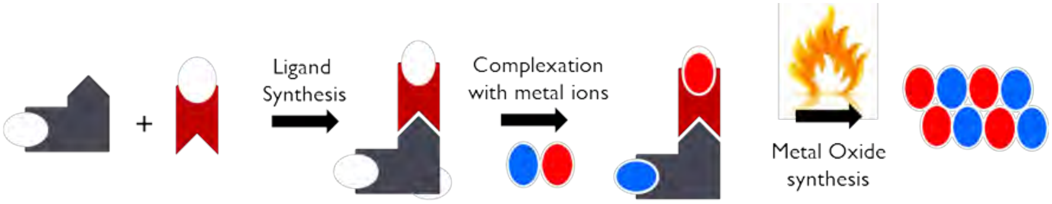
[1]University of Fribourg

The research interest in mixed metal oxides is increasing in material science, as they have multiple applications, such as in batteries, ceramics, pigments, high-Tc superconductors or transparent conductors.

However, the two main challenges for the synthesis of such compounds are the lack of control on the ratio of the different metal components and the extreme conditions (up to 900 °C) that many of these oxides require during their traditional solid state synthesis.

To overcome these issues, we propose a strategy for the synthesis of mixed metal complexes, which is based on precursors of coordination compounds, using the "multitopic ligand approach".

The aim is to design specific ligands with selective coordination sites to bind different metal ions. Due to the metal ion preorganization in the precursor thus formed, the stoichiometry of the final oxide material can be controlled and the extreme synthesis conditions diminished (pressure or temperature). These new mixed metal complexes will be finally combusted to oxide materials with possible new features and ideally at the nanoscale, allowing to access new and better properties in their applications.



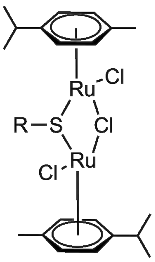
F. Gschwind, O. Sereda, K. M. Fromm, *Inorg. Chem.* **2009**, 48, 10535-10547
F. Gschwind, K. M. Fromm, *Z. Anorg. Allg. Chem.* **2011**, 1871-1879

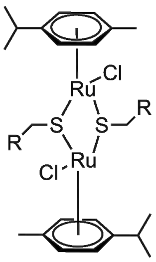
Stability and reactivity of dinuclear thiolato-bridged arene ruthenium complexes and their interactions with biological ligands

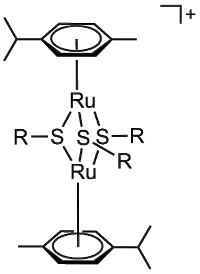
D. Stibal[1], F. Giannini[2], J. Furrer[2], G. Süss-Fink[1]*

[1]University of Neuchatel, [2]University of Bern

The dinuclear trithiolato arene ruthenium complexes discovered by our group are highly cytotoxic towards ovarian cancer cell lines [1]. However, the mode of action of these complexes still remains largely unknown. A recent *in vivo* study showed that they act predominantly as inhibitors of the aerobic metabolism and they also interact with intracellular glutathione [1,2]. The discovery of dithiolato [3] and monothiolato [4] complexes allowed us to compare the behavior of the three types of complexes in aqueous media and their interactions with biological ligands, such as amino acids or DNA.







The trithiolato complexes are inert towards most of the typical biological targets. The complexes do not undergo hydrolysis in aqueous solutions, and no interactions with amino acids, DNA or proteins are observed. The dithiolato and monothiolato complexes undergo hydration, the monothiolato complexes also show exchange between their thiolato and chloro ligands. Only the thiol-containing amino acid cysteine interacts with thiolato-bridged complexes, forming adducts with mono- and dithiolato complexes, while being oxidized by trithiolato complexes. These observations allowed us to synthesize several cysteine-containing trithiolato complexes and study their properties to gain insight into the mechanism of catalytic oxidation of thiol containing biological substrates.

[1] Federico Giannini, Julien Furrer, Anne-Flore Ibao, Georg Süss-Fink, Bruno Therrien, Olivier Zava, Mathurin Baquie, Paul J. Dyson, Petr Štěpnička, **2012**, *J. Biol. Inorg. Chem.*, 17, 951-960.
[2] Pavel Tomšík, Darina Muthná, Martina Řezáčová, Stanislav Mičuda, Jana Ćmielová, Miloš Hroch, René Endlicher, Zuzana Červinková, Emil Rudolf, Stephan Hann, David Stíbal, Bruno Therrien, Georg Süss-Fink, **2015**, *J. Organomet. Chem.*, 782, 42-51.
[3] Anne-Flore Ibao, Michaël Gras, Bruno Therrien, Georg Süss-Fink, Olivier Zava, Paul J. Dyson, **2012**, *Eur. J. Inorg. Chem*. 9,1531-1535.
[4] David Stibal, Bruno Therrien, Federico Giannini, Lydia E. H. Paul, Julien Furrer, Georg Süss-Fink, **2014**, *Eur. J. Inorg. Chem.*, 34, 5925-5931.

Using Oxidative Quenching of a Copper Photosensitizer for Light-Driven Hydrogen Production

J. Windisch[1], B. Probst[1], R. Alberto[1]*

[1]University of Zurich

Our research focuses on the reductive half-reaction of water splitting to produce hydrogen, using rhenium- or ruthenium-based photosensitizers (PS), cobalt-based water reduction catalysts (WRC) and a sacrificial electron donor (D) [1]. Since the photosensitizers contain rare and expensive metals, a cheaper and more abundant alternative is desirable. Copper(I)-bis-phenanthroline complexes seem to be very promising candidates for this purpose and they have been successfully applied very early, using platinum for water reduction [2]. In a more recent example the WRC was replaced by $Co(dmgH)_2(py)Cl$, however, other cobalt-based WRC are not applicable in this system [3]. Heteroleptic copper(I) complexes composed of a phenanthroline ligand and a bidentate phosphine ligand were also used for light-driven hydrogen production [4]. The main drawback of these photosensitizers is the limited absorption of visible light.

