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Using Coordination Complexes to Inhibit Mitochondrial Calcium Uptake

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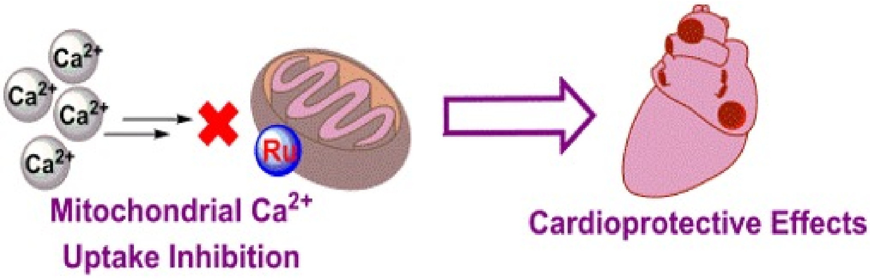
Mitochondrial calcium trafficking plays an important role in human health, and its dysregulation has been implicated in a wide range of pathological conditions [1]. In particular, mitochondrial calcium overload causes cell death. In this presentation, we will discuss our development of mitochondrial calcium uptake inhibitors, as both potential therapeutic agents for treating mitochondria-related disorders and tools for studying the role of calcium trafficking in this organelle [2]. Our research in this area has shown that both ruthenium and cobalt coordination complexes can act as potent inhibitors of mitochondrial calcium uptake [3, 4]. Furthermore, proper tuning of the properties of these complexes can lead to effective inhibitors that operate in intact cell systems and can be leveraged for eliciting cytoprotective effects. This work demonstrates the potential of simple coordination complexes as ion channel inhibitors with therapeutic potential.



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$Fe(TMP)_2$ - Synthesis, characterisation and tuneable reactivity of a new Fe(II) *bis*(amide) complex

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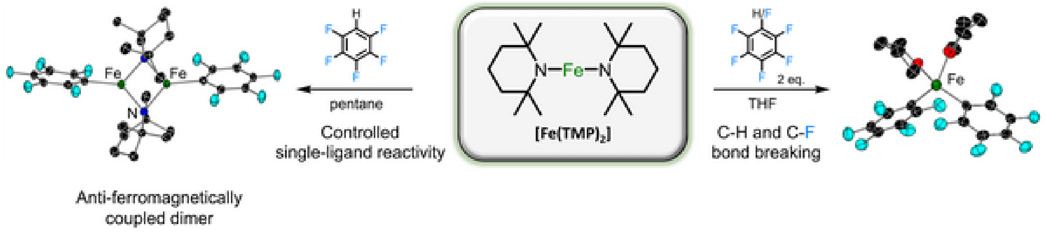
Two coordinate first-row transition metal complexes are rare but key class of reagent for the synthetic inorganic chemist. Such coordinatively unsaturated open-shell complexes are capable of displaying unique reactivity with small molecules, interesting coordination chemistry and often possess stimulating magnetic properties.[1] Since the introduction of the HMDS amido ligand (HMDS = hexamethyldisilazide) in the 1960's, $M^{II}(HMDS)_2$ complexes such as $Fe(HMDS)_2$, originally reported by Lappert and co-workers in 1988,[2] have been prepared and utilised to great extent as key synthetic precursors owing to their ease of synthetic access, high solubility and ligand lability. Recently we have utilised $Fe(HMDS)_2$, in combination with sodium amides, for the regioselective deprotonation and ferration of non-activated arenes.[3]

Breaking new ground in this field, here we introduce $Fe(TMP)_2$ as a new addition to the class of two-coordinate first-row transition metal complexes. Possessing highly basic TMP (TMP = tetramethylpiperidide) amido ligands, this iron *bis*(amide) exhibits unprecedented reactivity, capable of breaking C-H and strong C-F bonds, without the presence of a strong alkali-metal base. The synthetic routes to access this novel iron amide and its inherent properties, including structural, spectroscopic and magnetic characterisation will also be discussed. Furthermore, we detail its novel and tuneable reactivity towards fluoroarenes, providing mechanistic insight through DFT calculations.



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Iron and Cobalt Nitrilimide Complexes: Transformations to Nitride and Isocyanoamide Complexes *via* a Fleeting Diazomethanediide Intermediate.

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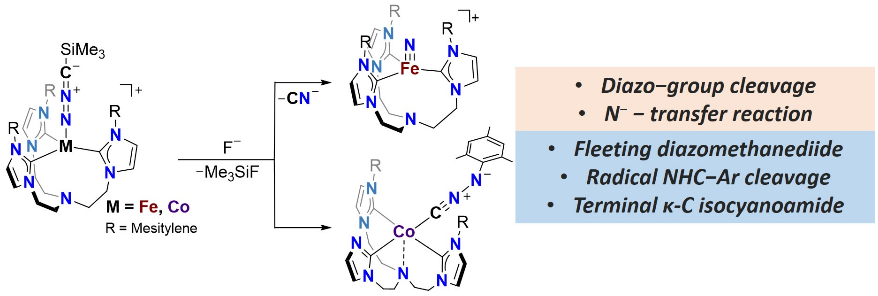
In a series of works, Rolf Huisgen and co-workers established that the thermal decomposition of tetrazole derivatives yields fleeting nitrilimines (RNNCR').[1] These intermediates were trapped upon their 1,3-dipolar cycloaddition with various substrates in a so-called Huisgen reaction. Guy Bertrand and co-workers isolated nitrilimines stabilized with bulky electron-withdrawing substituents at both C and N ends.[2] Building on the latter discovery, we envisaged that the redox of transition metals and the high reactivity of nitrilimines, brought together in transition metal nitrilimide complexes, potentially could give access to unique reactivity.

In this contribution, we will present a novel strategy to access transition metal nitrilimide complexes. Specifically, we have isolated Fe(II), and Co(II) nitrilimide complexes [$LM{-}N{=}N^{+}{=}C^{-}{-}SiMe_3$] stabilized within a *tris*-NHC ligand.[3,4] A suite of spectroscopic tools, crystallography analysis, and quantum-mechanical calculations revealed detailed electronic structures of nitrilimide complexes. The iron nitrilimide complex undergoes an unprecedented diazo group cleavage upon trimethylsilylium "$SiMe_3^{+}$'' group removal, giving entry to an iron nitride complex at mild reaction conditions.[3] Due to the inaccessibility of a cobalt nitride complex within the employed *tris*-NHC ligand, the cobalt nitrilimide complex engages in an alternative transformation upon "$SiMe_3^{+}$'' removal, forming a novel Co(II) complex featuring a terminal isocyanoamide ligand.[4] Quantum mechanical study suggests that the cobalt nitrilimide-to-isocyanoamide transformation proceeds via a fleeting intermediate featuring a diazomethanediide ligand. The understanding of the reactivity of nitrilimide complexes could be further implemented in designing alternative systems for unique element or group transfer reactions.



- *Diazo−group cleavage*
- *N− – transfer reaction*
- *Fleeting diazomethanediide*
- *Radical NHC−Ar cleavage*
- *Terminal κ-C isocyanoamide*

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Delivery of a masked uranium(II) by an oxide bridged diuranium(III) for multi-electron transfer reactions

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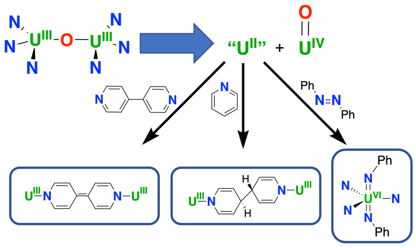
One of the main challenges chemistry currently faces in the transition to a sustainable economy is the activation and functionalization of small molecules, such as N_2, CO and CO_2, which requires multi-electron transfer processes. Low oxidation state uranium compounds have shown high reactivity in these transformations, but multimetallic complexes are often required, as uranium predominantly undergoes single electron transfer processes.[1] Recently in our group, the use of siloxide ligands allowed the isolation of two diuranium(III) complexes, which were bridged by a nitride or by an oxide, and both showed remarkable but different small molecule reactivity.[2,3] Besides the linker, also the ancillary ligands were shown to have an effect on the reactivity in a comparison of silylamide and siloxide ligands in nitride-bridged complexes.[4]

In this work, we continued to study silylamide supported complexes, resulting in the isolation of an oxide-bridged diuranium(III) complex.[5] Reactivity studies showed that the U–O bond is easily broken upon substrate addition, resulting in the delivery of a masked U(II) and a U(IV) terminal oxo co-product. The masked U(II) can effect cooperative single electron reductions of pyridine and bipyridines, affording unique examples of diuranium(III) complexes bridged by redox-active ligands, which can act as electron reservoirs. Furthermore, the masked U(II) is also able to effect multi-electron reductions of diphenylacetylene by two electrons and of azobenzene by four electrons.[6] This reactivity was shown to correspond to the reactivity displayed by the previously reported U(II) complex $[K\text{-}(2.2.2\text{-cryptand})][U\{N(SiMe_3)_2\}_3]$, showing the first example of a “clear-cut” single metal four-electron transfer in f-element chemistry.

These results provide new insight into how uranium can be used in multi-electron transfer processes, essential in the activation of small molecules.



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ALISI – Automated Light induced Synthesis of ^{89}Zr-Radiolabeled Antibodies for ImmunoPET

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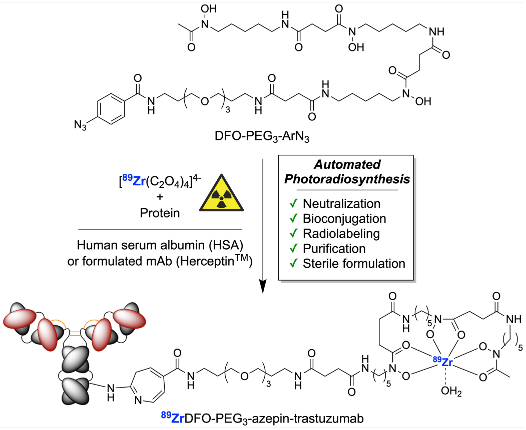
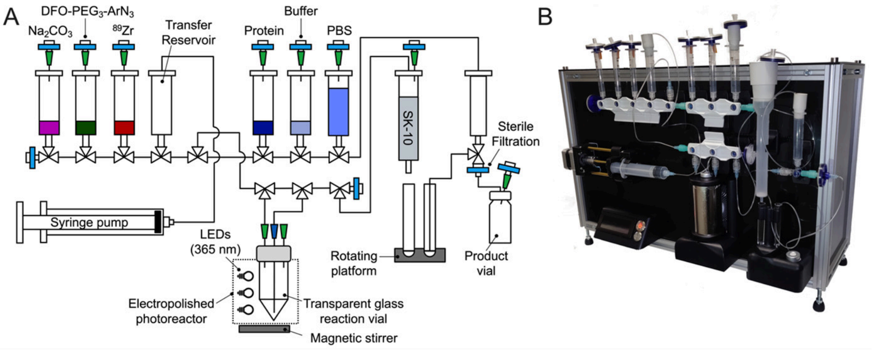
The standard production of ^{89}Zr-radiolabeled antibodies (^{89}Zr-mAbs) relies on the pre-conjugation of desferrioxamine B (DFO) to the purified protein, followed by isolation and characterization of the functionalized intermediate, and then radiosynthesis on demand. Although highly successful, this route entails several technological and economic hurdles that limit the more wide-spread development of ^{89}Zr-mAbs at smaller research and clinical facilities. Here, we adapted our one-pot photoradiosynthesis approach for automation and designed ALISI – a synthesis box that can produce and isolate ^{89}Zr-mAbs starting from $[^{89}Zr(C_2O_4)_4]^{4-}$ (^{89}Zr-oxalate), our photoactivatable DFO-PEG$_3$-ArN$_3$ chelate, and clinical-grade Herceptin without pre-purification of trastuzumab.



Methods: We constructed our prototype radiosynthesizer unit by using a combination of open-source microcontrollers (Arduino) and computer-aided design (CAD), coupled with additive manufacturing (3D-printing) techniques. Liquid handling components and fluidic pathways employ commercially available, single-use tubing and three-way switching valves operated by digital servo-motors. Liquid transfer is driven pneumatically with a syringe pump. For the in-line automated purification, we designed custom-made SK-10 that flow under gravity and allow for increased resolution between the small-molecule byproducts and the higher molecular weight ^{89}Zr-mAbs. **Results:** ALISI can produce ^{89}Zr-radiolabeled proteins formulated in sterile solution in 89Zr-oxalate stock, chelate radiolabeling, and light-induced protein conjugation, followed by ^{89}Zr-mAb purification, formulation and sterile filtration. **Conclusion:** Full automation of the simultaneous radiolabeling and photochemical bioconjugation process was demonstrated on a custom-made radiosynthesis unit. The ALISI box performs all of the essential steps required to make ^{89}Zr-mAbs in high radiochemical purity at the touch of a button.



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A Biomimetic Superreduced Iron-Sulfur Cubane and its Oxidized Analogues

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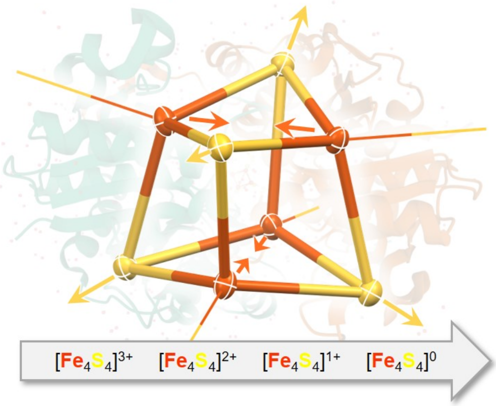
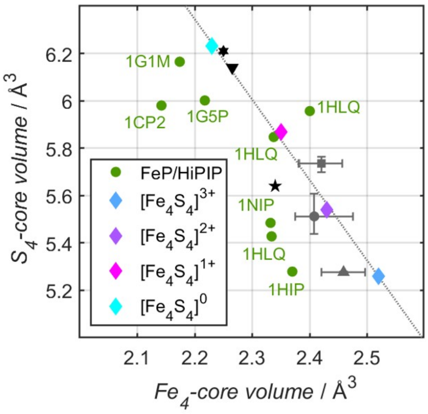
In nature, cystein-ligated iron-sulfur (FeS) cubanes of Ferredoxins (Fds) and High-Potential Iron-Sulfur Proteins (HiPIPs) mediate electron transfer and are known to exist in four different oxidation states, namely $[Fe_4S_4]^{0/1+/2+/3+}$.[1,2] Among these, the elusive “superreduced” all-ferrous state, $[Fe_4S_4]^0$, is only retained by the Iron Protein (FeP) of the Nitrogenase enzyme, which belongs to the Fd family.[3–5] Pioneered by R. Holm in the early 70s, bioinorganic chemists have isolated and characterized a variety of FeS cubanes. However, a systematically comparable redox series, which bears the same thiolate ligands and counter-cations and covers all biologically relevant oxidation states, including $[Fe_4S_4]^0$, is yet lacking.[6–8]





Herein we report the synthesis of $[Fe_4S_4(SR)_4]^{4-}$ *via* twofold chemical reduction of a novel cubane, $[Fe_4S_4(SR)_4]^{2-}$, in its traditional oxidation state. To the best of our knowledge, $[Fe_4S_4(SR)_4]^{4-}$ is the first example of an all-ferrous FeS cubane supported by thiolate ligands, that is isolable in substance and characterized by X-ray diffraction analysis. Its oxidation state assignment is supported by extensive spectroscopic characterization including UV-Vis, EPR, XAS, EXAFS as well as variable-temperature ^{57}Fe Mössbauer spectroscopy. Further, for the first time, using straightforward redox-chemistry, all biologically pertinent oxidation states of this new FeS cubane system, $[Fe_4S_4(SR)_4]^n$ (n = 1-, 2-, 3-, 4-), are accessible. X-ray diffraction analysis of all members of this biomimetic electron-transfer series reveals that reduction of the Fe_4S_4-core is accompanied by structural compression of the Fe_4-tetrahedron and a concomitant expansion of the S_4-tetrahedron in a linear relationship. Thereby, because the S_4-expansion supersedes the Fe_4-contraction, the overall FeS cubane-volume as well as its surface area are being maximized, which confirms the long-standing hypotheses of biological studies.[5]

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What is more important to enable efficient cyber-physical systems – Digital Twins or the degree of automation in RnD labs?

