CHIMIA

CHIMIA 2018, Volume 72
ISSN 0009-4293
www. chimia.ch
Supplementa to Issue 7-8/2018

SCS
Swiss Chemical
Society

SCS Fall Meeting 2018
Poster Abstracts

Session of Inorganic & Coordination Chemistry

September 7, 2018
École Polytechnique Fédérale de Lausanne (EPFL)
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New arene ruthenium metalla-assemblies for the transport of $^1O_2$ to treat hypoxic cancer

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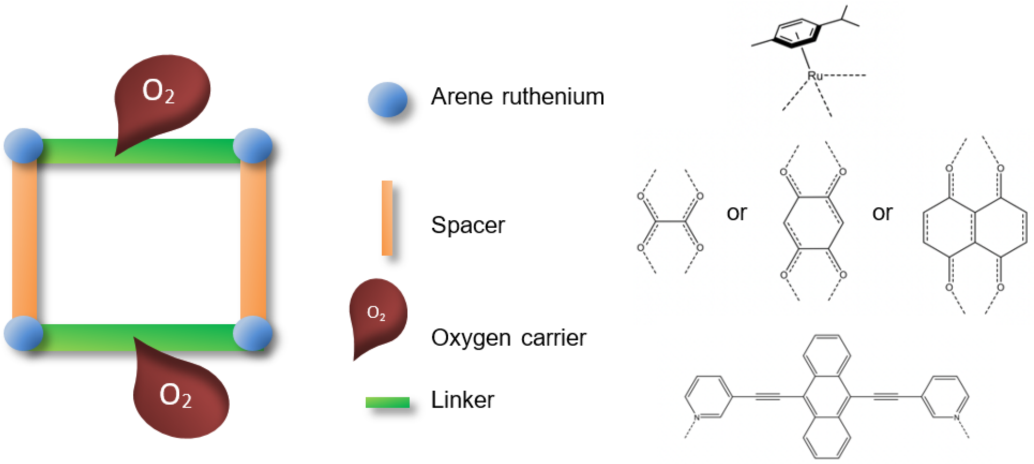
Oxygen is one of the key elements of photodynamic therapy (PDT), an emerging and promising treatment for cancers and other diseases, which involves the production of ROS by a photosensitizer upon light activation. PDT is expected to treat inoperable tumors, thanks to its high specificity and its non-invasive use. [1,2,3] Unfortunately, human solid cancers show hypoxic regions (with a critic oxygen concentration), which limits the use of PDT.[4] Arene ruthenium metalla-assemblies can be an answer to that issue.[5,6] In fact, it can potentially bring oxygen to tumors, thanks to anthracene moieties attached to them. In fact, anthracene is known for transporting oxygen through its endoperoxide form.[7,8] Therefore, we describe here the synthesis and characterization of three arene ruthenium metalla-assemblies containing 9,10-bis(3,3'-ethynylpyridyl)anthracene and show their potential as oxygen carriers.



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Carbon etching chemistry for the generation of nanopores in single-layer graphene for gas-sieving

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The single-layer graphene is the thinnest molecular barrier, impermeable to the smallest of molecules and ions.[1] To apply graphene as an ultrahigh-flux, molecular-sieving membrane, an idea that has fascinated many in the last decade, one needs to etch molecular-sized pores in graphene.[2] For separation of gases (for example, H_2 from CH_4), this entails a controlled etching of the graphene lattice such that the resulting pore-size is between 0.30 to 0.38 nm, and such that percentage of pores larger than 0.38 nm is less than a few ppm to obtain a reasonably high selectivity. In terms of the number of carbon atoms, this corresponds to removing 10 to 13 carbon atoms from the lattice.[3] As of now, there is no established chemistry that can achieve this. The state-of-the-art nanofabrication techniques are restricted to the resolution of 1 nm. Etching lattice using high-energy electron and ion-beam is neither scalable nor easy to implement or control. In this light, development of a controlled carbon etching chemistry, providing control on the pore-expansion rate in the range of 0.1-0.3 nm/s is highly promising. Such chemistry can pave the way to controlled etching of the lattice such that one can etch out pores with the resolution of 0.1 nm. Herein, we report a synergistic pore-generation and expansion/contraction strategy by utilizing oxygen plasma and ozone etching/functionalization which allows us to form pores with etching rates of 0.03 – 0.3 nm/s.

The porosity and pore size distribution were characterized and correlated with the gas transport properties (flux and gas pair selectivity) to understand the pore nucleation and expansion process.[4] With a short O_2 plasma exposure time, a low-density of vacancy as well as sp^3-defects (epoxy and carbonyl groups) were generated in the graphene lattice. Subsequently, by exposing the plasma-treated lattice to ozone, the sp^3-type defects were converted into vacancy defects, without expanding the pre-existing vacancy-defects. The resulting porous lattice yielded a remarkably enhanced gas permeance (2.05×10^{-6} mol m^{-2} s^{-1} Pa^{-1}) with an attractive H_2/CH_4 selectivity (15.6). This is one of the best performance among the reported gas separation membranes (**Figure 1).**

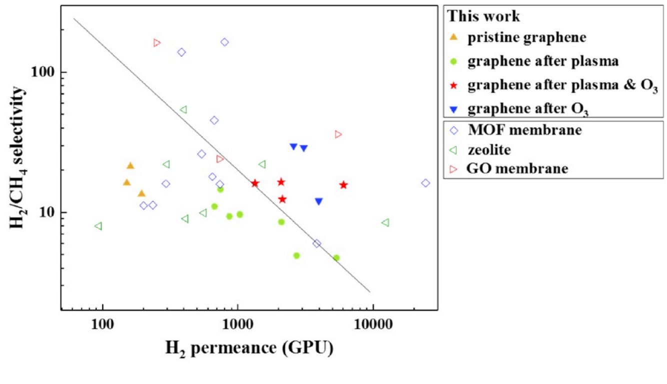

Figure 1. Comparison of graphene membranes in this work with other membranes (metal-organic frameworks (MOF), zeolite and graphene-oxide (GO) membranes) in literatures in terms of the H_2/CH_4 separation performance (the black line is the polymer upper bond assuming 1-µm-thick skin layer).

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Cu(I) Photoredox Catalyzed Trifluoromethylation Reactions

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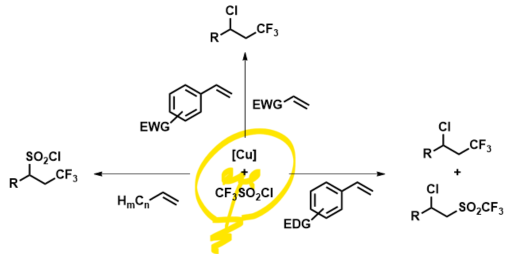
Interest in inexpensive and sustainable catalysts incentivizes the development of Cu-based photoredox catalysts. To date, only few Cu-based photoredox catalysts have been applied. Most of them consisting of one or two 1,10-phenanthroline based ligands. We have designed a new 4,6-disubstituted-2,2'-bipyridine ligand and synthesized and characterized two heteroleptic [Cu(N^N)(P^P)][PF_6] complexes (N^N = substituted 2,2'-bipyridine, P^P = bisphosphine ligand). They exhibit longer excited state lifetimes and higher Cu(I)/Cu(II) redox potentials compared to the standard [Cu(dap)$_2$]Cl photoredox catalyst. The complex with Xantphos as bisphosphine ligand is an efficient catalyst for chloro-trifluoromethylation, -trifluorosulfonation and trifluorochlorosulfonation reactions of alkenes. Especially styrenes were reactive, which had been elusive substrates for previously reported photoredox catalyzed trifluoromethylation reactions.[1,2] This method provides an easy way to introduce trifluoromethyl group into organic molecules under mild conditions.



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In-situ neutron diffraction study of carbon dioxide adsorption on M-BTT frameworks, a series of highly crystalline MOFs

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Metal Organic Frameworks (MOFs) are a class of porous materials that have shown record-breaking surface areas (up to 7000 m^2/gr),[1] allowing them to adsorb significant amounts of different gases like carbon dioxide. Considering the large number of potential MOFs that can be accessed, determining the relationship between their structural features and corresponding carbon dioxide adsorption properties is of utmost importance. In this regard, in-situ characterization can be advantageous. MOFs have a nonhomogeneous van der Waals potential energy landscape that dictates how incoming guest molecules arrange themselves on the internal framework surface.[2] This makes diffraction the most direct way to probe static site-specific binding properties. In this report a comprehensive study of the CO_2 adsorption in several of the metal-substituted M-BTT analogs is carried out. *In-situ* neutron diffraction studies reveal for the first time, a molecular level view of CO_2 adsorption in this framework family and allow rationalization of the observed CO_2 adsorption isotherms. The experimental results have further been compared with those obtained from DFT simulations and show excellent agreement in all cases regarding CO_2 binding geometries and isosteric heats of CO_2 adsorption. Combining synthesis, characterization, and computation, can render unique insight into CO_2 adsorption processes that will hopefully provide an accelerated search for materials with optimal properties for energetically relevant gas separations.

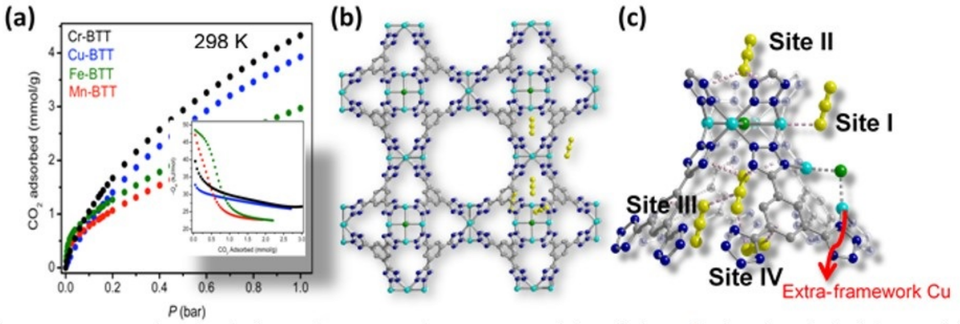

Figure 1- (a) CO_2 adsorption isotherms for M-BTT series at 298 K and isosteric heat of adsorption obtained from variable temperature adsorption data based on Clasius-Clapeyron equation. (b) The schematic figure of M-BTT frameworks with CO_2 adsorption positions. (c) The location of preferential CO_2 adsorption sites in the framework detected by in-situ neutron diffraction.

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Dinitrogen reduction and functionalization by uranium multimetallic complexes.

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The reduction of dinitrogen (N_2) and its transformation into ammonia (NH_3) or fine N-containing chemicals is a very difficult and important challenge in modern chemistry. The only industrial process so far that uses dinitrogen as a feedstock is the Haber-Bosch process to produce ammonia, required in the production of fertilizers, but requires harsh conditions and a metal catalysis, also consuming 2% of the world's annual energy supply. The conversion of N_2 into N-containing organic molecules would also be a sustainable alternative of the Haber-Bosch process. Very recently in our group the first example of a four-electron reduction of dinitrogen performed by a U complex has been reported[1]. In this work, a multimetallic uranium nitride complex performs the reduction and the reduced dinitrogen could be functionalized or converted into ammonia. Here we will present mutimetallic complexes of low valent uranium able to perform the four-electron reduction of dinitrogen. We will also describe how the nature of the bridging ligand affect the reactivity of the reduced dinitrogen.

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Bridging the Gap: crosslinking allosteric sites on the nucleosome

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As the repeating units of chromatin, nucleosomes represent key epigenetic targets. The nucleosome core consists of 145-147 base pairs of DNA encircling an octamer of pairs of H2A, H2B, H3 and H4 histone proteins. An allosteric relationship between RAPTA-T, an anti-metastatic ruthenium(II) complex, and Auranofin, a gold(I) anti-rheumatic drug, is observed on nucleosome core particle (NCP). The binding of RAPTA-T to specific sites on the surface of the H2A-H2B dimer induces a kink in the long α-helix of the H2A histone protein enabling Auranofin to bind to two previously inaccessible sites.[1],[2]

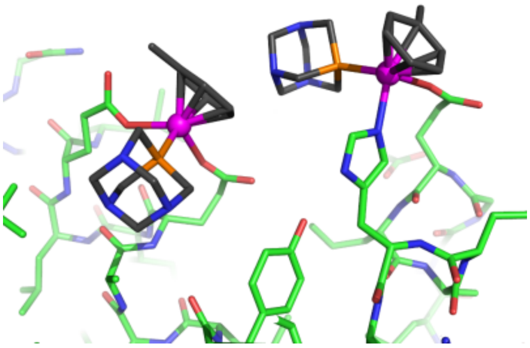

Figure 1. Binding sites of the RAPTA-T on the H2A-H2B dimer of the NCP.

This allosteric effect inspired the design, synthesis and evaluation of heterobimetallic ruthenium(II)-gold(I) complexes with the ability to simultaneously initiate the same conformational change as caused by the binding of mononuclear RAPTA-T and simultaneously bind with the corresponding Auranofin site. Further crosslinking of binding sites on the nucleosome has been explored with the development of other heterobimetallic complexes and gold(I)-peptide conjugates.

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A catalytic CO_2 scrubber that generates cyclic carbonates from simple epoxide:ionic liquid mixtures.

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Common CO_2-scrubbers consist of amine solvents or other basic species such as inorganic hydroxides and rely on an absorption-desorption process.[1] Hence, they can be used as a means to obtain pure CO_2. On the other hand, cyclic carbonates are industrially relevant compounds (used as solvents, electrolytes, etc.) that are routinely prepared from the coupling between epoxides and pure, pressurized CO_2.[2-3] We have combined both approaches and designed a catalytic CO_2-scrubber that directly incorporates the CO_2 contained in various gas streams including air to generate cyclic carbonates. Our results show that up to 100 % of the CO_2 contained in waste gas streams can be extracted, and hence our IL:epoxide mixture may serve as a cost-effective biogas upgrader.

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Phosphane tuning for [Cu(N^N)(P^P)][PF_6] complexes in Light Emitting Electrochemical Cells

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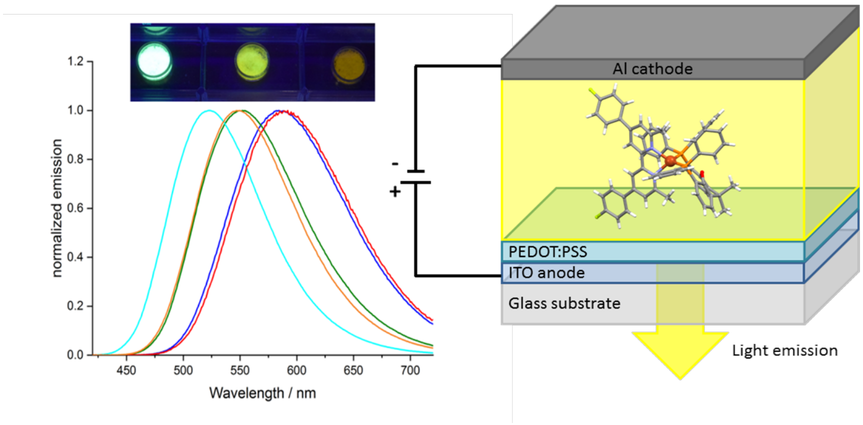
Light emitting electrochemical cells (LECs) are of growing importance in the field of flexible electronics and large surface lighting. Their simple device architecture and the use of air stable materials make them fundamentally suitable for large area lighting as well as display applications. The emissive layer can be easily deposited by solution based methods such as spin coating, which makes the fabrication of a LEC fairly simple and less complex than the fabrication of e.g. an OLED (organic light emitting diode). In the past iridium based transition metal complexes have been widely used in LECs but the low abundance and high cost of this rare metal demands the development of alternative materials for LEC applications.[1]

Heteroleptic copper complexes of the type [Cu(N^N)(P^P)][PF_6] where N^N is a chelating diimine and P^P is a chelating diphosphine ligand show good photo- and electroluminescence properties. Careful adjustment of the steric and electronic properties of the ligands leads to colour variations as well as enhanced device performance.[2] In this work a series of new heteroleptic copper complexes is presented in which the phosphane ligand is tuned sterically and electronically to alter the emissive properties of the compound as well as the device functionality and lifetime.



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Towards One-Photon Two-Electron Processes in Molecular Systems

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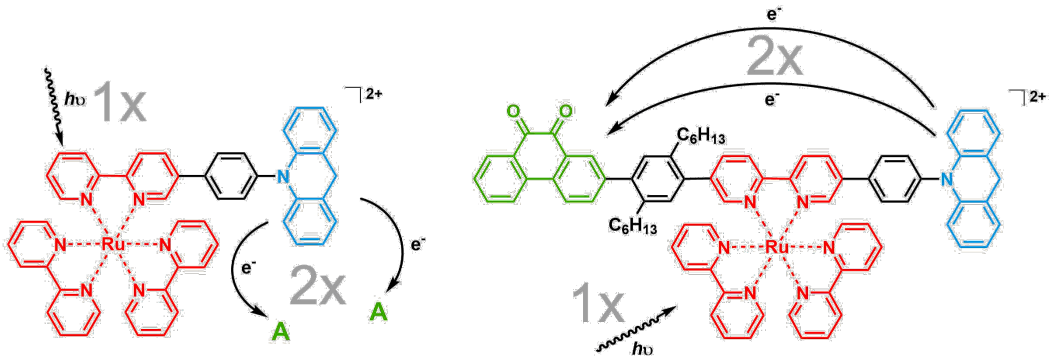
Light-driven accumulation of redox equivalents and multi-electron transfer is of key importance for artificial photosynthesis.[1,2] Usually multiple photons are required for such reactions. Here, acridan is investigated as a two-electron donor in order to accomplish the accumulation of two redox equivalents in a molecular system induced by the absorption of only a single photon. In combination with tris(bipyridine)ruthenium(II) acting as a photosensitizer and an acceptor, the first charge separated state is anticipated to generate the acridinyl radical. Being a stronger reductant than its parent species, a second, thermally-induced redox reaction is expected to occur between the acridinyl radical and the acceptor. The reducing power of the acridinyl radical is limited, hence suitable acceptors have to be found to accomplish the thermally-induced redox reaction.



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Catalytic activity and asymmetric induction of carbohydrate-functionalised transition metal–NHC systems

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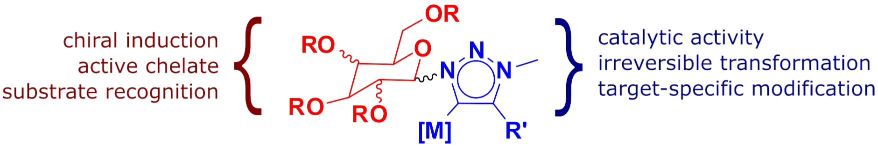
1,2,3-Triazolylidene NHC ligands have been demonstrated to have broad applications for materials science and biochemistry, but in particularly they show great promise as transition metal ligands in the field of homogeneous catalysis.[1] In order to advance these systems towards applications in asymmetric catalysis, functionalisation of mesionic donor ligands with optically pure wingtip groups is an attractive strategy. Carbohydrates represent a natural pool of chirality and functionality, offering a broad range of well-defined stereochemistry and water solubility. Introduction of these natural building-blocks into the structure of organometallic species offers the potential to investigate their interaction with biological systems. CuAAC click chemistry can be conveniently used to combine these two classes of molecule into hybrid systems, as illustrated schematically in Figure 1.



chiral induction
active chelate
substrate recognition

catalytic activity
irreversible transformation
target-specific modification

Figure 1. Carbohydrate-functionalised transition metal–NHC complexes

Only a handful of carbohydrate—NHC transition metal complexes have been investigated as catalysts,[2] although such decoration of phosphine and phosphinite ligands has been a promising avenue of research for asymmetric catalysis.[3] We present a series of new hybrid complexes and report their catalytic activity under mild conditions, with attention paid to the direct impact of the stereochemistry of the carbohydrate on the enantiomeric ratio of the products.

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The Importance of Subtle Steric Effects on Self-Assembled Coordination Cages

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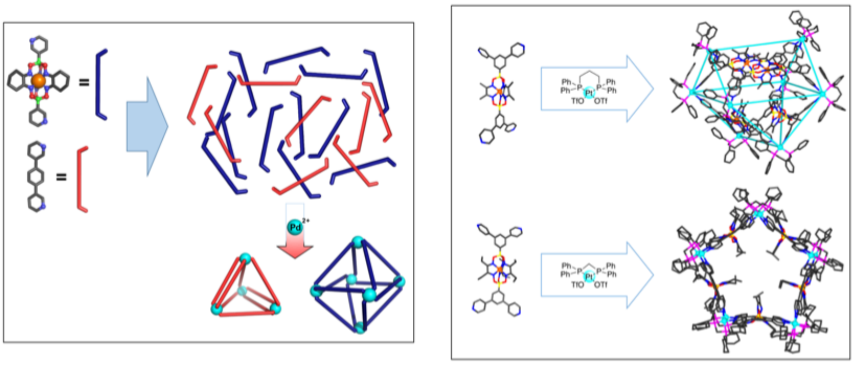
In recent years, different synthetic approaches have been developed, allowing for the efficient preparation of cages with diverse geometries and properties. The understanding of steric effects is a central point to the rational design of supramolecular assemblies. Clathrochelate-based metalloligands enable the role of the aspect-ratio of different building blocks to be explored. Moreover, the utilization of metalloligands instead of simple organic polypyridyl ligands results in the formation of uncommon structures; for example with ‘naked’ Pd^{II} ions, we observed octahedral complexes instead of tetrahedral ones (Figure 1 left).[1] However, *cis*-blocked Pt^{II} complexes combined with tetratopic metalloligands, gave cages with unusual geometries and we have started to futher explore the intricate structural chemistry of $M^{II}_{2n}L_n$-type assemblies (Fugure 1 right).[2,3] Our results provide further evidence that rather small structural modifications can have important effects on multicomponent self-assembly reactions. Ultimately, the control of such effects will enable chemists to predict and construct synthetic assemblies of unprecedented complexity and functionality.



