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Using Proximal Cations to Install Internal Electric Fields in Transition Metal

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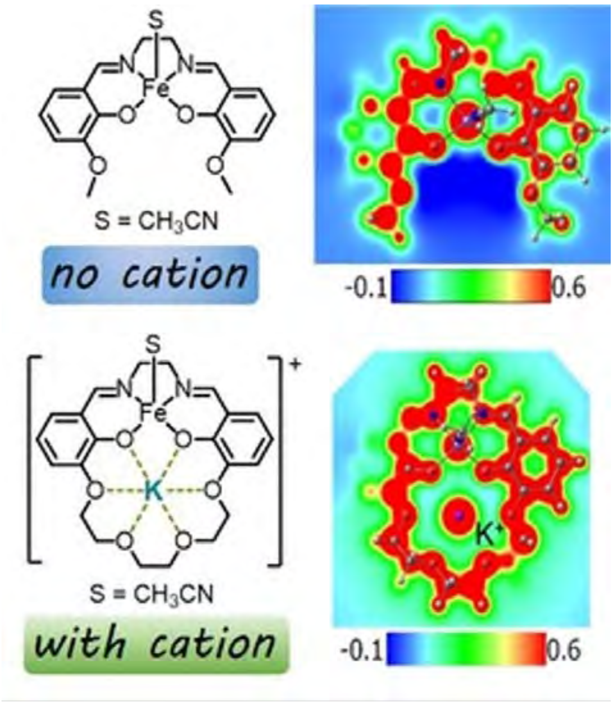
Non-redox active Lewis acidic metal cations play a key role in a diverse set of biological and synthetic transition metal complexes that mediate redox activity. One of their proposed roles in promoting reactivity is by tuning the redox potential of the reaction site. We investigated whether non-redox active cations engender this change through an inductive effect, which would change the electronic structure of the redox active cation, or through an electrostatic effect, which would uniformly shift the molecular orbitals on the redox active metal due to the electric field potential of the proximal cation. Our study, which utilized a Schiff base ligand with an appended crown-like functionality that incorporates a variety of alkali and alkaline earth metals, indicates an electrostatic effect is likely dominant. The effect of the electric field on reactivity and thermochemical properties will be discussed.



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Exploiting Cobalt(II) Amide Complexes in Deprotonative Metalation of Fluoroaromatic Molecules

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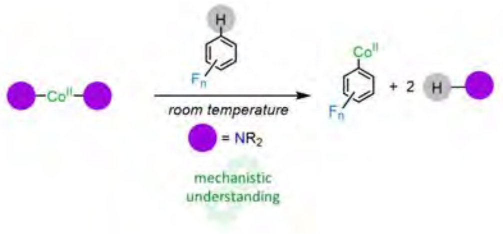
Fluoroaromatic compounds are increasingly heavily employed as scaffolds in agrochemicals and active pharmaceutical ingredients.[1] One of the most powerful methods for the incorporation of these molecules in more complex molecular scaffolds is deprotonative metalation. Typically these reactions have been the exclusive domain of group 1 and group 2 organometallics.[2] On the other hand, earth-abundant transition metals such as cobalt have shown excellent potential to selectively functionalize these molecules via C-H and C-F bond activation.[3]

Breaking new ground in this field, in this contribution, we present the synthesis and the reactivity potential of a new Co(II) amide complex. While deprotonation of fluoroarenes using conventional lithium bases can be challenging due to the exceptionally fragility of generated intermediates,[4] the cobaltation of a range of different fluoroarenes proceeds regioselectively enabling the isolation of Co-H exchange products while operating at room temperature.

Combining the isolation of key metalated intermediates with theoretical calculations, this work exploits the potential of a new Co(II) base in a field widely dominated by main group element complexes, opening up for possible future development of new chemical transformations in this area of research.



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Synthesis, Structure, Reactivity and Catalytic Activity of Octahedral Heteroleptic β-Diketonate Complexes of Molybdenum[1]

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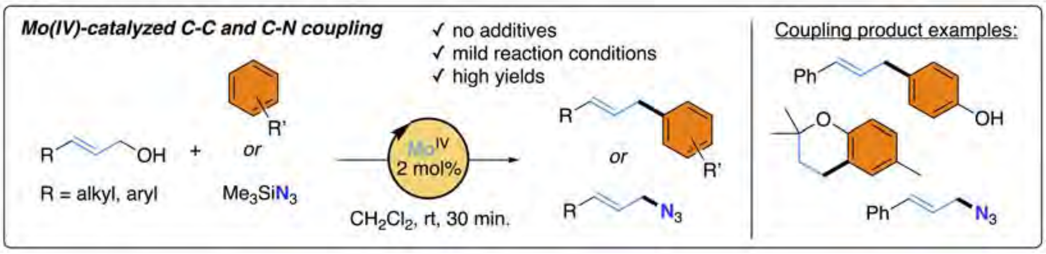
We present here the isolation, characterization and catalytic activities for C-C and C-N bond coupling of a new family of octahedral Mo(IV) compounds. In opposition to the well-developed π-allyl metal complex-based coupling reactions catalyzed by precious metals such as iridium and palladium,[2,3] molybdenum has found much fewer applications.[4,5] This stands in contrast to its earth abundancy, rich redox-chemistry, and capability to easily undergo metal-carbon bond formation and cleavage, rendering molybdenum an attractive choice for the development of new metal-based catalysts for a variety of different organic transformations.

We have optimized the preparation and fully analyzed a series of Mo(IV) bis-β-diketonate complexes.[6,7] Detailed solid- and solution state studies gave unprecedented insights into the geometry and coordination chemistry of these compounds, *e.g.* displaying solvent dependent dynamic equilibria involving *cis*- and *trans*-isomers in solution.

Reactivity and catalytic activity of the complexes were further explored, providing one of the most active and stable earth abundant metal-based molecular catalyst for the substitution of allylic alcohols by electron-rich carbon-centered nucleophiles (*e.g.* phenols). Reactivity studies involving the isolation of a catalytically active intermediate provided insights into the present mechanistic pathway.



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Cation assisted binding and cleavage of dinitrogen by uranium complexes

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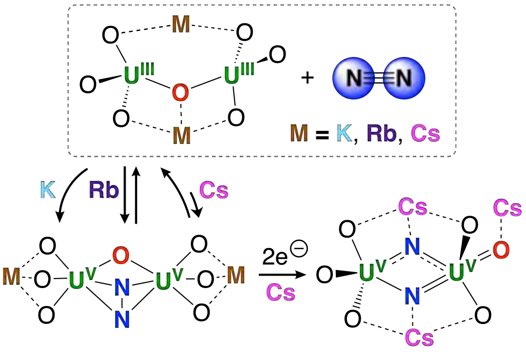
Dinitrogen (N_2) is a cheap and widely available molecule, however, its low reactivity complicates its use for the synthesis of high-added feedstocks. Notably, the industrial Haber-Bosch process uses N_2 to synthesize ammonia (NH_3), but requires harsh temperatures and pressures. Before the current Fe-based catalyst was implemented, uranium materials were reported to be highly effective in the transformation of N_2 into NH_3. Nevertheless, the N_2chemistry of uranium remains underdeveloped, with only a few examples of molecular uranium complexes that are capable of cleaving N_2 to nitridesupon addition of external reducing agent,[1-3] where uranium nitrides are considered important inrtermediates the Haber Bosch process. Recently, our group reported two bimetallic uranium(III) systems that were able to perform the four-electron reduction of N_2.[4,5] Moreover, we found that the N_2 bound in the bridging oxide system could be functionalized by addition of CO to yield a cyanamido complex, but the addition of acid or H_2 resulted only in the release of N_2.[5]

Here, we will present a series of alkali bound-oxo-bridged diuranium(III) complexes that provide a unique example of decreasing N_2 binding affinity with increasing cation size. We will show spectroscopic, electrochemical, and computational data, suggesting that the decreased reactivity is due to sterics rather than electronic effects. We also show that weak N_2 binding in ambient conditions does not prevent alkali assisted N_2 cleavage to nitride. Furthermore, we will present the first example of Cs-assisted dinitrogen cleavage by a metal complex.



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(Re)investigating ternary rare-earth β-diketonates complexes: making new insights out of old ones

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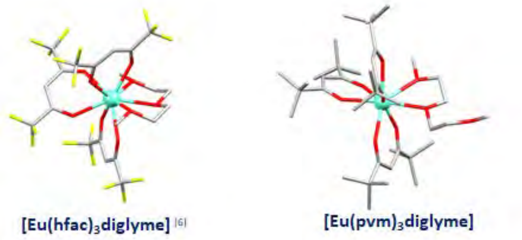
β-diketonates based rare-earth coordination complexes have enjoyed an expanding popularity ever since their discovery at the end of 19th century, which spans multiple applied research fields. Their multi-faceted chemical and physical properties have been successively harnessed for liquid extraction[1], bioanalytical imaging[2] as well as in light emitting devices[3]. Yet, the fast-paced development of rare-earth β-diketonates have at times been at the expense of in-depth solutions studies, undermining the trustworthiness of synthetic procedures as occasionally pointed out at in literature[4]. Within this context, our group dedicated efforts to describe the thermodynamic features of the association of [Ln(hfac)$_3$(diglyme)] precursors with different (single or multi-sites) N-heterocyclic tridentate receptors, in solution[5]. The study was subsequently extended to a new series of [Ln(β-diketonates)$_3$X] building-blocks (where X is a glyme), based on β-diketonates ligands displaying nuanced or contrasted electronic effects. A first part of the discussion will address the preparation of these new [Ln(β-diketonates)$_3$X] precursors, before assessing their structural, thermodynamic and luminescent properties. Then, the propensity of these precursors to form stable ternary complexes with a N-heterocyclic tridentate ligand will be considered.



[Eu(hfac)$_3$diglyme] [6]

[Eu(pvm)$_3$diglyme]

Figure 1. Crystallographic structures of selected [Ln(β-diketonates)$_3$diglyme] containers.

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Synthesis and Characterization of an Artificial Iron-Sulfur Metalloenzyme

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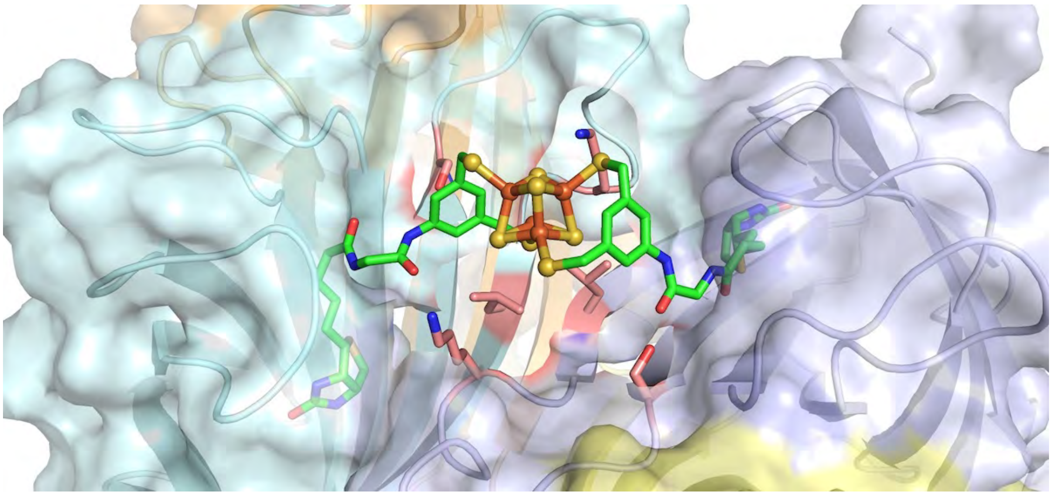
The study of synthetic iron-sulfur clusters has allowed elucidation of the molecular basis of the active sites of iron-sulfur proteins. Apart from their numerous biological activities, FeS-clusters have been utilized outside of their biological scaffold in an expanding number of areas such as biomimetic materials, redox mediators and catalysis. However, all of those active-site analogs suffer from poor solubility and limited stability in protic media. In order to bridge these synthetic and biological systems, we set out to synthesize an artificial iron-sulfur metalloenzyme by biotin-streptavidin technology. We have synthesized a bis-biotinylated-[Fe_4S_4] cluster (**$Biot_2$-Fe_4S_4** hereafter), which is, to the best of our knowledge, the first synthetic iron-sulfur cluster that is stable in aqueous solutions. Following the synthesis of the abiotic cofactor **$Biot_2$-Fe_4S_4**, it was anchored within homotetrameric streptavidin (Sav) to afford the artificial metalloenzyme **$Biot_2$-Fe_4S_4** · Sav, Scheme. Having these two systems at hand allowed us to scrutinize the effect of the second coordination sphere between the cofactor and the host protein. The influence of mutations in the binding pocket on the redox properties of the cluster was examined by cyclic voltammetry. Further, we evaluated the catalytic performance of **$Biot_2$-Fe_4S_4** and **$Biot_2$-Fe_4S_4** · Sav for CO_2-reduction to afford alkanes and found the protein environment to strongly affect the reactivity of the cluster.



Scheme: Close-up view of the docked model **$Biot_2$-Fe_4S_4** · Sav WT, close lying residues are highlighted as stick (flesh colour).

Toward CO_2-reduced Binders: Limestone Calcined Clay Cements with Improved Workability

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Limestone calcined clay cement (LC3) is one of the most promising ways to further reduce the clinker factor as it provides satisfying mechanical and durability properties compared to other (blended) cements. Clays are as well abundant, widely available, and don’t result in CO_2 emissions during their activation process besides the energy required to calcine and mill them. Moreover, cement composed with such materials doesn’t require high grade clay material and can therefore tolerate rather high amounts of impurities.

On the other hand, such materials usually come with very high specific surface area resulting in challenging rheological properties.

One of the goals of this work was to study and understand the reasons for the pronounced issue of loss of workability observed in the case of LC3 type of binders. It has been found that the intrinsic reactivity of the calcined clays leads to the formation of early aluminate hydrates, most presumably ettringite, and appears to be a major factor for the loss of workability.

At clinker replacement levels up to 30%, traditional superplasticizers are sufficient to extend the slump life. However, these superplasticizers prove much less effective for replacement levels reaching 50% and above, where the loss of workability is particularly distinct.

Nonetheless we found some carbohydrate derivatives being able to control the formation rate of these early hydrates, resulting in extended workability without dramatically affecting the strength development. Such approaches would enable the broader use of such novel binders and help decarbonize the construction sector.