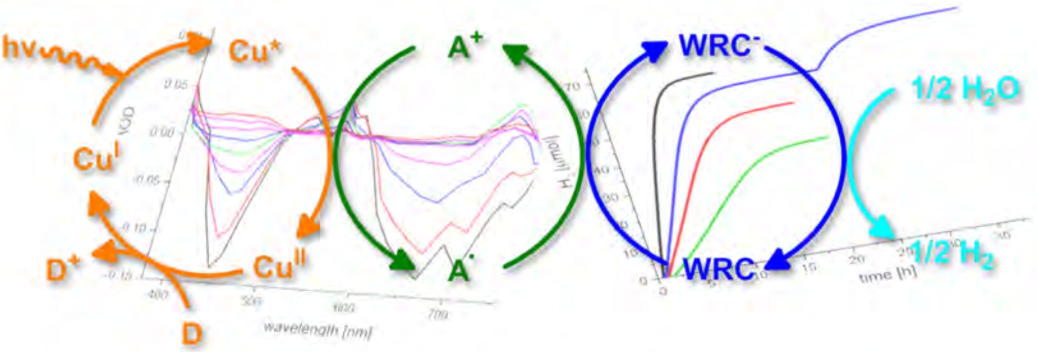


Fig.1 – Photocatalytic hydrogen evolution cycle based on oxidative quenching of the copper photosensitizer.

In this work a copper(I) bis-phenanthroline PS and cobalt based WRCs were coupled by an electron relay. The fast electron transfer from the PS to the relay drastically increases the lifetime of the charge separation. This provides much more time for the excited electron to be transferred to the WRC and therefore makes the PS/relay combination almost universal for the application with different WRCs. In order to minimize the energy loss from the additional electron transfer step, elaborate fine-tuning of the redox potentials of PS and relay was necessary. Not only photocatalytic hydrogen evolution experiments, but also quenching studies combined with transient absorption spectroscopy were applied to shed light on the mechanism and identify the strengths and limitations of the system.

[1] C. Bachmann, B. Probst, M. Guttentag, R. Alberto, *Chem. Commun.,* **2014,** 50, 6737.
[2] A. Edel, P.A. Marnot, J.P. Sauvage, *Nouv. J. Chim.,* **1984,**8, 495.
[3] R.S. Khnayzer, C.E. McCusker, B.S. Olaiya, F.N. Castellano, *J. Am. Chem. Soc.,* **2013,** 135, 14068.
[4] S. Luo, E. Mejía, A. Friedrich, A. Pazidis, H. Junge, A. Surkus, R. Jackstell, S. Denurra, S. Gladiali, S. Lochbrunner, M. Beller, *Angew. Chem. Int. Ed.,***2013,** 52, 419.

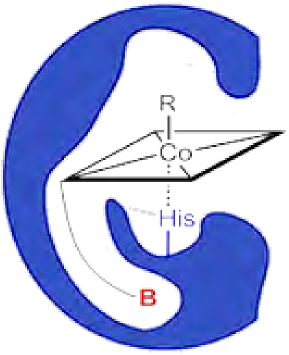
Peptide Backbone Vitamin B_{12} Derivative: a Biomimetic Model

M. Sonnay[1], F. Zelder[1]*

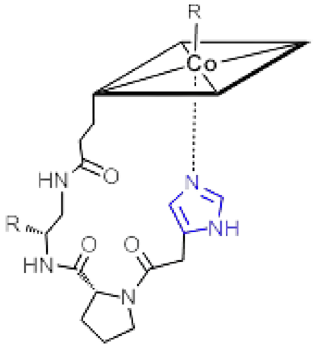
[1]University of Zurich

Vitamin B_{12} and its derivatives present an elaborate structure, allowing for interesting reversible modifications which lead to fine tuning of their physico-chemical properties.[1] B_{12} can thus act as molecular switches by reversibly coordinating the backbone to the cobalt center (base-on/base-off). Nature takes advantage of this special feature for B_{12}-dependent catalysis, where enzymes replace the natural backbone by coordinating their own histidine residue to the cobalt center. This direct coordination allows the enzyme to modulate and control the reactivity of its cofactor (figure A).[2]

A



B



Our group is interested in modifying the B_{12} backbone, and thus reach altered properties. Such derivatives have multiple applications: some can act as antivitamins B_{12} by inhibiting B_{12}-dependent enzymatic processes.[3] Others present definite structure, allowing mimicking the binding site of a specific enzyme and thus constitute a biomimetic model. The derivative presented here (figure B) aims at replicating the histidine-cobalt coordination found in several B_{12}- dependent enzymes, in order to further study the influence of this residue on the reactivity of the metal centre.[4] These insights will yield to a better understanding of specific catalytic processes, and contribute to the development of novel enzyme inhibitors.

[1] Felix Zelder, Kai Zhou, Marjorie Sonnay, *Dalton Transactions*, **2013**, 42, 854-862.
[2] Catherine Luschinsky Drennan, Sha Huang, James T. Drummond, Rowena G. Matthews, Martha L. Ludwig, *Science*, **1994**, 266, 1669-1674.
[3] Felix Zelder,Marjorie Sonnay, Lucas Prieto, *ChemBioChem*, **2015**,DOI: 10.1002/cbic.201500072.
[4] Marjorie Sonnay, Felix Zelder, **2015**, in preparation.

Synergistic antimicrobial effect of silver and other metals in bimetallic complexes

C. Paula[1], K. Fromm[1]*

[1]Department of Chemistry, University of Fribourg, Chemin du Musée 9, CH-1700 Fribourg, Switzerland

The precious metal silver is aging for its excellent antimicrobial properties as throwing silver coins in fountains is not only a lovely old tradition.[1] It has been recognized to play an important role concerning medical applications, for example the coating of implants with Ag^0 or Ag^I coordination compounds to avoid infections due to bacterial biofilms formation.[2] The recent research of the FROMM group with respect to antimicrobial silver compounds was focussed on silver coordination networks, meaning short PEG oligomers functionalized with (iso-)nicotinic acid as ligands.

Thus, the aim of the project is to create new Ag^I complexes with other bioinspired ligands, for example derivatives of phenylalanine, aminobenzoic acid or picolinic acid. Furthermore, we try to synthesize bimetallic complexes combining silver and another metal such as Zn or Cu withthe ambition to generate synergistic antimicrobial effects and to elucidate structural characteristics.

[1] Fromm, K. M., *Nat. Chem*. **2011**, *3*, 178.
[2] Vig Slenters, T. *et al. Materials* **2010**, *3*, 3407-3429.

