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Rationally Designed Long-Wavelength Absorbing Metal Complexes as Photosensitizers for Photodynamic Therapy

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Photodynamic Therapy (PDT) has expanded the range of treatment opportunities for some fungal and bacterial infections and cancer. The first clinically approved photosensitizer (PS) was Photofrin®, which is used to treat various types of cancer (e.g. non-small lung, bladder, oesophageal or brain cancer). As the majority of clinically accepted and investigated PSs are based on the same structural scaffold, these compounds are usually associated with similar drawbacks (e.g. poor water solubility, tedious synthesis and purification, photodegradation and slow clearance from the body causing photosensitivity). To overcome these limitations, existing PSs have been modified revealing a new class of PS. As an emerging class of compounds, Ru(II) polypyridyl complexes have gained much attention due to their attractive chemical and photophysical properties (e.g. high water solubility, high ROS production, chemical stability and photostability). Despite recent research efforts, the majority of investigated Ru(II) polypyridyl complexes lack absorption in the biological spectral window (600-900 nm), limiting their use for the treatment of large or deep-seated tumours. During this talk, we will present our latest results on the use of novel Ru(II) polypyridyl complexes as long wavelength absorbing PSs for PDT.[1-4]

[1] J. Karges, S. Kuang, F. Maschietto, O. Blacque, I. Ciofini, H. Chao,* and G. Gasser,* *Nature Commun.*, **2020**, *11*, 3262.
[2] J. Karges, F. Heinemann, M. Jakubaszek, F. Maschietto, C. Subecz, M. Dotou, R. Vinck, O. Blacque, M. Tharaud, B. Goud, E. Viñuelas Zahínos, B. Spingler,* I. Ciofini,* and G. Gasser,* *J. Am. Chem. Soc.*, **2020**, *142*, 6578-6587.
[3] A. Mani, T. Feng, A. Gandioso, R. Vinck, A. Notaro, L. Gourdon, P. Burckel, B. Saubaméa, O. Blacque, K. Cariou, J.-E. Belgaied, H. Chao, and G. Gasser, *Angew. Chem. Int. Ed.*, **2023**, *62* ,e202218347.
[4] E. Ortega-Forte, A. Rovira, M. López-Corrales, A Hernández-García, F.J. Ballester, E. Izquierdo-García, M. Jordà-Redondo, M. Bosch, S. Nonell, M. Dolores Santana, J. Ruiz, V. Marchán and G. Gasser, *Chem. Sci.*, **2023**, *accepted,* DOI : https://doi.org/10.1039/D3SC01844J

Synthesis and Reactivity of a Stable Organoazide Iron Complex and its Relevance to C–H Bond Amination

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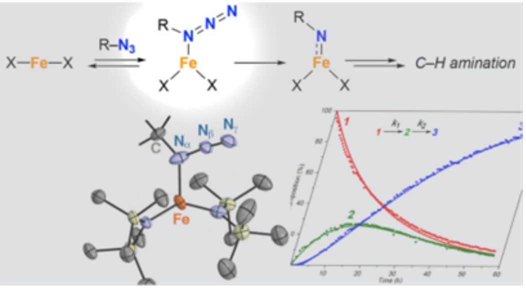
The formation of C–N bonds is of paramount importance for synthesis of pharmaceuticals, agrochemicals and natural products.[1] Complexes with organic azides are critical precursors for the formation of nitrene systems en route to the direct C–H amination, forming C–N bonds very efficiently and sustainably. Despite their relevance, first-row transition metals with α-organoazide coordinated are extremely rare,[2,3] and they have been elusive so far for iron, even though iron complexes are by far the most active C–H amination catalysts with organic azides.[4-6]



In this contribution we will show the first example of the full characterization of such an organoazide iron complex. We will demonstrate the further reactivity to a transient nitrene intermediate and discuss reactivity of the azide both in solution and in crystallo. The characterization of both these intermediates is of paramount importance for understanding the catalytic C–H amination reaction and for designing new and improved catalytic systems.

[1] Ryan Hili, Andrei K. Yudin, *Nat. Chem. Biol.,* **2006**, 2, 284–287.
[2] Lauren N. Grant, Maria E. Carroll, Patrick J. Carroll, Daniel J. Mindiola, *Inorg. Chem.*, **2016**, 55, 7997–8002.
[3] Yunjung Baek, Anuvab Das, Shao-Liang Zheng, Joseph H. Reibenspies, David C. Powers, Theodore A. Betley, *J. Am. Chem. Soc.*, **2020**, 142, 11232–11243.
[4] Wowa Stroek, Martin Keilwerth, Daniel M. Pividori, Karsten Meyer, Martin Albrecht, *J. Am. Chem. Soc.*, **2021**, 143, 20157–20165.
[5] Wowa Stroek, Lilian Hoareau, Martin Albrecht, *Catal. Sci. Technol.* **2023**, 13, 958-962
[6] Wowa Stroek, Martin Albrecht, *Chem. Sci.* **2023**, 14, 2849-2859

Behavior of silver(I) ion binding with peptides inspired from SilE protein

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Since many years, silver has been used in medicine for its antimicrobial properties.[1] However, as for antibiotics, bacteria can develop a certain resistance or tolerance to the antimicrobial action of silver.[2] For the *Salmonella Typhimurium*, this silver resistance is based on a silver efflux pump, composed of eight proteins which act together to export silver(I) ions, named Sil system.[2] While most of these proteins could be attributed in analogy to the copper efflux system Cus, the SilE protein is unique and proposed to act like a silver sponge.[2,3] SilE is composed by 143 amino acids (aa) and contains many histidine (His, H) and methionine (Met, M) residues, which are able to bind silver(I) ions.[4] The study of HXXM tetrapeptides has shown that the nature of the aa "X" influences the association binding constant $\log(K_{ass})$.[4]

Based on these observations and in order to gain a more basic understanding of silver ion binding in peptides and proteins, HXXM / MXXH / HXXH / MXXM tetrapeptides were synthesized and studied for their interactions with Ag^+. Differences and similarities in the coordination behavior between HXXH and MXXM, but also HXXM and MXXH were noticed. Some first trends will be presented in this work.

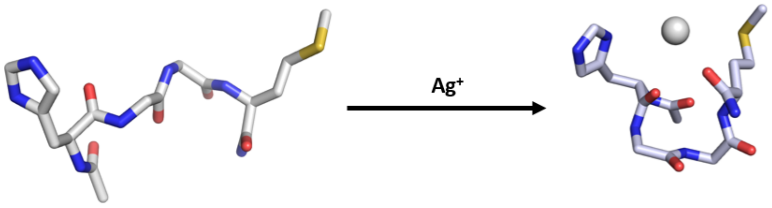

Fig. 1 : Folding of HXXM upon coordination with Ag^+

[1] Serenella Medici, Massimiliano Peana, Valeria M. Nurchi, Maria A. Zoroddu, , *J. Med. Chem.*, **2019**, 13, 5923-5943.
[2] Simon Silver, *FEMS Microbiol. Rev.*, **2003**, 27, 341–353.
[3] Karishma R. Asiani, Huw Williams, Louise Bird, Matthew Jenner, Mark S. Searle, Jon L. Hobman, David J. Scott, Panos Soultanas, *Mol Microbiol.*, **2016**, 101, 731-742.
[4] Valentin Chabert, Maggy Hologne, Olivier Sénèque, Aurélien Crochet, Olivier Walker, Katharina M. Fromm, *Chem. Commun.*, **2017**, 53, 6105-6108.

Orientational self-sorting in octahedral palladium cages: scope and limitations of the cis-rule

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Palladium-based metal-organic cages (MOCs) have been widely studied and have applications in medicinal chemistry as well as in catalysis. The understanding of their self-assembly is therefore of great importance. Ditopic N-donor ligands L and Pd(II) precursors form a variety of MOCs of the general formula $[Pd_nL_{2n}]^{2n+}$ in which the bend angle of L, for the most part, dictates the geometry of the cage. Using various low-symmetry heteroditopic ligands L with a bend angle of 90°, hexanuclear $[Pd_6L_{12}]^{12+}$ metal-organic cages (MOCs) were synthesized with $[Pd(CH_3CN)_4(BF_4)_{12}]$ in acetonitrile. Due to the low symmetry of the ligands many isomers can potentially be formed. The obtained structures provide additional evidence for orientational self-sorting[1,2]: Out of 112 possible isomers for $[Pd_6L_{12}]^{12+}$, we show the one isomer with *cis*-configuration at all Pd-centers is thermodynamically favored (Fig. 1a and 1b). Various characterization methods including ^{1}H NMR, ^{13}C NMR, COSY, NOESY, DOSY and single crystal XRD structure elucidation confirm the formation of a single isomer. Using ligands with different coordination vector ratios and donor groups (pyridyl-, triazolyl- and imidazolyl-donor) we discuss the scope and limitations of the aforementioned selectivity. A kinetically trapped product was obtained from imidazolyl-ligand **L5** (Fig. 1c). Furthermore, we provide a geometrical explanation using a coordination vector model for the experimentally observed *cis*-isomers.

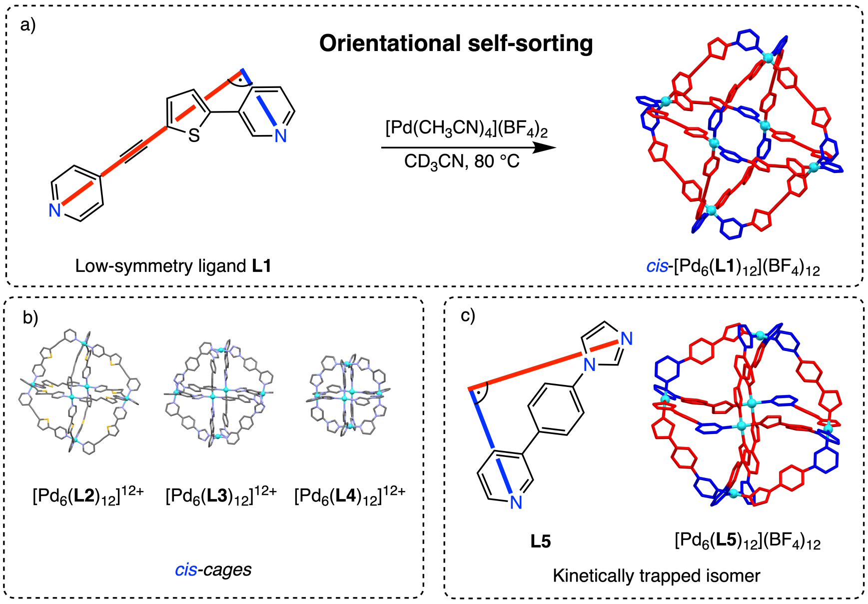

Fig. 1 Orientational self-sorting in $[Pd_6L_{12}]^{12+}$ cages using low-symmetry ligands. a+b) The thermodynamic isomers with *cis*-configuration at every Pd-center are obtained exclusively. c) A kinetically trapped isomer with *cis*-configuration at only 2 Pd-centers.

[1] Ru-jin Li, Andrew Tarzia, Victor Posligua, Kim E. Jelfs, Nicolas Sanchez, Adam Marcus, Ananya Baksi, Guido H. Clever, Farzaneh Fadaei-Tirani and Kay Severin, *Chem. Sci.*, **2022**, 13, 11912-11917.

[2] Ru-jin Li, Adam Marcus, Farzaneh Fadaei-Tirani and Kay Severin, *Chem. Commun.,* **2021**, 57, 10023-10026.

Surface Morphology and Interfacial Electric Fields of Inorganic Materials

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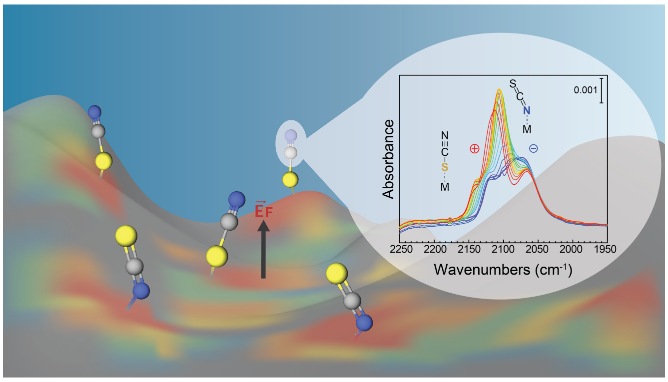
Sustainable energy conversion technologies often rely on an inorganic material as electrocatalyst. The activity and selectivity of such electrocatalysts critically depend on a complex interplay of the electric field at the solid-solution interface, the coordination of substrates and other solution components at the inorganic surface, the surface morphology that influences the diffusion of electrons and ions to the active surface sites, and other factors.[1-7] However, these interfacial fundamentals remain elusive, in part because many conventional characterization methods are either not surface-specific or cannot be assessed under reaction conditions. Here, we aim to disentangle the relationship between surface morphology, chemical binding of solution components and electric field effects at the surface of inorganic material electrocatalysts by a spectro-electrochemical approach.

We employed in situ surface-enhanced infrared absorption spectro-electrochemistry (SEIRAS) to probe the interfacial chemistry of thin electrode films of inorganic materials having different surface morphologies as a function of an applied potential. A series of probe molecules and chemical surface modification strategies were combined to report on the presence or absence of pinholes and other defects at the surface, to provide insight into the nature of coordinative surface binding for both earth-abundant inorganic materials and noble metals, and to measure the electric field locally at the surface on molecular-length scales. By careful analysis of the infrared spectra, we provide first clues on the complex behavior of the polarized surfaces of inorganic materials and provide tools to analyze their potential relevance in catalysis.



[1] Chen, L. D.; Urushihara, M.; Chan, K.; Nørskov, J. K. *ACS Catal.* **2016**, 6, 7133−7139.
[2] Murata, A.; Hori, Y. *Bull. Chem. Soc. Jpn.* **1991**, 64, 123−127.
[3] Resasco, J.; Chen, L. D.; Clark, E.; Tsai, C.; Hahn, C.; Jaramillo, T. F.; Chan, K.; Bell, A. T. *J. Am. Chem. Soc.* **2017**, 139, 11277−11287.
[4] Liu, M.; Pang, Y.; Zhang, B. *et al. Nature* **2016,** 537, 382–386.
[5] Li, F.; Medvedeva, X.V.; Medvedev; J.J. *et al. Nat Catal.* **2021,** 4, 479–487.
[6] Delley, M. F.; Nichols, E. M.; Mayer, J. M. *J. Am. Chem. Soc.* **2021**, 143, 10778−10792.
[7] Delley, M. F.; Nichols, E. M.; Mayer, J. M. *J. Phys. Chem. C* **2022**, 126, 8477–8488.

^{15}N NMR Anisotropy on Transition Metal Imido Complexes: Link between Spectroscopy and Reactivity

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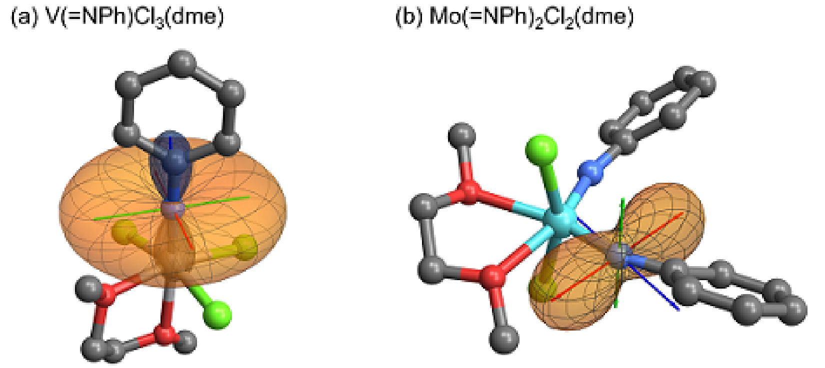
Imido ligands are one of the most fundamental ingredients in organometallic chemistry serving as supporting ligand, which can be typically found in Schrock-type olefin metathesis catalysts, and as a reactive site which facilitates numerous stoichiometric- and catalytic transformations such as cycloaddition with unsaturated bonds, nitrene transfer or C-H bond activation. Despite the diverse reactivity found among transition metal imido complexes across the periodic table, no general reactivity descriptor has been uncovered. In this context, solid-state NMR (ssNMR) has recently emerged as a powerful tool to link the spectroscopic signature, *i. e.* chemical shift tensors (CSTs), of specific nuclei to their electronic structures, which can be further tied with the reactivity.[1] In this work, we uncover the electronic structures of transition metal imido complexes using solid-state NMR augmented with DFT calculations and establish a spectroscopy-reactivity relationship.

The experimentally-collected ^{15}N ssNMR spectrum of the group 5 mono-imido species $V(={}^{15}NPh)Cl_3(dme)$, which has inert imido ligand, revealed an axial spectral pattern ($d_{11} \approx d_{22}$) while the highly reactive group 6 bis(imido) species $Mo(={}^{15}NPh)Cl_2(dme)$ exhibited an anisotropic spectrum ($d_{11} \neq d_{22}$). Natural Chemical Shift (NCS) analysis anchored on the experimentally-determined chemical shift anisotropy revealed the dominant and highly asymmetric development of p-contribution on the CSTs in $Mo(=NPh)_2Cl_2(dme)$, while s-bond only plays a marginal role. This contrasts with the symmetric distribution of s- and p-orbitals in the unreactive $V(=NPh)Cl_3(dme)$, in which the s(V-N) orbital dominates. The highly developed contribution from the p(Mo-N) orbital in $Mo(=NPh)_2Cl_2(dme)$ points out its high-lying nature. Visualization of the molecular orbitals revealed the competitive p-interaction between two imido ligands sharing the same orbital, which induces an increase HOMO energy and reactivity. Such scenario further supports the so-called concept of the "p-loading effect",[2] which is often referred as an activation strategy for imido complexes. The thus-obtained results show that ^{15}N chemical shift tensors are useful probe of reactivity for imido complexes.



(a) $V(=NPh)Cl_3(dme)$ (b) $Mo(=NPh)_2Cl_2(dme)$

Figure 1. Visualized ^{15}N Chemical Shielding Tensors for selected imido complexes

[1] (a) Czaja, K.; Biatek, M. *Macromol. Rapid Commun.* **1996**, *17*,253-260. (b) Mikenas, T. B.; Zakharov, V. A.; Echevskaya, L. G.; Matsko, M. A. *Macromol.Chem.Phys.* **2001**, *202*,475.

[2] Lapina, O. B.; Mats'ko, M. A.; Mikenas, T. B.; Zakharov, V. A.; Paukshtis, E. A.; Khabibulin, D. F.; Sobolev, A. P. *Kinetics and Catalysis*, **2001**, *42*, 553–560.