Anticancer rhenium di- and tricarbonyl complexes and synthesis of new α-diimine rhenium dicarbonyl complexes

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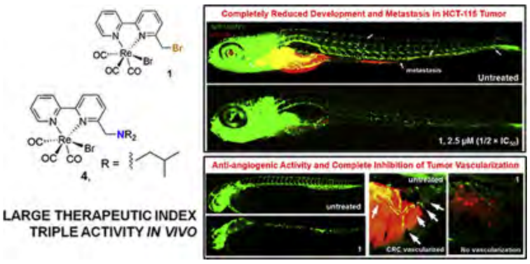
In our effort to discover novel selective and non-toxic agents effective against CRC, we synthesized a series of rhenium(I) tricarbonyl-based complexes with increased lipophilicity. Two of these novel compounds were discovered to possess remarkable anticancer, anti-angiogenic and antimetastatic activity in vivo (zebrafish-human HCT-116 xenograft model), being effective at very low doses (1-3 µM). At doses as high as 250 µM the complexes did not provoke toxicity issues encountered in clinical anticancer drugs (cardio-, hepato-, and myelotoxicity). In vivo assays showed that the two compounds exceed the anti-tumor and anti-angiogenic activity of clinical drugs cisplatin and sunitinib malate, and display a large therapeutic window.[1]



In another study, we reported a rhenium(II) dicarbonyl complex, which displayed better cytotoxicity against MCF-7 breast cancer cells than cisplatin.[2] We investigated later new synthetic routes to aerobically stable and substitutionally labile α-diimine rhenium(I) dicarbonyl complexes. The molecules were prepared in high yield from the *cis–cis–trans*-$[Re(CO)_2(^tBu_2bpy)Br_2]^-$ anion (where $^tBu_2$bpy is 4,4′-di-*tert*-butyl-2,2′-bipyridine), which could be isolated from the one electron reduction of the corresponding 17-electron complex. Ligand substitution of Re(I) complexes proceeded via pentacoordinate intermediates capable of Berry pseudorotation. In addition to the *cis–cis–trans*-complexes, *cis–cis–cis-* (all cis) isomers were also formed. $[Re(CO)_2(^tBu_2bpy)Br(L)]$ complexes may be considered as synthons for the preparation of a variety of new stable diamagnetic dicarbonyl rhenium *cis*-$[Re(CO)_2]^+$ complexes, offering a convenient entry in the chemistry of the core.[3]

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$[^{99m}Tc(\eta^6\text{-pharm})_2]^+$ synthesis with direct labelling of pharmaceuticals in water

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Sandwich complexes with unchanged pharmaceuticals are unprecedented in bioorganometallic or radiopharmaceutical chemistry. We recently prepared a larger series of homo- and hetero sandwiches with Tc with direct labeling of arene in water.[1]

We will now present the direct labelling of pharmaceuticals with ^{99m}Tc through η^6-coordination to phenyl rings and the confirmation of the structures with the rhenium homologues.[2] Pharmaceuticals with an arene and simple organic functions were first chosen such as carbazole and indole (unit presents in some anticancer drugs)[3, 4], 4-methoxyphenol (drug used in skin depigmentation), lidocaine (local anesthetic), but also more complexes drugs like lenalidomide (anticancer), erlotinib and gefitinib (tyrosine kinase inhibitor). (Figure).

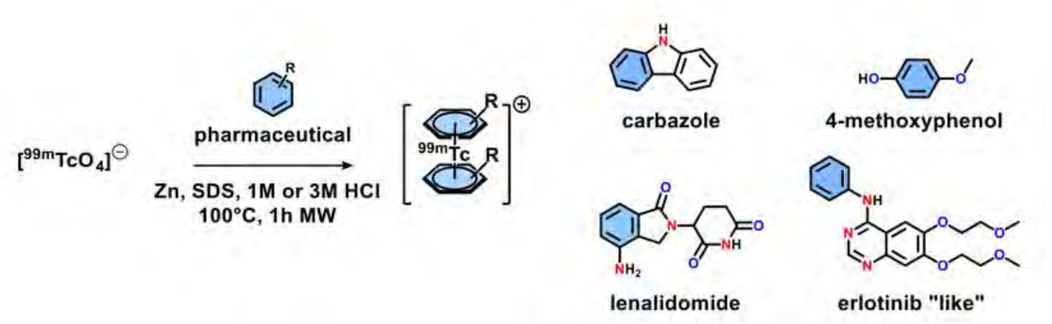

Figure. General scheme of the reaction towards $[^{99m}Tc\ (\eta^6\text{-pharm})_2]^+$.

Selected complexes display planar chirality since the two planes formed by the ligands are not equal; a feature that is very rare for rhenium or technetium if ever, but common for ferrocene or Ru-sandwich complexes.[1,5-7].

The direct labelling of pharmaceuticals with ^{99m}Tc through η^6-coordination to phenyl rings and the confirmation of the structures with the rhenium homologues opens a path into a wide variety of novel radiopharmaceuticals and molecular theranostics.

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Metal Amidinate Precursors for Easy Access to Supported Nanoparticles

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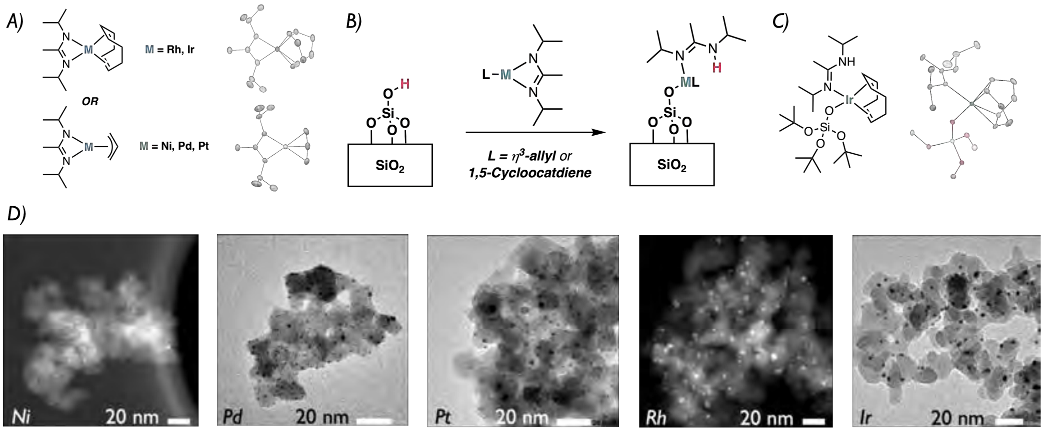
Platinum group metals (PGM) are of central importance in a variety of industrially relevant processes.[1] In most cases, the active phase is the metallic state, for instance in the form of colloidal nanoparticles, supported nanoparticles or thin films on a surface.[2]In order to establish meaningful structure activity relationships, a large research effort has concentrated over the years on the development of tailored organometallic or metalorganic precursors, that can be used for precise material synthesis, such as Atomic Layer Deposition (ALD) or Surface organometallic chemistry (SOMC).[3,4] Both of these methods require precursors that are stable during storage, yet reactive towards a specific surface functionality in a selective way, leaving no byproduct upon thermal/gas treatment. The combination of these requirements is challenging to be met by one single precursor family, especially for late 4d and 5d transition metals.[5]

We have explored the use of amidinate ligands for SOMC, which are a popular class of ligands in ALD applications. In this work, a scalable synthesis route for a series of amidinate-based organometallic precursors based on platinum group metals (Rh, Ir, Pd, Pt) as well as Ni was developed (*A*). These precursors readily react with oxide supports such SiO_2 in a well-defined way (*B*), as confirmed by the synthesis of a molecular analogue of the surface species (*C*). Upon treatment with hydrogen, they are converted into supported small and narrowly distributed nanoparticles in a traceless fashion, as confirmed by IR, TPR–TCD and TEM techniques (*D*).



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Molecular controllable cubane oxo cluster catalysts and their dynamic role on photoanodes for water oxidation

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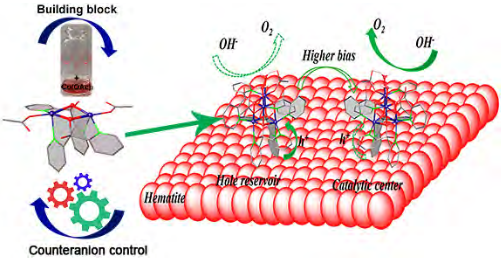
Photocatalytic water splitting by cuboidal {$CaMn_4O_5$} center is one of nature's most fascinating and important reactions.[1] Knowledge transfer from the key features of the {$CaMn_4O_5$} center to other oxo cubane-type water oxidation catalysts has attracted enormous attention due to its ability for direct solar energy-to-fuel conversion. Inspired by this concept, we successfully developed molecular {Co_4O_4} cubane-type catalysts through both ligand engineering and mixed metal centers.[2,3] To predictively access this highly active motif, we achieved an unprecedented level of synthetic control for the self-assembly of {Co_4O_4}.[4] Typical systems involving $Co(OAc)_2$ precursor and dpy{OH}O ligand were operated with systematically varied inorganic counteranion types and concentrations. After introducing a toolbox of straightforward inorganic counteranions, the self-assembly processes of oxo clusters revealed a surprisingly strong structure-directing effect of inorganic counteranions in solution. The type of {Co_4O_4} cubane exhibited a clear selectivity with respect to the counteranions used during the assembly process. Therefore, we opened up a strategy to molecular controllable {Co_4O_4} cubane synthesis for water oxidation. The combination of experimental screening and complemented DFT calculations were efficient used to track their pathways. These results are expected to provide insight into the widely unknown assembly mechanisms of organically ligated oxo clusters.

The dynamic role of {Co_4O_4} cubanes on photoanodes for water oxidation was investigated by loading molecular (Co_4O_4-dpk) on hematite photoanode surfaces.[5] Supported by both photoelectrochemical analyses and related rate law analyses, we revealed that the role of the {Co_4O_4} cubane cocatalysts alternated from predominate hole reservoirs to catalytic centers with the applied potential. Likewise, several other {Co_4O_4}-type molecules for heterogeneous cocatalysts were observed to display similar properties. Overall, our works provide a controllable and predictive access to highly performing oxo cluster catalysts via ligand engineering and counteranion selection, and further reveal the dynamic role of {Co_4O_4} cubanes on photoanodes for water splitting.



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β-X vs. β-H Elimination. Selection Rules for Chemoselectivity Enabled by Mechanistic Studies‡

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As transition metal chemistry advances, catalytic reactions will tackle more difficult transformations. Reactions involving alkyl-transition-metal species are particularly challenging, given the high reactivity of these species.[1] Many existing reactions employ such intermediates *e.g.* alkene hydrofunctionalisations, Mizoroki–Heck cross-coupling, alkyl C–H activation, alkene polymerisation and C(sp^3)- C(sp^3) coupling.[2] For these compounds, β-elimination - of either a hydride (β-H) or a heteroatom (β-X) - is the most common reaction pathway. These pathways can either lead to the desired reaction *cf.* Mizoroki–Heck, or they can hinder reaction progress *cf.* ethylene/vinyl halide co-polymerisations.[3] Despite the importance of these elimination processes, little mechanistic understanding exists with respect to the factors that control the competition between them.[4]

We describe a systematic mechanistic investigation of the competition between β-H and β-X using alkylpalladium complexes as a model system. The derivation of selection rules for achieving selectivity towards either elimination, as well as the development a predictive mechanistic mathematical model is presented. Finally, we outline how the ideas derived from this research could apply more generally to studying competing reactions and extending this work to other metals.

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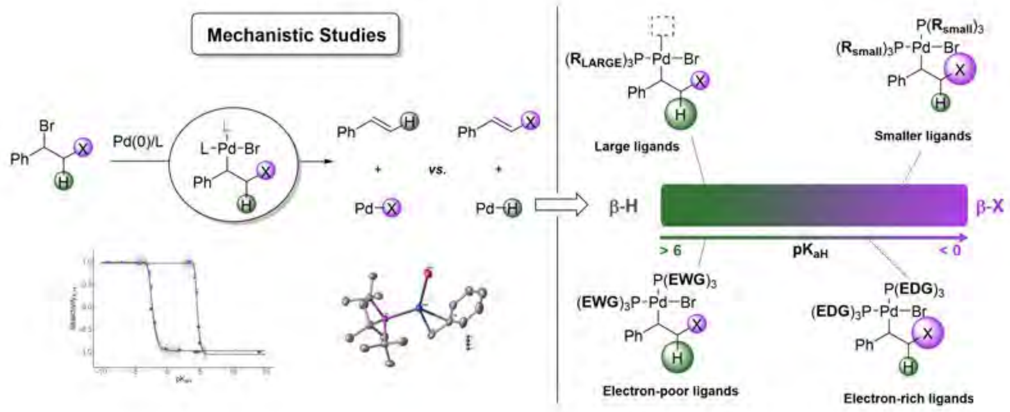

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Watching Ternary Oxides with Dual Eyes: an *in-situ* Two-Colour XES Studies of Photo-Electrocatalytic Water Oxidation Mechanisms in Ferric Pseudobrookite (Re_2Tio_5) Photoanodes

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The design of highly efficient, robust, and green water oxidizing catalysts is one of the most critical challenges in sustainable energy research. Due to the global climate change crisis and energy demand, solar assisted photo-electrocatalytic (PEC) water splitting has emerged as a promising approach towards producing clean chemical fuels and storable energy resources.[1] An ideal photo-electrode material should encompass a suitable energy bandgap for efficient sunlight absorption, good electrical conductivity, chemical stability, and non-toxicity.[2] Among the investigated photoanode materials, α-Fe2O3 had gained considerable interest in the field due to its suitable bandgap (1.9-2.2 eV) and earth abundance.[2] But the water oxidation efficiency of α-Fe2O3 is limited due to low carrier concentration and slow interfacial hole transfer. Doping α-Fe2O3 with tetravalent dopants such as Ti^{4+}, Zr^{4+} had been found to increase its carrier conductivity, thereby improving the PEC performance.[2] In this regard, ternary oxide materials have emerged as potential candidates for photoanode materials, as they provide diverse strategies for tuning the composition and electronic structure of photoanode materials compared to their binary counterparts.[3] Among these, the ferric pseudobrookite: Fe_2TiO_5 has received significant attention owing to its high thermodynamic phase stability, aqueous stability in a wide pH range, and suitable bandgap (1.9- 2.1 eV) for efficient solar light absorption.[4] Herein we report Fe_2TiO_5 inverse opals photoanodes with this which has shown improved performance and photocurrent density of 0.3 mA/cm^2 under solar light irradiation. We demonstrate the use of two-colour X-ray Emission Spectroscopy (XES) in identifying the catalytic intermediates and protonation events/species involved in solar water oxidation catalyzed by Fe_2TiO_5 photoanodes via Fe-Ti two-colour VtC-XES experiments under operational PEC conditions. XES being highly sensitive to metal-ligand atom coordination and protonation states, this in-situ two-colour study offers an excellent opportunity to simultaneously monitor the high valent catalytic Ti/Fe-Oxo species, Fe spin states, and dynamic behaviour of local coordination at Fe/Ti sites generated under real-time PEC conditions. In-situ XES studies indicated that the Ti sites acts as oxo-coordination site whereas the Fe site behaves as a redox regulator. Further post-catalytic XAS and XPS investigations also confirmed the change in local coordination at the Ti center, confirming its active role in driving the O-O bond formation.