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Gamification, Internet of the Lab Tools, Digital Twins, Machine Learning/ Artificial Intelligence combined with automation are pivotal tools to move chemical R&D processes and operations into the digital age.

Presented concepts and solutions will show that digital twins are disruptive for every lab and enable the AI/ML pipelines in the future. The presentation will show Chemspeed's top-down and bottom-up digitalization approach that is shaping the R&D sphere.

Fully Solvated, Monomeric Re^{II} Complexes: Insights into the Chemistry of [Re(NCCH$_3$)$_6$]$^{2+}$

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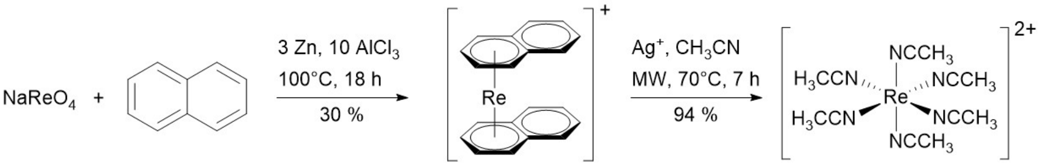
The coordination chemistry of the group 7 elements rhenium and technetium is very versatile and takes place across many different oxidation states, usually ranging from +VII to 0. Of course, not all oxidation states are encountered to a similar extent. The most prominent oxidation state is +V, whose d^2-system is stabilized by π-donors such as oxo or nitrido. Over the past few years the numbers of complexes with the oxidation state +I increased, especially due to the development of suitable precursor compounds such as the tricarbonyl-cores ({*fac*-M(CO)$_3$}$^+$, M = Re, $^{99(m)}$Tc). A relatively rarely encountered oxidation state is +II. One of the reasons for the small amount of Tc and Re complexes in the oxidation state +II is the lack of stable but also reactive precursor complexes. In general, Re^{II} and Tc^{II} compounds are produced by the oxidation of a M^I species or by the reduction of a higher valent complex (e.g. M^{III}). The development of suitable precursor complexes might therefore significantly contribute to the syntheses of novel rhenium and technetium complexes in the oxidation state +II.



Fully solvated metal centers are useful precursors in coordination chemistry, as they solely consist of the metal core surrounded by one specific type of ligand, namely solvent molecules. The solvent molecules stabilize the metal center in its oxidation state, but are still easily exchanged which enables substitution reactions. Examples for such fully solvated precursors are the hexaqua complexes of the first row transition metals such as [Co(H$_2$O)$_6$]$^{2+}$. Such hexaaqua complexes have so far not been found for Tc or Re, though there are some examples of fully solvated complexes with acetonitrile as ligand such as the dimeric [Re$_2$(NCCH$_3$)$_{10}$]$^{4+}$ or the monomeric [^{99}Tc(NCCH$_3$)$_6$]$^{2+}$.[1,2] Recently, we were able to synthesize the fully solvated and monomeric [Re(NCCH$_3$)$_6$]$^{2+}$ by Ag^I mediated oxidation of [Re(η^6-C$_{10}$H$_8$)$_2$]$^+$ in acetonitrile. The unexpectedly stable [Re(NCCH$_3$)$_6$]$^{2+}$ was fully characterized and its potential as a Re^{II} precursor complex was examined with various substitution reactions with phosphines and halides. Additionally, using DFT calculations we propose a possible mechanism for the formation of [Re(NCCH$_3$)$_6$]$^{2+}$.[3]

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Can early lanthanide sandwich complexes be efficient single-molecule magnets?

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Single-molecule magnets (SMMs) have unique properties that open new possibility in high-density data storage, spintronic devices as well as quantum computing.[1-4] Their defined feature is the slow relaxation of their magnetization in the absence of an applied field. In the so-called lanthanide sandwich complexes, the high intrinsic magnetic moment is combined with a strong axial coordination environment, which has proven to be favourable for SMMs and has led to the best reported magnetic properties so far.[4-8] State-of-the-art SMMs are based on lanthanide ions (mainly Dy^{3+}, Er^{3+} and Tb^{3+}) due to their highly anisotropic ground state and their intrinsic unquenched spin-orbit. Despite these clear advantages, the low natural abundance of late lanthanides renders SMMs based on these elements expensive and could prohibit their future industrial implementation. Conversely, the lighter elements of the series are substantially more abundant[9] and are already used commercially as permanent magnets (NdFeB and SmCo).[10-11] However, their usage in SMMs has been so far limited as light lanthanide complexes rarely exhibit slow relaxation of magnetization in zero field. In principle, this issue could be ameliorated by careful tailoring the coordination environment of the lanthanide ion. We decided to explore bulky ring-type organic moieties as ligands of choice for the design of neutral early lanthanides based SMMs. We hypothesized that a strong axial coordination environment in combination with the absence of ligands in the equatorial plane will engender formation of a zero-field SMM. Indeed, our results show that the successfully synthesized novel organometallic complex exhibits slow magnetic relaxation without applied external field at low temperatures. Furthermore, we show that the dilution of the complex in the diamagnetic matrix can further improve the relaxation properties of this system.

In conclusion, we have leveraged the design principles for known late lanthanide sandwich complexes to synthesize a novel zero-field SMM based on a less investigated element of the lanthanide series. We demonstrate that the use of bulky ligands can tailor the coordination environment to mitigate the fast relaxation of the magnetic moment.

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Chemical investigation with exotic radionuclides

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From the prediction of atomic and molecular properties to the understanding of the development of our universe, exotic radionuclides are nowadays of great interest in several research domains. Whereas these exotic elements are recently discovered transactinides, or long-lived lanthanides, the study of their chemical and nuclear properties represents a unique challenge. Transactinide elements can only be produced artificially in heavy-ion induced nuclear fusion reactions. The typically low production rates and short half-lives of these elements require rapid and selective chemical setups. This entails that a complete and unambiguous chemical characterization of a transactinide can only be achieved by studying – literally – one atom at a time [1, 2].

Different but no less challenging is the determination of nuclear properties, such as half-lives, of exotic lanthanides. Certain long-lived lanthanides (e.g., ^{146}Sm, ^{154}Dy, ^{148}Gd, ^{157}Tb) play a fundamental role in astrophysics and nuclear physics. For many of these studies, an accurate knowledge on the nuclear properties of the above-mentioned radionuclides is required. However, the currently available data for the half-life of ^{146}Sm, ^{148,150}Gd, ^{154}Dy, and ^{157,158}Tb are inconsistent, or affected by high uncertainty [3-5]. Reasons for these shortcomings in the nuclear databases are in many cases the limited availability of the isotopes of interest, often accompanied by difficulties in the preparation of samples with a high chemical purity. To overcome these limitations, the initiative "Exotic Radionuclides from Accelerator Waste for Science and Technology – ERAWAST", was launched in 2006 at Paul Scherrer Institute (PSI) [6, 7]. This long-term project aims to reprocess irradiated materials from the PSI accelerator-facilities, in order to obtain exotic radionuclides for scientific purposes. Detailed information can be found at the website: psi.ch/en/lrc/erawast. Among the several applications of ERAWAST, special focus is given to the improvement of the existent nuclear databases by re-determining the half-life of exotic radionuclides.

Here, the latest results on the chemical experiments with the transactinide dubnium (Z = 105) [8] in collaboration with the Japan Atomic Energy Agency (JAEA), together with the current developments related to the ERAWAST project, will be presented.

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DNA-ferrocene as two-step-mechanophore

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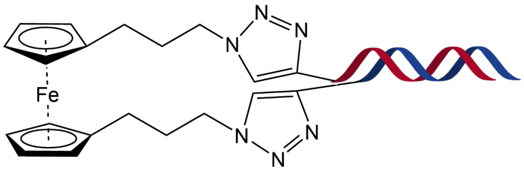
Since many years, researchers are interested in sandwich-type complexes that can be used in various areas like in catalysis, in electrochemistry, in agrochemical applications or for the production of pharmaceuticals and flavours.[1, 2] Recently, we have shown that ferrocene can be used as a mechanophore in polymers, hence as preferential breaking point in poly methyl-acrylate and polyurethane.[3]

We have now introduced additional functionality by associating the ferrocene moieties via a linker [4] to a DNA duplex. Embedding such an entity into a polymer is expected to give rise to a two-step mechanophore [5] (Figure 1) in which first the H-bonds of DNA, and then the sandwich-complex are cleaved as increasing force is exerted. Mismatches that have been introduced in the DNA pairing, have an influence on the mechanical strength of the mechanophore.



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New oxide group-9 transition metal superconductors in the filled-Ti_2Ni type structure

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The Ti_2Ni and the related η-carbide-type structures are known to exhibit various interesting physical properties [1, 2]. The Ti_2Ni structure is surprisingly complex for an intermetallic structure-type crystallizing in the space group Fd-3m with a unit cell containing 96 metal atoms [1]. The related η-carbide-type compounds of the general formula A_4B_2X or A_3B_3X correspond to a filled version of the Ti_2Ni structure. The role of the void filling light atom X, which can be carbon, oxygen, or nitrogen, has so far been unclear for the overall physical properties of these materials. Herein, we have successfully grown single crystals of Ti_2Co with the Ti_2Ni-type structure and single crystals of η-carbide-type oxide Ti_4Co_2O. We show that Ti_2Co displays a semimetallic behavior down to 0.75 K, and then a superconducting transition seems to occur at lower temperatures. Its oxygen filled-version Ti_4Co_2O is a bulk superconductor with a critical temperature of T_c = 2.7 K. We find that the interstitial oxygen plays a crucial role for the overall physical properties. By extending this concept to the other group 9 transition metals, we have successfully synthesized two new compounds, Ti_4Rh_2O and Ti_4Ir_2O. We, furthermore, show that both are new bulk type-II superconductors with superconducting transitions at T_c = 2.8 K and 5.3 K, respectively. We present detailed measurements on all three superconductors, showing that all three have remarkably high upper critical field in comparison with their critical temperatures. Most noteworthy Ti_4Ir_2O has an upper critical field of $\mu_0H_{c2}(0)$ =16.06 T, which is exceeding by far the weak-coupling BCS Pauli paramagnetic limit of μ_0H_{pauli} = 9.86 T.

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Targeted Design of Binuclear Copper Complexes for Efficient Electrocatalytic Water Oxidation

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Owing to the current global energy demands, electrochemical water splitting have emerged as a potential approach towards sustainable energy conversion and production of chemical fuels.[1] Following the understanding of nature's water splitting machinery: the {CaMn4O5} Oxygen Evolution Complex (OEC), many artificial chemical systems have been designed till date, so as to mimic the water oxidation pathway and thereby utilize the pool of generated electrons/protons for CO_2 fixation.[2] Although a sustainable approach, artificial water oxidation is both kinetically and thermodynamically challenging, which increases the need for superior water oxidation catalysts (WOCs).[3] Over the paste two decades, many transition metal-based homogeneous catalysts have been developed and have shown promising outcomes although they deal with stability issues over time, which effects their efficiency during turnover. In this regard, proper choice of active metal center and having stabilizing ligand environment is of utmost importance in the design of robust and efficient WOCs.[4] Copper being an earth abundant and less toxic metal is often accounted for its unique redox properties. Herein, we present three grenerations of novel Binuclear molecular WOCs based on Copper which shows enhanced water oxidation properties under electrocatalytic conditions. Additionaly, we show how ligand environment modulation and its electronic properties could enhance the water oxidation turnovers in Binuclear WOCs.

Keeping the dimeric Cu core, and modulating the ligand environment from Acetate to Alkoxypyridine, shows how the bimetallic core can be effectively stabilized and driven towards higher efficiency. Finally, addition of an extended conjugated system to the ligand have shown to enhance the water oxidation turnovers by the as designed Binuclear Cu WOCs. Detailed understanding of the electrocatalytic water oxidation turnover have been depicted by long-term Bulk electrolysis, which has shown efficient O_2 production without catalyst degradation on tuning the ligand environment from Acetate to Alkoxypyridine. We present herein, a mechanistic picture of the catalytic Metal core and its coordination changes via operando X-ray Spectroscopy, which has confirmed the presence of an high-valent Cu^{III} species as an active intermediate during water oxidation. Further we employed in-situ IR and Raman spectroscopic techniques to understand the mechanism of O-O bond formation and to deduce the plausible water oxidation pathway. All in all, we hereby communicate the importance of tarted tuning of ligand environment which greatly influence the strategic development of efficient water oxidation catalysts.