SwissCAT+ - Hub for Data-driven, Automated and High-throughput Catalysis R&D

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The ETH domain has recently launched the Catalysis Hub SwissCAT+, a technology platform dedicated to automated high-throughput and data-driven experimentation in the field of catalysis. The Hub located at ETH Zürich (SwissCAT+ East) focusses on heterogeneous catalysis and the Hub at EPF Lausanne on homogeneous catalysis. SwissCAT+ East hosts state-of-the-art robotic and high-throughput equipment to synthesize, characterize and evaluate catalysts augmented by artificial intelligence/machine learning algorithms to analyze data and optimize workflows.[1] As an open-access technology platform, SwissCAT+ East offers tools and expertise to the broad scientific community investigating catalytic processes, particularly for the production of sustainable fuels and chemicals.

In this presentation, the capabilities of SwissCAT+ East for performing automated high-throughput synthesis, characterization and testing of heterogeneous catalysts will be introduced. It includes the synthesis of materials via incipient wetness impregnation and zeolites as well as parallel fixed-bed reactor testing at up to 925 °C and 100 bars (e.g. for CO_2 hydrogenation, dry reforming, methanol-to-olefin, propane dehydrogenation). Finally, a case study for a closed-loop workflow for the synthesis and optimization of catalysts for CO_2-to-CH_3OH conversion guided by Bayesian optimization will be discussed.

[1] P. Laveille, P. Miéville, S. Chatterjee, E. Clerc, J.-C. Cousty, F. de Nanteuil, E. Lam, E. Mariano, A. Ramirez, U. Randrianarisoa, K. Villat, C. Copéret, N. Cramer, *Chimia* **2023**, *77*, 154, DOI: 10.2533/chimia.2023.154.

Synthesis and Anisotropic Magnetic Properties of $LiCrTe_2$ Single Crystals with a Triangular-Lattice Antiferromagnetic Structure

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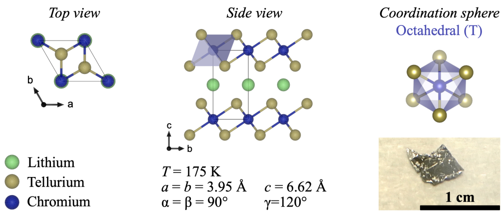
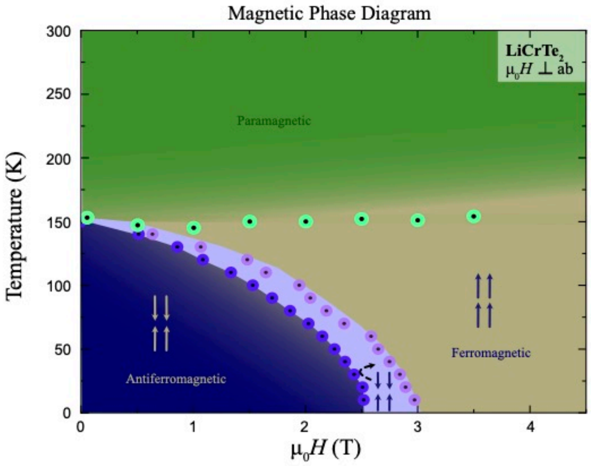
$LiCrTe_2$ is an antiferromagnetic compound and was synthesized as powder for the first time in 2016 by *Kobayashi et al* because of the expected exotic ground states and physical properties that come along with two-dimensional triangular-lattice compounds.[1,2] $LiCrTe_2$ can be understood as a Li intercalated version of the thermodynamically metastable 1T-$CrTe_2$ van der Waals compound and was believed to have a helical spin structure.[3]

We report on the single crystal synthesis of $LiCrTe_2$ employing a Te/Li-flux and find the transition temperature to be substantially higher (~150 K) then previously reported (70 K).[4]



With neutron powder diffraction measurements, we were able to determine the Li content as stoichiometric and elucidate the long-range low temperature magnetic structure as being A-type antiferromagnetic, with the easy axis along the *c*-direction. This is consistent with our DFT calculations. We have determined the magnetic phase diagram of this material using detailed orientation dependent magnetization measurements and reveal a pronounced metamagnetic transition for $H \perp ab$ with a critical field of $\mu H_{MM}(5\ K) \approx 2.5\ T$.

Our findings suggest that $LiCrTe_2$ is a promising material for exploring the interplay between crystal structure and magnetism, and could have potential applications in spin-based 2D devices.



1. Kobayashi S, Ueda H, Michioka C and Yoshimura K, *Inorg. Chem.*, **2016**, 55 7407–13.
2. Nocerino E, Kobayashi S, Witteveen C et al, *arXiv*, ***2022***, arXiv:2211.06864
3. Nocerino E, Witteveen C, Kobayashi S et al, *Sci. Rep.*, **2022**, 12 21657
4. Witteveen C, Nocerino E, López-Paz S et al, *arXiv*, **2023**, arXiv:2304.01767

Charge Transport via Redox Ligands in Quantum Dots

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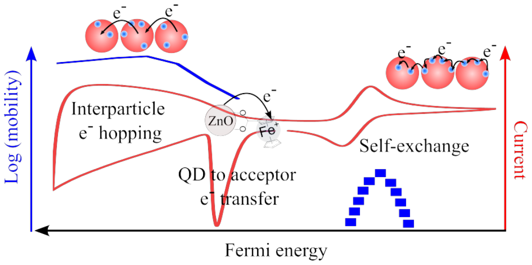
[1]Department of Chemical Engineering, Delft University of Technology

We present a strategy to actively engineer long-range charge transport in colloidal quantum dot (QD) assemblies by using ligand functionalities that introduce electronic states and provide a path for carrier transfer.[1] This is a paradigm shift away from the use of inactive spacers to modulate charge transport through the lowering of the tunneling barrier for interparticle carrier transfer. It has immediate implications in the design of QD lasers, light-emitting diodes, solar cells and photodetectors where charge transport determines the device performance.

The introduced states are narrow and only available at a certain Fermi energy, which makes it challenging to explore. To overcome this challenge, we turned to an electrochemical approach that allows to set the Fermi energy while simultaneously measure the rate of charge transport. We show that charge transport occurs through a succession of self-exchange reactions between the immobile redox ligands distributed at random positions in the assembly and their density is readily controllable. This allows to adjust the conductivity which is explained by a percolation model. Modulating the Fermi energy allows to switch between charge transport mechanisms, from self-exchange to electron hopping, and this is shown to be accompanied by ion transport.

Overall, the strategy presented here enables a means to actively control long-range charge transport in QD assemblies that remained until now unexplored.



[1] Yan B. Vogel, Maarten Stam, Jence T. Mulder, Arjan J. Houtepen, *ACS Nano*, **2022**, 16, 21216-21224.

Synthesis and antimicrobial activity of rhenium tricarbonyl complexes bearing medically relevant ligands and selected by computer-aided design

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For more than 30 years, no new class of antibiotics has reached the market, which has caused antimicrobial resistance (AMR) to increase in a concerning manner. Metal complexation of well-established drugs constitutes a promising strategy to overcome loss of medication sensitivity and induced resistance, as the coordinated derivatives of biologically active ligands have been known to show synergistic effect with certain metal cores [1]. The choice of the latter yet remains critical and, in particular, rhenium (Re) complexes feature interesting medical properties, especially because the final oxidation product of such species displays extremely low toxicity, comparable to the one of sodium chloride [2].

Examples of Re derivatives developed for antimicrobial purposes remain scarce in the literature. However, Mendes et al. recently studied the antibacterial mechanism of such a molecule (**1**) bearing the well-established clotrimazole ligand. They discovered that this promising complex inhibits cell wall synthesis by interfering in the MurG-mediated production of Lipid II from Lipid I (Figure 1A) [3].

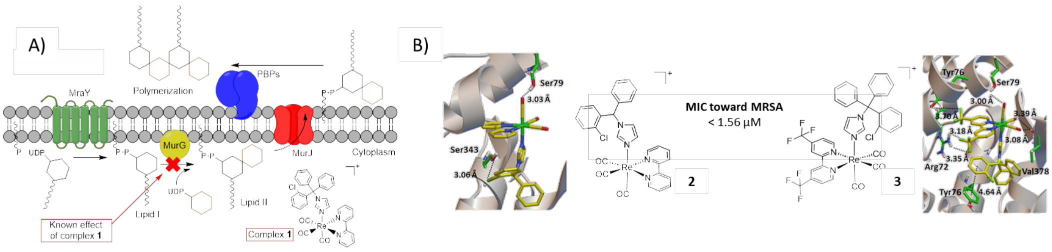

Figure 1. A) Peptidoglycan biosynthesis where the MurG-mediated reaction is inhibited by **1**. B) Interaction maps of the absolute lowest energy poses of **2** and **3** in SpsB catalytic site.

Using computational methods, our group has been investigating similar Re-containing enzyme blockers in order to develop new efficient antibiotics [4,5]. This computer-aided strategy consists in performing docking calculations followed by synthesis and finally antimicrobial assessment of the candidates with best docking scores in the selected enzyme pocket. Considering the results obtained so far (see *e.g.* complexes **2** and **3**, Figure 1B), we believe that this approach constitutes a viable strategy in the fight against AMR.

[1] Chellan, P.; Sadler, P.J. *Chem. Eur. J.* **2020**, *26*, 8676-8688.
[2] Haase, A.A.; Bauer, E.B.; Kuhn, F.E.; Crans, D.C. *Coord. Chem. Rev.* **2019**, *394*, 135-161.
[3] Mendes, S.S.; Marques, J.; Mesterházy, E.; Straetener, J.; Arts, M.; Pissarro, T.; Reginold, J.; Berscheid, A.; Bornikoel, J.; Kluj, R.M.; et al. *ACS Bio & Med Chem Au* **2022**, *2*, 419-436.
[4] Schindler, K.; Cortat, Y.; Nedyalkova, M.; Crochet, A.; Lattuada, M.; Pavic, A.; Zobi, F. *Pharmaceuticals* **2022**, *15*, 1107.
[5] Cortat, Y.; Nedyalkova, M.; Schindler, K.; Kadakia, P.; Demirci, G.; Nasiri Sovari, S.; Crochet, A.; Salentinig, S.; Lattuada, M.; Steiner, O.M.; Zobi, F. *Antibiotics* **2023**, *12*, 619.

Alkali-Metal Silyl Zincates: Synthesis, Structure and Reactivity

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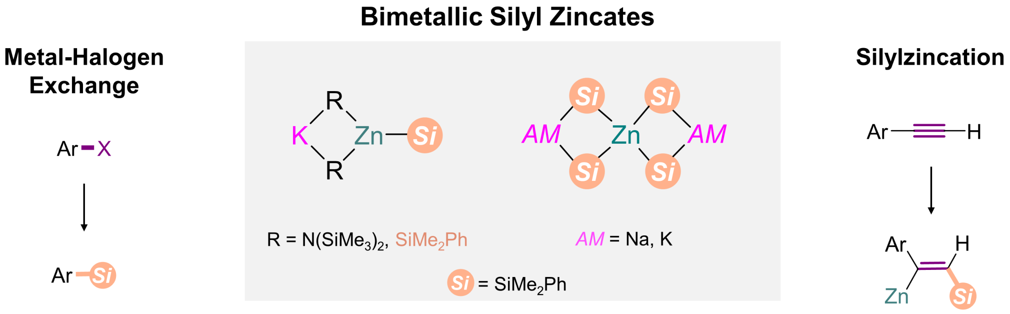
The high natural abundance of silicon and its non-toxic nature are just some of this element's advantages, strengthened by the popular use of organosilicon compounds within cross-coupling reactions.[1] Therefore, there stands a natural drive to easily access such useful organosilicon building blocks. While numerous pathways for the silylation of organic molecules have been designed using electrophilic silicon species (mainly using transition metals and/or harsh conditions), the use of nucleophilic silicon reagents is a lesser-employed alternative.[2] Current methods that have emerged within the past decade include nucleophilic addition or substitution reactions *via* silylmetalation,[3a] silylboration,[3b] defluorosilylation[3c] or nucleophilic silyl substitution[3d] using monometallic-silyl reagents. Despite these advances, a gap in the knowledge still exists with regards to (i) fundamental characterisation and understanding of these bimetallic reagents employed and (ii) the *modus operandi* which they follow.

In an effort to bridge this gap, this work exploits the high reactivity of alkali-metals (e.g. K) combined with the better selectivity of a lower-polarity metal (Zn) as a platform for accessing novel, nucleophilic silyl complexes. The results presented include X-ray crystallographic characterisation of these bimetallic silyl reagents, and our preliminary understandings surrounding their nucleophilic capabilities in the direct silylation of haloarenes or the silylzincation of phenylacetylene.



[1] Hannah F. Sore, Warren R. J. D. Galloway, David R. Spring, *Chem. Soc. Rev.*, **2012**, 41, 1845-1866.
[2] Takeshi Komiyama, Yasunori Minami, Tamejiro Hiyama, *ACS Catal.*, **2017**, 7, 631-651; Watchara Srimontree, Lin Guo, Magnus Rueping, *Chem.-Eur. J.*, **2020**, 26, 423-427.
[3] (a) Shinki Nakamura, Mitsuhiro Yonehara, Masanobu Uchiyama, *Chem. Eur. J.*, **2008**, 14, 1068-1078. (b) Yiting Gu, Yaya Duan, Yangyang Shen, Ruben Martin, *Angew. Chem. Int. Ed.*, **2020**, 59, 2061-2065. (c) Greg Coates, Hui Yee Tan, Carolin Kalff, Andrew J. P. White, Mark R. Crimmin, *Angew. Chem. Int. Ed.*, **2019**, 58, 12514-12518; d) Eiji Yamamoto, Satoshi Ukigai, Hajime Ito, *Synlett*, **2017**, 28, 2460-2464.

Novel (C^C) Zwitterionic Gold(III) Complexes: Synthesis and Insight into the Mechanism of the Cycloauration Step

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In the last years, gold(III) complexes have gained great attention due to their steadily increasing applications in a variety of fields, including catalysis, material science, and biomedicine. [1] Due to the tendency of Au(III) to be reduced to Au(I) or Au(0), stable Au(III) are often prepared in the form cyclometalated species based on pincer or bidentate ligands bearing aryl carbanions and pyridine moieties (e.g. [C^N^C], [C^N] and [N^N] type of ligands).[2] Some of these mono- or bis-cyclometalated species have been used for studying elementary steps in gold-catalyzed transformations, such as in transmetalation, insertion or reductive eliminations. Unfortunately, stable examples of precursors of carboauracycles of type [C^C]Au(III), which could be used to further unveil mechanistic intricacies of gold-promoted C–C bond-forming processes, are very scarce, and essentially limited to systems bearing biphenyl and other $C(sp^2)$-based ligands.

As part of our investigations on the reactivity of Au(III) with alkylidenecyclopropanes (ACPs) equipped with pyridine ligands[3], we have now discovered that substrates in which the ACP and the pyridine are connected through 1,2-phenyl tether exhibit a novel type of reactivity with Au(III) salts to deliver intriguing zwitterionic [C^C]Au(III) carboauracycles. These interesting spirocyclic auracycles result from a cascade process involving the nucleophilic addition of the pyridine moiety to the Au(III)-activated alkene and an intramolecular aromatic metalation of the resulting $C(sp^3)$-gold(III) intermediates.

Importantly, the isolation of the alkyl gold(III) intermediates that precede the cyclometallation, allowed us to use them as a proxy for carefully studying the subsequent aromatic auration. Importantly, our collected data allowed us to rule out a CMD process, previously proposed in related systems, while is fully compatible with a two-step S_EAr pathway in which the Au(III)- arene complexation, rather than the direct formation of the Wheland intermediate, is the rate-limiting step. This study provides a detailed insight into how the Au-C(sp2) bond formation step takes places and the factors that affect this process, which is an elementary step for gold-catalyzed oxidate cross-couplings.

[1] Luca Rocchigiani, Manfred Bochmann, *Chem. Rev.* **2021**, 121, 14, 8364-8451.
[2] Rupender Kumar, Cristina Nevado, *Angew. Chem. Int. Ed.* **2017**, 56, 1994-2015.
[3] Jorge A. González, Felipe Verdugo, José L. Mascareñas, Fernando López, Cristina Nevado, *Angew. Chem. Int. Ed.* **2020**, 59, 20049–20054.

Cesium Distribution in Perovskites revealed by ^{127}I NQR

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Formamidinium-based hybrid lead iodide perovskites ($FAPbI_3$) have recently led to significant improvements in the performance of perovskite photovoltaics. One of the remaining major hurdles is the instability of the black α-$FAPbI_3$, which undergoes a phase transition from the desired three-dimensional cubic perovskite phase to a non-perovskite one-dimensional hexagonal lattice. Partial substitution of FA with Cs is known to stabilize the material's cubic perovskite structure, as shown by X-ray diffraction. We address this problem by ^{127}I nuclear quadrupole resonance (NQR), which has been shown to be able to resolve structural changes with accuracies commensurate with synchrotron X-ray diffraction and scattering.[1] We report the ^{127}I NQR spectra of $FA_{1-x}Cs_xPbI_3$ (x = 0 - 0.1) crystals showing not only the averaged but all the local iodide structures.[2] Already minute quantities of Cs ions drastically change the observed ^{127}I NQR spectra. 5% of cesium ion incorporation leads to immense inhomogeneous line broadening and an additional species observable at lower frequencies. This new species could be assigned to iodide environments with one of the four FA neighbours being replaced by Cs, showing reduced quadrupolar coupling constants and increased asymmetry. For higher amounts of ion substitution, iodide environments with two cesium neighbours can be observed. This species is highly overrepresented with respect to a homogeneous halide distribution. This could be attributed to cesium clustering, foreshadowing the complete phase segregation occurring upon further cesium addition. These findings showcase the great potential of halide NQR for characterizing local structures of perovskite-based materials, enabling improved models for property calculations, as well as allowing for a better atomic picture of these complex materials.

[1] Piveteau L., *et al., ACS Cent. Sci.* **2020**, 6, 7, 1138–1149.
[2] Aebli, M., Porenta N., Aregger N., Kovalenko M.V., *Chem. Mater.* **2021**, 33, 17, 6965–6973.

