FMOCS VIII

Mainz, Germany,
July,
22nd – 25th 2025

FRONTIERS IN METAL OXIDE CLUSTER SCIENCE

JOHANNES GUTENBERG UNIVERSITÄT MAINZ

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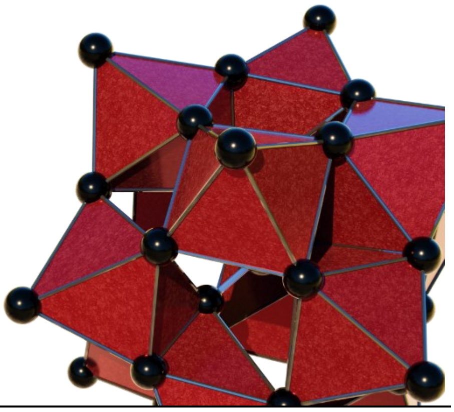

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Welcome to FMOCS VIII

Dear members of the FMOCS community,

It is with great pleasure that we welcome you to *Frontiers in Metal Oxide Cluster Science VIII* at Johannes Gutenberg University in Mainz. We are thrilled to see so many colleagues and friends from near and far, young and …well, still young. Especially in light of the many global challenges we continue to face, it is a pleasure to see everyone. Your presence reflects the strength and resilience of our scientific community and its commitment to advancing metal oxide cluster science.

This year’s meeting is hosted at Johannes Gutenberg University Mainz, one of Germany’s largest research universities. With a strong tradition in the natural sciences and a thriving interdisciplinary environment, JGU offers an inspiring setting for vibrant scientific exchange.

Mainz is a historic city nestled along the banks of the Rhine River. Founded as the Roman military stronghold *Mogontiacum*, it later rose to prominence as a powerful ecclesiastical center within the Holy Roman Empire. In the 17th century, Mainz played a key role in the emergence of German democracy. Over the centuries, the city has seen shifting sovereignties between France and Prussia before becoming the capital of the modern federal state of Rhineland-Palatinate. Today, Mainz seamlessly blends its rich cultural legacy—most notably as the birthplace of Johannes Gutenberg, inventor of the movable-type printing press—with a vibrant atmosphere, carnival celebrations and the scenic charm of the surrounding wine-growing country. We hope you’ll take the opportunity to explore the region and enjoy the special experiences we have prepared for you during the wine tasting, poster session, and conference dinner.

On behalf of the entire organizing team, we wish you a fantastic experience and I hope you enjoy your time here in Mainz.

Last, not least, I would like to thank the members of the scientific committee (Tatjana Parac Vogt, Kirill Monakhov), as well as the local FMOCS team for their hard work. Vielen Dank!

With best wishes,

Carsten Streb

Carsten Streb

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List of Oral Presentations

List of Poster Presentations

Synthesis And Characterisation Of Promising POM Catalyst Structures For Enhanced Biomass Valorisation

Maximilian J. Poller, Dorothea Voß, Jakob Albert*

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Enhanced biomass valorisation by engineering of polyoxometalate catalysts (BioValCat) shifts the borders for biomass valorisation techniques to so-far unexpected regimes up to 100% carbon efficiency by completely suppressing undesired total oxidation to CO2. The discovery that methanol as a (co-) solvent manipulates molecular POM catalysts in homogenously-catalysed oxidation reactions and consequently increases the product selectivity for formic acid (esters) to nearly 100% sets a disruptive innovation for engineering homogeneous biomass conversion processes. [1]

Developing medium-optimised POM structures showing superior performance in various aqueous-alcoholic solvents is one challenge for improving this technology. [2] Hereby, we want to combine high catalytic activity and selectivity of POMs with easy handling and high stability under oxidative conditions. Consequently, we prefer Keggin- ([XM12O40]) and Wells-Dawson-type ([X2M18O62]) structures as they do have great features based on synthesis procedure, stability, solubility in polar media and redox activity. The focus will be on (at least) non-precious, highly redox active, robust and long-term stable structures containing W or Mo as framework metals, substituted with highly redox-active transition metals like V.

The prepared POM catalysts will be characterised in detail with respect to their composition, structure and reactivity in order to understand the structure/composition relationships of the obtained materials and to develop material optimisation concepts for enhanced catalytic performance. This will be carried out by using sophisticated analytical tools for determining the elemental composition, performing structural analysis and revealing catalyst-solvent interactions.

This will answer the fundamental scientific question which material combinations (framework metal, heteroatom in combination with the redox active metal) in various POM structures (i.e. Keggin, Wells-Dawson), are most suitable to form active and stable POM-alcoholate complexes and where are the limitations with respect to thermal and chemical stability as well as robustness versus impurities in the substrate.

[1] S. Maerten, C. Kumpidet, D. Voß, A. Bukowski, P. Wasserscheid, J. Albert, Green Chem., 22 (2020), 4311-4320.
[2] S. Wesinger, M. Mendt, J. Albert, ChemCatChem, 13 (2021), 3662-3670.

Toward Distinguishing between the Superchaotropic and Hydrophobic Characters of Nanometric-Sized Ions in Interaction with PEGylated Surfaces

Christop Bruckschlegel[a], Coralie Pasquier[a], Guillaume Toguer[a], Luc Girard, Michael Odorico[a], Joseph Lautru[a], Oliver Diat[a] and Pierre Bauduin[a*]

[a] *ICSM, CEA, CNRS, ENSCM, Univ Montpellier, Marcoule, 30207 Bagnols sur Cèze Cedex, France.*

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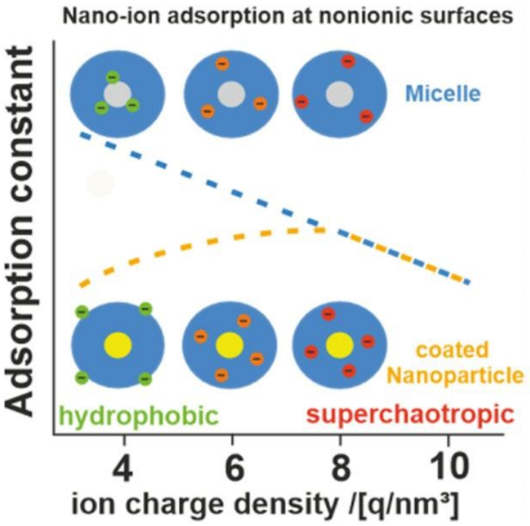
In this study,[1] we explore the superchaotropic effect of various poloxoometalate or boron cluster nano-ions on hydrophilic neutral surfaces. Thesee nanometric sized ions (nano-ions) with by low charge densities exhibit strong adsorption on non-ionic hydrophilic surfaces like PEGylated micelles. This adsorption phenomenon was attributed to the enthalpically favorable dehydration of nano-ions, the so-called superchaotropic effect. Here we investigate the adsorption of three nano-ions, α-$SiW_{12}O_{40}^{4-}$, α-$PW_{12}O_{40}^{3-}$ and $B_{12}I_{12}^{2-}$, with decreasing charge density or increasing superchaotropicity (or hydrophobicity), on hydrophilic solid surfaces, PEGylated gold nanoparticles, an PEGylated gold-coated quartz crystal. Solid surfaces are devoid of hydrophobic regions, enabling the study of the subtle nuance between hydrophobic and superchaotropic effects. Unlike adsorption on PEGylated micelles, the adsorption constant decreases with a reduced charge density, aligning with the well-established principle that hydrophobic ions do not adsorb on hydrophilic surfaces. This research improves our understanding of the subtle difference between superchaotropic and hydrophobic effects in nano-ion adsorption phenomena.



[1] Bruckschlegel, C.; Pasquier, C.; Toquer, G.; Girard, L.; Odorico, M.; Lautru, J.; Diat, O.; Bauduin, P., The Journal of Physical Chemistry Letters 2024, 15 (15), 4229-4236.

DFT Simulation of Complex Reaction Networks: New Insights into the Speciation and Formation of Polyoxometalates

Jordi Buils,[a,b], Diego Garay-Ruiz,[a] Laura S. Junkers [c], Enric Petrus [d], Mireia Segado-Centelles [b], Carles Bo [a,b]*

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In recent years our group has been working in the development of a new computational methodology, which we called POMSimulator, [1,7] to simulate the complex multi-species multi-equilibria taking place in the self-assembly processes leading to polyoxometalates. POMSimulator comprises automated workflows that rely exclusively on DFT-based results, and has been successfully applied to Mo, W, V, Nb and Ta isopolyoxometalates (IPAs). [2,3] The reaction networks can be applied to perform very long multi-time scale kinetic simulations on the formation of isopolyoxotungstanates, [4] what led to the discovery of a reation mechanism that transforms the kinetic product {W12} in the thermodynamic product {W10}. We released recently the first open-source version of the code. [5]

On the other hand, eteropolyoxoanions (HPAs) introduce far more complexity. We carried out a statistical analysis of the massive amounts of data produced by POMSimulator to reduce the reliance of the method on experimental formation constants. [6,7] More recently, we combined the predictions of our method with new Z-Ray total scattering data to investigate polyoxomolibdates speciation under hydrothermal conditions.[8]

[1] E. Petrus, M. Segado, C. Bo, Chemical Science 2020, 11, 8448–8456.
[2] E. Petrus, C. Bo, Journal of Physical Chemistry A 2021, 125, 5212–5219.
[3] E. Petrus, M. Segado-Centellas, C. Bo, Inorg. Chem. 2022, 61, 13708–13718.
[4] E. Petrus, D. Garay-Ruiz, M. Reiher, C. Bo, J. Am. Chem. Soc., 2023, 145, 34,18920-18930
[5] E. Petrus, J. Buils, D. Garay-Ruiz, M. Segado-Centellas, C. Bo, J Comput Chem 2024, 45, 2242–2250.
[6] J. Buils, D. Garay-Ruiz, M. Segado-Centellas, E. Petrus, C. Bo, Chem. Sci. 2024, 15, 14218-14227.
[7] J. Buils, D. Garay-Ruiz, E. Petrus, M. Segado-Centellas, C. Bo, Digital Discovery 2025, 4, 970-978.
[8] L. S. Junkers, D. Garay-Ruiz, J. Buils, R. S. Silberg, G. B. Strapasson, K. M. Ø. Jensen, Carles Bo,

Te(IV) Bicapped Vanadium-Containing Keggin Anion: From electron transfer engineering to Intimate Magnetic and Optical properties