CHIMIA
CHIMIA 2015, Volume 69
ISSN 0009-4293
www. chimia.ch

SCS
Swiss Chemical
Society

Supplementa to Issue 7-8/2015

SCS Fall Meeting 2015
Oral Presentation Abstracts Session of Inorganic & Coordination Chemistry

September 4, 2015
Ecole Polytechnique Fédérale de Lausanne (EPFL)
http://scg.ch/fallmeeting/2015

Swiss Chemical Society
Haus der Akademien
Postfach
3001 Bern
Switzerland
info@scg.ch
www.scg.ch

The Magic of Polypnictogen-based Chemistry

M. Scheer[1], C. Heindl[1], A. Seitz[1], F. Spitzer[1]

[1]Institute of Inorganic Chemistry, University of Regensburg, Regensburg, Germany;
manfred.scheer@chemie.uni-r.de

Organometallic polypnictogen compounds are an important class of compounds, valuable for many applications. Our interest is dedicated to pnictogen-rich organometallics, which usually can be synthesized from the E_4 allotropes (E = P, As). Therefore, we have developed special approaches for the activation of the E_4 molecules. Also, we created novel E_4-transfer reagents to avoid the handling hazardous starting materials. The talk will give an overview about the latest developments in the area of E_4 activation[1] and the stage of the use of the transfer reagents in main group and transition metal chemistry.

Moreover, pentaphosphaferrocene, [Cp*Fe(η^5-P_5)], the P-rich congener of ferrocene, can be used as a starting material in different directions: (i) in redox-processes where charged anionic and cationic polyphosphorus moieties are obtained, (ii) in the reaction with Cu(I) halides where nano-sized inorganic fullerene-like molecules are formed. Thus, the second part of the talk is dedicated to recent results in redox chemistry of pentaphosphaferrocene[2] and in the latest giant spheres obtained.[3]

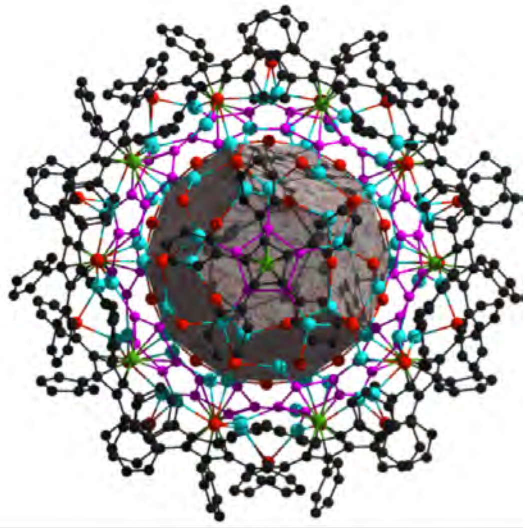


Figure 1. Molecular structure of an organometallic supersphere.

[1] (a) C. Schwarzmaier, A. Y. Timoshkin, M. Scheer, *Angew. Chem. Int. Ed.* **2013**, *52*, 7600. (b) S. Heinl, E. Peresypkina, A. Y. Timoshkin, P. Mastrorilli, V. Gallo, M. Scheer, *Angew. Chem. Int. Ed*. **2013**, *52*, 10887. (c) C. Schwarzmaier, A. Y. Timoshkin, G. Balàzs, M. Scheer *Angew. Chem. Int. Ed*. **2014**, *53*, 9077–9081. (d) F. Spitzer, M. Sierka, M. Latronico, P. Mastrorilli, A. V. Virovets, M. Scheer, *Angew. Chem. Int. Ed*. **2015**, *54*, 4392-4396.

[2] (a) M. V. Butovskii, G. Balázs, M. Bodensteiner, E. V. Peresypkina, A. V. Virovets, M. Scheer, *Angew. Chem. Int. Ed.* **2013**, *52*, 2972. (b) E. Mädl, M. V. Butovskii, G. Balázs, E. V. Peresypkina, A. V. Virovets, M. Seidl, M. Scheer, *Angew. Chem. Int. Ed*. **2014**, *53*, 7643–7646.

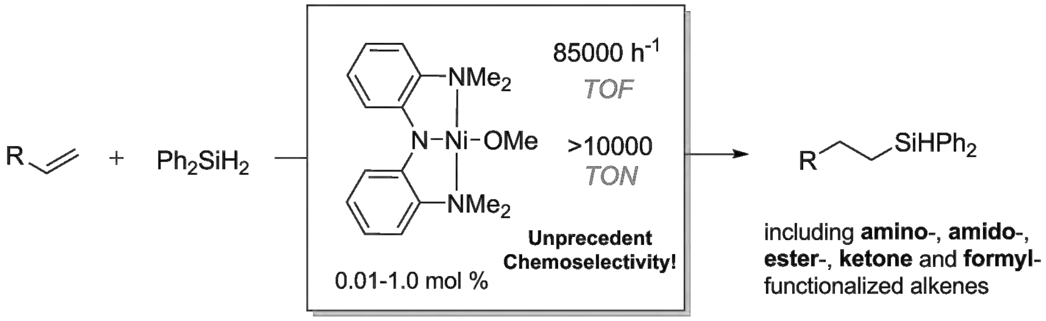
[3] (a) C. Schwarzmaier, A. Schindler, C. Heindl, S. Scheuermayer, E. V. Peresypkina, A. V. Virovets, M. Neumeier, R. Gschwind, M. Scheer, *Angew. Chem. Int. Ed*. **2013**, *52*, 10896. (b) F. Dielmann, C. Heindl, F. Hastreiter, E. V. Peresypkina, A. V. Virovets, R. M. Gschwind, M. Scheer, *Angew. Chem. Int. Ed*. **2014**, *53*, 13605–13608. (c) F. Dielmann, M. Fleischmann, C. Heindl, E. V. Peresypkina, A. V. Virovets, R. M. Gschwind, M. Scheer, *Chem. Eur. J.* **2015**, *21*, 6208-6214.

Chemoselective Alkene Hydrosilylation Catalyzed by Nickel Pincer Complexes

I. Buslov[1], X. Hu[1]*

[1]EPF Lausanne

Hydrosilylation of alkenes is widely used for the production of numerous consumer goods and fine chemicals.[1, 2] Platinum catalysts, such as Speier's [3] catalyst and Karstedt's [4] complex, are still most often used for this reaction. However, the high cost and low abundance of Pt motivates the development of alternative catalysts based on more abundant and economical metals.