Acetylene-Based Layered Hybrid Perovskites

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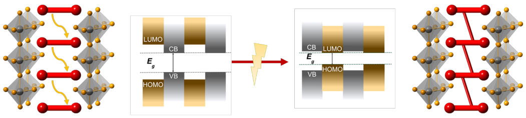
Hybrid organic-inorganic metal halide perovskites have become one of the dominant semiconductors in the field of photovoltaics. They are soft yet crystalline mixed ionic-electronic conductors that have unique optoelectronic and optoionic properties. However, they suffer from instability under device operating conditions.[1,2] This stimulated the development of low-dimensional and layered (2D) perovskites as a more stable alternative based on hydrophobic organic cations that act as spacers, templating halide perovskite slabs.[2] However, conventional organic spacers are mostly electronically insulating species that form quantum well electronic structures with charges confined within the inorganic layers, limiting their transport and lowering power conversion efficiency in solar cells.[2-4] This could be addressed by incorporating extended (opto)electronically active organic moieties within layered hybrid perovskite frameworks, which remains challenging. We demonstrate the capacity to extend the functionality of Ruddlesden-Popper and Dion-Jacobson 2D perovskite materials by incorporating acetylene-based organic spacers.[5] The formation of hybrid 2D perovskites is evidenced by a combination of techniques, including X-ray diffraction and solid-state NMR spectroscopy. Moreover, we assess their opto(electro)ionic characteristics by UV-vis absorption, photoluminescence emission, and impedance spectroscopy, showcasing changes in their functionality in response to light. This opens perspectives toward multifunctional hybrid materials in opto(electro)ionics.



Schematic representation of layered hybrid perovskites with their quantum well electronic structure (left) and light-induced changes of their functionality (right)

[1] A. K. Jena, A. Kulkarni, T. Miyasaka, *Chem. Rev.***2019**, *119*, 3036–3103.
[2] J. V. Milić, S. M. Zakeeruddin, M. Grätzel, *Acc.Chem. Res.* **2021**, *54*, 2729–2740.
[3] J. V. Milić, *J. Mat. Chem. C* **2021**, *9*, 11428–11443.
[4] W. Luo, G. AlSabeh, J. V. Milić, *Photochemistry* **2022**, *50*, 342–366.
[5] G. AlSabeh J. V. Milić, et al. **2023**, *manuscript in preparation*.

Nickel-Catalyzed Cyclopropanation of Unactivated Olefins

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Cyclopropanes have always been an appealing synthetic building block for any organic chemist. New Cyclopropanation methods have been investigated intensely through the last decades in order to avoid inorganic waste (Simmons-Smith reaction) and/or highly toxic chemicals (diazo-compounds)[1-6].

Our group proposed a Nickel-catalyzed cyclopropanation method of unactivated olefins using tetramethylammonium triflate as the methylene donor[7]. Compared to other catalytic systems (Pd/Pt, Zn, diazo-compounds) this proposed method makes use of cheap and abundant materials, making it safer and more atom economic. Good yields have been achieved by means of thorough mechanistic studies and reaction optimization, achieving now up to 75% yield for highly unactivated olefin (cyclooctene). It has been shown that the reaction can be performed using bench-stable reagents including the catalyst (excluding *n*-BuLi) giving similar yields than more cumbersome oxygen/temperature-sensitive Ni(0) sources.

Mechanistic studies showed that the catalyst retains its catalytic activity for several days after full consumption of tetramethylammonium triflate. Side reactions still seem to be a major problem in the reaction, consuming the methylene donor in a competitive reaction. Ongoing studies in order to reduce the side reaction (homocoupling) are taking place as well as parametrization efforts.

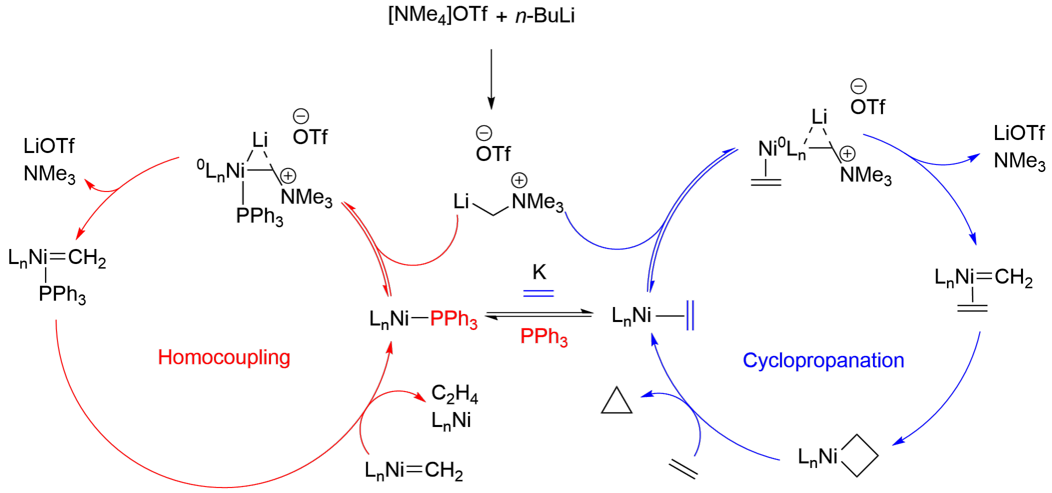

Figure 1: Cyclopropanation proposed catalytic cycle, involving Cyclopropanation (blue) and side reaction homocoupling (red).

[1] Pasco, M.; Gilboa, N.; Mejuch, T.; Marek, I. *Organometallics* **2013**, *32* (4), 942–950.
[2] Charette, A. B. In *The Chemistry of Organozinc Compounds*; John Wiley & Sons, Ltd, **2006**; pp 237–286.
[3] Zhou, Y.-Y.; Uyeda, C. *Angew. Chem., Int. Ed.* **2016**, *55*, 3171– 3175.
[4] Tomilov, Y. V.; Bordakov, V. G.; Dolgii, I. E.; Nefedov, O. M. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1984**, *33*, 533– 538.
[5] Denmark, S. E.; Stavenger, R. A.; Faucher, A.-M.; Edwards, J. P. *J. Org. Chem.* **1997**, *62*, 3375–3389.
[6] Nakamura, A.; Yoshida, T.; Cowie, M.; Otsuka, S.; Ibers, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 2108–2117.
[7] Künzi, S. A.; Gershoni-Poranne, R.; Chen, P. *Organometallics* **2019**, *38* (9), 1928–1938.

Dissolution-Precipitation Synthesis of Pyrochlore-Type Iron Hydroxy Fluoride for Low-Cost Lithium-Ion Batteries

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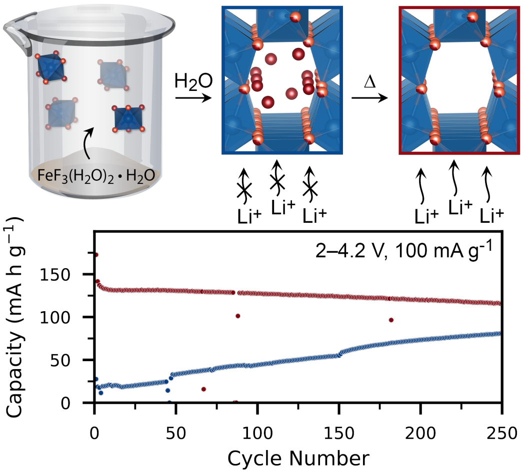
Iron (III) fluorides are appealing low-cost stationary energy storage materials due to the virtually unlimited supply of the constituting elements and high energy densities.[1] The pyrochlore modification is of particular interest because its 3D interconnected channels may potentially enable fast Li-ion diffusion.[2] However, the prohibitevely large cost for synthesis or cathode architecture prevent commercialization. Herein, we present a facile dissolution-precipitation synthesis to access pyrochlore iron (III) hydroxy fluoride (Pyr-IHF) from soluble iron (III) fluoride precursors, enabling to produce Pyr-IHF at a low cost of *ca*. 14 $ kg^{-1}.[3] Without the need for elaborate cathode designs, we demonstrate superior capacity retention of > 80% after 600 cycles at high current densities of 1 A g^{-1}. Guided by *operando* X-ray diffraction experiments, we selectively synthesize Pyr-IHF of different solvent content inside the channels. Rate capability tests of Pyr-IHF cathodes provide the first experimental evidence for Li-ion diffusion occurring through the 3D channels.



[1] F. Wu, G. Yushin, *Energy Environ. Sci.*, **2017**, 10**,** 435–459
[2] C. Li *et al., J. Am. Chem. Soc.* **2013**, 135, 11425–11428
[3] J. F. Baumgärtner *et al., Manuscript Submitted*, **2023**

Lead Halide Perovskite Nanocrystals passivated with guanidinium-based ligands

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Lead halide perovskite nanocrystals (LHP NCs) exhibit immense potential for optoelectronic applications. However, due to their labile lattice and dynamic binding of ligands, they are sensitive to polar solvents and humidity. This instability hinders the processibility of LHP NCs and calls for new passivation strategies. Ligand engineering enables improved device performance and stability by enhancing charge carrier lifetime, controlling film morphology, and facilitating efficient charge transfer. Ligands with better binding groups, such as zwitterions and quaternary ammoniums, have been shown to enhance colloidal stability and LED performance. A step forward from the ammonium-based ligands can be the ligands with guanidinium fragments which exhibit excellent thermodynamic stability, high basicity, and multiple strong hydrogen-bonding capabilities.[1]

This work presents a new class of ligands with guanidinium as the binding group that were developed and used in the synthesis of LHP NCs, such as $CsPbBr_3$, $FAPbBr_3$, and $CsPbI_3$. The new synthetic approach allows obtaining LHP NCs with quantum yields as high as 95% in colloidal solutions and up to 80% in compact films. One of the ligands, Oleylguanidinium Bromide, allows synthesizing of nearly-bulk NCs with barely present quantum confinement.[2] Furthermore, these ligands enable colloidal stability in a broader range of solvents than conventional ones, which is exemplified by $CsPbBr_3$ NCs retaining high quantum yield even after two months in tetrahydrofuran.

[1] Berezovska et al., In preparation.
[2] Tamarat, P., Prin, E., Berezovska, Y. et al., *Nat Commun,* **2023,** 14, 229.

Nickelate-Catalysed Alkynylation of (Poly)Fluoroarenes

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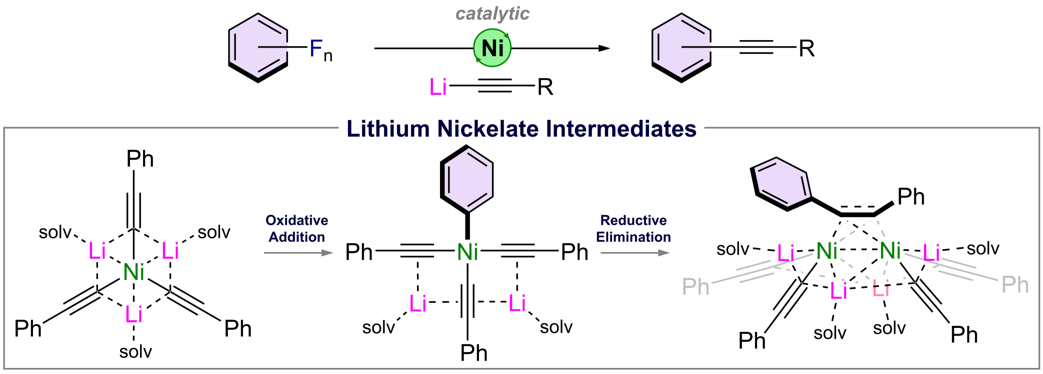
[1]Universitat Bern, [2]University of Bern

Nickel catalysis has the unique ability to functionalise inert substrates that are typically out of scope for Pd-catalysed methods. In contrast to traditionally accepted mechanisms, it has been proposed that low-valent nickelates that are derived from Ni(0)-olefin complexes (*i.e.* the pre-catalyst) and polar organometallics (*i.e.* the nucleophilic coupling partner) may be alternative intermediates that facilitate these challenging transformations.

In this context, we have recently provided detailed experimental and theoretical evidence to support the involvement of lithium nickelate intermediates in the Ni-catalysed cross-coupling of aryl ethers with PhLi.[1,2] Using this mechanistic knowledge, this work will reveal how tri-lithium nickelates[3] derived from lithium acetylides can facilitate the alkynylation of fluoro- and polyfluoroarenes.[4] Insights into the reaction mechanism have been gained through a series of stoichiometric, catalytic and kinetic studies.



[1] Andryj M. Borys, Eva Hevia. *Angew. Chem. Int. Ed.,* **2021**, *60*, 24659-24667.

[2] Haosheng Liang, Andryj M. Borys, Eva Hevia, Lionel Perrin, Pierre-Adrien Payard. *In preparation.*

[3] Andryj M. Borys, Lorraine A. Malaspina, Simon Grabowsky, Eva Hevia.*Angew. Chem. Int. Ed.,* **2022**, *61* e202209797.

[4] Andryj M. Borys, Luca Vedani, Eva Hevia. *In preparation.*

Introducing Isocyanide Ligands into the Cyclopentadienone Iron Complex Framework

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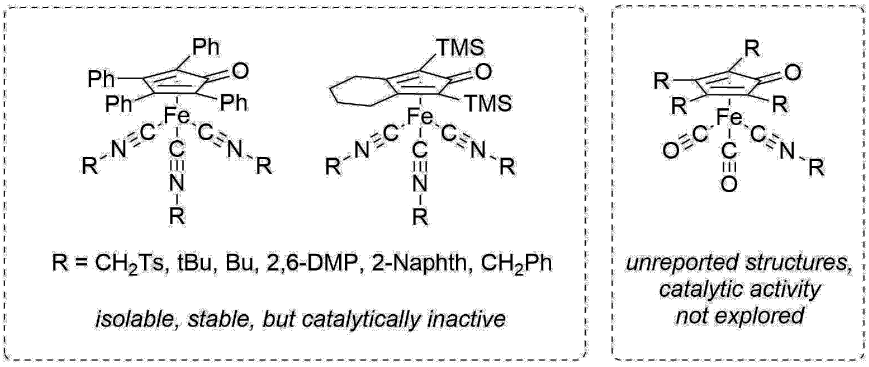
Cyclopentadienone iron complexes are well established as hydrogenation and transfer hydrogenation catalysts [1-2]. Most systems use a dicarbonyl complex with a free coordination site on iron as the active catalyst, although other configurations exist which replace one of the carbonyls by other ligands, such as, for example, phosphines [3] or NHC's [4].

Isocyanides (RNC, R = aryl, alkyl) are isoelectronic to CO and can be generally regarded as electron rich analogues to carbonyl ligands, i.e. they are better σ-donors and worse π-acceptors [5]. In contrast to CO, isocyanides offer a handle to vary the electronic and steric properties of the ligand by variation of the R substituent.



Recently, we have discovered that cyclopentadienone triisocyanide complexes can be easily prepared by irradiation (blue LED's) of the corresponding tricarbonyl complexes in the presence of the isocyanide of choice (R = CH_2Ts, ^{t}Bu, Bu, 2,6-DMP, 2-Naphth, CH_2Ph) (Ts = toluenesulfonyl, DMP = dimethylphenyl, Naphth = naphthyl) (*manuscript submitted*). These complexes constitute the first instance of incorporation of isocyanides into the cyclopentadienone iron complex framework. Although these complexes are catalytically inactive in hydrogenation, presumably because of the lack of a straightforward way to create an empty coordination site, they show that isocyanides can be used in place of carbonyls.

In this work, we explore the synthesis of dicarbonyl monoisocyanide complexes. By removal of a carbonyl ligand with trimethylamine oxide, a free coordination site is created, opening up the possibility of catalysis. We investigate the catalytic activity of the complexes in hydrogenation and transfer hydrogenation reactions depending on the chosen isocyanide ligands.

[1] Quintard, A.; Rodriguez, J., *Angew. Chem., Int. Ed.* **2014**, 53, 4044.
[2] Pignataro, L.; Gennari, C., *Eur. J. Org. Chem.* **2020**, 3192.
[3] Seck *et al.*, *ChemCatChem* **2017**, 9, 4410.
[4] Cingolani *et al.*, *Appl Organometal Chem.* 2019, 33, 4, e4779.
[5] Pruchnik, F.P., Duraj, S. A., Eds.; Modern Inorganic Chemistry; Springer US: Boston, MA, 1990; pp 617-645.

Structural investigation of chelating agents and their mercury, lead and cadmium (II) complexes

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Mercury (Hg) is one of the most toxic heavy elements present in the environment, which is mostly ingested/inspired insidiously in small quantities, causing chronic diseases. Excretion of high doses of inorganic Hg^{2+} mostly relies on chelation therapy, which consists in administering a chelator such as DMSA (dimercapto succinic acid, FDA-approved medication) or DMPS (2,3-Dimercapto-1-propanesulfonic acid). The naturally occurring enzyme cofactor R-alpha lipoic-acid (R-α-LA) and especially its reduced form dihydrolipoic acid (DHLA) [1] have been considered potential replacement chelators for DMSA and DMPS. Yet, little is known of the complex structure formed by the various ALA:Hg and DHLA:Hg complexes and it has been long debated for a long time. In the present study, we have prepared and synthesized various [R-α-LA:Hg] and [DHLA:Hg] and investigated their solution chemistry, their propensity to chelate mercury, and the complex structure formed followed by spectroscopic techniques. Overall, several complexes are formed with various coordination number such as polydentate complexes as well as non-crystalline solid. Subsequently, synthetical approach was also considered, where two or more aggregation phases were concluded. These complex phases derive from various species of the complex and hold a different oxidation/reduction behavior as disulfides and dithiols have the capability to act as a reducing agent also depending on different synthetic performance.

[1] Bridges C. C., Zalups R. K.; Toxicology and Applied Pharmacology, 2004 (2005) 274-308.
[2] Lin H., Han H., Sun W., Yang Y., Tang C., Lu G., Qi J. Wang X. Yang Y; European Journal of Medicinal Chemistry, 144 (2018) 137-150.
[3] Rivera M., Yheng W., Aposhian H., Fernando Q., Toxicology and applied Pharmacology 100, 96-106 (1989).

Investigation of Iron(III) Schiff-Based Complexes for Carbon Dioxide Reduction

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Carbon dioxide (CO_2) reduction is attracting great consideration due to environmental challenges[1] and the interest in its transformation into high-value-added chemicals,[2] such as urea, polycarbonate, salicylic acid and methanol. An attractive perspective for a carbon neutrality economy with a potential impact on the United Nations Sustainable Development Goals.[3] To achieve this ambitious aim, research primarily focuses on designing stable and robust catalysts that can efficiently perform the CO_2 reduction reaction (CO_2RR). Like other redox reactions involved in energy-related schemes,[4] a catalyst is required for the process to proceed at sustainable rates. Recent works on CO_2RR catalysts based on noble metals[5] have pushed active research on more attractive and cheap alternatives: earth-abundant transition metals like manganese, iron, cobalt, and copper. Iron stands out as a fascinating active site to catalyse CO_2RR[6] thanks to its rich chemistry, broad application in several redox processes, low cost and environmental compatibility. However, despite the high activity of molecular catalysts, they often suffer from deactivation mechanisms, resulting in metal nanoparticle formation.