Romain Canioni,[a] Mohamed Haouas,[a] Nathalie Leclerc,[a] Catherine Roch,[a] Clément Falaise,[a] Nicolas Suaud,[b] Laurent Ruhlmann,[c] R. John Errington[d] and Emmanuel Cadot,[a]

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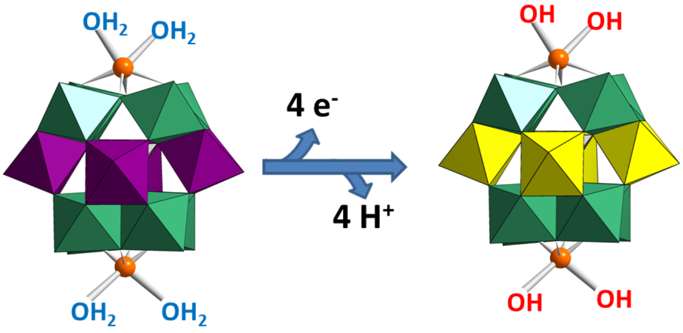
The development of efficient electrochemical devices for energy conversion processes requires a thorough understanding of the elementary sequences that pave the way of charge transfer reactions.[1] A wealth of evidences and examples has shown that electrons transfer promoted in metal oxides are strongly correlated with collateral effects contributing to local charge compensation, such as dynamic surface adsorption or alteration. In context, polyoxometalates (POMs), which are generally described as discrete groups of soluble metal oxides, can mimic to some extent the core-shell relationships behind the activity of functional MOx metal-oxide materials.[2]



In this communication, we report on an atomically precise Mo-V-Te Keggin-type assembly and we demonstrate how its magnetic, electrochemical and optical properties are counter-intuitive and highly correlated. Then electron transfer processes has been extensively studied by electrochemical methods in aqueous and non-aqueous solution. In addition, in situ and ex-situ characterization such as multinuclear NMR (^{29}Si and ^{125}Te), ESI-mass, UV-vis, magnetic studies, infrared and X-ray diffraction have been carried out. Data analysis and their interpretation were consistent with a PCET mechanism involving the concomitant hydrolysis of the externally exposed Te(IV) ion and the massive transfer of four electrons. In conclusion, the rich redox behavior of this Mo/V/Te compounds appears as ideal for modelling electrocatalytic dioxygen reduction, a key step within the fuel cell devices.

[1] S. Hou et al. *ChemElectroChem*, **2021**, *8*, 3433–3456.
[2] A. A. Fertig et al. *J. Am. Chem. Soc.*, **2021**, *143*, 15756–15768.

Conformational Analysis of Bidentate and Tridentate Ligands on Polyoxovanadates Modified by Coordination to The Vanadium

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Polyoxometalates are important in catalysis and as such will interact with a wide range of substrates and in many cases for intermediate structures covalently coordinated to the substrate. In some cases such substrates will stabilize the complex and an increasing number of such complexes are isolated and structurally characterized. In this work we examined the structural impact of the polyoxovanadates (POVs) on the conformation of bidentate and polydentate ligands. In this first analysis we focused on the selection of substrates that formed a six-membered ring with the vanadium atom. There are 386 structures in the Cambridge Crystallographic Data Centre (CCDC) with the O-V-O unit and only 28 structures with the O-V-N unit. In investigating these structures we categorize the structures based on the conformation of the six-membered ring being a chair (275 out of 386, 71%), a boat (59 out of 386, 15%), a half-chair (35 out of 386, 9%) and less than 5% of planar and non-POV structures. Therefore, it appears that the POV impact the conformation of the ligand bound to the POV. The 28 structures containing the O-V-N unit on the other hand show a very different conformations and in tetranuclear complex, the geometry change from a chair to a boat depending on whether the N-atom is exocyclic to the six-membered ring or bridging the six-membered ring. We seek to correlate these structural features to the reactivity of these complexes and their biological activities and our results will be discussed in this presentation.

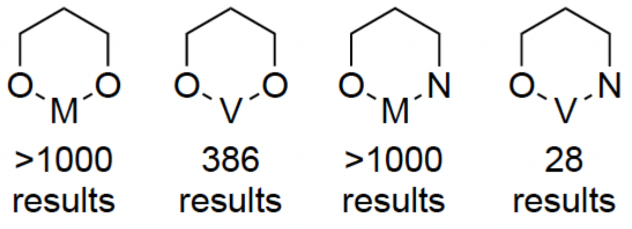

Figure 1: Overview of coordination complexes structures identified and categorized

Cybernetic Polyoxometalates

Leroy Cronin [a]*

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Here I report our conitnung quest to merge chemputer-controlled robotics, design-of-experiments, and machine learning to explore polyoxometalate (POM) architectures. By encoding synthetic steps as executable digital recipes, we present a paradigm where the platform iteratively explores multimetal oxide phase-space, executing and analysing many reactions per day while recursively updating a probabilistic map that links reagent stoichiometry, pH, redox history, and modular assembly pathways to emergent cluster nuclearities. Closed-loop optimisation steered by feedback prioritises reactions that appear novel. Together, this fusion of metal-oxide chemistry and autonomous reasoning lays the foundation for a scalable "operating system" for matter, where cybernetic feedback loops continuously refine both the molecular artefacts we make and the algorithms that make them, see Figure.

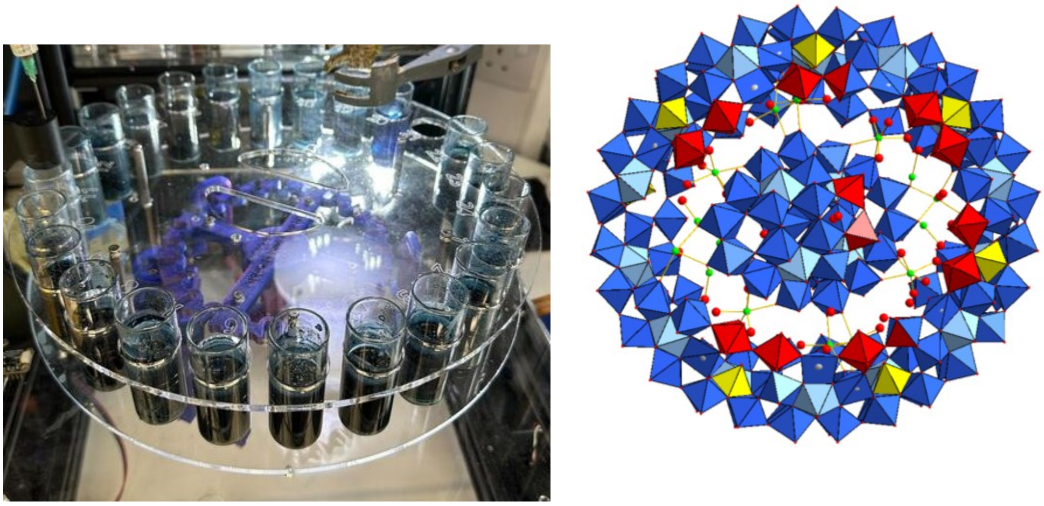

Figure: Photograph of the synthesis wheel in the POM-robot, left and the crystallisation of $\{Mo_{186}\}$ made in the robot

[1] D. He, Y. Jiang, M. Guillen-Soler, Z. Geary, L. Vizcaino-Anaya, D. Salley, M. D. C. Gimenez-Lopez, D. -L. Long, L. Cronin, *J. Am. Chem. Soc.*, **2024**, *146*, 28952–28960

[2] V. Lakhanpal, M. Guillén-Soler, L. Vilà-Nadal, D-L Long, L. Cronin, *J. Am. Chem. Soc.*, **2025**, *147*, 10.1021/jacs.5c00187

What's in Solution?

Insights into Non-Aqueous Tungstate Speciation.

Dominic Shiels,[a,b] Corinne Wills,[a] R. John Errington[a*]

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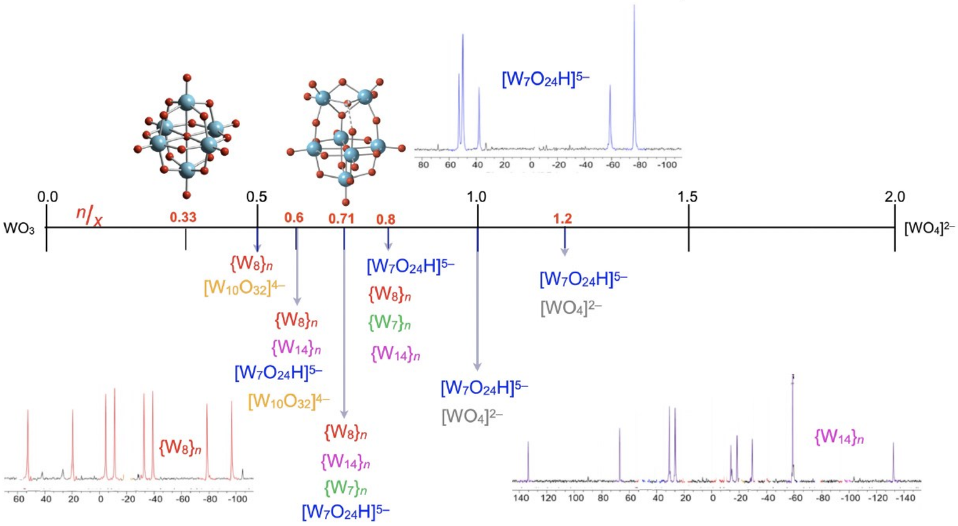
While our approaches to the synthesis of heterometal-substituted Lindqvist-type tungstates $[(L)MW_5O_{18}]^{n-}$ have facilitated a range of systematic reactivity studies, [1-4] they have also raised questions regarding the underpinning tungstate speciation in these non-aqueous solutions. [5] Our recent work has established that base degradation of $[W_6O_{19}]^{2-}$ provides a remarkably generic route to $\{MW_5\}$ substituted Lindqvist anions and prompted us to explore the intermediates generated during these reactions. The results of extensive ^{183}W NMR studies will be described and their implications for rational synthesis design will be discussed.

Figure: Representation of results from ^{183}W NMR studies of $[W_6O_{19}]^{2-}$ base degradation.