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Structure Elucidation of Colloidal Perovskite Nanocrystals by Solution NMR

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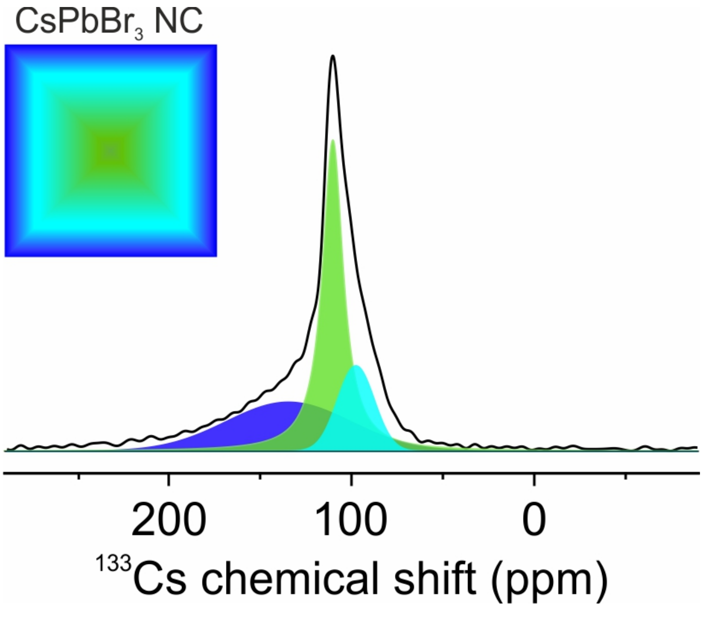
Cesium lead halide ($CsPbX_3$) perovskite semiconductor nanocrystals (NCs) increasingly mesmerize researchers because they exhibit outstanding optoelectronic properties. One of the remaining hurdles is atomistic structure determination due to their soft structure and their small size.[1] We address this challenge by using solution NMR spectroscopy. This easy-to-use technique can not only give insights into the elemental composition, but also into structural properties. Thanks to the incoherent tumbling of the NCs in in their colloidal state, the spectra of the crystalline cores resemble traditional solution NMR spectra. The identification of surface and core sites could be done by probing different size selected NCs. For mixed halide $CsPb(Br/Cl)_3$ NCs an anion segregation within the cores was observed, favoring the bigger bromide to be located on the more disordered and enlarged surface sites. The influence of the various available capping ligands on the structure in the NCs was studied, revealing an increased amount of disorder for zwitterionic, covalent-bonded ligands compared to their ionic-bonded counterparts which could be correlated with their optical properties. To corroborate our experimental data, we performed ab inito molecular dynamics simulations, which point to the role of the surface in causing the strain distribution and disorder within numerous sizes of NCs. These findings showcase the great potential of solution NMR in shedding light on the inorganic structure of colloidal NCs.



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Sulfur-Transfers on Transition Metal Phosphide Surfaces

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Transition metal phosphides have recently emerged as active catalysts in water splitting for the hydrogen evolution reaction (HER) and in hydrodesulfurization (HDS), i.e., the removal of sulfur from fuel feeds.[1,2,3] During HDS processes, the surfaces of transition metal phosphides become sulfided.[1] This surface sulfidation increases the activity of the material for HDS compared to bare phosphide surfaces. A similar promoting effect of sulfur at phosphide surfaces has been reported for HER applications.[2,3] Sulfidation clearly enhances the catalytic properties of transition metal phosphides, but the underlying physicochemical effect is not well understood. For a rational catalyst design fundamental insight into structure, thermochemistry, and reactivity of sulfided transition metal phosphides are critically needed.

Previously, we reported the bond strength distribution of hydrogen on cobalt phosphide measured via chemical equilibration of the material with molecular reagents.[4] In this poster, we present a related approach to probe the stoichiometry and thermochemistry of sulfur on transition metal phosphides. We discuss the sulfur transfer ability of phosphide surfaces and contextualize our findings with the reported promoting effect of sulfur.

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Effect of missing-linker defects on crystalline stability of UiO-66 under different gaseous conditions

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UiO-66 is a versatile zirconium based MOF, which is considered thermally stable up to 500°C. The crystalline stability of the MOF differs from thermal stability depending on various factors mainly on the defects of the MOF. Degradation patterns of various UiO-66 samples having varying “missing-linker” defects were studied under oxidative, reductive and inert conditions. The sample having the highest BET surface area (maximum number of defects) shows collapse of crystalline framework at lower temperature than those having less defects. TGA studies show that thermal mass loss of all the UiO-66 samples occurs above 450°C. After loss of crystallinity, the MOF remains in the form of an amorphous solid phase over a wide range of temperature (e.g. from 250°C to 450°C for UiO-66 having 1826 m^2/g BET surface area) before complete thermal decomposition.UiO-66 changes of tetragonal zirconia on heating up to 600°C under oxidative, reductive and inert conditions. On further heating up to 900°C under oxidative condition, the tetragonal phase changes to monoclinic phase but no phase change occurs under inert conditions. TEM images show that the shape of the UiO-66 crystals is maintained under inert and reductive conditions after heating to 600°C. These results will be helpful to design certain combinations of metals with zirconia on carbon support to get enhanced catalytic performance.

Key words: Missing-linker defects, UiO-66, crystalline stability, monoclinic zirconia, tetragonal zirconia.

Reactivity of a 5-Coordinated unsaturated Pya Reuthenium (II) Complex

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Flexible ligands have the ability to modify their donor properties. These characteristics offer opportunities for stabilizing different intermediates and make them of interest for catalytic applications. Pyridylideneamides (PYAs; Figure 1) are an innovative class of electronically flexible N-donor ligands and have been successfully used for catalysis, such as in transfer hydrogenation or water oxidation.[1,2] Here we will present a rare 5-coordinated unsaturated ruthenium (II) complex containing a PYA unit (Figure 1). We will discuss the reactivity of the complex towards external ligands and its applications in catalysis.

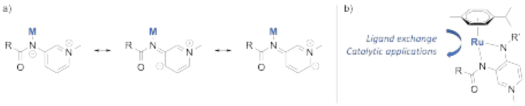

Figure 1. Limiting resonance structures of a *meta*-PYA unit (a), schematic representation of the unsaturated ruthenium (II) complex and its reactivity (b)

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Interaction of small molecules with ^{99}Tc pincer-type complexes

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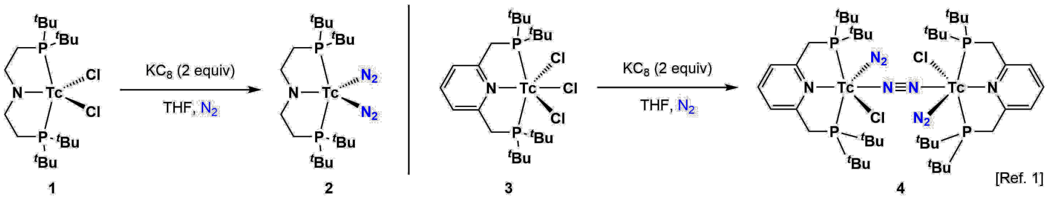
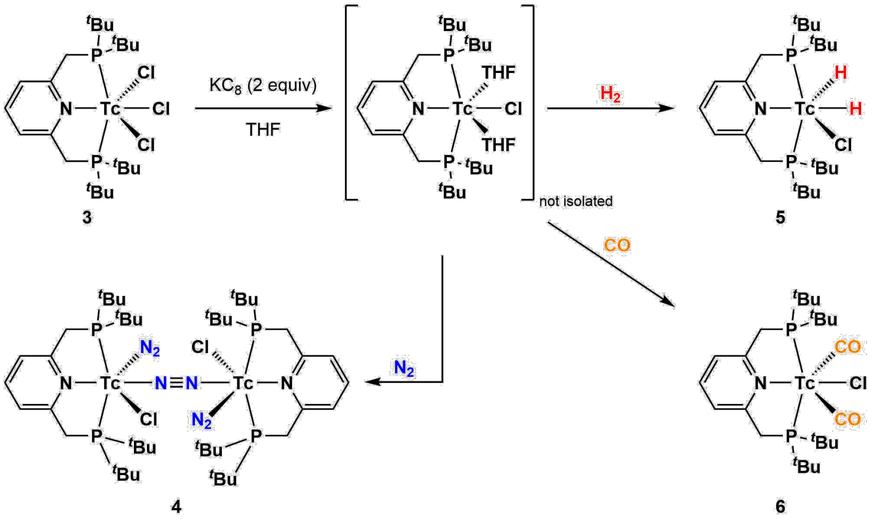
Small molecule activation (SMA) has become an increasingly relevant field of research and has been investigated with various transition metals. Despite the radioactive nature of technetium (^{99}Tc), which renders its application for large scale SMA most improbable, ^{99}Tc provides a wide range of stable, accessible oxidation states. These consequently form suitable coordination environments for a diverse palette of ligands. This special characteristic and the central position of Tc in the periodic table could be exploited as a highly attractive platform for investigations with small molecules. Recently, we reported the first pincer-type complexes (PNP) with technetium (**1** and **3**) and their interaction with N_2 (Complex **2** and **4**).[1] Pincer type ligands have been employed for various applications in the activation of N_2, H_2 and CO_2.[2-4]



The reduction of the precursor **3** (Tc^{III} to Tc^{I}) under argon leads to the formation of a highly reactive, intermediate species which is most likely a THF complex. This intermediate is electron deficient and coordinates small molecules introduced into the system. Experiments show reactivity with other small molecules such as H_2 (complex **5**) and CO (complex **6**). Complex **5** shows activity in hydrogenation reactions and the overall reactivity of the coordinatively unsaturated intermediate is under investigation.



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The Structurally Diverse Anionic Pathway in the Nickel-Catalysed Cross Coupling of Aryl Ethers

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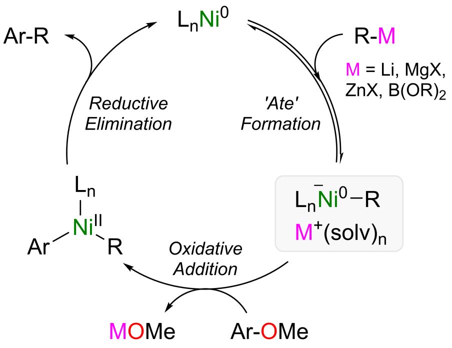
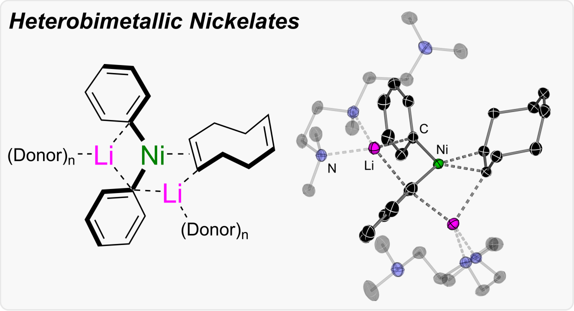
The Ni-catalysed cross coupling of aryl ethers has recently emerged as a powerful methodology to forge new C-C and C-heteroatom bonds using a range of nucleophiles.[1] The inert C(sp^2)-O bond, however, renders the canonical cross-coupling mechanism which consists of the initial oxidative addition of the electrophile to Ni^0 both thermodynamically and kinetically unfavourable, raising doubts as to the true mechanism involved in these transformations.[2]

In this presentation, we will provide spectroscopic and structural insights into an alternative anionic pathway which relies on the formation of electron-rich anionic nickelates from the addition of organometallic nucleophiles to Ni^0 sources.[3] Specifically, we have found that a number of polynuclear heterobimetallic anionic nickelates can be observed and isolated directly from PhLi and the ubiquitous Ni^0 source, Ni(COD)$_2$. Furthermore, we will highlight the dramatic solvent and donor effects which suggest that the cooperative activation of the aryl ether substrate by anionic heterobimetallic nickelate intermediates play an important role in the catalytic cycle.





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Crystal and Morphology Engineering of Poly (triazine imide) for Application in Molecular Separation

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Two-dimensional (2D) crystalline, nanoporous materials have attracted significant attention in the area of sensors, catalysis, energy storage, nanofiltration, and gas separation, etc., owing to its well-defined structures, high specific surface area, and chemical functionality. [1] Among these applications, 2D membranes are poised as the ultimate membranes due to the shortest possible diffusion path of the molecules, enabling orders of magnitude higher molecular permeance than conventional polymeric membranes. Poly(triazine imide) (PTI), belonging to the family of g-C_3N_4, is a promising candidate for making atom-thick membranes. PTI has outstanding chemical and thermal stability compared with polymer or MOF membranes, enabling its utility in harsh conditions. Furthermore, PTI hosts an atom-thick two-dimensional structure with a high density and order array of 3.4-Å-sized nanopores, which perfectly qualified for molecular sieving. Nonetheless, in our recent findings, the guest ions (Li^+ and Cl^-) in PTI frameworks increase the diffusion resistance, resulting in unexpectedly low permeance. [2] Thus, removal of guest ions in PTI framework is crucial to release the open pores for PTI membranes using in molecular separation. Herein, we have successfully reduced Li^+-ion content by 87% and Cl^--ion content by 74% in PTI framework using acid treatment compared with the reported chemical composition. The distinct structural difference between as-synthesized and acid-treated PTI were observed from the analysis of solid-state nuclear magnetic resonance (ssNMR) spectroscopy and X-ray diffraction (XRD). Moreover, the integrated differential phase contrast (iDPC) scanning transmission electron microscopy (STEM) was used to image the lattice structure of acid-treated PTI, revealing the desired open channels in PTI framework was achieved. The effective post treatment and the observation of the diffusion channels lay a solid foundation for developing high performance PTI membranes using in molecular separation.

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Size and Composition Controlled Intermetallic Nanocrystals via Amalgamation Seeded Growth

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Nanocrystals (NCs) of intermetallic compounds (IMCs, long-range ordered alloys) are a large family of emerging materials. They offer attractive characteristics originating from well-defined crystallinity, synergistically combined properties of the incorporated metals and unique size- and surface-related physical and chemical phenomena exhibited by NCs. Intermetallic NCs have recently acquired a large amount of research interest due to their extensive applications in catalysis, electronics, e.g. thermoelectric devices and memory technologies, superconductivity, energy storage and conversion technologies, photonics and in life sciences and medicine. For instance, they are promising plasmonic and magnetic materials and show great potential as selective catalysts. Nevertheless, a general synthetic method towards uniform intermetallic nanocrystals was still lacking.

We have developed a wet-chemical colloidal synthesis method towards uniform intermetallic nanocrystals based on the amalgamation of monometallic nanocrystal seeds with low-melting point metals [1]. We use this approach to achieve crystalline and compositionally uniform intermetallic nanocrystals of Au-Ga, Ag-Ga, Cu-Ga, Ni-Ga, Pd-Ga, Pd-In and Pd-Zn compounds. We demonstrate both compositional tunability across the phase spaces (e.g. $AuGa_2$, AuGa, Au_7Ga_2 and Ga-doped Au), size tunability (e.g. 14.0, 7.6 and 3.8 nm $AuGa_2$) and size uniformity (e.g. 5.4 % size deviations). In summary, the developed amalgamation seeded growth approach makes it possible to systematically achieve size and composition controlled intermetallic nanocrystals of excellent quality, opening up a multitude of possibilities for these materials.

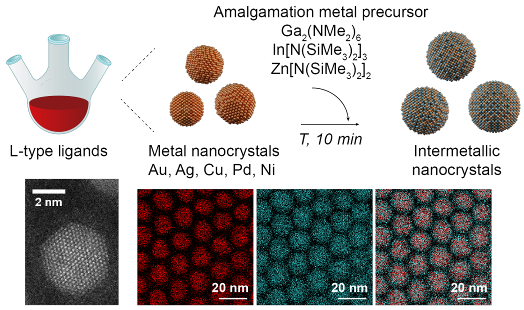

Figure 1. Scheme for the amalgamation seeded growth reaction (above) and examples of intermetallic nanocrystals shown in a HRSTEM image (PdZn NCs) and STEM EDX elemental mappings ($AuGa_2$ NCs) (below).

