CHIMIA 2014, Volume 68
ISSN 0009-4293
www. chimia.ch

SCS
Swiss Chemical
Society

Supplementa to Issue 7-8/2014

SCS Fall Meeting 2014
Poster Abstracts
Session of Inorganic & Coordination Chemistry

September 11, 2014
University of Zurich, Irchel Campus
http://scg.ch/fallmeeting2014

Swiss Chemical Society
Schwarztorstrasse 9
3007 Bern
Switzerland
info@scg.ch
www.scg.ch

Binding isotherms for modelling Lanthanide multiple complexation to polymeric scaffolds

Lucille Babel[1], Nhu Y Hoang[1], Homayoun Nozary[1], Laure Guénée[1], Claude Piguet[1] *

[1]University of Geneva

Since a few decades, macroscopic lanthanide-containing entities have been extensively developed for their numerous technological applications. [1] However, Wolf-type II lanthanidopolymers have less benefited from this interest despite that the metal loading of linear multi-sites receptors can be rationalized much more easily. In this work, thermodynamics of lanthanidopolymers $[\{Ln(hfac)_3\}_m\mathbf{L}]$ (hfac = hexafluoroacetylacetonate) are investigated (Figure 1).[2] To do so, a polymer **L** has been designed and synthetized to obtain a rigid and soluble scaffold with tridentate units. ^{19}F and/or ^{1}H NMR titrations of the polymer with $Ln(hfac)_3dig$ (dig = diglyme = 1-methoxy-2-(2-methoxyethoxy)ethane) in deuterated dichloromethane provides the lanthanide loading for each metal concentration. Using statistical mechanics, binding isotherms are expressed according to two microscopic thermodynamic parameters: (i) the intrinsic affinity of one lanthanide for a tridentate binding unit f^{Ln}_{N3} and (ii) the intermetallic interactions between two occupied neighboring sites $\Delta E^{Ln,Ln}_{1-2}$. Within the set of the three selected lanthanides (Ln = La, Y and Eu), various affinities and intermetallic interactions have been observed, which is promising for the design of f-f' materials. Photophysical studies were investigated for $[\{Eu(hfac)_3\}_m\mathbf{L}]$ and resulted in the observation of exploitable light-downshifting. Moreover, the disappearance of the emission arising from the ligand **L** with the increase in europium loading confirmed the thermodynamic model.

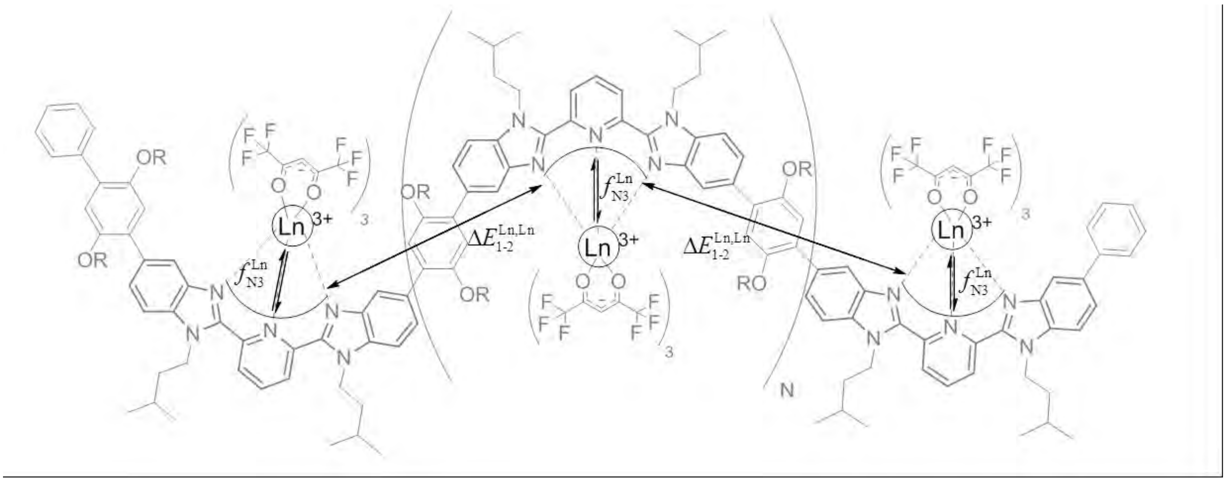


Figure 1 – Chemical structure of the lanthanidopolymers $[\{Ln(hfac)_3\}_m\mathbf{L}]$ (gray) highlighting the two microscopic parameters used in the thermodynamic model (black).

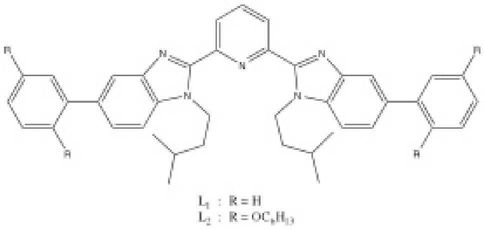
[1] Eliseeva, S. V. and Bünzli, J.-C. G., *New J. Chem.*, Vol. 35, (2011), pp 1165-1176.
[2] Babel L., Hoang T. N. Y, Nozary H., Salamanca J., Guénée L. and Piguet C.,*Inorg. Chem.* **2014**, 53, 3568.

Solvation effects and their consequences on ligand-metal binding events.

Karine Baudet[1], Claude Piguet[1] *

[1]University of Geneva

Thermodynamic laws consider solvent as having a constant activity in global binding equilibria, but totally neglecting solvent activity may be injurious for the comprehension of molecular binding processes. In this context, Castellano and Eggers[1] introduced a new thermodynamic framework, which treats solvent as a co-reactant in the development of common binding equations. The explicit consideration of solvent as a member of complexation equilibria can generate significant deviations in the law of mass action. Those will affect the stability constants, which characterize the formation of coordination complexes. With these facts in mind, we established theoretical methods which aim at separately evaluating solvent effects and “pure” binding affinity accompanying the reaction of tridentate ligands (**L_1** and **L_2**) with the saturated trivalent lanthanide carriers [Ln(hfac)$_3$(diglyme)]. Changes in solvent polarity, in ligand lipophilicites and in metallic sizes are investigated for deciphering robust trends in binding selectivity.[2]



[1] Brian M. Castellano, Daryl K. Eggers, *The Journal of Physical Chemistry B*, **2013**, 117, 8180-8188

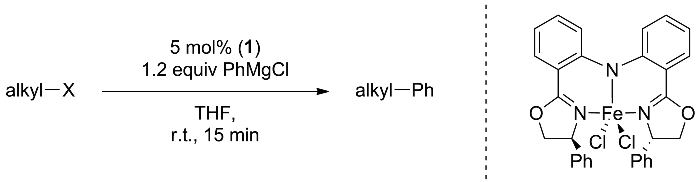
[2] Lucille Babel, Thi Nhu Y Hoang, Homayoun Nozary, Jasmina Salamanca, Laure Guénée, Claude Piguet, *Inorganic Chemistry*, **2013**, 53, 3568-3578.

From Welding to Cross-Coupling: How Iron Forms Bonds— the Story of a Mechanism.

Gerald Bauer[1], Matthew Wodrich[1], Rosario Scopelliti[1], Xile Hu[1] *

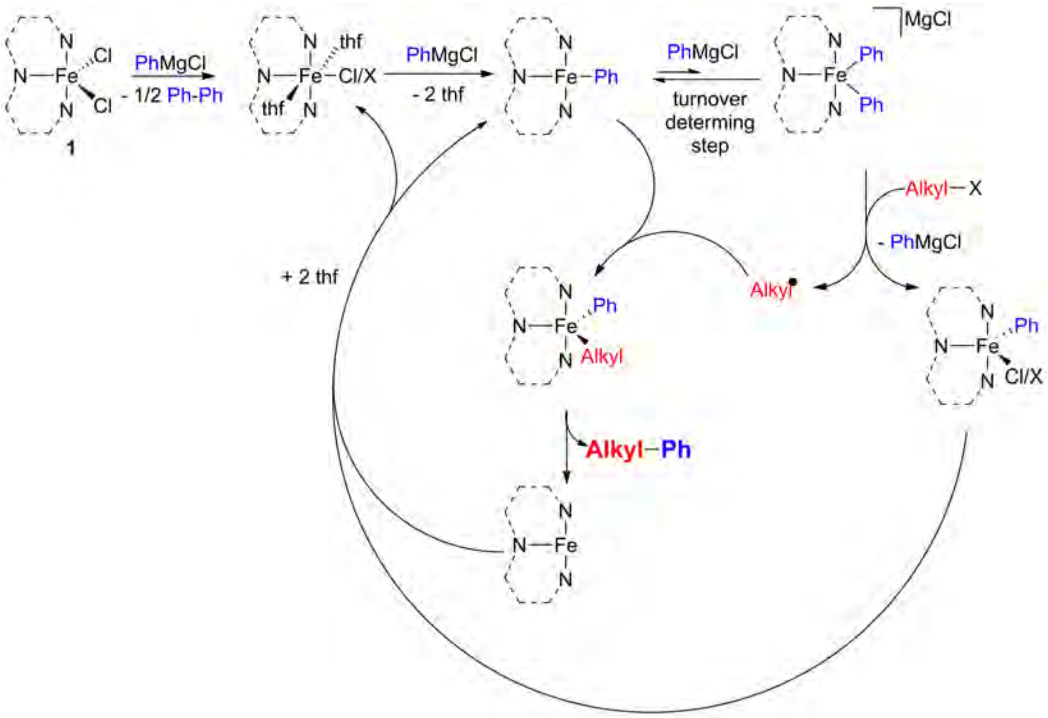
[1]EPFL Lausanne

The use of iron as a catalyst for the formation of new alkyl-aryl bonds via Kumada cross-coupling reactions developed into an efficient tool. Though its application is increasing, little is yet known about operating mechanisms. In the present work we apply a bisoxazolinylphenylamido pincer ligand (Bopa) to stabilize the catalytically active Fe center in the catalytic cross-coupling of *sec*. alkyl halides with aryl-Grignard compounds.



1

Stoichiometric reactions with PhMgCl allowed the isolation and characterisation of the octahedral [Fe^{II}(Bopa-Ph)Cl$(THF)_2$] (**2**) and the tetrahedral [Fe^{II}(Bopa-Ph)Ph] (**4**). Their catalytic relevance was further probed and confirmed. Reactivitiy studies showed the formation of an anionic Fe(II) "ate" species, [Fe(Bopa-Ph)$(Ph)_2$]$^-$, as the active species in the oxidative addition of alkyl halides. Further experiments using radical probes and DFT calculations revealed a radical bimetallic mechanism for the oxidative addition. Kinetic experiments of the coupling reaction of PhMgCl with alkyl iodides showed that the "ate" complex formation rather than the oxidative addition is the turn over determining step.

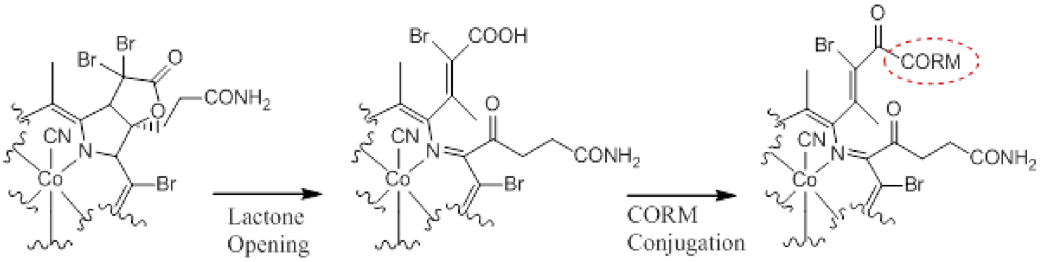


Modifications of Vitamin B12 as a Drug Delivery System for CORMs

Ruben Beltrami[1], Fabio Zobi[1] *

[1]University of Fribourg

Carbon monoxide releasing molecules (CORMs) are an evolving class of pharmaceutical compounds currently evaluated in several preclinical disease models. The cellular internalization of CORMs is a critical event in their therapeutic action. To allow cellular internalization, vitamin B12 is used as a biocompatible water soluble scaffold [1]. The main focus of this work pivots around modifications of vitamin B12 for the synthesis of new biocompatible CORM conjugates.



B ring modified B12 derivatives are used for therapeutic applications [2-4]. We followed a synthetic pathway for B ring opening of 7,8-seco-cyanocobalamins by hydrolysis of a c-lactone derivative which in turns generates a β-bromo alcoholate subunit with a pending carboxylic group [5]. The functional group generated by this reaction (figure 1) allows a new functionalization of the vitamin in addition to generally addressed 5’-OH ribose group. By this strategy a new class of vitamin B12-CORMs conjugates may be explored.

[1]Fabio Zobi; Olivier Blacque; Luca Quaroni; Giuseppe Santoro; Blagoj Sarafimov; Marcus C Schaub; Theodora Zlateva; Anna Yu Bogdanova, *Journal of medicinal chemistry*, **2013**; 56(17):6719-31

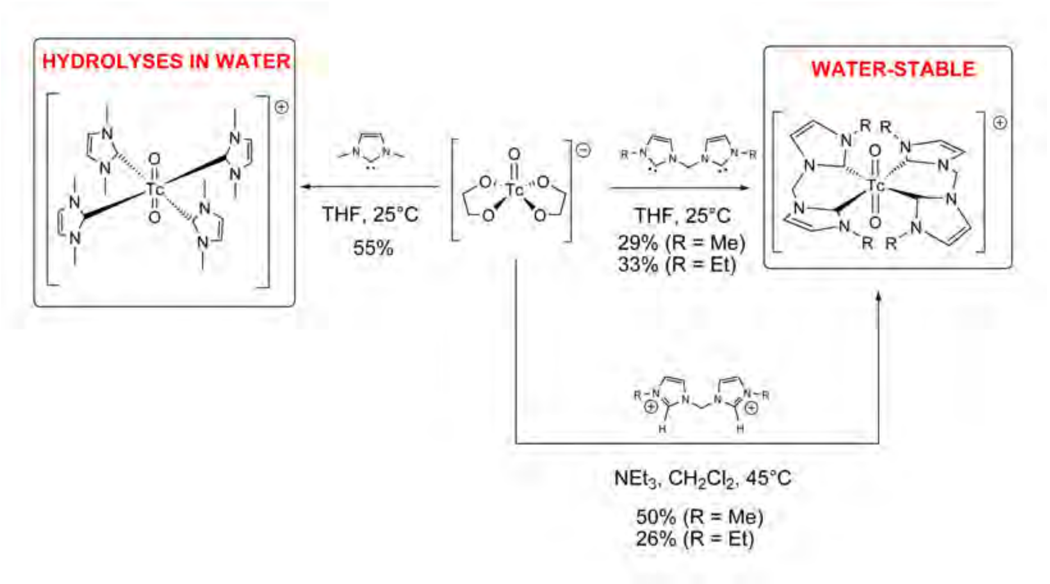
[2]Fedosov, S.N.; Ruetz, M.; Gruber, K.; Fedosova, N. U.; Kräutler,B., *Biochemistry*, **2011**, 50, 8090
[3]Kurcon, S.; ó Proinsias, K.; Gryko, D., *J. Org. Chem.*, **2013**, 78, 4115
[4] Zelder, F.; Zhou, K.; Sonnay, M., *Dalton Trans.*, **2013**, 42, 854
[5] René M. Oetterli ; Lucas Prieto ; Bernhard Spingler and Felix Zelder, *Org. Lett.*, **2013**, Vol. 15, No. 18

Synthesis of Water Stable $\{M^{(V)}O_2\}^+$-N-Heterocyclic Carbene Complexes (M = Re, ^{99}Tc)

Michael Benz[1], Henrik Braband[1], Roger Alberto[1] *

[1]University of Zurich

Recently, the scope of N-heterocyclic carbenes (NHCs) has been extended from catalytic application to the field of *bioinorganic chemistry* and *metals in medicine*. In this context, the NHC chemistry of technetium came into our research focus. However, ^{99}Tc-NHC complexes are scarce.[1] While $\{Re^{(V)}O_2\}^+$ complexes, which contain monodentate NHCs, are hydrolytically stable, the corresponding $\{Tc^{(V)}O_2\}^+$-NHC complexes show rapid hydrolysis in the presence of trace amounts of H_2O.[2] We present novel synthetic pathways for the synthesis of water stable $\{M^{(V)}O_2\}^+$-NHC complexes.[3] The key link for these general procedures is $[M^{(V)}O(glyc)_2]^-$ (M = Re, ^{99}Tc; glyc = ethylene glycolato). The high water stability of the products allows conversion of the $\{M^{(V)}O_2\}^+$ core into $\{M^{(V)}OCl\}^{2+}$ with HCl as the H^+ and Cl^- source. The remarkable stability and pH-controllable reactivity of the new complexes underline the potential of NHCs as stabilizing ligands for ^{99}Tc complexes and paves the way for the first ^{99m}Tc-NHC complexes in the future.



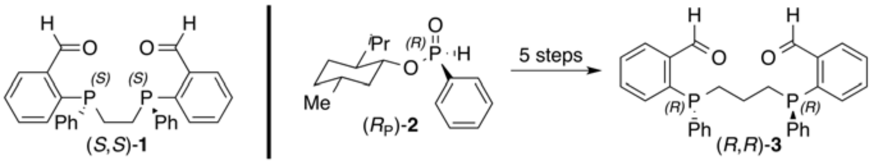
[1] Sebastian J. Hock, Lars-Arne Schaper, Wolfgang A. Herrmann, Fritz E. Kühn, *Chemical Society Reviews*, **2013**, 42, 5073-5089.
[2] Henrik Braband, Theresa I. Kückmann, Ulrich Abram, *Journal of Organometallic Chemistry*, **2005**, 690, 5421-5429.
[3] Michael Benz, Bernhard Spingler, Roger Alberto,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

Synthesis of C_2-Symmetric N_2P_2 Macrocycles and their Fe(II) Complexes

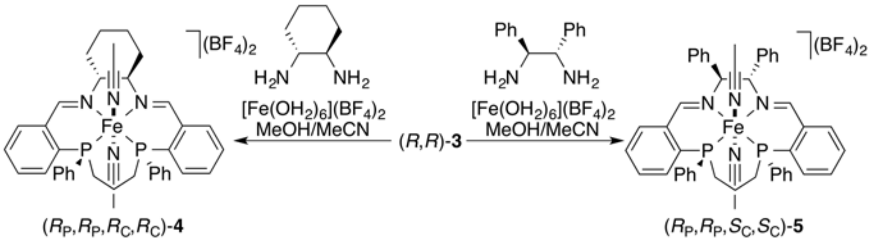
Raphael Bigler[1], Marco Stöckli[1], Antonio Mezzetti[1] *

[1]ETH Zurich

Following our interest in open-chain and macrocyclic PNNP ligands [1,2], we have recently prepared enantiomerically pure dialdehyde (*S*,*S*)-**1**, which was condensed with diamines to give N_2P_2 macrocycles with an ethylene bridge between the phosphine donors. The corresponding Fe(II) bis(isonitrile) complexes catalyze the transfer hydrogenation of aromatic ketones with up to 91% *ee* and are therefore promising catalyst systems. We present here a more general route to similar macrocycles with a varying bridge length.



A first example is dialdehyde (*R*,*R*)-**3**, which was prepared from phosphinate (R_P)-**2**. The N_2P_2 macrocycles and the corresponding Fe(II) complexes *trans*-**4** and *trans*-**5** were prepared by template synthesis. The derivatization of the resulting bis(acetonirile) complexes and their application in transfer hydrogenation of ketones will be presented.



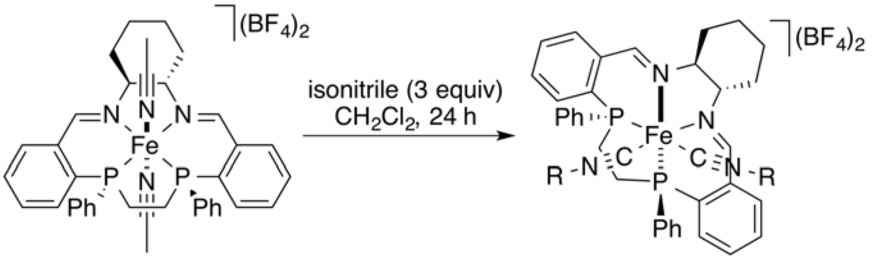
[1] A. Mezzetti, *Dalton Trans.*, **2010**, *39*, 7851-7869.
[2] M. Ranocchiari, A. Mezzetti, *Organometallics*, **2009**, *28*, 1286-1288.

Macrocyclic Iron(II) Complexes in Asymmetric Transfer Hydrogenation

Raphael Bigler[1], Antonio Mezzetti[1] *

[1]ETH Zurich

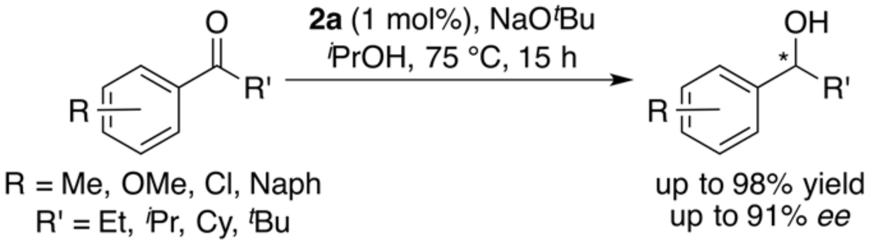
The use of iron with chiral PNNP ligands has lately developed as a powerful combination in asymmetric transfer hydrogenation [1]. However, early systems have been found to decompose to iron nanoparticles thereupon [2]. We have recently prepared diamagnetic Fe(II) complexes bearing chiral, macrocyclic N_2P_2 ligands. Exchange of acetonitrile by isonitrile as ancilliary ligands gave complexes **2a**-**e** as diamagnetic solids which are robust under the transfer hydrogenation conditions.