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$(RO)_2W(O)(pyridine)_3$: Activity in Alkene Metathesis and Mode of Initiation

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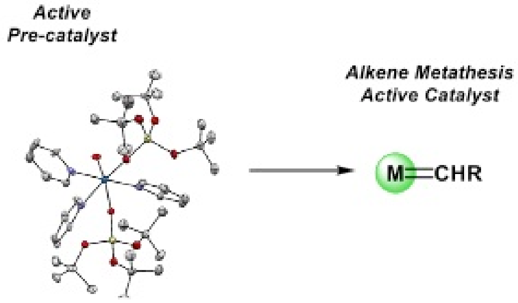
[1]ETH Zürich, [2]Ens de Lyon, [3]UCLA, [4]Paul Scherrer Institute

Supported MO_3/SiO_2 (M = Mo or W) are heterogeneous alkene metathesis catalysts used in industrial processes, but these catalysts usually require high activation temperatures. Recently, a new method of activating MO_3/SiO_2 using organosilicon reducing agents had been established. This method allows generating highly active metathesis catalysts at low temperature. Furthermore, this study supports that the active sites are generated in situ upon reaction of olefins with the reduced M(IV) centers.[1,2]

Here, we describe the syntheses of a new class of W(IV) complexes, which are active in metathesis with comparable activities with the homogeneous metathesis catalysts containing alkylidene ligands. Detailed experimental and computational studies provide molecular understanding on how to generate the required alkylidene ligand for metathesis in situ from W(IV) and also clues about how heterogeneous catalysts work.[3]



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A nanoporous two-dimensional silicate: synthesis and application in molecular-sieving

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Two-dimensional (2D) nanoporous materials are highly attractive for the synthesis of the next generation membranes. However, synthesis of such two-dimensional nanoporous sheets with a precise array of molecular hugging nanopores is not trivial. One of the leading approaches to synthesize 2D materials is the top-down synthesis. Herein, for the first time, we report a nm-thick, 2D silicate, RUB-15-nanosheet, consisting of atomically bridged arrays of 4- and 6-member silica rings, synthesized by exfoliation of layered RUB-15, a precursor to the sodalite zeolite.

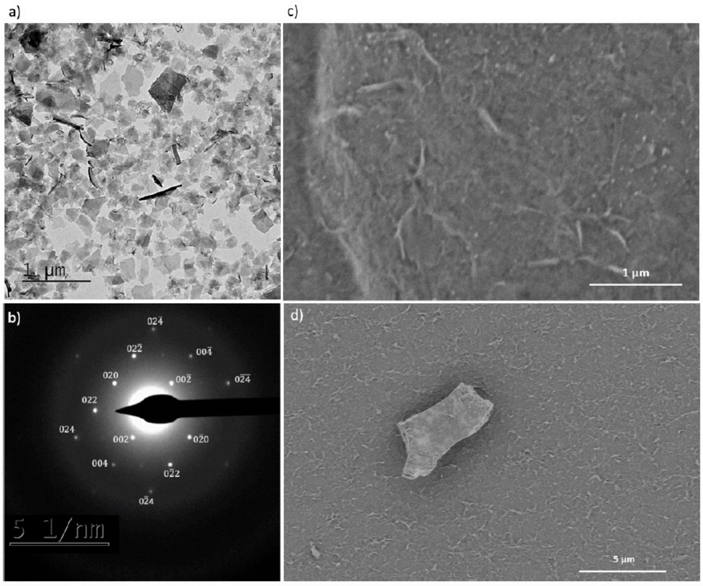

Figure 1. Processing of RUB-15 nanosheets into membranes for gas separation. 1a) TEM of exfoliated RUB-15 nanosheets. 1b) Electron diffraction of RUB-15 nanosheets. 1c) SEM of the packing of nanosheets using hot drop coating technique at 150 °C. 1d) SEM of the packing of nanosheets using Langmuir-Schaeffer deposition.

RUB-15 layers were synthesized by the hydrothermal synthesis route using a modified method [1-2]. The as-made material was confirmed to be RUB-15 using X-ray diffraction, ^{29}Si MAS NMR and ED. Ion-exchange of RUB-15 with a C_{16} cationic surfactant was performed in order to increase the interlayer spacing from 14.2 Å to 30 Å (Fig. 1a). Finally, exfoliation of the nanosheets was carried out by melt compounding technique (Fig. 1a) [3-4]. ED confirmed the crystallinity of exfoliated RUB-15 (Fig. 1b).Gas-separation preliminary results of RUB-15 membranes obtained by filtration of the nanosheets suspension on a porous support showed promising results: a H_2 permeance of about 2.0×10^{-6} mol m^{-2} s^{-1} Pa^{-1} and a H_2/CO_2 ideal selectivity of 7.4 were achieved. To exploit the high potential of nanosheets as molecular sieves, interstices between the nanosheets need to be minimized. We are currently working on enhancing the packing efficiency using the hot drop coating technique (Fig. 1c) [5]. Interaction between nanosheets based on drop casting results to be more effective than the simple filtration due to the restacking of nanosheets during the filtration. To further thin down the membrane thickness, we are using Langmuir-Schaeffer technique, which will drastically reduce the gases diffusion path, and, hence, results in an improved flux (Fig. 1d).

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Asymmetric Transfer Hydrogenation of Ketones: The Long-Standing Issue of the Base and its Solution

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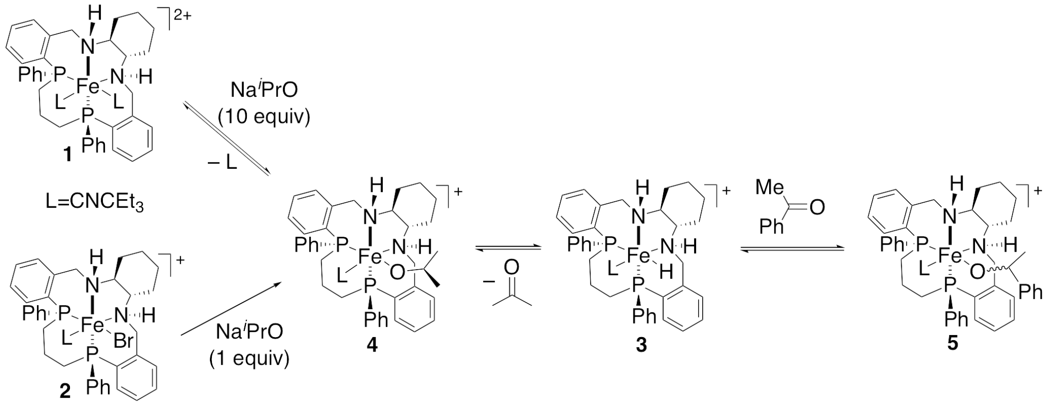
The overwhelming majority of catalysts for the asymmetric transfer hydrogenation (ATH) of ketones require base activation to form the catalytically active hydride, which reduces the carbonyl function in combination with a NH moiety present on the ligand via the Noyori's bifunctional mechanism [1]. Our group has developed the bis(isonitrile) complex $[Fe(CNR)_2(N_2P_2)]^{2+}$ (**1**) for the ATH of a broad scope of ketones with excellent enantioselectivity (up to 99% ee) upon activation with Na^{t}BuO (10 equiv). Recently, we reported the synthesis and characterization of $[FeBr(CNR)(N_2P_2)]^+$ (**2**) and $[FeH(CNR)(N_2P_2)]^+$ (**3**). Hydride **3** is active in ATH without the need of base activation and reduces acetophenone with the same activity and enantioselectivity as **1** [3] suggesting its direct involvement in the catalytic cycle. As herein reported, hydride **3** reacts with acetone and acetophenone to give the 2-propoxo and 1-phenylethanolato complexes **4** and **5**, respectively, which were characterized in solution by 1D and 2D NMR spectroscopy. These reactions confirm that hydride **2** is the active species of the catalytic cycle and show that the excess of base is needed to shift the equilibrium toward the hydride **3**.



Further intermediates of the catalytic cycle will be identified by DFT calculations.

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The Effect of Iron Binding on Pentavalent Uranyl(V) Stability.

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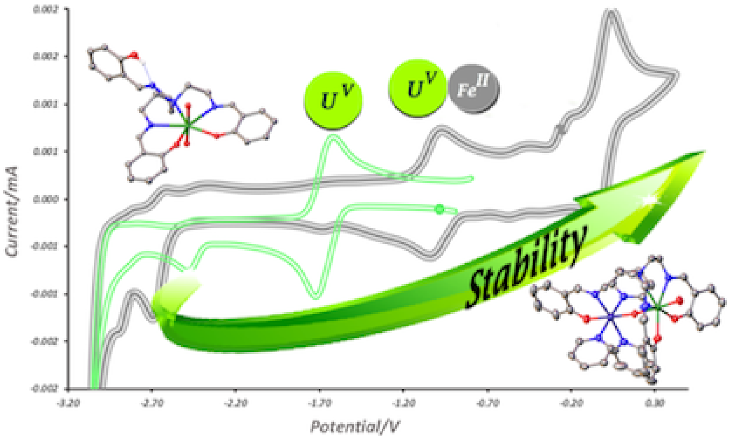
Pentavalent uranyl has been proposed as an important transient intermediate in the biological or abiotic mineral-mediated transformation of soluble uranyl(VI) compounds into the insoluble uranium(IV) dioxide (UO_2), a very important process for ground-water remediation. Recent studies indicate that U(V) species are incorporated in iron oxo-hydroxide minerals such as goethite and magnetite and the presence of iron as second nearest neighbour has been identified.[1] Several heteropolymetallic uranyl(V) complexes stable in organic solution have been isolated in recent years, with only few examples of a $UO_2^{+-----}Fe^{2+}$ interaction[2]. However, the role of iron binding to uranyl(V) species in their stabilization remains ambiguous in spite of its importance for the correct speciation of uranium in the environment.

Here we report the synthesis of stable complexes of pentavalent uranyl supported by the tripodal Schiff base ligand H_3trensal (2,2',2" -tris(salicylideneimino)triethylamine). The reactivity, chemical as well as redox stability of potassium complex [UO_2(trensal)K]K and the iron(II) heterometallic uranyl(V) complexes ([UO_2 (trensal)Fe(py)$_3$]; [UO_2(trensal)Fe(py)$_3$U(trensal)]I; [(UO_2(trensal)Fe(py)$_3$)$_2$Fe(py)$_3$]I_2) was investigated.This study demonstrated that Fe^{2+} stabilizes the U(V) toward proton induced disproportionation and redox reactions. Moreover, cation-cation interaction between the uranyl(V) oxygen and the Fe^{2+} is essential for the stabilization of U(V) while the presence of a Fe(II) bound through the ligand has no significant effect on the redox properties of the uranyl(V).



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Non-innocent behavior of pyridylideneamide (PYA) ligands

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Classically, ligands of homogeneous catalysts have a set of intrinsic and static electronic properties that stabilize the metal center and impart specific activity and selectivity.[1] In contrast, pyridylideneamides (PYAs) are comprised of electronically flexible N-donor sites that may coordinate to the metal center either as a π-acidic imine, or as a π-basic zwitterionic pyridinium amide, therefore stabilizing metals in low- and high-oxidation state (see Figure).[2] Such stabilization of different electronic configurations is particularly attractive for redox catalysis, which requires the metal to change oxidation state during the catalytic cycle. Moreover, the PYA ligand alters its reactivity. Here we demonstrate the reactivity of PYA ligands towards electrophiles which suggests that these ligands are not only electronically flexible, but also that they are non-innocent and have potential in reversible proton storage. We will discuss selectivity aspects as well as synthetic opportunities emerging from this ligand-based reactivity.

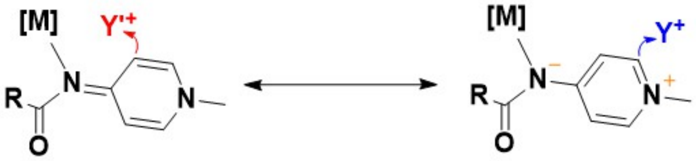

Figure 1. Schematic representation of the PYA ligands coordinate to the metal either as a π-acidic imine (left), or as a π-basic zwitterionic pyridinium amide (right).

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A facile chemistry route for in situ passivation of hybrid imidazolium/methylammonium lead iodide perovskite solar cells

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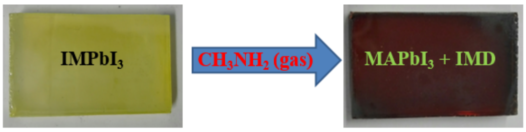
Passivation is important in the growth of perovskite films employed in high performance solar cells, but the known passivation techniques are mostly based on physical mixing/alloying processes, rather than chemical reactions.[1]

We describe the use of a facile chemistry route for the *in situ* passivation of hybrid imidazolium/methylammonium lead iodide $IM_xMA_{1-x}PbI_3$ (X = 0.1-0.3) films that afford high efficiency perovskite solar cells. Because methylamine is a stronger Lewis base (pK_b = 3.24) than imidazole (pK_b = 7), [2] exposure of the hybrid imidazolium/methylammonium lead iodide films to methylamine gas results in the deprotonation of IM cations and the concomitant formation of MA cations, releasing neutral imidazole (IMD):



The structure of the key imidazolium lead iodide salt ($IMPbI_3$) (i.e. formed in the absence of the methylammonium cation) has been determined. Employed in solar cells, a power conversion efficiency of up to 20.14% is demonstrated. Overall, this work shows that classical perovskite materials can potentially be doped with many different organic cations using facile chemistry routes.

Acknowledgement: We thank the EPFL and Swiss National Science Foundation for financial support.

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New Star Shape Organometallic Complexes Contaning Three Dinuclear Trithiolato-Briged Ruthenium(II) Arene Units – Synthesis and Characterisation

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[1]University of Bern, Department of Chemistry and Biochemistry

The high cytotoxicity against human cancer cells [1] of cationic trithiolato-briged dinuclear ruthenium(II) arene complexes (general formula $[(\eta^6\text{-arene})_2Ru_2(\mu_2\text{-SR})_3]^+$) make them interesting scaffolds for the development of new compounds with potential biological activity. The controlled synthesis of 'mixed' cationic trithiolato precursors allowing further modification (general formula $[(\eta^6\text{-}p\text{-MeC}_6H_4Pr^i)_2Ru_2(\mu_2\text{-S-CH}_2\text{-C}_6H_4\text{-}p\text{-Bu}^t)_2(\mu_2\text{-S-C}_6H_4\text{-XH})]Cl$, where -XH = -OH, -SH, $-NH_2$, $-CH_2CO_2H$) [2] enables the design of a large variety of conjugates. [3,4]

Polynuclear compounds are a relatively new and successful approach in metal-based cancer chemotherapy as they offen exert different modes of action compared to the respective mononuclear complexes.A typical example is the linear trinuclear platinum compound BBR3464, shown to exhibit potent cytotoxicity and efficacy against cisplatin-resistant tumors, and which has reached phase II clinical studies. The biological properties of various star-shape monometallic trinuclear platinum, ruthenium,iridium, and rhodium compounds were also reported. On this background, we have extended of this concept to the synthesis and characterisation of new organometallic compounds containing three thiolatho-bridged dinuclear ruthenium(II) arene moieties distributed in a tri-geminal star-like arrangement. As the size of the pendant arms attached to the core proved to be very important to avoid sterical hindrance and allow the anchoring of the three metalorganic units, a two steps synthetic strategy was used. First, specific linkers were attached in a symmetrical manner on a trifunctional central core. These connectors allowed further attachment of judiciously functionalized 'mixed' thiolatho-bridged dinuclear ruthenium(II) arene moieties in a second step. The importance of the nature/rigidity of the central core and of the length of the spacers was assessed.

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Tuneable Exciton Binding Energy in New Fluorous Two Dimensional Perovskites

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Perovskite solar cells (PSCs) are promising alternatives toward clean energy because of their low processing cost and high-power conversion efficiency (PCE) nowadays approaching 23%.[1] However, their commercialization and practical applications are still restricted by insufficient long-term stability in ambient atmosphere. Reduced-dimensional metal-halide perovskites have attracted significant attention in recent years due to light harvesting and emissive properties. In particular, the so-called *Ruddlesden-Popper*-phase 2D hybrid perovskites (2D HP) have also demonstrated higher environmental stability.[2] Their structure reads as R_2BX_4 where R is the organic molecule acting as a spacer between the inorganic layers; B the divalent metal and X the halogen atom.[3]

Influence of different components, in particular the organic moieties, on the structural and optical properties of the 2D HP were investigated. In this work, we synthesized a new family of fluorous ammonium cations as organic spacer to create new stable 2D HP with enhanced hydrophobic character. Our design approach demonstrates an easy and robust method to control and tune the optoelectronic properties of 2D HP (exciton binding energy and band gap among others), a figure of merit which is paramount for device optimization, either solar cells or light emitting devices.

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Light-driven base-promoted homolytic aromatic substitution reactions catalysed by a Mo^0 complex

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Photoredox chemistry has been established as a versatile method in organic synthesis during recent years.[1] Milder conditions, new synthetic pathways and more sustainable chemical transformations combined with a broad functional group tolerance are the main advantages of these processes in many cases.[2,3]

We have previously demonstrated that a homoleptic Mo^0 complex bearing chelating diisocyanide ligands can be used as a strong photoreductant able to perform net redox-neutral transformations beyond the capability of the popular *fac*-[Ir(ppy)$_3$] catalyst.[4,5] In this study, we report a net redox-neutral base-promoted homolytic aromatic substitution (BHAS) reaction catalysed by this same Mo^0 catalyst that cannot be performed with *fac*-[Ir(ppy)$_3$], and have systematically investigated different substrates with altered geometric and electronic properties to gain deeper mechanistic insight (Figure 1).

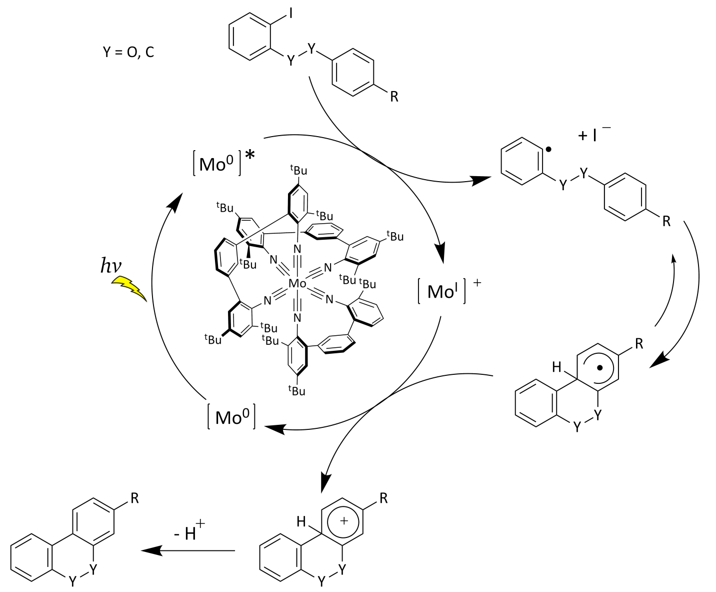

Figure 1. Catalytic cycle for the light-driven base-promoted homolytic aromatic substitution reaction catalysed by [Mo((^{t}Bu)CNAr$_3$NC(^{t}Bu))$_3$].

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

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

Since the pioneering work about molecular magnetism on $[Mn_{12}O_{12}(O_2CMe)_{16}(H_2O)_4]$, $\{Mn_{12}\}$, by *Sessoli* et *al.*[1], and the observation of a slow magnetic relaxation process in a molecular material, the number of reported single molecule magnets (SMMs) has not ceased to grow over the last two decades. Several examples have been reported, including 3d, 4f and mixed 3d-4f complexes.[2] The first mononuclear lanthanide complex $[Ln(W_5O_{18})_2]^{9-}$ (Ln = Ho, Er) unveiling SMM behaviour was reported by *Coronado* et *al.* in 2008.[3] After this breakthrough, similar approaches have been extended to the Preyssler-type series $[Ln(P_5W_{30}O_{110}]^{12-}$ (Ln = Tb, Dy, Ho, Er, Tm, Yb) and the Keggin-type structures $[Ln(\beta_2\text{-}SiW_{11}O_{39})_2]^{13-}$ (Ln = Dy, Ho, Er, Yb). Here, we highlight a new family of mononuclear-type 4f polyoxometalates with a large variety of lanthanide ions (Ln = Gd, Tb, Dy, Ho, Er, Yb, Eu). The crystal structure of all new-fangled POMs was successfully resolved and full magnetic characterization with alternating and direct current (ac-dc) has been performed. The results reveal that the $[Er(\beta_2\text{-}GeW_{11}O_{39})_2]^{13-}$ compound exhibits SMM like-behaviour. Detailed studies on the atomic coordination of erbium indicate that the Er^{3+} ion is embedded in a favourable antiprismatic geometry. To slow down the dynamics of the magnetization the sample was doped with the isostructural diamagnetic Yttrium.