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Developing the biological potential of organometallic cages

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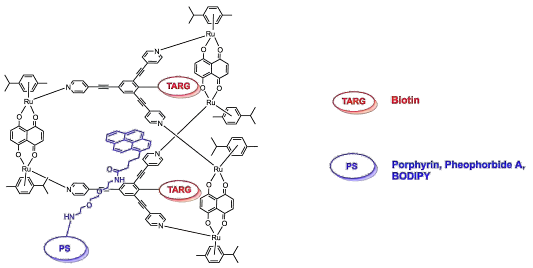
Ruthenium-based metalla-assemblies have been found to possess very promising features for biological and medicinal applications. Among these, water solubility, good anticancer activity and even the strong interaction with DNA are especially relevant.[1] Together with these properties, metalla-assemblies offer the possibility of encapsulation of interesting guest molecules. In this project, synthesis and characterization of high molecular weight metalla-assemblies is performed, aiming to exploit the benefits of the Enhanced Permeability and Retention effect (EPR effect), by which large and heavy molecular structures are directed in a selective manner to cancerous tissues.[2]

To obtain high molecular weight metalla-assemblies, different strategies are exploited such as functionalization with high molecular weight appendages of a guest molecule and the precursor panels, or the use of a common core that connects several metalla-assemblies in a single bigger system. Pyrene has been shown to be a very good guest for hexanuclear (arene)ruthenium metalla-prismatic cages[2], and it offers the possibility to be functionalized with one, two or even four arms containing high molecular weight functional groups.

Functionalization of these metalla-assemblies offers aswell the possibility of giving enhanced properties to the metalla-assembly, such as targeting, imaging, or the exploitation of photodynamic therapy using photosensitizers. In this context, a new set of metalla-assemblies containing biotinylated panels (targeted delivery[3]) and pyrenyl guests containing photosensitizers (photodynamic therapy) are obtained (figure 1).



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Redox Chemistry of Corrin-Based F430 Mimics

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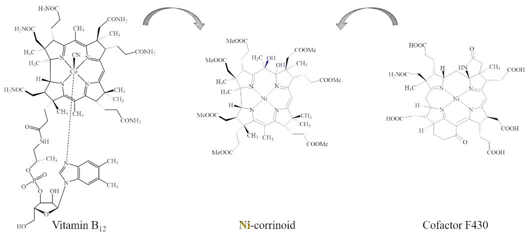
In nature are encountered important metal porphyrinoid cofactors such as heme, chlorophyll, vitamin B_{12} and cofactor F430 with essential biological functions. They consist of related, but structurally different tetradentate ligands and metal ions (i.e. Fe, Mg, Co and Ni).[1, 2] Based on the particular combination, they play different roles in nature ranging from reversible dioxygen binding to C-H activation chemistries.

Recently we described the synthesis, structure-property and structure-reactivity relationships of semi-artificial nickel-containing corrin derivatives (Figure middle).[3, 4] In our efforts to control metal vs. ligand centered redox chemistry in this new class of prophyrinoids, we report on the synthesis and reduction chemistry of new metallo-corrinoids.



Vitamin B_{12} Ni-corrinoid Cofactor F430

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Series of low-valent uranium-based coordination polymers based on tritopic carboxylic acids

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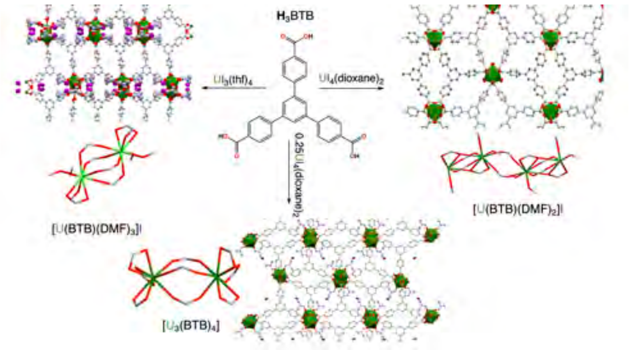
Although a vast majority of coordination polymers are based on transition metals, the motivation in obtaining MOFs with more complex structural motifs prompted an investigation on the use of f-elements. However, frameworks build on f-elements and especially based on 5f-elements are considerably less studied than d-metals based MOFs. For uranium, the most abundant and environmentally significant of 5f-elements, oxidation states vary from +2 to +6. The chemistry of uranium-based coordination polymers containing uranium(VI) ions is comparatively developed.[1] The most common form of the metal nodes in these U(VI) frameworks is the uranyl ion $(UO_2)^{2+}$. This makes it difficult to form 3D frameworks due to the positioning of oxo atoms in the axial plane of the ion, which leads to a prevalence of 1D or 2D coordination polymers.[2] In contrast to frameworks containing the U(VI) ion, lower-valent U MOFs are less studied. However, some examples of uranium-based organic coordination polymers in lower oxidation states are known. In particular, the +4 oxidation state has also been studied over the years.[3] While several carboxylates were employed as ligands in investigation of the frameworks' formation, still, the majority of the used carboxylate ligands are ditopic.[4] However, the use of carboxylates with a higher number of carboxylic groups can lead to the formation of more open polymeric structures exhibiting structures with higher surface area, increased pores' size, and could lead to an unprecedented coordination environment of the metal nodes.

Here we will describe the isolation and characterization of the 2D and 3D U(IV) coordination polymers based on a series of tritopic carboxylic acids. The influence of the reaction's parameters and conditions such as temperature, solvent, pH, modulation, on the products will be shown. Structural differences of the U(IV) coordination polymers will be described and their expected properties will be discussed.



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Controlled Modification of Cobalt Phosphide Catalysts by Sulfur

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Transition metal phosphides have shown excellent catalytic properties for the catalysis of water splitting and hydrodesulfurization with similar catalytic activity as the traditional noble metal catalysts.[1-2] In both current catalytic applications of the phosphide materials an enhanced catalytic activity was observed when a bit of sulfur is incorporated in the material.[3-4] However, current preparation methods of sulfur-modified phosphides lack control over the distribution of sulfur in the material. This hampers our understanding of how sulfur enhances catalysis by phosphides and thereby precludes the rational design of modified transition metal phosphides for actual implementation in industrial processes.

We developed a controlled method to modify transition metal phosphides with sulfur using a molecular approach. Use of molecular S-transfer reagents of varied strength enables us to control the amount of sulfur transferred and track the modification reaction by NMR spectroscopy. We show that there is a distribution of different sulfur sites possible at the phosphide surface and how this sulfur site distribution influences catalysis.

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Quantum crystallographic evaluation of S-C and P-C bonds in sulfur and phosphorus ylides

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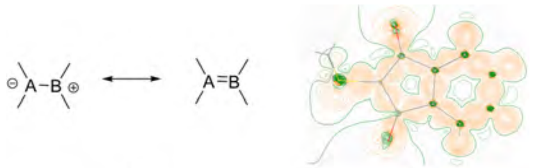
An ylide compound is a neutral molecule containing a formal double bond for which actually the charge-separated resonance form has a high stabilizing contribution (see Figure 1a). The negative charge is usually located at a carbon atom connected to a heteroatom with a formal positive charge (usually nitrogen, phosphorus or sulfur). This charge distribution has direct consequences on the reactivity of ylides leading to a lot of applications in organic synthesis as reagents or reactive intermediates. Phosphorus ylides or phosphonium ylides have been widely used in organometallic and organic synthesis, most famously as Wittig reagents in the Wittig reaction.[1] Sulfur ylides (sulfonium ylides and sulfoxonium ylides) are also employed in organic synthesis, e.g. in the Johnson–Corey–Chaykovsky reaction.[2]



(a) (b)

For those reasons, ylides are textbook examples for the interplay between Lewis resonance forms and molecular reactivity/ function. Hence, a full complementary bonding analysis[3] revealing the nature and character of the P-C and S-C bonds in ylides in detail is of practical importances and will also clarify concepts such as hypervalency of P and S atoms as well as the interplay between covalency and ionicity of heteroatom bonds. To the best of our knowledge, there are four experimental charge density studies about these bonds using multipole refinement[4] [5], and there is no Hirshfeld atom refinement (HAR) and X-ray wavefunction (XCW) fitting study about these bonds. In this study, our aim is to perform full X-ray wavefunction refinements (HAR + XCW fitting)[6] plus complementary bonding analyses to evaluate the C-S and C-P bonds in two ylide compounds measured at 100K with Ag Kα radiation to high resolution (Figure 1b).

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Structure and characterisation of a series of bipyrimidine-bridged diuranium complexes

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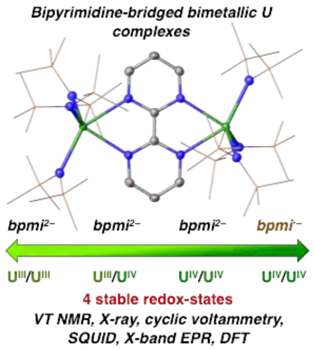
Single-molecule magnets (SMMs) possess a wide range of perspective applications in areas such as data storage, quantum computing and spintronics. Recently, the interest in this field has prompted in-depth analysis of structural correlations and physical phenomena, such as magnetic coupling, contributing to a high-performance SMM. It was shown that by bridging two lanthanide ions with a redox-active ligand 2,2’-bipyrimidine bearing different substituents it is possible to modulate the degree of exchange coupling, accessing larger SMM benchmark values such as relaxation barrier U_{eff}**[1]**. While radical-bridged lanthanide species and their magnetic properties are reasonably well-studied, the area of radical-containing uranium SMMs remains unexplored, despite its great potential interest. For example, introducing the azobenzene radical into a U(IV) system has allowed the enhanced slow magnetic relaxation to be observed**[2]**. In general, few examples of uranium SMMs containing radicals are known and no radical-bridged uranium species featuring strong magnetic communication have been reported thus far.

Here, a series of hexamethyldisilazane-supported bipyrimidine-bridged bimetallic uranium complexes is presented. The system is highly red-ox active, allowing to isolate four stable redox states, including a radical-bridged U(IV)/U(IV) and a mixed-valent U(III)/U(IV) complexes. X-ray crystallography, DC susceptibility data, DFT calculations and X-band EPR spectra all support their respective oxidation state assignments, and cyclic voltammetry shows complete red-ox reversibility and potential magnetic communication between the two uranium ions. The susceptibility data shows no direct indication of magnetic coupling in any of the complexes, and in the case of a U(IV)/U(IV) radical compound this can potentially be attributed to fast flipping of the radical spin, as evidenced by DFT-probed electronic state degeneracy; nevertheless, the complexes did show frequency-induced responses in alternating current (AC) magnetometry.



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Selective Olefin Transfer Hydrogenation of Unsaturated Carbonyls with EtOH using a PYA-based Ruthenium (II) Complex

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Pyridylideneamides (PYAs) are an innovative class of electronically flexible N-donor ligands and have been successfully used for catalysis, such as transfer hydrogenation of ketones or water oxidation.[1,2] While the catalytic transfer hydrogenation of ketones has been widely studied during the last years, the selective hydrogenation of olefins conjugated to an electron-withdrawing group such as carbonyl, ester or amide still remains a challenging reaction.[3] Here, we will present a 5-coordinated unsaturated ruthenium (II) complex containing a PYA unit and its application in selective olefin transfer hydrogenation of unsaturated carbonyls using ethanol as solvent and hydrogen source (Figure 1).

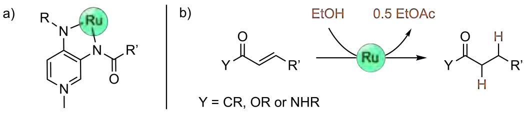

Figure 1. Schematic representation of the unsaturated ruthenium (II) complex (a), and its application in olefin transfer hydrogenation of unsaturated compounds (b).

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^{99}Tc-PNP Pincer Complexes interacting with Small Molecules

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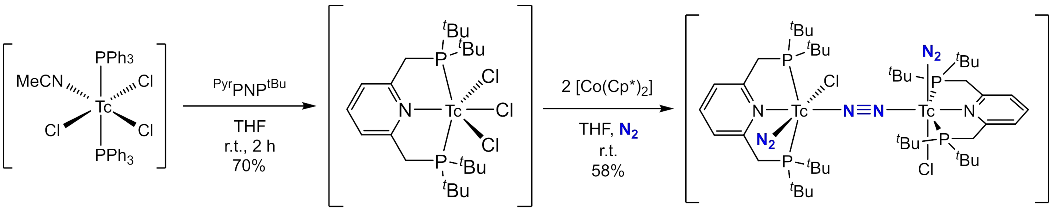
In the past years, the activation of small molecules (SMA) with transition metal catalysts has gathered increased attention. The introduction of non-fossil fuel based feedstocks into industrial processes is one step in this direction but requires activation of small molecules such as H_2, N_2 or CO_2. Tailor-made transition metal complexes are the underlying base. Pincer-type ligands are one class of versatile co-ligands which stabilize meridional coordination geometry. Respective complexes have generated exciting results such as the fixation of N_2 to produce NH_3 with a Mo-pincer catalyst.[1] Recently, we reported the synthesis of the first *mer*-Tc^{III}-PNP pincer complex $[Tc^{Pyr}PNP^{tBu}Cl_3]$ from the readily accessible precursor $[Tc(PPh_3)_2Cl_3MeCN]$. $[Tc^{Pyr}PNP^{tBu}Cl_3]$ coordinates N_2 upon reduction to Tc^{I} (Scheme 1).[2]



Scheme 1: *The PNP-pincer ligand $^{Pyr}PNP^{tBu}$ is added to $[Tc(PPh_3)_2Cl_3MeCN]$ in THF to form the Tc^{I} pincer complex $[Tc^{Pyr}PNP^{tBu}Cl_3]$. Two-fold reduction of this complex with $[Co(Cp^*)_2]$ under N_2 atmosphere leads to the dinuclear Tc^{I}-N_2 complex $[(Tc^{Pyr}PNP^{tBu}Cl(N_2))_2(\mu\text{-}N_2)]$.*

The two electron reduction of $[Tc^{Pyr}PNP^{tBu}Cl_3]$ with $[Co(Cp^*)_2]$ under N_2 leads to the formation of a reactive, electron-deficient intermediate. It coordinates N_2 to form the dinuclear complex $[(Tc^{Pyr}PNP^{tBu}Cl(N_2))_2(\mu\text{-}N_2)]$. This unprecedented example of a Tc complex coordinating multiple N_2 ligands represents the first *mer*-pincer-type complex with technetium. The findings sparked the motivation to investigate the interaction of other small molecules with the reported Tc-PNP frameworks. Accordingly, CO and H_2 have been coordinated to or activated by this moiety. Recently, we extended reactivity schemes by exploration of a metal-ligand cooperativity (MLC) pathway. The nature of this project is fundamental and aims at providing insights that enable systematic understanding of periodic trends, mainly in the Mn triad.