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Role of the Apparently Non-Interacting Substrate in Dioxygen Activation at Rieske Dioxygenases

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Rieske Dioxygenases (RDOs) are the primary oxygenases responsible for the hydroxylation of aromatic hydrocarbons. [1] 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 any direct interaction with the non-heme iron center. [2] 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 "innocent" substrate. This tight control over dioxygen reactivity is biologically plausible as possible control of unproductive O_2 activation, yet the mechanistic and electronic implications are not understood.

In this study, we elaborate on the modulation of O_2 activation through the presence of the substrate in a bottom-up approach, for which we choose naphthalene 1,2-dioxygenase as prototypical RDO. [3] In a purely quantum chemical study combining both Density Functional Theory and first-principle Coupled Cluster reference calculations, we analyze all steps leading to dioxygen activation in a generic local structural model. We subsequently expand our findings to the QM/MM scale making use of the fully automated protocols of model parametrization (SFAM [4]) and QM region selection (QM/SFAM [5]) developed in our group and available through the SWOOSE module within the SCINE [6] framework.We show 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. The incoming electron is intermediately transferred to the spectator substrate via an axially coordinated solvent molecule as mediator. On the substrate, the electron is resonance-stabilized and can react in a spin-allowed process with O_2.

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Spectral Signatures of Ga Species Enabled by ^{71}Ga Nuclear Magnetic Resonance and ^{69}Ga/^{71}Ga Nuclear Quadrupole Resonance Spectroscopies

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Gallium-containing materials are employed as catalysts in an array of industrially-relevant reactions, including the dehydroaromatization of alkanes and alkane dehydrogenation, amongst others.[1,2] Furthermore, Ga has been shown to be an effective dopant for enhancing the selectivity of noble metal based catalysts for reactions ranging from alkane dehydrogenation, to CO_2 hydrogenation to methanol, and acetylene semi-hydrogenation.[3,4] However, significant debate remains regarding the role and structure of Ga in these materials, with an array of oxidation states, geometries and charge states invoked across the existing literature. Thus, there is an interest in the development of spectroscopic techniques that enable the unambiguous identification and structural characterization of the catalytically relevant sites.

In recent years, nuclear spectroscopy of quadrupolar nuclei ($I > 1/2$) has been used to gain structural insights and geometric information for an array of molecules and materials in the solid state. Acquisition of this information is often hampered by poor signal-noise ratio, signal broadening due to the magnitude of the quadrupolar coupling constant (C_Q), and structural disorder at a molecular level.[5] Here, we demonstrate a broad-ranging strategy for the structural characterization of Ga-containing molecules and materials using a combination of ^{71}Ga Solid-State Nuclear Magnetic Resonance (NMR) and ^{69}Ga/^{71}Ga Nuclear Quadrupole Resonance (NQR) spectroscopies. Using a series of well-defined molecular compounds that reflect likely surface species, we demonstrate a combined experimental and theoretical approach for the prediction and acquisition of spectroscopic signatures of Ga nuclei in a range of coordination environments, with a broad range of C_Q values (0-110 MHz). The approach is then applied to catalytically relevant Ga-containing species as a proof of concept.

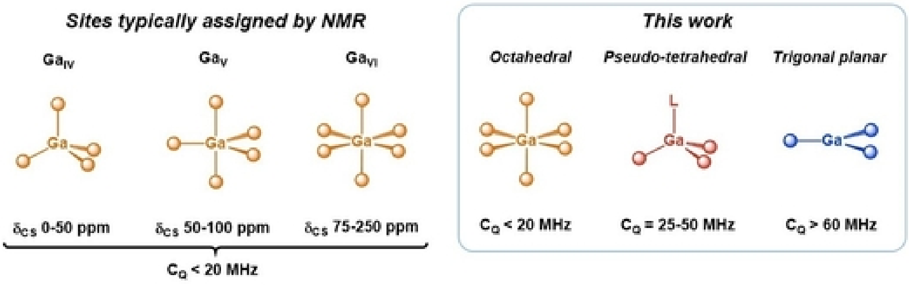

Figure 1. *(L) Ga sites typically observed by ss-NMR; (R) expanded range of geometries explored*

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Development of an electrochemical method to separate radioisotopes of cobalt and nickel

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^{60}Co and ^{63}Ni are often present in trace amount along with other activation products in irradiated matrices (e.g., activated steel). A reliable quantification of ^{60}Co and ^{63}Ni in radioactive waste is essential to provide a reliable risk assessment for decommissioning of nuclear power plants due to the β-activity of those two radionuclides. A radiochemical separation of ^{60}Co from ^{63}Ni is necessary in order to prevent any interferences of ^{60}Co during the analysis of ^{63}Ni by liquid scintillation counting. Moreover, ^{60}Co as well as ^{63}Ni can both cause interferences during the analysis of other radionuclides. Therefore, a suitable method is needed to separate them from other radionuclides in complex samples of nuclear waste. In addition to radioanalytical aspects, a fast and efficient radiochemical separation method may proof useful for the retrieval of ^{57}Co after fast neutron irradiation of nickel for Mössbauer spectroscopy with ^{57}Fe.

Here we present the development of a radiochemical separation method using selective electrodeposition of nickel and cobalt. In basic media, cobalt and nickel can form a complex with dimethylglyoxime ligands. These complexes can be electrochemically adsorbed and the metals reduced to their metallic state at a bismuth film electrode. Therefore, an electrochemical method for the separation of cobalt and nickel based on the use dimethlyglyoxime ligands in combination with a bismuth film electrode has been investigated. Furthermore, the selectivity of electrodeposition of cobalt and nickel onto bare glassy carbon electrodes has also been evaluated for separation of cobalt and nickel from other elements.

Rigidifying Bis(Benzimidazole)Pyridine Scaffolds: the Key to Improve Stability in Linear Lanthanidopolymers

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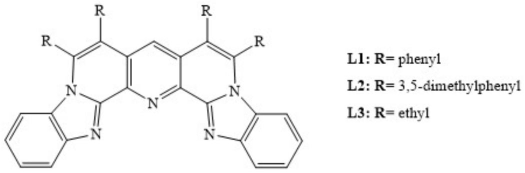
Supramolecular interactions (H-bond, solvation effects, dative bonds, etc.) have some unique potential for programming the free-energy drift due to the formation of host-guest assemblies.[1] The free-energy changes (ΔG) corresponding to the formation of such assemblies can be splitted into two major parameters:[2] (i) the statistical changes in entropy accompanying the complexation process,[3] and (ii) chemical intercomponent interactions such as host-guest (H-G), guest-guest (G-G) and host-host (H-H).[4] Employing these two parameters offers the opportunity to control the metal loading in linear lanthanidopolymers, that can lead to two opposite trends. Firstly, the formation of metallic clusters via the systematic loading of neighboring sites; an arrangement which finds applications in sensing[5] and in the programming of intermetallic energy migration processes with emissive trivalent lanthanide cations.[6] Secondly, the alternation of free and occupied sites which is highly desired for drug sensing,[7]light-upconversion[8] and metal segregation.[9]

Therefore intermetallic cooperativity plays a crucial role in selecting the output of the polymer metal loading. A rational control of the latter parameter requires improved preorganization and rigidity in the tridentate binding sites dispersed along the polymeric backbone. As a first step toward this goal, we have built on well-known bis(benzimidazole)pyridine scaffolds for designing new neutral tridentate, but highly preorganized and rigid ligands (**L1**-**L3**) (Figure 1). In addition to their synthesis via C–H activation and alkyne annulation, the effect of the ligand preorganization on the thermodynamic stability of 1:1 adducts with different trivalent lanthanide containers [Ln(hfac)$_3$(diglyme)] will be discussed.



L1: R= phenyl
L2: R= 3,5-dimethylphenyl
L3: R= ethyl

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Competitive Csp^2-H versus Csp^3-H activation from Ph-PYA based Pt(IV) complexes

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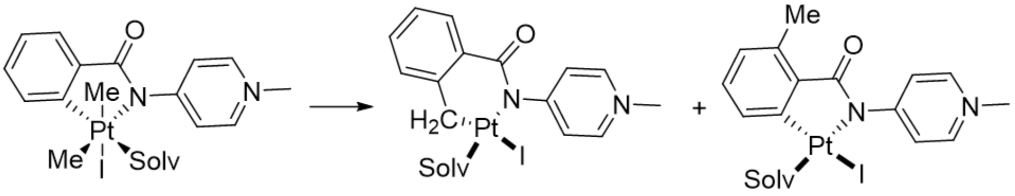
Pyridylideneamides (PYAs) are unique ligands that are comprised of an electronically flexible N-donor site that may coordinate to a metal center either as a π-acidic imine, or as a π-basic zwitterionic pyridinium amide (Fig). Therefore, PYAs are suitable for stabilizing metals in low- and high-oxidation state.[2] Such stabilization of different electronic configurations is particularly attractive for redox catalysis, which requires the metal to change oxidation state during the catalytic cycle. In order to probe the implications of PYA ligands on reduction steps, we synthetized a new Pt(IV) complex containing an aryl-PYA ligand and studied its reactivity, which entails competitive C(sp^2)-H versus C(sp^3)-H bond activation leading to 5 and 6 membered platinacycles, respectively. We will discuss mechanistic and kinetic aspects of this reactivity and the key factors that govern the selectivity of the bond activation process leading to the Pt(II) products.



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Cyclotron production and radiochemical purification of the radiolanthanide terbium-155 for potential application in nuclear medicine

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Terbium-155 ($T_{1/2}$= 5.32 d, Eγ = 87 keV (32%) 105 keV (25%) [1]) is an interesting radionuclide suitable for single-photon emission computed tomography (SPECT) and, therefore, could be used in the diagnosis of several diseases in nuclear medicine. Moreover, it could form part of the perfect "matched pair" with the therapeutic radionuclide terbium-161 [2,3], enabling the concept of true radiotheragnostics in nuclear medicine [4]. Therefore, the aim of this study was to investigate, for the first time, the production and radiochemical purification of terbium-155 via the ^{155}Gd(p,n)^{155}Tb and ^{156}Gd(p,2n)^{155}Tb nuclear reactions, in order to obtain a final product in quantity and quality sufficient for preclinical and potential clinical application.

In this study, terbium-155 production was achieved by proton irradiation of enriched gadolinium-155 and gadolinium-156 oxide targets, resulting in higher production yields when the ^{156}Gd(p,2n)^{155}Tb nuclear reaction was performed. However, up to 1.7 GBq of terbium-155 was produced and finally separated from the target material using cation exchange and extraction chromatography. The radiochemical purification process provided up to 1.0 GBq of [^{155}Tb]TbCl$_3$ in a small volume of 0.05 M HCl (0.02 - 1.0 MBq/μL), suitable for radiolabeling purposes. The high chemical purity of the purified terbium-155 was proved by successful radiolabeling experiments where DOTATOC was labeled at molar activities up to 100 MBq/nmol with >99% radiolabeling yield. With this quality of product, it was possible to perform a preliminary study for cell uptake and internalization of [^{155}Tb]Tb-PSMA-617 and [^{155}Tb]Tb-Ibu-DAB-PSMA, which showed specific uptake of the radiolabeled ligands in PSMA-positive cells. Furthermore, SPECT/CT imaging studies were carried out in tumor-bearing mice with the same ^{155}Tb-labeled compounds and showed excellent tumor visualization up to 24 h after injection.

In conclusion, this study has shown two possible routes for the production of high activities of terbium-155 via cyclotron irradiation. The developed method for terbium-155 radiochemical purification from the target material provided terbium-155 in quality and quantity suitable for radiolabeling at high molar activities, relevant for future preclinical and, potentially, clinical application. Initial in vitro and in vivo studies have already shown particularly promising results.

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Stabilizing $CsPbBr_3$ Nanocrystals: AlO_x Gel Capping from a Non-Hydrolytic Sol-Gel Reaction

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$CsPbBr_3$ nanocrystals have emerged as promising light sources for classical and quantum light applications [1]. Their commercial deployment as, for instance, luminescent downconverters in LCD displays is hindered by the limited environmental stability, foremost with regard to moisture. Despite a rapid surge of publications in this topic, there exist no reliable shelling method for stabilization of perovskite nanocrystals and without compromising their colloidal and morphological integrity. [2] In our work, we employ non-hydrolytic sol-gel reactions, intended as a minimally invasive method for shelling $CsPbBr_3$ NCs as compared to the hydrolytic approaches. Specifically, we propose a non-hydrolytic sol-gel reaction capable of wrapping individual NCs with an AlO_x gel. This shell provides colloidal stability in polar solvents such as alcohols, which otherwise degrade NCs within seconds. The colloidal integrity is retained for over a year, with photoluminescence spectra and quantum yields unchanged. The improved stability was investigated on the ensemble and single particle level with temperature and time resolved photoluminescence spectroscopy. Analyzing an amorphous and only few nanometer thick layer is approached with TEM, NMR, IR and zeta potential measurements.

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Interdependence of structural and compositional parameters on up-converting hafnia nanoparticles

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NIR-Vis up-conversion (UC) plays a key role in many emerging applications such as theranostics, solar energy harvesting, sensing and others.[1] While rare earth (RE) up-conversion luminescence in fluoride nanoparticles is extensively studied,[2] fewer reports are available on RE-doped metal oxide-based UC nanoparticles, despite their higher chemical stability. In particular, HfO_2 nanocrystals seem to be a promising alternative because of their high stability and biocompatibility.[3] Nevertheless, the polymorphism observed in hafnia when high RE doping levels are used, prevents a clear understanding of the parameters relevant for controlled and improved UC. Therefore, a finer control over doping levels and crystal structure is necessary to optimize the optical performance.

In this work, we studied the influence of structural and compositional modifications on the up-conversion luminescence (UCL) recorded in Er/Yb co-doped hafnia nanocrystals obtained by a colloidal solvothermal synthesis. The up-conversion characteristics of the materials were monitored in dependence of structural parameters such as crystal size and lattice symmetry, determined by means of X-ray diffraction and transmission electron microscopy (TEM), and originating from the multifunctional doping.[4] We report that the cubic polymorph of hafnia expresses much higher up-conversion efficiency with respect to monoclinic nanoparticles. On the other hand, the elemental analysis carried out by TEM energy diffusive X-ray spectroscopy (EDS) allowed us to correlate the composition of Er/Yb/Lu:HfO_2 with the main UC features like efficiency and the ratio between green and red emission deriving from radiative recombination on Er^{3+} centres. Moreover, the experimental platform described here permitted to possibly explain the inhomogeneity of doping in mixed polymorphs by analysing UCL profiles as probes of the local rare earth environment. These results give useful insights about the phenomena responsible for UCL features in hafnia nanocrystals, enabling their employment in various fields, thanks to improved UC intensities and control over the emission profile.