Synthesis and characterization of metal complexes for their catalytic use in electrochemical CO_2 reduction are discussed here. A family of Salen-like tetradentate Schiff-base iron(III) complexes, $Fe(L_{N2O2})Cl$, were explored. These catalysts exhibit peculiar stability due to ligand-to-metal electronic polarization and the participation of iron in the π-bond systems. These complexes show the possibility of electrochemically generating iron(I) species: the key intermediate capable of reacting with CO_2, forming carbon monoxide (CO) and formic acid (HCOOH) while competing with dihydrogen evolution reaction (HER). As a result, the reaction selectivity is guided by the complexes reactivity and by the co-catalyst effect, which way the role of the proton-donors is so important.

These $Fe(L_{N2O2})Cl$ complexes mediate the two-electron two-proton CO_2 reduction to CO by means of an iron(I) intermediate, upon the addition of a suitable proton source. This was proven with gas chromatography and spectroscopy techniques and further evidenced by cyclic voltammetry (CV) through increased catalytic current density. Moreover, target CVs studies and chronoamperometry analysis allow the evaluation of different key parameters, such as the overpotential, the rate constant, faradaic yield, selectivity and the turnover frequency; these are useful tools to characterize the catalytic behaviour of these compounds. Then, based on the analysis of the supernatant composition, and morphological and electrochemical investigation of the electrode after the electrolysis, the complexes were shown to undergo competitive degradation, limiting their activity and lifetime.

[1] https://gml.noaa.gov/ccgg/trends, **20/06/2023.**
[2] Iwao Omae, *Coordination Chemistry Reviews*, **2012**, 256, 1384-1405.
[3] https://www.un.org/sustainabledevelopment/energy, **22/06/2023.**
[4] Jingguo Li, Carlos. A. Triana, Wenchao Wan, Devi P. Adiyeri Saseendran; Yunggui Zhao; S. Esmael Balaghi, Sima Heidari, Greta. R. Patzke, *Chem. Soc. Rev.*, **2021**, 50, 2444-2485.
[5] Andrea Álvarez, Atul Bansode, Atsushi Urakawa, Anastasiya V. Bavykina, Tim A. Wezendonk, Michiel Makkee, Jorge Gascon, Freek Kapteijn, *Chem. Rev.*, **2017**, 117, 9804–9838.
[6] Federico Franco, Clara Rettenmaier, Hyo S. Jeon, Beatriz R. Cuenya, *Chem. Soc. Rev.*, **2020**, 49, 6884-6946.

Redox-Transmetalation and Associated Bimetallics Based on an Al/Zn System

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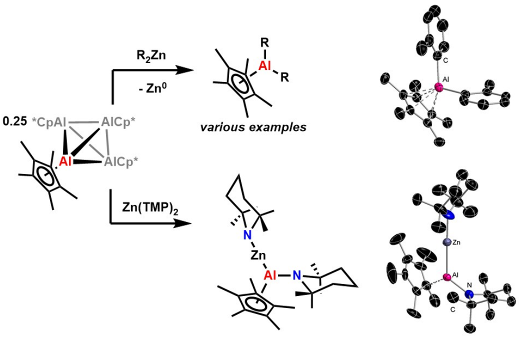
In the last decade, the chemistry of low-valent aluminum has significantly aroused the interest of many different groups around the globe.[1] As the chemistry of group13 low-valents has evolved, it was also put into context of bimetallics. So does the deft combination of aluminyl precursor and metallic partner yield various combinations of compounds which contain a metal-metal bond. The unsupportive nature of these bonds facilitates unique reactivity. A recent breakthrough is for instance the nucleophilic behaviour of beryllium across an [Al]-[Be] bond.[2] To establish such metal-metal bonds, however, usually requires large, bulky ligands to kinetically stabilize these systems.



In our group, we are currently interested in downsizing ligand bulk which would e.g., be promising for the formation of main-group oligomers and multiple bond activations. Therefore, we currently investigate the reactivity of $[AlCp^*]_4$ towards various small organometallics and homoleptic complexes of small molecules. Here, we demonstrate the reactivity towards diorgano-zinc compounds (=ZnR_2) as well as $ZnTMP_2$. In case of ZnR_2 we could observe the selective transfer of "AlCp*" forming $AlCp^*R_2$ *via* reductive transmetalation. The use of bis amide $ZnTMP_2$, however, gives rise to the formation of a compound with an exceptionally short, rarely[3] observed Al-Zn bond of 239.2(3) pm. We are currently having a look into the reactivity of such simpler systems.

[1] see e.g. *Chem. Sci.*, **2020**, *11*, 6942-6956, *Chem. Commun.*, **2023**, *59*, 503-519; *ChemCatChem*, **2018**, *10*, 4213-4228. [2] *JACS*, **2023**, 145, 8, 4408–4413. [3] *ACIE*, **2021,** *60(41)*, 22301-22306.; *Chem. Sci.,* **2018***, 9,* 2348–2356; *Chem. Commun.* **2022**, *58*, 10091–10094; *Inorg. Chem.* **2018***, 9,* 2348–2356.

Intrinsic formamidinium tin iodide nanocrystals by suppressing the Sn(IV) impurities

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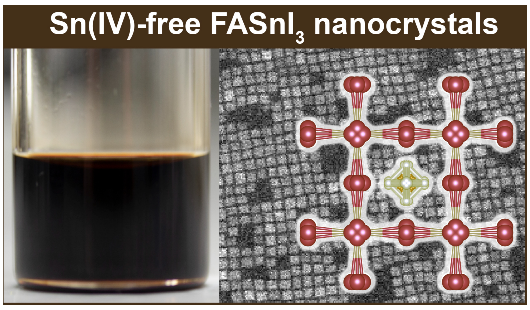
Lead halide perovskites successfully advance toward applications in solar cells, light-emitting devices, and high-energy radiation detectors. Recent progress in understanding their uniqueness highlights the role of optoelectronic tolerance to intrinsic defects, particularly long diffusion lengths of carriers, and highly dynamic 3d inorganic frameworks. This picture indicates that finding an analogous material among non-group-14 metal halides can be very challenging, if possible at all. On the other hand, a judicious choice of chemistry made it possible to noticeably increase the performance of formamidinium tin iodide perovskites when integrated into thin-film photovoltaic devices. The main challenge with this material originates from the easiness of the trap states generation, which is typically ascribed to the oxidation of Sn(II) to Sn(IV). In this work, we describe the synthesis of colloidal monodisperse $FASnI_3$ NCs, whereby thorough control of the purity and redox chemistry of the precursors allows the concentration of Sn(IV) to be reduced to an insignificant level, to probe the intrinsic structural and optical properties of these NCs. Intrinsic $FASnI_3$ NCs exhibit unusually low absorption coefficients of $4 \bullet 10^3$ cm^{-1} at the first excitonic transition, a 190 meV increase of the bandgap as compared to the bulk material, and a lack of excitonic resonances. These features are attributed to a highly disordered lattice, distinct from the bulk $FASnI_3$ as supported by structural characterizations and first-principles calculations.



The Co-C Bond in the Gas Phase

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The Co-C bond in adenosylcobalamin (AdoCbl) is considered to be a weak bond. The homolytic bond cleavage is measured to be at most 16 kcal/mol in an enzymatic environment and 34 kcal/mol in aqueous media.[1] Threshold collision-induced dissociation (T-CID) is a method used to measure reactive cross-sections in the gas phase. From the reactive cross-sections, bond dissociation energies (BDEs) are deconvoluted using ligand collision-induced dissociation (L-CID)[2], a program written in-house. Our group previously measured the Co-C bond of the structurally similar adenosylcobinamid (AdoCbi) with T-CID/L-CID and obtained a BDE value of 41 kcal/mol.[3] When changing the adenosyl to a phenyl, *i.e.* changing a sp^3-hybridized carbon to a sp^2 one, we would expect the bond strength to increase. However, T-CID measurements of PhCbi reveal a decrease of the bond strength – from 41 kcal/mol to 38 kcal/mol.[4] To rationalize this observation, we hypothesize that the bond strength is modulated significantly through London dispersion by the presence of the sidechains on Cbl/Cbi. To test this hypothesis, Costa[5] complexes, which feature a similar chemical environment around cobalt but no such sidechains, are employed to obtain the unmodulated Co-C bond-strengths in the gas phase using T-CID/L-CID. The measurements reveal the BDE of sp^3-hybridized carbons to be 38 kcal/mol and 35 kcal/mol for methyl- and ethyl-Costa complexes, respectively, compared to 45 kcal/mol for the phenyl complex, which is in line with the expectation that the sp^3-hybridized carbons should be bound weaker to cobalt than the sp^2 ones. However, the trend appeared, at first, to be broken when we reach sp-hybridized carbons, as they go through a different dissociation and thus end up having similar BDEs to sp^3-hybridized ones. The BDEs for sp^3 and sp^2-hybridized carbons bound to cobalt compare favorably to calculations at the DFT level, while the gas phase structure of the sp Costa complexes remains unclear.

[1] Benjamin P. Hay, Richard G. Finke, *J. Am. Chem. Soc.* **1987**, *109*, 8012.
[2] Sanja Narancic, Andreas Bach, Peter Chen, *J. Phys. Chem. A* **2007**, *111*, 7006.
[3] Ilia J. Kobylianskii, Florian J. Widner, Bernhard Kräutler, Peter Chen*J. Am. Chem. Soc.* **2013**, *135*, 13648.
[4] Alexandra Tsybizova, Christopher Brenig, Christoph Kieninger, Bernhard Kräutler, Peter Chen, *Chemistry – A European Journal* **2021**, *27*, 7252.
[5] G. Costa, G. Mestroni, E. de Savorgnani, *Inorganica Chimica Acta* **1969**, *3*, 323.

The electronic structure of molecular Pt clusters from solid-state ^{195}Pt NMR, one atom at the time.

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Atomically-precise metal clusters show unique properties which make them appealing for the preparation of optical devices and for biomedical applications. Furthermore, some of these species are proposed to be catalytically active for the activation of small molecules and for selective transformations of organics. As such, they provide fundamental knowledge on the bonding and reactivity of complex systems.[1]

Common characterization techniques of metal clusters involve mass spectrometry, optical and X-ray spectroscopies.[2,3] While these tools can describe a system in its totality, they only provide an averaged information of the different metal sites. Conversely, solid-state NMR (ss-NMR) spectra encode information on the electronic structure of a specific nucleus, as the shape and orientation of the chemical shift (shielding) tensor (CST) is strictly related to its valence orbitals (fMOs).[4]

In this work, we show how ^{195}Pt ss-NMR can be used to understand the bonding situation of metal nuclei in a library of $Pt_n(0)$ species with different nuclearity (n= 1 to 5) and connectivity.[5] ss-NMR can be therefore applied as a general tool to distinguish among the metal sites of clusters. Additionally, the analysis of the CST of a nucleus in a cluster can provide information on its local electronics and environment (**Figure 1**).

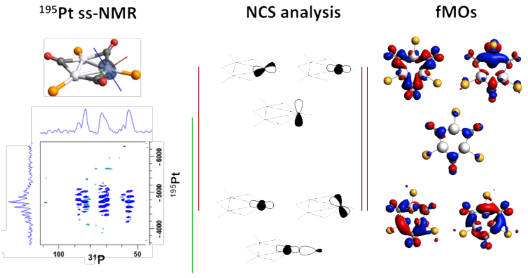

Figure 1: Investigation of a $Pt_3(CO)_3(PR_3)_3$ cluster: $^{31}P\{^{195}Pt\}$ ss-NMR, CST and MOs responsible for the (de)shielding.

[1] Chakraborty, I.; Pradeep, *T. Chem. Rev.*, **2017**, 117, 8208-8271.
[2] Joshi, C. P.; et.al, *J. Am. Chem. Soc.*, **2015**, 137, 11578-11581.
[3] Zhang, B.; et. al., *ChemCatChem*, **2018**, 10, 5372-5376.
[4] Venkatesh, A.; Gioffrè, et. al., *J. Am. Chem. Soc.*, **2022**, 144, 13511-13525.
[5] Chatt, J.; Chini, *P., J. Chem. Soc. Inorg. Phys. Theor.*, **1970**, 0, 1538-1542.

Iron-mesoionic carbene complexes for catalytic intramolecular C-H amination: novel ligand synthesis

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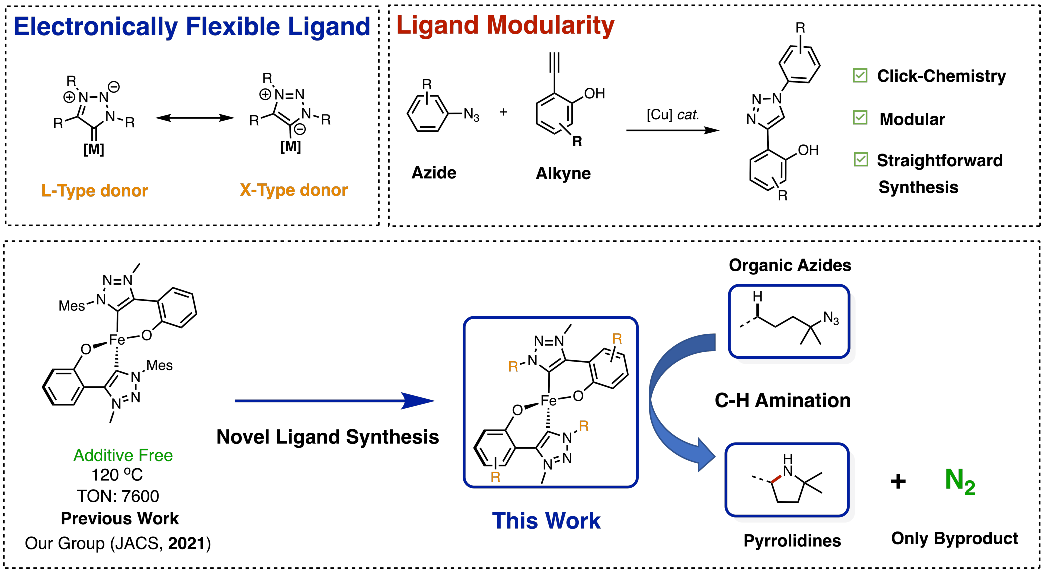
Nitrogen containing heterocycles are ubiquitous across nature and industry with C-N bonds being found in numerous natural products and pharmaceutically relevant molecules.[1,2] Therefore carbon-nitrogen bond formation is of utmost importance with catalytic and atom economical syntheses being particularly attractive. In this context, Betley in 2013 reported and iron-catalysed direct C-H bond amination using an iron-dipyrrinato catalyst to yield a range of pyrrolidines.[3] However, the activity was limited to only single digit TONs requiring 20 mol% catalyst loading and an equivalent of Boc_2O to prevent product inhibition. More recently, Betley also reported the additive-free C-H amination of nickel-dipyrrin complexes.[4] In 2021, our group disclosed a highly efficient iron(II) mesoionic carbene complex, which afforded a range of C-H aminated pyrrolidine products in excellent yield with no need of additives, generating only N_2 as the sole side product with TONs exceeding the state of the art by an order of magnitude.[5]

Herein, we aim to better understand the influence of the ligand and to improve the catalytic performance of the iron complex by designing and synthesising novel ligands. Our data shows that appropriate ligand substitution enhances both the activity and selectivity of C-H amination.



[1] R. Hili and A. K. Yudin, Nat Chem Biol, 2006, 2, 284–287.
[2] E. Vitaku, D. T. Smith and J. T. Njardarson, J. Med. Chem., 2014, 57, 10257–10274.
[3] Betley, Hennessy, Science, 2013, 340, 591–595.
[4] Y. Dong, R. M. Clarke, G. J. Porter and T. A. Betley, J. Am. Chem. Soc., 2020, 142, 10996–11005.
[5] W. Stroek, M. Keilwerth, D. M. Pividori, K. Meyer and M. Albrecht, J. Am. Chem. Soc., 2021, 143, 20157–20165.

Exploring Trans(amination) Reactions in Co(II) Chemistry

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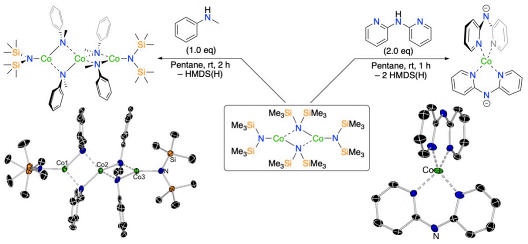
Pioneered over 60 years ago,[1] cobalt (II) amide Co(HMDS)$_2$ (HMDS= N(SiMe$_3$)$_2$) has found widespread applications in synthesis and catalysis as a precursor of Co(II) complexes.[2] Previous studies have reported the ability of this complex to undergo trans(amination) reactions with primary amines in the presence of sterically demanding N-heterocyclic carbenes although harsh reaction conditions are required in order to promote the activation of both HMDS groups.[3]

Breaking new ground in this field, here we systematically study the reactivity of Co(HMDS)$_2$ towards a range of different amines uncovering its polybasic behaviour when reacted with 2,2'-dipyridylamine (DPA(H)) (see Figure) whereas with other amines like piperidine and *N*-methylaniline it can only undergo hemi(transamination) reactions even under forcing reaction conditions. Isolation and structural characterisation of key reactive intermediates has revealed the remarkable structural diversity of Co(II) amide complexes. Initial reactivity studies have also shown that while Co(HMDS)$_2$ can react with two equivalents of mesitylacetophenone to form a novel Co(II) enolate complex via deprotonative metalation, Co(DPA)$_2$ is completely inert towards this substrate.



[1] H. Bürger, U. Wannagat, *Monatshefte für Chemie.* **1963**, *94*, 1007–1012.

[2] (a) H. Hope, M. M. Olmstead, B. D. Murray, P. P. Power, *J. Am. Chem. Soc.* **1985**, *107*, 712–713. (b) A. M. Bryan, W. A. Merrill, W. M. Reiff, J. C. Fettinger, P. P. Power, *Inorg. Chem.* **2012**, *51*, 3366–3373. (c) Y. Liu, L. Deng, *J. Am. Chem. Soc.* **2017**, *139*, 1798–1801.

[3] A. Massard, P. Braunstein, A. A. Danopoulos, S. Choua, P. Rabu, *Organometallics* **2015**, *34*, 2429–2438.