[1] D. Lebbie, T. Izuagie, M. Pascual-Borràs, B. Kandasamy, C. Wills, B. R. Horrocks and R. J. Errington, Inorg. Chem. 2025, 64, 2379-2393.
[2] N. V. Maksimchuk, V. Y. Evtushok, O. V. Zalomaeva, G. M. Maksimov, I. D. Ivanchikova, Y. A. Chesalov, I. V. Eltsov, P. A. Abramov, T. S. Glazneva, V. V. Yanshole, O. A. Kholdeeva, R. J. Errington, A. Solé-Daura, J. M. Poblet, and J. J. Carbó, ACS Catalysis, 2021, 11, 10589-10603.
[3] N. V. Maksimchuk, I. D. Ivanchikova, G. M. Maksimov, I. V. Eltsov, V. Yu. Evtushok, O. A. Kholdeeva, D. Lebbie, R. J. Errington, A. Solé-Daura, J. M. Poblet, and J. J. Carbó, ACS Catalysis, 2019, 9, 6262-6275.
[4] B. Kandasamy, P. G. Bruce, W. Clegg, R. W. Harrington, A. Rodríguez-Fortea, M. Pascual-Borrás and R. J. Errington, Chem. Eur. J. 2018, 24, 2750-2757.
[5] D. Shiels, M. Pascual-Borràs, P. G. Waddell, C. Wills, J. M. Poblet and R. J. Errington. Chem. Commun. 2023, 59, 7919-7922.

The Renaissance of super-reduced polyoxometalate chemistry

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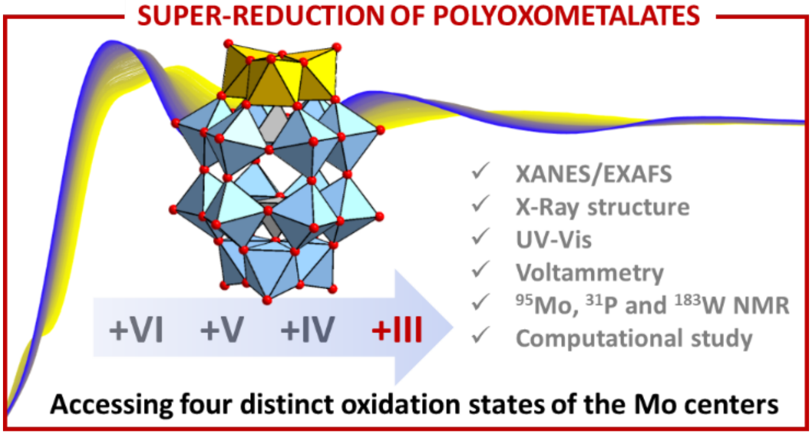
The increasing interest in polyoxometalates (POMs) for energy storage raises fundamental questions about their behavior when storing large numbers of electrons. Understanding how injected electrons influence POM structures and properties bridges the gap between theory and application. This field was pioneered by the "French school" of POM chemistry, yet many of its key claims remain unverified.[1] For instance, some studies suggest that Keggin-type POMs can accommodate 18, 20, 24, or even 32 electrons without significant structural changes.[2] However, structural data is currently available only for POMs reduced by up to six electrons. This highlights two major challenges: elucidating the structures of super-reduced species and uncovering structure-reducibility relationships.

In this communication, we present our latest discoveries in super-reduced POMs. First, we demonstrate that electron storage within metal-metal bonds is not exclusive to Keggin-type POMs, but to any other POM structures containing the triad unit {M_3O_{13}}, M = Mo or W.[3] Next, we show the first structural elucidation of super-reduced POMs containing multiple metal-metal bonded triads. Finally, we provide experimental and theoretical evidence for the gradual transition of the Mo oxidation state in a triad from VI to III without compromising the integrity of the POM structure.



[1] C. Falaise, *Eur. J. Inorg. Chem.* **2025**, e202400827.
[2] G. Hervé, *Ann. Chim.* **1971**, 287–296.
[3] G. Mpacko Priso *et al. Angew. Chem. Int. Ed.* **2023**, *62*, e202312457.

Polyoxometalate-Derived Material Systems for Sustainable Chemistry

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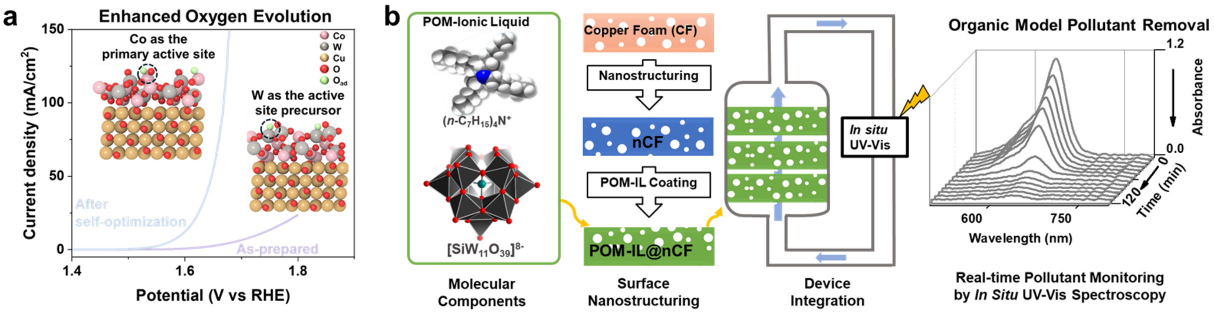
Polyoxometalates (POMs) have been widely used as well-defined single-source-precursors for water splitting electrocatalysts.[1] The anchoring of these catalysts to proper substrate surfaces is a key challenge to enable advanced water splitting performance. Here, we report self-assembled Co-W oxide nanostructures on a lab-synthesized CuO substrate through a single-step deposition approach. The resulting composite exhibits remarkable self-optimization behavior for OER, shown by significantly reduced overpotentials and enhanced current densities, accompanied with substantial increase in OER kinetics, electrocatalytically active surface area, surface wettability, and electrical conductivity. Under operating conditions, interfacial restructuring of the electrocatalyst reveals the in-situ formation of oxidized cobalt species as the true active site. Complementary density functional theory (DFT) calculations further demonstrate the formation of *OOH intermediate as the rate-determining step of OER, and highlight the adaptive binding of oxygen intermediates, which transitions from tungsten to cobalt sites during OER process (**Figure 1a**).[2]

Recently, polyoxometalate ionic liquid hybrid materials have been developed for multiple water pollutants removal in lab-scale small volumes, in which commercial silica was used as the support phase.[3]In order to achieve scalable water purification under operation, we have developed a 3d-printed open source flow-through device (**Figure 1b**).[4] In this work, a novel composite filter was designed based on nanostructured Cu foam, which was functionalized with a polyoxometalate ionic liquid (POM-IL) before being integrated into a modular flow reactor. The resulting composite filter (POM-IL@nCF) is highly efficient for both organic and inorganic pollutants removal from large water volumes (6 runs, 900 mL in total) under flow. Importantly, the open-source 3D printed device design allows the integration of in situ spectroscopy (e.g., UV-Vis) to monitor real-time reaction progress for mechanistic studies.

Figure: (a) Self-optimizing Co-W oxide deposited on CuO for enhanced OER. (b) continuous-flow water purification designed by integrating nanostructured Cu-foam surface-functionalized with POM-IL in 3D printed flow device.



[1] **D. Gao**, I. Trentin, L. Schwiedrzik, L. González, C. Streb*, *Molecules* **2020**, *25*, 157.
[2] C. Nickel, D. Troglauer, Z. Dallos, D. Abid, K. Sowa, M. Cichocka, U. Kolb, B. Mashtakov, B. FeiziMohazzab, S. Han, L. Prädel, L. Ci, D. Li, X. Lin, M. Hua*, R. Liu*, **D. Gao***, *Angew. Chem. Int. Ed.* **2025**, e202424074.
[3] S. Herrmann, L. De Matteis, J.M. de la Fuente, S.G. Mitchell, C. Streb*, *Angew. Chem. Int. Ed.* **2017**, *56*, 1667–1670.
[4] E. Oseghe, F. Guba, A. Misra, R. Gong, R. Liu, S. R. Waldvogel, D. Ziegenbalg*, C. Streb* and **D. Gao***, *Device* **2023**, *1*, 100020.

Electron And Proton Transfers To and From (Hybrid)–Polyoxotungstates

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The accumulation of reducing equivalents at a single–site is seen as a key step towards the development of catalytic materials that meet environmental and energy challenges.[1] Thus, the ability of polyoxometalates (POM) to behave as multi-electron acceptors makes them particularly attractive as (electro)catalysts or redox mediators for many important scientific and technological applications, including redox-flow batteries and artificial photosynthesis.

Within the POM-team@Paris, we have developed a special interest in studying the reduced forms of POMs, particularly in the context of photoinduced charge accumulation (use of a sacrificial electron donor) and the hydrogen evolution reaction (in the presence of protons).[2] To this end, photosensitised derivatives of W and Mo based Keggin and Wells–Dawson series have been designed but, to date, the mechanism and parameters favouring hydrogen evolution remain poorly defined. We are therefore interested in determining the conditions under which protons trigger the release of electrons from reduced POMs prepared by chemical, electrochemical or photochemical means.[3] Understanding these mechanisms is of major importance with a view to developing photo-assisted reduction catalysis in which the POM can act as a carrier of hydrogen atom for the selective interconversion of small molecules such as O_2/H_2O_2 and the transfer hydrogenation of organic substrates. Some of our results and perspectives will be presented in this communication.

