CHIMIA
CHIMIA 2016, Volume 70
ISSN 0009-4293
www. chimia.ch

SCS
Swiss Chemical
Society

Supplementa to Issue 7-8/2016

SCS Fall Meeting 2016

Poster Abstracts Session of Inorganic & Coordination Chemistry

September 15, 2016
University of Zurich, Irchel Campus
http://scg.ch/fallmeeting/2016

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Multitopic precursors for oxide materials' synthesis

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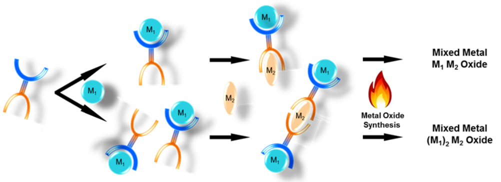
The research interest in mixed metal oxides is increasing in material science, as they have multiple applications, such as in batteries, ceramics, pigments, high-Tc superconductors or transparent conductors. However, the two main challenges for the synthesis of such compounds are the lack of control on the ratio of the different metal components and the extreme conditions (up to 900 °C) that many of these oxides require during their traditional solid state synthesis. To overcome these issues, we propose a strategy for the synthesis of mixed metal complexes, which is based on precursors of coordination compounds, using the "multitopic ligand approach" .



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

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Pressure induced chemisorption in isoreticular Metal Organic Frameworks

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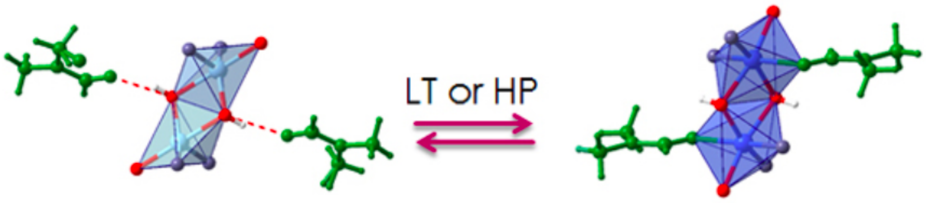
Metal organic frameworks (MOF) with stereochemically accessible unsaturated metal centres may enable chemisorption of small molecules at the metal sites, to be distinguished from the classical physisorption occurring through weaker interactions between the guest and the internal active surface of the network. Chemisorption and framework flexibility are desirable features for the design of promising catalysts, selective sieves or absorbents. Moreover, by varying metal centers, oxidation states, organic linkers, guest molecules, stereochemical features etc., the potential and complexity of MOFs can be tuned towards to the desired properties. Efforts to rationalize the synthesis of frameworks with specific features would therefore benefit from comparative studies involving systematic variations of their structure, which can be induced by external stimuli (temperature, pressure) as well as chemical modifications.

In this work, we investigated the role of controlled structural modifications on the physico-chemical properties of a family of isostructural MOFs.We discuss here about isomorphic, iso-reticular MOFs based on M^{II} connectors (Co^{II}, Zn^{II} or Mn^{II}) and benzotriazolide-5-carboxylato (btca) linkers that were found to selectively react with guest molecules (like methanol or dimethylformamide) trapped in the channels during the sample preparation or after an exchange process. A mild compression or cooling are enough to induce a reversible nucleophilic addition of the guest molecules to the metal ion. Depending on the guest or the metal, the coordination may increase stepwise up to saturation. A preliminary study on the CoII MOF was recently published.[1]



[1] Arianna Lanza, Luzia Germann, Martin Fisch, Nicola Casati, Piero Macchi,*J. Am. Chem. Soc.*, **2015,** 137, 13072–13078

Controlling architecture of coordination cages via the aspect ratio of the ligands

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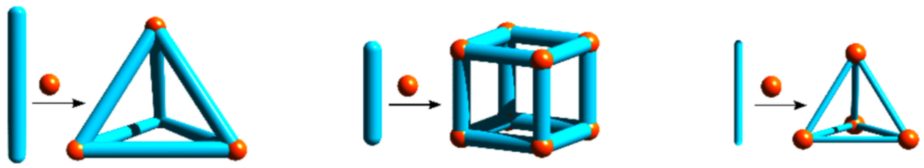
It is possible to control the geometry of metallasupramolecular assemblies via the aspect ratio of rod-like metalloligands. Functionalized clathrochelate complexes were used with a variable aspect ratio. A cubic Fe_8L_{12} cage was obtained, when ligand aspect ratios are intermediate. By increasing the length or by decreasing the width of the ligand, the self-assembly process resulted in the formation of tetrahedral Fe_4L_6 cages instead of a cubic one.



J. Am. Chem. Soc., 2016, 138 (6), pp 2046–2054.

A Homoleptic Molybdenum(0) Complex with Chelating Isonitrile Ligands as a $[Ru(bpy)_3]^{2+}$ Analog

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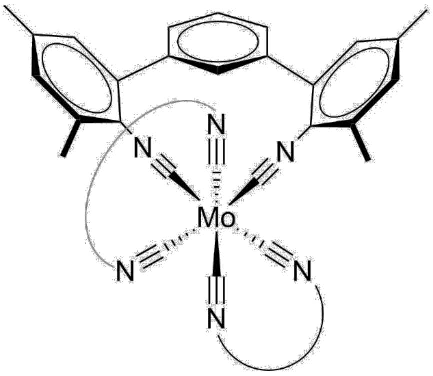
One of the best studied classes of photoredox catalysts and photosensitizers are complexes derived from the ruthenium(II) tris(2,2'-bipyridine) parent complex. These compounds are chemically robust, exhibit MLCT absorptions in the visible spectral range and their properties are tunable by altering their ligands. [1]

Cr(0), Mo(0) and W(0) complexes with monodentate aromatic isonitrile ligands have long been known as isoelectronic analogs to Ru(II)-based d^6 metal a-diimines, but they are prone to photoinduced ligand dissociation. [2-3]



We report on the first homoleptic Mo(0) complex with chelating isonitrile ligands (Figure 1). Our complex is isoelectronic to $[Ru(bpy)_3]^{2+}$ and exhibits similar optical spectroscopic properties. The chelating ligands make the complex comparatively robust. Our complex was employed in photoredox chemistry, and was found to be a much stronger photoreductant than $[Ru(bpy)_3]^{2+}$.

Our Mo(0) complex is a strongly reducing, chemically robust alternative to $[Ru(bpy)_3]^{2+}$, but made from an earth-abundant metal.

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Synergistic antimicrobial effect of silver and other metals in bimetallic complexes

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The precious metal silver is aging for its excellent antimicrobial properties as throwing silver coins in fountains is not only a lovely old tradition.[1] It has been recognized to play an important role concerning medical applications, for example the coating of implants with Ag^0 or Ag^I coordination compounds to avoid infections due to bacterial biofilms formation.[2]

The research of the FROMM group with respect to antimicrobial silver compounds was focused on silver coordination networks, meaning short PEG oligomers functionalized with (iso-)nicotinic acid as ligands.

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

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Thermodynamic and Photophysical Properties of Dual VIS/NIR Luminescent Erbium Complexes

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The luminescence properties of lanthanide complexes are a subject of great interest mainly due to their applications as building blocks for construction of functional materials.[1] Since the Er(III) ion possesses several closely spaced exited states that cover the infrared to ultraviolet range, Er(III) complexes have been exploited as activators in linear optics for molecular up-conversion.[2] In this perspective, a series of nine- and eight-coordinated mononuclear Er(III) complexes with tridentate ligands of increasing steric demand **L1-L6** (Figure 1) have been synthesized and characterized. Spectrophotometric titrations with ErX_3 (X = $CF_3SO_3^-$, ClO_4^-, tetraperfluoroalkoxyaluminate) in aprotic organic solvents show the successive formation of ML, ML_2 and ML_3 complexes, the speciation of which can be rationalized by using the site-binding model. Photophysical investigations reveal a very unusual dual VIS/NIR Er-centered emission sensitized via ligand excitation. Whereas the NIR emission arising from the Er($^4I_{13/2}$®$^4I_{15/2}$) may be classified as 'standard', the nanosecond green emission occurring at 540 nm (Er($^4S_{3/2}$®$^4I_{15/2}$)) is much more challenging and rarely reported for coordination complexes possessing high-energy oscillators. The special conditions required for implementing Er-centered visible emission in coordination complexes will be discussed in this work.

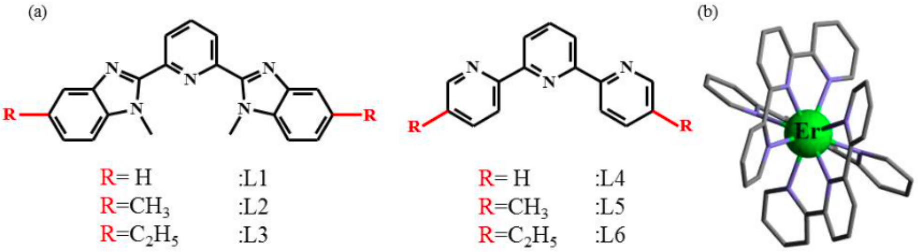

Figure 1. a) Chemical structures of the ligands **L1-L6.** b) Crystal structural of [Er(**L4**)$_3$](CF$_3$SO$_3$)$_3$

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Hydrolytic behaviour of mono-and dithiolato-bridged dinuclear arene ruthenium complexes and their interactions with biological ligands

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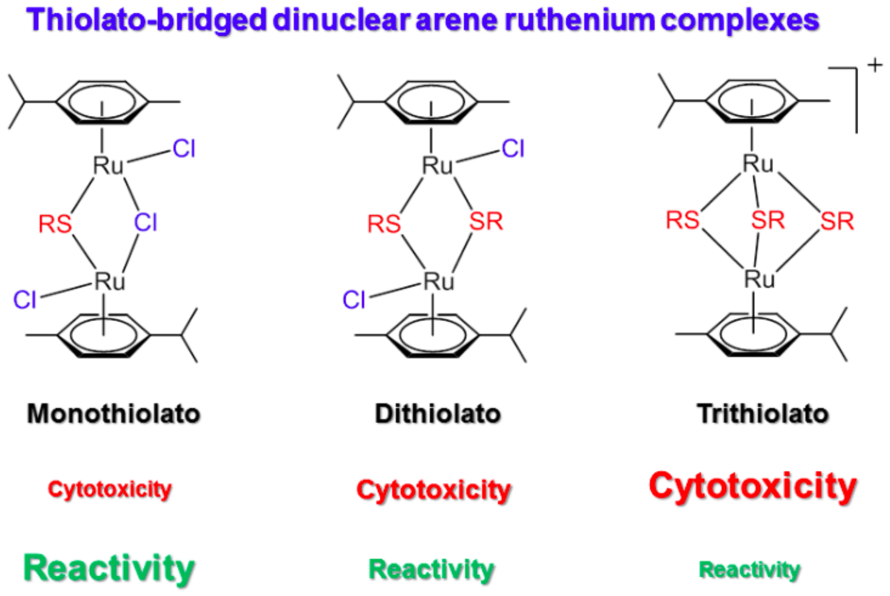
[1]University of Bern, [2]University of Neuchâtel

In this contribution, the hydrolysis and the reactivity of two dinuclear *p*-cymene ruthenium monothiolato complexes$[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{Pr}^i)_2\text{Ru}_2\text{Cl}_2(\mu\text{-Cl})(\mu\text{-SR})]$ and of two dinuclear *p*-cymene ruthenium dithiolato complexes $[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{Pr}^i)_2\text{Ru}_2(\mu\text{-SR})_2\text{Cl}_2]$ towards amino acids, nucleotides, and a single-stranded DNA dodecamer were studied. In aqueous solutions, the monothiolato complexes undergo rapid hydrolysis, irrespective of the pH value, while the dithiolato complexes are stable under acidic conditions, but undergo slow hydrolysis under neutral and basic conditions.



Surprisingly, no adducts are observed upon addition of an excess of L-methionine or L-histidine to the aqueous solutions of the complexes. Upon addition of an excess of L-cysteine, on the other hand, the monothiolatho complexes form unusual cationic trithiolato complexes $[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{Pr}^i)_2\text{Ru}_2\{\mu\text{-SCH}_2\text{CH(NH}_2\text{)COOH}\}_2(\mu\text{-SR})]^+$ containing two bridging cysteinato ligands, while the dithiolato complexes yield cationic trithiolato complexes $[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{Pr}^i)_2\text{Ru}_2[\mu\text{-SCH}_2\text{CH(NH}_2\text{)COOH}](\mu\text{-SR})_2]^+$ containing one bridging cysteinato ligand. Moreover, the complexes are inert toward nucleotides and DNA, suggesting that DNA is not a target of cytotoxic thiolato-bridged arene ruthenium complexes. In contrast to the trithiolato complexes, monothiolato and dithiolato complexes hydrolyse and react with L-cysteine. These results may have important implications for the mode of action of thiolato-bridged dinuclear arene ruthenium drug candidates, and suggest that their modes of action are different to those of other arene ruthenium complexes.[1]

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Screening of Dopants for Ceria-Based Materials for Solar Thermochemical Two-Step CO_2-Splitting

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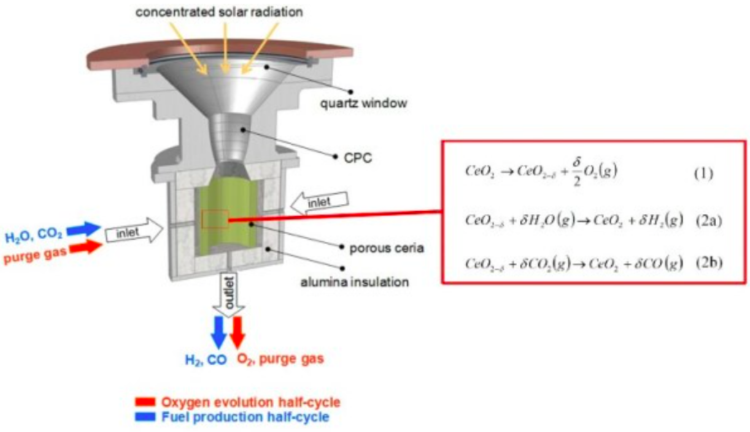
[1]University of Zurich, [2]ETH Zurich, [3]ETH Zurich/PSI Villigen

Fueling the planet with clean and sustainable energy is a fundamental challenge of the 21st century in which solar energy as our main inexhaustible resource plays a key role. Thermochemical water splitting is one of the most elegant approaches to generate solar fuels: The collected solar energy of a heliostat field is focused on a solar reactor which contains a metal-oxide (ceria[1,2],perovskite[3,4,5,6] or spinel[7]).Through cycling of the oxide material between reduction and oxidation steps at different temperatures (Fig. below), water and CO_2 are split into H_2 and CO (syngas), respectively,[1] which can further be converted into fuels (alkanes, e.g. gasoline) by the Fischer-Tropsch process. However, the efficiency is not yet sufficient to produce CO_2 neutral fuels economically. In order to improve the solar-to-fuel conversion efficiency three different types of additives can be used: Tetravalent or trivalent dopants and anti-sintering agents.

We herein report the investigation of all potential tetravalent, eight-fold coordinated dopants for ceria by thermogravimetric analysis (TGA). The influence of the dopants on the oxygen storage capacity (OSC) was studied and a relationship between the effective ionic radius of the dopant and the OSC was established.



$$CeO_2 \rightarrow CeO_{2-\delta} + \frac{\delta}{2} O_2(g) \quad (1)$$

$$CeO_{2-\delta} + \delta H_2O(g) \rightarrow CeO_2 + \delta H_2(g) \quad (2a)$$

$$CeO_{2-\delta} + \delta CO_2(g) \rightarrow CeO_2 + \delta CO(g) \quad (2b)$$

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Tuning the liquid-crystaline properties of pyrenyl-dendrimers by encapsulation in metallacycles

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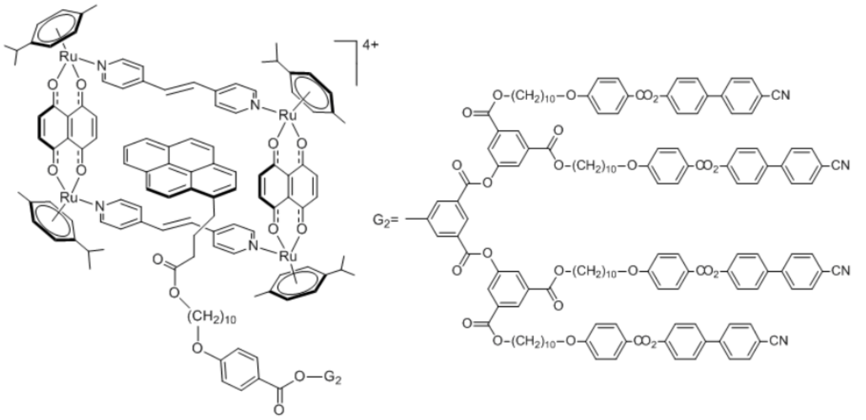
The construction of metallacontainers has garnered great deal of attention owing to their prominent applications in different fields like molecular recognition, host-guest chemistry, crystal engineering, biomedical, and molecular devices.[1] Herein, arene ruthenium metallacycles containing pyrenyl-dendrimers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



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Studies of Iridium Hydride Complexes and Recovery of Iridium Catalysts from Hydrogenation Reactions

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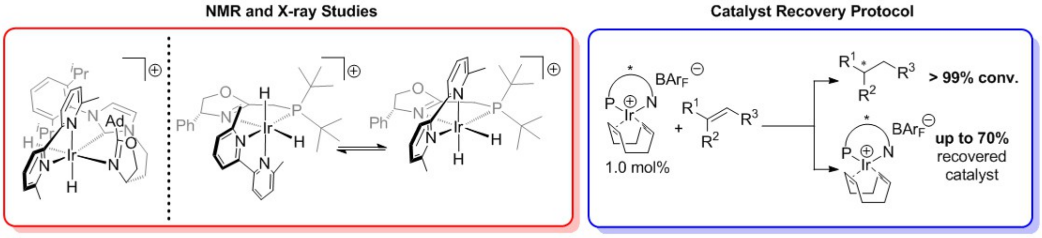
[1]University of Basel, [2]ETH Zurich

Iridium complexes derived from chiral N,P or C,N ligands have emerged as highly effective catalysts for the asymmetric hydrogenation of a wide range of functionalized as well as unfunctionalized alkenes, furans, and imines.[1] Despite the vast amount of literature on this area, the mechanistic details of the iridium-catalyzed asymmetric C=C bond hydrogenation remain to be clarified. Therefore, iridium(III) dihydride complexes continue to be of considerable interest and further studies will be necessary for a better understanding of their chemistry. In recent studies[2] we found reliable procedures for the controlled formation of dinuclear iridium(III) hydride-bridged complexes and experimentally identified previously elusive iridium(III) dihydride olefin complexes.

Herein, we present our results on the synthesis and characterization of new C,N and N,P derived iridium(III) dihydride complexes that are formed under hydrogen gas.[3] Furthermore, based on our current and previous investigations, we have developed a procedure that allows the catalyst recovery as COD complex. Importantly, the recovered catalyst exhibited the same activity and enantioselectivity as the original catalyst.[4]



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Development of new organometallic assemblies for photodynamic therapy applications

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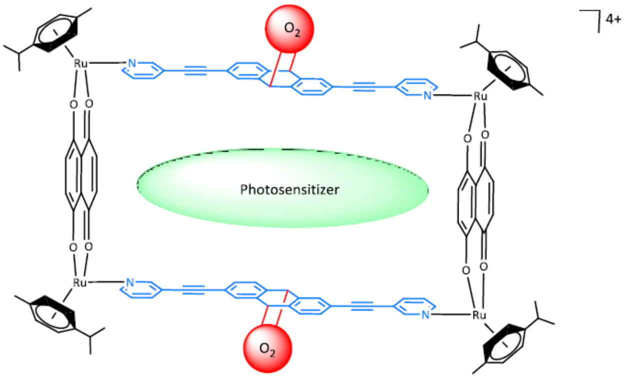
Photodynamic therapy (PDT) treatments involve the injection of a photosensitizer, which is later on activated by light at a specific wavelength. Upon irradiation in a spatial-controlled area, the photosensitizer reaches a high-energy triplet state, and when returning to its ground state, an energy transfer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

Anthracene units are already known for transporting and releasing singlet oxygen ($^1O_2$) via their endoperoxide form, [2] and also for sensing $^1O_2$ during photodynamic treatments. [3] So, the reversible coordination of $^1O_2$ to an anthracene unit, or all other patterns which can play the same role, offers great perspectives for biological applications, especially for PDT.

The project consists of preparing metalla-cages to transport the two components of PDT treatments into cancerous cells. Anthracene units can be attached to the cage as connectors between the dinuclear arene ruthenium clips or inserted as appendages on the different building blocks. The cavity of the metalla-assembly can also be used to transport the photosensitizer.[4]



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Site-specific labeling of large RNA with fluorophores for the application in single molecule FRET studies

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

[1]University of Zurich

A prerequisite of smFRET study of biomolecules is fluorophore installation. For the large RNAs which features more than 200 nucleotide units, a facile method for the site-specific labeling at internal sites is still unavailable. The demand for such a method is high since non-coding RNAs were found to have important biological functions which can be understood well at the single molecule level. Our interest focuses on the btuB riboswitch from E. coli which is over 200 nucleotides in length. Their re-structuring upon metabolite binding regulates gene expression and metabolite maintenance.[1] Recently, we developed a post-transcriptional method that enable the site-specific labeling of large RNA.[2] By applying this method, we prepared several btuB riboswitch constructs with varying labeling schemes. Each of these constructs carries Cy3 as Förster resonance energy transfer (FRET)-donor and Cy5 as FRET-acceptor fluorophore. These differently labeled btuB riboswitches were characterized at the single molecule level. The observed FRET traces point to successful application of our labeling method to large RNAs. Details will be presented during conference. Financial support from the Swiss National Science Foundation (EF), the UZH Forschungskredit (FK-14-096, RB), the European Research Council (RKOS), the University of Zurich (EF, RKOS), and the SBFI (COST Action CM1105; EF, RKOS) is gratefully acknowledged.

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In situ X-ray diffraction monitoring of the room temperature growth of $Bi_2O_2CO_3$

R. Moré[1], M. Olah[1], Y. Zhou[2], G. R. Patzke[1]*

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Functional metal oxide materials are in the focus of several environmentally relevant processes, such as sensor applications and photocatalytic wastewater cleaning.[1-3] A deeper insight into the formation mechanism of such materials is essential for their rational design and optimization. In-situ X-ray diffraction is a proper technique for acquiring the missing knowledge about the reaction mechanisms behind the growth of functional oxide materials under different reaction conditions. [4]

Bismuth oxycarbonate nanosheets obtained from room temperature conversion of bismuth oxide (β-Bi_2O_3) and atmospheric carbon dioxide (CO_2) show interesting humidity sensing properties and high photocatalytic activity.[2] This room temperature formation of $Bi_2O_2CO_3$ offers also an attractive way to CO_2 capture, which is an interesting solution strategy to the global greenhouse effect. This room temperature transformation was studied by in situ techniques at the beamline P02 of the PETRA III storage ring at HASYLAB. [5] The experiments were performed in carbonate buffer solution in order to control the pH value and to simulate a high CO_2 partial pressure. Our in situ X-ray diffraction experiments indicate a strong pH dependence of the reaction mechanism. The in situ PXRD data were compared with ex situ Raman spectroscopy and scanning electron microscopy. This mechanistic information is an important step toward the selective optimization of this multifunctional material.

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New Light Emitting Electrochemical Cells with halogen containing $[Cu(N\^{}N)(P\^{}P)][PF_6]$ complexes

F. Brunner[1], S. Keller[1], A. Pertegás[2], H. J. Bolink[2], E. C. Constable[1]*, C. E. Housecroft[1]*

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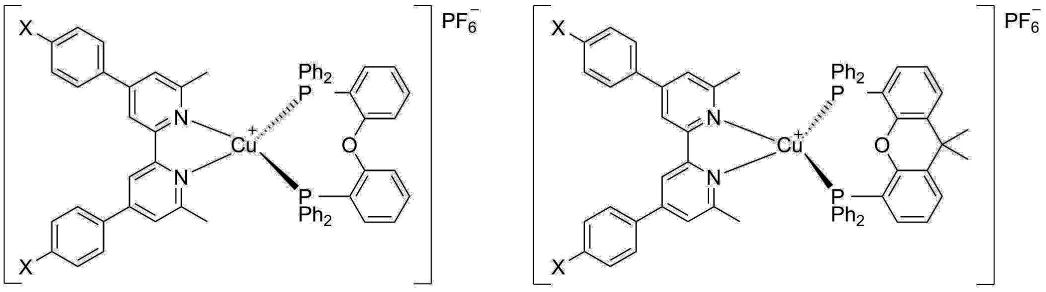
Light emitting electrochemical cells (LEECs) are of growing importance in the field of flexible electronics and large surface lighting devices. The advantage of LEECs over OLEDs is their simple architecture and the usage of air stable electrode and luminescent materials. During the last few years $[Cu(N\^{}N)(P\^{}P)][PF_6]$ type complexes have been proven to perform surprisingly well in LEEC devices. A series of ten new copper (I) complexes with 4,4'-bis(4-halophenyl)-6,6'-dimethyl-2,2'-bipyridine as chelating diimine ligands and POP (bis(2-diphenylphosphinophenyl)ether) or xantphos (4,5-bis(diphenylphosphino)-9,9-dimethylxanthene) as chelating diphosphine ligands were prepared. The resulting complexes adopted a distorted tetrahedral geometry in the solid state; their photophysical properties will be presented. Photoluminescent quantum yield (PLQY) and excited state lifetime measurements revealed a trend towards higher quantum yields and longer lifetime with increasing electronegativity of the halogen on the bpy ligand. LEEC devices were prepared and characterized.