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Strongly confined $CsPbBr_3$ perovskite quantum dots as quantum emitters and building blocks for highly ordered rhombic superlattices

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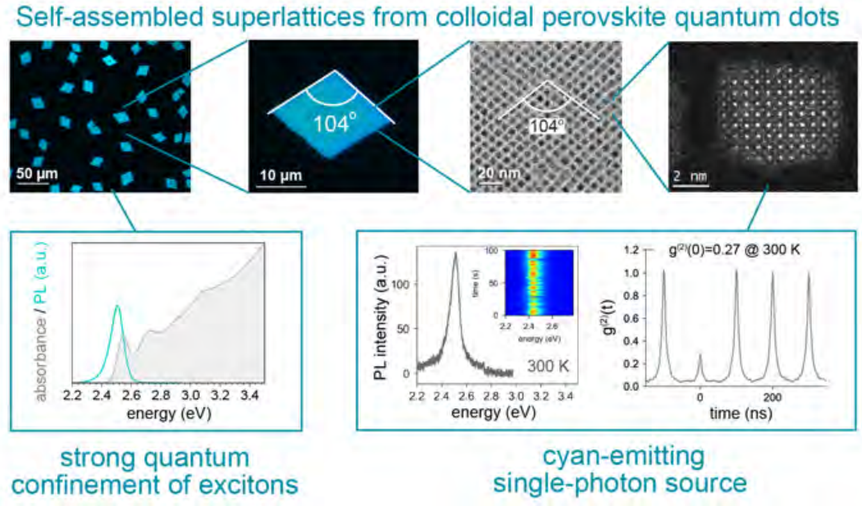
The success of the colloidal semiconductor quantum dot (QD) field is rooted in the precise synthetic control of QD size, shape, and composition, enabling electronically well-defined functional nanomaterials that foster fundamental science and drive diverse fields of applications. While the exploitation of the strong confinement regime has been driving commercial and scientific interest in InP or CdSe QDs, a thorough exploration of such a regime has still not been achieved for lead-halide perovskite QDs. Here, we overcome previous challenges of insufficient chemical stability and monodispersity of small perovskite QDs via a post-synthetic treatment employing didodecyldimethylamonium bromide ligands. The achieved high monodispersity in both size and shape enables us to prepare self-assembled QD superlattices of exceptional long-range order and uniform thickness, with an unusual rhombic packing, and with narrow-band cyan emission. Their enhanced chemical stability allows us to explore strongly confined perovskite QDs at the single-particle/single-photon level.



Synthesis, Structure and Bonding of Alkali-Metal Nickelates

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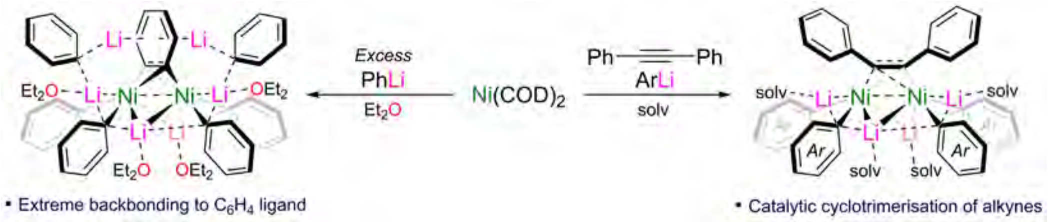
Heterobimetallic nickelates derived from Ni(0)-olefin complexes and polar organometallics were widely studied during the spawn of low-valent organonickel chemistry but have remained largely dormant in modern literature.[1] Recently, we have demonstrated that heterobimetallic nickelates are key intermediates in the nickel-catalysed cross-coupling of aryl ethers under mild conditions,[2] prompting us to further explore this structurally diverse class of compound.

In this presentation, we will unveil the synthesis, structures and bonding of a family of polynuclear alkali-metal nickelate clusters that can be readily accessed from $Ni(COD)_2$ and simple organolithium reagents. This includes an exotic octanuclear complex which contains a bridging C_6H_4-ligand and exhibits unique structural and bonding features that have been investigated by computational studies and solution-state NMR studies.[3] Related dinickel-alkyne complexes can be prepared in a similar fashion and are competent catalysts for the cyclotrimerisation of alkynes.[4]



- Extreme backbonding to C_6H_4 ligand
- Catalytic cyclotrimerisation of alkynes

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An Orthogonal Labeling Strategy to Accelerate Bioconjugation of [^{99m}Tc]-Building Blocks

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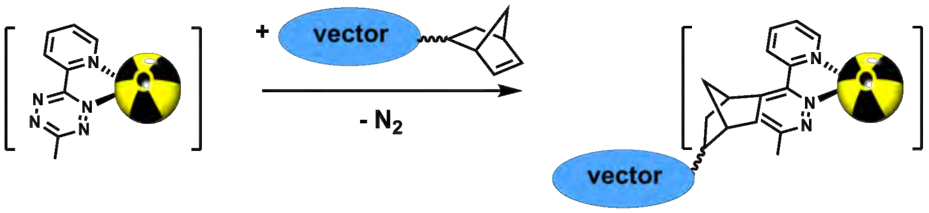
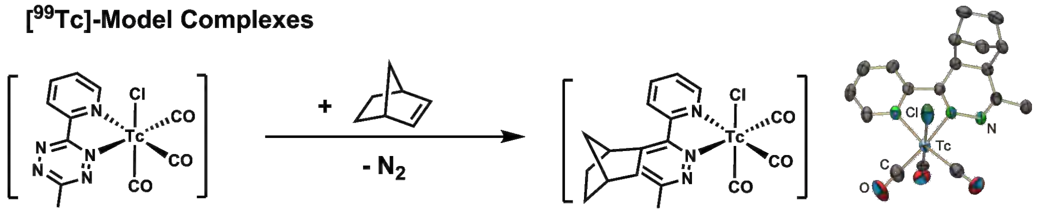
Fast and efficient bioconjugation of technetium and rhenium still represents a challenge for radio probe synthesis. Click chemistry had an enormous impact on this field and lead to fascinating new labeling techniques such as the click to chelate approach.[1] However, in clinical settings cupper free reactions are preferred. The inverse electron demand *Diels-Alder* reaction (iEDDA) of 1,2,4,5-tetrazines with dienophiles is an attractive new approach for the synthesis of bioconjugates.[2] Schnierle et al. showed that the coordination of 3-(2-pyridyl)-1,2,4,5-tetrazin (TzPy) to the $\{Re(CO)_3\}^+$ core boosts rate and regioselectivity of the iEDDA.[3] Based on these results complexes of the type $[MX(CO)_3(TzPy)]$ (M = ^{99m}Tc, X = H_2O; M = Re, X = Br) will enable a very fast bioconjugation of $\{M(CO)_3\}^+$ fragments (M = ^{99m}Tc, Re), which have a small steric foot print and multiple opportunities for fine tuning. We present the synthesis and characterization of novel ^{99}Tc-tricabonyl complexes containing the 1,2,4,5-tetrazine motif and their reactivities with norbornene and *trans*-cyclooctene.

Labeling via Diels-Alder reaction of 1,2,4,5-Tetrazine derivatives



[^{99}Tc]-Model Complexes



[^{99}Tc(CO)$_3$Cl(MeTyPy)]

[^{99}Tc(CO)$_3$Cl(MeDzNorboPy)]

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Investigation of Different Deposition Techniques of Holmium Sources for the Measurement the Electron Neutrino Mass

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The radioisotope ^{163}Ho decays by electron capture with a low transition energy, which makes it a promising candidate for the direct measurement of the electron neutrino mass. The HOLMES project aims at such a neutrino mass determination by means of calorimetric decay measurements of implanted ^{163}Ho with a sub-eV sensitivity [1]. The needed ^{163}Ho-implanted microcalorimeters are prepared by Ar-sputtering from a Ho sputter target (as cathode) in a Penning ion source followed by mass separation and implantation of ^{163}Ho in an array of 1024 calorimetric pixels [2]. The method for the production of the needed ^{163}Ho source is of vital importance and it has to meet three requirements: uniform surface distribution, chemical homogeneity, and high yields.

In this work, different techniques for the preparation of adequate Ho sputter targets were used. The morphology of the obtained sources was characterized by autoradiography and scanning electron microscopy, while the chemical composition of the deposited Ho was investigated by energy dispersive X-ray spectroscopy.

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Electric Field Effects on the Surface Chemistry of Inorganic Materials

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For the development of sustainable energy conversion technologies we need earth-abundant alternatives to the typical noble metal electrocatalysts and control over the reactivity at their surfaces. In electrocatalysis, electric fields at the metal electrode surface have been suggested to be a key factor influencing the surface reactivity and selectivity.[1-3] For instance, some of us have recently shown that interfacial electric fields can dramatically change the surface acidity of organically modified gold layers.[4] Rather than the applied potential, it is the electric field and potential experienced at the surface that is more relevant to the surface chemistry. These electric field effects are significantly influenced by interfacial interactions.[5] Hence, electric field effects and interfacial interactions have to be understood not only for the conventional metal electrodes but also for alternative earth-abundant materials in order to control catalysis.

Here, we describe an infrared spectro-electrochemical approach to measure electric fields at the surface of a cobalt sulfide film. We use the so-called Vibrational Stark Effect that connects vibrational shifts to electric fields and introduce direct Stark reporters of electric field to the surface by chemical modification of the sulfide surface. Furthermore, we show how interfacial interactions vary as a function of electric field. This study provides first clues on electric field effects at the surface of inorganic metal sulfide materials and their potential relevance for the catalysis by inorganic materials.

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[5] Murielle F. Delley, Eva M. Nichols, James M. Mayer, *Journal of Physical Chemistry C*, **2022**, 126, 8477–8488.

Structure-function correlations in a new family of homoleptic tris-didentate Cr(III) complexes.

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Over the past decade, the quest for earth-abundant phosphorescent emitters has renewed interest for Cr(III) coordination chemistry. The long emission lifetimes of the spin-forbidden transitions of Cr(III) complexes in the near-infrared region appear valuable in diverse applications such as in optical devices, catalysis or even bioimaging [1]. Yet, these emission lifetimes seem to show some sensitivity to the deviation of the complex coordination sphere from the ideal octahedral geometry [2, 3]. In this context, we have investigated new homoleptic tris-didentate Cr(III) complexes with imidazole-based ligands, presenting either a 5-membered or a 6-membered chelate ring (Figure 1). We successively examined the structural properties of these complexes along with their photophysical features (e.g. emission lifetimes, quantum yields, and Racah parameters). The benefit of 6-membered chelate ring over the 5-membered chelate rings is discussed in regard to different archetypal Cr(III) complexes, such as $[Cr(phen)_3]^{3+}$ and $[Cr(bpy)_3]^{3+}$, previously reported in literature [4]. Finally, this study of model compounds will provide information in support of a further design of (d-f) multicomponent assemblies for addressing light upconversion challenge at the molecular scale.

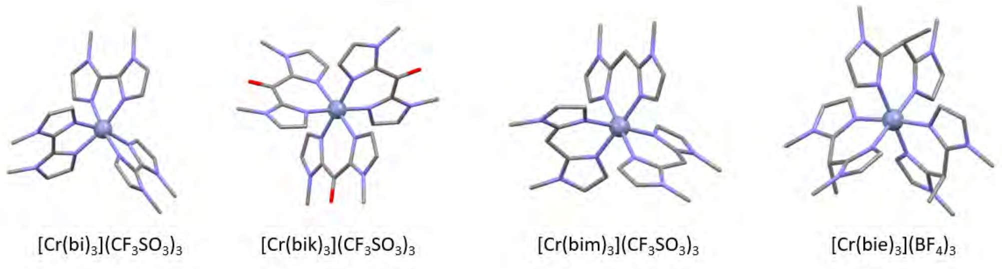

Figure 1: Crystallographic structures of homoleptic tris-didentate Cr(III) complexes.

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Diimine Re(I) tricarbonyl complexes: toward novel highly potent and non-toxic antimicrobial agents

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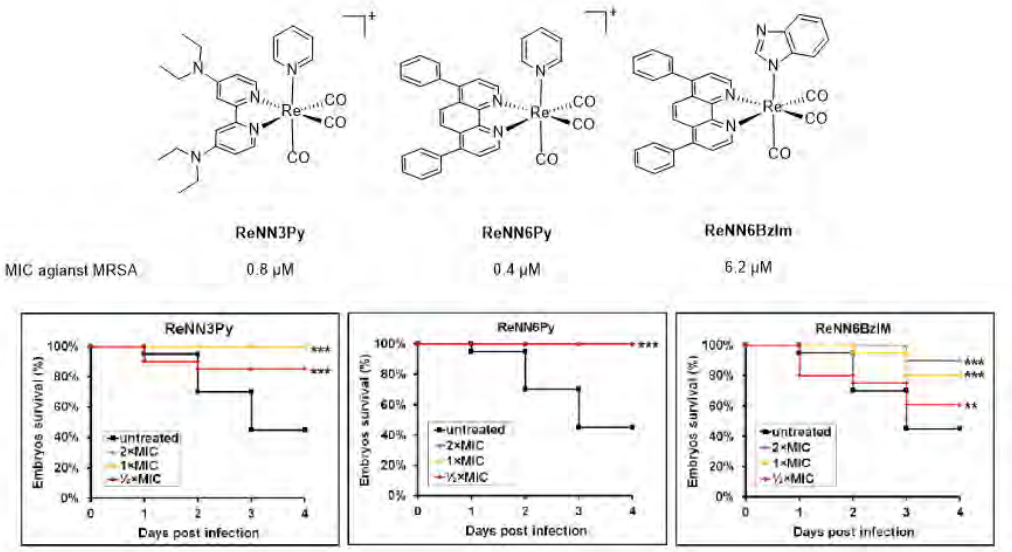
The current increase of antimicrobial resistance (AMR) poses a serious need for new classes of therapeutic compounds. For this purpose, our group has been interested in organometallic antimicrobial agents and more precisely in rhenium(I) tricarbonyl (RTC) molecules, which have been known for possessing promising therapeutic properties against a variety of bacteria and fungi.[1,2] Our work features the synthesis of various RTC complexes bearing a diimine moiety as bidentate ligand and a pyridine or imidazole derivative as monodentate ligand. The biological activity of these compounds is tested against several strains of bacterial and fungal pathogens.[3,4]



The already obtained results suggest great potential, as some RTC species exhibit excellent activity against methicillin-resistant *Staphylococcus aureus* (MRSA), *Candida albicans* or MRSA-*C. albicans* co-infection with a minimum inhibitory concentration (MIC) in the nanomolar range. Furthermore, *in vivo* tests using zebrafish as model organism show no toxicity toward the embryos, increasing the infected fish rate survival up to 100 %.