[1] L. Hammarström, Acc. Chem. Res. 2015, 48, 840–850.
[2] C. Cariño, N. Moussa, S. Blanchard, A. Solé Daura, A. Proust, G. Izzet, submitted
[3] L. K/Bidi, A. Desjonquères, G. Izzet, G. Guillemot, Inorg. Chem. 2023, 62, 1935–1941

Speciation and Decomposition Pathways of Keplerate-Type Polyoxometalates in Aqueous Environments

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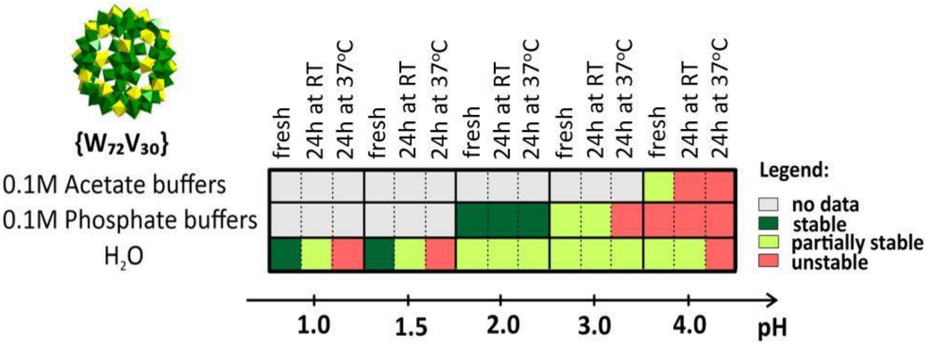
Understanding the solution behavior of large, reduced polyoxometalates (POMs) remains a major challenge, particularly for nanosized clusters such as Keplerate-type structures. POMs are known to be highly sensitive to changes in pH, redox conditions, and other environmental factors, which can lead to structural rearrangement or decomposition.[1] A more systematic approach is needed to reveal how these giant clusters behave under relevant solution conditions and to support their rational design for future applications. In this work, we present a comparative speciation analysis of two structurally related Keplerate-type compounds $\{Mo_{72}V_{30}\}$ and $\{W_{72}V_{30}\}$. Using a combination of ^{51}V and ^{31}P NMR, Resonance Raman spectroscopy, Electrospray Ionization Mass Spectrometry, and UV-VIS spectroscopy, we assessed their behavior under a wide range of experimental conditions, including variations in pH, buffer type, temperature, and incubation time. Each method provides complementary information, yet none alone is sufficient to fully characterize these complex systems. Only by integrating data from multiple sources can we achieve a comprehensive understanding of the structural transformations and stability of large POMs in solution. Our findings suggest that even subtle changes in composition can significantly impact solution stability and speciation pathways. $\{W_{72}V_{30}\}$ appears to be more resilient to decomposition (Figure 1), maintaining structural integrity across a broader range of conditions. These insights contribute to a more complete picture of the dynamic behavior of large POMs in solution and offer guidance for future synthetic and application-focused studies.



pH	1.0			1.5			2.0			3.0			4.0		
	fresh	24h at RT	24h at 37°C	fresh	24h at RT	24h at 37°C	fresh	24h at RT	24h at 37°C	fresh	24h at RT	24h at 37°C	fresh	24h at RT	24h at 37°C
0.1M Acetate buffers	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	🟨	🟥	🟥
0.1M Phosphate buffers	⬜	⬜	⬜	⬜	⬜	⬜	🟩	🟩	🟩	🟨	🟨	🟥	🟥	🟥	🟥
H_2O	🟩	🟨	🟥	🟩	🟨	🟥	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟥

Legend:
- ⬜ no data
- 🟩 stable
- 🟨 partially stable
- 🟥 unstable

Figure: Overview of stability of $\{W_{72}V_{30}\}$ Keplerate in highly acidic environment.

[1] N. I. Gumerova, A. Rompel, "Speciation Atlas of Polyoxometalates in Aqueous Solutions" Sci. Adv. 2023, 9, eadi0814.

The research reported in this work was funded by the Austrian Science Fund (FWF) (DOI 10.55776/P33927).

Viewing Biomolecular Interactions of Big Inorganic Molecules via Small Ones

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Life has evolved in the presence of mineral nanoparticles (NPs)—large inorganic species formed during the nucleation of sand minerals and metal oxides from solutions—suggesting a potentially significant role in metabolic processes. These particles exhibit striking size uniformity and enhanced surface charge, traits they share with the smallest oxide molecules, such as polyoxometalate ions (POMs), notably, Keggin ions falling themselves within the nanoscale. Our research systematically explored NP-protein interactions through structural and reactivity studies of POM-peptide and oligonuclear metal oxo-carboxylate-peptide complexes, using single-crystal X-ray diffraction, electrospray-MS, and NMR. We examined factors influencing peptide binding, including the polarity of metal-oxygen bonds and solution thermal history [1], peptide hydrophilicity/hydrophobicity [2], solution acidity and salinity [3], and the strength of intermolecular peptide bonding [4]. We focused particularly on revealing molecular mechanisms behind nanozyme activity in amino acid oxidation by nano tungsten and cerium oxides [5-7]. Additionally, we investigated the antiviral mechanisms of metal oxide NPs [8,9], identifying competition between protein and membrane phospholipid complexation as the key driving force.

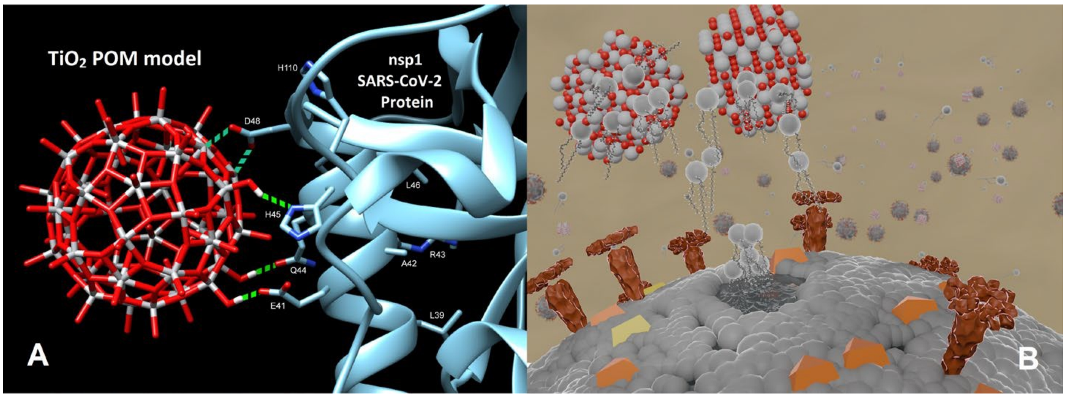

Figure: Anti corona virus activity of mineral NP via protein binding (A) [7] and via phospholipid binding (B) [8].

[1] Rominger K.M., Kessler V.G. et al., Eur. J. Inorg. Chem., 2019, 4297-4305.
[2] Greijer B., Kessler V.G. et al., Eur. J. Inorg. Chem., 2021, 54-61.
[3] Greijer B., Kessler V.G. et al., Dalton Trans., 2022, 51, 9511-9521.
[4] Greijer B., Kessler V.G. et al., Cryst. Growth Des. 2024, 24, 15, 6483–6491.
[5] Greijer B.H., Kessler V.G., CrystEngComm, 2025, 27, 1679-1686.
[6] Nefedova A., Kessler V.G. et al., Inorg. Chem. 2024, 63, 19, 8556–8566.
[7] Targonska S., Kessler V.G. et al., Inorg. Chem. 2025 (accepted).
[8] Agback P., Kessler V.G. et al., Nanoscale Adv., 2022,4, 1527-1532.
[9] Greijer B.H., Kessler V.G., Nanoscale, 2025, 17, 3728-3738.

Role of Included Moieties of VO_5-Based Polyoxovanadates

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Polyoxovanadates are the family of vanadium-oxygen cluster anions with high molecularity. Square-pyramidal VO_5 units show unique electrostatic interaction with the central moiety. Recently, we focused on the chemistry of the inside of the VO_5-based polyoxovanadates. With half-spherical dodecavanadates, $[V_{12}O_{32}]^{4-}$, the affinity of the organic molecules was evaluated. On the other hand, it is difficult to discuss the other properties of dodecavanadates with or without central moieties due to the low stability and the easy guest-exchange. We have successfully synthesized the fully spherical polyoxovanadate with an organic molecule (Figure). By the removal of the included neutral molecule, one of the VO_5 units was flipped. The flipped structures acted as a more efficient catalyst than the original one. [1] In addition, we found that the mobility of the inside nitrate was different among the octadecavanadate derivatives with the same structure. [2,3]

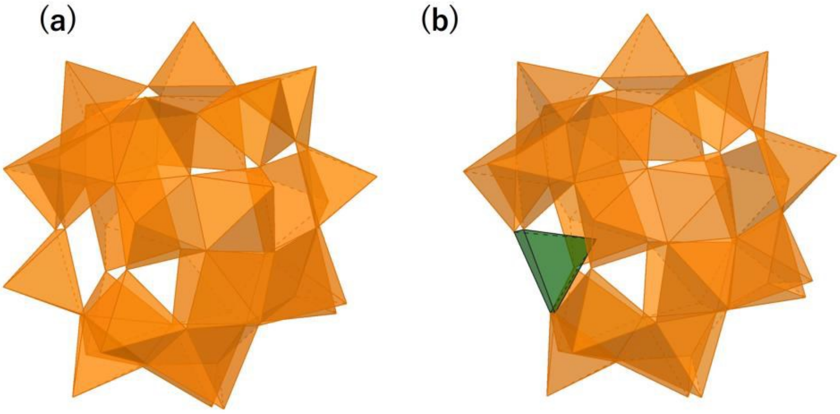

Figure: Structures of polyoxovanadates (a) with and (b) without an organic molecule

[1] Y. Kikukawa, M. Taga, Y. Horikawa, R. Mitsuhashi, Y. Hayashi, *Inorg. Chem*. **2025**, *64*, 344.
[2] I. Yoshida, R. Mitsuhashi, Y. Kikukawa, Y. Hayashi, *Inorganics*, **2024**, *12*, 61.
[3] I. Yoshida, Y. Kikukawa, R. Mitsuhashi, Y. Hayashi, *Nanoscale*, **2024**, *16*, 10584.

Recent Developments in Noble Metal-Oxo Cluster Chemistry

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Polyoxometalates (POMs) are discrete, anionic metal-oxo complexes and the conventional derivatives comprise early *d*-block metal ions in high oxidation states (e.g. $PMo_{12}O_{40}^{3-}P_2W_{18}O_{62}^{6-}$). In 2008 the first example of a POM based exclusively on square-planar coordinated Pd^{II} addenda was reported ($Pd_{13}O_8(AsO_4)_8H_6^{8-}$), which opened the door to the class of polyoxopalladates (POPs).[1] Over the year POP chemistry has developed rapidly due to the fundamentally novel structural and compositional features of POPs resulting in unprecedented electronic, spectroscopic, magnetic, and catalytic properties.[2] Besides the structural variety of POPs (e.g. cube, star, open-shell, dumbbell, bowl, wheel) their chemical composition can be modified by incorporation of different metal ion guests or substitution of the external hetero groups, resulting in around distinct 100 POPs known to date. More recently, neutral palladium(II)-oxo clusters (POCs) could be prepared,[3] followed by the first examples of cationic POCs.[4] Also, it was demonstrated that the aqueous POP chemistry can be extended to platinum and gold, resulting in the anionic, mixed platinum-palladium cluster $\{Pt^{IV}Pd^{II}_6\}$ and the platinum-gold cluster $\{Pt^{IV}Au^{III}\}$, as well as the mixed-valent derivatives $\{Pt^{IV}Pt^{II}\}$ and $\{Pd^{IV}Pd^{II}\}$, all prepared in aqueous solution using one-pot procedures.[5] The first examples of metal-organic frameworks (MOFs) using POPs as secondary building units (POP-MOFs) were also reported.[6] Here we present some recent developments in noble metal-oxo cluster chemistry.