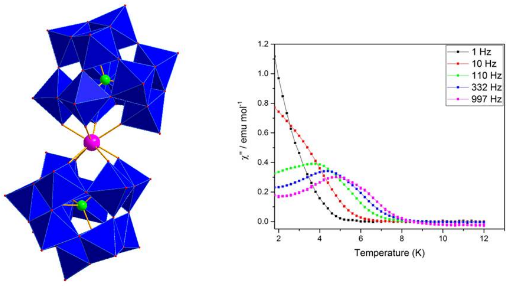

Fig. 1: Ball and stick and polyhedral representation of $[Er(\beta_2\text{-}GeW_{11}O_{39})_2]^{13-}$ and temperature dependence of the out-of-phase (χ’’) signal.

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$[Re(\eta^6\text{-benzene})_2]^+$ as scaffold for artificial photosynthesis

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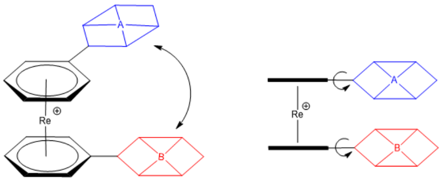
For more than 50 years the chemistry of $[Re(\eta^6\text{-arene})_2]^+$ complexes has remained mostly undeveloped. In the last few years, novel synthetic and analytical methods revealed these complexes to be building blocks of great interest for organometallic chemistry [1, 2]. The extraordinary stability and the structural flexibility of Re(I) bis-arene complexes [1, 2] are well known. Rotation around the rhenium axis and tilting of pendent functionalities are possible for such sandwich complexes without a notable energetic barrier. Combination of one or two identical or different complexes, separated by ring-ring distance is also possible. Those properties make $[Re(\eta^6\text{-arene})_2]^+$ complexes ideal scaffolds for the development of H_2O or CO_2 reduction photocatalysts.



In order to introduce other catalytically active metal centers, functionalization of complex $[Re(\eta^6\text{-benzene})_2]^+$ was explored. Symmetric introduction of five and six *N*-heterocyclic rings to the basic sandwich was successfully achieved and a number of new complexes were synthetized. Sandwich complexes with one, two and four pyridines were synthetized. Moreover, complexes with a pendent ligand combining pyrazoles and pyridines were also synthetized. Crystal structure determinations confirmed the expected structures. Furthermore, the synthetized complexes chelate metal centers such as Re(I) and Co(II). Catalysis studies with complexes containing a Co(II) center show hydrogen evolution. Further investigation in this direction will be the focus of this project in the near future.

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Synthesis and transfer of single-layer nanoporous graphene for molecular separation

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Atom-thick graphene film with molecular-sized pores is regarded as the ultimate membrane, yielding attractive gas selectivity, orders of magnitude higher permeance than the conventional membranes.[1] However, the demonstration of gas separation from single-layer graphene membrane has remained elusive. The major bottlenecks have been a) incorporate molecular-selective pores and b) crack-free transfer of graphene on a porous substrate. Herein, we report significant advances in the synthesis of nanoporous graphene as well as fabrication of crack-free graphene membrane.[2] We synthesized nanoporous graphene by the chemical vapor deposition (CVD) technique in the presence of a trace amount of oxygen, leading to a low-density (0.025%) of sub-nanometer pores in graphene (Fig.1a-c). Further, we developed a novel nanoporous-carbon-assisted transfer technique, leading to crack-free, single-layer graphene membranes with a relatively large area. Due to the development of the crack-free transfer method, for the first time, gas-separation from the graphene nanopores was observed. An attractive gas separation performance was observed (H_2 permeance up to 4.1 x 10^{-7} mol m^{-2} s^{-1} Pa^{-1} and H_2/CH_4 selectivity up to 25), where the H_2 transport was in the activated mode (Fig. 1d). We further show that the performance of membrane improves by increasing the porosity, or shrinking the size of graphene nanopores by developing a novel, ozone-based pore-etching and functionalization chemistry, improving H_2 permeance (up to 300%) and H_2/CH_4 selectivity (up to 150%) (Fig. 1e). Overall, the pore-etching and pore-modification chemistry developed herein is expected to bring the implementation of nanoporous two-dimensional membranes a step closer to reality.

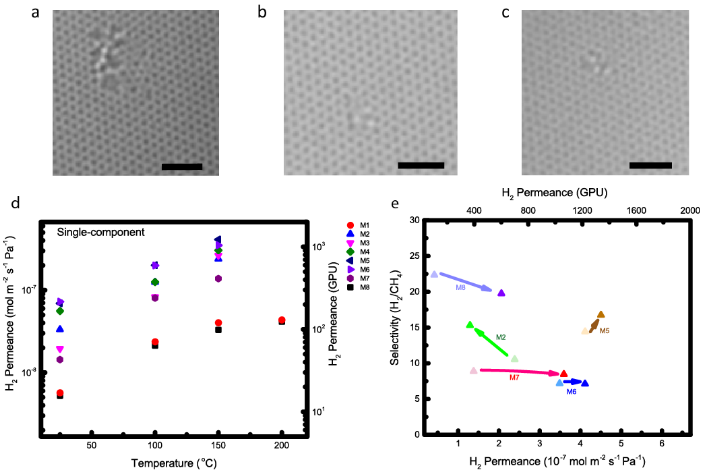

Fig. 1 a-c) HRTEM images of the intrinsic defects in graphene lattice (scale bar is 1 nm); d) H2 permeance through intrinsic defects; e) The trajectory of gas performance after different ozone treatments.

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Synthesis and light-induced disassembly of coordination cages

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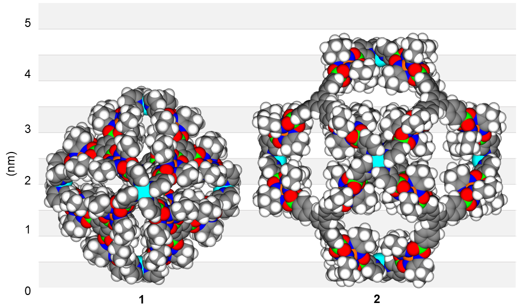
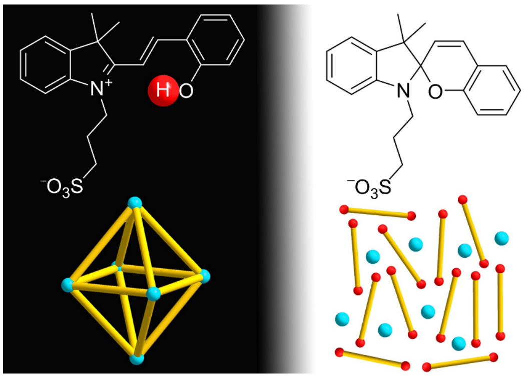
[1]EPFL SB ISIC LCS

Large metalloligands were obtained via a straightforward synthesis and used to form heterometallic Pd_6L_8-type coordination cages (**1** and **2**). With maximum Pd···Pd distances of 3.3 nm (**1**) and 4.2 nm (**2**), these complexes are among the largest Pd_6L_8 cages described to date. [1]



The addition of a metastable-state photoacid to solutions containing metal–ligand assemblies renders the systems light responsive. Upon irradiation, proton transfer from the photoacid to the ligand is observed, resulting in disassembly of the metallasupramolecular structure. In the dark, the process is fully reversed. Light-induced switching was demonstrated for six different metal–ligand assemblies containing Pd^{II}, Pt^{II} or Ru^{II} complexes and bridging polypyridyl ligands. The methodology allows liberating guest molecules with light. [2]



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Stepwise introduction of large bite angle ligands in Cr(III) complexes: from terpyridine to dipyridine-2-yl-pyridine-2,6-diamine

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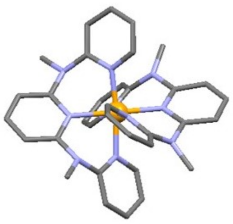
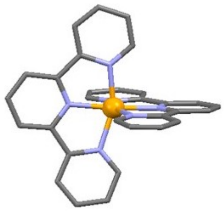
Polypyridine-Cr(III) complexes are well known to exhibit interesting photophysical and photochemical properties. For instance, they can be used as luminophores and dyes for solar cells, as sensitizers in up-conversion or downshifting processes and in photoredox catalysis. Such appealing features arise from the remarkable long-lived excited-state displayed by some of these complexes, which range from the nano- to the microsecond regime. In this regard, Heinze et *al.*, reported the $[Cr(ddpd)_2]^{3+}$ complex **(1)** showing efficient NIR photoluminescence with a ^2E excited-state lifetime (t) of 898 ms,[1] much longer than $[Cr(tpy)_2]^{3+}$ **(2)**, t < 35 ms.[2] This remarkable difference is mainly due to the capability of the 'ddpd' ligand to chelate to Cr(III) with larger N-Cr-N bite angles. Thus, the more efficient orbital overlapping (M-L) together with the strong σ donating character of the 'ddpd' increases the ligand field splitting of the complex. This allows preventing the non-radiative relaxation pathways and the enhancement of the lifetime of ^2E excited-state. In order to study the effect of replacing one 'tpy' ligand by a 'ddpd' ligand in **2**, the heteroleptic $[Cr(ddpd)(tpy)]^{3+}$ complex **(3)** has been synthesized. In this contribution we will discuss and compare the structural and photophysical properties of **1**, **2** and **3**.

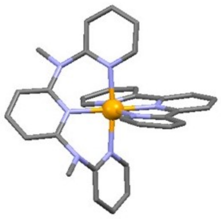
$[Cr(ddpd)_2]^{3+}$ **(1)**



$[Cr(tpy)_2]^{3+}$ **(2)**



$[Cr(ddpd)(tpy)]^{3+}$ **(3)**



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Cuprophilia: dye-sensitized solar cells with copper(I) dyes and copper(I)/(II) redox shuttles

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Today, the efficient and economic access to renewable energy sources is one of the fundamental challenges to every industrialized country. Besides the use of wind and water, the access to solar energy is of key importance, which is displayed by the broad scientific field of photovoltaics. Even though rare-metal containing solar cell systems have existed since 1993, they suffer from several drawbacks the most crucial of which is high cost and the use of a non-Earth abundant metal.

Our group focuses its research on n-type dye-sensitized solar cells (DSCs), which combine the use of Earth abundant metal complexes as dyes and electrolytes to address the current limitations of the known photovoltaic systems [1]. In one of the recent publications, DSCs with heteroleptic copper(I)-based dyes and homoleptic copper(I)/(II) redox shuttles have been investigated (Figure 1) [2].

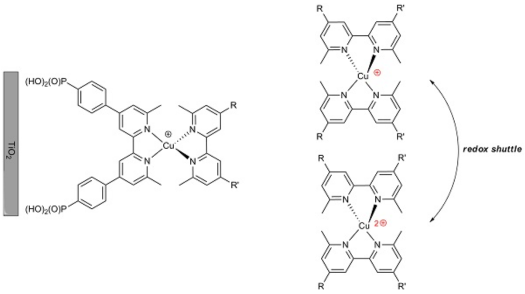

Figure 1. Heteroleptic copper-dye coupled with a homoleptic copper (I)/(II) redox shuttle.

In this work, new heteroleptic dyes based on the 6,6'-dimethyl-2,2'-bipyridine scaffold and with functionalizations in the 4,4'-positions have been developed. In combination with homoleptic copper complexes as electrolytes having the same scaffold, our DSCs showed promising performances (up to 2.06% photoconversion efficiency, 38.1% relative to N719 set at 100%).

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Modifying spacers and anchoring groups for heteroleptic bisdiimine copper(I) based DSSCs

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Heteroleptic $[Cu(6,6'\text{-dimethyl-}2,2'\text{-bipyridine})_A(6,6'\text{-dimethyl-}2,2'\text{-bipyridine})_C]^+$ (A: anchoring ligand, C: capping ligand) complexes in which the bpy units are functionalized in the 4- and 4'-positions are known to be good light harvesting materials in dye-sensitized solar cells (DSSCs). Our group has developed a stepwise build-up of DSSCs (Figure 1a): a 'surface-as-ligand, surface-as-complex' approach.[1] For the first step a 6,6'-dimethyl-2,2'-bipyridine ligand, which is modified in the 4 and 4'-positions by a spacer bearing an anchoring group (e.g. 4-phenylphosphonic acid, Figure 1b) is bound to a TiO_2 surface. Afterwards Cu(I) and a capping ligand are introduced by a ligand exchange reaction between the anchored bpy_A and a bpy_C of the homoleptic $[Cu(bpy_C)_2]^+$ complex. The standard anchoring ligand with the best performance, which is currently used in our group is shown below. Changing the anchoring group from phosphonic acid to alternative groups[2], 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.

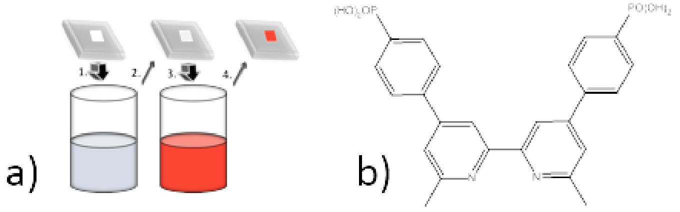

Figure 1: a) Preparation of heteroleptic $[Cu(bpy)_A(bpy)_C]^+$ complexes on TiO_2 b) Current standard anchoring ligand bearing two 4-phenylphosphonic acid groups in the 4- and 4'-positions.

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Non-Aqueous Aluminium-Graphite Batteries: Status, Prospects and Future

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[1]ETH Zurich, [2]Empa – Swiss Federal Laboratories for Materials Science and Technology

Due to limited natural abundance of lithium, novel battery technologies are needed for large-scale, stationary storage of electricity [1]. Such batteries can then be combined with renewable sources of electricity, for the best integration of a variety of sources into electrical grid. We will discuss the utility of graphite as cathode material in non-aqueous aluminum batteries as a highly promising post-Li-ion technology for low cost and/or large scale storage of electricity [2, 3]. In particular, the focus will be on a balance between structural perfection of the graphite, its electrochemical performance and material's synthesis costs. In this regard, we provide a balanced analysis of the overall cell-level energy density of graphite based aluminum batteries. In view of its non-rocking chair operation mechanism, we show the achievable energy densities as a function of the composition of chloroaluminate ionic liquid ($AlCl_3$ content) and compare it with other battery electrochemistries suited for stationary storage of electricity (such as lead-acid or vanadium redox flow). We will discuss also other issues associated with this technology, one being the incompatibility of most metallic current collectors with the corrosive $AlCl_3$-based ionic liquids. Finally, we will present a novel concept of flexible aluminum-graphite battery using current collectors from earth-abundant elements and point to further avenues to commercialization of aluminum-graphite batteries as a potential grid-level energy storage technology [4].

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Novel post-modification strategy of triazolylidene metal complexes to efficiently enhance catalytic activity

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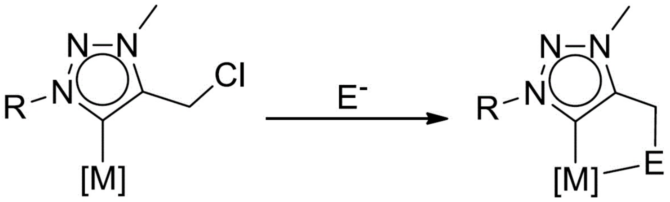
N-heterocyclic carbene (NHC) metal complexes have shown versatile applicability in a wide variety of catalytic transformations, partially due to their strong σ-donating abilities.[1] A sub-class of NHCs are mesoionic NHCs, which includes 1,2,3-triazolylidenes. These are even stronger electron donors and exhibit additional beneficial properties in, for instance, redox catalysis, as they can act as 'charge reservoirs'.[2] These features make them an interesting class of ligands and significant research has been devoted into tailoring the carbene ligands by introduction of functional groups for chelation or other purposes. However, functionalization of such a ligand is often a challenging multi-step synthesis.[3] We have developed a system, based on a chloro-functionalized triazolylidene ligand that allows modification of the ligand in the very last stages of the synthesis with a wide variety of nucleophiles (Figure 1).[4] Synthetic procedures are significantly simplified and rapid screening of different functional groups for catalyst optimization is facilitated. Thus, tedious ligand synthesis is circumvented, making it very time-efficient and potential synthetic incompatibilities are avoided.[5]

We will demonstrate the potential of this approach by the synthesis and catalytic screening of a variety of donor-functionalized triazolylidene metal complexes. The versatility of this post-functionalization method will be discussed as it efficiently allows to screen a large set of catalysts and to identify the best catalysts for various transformations.



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Coordination-induced evolution of single gold atoms on nitrogen-doped carbon for alkyne semi-hydrogenation

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Deriving structure-performance relations relies on the ability to design materials with well-defined active sites, an aspect tremendously challenging in heterogeneous catalysis. Supported single-atom metal catalysts are promising candidates to tackle this point.[1,2] Nonetheless, current efforts are exclusively devoted to stabilization strategies, while the fundamentals of tuning the nature of the single-atom metal sites for targeted applications is still at the primordial stage. Here we report a novel approach for tailoring the metal oxidation state and the coordination sphere of single gold atoms by using nitrogen-doped carbon as the host.[3] Atomic dispersion of gold can be ensured in an exceptionally wide temperature range 413-1073 K due to the surface migration of gold atoms over different anchoring sites, which allows to finely tailor their coordination environments. This structural evolution of single gold atoms on the host is clearly depicted by coupling comprehensive characterization techniques with density functional theory studies. When assessed in the three-phase alkyne semi-hydrogenation, a relevant transformation in industrial organic synthesis, the single-atom gold catalysts display distinct linear or volcano-like catalytic responses, depending on both the gold-cavity ensembles and the substrate functionalities. Theoretical analysis links this unprecedented behavior to the strong adsorption of alkynol molecules at specific ensembles, resulting in what we denote a ‘catalytic titration’ of the different single-atom gold sites (Figure 1). This study illustrates how coordination control can be employed in the precise design of innovative catalysts for hydrogenations and beyond.

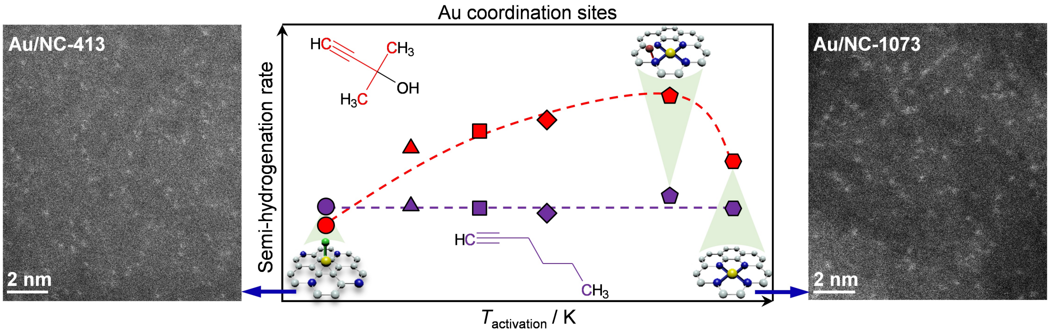

Figure 1 Nitrogen-doped carbon (NC) supported single-atom gold catalysts of varying structure display distinct substrate sensitivity in the semi-hydrogenation of alkynes.

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Trimethylsilyl-Induced N–O Bond Cleavage in Nitrous Oxide-Derived Aminodiazotates

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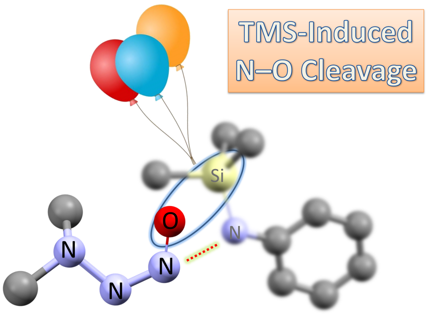
Upon chemical activation, nitrous oxide (N_2O) typically acts as a clean O-atom transfer reagent with dinitrogen as the benign byproduct.[1] Utilization of N_2O as an N-atom donor, on the other hand, has received much less attention. For such purposes, both nitrogen- and carbon-based nucleophiles have been explored but with only limited success, except for *N*-heterocyclic carbenes (NHCs) which form stable covalent adducts with N_2O and can be further functionalized into azo dyes, with the azo group originating from N_2O.[1] Recently, we have found that lithium dialkylamides, for example lithium diisopropylamide, readily capture N_2O to give metastable lithium dialkylaminodiazotates.[2] These diazotates undergo N–O Bond Cleavage when treated with Grignard reagents, preserving the N atoms from N_2O in the trisubstiuted triazenes products, the latter of which represent highly useful reagents in synthetic organic chemistry. In this study,[3] we demonstrate that *N*-trimethylsilyl (TMS)-substituted amides can also form covalent adducts with N_2O. The resulting aminodiazotes undergo spontaneous N–O bond cleavage, giving inorganic or organic azides accompanied with Si–O bond formation. *N*-TMS-substituted amide was also found to effect N–O bond cleavage in N_2O-derived dialkylaminodiazotates, generating unsymmetrical tetrazene monoanion salts. These results indicate the potential of TMS in devising N_2O transformations where value-added N-containing chemicals can be obtained.