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Dioxygen Activation in Rieske Dioxygenases: A Model Study Towards Automated QM/MM Protocols

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Quantum mechanics/molecular mechanics (QM/MM) hybrid methods allow one to address chemical phenomena in complex molecular environments. Such hybrid models are tedious to construct and require specific knowledge on the considered problem, which is why it has been difficult to provide automated procedures of controllable accuracy, making such type of modelling far from being of a black-box type.

Here, we present an automated QM/MM model construction protocol on the basis of fully automated structure preparation, model parametrization (SFAM[1]) and QM region selection (QM/SFAM[2]) developed as *SWOOSE* module within out *SCINE* software framework.[3]

We apply this protocol to QM/MM-based evaluation of oxygenations reactions catalyzed by Rieske dioxygenases (RDO), which are the primary enzymes responsible for the hydroxylation of aromatic hydrocarbons.[4] In contrast to other mononuclear non-heme iron oxygenases, substrates of RDOs are held in substrate pockets in proximity of the active site but lack direct interaction with the non-heme iron center.[5] Despite this apparently missing interaction, it was observed experimentally that coordination of O_2 to the metal center is gated by the presence of the apparently unreactive substrate. This tight control over O_2 reactivity appears biologically plausible to avoid unproductive O_2 activation, yet the role of the substrate in the formation of reactive iron-oxygen species is not understood.

We recently discussed all steps leading to substrate-modulated dioxygen activation in a purely quantum chemical study combining both Density Functional Theory and first-principle reference calculations.[6] We find that binding of dioxygen to a mononuclear non-heme iron center requires prior reduction of the active site through electron transfer from the nearby Rieske cluster. We utilize our findings to reproduce critical reaction steps in the active site on the QM/MM scale and, by that, validate our QM/MM modelling protocol.

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Tuning spin-crossover transition temperatures in non-symmetrical homoleptic meridional/facial [Fe(didentate)$_3$]$^{2+}$ complexes

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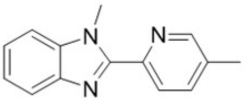
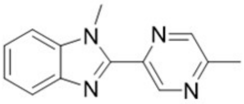
[1]University of Geneva, Department of Inorganic and Analytical Chemistry, [2]University of Geneva, Laboratory of X-Ray Crystallography

In an effort to develop *tris*-diimine Fe^{II} complexes displaying spin crossover properties in solution at room temperature, several unsymmetrical didentate units were investigated (ligands **L1**-**L4**). By changing the number of nitrogen atoms or their position within the 6-membered *N*-heterocyclic ring, the spin transition can be finely tuned. The construction of ligands **L3** and **L4** containing pyrimidine rings bound at positions 2 or 4 to *N*-methyl-benzimidazole units is a prerequisite for the thermodynamic programming of [Fe(**L*x***)$_3$]$^{2+}$ complexes, the transition temperatures ($T_{1/2}$) of which are lower than those found in the complexes [Fe(**L1**)$_3$]$^{2+}$ ($T_{1/2}$ = 309(6) K) and [Fe(**L2**)$_3$]$^{2+}$ ($T_{1/2}$ =349(5) K)[1]. The [Fe(**L3**)$_3$]$^{2+}$ unit, considered as its mixture of *mer*/*fac* isomers, exhibits spin crossover in solution with $T_{1/2}$ = 273(3) K, which makes this complex suitable for the potential modulation of lanthanide-based luminescence in polymetallic helicates. Furthermore, the explicit analysis of the isomeric equilibrium involving the *mer* and *fac* isomers of [Fe(**L3**)$_3$]$^{2+}$ offers an unprecedented opportunity for assigning specific thermodynamic spin-crossover parameters to each isomer[2]. Due to the thermodynamic *trans* effect (*trans* influence) the enthalpic driving forces favour the low-spin isomer for the facial isomer, a trend reinforced by entropic consideration based on solvation effects. In other words, spin crossover occurs systematically at lower temperature for the meridional isomer.


L1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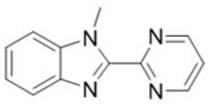
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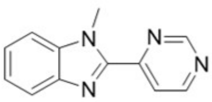
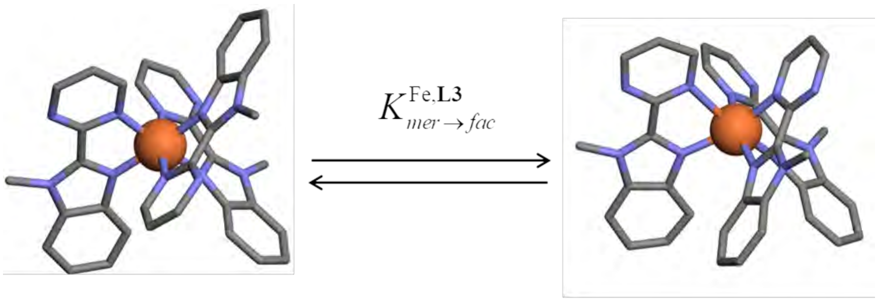

L4

In the solid-state, these isomers could be crystallised separately. Cleared of solvation effects, but submitted to strong intermolecular packing effects, *fac*-[Fe(**L3**)$_3$]$^{2+}$ undergoes an abrupt transition ($T_{1/2}$ = 207(16) K), while *mer*-[Fe(**L3**)$_3$]$^{2+}$ shows a two-step transition ($T_{1/2}$ = 178(4) K and 251(12) K) with accompanying phase-transitions characterized by XRD-analysis, indicating a peculiar process explaining the stepwise transition. This presentation aims to highlight the nuanced modification of complex properties, which results from the apparently negligible flipping of a didentate ligand in going from facial to meridional Fe^{II} spin-crossover complexes.


$K^{\text{Fe},\mathbf{L3}}_{mer\rightarrow fac}$

mer-[Fe(**L3**)$_3$]$^{2+}$

$T_{1/2}^{\text{SCO}} = 258\text{K}$

fac-[Fe(**L3**)$_3$]$^{2+}$

$T_{1/2}^{\text{SCO}} = 309\text{K}$

[1] T. Lathion, L. Guénée, C. Besnard, A. Bousseksou and C. Piguet, *Chem. Eur. J.*, **2018**, *24*, 16873–16888.

[2] N. Deorukhkar, C. Besnard, L. Guénée and C. Piguet, *Dalton Trans.*, **2021**, *50*, 1206–1223.

Redesigning nanocrystal synthesis - Critically evaluating the use of solvents and ligands

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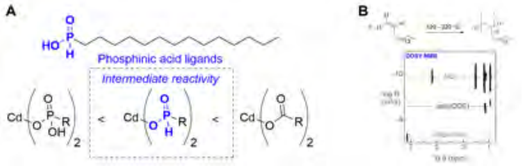
In every colloidal nanocrystal synthesis ligands and solvent play a crucial role. For the former, only a handful molecules are currently used, of which oleic acid being the most typical example. Here we show that monoalkyl phosphinic acids are another ligand class. For the latter, *1*-octadecene (ODE) is a widely used solvent for high temperature nanocrystal synthesis (120 –320 °C), but it is not innocent.

First, we put forward monoalkyl phosphinic acids as an alternative ligand class, similar to carboxylic acids and phosphonic acids (Figure A). After presenting the ligand synthesis for several selected substrates, we proceed to show the intermediate reactivity of the phosphinic acids in CdSe quantum dot syntheses. The nanocrystals synthesized with phosphinic acids are also easier to purify since there is no gel formation. Very small (2–3 nm) CdSe quantum dots with low polydispersity and high photoluminescence quantum yields can be easily accessed with phosphinic acid ligands. CdSe and CdS nanorods were also synthesized using phosphinic acids, whereby the rods showed high purity an d uniformity. In addition, given their intermediate acidity, phosphinic acids (pKa ≈ 3.08) bind to the surface with an affinity between carboxylic and phosphonic acids. Using solution NMR, we quantify the X-for-X ligand exchange and conclude that the monoalkyl phosphinic acids quantitatively displace carboxylate ligands and are in equilibrium with phosphonates (although phosphonate binding is favored).



Second, we show that ODE polymerizes at temperatures relevant for nanocrystal synthesis (Figure B). Using NMR spectroscopy, we detect its presence in five different nanocrystal syntheses: ZnS:Mn/ZnS, $CuInS_2$, CdS, TiO_2, and Fe_3O_4. The resulting poly(ODE) has a comparable solubility and size to nanocrystals stabilized by hydrophobic ligands, thus hampering typical purification procedures. To avoid formation of poly(ODE), we replaced *1*-octadecene with saturated, aliphatic solvents. Alternatively, the native ligands are exchanged for polar ligands, leading to significant solubility differences between nanocrystals and poly(ODE), therefore allowing isolation of pure nanocrystals, free from polymer impurities.

In conclusion, by introducing a third and intermediate class of surfactants, we enhance the versatility of surfactant-assisted syntheses and post-synthetic stabilization. In addition, the inertia of solvents should not be taken for granted. Side reactions can seriously compromise the purity of the nanocrystal product, with consequences for ensuing applications.

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Development of an electrochemical strategy for routine separations of radionuclides

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Radionuclide-specific radioactivity measurements are necessary in order to give an accurate evaluation for the decommissioning of nuclear facilities, radioactive waste management or contamination monitoring. Measurements are commonly carried out with liquid scintillation counting, α-, γ-, and mass-spectrometry. However, all these analysis techniques usually require a thorough chemical pretreatment, targeting the removal of interfering radionuclides. Common strategies for routine analytical separations of radionuclides are based on ion-exchange or extraction chromatography, as well as precipitation/co-precipitation methods. The objective of the herein presented project is to explore a so far less commonly used separation route, which is based on selective electrodeposition. We report on promising results obtained by controlled-potential electrolysis for the separation of radionuclides in simple mixtures (e.g., ^{60}Co and ^{137}Cs) using an ordinary undivided cell. In addition, an electrochemical flow-cell has been designed and tested in order to reach faster electrolytic separations. Such an electrochemical approach is expected to lead to fast routine radioanalytical methods, which will be used for the analysis of radionuclide mixtures of increasing complexity. Thus, the herein presented results may pave the way to a viable alternative for traditional separation techniques.

Reversible *fac-mer* Isomerization of Luminescent Ir(III) Complexes

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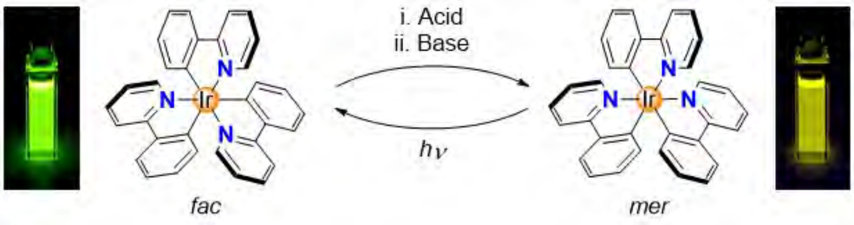
Iridium(III) complexes are of everlasting interest due to their unique chemical and photophysical properties including remarkable chemical and thermal stability, reversible redox transformations, high luminescence quantum yields, and easily tunable emission color and lifetime. These features have allowed these complexes to be widely used in optoelectronics, photonics, photoredox catalysis, oxygen and sensing etc.[1]

Structurally, luminescent Ir(C^N)$_3$ complexes (C^N = cyclometalated arylpyridyl ligand) exist as two stable geometrical isomers with distinct photophysical properties: facial (*fac*) and meridional (*mer*).[2] The *mer* isomer tends to be thermodynamically less stable than the *fac* isomer. Varying the reaction conditions, the *mer* isomer can be obtained in a kinetically controlled reaction and transformed to the *fac* form at elevated temperatures or under light irradiation.[3] The opposite *fac*→*mer* isomerization has not been reported so far.

Herein we demonstrate that *fac*-Ir(C^N)$_3$ complexes can be converted into their *mer* isomers by a successive reaction with acid and then base as shown below.



This chemically induced *fac*→*mer* isomerization is fast, clean, quantitative, tolerant to different substituents, stereoselective, and it can be reversed by light irradiation.

The cleanliness and reversibility of the new *fac*→*mer* isomerization provide the possibility to use luminescent Ir(C^N)$_3$ complexes as substrates for rewritable data storage devices or as a basis for molecular machines. Another application direction of this isomerization is the synthetic accessibility of *mer* isomers, which are difficult to prepare using published procedures.

The authors greatly appreciate a financial support from Swiss National Science Foundation (SNSF) and EPFL as well as facility/equipment available within EPFL.

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^{109}Ag NMR Chemical Shift: A Descriptor of Brønsted Acidity from Molecular Ag-NHC-Complexes

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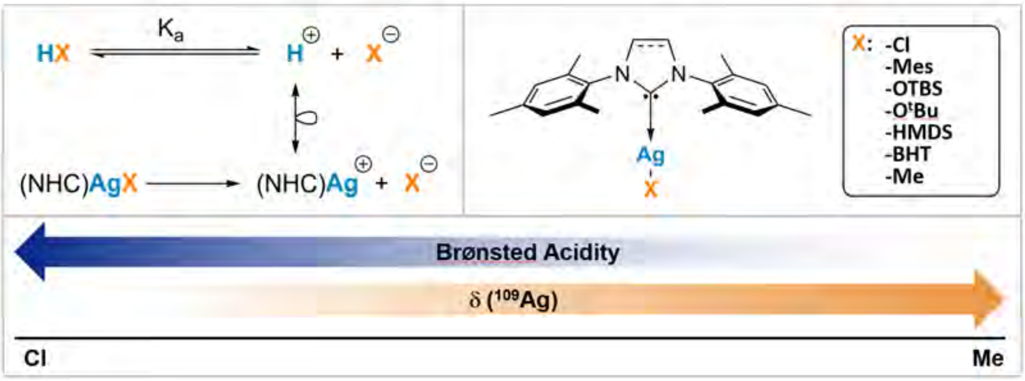
For group 11 metals (Cu, Ag, Au) in the 1+ oxidation state, it has been suggested that the molecular fragment [LM$^+$] can be considered isolobal to a proton (H$^+$), due to the closed-shell nature of the d^{10} electron configuration.[1], [2] On this basis, we investigated ^{109}Ag chemical shift of [LAg$^+$] as a descriptor for the pKa of Brønsted acid sites.