Alkene Hydrosilylation
Tandem Isomerization-Hydrosilylation

The bis(amino)amide nickel alkoxy complexes, [($^{Me}N_2N$)Ni-OR] (R = Me, iPr, tBu), efficiently catalyse anti-Markovnikov hydrosylilation of terminal alkenes without pre-activation. An excellent functional group tolerance was demonstrated: alkenes containing halogens, ester-, amido-, sulfonylamido- and free amino-groups were hydrosilylated with good yields. Furthermore, in contrast to previously reported Ni-catalyzed hydrosylilations of C=O, keto- and formyl groups were tolerated. Also, the system showed ability to promote isomerization-hydrosilylation of functionalized internal alkenes to give terminal alkylsilanes. The starting [($^{Me}N_2N$)Ni-OR] complex *in situ* produces [($^{Me}N_2N$)Ni-Alkyl] which is identified as the resting state of the catalysis. The mechanistic studies, as well as development of other Ni-based catalytic systems for hydrosilylation are ongoing.

[1] Bogdan Marciniec, Hydrosilylation: A Comprehensive Review on Recent Advances, Springer, Berlin, **2009**.
[2] Kohei Tamao, Neyoshi Ishida, Tatsu Tanaka, Makoto Kumada, *Organometallics,* **1983**, 2, 1694-1696.
[3] John L. Speier, James A. Webster, Garrett H. Barnes, *J. Am. Chem. Soc.,* **1957**, 79, 974-979.
[4] Peter B. Hitchcock, Michael F. Lappert, Nicholas J. W. Warhurst, *Angew. Chem. Int. Ed.,* **1991**, 30, 438-440.

Chiral $(NH)_2P_2$ Macrocyclic Iron(II) Complexes: Design and Application in the Highly Enantioselective Transfer Hydrogenation of Ketones

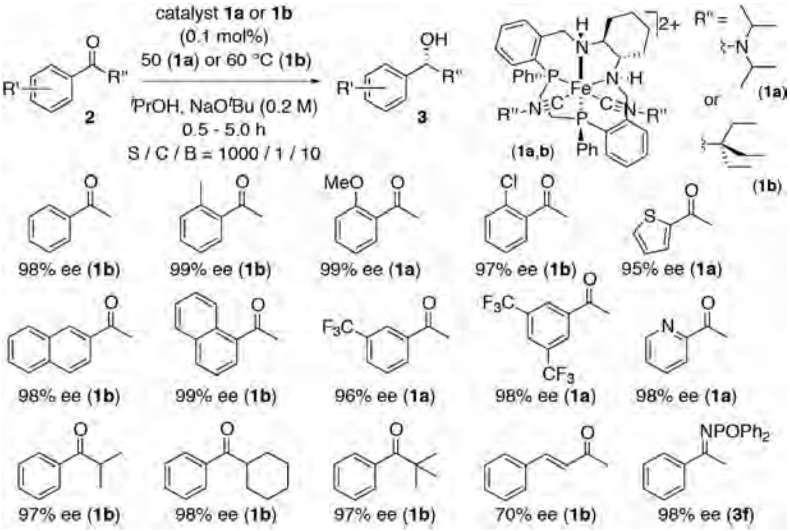
R. Bigler[1], R. Huber[1], E. Otth[1], A. Mezzetti[1]*

[1]ETH Zurich

In the past decade, great progress has been made to find cheap, environmentally benign 3d metal analogues as alternatives to expensive and often toxic precious metal catalysts, and iron is of central interest.[1] However, a major problem still is the inherent lower stability of these complexes as the metal-ligand bonds are weaker if compared to their 4d and 5d analogues. To this end, we recently developed chiral tetradentate N_2P_2 macrocyclic ligands that give stable, diamagnetic iron(II) complexes.[2,3]

We show here that the corresponding bis(isonitrile) iron(II) complexes bearing a C_2-symmetric diamino $(NH)_2P_2$ macrocyclic ligand efficiently catalyze the asymmetric transfer hydrogenation of polar bonds of a broad scope of substrates (ketones, enones, and imines) in high yield (up to ›99.5%) and with excellent enantioselectivity (up to 99% ee).[4] The substrate scope includes challenging ketones like arylalkyl ketones containing bulky alkyl groups, *ortho*-substituted acetophenones, acetonaphthones, and acyl-substituted heterocycles, i.e. acyl pyridines and acyl thiophenes. Turnover frequencies of up to 1950 h^{-1} were achieved while keeping the catalyst loading low (generally 0.1 mol%). The ancilliary isonitrile ligand (*C*-isonitriles and *N*-isonitriles were used) have a large and unprecedented influence on the activity and selectivity of the catalyst, which is exploited for the fine-tuning of the catalyst to achieve optimal results for specific substrates. Furthermore, preliminary tests support a homogeneous mechanism.

In sum, this is the first chiral iron(II) catalyst for the transfer hydrogenation of ketones that combines high activity and excellent enantioselectivity for a wide scope of substrates.



[1] R. Morris Bullock, *Science*, **2013**, *342*, 1054-1055.
[2] Raphael Bigler, Elisabeth Otth, Antonio Mezzetti,*Organometallics*,**2014**, *33*, 4086-4099.
[3] Raphael Bigler, Antonio Mezzetti, *Org. Lett.*, **2014**, *16*, 6460-6463.
[4] Raphael Bigler, Raffael Huber, Antonio Mezzetti, *Angew. Chem. Int. Ed.*, **2015**, *54*, 5171-5174.

Cobalt Complexes of Tetradentate, Bipyridine-Based Macrocycles for Highly Active Hydrogen Evolution in Aqueous Photocatalysis

E. Joliat[1], S. Schnidrig[1], B. Probst[1], C. Bachmann[1], B. Spingler[1], K. Baldridge[1], F. von Rohr[1], A. Schilling[1], R. Alberto[1]*

[1]University of Zurich

In the field of photocatalytic hydrogen production, cobalt complexes have proven to be active water reducing catalysts (WRCs) (Fig. 1).[1] As the stability of current WRCs is still insufficient, we introduce a new class of homogeneous cobalt WRCs based on a tetradentate, macrocyclic polypyridine framework (Fig. 2).[2, 3] The complexes are called cobalt pyrphyrins because the ligand resembles porphyrins but consists of *pyr*idine units only. The synthesis and full characterisation (cyclic voltammetry, crystal structures, UV-Vis and SQUID) of *mono*-butyl- as well as *cis*- and *trans*-dibutyl-Co-pyrphyrin-complexes (**1**-**3**, Fig. 2) are presented. All complexes are highly active WRCs in an aqueous system with $[Ru(bipy)_3]Cl_2$ as photosensitiser (PS) and TCEP/NaAsc [4] as sacrificial electron donor and shuttle, respectively. As more than 20’000 TON(H_2/WRC) are reachable, the stability of **1**-**3** is far superior to previously used cobaloximes.[5] Interestingly, *trans*-complex **3** performs significantly better in photocatalysis than its *cis*-counterpart **2**. This remarkable finding opens up new perspectives to elucidate the mechanism of hydrogen evolution at the cobalt centre.