1

R = ^{t}Bu (**2a**), Ad (**2b**), ^{neo}Oct (**2c**), Ph (**2d**), Cy (**2e**)

Of the new complexes **2a**-**e**, the best performance was obtained with the bis(*tert*-butylisonitrile) derivative **2a**, which reduced acetophenone in good yield and enantioselectivity (93%, 83% *ee*). Complex **2a** hydrogenates a variety of ketones with overall good yields and up to 91% *ee* (for 2-methoxyacetophenone and 1-acetylnaphthalene). We are currently investigating the mechanism of the transfer hydrogenation, and preliminary results will be presented.



[1] W. Zuo, A. J. Lough, Y. F. Li. R. H. Morris, *Science,* **2013**, *342*, 1080-1083.

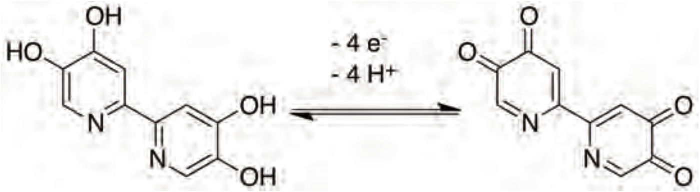
[2] J. F. Sonnenberg, N. Coombs, P. A. Dube, R. H. Morris, *J. Am. Chem. Soc.*, **2012**, *134*, 5893-5899.

d^6-Metal Complexes with Bifunctional Catechol-like Bipyridine Ligands

Laura A. Büldt[1], Oliver S. Wenger[1] *

[1]University of Basel

In recent years light driven redox catalysis showed some promising results in conducting sustainable water oxidation[1]. In this context bipyridine-based ruthenium complexes are extensively investigated. A general approach to tuning potential of a complex is varying its ligands.[2] The ligands can also provide functional moieties such as proton accepting or donating sites. The release of a proton coupled to an oxidation step helps avoid a build-up of charge in the system and may influence the energy profile of the overall reaction in a beneficial way. Proton-coupled electron transfer (PCET)[3] is a common process in nature. One prominent example is photosystem II, which performs the multistep redox process of water oxidation via several PCET processes.[4]



This project aims at the development of a ligand (shown above), which contains proton-donating sites and, in addition, is redox active itself.[5, 6] As a first step we investigated the influence of the methoxy-protected ligand on the redox and spectroscopic properties in different transition metal complexes. In a second step we developed the heteroleptic complex (below) with a nonsymmetrical bipyridine ligand, which contains only one bifunctional moiety. Using this model system, our research focuses on elucidating the stability of the individual redox and protonation states of this complex under various conditions.

[1] N. Kaveevivitchai et. al., *J. Am. Chem. Soc.* **2012**, 134, 10721-10724.
[2] S. Romain et al., *Acc. Chem. Res.* **2009**, 42, 1944-1953.
[3] Sharon Hammes-Schiffer, *Acc. Chem. Res.* **2009**, 42, 1881-1889.
[4] C. J. Gagliardi et al., *Energy Environ. Sci.* **2012**, 5, 7704-7717.
[5] S. Klein et al., *Inorg. Chem.* **2011**, 50, 2754-2763.
[6] M. J. Fuentes et al., *Dalton Trans.* **2012**, 41, 12514-12523.

Cyclometallated Ir(III) based Light-emitting Electrochemical Cells - A new Technology for Lighting Applications

Andreas Bünzli[1], Daniel Tordera[2], Enrique Ortí[2], Henk J. Bolink[2], Edwin C. Constable[1], Catherine E. Housecroft[1] *

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

The worldwide consumption of artificial light has to be reduced by new, more efficient technologies, resulting in huge environmental and economic savings. Octahedral iridium(III) complexes of the type $[Ir(C^\wedge N)_2(N^\wedge N)][PF_6]$ show promising properties for applications in light-emitting electrochemical cells (LEEC).

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 ultrathin 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.

By modifying the set of ligands, cyclometallated Ir(III) complexes offer a unique opportunity to tune the emission colour, and due to the strong spin-orbit coupling almost quantitative photoluminescence quantum yields (PLQY) over 95 % can be reached. A major drawback remains the limited stability of the Ir(III) emitters in LEEC devices and that most of the complexes emit in the yellow-orange region.

Herein the synthesis of several series of cyclometallated Ir(III) complexes emitting over the whole visible spectrum is presented[1],[2]. Additionally, by introducing π-stacking phenyl rings on the ligands the stability of such complexes and thus the lifetime of the devices was enhanced.

[1] A. M. Bünzli, H. J. Bolink, E. C. Constable, C. E. Housecroft, J. M. Junquera-Hernández, M. Neuburger, E. Ortí, A. Pertegás, J. J. Serrano-Pérez, D. Tordera, and J. A Zampese, *Dalton transactions*, **2014**, 43, 738–750
[2] D. Tordera, A. M. Bünzli, A. Pertegás, J. M. Junquera-Hernández, E. C. Constable, J. A Zampese, C. E. Housecroft, E. Ortí, and H. J. Bolink, *Chemistry - A European .Journal.,* **2013**, 19, 8597–8609.

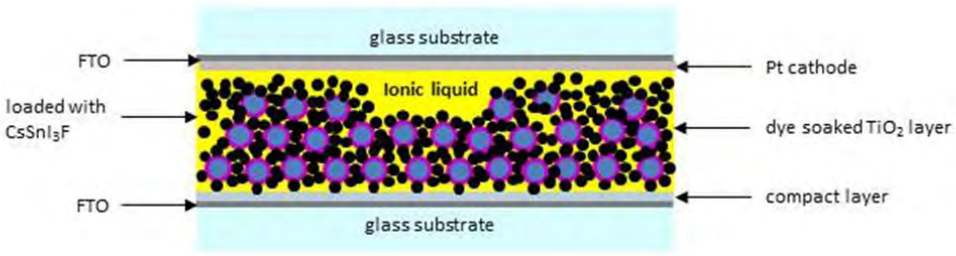
Tin based P-type direct band-gap semiconductor material for application in solid-state dye-sensitized solar cells

Annika Büttner[1], Edwin C. Constable[1], Catherine 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 main problem in the general construction of a DSC is the electrolyte contained within due to its corrosive nature. Replacing this by a solid state material therefore is of high interest. In order to do this via the construction of an all-solid-state dye-sensitized solar cell (ssDSC) we have implemented a tin containing p-type band-gap semiconducting material $CsSnI_{3-X}F_X$ into the solid electrolyte layer. The 3D perovskite structure is known to act as a direct band-gap semiconductor which inspired us to choose this material. [2] In addition to that, p-type conduction behavior and high hole mobility are characteristic of this material. The preparation of the pure black $CsSnI_{3-X}F_X$ was achieved via a solid state reaction. [3]



By incorporating an ionic liquid into the cell, improved contact between the working and the counter electrodes was achieved. Through this change in construction it was possible to increase the efficiency of the cell from 0.09 up to 0.73 %. For further enhancement of the power conversion efficiency a second compact layer was applied to reduce the electron recombination.

Investigation of applying a gold-coated counter-electrode may improve the contact and therefore the power conversion efficiency. Along with this copper(I) complexes will be tried as sensitizers within these setups.

[1] Kuppuswamy Kalyanasundaram , "*Dye-Sensitized Solar Cells",* 1st edition, CRC Press and EPFL Press, **2011**.

[2] In Chung, Byunghong Lee, Jianqing He, Robert P.H. Chang, Mercouri G. Kanatzidis, *Nature*, **2012**, 485, 486-489.

[3] In Chung, Jung-Hwan Song, Jino Im, John Androulakis, Christos D. Malliakas, Hao Li, Arthur J. Freeman, John T. Kenney, Mercouri G. Kanatzidis, *Journal of the American Chemical Society*, **2012**, 134, 8579-8587.

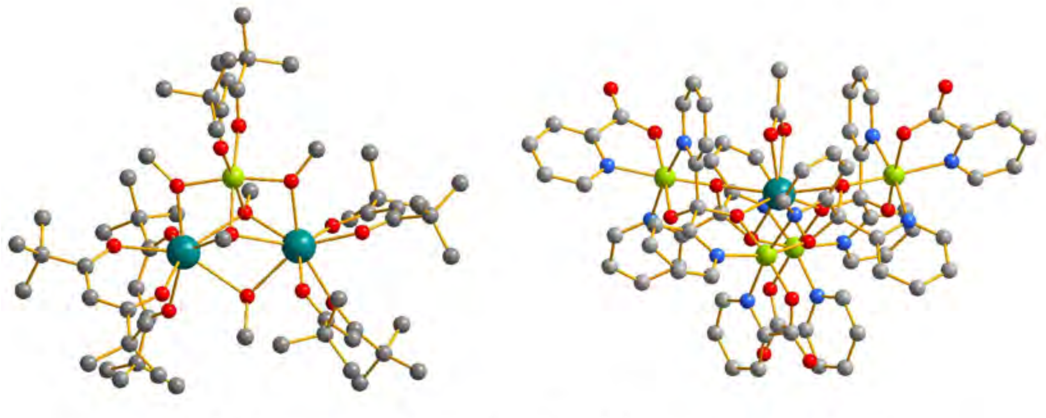
Chromium-Lanthanide complexes: a fascinating class of compounds. Crystal structures and magnetic property investigations

Pierre-Emmanuel Car[1], Olivier Blacque[1], Andrea Caneschi[2], Roberta Sessoli[2], Greta Ricarda Patzke[1] *

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

In 1991[1], Sessoli *al.* reported the first observation of a magnetic bistability in a molecular cluster $[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4]$ currently known as "Mn_{12}". This pioneering result followed by several examples based on 3d and/or 4f elements opened the way to a new family of compounds known today as single molecule magnets (SMMs). Since this date, the SMM family did not cease to grow, has been widely investigated but continues to lead to promising and fascinating results.[2] In this structurally diversified family of compounds, the "chromium-lanthanide" family is still widely unexplored mainly to the difficulty for reacting in solution a chromium salt with lanthanide ions. Up to know, only very few examples of Cr-Ln complexes have been reported.[3]

Nonetheless, we herein report the syntheses, the crystal structures and the magnetic property investigations of new chromium-lanthanide complexes: $[CrDy_2(OCH_3)_4(dpm)_5(CH_3OH)]\cdot CH_3OH$ **(1)**[4a] and $[Cr_4Ln(CH_3COO)(pyCOO)_4((py)_2COO)_4](NO_3)_2\cdot 19\text{-}20H_2O$ **(2)**[4b] (with Ln = Dy^{3+}, Tb^{3+}, Gd^{3+}; and py = pyridine). Complexes **1** and **2** were characterized by single crystal X-ray diffraction techniques. Magnetic measurements on **1** have been carried out in an applied field of 1 kOe between 1.8-45 K and under 10 kOe between 45-300K for the dc (direct current) susceptibility measurements, and under zero-dc field as function of temperature (1.8-6 K) under frequencies in the range of 0.1-60 KHz for the ac (alternative current) susceptibility measurements. The evaluation of the magnetic data for **1** reveals that **1** exhibits a single molecule magnet behaviour. Structural studies revealed that complexes **2** crystallized interestingly into two polymorphs in a triclinic *P*-1 and in a monoclinic *P*2$_1$/*n* space groups. The magnetic behaviour of **2** is still under investigation.



Ball and stick representations of complexes (**1**) and (**2**), respectively in left and in right.

[1] A. Caneschi, D. Gatteschi, R. Sessoli, A.-L. Barra, L.-C. Brunel, M. Guillot, *J. Am. Chem. Soc.*, **1991**, 113, 5873-5874.

[2] (a) N. Ishikawa, M. Suguta, T. Ishikawa, S. Y. Koshihara, Y. Kaizu, *J. Am. Chem. Soc.*, **2003**, 125, 8694-8695; (b) M. Mannini, F. Pineider, P. Sainctavit, C. Danieli, E. Otero, C. Sciancalepore, A. M. Talarico, M. A. Arrio, A. Cornia, D. Gatteschi, R. Sessoli, *Nat. Mater.*, **2009**, 8, 194-197; (c) M. Mannini, F. Pineider, C. Danieli, F. Totti, L. Sorace, P. Sainctavit, M. A. Arrio, E. Otero, L. Joly, J. C. Cezar, A. Cornia, R. Sessoli, *Nature*, **2010**, 468, 417-421.

[3] S. K. Langley, D. P. Wielechowski, V. Vieru, N. F. Chilton, B. Moubaraki, B. F. Abrahams, L. F. Chibotaru, K. S. Murray, *Angew. Chem. Int. Ed.*, **2013**, 52, 12014-12019.

[4] (a) P.-E. Car, A. Favre, J. F. Soares, A. Caneschi, R. Sessoli. *To be submitted;* (b) P.-E Car, O. Blacque, A. Caneschi, R. Sessoli. *In preparation.*

Transition metal substituted polyoxometalates: crystal growth engineering and photocatalytic applications

Pierre-Emmanuel Car[1] *, Olivier Blacque[1], Greta Ricarda Patzke[1]

[1]University of Zurich

Polyoxometalates (POMs) are a fascinating class of oxoanions with transition metal ions (generally Mo, W, and V) in their high oxidation states. This family of compounds has been widely explored the last decades and remains in the center of international research due to their excellent efficiencies in a wide range of research fields, such as magnetism[1a], catalysis[1b] and water oxidation reaction.[1c] Despite these interesting results, the search for new polyoxometalates and new experimental approaches does not cease to grow.

In this context, we herein report a new crystallization approach for transition metal substituted polyoxometalates (TMSPs) based on the diffusion of a “POM solution” trough a gel media containing the appropriate counter-cation. This approach newly applied to the POM chemistry led[2] two the formation of two new cobalt polyoxometalates $K_{16}[\{Co_3(H_2O)(GeW_9O_{33}(OH)(GeW_8O_{29}(OH)\}_2Co(H_2O)_2Co(H_2O)_4]\cdot 30H_2O$ **(1)** and $K_9[\{Co_4(H_2O)_2\}(Si_2W_{19}O_{68}(OH)_3)]\cdot 20H_2O$ **(2)**, and the existing $K_{10}[Co_4(H_2O)_2(PW_9O_{34})_2]\cdot 21H_2O$ **(3)**. As a proof of concept of the crystal quality of the synthesized POMs, all compounds were characterized by single crystal X-ray diffraction techniques and fully characterized by a wide range of analytical techniques. The efficiency of all POMs as water oxidation catalyst (WOC) was evaluated and compared to similar existing POMs.

In the search of new efficient TMSPs water oxidation catalysts, containing abundant and low-cost transition metal ions, we reported[3] the synthesis and the characterization of a novel dimanganese substituted polyoxotungstate $K_6[Mn_2SiW_{10}O_{37}(OH)(H_2O)]\cdot 11H_2O$ **(4)**. Crystal studies revealed that the $\{SiMn_2W_{10}O_{38}\}$ fragment self-organize into a 1D chain-like POM architecture with rarely observed Mn-O-W bridges. This new polyoxometalate has been fully characterized, its magnetic property investigated as well as its efficiency as water oxidation catalyst.

Polyhedral representation of the 1D chain of $\{Mn_2SiW_{10}O_{38}\}$building blocks

[1] (a) E. Coronado, C. J. Gomez-Garcia, *Chem. Rev.*, **1998**, 98, 273-296; (b) N. Mizuno, M. Misono, *Chem. Rev.*, **1998**, 98, 199-218; (c) P.-E. Car, M. Guttentag, K. K. Baldridge, R. alberto, G. R. Patzke., *Green Chem.*, **2012**, 14, 1680-1688.

[2] P.-E. Car, O. Blacque, G. R. Patzke. *In preparation.*

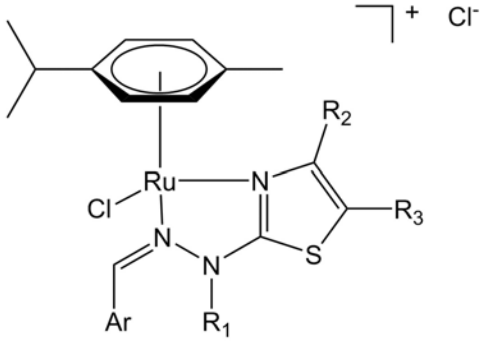
[3] P.-E. Car, B. Spingler, S. Weyeneth, J. Patscheider, G. R. Patzke, *Polyhedron*, **2013**, 52, 151-158.

Synthesis, characterization and biological activity of novel ruthenium-thiazolylhydrazone complexes

Thomas Cheminel[1], Adriana Ignat[2], Bruno Therrien[1]

[1]University of Neuchatel, [2]University of Cluj-Napoca

Research in our group is focused on the synthesis of ruthenium complexes[1] and cages[2] designed for biological applications, such as cytotoxicity against cancerous cells. Herein, thiazolylhydrazone derivatives, mainly used as inhibitory agents in biology,[3] are used to synthesize chelate ruthenium complexes. We report their synthetic procedure, spectroscopic characterization, crystal structure and biological activity to HeLa cancerous cells.



R_1 = H, COMe

R_2 = Me, Ph, CH_2COOEt

R_3 = H, COMe, COOEt

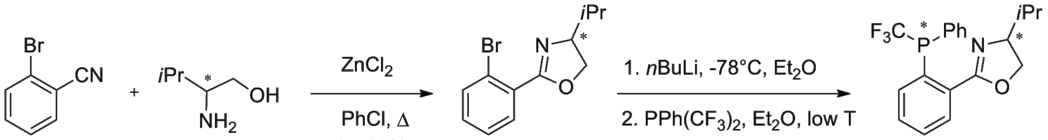
[1] G. Süss-Fink, *J. Organomet. Chem.*, **2014**, *751*, 2-19.
[2] B. Therrien, G. Süss-Fink, P. Govindaswamy, A. K. Renfrew, P. J. Dyson, *Angew. Chem. Int. Ed.*, **2008**, *47*, 3773-3776.
[3] A. Ignat, T. Lovasz, M. Vasilescu, E. Fischer-Fodor, C. B. Tatomir, C. Cristea, L. Silaghi-Dumitrescu, V. Zaharia, *Arch. Pharm. Chem. Life Sci.*, **2012**, *345*, 574-583.

Novel Trifluoromethylated P-Stereogenic Oxazoline Ligands

Rima Drissi[1], Antonio Togni[1] *

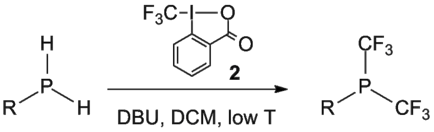
[1]ETH Zurich

Since the advent of chiral oxazoline ligands in asymmetric catalysis, the bidentate P-N ligand containing the phenyloxazoline (PHOX) backbone has been extensively used and has demonstrated its versatility in numerous asymmetric reactions [1]. Using this modular backbone, we sought to combine this exceptional chiral motif with a CF_3 group using a trifluoromethylation procedure developed in our group [2], thus introducing an additional stereogenic center, namely at the phosphorus atom. We initially achieved the synthesis of P-trifluoromethylated PHOX ligand **1** in two steps from the aminoalcohol in good yields.



1

The key step, namely nucleophilic substitution in order to introduce the trifluoromethylated phosphane on the aromatic backbone, was carried out using a bistrifluoromethylated phosphane prepared using our hypervalent iodine CF_3-transfer reagent **2** under low temperature conditions [3].



This straightforward synthetic pathway allows access to ligands with variation not only at the sidechain, but also at the phosphorus atom, which is particularly attractive as it allows modulation of the steric and electronic properties of the ligand in the last step.
After diastereomer separation, promising results are expected in metal-catalyzed asymmetric transformations using these novel ligands [4].

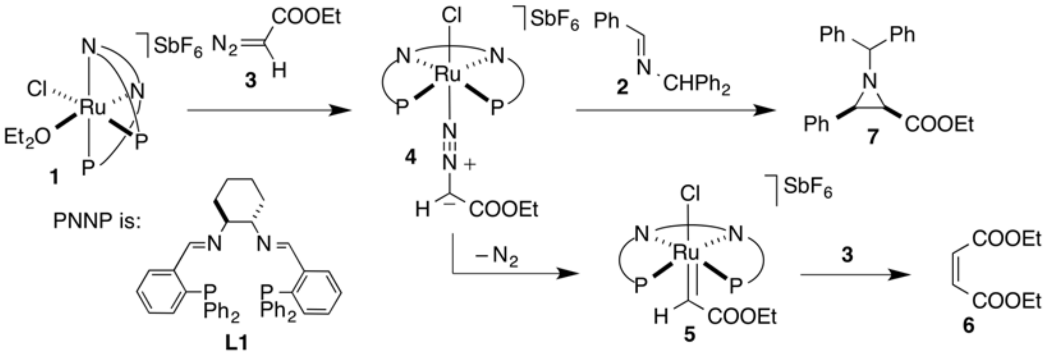
[1] G. C. Hargaden and P. J. Guiry, *Chem. Rev.* **2009**, *109*, 2505–50.
[2] J. Bürgler, Ph. D. Thesis Nr. 19513, ETH Zürich, **2011**, p.83.
[3] P. Eisenberger, I. Kieltsch, N. Armanino, and A. Togni, *Chem. Commun.* **2008**, 1575–7.
[4] Z. Hu, Y. Li, K. Liu, and Q. Shen, *J. Org. Chem.* **2012**, *77*, 7957–67.