By exploiting the modularity of N-Heterocyclic carbene (NHC) complexes of Ag(I) (general structure (NHC)AgX), we demonstrate that the ^{109}Ag chemical shift of a series of monomeric silver NHC complexes ((NHC)AgX) correlates (linearly) with the pKa of the conjugate acid of the anionic ligand (X$^-$). The relationship between isotropic chemical shift has been extended across a broad range of ligands (halides, alkoxides, amides, aryl, alkyl etc.), and provides a broad-ranging strategy for the estimation of pKa of a range of Brønsted acids. Analysis of solution NMR, solid-state NMR and calculations of chemical shift tensors illustrate clear trends between both experimental and calculated parameters with pKa of the corresponding Brønsted acid. Furthermore, the broad range of ^{109}Ag chemical shifts obtained (ca. 300 ppm) provides a basis to evaluate the acidity of various compounds; a path that we are currently further exploring, and that we hope to extend to the surface chemistry of heterogeneous catalysts.



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Lanthanide Isotopes in Uranium Products

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The enrichment of uranium for civil and military purposes has led to the accumulation of uranium by-products with reduced abundance of ^{235}U, which is known as depleted uranium (DU). Due to its high density (≈18 g/cm^3), DU has found its broad application in the fabrication of counter balances for airplanes, armored vehicles and armor-piercing ammunition [1,2]. Meanwhile, the content of chemically similar behaving rare earth elements (REEs) can be used to match the geolocation of a source of uranium ore. Further processing routes and especially activation products, as derived from plutonium production, can give hints on corresponding process routes [3-5]. In recent publications of nuclear forensics, impurities at concentration levels of several percent were predominantly investigated by energy-dispersive X-ray spectroscopy (EDX) [1]. Unfortunately, the concentration of REEs in DU lays below the detection limit of EDX, thus demanding for alternative methods of analysis, such as inductively coupled plasma mass spectrometry (ICP-MS).

Recently, Roach et al. [6] developed promising methods to quantitatively separate Ce, Pr, Nd, Sm, Eu, and Gd using ion chromatography, coupled to ICP-MS for ultra-trace nuclear forensic applications. Our own preliminary results revealed promising chemical yields for the separation of the problematic contaminant Ce, together with the transuranium elements Am and Cm, from other REEs. With this in hand, we aim at investigations similar to works as published by Varga [7] and colleagues. They studied REE patterns in uranium ores and the influences from milling and pre-concentration of uranium on REE patterns. Finally, the acquired data will be used to establish a library of potential uranium sources and processing routes. This library in connection with a thorough understanding of the involved processing routes will help to find source and process-specific patterns as well as it will help to study statistically significant differences. Furthermore, we will try to understand the influences on patterns derived from mixing different uranium sources and processing routes during manufacturing. This will pave the way for nuclear forensic studies of unknown samples.

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Reactivity of Multimetallic Thorium Nitrides Generated by Reduction of Thorium Azides

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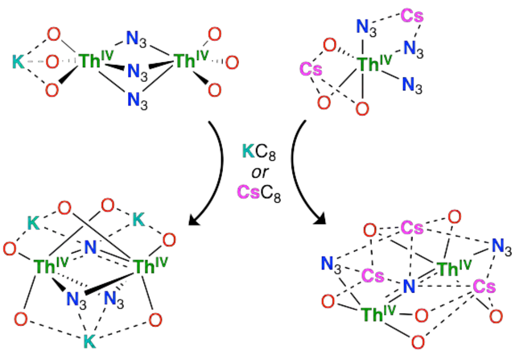
Thorium nitrides are likely intermediates in the reported cleavage and functionalization of dinitrogen by molecular thorium complexes and are attractive compounds for the study of multiple bond formation in f-element chemistry, but only one example of thorium nitride isolable from solution was reported.[1] Here, we show that stable multimetallic azide/nitride thorium complexes can be generated by reduction of thorium azide precursors, a route that has failed so far to produce Th nitrides.[2][3]

Here, we investigated the reduction of azide precursors with excess KC_8 and CsC_8, allowing the isolation of bis-azide, mononitride, with different counterions.[4] Both complexes were characterized by X-ray crystallography, NMR spectroscopy and density functional theory calculations. In the solid-states structure, they both display a dinuclear Th(IV) complex, featuring a bridging nitride and two azide ligands, but in the presence of two different counterions gives rise to paramount structural differences in the two complexes. We also investigated the reactivity toward CO. Both complexes reacted with excess ^{13}CO, yielding $^{13}CN^-$ in 30% and 22%, after hydrolysis with D_2O (pD = 13). Furthermore, removal of the alkali ions might favor the loss of the azide ligands, affecting the reactivity of complex toward CO. The yield of $^{13}CN^-$ increased to 70% after hydrolysis. In conclusion, we have synthesized the first multimetallic Th_2K_3 and Th_2Cs_3 azido/nitrido complexes, which are the second examples of isolable molecular thorium nitrides and studied the reactivity toward CO.



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Potassium Alkoxide Mediated Zincations of Aromatic Substrates

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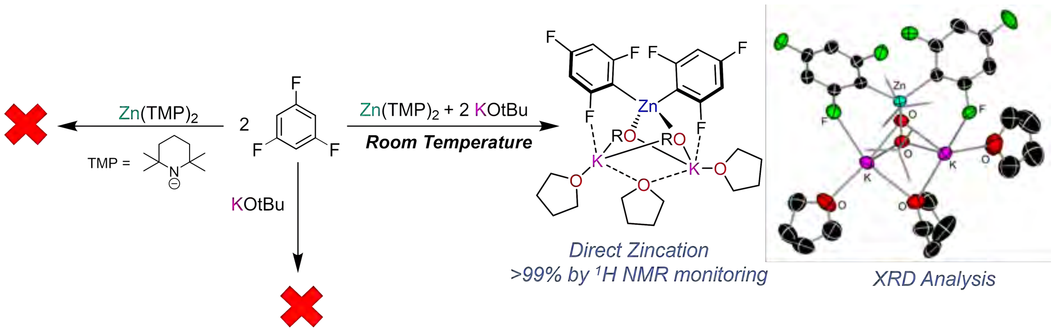
The unique activating effects of alkali-metal alkoxides when added to other s-block organometallics is a well-established phenomenon in polar organometallic chemistry.[1] Typified by the LIC-KOR (Lochmann-Schlosser) superbase, combining potassium *tert*-butoxide with *n*-butyllithium greatly enhances the metalation capabilities of this mixture when compared to those of their monometallic counterparts.[2,3] Extending these reactivity enhancement effects beyond group 1 organometallics, our group has recently demonstrated the ability of alkali-metal alkoxides to activate dialky magnesium or zinc reagents towards metal halogen exchange reactions of bromo and iodoarenes. Mechanistic studies indicate that these special behaviors can be attributed to the formation of more reactive mixed-metal mixed-aggregate complexes. [4–6]

Building on this work, this contribution showcases recent advances on the development of a new bimetallic base which allows for the direct zincation of a broad range of aromatic substrates. By combining the Zn amide $Zn(TMP)_2$ (TMP = 2,2,6,6-Tetramethylpiperidide) with two equivalents of KOtBu effective zincation of sensitive substrates such as 1,3,5-trifluorobenzene can be achieved while operating at room temperature (see Figure). Trapping of key reaction intermediates and NMR monitoring of the reactions have uncovered the close interplay between the different components of this bimetallic mixture to facilitate the success of the Zn-H exchange reaction and the stability of the metalated intermediates.



Direct Zincation
>99% by ^1H NMR monitoring

XRD Analysis

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From Macrocycles into Assembled Chain-mails!

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Knots and links, being part of the mechanically interlocked molecular architectures, are related to three-dimensional space. Nevertheless, links are less studied and are not as well classified as knots [1]. Nature shows examples of strong relations between topology and function [2,3]; for instance, complex topological structures such as those present in the chain-mail like bone armour lying under a Komodo dragon's skin are extremely robust [4], as is the non-covalent interlaced protein structure forming the capsid of the virus HK97 [5].

To achieve chain-mail type structures, macrocycles need to interlink with each other. Such complex topologies of links can be analyzed for example by looking at their two-dimensional assemblies at the atomic level. This is achieved by applying imaging techniques, such as AFM and STM.

Scheme 1: New macrocyclic ligands as synthons for interlaced structures

New synthons like a new family of macrocycles with alternating aromatic and polyether chains, have been synthesized and characterized with the aim of obtaining a controlled complex chain-mail structure (scheme 1). Such flexible and robust macrocyclic structures are formed by alternating the mechanical and physical properties resulting from the different building blocks. Their optimal packing arrangement on atomically flat 2D structures have been investigated and compared with the 3D structures obtained from single crystal analyses of the macrocycles and its/their solvates.

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Isocyanides and their Strong Affinity to Gold

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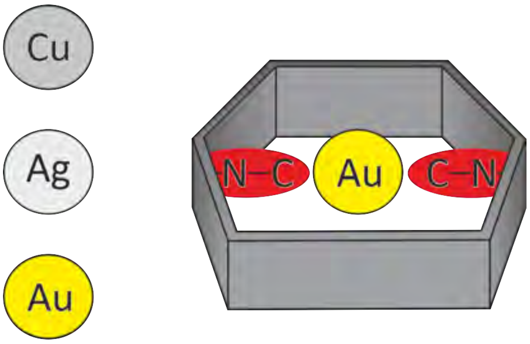
The isocyanide is a versatile functional group which is widely employed in the field of organic and combinatorial chemistry including catalysis, photochemistry and transition metal chemistry. The isocyanide is furthermore getting increasing attention in the field of medicinal chemistry as well as molecular electronics.[1]

The unique structural property of this functional group is given by the lone pair on the carbon atom, which allows to coordinate in a linear fashion via σ-bond donation to metals. Based on these characteristics the isocyanide seems to have a particular high affinity to copper, silver and gold, while increasing in the listed order.[2]

To investigate the affinity of the isocyanide to the different metals we designed and synthesized a macrocyclic bidentate diisocyanide ligand. The distance between the isocyanides was optimized for the complexation with gold, while a compromise was found with butadiynes as spacing units. Complexation with copper, silver and gold was performed and analyzed via NMR and IR experiments. Of particular interest was the affinity of the isocyanide towards gold(I). For this purpose, UV-vis titration experiments were carried out. These showed, that the K_a value was too high to be determined ($>10^{20}$).[3]



Macrocyclic bidentate ligand for the complexation with copper, silver and gold.

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Photoinduced Electron-Transfer Through the Mechanical Bond in a Supramolecular Dyad

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Photoinduced Electron transfer (PET) has been widely explored in covalently connected molecular motifs, mostly focusing on how various bridging motifs facilitate PET.[1] Although research has predominantly focused on PET through covalent bridges, an emerging field is through-space PET.[2] Within this framework, mechanically-interlocked molecules such as catenanes and rotaxanes represent a particularly interesting scaffold for PET, due to their unique three-dimensional topology and dynamic nature.[3]

Despite interest in PET in rotaxanes dating back to Sauvage's original work in the field,[4] fundamental insight into PET in mechanically-interlocked systems remains underdeveloped. To address this, herein is presented a systematic spectroscopic investigation on PET through the mechanical bond, using a supramolecular dyad comprised of a $[Ru(bpy)_3]^{2+}$ photosensitizer and a triarylamine (TAA) donor, situated on different components of a [2]rotaxane.

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Bifunctionalised Vitamin B_{12} Derivatives for Medicinal Applications

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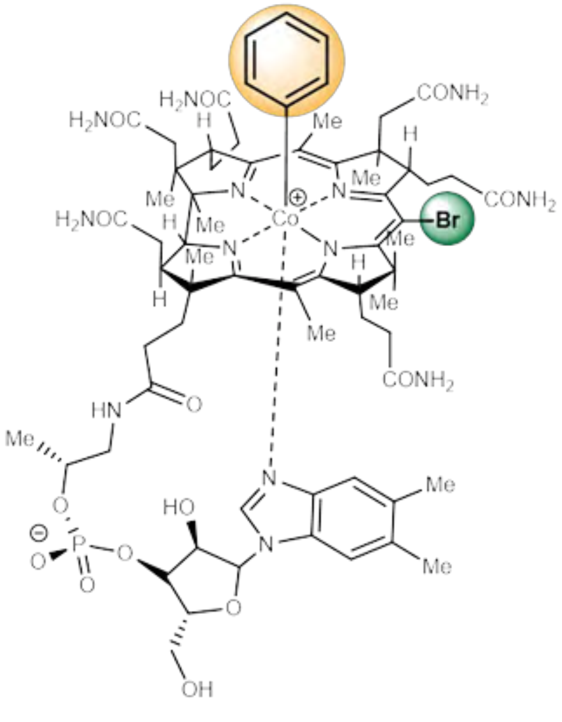
Antimetabolites and antivitamins are molecules that diminish or abolish the specific metabolic functions of vitamins.[1] In the case of vitamin B_{12}, designing an antimetabolite that inhibits B_{12}-dependent metabolism by competitive binding is a challenging task.[2] In the Zelder group, we have set out to explore novel routes towards bifunctionalised B_{12} antimetabolites by combining chemical modifications of the corrin scaffold and the upper (β-) axial ligand to design the most powerful antivitamins against specific biological targets, namely bacteria and cancer cells.[2,3]

In the poster, we present a substance library of bifunctionalised cobalamin derivatives as promising new antibacterial agents.[4] It is demonstrated that the upper (β-) axial organometallic ligand controls the antimetabolic effect. Some of the derivatives do not only represent powerful “antivitamins B_{12}”, but also allow for further functionalization. With such tools in hand, further progress in vitamin B_{12} chemistry to utilize B_{12} derivatives as antibiotic and antiproliferative agents in real-live applications becomes foreseeable.



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The development of new luminescent MOFs for molecular detection.