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Fighting Cancer with the Next Generation of Organometallic Assemblies Using the EPR-Effect

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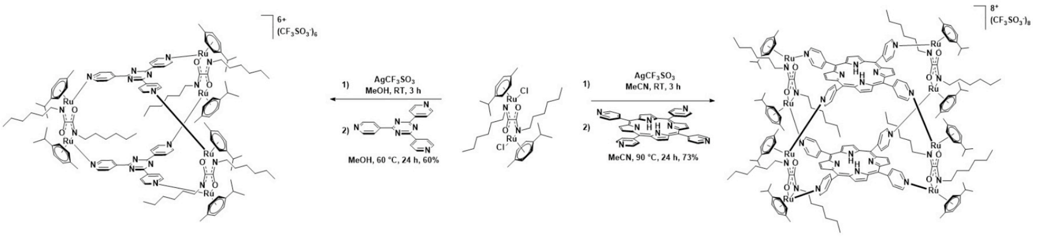
Solid tumors have a unique architecture and tumor blood vessels are more dynamic and variable than healthy blood vessels. They are able to extravasate macromolecules from the blood into the tumor tissue due to the excessive production of vascular mediators. An impaired lymphatic drainage causes accumulation of such macromolecules, which can operate locally to fight tumors. These two findings are the key elements of the enhanced permeability and retention effect (EPR).[1,2] This EPR-effect can be used as a selector for bioactive macromolecules and ultimately keeping healthy tissues untouched and therefore reducing side effects.[3] Arene ruthenium complexes show a high potential to treat cancers, and in recent years we have developed a strategy to build arene ruthenium metalla-assemblies. Herein, we communicate the synthesis of novel arene ruthenium complexes with peripheral alkyl chains as the next generation of arene ruthenium metalla-assemblies with the view of exploiting the EPR-effect. The scheme below shows the preparation of a hexanuclear and an octanuclear metalla-assembly starting from the dinuclear molecular clip. Coordination between the ruthenium and the panel ligands result in cage-like structures.



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Characterization and improvement of p-type dye sensitized solar cells

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[1]Department of Chemistry, 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.

Facile modification towards powerful transfer hydrogenation catalysts

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Ligand systems that offer flexibility and assist the metal in catalytic bond making and breaking have recieved much attention recently.[1] Pyridylidene amide (PYA) ligands have been shown to be electronically flexible N-donor sites and have sucessfully been used for several applications in homogeneous catalysis, such as in challenging water oxidation and transfer hydrogenation.[2,3] Here we will present new pincer-type ligands containing two PYA units (see Figure 1). We will discuss the influence of different PYA ligand systems and the variation of spectator ligands on the electrochemical and photochemical properties of the ruthenium(II) complexes, as well as the evolution of catalytic performance of these PYA-pincer complexes to attractive transfer hydrogenation catalysts.

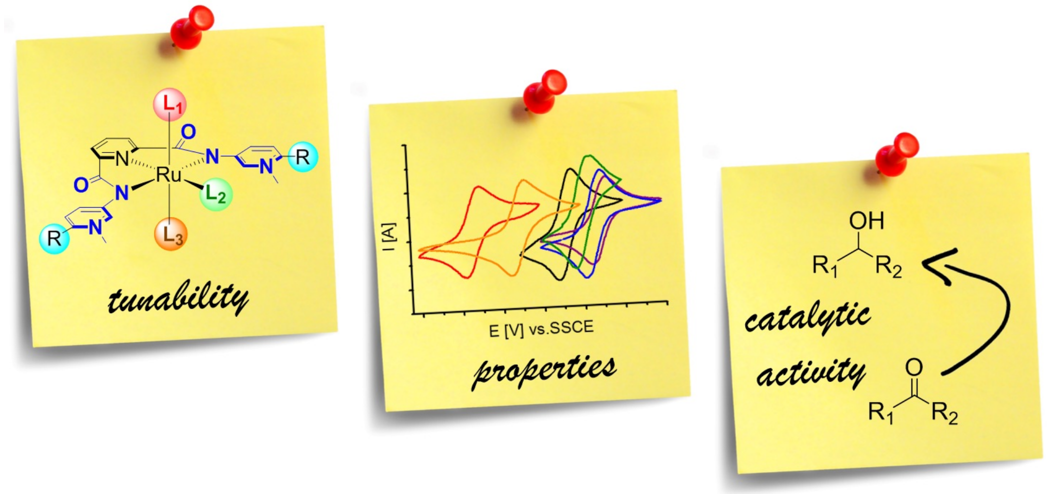

Figure 1. Tunable Ru(II) complexes containing pincer-type PYA ligands with tailored properties and high catalytic activity in transfer hydrogenation catalysis.

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Earth alkaline ion selectivity in marine Acantharia

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Separating various earth alkaline ions from each other poses a technological challenge. While most living organisms show an indiscriminate transport of Ca^{2+}, Sr^{2+} and Ba^{2+}, the marine protists Acantharia build their entire skeleton from strontium sulfate ($SrSO_4$) in their unicellular body. A key question to be addressed is how Acantharia selectively sequester $SrSO_4$ mineral despite the very low levels of strontium compared to calcium salts in the oceans. Within the small compartment of the specialized vesicle, the local Sr^{2+} and SO_4^{2-} ion concentration has to exceed supersaturation to allow for $SrSO_4$ mineral deposition. Desmid green algae achieve high selectivity towards Ba^{2+}/Sr^{2+} by a sulfate trap mechanism[1]. Towards the goal of understanding the principles of ion-selection in Acantharia, we map the elemental composition across the cellular tissue at sub-micrometer resolution using scanning synchrotron X-ray fluorescence (Advanced Photon Source, Argonne National Laboratory)[2]. We speculate that specific sites (e.g. anionic moieties) in the vesicle enclosing the $SrSO_4$ crystals may be involved in ion complexation. State-of-the-art analytical tools (e.g. Atom Probe Tomography) allow us to fully characterize the inorganic/soft tissue interfaces. Based on Raman and sulfur K-edge µ-XANES spectroscopy[3], free sulfate ions in the cellular tissue can be clearly discerned from solid $SrSO_4$ minerals, which offers further insights into possible ion transport pathways across the semipermeable membranes. Fundamental insights into the biological system will help us find engineered solutions for a broad range of chemical separation problems, as in drinking water purification, nuclear waste management, or the chemical industry.

Acknowledgement: V. M. thanks the Swiss National Science Foundation for financial support.

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"Liquid Perovskites": highly luminescent lead(II) halide ionic liquids

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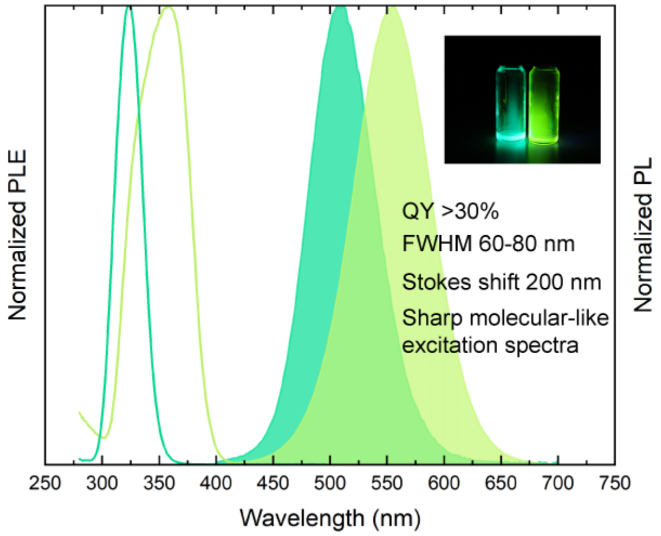
Low-dimensional hybrid organic-inorganic lead(II) halide perovskite-related structures have recently been drawing more attention due to their vast potential for structural engineering and optical properties.[1] It is known that, for example, bulk $APbX_3$ compounds (where A = Cs, MA, FA, and X = Cl, Br, I) do not exhibit luminescence at room temperature, presumably due to the extended 3D structure. The confinement of the exciton becomes possible in hybrid organic-inorganic compositions when inorganic fragments are separated with insulating organic cations.[2] In this research, we attempt to push the lead halide perovskite-related structures research even further and for the first time discover luminescent properties of room-temperature liquid salts in systems TAPX-PbX_2 (where TAP = tetraalkylphoshonium) and low-melting point salts (below 100 deg C) in systems TAAX-PbX_2 (TAA = tetraalkylammonium). We speculate on the basis of the optical properties and structural analysis (EXAFS, ^{207}Pb NMR) that highly Stokes shifted broad emission results from low-dimensional lead(II) halide framework. We anticipate that this work will further improve the understanding of the optical properties of low-dimensional lead halide perovskites.



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Artificial Photosynthesis: Immobilization Strategy on Metal Oxides

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Artificial photosynthesis using catalysts in homogeneous solution is interesting from a mechanistic point of view, but suffers from a vast number of possible non-productive electron transfer processes (cross and back electron transfers) between the O_2 and H_2 evolving half reactions leading to self-inhibition of such systems.[1] The use of composite materials consisting of molecular (photo)catalysts immobilized on solid supports circumvents some of this issues by creating a potential gradient by design, and has thus become a topic of intense research. Covalently and non-covalently immobilized molecular systems on nanomaterials have shown considerable performance in terms of turnover numbers (TONs), stability and H_2 production efficiencies.[2–4]

In our group, a series of molecular cobalt polypyridyl based hydrogen evolution catalysts (HECs) has been developed and studied.[5] Synthesis of different benzylic linker molecules with a varying number of phosphonate anchoring groups attached to the HEC's polypyridyl framework thus allowed for heterogenization on metal oxide supports – for applications either on (photo-) electrodes or nanoparticles. The stability of the linker-polypyridyl constructs on TiO_2 was studied as a function of the number of phosphonate groups and performance of the heterogenized systems in hydrogen evolution experiments were investigated in comparison to the corresponding homogeneous systems.

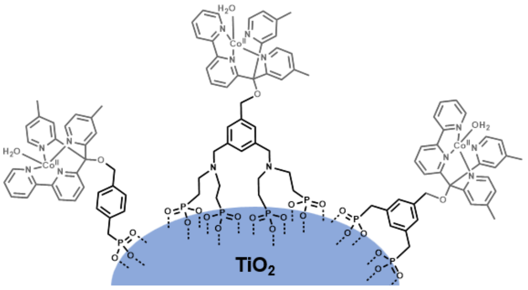

Figure 1: Cobalt polypyridyl based HEC (grey) immobilized on TiO_2 via different benzylic linkers.

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The Influence of the Bridging Position in Cobalt Poly-pyridyl Water-Reduction Catalysts Towards Activity

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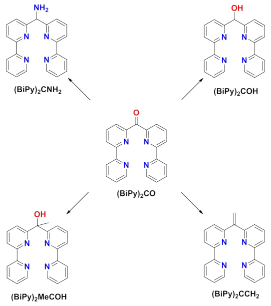
The investigation of homogeneous water reduction catalysts (WRCs) is an important step towards the development and synthesis of heterogeneous WRCs. Cobalt polypyridine based WRCs are promising structures in terms of rate and stability[1], but never the less a few polypyridine based WRCs are known, there is still room for improvement. Next to mechanistic studies of the photo-catalytic cycle, it is of great importance to understand the influence of the different positions in the ligand-framework. In the presented tetrapyridyl ligand-framework, a rather easy accessible and modifiable position is the bridging position between the two bipyridine moieties.

[Co((BiPy)$_2$CO)]Br$_2$ is one of our most promising WRC in terms of rate and therefore an interesting framework to investigate[2].



The five ligands, respective the corresponding five Co-complexes were measured in our established catalytic system containing water reduction catalyst (5 uM), photosensitiser (500 uM), sacrificial electron donor (0.1 M) and Sodium ascorbate (0.1 M) in water, to compare the catalytic activity and therefore study the influence of the bridging position in those polypyridyl-based systems.

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Reactive stability of promising scalable doped ceria materials for solar thermochemical two-step CO_2 dissociation.

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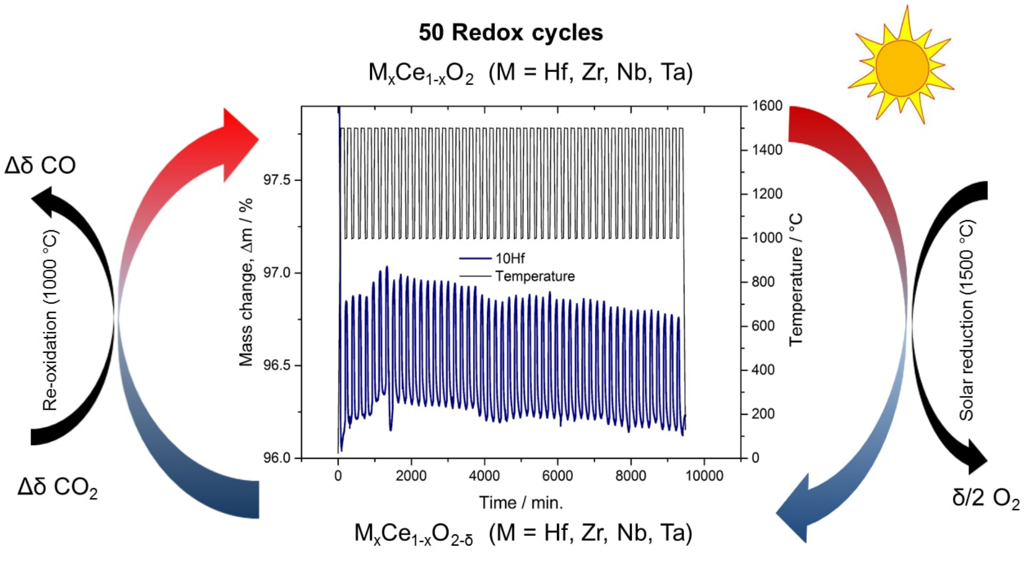
Solar thermochemical fuels production from CO_2 and water are a topic of current large scientific and industrial interest. Thermochemical approaches for splitting CO_2 using concentrated solar power plants inherently operate at high temperatures and utilize the entire solar spectrum, and as such provide a favourable thermodynamic path to solar fuel production with potentially high efficiencies. Ceria is considered as the state of the art redox material for the operation of solar thermochemical reactors. Two step thermochemical redox cycling of ceria encompasses a endothermic reduction step at low O_2 partial pressures followed by exothermic re-oxidation step using CO_2 and H_2O to generate a mixture of CO and H_2 (synthesis gas), which can then be processed to desired liquid hydrocarbon fuels via the well-established Fischer-Tropsch synthesis. Increasing the oxygen exchange capacity (OEC) of ceria though doping is one of the key performance parameters to enhance the solar-to-fuel energy efficiency. In our previous studies, we screened all potential tetravalent dopants (comprising 26 elements) for enhanced OEC of ceria, and only three of all tested metal cation dopants (Hf, Zr, and Nb) were found to combine higher OEC values with thermal stability. Furthermore, the obtained experimental trends pointed to an optimal dopant radius around 0.8 Å for maximum OEC. As a further step on the way to commercial production of doped ceria for thermochemical CO_2 splitting, we here present the first comprehensive long-term stability study of a series of systematically optimized co-doped ceria samples. Hf-, Zr- and Nb-doped ceria materials had been subjected to thermogravimetric analysis (TGA) cycling experiments with 50 cycles between 1000 ^oC and 1500 ^oC, and their OEC under long term conditions (10,000 mins) were evaluated.



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Modulated-Excitation Spectroscopy of Vanadia-Based Catalysts

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Transition metal oxides constitute the largest family of catalytic materials used in the industry. Due to their highly polarizable and predominantly covalent M-O bonds, they are preferentially characterized by Raman spectroscopy [1]. Raman studies can reveal the nature of M-O bond, type of surface MO_x species, and the coordination environment of the metal. Typically, *in situ/operando* Raman studies are performed under steady state or static conditions, which are not suitable to capture meaningful mechanistic and kinetic features. In this work, we apply the technique of modulated excitation (ME) [2] in Raman spectroscopy to extract mechanistic information about the V_2O_5/TiO_2 system, the catalyst of choice for the selective catalytic reduction (SCR) of NO_x from stationary sources.

ME was performed by repeatedly pulsing NH_3 in a gas feed of $NO/H_2O/O_2/Ar$ at 250 °C while recording Raman spectra simultaneously. In the time-resolved spectra of the catalysts, no obvious spectral changes were apparent. However, after applying phase-sensitive detection (PSD) [3], changes around the V=O and TiO_2 (395, 512, and 636 cm^{-1}) peaks were amplified. In particular, while the V=O peak broadened in the presence of NH_3 and H_2O in the time-resolved spectra, a sharp peak appeared at 1031 cm^{-1} in the phase-resolved spectra. Hence, only a defined fraction of the VO_x species contributes to the SCR process, and these active species correspond to coordinatively unsaturated VO_x sites.

When TiO_2 alone was subjected to the same pulsing procedure, no significant spectral changes were observed, confirming that NH_3 is adsorbed strongly on the TiO_2 surface and does not react in the absence of VO_x sites. This observation, together with the fact that TiO_2 peaks were present in the phase-resolved spectra of V_2O_5/TiO_2, implies that NH_3 adsorbed on the TiO_2 surface can be delivered to the active VO_x sites to react with NO, i.e. TiO_2 acts as a reservoir of NH_3 molecules.

These novel mechanistic insights could be extracted from the Raman spectra only due to the increased sensitivity offered by ME and PSD. Therefore, this approach opens up new possibilities in deciphering structure-reactivity relationships of mixed oxide catalyst systems.

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Tackling Water Oxidation using Mesoionic Carbene Iridium Complexes

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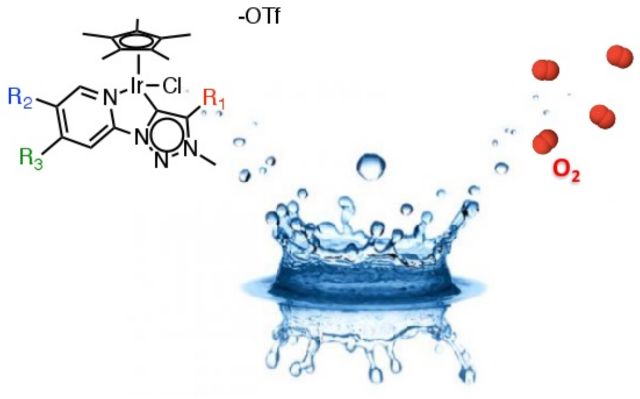
Water oxidation is one of the two half reactions of water splitting and the critical step due to its complexity and high potential required.[1] Iridium-based complexes show remarkably high activity for water oxidation, and homogeneous catalysis has demonstrated in various cases.[2,3] Here we will discuss a new family of iridium(III) complexes containing mesoionic carbene ligands. These ligands have been modified selectively by introducing substituents (see Figure), and the influence of various functional groups on catalytic water oxidation has been investigated. This methodology provides a rational approach for increasing catalytic water oxidation activity. We will present results from CAN-mediated chemically driven water oxidation and critical compare these results with electrochemically driven water oxidation.



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Amide and Siloxide Ligand Influences on f-Element Redox Chemistry

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Understanding basic chemistry of *f* elements could improve materials development for more efficient nuclear and chemical energy conversion.[1,2] Electron transfer reactions are fundamental to the synthesis of uranium materials, such as uranium containing ceramics for nuclear fuel applications[3-5] and molecular compounds used to study *f* electron bonding and catalysis.[6-11] Catalysis using *f* elements is less developed than with transition metals; however, the unique properties of *f* electrons could allow new types of transformations.[12] We report work that examines influences of amide and siloxide ligands on the redox chemistry of uranium and the ability of its complexes to perform thermodynamically difficult transformations. Also presented is a new class of heterobimetallic complexes which combines *f* element redox chemistry with that of transition metals.

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Mn(I) Complexes with P-Stereogenic Pincer Ligands in the Asymmetric Hydrogenation of Ketones

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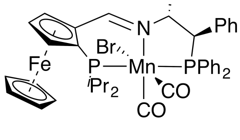
In 2017, the first Mn(I) pincer catalysts for the asymmetric hydrogenation of ketones were reported, which is an appealing application as manganese is cheap and non-toxic. Complex **1** is active under hydrogen transfer conditions (ATH), whereas **2** and **3** operate under H_2 (AH). [1]



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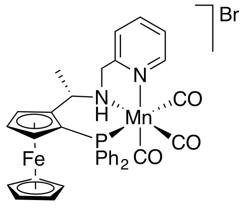

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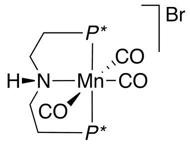

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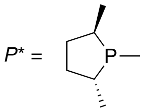
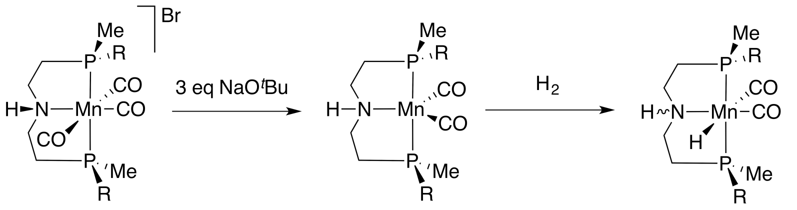


We report here the first Mn(I) complexes with P-stereogenic PN(H)P pincer ligands (**4**), which catalyze the AH of ketones. Catalyst **4b** (1 mol%, 3 mol% KH, 50 bar H_2, toluene, 80 °C) hydrogenates acetophenone to 1-phenylethanol with 99% yield and 55% ee after 16 h reaction time.

Upon reaction with NaO^{t}Bu (3 equiv), complexes **4** give the amido derivatives **5**, which react with H_2 to hydrides **6**. Hydrides **6** react with acetophenone to give 1-phenylethanol. Accordingly, DFT calculations show that **5** and **6** have comparable energies.