[1] E. V. Chubarova, M. H. Dickman, B. Keita, L. Nadjo, M. Mifsud, I. W. C. E. Arends, U. Kortz, *Angew. Chem. Int. Ed.* **2008**, *47*, 9542.

[2] (a) P. Yang, U. Kortz, *Acc. Chem. Res.* **2018**, *51*, 1599−1608; (b) N. V. Izarova, M. T. Pope, U. Kortz, *Angew. Chem. Int. Ed.* **2012**, *51*, 9492.

[3] (a) S. Bhattacharya, U. Basu, M. Haouas, P. Su, M. F. Espenship, F. Wang, A. Solé-Daura, D. H. Taffa, M. Wark, J. M. Poblet, J. Laskin, E. Cadot, U. Kortz, *Angew. Chem. Int. Ed.* **2021**, *60*, 3632; (b) S. Bhattacharya, X. Ma, A. S. Mougharbel, M. Haouas, P. Su, M. F. Espenship, D. H. Taffa, H. Jaensch, A.-J. Bons, T. Stuerzer, M. Wark, J. Laskin, E. Cadot, U. Kortz, *Inorg. Chem.* **2021**, *60,* 17339.

[4] S. Bhattacharya, A. Barba-Bon, T. A. Zewdie, A. B. Müller, T. Nisar, A. Chmielnicka, I. A. Rutkowska, C. J. Schürmann, V. Wagner, N. Kuhnert, P. J. Kulesza, W. M. Nau, U. Kortz, *Angew. Chem. Int. Ed.* **2022**, e202203114.

[5] (a) J. Zhang, S. Bhattacharya, T. Nisar, V. Wagner, U. Kortz, *Inorg. Chem.* **2023**, *62*, 19603; (b) J. Zhang, S. Bhattacharya, B. E. Khsara, T. Nisar, A. B. Müller, M. Besora, J. M. Poblet, V. Wagner, N. Kuhnert, U. Kortz, *Inorg. Chem.* **2023**, *62*, 13184; (c) J. Zhang, S. Bhattacharya, A. B. Müller, L. Kiss, C. Silvestru, N. Kuhnert, U. Kortz, *Chem. Commun*. **2023**, *59*, 5918; (d) X. Ma, S. Bhattacharya, T. Nisar, A. B. Müller, V. Wagner, N. Kuhnert, U. Kortz, *Chem. Commun.* **2023**, *59,* 904.

[6] S. Bhattacharya, W. W. Ayass, D. H. Taffa, A. Schneemann, A. L. Semrau, S. Wannapaiboon, P. J. Altmann, A. Pöthig, T. Nisar, T. Balster, N. C. Burtch, V. Wagner, R. A. Fischer, M. Wark, U. Kortz, *J.* Am. Chem. Soc. **2019**, 141, 3385.

Structural Characterization and Controlled Deposition of Metal Oxide Ions onto Surfaces Using Mass Spectrometry

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Controlled deposition of complex ions onto surfaces enables the study of fundamental processes essential for designing functional 2D and 3D interfaces, with applications spanning materials science, energy production, and other fields. Ion soft landing, a technique that deposits intact polyatomic ions onto surfaces with or without charge retention, is a powerful tool for exploring the mechanisms underlying ion deposition. The precise control of ion composition and kinetic energy in soft landing makes it an attractive approach for surface modification. We have demonstrated the unique potential of this technique by designing high-performance 3D electrochemical interfaces through the mass-selective deposition of metal oxide ions onto porous carbon electrodes.[1] Additionally, mass-selective ion deposition onto specially designed electrochemical cells has enabled the investigation of redox properties in substituted metal oxide species that are otherwise challenging to isolate using conventional methods.[2] Mass spectrometry further enhances these studies by providing detailed insights into the structures of isolated metal oxide clusters in the gas phase. Using tandem mass spectrometry (MS/MS) and ion mobility spectrometry, we can analyze the structures of metal oxides in complex multicomponent mixtures without the need for prior separation.

[1] Das, A.; Samayoa-Oviedo, H. Y.; Mohapatra, M.; Basu, S.; Laskin, J. Enhancing Energy Storage Capacity of 3D Carbon Electrodes Using Soft Landing of Molecular Redox Mediators. Small **2024**, 20, 2311585.

[2] Wilson, S. M.; Petel, B. E.; Schreiber, E.; Maiola, M. L.; Su, P.; Matson, E. M.; Laskin, J. Electrochemical and Structural Characterization of Soft Landed Tungsten-Substituted Lindqvist Polyoxovanadate-Alkoxides. Chemistry – A European Journal **2023**, 29, e202203440.

An ultra-stable heteropoly blue built by covalent grafting of arylamines to Ta/W POM via boronic acids

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Heteropoly blues (HPBs) are a subclass of reduced polyoxometalates (POMs). Their unique electronic structure, wide spectral absorption and efficient light response make them promising photosensitive materials. However, their susceptibility to oxidation and instability in air have limited their applications. The design and synthesis of stable HPBs are therefore of high importance[1]. Recently, we developed a new synthetic strategy to functionalize POMs with aromatic boronic acids and reported a range of interesting compounds including POM nanocapsules, a POM-boronic acid-polymer and POM-boronic acid supramolecules[2, 3].

Here, an ultra-stable HPB $NaH_{27}[P_2W_{15}Ta_3O_{62}]_4 \cdot (C_6H_4BNH_2)_4 \cdot nH_2O$ (**1**) was obtained by covalently modifying $[P_2W_{15}Ta_3O_{62}]^{9-}$ with 3-aminophenylboronic acid (3-APBA). The polyanion of **1** is constructed by four $\{Ta_3W_{15}\}$ units linked by four 3-APBA moieties resulting in a tetrahedral aggregate. The short N···O distance of 2.83 Å indicates the presence of intramolecular hydrogen bond interaction (Fig. 1a). It is interesting that the almost colorless crystals of **1** are photoactive even under indoor lighting and quickly change to dark blue or even black (**1-HPB**). **1-HPB** is extremely stable and the dark color of **1-HPB** does not fade when exposed to air or pure oxygen, even under heating (Fig. 1b). XPS analysis suggests the presence of W^{5+} in **1-HPB**. In addition to the signal of W^{5+} at g = 1.908, the EPR spectrum of **1-HPB** shows a significant signal at g = 2.003, which is assigned to the aniline radical (Fig. 1c). Based on a series of experimental and theoretical calculations results, we propose that the intramolecular proton coupled electron transfer between 3-APBA and $\{Ta_3W_{15}\}$ as well as the presence of stable aniline radicals stabilize the electron-hole separation state in **1-HPB**. **1-HPB** showed high photothermal conversion efficiency and reached a temperature of 190 °C within one minute under irradiation with an 808 nm infrared laser (Fig. 1d). Studies on the photothermal catalytic performance of **1-HPB** are ongoing in our laboratory.

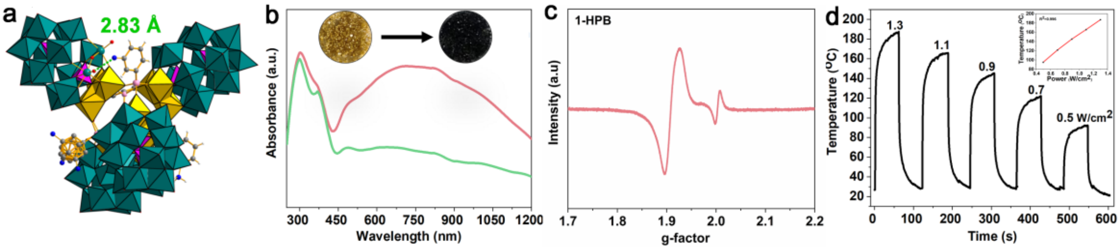

Figure 1: a) Combined polyhedral/ball-and-stick representation of **1**; (b) Diffuse reflectance spectra of **1** and **1-HPB**; (c) EPR of **1-HPB**; and (d) Temperature rises of **1-HPB** at different NIR laser intensities.

[1] T. Yamase, *Chem. Soc. Rev*. 1998, 98, 307-325.
[2] S. Li, Y. Zhou, N. Ma, J. Zhang, Z. Zheng, C. Streb, X. Chen, *Angew. Chem. Int. Ed.* 2020, 59, 8537–8540.
[3] S. Li, Y. Ma, Y. Zhao, R. Liu, Y. Zhao, X. Dai, N. Ma, C. Streb, X. Chen, Angew. Chem., Int. Ed., 2023, 62, e202314999.