Asymmetric Imine Aziridination with Ru/PNNP Catalysts

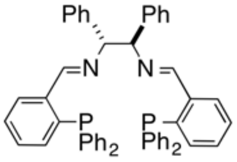
Joël Egloff[1], Antonio Mezzetti[1] *

[1]ETH Zurich

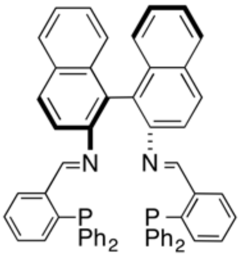
Our group has recently reported that [RuCl(OEt$_2$)(PNNP)]SbF$_6$ (**1**) catalyzes the asymmetric aziridination of imine **2** with ethyl diazoacetate (**3**) with the intermediacy of the diazoester complex **4** [1, 2]. Complex **4** either transfers carbene to the imine or decomposes to the carbene complex **5,** whose reaction with **3** gives diethyl maleate (**6**) and lowers the yield of aziridine **7**, which is obtained in 93% enantiomeric excess and 24% yield.



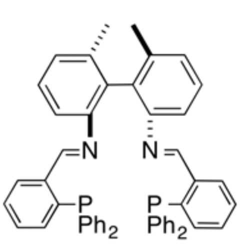
Sterically crowded diazoalkane complexes are more stable towards decomposition to the carbene complex (**5**) as shown by Milstein. Carbene formation requires dissociation of the diazoalkane and its recoordination in a η^2-C,N fashion [3]. Preliminary molecular modeling studies (Materials Studio 7), suggest that increasing the bulk on the imine backbone of the ligand inhibits the η^2-C,N coordination mode, which led us to investigate the ligands **L2** - **L4** for imine azirdination. First results with **L2** showed no improvement in the aziridine to maleate ratio. The BINAM backbone (**L3**) gives a higher ratio of aziridine to maleate, but shows a reduced activity. Further experimental studies of these ligands will be presented.



L2



L3



L4

[1] M. Ranocchiari, A. Mezzetti, *Organometallics*, **2009**, 28, 3611-3613.
[2] J. Egloff, M. Ranocchiari, A. Schira, C. Schotes, A. Mezzetti, *Organometallics*, **2013**, 32, 4690-4701.
[3] R. Cohen, B. Rybtchinski, M. Gandelman, H. Rozenberg, J. M. L. Martin, D. Milstein, *J. Am. Chem. Soc.*, **2003**, 125, 6532-6546.

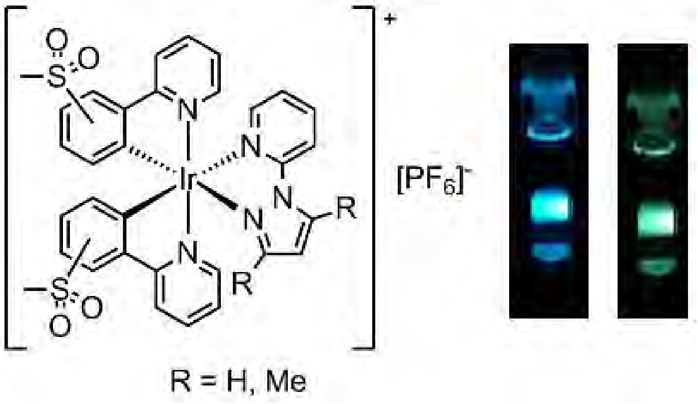
Fluorine-Free Blue and Green Emitting Iridium(III) Complexes for Light Emitting Electrochemical Cells

Cathrin Ertl[1], Catherine E. Housecroft[1], Edwin C. Constable[1] *

[1]University of Basel

Due to their excellent photophysical properties and easy colour tunability, iridium(III) complexes are very well suited for solid state lighting devices such as light emitting electrochemical cells (LEECs). Charged Ir(III) complexes containing two cyclometallating and one ancillary ligand already meet the requirement of mobile ions necessary for functional LEEC devices. New 2-phenylpyridine based cyclometallating ligands containing methylsulfonyl groups in various positions of the phenyl ring have been synthesised. Heteroleptic Ir(III) complexes of these ligands (Figure 1) have been prepared in order to investigate the influence of the sulfur substituents on the photophysical properties of the complexes.

In combination with electron-rich ancillary ligands such as 2-(1*H*-pyrazol-1-yl)pyridine, significant shifts of the emission maxima into the green and even blue region were achieved. If the new complexes prove to be stable under LEEC conditions, sulfone functional groups will become promising alternatives to fluorine substituents in the pursuit of stable and efficient blue/green emitters based on cyclometallated Ir(III) complexes.



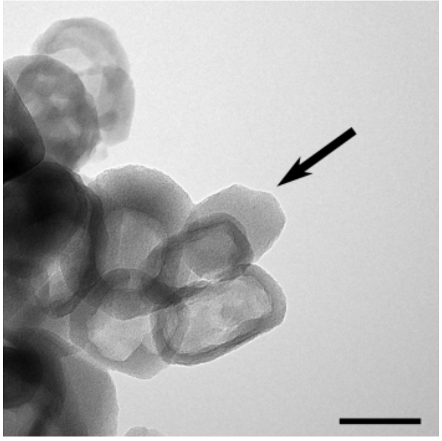
[1] Edwin C. Constable, Cathrin D. Ertl, Catherine E. Housecroft, Jennifer A. Zampese, *Dalton Trans.* **2014**, 43, 5343.

Dissolution of nano-size ZSM-5 crystals in alkaline solution: Identification of structural differences between crystals

Daniel Fodor[1], Jeroen A. van Bokhoven[1] *

[1]ETH Zurich

Zeolite properties heavily depend on synthesis conditions. One of these properties of ZSM-5 crystals is that a gradient exists regarding the distribution of aluminum sites [1, 2]. When using tetrapropylammonium (TPA) salts as template [3], enrichment of aluminum in the crystal rim is generally observed [4, 5]. By dissolving the silicon rich interior of aluminum zoned crystals in alkaline solution, one gets information about the distribution of aluminum. We reported the synthesis of hollow zeolites below 100 nm by leaching the crystals in 0.1 M NaOH solution at 80 °C [6]. During this process dissolution of the silicon rich interior takes place and at the same time aluminum rich species redeposit on the surface of the crystals. These deposits are removed by acid treatment in 0.1 M HCl at 65 °C. The base leaching was investigated in detail and we found evidence for the inhomogeneous dissolution of ZSM-5 crystals. The hollow formation occurs in a stepwise fashion, meaning that the crystals are either hollow or non-hollow and as time proceeds, the relative ratio of hollow crystals increase. We observed this phenomenon also in micrometer large commercial zeolites at various Si/Al ratios and even after one week of leaching intact and nearly intact crystals were visible in TEM images. The conclusion is that within a single synthesis batch, the individual zeolite crystals are dissimilar and display different properties.



The zeolites were investigated with TEM, SEM, XRD, AAS, solid state NMR and nitrogen physisorption.The figure shows a TEM micrograph of hollow ZSM-5 crystals (Scale bar: 50 nm). The arrow points to a crystal which was not attacked by NaOH.

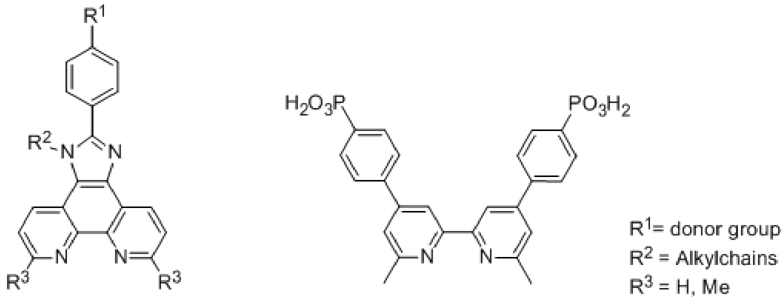
[1] R. von Ballmoos, W.M. Meier, *Nature*, **1981**, 289, 782.
[2] R.M. Dessau, E.W. Valyocsik, N.H. Goeke, *Zeolites*, **1992**, 12, 776.
[3] A. Tissler, P. Polanek, U. Girrbach, U. Müller, K.K. Unger, *Stud. Surf. Sci. Catal.*, **1989**, 46, 399.
[4] R. Althoff, B. Schulz-Dobrick, F. Schüth, K. Unger, *Microporous Mater.*, **1993**, 1, 207.
[5] N. Danilina, F. Krumeich, S.A. Castelanelli, J.A. van Bokhoven, *J. Phys. Chem. C*, **2010**, 114, 6640.
[6] D. Fodor, L. Pacosová, F. Krumeich, J.A. van Bokhoven, *Chem. Commun.*, **2014**, 50, 76.

New Phenanthroline Copper Dyes and their Application in Dye Sensitized Solar Cells

Sebastian Fürer[1], Edwin C. Constable[1], Catherine E. Housecroft[1] *

[1]University of Basel

Dye sensitized solar cells (DSSCs) are of great interest as a valuable alternative to commercial silicon solar cells. Copper(I)-based dyes have shown promising performances in DSSCs and are therefore interesting candidates for low-cost solar cells [1]. By exchanging the commonly used I^-/I_3^- mediator by $Co^{2+/3+}$, higher open circuit voltages and performances can be achieved. Recombination and mass transport issues that have previously been shown to be limiting factors for cobalt electrolytes can be avoided by attaching sterically demanding alkyl chains to the dyes and by adjusting the pore and particle size of the TiO_2 semiconductor [2,3]. Recently, cobalt-based electrolytes have been successfully implemented in copper DSSCs [4].



1 2

Different donor groups were introduced at the R^1 position of L1 and the respective homoleptic Cu(I) complexes applied in solar cells. Heteroleptic copper(I) complexes were synthesized on the TiO_2 semiconductor by exchanging homoleptic copper(I) complexes $[Cu(L1)_2][PF_6]$ with surface-bound anchoring ligand 2 (Fig. 1). The influence on the performance of the alkyl chain length of the heteroleptic complexes as well as the necessity of methyl groups in the 2 and 9 position of the phenanthroline unit is being studied in DSSCs using optimized I^-/I_3^- and $Co^{2+/3+}$ electrolytes.

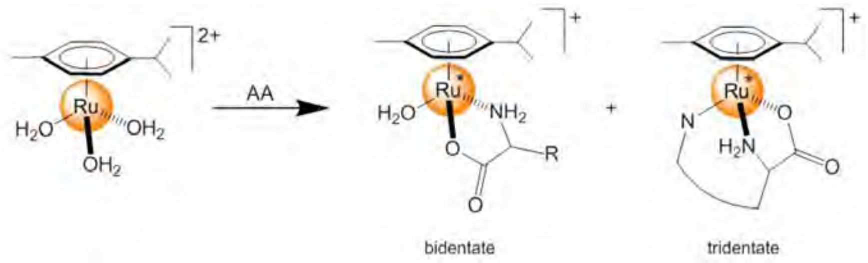
[1] Biljana Bozic-Weber, Sven Y. Brauchli, Edwin C. Constable, Sebastian O. Fürer, Catherine E. Housecroft, Iain Wright, *Phys. Chem. Chem. Phys.*, **2013**, 15, 4500-4504.
[2] Aswani Yella, Hsuan-Wei Lee, Hoi N. Tsao, Chenyi Yi, Aravind K. Chandiran, Mohammad K. Nazeeruddin, Eric W. –G. Diau, Chen-Yu Yeh, Shaik M. Zakeeruddin, Michael Gratzel,*Science*, **2011**, 334, 629-634.
[3] Sandra M. Feldt, Elizabeth A. Gibson, Erik Gabrielsson, Licheng Sun, Gerrit Boschloo, Anders Hagfeldt, *J. Am. Chem. Soc.*, **2010,** 132, 16714-16724.
[4] Biljana Bozic-Weber, Edwin C. Constable, Sebastian O. Fürer, Catherine E. Housecroft, Lukas J. Troxler, Jennifer Zampese, *Chem. Comm.*, **2013**, 49, 7222-7224.

Synthesis, characterization and cytotoxicity of (η^6-p cymene) ruthenium(II) complexes of α-amino acids

Julien Furrer[1], Lydia Paul[1], Bruno Therrien[2]

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

Arene ruthenium complexes of a-amino acids, obtained by mixing aqueous solutions of $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ in the presence of $AgCF_3SO_3$with various amino acids, have been studied at 37 °C using NMR spectroscopy and electrospray ionization mass spectrometry (ESI-MS). Presumably, complexes with the general formula $[(\eta^6\text{-}p\text{-cymene})Ru(AA)_2]^{n+}$ and bridged complexes with the general formula $[((\eta^6\text{-}p\text{-cymene})Ru)_2(\mu\text{-}AA)_2(\mu\text{-}OH)]^+$ are formed together with the expected bi- and tridentate chelate complexes. All complexes are highly cytotoxic, with IC_{50} values ranging from 0.16 to 19.8 µM. Interestingly, all complexes exhibit selectivity towards A2780 versus A2780cisR cells, indicating a distinct mechanism of action, different from that of many previously reported cytotoxic ruthenium complexes. No direct correlation between the kinetics of formation and the cytotoxicity could be evidenced, suggesting that other physico-chemical parameters such as the stability and ligand exchange kinetics may play an important role in their biological activity [1].



[1] Folake A. Egbewande , Lydia E.H. Paul , Bruno Therrien , Julien Furrer , *Eur. J. Inorg. Chem.* **2014,** 2014, 1174-1184.

Reducing Aggregation of Silicon Nanoparticles by Shell Designing.

Almudena Gallego[1], Marcel Mayor[2] *

[1]University of Basel, [2]University of Basel

Silicon nanoparticles (Si NPs) are in the focus of interest due to its tunable photoluminescence, its compatibility with current silicon-based electronic devices and its low toxicity. Many works are centered on stabilizing and gaining size-control by ligand coating, usually with long alkylchains [1]. Although it is a good strategy which also increases the solubility and thus makes its processability easy, this approach usually leads to aggregation of the NPs. It is not desirable for experiments with individual NPs, which could lead on the better understanding and its possible application in nanodevices. Thus, we prepared and fully characterized non-aggregated Si NPs by using perfluoroalkyl/aryl ligands as coating (figure 1).

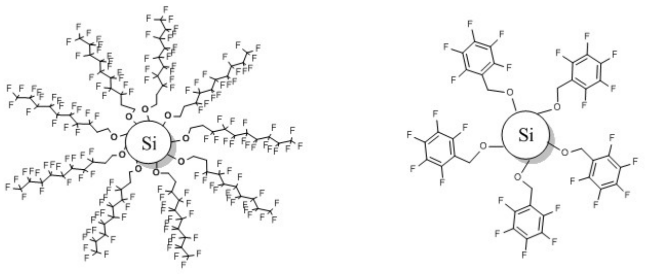


Figure 1

Perfluorinated ligands reduce the delocalized electron density on the carbon frame of the ligand and thus its polarizability and intermolecular interactions. It leads to a high-monodispersed multifuctional nanomaterial suitable for subsequent quantum experiments as the sublimation temperature can thus be shifted to below the decomposition temperature [3]. The study of the quantum effects of isolated fluorescence nanoparticles is a challenge which could lead on developing new fluorescent nanomaterial as a platform for energy and/or biological applications.

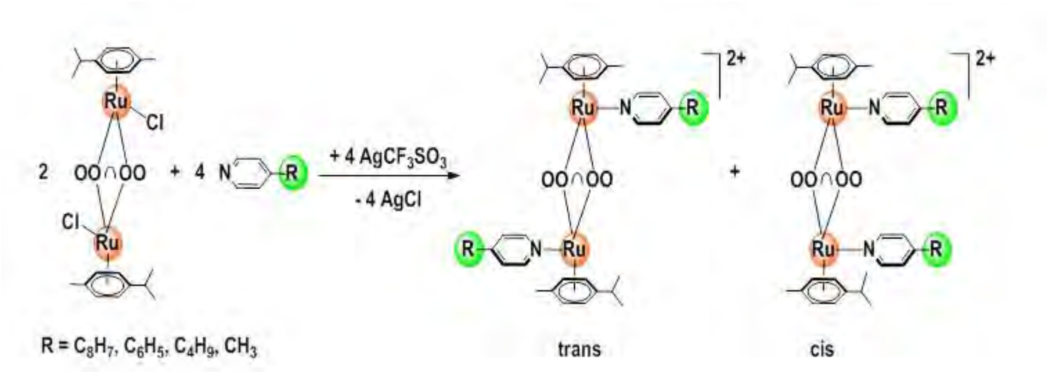
[1] [a] Priolo, F. *et al., Nature*, **2000**, 408, 440−444. [b] Bard, A. J. *et al., Science,* **2002**, 296, 1293−1297. [c] Lieber, C. M. *et al., Science*, **2006**, 313, 1100−1104. [d] Lauhon, L. J. *et al., Nat. Nanotechnol.*, **2008**, 3, 168−173. [e] He, Y. *et al., ACS Nano*, **2012**, 6, 2582−2590.
[2] [a] H. Hajjaji *et al. Nanoscale Res. Lett.* **2014**, 9, 94. [b] Andrew Heintz *et al.,Adv. Mater.* **2007**, 19, 3984
[3] Mayor, Marcel *et al., Nature Physics*, **2007**, 3, 711-715.

Arene ruthenium metalla-assemblies: A mechanistic study

Amine Garci[1], Gajendra Gupta[1], Claudio Dalvit[1], Bruno Therrien[1] *

[1]University of Neuchatel

Two main strategies have been employed to generate metalla-assemblies from arene ruthenium complexes; by mixing tritopic ligands composed of a bidentate and a monodentate ends with “naked” arene ruthenium corners [1], and by forming stable dinuclear arene uthenium clips prior to the final assembly step involving various connectors [2]. Both methods have successfully produced esthetical architectures as well as metalla-assemblies with functions. In recent years, we have extensively used the second strategy to prepare metalla-assemblies with biological functions [3]. The combination of dinuclear arene ruthenium clips with bidentate, tridentate and tetradentate connectors have generated metalla-rectangles, metalla-prisms and metalla-cubes. These two- and three-dimensional assemblies are well defined and they have been fully characterized. Several examples possess cavities large enough to encapsulate guest molecules, thus giving rise to carceplexes or host-guest systems [4]. However, the exact nature of the intermediate species leading to the final metalla-assemblies remains unknown.



Herein, we present the synthesis and characterization of several dinuclear arene ruthenium complexes as models of the intermediate species formed during the supramolecular assembly of arene ruthenium metalla-rectangles. The kinetic and thermodynamic aspects dictating the formation of these dinuclear complexes have been studied in solution using NMR spectroscopy, thus giving valuable answers of the probable mechanism leading to the formation of arene ruthenium metalla-assemblies.

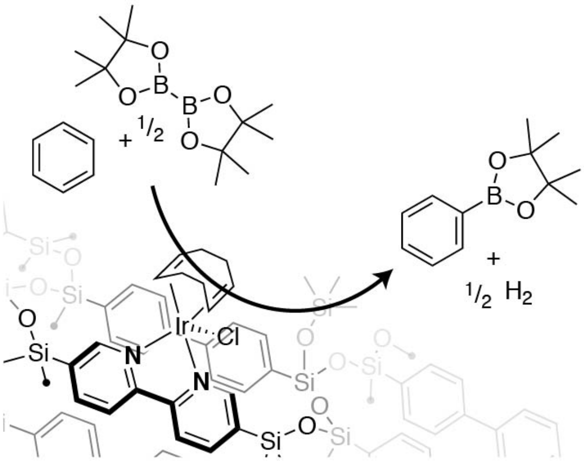
[1] L.-M. Lehaire, R. Scopelliti, L. Herdeis, K. Polborn, P. Mayer, K. Severin, *Inorg. Chem.,* **2004**, 43, 1609-1617
[2] H. Yan, G. Süss-Fink, A. Neels, H. Stoeckli-Evans, *J. Chem. Soc., Dalton Trans*., **1997**, 4345-4350.
[3] F. Schmitt, J. Freudenreich, N. P. E. Barry, L. Juillerat-Jeanneret, G. Süss-Fink, B. Therrien, *J. Am. Chem. Soc.,* **2012**, 134, 754-757.
[4] B. Therrien, G. Süss-Fink, P. Govindaswamy, A. K. Renfrew, P. J. Dyson, *Angew. Chem. Int. Ed.,* **2008**, 47, 3773-3776.