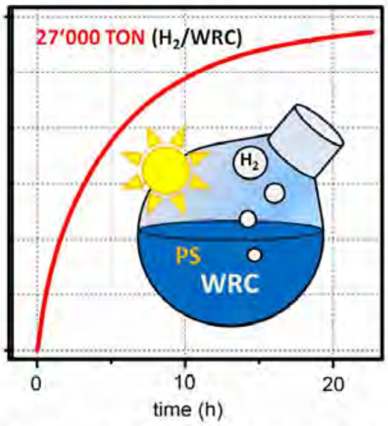


Fig. 1 – Flask: Photocatalytic water splitting with a water reduction catalyst (WRC) and a photosensitiser (PS). Graph: Hydrogen evolution of complex **1** as WRC.

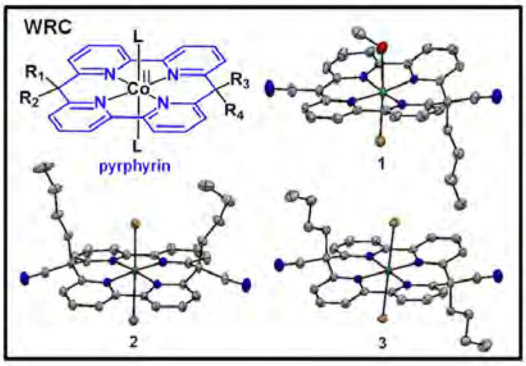


Fig. 2 – General structure of Co-pyrphyrins. - X-ray crystal structures of **1**: *Mono*-butyl-Co-pyrphyrin, **2**: *cis*-dibutyl-Co-pyrphyrin, **3**: *trans*-dibutyl-Co-pyrphyrin.

[1] Miguel Guttentag, Alexander Rodenberg, Cyril Bachmann, Anna Senn, Peter Hamm, Roger Alberto, *Dalton Trans*., **2013**, 42, 334-337.
[2] Shojiro Ogawa, Ryoichi Narushima, Yoshie Arai, *J. Am. Chem. Soc.*, **1984**, 106, 5760-5762.
[3] Shojiro Ogawa, Tokiko Uchida, Tomoaki Uchiya, Teruyoshi Hirano, Masahiko Saburi, Yasuzo Uchida, *J. Chem. Perkin Soc. Trans. 1,* **1990**, 1649-1653.
[4] Cyril Bachmann, Benjamin Probst, Miguel Guttentag, Roger Alberto, *Chem. Commun.*, **2014**, 50, 6737-6739.
[5] Theodore Lazarides, Milan Delor, Igor V. Sazanovich, Theresa M. McCormick, Irene Georgakaki, Georgios Charalambidis, Julia A. Weinstein, Athanassios G. Coutsolelos, *Chem. Commun.*, **2014**, 50, 521-523.

Two Synthetic Approaches for one target: Single Molecule Magnet Behaviour

P. E. Car[1], R. Güttinger[1], O. Blacque[1], L. Sorace[2], A. Caneschi[2], G. R. Patzke[1]

[1]Department of Chemistry, University of Zurich, [2]University of Florence, Italy

The first observation of a magnetic bistability phenomenon from a purely molecular origin has been reported by Sessoli al.[1] in 1991, on Mn_{12} acetate complex. Since this pioneering result, molecules exhibiting a slow relaxation of their magnetization are named single molecule magnets or SMMs and have been widely studied. Single molecule magnet behaviour is generally associated and represented by two characteristics: **(1)** a large magnetic anisotropy characterized by a large negative value (*D*) and **(2)** a large ground state spin (*S*). Up to now, peculiar attentions have been devoted to the synthesis of 3d and heterometallic 3d-3d' complexes.[2] But recently, in the search for more efficient SMMs, it has been demonstrated that the incorporation of a highly anisotropic 4f ions into 3d matrices can enhance the SMM properties.[3] Furthermore, Powell *al*.[4] in 2008, revealed that the combination of a highly anisotropic 4f ion with a highly isotropic 3d ion such as Cr^{III} ion can led to the formation of 3d-4f clusters with higher blocking temperature.

In the quest of new efficient SMMs, two synthetic approaches are currently under exploration in our group: **(1)** synthesis of heterometallic Cr-Ln molecular materials and **(2)** polyoxometalate materials. As metal-oxo cluster materials containing transition metal ions in their higher oxidation state (mainly Mo and W), polyoxometalates or POMs are a virtually inexhaustible reserve of robust and structurally diverse compounds for future applications in catalysis[5] and electronic devices.[6]

We will present herein new developments and promising results in molecular magnetism based on the two approaches cited above. In a first instance, we will show a new family of isostructural mononuclear 4f polyoxometalates. All compounds have been fully characterized by single crystal X-ray diffraction techniques, ATR-FTIR spectroscopy and photoluminescent properties were also investigated. The full magnetic behaviour (dc and ac magnetic susceptibility measurements) of each compound was studied in detail. We also report here a new family of heterometallic Cr^{III}-Ln^{III} complexes. Crystal structure determinations revealed that the dysprosium and the terbium derivatives crystallize both into two polymorph forms (crystal systems: triclinic and monoclinic). Full magnetic behaviour investigations showed that the Dy^{III} and Tb^{III} complexes exhibit single molecule magnet behaviour.

[1] A. Caneschi, D. Gatteschi, R. Sessoli, A.-L. Barra, L.-C. Brunel, M. Guillot, *J. Am. Chem. Soc.*, 1991, **113**, 5873.
[2] (a) L. Lisnard, F. Tuna, A. Candini, M. Affronte, R. E. P. Winpenny, E. J. L. McInnes, *Angew. Chem. Int. Ed.*, 2008, **47**, 9695; (b) J. Martinez-Lillo, N. Dolan, E. K. Brechin, *Dalton Trans.*, 2014, **43**, 4408.
[3] L. Ungur, M. Thewissen, J.-P. Costes, W. Wernsdorfer, L. F. Chibotaru,*Inorg. Chem.*, 2013, **52**, 6328
[4] J. Rinck, G. Novitchi, W. Van den Heuvel, L. Ungur, Y. Lan, W. Wernsdorfer, C. E. Anson, L. F. Chibotaru, A. K. Powell, *Angew. Chem. Int. Ed.*, 2010, **49**, 7583
[5] P.-E. Car, M. Guttentag, K. K. Baldridge, R. Alberto, G. R. Patzke, *Green Chem.*, 2012, **14**, 1680.
[6] M. A. AlDamen, J. M. Clemente-Juan, E. Coronado, C. Marti-Gastaldo, A. Gaita-Arino, *J. Am. Chem. Soc.*, 2008, **130**, 8874.