Dinitrogen cleavage by a multinuclear U(III) complex in absence of cations

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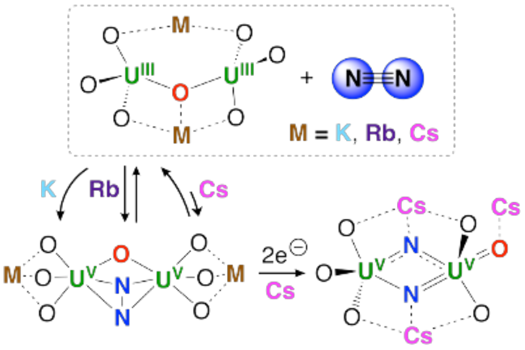
Dinitrogen (N_2) is a cheap and widely available molecule, however, its low reactivity complicates its use for the synthesis of higher-added products. Notably, the industrial Haber-Bosch process uses N_2 to synthesize ammonia (NH_3), but requires harsh temperatures and pressures. Before the currentFe-based catalyst was implemented, uranium materials were reported to be highly effective in the transformation of N_2 into NH_3. Nevertheless, the N_2chemistry of uranium remains underdeveloped, with only a few examples of molecular uranium complexes that are capable of cleaving N_2 to nitridesupon addition of external reducing agent,[1-3] where uranium nitrides are considered important inrtermediates the Haber Bosch process. Recently, our group reported two bimetallic uranium(III) systems that were able to perform the four-electron reduction of N_2.[4,5] Moreover, we found that the N_2bound in the bridging oxide system could be functionalized by addition of CO to yield a cyanamido complex, but the addition of acid or H_2 resulted only in the release of N_2.[5]

Here, we will present a series of alkali bound-oxo-bridged diuranium(III) complexes that provide a unique example of decreasing N_2 binding affinity with increasing cation size. We will show spectroscopic, electrochemical, and computational data, suggesting that the decreased reactivity is due to sterics rather than electronic effects.[6]



We also show the first example of Cs^+-assisted cleavage of dinitrogen to nitrides by a molecular complex. Furthermore, we will show spectroscopic and computational data that confirms that the removal of the alkali metal counter ions from the core of the complex facilitates the N-N bond cleavage, resulting in the first example of U(III) complex able to perform the N-N bond cleavage in absence of external reducing agents.

[1] I. Korobkov, S. Gambarotta and G. P. A. Yap, *Angew. Chem. Int. Ed. Engl.*, **2002**, 41, 3433-3436
[2] X. Q. Xin, I. Douair, Y. Zhao, S. Wang, L. Maron and C. Q. Zhu, *J. Am. Chem. Soc.*, **2020**, 142, 15004-15011
[3] N. Jori, L. Barluzzi, M. Mazzanti *et al.*, *J. Am. Chem. Soc.*, **2021**, 143, 11225-11234
[4] M. Falcone, L. Chatelain, M. Mazzanti, *et al.*, *Nature*, **2017**, 547, 332–335
[5] M. Falcone, L. Barluzzi, M. Mazzanti, *et al.*, *Nature Chem.* **2019**, 11, 154–160.
[6] N. Jori, M. Mazzanti *et al.*, *Chem. Sci.* **2022**, 13, 9232–9242.

Alkali-Metal-Alkoxide Powered Zincation of Fluoroarenes Employing Zinc Bis-Amide Zn(TMP)$_2$

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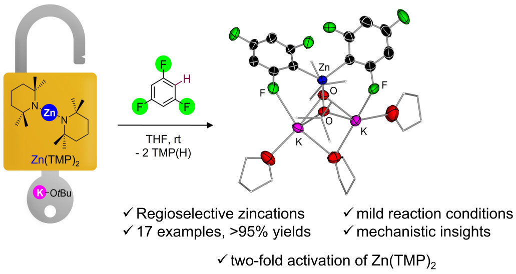
The unique activating effects of alkali-metal alkoxides when added to other s-block organometallics is a well-established phenomenon in polar organometallic chemistry.[1] Typified by the LIC-KOR (Lochmann-Schlosser) superbase, combining potassium *tert*-butoxide with *n*-butyllithium greatly enhances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

Building on this work, we have recently developed a new bimetallic base which allows for the direct zincation of a broad range of aromatic substrates.[7] By combining the Zn amide Zn(TMP)$_2$ (TMP = 2,2,6,6-Tetramethylpiperidide) with two equivalents of KO*t*Bu effective zincation of sensitive substrates such as 1,3,5-trifluorobenzene can be achieved while operating at room temperature (see Figure). Trapping of key reaction intermediates and NMR monitoring of the reactions have uncovered the close interplay between the different components of this bimetallic mixture to facilitate the success of the Zn-H exchange reaction and the stability of the metalated intermediates. Showcasing its metalating power, this bimetallic KO*t*Bu/Zn(TMP)$_2$ partnership, can even effect benzylic zincation of toluene and benzene at room temperature.[7]



[1] L. J. Bole, E. Hevia, *Nat. Synth.* **2022**, *1*, 195–202.
[2] M. Schlosser, *J. Organomet. Chem.* **1967**, *8*, 9–16.
[3] M. Schlosser, *Angew. Chem. Int. Ed.* **2005**, *44*, 376–393.
[4] M. Balkenhohl, D. S. Ziegler, A. Desaintjean, L. J. Bole, A. R. Kennedy, E. Hevia, P. Knochel, *Angew. Chem. Int. Ed.* **2019**, *58*, 12898–12902.
[5] L. J. Bole, N. R. Judge, E. Hevia, *Angew. Chem. Int. Ed.* **2021**, *60*, 7626–7631.
[6] N. R. Judge, L. J. Bole, E. Hevia, *Chem. Eur. J.* **2022**, e202104164.
[7] N. R. Judge, E. Hevia, *Angew. Chem. Int. Ed*. **2023**, 62, e202303099.

Phosphine Oxide-Functionalized Terthiophene Redox Systems

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Redox systems based on main group elements are emerging as next-generation building blocks for organic batteries, electrochromic materials, magnets, photovoltaics, and sensors.[1] Although they are attractive from economic and sustainability perspectives,[2] main group elements typically feature a lower density of redox states compared to transition metals and consequently yield difficult-to-control, highly reactive radical species upon electron transfer.[3] Despite their reactivity, main group redox systems could prove especially valuable in energy storage devices as chargeable electrolytes. In particular, oligothiophenes, one of the most widely studied structural motifs in organic electronics,[4] offer the possibility of multi-electron storage at extremely negative potentials. However, studies on the electrochemical reduction of oligothiophenes have established the instability of the formed anions upon charging.

Here, we present our finding that diarylphosphine oxide functionalization of terthiophenes stabilizes their respective anions formed upon reduction. A crystalline phosphine oxide-functionalized terthiophene radical anion was synthesized wherein the redox-responsive nature of the platform was established using combined structural, spectroscopic, and computational characterization. Structural modification led to the identification of a variant that exhibits exceptional stability during bulk two-electron galvanostatic charge-discharge cycling, indicating that phosphine-oxide functionalized terthiophenes could be a promising new class of main group electrolytes for energy storage applications.[5]

[1] Thomas Baumgartner, Frieder Jaekle *Main Group Strategies towards Functional Hybrid Materials*, Wiley, New York, **2018**.
[2] Dierk Raabe, *Chem. Rev.* **2023**, *123*, 2436–2608.
[3] Philip P. Power, *Chem. Rev.* **2003**, *103*, 789−810.
[4] Igor F. Perepichka, Dmitrii. F. Perepichka, Hong Meng in *Handbook of Thiophene–Based Materials*, John Wiley & Sons, Ltd: Chichester, **2009**, pp. 695–756.
[5] Daniel Käch, Aurelio C. Gasser, Lionel Wettstein, Clara Schweinzer, Máté J. Bezdek, *Angew. Chem. Int. Ed.* **2023**, e202304600.

Activation of Methyltrioxorhenium for Olefin Metathesis by a Frustrated Lewis Pair

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Methyltrioxorhenium (MTO) supported on Al_2O_3 or SiO_2-Al_2O_3 is an efficient heterogenous alkene metathesis catalyst that works at room temperature and in the presence of various functional groups.[1] The catalytically active rhenium-methylidene species in MTO based catalysts has not yet been observed. Surface studies revealed that MTO interacts with highly Lewis-acidic tricoordinate aluminum centers on the support surface, and that its methyl group is C–H activated resulting in rhenium-methylidene species.[2] The exact structure of the catalyst resting state and the active species is subject to active scientific debate.[2]

Our group focuses on developing homogeneous model systems for rhenium(VII)-based metathesis catalysts.[3] Previous model systems mainly aimed to mimic the electron deficient nature of the support surface.[4] Here we report on the activation of MTO by 2,6-Lutidine and $B(C_6F_5)_3$, a frustrated Lewis pair (FLP) in solution. The MTO/FLP catalyst is active in ring-opening metathesis polymerization of norbornene, and in the cross-metathesis of internal olefins. ESI-MS and NMR studies found that MTO coordinates to $B(C_6F_5)_3$, and the adduct is activated via the deprotonation of the methyl group by 2,6-lutidine. Moreover, we were able to detect metathesis active rhenium-alkylidenes by ESI-MS experiments during the ring-opening metathesis reaction of rigid cycloalkenes. A rapid second deprotonation of the initially formed methylidene, which yields a rhenium-methylidyne, was identified to be a major catalyst decomposition pathway.

[1] Herrmann, W. A.; Wagner, W.; Flessner, U. N.; Volkhardt, U.; Komber, H. *Angew. Chem. Int. Ed.* **1991**, *30,* 1636.
[2] a) Salameh, A.; Joubert, J.; Baudouin, A.; Lukens, W.; Delbecq, F.; Sautet, P.; Basset, J. M.; Copéret, C. *Angew. Chem. Int, Ed.* **2007**, *46*, 3870. b) Valla, M.; Wischert, R.; Comas-Vives, A.; Conley, M. P.; Verel, R.; Copéret, C.; Sautet, P. *J. Am. Chem. Soc.* **2016**, *138*, 6774.
[3] Lai, Y.-Y.; Bornand, M.; Chen, P. *Organometallics* **2012**, *31*, 7558.
[4] Commereuc, D. *J. Chem. Soc., Chem. Commun.* **1995**, *7*, 791

Understanding the preparative green MOF-74 synthesis by time-resolved ATR-IR and XRD measurements

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Metal-organic frameworks (MOFs) show great promise among nano- and micro-porous materials due to their intrinsic tunability and structural versatility, leading to their use in numerous applications such as gas separation and storage as well as catalysis.[1] While the MOF field offers a great choice of materials, one of the remaining challenges for their practical implementation is the development of reliable synthetic procedures with speed, scale, and quality matching the industry requirements. Recently, promising aqueous-based room-temperature syntheses of MOF-74/CPO-27 analogs were developed, allowing outstanding space-time yields of up to 18 720 kg m^{-3} day^{-1}.[2] However, there is still a lack of knowledge of the underlying mechanisms, which is crucial for further extension and optimization to other MOF families and the fundamental understanding of MOF formation pathways.

In this work, we studied the mechanism of formation of the MOF-74 family in aqueous solution on a preparative scale (> 0.5 g) using time-resolved Attenuated Total Reflection IR spectroscopy (ATR-IR) in a custom-made stainless steel batch reactor cell equipped with a ZnSe crystal (30°, 50x44x2 mm). An external probe loop of this cell was used for the acquisition of time-resolved (50 ms) powder X-ray diffraction (XRD) data. Multivariate curve resolution-alternating non-negatively constrained least squares (MCR-AR-NNLS)[3] of the ATR-IR data was utilized to extract the kinetic profiles of the species in the reaction mixture, while time-resolved peak profile fitting of both datasets was used to gain information on the speciation as well as nucleation and growth processes.

The MOF synthesis was found to proceed via the formation of a molecular intermediate containing a twofold deprotonated ligand molecule. The width of the growing ν(C=C) mode of the MOF along synthesis time was mirrored by changes in specific XRD peaks indicating that growth of the MOF crystals occurred along the *c* axis. Fitting the XRD data using the Gualtieri model[4] allowed to determine the nucleation and growth constansts for MOF synthesis and establish their dependence on the reaction conditions. The ATR-IR experiments also revealed that zinc salts with non-coordinating anions enhance the reaction rate and completion time by a factor of 5. The products of the synthesis in the spectroscopy cell exhibited BET areas close to the theoretical limit of 1350 m^2 g^{-1}.

The information obtained in the spectroscopic study enables us to propose optimized synthetic protocols for MOF-74 materials.

[1] Q. Wang, D. Astruc, *Chem. Rev.* **2020**, *120*, 1438-1511.
[2] L. Garzón-Tovar, A. Carné-Sánchez, C. Carbonell, I. Imaz, D. Maspoch, *J. Mater. Chem. A* **2015**, *3*, 20819-20826.
[3] C. H. J. Camp, *J. Res. Nat. Inst. Standards Technol.* **2019**, *124*, 124018.
[4] A. F. Gualtieri, *Phys. Chem. Miner.* **2001**, *28*, 719-728.

Colloidal ternary telluride quantum dots for tunable phase change optics in the visible and near-infrared

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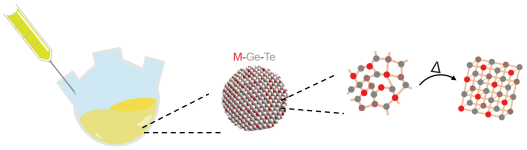
Phase change memory (PCM) materials have gained major interest and revival since their utility in optical data storage discs. This is due to the tunable contrast in material properties such as complex refractive index and electrical conductivity between amorphous and crystalline states. PCM materials are widely deposited using sputtering techniques and most of these materials fall in the pseudo-binary tie line of GeTe and Sb_2Te_3. Therefore, there is a need for inexpensive fabrication of PCM materials and a wider material choice to improve power efficiency, long-term stability, and to persevere nanoscale device configurations to fabricate high-density devices.

Here, we present a new library of colloidal-based ternary telluride M−Ge−Te (M is Sn, Pb, In, Bi, Ag, and Co) quantum dot PCM (QD PCM) by showing the detailed high-throughput synthesis, comprehensive characterization of QD PCM and their device fabrication. We majorly focus on Sn-Ge-Te (SGT) QD by studying the chemical tunability of the synthesis to achieve varied compositions and phases in the SGT QD. Using high-temperature *in-situ* XRD and XAS, we study the Sn doping effect on the crystallization temperature and local atomic arrangement, which are responsible for aging properties and ultrafast crystallization kinetics in the devices. We find that the SGT QD shows composition dependent crystallization temperature, which is higher than bulk SGT thin film, and outstanding reflectivity contrast of >0.7 between amorphous and crystalline SGT QD thin film in the near-IR spectrum. We utilize these excellent properties in two proof-of-concept type devices that are fabricated through solution-based deposition-1. Nonvolatile multicolor reflective stack with color tunability in the visible spectrum 2. Electro-optical PCM device operating in the near-IR spectrum for multi-factor emulation as shown by biological synapses. Our approach offers faster and cheaper customization of material choice along with facile device fabrication methods for advance PCM QD electronics in the sub-10nm scale in the future.



1. Kumaar, D. et al., ACS Nano 17, 6985–6997 (2023).

Metal Template Synthesis of Aromatic Preorganized Ligands for Tuning Stability Constants in Lanthanide Adducts

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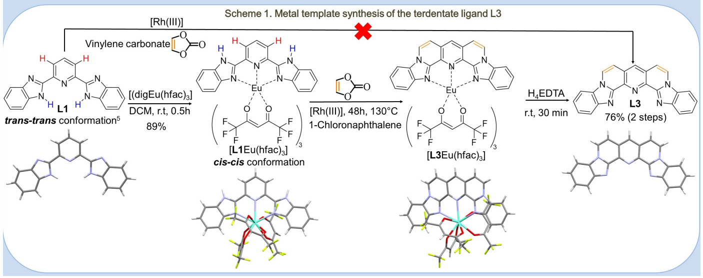
Among the multifactorial parameters affecting the stability and geometry of complexes for a given metal, the structural conformation of ligands displays a crucial influence.[1] A ligand preorganized in an orientation close to the conformation required to complex a metal ion tends to result in increased affinity for the entering guest thanks to the removal of the conformational change energy produced upon complexation.[2] With this in mind, ligand **L3** was synthesized from **L1** *via* a metal template strategy,[3] in which the *cis-cis* bound terdentate ligand in [**L1**Eu(hfac)3] undergoes intermolecular rhodium-catalyzed reactions aiming at intercalating a vinylene carbonate between the N-H groups of the benzimidazole side arms and the C-H units of the central pyridine ring.[4] Comparing the affinity of ligands **L1**, **L2** and **L3** with trivalent lanthanides in both solution (NMR studies) and solid state (X-ray analysis) allowed to determine the relationship of the level of structural preorganization with complexes stability constants.


Scheme 1. Metal template synthesis of the terdentate ligand L3

The *trans-trans* conformation in ligand **L1** leads to the failure of rhodium-catalyzed N-H/C-H activation reaction (red cross in Scheme 1) when **L1** is simply reacted with vinylene carbonate. In order to overcome this limitation, the complexation of **L1** to [(dig)Eu(hfac)3] have been considered for forcing the coordinated terdentate ligand **L1** to accommodate the unfavorable *cis-cis* orientation required for intermolecular rhodium-catalyzed reactions between vinylene carbonate and NH, CH of bound ligand **L1**. As expected, carrying out the rhodium-catalyzed annulation of [**L1**Eu(hfac)3] with vinylene carbonate, followed by demetallation with H4EDTA, finally generates the target ligand **L3** in 76% yield.

Increasing the level of preorganization in ligand scaffold along the **L1→L2→L3** series gives rise to (i) improved binding constants with trivalent lanthanides in CD2Cl2 solution due to the removal of the energy cost for rotating the benzimidazole side arms to reach the high-energy *cis-cis* organization required for metal complexation reaction, and (ii) significant decreased Ln-N affinity in solid state due to a limited match between the lanthanide size and the larger cavity of the rigid terdentate ligand with 5-membered chelate rings.