C–H Activation with Iridium(I) on Bipyridine-Containing Periodic Mesoporous Organosilicas

Wolfram R. Grüning[1], Georges Siddiqui[1], Olga V. Safanova[2], Christophe Copéret[1] *

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

Periodic Mesoporous Organosilicas (PMO) are hybrid organic inorganic materials with a high density of organic linkers in the walls.[1–4] For aromatic groups supramolecular ordering is observed to give crystal-like structures. [5]



We describe the preparation of a new PMO containing bipyridine moieties as ligands. The material exihibits a high surface area and ordering with in the pore walls. After passivation and functionalization with $[IrCl(COD)]_2$ we obtain a material with molecularly defined iridium surface complexes.
The materials catalyze the reaction of arenes with diboranes to aryl boronic acids with identical activity and selectivity as their homogenous analogues.[6]

[1] T. Asefa, et. al., *Nature* **1999**, *402*, 867
[2] B. J. Melde, et. al., *Chem. Mater.* **1999**, *11*, 3302
[3] S. Inagaki, et. al., *J. Am. Chem. Soc.* **1999**, *121*, 9611
[4] F. Hoffmann, M. Fröba, *Chem. Soc. Rev.* **2011**, *40*, 608
[5] S. Inagaki, et. al., *Nature* **2002**, *416*, 304
[6] W. R. Grüning, et. al.. *Adv. Synth. Catal.*, **2014**, *356*, 673
For work on closely-related materials published at the same time see:
[7] M. Waki, et. al., *J. Am. Chem. Soc.* **2014**, *136*, 4003

News on Quasi-One-Dimensional Antiferromagnetic Chain Compounds

Nora Hänni[1], Mattia Mena[2], Christian Rüegg[2], Karl Krämer[1] *

[1]University of Berne, [2]Paul Scherrer Institute, Villigen

Recent research on Co^{2+}- and Ti^{2+}- based 113-halides of the diverse family of hexagonal perovskite type compounds would teach us that old compounds might still raise new questions. The long-known $RbCoCl_3$ [1-2] not only turns out to be a good antiferromagnetic Ising chain model system [3], but also has a complex magnetic structure with an interesting temperature dependence as we learned from a series of neutron diffraction measurements performed at the Swiss Spallation Neutron Source (SINQ) at Paul Scherrer Institut (PSI) [4]. Subsequent studies revealed that the magnetic structure changes in a transverse magnetic field. The critical field is accessible using state-of-the-art magnets both at neutron scattering facilities and in Physical Property Measurement Systems (PPMS). Figure 1 shows the partial suppression of the three-dimensional magnetic order in $RbCoCl_3$ in transverse fields as high as 13 T.

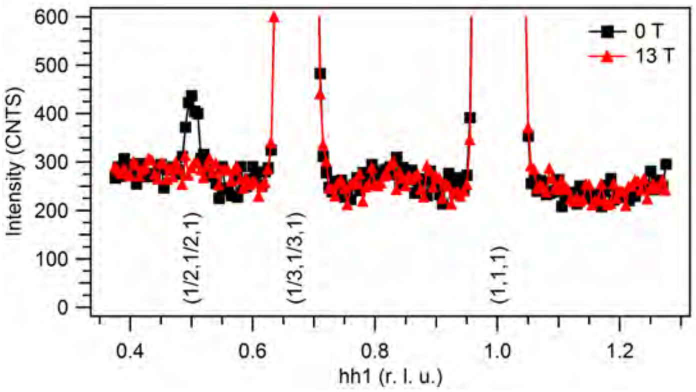


Fig. 1. Magnetic field dependence of the magnetic structure of $RbCoCl_3$. The different characteristic magnetic Bragg peaks are shown for 0 and 13 T, as they were measured on a single crystal sample on the triple axis spectrometer EIGER at SINQ, PSI. The intensity scale is adjusted to the weak magnetic peak at (1/2,1/2,1) which is suppressed in a 13 T transverse magnetic field.

Related to that, we are investigating $RbTiCl_3$ and $CsTiCl_3$. Not much is known about the magnetic behavior of Ti^{2+}-based compounds [5-6]. First magnetic property measurements on both of the above compounds reveal strong antiferromagnetic interactions between neighboring Ti^{2+} ions in the chains. But there is no feature of magnetic order in three dimensions so far. This question is due to be answered conclusively by the results of ongoing neutron powder diffraction measurements at SINQ, PSI.

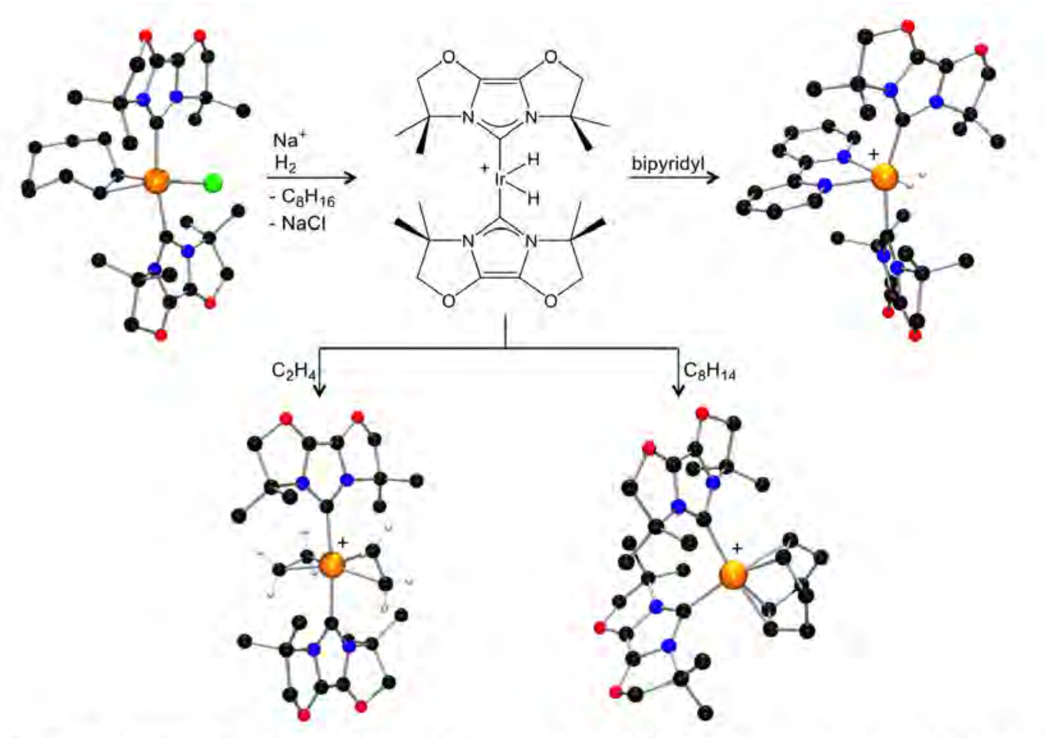
[1] Å. Engberg, H. Soling, *Acta chem. Scand.* **1967**, 21, 168.
[2] F. Matsubara, S. Inawashiro, H. Ohhara, *J. Phys. Condens. Mat.* **1991**, 3, 12, 1815.
[3] M. Mena, E. Hirtenlechner, N. Hänni, et al., in preparation.
[4] N. Hänni, D. Sheptyakov, et al., *Phys. Rev. B*, to be submitted.
[5] G. Meyer, T. Gloger, J. Beekhuizen, *Z. Anorg. Allg. Chem.* **2009**, 635, 1497.
[6] L. Jongen, T. Gloger, J. Beekhuizen, G. Meyer, *Z. Anorg. Allg. Chem.* **2005**, 631, 582.

Synthesis and reactivity of bis-IBioxMe$_4$ iridium complexes

Simone Hauser[1], Adrian Chaplin[1] *

[1]University of Warwick, Department of Chemistry, Gibbet Hill Road, Coventry, CV4 7AL, UK

N-heterocyclic carbenes (NHC) are a remarkable class of carbon-based ligand in organometallic chemistry.[1] These ligands form strong bonds with transition metals and simple and efficient synthetic protocols allow for facile variation of their electronic and steric properties. Notably, Glorius and co-workers have recently described a series of bioxazoline derived NHC ligands (IBiox) that are characterised by high conformational rigidity,[2] thus allowing to access low-coordinate transition metal complexes.[3] Given the growing use of NHC complexes in transition metal catalysed reactions, the organometallic chemistry of such coordinatively unsaturated NHC species has topical mechanistic importance.[4]



Scheme 1. Reactivity of bis-IBioxMe$_4$ iridium complexes ($[BAr^F{}_4]^-$ anions are omitted for clarity).

As part of our research focusing on the organometallic chemistry of reactive group 9 complexes, in this report we describe the synthesis and reactivity of iridium complexes containing the conformationally rigid IBioxMe$_4$ ligand, derived from $[Ir(IBioxMe_4)_2(COE)Cl]$ (Scheme 1).

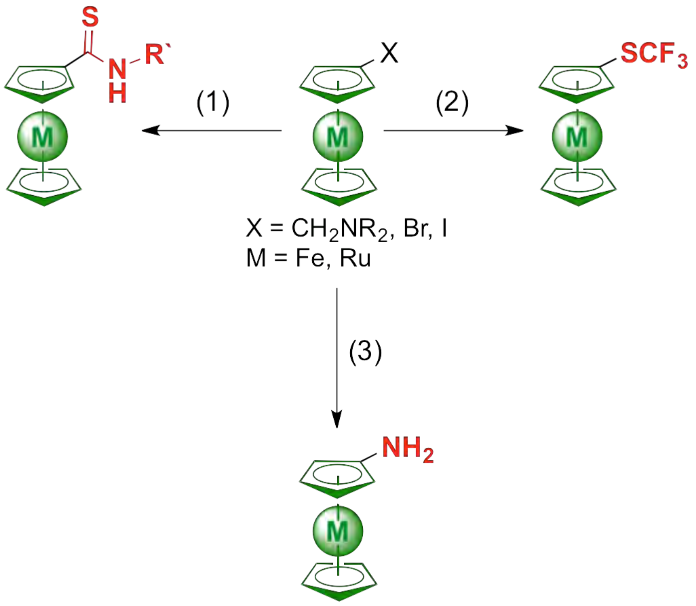
[1] F. Ekkehardt Hahn, Mareike C. Jahnke, *Angew. Chem. Int. Ed.,* **2008**, 47, 3122-3172. [2] Gereon Altenhoff, Richard Goddard, Christian W. Lehmann, Frank Glorius,*J. Am. Chem. Soc.,* **2004**, 126, 15195-15201. [3] Adrian B. Chaplin, *Organometallics,* **2014**, 33, 624-626. [4] Silvia Díez-González, Nicolas Marion, Steven P. Nolan, *Chem. Rev.,* **2009**, 109, 3612-3676.

Novel Straightforward Synthesis of Biologically Relevant Metallocene Derivatives

Jeannine Hess[1], Malay Patra[1], Anna Leonidova[1], Vanessa Pierroz[1], Stefano Ferrari[1], Gilles Gasser[1] *

[1]University of Zurich

In the last decades, several bioactive metallocenes have been reported as promising drug candidates. Such small pharmacophores can indeed play a pivotal role for drug uptake, intracellular localization and can hence determine the biological effect of a drug molecule. The facile and efficient synthetic modification of metallocenes is therefore a crucial tool for the construction of organometallic drug candidates. Our group has recently reported three straightforward and effective synthetic procedures for the derivatization of such metallocenes derivatives: (1)[1] efficient syntheses of various metallocenyl thioamides via a single-step three-component condensation; (2)[2] a mercury-free synthesis for trifluoromethylthio-substituted metallocenes; (3)[3,4] a facile "green-chemistry" preparation of aminometallocenes.



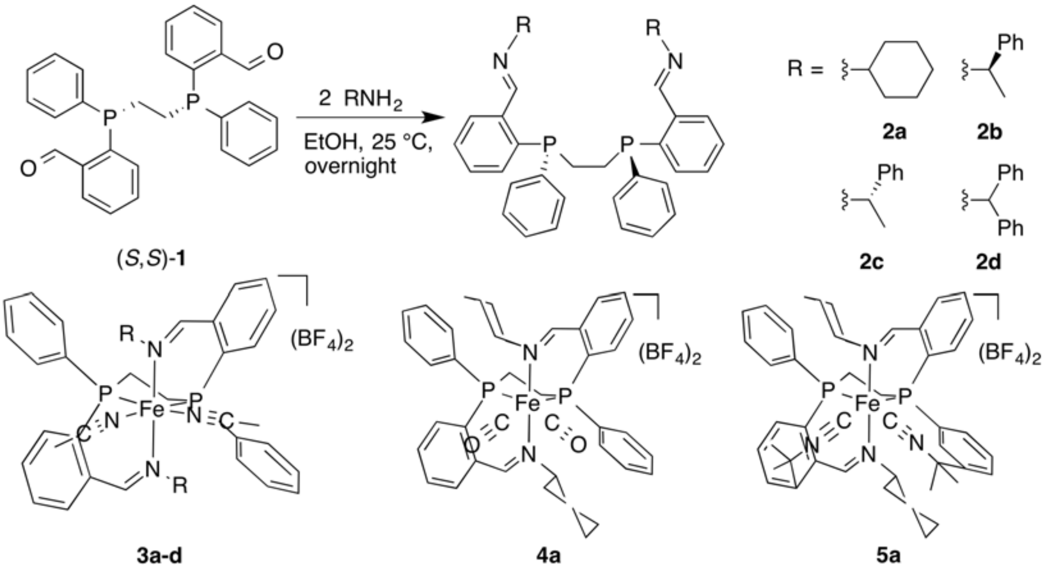
[1] Malay Patra, Jeannine Hess, Sandro Konatschnig, Bernhard Spingler, Gilles Gasser, *Organometallics*, **2013**, 32, 6098-6105.
[2] Jeannine Hess, Sandro Konatschnig, Sandra Morard, Vanessa Pierroz, Stefano Ferrari, Bernhard Spingler, Gilles Gasser, *Inorganic Chemistry*, **2014**, 53, 3662-3667.
[3] Anna Leonidova, Tanmaya Joshi, David Nipkow, Angelo Frei, Johanna-Elena Penner, Sandro Konatschnig, Malay Patra, Gilles Gasser, *Organometallics*, **2013**, 32, 2037-2040.
[4] Gilles Gasser, Anna Leonidova, Tanmaya Joshi, David Nipkow, Angelo Frei, Johanna-Elena Penner, Sandro Konatschnig, Malay Patra, *Eur. Pat. Appl.*, **2013**, EP13157319.

P-Stereogenic Open-Chain NPPN Fe(II) Catalysts for the Strecker Reaction of Azomethine Imines

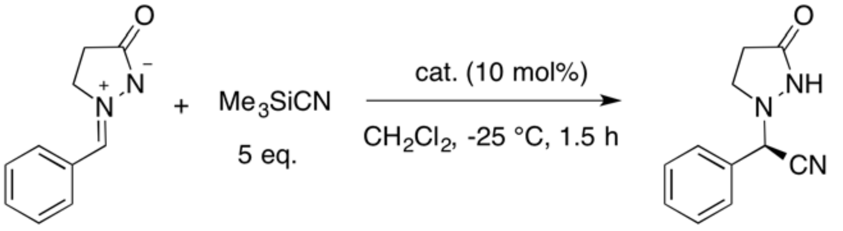
Raffael Huber[1], Antonio Mezzetti[1] *

[1]ETH Zurich

Our group has recently prepared enantiomerically pure dialdehyde (*S*,*S*)-**1**, which gives the C_2-symmetric NPPN ligands **2a-d** by condensation with a variety of amines. These ligands smoothly react with $[Fe(OH_2)_6](BF_4)_2$ in acetonitrile at 25 °C to give the diamagnetic complexes **3a-d**. They feature a *cis*-α geometry, as unambiguously determined by X-ray crystallography and NMR spectroscopy. Complex **3a** was converted to dicarbonyl complex **4a** using CO gas, and to **5a** by addition of *tert*-butylisonitrile.



The remarkable azaphilicity of the systems was exploited in the enantioselective Strecker-type addition of trimethylsilyl cyanide to azomethine imines. As a previous report uses a cinchona-derived organocatalyst [1], this is the first metal-catalyzed example.



cat.	%*ee*
3a	22
3b	10
3c	2
3d	2
4a	11

[1] Nai-Kai Li, Zhao-Min Liu, Xiao-Fei Huang, Jin-Xin Zhang, Xiang Chen, Yong Wang, Xing-Wang Wang, *RSC Adv.*, **2013**, 3, 9154-9157.

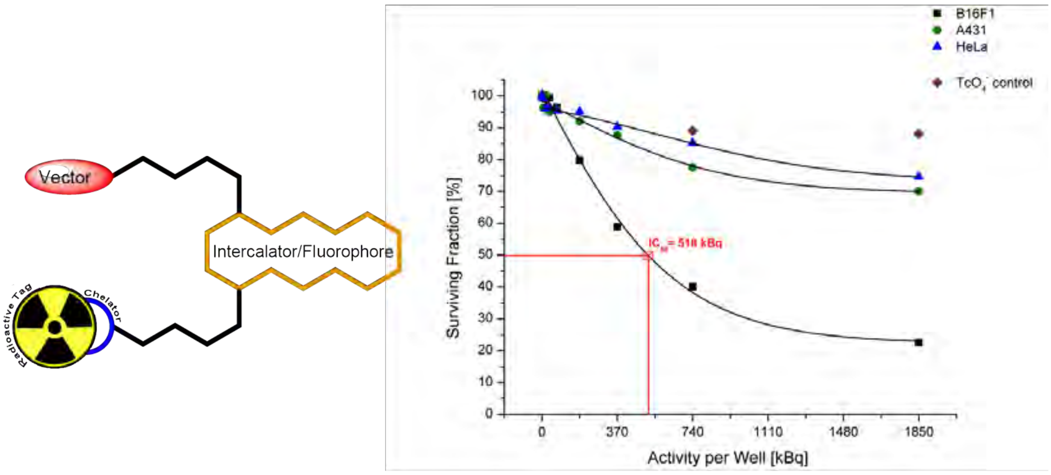
Towards Radionuclide Therapy with Doxorubicin Conjugated Tc-99m Compounds

Sebastian Imstepf[1], Roger Alberto[1] *

[1]University of Zurich

Certain organic small molecules, usually planar and extended π-conjugated systems are known to form stable adducts with DNA of various forms. Frequently encountered modes of interaction are groove binding and intercalation. Common to both modes is the proximity of the small molecule to its target.[1]

We want to take advantage of the emission of Auger electrons from Tc-99m to induce double strand breaks (DSBs) in the DNA. Since Auger electrons are densely ionizing, this process can inflict irreparable DSBs. Auger electrons of Tc-99m have initial energies in the eV-range, hence their entire energy is deposited within an ultra-short length of their origin.[2] In order to make use of the Auger electron activity to induce DSBs, the decay needs to happen right at the target – the DNA. To exploit this feature we want to apply intercalators to hold the nuclide firmly in the vicinity of its target, for the time of the radioactive decay.



A small library of different Doxorubicin derivatives was synthesized and the *in vitro* properties of the corrresponding Re complexes studied. Therafter, the derivatives were successfully labelled with Tc-99m, purified (RCP 95%) and upon formulation incubated with different cancer cell lines to assess their **radiocytotoxicity**.

Especially one of the derivatives exhibited a promising cytotoxicity profile wich can be assigned to the damage inflicted by the Auger electron activity of Tc-99m only.

With our concept we confirm that Re/Tc99m is indeed a theragnostic pair and take yet another step towards radionuclide therapy with Tc-99m, in theory a highly advantageous form of treatment: maximal damage at the ultra-short range while sparing systemic tissue dose.

[1] Zeglis, B.M.; Pierre, V.C.; Barton, J.K., *Chem. Commun.* **2007**, 44, 4565.
[2] Tavares, A.A.S., Tavares, J.M., *Int. J. Radiat. Biol.*, **2010**, 4, 261.

Ceria- and Perovskite- Based Materials for Solar Thermochemical Two-Step CO_2-Splitting

Roger Jacot[1], Jonathan R. Scheffe[2], Konstanze Hahn[1], Aldo Steinfeld[3], Greta R. Patzke[1] *

[1]University of Zurich, [2]ETH Zurich, [3]ETH Zurich and Paul Scherrer Institute, Villigen

In order to address the constant decreasing of natural resources and to solve environmental issues, new alternative and renewable energies are required. In this highly competitive context, solar energy is a powerful and inexhaustible resource, which is already used for devices, such as photovoltaic cells to convert solar energy into electricity. We herein report the investigation of new transition-metal oxide materials for the thermo-chemical water and CO_2 splitting processes via two step redox reactions.[1] In the first step, the transition-metal oxide is reduced at around 1500°C and oxygen is released (Eq. (1)). In a second step, the reduced transition-metal oxide reacts at lower temperature with either H_2O or CO_2 to produce H_2 or CO (Eq. (2a and 2b)).

$$MO_x \xrightarrow{1500°C} MO_{x-\delta} + \frac{\delta}{2}O_2 \qquad (1)$$

$$MO_{x-\delta} + H_2O \xrightarrow{1000°C} MO_x + H_2 \qquad (2a)$$

$$MO_{x-\delta} + CO_2 \xrightarrow{1000°C} MO_x + CO \qquad (2b)$$

The produced CO and H_2, also called syngas, can be converted into fuels by the Fischer-Tropsch synthesis.

It has been shown that the ceria (CeO_2) and perovskite materials are among the best candidates for this thermochemical redox process.[2] Interestingly, we have recently demonstrated that ceria can be doped with Hf^{4+} and Zr^{4+} to improve the performance of the thermochemical redox process with $Ce_{0.9}Hf_{0.1}O_2$ displaying the highest efficiency in CO_2 reduction.[3] To further improve and systematically screen materials, we have performed DFT calculations on oxygen vacancy formation energy and compared these results with the reduction behavior of the corresponding doped ceria containing tetravalent cations from thermogravimetric (TGA) analysis. We postulate that the vacancy formation energy is directly related to the ionic radius of the dopant, leading to an optimum where the oxygen vacancy formation energy is large enough to efficiently oxidize the ceria, but sufficiently low that reduction occurs under favorable conditions (e.g. lower temperatures). Analytical characterization is performed (Raman, XRD, SEM etc.) before and after thermochemical cycling to better understand crystallographic and morphological changes associated with cycling.

[1] W.C. Chueh, C. Falter, M. Abbott, D. Scipio, P. Furler, S.M. Haile, A. Steinfeld, *Science* **2010**, 330,1797-1800.
[2] J.R. Scheffe, D. Weibel, A. Steinfeld, *Energy Fuels* **2013**, 27, 4250-4257.
[3] J.R. Scheffe, R. Jacot, G.R. Patzke, A. Steinfeld, *J. Phys. Chem. C* **2013**, 117,24104-24114.