$[Cu(\mathbf{1})(POP)][PF_6]$ and $[Cu(\mathbf{1})(xantphos)][PF_6]$	X = F
$[Cu(\mathbf{2})(POP)][PF_6]$ and $[Cu(\mathbf{2})(xantphos)][PF_6]$	X = Cl
$[Cu(\mathbf{3})(POP)][PF_6]$ and $[Cu(\mathbf{3})(xantphos)][PF_6]$	X = Br
$[Cu(\mathbf{4})(POP)][PF_6]$ and $[Cu(\mathbf{4})(xantphos)][PF_6]$	X = I
$[Cu(\mathbf{5})(POP)][PF_6]$ and $[Cu(\mathbf{5})(xantphos)][PF_6]$	X = H

Nitrous oxide as hydrogen acceptor for the dehydrogenative coupling of alcohols catalyzed by Rh(I)

T. Gianetti[1], S. P. Annen[1], G. Santiso-Quinones[1], M. Reiher[1], H. Grützmacher[1]*

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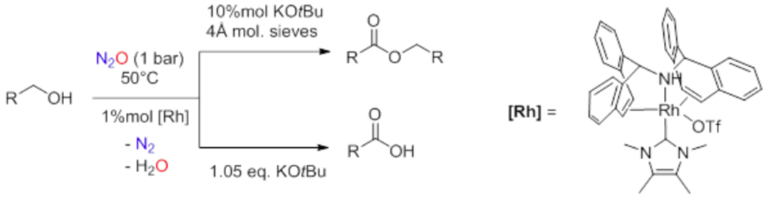
Nitrous oxide (N_2O) is an industrial waste product[1] which massively depletes ozone[2] and has a greenhouse gas effect 300 times higher than CO_2.[3] Its transformation to less harmful chemicals is therefore of particular interest and attractive when at the same time useful/ value-added products are generated. Herein we present the use of N_2O as hydrogen acceptor during dehydrogenocoupling of primary alcohols which led to N_2 and H_2O as only side product. The reaction, which is catalysed by low loading of diolefin-amine rhodium(I) complex under mild condition, proved to be efficient for a large scope of substrates. Mechanistic study suggests N_2O activation via a metal hydride leading to a metal hydroxide species and N_2.



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Hydrogen Bonded Arene Ruthenium Metalla-Assemblies.

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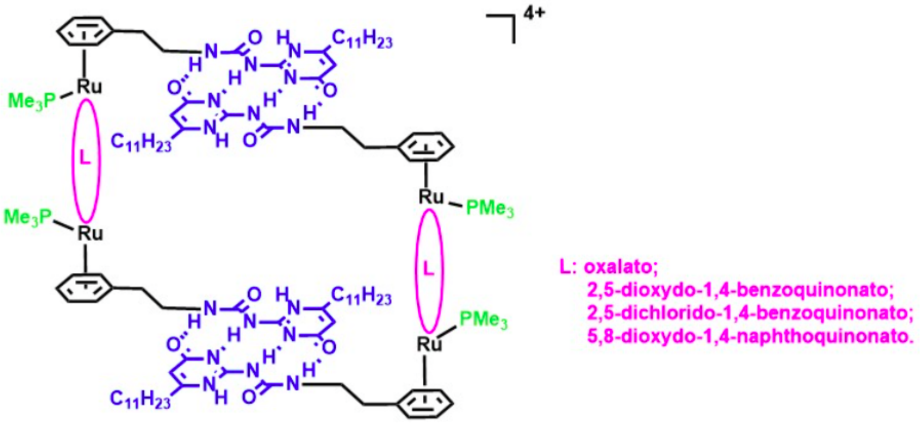
Hydrogen bonds are the most utilized non-covalent interactions in biological systems, due to their directionality, stability, reversibility and diversity. The weak strength of hydrogen bonding can be modified by combining several hydrogen bonds in the same unit like the 2-ureido-4-[1H]-pyrimidinone motif.[1]

Arene ruthenium metalla-assemblies have showed great biological potential. They can not only possess anticancer properties themselves, but also encapsulate and transport drugs in vitro.[2,3] Inspired by the combination of Hbonding and metal complexation from the group of de Mendoza,[4] we have recently prepared a series of hydrogen bonded metalla-assemblies.[5]

This project aims at developing the concept of hydrogen bonded arene ruthenium metalla-assemblies by designing new building blocks with Hbonding units. Our first results will be discussed.



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Highly active and stable iridium oxide and pyrochlore materials for oxygen evolution reaction

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Energy storage is a significant challenge due to the continuous growth of energy production from intermittent renewable energy sources. Water electrolysis is a promising solution allowing for a direct production of hydrogen, which can be easily stored and used either directly as a fuel (e.g. in the vehicles) or in the fuel cells to generate electricity. Proton exchange membrane water electrolysis (PEMWE) uses the solid proton conductive electrolyte and produces pure hydrogen at high pressures.[1] Moreover PEM water electrolyzers operate in acidic environment and thus benefit from fast kinetics of the cathodic hydrogen evolution reaction and high-voltage efficiencies at high current densities. At the same time, acidic environment strongly influences stability of the anodic water oxidizing material, limiting the pool of possible oxygen evolution reaction (OER) catalysts to mainly noble metal oxides (such as RuO_2, IrO_2 and their solid solutions).[2] The high cost and low abundance of the latter hinders the wide implementation of the PEMWE technology making the development of the active, stable, and cheap OER catalysts an extremely important issue.

The present work addresses the synthesis and study of high surface area iridium oxide and iridium pyrochlore materials as anodes for PEMWE. The OER catalysts were synthesized by the modified Adams fusion method which utilizes molten sodium nitrate for oxide nanoparticles formation. Chlorine-free IrO_2 nanoparticles of different size and shape were synthesized from $Ir(acac)_3$ at temperatures from 350 °C to 600 °C. The applied approach allowed controlling the effect of the particle size, morphology, and nature of the surface species on the oxygen evolution reaction (OER) activity of IrO_2 catalysts. Iridium oxide synthesized at 350 °C, consisting of 1.7 ± 0.4 nm particles with a specific surface area of 150 m^2g^{-1}, shows the highest OER activity: E = 1.499 ± 0.003 V to reach 10 $Ag_{ox}{}^{-1}$. Operando X−ray absorption spectroscopy in addition to X−ray photoelectron spectroscopy studies of this oxide catalyst indicate the presence of Ir^{3+} surface sites which was correlated with the formation of the iridium hydroxo (Ir−OH) surface species. Evaluation of TOF (per unit of area) of the IrO_2 catalysts revealed importance of the surface hydroxide layer for OER catalysis.

Iridium pyrochlore materials of the general formula $A_2Ir_2O_{6.5+x}$, where A is Bi, Y or Pb, were synthesized at 500−575 °C from metal nitrates and iridium chloride. Conventional solid-state synthesis of iridium pyrochlores requires high temperatures to approach phase pure materials (typically ≥ 800 °C), which yields catalysts with low surface area (≤ 2 m^2g^{-1}). The use of the modified Adams fusion method allowed synthesis of the materials with surface areas up to 40 m^2g^{-1}. Obtained catalysts show high activity and stability in OER, the lowest overpotentials were observed for $Y_2Ir_2O_7$ and $Bi_2Ir_2O_7$. $Y_2Ir_2O_7$ shows an overpotential about 50 mV lower than that of a similar surface area iridium oxide (30 m^2g^{-1}), which corresponds to about 10 times gain in the current. This suggests that the OER materials with pyrochlore structure allow improving the specific activity of Ir-based catalysts, offering a possibility to develop cheap, active and stable anodic catalysts for PEMWE.

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Fighting Cancer with the Next Generation of Organometallic Assemblies

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Tumor blood vessels are better in extravasating large molecules from the blood, and tumors show a poor lymphatic drainage.[1] Therefore, these two features are the bases for the EPR (Enhanced Permeability and Retention) effect. Due to this enhanced permeability, large molecules are able to enter into the tumor tissue and accumulate locally due to the poor lymphatic drainage, thus increasing the selectivity.[2] Our research uses organometallic assemblies that are likely better taken up by tumor tissues. Therefore, to better exploit the EPR effect, we have designed larger arene-ruthenium metalla-assemblies.[3] These large compounds are composed of three metalla-clips that are connected by two tridentate panels. Functional groups can be anchored on the building blocks to enhance the size, activity and physiological property. In the example below, octyl chains are anchored on the clip, thus increasing significantly the volume of the assembly. In the future, the influence of introducing longer and/or shorter, alkyl- and/or PEGylated chains, will be evaluated.

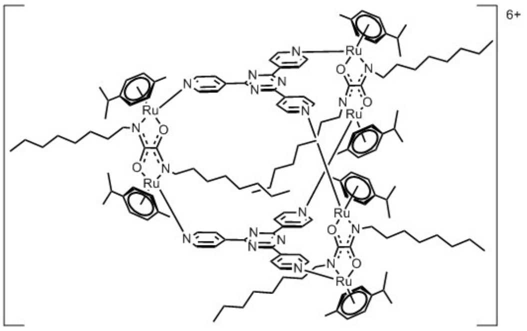

Figure 1: Hexanuclear Arene-Ruthenium Metalla-Assembly.

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Nucleophilic Reactivity of a Nitride-Bridged di-Uranium(IV) Complex: small molecules activation.

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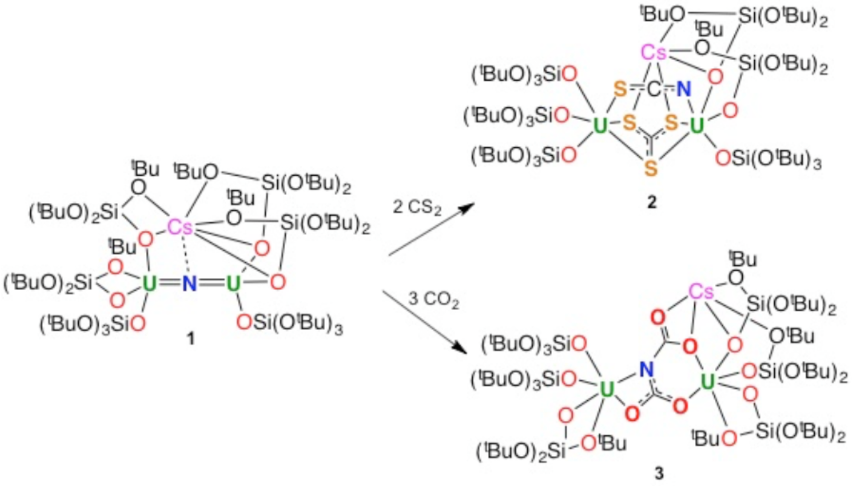
[1]EPF Lausanne

Uranium nitrides are attractive candidates for stoichiometric and catalytic N-transfer reactions, small molecule transformation,[1] and for advanced nuclear fuels. In recent years an increasing number of molecular nitride compounds of uranium has been synthetized [2]. However, the reactivity of bridging nitrides remains practically unexplored. The N-C bond formation reactions are very important in the construction of value-added chemical compounds such as amino acids, pharmaceuticals or agrochemicals. Synthetic methods using cheap and largely available feedstock such as carbon dioxide or carbon monoxide are particularly desirable.[3] So far the reactivity of molecular nitride compounds of *f* elements with CO_2 has not been investigated. Our group has recently shown that *tert*-butoxysiloxides are very effective ligands in supporting the reactivity of low valent f elements with small molecules.[4],[5] Here we will report the ability of the previously described nitride bridged diuranium(IV) complex $Cs\{(\mu\text{-}N)[U(OSi(OtBu)_3)_3]_2\}$, **1** [6] to promote N-C bonding formation and more in particular the reactivity with CO_2 and CS_2,and CO.

The nitride-bridged diuranium(IV) complex, $Cs\{(\mu\text{-}N)[U(OSi(O^tBu)_3)_3]_2\}$ (**1**), displayed reactivity towards CS_2 and CO_2 that is unprecedented in f-element chemistry, affording diverse N-functionalized products (Figure 1), the thiocyanate/trithiocarbonate complex, (**2**) and the unprecedented dicarbamate product, (**3**). Moreover, the reaction with charged electrophile as MeOTf, leads to a change in the electrons distribution within the bridging nitride yielding to two different products of trivalent and pentavalent uranium, respectively. This reaction may lead to a further understanding of the bonding in complex **1**. The high reactivity of complex **1** is also confirmed by its ability to cleave one of the strongest bonds in nature, the carbon oxygen bond in carbon monoxide. We will present an overview of the reactivity of uranium nitrides with small molecules.



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Heterometallic single precursor of oxides for Na-ion battery cathode materials

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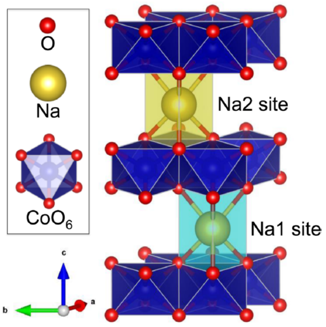
[1]University of Fribourg

After decades of improvements of and investments in the Li-ion battery technology, attention has been shifted toward Na-ion battery, mainly because of sodium's low cost. A lot of different materials are investigated as potential cathode for Na-ion batteries, especially the layered oxides of transition metals, NaT_MO_2 (with T_M = Ti, V, Cr, Mn, Fe, Co, Ni…), which are traditionally synthesized via solid state techniques.

These solid state techniques involve high energy ball-milling of several precursors (usually sodium carbonate and transition metal oxide) followed by calcination at high temperature (800-1000°C) for long reaction times, (8-12 hours) [2]. This long and energy consuming process was required in order to obtain a homogeneous mixing of the precursors. Recently, it was reported that synthesizing heterometallic single precursor can reduce the duration and the calcination temperature due to the pre-organized precursor design [3]. The high temperature phase of lithium cobalt oxide (HT-$LiCoO_2$) was obtained using heterometallic Li-Co alkoxides/aryloxide complexes as precursors [3] at as low temperatures as 350-450°C instead of 600-900°C required for the solid state synthesis [4].



The crystal structure of Na_xCoO_2 (x ‹1) has octahedral CoO_2 layers and prismatic coordinated sodium ions (Figure 1)[1]. The content of sodium influences the crystal structure and the lattice parameters of the unit cell. In the end, the amount of sodium in the structure also determines the specific capacity of sodium ion batteries.

We synthesized the Na_xCoO_2 starting from heterometallic complexes of sodium and cobalt. The method of heterometallic complexes is also applied to other transitions metals: nickel, iron and manganese. The obtained oxides will be characterized and tested as sodium ion battery cathode materials. We will present our first efforts, results of syntheses and characterizations.

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Monodisperse Co-Sn, Fe-Sn, Co-Sb Alloy NCs as High Performance Li-Ion Battery Anodes

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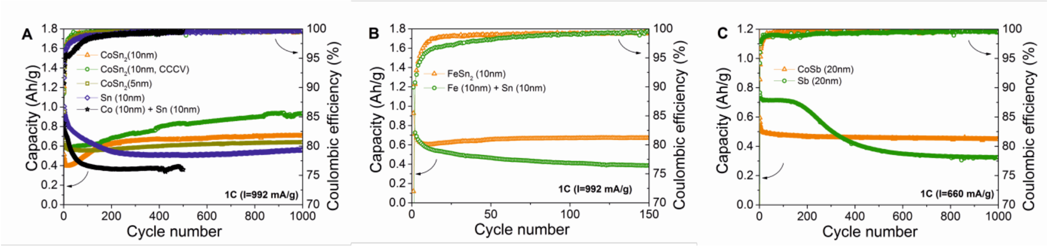
The combination of Sb or Sn with an inert-matrix of Co or Fe is a promising way for fabricating high-capacity anodes for Li-ion batteries. Here we present a facile colloidal synthesis of monodisperse $CoSn_2$, $FeSn_2$ and CoSb nanocrystals (NCs) via reaction between Co or Fe NCs and $SnCl_2$ or $SbCl_3$ in oleylamine under reducing conditions.[1] In comparison with individual Sn,[2] Sb[3] NCs, or even the nanoscale mixtures of Sn/Sb and Fe, Co NCs, we show that monodisperse $CoSn_2$, $FeSn_2$ and CoSb alloy NCs have enhanced Li-ion storage properties. In particular, $CoSn_2$, $FeSn_2$ and CoSb NCs show capacity levels of 705, 669 and 450 mAh g^{-1} with moderate decay after hundreds of cycles. In addition, a long cycle life exceeding 5000 cycles (690 mAh g^{-1}) at 2C rate with a low capacity decay rate (0.0014% per cycle) is demonstrated for $CoSn_2$ NCs.XRD measurements reveal that this stable behavior could be attributed to the in-situ formation of amorphous matrix containing Sn (Sb) and Co (Fe) during cycling, which are mixed on the nanoscale level. Such amorphous structure contains Li-ion active (Sn, Sb) and inactive metals (Co, Fe), which could buffer the large volume expansion and aggregation of active Sn or Sb nanoparticles, and therefore reduce capacity fading.



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Increasing kinetic inertness in polynuclear lanthanide complexes

D. Zare[1], Y. Suffren[1], L. Guénée[1], H. Nozary[1], S. V. Eliseeva[2], S. Petoud[2], A. Hauser[1], C. Piguet[1]*

[1]University of Geneva, [2]Centre de Biophysique Moléculaire, CNRS

The upconversion phenomenon operating in discrete molecular complexes has been reported for the first time in di- and trinuclear d-f triple helicates.[1,2] In this context, the upconverted erbium-centred green emission (Er($^4S_{3/2}$→$^4I_{15/2}$) transition at 542 nm) was detected in the 5-150 K range for CrErCr and CrEr samples in frozen solutions and in the solid state. The lability of the europium (III) cation in di- and trinuclear complexes in the non-luminecent GaY and GaYGa matrices have been investigated with the ultimate goal of preparing solid-state solutions of the luminescent Cr$_n$Ln complexes in Ga$_n$Y. In this contribution, we show that the rate constants of the reversible lanthanide exchange reaction Ga$_n$Y + Eu(III) ↔ Ga$_n$Eu + Y(III) strongly depend on the nuclearity of the complex. For the trinuclear system, the preparation of a solid-state solution of CrLnCr into GaYGa indeed provides a mixture of intact complexes. On the contrary, the dinuclear system is too labile to allow dilution without severe scrambling and mixing (Figure).

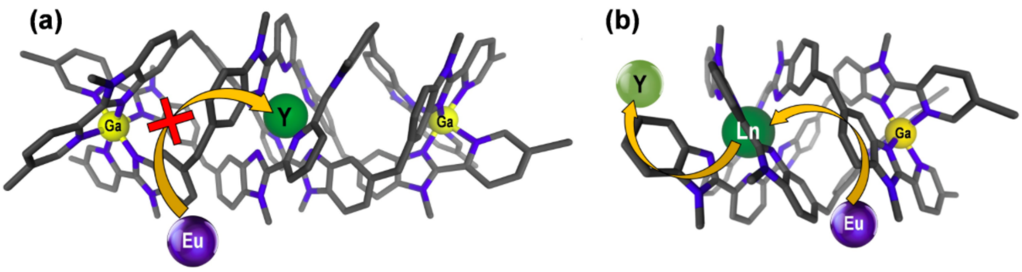

Figure: A schematic mechanism responsible for the change in lanthanide exchange rate constants in (a) trinuclear GaLnGa and (b) dinuclear GaLn complexes (Ln = Y and Eu)

[1] Davood Zare, Yan Suffren, Svetlana V. Eliseeva, Laure Guénée, Homayoun Nozary, Timothée Lathion, Lilit Aboshyan-Sorgho, Stéphane Petoud, Anderas Hauser, and Claude Piguet, *J. Phys. Chem. C,* **2013**, 117, 26957-26963.

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Improved spectral response does not lead to improved DSC performance: Studies on a ruthenium porphyrin-terpyridine conjugate

A. Lanzilotto, L. A. Büldt[1], H. Schmidt[1], A. Prescimone[1], O. S. Wenger[1], C. E. Housecroft[1]*, E. C. Constable[1]*

[1]University of Basel

The presented work[1] focuses on the synthesis of a new inorganic dye for application in dye-sensitized solar cells (DSCs), illustrated in Fig. 1 and hereafter referred as **Ru**. The choice of the two domains is such that the absorption arising from the {$Ru^{II}(tpy)_2$} chromophore is complementary to that of {ZnTPP}. The ester functionality has been proven to anchor to a nanoparticulate TiO_2 surface, however, once incorporated into DSCs, the dye shows poor photoconversion efficiencies.

Detailed investigation shows that after absorption of light, a deactivation mechanism dissipates the energy, competing with electron-injection into the semiconductor. Absorption experiments on **Ru** allowed us to assign the deactivation mechanism to a triplet-to-triplet energy transfer. Upon absorption and relaxation to the triplet metal-to-ligand charge-transfer state (^{3}MLCT), an energy transfer occurs to the energetically low-lying {ZnTPP} triplet. The transfer is so fast to be within the instrumental picosecond resolution (‹ 50 ps, rate constant of › 2 x 10^{10} s^{-1}). A rate constant of this magnitude accounts for a complete quenching of the charge-separated state, in favour of a porphyrin centred excited state. Here the energy is localised far from the semiconductor surface and, therefore, dissipated.

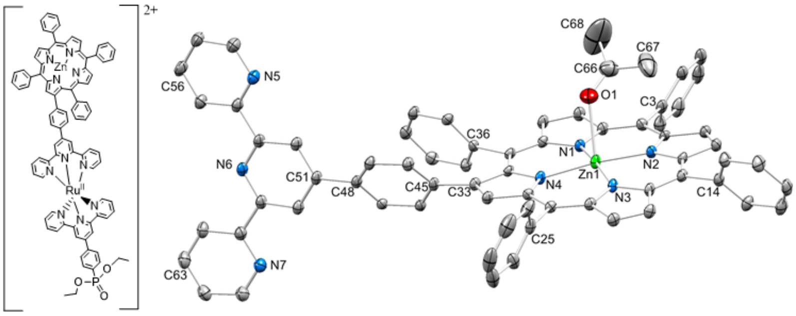

Fig. 1. Structure of **Ru** (left) and crystal structure of the porphyrin-bearing terpyridine ligand (one molecule of acetone is coordinated to the zinc) (right).

[1] Angelo Lanzilotto,Laura A. Büldt, Hauke C. Schmidt, Alessandro Prescimone, Oliver S. Wenger, Edwin C. Constable and Catherine E. Housecroft,*RSC Advance*, submitted.

Direct, aqueous carbon dioxide transformation to formic acid and methanol at room temperature

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[1]EPF Lausanne, [2]National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki, Japan, [3]National Institute of Advanced Industrial Science and Technology, Miyagino-ku, Sendai, Japan

The choice of energy resource and the reduction of greenhouse gas emissions, primarily carbon dioxide (CO_2), are key parameters in sustainable development. The transformation of CO_2 into value-added chemicals such as formic acid and methanol could provide a pathway for the utilization of this troublesome, yet inexpensive and widely available carbon source.[1] In addition, CO_2 hydrogenation can be employed for sustainable hydrogen storage in easy-to-handle liquid, organic chemical carriers (Figure 1).[2] Hydrogen is an energy vector with the potential of “green” production and utilization, in addition to having attractive inherent fuel properties.

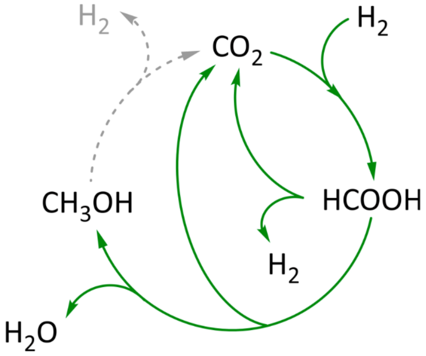

Figure 1. CO_2 for reversible hydrogen storage based on formic acid and methanol

We investigated direct CO_2 transformation to methanol, where formic acid was produced as an intermediate, in water as the solvent and at ambient temperature. Formic acid formation occurred in aqueous solution without additives or organic solvents with a homogeneous iridium catalyst, which also catalyzed formic acid disproportionation into methanol. Under optimized conditions, formic acid conversions of 98% and methanol selectivities of 96% were achieved in the disproportionation reaction. The catalyst operating in water endorses its environmental character. Conveniently, methanol-water solutions do not form an azeotropic mixture, facilitating their separation via distillation. In the field of homogeneous catalysis, the catalyst reported herein, overcame limitations such as high reaction temperatures, poor methanol selectivities in the formic acid disproportionation reaction, utilization of organic solvents and formation of cumbersome by-products (due to CO_2-like substrates).

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

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[1]University of Basel

Heteroleptic [Cu(6,6'-dimethyl-2,2'-bipyridine)$_A$(6,6'-dimethyl-2,2'-bipyridine)$_C$]$^+$ (A: anchoring ligand, C: capping ligand) complexes in which the bpy units are functionalized in the 4- and 4'-positions are known to be good light harvesting materials in dye-sensitized solar cells (DSSCs). When the formation of isolated heteroleptic [Cu(bpy)$_A$(bpy)$_C$]$^+$ complexes is attempted, equilibration occurs giving mixures of homo- and heteroleptic complexes; separation is very difficult. Therefore our group has developed a stepwise build-up of DSSCs (Figure 1a): a 'surface-as-ligand, surface-as-complex' approach.[1] For the first step a 6,6'-dimethyl-2,2'-bipyridine ligand, which is modified in the 4 and 4'-positions by a spacer bearing an anchoring group (e.g. 4/5-thiophenephosphonic acid, Figure 1b) is bound to a TiO_2 surface. Afterwards Cu(I) and a capping ligand are introduced by a ligand exchange reaction between the anchored bpy$_A$ and a bpy$_C$ of the homoleptic [Cu(bpy$_C$)$_2$]$^+$ complex. In previous work done by our group, much focus was put on the modification of the capping ligand to enhance photo to current efficiencies. The standard anchoring ligand with the best performance, which is currently used in our group is a 6,6'-dimethyl-2,2'-bipyridine ligand with 4-phenylphosphonic acid in 4 and 4' position. Changing the anchoring group from phosphonic acid to alternative groups, as well as modifying the phenyl spacer to a thiophene spacer has been investigated[1] with a goal of enhancing solar cell performance for [Cu(bpy)$_2$]$^+$ complexes. Targets are to gain better affinity of the anchoring group to TiO_2, better electron transport through the spacer, less electron recombination between dye and electrolyte and an overall longer electron lifetime within the complex.