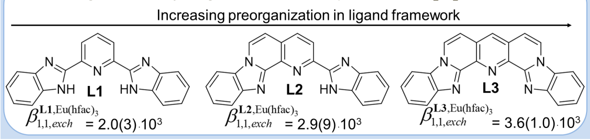


Figure 1. Affinity of ligands L1-L3 to europium ion in CD_2Cl_2 solution

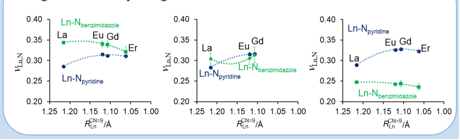


Figure 2. Affinity of ligands L1-L3 to lanthanide ions in solid state

[1] A. N. Carolan, G. M. Cockrell, N. J. Williams, G. Zhang, D. G. Vanderveer, H.-S. Lee, R. P. Thummel, R. D. Hancock, *Inorg. Chem.***2013**, , *52*, 15-27.
[2] S. Naseri, M. Mirzakhani, C. Besnard, L. Guénée, L. Briant, H. Nozary, C. Piguet,*Chem. Eur J.*, **2023**, DOI 10.1002/chem.202202727.
[3] C. O. Dietrich-Buchecker, J.-P. Sauvage, *J. Am. Chem. Soc.*, **1984**, *106*, 3043-3045.
[4] N. Nishii, M. Miura*, ACS Catal.,* **2020**, *10*, 9747–9757.
[5] H. Wu, X. Huang, J. Yuan, F. Kou, F. Jia, B. Liu, K. Wang, *Eur. J. Med. Chem.*, **2010**, *45*, 5324-5330.

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

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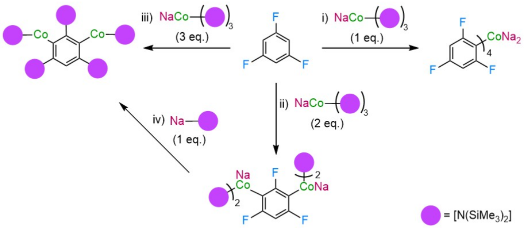
Fluoroaromatic compounds are increasingly heavily employed as scaffolds in agrochemicals and active pharmaceutical ingredients.[1] One of the most powerful methods for the incorporation of these molecules in more complex molecular scaffolds is deprotonative metalation. Typically these reactions have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

Breaking new ground in this field, in this contribution, by pairing a seemingly toothless cobalt (II) amide with their sodium congener, we report a new bimetallic approach, which enables the regioselective functionalisation of C-H as well as C-F bonds of a wide range of fluoroarenes. While deprotonation of fluoroarenes using conventional lithium bases can be challenging due to the exceptionally fragility of generated intermediates,[4] these cobaltation reactions occur regioselectively at room temperature. Combining the isolation of key metalated intermediates with theoretical calculations, unique mechanistic insights on how the alkali-metal and cobalt can cooperate in a synchronised manner to induce these processes that neither group 1 or cobalt amides are capable of facilitating on their own.



[1] Ahrens, J. Kohlmann, M. Ahrens, T. Braun, *Chem. Rev.* **2015**, 115, 931
[2] D. Robertson, M. Uzelac, R. E. Mulvey, *Chem. Rev.* **2019**, *119*, 8332
[3] (a) J. V. Obligacion, M. J. Bezdek, P. J. Chirik, *Am. Chem. Soc.* **2017**, *139*, 2825; (b) T. R. Dugan, X. Sun, E. V. Rybak-Akimova, O. Olatunji-Ojo, T. R. Cundari, P. L. Holland, *J. Am. Chem. Soc.* **2011**, *133*, 12418; c) O. Eisenstein, J. Milani, R. N. Perutz, *Chem. Rev.* **2017**, 117,8710
[4] Schlosser, L. Guio, F. Leroux, *J. Am. Chem. Soc.* **2001**, 123, 3822

Crystal growth of new van der Waals materials solid solutions ($TM´$, $TM´´$)I_2 (TM = Co, Fe, Ni) with tuned magnetic properties

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Magnetic van der Waals materials have emerged as a class of materials that offer exciting possibilities due to their distinctive interplay of magnetic interactions and van der Waals forces, leading to a rich and diverse range of functionalities. In the growing family of novel magnetic van der Waals materials, transition metal di-iodides (TMI_2, TM = Co, Fe, Ni) represent an exciting group of compounds in which different magnetic ground states are stabilized by subtle differences in their crystal structure [1-3]. Competing AFM and FM magnetic orders are the origin of magnetic frustrations at low temperatures. Despite prior investigations of these frustrated states in some of these compounds, the elusive interconversion between magnetic ground states within solid solutions of these materials remains unresolved.

Crystal growth of these compounds requires careful adjustment of precursor composition, growth temperature, and thermal gradient all along the solid solution. The choice and control of synthesis conditions are crucial to avoid phase separation in a reactor. We have successfully grown crystals of the solid solutions ($TM´$, $TM´´$)I_2 (TM = Co, Fe, Ni) with the aim of tuning the magnetic transitions and searching for new magnetic ground states. Plate-like crystals up to 6x10 mm^2 in size could be obtained by chemical vapor transport. Interestingly, with this technique, TMI_2 crystals were found to grow both from the vapor at the cold end of the reactor and from the melt at the hot end. All these crystals are extremely air sensitive and require handling inside a glovebox under an inert atmosphere.

Bulk crystals of ($TM´$, $TM´´$)I_2 can be exfoliated into 2D thin flakes expected to have thickness-dependent magnetic behavior down to a monolayer, thus opening the possibility of fabricating new 2D magnetic devices with novel magnetic properties.

[1] Xiaojian Bai et al, *Nature Physics*, **2021**, 17, 467-472.

[2] Qian Song et al, *Nature*, **2022**, 602, 601-605.

[3] T. Kurumaji et al, *Physical Review B*, **2013**, 87(1), 014429(9).

Unlocking Cyclometalation: Catalytic Transmetalation Towards Cyclometalated Gold(III) Complexes

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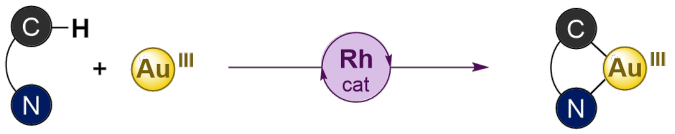
Gold(III) complexes have a significant impact on several fields, including materials science, biomedical research, and catalysis.[1] Despite the strongly oxidizing nature of this metal, bidentate or tridentate ligands can stabilize gold(III) complexes against reduction, making them more durable and robust for translational applications. In this context, cyclometalated gold(III) species containing bidentate (C^N) ligands play a prominent role as tunable photochemical dopants in OLEDs and as antitumoral agents.[2] Unfortunately, only a few strategies tackling their synthesis are available to date. They rely on organomercury reagents, silver salts, or harsh conditions thus severely limiting the functional group compatibility, synthetic efficiency, and applicability of these systems in the abovementioned areas.

To overcome this challenge, we have successfully developed a catalytic, environmentally friendly and redox-neutral approach to synthesize a broad array of cyclometalated (C^N)gold(III) complexes. Our methodology relies on the catalytic Csp^2-H bond activation of 2-aryl-pyridine ligands using a commercially available and stable rhodium complex, followed by an unprecedented Rh-to-Au(III) transmetalation step. Detailed mechanistic investigations using kinetic measurements, control experiments, and DFT calculations revealed a rate-determining stepwise (C-then-N) transmetalation process underlying these transformations.[3]

Catalytic Rhodium to Gold(III) Transmetalation



✓ Catalytic ✓ Environmentally friendly ✓ Mild conditions ✓ Broad scope

✓ No prefunctionalization ✓ 1st Example of **Rh**-to-**Au(III)** transmetalation

✓ Rate-determining, stepwise (first C, then N) ligand transfer

[1] Luca Rocchigiani, Manfred Bochmann, *Chemical Reviews,* **2021**, 121, 8364-8451.

[2] Roopender Kumar, Cristina Nevado, *Angewandte Chemie International Edition,* **2017**, 56, 1994-2015.

[3] Jaime Martín, Enrique Gómez-Bengoa, Alexandre Genoux, Cristina Nevado, *Angewandte Chemie International Edition*, **2022**, 61, e202116755.

Synthesis, Characterization and Reactivity of 7-Coordinate Molybdenum Alkyl Complexes Supported by β-Diketonates

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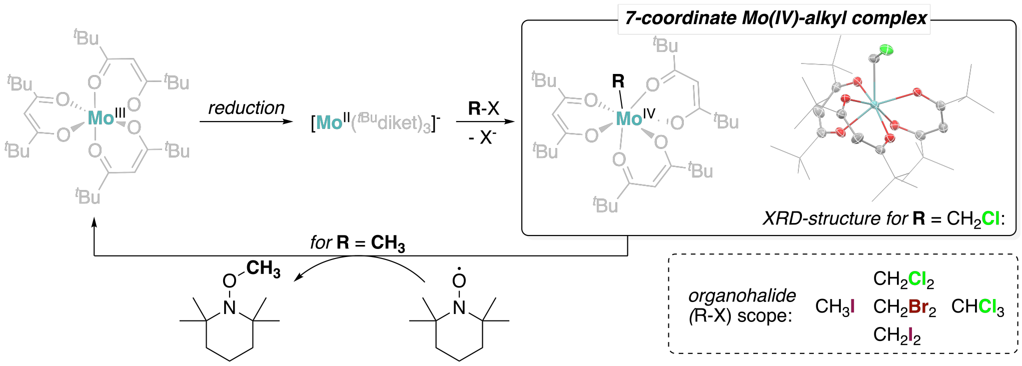
The selective C-X bond activation of simple organohalide substrates (*e.g.* dichloromethane) by low-valent transition metals is an attractive strategy for the preparation of (halogen-)alkyl complexes. The latter have been recognized as an important class of compounds, acting as precursors for the generation of methylene and methylene-bridged complexes, which represent proposed intermediates in a variety of important catalytic processes such as alkene metathesis, Fischer-Tropsch Synthesis or cyclopropanation.[1]

During the study of low-valent molybdenum complexes supported by β-diketonates,[2,3] we have found the selective reactivity of a homoleptic and anionic Mo(+II) complex with short-chain alkylhalides (R-X) such as dichloromethane. XRD solid state structure revealed the formation of a molybdenum-carbon bond as part of a novel 7-coordinate Mo(+IV) complex. Next to cyclopentadienyl supported complexes of the type $[MoCp(NO)_2(CH_2X)]$,[4] this is the only second report of molybdenum halomethyl complexes.

While isolated as pure compounds in the solid state, we have observed fast decomposition in solution. In order to better understand the reactivity of these Mo(+IV) alkyl complexes, the use of deuterated alkylhalide substrate allowed for the preparation of deuterated analogues. ^2H NMR spectroscopy has been used as a selective probe to follow the alkyl ligand's reactivity. Its radical-type character favors hydrogen abstraction *e.g.* from THF and allows for facile methyl radical transfer reactions to various acceptors such as TEMPO.



[1] Friedrich, H. B.; Moss, J. R. *Advances in Organometallic Chemistry* **1991**, *33*, 235-290.
[2] Masero, F.; Mougel V. *Chem. Commun.* **2023**, *59*, 4636-4639.
[3] Masero, F; Mougel V. *manuscript in preparation*.
[4] Elcesser, W. L.; Sörlie, M.; Hubbard, J. L. *Organometallics* **1996**, *15*, 2534-2542.

Cyclometalated ligand affords highly reducing U(III) complex

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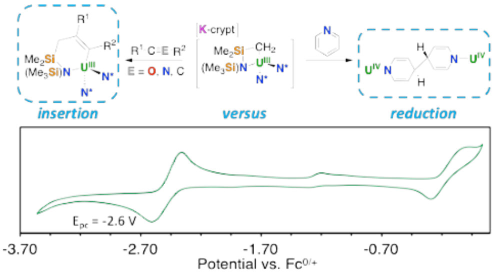
Uranium complexes have attracted interest for their reactivity with small molecules, such as N_2, CO and CO_2.[1] To activate these small molecules, highly reducing complexes are required. In order to obtain these type of complexes, alkyl ligands are of interest, thanks to their strong electron-donating properties. Even though U(IV) cyclometalated complexes have been long known[2] and show a broad range of reactivity, low oxidation state uranium cyclometalated complexes remain rare and not well studied.

We report the isolation of $[K(2.2.2\text{-cryptand})][U^{III}\{N(SiMe_3)_2\}_2(\kappa^2\text{-C,N-}CH_2SiMe_2NSiMe_3)]$, **1**, from the reduction of $[U^{III}\{N(SiMe)_2\}_3]$ with KC_8 and 2.2.2-cryptand at room temperature. Electrochemical experiments demonstrated that complex **1** has a reduction potential similar to that of the previously reported $[K(2.2.2\text{-cryptand})][U^{II}\{N(SiMe)_2\}_3]$ complex[3] (E_{pc} = -2.6 V versus $Fc^{0/+}$ and E_{pc} = -2.8 V versus $Fc^{0/+}$, respectively). Complex **1**, indeed, shows similar reducing abilities upon reactions with 4,4'-bipyridine, 2'2-bipyridine, 1-azidoadamantane and, most interestingly, pyridine ($E_{1/2}$ = -2.76 V versus Ag/AgCl), being the first example of a mononuclear U(III) complex that is capable of reducing pyridine. Remarkably, complex **1** is considerably more stable in solution at room temperature than the U(II) complex despite its similar reactivity. In addition, various substrates, such as CO, acetonitrile and PhCCH can be inserted into the U–C bond of complex **1**, demonstrating C-O, C-N and C-C insertion and forming new U(III) metallacycles. These results show that cyclometalated U(III) complexes can be interesting precursors to assemble a wide variety of chemical architectures.



[1] Benedict M. Gardner, Stephen T. Liddle, *European Journal of Inorganic Chemistry*, **2013**, 22-23, 3753-3770.
[2] Stephen J. Simpson, Howard W. Turner, Richard A. Andersen, *Angewandte Chemie*, **1981**, 20, 2991-2995.
[3] Austin J. Ryan, Mary A. Angedol, Joseph W. Ziller, William J. Evans, *Chemical Science*, **2019**, 55, 2325-2327.

Study of the Anticancer Activity of Polyoxometalates

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Polyoxometalates (POM) are polynuclear transition metal oxo-clusters, commonly composed of V^{5+}, Nb^{5+}, Ta^{5+}, Mo^{6+}, and W^{6+}, making up a class of coordination complexes that can take on a broad range of compositions and structures.[1,2] They have previously proven themselves as suitable drug candidates against cancers;[3-7] their suitability arises from the modularity of their structure and tunability of their properties.[5,7]

Despite the growing field of research on the anticancer activity of POMs, the mechanisms leading to the POMs' cytotoxicity are not well understood,[4] nor are the stability of the POMs in the cellular environment,[8] and therefore the active species leading to the therapeutic effects are unknown.[4]

With this work, these shortcomings aim to be addressed. The stability and speciation of various, common POMs in aqueous solution and cell culture medium have been investigated by NMR. Then the effects of the POM species and relevant reference compounds on different cell lines were investigated using PrestoBlue assays. In this way, the features of the POMs' structures causing the anti-cancer activity can be derived and an effective and selective POM-drug candidate can be developed.

1. Pope, M. T. *Heteropoly and Isopoly Oxometalates*, Vol. 8; Springer-Verlag, 1983.
2. Pope, M. T.; Müller, A. Polyoxometalate Chemistry: An Old Field with New Dimensions in Several Disciplines. *Angew. Chem. Int. Ed. Engl.* **1991**, *30* (1), 34–48. DOI: 10.1002/anie.199100341.
3. Liu, Y.; Tian, S.; Liu, S.; Wang, E. In vitro inhibitory effect of polyoxometalates on human tumor cells. *Transition Met. Chem.* **2005**, *30* (1), 113–117. DOI: 10.1007/s11243-004-3825-1.
4. Bijelic, A.; Aureliano, M.; Rompel, A. Polyoxometalates as Potential Next-Generation Metallodrugs in the Combat Against Cancer. *Angewandte Chemie (International ed. in English)* **2019**, *58* (10), 2980–2999. DOI: 10.1002/anie.201803868. Published Online: Oct. 12, 2018.
5. Čolović, M. B.; Lacković, M.; Lalatović, J.; Mougharbel, A. S.; Kortz, U.; Krstić, D. Z. Polyoxometalates in Biomedicine: Update and Overview. *Current medicinal chemistry* **2020**, *27* (3), 362–379. DOI: 10.2174/0929867326666190827153532.
6. Mukherjee, H. N. Treatment of Cancer of the Intestinal Tract with a Complex Compound of Phosphotungstic Phosphomolybdic Acids and Caffeine. *J. Indian Med. Assoc* **1965**, *44*, 477–479.
7. Hill, C. L.; Weeks, M. S.; Schinazi, R. F. Anti-HIV-1 activity, toxicity, and stability studies of representative structural families of polyoxometalates. *Journal of medicinal chemistry* **1990**, *33* (10), 2767–2772. DOI: 10.1021/jm00172a014.
8. Gumerova, N. I.; Rompel, A. Polyoxometalates in solution: speciation under spotlight. *Chem. Soc. Rev.* **2020**, *49* (21), 7568–7601. DOI: 10.1039/D0CS00392A. Published Online: Sep. 29, 2020.