Self-assembly of 3d-5f Molecular Magnets from Pentavalent Uranyl

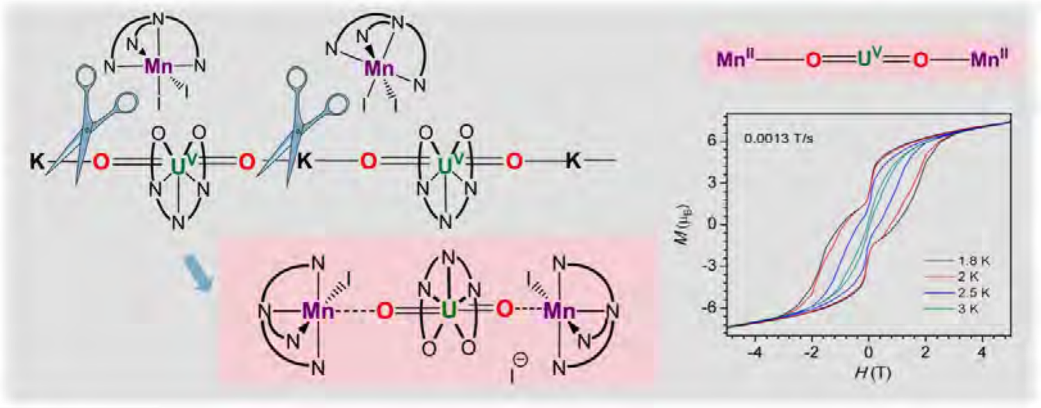
L. Chatelain[1], M. Mazzanti[1]*

[1]Ecole Polytechnique Fédérale de Lausanne

The design of multinuclear molecular actinide complexes is of high current interest for the development of actinide based single molecule magnets. A key property of an uranyl(V) moiety is its ability to bind another metallic center through the axial oxygen (commonly known as cation-cation interaction, CCI) leading to homometallic or heterometallic assemblies. We have recently shown that a suitable choice of ligand and conditions can lead to the isolation of assemblies with various topologies and nuclearities.[1,2]

Such assemblies show unambiguously an intermetallic communication that can be tuned by appropriate structural modifications to design complexes behaving like single molecule magnets (SMM). SMM are attractive molecules with a slow relaxation of the magnetization from a purely molecular origin. To improve the properties of SMM, a high spin ground state and a high magnetic anisotropy are required. In spite of the high single ion anisotropy of uranium, only few uranium based SMMs have been reported to date. We have recently shown that an SMM with enhanced properties can be obtained from the association of the high spin Mn^{2+} ion and of the highly anisotropic uranyl(V) in a large wheel shaped Mn_6U_{12} cluster.[3]

Here we will report that the topology of 3d-5f assemblies built from pentavalent uranyl can be tuned by the stoichiometry and the control of the coordination sphere of the d-block metal. This novel rational synthetic approach leads to the formation of a polymeric structure[4] with single chain magnet properties and to the assembly of discrete trinuclear heterometallic 3d-5f uranyl(V) based complexes. In particular, a TPA-capped Mn(II) complex allows the controlled formation of a UMn_2 trinuclear complex[5] that exhibits SMM behaviour with the highest relaxation barrier reported to date for a mono-uranium system (barrier of 81 ± 0.5 K arising from intramolecular Mn-U exchange interaction) and a open magnetic hysteresis loop at T ‹ 3 K.



1. V. Mougel, P. Horeglad, G. Nocton, J. Pécaut, M. Mazzanti,*Angew. Chem. Int. Ed.*,**2009**, 48, 8477.
2. L. Chatelain, V. Mougel, J. Pécaut, M. Mazzanti,*Chem. Science,***2012, 3, 1075.**
3.V. Mougel, L. Chatelain, J. Pécaut, R. Caciuffo, E. Colineau, J-C. Griveau, M. Mazzanti,*Nat. Chem.*,**2012**,4,1011.
4. V. Mougel, L. Chatelain, J. Hermle, R. Caciuffo, E. Colineau, F. Tuna, N. Magnani, A. Degeyer, J. Pécaut, M. Mazzanti, *Angew. Chem. Int. Ed.*,**2014**, 53, 819.
5. L. Chatelain, J. P. S. Walsh, J. Pécaut, F. Tuna, M. Mazzanti, *Angew. Chem. Int. Ed.,* **2014**, 53, 13434.

On the Synthesis, Biological Evaluation and Use of Metallocenyl Derivatives

J. Hess[1], M. Patra[1], A. Leonidova[1], V. Pierroz[1], S. Ferrari[1], G. Gasser[1]*

[1]University of Zurich

In the last years, metallocene-containing compounds have been intensively explored as promising anticancer or antimalarial drug candidates.[1] An improvement in the pharmacokinetic properties of the original drug was achieved through the conjugation of metallocenyl moieties to the initial drug. This is exemplified by ferroquine, which is a ferrocene derivative of the antimalarial drug chloroquine, which was found to be active on chloroquine-resistant strains. Thus, there is doubtlessly a high demand on novel synthetic strategies to prepare new functionalized metallocenyl derivatives. With this in mind, our group has recently reported the synthesis of diverse biologically relevant metallocenyl derivatives. These synthetic pathways give access to new organometallic conjugated moieties, which are valuable chemical entities in a broad biological context. [2], [3], [4]

[1] Gasser, G.; Metzler-Nolte, N. *Curr. Opin. Chem. Biol.* **2012**, *16*, 84 and references therein.
[2] Patra, M.; Hess, J.; Konatschnig, S.; Spingler, B.; Gasser, G. *Organometallics* **2013**, *32*, 6098.
[3] Hess, J.; Konatschnig, S.; Morard, S.; Pierroz, V.; Ferrari, S.; Spingler, B.; Gasser, G. *Inorg. Chem.* **2014**, *53*, 3662.
[4] Leonidova, A.; Joshi, T.; Nipkow, D.; Frei, A.; Penner, J.-E.; Konatschnig, S.; Patra, M.; Gasser, G. *Organometallics* **2013**, *32*, 2037.