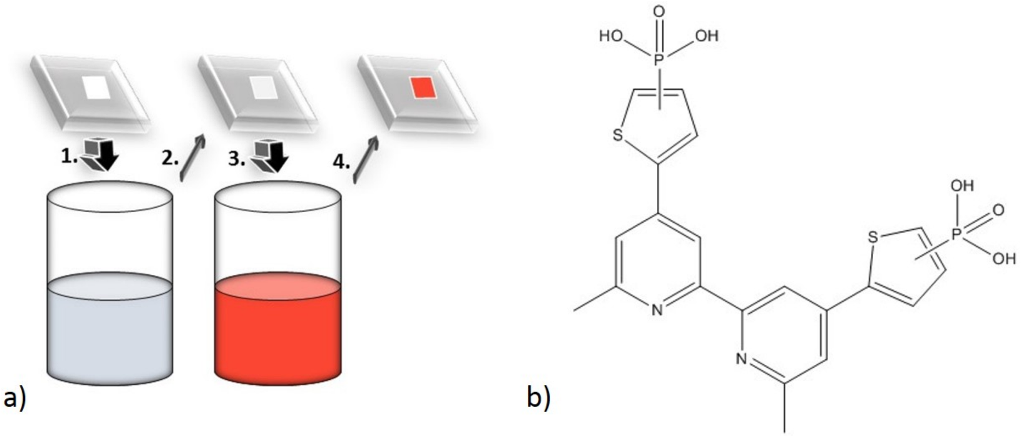

Figure 1: a) Preparation of heteroleptic [Cu(bpy)$_A$(bpy)$_C$]$^+$ complexes on TiO_2: 1. One day treatment of the TiO_2 coated glass plate in a solution of the anchoring ligand (1 mM in DMSO), 2. Cleaning, 3. Three days treatment of the modified TiO_2 surface with a homoleptic [Cu(bpy$_C$)$_2$]$^+$ complex, 4. Clean and fabrication of the DSSC. b) New anchoring ligand bearing two 4/5-thiophenephosphonic acid groups in the 4- and 4'-positions of 6,6'-dimethyl-2,2'-bipyridine.

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Combining acid functionalized anchoring ligands with symmetric ancillary ligands in bis(diimine)copper(I) dyes in dye-sensitized solar cells – influence of the symmetry on the performance

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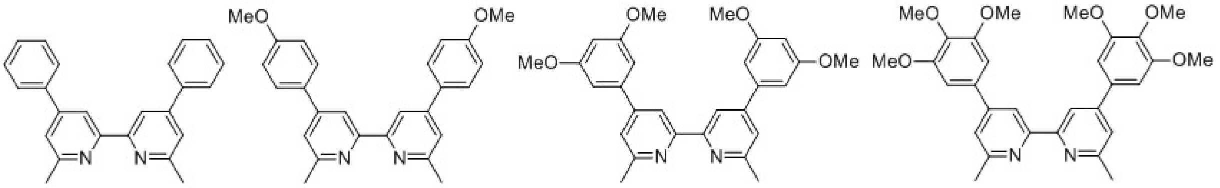
[1]University of Basel

The development of n-type dye-sensitized solar cells (DSCs) has made significant progress incorporating copper(I)-based dyes in order to replace the highly studied ruthenium(II) sensitizers used in conventional Grätzel cells which were first reported around two decades ago.Replacing the ruthenium(II) sensitizers by copper(I) dyes is of high interest in order to use more abundant materials and shift from rare metal sources on earth.

Our group has recently reported that phosphonic acid anchoring groups are preferential over carboxylic acids in copper(I) dyes. Moreover we have shown that by introducing phenyl substituents in the 6,6´-position of the bipyridine anchoring moiety, the light absorption can be improved towards the red-end of the visible spectra, additionally the bulkier substituents help to shield the copper(I) centre.

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



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

A. Büttner, S. Y. Brauchli, R. Vogt, E. C. Constable and C. E. Housecroft, *RSC Advances*, 2016, **6**, 5205.

Chloro Ligand Enhancement of Water Oxidation Catalysis with a Pentapyridyl Ruthenium Complex

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[1]University of Zurich

Artificial Photosynthesis, which uses solar energy to convert abundant natural resources (H_2O and CO_2) into fuels (e.g. H_2 and MeOH), has great potential to meet our future energy demands without increasing atmospheric CO_2 levels and causing further climate change.[1] However, for this process to be practical, we must make further progress in many research areas, particularly in catalytic water oxidation. Water oxidation is the underlying reaction that provides the reducing equivalents for the formation of solar fuels and is therefore crucial for all devices based on this concept.[2] Ruthenium complexes have played a defining role in advancing this area of research and the combination of polypyridyl ligands with ruthenium metal centres has produced many effective water oxidation catalysts.[3,4]

This work reports findings from our studies of ruthenium complexes containing the pentapyridyl ligand, Bpy_2PyOMe (6,6''-(methoxy(pyridin-2-yl)methylene)di-2,2'-bipyridine). The ruthenium aquo complex, $[Ru(Bpy_2PyOMe)OH_2](ClO_4)_2$, demonstrated only moderate activity for water oxidation, whereas the catalytic activity of the chloro precursor, $[Ru(Bpy_2PyOMe)Cl]Cl$, was unexpectedly enhanced. The synthesis, characterisation and initial catalytic studies for the chloro and aquo complexes are presented.

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Hierarchical graphene-based aerogels for long-life Li-ion batteries at high rates

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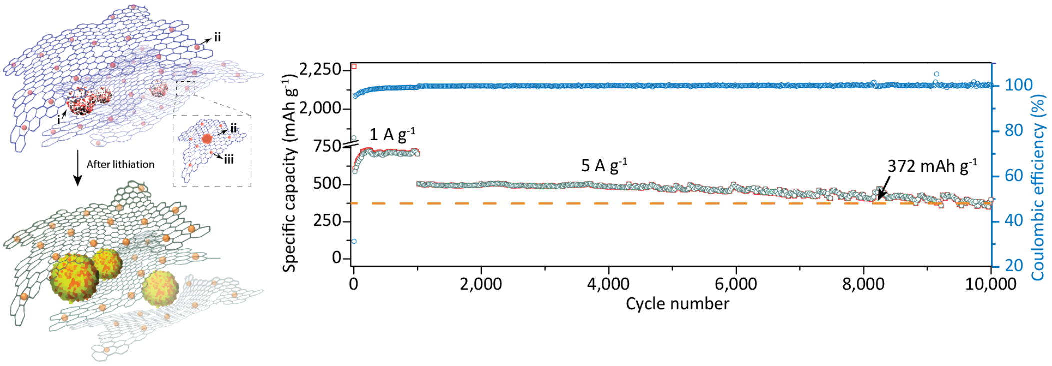
[1]ETH Zurich

Graphene and its derivatives have attracted great attention owing to its highly appealing properties since its first isolation in 2004; however, it has been lately occasionally criticized as ‘graphene fever’ due to the shortage of ‘killer’ applications. Among all potential applications, electrochemical energy-storage devices, particularly lithium-ion batteries (LIBs), are one of the most popular fields for graphene. Despite huge efforts, graphene battery performance is still far from satisfactory in terms of capacity, rate-performance and long-term stability. Here we present a general and facile way to fabricate hierarchical graphene-based aerogels as binder-free anodes for ultra long-life LIBs. In this approach, different types of active anode materials can be easily incorporated as spacer/pillar between graphene layers, e.g. spinel-type metal oxides, or Mo_xS_y/C hybrids. Benefitting from the hierarchical porosity of reduced graphene oxide (rGO) aerogel and its mechanical stability, the hybrid system synergistically enhances the intrinsic properties of each component, yet robust and flexible. As a result, the composite aerogels demonstrate outstanding electrochemical performance and ultra-long cyclability. For instance, the Mo_xS_y/C/rGO composite aerogels were found to enable high capacity (1060 mAh g^{-1} at 0.35 A g^{-1}), fast rate performance (425 mAh g^{-1} at 10 A g^{-1}) and ultra-long stability. At 5 A g^{-1}, the capacity can be retained at 336 mAh g^{-1} (71.3% of the initial) after 10,000 cycles. The excellent results pave an avenue for practical application for graphene in battery industry, and the versatile strategy developed here can be easily extended to the co-assembly of rGO with other functional materials for diverse applications as e.g. supercapacitors or in catalysis.



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

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

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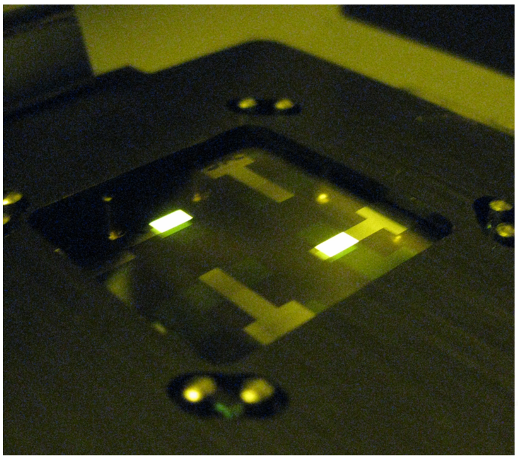
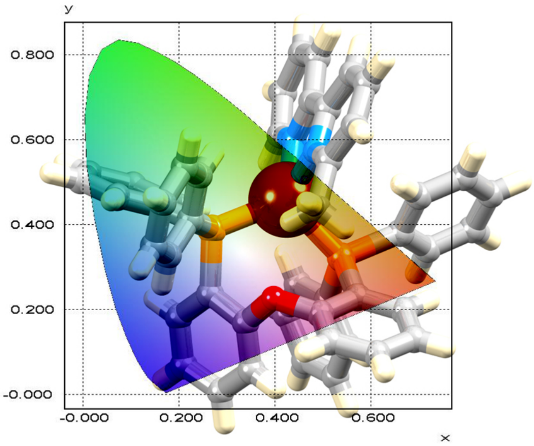
Artificial light sources are crucial for our modern society and the development of new lighting devices such as LECs (Light-Emitting Electrochemical Cells) and OLEDs (Organic Light-Emitting Diodes) promises considerable savings in terms of both energy and resources. We present the synthesis and investigation of light-emitting copper(I) complexes, which are a low-priced alternative to materials based on less abundant elements. In order to stabilize the d^{10} state of copper(I) and enhance the emissive properties of the complex, the ligands should be coordinated in a tetrahedral geometry. Encouraging results have been obtained with P^P chelating bisphosphanes such as POP (bis[(2-diphenylphosphino)phenyl]ether) and xantphos (4,5-Bis(diphenylphosphino)-9,9-dimethylxanthene), in combination with 2,2'-bipyridines and other chelating N^N-donors [1]. The copper(I) systems are very susceptible to the steric demand and electronic properties of the ligands. Due to sensible ligand tuning involving for example alkyl or aryl groups at the N^N ligands, we prepared copper(I) complexes with quantum yields of 37 % and improving, with the respective LECs exceeding device lifetimes of 80 hours [2]. Further alteration of the ligands will provide much needed insights into their influence on the important complex properties such as electroluminescence, lifetime of the excited state, quantum yield and stability, which then allows the fabrication of even more efficient light-emitting devices.





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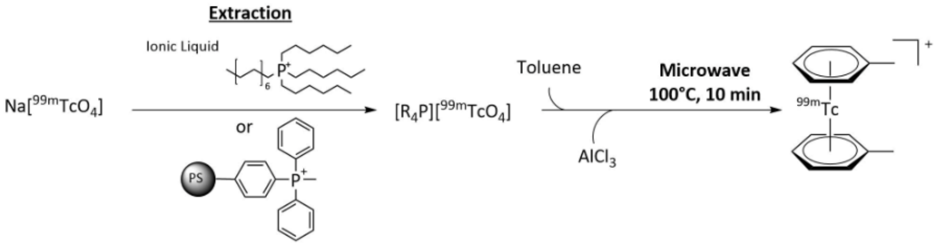
New Synthetic Strategies for $[M(\eta^6\text{-arene})_2]^+$ (M = Re, ^{99m}Tc) Complexes

C. Gotzmann[1], H. Braband[1], R. Alberto[1]*

[1]University of Zurich

Functionalised bis(arene)-complexes of transition metals are used as precursors for numerous reactions with applications in different fields, including medicinal inorganic chemistry.[1-3]

Benz *et al*. established a practical one step synthesis of $[^{99m}Tc(arene)_2]^+$ complexes in high yields and radiochemical purities. The generator-produced aqueous $Na[^{99m}TcO_4]$ was first extracted into an ionic liquid (IL) trihexyltetradecylphosphonium bromide, which acts as phase transfer reagent and is soluble in any liquid arene.[1] After addition of $AlCl_3$ and short microwave heating, the desired $[^{99m}Tc(arene)_2]^+$ complex was obtained.



Aiming at a one-pot reaction in aqueous media for routine radiopharmaceutical application, this reaction has to be carried to the next level, avoiding water sensitive reagents.

Therefore, profound insights into this reaction are essential. To obtain a more detailed picture, the reaction conditions were optimised to elucidate the yield relevant components. The formation of $[^{99m}Tc(toluene)_2]^+$ has been chosen as standard reaction. Higher yields and purities were achieved by decreasing the amounts of IL and $AlCl_3$. However, some IL led to side products. Alternative extraction strategies are presented. By extracting $[^{99m}TcO_4]^-$ with a polymer-bound $[P(CH_3)(C_6H_5)_3]I$ into the organic phase, only the desired $[^{99m}Tc(toluene)_2]^+$ complex was obtained.

In a next step, $AlCl_3$ was replaced as activation agent (Lewis acid) to make this reaction water fully compatible. Thereby a new perspective for organometallic radiopharmaceutical and medicinal chemistry develops. This procedure is also applied to the preparation of $[Re(arene)_2]^+$ complexes.

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Target Specific Multimodality Silica Nanoparticles for (Nano)Medical Applications

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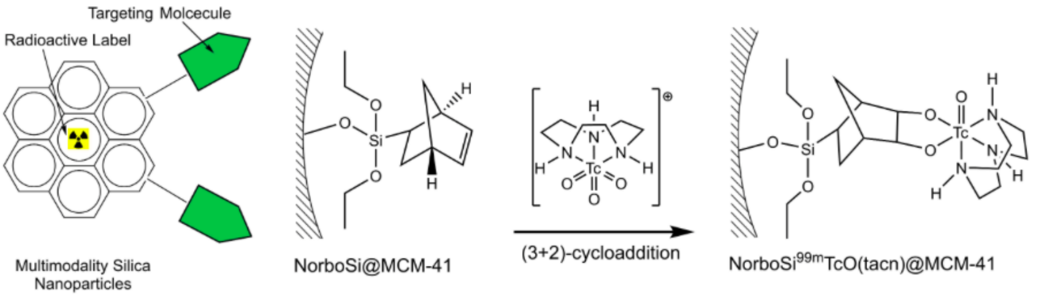
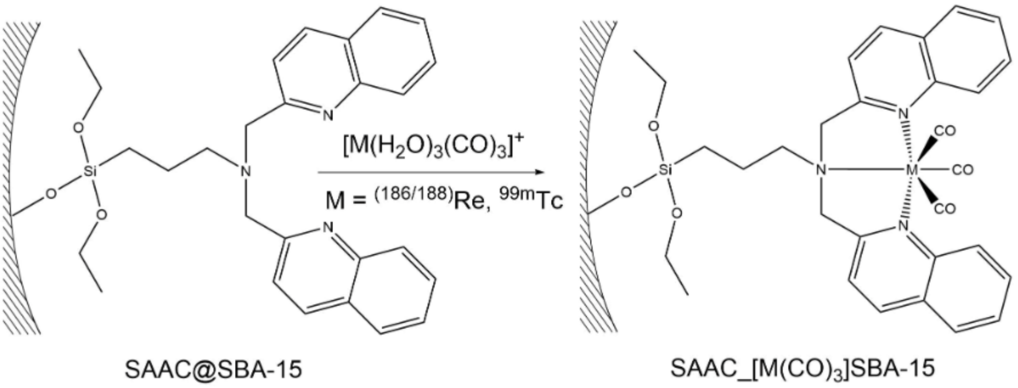
Silica nanoparticles, are currently under intense exploration in nanomedicine. In this context we are aiming at the development of novel synthetic pathways for the synthesis of^{99m}Tc- and/or $^{186/188}$Re-containing multimodality probes. Targeting moieties, imaging functions (radiolabels), and drug loading can be efficiently combined on mesoporous silica nanoparticles. This creates a promising multifunctional nanoplatform for the combination of therapy and diagnostic applications (theranostics). Recently we established a novel labelling procedure for silica based particles which proceeds via the reaction ofhigh-valent *fac*-$\{^{99m}TcO_3\}^+$ complexes with alkenes ((3 + 2)-cycloaddition)[1]. Currently, our research is focused on determining the most suitable type of silica particles to optimize the labelling procedure. The bifunctionalization and attachment of promising targeting functions is under development. These silica particles will be selectively labelled by radio nuclides at the inner pore surface. The desired targeting functions will exclusively be attached onto the outer surface of the particles.



Another silica nanoparticle based system has been developed which provides the possibility for multimodal imaging and the combination of (radio)therapy and diagnostics (theranostics). For this purpose a tridentate SAAC[2]-like ligand attached onto silica particles can be reacted with the $[M(H_2O)_3(CO)_3]^+$ (M = ^{99m}Tc, $^{(186/188)}$Re) complex. The choice of the metal leads to different imaging techniques (^{99m}Tc for radioimaging and Re for fluorescent imaging) or even radiotherapy ($^{186/188}$Re).



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Light-induced electron accumulation in a molecular triad

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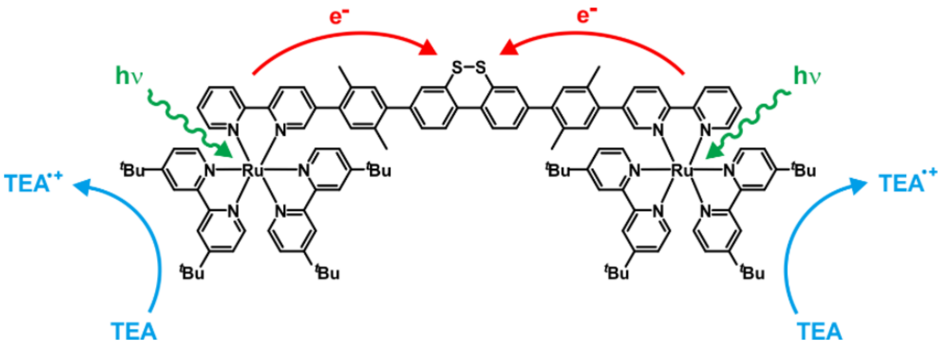
Charge accumulation is a crucial aspect in view of artificial photosynthesis, for instance for water splitting or carbon dioxide reduction.[1] Due to potential inversion, dibenzo[1,2]dithiin is a promising molecular unit for photo-driven electron accumulation. The reason why the second reduction step is much easier to perform than the first is the structural change which occurs upon two-electron reduction, leading to cleavage of the disulfide bond and rotation of the thiolate groups away from each other.[2,3]



In this work, photoinduced charge accumulation in a triad, which contains a central dibenzo[1,2]dithiin unit, was achieved (see figure). Spectroelectrochemical reduction measurements of the complex and different reference molecules were performed as well as irradiation experiments of the triad in presence of triethylamine (TEA) as a sacrificial electron donor. The comparison of the resulting absorption spectra indicated that dibenzo[1,2]dithiin is indeed accepting two electrons under steady-state photoirradiation. In following studies, we intend to replace TEA by an internal (non-sacrificial) electron source.

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Silica nanoparticles functionalised with lanthanide luminescent complexes

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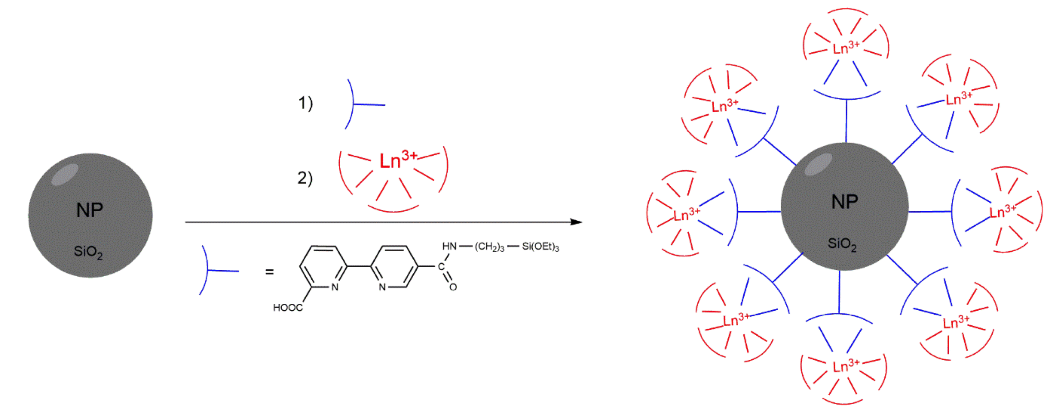
[1]Haute Ecole d'Ingénierie et d'Architecture Fribourg

Lanthanide ions are important and attractive candidates for luminescent materials as they can exhibit sharp fluorescent emissions through intra-4f or 4f−5d transitions and long lifetimes of the excited state.[1] On the other hand, however, direct excitation of lanthanide ion (Ln^{3+}) is a relatively inefficient process so in order to increase the quantum yield of lanthanide-containing compounds, antenna ligands have been used extensively.[1] These ligands need to bind strongly to the Ln^{3+} ions in order to form stable complexes. For this reason, chelating ligands are favoured. Moreover, oxygen-containing ligands are preferred because of their hard character.

A way of exploiting the interesting properties of lanthanide complexes is through nanoparticle functionalization, leading to new materials useful in imaging, molecular recognition and in the printing industry.[2,3] We are interested in their use as luminescent inks for inkjet applications.

Inspired by a recent work,[4] but using as starting material the dipicolinic acid, we developed a multistep synthetic route leading to a new UV-harvesting ligand, which was used for the synthesis of luminescent nanoparticles functionalised with Eu(III) and Tb(III) complexes. We will present the full characterisation (^1H, ^{13}C NMR, HRMS, luminescence spectra) of the molecular complexes and of the nanoparticles (TEM, DLS) functionalised with these complexes.



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Photocatalytic hydrogen production using Co(II)-Complexes and Semiconductor Quantum Dots

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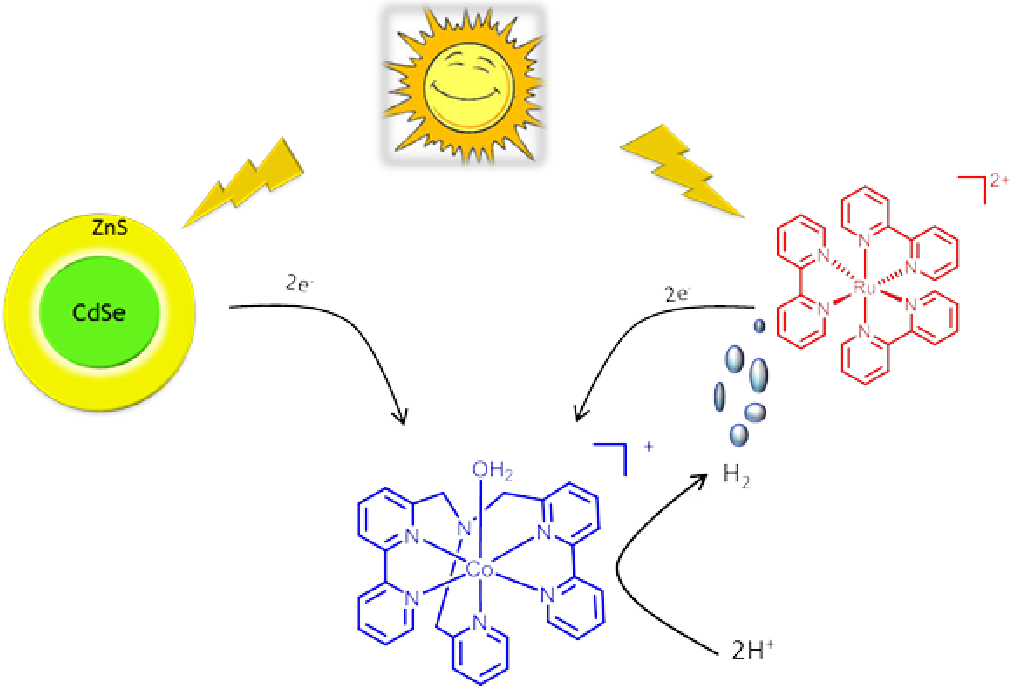
[1]University of Fribourg

The development of systems based on the use of abundant and renewable resources (e. g. water and sunlight) is perhaps the most promising, although challenging, solution to the growing demand of energy. Natural photosynthesis is a great source of inspiration to design systems able to use sunlight as an energy source for splitting water into hydrogen and oxygen.[1]

Our research is focused on the development of conjugated systems (dyads) capable of reducing protons into molecular hydrogen via photoexcitation. Promising results have been reported using semiconductor Quantum Dots (QDs) as light harvesting materials instead of $[Ru(bpy)_3]^{2+}$, one of the most popular sensitizers.[2]

We present here our preliminary results concerning the synthesis and photoelectrochemical investigation of a new Co-based polypyridine complex and the comparison of its catalytic efficiency in two multicomponent (i.e. non-conjugated) systems using CdSe/ZnS core/shell QDs and $[Ru(bpy)_3]^{2+}$ as sensitizers.