Salen-derived multi-metallic complexes

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Salen is one of the most studied ligands in chemistry, notably for its straightforward synthesis and its ability to coordinate a variety of metal ions.[1] This Schiff base compound has a N_2O_2 chelate site allowing the coordination of one metal ion. Salen is an interesting ligand in that it can be functionalized providing a panoply of new ligand structures. The main application of salen-metal complexes is in the field of catalysis,[2] the most well-known being the Jacobsen catalyst for its enantioselective epoxidation of alkenes.[3]

In our studies, we aim at synthesizing multi-metallic complexes with two or three different metal ions. To achieve this goal, salen can be functionalized with glycol chains creating e.g. a O_3O_3 recognition site for a second metal ion. The combination of different metal ions can provide enhanced chemical and biological properties.[2] For instance, the synthesized multi-metallic complexes could be used as mixed metal oxide precursors or show potential synergic antibacterial properties.[4]

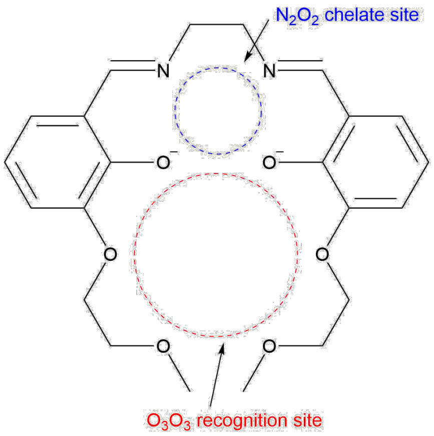

Fig. 1 : Representation of salen-derived ligand with N_2O_2 chelate and O_3O_3 recognition sites

[1] Ashish K. Asatkar, Mamta Tripathi, Deepali Asatkar, *IntechOpen*, **2020,** 1, Ch. 7
[2] Ramananda Maity, Bernhard S. Birenheide, Frank Breher, Biprajit Sarkar, *ChemCatChem*, **2021,** *13*, 2337-2370
[3] John Hanson, *J. Chem. Educ.*, **2001**, 78, 9, 1266-1268
[4] Alba Finelli, Sarah-Luise Abram, Nelly Hérault, Aurélien Crochet, Katharina M. Fromm, *Cryst. Growth Des.*, **2020**, 20, 4945-4958

Pulsed laser deposition of Ho_2O_3 Röntgen Thin Films

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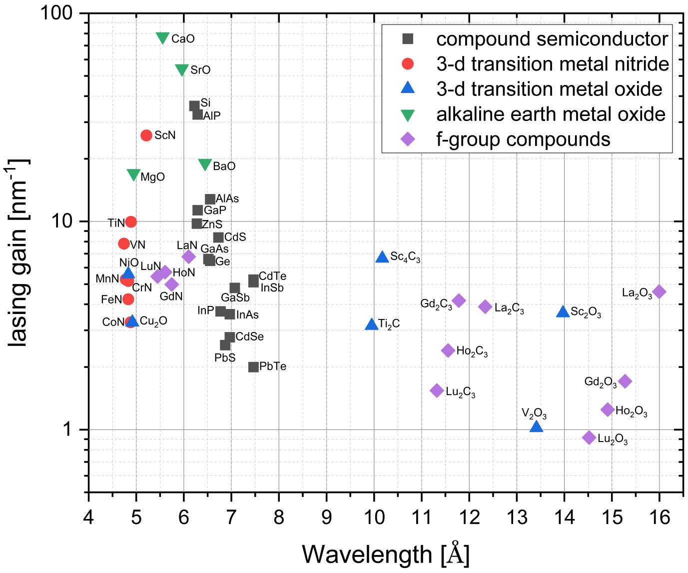
In 1974, Fisher [1] proposed the concept of utilizing single crystals for an ultra-small X-ray laser. He has proposed several crystals utilizing O-K_a as a resonant wavelength. Ho_2O_3 is one among them. Yariv [2] calculated the lasing parameters in the single crystals to achieve distributed feedback. The main working principle of this X-ray laser relies on resonant matching between the wavelength and the interplanar distance in the crystal. That theoretical foundation never come to an experimental system, mainly due to the strict requirements of crystal quality and stoichiometry.

The main goal of this work is to experimentally realize such compact X-ray laser using single crystals as a suitable "Röntgen material". Detailed calculation on various ''Röntgen materials'' have been performed to evaluate the performance of various materials [3]. From those materials which was illustrated in Fig.1, one of the potential candidate was selected for this experimental work, namely Ho_2O_3. The calculated results provided the dimension for the single crystal, which turns to be around 100 nm. To create such a tiny crystals, we employed pulsed lased deposition (PLD) to grow epitaxial thin film. PLD is well known for its stoichiometry transfer and epitaxial growth of thin film [4]. This is most important in our case. Ho_2O_3 is an interesting candidate to grow as a thin film due to its chemically stability.



1. Fisher, Robert A. *Applied Physics Letters* 24, **1974**, 12, 598-599.
2. Yariv, Amnon. *Applied Physics Letters* 25, **1974**, 2, 105-107.
3. Sharath Rameshbabu, Davide Bleiner. SPIE Optics and Optoelectronics **2023**, 2, 12582-42 (In-press).
4. Shepelin, Nick A., Zahra P. Tehrani, Natacha Ohannessian, Christof W. Schneider, Daniele Pergolesi, and Thomas Lippert. *Chemical Society Reviews*, **2023**.

Efficient alcohol oxidation with novel manganese(III) complexes with bis(phenolate)-NHC ligands

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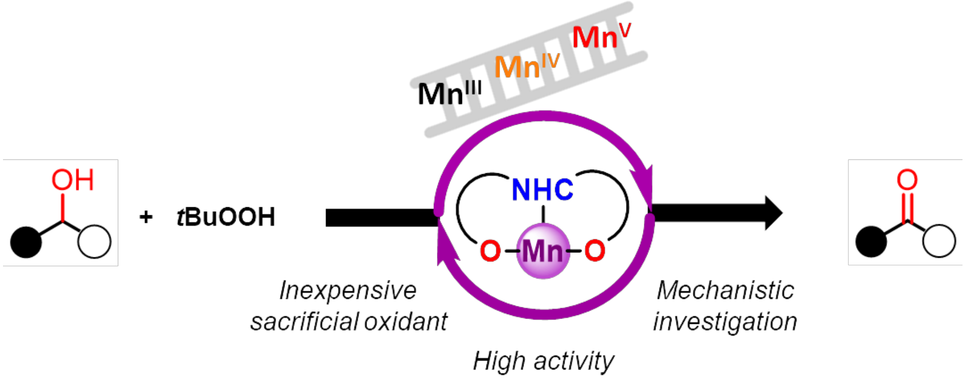
Oxidation chemistry plays a critical role in the synthesis of pharmaceuticals and value-added products, such as perfumes. A catalytic approach based on Earth-abundant metal complexes and inexpensive oxidants such as peroxides currently represents the most attractive strategy to perform this transformation.[1] Our group recently prepared a new class of N-heterocyclic carbene ligands bearing phenolate moieties and their corresponding metal complexes, investigating the potential benefit of the electronic flexibility of the carbene fragment in catalytic applications involving redox events.[2,3] Here, we decorated imidazole- and triazole-derived carbenes with phenolate substituents[4,5] to access Mn(III) complexes, which efficiently catalyze the oxidation of alcohols in the presence of *t*BuOOH as terminal oxidant. In addition, we will present the versatility of the catalytic system and mechanistic investigations in order to disclose the nature of the active species.



[1] C. Miao, X.-X. Li, Y.-M. Lee, C. Xia, Y. Wang, W. Nam, W. Sun, *Chem. Sci.* **2017**, *8*, 7476–7482.
[2] S. Bertini, M. Rahaman, A. Dutta, P. Schollhammer, A. V. Rudnev, F. Gloaguen, P. Broekmann, M. Albrecht, *Green Chem.* **2021**, *23*, 3365–3373.
[3] W. Stroek, M. Keilwerth, D. M. Pividori, K. Meyer, M. Albrecht, *J. Am. Chem. Soc.* **2021**, *143*, 20157–20165.
[4] E. Borré, G. Dahm, A. Aliprandi, M. Mauro, S. Dagorne, S. Bellemin-Laponnaz, *Organometallics* **2014**, *33*, 4374–4384.
[5] M. Baltrun, F. A. Watt, R. Schoch, C. Wölper, A. G. Neuba, S. Hohloch, *Dalton Trans.* **2019**, *48*, 14611–14625.

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

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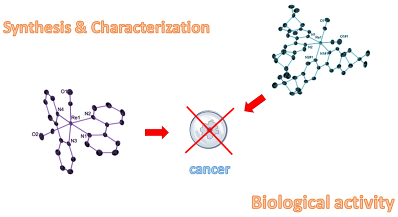
In our effort to discover novel selective and non-toxic agents effective against CRC, we synthesized a series of rhenium(I) tricarbonyl-based complexes with increased lipophilicity. Two of these novel compounds were discovered to possess remarkable anticancer, anti-angiogenic and antimetastatic activity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



In another study, we reported a rhenium(II) dicarbonyl complex, which displayed better cytotoxicity against MCF-7 breast cancer cells than cisplatin.[2] We investigated later new synthetic routes to aerobically stable and substitutionally labile α-diimine rhenium(I) dicarbonyl complexes. The molecules were prepared in high yield from the *cis–cis–trans*-$[\mathrm{Re(CO)_2}(^t\mathrm{Bu_2bpy})\mathrm{Br_2}]^-$ anion (where $^t\mathrm{Bu_2bpy}$ is 4,4′-di-*tert*-butyl-2,2′-bipyridine), which could be isolated from the one electron reduction of the corresponding 17-electron complex. Ligand substitution of Re(I) complexes proceeded via pentacoordinate intermediates capable of Berry pseudorotation. In addition to the *cis–cis–trans*-complexes, *cis–cis–cis-* (all *cis*) isomers were also formed. $[\mathrm{Re(CO)_2}(^t\mathrm{Bu_2bpy})\mathrm{Br(L)}]$ complexes may be considered as synthons for the preparation of a variety of new stable diamagnetic dicarbonyl rhenium *cis*-$[\mathrm{Re(CO)_2}]^+$ complexes, offering a convenient entry in the chemistry of the core.[3]

[1] Joachim Delasoie, Aleksandar Pavic, Noémie Voutier, Sandra Vojnovic, Aurélien Crochet, Jasmina Nikodinovic-Runic, Fabio Zobi, *Eur. J. Med. Chem.*, **2020**, 204, 112583.
[2] Jérémie Rossier, Daniel Hauser, Emmanuel Kottelat, Barbara Rothen-Rutishauser, Fabio Zobi, *Dalton Trans.*, **2017**, 7, 2159.
[3] Kevin Schindler, Aurélien Crochet, Fabio Zobi, *RSC Adv.*, **2021**, 13, 7511.

Synthesis and Characterization of POM-Cubane Hybrids

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Polyoxometalates (POMs) have a wide variety of applications due to their structural diversity and tunability and therefore are of high interest in many different research areas. To improve the desired properties of the POMs, hybrid materials with covalent and non-covalent bonds can be synthesized. Herein, the formation of POM hybrids derived from a combination of POMs with different metal oxo-clusters are described. Mainly the negatively charged full-Keggin POM $\{Co(II)W_{12}O_{40}\}$, with {Na}, {K}, $\{NH_4\}$, and $\{(NCH_3)_4\}$ as counterions, was used as a starting material and combined with the positively charged $\{Co(II)_4O_4\}$ cubane $[Co(II)_4(dpy\{OH\}O)_4(OAc)_2(H_2O)_2](BF_4)_2$ (Co_4O_4-dpk). Different counterions for the cubane formation were tested in combination with the POM and influenced the crystallization process. Replacing the starting POM with an unsaturated Keggin POM $\{BiW_9O_{34}\}$ resulted in a mixture of different crystal structures, including a structure with a sandwich-type POM and a mono nuclear cobalt(III) complex as a counter cation. The structures were determined using SC-XRD and PXRD. The redox reactions and stability of the compounds were studied by cyclic voltammetry.

Designing Advanced Battery Materials Beyond Lithium-Ion Technology

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Achieving a sustainable energy future is one of the key challenges facing humanity today. Metal-sulfur batteries represent very attractive energy storage systems, as their energy density and elemental abundance are much higher than that of lithium-ion batteries today. However, these batteries are plagued with problems relating to dendrite growth, polysulfide dissolution, and poor conductivity, necessitating advanced material design strategies. I will present our recent work on anode, cathode and electrolyte development, including protection of metal anodes using artificial interphases, inhibition of polysulfide dissolution at sulfur cathodes, and discovery of new promising electrolytes. The combination of these strategies result in metal-sulfur batteries with stable capacity and long lifetime over 1000 cycles.

Defined patches of interwoven materials

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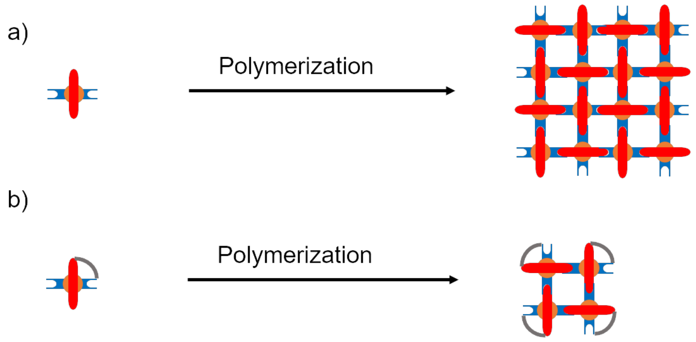
[1]University Basel

The simplest way of producing a textile is by orthogonally interlacing two yarns. The resulting material possesses stability, flexibility, and shape adaptability due to its interwoven structure. The concept of interwoven materials has been adapted to the molecular level in for example tailor-made DNA tiles, coordination polymers and tailor-made organic structures. [1]

A first step towards the bottom-up, self-assembled synthesis of polymer fabrics was done by Wöll *et a*l. by designing textile sheets through pre-orienting the coupling partners to a MOF layer, reacting them, and then removing the metal ions to get the organic textile layer.[2]

We designed a heteroleptic, amphiphilic metal complex to take advantage of its pre-organization to assemble a molecular textile from bottom-up. The octahedral geometry of the metal complex and the rigidity of the tri-dentate ligands ensure angles in between the ligands of close to 90°. [3] By choosing amphiphilic ligands with different functional groups, which can be linked with each other, a moiety that can form an interwoven 2D material by polymerization was designed. Fixing the orientation of the monomer by using an water-air interface to orientate the hydrophilic ligand to the water allows us to have the necessary groups for the polymerization pre-organized in one plane to later form the 2D interlocked material.

In an effort to gain further insight into interwoven materials, we also designed a heteroleptic complex that can only interlink on two sides. To ease the separation of the possible enantiomers, a linker which is chiral itself was chosen. Polymerizing this restricted moiety, a defined patch of an interwoven material is formed. This defined patch would allow a variety of analytical measurements, which are not possible with the polymeric material, to give immense insight into this type of materials.



[1] A. Di Silvestro, M. Mayor, *Chimia*, **2019**, 73, 455-461.
[2] Z. Wang, A.Blaszczyk, O. Fuhr, S. Heissler, C. Wöll, M. Mayor, N*ature Comm.,* **2017**, 8, 14442.
[3] G. Harzmann, M. Neuburger, M.I Mayor, *Eur. J. Inorg. Chem.,* **2013**, 2013, 3334-3347.

Inside or outside the box? Confinement-driven and surface catalysis with coordination cages

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Coordination cages, consisting of a self-assembled combination of metal ions and ligands into a porous, three-dimensional arrangement are attractive candidates for catalysis applications.[1,2] Much as enzymes control reactivity through trapping the substrates in their cavities, coordination cages are able to include one or two guests and direct them through various supramolecular interactions towards reaction-ready configurations, while also lowering the activation energy of various reactions due to the confinement effect.

More recently though, surface catalysis has also been explored for these assemblies.[3] Even if to a lesser extent compared to the hollow cavity of a coordination cage, the cage exterior provides an anisotropic environment which is suitable for various chemical transformations.[4] Even more, the cage can be employed both as a platform and a “nanoreactor” when both cavity-bound and surface-bound guests are employed concomitantly.

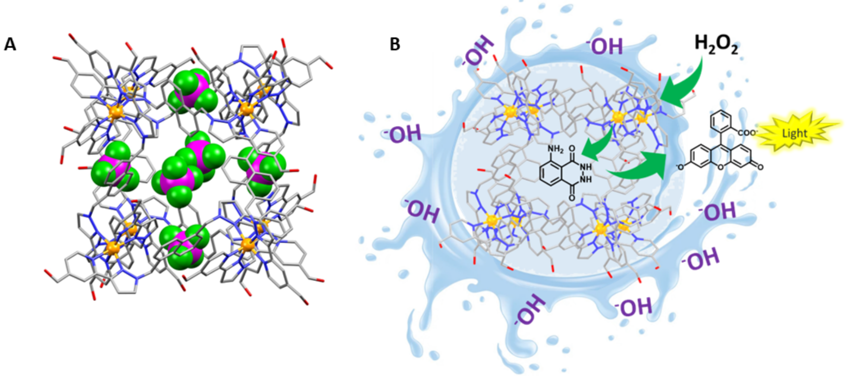

Figure 1. A. Molecular structure of the $[Co_8L_{12}](BF_4)_{16}$ cage determined by single-crystal X-ray diffraction (The H atoms were removed for clarity). B. Schematic representation of the oxidation of luminol and generation of chemiluminescence resonance energy transfer in the presence of the cage.

The high hydrophobic surface of the cage with the general formula $Co_8L_{12}^{16+}$, (where L is a pyrazole-pyridine-type ligand) (Figure 1A), as well as its high positive charge, allows it to act as a co-locator of both the fluorescein diacetate substrate and the hydroxide anions, promoting ester hydrolysis and formation of the fluorescein dianion, whose formation can be monitored by UV-Vis. We have found that the hydrophobic effect leads to a high association constant of 15000 (±2000) M^{-1}, while the rate of the reaction is accelerated 50 times compared to the uncatalyzed reaction.[4] Moreover, the Co^{2+} ions, in the presence of the surface bound hydroxide ions and reactive oxygen species catalyse the oxidation of cavity-bound luminol to generate chemiluminescence (Figure 1B). The cage acts as both a nanoreactor and as a platform for bringing all the components together so when an additional guest is bound to the surface, the cavity-bound luminol can transfer its excitation energy to the surface-bound fluorescein in the first example of Chemiluminescence Resonance Energy Transfer (CRET) involving coordination cages.[5]

[1] M. D. Pluth, R. G. Bergman, K. N. Raymond, *Angew. Chem. Int. Ed.* **2007**, 46, 8587–8589. [2] Y. Xue, X. Hang, J. Ding, B. Li, R. Zhu, H. Pang, Q. Xu, *Coord. Chem. Rev.* **2021**, 430, 213656. [3] M. D. Ludden, C. G. P. Taylor, M. B. Tipping, J. S. Train, N. H. Williams, J. C. Dorrat, K. L. Tuck, M. D. Ward, *Chem. Sci.* **2021**, 12, 14781–14791. [4] A. B. Solea, B. Sudittapong, M. D. Ward, *Dalton Trans.*, **2022**, 51, 11277-11285. [5] A. B. Solea, M. D. Ward, *Dalton Trans.*, **2023**, 52, 4456-4461.

Computational Design of Surface Capping Ligands for Structurally Soft Metal Halide Nanocrystals

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[1]Laboratory of Inorganic Chemistry, Department of Chemistry and Applied Biosciences, ETH Zürich, Vladimir Prelog Weg 1, CH-8093 Zürich, Switzerland, [2]Laboratory for Thin Films and Photovoltaics, Empa – Swiss Federal Laboratories for Materials Science and Technology, Überlandstrasse 129, CH-8600 Dübendorf, Switzerland, [3]Institute for Condensed Matter Physics, NAS of Ukraine, 1 Svientsitsky, Lviv 79011, Ukraine

Versatile surface functionalization of highly ionic surfaces, ubiquitous among inorganic nanomaterials, remains a formidable challenge in view of inherently non-covalent surface bonding. Colloidal lead halide perovskite nanocrystals (NCs), which are of interest for classical and quantum light generation,[1,2] are a prominent example.[3] One of the reasons is a limited atomistic understanding of the NC-ligand-solvent interface. We would like to present how classical molecular dynamics simulations can be used in combination with experimental techniques to aid in understanding surface chemistry of ionic nanomaterials and to guide experimental discovery of new better capping ligands. In particular, we will present the first structural investigation of perovskite NC surfaces capped with zwitterionic phospholipid molecules. Combined computational and experimental evidence suggests that the phospholipid ligands bind to the surface of the NCs with both head-groups by displacing native ions of the perovskite. The ligand head-group affinity to the surface is primarily governed by the geometric fitness of its cationic and anionic moieties into the surface lattice sites. As a result, stable and colloidally robust nanocrystals of inherently labile hybrid perovskites – $FAPbX_3$ and $MAPbX_3$ (X – Cl, Br, I) – can be obtained for the first time using lattice-matched phosphoethanolamine head-group. Improved surface stability enables excellent optical performance of the NCs. Thoroughly purified NCs retain their stable emission with above 95% photoluminescence quantum yield in a broad concentration range, as well as in thick films. Ligand tail engineering, on the other hand, allows diverse surface functionalization of the NCs, for example control over the compatibility with solvents of diverse polarity, from hydrocarbons to acetone and alcohols.