Vibrational spectroscopy on functionalized and chiral monolayer protected gold clusters

B. Varnholt[1], I. Dolamic[1], P. Oulevey[1], T. Bürgi[1]*

[1]University of Geneva

The structure of monolayer protected gold clusters can be described by the divide-and-protect-model,[1] i.e. they are built up from a gold core and a protecting shell of gold-thiolate units.

Vibrational spectroscopy is one way to discriminate bond strengths and geometry sensitively.[2,3] The low-wavenumber region, which contains the Au-S and Au-S-C vibrations, can be investigated with far-infrared and Raman spectroscopy. With these means we studied thiolate-protected gold clusters with surface structures composed of monomeric (S-Au-S) and dimeric (S-Au-S-Au-S) binding units.

DFT calculations on the well-known $Au_{38}L_{24}$ cluster allow discriminating the spectral contributions of such units. The assignment can be transferred to clusters with different surface composition. A systematic shift of the Au-S-C bending allows estimating the number of monomeric and dimeric units. Further, vibrational spectra of bimetallic Au-Ag clusters were studied and Au-S and Ag-S vibrations were discriminated. The catalytic activity of bimetallic clusters depends on the availability of the active metal (core vs. staples) to the substrate and vibrational spectroscopy is therefore a valuable tool for their characterization. Moreover, the ligand type used for the stabilization of the cluster influences the low-wavenumber range of the vibrational spectrum. Raman measurements reveal information about ligand-ligand interactions between long aliphatic chains. The distortion of the shell upon partial ligand exchange with di-thiolate ligands is reflected in the spectra.

It was found that intrinsic chirality is a common feature of monolayer protected gold clusters. The enantiomers of $Au_{38}L_{24}$ could recently be separated by high performance liquid chromatography.[4] Vibrational circular dichroism measurements on the enantiomers show that the chiral cluster transfers its handedness to the achiral ligand.[5] Chirality transfer of surfaces to adsorbed molecules is a phenomenon playing an important role in asymmetric catalysis.

[1] H. Häkkinen, M. Walter, H. Grönbeck, J. Phys. Chem. B **2006**, 110, 9927–9931.
[2] I. Dolamic, B. Varnholt, T. Bürgi, Phys. Chem. Chem. Phys. **2013**, 15, 19561–19565.
[3] B. Varnholt, P. Oulevey, S. Luber, C. Kumara, A. Dass, T. Bürgi, J. Phys. Chem. C **2014**, 118, 9604–9611.
[4] I. Dolamic, S. Knoppe, A. Dass, T. Bürgi, Nat. Commun. **2012**, 3, 798–804.
[5] I. Dolamic, B. Varnholt, T. Bürgi, Nat. Commun. **2015**, in press

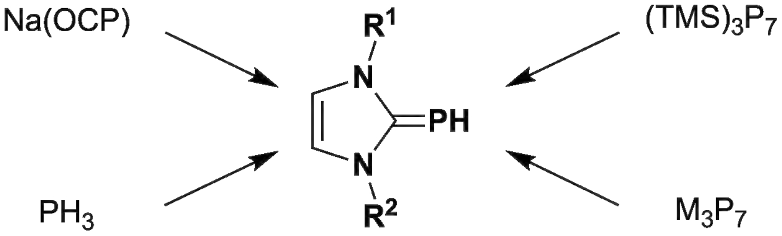
Carbene insertion into a P–H bond: Parent phosphinidene-carbene adducts from PH_3

M. Bispinghoff[1], H. Grützmacher[1]*

[1]ETH Zurich

Phosphinidenes, the phosphorus analogues of carbenes, are highly reactive species and eluded isolation so far. In 1997, Arduengo and co-workers showed that substituted phosphinidenes can be stabilized by adduct formation with N-heterocyclic carbenes (NHC).[1] We have recently prepared the parent NHC=PH adduct from imidazolium chlorides and the easily accesible P^- transfer agents $(TMS)_3P_7$ or Na(OCP) and applied this building block in the formation of carbene-supported P_3-cations and radicals.[2]

Herein, we report the synthesis of numerous parent phosphinidene-carbene adducts from halogen-free phosphorus transfer agents. Furthermore, we describe the insertion of a carbene into a P-H bond, giving access to NHC=PH adducts from PH_3 gas (Scheme 1)[3]. Finally, the influence of the steric and electronic properties of the NHC on the properties, reactivity and coordination behavior of the adducts will be discussed and their use as synthetic reagents demonstrated.



Scheme 1: Synthesis of parent phosphinidene-carbene adducts from different phosphorus transfer agents and PH_3 gas. R = Me, Et, *i*Pr, 2,6-diisopropylphenyl, 2,4,6-trimethylphenyl.

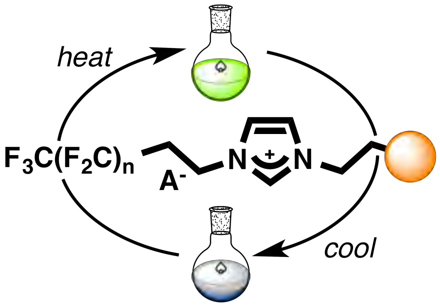
[1] A. J. Arduengo, J. C. Calabrese, A. H. Cowley, H. V. R. Dias, J. R. Goerlich, W. J. Marshall, B. Riegel, *Inorg. Chem*. **1997**, *36*, 2151.
[2] A. M. Tondreau, Z. Benkő, J. R. Harmer, H. Grützmacher, *Chem. Sci*. **2014**, *5*, 1545.
[3] M. Bispinghoff, A. M. Tondreau, H. Grützmacher, C. Faradji, P. G. Pringle, Dalton Trans., submitted.

Design and Synthesis of Perfluorous Ionic Liquids

V. M. Manzanares[1], Z. Fei[1], P. J. Dyson[1]*

[1]EPF Lausanne

Perfluorinated solvents display many desirable properties, of which*thermomorphism* is especially interesting for catalytic applications.[1] Although this approach can be generalized for catalystsand, to some extent, used in medicinal chemistry,[2] examples with perfluorinated ionic liquids are scarce.



We are currently investigating a series of task-specific ionic liquids bearing perfluorinated side chains along with other functional groups, which display UCST with organic solvents at higher temperatures.