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Rhodium-Complexes for the Photochemical NAD(P)H Regeneration

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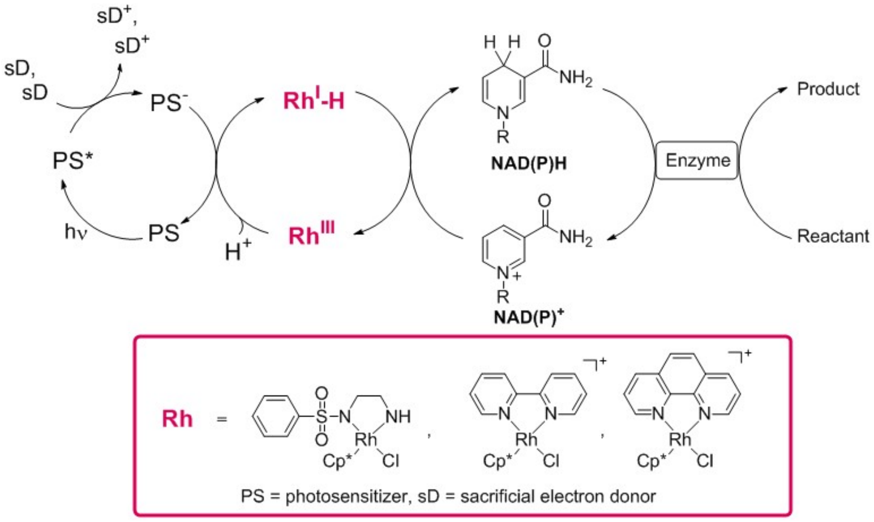
[1]University of Basel

The efficient photochemical regeneration of nucleotide co-factors is one key-component in mimicking natural photosynthesis.[1] Due to its importance as co-factor in biotransformations, the photoreduction of NAD(P)$^+$ to NAD(P)H using easily accessible reductants has been extensively studied in recent years, but there is still much room for improvement.[2] In a photochemical approach, the two-electron reduction of NAD(P)$^+$ can be achieved using a photosensitizer (PS) and a sacrificial electron donor (sD). Upon light excitation, two electrons are transferred to the nucleotide co-factor NAD(P)$^+$ *via* a redox mediator (Rh catalyst) that enables the formation of the desired nucleotide co-factor in high regioselectivity. For this purpose, [Cp*Rh(bpy)Cl]$^+$ was found to be suitable for the regioselective transfer hydrogenation of NAD$^+$ to 1,4-NADH.[3]



This work focuses on the evaluation of various rhodium-catalysts as possible redox mediators according to their turnover frequency in terms of NADH regeneration. As a final goal, this project aims to combine the depicted photocatalytic cycle with an enzymatic reaction, in order to mimic natural photosynthesis.

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Investigation of the interaction between platinum metal complexes and RNA G-quadruplex

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As non-canonical secondary structures of nucleic acids, G-quadruplexes seems to play a crucial role in gene regulation[1]. In contrast to DNA G-quadruplexes, which have been extensively investigated, few studies have been conducted on RNA G-quadruplexes till date. RNA G-quadruplexes are more likely to occur *in vivo* than their DNA counterparts due to their single-stranded nature. In addition, various clinically relevant genes are known to harbor RNA G-quadruplex forming sequences. Therefore, designing metal complexes to stabilize RNA G-quadruplexes could be a promising strategy to regulate gene expression, which may further expand into chemo-therapy of cancer[2].

In this study, we investigated the interaction between an RNA G-quadruplex sequence and two platinum complexes. The proposed RNA sequence is the 6A8U17U mutant of BCL2 RNA, present at the 5’ UTR of the mRNA of the BCL2 onco-gene and which proteins are aberrantly overexpressed in a wide range of human tumors[3]. The proposed metal complexes, P1 and P2 (Fig. 1), have proved outstanding binding affinities to DNA G-quadruplexes. Preliminary spectroscopic results show that both complexes are able to interact with this RNA G-quadruplex. Further investigation will deeply explore the structural details and the dynamics of these interactions.

Fig. 1. Formula of the proposed platinum complexes P1 and P2.

Financial support from the China Scholarship Council (ZH, No. 201506190127), the Swiss National Science Foundation (RKOS), the UZH Forschungskredit (ADM, RB), the European Research Council (RKOS), the University of Zurich (RKOS, SJ) is gratefully acknowledged.

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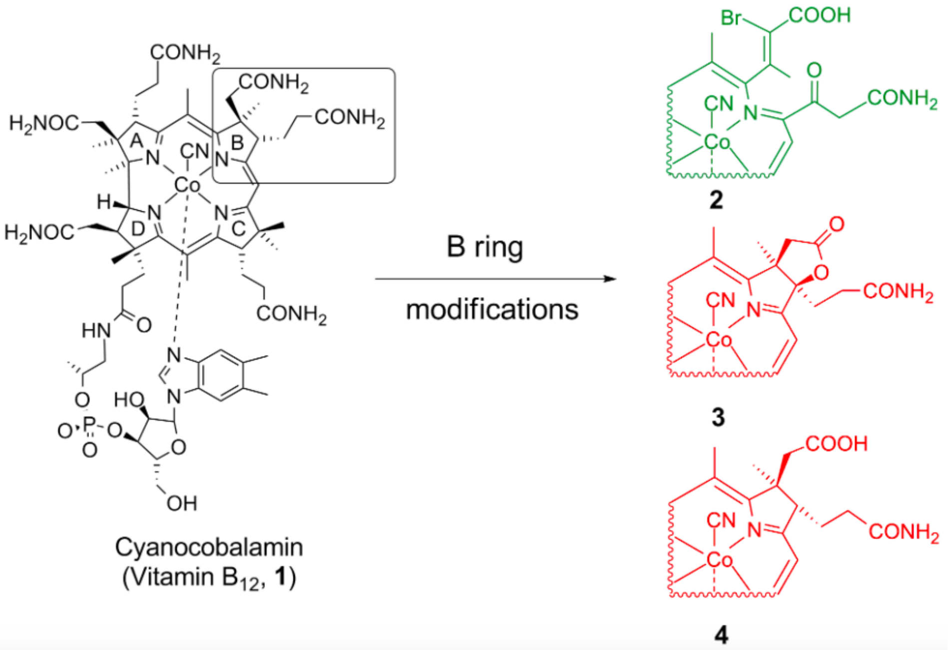
Ring-modified Vitamin B_{12} Derivatives as Potential Therapeutic Agents

L. Prieto[1], R. Oetterli[1], B. Spingler[1], H. Brandl[2], M. Neuburger[3], F. Zelder[1]*

[1]University of Zurich, [2]University of Zurich , [3]University of Basel

Vitamin B_{12} (**1**) is one of the most complex natural products and acts as an essential cofactor in many forms of life, including humans.[1] The enzymatic activity of this nutrient is dominated by cobalt-dependent organometallic reactions and the electronic and kinetic properties of the metal centre are strongly influenced by the equatorial corrin ligand. Therefore, well-designed modifications of this sophisticated macrocycle offer huge potential for the development of new B_{12}-based therapeutic agents. [2]



Based on pioneering studies by Kräutler et al,[3] we present procedures to disrupt and functionalize the corrin macrocycle of vitamin B_{12}.[4,5] Thus, we have gained access to a series of semi-artificial corrinoids (**2**, **3**, **4**) with modified electronic and redox properties. The general reactivity and biological activity of these B_{12} derivatives will be presented.

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Formic Acid Dehydrogenation Using Iron(II) Based Catalysts in Aqueous Media

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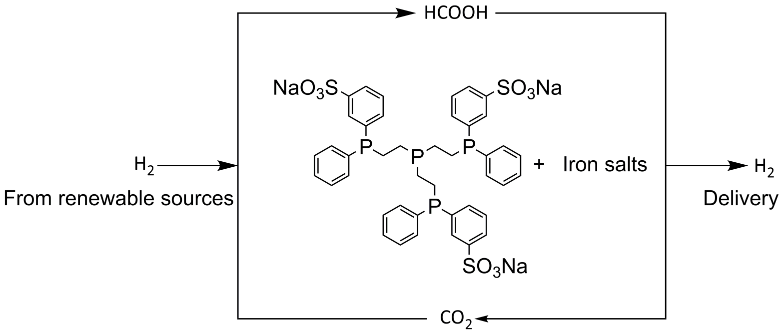
[1]EPF Lausanne

Within the actual context of sustainable energy development, one of the challenges for the scientific community is the development of new hydrogen storage methods. Currently, hydrogen is most commonly stored in pressurized vessels or liquefied at low temperatures which present safety hazards, are difficult to handle and can therefore not constitute a convenient solution for H_2 storage for small and mobile applications.[1–3] In 2008, our group presented a novel approach of hydrogen generation from formic acid (FA), H_2 is released on demand using a robust and effective ruthenium catalyst.[4] We present here the results of our investigation on FA dehydrogenation using non-noble metal based pre-catalysts in aqueous media.[5] This necessitated the synthesis of a hydrosoluble polydentate ligand, trisulfonated-tris[2-(diphenylphosphino)ethyl]phosphine sodium salt (PP_3TS). New catalysts, particularly those with iron(II), were formed *in situ* and generated H_2 and CO_2 from aqueous FA solutions, without of any organic co-solvents, bases or other additives. Techniques such as manometry, multinuclear NMR and FT-IR were used to follow the dehydrogenation reactions, calculate various kinetic parameters, and analyze the gas mixtures for purity. The catalysts are selective and the gaseous products are free from CO, which is a harmful for PEM hydrogen fuel cell. To the best of our knowledge, these represent the only example of first row transition metal based catalysts that dehydrogenate quantitatively formic acid in aqueous solution.



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Synthesizing Functionalized [M(η^6-arene)$_2$]$^+$ (Re,$^{99(m)}$Tc) Complexes as Highly Stable Bioorganometallic Scaffolds for Receptor Targeting

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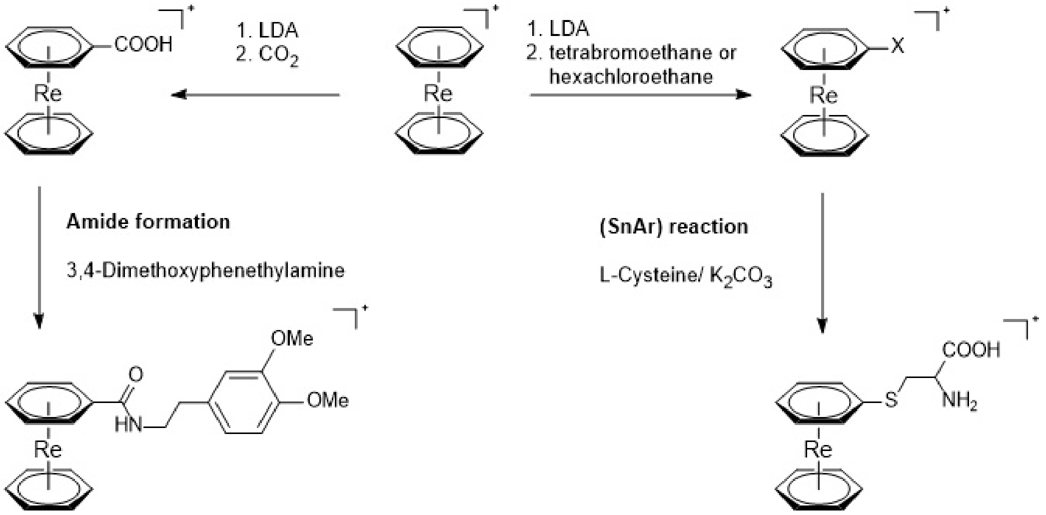
[1]University of Zurich

The field of medicinal inorganic or bioorganometallic chemistry is dominated by bis/mono-arene complexes of ruthenium and ferrocene (derivatives).[1],[2] These compounds represent fundamental precursors for numerous reaction and show interesting biological behaviour.[3] However, these complexes are not suited for “theranostic” applications, including radio imaging. Recently, [M(arene)$_2$]$^+$ type complexes (M = Re, $^{99(m)}$Tc) of rhenium and technetium came into the focus of our research, because these homologues metals are established matched pair for radiodiagnostic and (radio)therapy. Hence the synthesis of [Re(arene)$_2$]$^+$ type complexes (arene = benzene, toluene, mesitylene, *o*-xylene, *p*-xylene and naphtalene) was optimized and an efficient and practical one-step synthesis for [$^{99(m)}$Tc(arene)$_2$]$^+$ compounds was developed.[4],[5] Furthermore, novel synthetic pathways for the functionalization of this basic class of coordination compounds have been developed, which led to a variety of mono- and bi-functionalized [Re(C_6H_5R)($C_6H_{6-n}R_n$)]$^+$ compounds (R = -COOH, -Br, -Cl, -F, -COC_2H_5, -CH(OH)Ph, -C(OH)Ph_2). These introduced functional groups enable the rational design of metal modified biomolecules via amide bond formation or nucleophilic aromatic substitution (SnAr). Following this strategy, new classes of organometallic compounds were synthesized with high potential for therapeutic and diagnostic applications (inorganic drugs), in the future.



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Hybrid lead and tin halide perovskites with guanidinium cation

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Exploration of halide perovskites such as $RNH_3(Pb,Sn)(I,Br)_3$-type of materials, developed into a flourishing field with an immense practical potential for optoelectronics. Highly efficient photovoltaics with power conversion efficiencies above 20%[1] were enabled by high absorption coefficients, broad absorption range, high charge carrier mobility, long carrier diffusion length and low trap densities.

So far, most of work has been conducted on methylammonium and formamidinium lead halides. Another successor that could facilitate a formation of promising hybrid compounds is guanidinium cation.

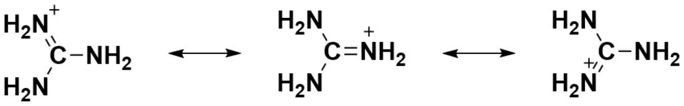

Fig.1. Guanidinium cation, canonical forms

Guanidine is a strong base (pK_b=0.4), has a high symmetry (D_{3h}) and is capable of hydrogen bonding. According to Goldschmidt's tolerance factor concept the guanidinium cation is too large for the formation of a three-dimensional cubic structure, as required for perovskites of ABX_3 formula[2]. Nonetheless, in combination with cesium promising two-dimensional hybrid structures could be envisaged.

Herein we demonstrate a synthesis and properties of hybrid two dimensional $Cs(CN_3H_6)PbI_4$ (**1**), $Cs(CN_3H_6)PbBr_4$ (**2**), $Cs_2(CN_3H_6)Pb_2Br_7$ (**3**), $Cs_2(CN_3H_6)Sn_2Br_7$ (**4**) perovskites. Compounds **1**-**3** exhibit intense photoluminescence at moderate cooling (**Fig.2b** PL_{max}= 457nm). **1**-**3** are stable in air and do not thermally decompose until 300°C (DTA/TG conducted under inert conditions). The corresponding tin(II) analogue **4** is surprisingly an air stable compound as well.

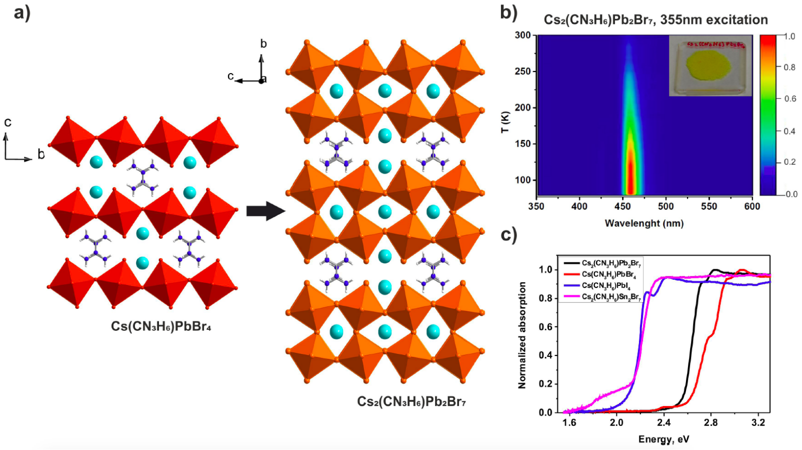

Fig.2. a) Crystal structure of two-dimensional cesium guanidinium lead halide perovskites.; **b)** Photoluminescence of polycrystalline $Cs_2(CN_3H_6)Pb_2Br_7$ from 100 to 300K; **c)** Optical absorption spectra of polycrystalline samples of two dimensional perovskites.

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Quantum Dots-sensitized Water Oxidation: Trick or Treat?

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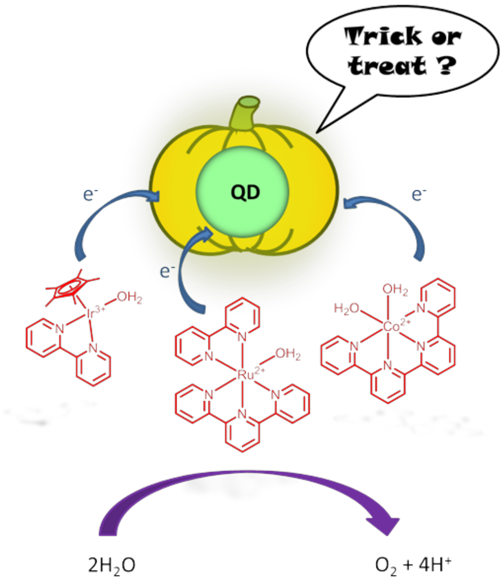
[1]Université de Fribourg

Semiconductor Quantum Dots (QDs) have been recently applied to the realization of systems for artificial photosynthesis: the remarkably high molar extinction coefficient and the tunability of their photoelectronic properties make them ideal candidates as light harvesting units (sensitizers).[1] However, in spite of the great performances shown by QDs for light-driven hydrogen generation, the investigation of their performance as sensitizers for water oxidation still remains a basically unexplored topic.

We present here some preliminary results concerning the interaction of CdSe/ZnS core/shell QDs with three different complexes, which are known to be capable of catalyzing water oxidation.[2] The possibility of realizing QD-sensitized water oxidation is investigated in terms of electron transfer efficiency (studied with time-resolved fluorescence and electrochemical techniques) and from the study of light-driven oxygen evolution in the presence of sacrificial species.



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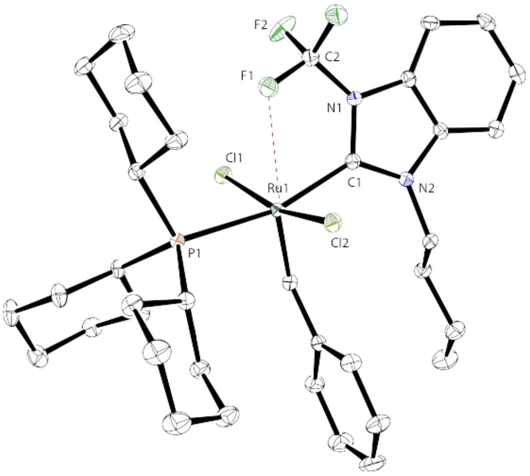
N-Trifluoromethyl NHC Ligands Provide Selective Ruthenium Metathesis Catalysts

P. Engl[1], A. Fedorov[1], C. Copéret[1], A. Togni[1]*

[1]ETH Zurich

A series of ruthenium metathesis catalysts containing unsymmetrical N-trifluoromethyl NHC ligands has been synthesized. These complexes have been fully characterized and a Ru–F interaction identified in the solid state by X-ray crystallographic analysis for three catalysts with Ru–F distances between 2.629(2) and 2.652(2) Å. The influence of the N-trifluoromethyl NHC ligands on the initiation rates and activation parameters was studied. The activity of these catalysts was evaluated in benchmark olefin metathesis reactions and compared to the standard 2nd generation Grubbs catalyst. Remarkably, N-trifluoromethyl catalysts display an unusually high selectivity for the formation of terminal olefins (up to 90%) in the ethenolysis of ethyl oleate. Much improved selectivity is demonstrated for alternating copolymerization of cyclooctene and norbornene as well. These results underline the importance of electronic effects exerted by the NHC ligand.



Ru1-F1 = 2.629(2) Å

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Investigating the benfits of incorporating carbohydrates into NHC systems for catalytic applications

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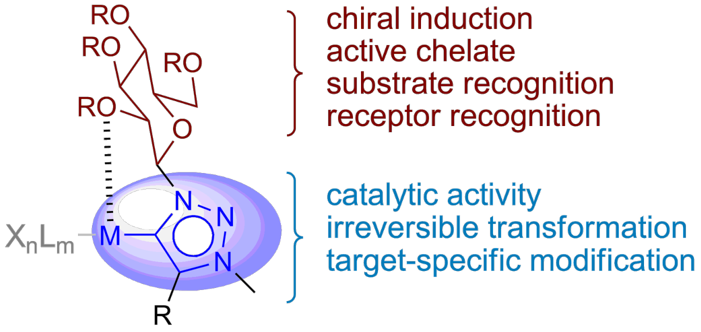
[1]Universität Bern

N-Heterocyclic carbenes (NHC) have been shown to act as versatile ligands for catalysis[1]. In particular, we have shown the promise of 1,2,3-triazolylidines as a class of NHC with wide-ranging applications in catalysis, as well as materials science and biochemistry.[2] This class of NHC may be conveniently constructed through the modular CuAAC ‘click’ reaction, thereby giving access to a broad range of functionality compared to ligand systems which must be prepared *via* harsher reaction conditions. Carbohydrates come from the natural pool of chirality and functionality and therefore represent an attractive class of substituent for providing defined stereochemistry and geometry to ligands, as well as being readily available; indeed carbohydrates have been used as scaffolds for phosphine and phosphinite ligands and shown promise for catalysing asymmetric transformations.[3] Similar work with NHCs is scarce.[4] Combining these two important classes of compound into a hybrid system will give rise to synergistic advantages. Here, we present a number of new carbohydrate-NHC hybrid ligands for catalysis and report preliminary investigations into their activity, exploring relationships between activity and structure.



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Chiral Iron(II) PNP Pincer Complexes for Enantioselective Direct Hydrogenation

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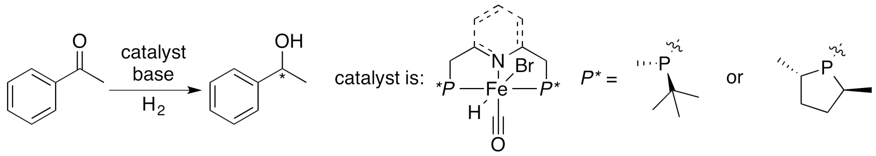
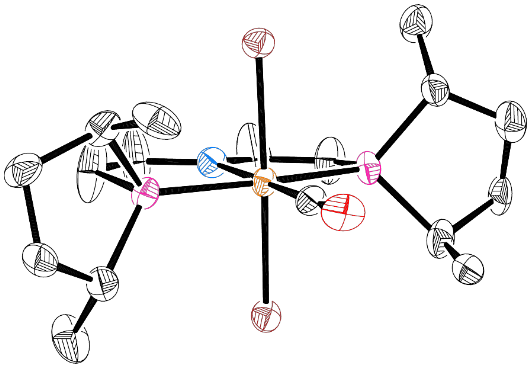
[1]ETH Zurich, Dept Chem. & Appl. Biosciences

In view of the success of iron(II) precatalysts containing neutral, achiral PNP pincer ligands with a pyridine[1] or an amine[2] moiety for the direct hydrogenation of ketones, we engaged in the challenge of preparing chiral, enantiopure analogues of such ligands and of studying their coordination chemistry with iron(II).



First, we prepared a pyridine-derived PNP as well as an amino-PN(H)P pincer ligand with enantiopure *tert*-butylmethylphosphine. The resulting Fe(II) dibromocarbonyl complexes were transformed into their hydrides using sodium triethylborohydride. In contrast to their bis(diisopropylphosphine) analogues, these precatalysts are inactive in the hydrogenation of acetophenone. Surprisingly, also the bis(2,5-dimethylphospholane) PNP and PN(H)P pincer Fe(II) complexes (see X-ray structure below) showed no activity in the hydrogenation of acetophenone despite the close analogy to the active bis(diisopropylphosphine) derivative. We presume that the larger s-character in the phosphorus lone pair weakens the Fe-P bond, thus reducing the catalyst stability. We are currently investigating other stereogenic phosphorus moieties that do not suffer from this drawback.



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Luminescence study of an anthracene derivative and its complexes with silver

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[1]University of Fribourg

An excimer, or excited dimer, is formed when a fluorophore in its ground state interacts with a fluorophore in its excited state. For this to happen, the two fluorophores should be within Van der Waals contact distance (3 to 6 Å). The fluorescence of such a dimer is usually shifted to lower energies, and shows a broader band. This difference in emission makes such a system an interesting candidate for sensor application[1]. Anthracene, due to its luminescence properties and possible formation of excimer, has been studied as sensor for selective recognition[2,3]. In our group, an isonicotinic derivative of anthracene has shown interesting fluorescence properties for itself and after self-assembly into coordination polymers with silver ions. The latter compounds were designed to be used as luminescent tracers in an antibacterial implant coatings[4,5].

We here study the synthesis and properties of an anthracene molecule functionalized with nicotinic acid, and its complexes with silver nitrate and silver triflate. We investigate the influence of the anions and the presence (or not) of solvent molecules on the solid state structure, and hence on the packing of the molecules (fig 1), and on their luminescence.

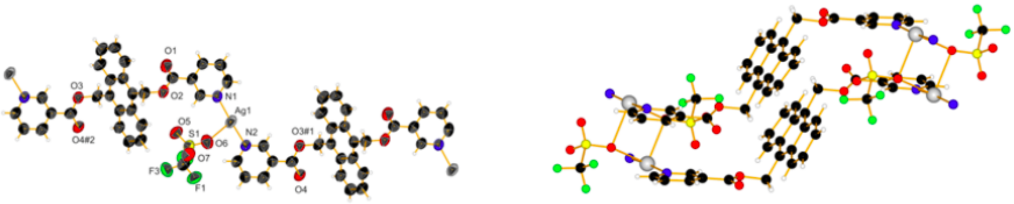

Figure 1:
(Left) ORTEP of the anthracene derivative, anthracene-9,10-diylbis(methylene) dinicotinate with silver triflate (50% ellipsoids).
(Right) Packing of the derivative in the crystal (carbon in black, hydrogen in white, oxygen in red, nitrogen in blue, sulfur in yellow, fluorine in green and silver in grey).