4a: R= Cy
4b: R= ^{t}Bu

5a: R= Cy
5b: R= ^{t}Bu

6a: R= Cy
6b: R= ^{t}Bu

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Neclu_MT1: a combined approach

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Metallothioneines (MTs) are a large super-family of small, cysteine-rich metalloproteins. Due to the high content of cysteine residues, and sometimes assisted by histidine, these tiny proteins are able to efficiently coordinate most of the transition metal ions, from the essential Zn(II) and Cu(I) to the most toxic such as Cd(II) and Hg(I).[1]

Thanks to their great metal ion binding capacity, many biological roles were proposed for MTs: they are involved in metal ion transportation, resistance against oxidative stress and detoxification processes. Neclu_MT1, for example, is one of the smallest MTs (only 24 amino acids of which eight are cysteines), and it is produced by the fungus *Heliscus lugdunensis*, which is able to survive in a German polluted spring with metal ion concentrations such high as 25 µM of Cd(II) and 30 mM of Zn(II).[2,3]

Neclu_MT1 was proven to be the first cadmium specific MT, since only this metal is able to trigger and regulate protein expression and translation. Besides this specificity, what caught the attention was the presence of one histidine at precisely the C-terminal end of the protein. In order to investigate the role of this ‘special guest’ in our sequence, the histidine was mutated to a non-coordinating arginine (*H24R*) and both, potentiometric studies and 2D-heteronuclear NMR experiments, were performed for the mutant and the wild-type protein.

On one side, potentiometry allows us to calculate the consecutive, individual pK_a values for many residues and to observe, how these values are affected by the mutation. It also allows to observe the stepwise coordination of metal ions. On the other side, when we follow the pH titration of the proteins by NMR, we are able to explicitly observe the protonation event of the histidine, and in this way could identify a distinct difference in the coordination pathway of Zn(II) compared to Cd(II).

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Cr^{III} tris-didentate sensitizers for energy converting devices

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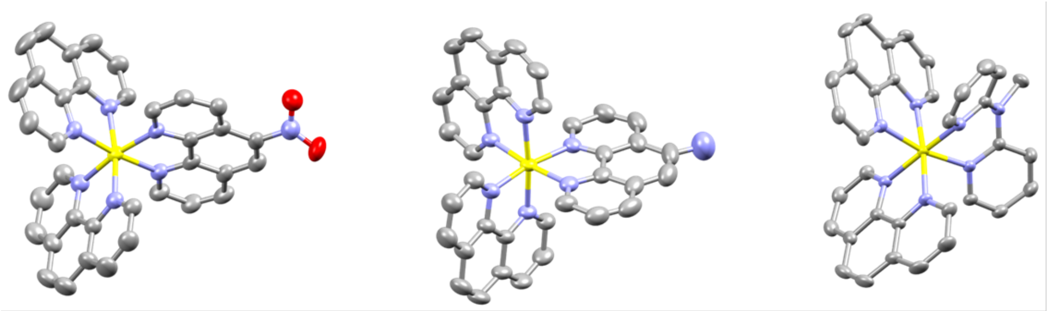
Energy conversion received increasing interest during the last decades and chemists took advantages of the toolkit of supramolecular chemistry for designing polymetallic architectures working as energy converting devices. The introduction of specific metal ions as sensitizers and activators in molecular systems permitted to observe down-shifting[1] and up-conversion phenomena.[2] Despite their particularly appealing photo-physical features with long excited state lifetimes,[3] sensitizers based on Cr^{III} complexes remain under-represented in multimetalic supramolecular architectures performing energy conversion, while Ru^{II} analogues are widely exploited for this purpose. We decided to overcome the Cr^{III} chemistry complexity in order to permit its use as sensitizer in heteroleptic polypyridine-based architectures.[4] In order to study the structural and electronic impact of the ligands on the photophysical properties of Cr^{III} complexes, the synthesis of a family of Cr^{III} tris-didentate heteroleptic complexes was performed (Figure). The structural and photophysical studies allowed to identify the chemical or structural parameters affecting the excited state lifetime. Altogether, the chemical versatile method used to synthetize Cr^{III} tris-bidentate sensitizers will be presented, as well as the studies highlighting the Cr^{III} complex displaying the best features for collecting and transferring energy.



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Towards a Better Understanding of Lead-Halide-Perovskite Structures with NMR

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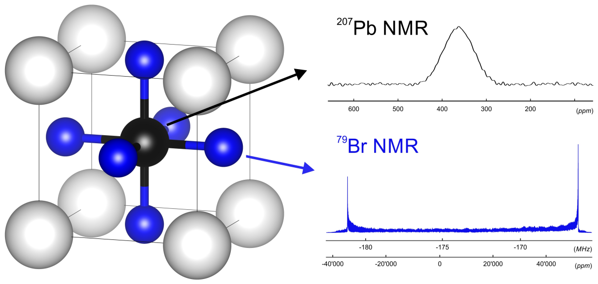
Lead halide perovskites $APbX_3$ ($A=CH_3NH_3$, $CH(NH_2)_2$, Cs; X= Cl, Br, I) have recently risen enormous interest in the scientific community as bulk $CH_3NH_3PbI_3$ solar cells outperformed the well-established and intensively studied silicon solar cells in only five years.[1] Also nano-sized perovskite materials have lately become the object of numerous research studies because they exhibit outstanding optoelectronic properties making them particularly appealing for a vast variety of potential applications such as light-emitting devices, lasers, photodetectors, and field-effect transistors.[2]

High defect tolerance, rich structural dynamics over a broad range of timescales and subtle changes in the structure[3] are assumed to be responsible for the attractive properties of bulk and nano-sized perovskite materials. However, to date, tracing such structural variations has always involved the use of synchrotron radiation, and was focused on bulk materials.[4-6] Nuclear magnetic resonance (NMR) can serve as a tool to better understand and track changes in perovskite materials as some of the spin-interactions have proven to be highly sensitive to small structural and dynamical deviations. We are using a multinuclear approach to study the different components within perovskite structures (i.e. A-cations, Pb and halides) which are all NMR active (^{1}H, ^{13}C, $^{14/15}N$, ^{133}Cs, ^{207}Pb, $^{35/37}Cl$, $^{79/81}Br$, ^{127}I). We utilize the strong spin-spin (J- and dipole-couplings), chemical shift and quadrupolar interactions to access information about the perovskite structure, the dynamics within the material and the relaxation processes present. The ultimate goal is the correlation of structural and dynamical insights from NMR to the optoelectronic properties of perovskites in order to better understand the still elusive origin of the exceptional properties of these materials.



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Synthetic route of trithiolato-bridged dinuclear arene ruthenium(II) complexes $[(h^6\text{- p-MeC}_6H_4Pr^i)_2Ru_2(m\text{-SR})_3]^+$: DFT calculations and synthesis of previously unreported complexes

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In the last fifteen years we have synthesized and characterized numerous water-soluble trithiolato-bridged dinuclear arene ruthenium complexes $[(h^6\text{-}p\text{-MeC}_6H_4Pr^i)_2Ru_2(m_2\text{-SC}_6H_4\text{-R})_3]^+$ and $[(h^6\text{-}p\text{-MeC}_6H_4Pr^i)_2Ru_2(m_2\text{-SC}_6H_4\text{-R}^1)_2(m_2\text{-SC}_6H_4\text{-R}^2)]^+$.[1] Remarkably, almost all trithiolato compounds tested so far are highly cytotoxic against several cancer cell lines, with the IC_{50} values in the submicromolar range,[1] as well as against several protozoan parasites.[2]

The current synthesis route to symmetrical diruthenium complexes $[(h^6\text{-}p\text{-MeC}_6H_4Pr^i)_2Ru_2(m_2\text{-SC}_6H_4\text{-R})_3]^+$ involves the reaction of $[(h^6\text{-}p\text{-MeC}_6H_4Pr^i)Ru(m_2\text{-Cl})Cl]_2$ with an excess of the corresponding thiol. It has been previously reported that some envisaged trithiolato complexes could not be obtained, presumably due to steric reasons,[3] while some other were obtained with only moderate yields.[4]. These experimental facts were the starting point of our investigations aiming at (i) understanding the likely synthetic route using DFT calculations and (ii) optimizatiing of the synthetic route to (a) increase the yields, (b) reduce the overall reaction time, and (c) to synthesize new trithiolato complexes.

DFT calculations show that formation of a mono- and dithiolato complex is relatively facile with sizable energy gains of the order of 18 and 16 kcal/mol and barriers of 20 and 25 kcal/mol, respectively. The mechanism proceeds by substitution of a chlorine by the protonated thiol group followed by the deprotonation once incorporated. The presence of a polar solvent can lead to smaller barriers and hence more rapid kinetics. The formation of the trithiolato complex on the other hand has a much smaller thermodynamic driving force and a fairly high barrier of (33 kcal/mol), linked to large rearrangements of the remaining ligands.

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Bridging the gap with silica-supported molybdenum-Oxo alkylidene for Olefin Metathesis

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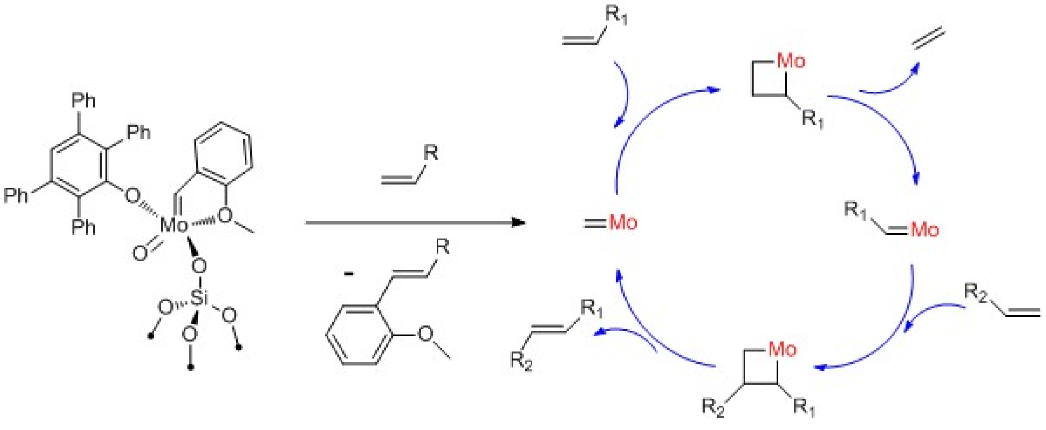
[1]ETH Zurich, [2]ETH Zürich

Despite significant advances in the last years, designing supported alkene metathesis catalysts with high activity and stability is still a challenge. In the past years, several well-defined W=NAr, W=O, Mo=NAr alkylidene have been developed as homogeneous and supported systems.[1] While W- and Mo-Imido show similar reactivity towards internal olefins,[2] W Oxo species display greatly improved activity for terminal olefin metathesis,[3] in particular for cationic species containing NHC ligand.[4] This has been explained with the less favorable formation of the unsubstituted metallacyclobutane with ethylene, produced in the reaction as a byproduct, thanks to the presence of a strong σ donor ligand (oxo and NHC).

After years of research, well-defined Mo-oxo alkylidenes have emerged as a new class of catalyst[5], with a structure resembling the putative active sites of supported Mo oxides. Here, we investigated the formation of the corresponding well-defined supported species and their activity in olefin metathesis.



1@SiO$_2$

Olefin Metathesis

High Activity

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Olefin dimerization and isomerization catalyzed by pyridylideneamide palladium complexes

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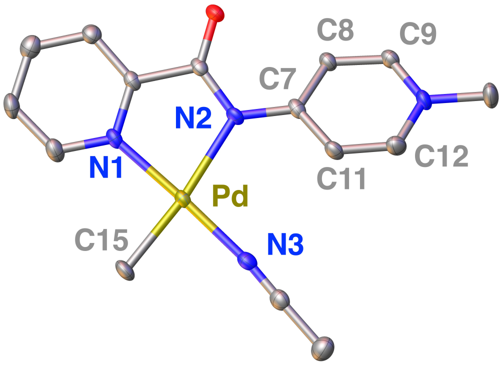
Palladium is the metal of choice for the homogenously catalysed copolymerization of ethylene with polar vinyl monomers, and the two main systems reported are based either on symmetric N-donor α-diimine ligands,[1] or dissymmetric P-O bidentate ligands.[2] Our group recently combined the two strategies by developing a family of C,N-bidentate ligands having a N-heterocyclic carbene as strong donor and a pyridine arm as N-donor; the related palladium complexes are active in the ethylene dimerization and oligomerization.[3] To further expand this trend, we designed a series of donor-flexible pyridylideneamides with a chelating pyridine unit, and used them as ancillary ligands for palladium(II) complexes. These complexes were fully characterized, investigating in particular the coordination mode of the ligand depending on the position of the N-alkyl pyridinium moiety. We will discuss their activity in terminal alkene dimerization, focusing in particular on the mechanistic aspects of the target reaction, and the competition between polymerization and isomerization of alkenes.



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A two-output signal Boolean logic-gate based on a blue colored [Ni(PCV)]Cl_2] complex for naked-eye detection of phosphate or thiol based molecules

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Thiols, containing molecules such as Glutathione (GSH) or cysteine (Cys), are generally aim at targeting metals according to the literature. For example, GSH - a thiol containing peptides - is produced in human cells for the detoxification of poisonous metals such as cadmium. Even if it is well accepted that GSH targets metals, the coordination modes are numerous and differ depending on metals. Moreover, very few modes are reported for precious metals such as Ruthenium or Palladium. [1] Here, we show that nickel complexes, bearing pyrocathecol violet (PCV) as a ligand, can be easily formed in buffered conditions. [2] These blue nickel complexes can be scrutinized using a so-called Indicator Displacement Assay (IDA) to recognize phosphate or thiols containing molecules such as pyrophosphate or GSH/Cys. The PCV ligand forming the Ni-complex is also a 1,4-Michael acceptor, therefore a competition with an indicator displacement and a 1,4 - Michael addition (1,4-MA) for recognition may take place. We show that, for both cysteine and GSH, the 1,4-MA is surprisingly preferred to the IDA, suggesting that thiol containing molecules are more likely to engage a 1,4-MA than a ligand exchange, even in presence of a metal. When in presence of pyrophosphate, the indicator displacement assay is preferred though. The one-complex two mechanisms possible reaction gives birth to a molecular two-output signal Boolean logic gate.

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Pyridylidene amide ligands for ruthenium(ii) catalyzed CO_2 reduction

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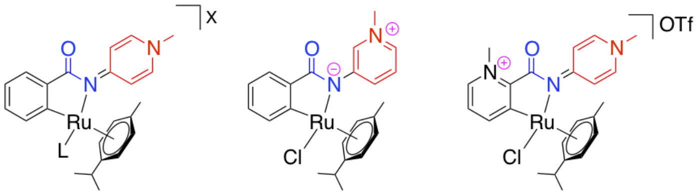
Non-innocent ligands can play a crucial role in catalysis, because they can display varying degrees of donor ability and may stabilize several intermediates of the catalytic cycle. Pyridylideneamides (PYAs, see Figure 1) are an innovative class of such non-innocent ligands. They show a flexible electronic character depending on their environment and are suitable for metal coordination.[1,2] Their synthetic versatility can also be easily exploited by changing the chelating donor group or by changing the PYA position, resulting in different donating properties. Here we introduce phenyl-PYA and pyridylidene-PYA ligands coordinated to the $[Ru(p\text{-}cym)Cl_2]_2$ precursor, which affords catalysts suitable for catalytic CO_2 reduction to formic acid.



L = Cl, MeCN
X = -, OTf

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Charge Accumulation through Potential Inversion in a Molecular Heptad

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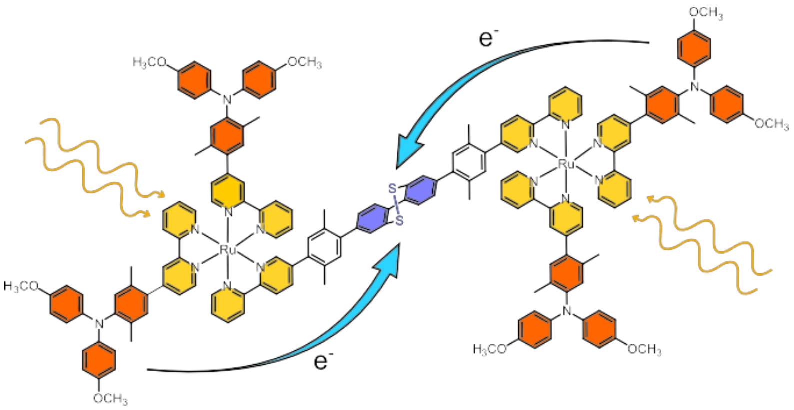
Charge accumulation lies at the basis of many important processes in nature. For example, photosynthesis relies on the temporary storage of redox equivalents on plastoquinone and the oxygen-evolving complex.[1] In context of the need for sustainable energy sources, where artificial photosynthesis is a promising approach, it is highly important to understand the fundamental underlying processes of electron accumulation.



In this project, a central dibenzo [1,2] dithiin was incorporated between two $Ru(bpy)_3^{2+}$ photosensitizers with triarylamine subunits as electron donors on the bipyridine ligands. Upon excitation of both photosensitizers, two electrons are transferred from the triarylamine-donors to the central electron-accepting unit.[2] The advantage of the sulfur-bridged acceptor is its unusual potential inversion in the two-electron reduction, where the second reduction is observed at a significantly less negative potential than the first one.[3]

However, to drive the water splitting reaction, it is necessary to accumulate four electrons on an acceptor unit.[1] Therefore, electron acceptors with two disulfide bridges are currently investigated.

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Photoinduced Multielectron Accumulation in Hexakispyridylbenzenes

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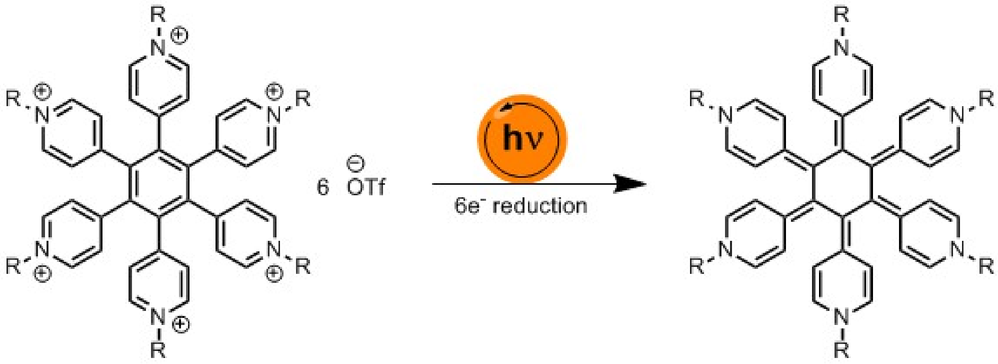
Efficient charge accumulation is one key-step towards mimicking natural photosynthesis, as many of the processes involved such as CO_2 reduction or water oxidation are multielectron transfer reactions.[1] While photo-induced accumulation of two electrons on an acceptor moiety has been successfully achieved, the accumulation of more than two electrons driven by light remains challenging.[2,3]

In this project, hexakis(4-(*N*-alkylpyridylium))benzenes are investigated as possible multi-electron acceptors that should be able to accept up to six electrons. Previous reports have shown that hexakis(4-(*N*-butylpyridylium))benzene triflate can be reduced to its corresponding neutral form both chemically and electrochemically.[4] However, to this date, photoinduced reduction of the sixfold charged core structure remains unknown. To achieve the desired multielectron accumulation, a suitable photochemical system is established, that is able to transfer up to six electrons from a sacrificial donor to the substrate driven by visible light.



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N-Heterocyclic carbene ligands for oxidation catalysis with copper complexes

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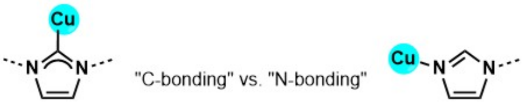
Copper enzymes are efficient catalysts for electron transfer and dioxygen activation.[1] Histidine is the common amino acid in the different active site types (Type 1, 2, 3 and CuA), and binds copper through a well-established N-bonding mode.[2] In synthetic complexes, C-bonding by N-Heterocyclic Carbenes (NHC) to different metal centers has considerable impacts on homogeneous catalysis.[3]



We are interested in studying C-bonding rather than N-bonding of an imidazole to copper(II) and in investigating its effect on the activity of selected copper enzymes. For this purpose, N,N'-dimethylimidazolium-2-carboxylate (DMI-CO_2) has been used as an N-heterocyclic carbene (NHC) precursor.[4] We first focused on the preparation and characterization of different copper(II)-NHC complexes as model complexes for C-bonding, and studied for oxidation catalysis. Detailed EPR and electrochemical characterizations will be presented.

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New chiral ligands derived from terpenes

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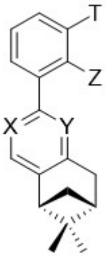
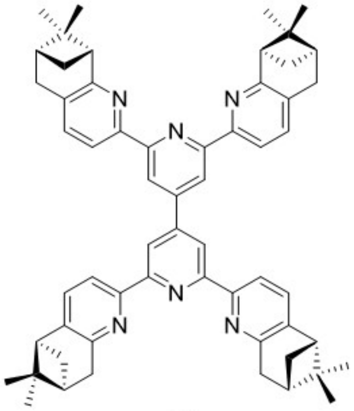
Ligands with a pinene backbone have found vast applications in catalysis[1] and in the design of chiral metallosupramolecular architectures.[2] The reason for this is their efficient chiral induction in various coordination complexes, spanning from *d* to *f* metals.