[1] Mingming Liu, et al. *Nature Photonics*, **2021**, 15, 379-385.
[2] Gabriele Raino, et al. *Nature*, **2018**, 563, 671-675.
[3] Quinten A. Akkerman, et al. *Nature Materials*, **2018**, 17, 394-405.

The ion-funnel-to-IVAC system for chemistry experiments with radionuclides having half-lives in the sub-second regime

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The chemical characterization of superheavy elements (SHEs, $Z \geq 104$) is limited by low production rates of aimed at nuclear reaction products (NRPs) and the low half-lives of the produced radioisotopes of said elements. A state-of-the-art approach, used for such studies, is gas adsorption (thermo)chromatography, which reaches its limit with radionuclides featuring half-lives of [1]. Thus, radioisotopes of SHEs with half-lives in the sub-second regime cannot be addressed with the currently available technique. A promising alternative is the transfer of the NRPs into an evacuated environment (molecular flow regime), which may allow for the characterization of more short-lived radionuclides well below one second ($t_{1/2} \leq 1$ s) [2]. However, the transfer of NRPs requires a suitable interface between the physical pre-separation and, e.g., an isothermal vacuum adsorption chromatography (IVAC) experiment.

Here, we present the development of a buffer gas cell (BGC), comprising a DC cage, an ion-funnel as well as a radio-frequency quadrupole, for the stopping and transfer of NRPs behind a gas-filled separator into vacuum. Preliminary results of chemical experiments with very short-lived radioisotopes of homologs of SHEs on fused silica surfaces are targeted as a benchmark for the suitability of IVAC for addressing even shortest lived SHEs beyond flerovium.

[1] A. Türler, R. Eichler, A. Yakushev, *Nucl. Phys. A,* **2015,** 944, 640-689.
[2] P. Steinegger et al., *J. Phys. Chem. C,* **2016,** 120, 7122-7132.

Tailoring Sodium Organometallic Reagents for Arena Functionalization

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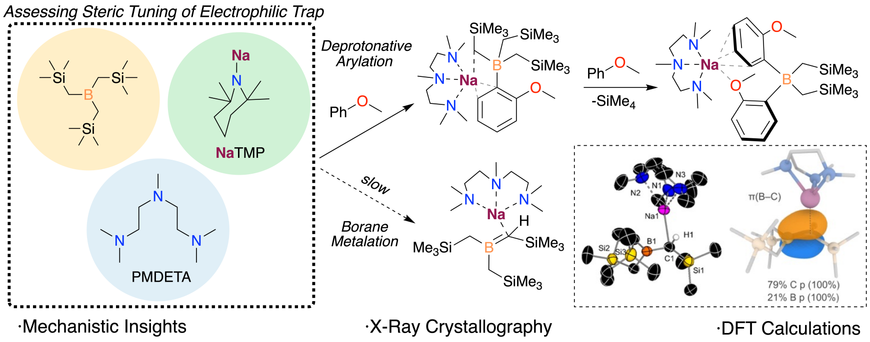
Organosodium compounds have attracted the attention of the scientific community in recent years as an alternative to widely used organolithium reagents.[1] Lithium alkyls and amides reside at the front of organometallic synthesis as key players in countless transformations, owing to their availability, substantial stability and solubility in hydrocarbon solvents.[2][3] However, these desirable traits are often pitfalls of heavier alkali-metal organometallics, meaning that their applications have remained underexplored.

Filling this gap in the knowledge, the preparation of organosodium compounds soluble in hydrocarbon solvents and the isolation and characterization of reactive sodium organometallic intermediates in the solid state and in solution by X-Ray crystallography and ^{1}H DOSY (Diffusion Ordered SpectroscopY) have allowed the development of new protocols for the functionalization of organic molecules. Our efforts have been focused on selective deprotonative metalation reactions of synthetically attractive arenes, providing access to the selective functionalization of these scaffolds, including the borylation[4] and the deuteration of the aromatic substrates.[5] Extending the application of this methodology, we have observed that the use of bulkier trialkyl boranes in deprotonative borylation opens new reactive pathways, from unlocking polybasic behaviour to obtaining competitive lateral borane sodiation.[6]



[1] P. B. De, S. Asako, L. Ilies, *Synthesis* **2021**, *53*, 3180–3192.
[2] (a) T. 'Li' Rathman, J. A. Schwindeman, *Org. Process Res. Dev*. **2014**, *18*, 1192–1210. (b) Lithium Compounds in Organic Synthesis – From Fundamentals to Applications, (Eds.: R. Luisi and V. Capriati), Wiley-VCH, Weinheim **2014**
[3] (a) S. Asako, M. Kodera, H. Nakajima, K. Takai, *Adv. Synth. Catal.* **2019**, *361*, 3120–3123. (b) S. Asako, H. Nakajima, K. Takai, *Nat Catal* **2019**, *2*, 297–303.
[4] L. J. Bole, A. Tortajada, E. Hevia *Angew. Chem. Int. Ed.* **2022**, *61*, e202204262.
[5] A. Tortajada, E. Hevia *J. Am. Chem. Soc.* **2022**, *144*, 20237–20242.
[6] A. Tortajada, L. J. Bole, M. Mu, M. Standford, M. N. Peñas-Defrutos, M. García-Melchor, E. Hevia *Chem. Sci.* **2023**, DOI: 10.1039/D3SC01705B.

Surface Functionalization of Carbon Substrates with Host-Guest Complexes for Electrocatalysis

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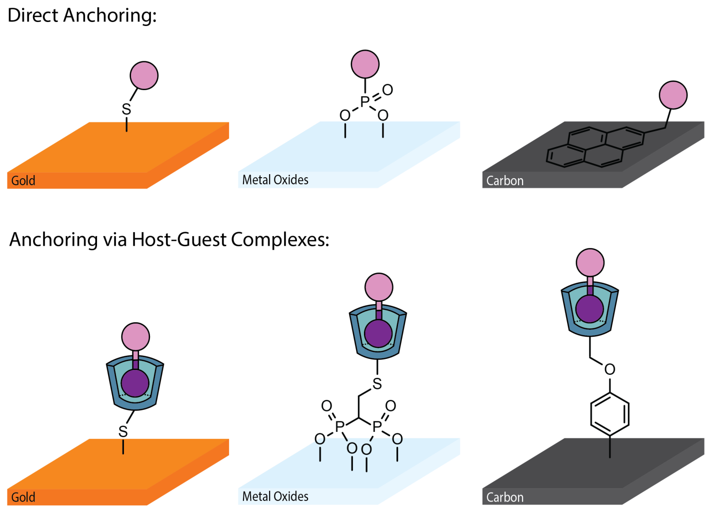
Catalysts can be classified into two main categories: heterogeneous and homogeneous. Heterogeneous catalysts offer the advantage of greater stability, whereas homogeneous catalysts exhibit higher activity and selectivity. The advantages of both types of catalysts can be brought together by anchoring molecular (homogeneous) catalysts on electrode surfaces. The state-of-the-art immobilization strategy is to alter the structure of the molecular catalyst such that it can bind to the surface via covalent bonding, non-covalent interactions or polymerization.[1] Different alterations are necessary for different substrates and these alterations can impact the activity of the catalyst.

In our research, we explore host-guest interactions as a novel and universal immobilization strategy. Host-guest complexes form via non-covalent interactions where the guest molecule enters the cavity of the host molecule through hydrophobic interactions and/or hydrogen bonding. By using these complexes, we can immobilize the same catalyst on different substrates without having to alter the catalyst structure depending on the substrate. The only modification necessary for the catalyst is the binding unit that goes inside of the host cavity. However, the binding unit remains the same regardless of the substrate.


Direct Anchoring:

Anchoring via Host-Guest Complexes:

In our previous study[2], we successfully performed electrocatalysis on metal oxide and gold substrates by using the host-guest strategy. These studies also showed that this system leads to stable catalyst binding on the surface. Additionally we proved that the catalytic activity can be regenerated by releasing degraded catalysts from the host cavity and subsequently adsorbing fresh catalysts. Our current work focuses on extending the host-guest binding approach to carbon substrates. We are investigating if similar benefits can be achieved, whether the host-guest system has any limitations depending on different substrates and if electrocatalysis is possible.

[1] Biaobiao Zhang, Licheng Sun, *Chem. Soc. Rev.*, **2019**, 48, 2216–2264.

[2] Laurent Sévery, Jacek Szczerbinski, Mert Taskin, Isik Tuncay, et al., *Nature Chemistry*, **2021**, 13, 523-529.

Band-Edge Modification of Quantum Dots by Solvation

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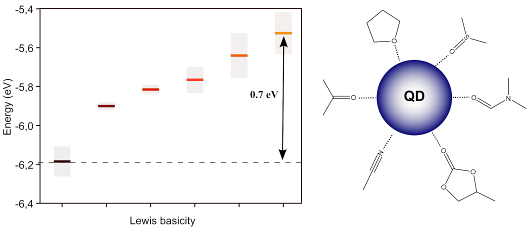
We show that band edge positions of colloidal quantum dots (QDs) shift over 0.6 eV depending on the solvent they are immersed in. We find that the direction of this energy shift is not purely a dielectric effect, and instead scales with the solvent Lewis basicity. This trend is independent on the QD material, and passivating ligand and matches well density functional theory calculations. This finding has immediate implications for the design of many emerging optoelectronic devices such as light emitting electrochemical cells, photocatalysts, and chemical sensors, where QDs are solvated, and the band edge positions determine device functionality. It also provides a means for stable electrochemical doping, as in-gap states related to material degradation are less sensitive to solvation than band edges.

Measurement of the band edge position is usually performed under ultrahigh vacuum, preventing inclusion of solvents. We overcome this challenge by developing a spectroelectrochemical approach that allows to measure the number of electrons/holes in solvated QD as the Fermi level is electrochemically shifted. This yields good agreement with expected shifts on the conduction band edge position with the QD size and the presence of different passivating ligands. Using this method, we demonstrate that the conduction band edge shifts up in energy as the solvent Lewis basicity increases.

Finally, we explore the implication of solvation for electrochemical doping. Electrochemical doping is arguably the most controllable way to regulate charge density in QDs, but the injected charges often end up localizing to in-gap states leading to material degradation. We find that the energetic position of these in-gap states can be brought outside the bandgap by leveraging solvation effects, providing a means to stabilize electrochemical doping.



Group-subgroup relation and superconductivity in ternary compounds with AlB_2-type structure

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In this work we summarize the abundance of the compounds with the AlB_2-type and related structures, which include ZrBeSi-, $CaIn_2$-, and YPtAs-type. These structures can be obtained by changing the stacking of the honeycomb layers and are connected via simple symmetry operations on the tree of the group-subgroup relations. In this class of compounds, we focus here on the ternary 111 honeycomb phases which exhibit superconductivity. Specifically, we investigate the evolution of the electronic, the superconducting and the structural properties upon exchange of the interlayer atoms in the $Ca_{1-x}Sr_xAlSi$ solid solutions. Furthermore, we present the structural phase transition in BaGaGe, where we describe a transition from 1H to 2H-BaGaGe correlated with the disorder-to-order transition of the atoms within the honeycomb layers. The structural phase transition is then followed by a transition to the superconducting state which we characterize in detail by means of magnetization, resistivity, and specific heat measurements.

Gas-Phase Adsorption Chromatography of Thallium on Dehydroxylated Fused Silica Surfaces

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Superheavy elements (SHEs, Z 104) hold the key to understanding relativistic effects and their influence on the chemical and physical behavior of particularly heavy elements. Since these effects scale with the atomic number [1], the chemical study of SHEs give insights in the extreme, and thus further our understanding of physicochemical properties of heavy elements in general. The yellow appearance of Au is a classic example of the relativistic influence on physical properties [2]. Unfortunately, SHEs have yet to be found in nature, thus they must be produced with accelerated heavy-ions in very-low-probability nuclear fusion-evaporation reactions. Depending on the target-projectile combinations, the yield of SHEs may be as low as an atom per day or week. Consequentially, preparation experiments with the lighter homologs of the SHE in question are extremely important. With nihonium (Nh, $Z = 113$) currently attracting the interest of chemists, the lighter homolog thallium is of primary interest. Despite previous Tl experiments preparing for Nh [3], recent attempts at a chemical characterization of the SHE have not yet yielded unambiguous results [4,5]. Presented here are the most recent results from an online isothermal chromatography experiment with short-lived radioisotopes of Tl isotopes. The experiments were conducted at the Tandem accelerator facility of the Japan Atomic Energy Agency through the Japan Society for Promoting Science fellowship program.

[1] P. Schwerdtfeger, L. F. Pasteka, A. Punnett, P. O. Bowman, *Nuclear Physics A*, **2015**, 944, 551-577.

[2] P. Pyykkö, *Chemical Reviews*, **1988**, 88, 563-594.

[3] A. Serov, R. Eichler, R. Dressler, D Piguet, A. Tüler, A. Vögele, D. Wittwer, H. W. Gäggeler, *Radiochimica Acta*, **2013**, 101, 421-425.

[4] S. N. Dmitriev, N. V. Aksenov, Y. V. Albin, G. A. Bozhikov, M. L. Chelnokov, V. I. Chepygin, R. Eichler, A. V. Isaev, D. E. Katrasev, V. Y.Lebedev, O. N. Malyshev, O. V. Petrushkin, L. S. Porobanuk, M. A. Ryabinin, A. V. Sabel'nikov, E. A. Sokol, A. V. Svirikhin, G. Y. Starodub, I.Usoltsev, G. K. Vostokin, A. V.Yeremin, *Mendeleev Communications*, **2014,** 24, 253-256.

[5] A. Yakushev, L. Lens, Ch. E. Düllmann, M. Block, H. Brand, T. Calverley, M. Dasgupta, A. Di Nitto, M. Götz, S. Götz, H. Haba, L. Harkness-Brennan, R. D. Herzberg, F. P. Heßberger, D. Hinde, A. Hübner, E. Jäger, D. Judson, J. Khuyagbaatar, B. Kindler, Y. Komori, J. Konki, J. V. Kratz, J. Krier, N. Kurz, M. Laatiaoui, B. Lommel, C. Lorenz, M. Maiti, A.K. Mistry, Ch. Mokry, Y. Nagame, P. Papadakis, A. Såmark-Roth, D. Rudolph, J. Runke, L.G. Sarmiento, T.K. Sato, M. Schädel, P. Scharrer, B. Schausten, J. Steiner, P. Thörle-Pospiech, A. Toyoshima, N. Trautmann, J. Uusitalo, A. Ward, M. Wegrzecki, V. Yakusheva, *Frontiers in Chemistry,* **2021**, 9.

Ultrafast-sintered self-standing LLZO membranes for high energy density Li-garnet solid-state batteries

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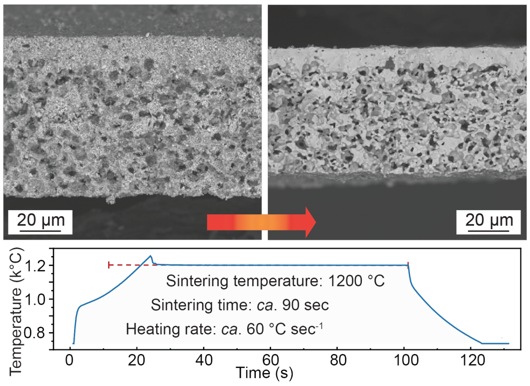
Towards building non-flammable and temperature-tolerant Li-ion batteries with high energy density, $Li_7La_3Zr_2O_{12}$ (LLZO) has recently attracted considerable attention as a compelling solid-state Li-ion electrolyte (SSE) due to its high thermal stability, Li-ion conductivity of up to 1 mS cm^{-1} (RT), and a wide electrochemical operation window of 0–6 V *vs.* Li^+/Li.[1, 2] Additionally, unlike other Li-ion soft solid conductors such as those based on sulfides, LLZO SSE can be manufactured with a bilayer dense-porous microstructure, which prevents the issues of dynamic volume change of the Li anode and the formation of voids at the Li/SSE interface during cycling and thus eliminates the need for external pressure.[3, 4] Here we report a facile, ultrafast sintering methodology for the fabrication of LLZO solid-state electrolyte in the form of self-standing bilayer dense-porous LLZO membranes. The thickness of the produced dense and porous layers was *ca*. 8 µm and 55 µm, which hypothetically allows to achieve high gravimetric and volumetric energy densities of Li-garnet batteries of 218 Wh kg^{-1} and 769 Wh L^{-1} (in combination with an NMC811/LiFSI-Pyr_{13}FSI cathode). Electrochemical measurements confirmed that produced LLZO membranes possess high critical current density up to 1.7 mA cm^{-2} and cycling stability of over 160 cycles at a current density of 0.4 mA cm^{-2}.



[1] Romain Dubey, Jordi Sastre, Claudia Cancellieri, Faruk Okur, Alex Forster, Lea Pompizii, Agnieszka Priebe, Yaroslav E. Romanyuk, Lars P. H. Jeurgens, Maksym V. Kovalenko, Kostiantyn V. Kravchyk, *Adv. Energy Mater*. **2021**, 2102086.
[2] Semih Afyon, Kostiantyn V. Kravchyk, Shutao Wang, Jan van den Broek, Christian Hänsel, Maksym V. Kovalenko, Jennifer L. M. Rupp, *J. Mater. Chem*. A **2019**, 7, 21299.
[3] Kostiantyn V. Kravchyk, Faruk Okur, M. V. Kovalenko, *ACS Energy Lett*. **2021**, 2202.
[4] Kostiantyn V. Kravchyk, Huanyu Zhang, Faruk Okur, Maksym V. Kovalenko, *Acc. Mater. Res.*, **2022**, 3, 4, 411–415.