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Synthesis and catalytic applications of chelating dicarbene iridium complexes.

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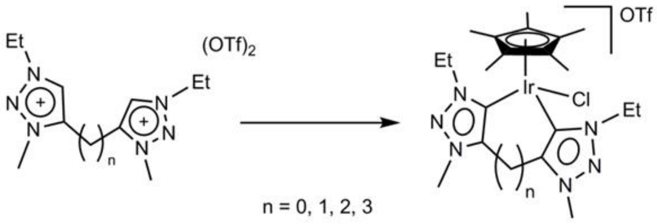
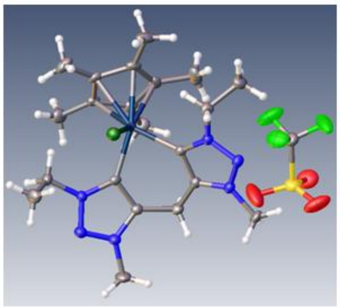
[1]Departement für Chemie und Biochemie, Universität Bern

Triazolylidenes are versatile ligands that are readily available through click chemistry. They are a subclass of N-heterocyclic carbenes that impart high electron density at the metal center due to the very strong donor properties, allowing the synthesis of complexes with a broad array of applications such as in catalysis.[1] Despite the kinetic and thermodynamic stability imparted by chelation, chelating ditriazolylidenes are still underexplored.[2]

Here we have synthesized a series of bis(triazolylidene) ligands through [2+3] click reaction of different dialkynes and azides. The corresponding dicarbene iridium (III) complexes, containing flexible alkyl- or ether-linker between the triazolylidine rings, are obtained via formation of the silver carbene complex and subsequent transmetallation.

Depending on the reaction conditions, monocarbene, dicarbene or bimetallic complexes can be obtained. Evaluation of the dicarbene complexes as catalysts in transfer hydrogenation shows a substantial influence of the triazolylidene linker on the catalytic activity.





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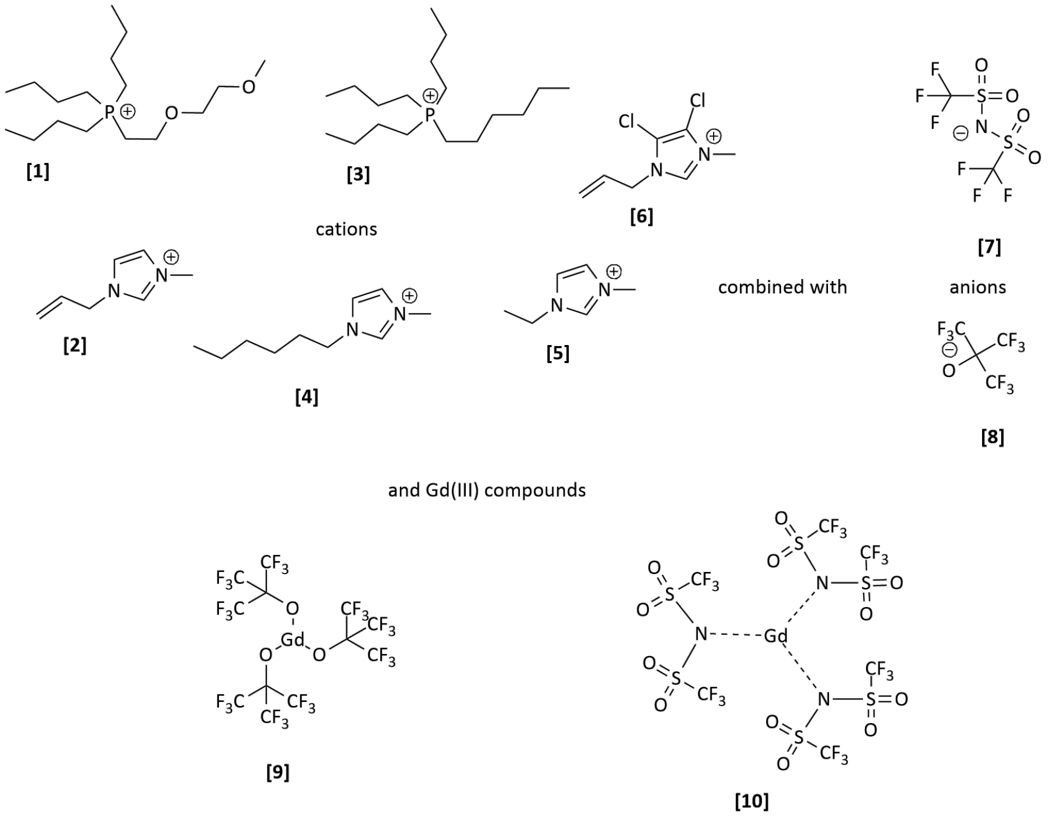
Highly Homo-perfluorinated Paramagnetic Ionic Liquids for NMR Field Probes for Magnetic Field Monitoring in MRI

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

[1]University of Zurich

Magnetic resonance imaging (MRI) techniques rely on observing nuclear magnetic resonance (NMR) during complex choreographies of time-varying magnetic fields. These field evolutions are subject to hardware imperfections and various external perturbances limiting image quality and the feasibility of high-performance methods. Continuous concurrent magnetic field monitoring[1] is a method for probing the spatiotemporal magnetic field evolution in an MR system with a set of NMR field sensors. For these sensors highly homo-perfluorinated liquid compounds with short fluorine NMR relaxation times (T_1 and T_2 ‹ 1 ms) are required. Herein we present different ionic liquids (ILs), containing homo-perfluorinated anions in combination with paramagnetic additives and functionalised phosphonium and imidazolium cations (scheme 1), as promising candidates for NMR field sensors. Homo-perfluorinated mono-anionic mixtures with high Gadolinium concentrations show the aspired relaxation times. Investigations into the relation between the paramagnetic metal content, relaxation behaviour and viscosity have been performed and will be presented.



Scheme 1: Building blocks for the homoperfluorinated paramagnetic ILs: Functionalised cations [1]-[6] in combination with homoperfluorinated anions [7] and [8] and Gd(III) compounds [9] and [10].

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Reversible Quinone-based Relays as Electron Transporter in Artificial Photosynthesis

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We recently showed that reversible quinone/hydroquinone redox couples, in analogy to the plastoquinone in the natural electron transport chain between PS II and PS I, are capable of acting as electron relay between photosensitizer and sacrificial electron donor in photocatalytic proton reduction (Fig.1).[1]

Usually, the two half reactions of artificial photosynthesis are studied separately using sacrificial agents as electron donor or acceptor.[2] This practice was established on one hand to optimize the catalysts and efficiency of the individual side. On the other hand, possible shortcuts between the vast number of oxidized and reduced species coming with a full system are minimized. Imposing an electron relay between the sacrificial agent and active species of the respective half reaction is a first step towards the goal of linking both sides to a full system.[3–5]

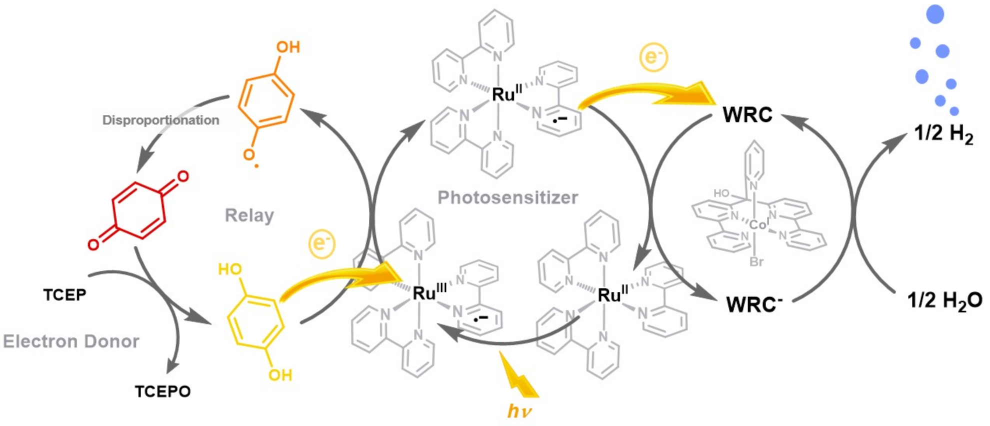

Fig. 1. Reductive half reaction of artificial photosynthesis with TCEP as sacrificial electron donor, a quinone-based relay, a Ru-photosensitizer and a Co-based water reduction catalyst (WRC).

In this work, various substituted hydroquinones and catechols were screened in photocatalytic proton reduction experiments to evaluate their performance as electron relay. Furthermore, their interactions with a ruthenium-based photosensitizer were investigated by spectroscopic means and the regeneration rates of the oxidized form determined.

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Low Temperature Wet Conformal Nickel Silicide Formation on Silicon Wafer through an Organometallic Approach

T.-H. Lin[1], T. Margossian[1], M. d. Marchi[2], M. Thammasack[2], S. Kumar[1], C. Shih[1], D. Giovanni[2], D. Baudouin[1], P. Gaillardon[3]*, C. Copéret[1]*

[1]ETH Zurich, [2]EPF Lausanne, [3]University of Utah

The formation of metal silicides, which are indispensable materials involved in the fabrication of all field effect transistors to reduce the contact resistance of the source and drain regions[1], has been identified as one of the most critical steps in current fabrication process flows[2]. Among all the possible metal silicides, nickel silicide ($NiSi_x$) is widely used by the industry thanks to its low resistivity, its material compatibility, and its good stability[3,4]. However, the transition towards devices using advanced 3D geometries makes it challenging to form homogeneous silicides using classical silicidation processes such as sputtering.Therefore, a one-pot chemical approach has been proposed to synthesize $NiSi_x$ layer onto silicon wafer allowing a homogenous coverage of 3D-structure device in this work.A 175-nm metal rich layeron Si (100) wafer was observed by electron microscopy (STEM-EDX), but XPS spectroscopy showed the presence of some carbon contamination. However, high temperature post-treatment lead to a decrease in carbon content and a lower surface roughness (R_a=6.5 nm) according to AFM and induced a lower value of sheet resistivity (R_s=0.4 kΩ/☐) measured by 4-point probe measurement. In addition to forming the $NiSi_x$ layer onto the flat Si (100) surface, the method was applied to 3D-patterned wafers, in which the TEM results showed that a promising aspect ratio could be obtained.

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Energy efficient, low temperature hydrothermal synthesis of battery-grade $LiFePO_4$ platelet particles

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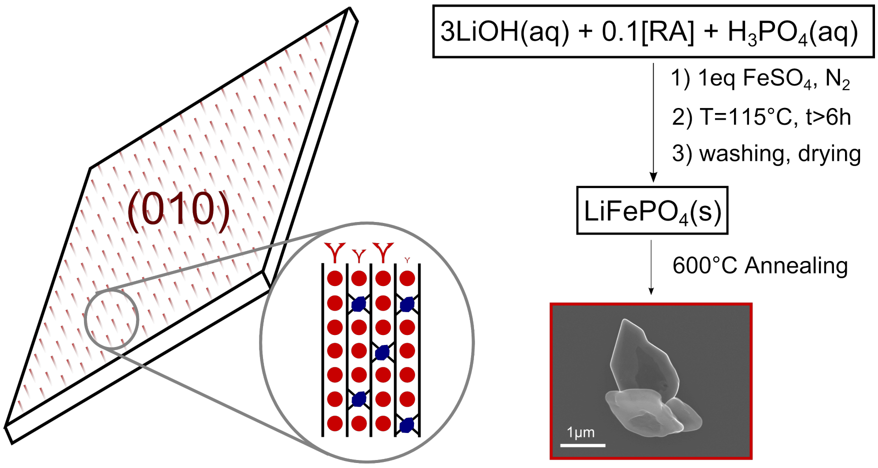
$LiFePO_4$ (LFP) is an important, commercially-used cathode material in lithium ion batteries that offers high rate capability and low toxicity. LFP crystalizes in an olivine-type structure having a highly stable $FePO_4$ backbone with one-dimensional channels along which the main Li ions diffusion occurs [1]. Due to the one dimensional diffusion, single defects in a channel can hinder Li ions from (de)intercalation (Figure 1, left). Typically, due to sluggish kinetics and solvent molecule incorporation, low synthesis temperatures lead to more defects. But typical hydrothermal syntheses have reaction temperatures of around 180°C, which implies high-energy consumption and associated material costs.

Here, we report a high-concentration hydrothermal reaction at only 115°C, which leads to an energy reduction of 40%, while still producing high quality materials with an electrochemical performance comparable to those prepared at high temperature syntheses. As indicated in Figure 1, our synthesis is based on the hydrothermal synthesis of LFP proposed by [2], but with reducing agent (RA) additives such as ethylene glycol and ascorbic acid. Using characterization techniques including SEM, XRD, and FTIR, we show that additives during the synthesis enable us to regulate the particle thickness (i.e. channel length) from 100 nm to 250 nm and decrease the defect concentration. Following annealing at 600°C, these hydrothermal syntheses exhibit capacities of up to 150 mAh/g, close to the theoretical capacity of LFP.



$3LiOH(aq) + 0.1[RA] + H_3PO_4(aq)$

1) 1eq $FeSO_4$, N_2
2) T=115°C, t>6h
3) washing, drying

$LiFePO_4(s)$

600°C Annealing

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Metal Oxide Catalysts for Alkane Functionalization

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Developing methods for alkane functionalization is a challenge across all of chemistry, and understanding the mechanism of such processes at a molecular level is particularly difficult. The development of alkane functionalization methods is discussed using heterogeneous catalysts based on metal oxides. This class of catalysts has been shown to activate C-H bonds, as seen in the H/D exchange of methane. The C-H bond is proposed to be broken heterolytically, forming a [M]-CH_3 bond, and this C-H bond activation mechanism is the same as proposed for H_2 bond activation, in which a [M]-H bond is formed. In developing novel reactions for alkane functionalization, we propose that processes known to activate H_2, such as hydrogenation and hydrogenolysis, will also activate methane. This poster details our exploration of this hypothesis using a variety of bulk, supported, and single-site metal oxide catalysts.

New routes to highly efficient copper(I)-based dye-sensitized solar cells: N^NX ligands as ancillary ligands

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

[1]University of Basel

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

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

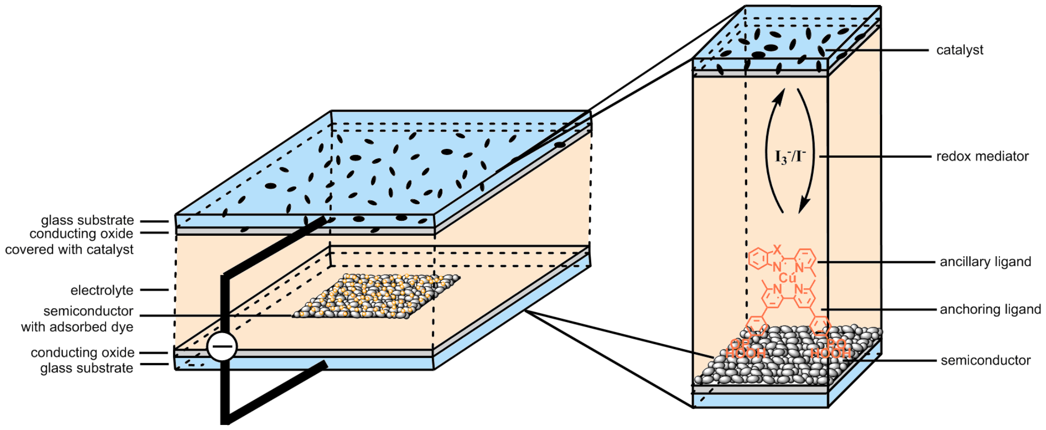

Figure 1: Structure of a dye-sensitized solar cell with zoom-in example for investigated copper(I) dye-sensitized solar cells.

The most important part of a dye-sensitized solar cell is the dye. It consists of two parts – the anchoring and the ancillary ligand. A series of heterocyclic N^NX ancillary ligands has been examined for the first time in copper(I) dye-sensitized solar cells. The relatively high efficiencies show the huge potential of copper(I) dye-sensitized solar cells.

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Controlling the Size of Nanocrystals of Metal-Organic Framework UiO-66

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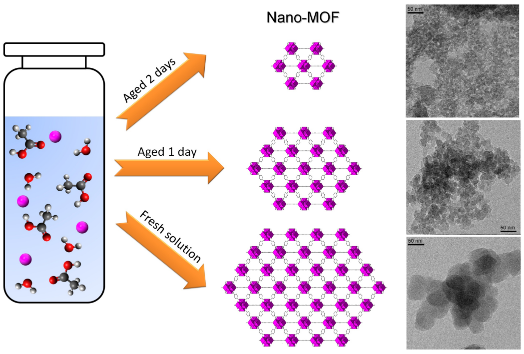
[1]Paul Scherrer Institute, Villigen, [2]ETH Zürich

Metal-organic frameworks (MOFs) are a class of highly porous materials based on the connection of metal atoms and organic linkers. They can be employed in a wide range of applications, including gas sorption/separation, heterogeneous catalysis, and drug delivery.[1, 2] More recently, MOF nanocrystallites have gained attention for their potential applications in drug delivery, sensing, contrast agents, thin films, electronic devices and photocatalysis.[3] The ability to precisely control crystallite size is therefore essential to optimize their use. UiO-66, based on zirconium-oxo clusters and terephthalic acid, is one of the most-studied MOFs, thanks to its chemical and thermal stability and to the easy functionalization of the framework, which make it very attractive for practical application.[4] We developed a new, simple way to tune the crystallite size of UiO-66. Our method enables synthesis of crystals as small as ten nanometer.[5] This is done by exploiting controlled aging of stock solutions of Zr^{4+} in *N*,*N* -dimethylformamide in the presence of variable amounts of water and acetic acid prior to addition of the linker and heating at 120 °C for 24 hours. Upon aging of the stock solution, the crystallite size of the final product decreases. Water is the main factor responsible for the aging effect. Acetic acid plays an essential role in modulating both the aging process and the crystallization of the MOF upon addition of terephthalic acid to the zirconium stock solution, avoiding the formation of amorphous non-porous phases. With this method we were able to synthesize nano-sized UiO-66 in the range between 10 and 125 nm with very high yield.



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Sn/C composite anode materials for high energy batteries

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Introduction:
Metallic tin (Sn) is one of the most promising anode materials for lithium ion batteries (LIBs) due to its high theoretical capacity of 991 mAh g^{-1} or 7313 mAh cm^{-3}, multiple times that of graphite anode materials. However, the huge volume expansion (up to 360%) causes cracking and pulverization of the active material, consequently leading to the dramatic mechanical stress of Sn during cycling (figure 1) and the loss of conductivity at the electrode, resulting in huge capacity fading and thereby letting down its application in LIBs[2, 3]. A composite electrode which could facilitate a buffer volume to survive the volume expansion will be the call of the moment. We have adopted a novel synthesis method to form a nano-rattle composite anode made of Sn nano metal encapsulated in a carbon shell as shown in figure 2.

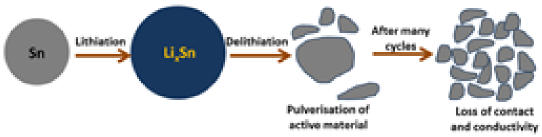

Figure 1: Pulverization of the active material

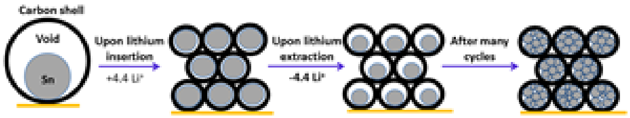

Figure 2: Sn/C nano rattle composite anode setup

Reverse micelle micro emulsion synthesis:
A reverse micelle micro emulsion technique has been developed to form Sn encapsulated into silica shell where the silica shell serves as the substrate for carbon coating[4]. Figure 3A and B show the SEM picture and the coupled EDS spectra of as-obtained Sn@SiO_2 material respectively, whereas figure 3C shows the TEM picture of the same. Also, figure 3D shows the Sn@SiO_2@C material after thermal treatment. After obtaining the Sn@SiO_2@C core-shell setup, the further step of the removal of SiO_2 template has been done. During the SCS presentation, the electrochemical tests will be shown after assembling half cells out of the electrode formulated from Sn@C nano-rattle type composite anode material.

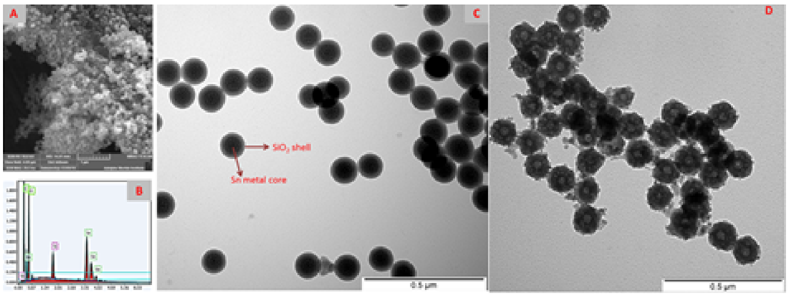

Figure 3: SEM (A), EDS (B) and TEM (3C) showing core-shell Sn@SiO_2, 3(D) showing Sn@SiO_2@C after thermal treatment

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Synthesis and characterization of novel imidazolium-based ionic-polystyrenes and their application as supports for Pd nanoparticles.

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[1]EPF Lausanne

Ionic polymers have emerged as a class of materials with interesting properties that make them suitable for several applications including recyclable catalyst supports [1]. Herein, Imidazolium-based cross-linked ionic polymers containing a N-donor ligand were synthesized, characterized and used as supports for Pd- catalysts. The synthesis requires three steps: synthesis of pure ionic monomers, polymerization of the monomers employing radical polymerization, and palladation of the polymer by reaction of the polymer with a suitable palladium salt. The obtained polymers were characterized and used to catalyze the reaction of aryl halides, CO_2 and hydrosilanes to form benzaldehydes.

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Highly Stable Red Light Emitting Electrochemical Cells Based on Cyclometallated Iridium(III) Complexes

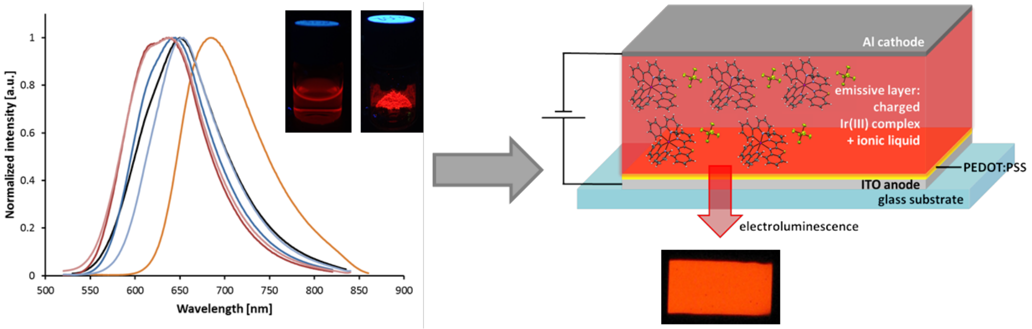
C. D. Ertl[1], C. Momblona[2], A. Pertegás[2], H. J. Bolink[2], E. Ortí[2], C. E. Housecroft[1]*, E. C. Constable[1]*

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

Cationic iridium(III) complexes of the type $[Ir(C^\wedge N)_2(N^\wedge N)]^+$ are the most intensely studied emissive compounds for light emitting electrochemical cells (LEECs). In addition to their good photophysical and chemical properties and ionic nature, emission colour tuning is straightforward due to spatial separation of the frontier orbitals, making these complexes well suited for LEEC applications.[1]

Nonetheless, there is still a lack of stable and efficient red emitters, crucial also for the production of white LEECs. By the introduction of a benzothiazole unit it was possible to effectively red-shift the emission maximum by 50 nm when compared to the archetypal complex $[Ir(ppy)_2(bpy)][PF_6]$.

Based on these findings, a series of related iridium complexes with different cyclometallating and ancillary ligands was investigated. All complexes are orange to deep red emitters, both in solution and in the solid state. For selected complexes in this series, highly stable LEECs were prepared, resulting in the longest reported lifetimes for red emitting iridium(III) complexes.



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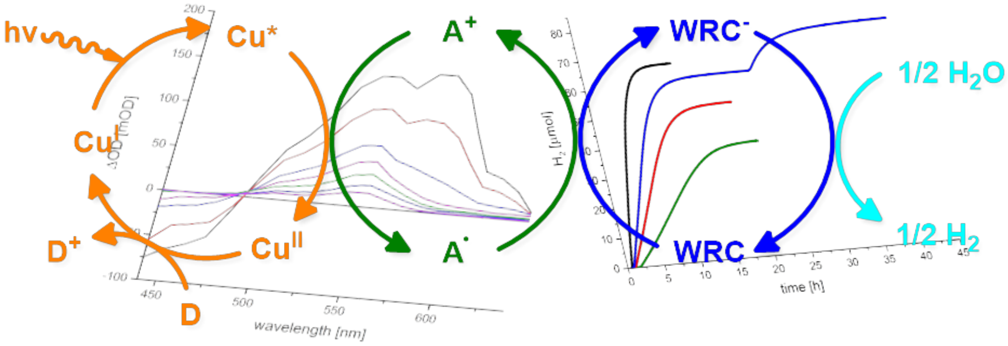
A General Scheme for Oxidative Quenching of a Copper-bis-phenanthroline Photosensitizer for Light-Driven Hydrogen Production

J. Windisch[1], M. Orazietti[1], P. Hamm[1], B. Probst[1], R. Alberto[1]*

[1]University of Zurich

A new, general reaction scheme for photocatalytic hydrogen production is presented based on oxidative quenching of a homoleptic copper(I) *bis*-1,10-phenanthroline[1] type photosensitizer (PS) by an electron relay, and subsequent regeneration of the so formed copper(II) complex by a sacrificial electron donor. Electron transfer from the relay to various cobalt based water reduction catalysts (WRC),[2] and subsequent H_2 production was shown to close the catalytic cycle.