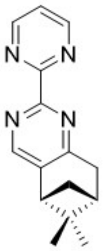
We have recently designed a library of ligands derived from α-pinene, which could be promising candidates either for chiral cyclometallated Ir(III) complexes or for lanthanide-containing complexes. The versatile synthesis of these ligands is mostly based on Kröhnke syntheses,[3] whereas the bipyrimidine ligands are synthetized through coupling reactions between a nitrile and an enaminoaldehyde. Synthetic procedures and full spectroscopic characterizations will be presented.



L1-L3



L4



L5

X = CH, Y = N, Z = COOH, T = H
X = CH, Y = N, Z = H, T = COOH
X = N, Y = CH, Z = H, T = H

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Engineered Defect sites on Silica: Preparation, Structure and Reactivity

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

Amorphous silica is among the most studied oxide supports in a heterogeneous catalysis but also has wide use in other disciplines (e.g. construction engineering, glass industry, tire manufacturing, pharmaceutical industry etc.). Preparation of amorphous silica can be achieved by sol-gel processes or by flame pyrolysis. [1] The structure consists of cross-linked Si-O-Si bridges, where silicon atoms adopt tetrahedral geometry. These siloxane moieties form ring structures (4-membered to 12-membered, where the ring size creates/alleviates strain in the structure) and are often terminated by silanol groups (geminal, vicinal, isolated). [2]

Presence of defects in the structure multilaterally influences physical and chemical properties of the material. Defect sites localized on the surface are source of interest within field of heterogeneous catalysis/surface chemistry, since such reactive species might be a source of catalytic activity. In this work, we will describe how high-temperature treatment of silica terminated with hydrosilane functionality (prepared by sol-gel deposition method) introduces extensive changes to the surface structure. During the treatment, paramagnetic and diamagnetic defects are generated, which correspond to the silicon-centered radicals and silylene groups. Aforementioned process also leads to removal of majority of H-based species (silane and silanol), while maintaining a relatively large surface area (> 150 m^2/g). The defect sites proved to be able to activate a broad range of small molecules such as H_2, O_2, CH_4 and allow the grafting of organometallic compounds.

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Porous Molecular Networks from Dative B-N Bonds

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[1]ISIC, École Polytechnique Fédérale de Lausanne (EP

Porous networks constructed with supramolecular interactions benefit from self-healing properties, alongside other properties (rheology, hydrolytic stability, permeability etc.) that can be directly addressed by the electronic tuning of bonding interactions. Previous examples of networks formed through dative B-N bonds have been shown to rapidly collapse following solvent removal, rendering them non-porous regardless of any crystallographically observed channels or cavities. Here, we demonstrate the use of imidazole adducts as N-donors to increase B-N bond strength (Figure 1a), which, in combination with suitable boronate esters, affords networks with high surface areas (up to 420 m^2g^{-1}). A systematic study revealed that the measured surface area is dependent on the chelating angle and length of the imidazole ligands used, whilst modification of the geometry / valency of the ligands resulted in the first examples of well-defined three-dimensional polymers from B-N bonds (Figure 1b), as well as n-fold interpenetrated two- and three-dimensional networks (Figure 1c).

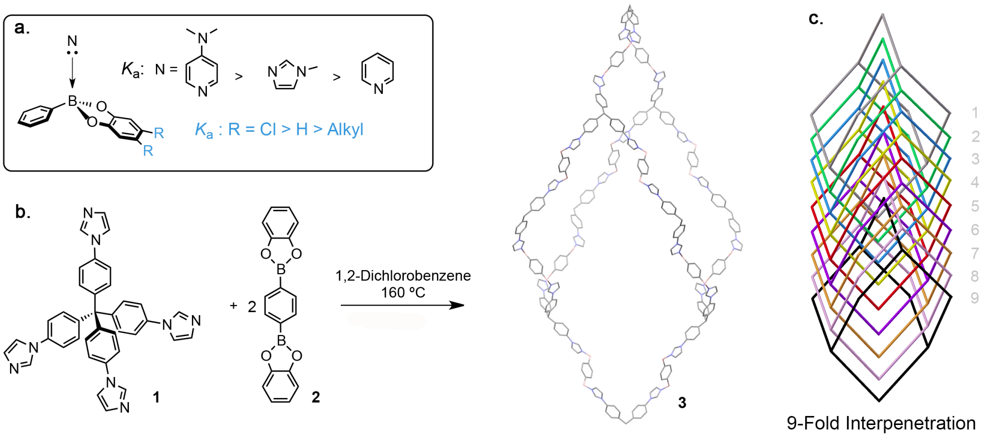

Figure 1 – (**a**) Factors influencing the strength of B-N bonding. (**b**) The self-assembly of 3D network from BN Bonds (catechol and protons are omitted from the crystal structure). (**c**) Representation of the interpenetration displayed by the network.

New Organometallic Complexes Containing Two Dinuclear Trithiolato-Bridged Ruthenium(II) Arene Units

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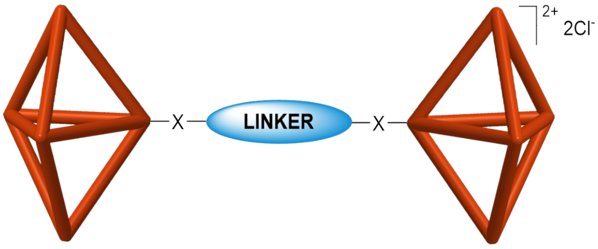
Cationic trithiolato-bridged dinuclear ruthenium(II) arene complexes of general formula $[(\eta^6\text{-arene})_2Ru_2(\mu_2\text{-SR})_3]^+$ are highly cytotoxic against human cancer cells (low micromolar range IC_{50} values).[1] The easy synthesis of 'mixed' cationic trithiolato compounds (general formula $[(\eta^6\text{-}p\text{-}MeC_6H_4Pr^i)_2Ru_2(\mu_2\text{-S-CH}_2\text{-C}_6H_4\text{-}p\text{-Bu}^t)_2(\mu_2\text{-S-C}_6H_4\text{-XH})]Cl$), bearing different functionalisable groups (-XH = -OH, -SH, $-NH_2$, $-CH_2CO_2H$)[2] opened the door to the obtainment of a large variety of ruthenium conjugates.[2,3]

Symmetric dinuclear metal complexes, in which two identic organometallic moieties are connected *via* linkers of variable nature/length, have emerged as a promising class of anticancer compounds. In some cases, the dinuclear complexes were considerably more cytotoxic compared to their mononuclear counterparts and a correlation between the length/lipophilicity of the linker and the cytotoxicity was observed.[4-5]

This concept was extended to the obtainment of new organometallic compounds containing two thiolatho-bridged dinuclear ruthenium(II) arene moieties. A one-step approach involving the reaction of a symmetrically substituted linker bearing two reactive groups with two units of functionalized 'mixed' trithiolato bridged dinuclear arene ruthenium precursor was used. The impact of the type of connection (ester *vs* amide), nature of the linker (aliphatic *vs* aromatic), as well as length of the aliphatic spacer was assessed.



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Multi-decker Arene Bridged Complexes of Lanthanides

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[1]ISIC, École Polytechnique Fédérale de Lausanne (EPFL), [2]University of Toulouse

The synthesis of multi-decker arenes complexes has attracted attention in fundamental research for their potentially magnetic or electronic properties.[1,2] Dinuclear arene-bridged $Ln^{II/III}$ complexes are obtained from the reduction of trivalent ($Ln(Cp^R)_3$) complexes (with $Cp^R = Cp' = C_5H_4(SiMe_3$ or Cp" or $Cp^{tt} = C_5H_31,3(tBu)_2$-1,3 and arene = C_6H_6 or C_7H_8 and Ln = Ce or La) in benzene or toluene with K or KC_8.[3] Recently our group reported the first example of a divalent cerium multi-decker complex obtained from the reduction of $[KCe((OSi(O^tBu)_3)_4]$ with KC_8 proving the ability of siloxide ligand to stabilize arene complexes of lanthanides (Figure 1A).[4] Moreover, the versatility of siloxide ligands allowed the isolation of cerium complexes in different oxidation state. We have now investigated the possibility of extending this chemistry to other lanthanide ions (Figure 1B). Here we will present new results on arenes-bridge multi-decker complexes with different lanthanide ions.

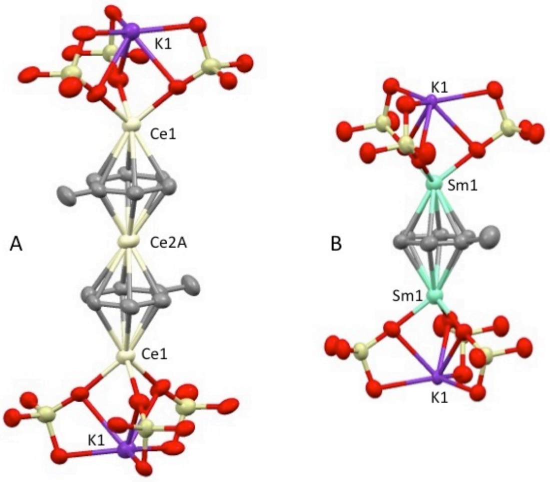

Figure 1. Molecular structure of $[K(2.2.2\text{-crypt})]_2[\{(KL_3Ce)(\mu\text{-}\eta^6\text{:}\eta\text{-}C_7H_8)\}_2Ce]$ (A) and of $[\{KSmL_3\}_2(\mu\text{-}\eta^6\text{:}\eta\text{-}C_7H_8)]$ (B) with ellipsoids set at 50% probability (L = $OSi(O^tBu)_3$). The $[K(2.2.2\text{-crypt})]^+$ counterions, disordered components, ^{t}Bu groups, and hydrogen atoms have been omitted for clarity.

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Luminescent p-p-assembled complexes of Zn and Cd with anthracene functionalized azole ligands

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The most promising materials nowadays in the field of soft materials coordination compounds are the compounds able to produce and harvest great luminescent properties. In this respect coordination polymers with highly emissive light fluorophores are the most attractive. Introducing highly luminescent fluorophores into rigidifying net or framework could enhance the stability and versatility of the material in application in different fields of technologies such as sensors [1-3], non-linear optics [4], up-conversion materaials [5,6], bioimaging.

The main goal of this study is to investigate the luminescent properties of new coordination polymers of Zn(II) and Cd(II) with highly luminescent new anthracene fluorophores. The study of photoluminescent properties with quantifying the lifetime and quantum yield with respect to the crystal structure of Zn(II) and Cd(II) coordination polymers will be presented. The first part will include fundamental studies to understand structure integrity with optical properties observed. And the second will include the part of tight description of this correlation with a stepwise tunable approach to luminescence by inserting different guest molecules. The response of luminescence of such host-guest interaction will be also described and studied.

Different coordination polymers with Zn(II) and Cd(II) will be presented, synthesized on the basis of 9,10-substituted anthracene building blocks, their luminescent properties will be discussed as well.

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Study of Plasmon-enhanced water splitting in a hematite photoanode

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Photoelectrochemical water splitting can use sunlight energy to produce hydrogen gas from water through the electron transfer between an aqueous electrolyte and a semiconductor electrode [1]. Metal oxides are very abundant and stable in aqueous conditions, however their use as semiconductor electrode has been subject to some limitations so far, either because they absorb only short wavelength light (TiO_2, WO_3) or because their charge transport properties are poor ($\alpha - Fe_2O_3$, $BiVO_4$). A suitable hematite ($\alpha - Fe_2O_3$) photoanode needs to be designed with very small features such that most light is absorbed close to the semiconductor/electrolyte interface [2]. Addition of plasmonic nanoparticles as the potential of increasing the quantity of light absorbed in such thin films, through the high near field intensity produced at resonance [3]. Electromagnetic simulations with a surface integral equation method are performed to compare different designs and different possible plasmonic material in combination with hematite. A fabrication technique for making a porous hematite film with electrospinning is presented and the effect of adding plasmonic nanoparticles to it is studied.

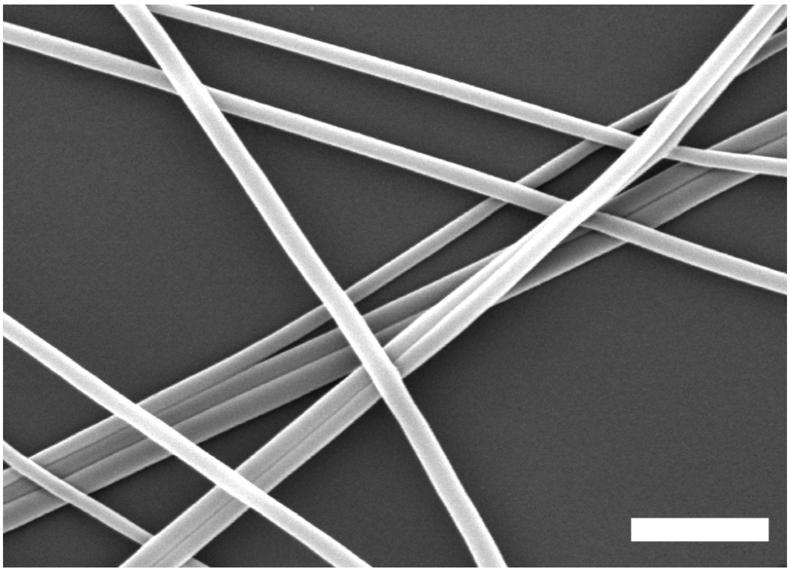

Fig 1: SEM image of composite PVA/$Fe(NO_3)_{3.9}H_2O$ fibers deposited with electrospinning (scale bar : 2µm)

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Scalable synthesis and exfoliation of poly(triazine imide) for nanometer-thick, molecular-sieving membranes

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g-C_3N_4 are highly promising materials for energy storage and conversion, sensors, and energy-efficient two-dimensional (2-d) membranes.[1] They are attractive for such applications because they have tunable photocatalytic and electronic properties, and an inherent porosity with pores in a size-range useful for several industrially relevant separations (e.g., CO_2 capture, H_2 recovery, etc.). However, their full potential can only be harnessed by a) developing a scalable synthesis route, b) exfoliating them into atom-thick nanosheets, and c) developing strategies to process such nanosheets into thin films with a controlled number of layers. This contribution will describe efforts in such directions: (i) scalable fabrication of poly(triazine imide) (PTI), one of the few truly crystalline graphitic carbon nitrides synthesized so far[2]; (ii) mild and simple exfoliation, and purification processes to obtain PTI nanosheets; (iii) and finally coating strategies to form continuous PTI films. We will present a scalable approach to obtain PTI crystals with a high degree of crystallinity and a strategy to control their size—up to 250 nm of lateral size, 5-fold larger than the state-of-the-art (Fig. 1a). Additionally, we will show a mild scheme to exfoliate PTI with a high yield (Fig. 1b), and how to processes PTI nanosheets into thin films. Finally, we will demonstrate how to further grow the nanosheets that form the PTI films to close the intersheet gaps (Fig. 1c).

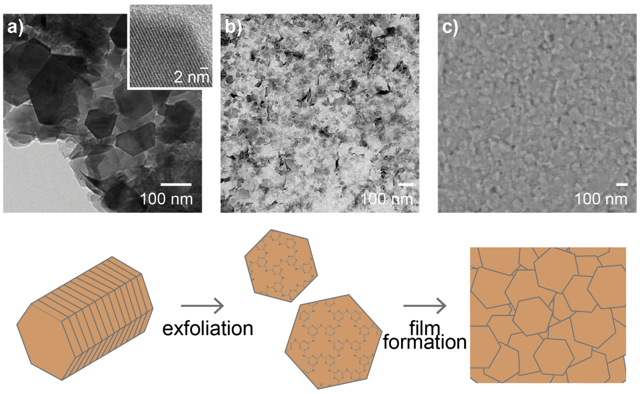

Figure 1. Processing of PTI crystals into nanometer thick-films. a) Transmission electron microscopy (TEM) image of the PTI crystals, inset shows a high-resolution TEM (HRTEM) image of a crystal; b) TEM image of the exfoliated PTI nanosheets; c) scanning electron microscopy (SEM) image of the surface of a PTI thin film.

PTI membranes of exfoliated sheets are expected to outstand in several separations; ab-initio simulations show that exfoliated PTI is extremely promising for H_2/N_2, H_2/CH_4, O_2/N_2, CO_2/N_2 & CO_2/CH_4. Moreover, PTI is an extremely stable material that can withstand acidic and basic environments[3], and temperatures of up to 600 °C[4]. This opens up the possibility of using PTI films for H^+ and OH^- transport in electrolytic cells, and to recover H_2 directly from the effluent of the steam reforming without having to cool it down.

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Current Collectors from Earth-Abundant Elements for Aluminum Chloride-Graphite Batteries

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[1]ETH Zürich, [2]EMPA

In the search for low-cost and large-scale stationary storage of electricity, non-aqueous, aluminum chloride-graphite batteries ($AlCl_3$-GB) receive a great deal of interest owing to the natural abundance of its primary constituents and substantially high energy densities. While notable recent advances in performance of $AlCl_3$-GB have been accomplished through the studies of various graphite cathode materials, further progress of this technology fully relies on finding oxidatively stable earth-abundant current collectors in chloroaluminate ionic liquid. This study presents a fully abundance concept of $AlCl_3$-GB with TiN as earth-abundant current collector which can be fabricated by utmost simple and inexpensive scalable technique such as magnetron sputtering whether on stainless steel or flexible polyimide substrates to be used in coin- or pouch-type cell configuration. Comprehensive characterization of TiN current collector by cyclic voltammetry and XPS spectroscopy means revealed its high oxidation stability of 2.5 V *vs.* Al/Al^{3+}. $AlCl_3$-GB with TiN current collector were characterized by high coulombic efficiencies of 99.5%, high power density of 4500 W kg^{-1} and stable cyclic stability for at least 500 cycles. In view of abundancy, high electronic conductivity and production scalability of TiN as current collector, this work provides further impetus for commercialization of $AlCl_3$-GB.

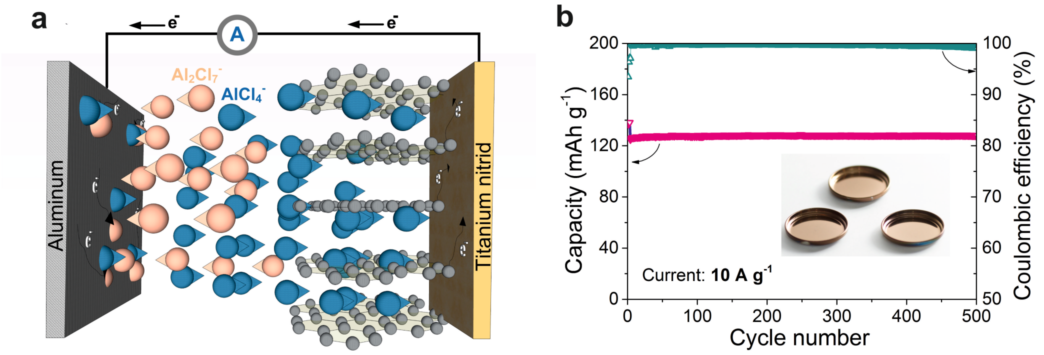

Figure. An aluminum chloride-graphite battery with TiN current collector. (a) schematics of the charging process of Kish graphite flake, and (b) cyclability of kish graphite flakes measured by a CCCV protocol at 10 A g^{-1} using $AlCl_3$:EMIMCl ionic liquid (r = 2) (first three cycles measured at 0.05 A g^{-1}); Insert in (b): the photograph of TiN current collector.

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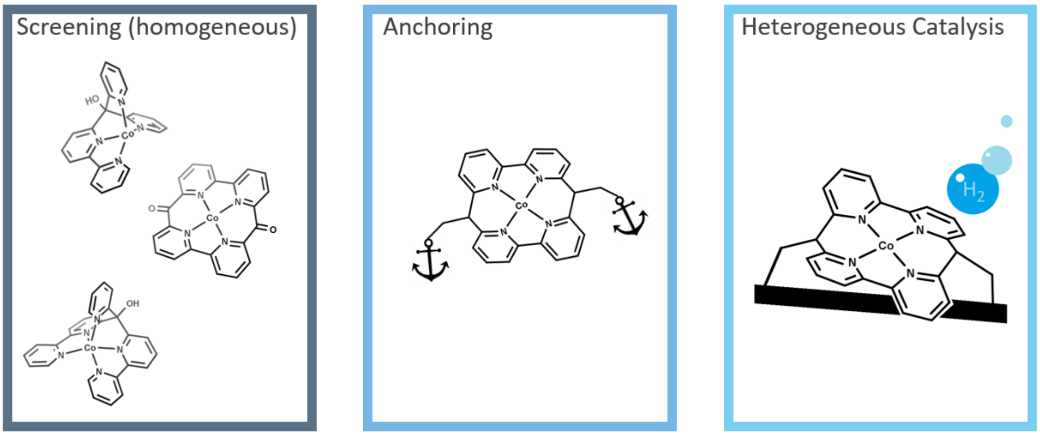
Synthesis Towards Heterogeneous Cobalt Water Reduction Catalysts

N. Weder[1], B. Probst[1], R. Alberto[1]*

[1]University of Zurich, Department of Chemistry, Win

Cobalt polypyridyl complexes have proven themselves as both, stable and efficient molecular water reduction catalysts. Especially ligand frameworks with more than one bipyridyl-moiety have drawn great attention, since their catalytic stability exceeds the ones of previous tetrapyridyl complexes by far.[1]

However, the major drawback of molecular catalysis is the requirement of a sacrificial electron donor, replacing the oxidative half reaction of the full water splitting system. Electron short-cuts from the reductive to the oxidative half reaction, which quench the water splitting, are inevitable in a one-pot, full-catalytic system. As a consequence, spatial separation of the two half-cells, connected via a light-harvesting, electron transferring site as well as a proton-permeable membrane circumvent this issue, however, require the molecular catalysts to be adsorbed on a semi-conducting surface.