Robotic Exploration of Molybdenum Blue Polyoxometalates

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The enormous chemical space for assembling gigantic polyoxometalates (POMs) presents a major challenge for systematic exploration, as many synthetic procedures are empirically derived with limited rationale. Investigating the complex multicomponent reactions that yield new-dimensional POMs demands precise control over molecular self-assembly and crystallization. This is especially true for discovering Molybdenum Blue POMs (MBs), which consist of multiple building blocks and supporting units formed through self-assembly or modified by organic ligands. Such discoveries require multi-parameter optimization across intricate reaction conditions. In this study, a robotic platform enabled rapid exploration of MB formation, conducting around 1000 experiments efficiently. This approach identified a group of MB POMs that are difficult to obtain through conventional random synthesis, demonstrating the platform's potential for targeted discovery. The resulting MBs incorporate diverse guests via supramolecular interactions or covalent bonding with organic ligands (e.g., amino acids). Their macrocyclic structure allows the formation of varied architectures, including 0D units, 1D arrays, and 2D layers—exemplified by the $\{Mo_{154}\}$ macrocycle forming a 2D mesh, shown in Figure 1. Detailed robotic experimental designs and dat analyses are presented

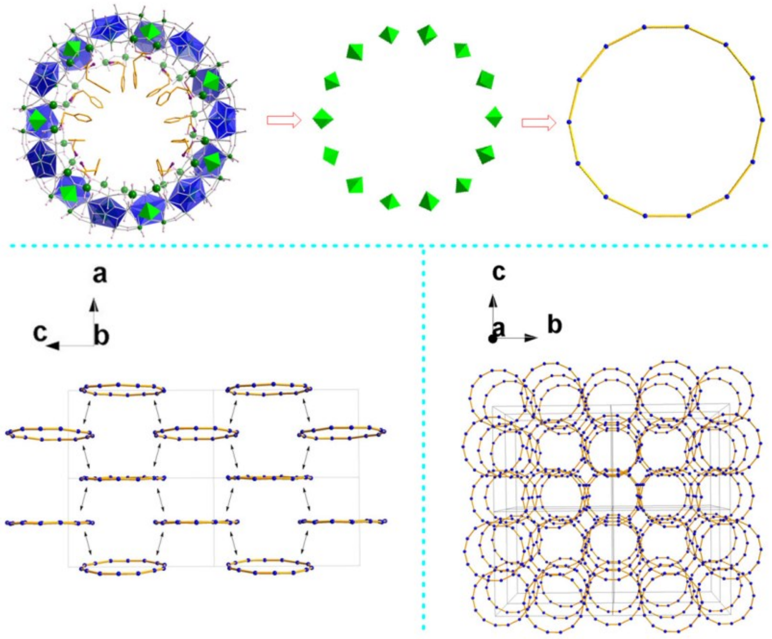

Figure 1: Representative packing diagrams of {Mo154} wheels in solid states. Up) {Mo154} wheels are symbolised by the ring of the 14 backbone {Mo1} centres; bottom-left) 2D layer of wheels on the crystallographic ac plane, the dual arrows indicate the places of single Mo-O-Mo bridges between {Mo154} wheels; bottom-right) view down along the crystallographic a axis.

[1] A. Muller, J. Meyer, E. Krickemeyer and E. Diemann, Angew. Chem. Int. Ed. Engl., 1996, 35, 1206-1208.
[2] D.-L. Long and L. Cronin, Adv. Inorg. Chem., 2021, 78, 227-267.
[3] D. He, Y. Jiang, M. Guillen-Soler, Z. Geary, L. Vizcaino-Anaya, D. Salley, M. D. C. Gimenez-Lopez, D.-L. Long and L. Cronin, J. Am. Chem. Soc., 2024, 146, 28952-28960.

DESC: an Automated Computational Strategy to Efficiently Account for the Counterion Effect in Solution. Application to the Electronic Structure of POMs

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Molecular properties and dynamics in solution are influenced by the solvent and other species, such as electrolytes, which can lead to (co-)solute aggregation. Quantum Mechanical (QM) calculations incorporating ordinary implicit solvent models (ISM) generally provide a good description of a molecule's electronic structure in solution. However, ISMs lack the specificity to differentiate effects due to various cation types (e.g., Cs^+ vs TBA^+), failing to capture these variations at the electronic level. Addressing this limitation often involves explicitly adding counterions to QM calculations, which presents multiple challenges including the accurate positioning of counterions, numerical convergence, prolonged computational times for large counterions, and the necessity of computing several replicas to achieve reliable average properties.

To overcome these obstacles, we propose a novel, automated approach called DESC (Dynamic Environment in Solution by Clustering) [1] that integrates extensive data from classical Molecular Dynamics (MD) simulations directly into routine QM calculations. This method allows for detailed, counterion-specific consideration, providing a more precise and cost-effective solution than ISMs and traditional explicit counterion models. Particularly advantageous for systems where counterions and the target solute aggregate, our approach facilitates significant physicochemical insights with low computational demands. This contribution presents MD data for several polyoxometalate/counterion/solvent systems, the modus operandi of our approach and its performance. Our results are compared to conventional QM/ISM calculations, showcasing its chemical representativeness and the saving in computational cost.

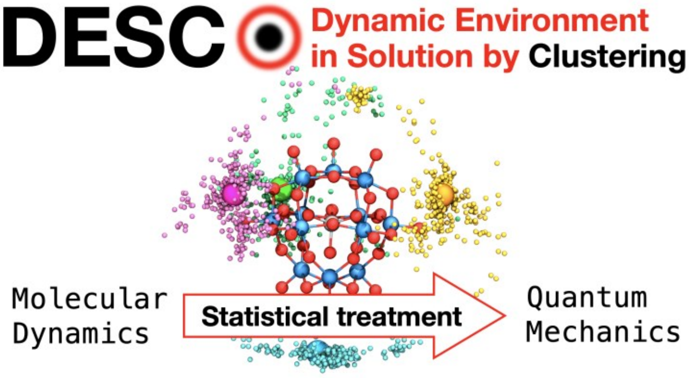

Figure: DESC: a user-friendly program that takes a Molecular Dynamics simulation, analyzes aggregation in a few seconds, and generates ready-to-run quantum mechanical routine

[1] A. Masip-Sánchez, J. M. Poblet, X. López, J. Chem. Theory Comput. 2025, 21, 2472-2486

Proton Coupled Electron Transfer in Polyoxometalates

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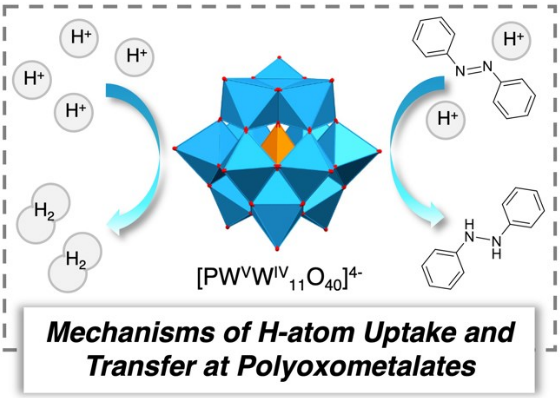
While the dynamics of proton- and electron-transfer at metal oxides have been studied extensively in the field of electrochemical energy storage, researchers have only very recently begun to understand how these process play out on molecular length scales and in the presence of small-molecule substrates. The latter is notable, considering that redox-active metal oxides are widely used in thermal and electrochemical catalytic processes. Further advances in the effective use of metal oxides in electrochemical catalysis will require improved understanding of elementary charge-transfer reaction mechanisms. Our research team has been studying the interfacial reactivity of reducible metal oxides using atomically precise, polyoxometalate clusters as models for extended materials. These self-assembled clusters are well-positioned to provide insight into the surface chemistry of reducible metal oxides. This talk will focus on the synthesis and characterization of reduced POMs, which have provided our research group with opportunities to investigate factors that dictate mechanisms of H-atom uptake and transfer at metal oxide surfaces. Emphasis will be placed on structural modifications to POMs that result in perturbations of the *mechanism* of H-atom uptake at the surface of the cluster. Collectively, these studies inform our understanding of proton-dependent reactivity of metal oxide surfaces, toward the design of materials capable of converting chemical pollutants into energy-rich fuels.



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Design & Heterogenization of Molecular Chalcoxides for Electro- & Photochemical H2 Production

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The requirement for novel materials with excellent electrochemical and/or photochemical performance to meet these needs for alternative clean energy sources has never been so crucial. Demand for energy is predicted to double by 2050, and the associated increase in CO2 emissions could have calamitous effects on the environment.[1] Utilization of hydrogen as energy source is a viable alternative to fossil fuels however, the sustainable electrochemical production of hydrogen presents a great challenge. Here, we present a design approach that demonstrates the high efficiency and stability of molecular catalysts and our endeavours to optimize these molecular moieties for the hydrogen evolution reaction.[2] Crucially, the development of a straightforward and cost-effective synthetic strategy for composite catalytic systems is essential to guarantee scalability for larger-scale applications.[3]

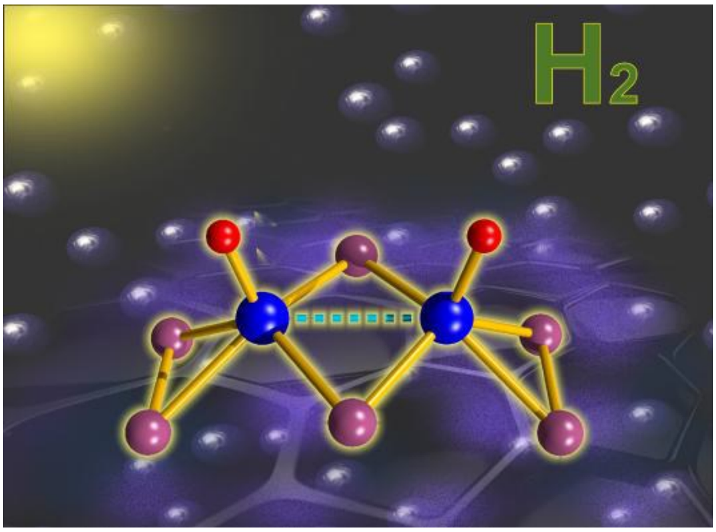

Figure: Ball-and-stick representation of: $[Mo_2O_2(\mu\text{-}Se)_2(Se_2)_2]^{2-}$@SWCNT. Colour code: Mo, Blue; X (S, Se), plum; O, red.

[1] N. S. Lewis, D. G. Nocera. Proc. Natl. Acad. Sci. USA, 2006, 103, 15729.
[2] J. McAllister, N. A. G. Bandeira, J. McGlynn, A. Ganin, Y-F. Song, C. Bo, H. N. Miras Nature Commun. 2019, 10, 370.
[3] M. Gray, Y-F. Song, H. N. Miras Chem. Commun., 2025, 61, 1822.