Coordination of metal ions by the two cysteine-rich domains of the plant metallothionein-3 from Musa acuminata (banana)

Jovana Jakovleska[1], Eva Freisinger[1] *

[1]University of Zurich

Metallothioneins (MTs) are a superfamily of small cysteine-rich proteins involved in metal ion homeostasis and detoxification. As shown previously by our group the MT3 form expressed in the banana tree, baMT3, has the ability to coordinate three divalent metal ions in two separate domains [1]. To obtain more precise information about the metal ion coordination properties and the structures formed, we are performing metal ion binding studies with the two separately prepared domains N- and C-terminal domains. The work presented here includes the study of the complexes formed in presence of Zn(II), Cd(II), Cu(I), and Ag(I) ions.

In addition we will present also our 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, H46C-baMT3, thereby studying the relevance of non-cysteine residues for the metal ion binding properties of MTs.

Studies are complemented with potentiometric pH titrations allowing the analysis of the thermodynamic stabilities of the formed metal clusters and of the metallation process.

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

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

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

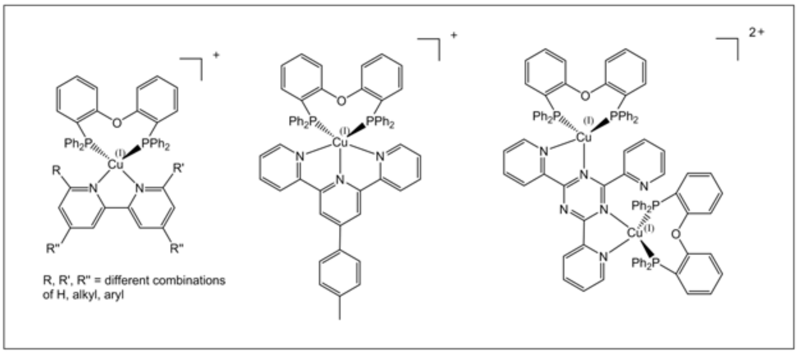
Sarah Keller[1], Edwin C. Constable[1], Catherine E. Housecroft[1] *

[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.

This poster will present new results on the synthesis and investigation of light-emitting copper(I) complexes: For LECs, charged complexes with $[PF_6]^-$ or other counter ions are required, whereas OLEDs also work with neutral, uncharged compounds.

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. In figure 1 below, an overview of the copper compounds which were synthesized and tested on their suitability for light-emitting systems in our group are illustrated. The 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.



[1] R. D. Costa, D. Tordera, E. Orti, H. J. Bolink, J. Schönle, S. Graber, C. E. Housecroft, E. C. Constable, J. Zampese, “Copper(I) complexes for sustainable light-emitting electrochemical cells”, *J. Mater. Chem.*, Vol. 21, (2011), pp. 16108 - 16118.

Coordination polymer or discrete complex? – The change of assembly in ZN(OAc)$_2$ complexes combined with a series of substituted 4,2':6',4''-terpyridine ligands

Maximilian Klein[1], Jennifer A. Zampese[1], Catherine E. Housecroft[1], Edwin C. Constable[1] *

[1]University of Basel

Coordination polymers of Zn(OAc)$_2$ with 4' substituted 4,2':6',4''-terpyridines (4,2':6',4''-tpy) have been reported in literature and normally 1-D polymer chain are obtained[1]. Ligand 4'-(4-dodecyloxyphenyl)-4,2':6',4''-tpy (**1**) has a long alkoxy chain and with Zn(OAc)$_2$ a discrete complex is obtained[2]. For a proper investigation of this change in assembly, ten complexes of Zn(OAc)$_2$ with 4'-(4-alkoxyphenyl)-4,2':6',4''-terpyridines from methoxy to decoxy have been synthesized. Their packing interactions have been investigated by X-ray diffraction and compared with the structure of [Zn$_2$(OAc)$_4$(**1**)]. Six have grown as one dimensional coordination polymers and 4 discrete complexes have been obtained. A change from polymer to discrete complex occurs between [Zn$_2$(OAc)$_4$(**2**)] (Figure 1b) and [Zn$_2$(OAc)$_4$(**3**)] (Figure 1c) and explanations for this phenomenon are given in this work.

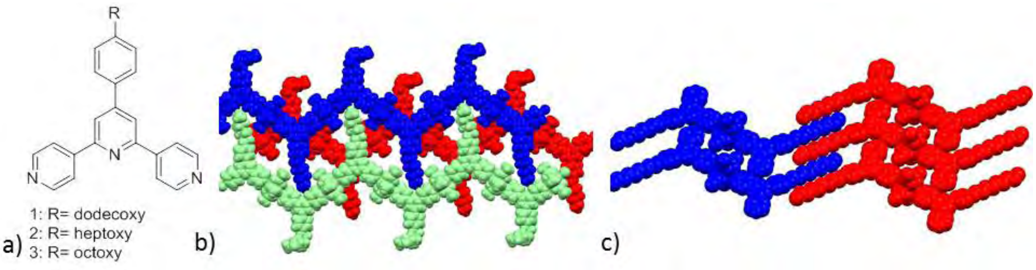


Figure 1: a) 4' substituted 4,2':6',4''-terpyridines. b) Coordination polymer arrangement in [Zn$_2$(OAc)$_4$(**2**)]. c) Assembly of the discrete complex [Zn$_2$(OAc)$_4$(**3**)].

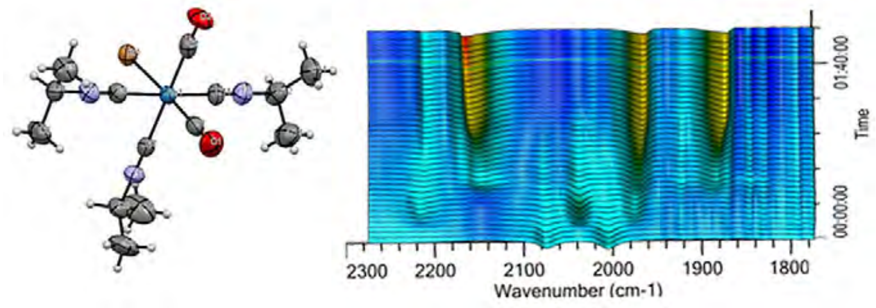
[1] C. E. Housecroft, *Dalton Trans.* **2014**, *43*, 6594.
[2] E. C. Constable, G. Zhang, C. E. Housecroft, J. A. Zampese, *Inorg. Chem. Commun.* **2012**, *15*, 113-116.

Carbonyl Isocyanide Complexes of Rhenium and Manganese: A Redox Struggle towards CORMs

Emmanuel Kottelat[1], Fabio Zobi[1] *

[1]University of Fribourg

CO releasing molecules (CORMs) are widely used as therapeutic agent. Medical applications of CORMs rage from the treatment of inflammations or microbial infections to cardiovascular diseases and organ transplantation and preservation [1]. CORMs can release CO in the body under controlled conditions and permit to avoid the toxicity of CO gas [2]. We describe in this contribution the synthesis and characterization of novel type of CORMs based on Re and Mn complexes with isocyanide ligands.



An experimental and theoretical approach is followed in the substitution reactions leading to the complexes. In-situ liquid IR spectroscopy revealed clean conversions from starting materials to products, usually via a single intermediate (Fig. 1, right). Structures were determined by mass spectroscopy, NMR and X-ray crystal structure determination. DFT calculations were then carried out in order to gain useful insights in the redox-coupled substitution mechanisms. Finally, CO releasing properties are tested by means of the myoglobin assay.

[1] Roberto Motterlini, Leo Otterbein, *Mat. Rev. Drug Discovery*, **2010**, 9, 728 - 743.
[2] Roger Alberto, Roberto Motterlini, *Dalton Trans*, **2007**, 1651- 1661.

New dyes for dye sensitized solar cells application

Angelo Lanzilotto[1], Edwin C. Constable[1], Catherine E. Housecroft[1] *

[1]University of 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. In fact 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 centered transitions in the UV, while complexation to a metal ion adds, for example, a metal to ligand charge transfer band, typically in the visible. This work will report new ligands, the electronic properties of which can be easily tuned according to the metal cation to which it complexes. By using mixtures of complexes in a dye, it should be possible improve the photoresponse of the dye, ensuring absorption of photons over the largest energy range possible.

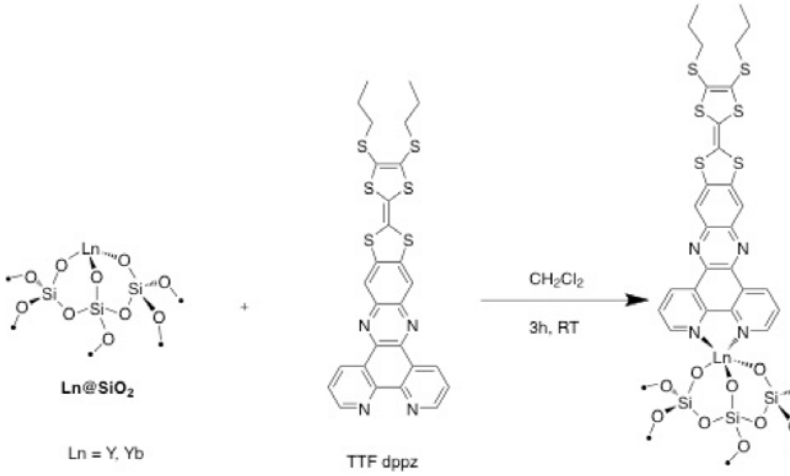
Another challenging target is the efficient anchoring of new dyes to the n-type semiconductor in the DSC. Once in the excited state, the dye should perform a charge separation through an electron transfer to the titania layer. It is crucial to delay the charge recombination, increasing the electron mobility to the anode and reducing the oxidized dye so that it could no longer accept the electron back.

Silica nanoparticles doped with well-defined TTF dppz ligated Yb(III) centers.

Giuseppe Lapadula[1], Shi-Xia Liu[2], Silvio Decurtins[2], Olivier Maury[3], Christophe Copéret[1] *

[1]ETH Zurich, [2]University of Berne, [3]ENS Lyon

Silica nanoparticles absorbing and emitting in the near infrared are important for bioimaging[1], (λ_{abs} = 700 nm, λ_{em} = 983 and 1050 nm). Those particles were synthesized by doping the surface of 12 nm amorphous silica nanoparticles via surface organometallic chemistry approach,[2] with more than 300 4’,5’ - bis(propylthio)tetrathiafulvenyl[i]dipyrido-[3,2-a:2’,3’-c]phenazine (TTF-dppz)[3] Yb(III) complexes. The system was fully characterized using various spectroscopic techniques (IR, NMR, UV-vis, luminescence and lifetime). To get further insights about the structure of the Yb (III) complexes on the surface, molecular equivalents were synthesized and characterized with the same spectroscopic techniques, and in addition with single crystal X – ray crystallography. Once the properties and the structure of the surface compounds were established the concept of the surface doping was extended to a more defined support and the same synthetic strategy was followed for silica nanospheres with a diameter of ca. 100 nm. Those particles have similar photophysical properties which opens the possibility to apply the same strategy to other silica supports with different morphologies.



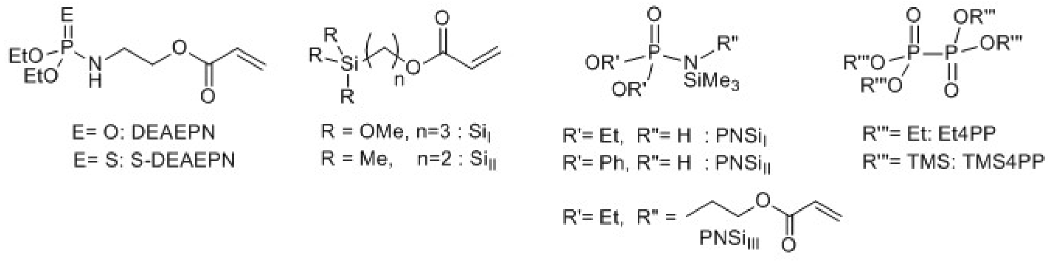
[1] Yuste, R. *Nat. Methods* **2005**, *2*, 902. (b) Campagnola, P. J.; Loew, L. M. *Nat. Biotechnol.* **2003**, *21*, 1356. (c) Zipfel, W. R.; Williams, R. M.; Web, W. W. *Nat. Biotechnol.* **2003**, *21*, 1356.
[2] Copéret, C.; Chabanas, M.; Petroff Saint-Arroman, R.; Basset, J.-M. *Angew. Chem., Int. Ed.* **2003**, *42*, 156.
[3] Jia C., Liu S.-X., Tanner C., Leiggener C., Neels A., Sanguinet L., Levillain E., Leutwyler S., Hauser A., and Decurtins S. *Chem. Eur. J.* **2007**, *13, 3804 – 3812*

The Effect of Other Elements Along with Phosphorus on the Flame Retardance of Cellulose-based Cotton Textiles

Jia En Low[1], Joëlle Levalois-Grützmacher[1] *

[1]ETH Zurich

As a common naturally available material for numerous uses, the application of suitable wash durable flame retardant coatings on cotton is an important issue that needs to be addressed. Using cotton fabrics as substrates, we report using phosphate-based compounds containing at least one phosphorus atom, and an additional element as flame retardant coatings onto these cellulose-based textiles. In order to confer washing durability of these additive compounds on cotton fabrics, we employed the Plasma-Induced Graft Polymerization (PIGP) technique [1] [2]. This study is carried out to explore possible synergistic effects that these elements could, together with phosphorus, contribute to achieve lower flammability of cotton textiles. Insofar, we have investigated the potential of phosphorus [3] [4], nitrogen [1], silicon [5] [6] and sulphur [7]. For silicon, we employed two general strategies: first, as physical mixtures of silicon-containing monomers and phosphoramidate monomers containing phosphorus-nitrogen bonds; second, with silicon being chemically incorporated into a range of phosphoramidate monomers. With various techniques such as Limiting Oxygen Index (LOI), Pyrolysis Combustion Flow Calorimetry (PCFC) and Thermogravimetric Analysis (TGA), we then measured and characterized the flammability of the surface modified cotton textiles. In general, we found that the chemical incorporation of elements onto the monomers gives more promising results in lowering the flammability of cellulose-based cotton textiles.


E= O: DEAEPN
E= S: S-DEAEPN

R = OMe, n=3 : Si_I
R = Me, n=2 : Si_{II}

R'= Et, R''= H : $PNSi_I$
R'= Ph, R''= H : $PNSi_{II}$
R'= Et, R'' = $PNSi_{III}$

R'''= Et: Et4PP
R'''= TMS: TMS4PP

[1] M. J. Tsafack, J. Levalois-Grützmacher, *Surface and Coatings Technology,* **2006**, *201,* 2599.
[2] M. J. Tsafack, J. Levalois-Grützmacher, *Surface and Coatings Technology,* **2007**, *201,* 5789.
[3] Y. Zhou, S. Yin, Y. Gao, Y. Zhao, M. Goto, L.-B. Han, *Angewandte Chemie International Edition,* **2010**, *49*, 6852.
[4] C. Ruflin, U. Fischbach, H. Grützmacher, J. Levaois-Grützmacher, *Heteroatom Chemistry* **2007**, *18*, 721.
[5] Q. Li, P. Jiang, Z. Su, P. Wei, G. Wang, X. Tang, *Journal of Applied Polymer Science,* **2005,** *96,* 854.
[6] A. Quédé, B. Mutel, P. Supiot, C. Jama, O. Dessaux, R. Delobel, *Surface and Coatings Technology,* **2006**, *181*, 265.
[7] S. K. Verma, I. Kaur, *Journal of Applied Polymer Science,* **2012**, *125*, 1506.

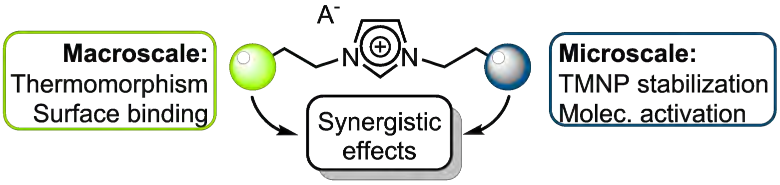
Bi-functionalized ionic liquids as active reaction media

Valentin Manzanares[1], Zhaofu Fei[1], Paul Dyson[1] *

[1]EPFL Lausanne

Task-specific ionic liquids (TSILs), which incorporate functional groups, have come under increasing focus during the last decade.[1] While TSILs can be used in a wide variety of applications, one of the most discussed use of these products is as reaction media for transition metal-catalyzed reactions. We have already shown that TSILs can be used to stabilize nanoparticular catalysts or prevent catalyst poisoning.[2]

Based on these known TSILS, we are developing several task-specific ionic liquids bearing a second moiety in order to benefit from both macro- and microscale effects in transition metal-catalyzed reactions.



V. M. M. would like to thank the SNSF for financial contribution.

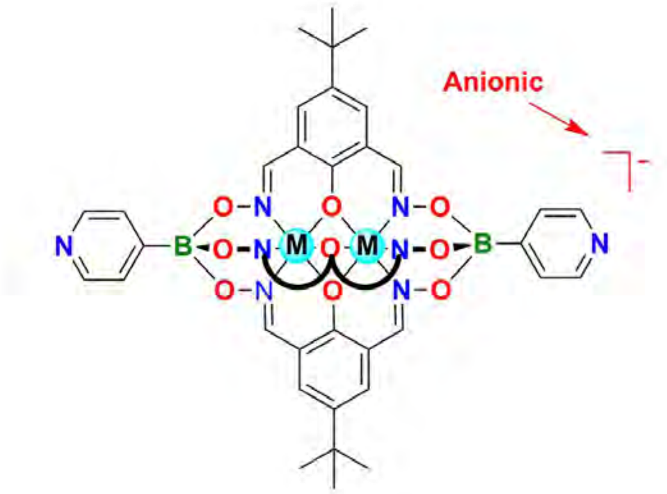
1. *a)* Fei, Z.; Geldbach, T. J.; Zhao, D.; Dyson, P. J. *Chem. Eur. J.* **2006**, *12*, 2122–2130.*b)* Lee, S.-G. *Chem. Comm.* **2006**, 1049–1063.
2. *a)* Geldbach, T. J.; Scopelliti, R.; Chiappe, C.; Dyson, P. J.; Fei, Z.; Zhao, D.; Pieraccini, D.; Ang, W. H. *Organometallics* **2007**, *26*, 1588–1598. *b)* Yang, X.; Fei, Z.; Geldbach, T. J.; Phillips, A. D.; Hartinger, C. G.; Li, Y.; Dyson, P. J. *Organometallics* **2008**, *27*, 3971–3977. *c)* Yan, N.; Yang, X.; Fei, Z.; Li, Y.; Kou, Y.; Dyson, P. J. *Organometallics* **2009**, *28*, 937–939.

Anionic Bipyridyl Ligands for Applications in Metallasupramolecular Chemistry

Mathieu Marmier[1], Mirela Pascu[1], Rosario Scopelliti[1], Julian Holstein[2], Gérard Bricogne[2], Kay Severin[1] *

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

Bipyridyl ligands are among the most frequently used building blocks in metallasupramolecular chemistry. From the original simple 4-4’-bipyridyl (bpy), many structural variants have been explored over time. Our group recently introduced clathrochelate-based bipyridyl ligands.[1] These ligands are rigid, long (between 1.5 and 5.4 nm), well soluble, and easily accessible in a one-pot reaction from commercially available starting materials. We describe here a different class of bipyridyl clathrochelate complexes. The new bipyridyl ligands display an interesting characteristic for applications in metallasupramolecular chemistry: they are negatively charged. These building blocks are compatible with metallasupramolecular chemistry, as evidenced by the synthesis of homometallic, two-dimensional coordination polymers.[2]



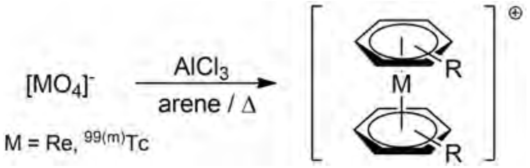
[1] M. D. Wise, A. Ruggi, M. Pascu, R. Scopelliti, K. Severin, *Chem. Sci.* **2013**, *4*, 1658.
[2] M. Pascu, M. Marmier, C. Schouwey, R. Scopelliti, J. Holstein, K. Severin, *Chem. Eur. J.* **2014**, *20*, 5592-5600.

Facile Synthesis of $[M(arene)_2]^+$ complexes (M = Re, $^{99(m)}$Tc)

Giuseppe Meola[1], Michael Benz[1], Paul Schmutz[1], Henrik Braband[1], Roger Alberto[1] *

[1]University of Zurich

Ru-arene complexes play an important role in the field of medicinal inorganic chemistry and have been known for many years.[1] Bis-arene complexes are of particular interest, since they represent fundamental precursors for numerous, subsequent reactions.[2] Recently, $[M(arene)_2]^+$ type complexes (M = Re, $^{99(m)}$Tc) came into the focus of our research, because these complexes bear the potential for a 'theranostic' approach in (nuclear) medicine. On the basis of a known synthesis for $[Re(arene)_2]^+$ (arene = benzene, toluene, mesitylene, o-xylene, p-xylene and naphtalene) complexes, we developed a new one step synthesis for $[M(arene)_2]^+$ complexes (M = Re, $^{99(m)}$Tc).[3] This new procedure uses only $AlCl_3$ as activating and reducing agent, leading to high yields. Starting from $[MO_4]^-$ (M = Re, $^{99(m)}$Tc) a series of bis-arene complexes $[M(arene)_2]^+$ (arene = benzene, toluene, mesitylene and tetralin) has been prepared. These syntheses will lead to a deeper understanding of the fundamental chemical properties of these complexes, while at the same time the more versatile synthesis of $[^{99m}Tc(arene)_2]^+$ compounds paves the way for new possibilities in radiopharmaceutical developments.