In this context, we are developing different cobalt coordinating ligand frameworks suitable for adsorption on different surfaces. Starting from macrocyclic polypyridyl ligands, suitable reaction sites are modified by phosphate or thiol anchor groups, which both have been found to adsorb well on TiO_2 or gold electrodes, respectively. A very straightforward synthesis of a stable, active and most of all *cis*/*trans* isomeric pure cobalt complex with two phosphate anchor groups is presented.

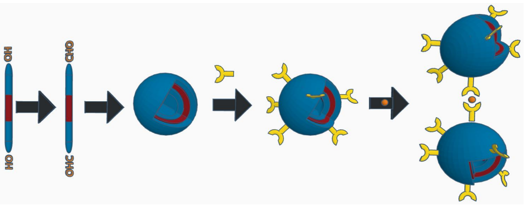
[1] S. Schnidrig, C. Bachmann, P. Müller, N. Weder, B. Spingler, E. Joliat-Wick, M. Mosberger, J. Windisch, R. Alberto, B. Probst

Functionalized surfaces: Interfacing electronic components with artificial organelles

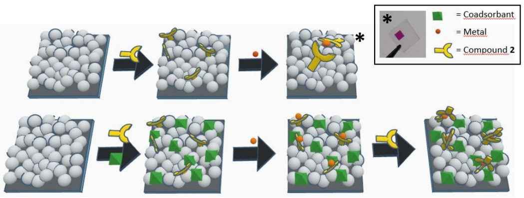
A. Wiesler[1], I. A. Dinu[1], M. Garni[1], S. Stolarov[1], C. E. Housecroft[1]*, E. C. Constable[1], C. G. Palivan[1]

[1]Department of Chemistry, University of Basel

We exploit the ability of tpy ligands to form stable complexes with metal ions by attaching a tpy domain to the hydrophilic part of an amphiphilic di- or triblock block copolymer. These modified polymers are self-assembled into nanostructures with the tpy domains pointing outwards. Upon addition of a metal ion, a M(tpy)2-complex forms, zipping together the nanostructures. Depending on the metal, this process can either be reversible or irreversible.



The outlined project is a collaboration between the Housecroft and the Palivan research groups, in which we aim to lay down predetermined patterns of reaction containers on a surface. The containers are, essentially, models for cells. The Palivan group`s expertise is in the combination of amphiphilic block copolymers, that have the ability to self-assemble into different nanostructures, e.g. micelles, vesicles, worm-like structures with active compounds. Within the NCCR, we combine this with our expertise in coordination chemistry, synthesis of functional ligands and on-surface to produce functionalized surfaces for platforms in molecular factories.



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Transition Metal Polypyridyl Complexes as Electrolytes in Combination with Copper(I) Dyes in Dye Sensitized Solar Cells

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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 transition metal complexes, e.g. 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 for example 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 transition metal electrolytes whilst optimizing the concentration, solvent and changing the additives of the electrolyte.

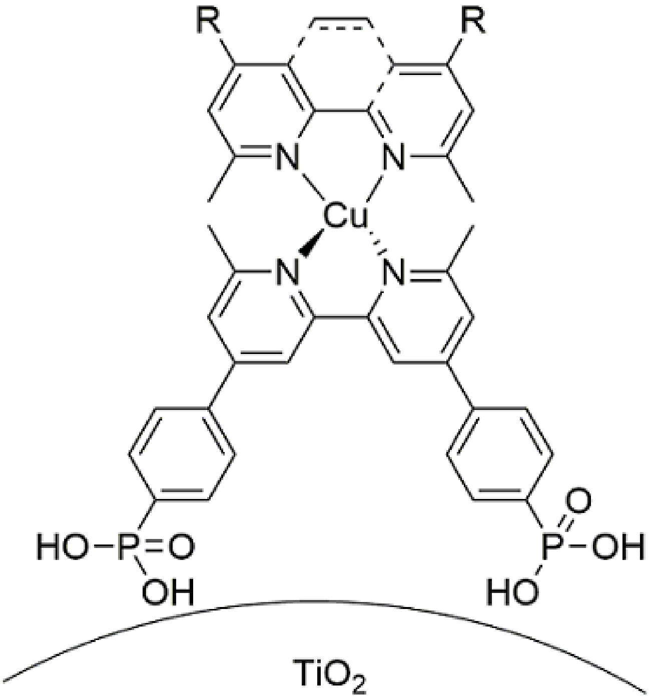

Figure 1: Cu(I) dye adsorbed on semiconductor surface for solar energy conversion

Disordered dolomite mesocrystals: Direct synthesis from solution at ambient temperature and pressure

J. Xto[1,3], D. Huachuan[2], C. Borca[1], J. A. van Bokhoven[3], T. Huthwelker[1]

[1]Paul Scherrer Institute, [2]EPFL Lausanne, [3]ETH Zürich

Disordered dolomite and very high magnesium calcites are major constituents of Holocene sediments of numerous hypersaline lagoons like Lagoa Vermelha, Rio de Janeiro, Brazil [1]and continental playa lakes of south east Australia[2]. Despite the fact that disordered dolomites precipitates in these environments at ambient conditions, it has been enigmatic to synthesis them in the laboratory. Understanding the nucleation conditions and mechanism is pertinent in geochemistry and sedimentary geology because dolomite rocks are linked to petroleum, aquifers and a variety of base metal deposits.

With an aim of linking inorganic solution chemistry to the nucleation of very high magnesium calcite and disordered dolomite, we did a systematic study on the influence of pH, carbonate concentration and total effective concentration at magnesium: calcium ratio of ~5:1 approximately the prevailing ratio in most oceans. Based on our experiments, we were able to identify conditions favouring the formation of disordered dolomite mesocrystals under ambient conditions. Further, through in situ X-ray absorption spectroscopy we could infer that the formation mechanism of magnesium calcium carbonates occurs via the formation of a metastable amorphous phase.

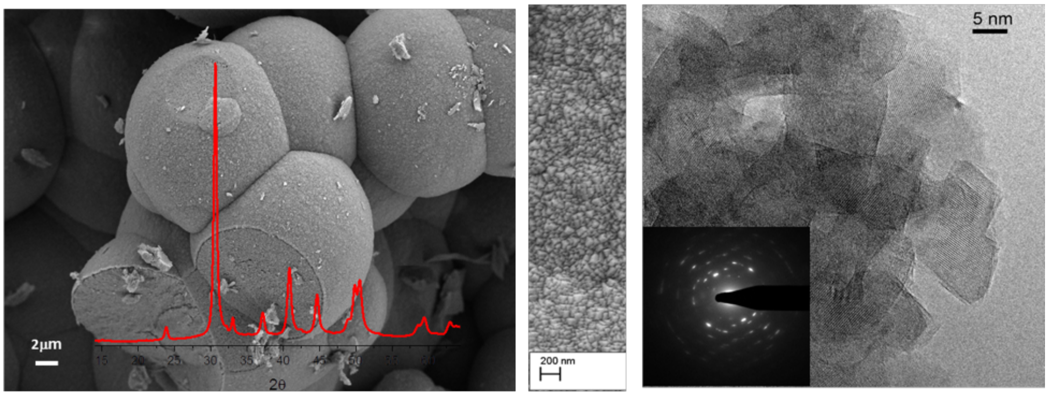

Figure 1: disordered dolomite mesocrystals

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

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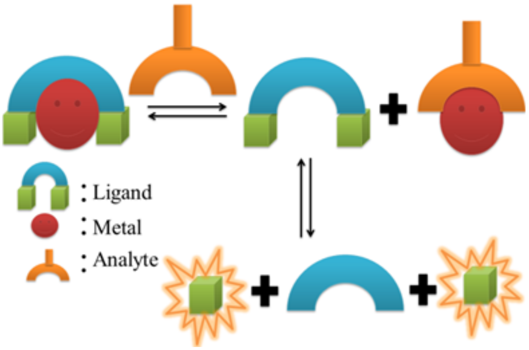
A stimulus-induced disassembly approach is presented for detection of analytes in living cells[1]. Particularly, we demonstrate that Fe^{III} salen complexes fluorometrically detect endogenous pyrophosphate (PPi), an important diagnostic marker for cancer and many other diseases. [1-4] In our approach, PPi sequesters the Fe^{III} centre from the salen complex and the "unlocked", metal-free ligand then subsequently hydrolyses into its molecular subunits ethylenediamine and salicyaldehyde. Initially, the intrinsic fluorescence of the salicyaldehyde subunit is quenched by the paramagnetic metal ion, but turns on back during the disassembly of the complex.



Our group studies how structural modifications in the design of the ligand affect solubility, reactivity, selectivity and the quantum yield of the complex.

Acknowledgement: The project has been assisted by SNF Funding (200021_169216) and CMSZH Graduate School (UZH).

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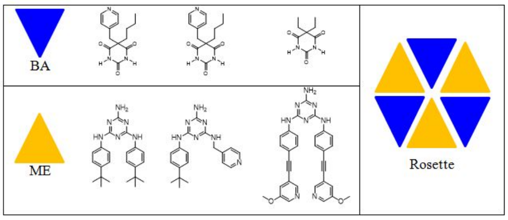
Hydrogen Bonded Metalla-Assemblies

F. ZHANG[1], B. Therrien[1]

[1]Université de Neuchâtel

style="text-align: justify;">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-bond can be modified by combining several hydrogen bonds in the same unit, like in the melamine•cyanuric/barbituric acid rosette-type system.[1] Arene ruthenium metalla-assemblies have showed a great biological potential.[2,3] Inspired by the combination of hydrogen bonding and metal complexation from the group of de Mendoza,[4] we have recently prepared a series of hydrogen bonded metalla-assemblies.[5,6] Therefore, to further investigate hydrogen bonded metalla-assemblies, we used the melamine/barbituric rosette-type system with piano-stool complexes or dinuclear metalla-clips. The introduction of a pyridyl group on the barbituric acid moiety or the melamine moiety allows coordination of metals at the periphery of the rosette.



New rosette-type metalla-assemblies have been prepared and characterized. Neutral and cationic trinuclear rosette-type metalla-assemblies have been synthesized, [7] as well as hetero-hexanuclear rosette-type metalla-assemblies.[8] Coordination of dinuclear metalla-clips have produced cationic hexanuclear metalla-assemblies. Overall, rosette-type assemblies with piano-stool complexes offer great opportunities in the field of supramolecular chemistry.

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CHIMIA

CHIMIA 2018, Volume 72
ISSN 0009-4293
www. chimia.ch
Supplementa to Issue 7-8/2018

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From High-Valent Iron Nitrides to a Pentad of Low-Valent Iron Nitrosyls

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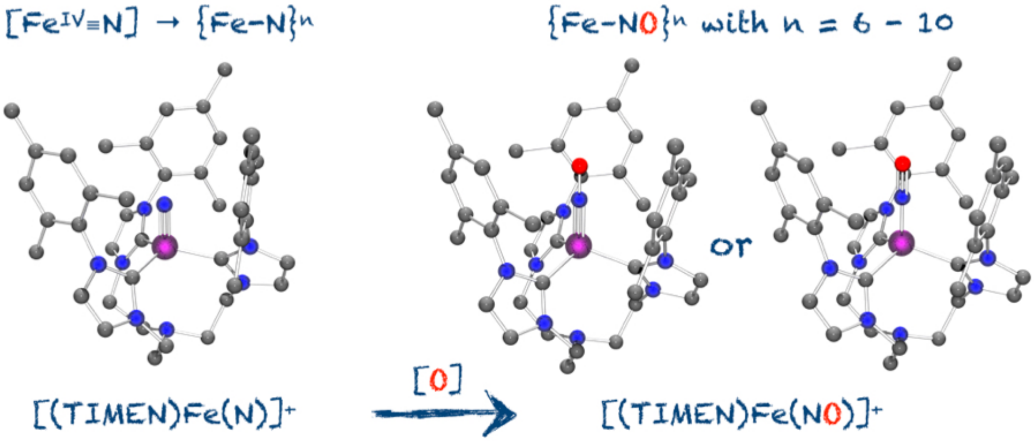
We present our work on the synthesis and reactivity of iron nitrido and nitrosyl complexes. First, we briefly discuss our work on Fe(IV) and Fe(V) nitrido complexes, synthesized *via* photolytic azide cleavage and N_2 evolution. In these complexes, the nitrido ligand is stabilized by sterically encumbered, tripodal tris-*N*-heterocyclic carbene chelates. Based on the iron nitrido complex $[(\mathrm{TIMEN})\mathrm{Fe}^{IV}(\mathrm{N})]^+$, we then address the question to what extent the complexes' electronic and structural properties change when – formally – atomic oxygen is added to the nitrido ligand; thus, transforming a high valent metal nitrido to a low valent metal nitrosyl complex.



This discussion was initialized by Bendix & Wieghardt in 1998,[1] who – similar to the Enemark & Feltham $\{\mathrm{Fe–NO}\}^n$ nomenclature for nitrosyl species – had proposed an analogous approach for nitrido complexes, using the $\{\mathrm{M–N}\}^n$ formalism, where n is the number of d-electrons in the diatomic unit if the N^{3-} ligand is considered a two-electron donor. Formally, the transformation of $\{\mathrm{Fe–N}\}^4$ to $\{\mathrm{Fe–NO}\}^6$ or $\{\mathrm{Fe–NO}\}^{10}$ would have to be considered a two- or even six-electron reduction, which is expected to be associated with striking structural changes. Accordingly, and independently, a series of iron nitrosyl complexes $[(\mathrm{TIMEN})\mathrm{Fe}(\mathrm{NO})]^m$ (m = 3+ to 1–) was synthesized. Treatment of coordinatively unsaturated $[(\mathrm{TIMEN})\mathrm{Fe}]^{2+}$ with NOBF_4 yielded the corresponding $\{\mathrm{FeNO}\}^6$ precursor complex. Subsequent reduction with Zn, Mg, and Na/Hg gave access to $\{\mathrm{FeNO}\}^7$, $\{\mathrm{FeNO}\}^8$, and $\{\mathrm{FeNO}\}^9$, respectively. Finally, reaction of $\{\mathrm{FeNO}\}^9$ with the electride $\mathrm{Cs}(18\text{-crown-}6)_2 \bullet e^-$ provided the highly reduced $\{\mathrm{FeNO}\}^{10}$. All new compounds were thoroughly characterized, including X-band EPR and VT-VF ^{57}Fe Mößbauer spectroscopy as well as by SQUID magnetization, electrochemistry, and single-crystal X-ray diffractometry; except for the $\{\mathrm{FeNO}\}^{10}$, for which a solid-state structure remains elusive (as of now). The study was complemented with computational analyses to provide insight into the electronic structure of the currently most complete series of iron nitrosyl complexes with an $\{\mathrm{FeNO}\}^{6–10}$ core unit.

[1] J. Bendix and K. Wieghardt *et. al.*, *Inorg. Chem.*, **1998**, *37*, 1767–1775.

Electrophoretic nuclei assembly: A versatile and reproducible crystallization chemistry for the synthesis of intergrown polycrystalline membranes

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The development of a robust crystallization process for the synthesis of defect-free inorganic films is highly attractive for many applications including electro- and photo-catalysis, sensors, membranes, etc. An ideal crystallization chemistry for the synthesis of polycrystalline films should allow one to synthesize defect-free film with an independent control on the heterogeneous nucleation and growth, allowing morphology engineering (grain-size, film thickness, orientation, etc.) while eliminating pinhole defects. Here we report the development of one such crystallization method, which we refer to as electrophoretic nuclei assembly for crystallization of highly-intergrown thin-films (ENACT), for the synthesis of high-quality metal-organic frameworks (MOF) films, in particular, zeolite imidazole frameworks-8 (ZIF-8) films and membranes.[1] ZIFs are one of the most promising class of materials due to their high chemical and thermal stability, large surface area and a rich host-guest interaction (e.g. molecular sieving) owing to their sub-nanometer pores.[2] The general approach for synthesizing pinhole-free, intergrown polycrystalline membranes is by decoupling the nucleation and growth steps. Critical to the success of this route is a high-density of heterogeneous nucleation, which is typically realized by modifying the substrate. However, this complicates the crystallization and reduces the versatility of the approach. In this context, our ENACT approach is simple and highly reproducible.[1] A high-density of uniform heterogeneous nucleation is obtained by electrophoretic deposition, where nuclei size and density is controlled by nuclei induction time, and electrophoretic assembly parameters. Highly intergrown, ultrathin, crack free ZIF-8 membranes are obtained after the growth stage with a remarkably high H_2 permeance of 8.3 x 10^{-6} mol m^{-2} s^{-1} Pa^{-1} and ideal gas selectivities of 7.3, 16.2, 2655 for H_2/CO_2, H_2/CH_4 and H_2/C_3H_8 respectively. Furthermore, by controlling the Ostwald ripening, an unprecedentedly high H_2/C_3H_8 ideal selectivity (greater than 8000) and C_3H_6/C_3H_8 mixture selectivity of 40 is realized. The versatility of the current approach is demonstrated by growing ZIF-8 films on a range of substrates (ceramic, polymer, metal, carbon and graphene) as well as by extending the process for the synthesis of ZIF-7 and UiO-66 films.

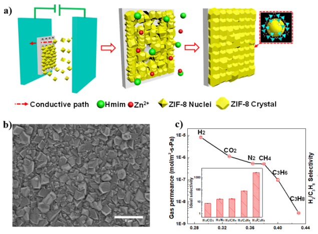

Figure 1. Schematic illustration of the electrophoretic process for the synthesis of ZIF films. b) SEM image of highly-intergrown ZIF-8 film c) gas permeances and ideal selectivities as a function of the gas kinetic diameter for the ZIF-8 membrane at 25°C

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NMR Chemical Shift Analysis Predicts Olefin Oligo- and Polymerization Activity of d^0 Group 4 Metal Complexes.

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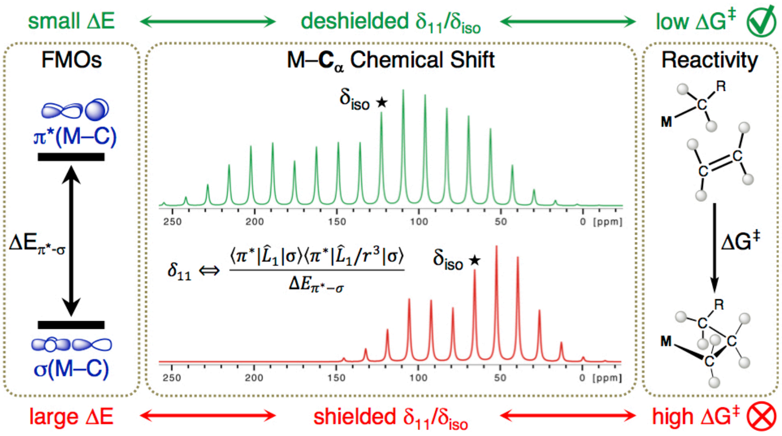
d^0 Metal alkyl complexes (M = Ti, Zr, and Hf) show specific activity and selectivity in olefin polymerization and oligomerization depending on their ligand set and charge. Here, we show by a combined experimental and computational study that the ^{13}C NMR chemical shift tensor provides a powerful tool for rationalization and prediction of the activity of these compounds towards olefin insertion. In particular, the ^{13}C NMR chemical shift tensors of the α-carbon of metal-alkyls, that undergo olefin insertion, signal the presence of partial alkylidene (double bond) character in the metal-carbon bond, which facilitates this reaction. The alkylidene character is traced back to the π-donating interaction of a filled p-orbital on the alkyl group with an empty low-lying metal d-orbital of appropriate symmetry. This molecular orbital picture establishes a connection between olefin insertion into a metal-alkyl bond and olefin metathesis, and a close link between the Cossee-Arlmann and Green-Rooney polymerization mechanisms. This further provides evidence that olefin insertion and olefin metathesis are in fact isolobal reactions. The ^{13}C NMR chemical shifts, the α-H agostic interaction, and the low activation barrier of ethylene insertion are therefore the results of the same orbital interactions, thus establishing chemical shift tensors as a descriptor for olefin insertion.



Relation of frontier molecular orbitals, chemical shift, and reactivity towards olefin insertion into metal-carbon bonds.

Carbene- rather than Nitrogen-metal bonding mode alters metallo-enzymes features

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In metalloenzymes, histidine is typically assumed to bind to the metal via a nitrogen atom. Tautomerization to a carbon-bonding mode requires only little structural modifications, yet C-bonding substantially alters the reactivity of the metal center. Here we investigated the azurin from *Pseudomonas aeruginosa*,[1] a small T1-type copper protein, as a model enzyme to demonstrate for the first time the implication of such C-bonding by using an N-heterocyclic carbene as a surrogate for C-bound histidine, which cannot tautomerize back to the N-bonding mode.[2] We have recently obtained evidence that replacing a histidine in a mutant azurin, with an extraneous carbene ligand markedly facilitates redox processes. The carbon coordination to the copper has been unequivocally determined by EPR with a ^{13}C-labelled carbene.