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The Bi^{3+} Lone Pair Effect in $(H_3O)Bi(SO_4)_2$, $Bi(HSO_4)_3$ and $Bi_2(SO_4)_3$

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Bi^{3+} based materials feature a possibly stereochemically active lone pair due to the electronic configuration of the Bi^{3+} cation of $6s^2$. Depending from the counter-anions this may result in structural distortions caused by the lone pair effect. The influence of this effect is investigated on three new members in the Bi_2O_3-SO_3-H_2SO_4 system: $(H_3O)Bi(SO_4)_2$, $Bi(HSO_4)_3$ and $Bi_2(SO_4)_3$. Further, it is compared to the recently published first bismuth borosulfates $Bi(H_3O)[B(SO_4)_2]_4$ and $Bi_2[B_2(SO_4)_6]$.[1]

The lone pair activity is proven by DFT and ELF calculations including both strength and direction of the effect. These results can be correlated to simple geometrical parameters deduced from the crystal structure by the method of Balic-Zunic and Makovicky based on all ligands enclosing spheres.[2] Exemplarily, this is shown for $Bi_2(SO_4)_3$ in Fig. 1. The centroid deviation coincides well with the direction of the asymmetric electron density distribution around the Bi^{3+} cation from the ELF calculations.

We could show that these simple geometrical calculations are able to assess the presence and significance of lone pair activity in several compounds related to our research containing Bi^{3+} cations requiring basic structural information, only.

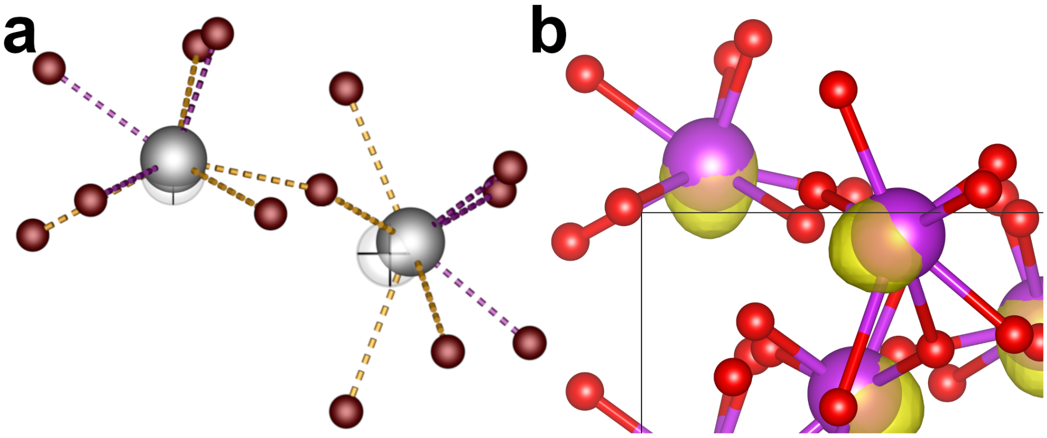

Fig. 1. The lone pair activity of $Bi_2(SO_4)_3$ viewed along (100): (a) shows two BiO_7 polyhedra including the centroids (semi-transparent octant) (Bi(2) left, Bi(1) right); Bi grey, oxygen red; shortest bonds that are part of the BiO_3E distorted tetrahedron according to the VSEPR model violet, residual bonds yellow; (b) depicts a detail of the ELF of $Bi_2(SO_4)_3$ the same BiO_7 polyhedra; oxygen red, bismuth violet,; ELF semi-transparent yellow.

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Mechanistic Study on Thermally Induced Lattice Stiffening of ZIF-8

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Zeolitic imidazolate framework-8 (ZIF-8), which hosts 3.4-Å-sized windows, is a highly promising metal-organic framework (MOF) for a number of molecular separations.[1] Unfortunately, the framework flexibility of ZIF-8,[2] allows the diffusion of molecules much larger than its 3.4-Å-window such as N_2, CH_4, C_3H_6, C_3H_8, n-C_4H_{10}, etc. As a result, selectivities of CO_2 (3.3 Å) over N_2 (3.64 Å) and CH_4 (3.8 Å) from polycrystalline ZIF-8 membranes have been limited. To overcome this, we have developed a post-synthetic rapid heat treatment (RHT) involving heating between 300-400 ºC for a few seconds. This has been effective in stiffening the ZIF-8 lattice, leading to significantly improved selectivities of the CO_2/N_2 and CO_2/CH_4 gas pairs.[3] However, the mechanism responsible for the lattice rigidification of ZIF-8 remains elusive.

Systematic gas permeation studies (Figure 1a-1c) show that lattice stiffening is only manifested in increased gas pair selectivity when the polycrystalline ZIF-8 membrane is treated under slightly humid environment (1.0% water vapor).[4] Using *ex situ* and *in situ* experiments, we determine that a small shrinkage of the unit-cell parameter, ~0.2%, is mainly responsible for the lattice stiffening (Figure 1e). In addition, one needs to achieve this shrinkage without a disproportionately large shrinkage in the grain size of the polycrystalline film to avoid the formation of cracks. We find that the lattice stiffening coincides with the incorporation of linker-vacancy defects and size-shrinkage of the ZIF-8 crystals (Figure 1d, f). In the absence of humidity, unit-cell parameter changes are minimal and linker-vacancy defects are absent.

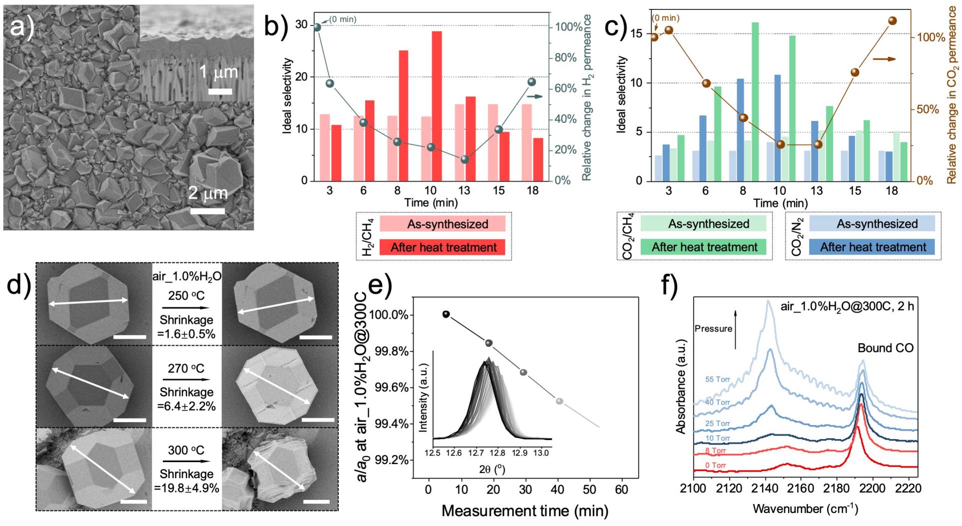

Figure 1. a) SEM image of the ZIF-8 membrane synthesized in this work. The inset is the cross-sectional view of the membrane. b) H_2/CH_4, c) CO_2/CH_4 and CO_2/N_2 ideal selectivities and the corresponding change in the H_2 (b) and CO_2 (c) permeances from polycrystalline ZIF-8 membranes after heat treatment in air_1.0%H_2O@300C for dwell time of 3 to 18 min. All of the permeation data were collected at 25 °C and 1.4 bar. d) SEM images of ZIF-8 crystals before and after heat treatment in air_1.0%H_2O for 2 h at 250, 270, and 300 °C, respectively. All scale bars: 5 micron. e) The ratio change of the *a*-axis obtained from *in situ* XRD measurement of ZIF-8 crystals after directly heating in air_1.0%H_2O@300C. The inset is the XRD patterns of the ZIF-8 (211) peak. f) *In situ* DRIFTS spectra obtained after by dosing ZIF-8 treated in air_1.0%H_2O@300C for 2 h to CO.

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Angstrom-scale etching and functionalization of porous graphene lattice

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Single-layer graphene (SLG) is regarded as one of the promising nanomaterials due to its atomic thickness, ordered lattice, and excellent electronic and mechanical properties. The pristine graphene lattice is impermeable to the smallest of the gas molecules, and one needs to create vacancy defects (nanopores) in graphene for gas permeation[1]. These angstrom-scale defects can potentially modified with functional groups to tailor the permeation properties of the nanopores.

Currently, a controlled etching of the graphene lattice for application in gas sieving remains a bottleneck[2]. Chemical etching such as treatment with oxygen plasma[3,4] and ozone[5,6] do incorporate sub-nanometer vacancy defects in SLG[7]. However, non-uniform plasma exposure limits the control on pore generation. Generally, lattice etching involving nucleation and expansion of vacancy defects happens simultaneously, leading to a broad pore size distribution (PSD). To achieve a better control on PSD, we recently reported a millisecond gasification reactor (MGR)(Figure 1). We also developed a mathematical model to predict the evolution of PSD[5]. The model predicts the number of missing carbon atoms leaving from the defects as a function of etching parameters. It allowed us to screen several etching conditions to optimize the PSD for post-combustion capture (CO_2/N_2 separation). With such an approach, we could achieve CO_2/N_2 separation up to 40 with CO_2 permeance 2932 gas permeation unit (GPU).

In our next example, functionalization of nanopores with CO_2-philic polymers was carried out to enhance CO_2 adsorption over less absorbing gases such as N_2 and CH_4. Briefly, the functionalization was carried out by the ring-opening chemistry between epoxy groups in the vicinity of nanopores and the amine groups in the polymer chains[3]. This led to high permeance membranes where the CO_2/N_2 selectivity was improved. CO_2 permeance of 8730 GPU and CO_2/N_2 separation factor of 33.4 could be obtained from this strategy.

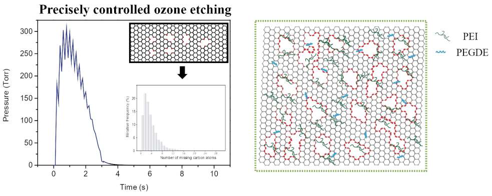

Figure 1. schematic illustration of precisely controlled ozone-led etching and polymer functionalization on graphene lattice

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Superheavy Element Chemistry and the Residual Gas Effects on the Chromatographic Yield of Homologs Hg and At

P. Ionescu[1,3], P. Steinegger[2,3], R. Eichler[3], R. Dressler[3], N. M. Chiera[3], A. Türler[1]*

[1]University of Bern, [2]ETH, [3]PSI

Challenges in the study of transactinide elements (Z ≥ 104) are low production rates at single-atoms per week and shortening half-lives as Z increases. Transactinide research uses on-line gas adsorption chromatography experiments, such as the Cryo-On-Line Detector (COLD) as the primary method of identification of superheavy elements (SHE) by chemical means. These state-of-the-art gas phase thermochromatography experiments provide the necessary detection sensitivity for single atoms, while experiments can be performed on radioisotopes with half-lives as low as ≈ 1 s. The SHEs Cn(Z = 112) and Fl(Z = 114) can thus be chemically studied [1,2]. During experiments, mercury is produced simultaneously in nuclear fusion-evaporation reactions for homolog studies of Cn, while acting at the same time as a tracer to monitor experimental conditions. Astatine, as a by-product of multinucleon-transfer reactions, provides similarly useful data. Results gathered during past experiments have strongly indicated that even minor changes in the experimental conditions can drastically affect chromatographic yields. The inclusion of atmospheric mass spectrometry for gas composition analysis have shown that there is a strong correlation between the composition of unwanted residual trace gases and transport yields of different elements (Fig. 1).

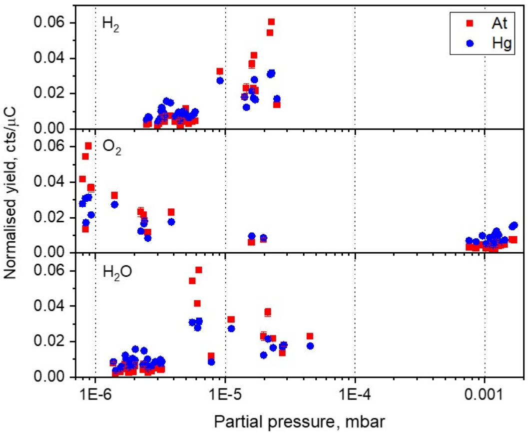

Figure 1: The effect of hydrogen, oxygen and water impurities on the normalized yields of different Hg and At radioisotopes.

The effect of carrier gas impurities on the chromatographic yield is presented in this work. These observations are of high significance as they highlight the importance of tightly controlling the purity of gases used in experiments at the single-atom scale. This knowledge can therefore be used to prevent unwanted side-reactions, or to increase transport yields in the future. This has led to the development of a new experimental setup Trace-gas Reaction Analysis for Chromatography (TRACY) designed specifically for this purpose [3].

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Stepwise reduction of dinitrogen to nitride by a uranium-potassium complex

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[1]EPFL Lausanne, Institut des Sciences et Ingénierie Chimiques, [2]INSA Toulouse, Laboratoire de Physique et Chimie des Nano-objets,, [3]EPFL Lausanne, Laboratory for Quantum Magnetism

The synthesis of ammonia from N_2 remains one of the key challenges in modern chemistry. Even though dinitrogen is a cheap and widely available molecule, its low reactivity complicates its use as a feedstock for the synthesis of high-added value products. Notably, the only industrial process that uses N_2 is the Haber-Bosch that converts it into ammonia, but requires really harsh conditions. Before the Fe-based catalysts were implemented, uranium materials were reported to actively effect the transformation of dinitrogen into ammonia.[1] Nevertheless, the dinitrogen chemistry of uranium remains underdeveloped. So far, only two uranium complexes were reported to cleave N_2 forming uranium nitrides (intermediates in the Haber Bosch process)upon addition of external reducing agent. Moreover, subsequent reactivity of the nitrides was not reported.[2],[3]Recently in our group two dimetallic uranium(III) systems that were able to perform the four electron of dinitrogen were reported.[4],[5] In particular, 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 report a new example of six electron reduction of dinitrogen to nitride effected by the combination of a uranium complex with KC_8 as an additional reducing agent, and the first one to generate a U(VI) nitride.

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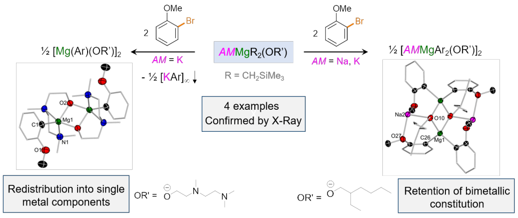
Exploring the alkali metal and alkoxide effects in Mg-Br exchange reactions using mixed alkly/alkoxy alkali metal magnesiates.