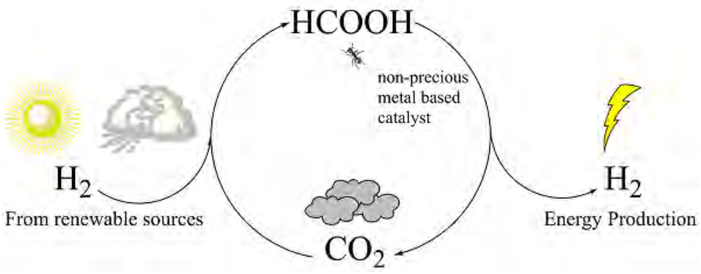
[1] Yaw Kai Yan, Michael Melchart, Abraha Habtemariam, Peter J. Sadler, *Chemical Communications*, **2005**, 38, 4764-4776.
[2] Guido Pampaloni, *Coordination Chemistry Reviews,* **2010**, 254, 402-419.
[3] Eveniya A. Trifonova, Dmitry S. Perekalin, Konstantin A. Lyssenko, Alexander R. Kudinova, *Jourrnal of Organometallic Chemistry*, **2013**, 727, 60-63.

Formic acid dehydrogenation catalyzed by non-precious metal based catalysts.

Mickael Montandon[1], Gábor Laurenczy[1] *

[1]EPFL Lausanne

An important challenge for the scientific community is the development of new hydrogen storage methods. Currently, hydrogen is stored in pressurized vessels that present safety hazards and are inconvenient to handle[1-3]. In 2008, our group presented a novel approach of hydrogen generation from formic acid (FA) that is released on demand using a robust and effective ruthenium catalyst[4]. Herein we present the results of our investigation on the dehydrogenation of formic acid using catalysts based on non-precious first row transition metals. The new *in situ* formed catalysts are capable to produce H_2 and CO_2 from an aqueous solution of FA without any additives.



Acknowledgements: EPFL and SCCER are thanked for financial support.

[1] A. Léon. *Hydrogen Technology Mobile and Portable Applications*; Green Energy and Technology; Springer-Verlag Berlin Heidelberg, **2008**.

[2] A. F. Dalebrook, W. Gan, M. Grasemann, S. Moret, G. Laurenczy, *ChemComm,* **2013,** *49*, 8735.

[3] M. Grasemann, G Laurenczy, *Energy Environ. Sci.*, **2012**, *5*, 8171

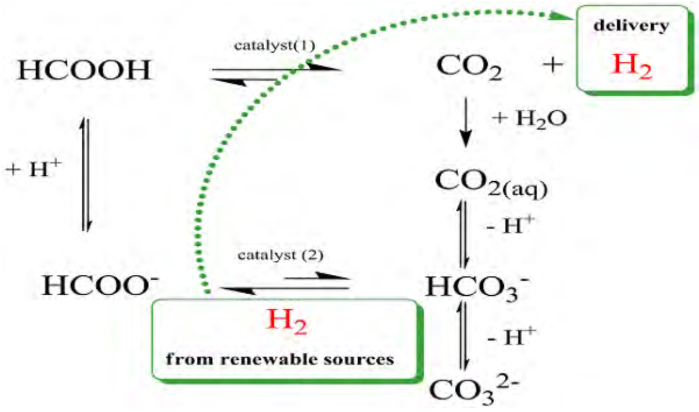
[4] C. Fellay, P. J. Dyson,G. Laurenczy, Angewandte Chemie, Int. Edition, **2008**, *47*, 3966.

Direct Carbon Dioxide Hydrogenation in the Hydrogen Storage under the Formic Acid/Carbon Dioxide Cycle

Séverine Moret[1], Gábor Laurenczy[1], Paul Dyson[1] *

[1]EPFL Lausanne

One of the main challenges of our time is to have a convenient energy supply from renewable sources. In this context hydrogen is among the candidates as an energy carrier for mobile applications and HCOOH has been proposed as a hydrogen storage material.[1, 2]



For hydrogenation of carbon dioxide in basic aqueous solutions/conditions to formates and other formic acid derivatives a large number of investigations have been reported. Despite of the fact that in reality bicarbonates or carbonates are the real substrates under basic conditions, these reactions were titled/called as carbon dioxide hydrogenations.

For the first time, the direct hydrogenation of CO_2 in acidic media, in aqueous solution and in DMSO, have been successfully carried out, in the absence of amines or other additives.[3, 4] The rate of CO_2 reduction has shown to be strongly dependent on the temperature and the gas pressures.

Acknowledgements: We thank EOS Holding and EPFL for financial support

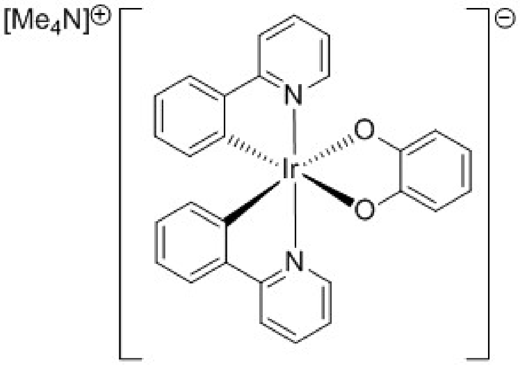
[1] C. Fellay, P. J. Dyson, G. Laurenczy, *Angew. Chem. Int. Ed.*, **2008**, *47*, 3966.
[2] M. Grasemann, G. Laurenczy, *Energy Environ. Sci.*, **2012**, *5*, 8171.
[3] EOS Holding, S. Moret, P. J. Dyson, G. Laurenczy, Patent application No. 13155490.9, **2013.**
[4] S. Moret, P. J. Dyson, G. Laurenczy, *Nat. Commun.* 5:4022 doi: 10.1038/ncomms5017 **2014**

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

Collin Morris[1], Edwin C. Constable[1], Mariana Spulber[1], Cornelia Gabriela Palivan[1], Catherine 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 typically comprised 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/, **2005**.
[2] R. D. Costa, E. Orti, H. J. Bolink, F. Monti, G. Accorsi, and N. Armaroli,*Angew. Chem. Int. Ed.*, **2012**, 51, 8178-8211.
[3] M. K. Nazeeruddin, R. Humphry-Baker, D. Berner, S. Rivier, L. Zuppiroli, and M. Graetzel, *J. Am. Chem. Soc.*, **2003**, 125, 8790-8797.
[4] H-F. Chen, C. Wu, M-C. Kuo, M. E. Thompson, and K-T. Wong, *J. Mater. Chem.*, **2012**, 22, 9556-9561.

Coordinating anchoring ligands for surface functionalisation

Steffen Müller[1], Catherine E. Housecroft[1], Edwin C. Constable[1] *

[1]University of Basel

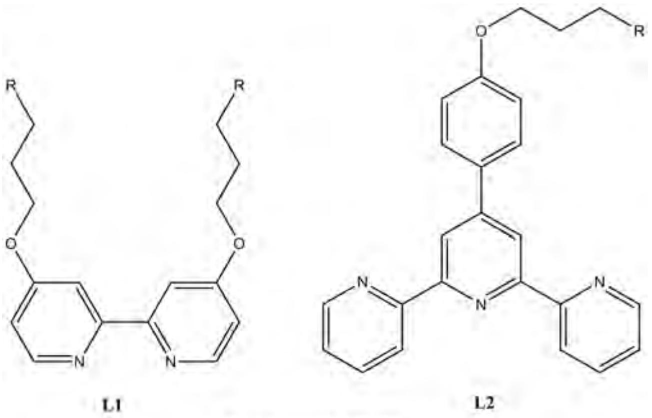
Transition metal complexes containing polypyridyl ligands can be found in nearly every area of modern chemistry. The possible applications range from sunlight harvesting to water splitting to reaction catalysts and lighting applications. In some cases it can be advantageous if the metal complex can be bound covalently to a surface. This can be achieved with coordinating anchoring ligands.

Here we describe the synthesis of a series of 2,2`-bipyridine (bpy) and 2,2';6',2"-terpyridine (tpy) based ligands. These ligands are comprised of an ether-bridged alkyl chain with variable anchoring group at its end[1–6]. The usage of different kinds of anchoring groups allows functionalization of several surface types. Thiol end groups were chosen for gold whereas carboxylic acid and phosphonic acid groups can be used for metal oxides as TiO_2 or SiO_2.

Functionalisation can be achieved be dipping the surface into a solution of the anchoring ligand for 1-2 days, followed by washing and drying. Afterwards complexation on the surface is possible. This can be obtained by using metal salts or not fully coordinated transition metal complexes.

The current synthetic progress towards the ligands and transition metal complexes will be discussed, alongside relevant physical data and planned future work.

We acknowledge the support of the European Commission of HYSENS (FP7-NMP-2010-SMALL-4, Project 263091)



R = SH, CO_2H, $PO(OH)_2$

[1] A. Baber et. al., *Dalt. Trans.*, **2006**, 4821.
[2] E. C. Constable et. al. , *Inorg. chem.*, **2004**, 43, 4817–9.
[3] Y. Hong and C. B. Gorman, *J. Org. Chem.*, **2003**, 8204, 9019–9025.
[4] H. J. Jung et.al., *Chem. Comm.*, **2010**, 46, 3863–5.
[5] A. Marra et. al., *Eur. J. Org. Chem.*, **2013**, 1144–1149.
[6] J. Wang and G. S. Hanan, *Synlett*, **2005**, 1251–1254.

Molybdenum/Tungsten-Oxide Nanomaterials for Gas Sensing

Michael Olah[1], Greta Ricarda Patzke[1] *

[1]University of Zurich

Semiconducting metal oxide (SMO) gas sensors have attracted much attention in the field of gas sensing due to their small dimensions, economic production, low power consumption and high compatibility with microelectronics processing. The fundamental sensing mechanism of SMO gas sensors is based on a change in electrical conductivity due to surface redox reactions by gas exposure. Among the most important metal oxides for gas sensing hexagonal molybdenum and tungsten oxides with related tunnel structures have attracted much interest due to their manifold electrochemical and catalytic properties. Formation of these channel structures is often supported by incorporation of alkali or alkaline earth guest cations. We have studied the hydrothermal growth processes of structurally related W/Mo-nanomaterials in the presence of alkali chlorides in detail.[1] In our previous work, the NH_3 sensing properties of alkali-containing hexagonal W/Mo-oxides indicated promising sensing performance.[2] We herein report on the results of the gas sensing performance of alkali-containing hexagonal Mo-oxide (h-MoO_3) nanorods. Starting from a hydrothermal approach, their particle size and morphology were optimized for NH_3 sensing applications by varying the addition of alkali additives. The underlying mechanisms of interaction between oxide surface and test gas are still under investigation.

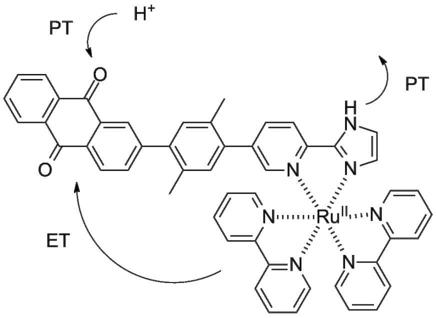
[1] Y. Zhou, N. Pienack, W. Bensch, G. R. Patzke, *Small* **2009**, 17, 1978-1983.
[2] Y. Zhou, K. Zheng, J.-D. Grunwaldt, T. Fox, L. Gu, X. Mo, G. Chen, G. R. Patzke, *J. Phys. Chem. C* **2011**, 115, 1134-1142.

Light-Induced Long-Range Electron Transfer Coupled to Two Proton Transfers

Andrea Pannwitz[1], Oliver S. Wenger[1] *

[1]University of Basel

Proton coupled electron transfer (PCET) plays a crucial role for example in hydrogenation reactions, water oxidation, and carbon dioxide reduction. Research in the field of PCET is currently aiming to understand and control redox processes which are proton coupled. One approach is the investigation of model compounds.[1,2] In the excited state, purely organic molecules as well as metal organic complexes can change their redox and acid-base properties. Therefore, by excitation with light, charge electron and transfer can be facilitated.[3]



The ruthenium-complex in Fig. 1 has functional units which initiate the following process:
In the excited state, the ruthenium moiety is oxidized by the covalently attached anthraquinone unit. Upon oxidation the pK_A value of the coordinating imidazole unit drops four orders of magnitude and a proton is released. The anthraquinone monoanion is protonated in the presence of water and other proton sources because it is more basic than in its neutral form.
In summary the long range electron transfer takes place and it is coupled to two proton transfers. The detailed mechanism of this unusual charge transfer is now investigated. To differentiate between concerted and stepwise PCET, spectroscopic methods such as transient absorption, steady state and time-resolved luminescence measurements are performed. Isotope labeling experiments will provide further insight.
Similar two-proton-one-electron reactions are reported to occur in enzymes, for example in Ribonucleotide Reductase.[4]

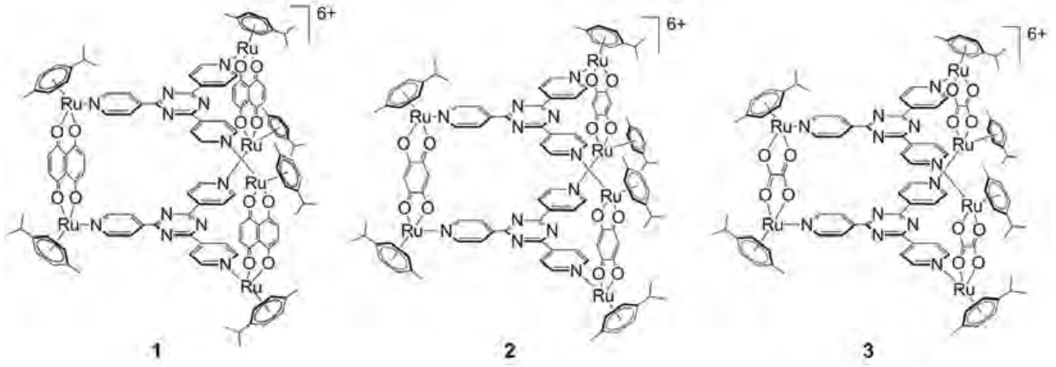
[1] C. J. Gagliardi, B. C. Westlake, C.A. Kent, J. J. Paul, John M. Papanikolas, T. J. Meyer, *Coord. Chem. Rev.* **2010**, 254, 2459–2471.
[2] L. Hammarström, S. Styring *Energy Environ. Sci.* **2011**, 4, 2379-2388.
[3] O. S. Wenger, *Acc. Chem. Res.* **2013**, 46, 1517-1526.
[4] E. Minnihan, D. Nocera, JoAnne Stubbe, *Acc. Chem. Res.* **2013**, 46, 2524-2535.

How do hexaruthenium assemblies interact with proteins?

Lydia Paul[1], Bruno Therrien[2], Julien Furrer[1] *

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

Since the 1980s, ruthenium-based drugs have gradually attracted attention, mainly due to their less severe side effects compared to platinum-based drugs.[1-3] In recent years, we have designed different hexacationic hexaruthenium assemblies that can encapsulate planar and bioactive molecules, making them a potential new class of drug delivery vectors.[4] Previous studies conducted within our group have shown that the assemblies **1-3** interact rapidly with amino acids and rather weakly with deoxyguanosine-5’-monophosphate and deoxyadenosine-5’-monophosphate.[5-7] In line with these previous investigations, we report here the interaction between the assemblies shown in the chart and human serum albumin, transferrin, myoglobin, ubiquitin and Cytochrome C.



[1] M. J. Clarke, *Met. Ions Biol. Syst.* **1980**, 11, 231-283.
[2] B. Rosenberg, L. van Camp, E. B. Grimley, A. J. Thomson, *J. Biol. Chem.* **1967**, 242, 1347-1352.
[3] G. Süss-Fink, *Dalton Trans*. **2010**, 39, 1673-1688.
[4] B. Therrien, G. Süss-Fink, P. Govindaswamy, A. K. Renfrew, P. J. Dyson, *Angew. Chem. Int. Ed.* **2008**, 47, 3773-3776.
[5] L. E. H. Paul, B. Therrien, J. Furrer, *Inorg. Chem.* **2012**, 51, 1057-1067.
[6] L. E. H. Paul, B. Therrien, J. Furrer, *J. Biol. Inorg. Chem.* **2012**, 17, 1053-1062.
[7] L. E. H. Paul, B. Therrien, J. Furrer, *J. Organomet. Chem.* **2013**, 734, 45-52.

The Impact of Structure and Bonding on The Reactivity of λ3-Iodanes: Theoretical Study of Competing Reactions Mechanisms

Halua Pinto de Magalhães[1], Hans Peter Lüthi[1], Antonio Togni[1] *

[1]ETH Zurich

Hypervalent iodine compounds are very useful for many organic transformations, both as reagents for a variety of functionalizations and as catalysts for oxidative reactions. Diaryliodonium salts, in particular, are versatile reagents for a number of arylation reactions. [1] Mechanistic studies of the functionalization of arenes using this reagents have shown that the formation of hypervalent iodine intermediates (λ3-iodanes) takes a key role, as they determine the course and the selectivity of the reaction. [2] Bridged diaryliodonium salts, featuring a heterocyclic moiety involving the iodine atom, were shown to exhibit a distinctly different reactivity leading to different products. [3] These products are not just the result of reductive elimination reactions i.e. heterolytic cleavage, but also involve different radical mechanisms (homolytic cleavage, SET). Furthermore, a relation between the size of the bridge connecting the two aryl groups, and the reaction products was established.

In the present work, we investigate these mechanisms using quantum chemical calculations. Our study reveals that the λ3-iodane intermediate is the ”gateway”, which plays a crucial role also for reaction pathways that are only observed for strained bridges systems. The preference for a certain reaction pathway can be ascribed to different features such as the remarkable affinity of the hypervalent region to planarity. Furthermore, the energetics of these competing reactions are clarified by analysis of the mechanisms of the various reaction pathways. Finally, using model compounds, some of the basic features governing the reactivity of λ3-iodanes are discussed.

[1] E. A. Merritt and B. Olofsson, *Angew. Chem. Int. Ed.*, **2009**, 48, 9052-9070.
[2] H. Pinto de Magalhães, H. P. Lüthi, A. Togni, *Org. Lett.*, **2012**, 14, 3830-3833.
[3] V. R. Grushin, *Acc. Chem. Res.*, **1992**, 25, 529-536.

Cyclodextrin, a Host to Welcome Organic Chlorinated Pesticide(s)

Vijay Kumar Rana[1], Joëlle Levalois-Grützmacher[1] *

[1]ETH Zurich

Organic chlorinated pesticides namely as chlordecone (CLD), β-hexachlorocyclohexane (HCH) and dieldrine have been extensively used during 1973 to 1992 to control the proliferation of banana weevil (Cosmopolite sordidus) pest at two islands of French West Indies, Guadeloupe and Martinique[1]. Catastrophically, extensive use of these pesticides (mainly chlordecone) consequences a large scale contamination of soils, rivers and crops, which is obviously very harmful for local population. Hence, in order to remove chlordecone and to avoid its impregnation into human being, drinking water sources and other production plants were equipped with activated carbon filters. However, eventually, recent data show that chlordecone is still present in the blood of adult men, pregnant women and newborns[2]. That is why; adsorption of these pesticides selectively is a very hot research topic. Thus, we are very glad to propose an alternate which adsorb the chlordecone preferentially.

Cyclodextrins (CDs) are a family of naturally occurred cyclic oligosaccharides consisting of six (α-CD), seven (β-CD) and eight (γ-CD) or more sugar units where α-(1,4) bonds hold them together and make them chemically stable, nontoxic, biodegradable and biocompatible macromolecules[3]. Moreover, cyclodextrins have toroid shape which allows them to form inclusion complexes (host-guest complex) with a wide variety of hydrophobic guest molecules. Here in, we have used (β-γ) cyclodextrin which has an appropriate shape to accommodate a single molecule of hydrophobic chlordecone. The 1:1 CLD_CDs complex formation was confirmed with the help of elemental analysis, thermogravimetry analysis and ^{1}H NMR characterization techniques. However, isothermal titration calorimetric (ITC) has also been used to confirm the 1:1 complex formation with chlorendic acid (having similar dimensions as that of CLD) instead of chlordecone, since cyclodextrins and chlordecone are not soluble in identical solvents.

Moreover, cyclodextrin has been attached on the surface of graphitic carbons in order to check any further improvement in adsorption of CLD. The cyclodextrin attached graphitic carbons were also characterized by several spectroscopy techniques such as X-ray photoelectron spectroscopy (XPS) and thermogravimetric analysis etc.