Such C-bonding of histidine should be considered for other redox-active metalloenzymes, therefore a similar approach was then taken for the nitrite reductase (NiR) from *Alcaligenes faecalis*,[3] an active enzyme with an azurin-like copper centre and the ability to catalyse the reduction of nitrite to nitric oxide.[4] Thus, as well as by spectroscopic and electrochemical analysis, the carbene-metal coordination can be monitored from a catalytic perspective. The H145G variant of the enzyme was used to generate the copper-carbon coordination stabilised by an exogenous NHC ligand in order to evaluate the effect on the enzyme catalytic efficiency. Although the activity was lower than the WT NiR, the mutant rescued with NHC showed a three-fold increase when compared to the H145G variant, similarly to what was observed when imidazole is used as exogenous ligand. This confirms that C-bonding of His in copper proteins may be indeed a more general feature which has been completely overlooked in the past.

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Glucose conversion with metal-organic frameworks in water

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Carbohydrate conversion is an essential technology for the widespread production of sweeteners, health-care intermediates and biofuels. Glucose-to-fructose catalytic isomerization is extensively studied in the literature to date overcoming 50% yields. In contrast, glucose-to-mannose catalytic epimerization is limited by 10% yields and still requires optimization, being, in most cases, a side process of a fructose formation. Most epimerases are only active on sugars substituted with phosphate or nucleotide groups, thus drastically restricting their use. In a contrast, MOFs represent an ideal platform for developing efficient and selective catalysts for carbohydrate isomerization and epimerization that overcomes the main disadvantages of currently employed enzymatic systems.

Herein, we present a series of stable MOF-based catalysts with highly reactive Lewis acid sites such as Zr(IV) and Hf(IV), which are capable to promote the selective conversion of sugars. As an example, a porphyrin-based Zr-MOF showed selective conversion of glucose to mannose in water, reaching 20% yields with over 70% selectivity, the highest value observed to date (Figure 1).

Exploring the chemistry of these materials, we aim to refine the catalytic performance of MOFs by varying pore size/shape and surface functionality of these solids. Further, given the complex nature of these materials, we carry out structure-property correlations using in-situ IR and solid state NMR spectroscopy to help understand how minor changes in the framework structure direct the materials catalytic activity. We aim to unveil mechanisms associated with these chemical transformations and hence promote the advancement of MOFs in the bio-refining processes for continuous MOFs design and future commercialization.

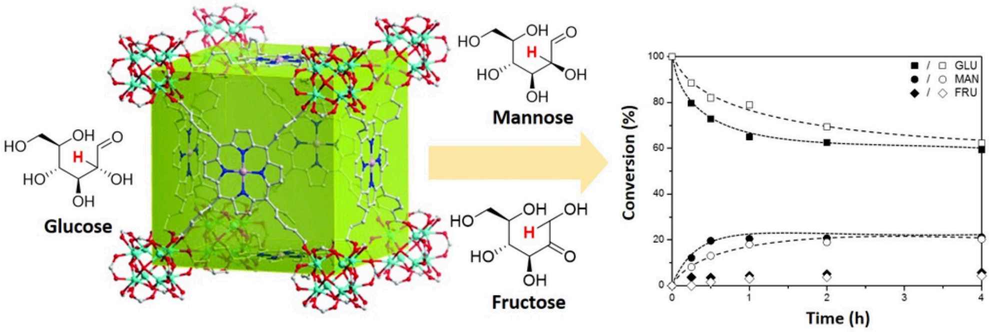

Figure 1. Zr-MOF-catalyzed glucose conversion to mannose and fructose.

Designing ultra-stable and highly crystalline two-dimensional organic networks based on calixarenes

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Two-dimensional (2D) organic thin films, fabricated with molecular precision via bottom-up methods, are highly attractive as functional surfaces to investigate host-guest interactions in a wide range of applications.[1] Recently, we reported the first crystalline 2D metal organic coordination network of a complex amphiphile, i.e. 5,11,17,23-tetra-carboxy-25,26,27,28 tetrapropoxycalix[4]arene (**1**) and a copper metal node at the air-liquid interface.[2] In this lecture, we show the first reported two-dimensional supramolecular organic network stabilized via only weak dipole-dipole interaction. Herein we replaced the carboxy groups of **1** with methyl cyano functional groups; i.e. *p*-methyl cyano-calix[4]arene (**2**). In absence of any organic/inorganic linkers, macromolecules of **2** form a free-standing and crystalline 2D supramolecular organic network.[3] Using the Langmuir balance and Brewster angle microscopy, we studied the interfacial behavior of amphiphiles at the air-liquid interface. The crystalline 2D organic networks were successfully transferred, with a transfer ratio of ~1, from the interface onto a solid substrate. Characterization of the transferred monolayers onto solid substrates have been carried out by means of atomic force microscopy (AFM), surface ellipsometry, contact angle measurements, transmission electron microscopy, *X*-ray photoelectron and near-edge *X*-ray absorption fine structure spectroscopy.

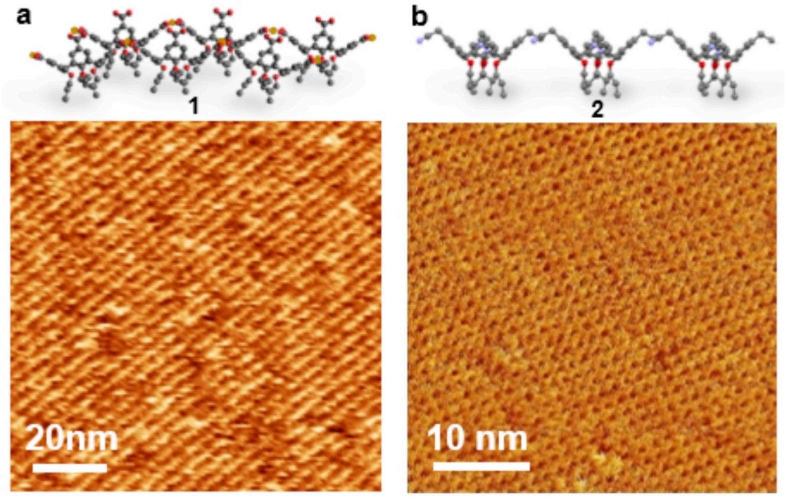

Figure 1. AFM images of the crystalline self-assembled networks of **1** (**a**) and **2** (**b**) and the corresponding molecular models.

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Insights on the $Pd(OAc)_2$/XPhos Catalytic System

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[1]Janssen R&D, Discovery, Product Development and Supply, Cilag AG, Hochstrasse 201, 8205 Schaffhausen, Switzerland, [2]PASTEUR, Département de Chimie, École normale supérieure, PSL University, Sorbonne Université, CNRS, 75005 Paris, France, [3]Janssen R&D, Discovery, Product Development and Supply, Turnhoutseweg 30, 2340 Beerse, Belgium, [4]Swagscha@its.jnj.com, anny.jutand@ens.fr, laurence.grimaud@ens.fr

Understanding the nature of the intermediate species operating within a palladium catalytic cycle is crucial to develop efficient cross-coupling reactions. The XPhos/$Pd(OAc)_2$catalytic system has found numerous synthetic applications, however, the nature of the active catalytic species remains elusive. An XPhos-ligated Pd(0) has been detected and characterized *in situ*for the first time using cyclic voltammetry and NMR techniques. This study also sheds light on the formation of a Pd(I)-Pd(I) dimer and an overall mechanism of the active species formation is proposed. Finally, a kinetic study probed a dissociative mechanism for the oxidative addition of XPhos-ligated Pd(0) with aryl halides.[1]

[1] S. Wagschal, L. A. Perego, A. Franco-Espejo, C. Tocqueville, J. Albaneze-Walker, A. Jutand, L. Grimaud, *Manuscript in preparation*.

Photoinduced Long-range Electron Transfer Across ortho-oligo-Phenylenes

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Long-range electron transfer plays a crucial role in many naturally occurring processes, such as photosynthesis.[1] Due to its importance and complexity, researchers strive to find simple model systems that can undergo photoinduced electron transfer to study charge separation with time resolved measurements. In this regard, many donor – bridge – acceptor compounds were prepared and their electron transfer properties characterised.[2]

In this presentation the first set of molecular dyads with a bridging unit made of 2 – 6 *ortho* -phenylenes, a Ru(II) chromophore and a triarylamine (TAA) electron donor moiety shall be introduced. The photoinduced forward as well as the thermal backward reaction were investigated with time resolved laser spectroscopy. It will be shown that these new bridges mediate electron transfer even better than their *para*-relatives. This is reflected in the very low β value that is the so called distance decay parameter. The value is as low as 0.04 Å^{-1}, whereas known *para*-phenylene connected systems have β-values between 0.4 – 0.8 Å^{-1}.[2]

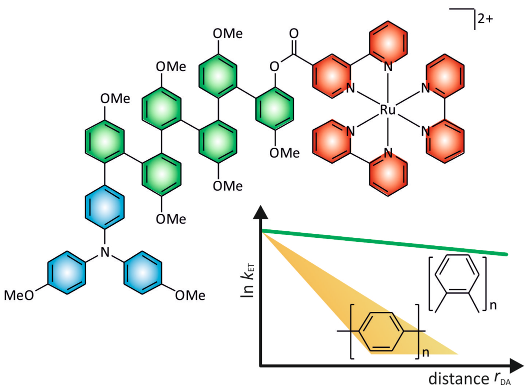

Figure 1 Top: Longest dyad investigated in this study. Bottom: Electron transfer rates of *para* -phenylene bridged systems versus the donor acceptor distances (yellow cone) in comparison to the herein presented *ortho*-phenylene system (green line).

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Porous Molecular Networks from Dative B-N Bonds

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Porous networks constructed with supramolecular interactions benefit from self-healing properties, alongside other properties (rheology, hydrolytic stability, permeability etc.) that can be directly addressed by the electronic tuning of bonding interactions. Previous examples of networks formed through dative B-N bonds have been shown to rapidly collapse following solvent removal, rendering them non-porous regardless of any crystallographically observed channels or cavities. Here, we demonstrate the use of imidazole adducts as N-donors to increase B-N bond strength (Figure 1a), which, in combination with suitable boronate esters, affords networks with high surface areas (up to 420 m^2g^{-1}). A systematic study revealed that the measured surface area is dependent on the chelating angle and length of the imidazole ligands used, whilst modification of the geometry / valency of the ligands resulted in the first examples of well-defined three-dimensional polymers from B-N bonds (Figure 1b), as well as n-fold interpenetrated two- and three-dimensional networks (Figure 1c).

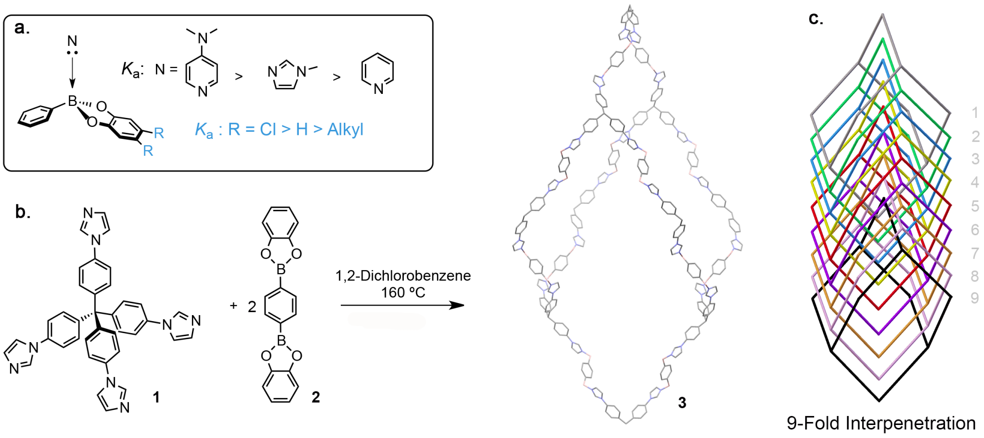

Figure 1 – (**a**) Factors influencing the strength of B-N bonding. (**b**) The self-assembly of 3D network from BN Bonds (catechol and protons are omitted from the crystal structure). (**c**) Representation of the interpenetration displayed by the network.

$Au_{25}(SR)_{18}$ cluster assembly in multiple dimensions

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Designing new generations of superstructures by controlled self-assembly of nanosized objects has great potential in applications such as molecular electronics or sensors.[1] Monolayer protected gold clusters are optimal building blocks due to their well-defined structure, high stability and unique size-dependent characteristic.[2] Formation of superstructures without modification the original clusters structure could however be a challenging task. Ligand exchange reactions are a valuable solution for this problem. It involves the replacement on the $Au_n(SR)_m$ cluster surface of one of the protecting thiol (ligand) with a new entering ligand SR'. As bridging agent rigid linear aryl dithiols were chosen, replacing two original protecting ligands. This dithiol is expected to create a conducting system, which allows communication between the covalently bonded $Au_{25}(SR)_{18}$ clusters.

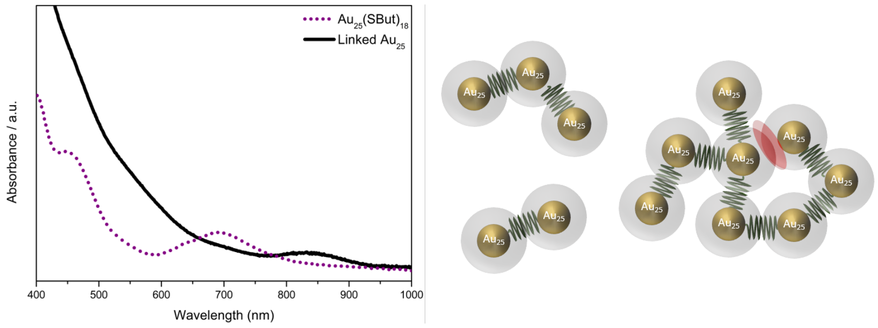

Figure 1: Absorption spectra of pure and linked $Au_{25}(SBut)_{18}$ clusters (left) and schematic representation of the linked clusters (right)

Several techniques (e.g. NMR and SAXS) confirmed a successful assembly into dimers, trimers and large networks of linked clusters, separated by a well-defined distance. The absorption spectra of these larger aggregates are drastically different from the original clusters, the former absorbing at lower energies. We ascribe this drastic change of the absorption spectra to the communication between the clusters in the aggregates through the aromatic linker. Additionally, the size of these aggregates could be reduced through the unlinking reaction, resulting in a shift of the absorption band in direction of the original Au_{25} spectrum. This formation of communicating clusters gives interesting perspectives for the creation of conducting two dimensional arrays. The development of these superstructures and their electrical properties could be an important step towards the use of well-defined metal clusters in molecular electronics.

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Guanidinium-formamidinium lead iodide: a layered perovskite-related compound with red luminescence at room temperature

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Hybrid layered perovskite-related lead halide compounds with a general formula $A_{n+1}Pb_nX_{3n+1}$ (A-monovalent cation, X-halogen ion) are under a focus of researchers due to their tunable optoelectronic properties and tailorable structures. The crystal structure of such compounds is made of perovskite layers consisting of corner sharing Pb-X octahedra, and large organic ammonium cations situated in the interlayer space (an isolating layer). To modify the thickness of slabs (n>1) a mixture of small and large cations is used where small cations, *i.e.* methylammonium (MA) would fill the voids within the layers. A use of rather compact interlayer cations leads to reduced volume of the interlayer space and to the reduction of the optical bandgap energy, as was previously shown on MA/G system and in our previous work on Cs^+/G system.[1,2] In our current study, we used highly symmetric guanidinium (G) cation that is not able to sustain a three-dimensional (3D) $APbI_3$ perovskite network, and a slightly smaller formamidinium cation (FA). G and FA cations are excellent donors of hydrogen bonds. We obtained a new compound where both G and FA are incorporated – $FAGPbI_4$. Its structure is composed of stair-like arranged layers of corner-sharing Pb-I octahedra, FA and G cations are situated in the interlayer space (Fig.1a).[3] $FAGPbI_4$ is luminescent at 298 K in red region under UV excitation (Fig.1b, c). The optical bandgap was estimated using the Kubelka-Munk function to be 2.32 eV. The purity of $FAGPbI_4$ was studied with powder X-ray diffraction, optical methods and ^{207}Pb ssNMR (Fig.1c). $FAGPbI_4$ is photoconductive and thermally stable up to 255 ℃.

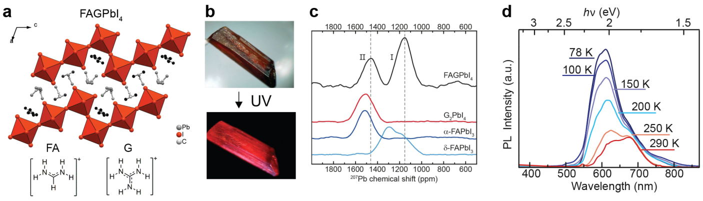

Figure 1. (a) Crystal structure of $FAGPbI_4$.(b) Photographs of a $FAGPbI_4$ crystal taken under day light and under UV illumination in dark. (c) ^{207}Pb ssNMR spectra. (d) Temperature-dependent PL spectra measurements performed on powdered crystals

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Derivatisation of $[Re(\eta^6-C_6H_5COOH)_2]^+$ Complexes for DNA-targeting

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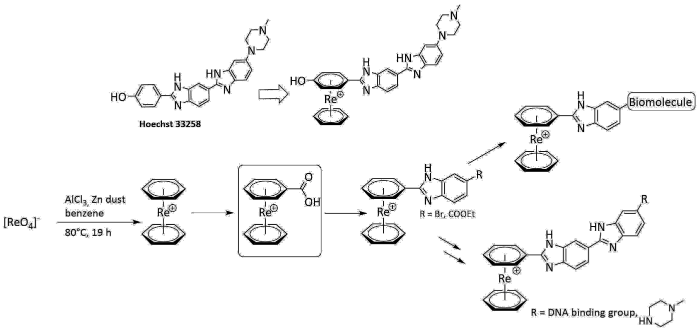
Cancer has become the disease with the highest mortality worldwide, therefore novel effective anticancer drugs with fewer side effects are urgently needed.[1] DNA has been established as a primary target for chemotherapeutic drugs by either intercalation between adjacent DNA base pairs or binding to the minor groove causing perturbation of the DNA structure.[2] The fluorescent Hoechst dyes (especially Hoechst 33258), containing two benzimidazole groups linked in a head-to-tail manner, bind specifically to AT-rich DNA minor groove sequences and were found to be effective inhibitors of mammalian DNA topoisomerase I.[3,4]

Functionalised transition metal bis-arene complexes ($[M(\eta^6\text{-arenes})_2]^{n+}$) are already used as precursors for numerous reactions with applications in different fields, including medicinal inorganic and bioorganometallic chemistry.[5]



In the search for new organometallic building blocks for imaging (^{99m}Tc) and therapy (Re) in the context of theranostics, this work focuses on the derivatisation of the sandwich type complex $[Re(\eta^6-C_6H_5COOH)_2]^+$ using the advantage of its high chemical stability and inertness towards oxidation and hydrolysis. The carboxylic acid groups represent a core feature for derivatisations with targeting moieties which can conveniently be introduced via amid bond formation.

New complexes with a connected benzimidazole moiety allow a prospective introduction of the Hoechst dye core to investigate the metal-containing behaviour of a Hoechst dye in DNA. Further-on, the compounds will be tested for their biological and physico-chemical behaviour.

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[2] A. Rescifina *et al.*, *Eur. J. Med. Chem.* **2014**, *74*, 95-115
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Small Molecule Activation at Multimetallic Uranium Nitrides

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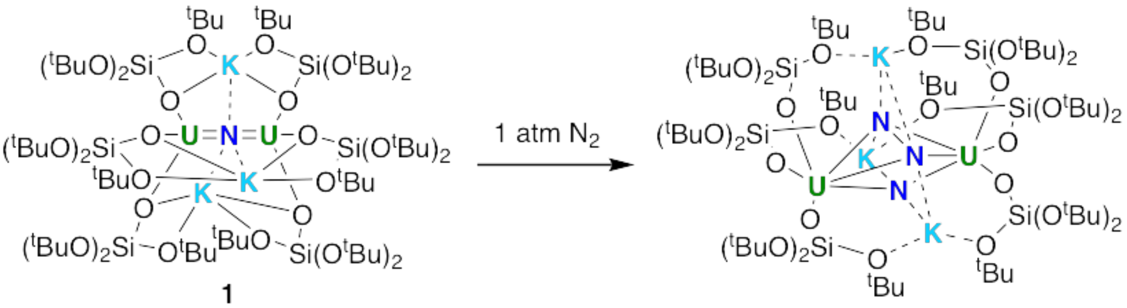
Uranium nitrides are attractive candidates for stoichiometric and catalytic N-transfer reactions, small molecule transformation, [1] and for advanced nuclear fuels.The N-C bond formation reactions are key steps in the construction of value-added chemical compounds. Recently we reported remarkable reactivity studies in f-element chemistry. Particularly desirable are the synthetic methods using cheap and available C_1feedstock such as carbon dioxide or carbon monoxide. [2] T*ert*-butoxysiloxides were shown to be very effective ligands in supporting the reactivity of low valent *f*elements with small molecules. [3],[4] In particular, it was recently reported the remarkable reactivity of the previously described nitride bridged diuranium(IV) complex $[Cs\{[U(OSi(O^tBu)_3)_3]_2(\mu\text{-}N)\}]$with CO_2, CS_2, and CO, yielding to diverse N-functionalized products. [5],[6] Moreover, very recent results show that increasing the electron density by reducing the metal centers leads to a multimetallic K_3UNU nitride bridged diuranium(III) complex, **1**(Figure 1) which shows extraordinary reactivity towards the dinitrogen molecule. The reduction and further functionalization of dinitrogen in ambient condition by a uranium nitride will be presented [7].



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