[1] a) Horváth, I. T.; Rábai, J. *Science* **1994**, *266*, 72–75. b) Gladysz, J. A.; Corrêa da Costa, R. In *Handbook of Fluorous Chemistry*; Gladysz, J. A., Curran, D. P., Horváth, I. T., Eds.; Wiley-VCH Verlag GmbH Co. KGaA: Weinheim, FRG, 2005; pp 24–40.
[2] a) Clavel, C. M.; Zava, O.; Schmitt, F.; Halamoda Kenzaoui, B.; Nazarov, A. A.; Juillerat-Jeanneret, L.; Dyson, P. J. *Angew. Chem. Int. Ed.* **2011**, *50*, 7124–7127. b) Clavel, C. M.; Păunescu, E.; Nowak-Sliwinska, P.; Dyson, P. J. *Chem. Sci* **2014**, *5*, 1097–1101.

Going to Extremes: From Fluorine-Free Blue to Stable Red Emitting Iridium Complexes for LEECs

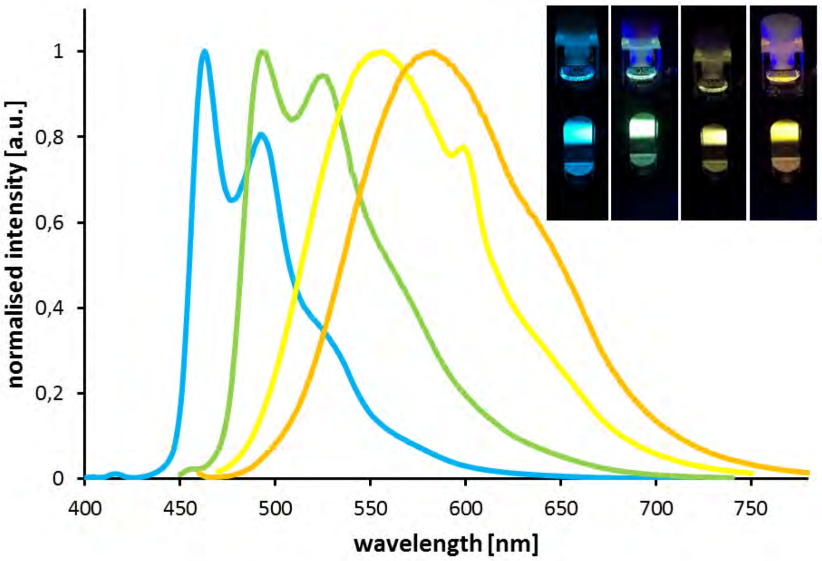
C. D. Ertl[1], A. Pertegás[2], H. J. Bolink[2], E. Ortí[2], E. C. Constable[1]*, C. E. Housecroft[1]*

[1]University of Basel, [2]Universidad de Valencia

Cationic iridium(III) complexes of the type $[Ir(C^\wedge N)_2(N^\wedge N)]^+$ are the most intensely studied emissive compounds for light emitting electrochemical cells (LEECs). In addition to their good photophysical and chemical properties and ionic nature, emission colour tuning is straightforward due to spatial separation of the frontier orbitals, making these complexes well suited for LEEC applications.

Nonetheless, there is still a lack of stable blue and red emitters. We have introduced a series of thioether and sulfone groups on the cyclometallating ligands to investigate the influence on the emission colour.[1] Electron-withdrawing sulfone groups yielded a large blue-shift in the emission maximum and were combined with electron-rich pyrazolylpyridine ancillary ligands[2] to further blue-shift the emission without the need of fluorine groups, which have been reported to have a detrimental effect on device stability both in OLEDs[3] and LEECs.[4]

Emission red-shifts on the other hand were achieved by the introduction of benzothiazolylpyridine ancillary ligands, leading to extremely stable LEECs with the longest reported lifetimes for red-emitting iridium complexes.



[1] E. C. Constable, C. D. Ertl, C. E. Housecroft and J. A. Zampese, *Dalton Trans.*, **2014**, 43, 5343.
[2] C. D. Ertl, J. Cerdá, J. M. Junquera-Hernández, A. Pertegás, H. J. Bolink, E. C. Constable, M. Neuburger, E. Ortí, C. E. Housecroft, *RSC Adv.*, **2015**, accepted.
[3] S. Schmidbauer, A. Hohenleutner, B. König, *Adv. Mater.*, **2013**, 25, 2114.
[4] D. Tordera, J. J. Serrano-Pérez, A. Pertegás, E. Ortí, H. J. Bolink, E. Baranoff, Md. K. Nazeeruddin, J. Frey, *Chem. Mater.*, **2013**, 25, 3391.

Application of ferrocene derivatives for stimuli-responsive polymers and for biosensor

M. Di Giannantonio[1], K. Fromm[1]*

[1]University of Fribourg

Since long time ferrocene and its derivatives have attracted the attention of the scientific and technical community because of its fascinating chemistry. Due to its easy functionalization and unusual and attractive properties, ferrocene derivatives have found different applications in material science, such as sensors, catalysts, polymers, electroactive materials and medicinal chemistry[1,2].

We propose two different research subjects: ferrocene-containing polymers as stimuli-responsive material and ferrocene-based trigger as biosensor.

The aim is to synthesize stimuli-responsive polymerswith several ferrocene units in a linear polyurethane chain or in a linear poly(methyl methacrylate) chain and to analyze their physico-chemical changessubjectingthe polymerto mechanical stress (sonication or stretching) or using techniques such as the Atomic Force Microscope.

Ferrocene derivatives can also be exploited for biomedical applications: the formation of resistant biofilms causes infection problems in the internal fixation devices[3]; the aim of this project is to synthesize an unsymmetrical ferrocene that could be a precursor of a new type of sensor for biomolecules, accounting for the presence of bacteria. Exploiting therotational freedom of ferrocene, temporally restricted by intramolecular-DNA near-match pairing and then quicklyreleased by hybridization with a fully-matching DNA strand, it is possible to identify the presence of bacteria.

[1] S. Zhai, J. Shang, D. Yang, S.Wang, J. Hu, G. Lu, X. Huang, *J. Polym. Sci. Part Polym.Chem.* **2012**, *50*, 811–820.
[2] C. Herfurth, D. Voll, J. Buller, J. Weiss, C. Barner-Kowollik, A. Laschewsky, *J. Polym. Sci. Part Polym.Chem.* **2012**, *50*, 108–118.
[3] *Science,* 8 February, **2002***: Vol. 295* no. 5557 p. 995.