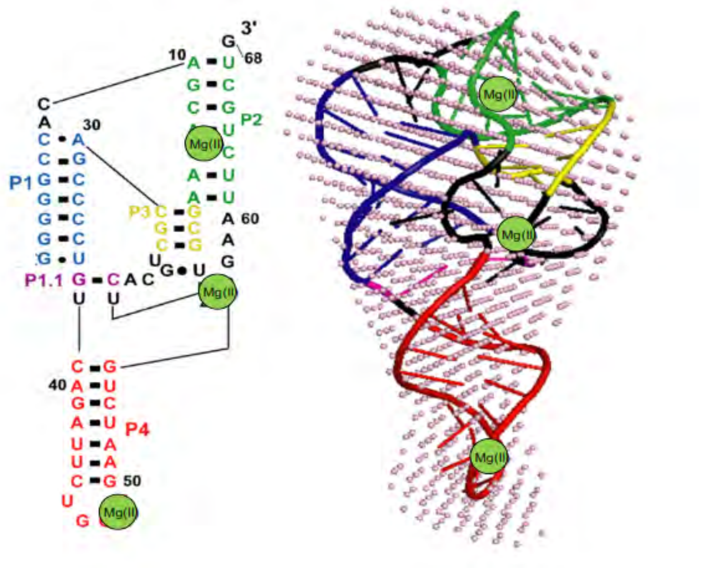
1. A. Durimel, S. Altenor, R. Miranda-Quintana, P. Couespel Du Mesnil, U. Jauregui-Haza, R. Gadiou and S. Gaspard, *Chemical Engineering Journal,* **2013**, 229, 239–249.
2. R. Dallaire, G. Muckle, F. Rouget, P. Kadhel, H. Bataille, L. Guldner, S. Seurin, V. Chajès, C. Monfort, O. Boucher, J. P. Thomé, S. W. Jacobson, L. Multigner and S.Cordier, *Environmental Research*, **2012**, 118, 79–85.
3. E.M. Martin Del Valle, *Process Biochemistry* **2004**, 39, 1033–1046.

Metal ions and the mammalian CPEB3 ribozyme – a complicated relationship

Magdalena Rowińska-Żyrek[1], Miriam Skilandat[1], Roland K. O. Sigel[1] *

[1]University of Zurich

Most of the available knowledge about the small, highly conserved, mammalian, self cleaving, non-coding CPEB3 ribozyme is based on comparative studies with the HDV (Hepatitis Delta Virus) ribozyme; both are predicted to fold into a similar pseudoknot structure and use a self-cleavage mechanism which employs a catalytic site cytosine [1,2].



In this study, we focus on the structural effects of metal ion binding to CPEB3, which is known to use Mg(II) for its catalytic mechanism. We present the first results in elucidating the structure of CPEB3 in solution and focus on understanding the metal ion requirements of the CPEB3 ribozyme. Several direct metal ion counting techniques show that there are at least three specific Mg^{2+} binding sites and NMR spectroscopy precisely shows their localisation. Mn^{2+} and $[Co(NH_3)_6]^{3+}$ are used as spectroscopic probes for Mg^{2+} inner- and outersphere binding, respectively.

The importance of these metal binding sites is underlined by co-transcriptional cleavage studies, which show the impact of single mutations of the predicted metal binding sites on the catalytical activity of the ribozyme.

Financial support by Marie Curie IEF (PIEF-GA-2012-329700 to MRZ) and the Swiss National Science Foundation (to RKOS) is gratefully acknowledged.

[1] K. Salehi-Ashtiani, A. Luptak, A. Litovchick, J.W. Szostak, *Science*, **2006**, 313, 1788-1792.
[2] C. Webb, N.J. Riccitelli, D.J. Ruminski, A. Luptak, *Science*, **2009**, 326, 953-932.

Ir(III)/Quantum Dots diads: en route to semiconductor-based photochemical water oxidation

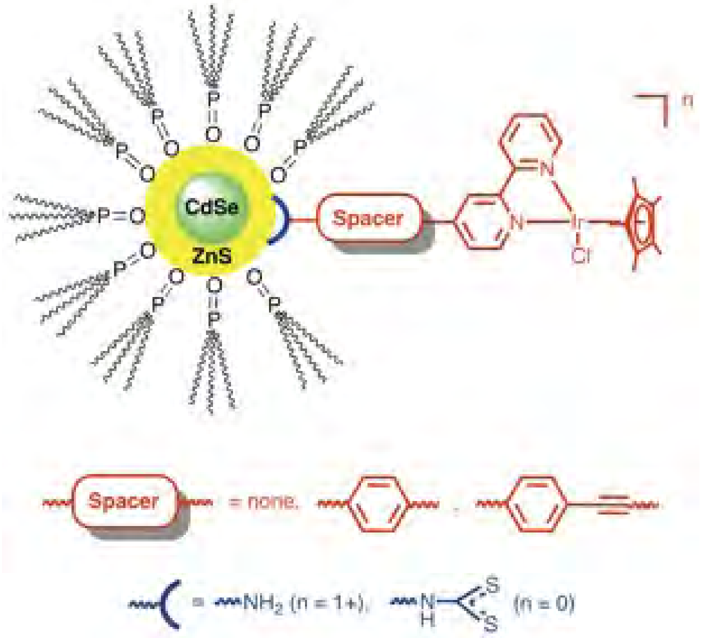
Albert Ruggi[1], Jérémie Rossier[1]

[1]University of Fribourg

The possibility of exploiting the immense and renewable energetic treasure constituted by solar radiation has pushed scientific research towards the realization of light-driven water splitting systems. The development of a system capable of efficiently performing the entire photoinduced water splitting process still constitutes the "Holy Grail" of modern scientific research and has captured the attention of scientists worldwide.

Semiconductor Quantum Dots (QDs) have recently proved to be highly efficient and stable sensitizers for light-driven hydrogen generation.[1] However, the possibility of using QDs as sensitizers for water oxidation remains unexplored.

We present here our preliminary results concerning the synthesis and photochemical behaviour of a diad based on CdSe/ZnS core-shell QDs functionalised with a family of Ir(III) complexes containing different spacers and connecting groups.



The Ir(III) complex used in this study has been already applied to electrochemical water oxidation, showing remarkable stability and catalytic efficiency.[2] Therefore, the coupling of this complex with QDs constitutes a promising model system for the realization of the first semiconductor-based system for light-driven water oxidation.

[1] Zhiji Han, Fen Qiu, Richard Eisenberg, Patrick L. Holland, Todd D. Krauss, *Science*, **2012**, 338, 1321-1324.

[2] Gerard W. Olack, Christopher D. Incarvito, Odile Eisenstein, Gary W. Brudvig, Robert H. Crabtree, *J. Am. Chem. Soc.*, **2010**, 132, 16017-16029.

Fluorescent Labels for Single Molecule Studies of RNA Structure and Folding

Anita G. Schmitz[1], Susann Zelger-Paulus[1], Gilles Gasser[1], Roland K.O. Sigel[1] *

[1]University of Zurich

We are interested in studying the dynamic folding behaviour of large functional RNAs via single molecule Förster Resonance Energy Transfer (smFRET). The systems that we are investigating with different labelling strategies are the group II intron of *Saccharomyces cerevisiae*, a catalytically active ribozyme, and the *btuB* riboswitch of *Escherichia coli*, a regulatory RNA that binds B_{12} as metabolite.[1,2] To investigate the process of RNA folding upon binding of the metabolite, we have labelled the B_{12} itself with various fluorophores suitable for FRET. Moreover, the large RNA constructs had to be labelled. To this end, the current state-of-the-art technique is to add short complementary DNA-sequences that carry the fluorophores. However, the binding strength of these labels is fairly weak and heavily dependent on the conditions. More efficient labelling techniques are therefore of great interest. Peptide nucleic acid (PNA) is a non-natural analogue of DNA. It has been used extensively due to its superior binding strength towards DNA and RNA. So far, the influence of PNA on the folding behaviour of flexible RNA constructs has not been sufficiently investigated and it remains unclear if it can be used as an unbiased probe in smFRET studies. Herein, we present first experimental evidence, that indeed the binding strength of PNA based labels is superior to DNA based ones. At the same time, the catalytic activity of the group II intron is not influenced by the labelling system. SmFRET studies show comparable general trends, but also differences between DNA- and PNA-labelled constructs. These differences have general implications for the interpretation of the dynamic RNA structures.[3] With these labelling strategies in hand we are a step closer to elucidate unknown RNA folding mechanisms.

Financial support by an ERC starting Grant 2010 (259092-MIRNA to R. K. O. S.), within the COST Action CM1105, and the University of Zurich is gratefully acknowledged.

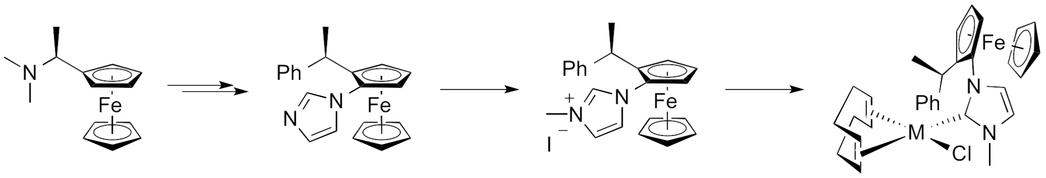
[1] M. Steiner, K. S. Karunatilaka, R. K. O. Sigel, D. Rueda, *Proc Natl Acad Sci USA*, **2008**, 105, 13853-13858.
[2] S. Gallo, M. Oberhuber, R. K. O. Sigel, B. Kräutler, *ChemBioChem*, **2008**, 9, 1408-1414.
[3] A. G. Schmitz, S. Zelger-Paulus, G. Gasser, R. K. O. Sigel, **2014**, submitted.

Chiral Ferrocenyl-Substituted N-Heterocyclic Carbenes in Asymmetric Catalysis

Lukas Sigrist[1], Antonio Togni[1] *

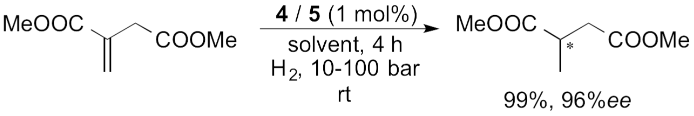
[1]ETH Zurich

Starting from Ugi's amine **1** [1], the ferrocenylimidazole **2** can be prepared *via* a Ullmann-type coupling in good yield. Quaternization of the imidazole is achieved using alkyl halides, for example methyl iodide, to give imidazolium salt **3**.
Activation of **3** with silver(I) oxide and subsequent transmetallation gives rise to the diene precatalysts **4** and **5** with a monodentate stereogenic NHC ligand. Both complexes are stable at ambient conditions and could be fully characterized.



1 **2** **3** **4**, M = Rh **5**, M = Ir

Employing the complexes **4** and **5** in hydrogenation reactions of C-C and C-N double bonds gives products in high yield and enantioselectivity. The presented catalytic system is a unique example of a monodentate, phosphane-free setup which only requires hydrogen pressure to activate the catalyst.



[1] G. W. Gokel, I. K. Ugi, *J. Chem. Educ.* **1972**, *49*, 294-296.

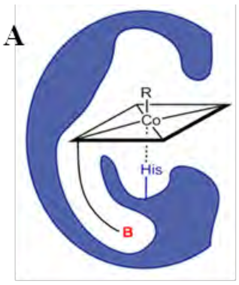
Accessing Modified Properties and Functions of Vitamin B_{12} through Backbone Alterations

Marjorie Sonnay[1], Kai Zhou[1], Felix Zelder[1] *

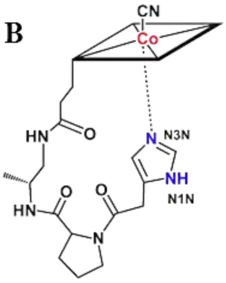
[1]University of Zurich

Vitamin B12 and its derivatives present an elaborate structure, allowing them to undergo important reversible structural modifications. They can thus act as molecular switches by reversibly coordinating the backbone to the cobalt center (base-on/base-off). This interesting feature allows B_{12} and B_{12} cofactors to finely tune their physico-chemical properties.[1] B12 dependent enzymes also take advantage of this characteristic by replacing the backbone with a histidine residue, which coordinates to the cobalt (figure A).[2]

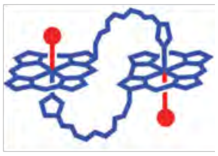
A



B



C



Our group is interested in synthesizing new B_{12} derivatives (peptide B_{12}), using peptides as artificial backbones. Such analog yield to interesting compound bearing modular redox and coordination properties. Furthermore, they brought important insights in various domains, and our recent research advancements will be presented in this occasion. Some biomimetic cobalamins are good potential enzymatic inhibitors [1] while others allow a better understanding of the B_{12} dependant catalytic cycles and cofactor activation (figure B). Moreover, a different peptide backbone derivative yields an interesting intermolecular coordination, leading to a dimeric structure (figure C).[3]

[1] F. Zelder, K. Zhou, M. Sonnay, *Dalton Transactions*, **2013**, 42, 854-862.
[2] C. L. Drennan, S. Huang, J. T. Drummond, R. G. Matthews, M. L. Ludwig, *Science*, **1994**, 266, 1669-1674.
[3] K. Zhou, F. Zelder, *Chemical Communications*, **2011**, 47(43), 11999-12001.

Hydrogen storage in formate-bicarbonate systems using new water-soluble ligands.

Katerina Sordakis[1], Geraldine Stauffer[1], Jonathan Thierry[1], Antonella Guerriero[2], Maurizio Peruzzini[2], Luca Gonsalvi[2], Gábor Laurenczy[1] *

[1]EPFL Lausanne, [2]ICCOM-CNR

Hydrogen storage, one of the enabling elements for a future hydrogen economy, remains a challenge from both a chemical as well as an engineering point of view.[1] Formate-bicarbonate systems are among the most promising scenarios towards the realization of a practical H_2 charge/discharge device, mainly due to their nontoxic and stable nature, as well as the use of water as a “green” solvent.[2][3][4]A series of new water soluble ligands in combination with ruthenium catalytic precursors were tested for their activity in this hydrogen storage cycle (Figure 1).

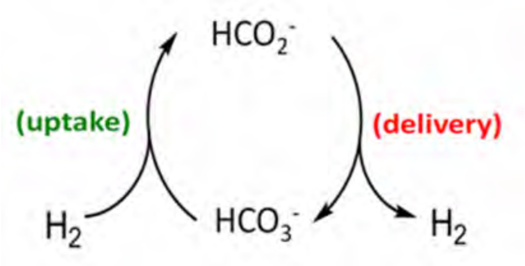


Figure 1. Overview of H_2 uptake and delivery based on formate-bicarbonate cycles.

Acknowledgements: EPFL and Swiss National Science Foundation are thanked for financial support. E. Monflier, H. Bricout andF. Hapiot of the Université Lille Nord de France are thanked for the ligand synthesis.

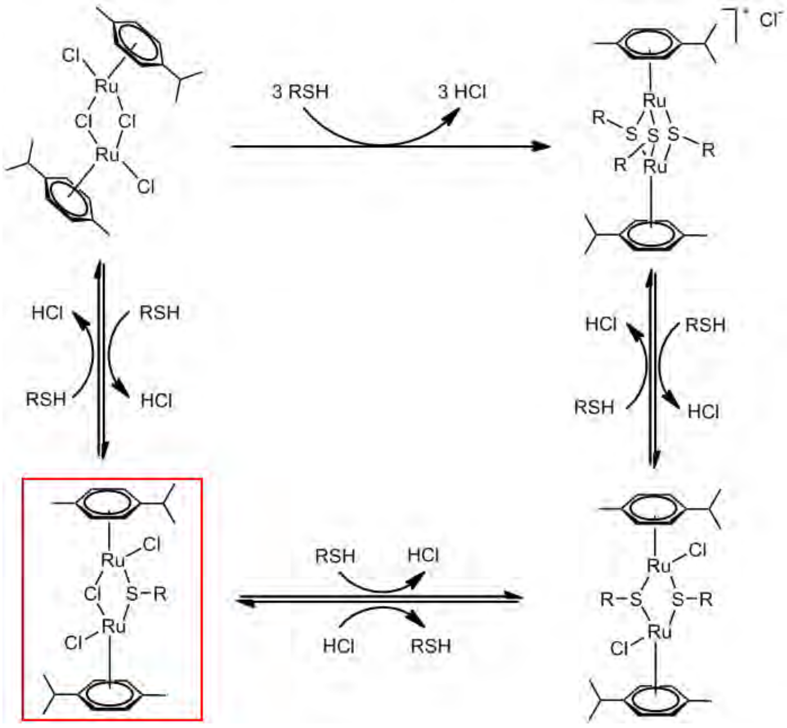
[1] Martin Grasemann, Gábor Laurenczy, *Energy Environ. Sci.* **2012**, *5*, 8171-8181.
[2] Mikael Erlandsson, Vanessa R. Landaeta, Luca Gonsalvi, Maurizio Peruzzini, Andrew D. Phillips, Paul J. Dyson, Gábor Laurenczy, *Eur. J. Inorg. Chem.* **2008**, *2008*, 620–627.
[3] Christopher Federsel, Albert Boddien, Ralf Jackstell, Reiko Jennerjahn, Paul J. Dyson, Rosario Scopelliti, Gábor Laurenczy, Matthias Beller, *Angew. Chem. Int. Ed.* **2010**, *49*, 9777–9780.
[4] Gábor. Papp, Jenõ Csorba, Gábor Laurenczy, Ferenc Joó, *Angew. Chem. Int. Ed.* **2011**, *50*, 10433–10435.

Monothiolato-Bridged Dinuclear Arene Ruthenium Complexes: The Missing Link in the Reaction of Arene Ruthenium Dichloride Dimers with Thiols

David Stibal[1], Bruno Therrien[1], Julien Furrer[2], Federico Giannini[2], Lydia Paul[2], Georg Süss-Fink[1] *

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

The reaction of *p*-cymene ruthenium dichloride dimer with thiols is well known to give the cationic trithiolato complexes $[(p\text{-MeC}_6\text{H}_4\text{Pr}^i)_2\text{Ru}_2(\text{SR})_3]^+$ or the intermediary dithiolato complexes $[(p\text{-MeC}_6\text{H}_4\text{Pr}^i)_2\text{Ru}_2\text{Cl}_2(\text{SR})_2]$, depending on the reaction conditions [1]. We have recently observed the formation of previously unknown monothiolato complexes of the general formula $[(p\text{-MeC}_6\text{H}_4\text{Pr}^i)_2\text{Ru}_2\text{Cl}_3(\text{SR})]$ which represent the missing link in the stepwise formation of the trithiolato complexes.



Four complexes of this type have been successfully synthesized and evaluated for their activity against human ovarian cancer (A2780) cells. Their catalytic activity in the oxidation of glutathione was also studied. Our results provide insight into the structure-activity relationship of thiolato-bridged arene ruthenium complexes.

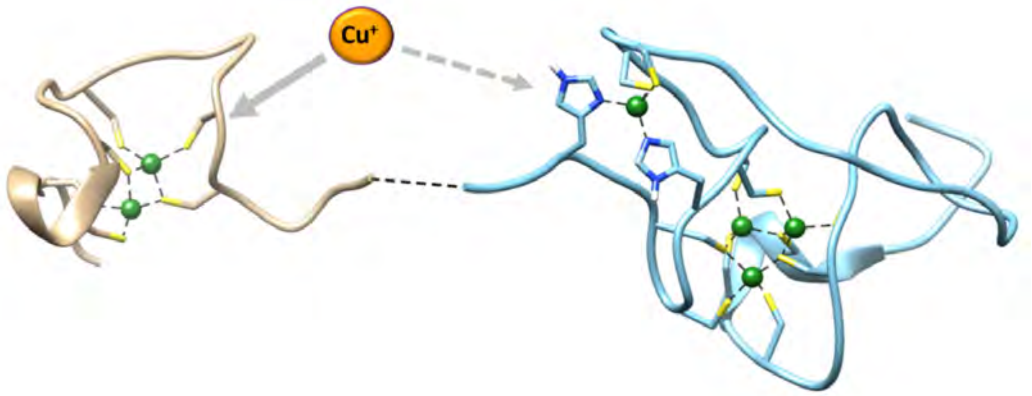
[1] Anne-Flore Ibao, Michaël Gras, Bruno Therrien, Georg Süss-Fink, Olivier Zava, Paul J. Dyson, *Eur. J. Inorg. Chem.* **2012**, 1531-1535

Biologically Relevant or an Artifact? The Copper Binding Site in Wheat Metallothionein

Katsiaryna Tarasava[1]

[1]University of Zurich

Metallothioneins (MTs) are small cysteine-rich proteins. MTs are suggested to be involved in metal tolerance and homeostasis, as they are able to bind metal ions through the thiol groups of cysteine residues. The early cysteine-labeled MT (E_c-1) from *Triticum aestivum* (common wheat) hosts two metal binding domains, γ and β_E, coordinating two and four divalent d^{10} metal ions, respectively (Fig.)[1]. E_c-1 is currently assumed to play a role in zinc homeostasis, as it is forming well defined species with Zn(II) upon *in vitro* reconstruction [1]. However recently the E_c-1 species containing also one copper ion were purified from the wheat germ [2]. The simultaneous binding of both Zn(II) and Cu(I) to MTs has been reported [3]. In many cases, additional Cu(I) binding to MTs has a function, for example predominant human MT subtype, MT-2A, is able to prevent copper-mediated aggregation of amyloid β-aggregates [4]. We assume, that Cu(I) binding to the specific site in the E_c-1 MT with formation of well-defined species could suggest a possible function. Our data suggest specific coordination of the first Cu(I) ion to the N-terminal γ-E_c-1 domain. It replaces one zinc ion and this binding is not affected by the other β-E_c-1 domain. The cluster structures formed upon addition of increasing amounts of Cu(I) to the separate γ-Ec-1 domain were investigated with UV/Vis, circular dichroism, and fluorescence spectroscopy. The same cluster structure is formed regardless if the apo-protein is used in the titration study or the metal-loaded and hence prefolded Zn_2- or Cd_2-γ-E_c-1 forms. Together with the reported occurrence of copper containing E_c-1 *in vivo* our results provide evidence about the possible functional importance of Cu(I)-species of wheat MT.