Due to its earth abundance, copper based PS's present a viable alternative to ruthenium, rhenium or platinum type PS.[1, 3] As compared to the latter, both, the excited state oxidation and reduction potential are shifted cathodically, thus prohibiting the use of common reductive quenchers. To turn this difference into an advantage, oxidative quenching was investigated for a series of organic acceptor molecules of varying redox potentials. For the best candidates, photocatalytic test runs were performed, confirming the shown reaction scheme. Further evidence was gathered from transient absorption experiments, which unambiguously confirmed the proposed reaction pathway. In summary, this new PS/relay system delivers very long lived reduction equivalents and therefore universalizes the applicability of copper(I) *bis* -1,10-phenanthrolines as photosensitizers.

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

N. Marinakis[1], C. E. Housecroft[1], E. C. Constable[1]

[1]University of Basel

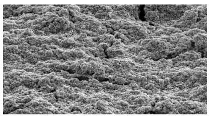
We present recent research that has been done in our group detailing the mechanism of a p-type cell. A p-type electrode will eventually be used as the cathode electrode in a tandem cell, in order to achieve that the performance of the cell has to be improved.

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

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

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

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



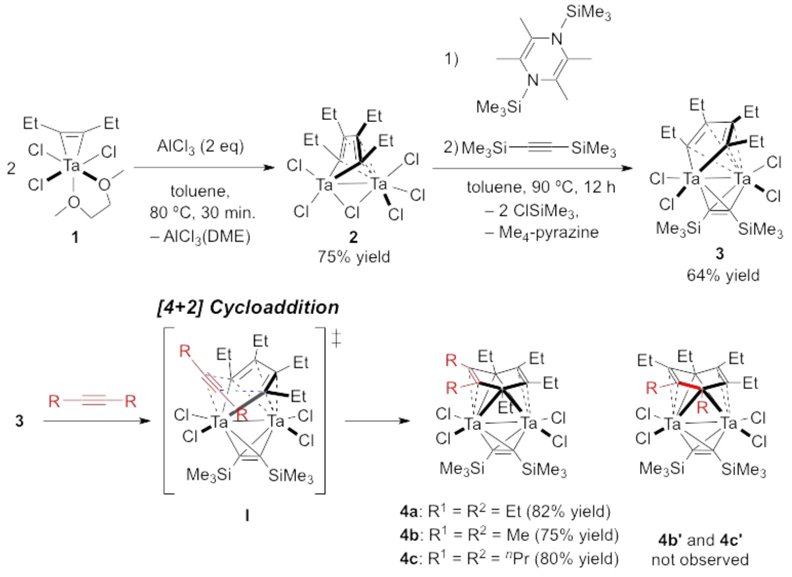
Evidence for [4+2] cycloaddition mechanism of alkynes to tantallacyclopentadiene as a model of alkyne cyclotrimerization

K. Yamamoto[1], H. Tsurugi[2], K. Mashima[2]

[1]ETH Zürich, [2]Osaka University

Cyclotrimerization of alkynes assisted by various transition metal catalysts is a straightforward synthetic method for constructing substituted aromatic compounds.[1] A well-established reaction mechanism involves the oxidative coupling of two alkynes at a low-valent metal center, giving a metallacyclopentadiene, following further addition of an alkyne to produce the corresponding benzene derivatives. Although [4+2] cycloaddition between a metallacyclopentadiene and an alkyne is an acceptable mechanism for constructing a six membered ring, experimental evidence of the [4+2] cycloaddition is limited for an intramolecular reaction.[2] Herein, we report our direct observation of the intermolecular [4+2] cycloaddition pathway during alkyne cyclotrimerization using a dinuclear tantalum metallacyclopentadiene scaffold. Suppression of the rotational behavior of the arene ligand at the dinuclear tantalum core was key for clarifying the [4+2] cycloaddition mechanism.

Reaction of **1**with anhydrous $AlCl_3$ in toluene afforded dinuclear tantalum metallacyclopentadiene complex **2**. Although complex **2** showed high catalytic activity of cyclotrimerization of alkynes such as 3-hexyne, 2-butyne and 4-octyne, any intermediate species were not detected. When metallacyclopentadiene complex **3**, which was prepared by ligand exchange reaction of two chloride ligands to a bis(trimethylsilyl)acetylene, was used for the arene ring formation by the addition of 3-hexyne, 2-butyne and 4-octyne, the corresponding arene-coordinating complexes **4a**-**c** were obtained in good yield. No formation of isomers such as **4b’** and **4c’** indicated that this reaction proceeded through the [4+2] cycloaddition transition state **I**. In addition, further isomeric rotational behavior of **4b** to **4b’** was observed by heating **4b** in toluene at 80 ºC, without dissociation of the $C_6Et_4Me_2$ ligand.



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Isonitrile Iron(II) Complexes with Chiral $(NH)_2P_2$ Macrocycles in the Enantioselective Transfer Hydrogenation of Polar Double Bonds

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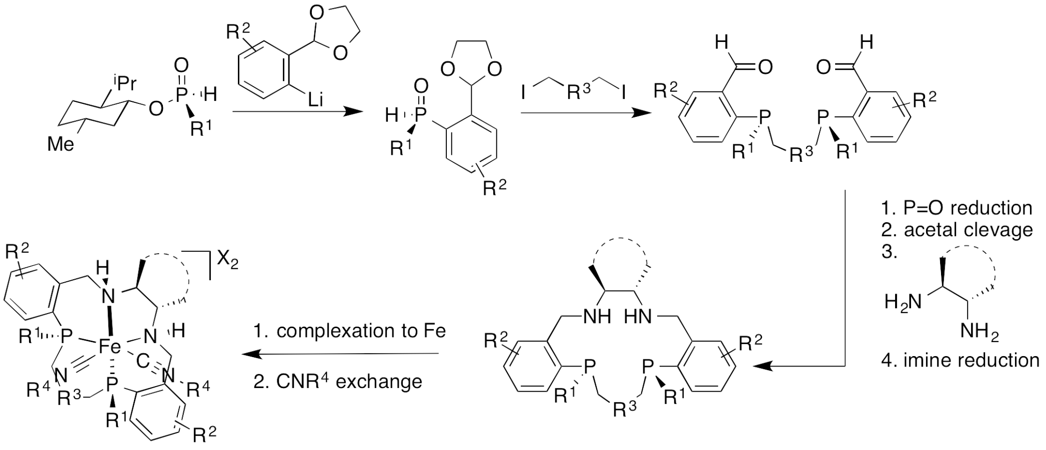
[1]ETH Zurich

Following our interest in C_2-symmetric N_2P_2 macrocycles,[1,2] we have recently reported an intriguing example of bis(isonitrile) iron (II) complexes bearing a C_2-symmetric diamino $(NH)_2P_2$ macrocyclic ligand, which efficiently catalyze the asymmetric transfer hydrogenation of polar bonds of a broad scope of substrates (ketones, imines, and enones) in high yield (up to 99.5 %), excellent enantioselectivity (up to 99 % *ee*), and with low catalyst loading (0.1 mol %).[3]



Additionally to changing the isonitrile ligands, the new modular approach[4] to the synthesis of the ligand allows the facile tuning of the catalyst by modifying the macrocycle or changing the isonitrile ligands. Ligands with R^3= $-CH_2-$ and 3,5-substituted aromatic rings as R^1 have been screened in order to modulate the steric and electronic effects in the ATH of ketones.

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Cobalt(II)/Cobalt(III) Polypyridyl Complexes as Electrolytes in Combination with Copper(I) Dyes in Dye Sensitized Solar Cells

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

[1]University of Basel

In order to achieve higher efficiencies and prolong long-term stability in n-type dye sensitized solar cells (DSCs), the widely-used iodine/triiodide electrolyte is replaced by various cobalt(II)/cobalt(III) polypyridyl complexes. In our research we use heteroleptic copper(I) complexes of the type $[Cu(L_{anchor})(L_{ancillary})]^+$ as dye sensitizers; the dyes possess tetrahedral bis(dimine)copper(I) cores. The ancillary ligand $L_{ancillary}$ harvests the incident photons and the anchoring ligand L_{anchor} binds the complex to the semiconductor surface of the photoanode.

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

In this work, we show the results of testing the combinations of different copper(I) dyes with cobalt electrolytes whilst optimizing the concentration, solvent and changing the additives of the electrolyte.

Quasi-Solid Polymer Electrolytes reinforced by a Cellulose Nano Crystals to be used in Dye Sensitized Solar Cells

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

[1]University of Basel

Currently, a considerable amount of research is carried out all over the world to enable the usage of dye sensitized solar cell (DSSC) devices and make them more commercially passable. Among the challenges at hand is the electrolyte component within the DSSC which often contains volatile organic solvents. These solvents typically have the disadvantage, besides of being toxic and environmentally unfriendly, of evaporating and leaking out over time, lowering the performance and shortening the lifetime of the cell. One way to encounter this problem is to replace the liquid electrolyte with a quasi-solid constituent that can perform the same task of conducting the active redox couple. Over the years, poly(ethylene glycol), (PEG), has gained interest as the solid content of the electrolyte due to its good ion conducting abilities. The advantage of adding a reinforcing component to help the polymer matrix withstand geometry changes upon swelling with a liquid electrolyte in order to disperse the redox species in the polymer is also widely investigated.

In the work presented, cellulose nano crystals (CNC) is utilized as an environmentally friendly component to reinforce a low T_g poly(ethylene glycol) (PEG) matrix into a nano composite, which is UV-polymerized and finally activated by a liquid iodide electrolyte. The activated nano composite is then introduced to a copper sensitized DSSC. Results show the performance dependence on the CNC content in the composite, where the best compositions outperform the liquid control sample. Furthermore, the chosen CNC content of 40% by weight is superior to the control DSSC in terms of long time stability where characterization tests are carried out over a period of 60 days.

Full magnetic investigations of a novel mononuclear 4f polyoxometalateexhibiting single molecule magnet behaviour

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

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

Polyoxometalates (POMs) are a fascinating class of metal-oxo clusters containing transition metal ions in their high oxidation states. Over the last 50 years, POMs have been widely explored for numerous applications in catalysis, for biomedical and biological features and lately, magnetism. Truly, these metal-oxo clusters offer undeniable qualities for future applied devices such as a wide structural and compositional diversity. First reports on the observation of slow magnetic relaxation process in a molecular material were published by *Sessoli* et *al.*[1] on the $[Mn_{12}O_{12}(O_2CMe)_{16}(H_2O)_4]$, $\{Mn_{12}\}$. Interests in Single Molecule Magnets (SMMs) increased substantially when researchers realized that SMMs could be used for high-density information storage [2] and over the last two decades the number of reported SMMs did not cease to grow with several examples of 3d, 4f and even mixed 3d-4f complexes.[3]
Up to now, not many POMs exhibiting SMM behaviour have been reported. The first mononuclear lanthanide complex $[Ln(W_5O_{18})_2]^{9-}$ (Ln = Ho, Er) with SMM behaviour was published by *Coronado* et *al.* in 2008.[4] After this breakthrough, similar approaches were extended to the mononuclear family with the Preyssler-type series $[Ln(P_5W_{30}O_{110}]^{12-}$ (Ln = Tb, Dy, Ho, Er, Tm, Yb) and the Keggin-type structure $[Ln(\beta\text{-}SiW_{11}O_{39})_2]^{13-}$ (Ln = Dy, Ho, Er, Yb). As of now, only these three types of mononuclear 4f POM complexes showing SMM behaviour were observed and join a short list of published polyoxometalates exhibiting this magnetic property.
Here, we highlight[5] a new isostructural family of 4f mononuclear "sandwich" Keggin POMs with a large variety of lanthanide ions (Ln = Gd, Tb, Dy, Ho, Er, Yb). The crystal structure of the whole family was successfully solved and full magnetic investigations with alternating current (ac) and direct current (dc) were performed. The distinct out-of-phase signals of the ac measurements on the $[Er(\beta_2\text{-}GeW_{11}O_{39})_2]^{13-}$ and $[Dy(\beta_2\text{-}GeW_{11}O_{39})_2]^{13-}$ derivative revealed the presence of SMM behaviour.
Moreover, careful studies of the lanthanide coordination geometry show that the Ln^{3+} (Ln = Gd, Tb, Dy, Ho, Er, Yb) ion is embedded in a favourable square-antiprismatic geometry for SMM behaviour.

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Synthesis and catalytic applications of O-functionalized mesoionic NHC metal complexes.

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1,2,3-Triazolylidenes are a unique class of carbenes which have many advantages over classical N-heterocyclic carbenes (NHCs) including ease of synthesis and modification, and increased σ-donation properties.[1] Since *O*- and *N*-functionalization of classical NHCs has been shown to enhance the catalytic activity of the metal center, in particular for (transfer) hydrogenation reactions.[2,3] We aimed to explore the implication of such functional groups in combination with triazolylidene ligands. To this end, we have synthesized a range of metal complexes bearing *O* -functionalized 1,2,3-triazolylidene ligands. In this presentation, we will discuss the effects of this functional group, and the catalytic applications of the corresponding complexes in transfer hydrogenation and dehydrogenation reactions.

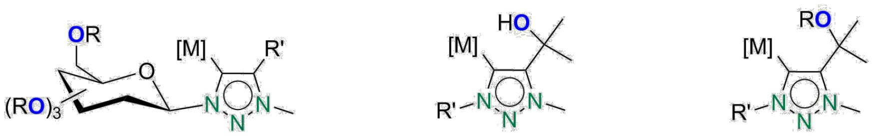

Figure 1: *O*-functionalized 1,2,3-triazolylidene metal complexes

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Strategies to solve the solution structure of the CPEB3 ribozyme through NMR spectroscopy

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

The hepatitis delta virus (HDV) ribozyme is one of the best studied small ribozymes. It folds in a nested double pseudoknot and catalyzes its own scission during the rolling circle replication of the hepatitis delta virus resulting in several copies of the genome. The cytoplasmic polyadenylation element binding protein 3 (CPEB3) ribozyme is an HDV-like ribozyme found in mammalian genomes including humans[1]. Its role has yet to be elucidated however it has been linked to episodic memory[2]. The HDV ribozyme shares biochemical properties and secondary structure with the CPEB3 ribozyme which leads to the hypothesis of these ribozymes being evolutionarily related[1]. These ribozymes, when properly folded, catalyze a transesterification reaction resulting in a 2'-3'cyclic phosphate and a liberated 5' hydroxyl. The crystal structure of the HDV ribozyme has been through X-ray crystallography but no atomic resolution structure of the CPEB3 ribozyme has been solved[3,4].

The goal of this project is to solve the solution structure of the CPEB3 ribozyme by NMR spectroscopy. Our lab already demonstrated by NMR the importance of Mg^{2+} ions to drive the CPEB3 ribozyme in its compact and active fold[5.] However, due to the length of 67 nts and the complex folding of this ribozyme, the NMR spectra of natural abundance CPEB3 constructs are affected by strong spectral overlap. Thus, a straightforward assignment procedure is not feasible and extended assignments strategies need to be applied. Here we discuss various strategies to assign such NMR spectra including different uniform and selective isotopic labeling routes, the usage of small model constructs and the stabilization of specific parts by mutating or elongating the constructs, by metal ions or by changing the temperature and pH conditions. ^1H-^1H NOESY spectra of the CPEB3 ribozyme are discussed including uniform isotopic labeling, A, G, C or U only labeled samples and three small model constructs based on the helical domains.

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New Perfluoroalkylated Reagents on the Basis of Hypervalent Iodine Compounds

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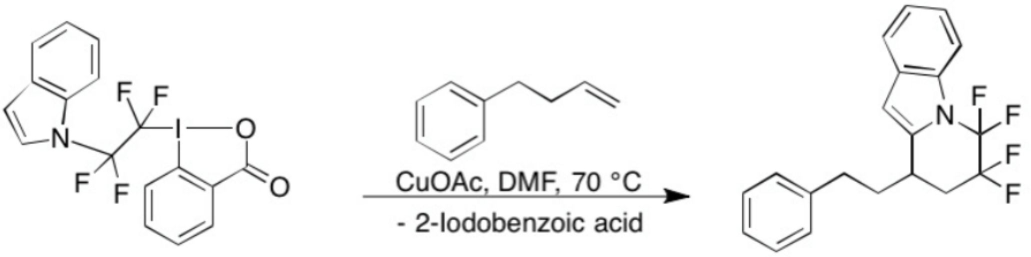
[1]ETH Zurich

Recently in our group a new synthetic pathway to perfluoroalkylated tetra-dihydro-imidazo-pyridines was described as a so called tandem fluoroalkylation-cyclization reaction.[1]

We were able to extend the scope of the corresponding *N*-heterocycle, to e.g. pyrazole triazole, or indole based reagents, as shown in Scheme 1. Furthermore, the mechanism of this type of reactions was investigated.

Non-fluorinated heterocycles are well known to be useful against different diseases[2] and it would be interesting to synthesize the fluorine analogues with the reported pathway.



Scheme 1: Tandem fluoroalkylation-cyclization with 4-Phenyl-1-butene.

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Growth of Zinc Oxide Rods on Wood Cross-sections to Fabricate Surfaces with Anisotropic Wettability

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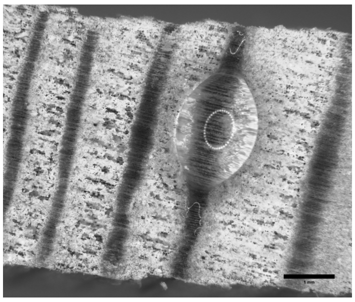
[1]ETH Zürich, [2]Empa

In certain applications, self-cleaning (super)hydrophobic surfaces can have the major disadvantage that water is lost as droplets roll away randomly from the homogeneous substrates. To prevent this, manufacturing techniques to obtain anisotropic wetting on surfaces by lithographic techniques [1-2] have been developed. However, additional insight and research are still needed to optimize and scale up fabrication approaches in order to achieve low cost and mass scaling for industrial applications [3]. Such issues could be potentially solved with the use of the widely available natural material wood.

Wood is a cellular, anisotropic, and hygroscopic material, consisting of biopolymers (cellulose, lignin, and hemicellulose) assembled in a complex hierarchical composite structure [4]. Our objective is to exploit the natural surface inhomogeneity as well as both intrinsic chemical and physical characteristics of the wood substrate, in order to create specific patterns of wettability on the surface (Fig.1).

To this end, zinc oxide rods are grown on wood surface using a sol-gel process. Based on density and porosity variations, the accessibility of early wood (EW) and late wood (LW) to the treatment solution during the hydrothermal reaction is different. As a result, ZnO rods preferentially grow in the EW regions. The EDS result confirms that most of the ZnO rods are essentially located within the EW, thereby implementing a higher roughness leading to clear differences in wetting properties between LW and EW. The later observation is confirmed by contact angle studies.

In the future, inspired by the example of desert beetle [5], we plan to show that wood cross-section has the potential in fog collection. We believe that the wettability pattern created on wood surface with our simple and green chemistry will allow applications in water drop nucleation and directional flow.



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Synthesis and reactivity of divalent lanthanide siloxide complexes

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[1]EPF Lausanne

Siloxide ligands have attracted scant attention in lanthanide chemistry, although a handful of complexes are known.[1] As such, we have been focusing on the use of bulky, electron-rich tris(*tert*-butoxy)siloxide ligands to prepare highly reactive divalent lanthanide complexes. The divalent complexes, $[Ln\{OSi(OtBu)_3\}_4K_2]$ (Ln = Eu, Yb), are potent reducing agents and they can effect the reduction of various substrates such as CS_2 and azobenzene. Additionally, $[Yb\{OSi(OtBu)_3\}_4K_2]$ (Fig. 1) can reduce CO_2 – the first example of CO_2 reduction by an Yb^{II} complex.[2]

In order to tune the steric and electronic environments around the lanthanide centres, the number of siloxide ligands or the type of siloxide ligand can be varied. With this in mind, we have now turned our attention to preparing divalent complexes with two or three tris(*tert*-butoxy)siloxide ligands, respectively, and we have also extended our focus to the triphenylsiloxide ligand. These syntheses are complicated by facile ligand rearrangement reactions and/or instability of the products. Here, we describe attempts to make new divalent lanthanide complexes with either tris(*tert*-butoxy)siloxide or triphenylsiloxide ligands, along with preliminary reactivity tests with small molecules. Interesting structural features and reactivity have been discovered so far.

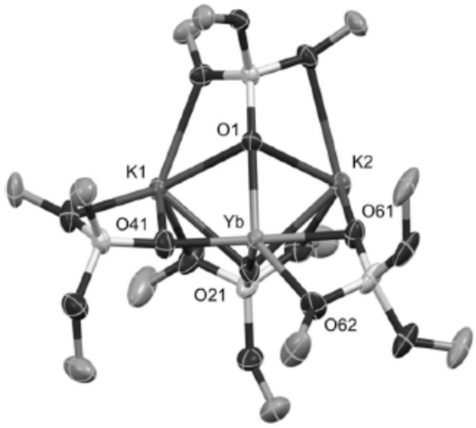

Fig. 1 Structure of $[Yb\{OSi(OtBu)_3\}_4K_2]$

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Facile post-modification to efficiently modulate the catalytic activity of triazolylidene iridium complexes

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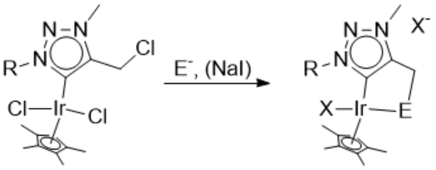
N-heterocyclic carbene (NHC) metal complexes have shown excellent activity in many systems, including a wide variety of catalytic applications.[1] A sub-class of NHCs are mesoionic NHCs, such as 1,2,3-triazolylidenes, which are stronger donating ligands and impart beneficial properties in, for instance, redox catalysis.[2] Functionalization of the carbene ligands is often a challenging multi-step synthesis, which can be simplified by a post-modification procedure.[3,4] Here we have developed a new post-modification approach that is based on a chloro-functionalized triazolylidene iridium complex (see Figure). From this organometallic building block, a wide range of donor-functionalized iridium complexes are readily accessible, thus substantially expediting tedious synthesis. We will discuss the versatility of this method and its suitability to fast catalytic screening and to optimize the impact of functional donor sites.



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A Cobalt-diketopyrphyrin complex as highly active catalyst for light-driven H2 evolution

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Cobalt complexes are common H^+ reducing catalysts for homogeneous photocatalytic hydrogen evolution in water (Fig. 1).[1] Our group recently introduced cobalt pyrphyrins [2, 3] as a new class of H_2 evolution catalysts. Here, a novel cobalt(II) complex based on a diketopyrphyrin ligand framework is presented. The complex is synthesized along a comparatively simple route in only 3 steps and is well soluble in water. This complex shows extraordinary activity as water reduction catalyst (WRC) when tested in an aqueous system with $[Ru(bpy)_3]Cl_2$ as photosensitizer (PS) and TCEP/NaAsc [4] as sacrificial electron donor and shuttle, respectively. Turnover numbers (TON) higher than 80'000 H_2/Co were achieved, thus excelling our previous polypyridyl and pyrphyrin based catalysts by far. [2, 4] The catalytic performance as well as insights into the mechanism of H_2 evolution are discussed.

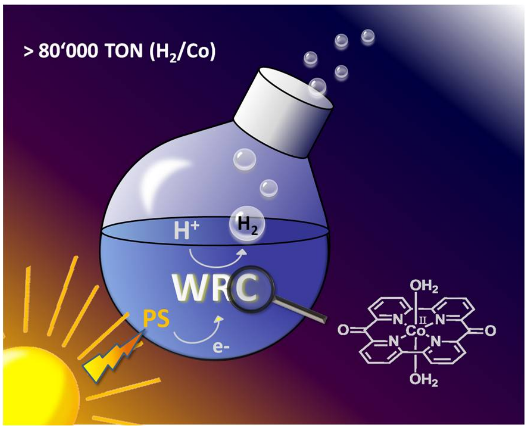

Fig. 1. Photocatalytic water splitting with cobalt-diketopyrphyrin as water reduction catalyst (WRC), achieving turnover numbers higher than 80'000 H_2/Co.

Synthesis of novel octadentate bifunctional chelating agents for ^{89}Zr immuno-PET.

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Cancer is the leading cause of death worldwide, killing nearly 8 million people annually. Thus, an early detection of the disease is crucial to increase survival. During the past years, Positron Emission Tomography (PET) has become an indispensable diagnostic tool in clinical oncology as a sensitive nuclear molecular imaging technique.[1] Several monoclonal antibodies (mAbs) against different tumor antigens have been approved for use as diagnostics and therapeutics in the clinic. Indeed, such antibodies allow the targeting of primary tumors and metastases.[2] Consequently, the combination of PET with mAbs (immuno-PET) is an attractive option to improve diagnostic tumor characterization.[3] The metallic radionuclide ^{89}Zr has a physical half-life of 78.4 hours, long enough to match the biological half-life of most antibodies (several days). As a radiometal, ^{89}Zr is linked to mAbs through a bifunctional chelating agent (BFCA). BFCAs are molecules able to coordinate stably the ^{89}Zr and covalently link the radiometal complex to an antibody.[4] Analogs of the chelator desferrioxamine (DFO) are currently used for this purpose. However, the incomplete coordination of ^{89}Zr by the hexadentate DFO results in instability of the radiolabeled conjugate in vivo.[5] Recently, a novel DFO analogue (termed DFO*) with an additional hydroxamic acid group has been designed to accomplish complete octadentate coordination of Zr^{4+}.[6] In comparison to DFO, the new chelator has been shown to yield radiometal complexes of significantly increased stability in vitro and in vivo. However, a remaining issue of DFO* is its low solubility in aqueous media which impedes to some degree with protein modification protocols. We will present novel DFO* derivatives of improved water solubility that will facilitate the development of ^{89}Zr-immunoPET imaging probes.