N. R. Judge[1], L. J. Bole[1], E. Hevia[1]*

[1]University of Bern

Mg-halogen exchange reactions constitute one of the most powerful methodologies for the functionalisation of aromatic halides since the emergence of Turbo Grignard reagents ($RMgCl\cdot LiCl$) promoting Mg-bromine exchange under mild reaction conditions.[1,2] More recently a new type of mixed alkyl/alkoxy lithium-magnesium reagent, namely $s\mathrm{Bu}_2\mathrm{Mg}\cdot 2\mathrm{LiOR}$ (R = 2-ethylhexyl), has been introduced which offers even more enhanced reactivities and greater functional group tolerance as well as being compatible with the use of toluene as a solvent.[3] We recently uncovered the hidden complexity of this system whereby a new bimetallic Schlenk like equilibrium was uncovered and this enhanced reactivity was due to the presence of an alkyl rich higher order lithium magnesiate ($\mathrm{Li}_2\mathrm{Mg}s\mathrm{Bu}_4$) and the mixed alkyl/alkoxy species ($\mathrm{LiMg}s\mathrm{Bu}_2\mathrm{OR}$) was inactive towards metal halogen exchange. [4]

Combining structural and spectroscopic methods we herein report the exploration into improving the reactivity of pure mixed alkyl/alkoxy magnesiates by virtue of changing the nature of the alkali metal. The intrinsic properties of the accompanying alkoxide ligand was also found to have a surprising effect on the constitution of the reactive intermediates from the metal-halogen exchange process (See figure).



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Macrocyclic Ligands: From Synthesis Towards On-Surface Topology, and their Candidacy as Synthons for Interlaced Structures

A. S. Kaiss[1], A. Hinaut[2], A. Crochet[1], E. Meyer[2], K. M. Fromm[1]*

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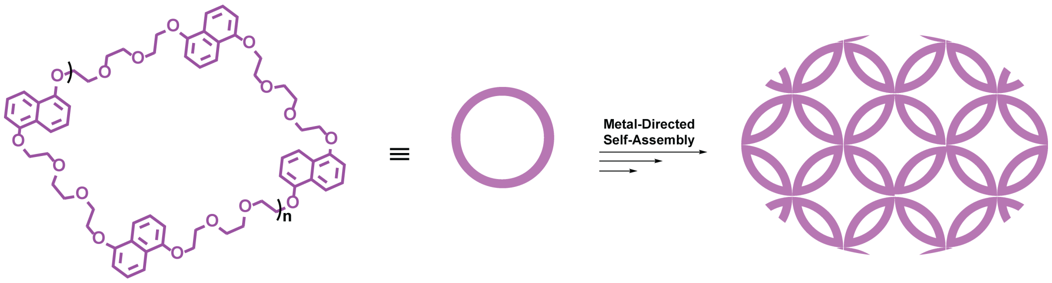
Knots and links, being part of the mechanically interlocked molecular architectures, are related to three-dimensional space (manifolds). Nevertheless, links are less studied and are not as well classified as knots.[1] Nature shows examples of strong relations between topology and function;[2,3] for instance, complex topological structures such as those present in the chain mail-like armour lying under Komodo warren's skin are extremely robust,[4] as is the 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 them 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 complex chain-mail structures (Scheme 1). These flexible and robust macrocyclic structures are formed by alternating the mechanical and physical properties resulting from the different building blocks. Their arrangement on atomically flat 2D structures have been investigated and compared with the 3D-structures obtained from single crystal analyses.

[1] Nils A. Baas, Nadrian C. Seeman, Andrew Stacy, *Journal of Mathematical Chemistry*, **2015**, 53(1), 183-199.

[2] Nadrian C. Seeman, *Journal of Theoretical Biology,* **1982**, 99, 237-247.

[3] Christopher S. Wood, Tanya K. Ronson, Ana M. Belenguer, Julian J. Holstein, Jonathan R. Nitschke, *Nature Chemistry,* **2015**, 7, 354-358.

[4] Jessica A. Maisano, Travis J. Laduc, Christopher J. Bell, Diane Barber, *The Anatomical Record,* **2019**, 302, 1675-1680.

[5] Robert L. Duda, *Cell,* **1998**, 94, 55-60.

Macrocyclic Ligands: From Synthesis Towards On-Surface Topology, and their Candidacy as Synthons for Interlaced Structures

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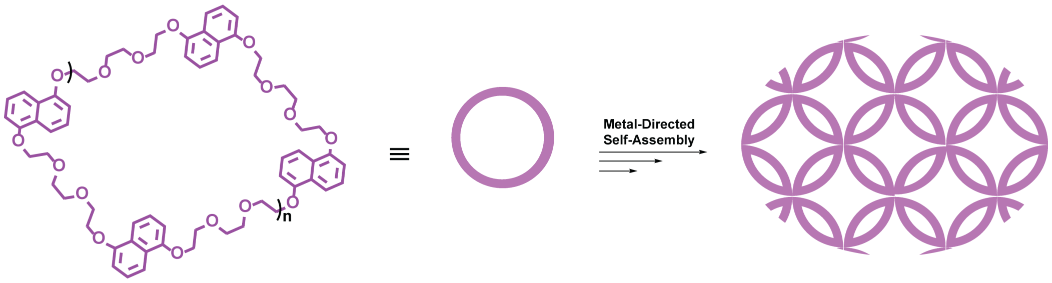

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Self Supporting Polymers of Ir-NHC Complexes

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[1]University of Bern

Immobilization of homogeneous iridium catalysts is of continuous interest because of this metal’s high activity in water oxidation[1,2] and hydrogenation[3] reactions, which are processes that can greatly benefit from heterogenized molecular catalysts.[4] Triazolylidene ligands are very promising candidates to enable immobilization as the strong sigma donation and electronic flexibility of the NHC can impart high catalytic activity[5] while the resilience of the metal-carbon bond renders the complexes highly stable and potentially suitable for prolonged applications. [4,6]

Here we present a new Ir-triazolylidene complex which is designed to be postmodified and immobilized with simple techniques. The approach allows immobilization in a variety of ways, both self supporting (Figure 1.) or by attachment to solid supports. We will discuss the immobilization process as well as the influence of heterogenization on the catalytic performance of the complex in water oxidation and hydrogenation reactions.

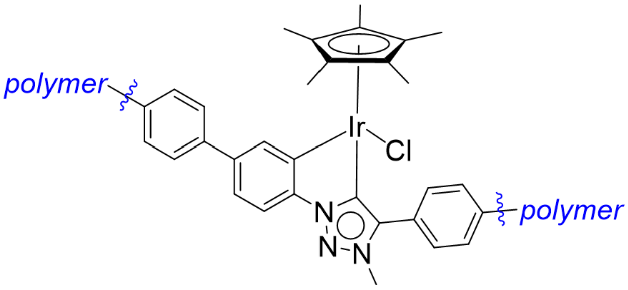

Figure 1. Iridium-NHC complex immobilized by integration into a self supporting polymer

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$CeZn_{2-\delta}Ge_2$: New Zn-deficient $CaBe_2Ge_2$-Type Phase with Rare Ce-based Ferromagnetism and Large Magnetoresistance

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In this presentation, we will report on a new compound $CeZn_{2-\delta}Ge_2$ which crystallizes in a $CaBe_2Ge_2$-type structure. The phase only forms Zn-deficiency on only one crystallographic site. This reduces the number of excess electron per unit-cell stabilizing the unusual compound. This new phase is metallic, displaying uncommon Ce-based ferromagnetism with a critical temperature of T_C = 6.7 K as confirmed by magnetic susceptibility measurement in form of an Arrott plot. We find this material to exhibit a large positive magnetoresistance peak of approximately 30 % at low temperature and still present up to 10 % below 30 K – a temperature much higher than the Curie temperature – hence the magnetoresistance is not only linked to the ordering of the magnetic moments, but likely connected to enhanced spin-fluctuations.

Cooperative bis(pyridylidene-amine) ligands for efficient palladium catalyzed formic acid dehydrogenation

N. LENTZ[1], M. Albrecht[1]

[1]University of Bern

Pyridylidene-amine (PYE) ligands are strong s-donors with exceptionally high electronic flexibility that ensures reliable coordination to the metal centre.[1] This electronical flexibility can stabilize several intermediates of the catalytic cycle and may play a crucial role in catalysis by assisting the metal in different challenging elementary steps.[2]

These unique properties coupled with a cooperative ligand are not only stabilizing and modulating the electronic environment of the metal centre, but also promote cooperatively chemical changes during catalysis.[3] In addition, the synthetic versatility is easily exploited by changing the ligand architecture and by modulating the cooperative ligand environment, resulting in different donor and acceptor properties.

Here we introduce a set of flexible bis-PYE ligands coordinated to different palladium precursors (Figure 1), which affords catalysts with activity for formic acid dehydrogenation as a methodology to implement hydrogen economy (Figure 2).

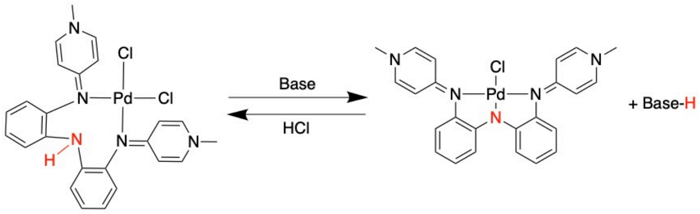

Figure 1 Cooperative-hemilabile behavior of the palladium bis-PYE complex.

$$HCOOH \xrightarrow[\text{Additives}]{\text{Cat (mol\%)}} H_2 + CO_2$$

Figure 2 Catalytic application of bis-PYE palladium complexes in formic acid dehydrogenation.

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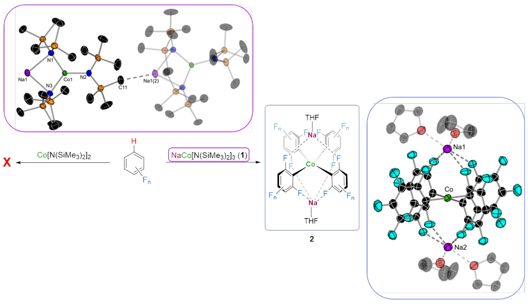
Direct Co-H exchange reactions of Fluoroarenes mediated by a mixed-metal Na/Co(II) base

A. Logallo[1], E. Hevia[2]*

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

The use of earth abundant cobalt complexes to perform selective C-H bond activation of fluoroaromatic compounds has gained increased attention as an effective method to obtain versatile fluorinated organic compounds.[1] Most of these reactions are controlled by the redox capabilities of Co and its ability to undergo oxidative addition processes. Breaking new ground in this field, here we report an unprecedented type of reactivity for Co(II) where by using the bimetallic base [NaCo(HMDS)$_3$] (**1**) [HMDS=N(SiMe$_3$)$_2$] which enables the direct Co-H exchange of a wide range of fluoroarenes, at room temperature with excellent stoichiometric control. Isolation of key reaction intermediates has revealed that when reacted with perfluoroarenes such as C_6F_5H in the presence of an extra equivalent of NaHMDS it is possible to activate all the amide groups towards the metallation reaction, affording the unique square planar Co(II) complex (THF)$_2$Na$_2$Co(C$_6$F$_5$)$_4$ (**2**). Reactivity studies have shown that **2** can be subsequently functionalized with HBpin to give the relevant borylated species as well as undergo oxidative homocoupling. This presentation also shows light on the mechanisms involved in these transformations and the key role of the alkali-metal to facilitate the Co-H exchange process.



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Low-Valent Molybdenum Complexes Supported by Redox-Active β-Diketonate Ligands

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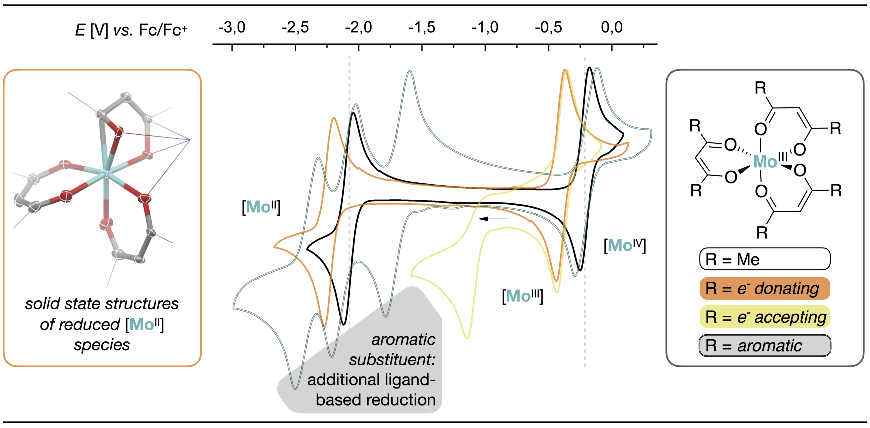
[1]ETH Zurich

Molybdenum is the sole second row transition metal that is essential for most living organisms and it is found as a component of many redox-active enzymes including the nitrogenase among others.[1] The Mo-center is often found in an octahedral coordination environment and stable in a variety of oxidation states. Advanced spectroscopic studies on the cofactor of the nitrogenase enzyme recently proved the presence of a low-valent Mo(III)-ion.[2]

The coordination chemistry of octahedral, low-valent Mo complexes is comparatively underexplored and only a handful of compounds were isolated.[3-5] We are currently studying low-valent Mo complexes supported by β-diketonate ligands[6] and derivatives thereof, aiming at creating a new platform which will allow for a better understanding of the structure and reactivity of such complexes.

We will present a whole series of new complexes bearing different substituents bound to the common diketonate motif and discuss their structural and electrochemical properties. Cyclic voltammetry studies revealed unprecented insights into the redox activity of β-diketonate ligands. The redox non-innocent behavior was further elaborated by isolation of reduced species as well as advanced spectroscopic techniques.



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Tandem Mn-I exchange and homocoupling processes mediated by Li/Mn cooperativity

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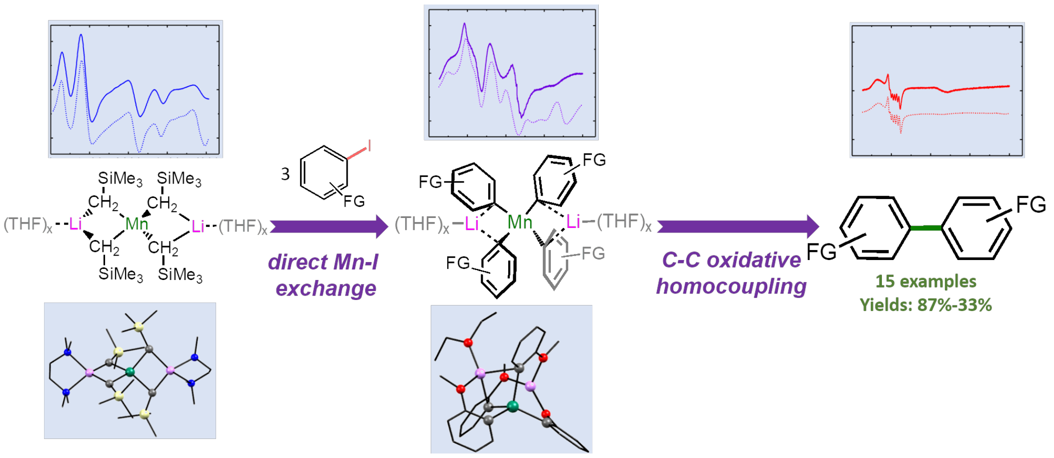
[1]Department für Chemie, Biochemie und Pharmazie, Universität Bern, Freiestrasse 3, 3012, Bern, (Switzerland). , [2]EastCHEM School of Chemistry, University of Edinburgh EH9 3FJ Edinburgh (UK)

Metal/halogen exchange is one of the most powerful and widely used methods for the functionalization of aromatic halides. For decades, this methodology has been the exclusive domain of the classical polar organometallic reagents such as organolithium and organomagnesium (Grignard reagents) [1]. In order to improve the functional group tolerance, in recent years, lower polarity metals such as Zn, La, Sm, and Ce in combination with Li were used for metal/halogen exchange [2]. Extending this reactivity to earth abundant transition metals here we report the first examples of Mn-I exchange for iodoarenes.