Financial support from the Swiss National Science Foundation (EF) and the Forschungkredit 2013 from Zurich University (KT) are gratefully acknowledged.

[1] E. Peroza, R. Schmucki, P. Guntert, E. Freisinger and O. Zerbe, *Journal of Molecular Biology* **2009**, 387, 207-218.
[2] O. Leszczyszyn, R. Schmid and C. Blindauer, *Proteins-Structure Function and Bioinformatics* **2007**, 68, 922-935.
[3] P. Chen, P. Onana, C. Shaw and D. Petering, *Biochemical Journal* **1996**, 317, 389-394.
[4] R. Chung, C. Howells, E. Eaton, L. Shabala, K. Zovo, P. Palumaa, R. Sillard, A. Woodhouse, W. Bennett, S. Ray, J. Vickers and A. West, *Plos One* **2010**, 5, 1-11

Gas Phase Investigations on the β-Hydride Elimination Step in a Pd(II)-based System for the Polymerization of Polar Olefins

Augustin Armand Tchawou Wandji[1], Peter Chen[1] *

[1]ETH Zurich

The controlled (co)polymerization of industrially relevant polar olefins has progressed considerably since the introduction of phosphine-sulfonate palladium(II)-based catalysts by Pugh and coworkers.[1] However, despite the huge potential exhibited by these catalysts, only relatively low molecular weight polymers are obtained and the deactivation of the catalysts strongly limits the (co)polymerization. It is known that both the short length of the polymers and the loss of catalytic activity originate from β-hydride elimination. An understanding of the mechanism by which β-hydride elimination takes place therefore becomes crucial for any rational and significant improvement of the (co)polymerization. Gas phase reactions allow us to examine individual elementary steps and herein, the isolation of catalyst (1) allowed a first qualitative mass spectrometry measurement of the β-hydride elimination step (Figure 1). Additional quantitative threshold measurements were performed to uncover the energetics of this process and the results were compared with DFT calculations.

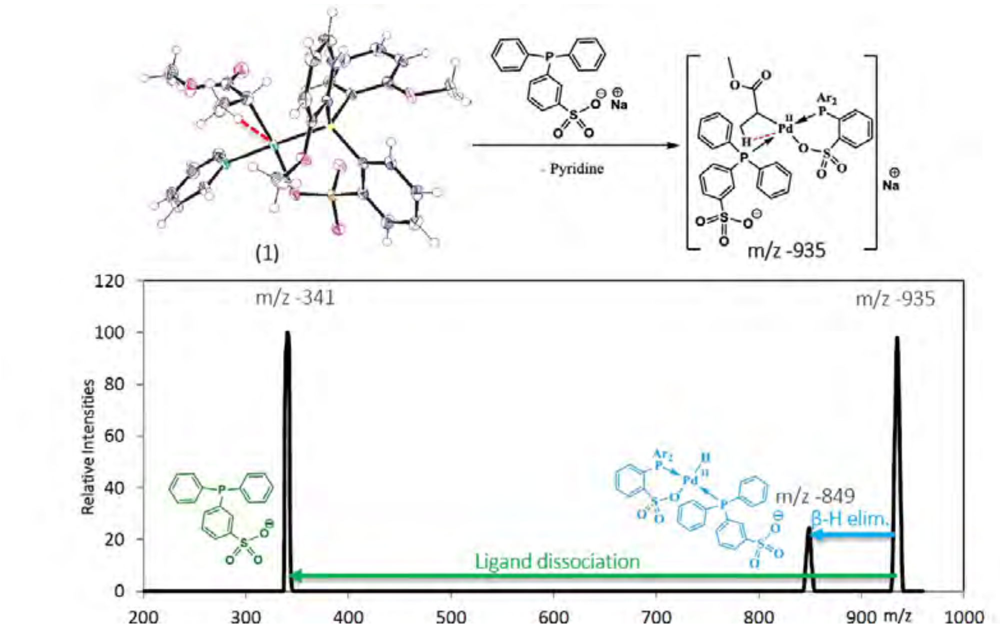


Figure 1: Qualitative mass spectrometry measurement (MS2) in the negative mode using ESI-MS.

[1] Drent, E.; van Dijk, R.; van Ginkel, R; van Oort, B; Pugh, R. I. *Chem. Commun.*, 2002, 744-745

Layered ionic liquid-crystalline organisations built from nano-capsules $[Mo_{132}O_{312}S_{60}(SO_4)_x(H_2O)_{132-2x}]^{(12+2x)-}$ and $DODA^+$ cations

Emmanuel Terazzi[1], Sébastien Floquet[2], Vladimir S. Korenev[2], Akram Hijazi[2], Laure Guénée[1], Emmanuel Cadot[2]

[1]University of Geneva, [2]University of Versailles

Two dimethyldioctadecylammonium ($DODA^+$) salts of a new keplerate with the general formula $[Mo_{132}O_{312}S_{60}(SO_4)_x(H_2O)_{132-2x}]^{(12+2x)-}$ (Figure) and abbreviated $DODA_n{-}Mo_{132}S_{60}$ ($n = 44, 56$) were synthesised and characterised. [1] [2] Both clusters were fully characterised by the combination of Polarised Optical Microscopy, Differential Scanning Calorimetry and Small-angle X-Ray Diffraction showing self-organisation in lamellar (L) liquid crystalline phases.

We demonstrated that the lamellar periodicity h of the mesophases can be controlled with the number of $DODA^+$ associated to the clusters. Finally, these new results were compared to those gained from a previously published analogue, the fully oxo keplerate noted $DODA_{36}{-}Mo_{132}$ that also self-organise with temperature, but in a slightly more structured lamellar liquid crystalline phase. [3]

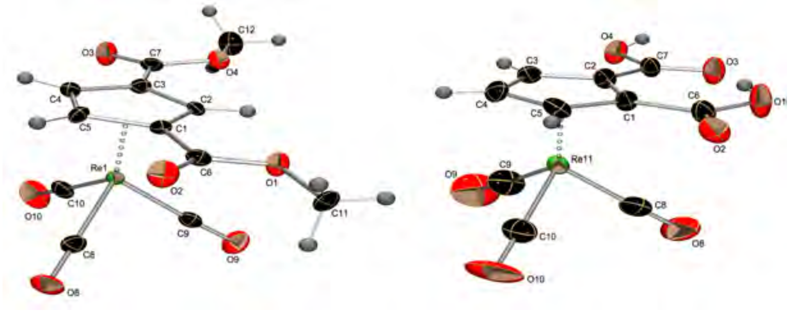
[1] V. S. Koronev, A. G. Boulay, M. Haouas, F. Bannani, V. P. Fedin, M. N. Sokolov, E. Terazzi, S. Garai, A. Müller, F. Taulelle, J. Marrot, N. Leclerc, S. Floquet, E. Cadot *Chem. Eur. J.* **2014**, *20*, 3097-3105.
[2] S. Floquet, E. Terazzi, V. S. Koronev, A. Hijazi, L. Guénée, E. Cadot. *Liq. Cryst.,* **2014**, *41*, 1000-1007.
[3] S. Floquet, E. Terazzi, A. Hijazi, V.S. Korenev, L. Guénée, C. Piguet, E. Cadot *New J. Chem.* **2012**, *36*, 865-868.

Aqueous Synthesis of Multi-Functional Cyclopentadienyl Complexes: [(η^5-Cp{COOR}$_2$)M(CO)$_3$] (M = Re, ^{99m}Tc) for Potential Theranostic Applications.

Samer Ursillo[1], Daniel Can[1], Harmel W. Peindy N'Dongo[1], Paul Schmutz[1], Bernhard Spingler[1], Roger Alberto[1] *

[1]University of Zurich

The sodium salt of Cp carrying two carboxylato groups Na[Cp(1,2-COOMe)$_2$] (**1**) was described in literature but its coordination chemistry is largely unexplored [1,2]. Retaining the principal coordinating properties of the Cp-ring, the two functional groups allow for the coupling to one or two chemical and biological functions. Moreover, **1** is water soluble, water stable and does not dimerize or polymerize in aqueous media. These properties which differ significantly from other cyclopentadienyl derivatives make it versatile for molecular imaging purposes. We developed a fully aqueous synthesis of [(Cp-R)^{99m}Tc(CO)$_3$] at T ≤ 100°C [3]. Recently, we reported detailed studies on similar complexes and their rhenium homologues [4-6].



The rhenium complexes [Re{Cp(1,2-COOMe)$_2$}(CO)$_3$], [Re{Cp(1,3-COOMe)$_2$}(CO)$_3$], [Re{Cp(1,2-COOH)$_2$}(CO)$_3$] and [Re{Cp(1,3-COOH)$_2$}(CO)$_3$] serve as potential building blocks for therapeutic agents. The ^{99m}Tc homologues [^{99m}Tc{Cp(1,2-COOMe)$_2$}(CO)$_3$], [^{99m}Tc{Cp(1,2-COOH)$_2$}(CO)$_3$] and [^{99m}Tc{Cp(1,3-COOH)$_2$}(CO)$_3$] have high potential for diagnostic applications in nuclear medicine.

[1] D. Peters, *J. Chem. Soc.,* **1959,** 0, 1757-1760.
[2] L. Busetto, M. C. Cassani, V. Zanotti, V. G. Albano, P. Sabatino, *Organometallics,* **2001,** 20, 282-288.
[3] Y. Liu, B. Spingler, P. Schmutz, R. Alberto, *J. Am. Chem. Soc,* **2008,** 130, 1554-1555.
[4] S. Sulieman, D. Can, J. Mertens, H. W. P. N`Dongo, Y. Liu, P. Schmutz, M. Bauwens, B. Spingler, R. Alberto, *Organometallics,* **2012,** 31, 6880-6886.
[5] D. Can, B. Spingler, P. Schmutz, F. Mendes, P. Raposinho, C. Fernandes, F. Carta, A. Innocenti, I. Santos, C. T. Supuran, R. Alberto, *Angew. Chem. Int. Ed.,* **2012,** 51, 3354-3357.
[6] D. Can, H. W. P. N`Dongo, B. Spingler, P. Schmutz, P. Raposinho, I. Santos, R. Alberto, *Chem. Biodivers.,* **2012,** 9, 1849-1866.

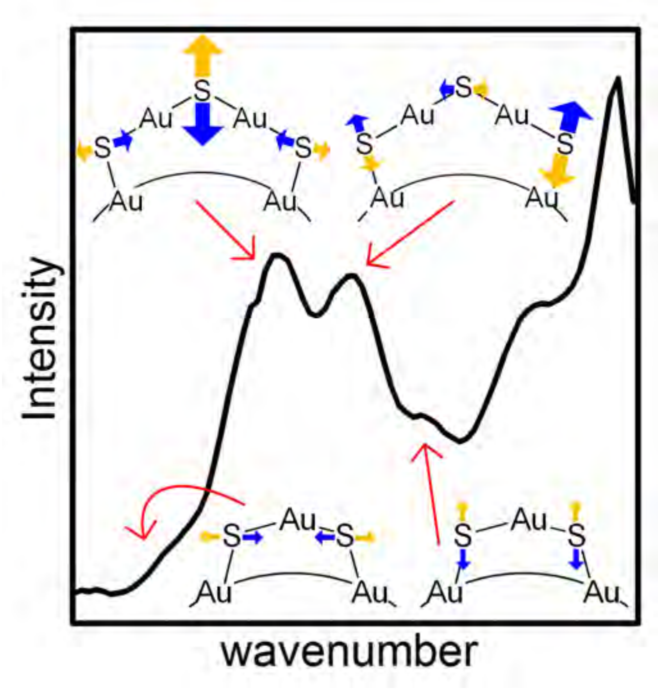
Towards a better understanding of the gold-sulfur interface by spectroscopic investigation on monolayer protected gold-nanoclusters

Birte Varnholt[1], Thomas Bürgi[1] *

[1]University of Geneva

Gold nanoclusters are well defined materials which consist of a metal core protected by a layer of gold-thiolate units. The atomically precise structure and our ability to separate different sizes and even enantiomers of chiral clusters make these a very interesting system for studying the gold-thiolate interaction.

A series of clusters of different sizes and protected with different ligands was synthesized and investigated by circular dichroism, HPLC, vibrational spectroscopy and other methods. Following the racemization of enantioseparated clusters by CD and HPLC we could show that the gold-sulfur interface is flexible and ligands can move.[1] This result is further confirmed by ligand exchange reactions and the spectroscopic study thereof. Au-Au and Au-S vibrations are expected in the low frequency region (30-600 cm^{-1}). Far-infrared[2] and Raman[3] spectra show subtle but consistent changes of position and form of these characteristic bands. Notably the Au-S-C bending and Au-S radial vibrations vary with cluster-size and ligand structure; a result which could prove useful for the structure determination of new cluster sizes.



[1] B. Varnholt, I. Dolamic, S. Knoppe, and T. Bürgi, *Nanoscale*, **2013**, 5, 9568–9571.
[2] I. Dolamic, B. Varnholt, and T. Bürgi, *Phys. Chem. Chem. Phys.*, **2013**, 15, 19561–19565.
[3] B. Varnholt, P. Oulevey, S. Luber, C. Kumara, A. Dass, and T. Bürgi, *J. Phys. Chem. C*, **2014**, 118, 9604-9611.

Polyoxometalates: Structural diversities and efficient catalysts for artificial photosynthesis

Kim von Allmen[1], Pierre-Emmanuel Car[1], Fabio Evangelisti[1], Olivier Blacque[1], Greta Ricarda Patzke[1] *

[1]University of Zurich

Polyoxometalates (POMs) are structurally versatile oxoclusters, preferably with Mo, W and V in their high oxidation states, with a wide range of applications such as in catalysis and bio-medical materials.[1] Lacunary POM derivatives act as flexible host ligands for the coordination of transition metal ions of the 1st and 2nd rows. We herein report on the synthesis and the characterization of two new gallium containing polyoxometalates $[Ga_6(H_2O)_3\{\alpha\text{-}SiW_9O_{35}(OH)_2\}_2]^{10-}$ **(1)** and $[Ga_4(H_2O)_2\{\alpha\text{-}SiW_{10}O_{38}\}_2]^{12-}$ **(2)** isolated from the reaction of the trilacunary precursor $[\alpha\text{-}SiW_9O_{34}]^{10-}$ and gallium nitrate.[2] In the search for new efficient water oxidation catalysts (WOCs), we have also investigated three new cobalt and manganese substituted tungstobismutates: $[\{Co(H_2O)_3\}_2\ \{CoBi_2W_{19}O_{66}(OH)_4\}]$ **(3)**, $[Co_{2.5}(H_2O)_6\{Bi_2W_{19.5}O_{66}(OH)_4\}]$ **(4)** and $[Mn_{1.5}(H_2O)_6\{Bi_2W_{20.5}O_{68}(OH)_2\}]$ **(5).** The activity of **1** and **2** as WOCs has been compared to the activity of compounds **3**-**5**. While POMs **1** and **2** did not show activity for visible light driven water oxidation, POM **3** is an efficient WOC. Structural studieson POM **3**, **4** and **5** have shown that a subtle disorder of the central metal core leads to an efficient or an inefficient WOC.[3] This structure-activity relationship of the newly reported POM is still under investigation.

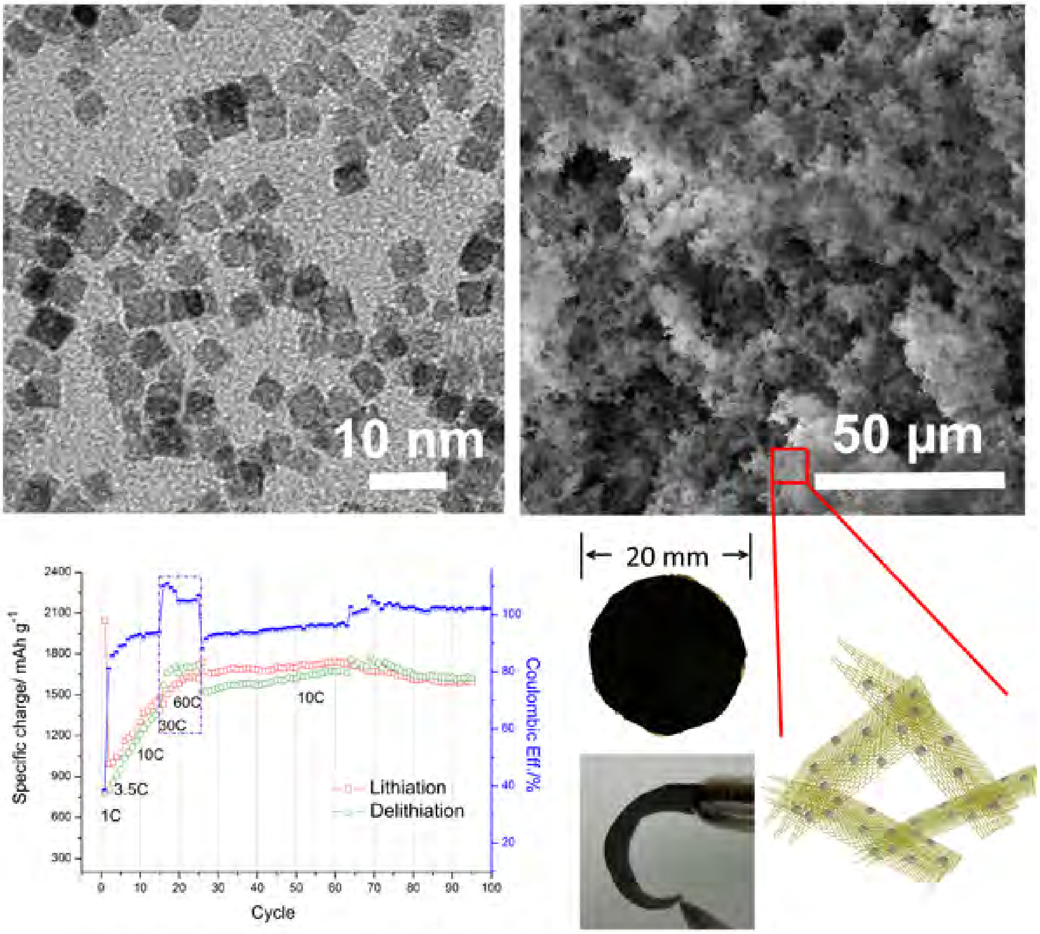
[1] A. Proust, R. Thouvenot, P. Gouzerh, *Chem. Commun*., **2008**, 1837.
[2] K. von Allmen, P.-E. Car, O. Blacque, T. Fox, R. Müller, G. R. Patzke, *Z. Anorg. Allg. Chem.* **2014**, 640, (5), 781–789.
[3] F. Evangelisti, P.-E. Car, O. Blacque, G. R. Patzke, *Catal. Sci. Technol*. **2013**, 3 (12*),* 3117 - 3129.

Flexible Co_3O_4/rGO Composite Aerogel as High-Performance Anode for Lithium-ion Batteries

Guobo Zeng[1], Markus Niederberger[1] *

[1]ETH Zurich, Laboratory for Multifunctional Materials, Department of Materials, Vladimir-Prelog-Weg 5, 8093, Zurich, Switzerland

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 transition metal oxides, particularly in the form of nanomaterials, have long been exploited as high capacity anode for LIBs; however, its poor Li^+ and e^- conductivity and huge volume change upon cycling impede the high-rate and cyclability performance towards its practical application. Here we present a facile approach to fabricate a flexible Co_3O_4/reduced graphene oxide (rGO) composite aerogel with hierarchical porosity as a binder-free high-performance anode where the Co_3O_4 nanocrystals are integrated within an interconnected rGO network. Beneficial 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 Co_3O_4/rGO composite aerogel demonstrates superior electrochemical performance up to 60C (1C = 1 A g^{-1}) and long-term stability up to 100 cycles at 10C rate.



Jiang, J.; Li, Y.; Liu, J.; Huang, X.; Yuan, C.; Lou, X. W., *Adv. Mater.* **2012,** 24, 5166-5180.

Direct labeling of thebtuB riboswitch for singlemolecule FRET studies

Meng Zhao[1], David Egloff[1], Igor Oleinich[1], Eva Freisinger[1], Roland K.O. Sigel[1] *

[1]University of Zurich

Riboswitches are highly conserved RNA sequences in the untranslated regions of bacterial mRNAs.[1] They specifically bind metabolites leading to a different three-dimensional structure to regulate gene expression and metabolite concentration in the cell. The 200 nucleotide long *btuB* riboswitch from *E. coli* folds into a complex tertiary structure in the presence of Mg^{2+}, resulting in a binding pocket of AdoCbl (adenosyl cobalamin).[2] Upon AdoCbl binding, transcription and translation of the *btuB* mRNA is down regulated, preventing further uptake of this metabolite. There is very limited knowledge on the folding and binding behavior of the *btuB* riboswitch at the atomic level. Here, we apply a recently developed strategy in our group[3] to directly label the *btuB* riboswitch with fluorophores at specific sites for single molecule FRET studies.

Financial support by the Swiss National Science Foundation (EF), the UZH Forschungskredit (DE), the European Research Council (RKOS), the University of Zurich (EF, RKOS), as well as the SBFI (COST Action CM1105; EF, RKOS) is gratefully acknowledged.

1. Alexander S Mironov, Ivan Gusarov, Ruslan Rafikov, Lubov Errais Lopez, Konstantin Shatalin, Rimma A. Kreneva, Daniel A. Perumov, Evgeny Nudler,*Cell*, **2002**, 111, 747–756
2. Pallavi K. Choudhary, Roland K.O. Sigel, *RNA*, **2014**, 20, 36-45
3. David Egloff, Eva Freisinger, *submitted*