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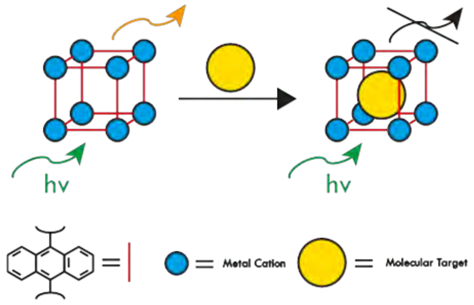
Metal-organic frameworks (MOFs) are a fascinating class of hybrid organic-inorganic porous crystalline nanomaterials built from metal-ions and organic bridging ligands [1]. Among the applications of MOFs in different prominent fields [2], the sensing and detecting of specific target components, including toxic and aromatic compounds, volatile organic compounds (VOC), pesticides and explosives, have attracted our attention. In our group, extensive research over the past few years has focused on the design, synthesis, and investigation of a new class of anthracene-based MOFs. Modification of different parameters of these compounds revealed them to very promising candidates for the molecular detection of analytes due to changes in their optical properties through host-guest interactions.



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Anti-Cancer Activity of Polyoxometalates and their Nanocomposites

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The medicinal applications of polyoxometalates (POMs) have long been investigated. More recently organic modification and encapsulation of POMs have been found to enhance the POMs' activity and selectivity towards malignant or infected/foreign cells. In this work, we investigate the anticancer activity of polyoxotungstates, with the aim of determining which features of the POM are biologically active and the targets of these features, so that the POM's structure can be modified systematically to optimize the treatment. For this, we use the anti-viral POM $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ as a model.

Moreover, we encapsulate the POM with a biocompatible polymer, carboxymethyl chitosan (CMC). Through ionotropic gelation, we can form nanoparticles ranging from 100 to 200 nm in diameter. The polymer has been chosen as it is minimally cytotoxic and, in some instances, can enhance the cellular uptake of drugs when it is employed as a drug carrier. We aim to understand how the polyoxometalate interacts with the polymer and to uncover how the entrapment in CMC modifies the POMs bioactivity.

The chemistry of Cu_3N and Cu_3PdN nanocrystals

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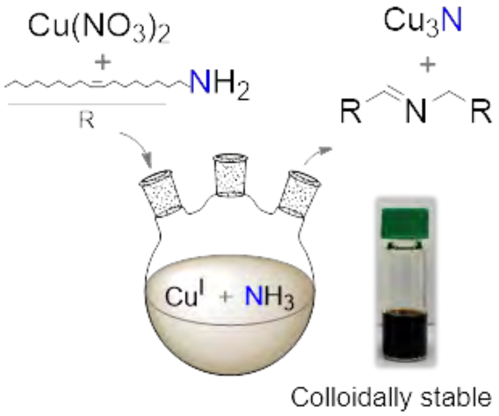
Cu_3N and Cu_3PdN nanocrystals are attractive materials with numerous applications ranging from optoelectronics to catalysis. However, their chemical formation mechanism and surface chemistry are unknown or contested. In this work, we first optimize the synthesis and purification to yield phase pure, colloidal stable Cu_3N and Cu_3PdN nanocubes. Second, we elucidate the precursor conversion mechanism that leads to the formation of Cu_3N from copper(II) nitrate and oleylamine. We find that oleylamine is both the reductant and nitrogen source. Oleylamine is oxidized to a primary aldimine and the latter reacts further with oleylamine to a secondary aldimine, eliminating ammonia. Ammonia reacts with Cu(I) to form Cu_3N. Third, we investigated the surface chemistry of the nanocrystals using solution NMR spectroscopy and X-ray photoelectron spectroscopy (XPS). We find a mixed ligand shell of aliphatic amines and carboxylates. The carboxylate is produced *in situ* during the synthesis. While the carboxylates appear tightly bound, the amines are easily desorbed from the surface. Finally, we analyze the optoelectronic properties by UV-Vis and XPS. Doping with palladium decreases the bandgap and the material becomes semi-metallic. These results bring insight into the chemistry of metal nitrides and will help the development of other metal nitride nanocrystals.



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Mechanistic insights into multi-photon driven photocatalysis and its application for challenging redox catalysis

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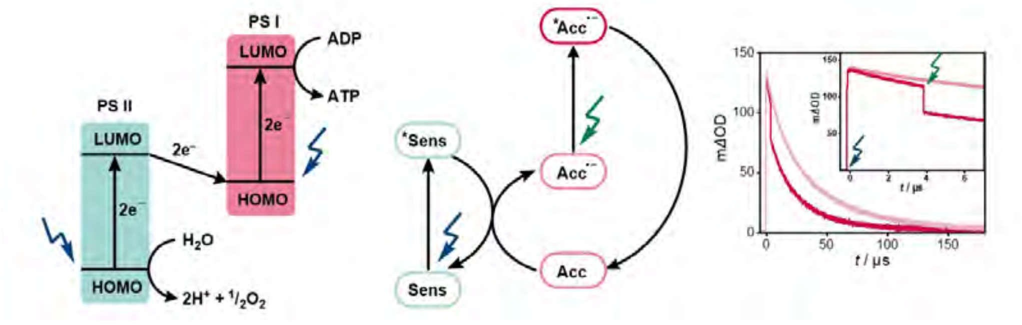
Photoredox catalysis has led to significant progress in organic synthesis by using visible light for the mild activation of small molecules but has an intrinsic energetic limitation of 3.1 eV, corresponding to the energy of blue photons. As a result, challenging chemical transformations cannot be initiated with a single visible photon and biphotonic excitation is needed, whereby the energy of two photons is combined to overcome the intrinsic limitation.[1, 2] However, elucidations of such multi-photon mechanisms in complex photocatalytic systems are rare but essential for the development of the growing field of biphotonic catalysis.[2-4] Here we report a biphotonic mechanism, mimicking the photosystem I and II, where two different light-absorbers are combined leading to an extremely strong reductant, yet using only visible photons, able to dehalogenate and detosylate challenging substrates in the presence of suitable electron donors. The investigated mechanism involves an electron transfer where an iridium(III) sensitizer absorbs the first photon and transfers one electron to a terphenyl-based redox catalyst forming an energy-rich radical anion that can be excited with a second photon forming a very reactive species. Using time-resolved spectroscopy we were able to investigate each step of the proposed mechanism including two-pulse experiments, where the depletion of the terphenyl-based radical anion could be observed upon the second laser pulse.



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Mechanistic Insight into the Precursor Chemistry of ZrO_2 and HfO_2 Nanocrystals; towards Size-Tunable Syntheses

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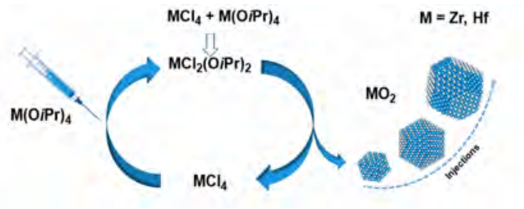
One can nowadays readily generate monodisperse colloidal nanocrystals, but a retrosynthetic analysis is still not possible since the underlying chemistry is often poorly understood. Here, we provide insight into the reaction mechanism of colloidal zirconia and hafnia nanocrystals synthesized from metal chloride and metal isopropoxide. We identify the active precursor species in the reaction mixture through a combination of nuclear magnetic resonance spectroscopy (NMR), density functional theory (DFT) calculations, and pair distribution function (PDF) analysis. We gain insight into the interaction of the surfactant, tri-*n*-octylphosphine oxide (TOPO), and the different precursors. Interestingly, we identify a peculiar X-type ligand redistribution mechanism that can be steered by the relative amount of Lewis base (L-type). We further monitor how the reaction mixture decomposes using solution NMR and gas chromatography, and we find that $ZrCl_4$ is formed as a by-product of the reaction, limiting the reaction yield. The reaction proceeds via two competing mechanisms: E1 elimination (dominating) and S_N1 substitution (minor). Using this new mechanistic insight, we adapted the synthesis to optimize the yield and gain control over nanocrystal size. These insights will allow the rational design and synthesis of complex oxide nanocrystals.



Novel Re (I) tricarbonyl complexes of thiazolhidrazinylidene-chroman-2,4-diones

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Rhenium complexes, mostly explored for their anti-tumor properties, were recently shown to possess promising antibacterial properties. A new strategy for designing metal complexes entails using ligands that already have biological activities. In medicinal chemistry, several derivatives of the coumarin core have already shown a wide spectrum of physiological and pharmacological activities. Based on that, a previous study in our group evaluated a series of arylcoumarin of *fac* -[Re(I)(CO)$_3$] complexes for their antimicrobial activities.[1] Some of these species showed remarkable antimicrobial activity against methicillin-resistant *S. aureus* (MRSA) with MIC values *in vivo* as low as 350 ng/mL (Fig 1, left). This encouraged us to explore the synthesis of new complexes of coumarin. In particular, derivatives of thiazolhidrazinylidene-chroman-2,4-diones and their corresponding bidentate and monodentate *fac*-[Re(I)(CO)$_3$] complexes were prepared (Fig 1, right).

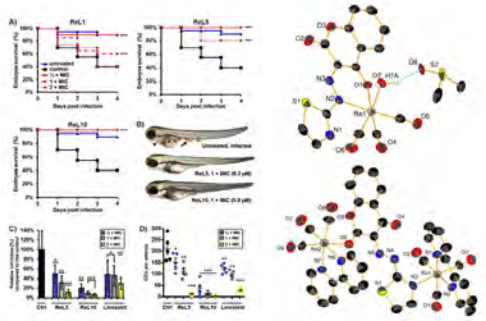

Fig.1 Left. Effect of arylcoumarin *fac-[Re(I)(CO)$_3$] complexes in efficiently rescuing zebrafish embryos of the lethal MRSA-infection. Right. New bidentate and monodentate fac-[Re(I)(CO)$_3$] thiazolhidrazinylidene-chroman-2,4-dione species prepared in this study.*

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Electronically flexible pyridyl-pyridylidene amide ligands for palladium-catalyzed α-arylation of ketones

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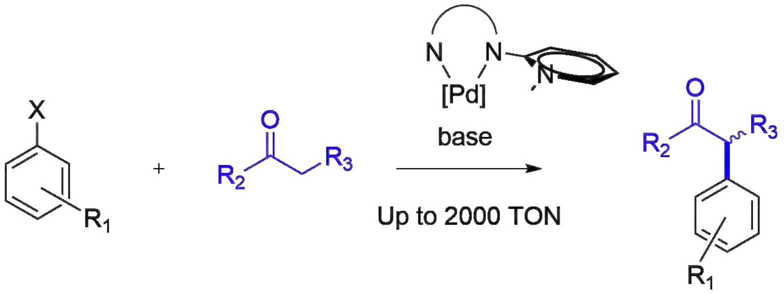
Electronically flexible ligands such as pyridylideneamides (PYAs, see Figure 1) can vary their degree of donor ability and may stabilize several intermediates of the catalytic cycle.[1] This ligand flexibility is a highly desirable feature in a process such as cross-coupling where different oxidation states are involved during the catalytic cycle[2]. In their zwitterionic form, these ligands exhibit strong donating properties that facilitates oxidative additions on the coordinated metal center. Furthermore, their ease of production, low-cost synthesis and high tunability make them efficient alternatives to carbenes and phosphines. Here we introduce different pyridyl-PYA ligands coordinated to palladium(II), which afford, highly active and robust ketone alpha-arylation catalysts. The herein reported TONs are unprecedented for N-based ligand for such a transformation[3].



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Demonstrating and unraveling a controlled nanometer-scale expansion of the vacancy defects in graphene by CO_2

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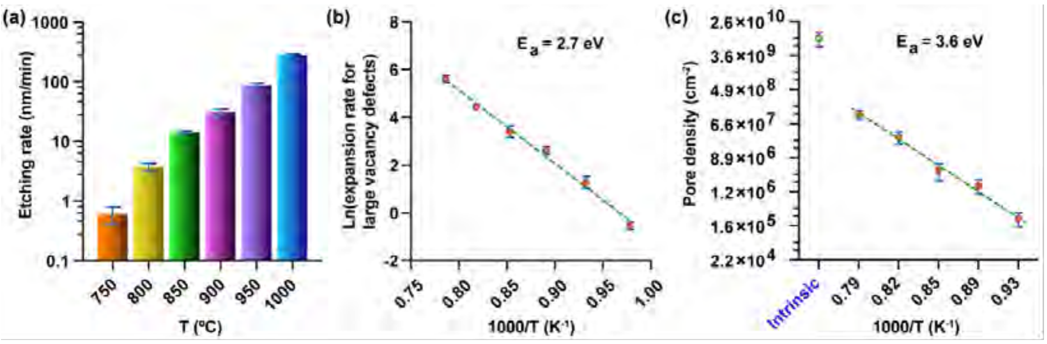
A controlled manipulation of graphene edges and vacancies is desired molecular separation, sensing and electronics applications. Unfortunately, available etching methods always lead to vacancy nucleation making it challenging to control etching [1]. Herein, we report CO_2-led controlled etching down to 2 – 3 Å per minute while completely avoiding vacancy nucleation. This makes CO_2 a unique etchant for decoupling pore nucleation and expansion. The theoretical literature predicts that CO_2 should not nucleate pores in graphene because of an extremely high energy barrier for its chemisorption on the basal plane of graphene [2]. This systematic pore expansion study, tracking the density of expanded pores as a function of etching condition, not only confirms the theoretical prediction but also reveals that only vacancy defects larger than 0.30 nm can be expanded by CO_2 [3]. So far, the energetics for CO_2 led etching of graphene edges were only studied by computational calculations and no experimental data was available. This study, for the first time, validates that CO_2 expands graphene edges with an energy barrier is 2.7 eV, close to that predicted for the dissociative chemisorption of CO_2 on the zigzag edges.



We demonstrate the presence of an additional configurational energy barrier for nanometer-sized vacancies resulting in a significantly slower rate of expansion. Finally, CO_2 etching is applied to map the location of the intrinsic vacancies in the polycrystalline graphene film where we show that the intrinsic vacancy defects manifest mainly as grain boundary defects where intragrain defects from oxidative etching constitute a minor population. These results present a novel tool for the manipulation of vacancy defects in graphene with an added advantage of highly controlled size manipulation decoupling pore nucleation from pore expansion. This will inspire and aid future studies aiming to tune the PSD in graphene for molecular separation and sensing studies. It will also aid efforts to manipulate the width of graphene nanoribbons to control their electronic properties. Finally, CO_2 etching will also find application in the mapping of the intrinsic vacancy defect with respect to grain boundaries, a method which can be extremely useful for researchers looking to control or manipulate the intrinsic defects.