Using novel lithium manganate $[Li_2Mn(CH_2SiMe_3)_4]$, enables the efficient direct Mn–I exchange of a wide range of iodoarenes, affording a transient (aryl)lithium manganate intermediate which in turn undergoes *in-situ* C-C oxidative homocoupling, to furnish symmetrical (bis)aryls in good yields under mild reaction conditions. Isolation of key intermediates, combining EPR with single crystal X-Ray crystallography, provides a unique mechanistic understanding of how Li and Mn work together to facilitate both the Mn-I exchange and C-C bond forming steps.



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Deciphering Coordination Sites Affinity in Linear Multi Site Metallopolymers

M. Mirzakhani[1], H. Nozary[1], C. Besnard[1], C. Piguet[1]*

[1]University of Geneva, Department of Inorganic Chemistry, 30 quai E. Ansermet, 1211 Geneva

Metallopolymers are a type of modern hybrid materials that are combining the advantageous properties of both classical metal complexes (such as catalysis, optics, electronics) and organic materials (such as processability, flexibility, scalability).[1] Despite the latter desirable properties, the absence of rational control over metal loading in multisite polymers significantly limits the design and reproducibility of the target metallopolymers.[2] To reap the greatest rewards from these hybrid materials we need to specify the parameters that govern both the organization and the final structure of the metallopolymers. In this context, a deep perception of the metallopolymers formation enables us to control or even program metal sequence in metallopolymers.[3] The complexation of a linear multi-site polymer with labile lanthanides consists in numerous successive and concurrent thermodynamic equilibria, which results in an intricate thermodynamic system. Thanks to the site binding model (Figure 1), these complicated equilibria can be summarized in terms of two independent quantifiable parameters: (i) the intermolecular affinity of a single site for the entering lanthanide (Ln) in the polymer ($f^{\mathrm{Ln,}\,\mathbf{P}}$) and (ii) the energetic penalty (or benefit) resulting from the fixation of a second metal to a neighboring free site in the polymer ($\Delta E^{\mathrm{Ln,\ Ln}}$). In this framework, we used tridentate 2,6-bis(benzimidazol-2-yl)pyridine receptor units to construct a linear multi-site polymer. The intrinsic metal-receptor affinity for the coordination units of a polymer, traditionally derived from some thought equivalent analogous monomeric ligand (**L3**). This oversimplified approach causes a significant discrepancy of the intrinsic affinity for the same binding unit taken either separately or within the polymeric backbone.[4] With this in mind, The investigation of the binding affinity of the model ligands **L1**-**L3** toward [Ln(hfac)$_3$] lanthanide containers, casts light on the different interactions pertinent to the internal and terminal coordination sites in the linear multisite polymer. Accordingly, the first oligomers of the series **L4** and **L5** have been prepared and we report a novel approach for implementing the site binding model in oligomers with the ultimate goal of mastering metal-binding site affinities ($f^{\mathrm{Ln,}\,\mathbf{P}}$) and intermetallic interactions ($\Delta E^{\mathrm{Ln,\,Ln}}$) along the polymeric backbone.

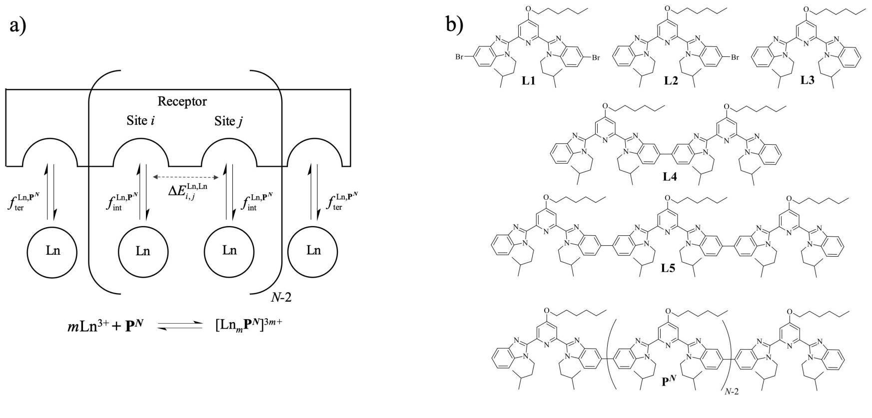

Figure 1.a) The site bonding model. b) Chemical structures of the monomers (**L1**-**L3**), dimer (**L4**), trimer (**L5**) and the polymer($\mathbf{P}^{N}$).

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Cooperative Generation of Metal hydride *via* Bioinspired Proton Coupled Electron Mediator: Application to CO_2 reduction

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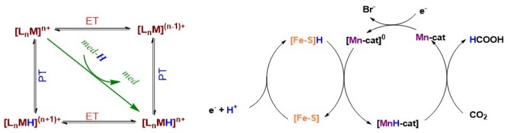
Facile generation of transition metal hydrides (M-Hs), key intermediate in several biological and chemical processes, are highly shouted to achieve greater reactivity and efficiency of various chemical reactions.[1-3] Electrochemical generation of M-Hs requires transfer of an electron to an oxidized metal complex, followed by a proton coupled electron transfer (PCET) step. The rate of PCET processes are highly influenced by the efficiency of the proton transfer (PT) or the electron transfer (ET), especially when electrons and protons are originating from different sources.[4] Often this requires highly reducing potentials or stronger proton sources, eventually lowers the energy efficiency of the overall processes. Attempts to enhance the ET *via redox mediator* or PT *via proton shuttle* have been established to be promising but limited to certain applications.[5, 6] Alternatively, an electron and a proton can be transferred together to the single reduced metal complex *via* a *concerted electron proton transfer (CPET) mediator* to generate M-H. In this work, a synthetic bioinspired iron-sulfur cluster (**Fe-S**)] has been employed as a *CPET mediator* for selective generation of highly reactive manganese hydride species electrochemically from well-established catalyst [bpyMn(CO)$_3$Br] (**Mn-cat**).[7] A composite system (**Mn-cat/Fe-S**) enables us to change the product selectivity of the **Mn-cat** from CO to formic acid during CO_2 reduction at higher rate and lower overpotential. Parallel investigations with other CPET mediators and observed product ratios during CO_2 electro-reduction perfectly demonstrate the key thermochemical boundaries for the catalytic M-H generation and ensures the high efficiency of **Fe-S** cluster as *CPET mediator*.



Scheme 1: (*left*) Mechanistic difference of *CPET mediated* process from *ET-PT* of *PT-ET* process. (*right*) Overall catalytic cycle of the reactivity observed in this work.

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To Low-Valency and Back: Initiation Pathway for High-Valent Molybdenum-Oxo Species in Olefin Metathesis through molecular model systems

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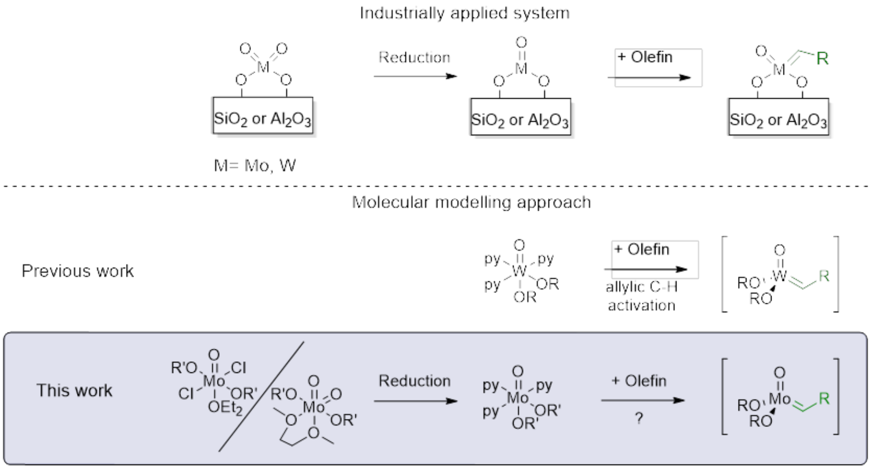
Olefin metathesis has found a large number of applications in both the fine chemical and petrochemical industries[1]. Metathesis catalysts are frequently based on Mo, that typically shows high activity and good functional group tolerance[2,3]. While it is accepted that the active sites for these catalytic systems are high-valent Mo alkylidenes, their mechanism of formation from metal oxo species in supported catalysts still remains unknown, with current literature invoking a number of possible pathways[4–8], most of them invoking a reduction of the high-valent, precatalytic site to a low-valent Mo(IV) intermediate. Initiation is then thought to proceed *in situ* from reaction with the olefin substrate. However, obtaining a detailed, molecular-level of understanding of these initiation processes has proven to be rather challenging, with further complications arising from the multitude of monomeric and oligomeric sites Mo(VI) sites in a number of coordination geometries that might serve as precatalytic sites. Recent works on W-based systems have shown the power of using molecularly-defined model systems to uncover the initiation mechanism[9]. Here, using experimental molecular model systems supplemented by DFT calculations, we evaluate the initiation mechanism of Mo-based catalysts and show that metallacyclopentanes are likely key reaction intermediates in forming alkylidenes, which sharply contrasts what has been found for W, where C-H activation and proton transfers were key steps.



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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.

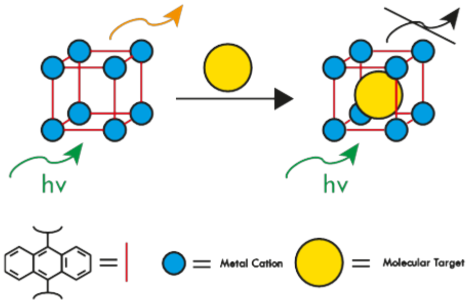

Figure 1: Concept of how MOFs materials based on anthracene building unit can detect the molecular targets by luminescence changes through host-guest interaction.

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Electronically asymmetric pyridyl-pyridylidene amide ligands for palladium-catalyzed copolymerization of alkenes and polar co-monomers

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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] In their zwitterionic form, these ligands exhibit strong donating properties resulting in a significant electronic contrast with the weaker pyridyl ligand site.[2] This flexible asymmetry is beneficial for the incorporation of polar co-monomers into growing alkyl chains in olefin polymerization.[3] Here we introduce the asymmetric pyridyl-PYA ligand coordinated to palladium(II), which affords, after in-situ chloride removal, a highly active polymerization catalyst. We will also discuss the tolerance of this system towards polar co-monomers insertion as well as higher alkene polymerization.

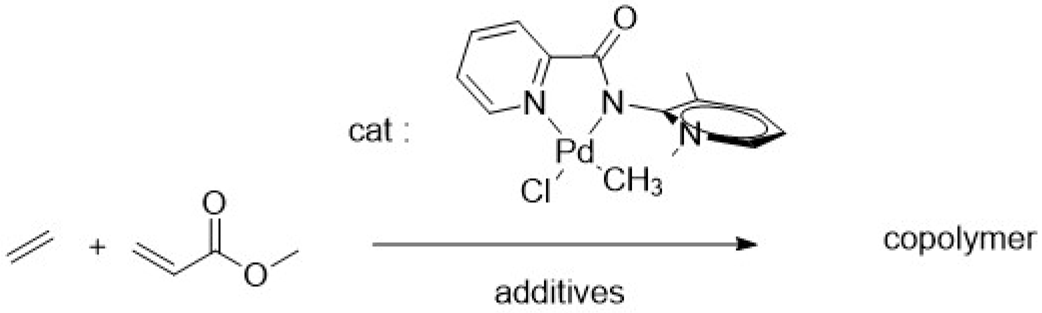

Figure 1 Schematic representation of a palladium complex containing a pyridyl-pyridylidene amide ligand that is active in the polymerization of (functionalized) olefins.

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Competitive etching and growth of graphene nanopores for molecular sieving

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Recent efforts in introducing gas sieving nanopores in graphene has been led to either wide pore size distribution (PSD) or low density of pores, attributing to simultaneous pore nucleation and expansion of the existing pores, hindering the true potential of this material.[1,2] To control the PSD for gas separation, we utilize CO_2 as an etchant to expand the existing defects in graphene. We show that CO_2 does not introduce new defects in the graphene basal plane. Next, we develop a method to fabricate porous graphene with a high pore-density while maintaining a narrow PSD. We expose highly porous graphene with a broad PSD to graphene growth conditions in the presence of CH_4 while at the same time, we introduced CO_2. It seemed that the pore expansion (as a result of etching) and shrinkage (as a result of growth) reached a comparable rate. We are able to control the graphene etching rate (down to Å/min) via manipulating T and P_{CO2} (Figure 1a-c). Moreover, we show that at the same T and P_{CO2}, for pores bigger than tens of nanometers, the etching rate is constant. However, for smaller pores, the etching rate is an order of magnitude smaller due to the confinement effect (Figure 1d). We fabricated several membranes with this method and mechanically reinforced by PTSMP, and observe that there is an optimum ratio of CH_4 to CO_2 to achieve the highest gas pair selectivities (H_2/C_3H_8 = 27 and H_2/CH_4 = 6) (Figure 1e-g). Moreover, regrowth decreases the defect density of the samples compared to that of plasma treated sample, and improves the graphene crystallinity (Figure 1h, i).