Developing Organo-POM Materials for Health, Heritage, and the Environment

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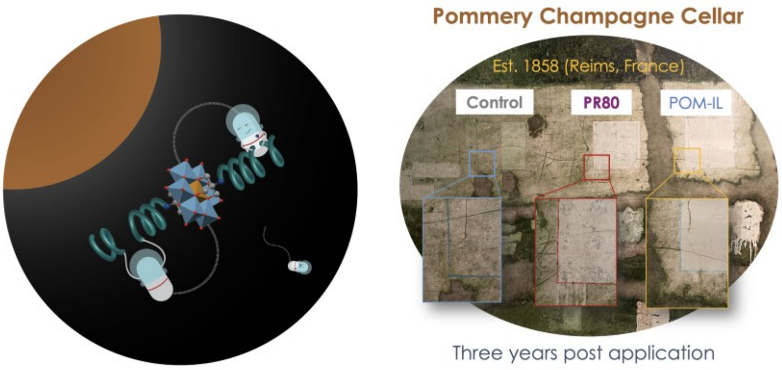
The organo-functionalization of polyoxometalates (POMs) represents an effective approach for obtaining diverse self-asembled structures and arrays of practical hybrid or composite materials with tailored surface chemistry, charge, polarity, and redox properties.[1] Such hybrid materials also possess relevant biological activity: they can cross lipid membranes, interact with proteins, and are producers of reactive oxygen species; making them suitable for a variety of end uses as functional materials for real-world applications.[2,3] Here I will show how we have been developing and applying POM-ILs as multifunctional coatings to prevent biodeterioration of stone-based cultural heritage objects and architectures (TRL 5-6).[4] Our research has shown how POM-based coatings eliminate specialist microorganisms like Cyanobacteria, Chlorophyta and Ascomycetes over a three-year period, but also stimulate the appearance of resistance genes in generalists such as Pseudomonadota.[5] I will also discuss our ongoing collaborative efforts to advance the incorporation of POM materials into universal pollutant removal devices using POM-functionalized porous substrates[6] and the development of functional materials for mitigating microbiologically-influenced corrosion (MIC) of metal surfaces.



Left: "POMlymers", covalent POM-polypeptide hybrids, prepared through the ring-opening polymerization of amino acid *N*-carboxyanhydrides on POM anions. Right: Modular POM-ILs act as precision biocides that prevent microbial colonization of lampenflora biofilm growth over a three year period *in situ* in the Pommery Champagne Cellar.

[1] H. Soria-Carrera, E. Atrián-Blasco, R. Martín-Rapún and S. G. Mitchell, *Chem. Sci.* **2023,** 14, 10-28.
[2] H. Soria-Carrera, E. Atrián-Blasco, S. G. Mitchell and R. Martín-Rapún, *Nanoscale* **2022**, 14, 5999–6006.
[3] C. McWilliams, I. Franco-Castillo, A. Seral Ascaso, S. García-Embid, M. Malefioudaki, J. G. Meier, R. Martín-Rapún, and Scott G. Mitchell, *RSC Pharmaceutics*, **2024**, 1, 755-764.
[4] S. Eyssautier-Chuine, I. Franco-Castillo, A. Misra, C. Streb, S. G. Mitchell, *STOTEN* **2023,** 884, 163739.
[5] S. Eyssautier-Chuine, S. G. Mitchell, et al, *ChemPlusChem* **2025** *(under review)*.
[6] C. Amonte, N. Gracia-Vallés, J. Gurauskis and S. G. Mitchell, *Device* **2025** 10.1016/j.device.2025.100725.

Polyoxovanadates as Redox-active Devices in Molecular Electronics Applications

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Polyoxovanadates (POVs) as molecular metal oxide nanoparticles have emerged within the last years to a very promising species for several applications in the field of molecular electronics like information data storage and sensor technology. Their supreme redox-activity in combination with high chemical stability and easy functionalization makes them to potential molecular multi-level switching devices, working at room temperature and at low electric potentials [1]. The discrete electronic nature of POVs is the ideal fundament for the development of new capacitive and resistive data memories based on molecular electronics [2]. By stabilizing additional electronic charge via electron absorption from external sources even their application for high-capacitive energy conversion and energy storage is possible [3,4]. POVs are typically polynuclear vanadium-oxygen anions, which results in the need of counter cations for charge stabilization. The interaction of both ionic components may also offer possibilities for their usage as neuromimatic emulators in future neuromorphic computing applications [5].

This presentation will give an introduction into the electronic properties of differently functionalized POVs and their adsorption behavior on various substrate surfaces. The complex interplay with the counter cations of the anionic POV species can make a controlled surface deposition in form of single molecules and closed layers to a challenging task. In that context, suitable deposition techniques of the charged POV/cation complexes from solution and from the gas phase together with the influence of deposition parameters will be discussed as well as feasible ways to integrate POVs into future technical devices.

[1] O. Linnenberg, M. Moors, A. Notario-Estévez, X. López, C. de Graaf, S. Peter, C. Baeumer, R. Waser, K. Monakhov, *J. Am. Chem. Soc.* 2018, **140**, 16635–16640.
[2] M. Moors, K. Monakhov, *ACS Appl. Electron. Mater.* 2024, https://doi.org/10.1021/acsaelm.3c01751.
[3] M. Anjass, G.A. Lowe, C. Streb, *Angew. Chem. Int. Ed.* 2021, **60**, 7522–7532.
[4] T. Zhou, L.-L. Xie, Y. Niu, H.-R. Xiao, Y.-J. Li, Q. Han, X.-J. Qiu, X.-L. Yang, X.-Y. Wu, L.-M. Zhu, H. Pang, X.-Y. Cao, *Rare Met.* 2023, **42**, 1431–1445.
[5] M. Moors, K. Monakhov, *Mater. Today* 2024, https://doi.org/10.1016/j.mattod.2024.10.007.

Polyoxometalates as Electrocatalysts for Small Molecule Activation

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The activation of small molecules such as O_2, H_2O, N_2 and CO_2 play an important role to towards more sustainable chemical transformations. Activation of these molecules requires a change in their oxidation state and thus are attractive for activation with first-row redox transition metals. Renewable energy resources can provide the driving force, leading to electrocatalytic transformations. Our research on the cathodic, reductive activation of O_2, N_2, and CO_2 as well as the anodic, oxidative activation of H_2O using transition metal substituted polyoxometalates as unique molecular electrocatalysts will be presented.

Cathodic activation of O_2: Paradoxically, monooxygenase enzymes activate O_2 typically via a twoelectron reductive pathway. Surprisingly, cathodic electrocatalysis using H_2O as a proton and electron source is almost unreported. We found that iron Keplerates, $\{Fe_{30}W_{72}\}$ can be used as electrocatalysts for the oxidation of light alkanes and alkenes in water, for example ethane to acetic acid. Mechanistic studies have revealed that reaction intermediates have reactivity profiles similar to those observed for Compound I of cytochrome P-450. We have also found that, tetra-copper substituted polyoxometalates also are very efficient electrocatalysts for the cathodic activation of O_2 and show reactivity profiles similar to those of the previously studied iron Keplerates.

Reduction of CO_2: The removal of CO_2 from the atmosphere through capture is a feasible technology, however, is not sustainable due to the high cost of the process and the low value of captured CO_2. Therefore, the transformation of CO_2 to a higher valued product is a requirement for the CO_2 abatement problem. we will focus on the two-electron reduction to CO, since the latter is an important intermediate in a multitude of energy and petrochemical related processes. We have prepared a series of trimetallo substituted polyoxometalates that can catalyze the reduction of CO_2 to CO with very low overpotentials using even low concentrations of CO_2 via a capture/reduction sequence.

Reduction of N_2: A N_2 to NH_3 electrocatalytic reduction using an inorganic molecular catalyst, a tri-iron substituted polyoxotungstate $\{SiFe_3W_9\}$ and H_2O as electron and proton donor will be presented. The catalyst requires the presence of Li_+ or Na_+ cations as promotors through their binding to $\{SiFe_3W_9\}$. Electrochemical studies show that the alkali metal cation enables the decrease of the redox potential of $\{SiFe_3W_9\}$ allowing the activation of N_2. Spectroscopic NMR, CV, Raman, IR and UV-vis measurements and MD/DFT calculations have lead to mechanistic insights.

H_2O as oxygen donor: Although water oxidation is widely researched via its four-electron oxidation as a necessary component for a hydrogen evolution reaction, we have found that reactive intermediates formed on electrode surfaces can be “captured” using cobalt-substituted polyoxometalates leading to important electrochemical transformations such as alkene epoxidation. This kind of reactivity and its simplicity obviates the use of even relatively benign oxidants such H_2O_2 since the latter is still produced using H_2 from steam reforming.

Hierarchical self-assembly of hybrid inorganic-organic polyoxometalate amphiphiles: from 0D micelles to 3D network materials

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Controlling the aggregation of functional molecules in solution allows the design and fabrication of nanomaterials with varied structures, dimensions, compositions, and properties. The controlled selfassembly of polyoxometalates into dynamic superstructures is a particularly attractive target given their potential application in photochemical and electrochemical energy devices. Herein, we report the hierarchical self-assembly of $K_6[P_2W_{17}O_{59}(C_6H_4PO_4R)_2]$ (where $R = C_nH_{2n+1}$ ($n = 10–20$)) organicinorganic hybrid polyoxotungstates. The clusters spontaneously self-assemble under aqueous conditions to from spherical or cylindrical micelles depending on the length of the carbon chain and the reaction conditions.

The cylindrical micelles demonstrate remarkable structural uniformity and are driven by electrostatic repulsion to self-organise into grid architectures. Intricate higher-order structures can be isolated in the solid state from aqueous solution of $\{W_{17}C_n\}$ micelles.

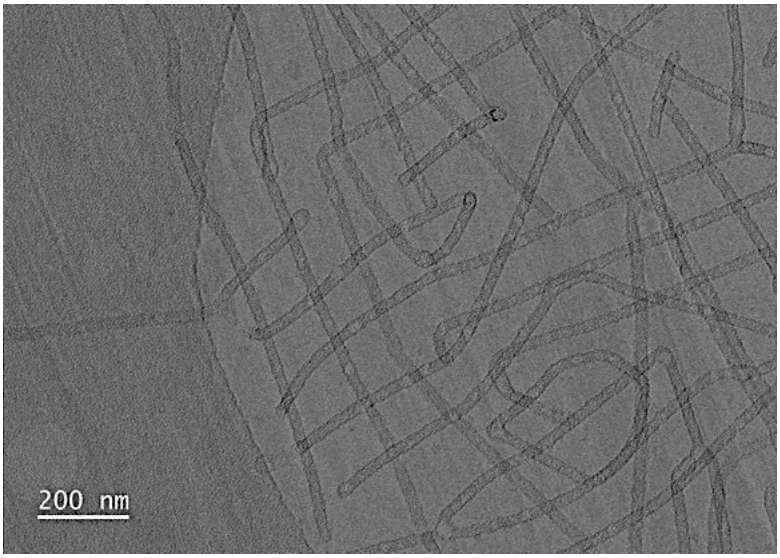

Figure 1: Cryo-TEM image of cylindrical POM micelles.