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Synthesis and catalytic activity of triazolylidene iron(II) piano stool complexes

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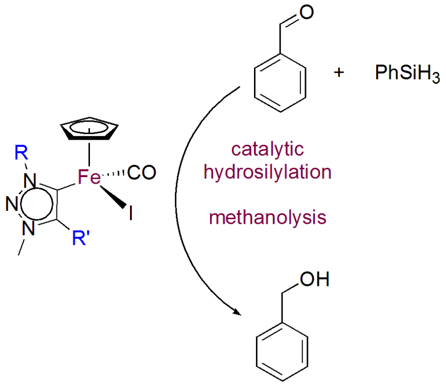
In recent years, mesoionic 1,2,3-triazolylidenes have emerged as a highly versatile subclass of N-heterocyclic carbene (NHC) ligands.[1] This NHC scaffold can be effectively tailored to specific functions as a consequence of the flexibility of the [3 + 2] cycloaddition of alkynes with azides. This feature, coupled with the ligands' strong σ-donor abilities have led to their diverse application in catalytic transformations.[2]

Despite the substantial economic advantages of iron based NHC catalysts *vs* the rare and heavy transition metals, examples are relatively scarce.[3] Herein we present a new class of triazolylidene iron(II) piano stool complexes and discuss their application in catalytic hydrosilylation reactions.



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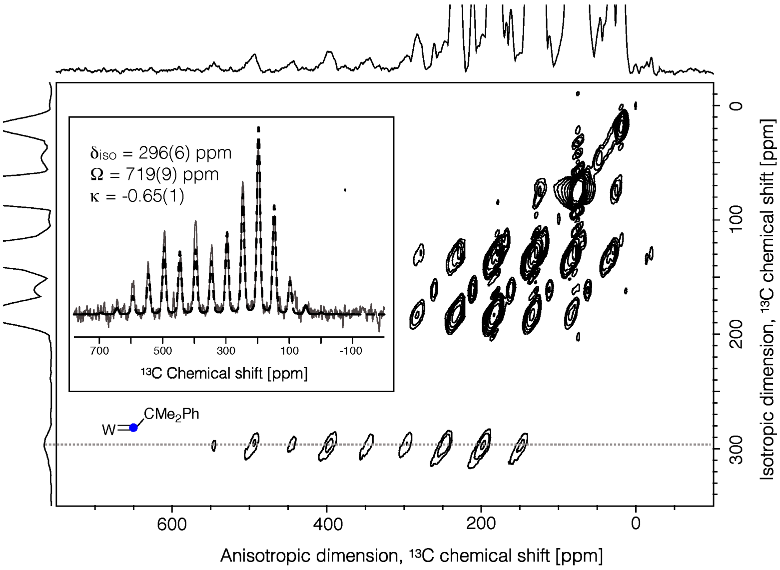
Direct Characterization of Highly Reactive Heterogeneous Alkene Metathesis Catalyst by DNP SENS

W.-C. Liao[1], T. Ong[1], D. Gajan[2], G. Casano[3], M. Pucino[1], O. Ouari[3], A. Lesage[2], P. Tordo[3], L. D. Emsley[4], C. Copéret[1]*

[1]ETH Zurich, [2]Centre de RMN à très hauts champs, [3]Institut de Chimie Radicalaire, Aix-Marseille Université / CNRS, [4]Ecole Polytechnique Federale De Lausanne, EPFL

Heterogeneous catalyst is key to industrial processes because of its streamline and simplified operating units (e.g. catalyst separation and regeneration). However, improving the catalyst is usually difficult because of the lack of understanding of the active site structures. Surface organometallic chemistry has thus aimed at generating well-defined surface sites to rationalize structure–activity relationships. A key tool to probe surface structures is solid-state NMR spectroscopy, but its intrinsic low sensitivity coupled with the low concentration of active sites on surfaces often impedes its application. Dynamic nuclear polarization surface enhanced NMR spectroscopy[1] (DNP SENS) is an effective method to increase NMR sensitivity by transferring the larger electron polarization of the paramagnetic dopant (usually nitroxide biradicals) to the smaller nuclear polarization of the nuclei under analysis. However, surface sites can be incompatible with the necessary radicals used in DNP.[2] Here we describe the synthesis of a series of bulky dendrimeric biradicals. We show that they are compatible with the highly reactive metal alkylidene[3], a key intermediate in olefin metathesis, making faster acquisition of NMR spectra possible. Combining ^{13}C enrichment and DNP enhancement, the gained sensitivity allows us to apply the 2D CPMAT experiment to extract the chemical shift anisotropy (CSA) of the alkylidene carbon. With additional analysis using DFT calculations, we can thus understand the electronic structure of a highly active metathesis catalyst.



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Heterometallic coordination cages with unusual geometries

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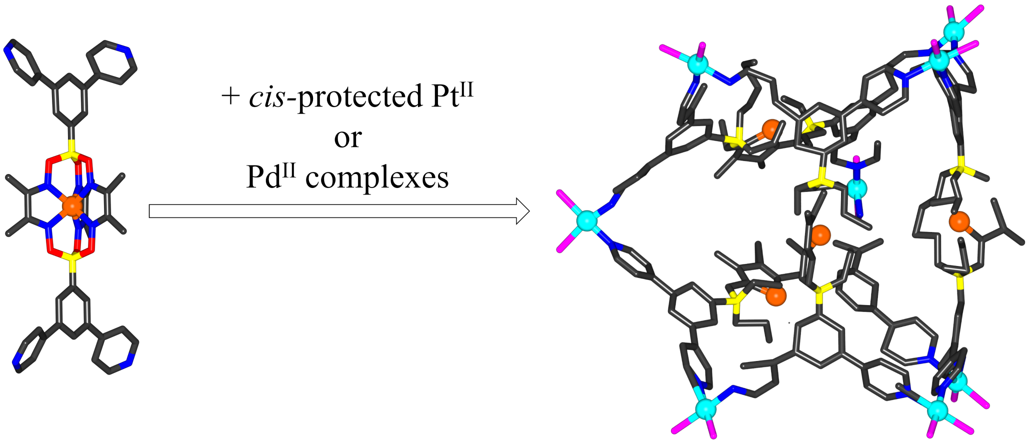
[1]EPFL Lausanne

The chemistry of coordination cages has advanced dramatically in recent years. Different synthetic approaches have been developed, allowing the efficient preparation of cages with diverse geometries and functions. Even though the rational design of coordination cages with well-defined structures has been successful in numerous cases, there is still ample room for surprises. We have prepared large, heterometallic coordination cages by combining clathrochelate-based metalloligands featuring terminal pyridyl groups with Pd^{II} and Pt^{II} complexes. The utilization of metalloligands instead of simple organic polypyridyl ligands resulted in the formation of unusual structures. With 'naked' Pd^{2+} ions, we observed octahedral complexes instead of tetrahedral ones,[1] and with *cis*-blocked Pt^{II} complexes we obtained cages with unusual gyrobifastigium geometries.[2]



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Molecular Knots and Links for Halide Binding and Allosterically Regulated Catalysis

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

The spontaneous formation of molecular entanglements in either biomacromolecules (e.g. DNA and proteins) or synthetic polymers can influence the overall stability and tensile strength of the molecule. Thus, a better understanding of the factors governing the formation and properties of such nanoscopic knots and links is desirable. Here, the synthesis of several new and fascinating molecular knot and link topologies is described[1] using self-assembled metal-organic circular helicates as precursor complexes. The product topologies are ultimately determined and studied using X-ray crystallography, and are shown to possess unprecedented levels of structural complexity. The topological chirality displayed by such molecules is investigated, along with their ability to strongly (and selectively) bind halide anions[2] and metal cations, and to allosterically regulate external reactions.[3]

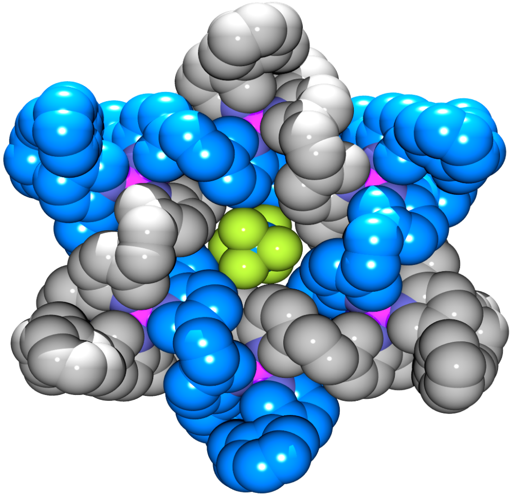

Figure: Crystal structure of a molecular link possesing the topology of a Star of David [2]Catenane. The carbon atoms of one discrete ring are shown in blue, and the other in light grey.

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New Polarization Matrices for Dynamic Nuclear Polarization with the Polarizing Agent Embedded in the Wall

D. L. Silverio[1], H. A. van Kalkeren[2], T. Ong[1], M. Yulikov[1], D. Gajan[4], G. Jeschke[1], M. V. Kovalenko[1], C. Thieuleux[2], C. Copéret[1]*, L. Emsley[4]*

[1]ETH Zurich, [2]CPE Lyon, [3]ETH Zürich, [4]Centre de RMN à très hauts champs

SBA-type materials containing a radical have been shown to polarize a solution containing analytes at low temperatures (1 – 100 K) via dynamic nuclear polarization (DNP). [1]. Importantly, DNP can be carried out in broad range of solvents including pure water and with any class of radicals because the radicals were isolated at the pore surface of a material, thus avoiding problems of glassing and required solubility of the radical.

Here we describe the development of a new class of polarizing matrix, where the radicals are incorporated in the wall of the materials. This separation from the radical can be crucial when the molecule being studied by DNP NMR would otherwise react in a deleterious manner with the radical, a problem for organometallics species, redox active biologically active molecules, and sensitive colloidal species.

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Formation of Formic Acid via CO_2 Hydrogenation with Silica-Supported Transition Metal Pincer Complexes

H.-K. Lo[1], I. Thiel[1], C. Copéret[1]*

[1]ETH Zurich

Over the past decades, the hydrogenation of CO_2 to more valuable products such as formic acid or methanol has been highly emphasized in the academic field because of the continuous increase of CO_2 in the earth's atmosphere. The challenge of converting CO_2 results mainly from its considerable Gibbs free energy ($\Delta G° = -394.4$ kJ/mol). Therefore active co-reactants and/or catalysts are usually needed. Formic acid, one of the CO_2 hydrogenation derivatives, is an efficient hydrogen carrier and hasgreat potential to be applied in fuel cells. Nowadays various efficient homogeneous catalytic systems have been developed to convert CO_2 to formic acid, such as the iridium complexes with PNP pincer-type[1, 2] and bipyridine-type ligands[3] or ruthenium complexes with N-heterocyclic carbenes.[4] However, the above-mentioned homogeneous catalysts were only applied in batch reactors, which are less favored in industrial continuous processes, and efficient well-defined immobilized catalysts are still sparse in CO_2 hydrogenation. Here, we aim at synthesizing new immobilized Ir-based catalysts, which are supported on well-defined silica-based hybrid materials or synthetic polymers, and applying them in a continuous CO_2 hydrogenation process.

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Molecular photocathodes for hydrogen evolution

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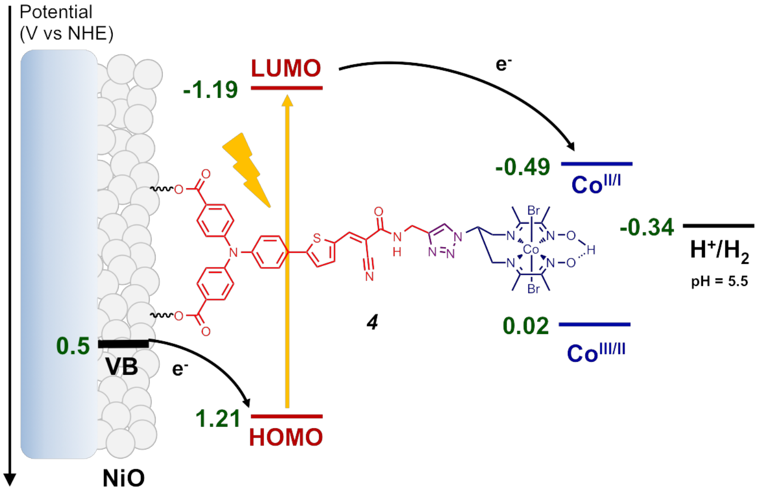
[1]ETH Zürich, [2]Universite Grenoble Alpes, CEA, CNRS, France

While market-grown technologies for splitting water into H2 and O2 mainly lay on catalysis through platinum, scientists now turn toward non-rare metals alternatives to produce such solar fuels. To go toward the possible utilization of sunlight as the energy source, we investigated the immobilization of a proton reduction catalyst, a cobalt diimine-dioxime complex, along with organic photosensitizers onto transparent conducting oxides. We exploited two strategies to join the photoactive and catalytic entities on the surface, either by co-grafting them or by a covalent coupling. We will report here on our efforts to construct such photocathodes for hydrogen evolution relying on molecular components only. Characterizations of these systems at the molecular level will be provided.



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Propane Dehydrogenation Utilizing Gallium-Based Catalysts

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[1]ETH Zurich

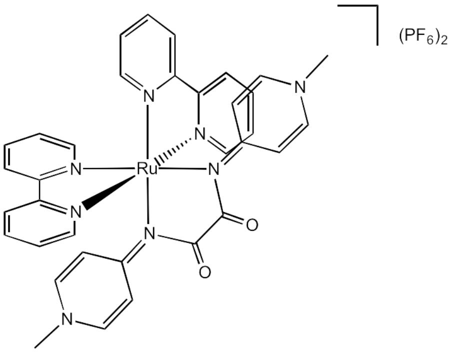
Gallium(III) oxide is an appealing catalyst for propane dehydrogenation (PDH) due to its high conversion and selectivity for propene. However, most catalysts based on this oxide suffer from relatively facile deactivation. Several studies have focused on varying the support on which gallium(III) oxide is dispersed utilizing incipient wetness impregnation methods for the preparation. Other studies have also investigated incorporating promoter elements to inhibit deactivation pathways. While these studies have assisted in developing a better understanding of PDH when utilizing gallium, a greater insight on the molecular level is required for future development of gallium-based catalysts. Here will be presented the preparation of gallium-based catalysts utilizing surface organometallic chemistry to generate well-defined gallium sites. The catalyst preparation involves the synthesis and characterization of several molecular complexes of gallium and their reactivity with silica and alumina supports. The catalytic performance of these materials for PDH will be evaluated with aims of understanding the reaction mechanism on a molecular level.

BIS-PYRIDYLIDENE AMIDE LIGANDS FOR RUTHENIUM-FACILITATED OXIDATION PROCESSES

K. Salzmann[1], C. Segarra[1], M. Albrecht[1]

[1]Universität Bern

The interest of redox-active ligands increases for photophysical and catalytic applications. Such noninocent ligands display varying degrees of donor ability and may stabilize several intermediates of the catalytic cycle. Pyridylideneamides (PYAs) are an innovative class of flexible ligands who show a neutral and a mesoionic resonance structure and are suitable for metal coordination.[1] Recent findings of our group showed that those ligands may be beneficial over tris(bipyridine) ruthenium and its analogues in charge separation for use in dye-sensitized solar cells (DSSCs).[2] Here we introduce a novel analogue of $[Ru(bpy)_3]^{2+}$ with one bipyridine ligand site substituted by chelating bis-PYA ligands and their coordination to a ruthenium(II) center. These new complexes were photo- and electrochemically measured and showed that the presence of PYA moieties facilitates oxidation processes.



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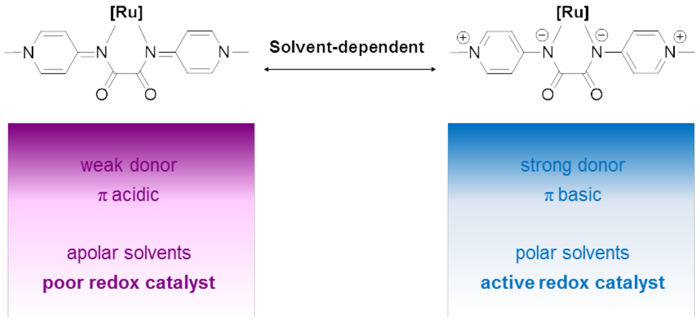
DONOR-ADAPTIVE N-MESOIONIC LIGANDS FOR RUTHENIUM-MEDIATED REDOX CATALYSIS

C. Segarra[1], N. Meisel[1], K. Salzmann[1], M. Albrecht[1]

[1]University of Bern

Redox-active ligands are becoming increasingly important for the development of improving the activity of transition metal complexes in their role as homogeneous catalysts.[1] These noninocent ligands, specifically ligands which display varying degrees of donor ability, are very attractive for catalytic applications, as they may stabilize several intermediates of the catalytic cycle. Pyridylideneamides (PYAs) are a new class of flexible ligands that provide access to a neutral and a mesoionic resonance structure, and which are suitable for metal coordination.[2] We have recently demonstrated the adaptiveness of these ligands in response to the external environment, such as the solvent polarity, and have exploited this donor-flexibility to enhance transfer hydrogenation catalysis.[3] Here we introduce novel chelating bis-PYA ligands and their coordination to a ruthenium(II) center. These new complexes benefit from having two mesoionic PYA moieties and their improved donor-flexibility has been explored in redox catalysis.



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Oriented crystallization of barite in hierarchical cell structures

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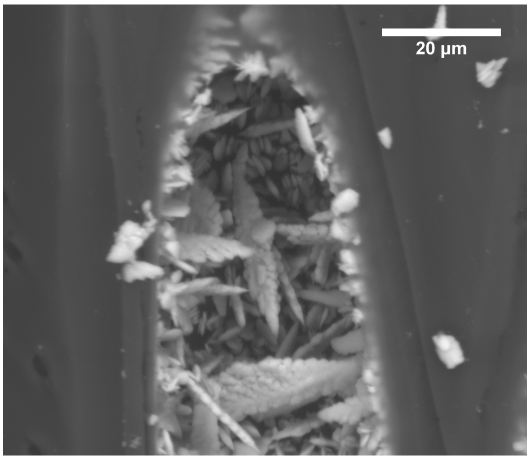
One of the most exciting topics discussed in the field of biomineralization is oriented crystal alignment in complex organic templates. Biomacromolecules, in particular proteins, are known to be involved in controlling crystallization processes, whereas the role of polysaccharides is yet largely unknown. As previously shown for the minerals calcium carbonate [1] or iron oxide [2], natural wood provides an intriguing scaffold for studying mineral formation in confinement. Scanning electron microscopy, Raman spectroscopic imaging and synchrotron-based wide-angle X-ray scattering (WAXS) allow to characterize the deposition pattern, morphology, and texture of barium sulfate at the cellular interface and inside the sub-microporous cell wall. Scanning WAXS-measurements reveal a crystallographic co-orientation of barite crystals and cellulose microfibrils. The experimental findings do not only help understanding inorganic crystallization in the presence of carbohydrates, but also seem highly promising for templated crystal engineering and bio-inspired materials design.



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A naked-eye $[Ce_2(HXTA)]^{3+}$ based biosensor for the detection of phosphate ions in water

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A novel indicator displacement assay[1] (IDA) was developed to probe phosphate ions in water using a dinuclear cerium based complex $[Ce_2(HXTA)]^{3+}$.[2] The homoleptic complex is able to detect phosphates ions in micromolar concentrations both spectrophotometricaly and with the naked-eye

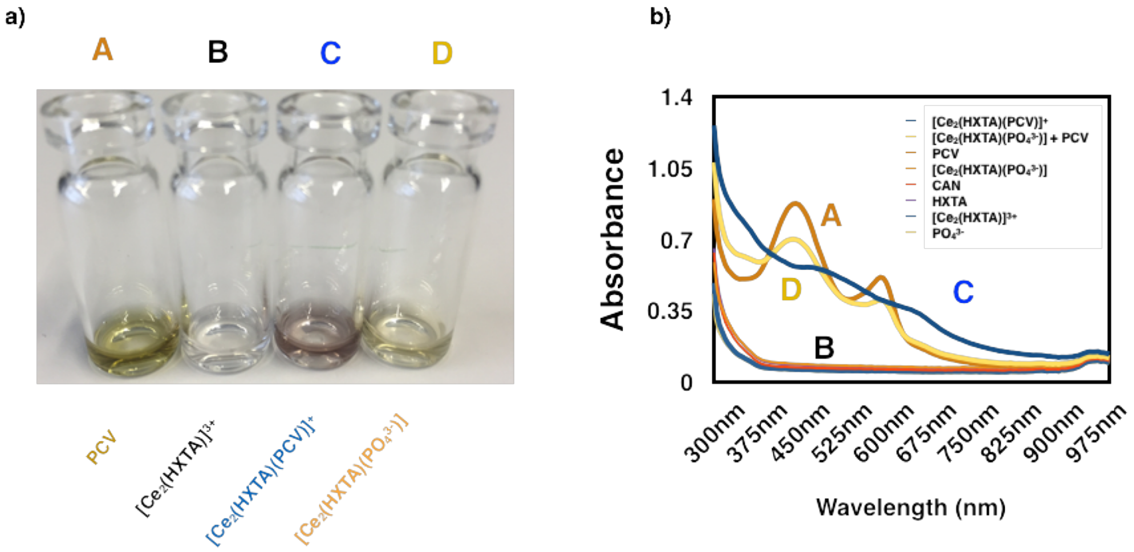

Figure Naked-eye (a) or spectrometric (b) detection of PO_4^{3-}. The assay is based on the violet coloured $[Ce_2(HXTA)(PCV)]^+$ **C**, which upon addition of PO_4^{3-}, changes colour to yellow **D** (a). **B** Is a 25 mM solution of $[Ce_2(HXTA)]^{3+}$ in aqueous buffer (HEPES 100 mM, pH 7.4) solution. The color of the pyrocathecol violet **A** changes from yellow (l_{max} = 445 nm) to violet (**C** l_{max} = 580 nm) upon formation of $[Ce_2(HXTA)(PCV)]^+$. Addition of phosphate anion (25 mM) displaces pyrocathecol violet $[Ce_2(HXTA)(PCV)]^+$ to form a pale yellow solution **D**.

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CHIMIA

CHIMIA 2016, Volume 70
ISSN 0009-4293
www. chimia.ch

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Natural Born Catalysts: Photocatalytic Water Oxidation by Molecular Metal Oxides

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The oxygen-evolving complex of photosystem II (PSII-OEC) in green plants, algae and cyanobacteria, is the unique catalytic site where, upon illumination, H_2O bonds are oxidized to form O_2. The natural OEC is a tetramanganese-calcium-oxo cluster (Mn_4O_5Ca), harbored within the PSII complex, with a flexible and adaptive coordination environment provided by the protein residues. In particular, carboxylate ligands play a major role in the assembly of the OEC cluster, bridging Mn ions and the Ca^{2+} hetero-site. In order to mimic the PSII-OEC structure and activity, special attention has been dedicated to tetra-nuclear metal catalysts, including also Mn-based complexes. However, only few ruthenium or cobalt tetra-metallic cores have been recognized as competent oxygen evolving catalysts under photocatalytic conditions.We focus herein on a unique tetra-manganese core stabilized by a hybrid set of ligands, including an all-inorganic tungstosilicate platform and three acetate bridges. The resulting polyanion, $[Mn^{III}{}_3Mn^{IV}O_3(CH_3COO)_3(A\text{-}\alpha\text{-}SiW_9O_{34})]^{6-}$ (**Mn₄POM**), displays striking similarities with the natural OEC in its S_0 state, *vis-à-vis* the Mn_4-oxo structure and its Mn^{III}/Mn^{IV} mixed-valency. Our results confirm that **Mn_4POM** undergoes fast and multiple electron transfers under visible light irradiation, leading to water photo-oxidation and oxygen evolution. The structural analogy with the natural photosynthetic catalyst is thus nicely complemented by a unique functional behavior, which follows a bio-inspired mechanism.[1-5]

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High Oxidation State N-Heterocyclic Carbene Molybdenum Alkylidene Complexes: Functional Group-Tolerant Olefin Metathesis Catalysts

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[1]University of Stuttgart

What is still a challenging task in olefin metathesis is a single site catalyst, which is highly active, both in terms of turn-over number (TON) and turn-over frequency (TOF), which is tolerant to water, air and number of functional groups with high stereo- and region-selectivity. In search for olefin-active metathesis catalysts based on a cheap metals and fulfill all the above mentioned criteria, the first N-heterocyclic carbene (NHC) complexes of *Schrock* molybdenum imido alkylidene bis(triflate) complexes have been synthesized. Unlike existing bis(triflate) complexes, the novel 5-fold coordinated 16-electron Mo-complexes contain two carbenes, *i.e.* a *Schrock* carbene and an NHC. Single crystal X-ray analysis revealed that the above mentioned complexes are distorted square pyramidal (SP) with one triflate (OTf) ligand *trans* to the NHC. In course of a metathesis reaction, this triflate leaves the complex and generates a trigonal bipyramidal cationic 14-electron Mo-NHC complex (^{19}F-NMR studies). The most important observation of this type of catalysts is active in ring-closing metathesis (RCM), cross-metathesis (CM), the cyclopolymerisation of α,ω-diynes and ring-opening metathesis polymerisation (ROMP). Monomers containing functional groups, *e.g., sec*-amine, hydroxy, and carboxylic acid moieties, which are not tolerated by the existing variations of *Schrock* catalysts, can be used. This novel class of catalysts displays substantial activity even at high temperatures (140 °C), *e.g.,* in RCM. Based on the observation that bistriflate complexes show a coalescence temperature for the two triflate groups, an activation mechanism based on a Berry-type pseudorotation, i.e. interconversion between trigonal biyramidal (TBP) configurations through a square planar (SP), is proposed. Activation of the catalysts through the release of one triflate in the SP configuration is in full accordance with the observed reactivity of both neutral and cationic Mo-imido alkylidene NHC complexes and with ^{19}F-NMR. Furthermore, reactions of the bis(triflate) NHC complexes with one equivalent of a fluorinated alkoxide(*e.g.,* $-OCH(CF_3)_2$, $-OC_6F_5$, $-OCCH_3(CF_3)_2$) or with $Ag^+B[3,5-(CF_3)_2C_6H_3]_4^-$ in dichloroethane afforded the corresponding monoalkoxide and the cationic imido alkylidene-NHC complexes. This particular feature is the presence of the NHC ligand, which delocalizes the cationic charge and stabilizes the molybdenum center. The structures of all compounds have been determined by single crystal X-ray diffraction and their reactivities in various olefin metathesis reactions have been explored. In selected metathesis reactions, TONs up to 545,000 have been reached. Nonetheless, Mo-imido alkylidene NHC complexes with one electron-withdrawing fluorinated alkoxide and the corresponding cationic complexes in which the remaining triflate replaced by $B[3,5-(CF_3)_2C_6H_3]_4^-$afforded remarkably active and functional-group tolerant metathesis catalysts. Employing different NHCs such as triazole-2-ylidene, benzimidazolylidene and CAAC (Cyclic Alkyl Amino Carbene) provides access to another novel class of Mo-NHC alkylidene complexes. It turned out that the Mo-imido alkylidene NHC complexes prepared very recently display a functional group tolerance that is unprecedented for high-oxidation state Mo-imido alkylidenes. These catalysts therefore hold great promise in both organic and polymer chemistry, where they allow for the use of protic monomers.