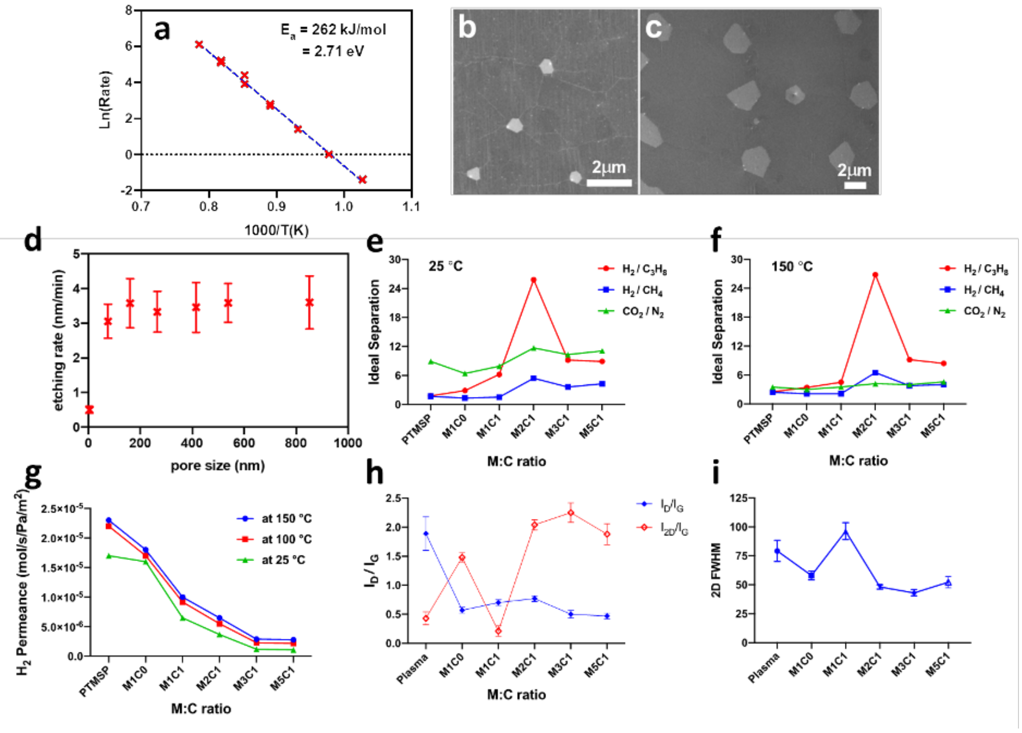

Figure 1. a) Etching rate versus 1/T at 500 mTorr CO_2. b,c) SEM image of the expanded pores (lighter areas) in graphene (darker areas) by CO_2. d) Evolution of etching rate versus pore size. e-g) Membrane performance for various CH_4 to CO_2 ratios during regrowth process. M:C shows the ratio of methane to carbon dioxide. h,i) Raman spectroscopy analysis of the samples.

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A simple cerium-based chemosensor for selective fluorescence phosphate detection in aqueous media

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Phosphate ions are key chemicals involved in crucial processes [1,2], for example in medicine or agriculture. However, their sensing with a chemosensor is arduous due to their chemical properties [1,2]. In the past, chemists addressed this problem by synthesizing complex chemical architectures as receptors, but with mixed results [3]. Here, we develop a simple fluorescent indicator displacement assay (FID) for phosphate detection, relying solely on commercially available chemicals. Cerium ammonium nitrate (CAN) is combined with a fluorophore to probe phosphate ions in aqueous mediums. We show that the inorganic complex detects phosphate ions in low micromolar concentrations, either spectrophotometrically, or with the naked-eye, with high selectivity and affinity over other anions [3]. To our knowledge, this is the first description of a simple, sensitive, selective and high affinity cerium-based chemosensor for the fluorescent selective naked-eye detection of phosphate in aqueous mediums. It proved useful for phosphate detection in Coca-Cola®.

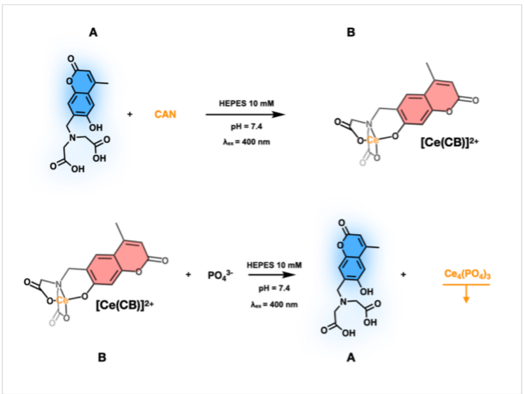

Figure 1: The proposed multi-step reaction mechanism presenting the fluorescent indicator displacement assay based on Calcein Blue (CB) (**A**) added to Cerium Ammonium Nitrate (CAN) forming $[Ce(CB)]]^{2+}$ (**B**) at 250 µM in HEPES pH = 7.4 for the detection of phosphate in 10 mM HEPES pH = 7.4.

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Characterization of the SINQ gas-jet facility as a source for fission products from ^{235}U

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The Swiss spallation neutron source SINQ of the Paul Scherrer Institute provides neutrons via proton-induced spallation in a lead target. These neutrons impinge on the ^{235}U-target, embedded in the outer wall of the SINQ. The thus triggered and well-described neutron-induced fission of ^{235}U, that takes place in the three-part target assembly, results in a variety of isotopes and chemically interesting elements.[1-3] These can be transported to a radiochemical laboratory using a pure or aerosol-loaded carrier gas. In the past, radioisotopes of Se, Br, Rb and Kr have already been identified and used mainly for environmental chemistry experiments.[4,5] Here, we present the characterization of the updated SINQ gas-jet facility in terms of recoverable volatile or non-volatile as well as long-lived or short-lived radioisotopes for radiochemical studies of all types.

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Bottom-up synthesis of films hosting atom-thick molecular-sieving apertures

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Membrane-based gas separation is expected to provide an energy-efficient gas separation technique provided that membranes can be developed that combine selective permeation with large permeance. The ultimate limit to this being two-dimensional (2D), atom thick selective layers hosting a high-density of molecular sieving apertures.[1] Graphene is a highly promising 2D membrane material, but existing techniques for its synthesis with high pore density are tedious because they rely on post-synthetic creation of pores in otherwise defect-free pristine graphene.[1-2]

In this work, we address this through the development of graphene crystallization conditions that promote the formation of nm and sub-nm-sized intrinsic defects.[3] Graphene films are formed through the precipitation of carbon dissolved in a Ni matrix with the carbon dissolution regulated by the controlled pyrolysis of precursors (polymers and/or sugar). The resulting porous nanocrystalline graphene (PNG) films were found to be made up of few-layer graphene, except near the grain edge where the grains taper down to single-layer and eventually terminate into vacancy defects at a node where multiple grains meet. The PNG-nanostructure and processes involved in PNG-formation were studied using transmission electron microscopy (TEM), nuclear magnetic resonance spectroscopy and thermogravimetric analysis. The high pore density (10^{12} cm^{-2}, comparable with state of post-synthetic etching strategies[1]) resulted in attractive gas separation performance with H_2 permeances up to 38000 GPU and attractive molecular sieving from CH_4 and N_2 (at 150 °C, H_2/CH_4 = 17.7 and H_2/N_2 = 16.0). Putting these numbers into perspective by comparison with gas permeance of other graphene membranes with solely intrinsic defects (Figure 1, right) further corroborates the highly porous nature of these PNG films. Post-synthetic masking of the PNG-pores with a CO_2-phillic PEGDE-swollen PEI-layer was shown to produce membranes with favorable CO_2/N_2 separation (CO_2 permeance of 5300 GPU and CO_2/N_2 selectivity of 31). Overall, the reported method improves the scale-up potential of graphene membranes by cutting down the processing steps.

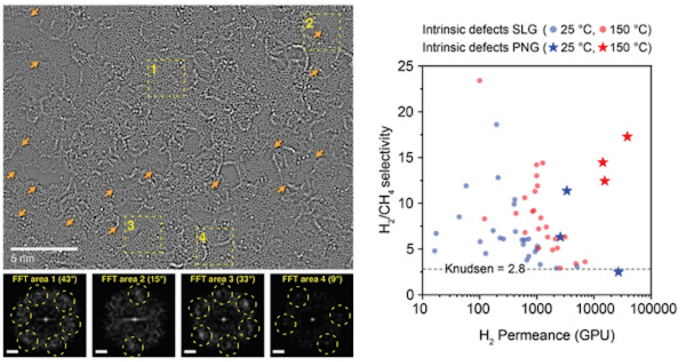

Figure 1. (left) AC-HRTEM image of a PNG-film synthesized by exposing a 25 µm nickel foil to the pyrolysis products of PS-b-P4VP and turanose (1:2 weight ratio) at 500 °C. Nanopores in the film are highlighted using orange arrows. FFT images of the areas highlighted with yellow squares are presented at the bottom (scale bar 2 nm-1). (right) Comparison of H2 permeance and H2/CH4 selectivity at 25 and 150 °C between PNG-membranes and literature single-layer graphene membranes with solely intrinsic defects.

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Radiochemical separation and purification of non-carrier-added silicon-32 for an accurate half-life redetermination.

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Silicon-32 ($T_{1/2}$ = 153(19) years) is an extremely rare, naturally occurring isotope that is considered as a geochronometer, suitable for radiometric dating regarding the time span of 100 to 1000 years - a time span that is currently not accessible (**Fig. 1 (a)**). Due to silicon's typical accumulation environment, it has been successfully employed to study environmental processes such as lacier dynamics, ocean and atmospheric circulation, and sedimentation in lakes and oceans[1]. However, one issue remained, namely the very imprecisely determined half-life, which is generally related to a lack of suitable sample material. Consequently, past attempts to determine the silicon-32 half-life showed both a wide range of values and significant uncertainties (**Fig. 1 (b)**).

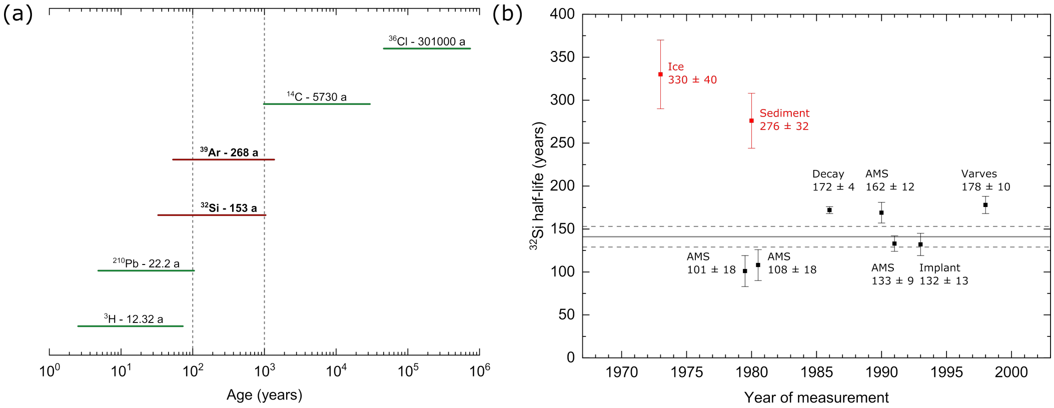

Fig 1: (**a**) Visible dating gap between 100 to 1000 years and (**b**) Compilation of previous half-life determinations. Modified after Fifield & Morgenstern[1].

Thus, utilizing the 590 MeV ring cyclotron at the Paul Scherrer Institut, Megabecquerel (x10^6 Bq) quantities of silicon-32 were artificially produced through spallation, exposing metallic vanadium discs to high-energy protons. As a result, with artificially produced silicon-32, a careful half-life redetermination becomes feasible, allowing the first step towards implementing the nuclide for precise radiochemical geochronology.

In the frame of the SINCHRON project, we present a radiochemical separation procedure that is based on a combination of ion exchange and extraction chromatography and has been successfully applied in order to process over 150 proton irradiated vanadium discs. The process has proven to be a reliable and robust method including a high chemical yield concerning the silicon-32 recovery[2]. Finally, radiochemically pure silicon-32 solutions with high activity concentrations of up to 100 kBq/g can be provided, allowing to perform individual measurements (AMS, ICP-MS, LSC), primarily focusing on the redetermination of the silicon-32 half-life.

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Planar or Buckled? - Structure-Property Relationships in Superconductors with Honeycomb Layers

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

In this project we successfully synthetized $Ca_{1-x}Sr_xAlSi$ and $Ca_{1-x}Sr_xGaGe$ solid solutions and investigated the superconducting properties of these materials. Both CaAlSi and CaGaGe crystallize in structures with slightly buckled Al-Si and Ga-Ge honeycomb layers. While SrAlSi and SrAlGe crystalize in prototypical AlB_2-type structures, with planar Al-Si and Ga-Ge honeycomb layers. We find that with an increasing Sr content the Al-Si and Ga-Ge layers become increasing planar in both solid solutions. Interestingly, while the two systems behave chemically very similar, they display very different electronic properties. We find that while the buckling in the $Ca_{1-x}Sr_xAlSi$ enhances the superconducting critical temperature, it decreases it in the $Ca_{1-x}Sr_xGaGe$ solid solution, accordingly.

Isothermal gas adsorption chromatography of different thallium species for further investigations of nihonium

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The discovery of nihonium has since prompted the investigation into its chemical properties[1,2]. To prepare for chemical investigations, offline experiments with its lighter homolog, thallium, have been conducted[3]. Reported here are the most recent results of online investigations with thallium. In collaboration with the Flerov Laboratory of Nuclear Reactions, Dubna, Russia, the experiment included their U-400 cyclotron facility in combination with the SHELS velocity filter for the separation of the nuclear reaction products[3]. Short-lived thallium radioisotopes were synthesized in the nuclear reaction ^{141}Pr(^{48}Ti, xn)$^{189-x}$Tl, where ^{184}Tl was the main radioisotope of interest[5]. Isothermal gas adsorption chromatography experiments gave new insights to the chemical behavior of thallium, as produced in nuclear fusion-evaporation reactions, on quartz. The chromatographic yields after the isothermal oven were measured using gamma- and alpha-spectroscopy. These results highlight the coming challenges to unambiguously identify the chemical state of nihonium.

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

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The use of liquid metals is an attractive proposition towards the development of generation IV nuclear power reactors. Such reactors can be employed both as breeder reactors, as well as for the transmutation of nuclear waste into shorter-lived nuclides.

In order to properly assess the safety of such systems, the distribution and behaviour of radionuclides, produced during operation, needs to be well understood. Especially for potential accident scenarios, a detailed knowledge about the release of radionuclides from the coolant is of utmost importance. Within the HORIZON2020 project PATRICIA, the ongoing research on the volatilisation of radionuclides from liquid lead-bismuth eutectic (LBE), crucial for the licencing and safety of future accelerator driven systems, is continued. Within the framework of PATRICIA the scope of work is extended towards the volatilisation behaviour of fission and spallation products. The studied elements within PATRICIA are extended to tellurium, ruthenium, rhenium and osmium in dilute solutions of LBE, whereas earlier investigations focused mainly on polonium. Furthermore, it is planned to utilize irradiated LBE material from the MEGAPIE target to investigate the influence of spallation products on the volatility of polonium and its compounds. Here, we will describe the methodological developments necessary for employing the transpiration method to study the volatilisation of the above-mentioned elements as well as discuss first results from those experiments. In addition, the evaporation behaviour of Te from LBE will be highlighted by results gathered from Knudsen-effusion-mass-spectrometry measurements of Te-containing LBE samples.