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Novel manganese complexes with phenolate-substituted NHC ligands: catalytic application in the oxidation of organic compounds

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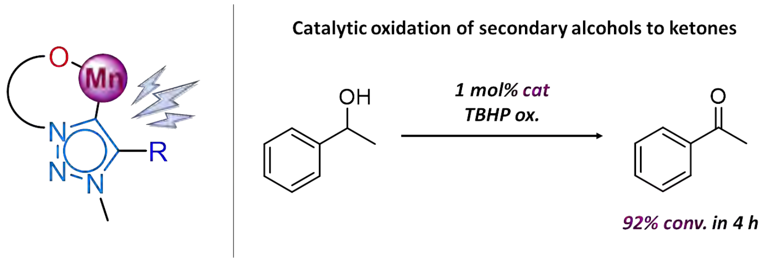
Oxidation chemistry keeps playing a critical role in organic synthesis for the production of pharmaceuticals and value-added products, such as fragrances. Catalytic approaches are more attractive than stoichiometric processes with hazardous inorganic oxidants, as well as the replacement of noble metals currently employed in industry with earth abundant metals such as Mn would be significantly convenient.

Our group recently synthesized a new class of 1,2,3-triazolylidene ligands bearing phenolate moieties and their corresponding Ni and Fe complexes were found promising for several catalytic applications.[1,2] We decided to evaluate the activity of the Mn analogues in the oxidation of selected substrates, which could benefit from the electronic flexibility of the mesoionic carbene fragment.[3] In this work, we show that a high-valent Mn/NHC system efficiently catalyses the oxidation of secondary alcohols and will discuss the effects of structural and electronic ligand variations.



- Air-stable Mn-NHC complexes thanks to *O*-coordination
- MICs as electronically flexible ligands
- R group for side functionalization

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Maturarbeit: Towards a copper-Azophloxine inorganic complex for the selective naked-eye detection of pyrophosphate in water

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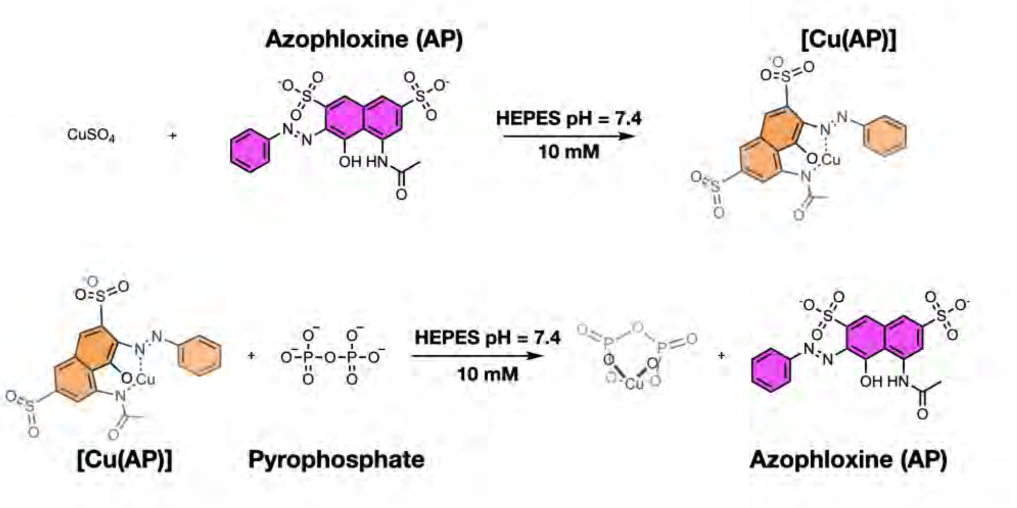
For the purpose of a high school thesis, we investigate with a student the possibility of detecting pyrophosphate with an indicator displacement assay using a copper-based inorganic complex. Our results indicate that real research with socially relevant results can be conducted at high school using very modest resources. [1]



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Initiation of Methyltrioxorhenium by C–H Activation in Homogeneous Olefin Metathesis Catalysts

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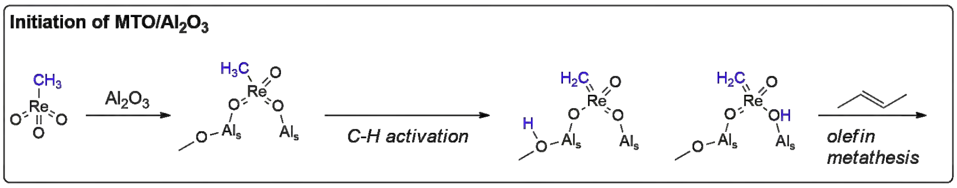
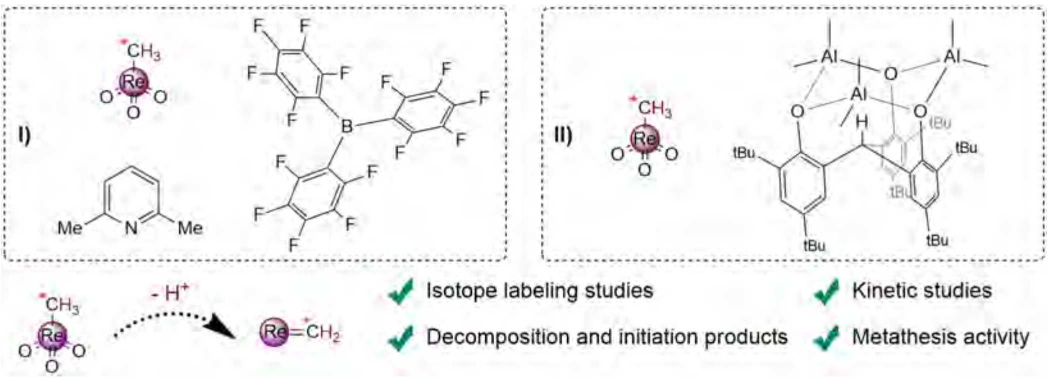
Olefin metathesis can be performed in homogeneous or heterogeneous fashion, mostly employing Ru, Mo, W, or Re catalysts. For the latter, methyltrioxorhenium (MTO) supported on alumina is a fairly well studied system [1]. The initiation of MTO/Al_2O_3 to form the metathesis active alkylidene is proposed to proceed via C–H activation of the MTO methyl group. This can take place either at a basic site on the support [1-3] or by tautomerization of the surface-coordinated MTO [4]. Mechanistic studies of heterogeneous catalytic reactions are often impaired by the fact that the surface species are ill-defined, and thus hard to investigate. We therefore sought to design homogeneous model systems, which enable us to study the C–H activation of MTO under metathesis conditions.



We looked at two model catalysts: **I)** a tri-component catalyst consisting of a frustrated Lewis pair (FLP) / MTO; and **II)** a trimetallic methyl aluminum phenoxide complex / MTO. The first one is inspired by small molecule activation chemistry with FLPs, while the second one is supposed to mimic an alumina surface on a molecular level. NMR studies using isotopically labeled MTO gave insight into the activation of the MTO methyl group by deprotonation. Tracking catalyst decomposition and metathesis initiation products allowed for indirect evidence on the initial active species. These experiments suggest that the initially formed alkylidene is indeed a rhenium methylidene, which originates from the MTO methyl group. In addition, the interconnection of these consecutive steps is corroborated by kinetic studies. The present study with the two homogeneous catalysts complements the work in the heterogeneous field consistently.



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Transactinide chemistry in the sub-second regime using vacuum adsorption chromatography

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The chemical characterization of superheavy elements (SHEs, $Z \geq 104$) demands for fast techniques and is conducted at the one-atom-at-a-time level. The state-of-the-art approach used for such studies is gas adsorption chromatography, which reaches its limit with radionuclides featuring half-lives of >1 s [1]. Thus, radioisotopes of heaviest elements beyond flerovium (Fl, $Z=114$) cannot be addressed with the currently available approach. However, a suitable alternative is vacuum adsorption chromatography, which may allow for the characterization of SHEs with radioisotopes having half-lives in the millisecond regime [2].

Here, we present the designs of a vacuum adsorption chromatography experiment, which set out to proof the expected short processing times. Two substantially different designs were compared using Monte Carlo simulations. Based on these simulations, a final design has been chosen for a planned experiment at the Cyclotron Institute of Texas A & M University.

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Zirconium and hafnium metal oxo clusters as smallest conceivable nanocrystals; from synthesis to application

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[1]University Basel, [2]University Ghent

Group 4 metal oxo clusters $[Zr_6O_4(OH)_4(RCOO)_{12}]$ are an interesting type of material with applications in 3D-printing, MOF's and catalysis.[1-3] They exist as a dimer or a monomer, depending on the ligand used during synthesis. These systems are often regarded as the smallest conceivable nanocrystals since they consist of an inorganic core capped with organic ligands, similar to nanocrystals.

Despite the vast amount of applications there is no consistency throughout the available synthesis. On top of this, complete characterizations are lacking in literature. In the past, crystal diffraction was the main characterization technique to obtain structural information. However, crystallizing these compounds becomes more and more challenging (if not impossible) when longer ligands are used. Making it impossible to study the structure with crystal diffraction techniques.

In order to overcome this problem Pair Distribution Function (PDF) was used. Since it allows for measuring liquid fatty acid capped clusters and still obtain structural data. The organic ligand shell on the other hand is probed via NMR, TGA and IR.

By improving the synthesis and purification of these clusters we developed an extended library of possible ligands which allows for solubility of these cluster in a large range of solvents with different polarities. By using our characterization toolbox, we found that the dimerization depends on the steric hindrance of the ligands itself and that hydrogen bonded ligands are inherent to the system on top of the coordinated ligands. Our results were found to be applicable for hafnium as well. Lastly, these clusters showed improved catalytic activity compared to nanocrystals which can be used as esterificaiton catalysts.[4]

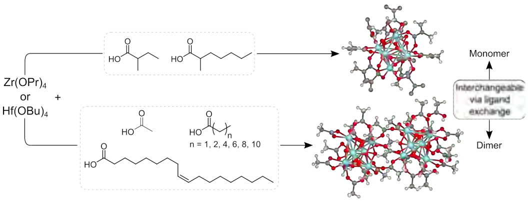

Figure 1. General scheme showing the control over monomeric versus dimeric clusters by changing the ligand reacting with the $M(OR)_4$ precursor. Via ligand exchange these 2 different cluster species can be converted into one another.

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High Temperature Studies with 4H-SiC α-Detectors for Future Superheavy Element Experiments

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The state-of-the-art technique for chemically classifying superheavy elements (SHEs, Z 104) is gas phase thermochromatography. Using this approach, the deposition temperature of the SHE under investigation within the chromatography channel relates to the element's adsorption enthalpy with the chosen stationary surface. To accommodate for short half-lives and low production rates, the chromatography channel consists of an array of detectors, whose surface acts as the stationary phase. This method has worked well for the characterizations of elemental copernicium (Cn, Z = 112) [1], elemental flerovium (Fl, Z = 114) [2], and $Sg(CO)_6$ (seaborgium, Z = 106) [3], where subzero temperatures are needed for the adsorption of the chemical species inside the detector array. A thermochromatography setup currently at Paul Scherrer Institut, the Cryo-OnLine Detection system (COLD), utilizes an array of Si-based α-detectors subjected to a negative temperature gradient from room temperature to approximately -180 °C. For comparably less volatile compounds and elements, e.g., Nh and NhOH (nihonium, Z = 113) [4], temperatures above the working range of Si-based detectors are required. The 4H-SiC semiconductor presents an affordable and expandable alternative α-detector option. The larger band gap (i.e., 3.23 eV for SiC vs. 1.14 eV for Si) makes 4H-SiC a suitable candidate for high temperature α-spectroscopy. Presented here are the results of high temperature tests up to 700 °C in preparation for future SHE chemistry experiments.

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Evaporation of polonium from heavy-liquid-metal-cooled reactors

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The use of liquid metals as a coolant is a potential development path for generation IV nuclear power reactors. This type of reactor is primarily intended for the use as a so-called breeder reactor or for the transmutation of nuclear waste, thus closing the nuclear fuel cycle. The distribution and behavior of radionuclides produced during operation are of the utmost importance for evaluating the safety of such systems. In order to make accurate predictions, the release of radionuclides from the coolant must be well understood, particularly for potential accident scenarios.

Within the HORIZON2020 project PATRICIA, previous research on the volatilization of radionuclides from liquid lead-bismuth eutectic (LBE), that is pertinent for the safety of future accelerator-driven systems, is continued. Previous investigations on polonium, the most radiotoxic element produced in the reactor, focused predominantly on its volatilization behavior from pure LBE. For the experiments carried out in the framework of PATRICIA, it is intended to use LBE from the MEGAPIE target to investigate the effect of spallation products on the volatility of polonium. The unique feature of this sample material lies in the fact that it contains a similar chemical composition and radionuclide inventory as found in the spallation zone of an actual accelerator-driven nuclear reactor, which encompasses most elements of the periodic table. It can therefore be used as a surrogate to study the complex chemical system of a heavy-liquid-metal-cooled reactor. Here, we describe the latest results regarding the volatilization studies of polonium from MEGAPIE, employing the transpiration method.

Dinuclear uranium nitride complexes for small molecule transformations

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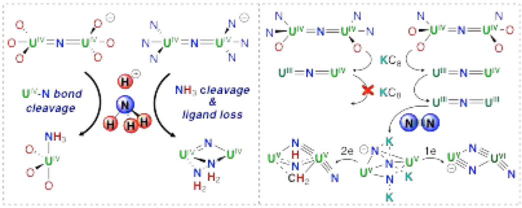
Uranium nitrides (UN_x) were identified almost 100 years ago as active catalysts in the industrial Haber-Bosch process for the conversion of dinitrogen (N_2) to ammonia (NH_3).[1] This has since generated significant interest in the dinitrogen chemistry of uranium, recently leading to the discovery of complexes capable of stoichiometrically converting N_2 to NH_3,[2-5] and even the catalytic conversion of N_2 to amine,[3] however, these types of transformations still remain relatively elusive. Herein, we present our work toward understanding the requirements necessary to undergo the 6e^- reduction and functionalization of N_2 to NH_3 utilizing well-defined diuranium complexes. First, we highlight our work for the comparative studies for the reactions of acid (H^+) and NH_3 with uranium nitrides containing different types of ancillary ligands, ultimately leading to contrast differences in reactivity.[6] This work allowed us to harness significant information for the design of diuranium complexes active in the H^+/e^- mediated catalytic transformation of N_2 to NH_3, as the conversion of uranium nitrides to NH_3 is an essential step in dinitrogen fixation. We will also present our work in probing ancillary ligand effects toward N_2 binding, by utilizing a series of heteroleptic diuranium nitride complexes containing different combinations of $OSi(O^tBu)_3$ and $N(SiMe_3)_2$ ligands.[7] In this work, we found by changing the number and type of ancillary ligands leads to contrast differences in reactivity, in which one complex is capable of N_2binding and cleavage, with subsequent functionalization to NH_3.



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