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Silver(I) N-heterocyclic complexes for C-C bond activation of alkylnitriles and catalytic application in oxazoline synthesis

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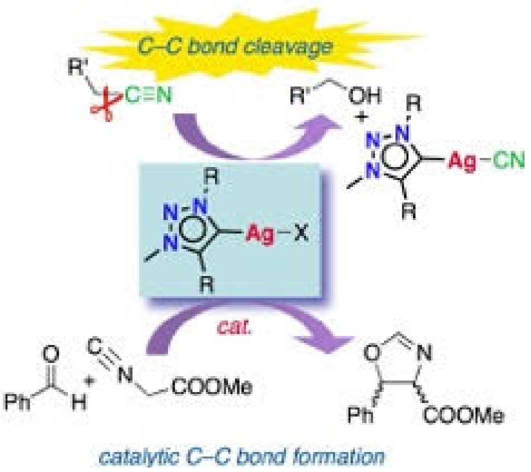
[1]University of Bern, [2]University College Dublin

N-heterocyclic carbenes (NHCs) have become increasingly prevalent ligands in the fields of organometallic chemistry and homogeneous catalysis [1]. A convenient route to form NHC transition metal complexes is the *in situ* generation of an Ag–NHC complex from reaction of azolium salts with Ag_2O, followed by transmetallation with a different metal [2]. However, to date little attention has been paid to the Ag–NHC intermediates regarding complex formation and potential catalytic applications [3].

We show that generation of Ag–NHC complexes from azolium salts in refluxing CH_3CN results in a selective C–C bond cleavage and the formation of [(NHC)Ag(CN)] complexes. This bond activation can also be extended to other alkyl nitrile reagents [4].

Furthermore, we will demonstrate the catalytic properties of a series of Ag–NHC complexes in oxazoline formation *via* aldol condensation. These highly active systems disclose new possibilities for applications of easily accessible silver carbene complexes.



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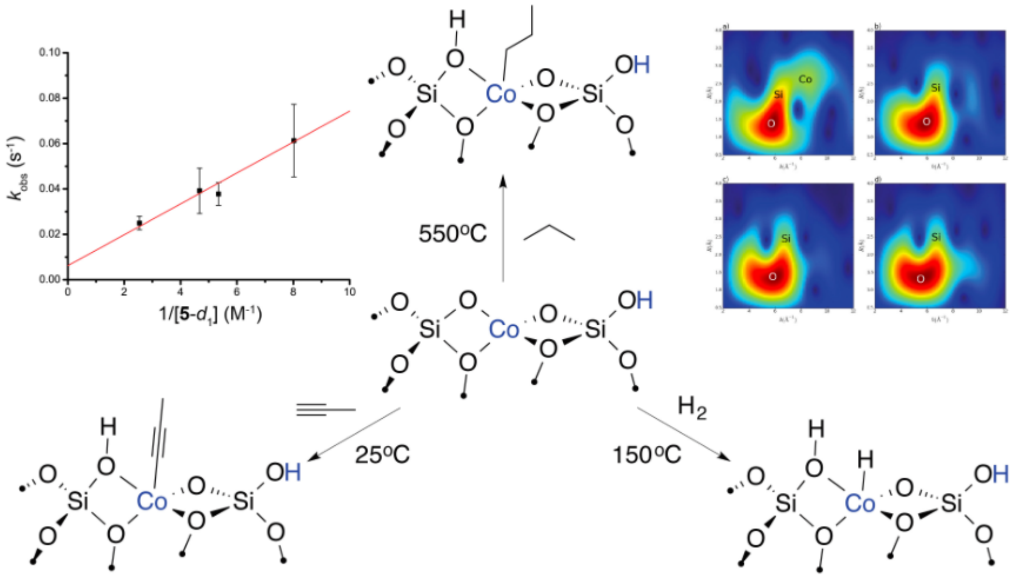
C-H Activations Catalyzed by Transition-Metal Ions Isolated on Metal Oxide Surfaces

D. P. Estes[1], G. Siddiqui[1], F. Allouche[1], K. V. Kovtunov[2], O. V. Safonova[3], A. Trigub[4], I. V. Koptyug[2], C. Copéret[1]

[1]ETH Zurich, [2]International Tomography Center, Novosibirsk, Russia, [3]Paul Scherrer Institute, Villigen, [4]National Research Centre “Kurchatov Institute

Transition metal ions supported on metal oxides have been shown to catalyze the conversion of hydrocarbons (e.g dehydrogenation of alkanes, alkane homologations). These reactions have to involve a C-H bond activation step, However, the mechanism of these transformations is still not well understood. Combining surface organometallic chemistry and thermolytic molecular precursor approaches, we have prepared isolated metal ions on silica surfaces (e.g. Fe, Co), which display good activity in the dehydrogenation of propane. Using these molecularly defined surface sites, we have performed detailed mechanistic investigations of this reaction as well as related reactions (propene hydrogenation (the reverse process) and alkyne trimerization. All data (kinetic measurements, isotopic labeling studies, kinetic isotope effects, and comparison with molecular analogues) are consistent with a C-H bond activation mechanism involving 1,2 addition across a M-O bond.



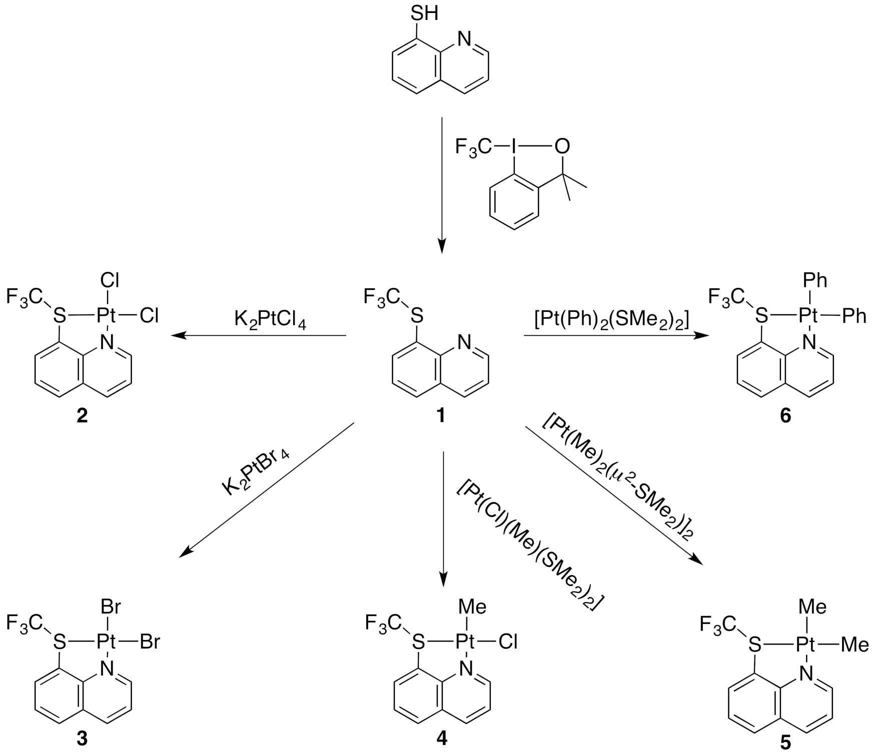
Exploring Trifluoromethylthioethers as ligands - Platinum(II) complexes of 8-(trifluoromethylthio)quinoline

C. P. Rosenau[1], F. Brüning[1], A. Togni[1]*

[1]ETH Zürich

To date, metal complexes with trifluoromethylthioether ligands ($RSCF_3$) are not well studied, due to the limited availability of synthetic methods in the past and the prominence of group 15 ligands.[1-3] Alkyl-, aryl- and perfluoroarylthioether ligands however are well known and have catalytic applications.[4-5]

To explore the properties of $RSCF_3$ ligands the N,S-bidentate ligand 8-(trifluoromethylthio)quinoline (**1**) was synthesized by electrophilic trifluoromethylation of 8-thioquinoline. Ligand **1** was reacted with platinum(II) precursors K_2PtCl_4, K_2PtBr_4, cis-$[Pt(Cl)(Me)(SMe_2)_2]$, $[Pt(Me)_2(\mu^2\text{-}SMe_2)]_2$ and cis-$[Pt(Ph)_2(SMe_2)_2]$ to form the corresponding complexes.



Complexes **2**-**6** were obtained in high yield, are air- and moisture-stable and soluble in most organic solvents with exception of strongly coordinating solvents such as MeCN and DMSO, which decoordinate the ligand.

Complexes **2**-**6** were characterized by elemental analysis, X-ray and ^1H, ^{13}C, ^{19}F, ^{195}Pt NMR spectroscopy and compared to their alkyl ($RSCH_3$) analogues and their reactivity investigated.

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D-Glucose-Platinum(II) Conjugates for Targeted Delivery of Platinum to Cancer Cells

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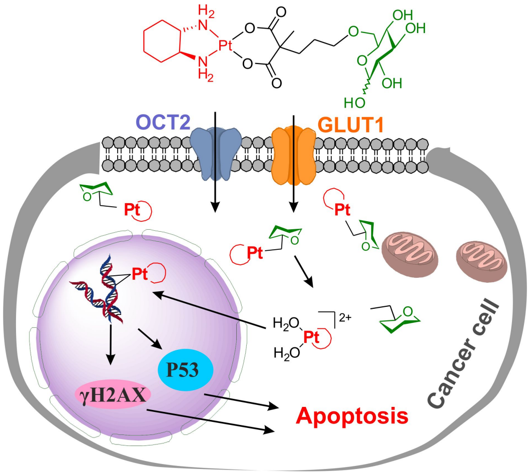
The three FDA approved platinum anticancer drugs, cisplatin, carboplatin and oxaliplatin, are widely used in the clinic to treat various forms cancer including testicular, ovarian, cervical, head and neck, non-small-cell lung, and colorectal cancer.[1] Despite their phenomenal clinical success, however, the undesired side effects such as nephrotoxicity, myelosuppression, peripheral neuropathy, ototoxicity, and nausea[1b,2] are main drawbacks of platinum-based chemotherapy.[1b,2] The side effectes can in principle be mitigated by introducing tumor-targeting properties into platinum anticancer compounds, thereby reducing nonspecific platinum accumulation in healthy tissues. Glucose transporter GLUT1 is overexpressed in many human cancers and its expression levels in tumor biopsy samples correlate well with poor prognosis.[3] Attachment of D-glucose to platinum anticancer compounds to target delivery to cancer cells has therefore been an attractive strategy for selective killing of the tumor over healthy tissue.[4] The design, synthesis, in vitro anticancer activity, in-depth characterization of the cellular uptake mechanism and the subcellular target of D-glucose-platinum(II) conjugates will be presented in this research seminar.[5] This work was supported by a grant from the US National Cancer Institute.



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Red-light activated photoCORMs of Mn(I) species bearing symmetric substituted 2,2'-azopyridines.

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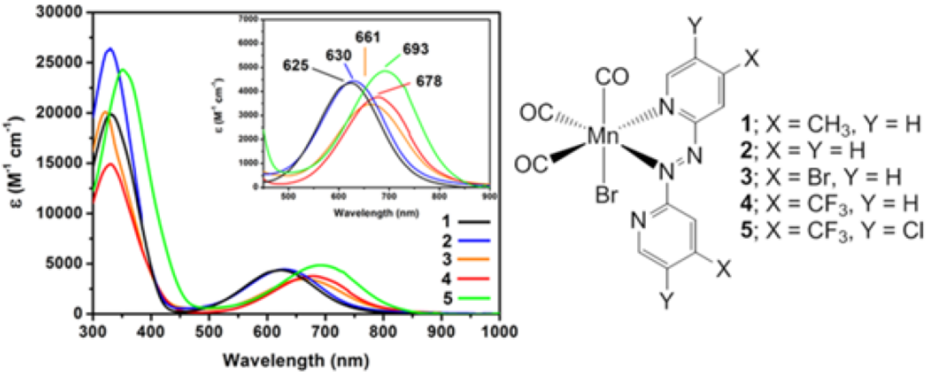
Carbon monoxide (CO) has been acknowledged as a fundamental neurotransmitter in humans and there is a growing interest in its pharmacological or medical applications. As nitric oxide and hydrogen sulfide, CO is endogenously produced in animals. These neurotransmitters are involved in several cellular, physiological and pathological pathways, such as vasodilatation, endothelial injuries, inflammation. Organometallic carbonyl complexes are best suited to play the role of CO carriers. Targeting of the molecules to local injuries can thus be achieved by modifying the coordination sphere of the metal ion via a proper selection of ligands or by appending CO releasing molecules (CORMs) to biomolecules. Manganese–based CORMs, for example, are activated by exposure to UV-light and are known as photoCORMs[1].

One of the great challenges in the design of photoCORMs lies in their sensitivity to visible light. Most of known photoCORMs have suffered from this fundamental drawback with few exceptions. In particular the group of Mascharak[2] has endeavored to develop rational strategies to visible light-activated CORMs and has introduced a series of carbonyl Mn(I) complexes with conjugated ligands of the 2-pyridyl-N-(2-methylthiophenyl) methylenimine and 2-phenylazopyrdine type which show MLCT bands with maxima at ca. 585 nm. These molecules represent probably the most significant improvement the field has seen in the recent years.

In this work, we report the synthesis, characterization and photochemical behaviour of the above mentioned complexes. The systematic substitution of the 2,2'-azopyridine with weak donating to strong deactivating substituents (EWG) lead to the progressive bathochromic shift of the MLCT absorption band maximum from 625 nm to 693 nm (Fig. 1). Exposure of solutions of complexes 1-5 to low-power visible light (≥ 625 nm, red light) resulted in CO photorelease as evidenced by the myoglobin assay. Furthermore, the MLCT band of complexes with strong EWG tails beyond the visible region of the spectrum in the near infrared and in one case photodecomposition could also be promoted at 810 nm.



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Not so similar after all. Fundamental differences in reactivity of fac-[M(solvent)$_3$(CO)$_3$]+ (M = Re, ^{99}Tc) with CO

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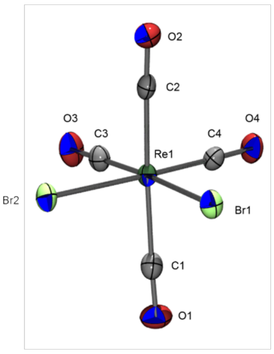
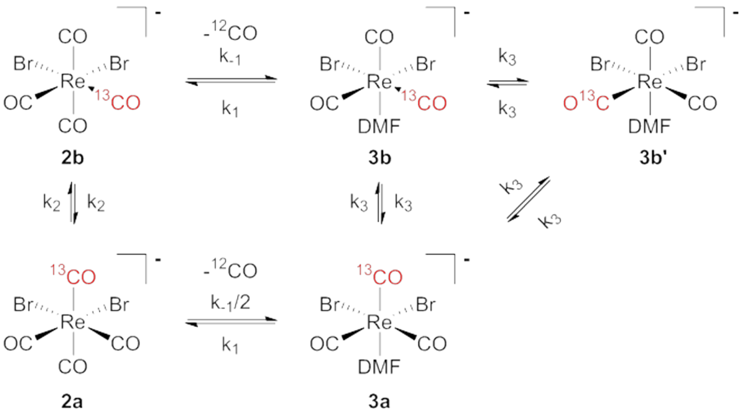
In the context of theranostics, the *fac*-[M(CO)$_3$]$^+$ (M = Re, Tc) core has proven promising due to its high kinetic stability and the relative ease of ligand exchange on the three non-CO coordination sites.[1] The substitution kinetics of these three labile sites have been studied extensively in the past. On the other hand, the exchange of carbonyl ligands has only been investigated very sparingly, most prominently in the complex *fac*-[^{99}Tc(CO)$_3$(H$_2$O)$_3$]$^+$.[2] To the best of our knowledge, no comparable studies have been performed with rhenium. To determine the ideal reaction conditions for the synthesis of radiopharmaceuticals it is imperative to understand in-depth the behavior of both the rhenium and technetium starting materials. We have conducted a systematic study of the self-exchange kinetics of the carbonyl ligands in [ReBr$_3$(CO)$_3$]$^{2-}$ and its respective solvato complexes. We present a complete mechanism for the self-exchange of the CO ligands based on both experimental and computational considerations. The stable intermediate complex [ReBr$_2$(CO)$_4$]$^-$ was isolated and fully characterized. Surprisingly, for ^{99}Tc a fundamentally different behavior was observed under comparable conditions. A dissociative-interchange mechanism for its formation is proposed based on the kinetic data.





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Controlling architecture of coordination cages via the aspect ratio of the ligands

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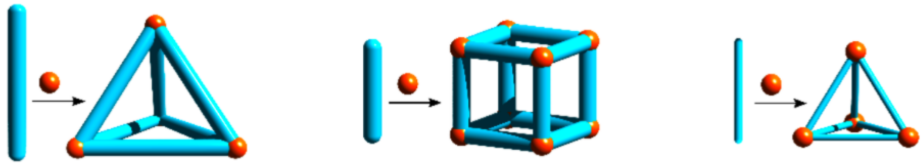
It is possible to control the geometry and the composition of metallasupramolecular assemblies via the aspect ratio of their ligands. This point is demonstrated for a series of iron- and palladium-based coordination cages. Functionalized clathrochelate complexes with variable aspect ratios were used as rod-like metalloligands. A cubic $Fe^{II}_8L_{12}$ cage was obtained from a metalloligand with an intermediate aspect ratio. By increasing the length or by decreasing the width of the ligand, the self-assembly process resulted in the clean formation of tetrahedral $Fe^{II}_4L_6$ cages instead of cubic cages.



J. Am. Chem. Soc., 2016, 138 (6), pp 2046–2054

Design Approaches to Blue and White Light Emitting Gold(III) Complexes

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During the past decennaries, transition metal complexes exhibiting interesting luminescent properties have been extensively investigated for applications in phosphorescent organic light emitting devices (PHOLEDs).[1] Organogold(III) complexes have been gaining increasing attention due to their promising emission properties.[2] The main problem being faced at the current time is the production of high-quality blue-emitting OLEDs. Three challenges emerge concerning the development of efficient blue triplet emitters. Poor chromaticity, low quantum efficieny and the short working lifetime. Recently, our group has demonstrated stable complexes based on monocyclometalated gold(III) framework displaying emission properties that rival the isoelectronic platinum(II) complexes.[3] Utilizing a rational design approach, we have been able to render gold(III) complexes with blue and white light emission properties that has been previously unprecedented.[4] These complexes have been investigated by detailed computational and photophysical studies and selected complexes by fabrication of devices. The tailored novel luminescent properties open-up further possibilities of applications of gold(III) complexes in light-emitting devices.

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Anthracene-based ligands for new luminescent coordination polymers

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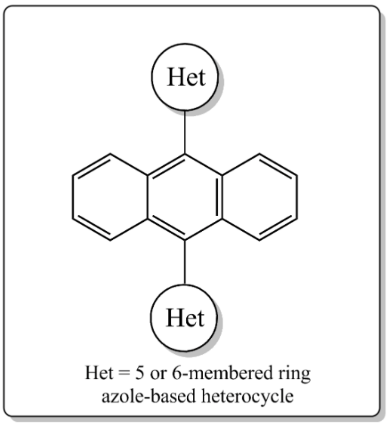
The design and synthesis of luminescent metal−organic complexes, polymers, and supramolecular frameworks are gaining interest as they find applications in molecular sensing, tunable emission for various light emitting devices (LEDs), and multiphoton upconversion devices [1, 2].

For numerous azole-based heterocyclic ligands it was shown that they can form a large panoply of building blocks which can be rigid or flexible [3]. As functional group, azole-based heterocycles have also potential in the design of new anthracene-based ligands. Anthracene derivatives with different azole-based heterocycles still have to be studied and explored.

The anthracene moiety is highly emissive in the UV-Vis region and involving this fragment into coordination polymers (CPs) can enhance the luminescent properties of the resulting materials [4]. Moreover, studying the crystal packing of the CPs with anthracene moieties will allow us to understand how different π-π stacking arrangements in the solid state influence the luminescent behavior of the compounds which are obtained. Furthermore, packing interactions between the anthracene fragment and the attached heterocycles will allow tuning the final luminescence properties. We will thus learn, using crystal engineering, which parameters bring significant influence on monomeric or dimeric emission inside of the solid CPs.

In this work we are going to present different bifunctional anthracene ligands which were designed for obtaining CPs with high potential for luminescent properties (Scheme 1). CPs of Cd(II) and Zn(II) will be presented. The studies of their luminescent properties are currently ongoing.



Scheme 1. Azole-based biheterocycle antracene ligands.

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Beyond size effects: composition-tunable properties for quaternary Cu-Zn-In-Se quantum dots

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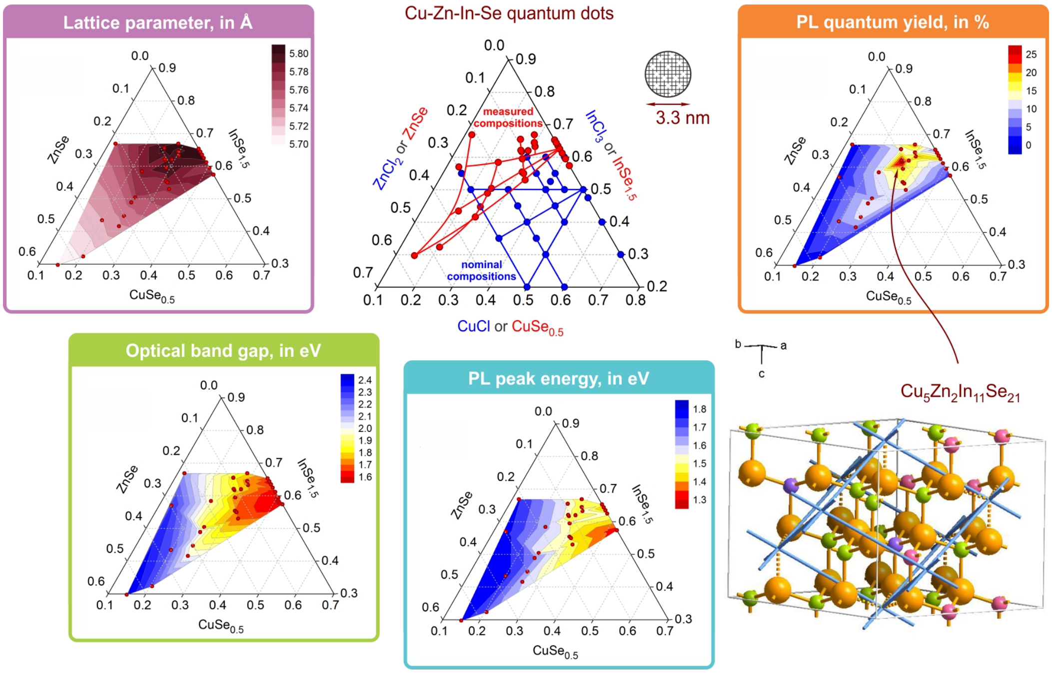
For multicomponent quantum dots (QDs), composition-dependent tuning of properties is superimposed on quantum confinement effects stemming for QD size. I-II-III-VI group semiconductor QDs represent excellent playground with broad miscibility ranges for binary chalcogenides and relatively large Bohr exciton radii, enabling size-dependent properties for QDs ‹ 5 nm. In addition, certain compositions allow cationic defects to order within the lattice (*i.e.*, ordered defect compounds, ODCs).

Here we present our investigation of the composition-dependent properties of quaternary Cu-Zn-In-Se (CZISe) colloidal quantum dots. [1] We employ an amide-promoted synthesis, which can provide independent composition and size control for multicomponent chalcogenides. [2] Applying same reaction conditions, and varying the amount of introduced metal salts, we are able to vary the composition of CZISe QDs over a broad range while keeping QD size similar (D_{QD} = 3.3 nm, see Figure). This allows us to map several optical and structural properties as a function of CZISe QD composition, such as lattice constant, optical band gap, PL peak position, or PL quantum yield (see Figure). We find that the PL quantum yield peaks at a composition close to $Cu_5Zn_2In_{11}Se_{21}$. Experimental and theoretical work suggests that the high PL efficiency of this composition originates from the fact that it belongs to a family of ODC structures with parent ternary composition of $Cu_2In_4Se_7$ and $^1/_7$ concentration of atomic vacancies on cation site. These results can guide the development of high PL quantum yield materials.



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