Contributions to Group VII oxocluster and POM chemistry

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Group VII including Mn, Tc and Re, lie at the crossroads between polyoxometalates and metal-metal bonded complexes, that are exemplified by dimers and hexamers of groups V through IX. Polyoxometalates can likewise contain metal-metal bonds; for example, Mo^V-Mo^V dimers in the molybdate Keplerates, and W^{IV}-W^{IV}-W^{IV} trimers in reduced tungstate Keggin derivatives. There have been inroads into Tc/Re in intermediate oxidation states (IV, V, VI) as polyoxometalates. For example, both Michael Pope and Lynn Francesconi have synthesized and characterized $Tc/Re^{V/VI}$ substituted POMs. During the past few years, there have been some advances in so-called pure group VII POM chemistry, in particular the isolation and characterization of Tc_{20}, $[Tc_4O_4(H_2O)_2(TcO_4)_{14}]^{4-}$. We have made additional advances including Tc-substituted POMs, hybrid uranyl-Tc clusters, and mixed metal Tc/Re clusters. In addition, we have isolated perrhenate/pertechnetate capped U^{VI} and U^{IV} isolated clusters and clusters linked into frameworks, some of which are highlighted in **figure 1**. I will present an overview and highlights of these recent studies, with a focus on reduction chemistry and coordination chemistry important to oxocluster assembly, determined through small-angle X-ray scattering, single-crystal X-ray diffraction and other supporting techniques. I will additionally compare reduction and coordination behavior of Tc and Re, which initially shows that rhenium is an imperfect surrogate for technetium. Computation helped define both orbitals of POM-Tc interactions, as well as Tc oxidation state in these studies.

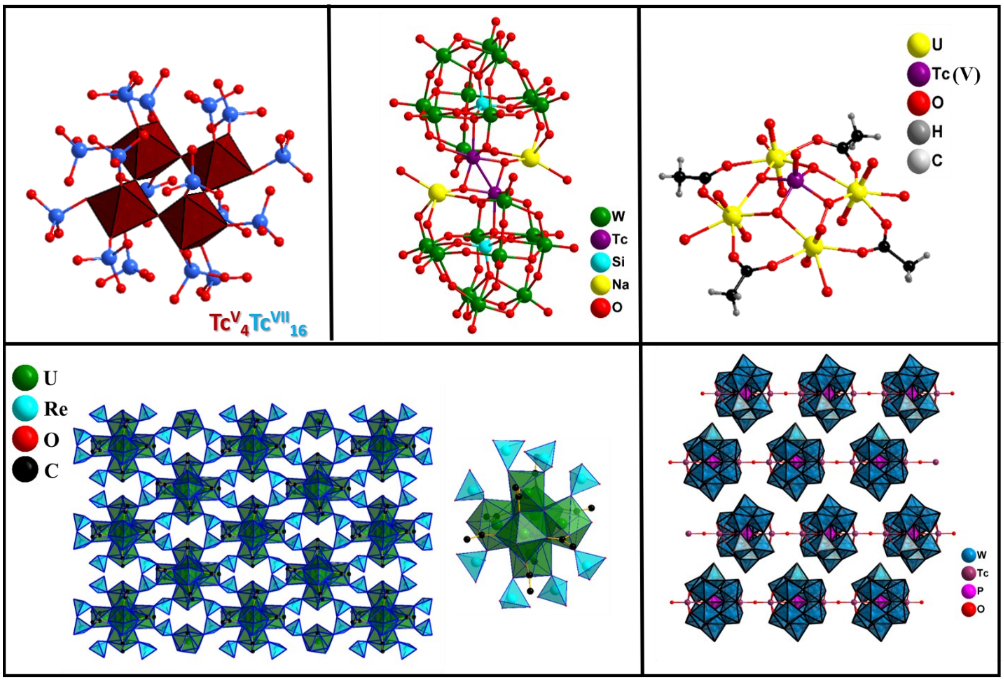

Figure 1: Array of Re/Tc containing oxoclusters and POMs..

Cyclic Silicomolybdate That Encapsulates Monoanions and Its Related Compounds

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The cyclic silicohexamolybate, $[HOSiO_3Mo_6O_{18}(O_2CCH_3)_3]^{6-}$, encapsulates various monoanions (Cl^-, Br^-, I^-, and NO_3^-) within its cavity, which is surrounded by the methyl groups of the acetate ligands. Its encapsulation preference follows the order of $Cl^- > NO_3^- > Br^- > I^- > H_2O > F^-$. Single crystal neutron diffraction revealed that H_2O was encapsulated in the sample intended for F^- encapsulation, suggesting that F^- can hardly be encapsulated. Notably, the similar compound $[HOPMo_6O_{21}(O_2CCH_2NH_3)_3]^{2-}$, reported by Kortz [1], encapsulates a K^+ cation in its cavity. Although the NCS^- anion was not encapsulated in the cavity, it co-crystallized with the cyclic silicohexamolybdate.

The N_3^- anion neither enters the cavity nor co-crystallizes. A similar preparation aimed at N_3^- encapusulation resulted in the formation of the tetramolybdate, $[Mo_4O_{12}(N_3)_2(O_2CCH_3)_2]^{4-}$. This is the second oxoazide of molybdenum(VI), following $[(bipy)MoO_2N_3]_2O$ [2], and the first azide of polyoxomolybdenum(VI). Based on the structures of $[Mo_4O_{12}(N_3)_2(O_2CCH_3)_2]^{4-}$ and other smaller polyoxometalates, factors influencing the nuclearity of polyoxometalates will be discussed.

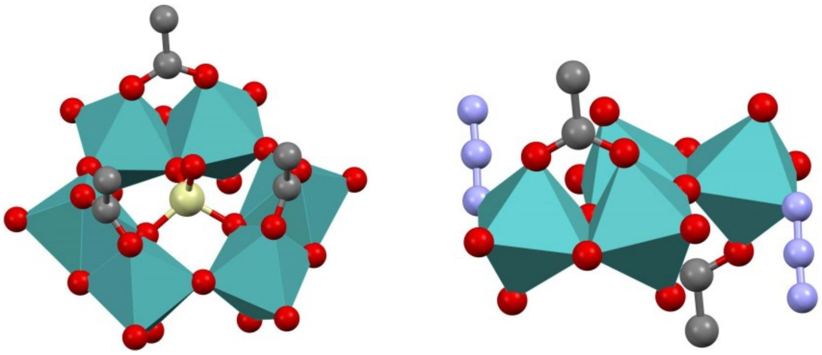

Figure: Structures of $[HOSiO_3Mo_6O_{18}(O_2CCH_3)_3]^{6-}$ and $[Mo_4O_{12}(N_3)_2(O_2CCH_3)_2]^{4-}$.

[1] U. Kortz, J. Vaissermann, R. Thouvenot and P. Gouzerh, *Inorg. Chem.*, **2003**, *42*, 1135-1139.
[2] R. Haiges, J. Skotnitzki, Z. Fang, D. A. Dixon and K. O. Christe, *Angew. Chem. Int. Ed.*, **2015**, *54*, 9581-9585.

Mechanochemical Approaches to Polyoxometalate Chemistry

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The use of mechanical forces to drive chemical reactions, *i.e.* mechanochemistry, has emerged during the last decade due to its potential to provide green and sustainable synthetic methods, involving solvent-free procedures, easy handling, high conversion rates and minimal waste production. In addition, it could enable access to compounds that are otherwise difficult or impossible to obtain in solution.[1] However, its application to the synthesis or reactivity studies in POM chemistry remains underexplored, with only a few reports describing the synthesis of molybdates, cation exchange or POM encapsulation within metal-organic frameworks. [2],[3]

In this talk, I will present a solvent-free, mechanochemical approach for the reduction and the addition of capping groups to Keggin-type POMs, enabling solvent-free access to reactive and electron-rich molecular metal oxides.[4] A variety of reducing agents and capping groups have been examined, and the electronic properties and reactivity of the resultant electron-rich nanoscale metal oxides have been analysed, including electron exchange rates in solution, where the nature of countercations was found to significantly influence electron exchange dynamics.

Additionally, I will discuss our recent advances in using mechanochemistry as a direct route to ^{17}O enrichment of different types of POMs. I will demonstrate how the type of POM, the identity of the addenda atom, and milling duration significantly affect enrichment efficiency, providing an alternative to traditional ^{17}O enrichment methods for ^{17}O NMR applications.

Overall, our findings highlight the potential of mechanochemistry as a sustainable, versatile, and scalable platform for the design and study of POM-based functional materials, opening new directions beyond conventional solution-based approaches.

[1] S. L. James, et al., *Chem. Soc. Rev.* **2012**, *41*, 413-447.
[2] M. Wilke, et al, *Chem. Sci.* **2022**, *13*, 1146-1151.
[3] X. Zhao, et al., *Inorg. Chem.* **2017**, *56*, 14506-14512.
[4] M. Pascual-Borràs, et al., *J. Am. Chem. Soc.* **2024**, *146*, 26485-26496.

Polyoxometalate-Loaded Carboxymethyl Chitosan Nanoparticles with Anticancer Activity

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Polyoxometalates (POMs) have emerged over the last half a century as promising biomedicinal agents ([1], [2], [3]), due to their ability to interact with biomolecules and the tunability of their properties ([1], [2], [4], [5], [6]) In this study, a small series of polyoxometalates and carboxymethyl chitosan nanoparticles are explored for their anticancer activity through extended viability assays, in which the cell viabilties are investigated for one or two days post 24 h of treatment. Cytotoxicity based on tungsten nuclearity and structure-type is investigated. Among the tested species, $[NaP_5W_{30}O_{110}]^{14-}$ exhibited significantly higher cytotoxicity towards the PC-3 prostate cancer cells, with an IC_{50} value ca. 5 times lower (per mole of tungsten) than smaller tungstates ($[WO_4]^{2-}$, $[PW_9O_{34}]^{9-}$, and $[PW_{12}O_{40}]^{3-}$). $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ showed generally reduced cytotoxicity, suggesting that the heteroatom influences the activity.

Encapsulation of POMs in 100-250 nm carboxymethyl chitosan nanoparticles ([7], [8]), characterized by cryo-TEM, DLS, and other spectroscopic techniques, typically enhances cytotoxicity compared to the pristine POM. Interestingly, a simple CMC/POM mixture was also found to enhance the activity. Additionally, a CMC-$[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ nanoparticle formulation showed selective toxicity towards HeLa cervical cancer cells over non-malignant MRC-5 cells in the extended viability assay. These findings highlight the potential of POM/CMC nanosystems for targeted anticancer therapies.

[1] A. Bijelic, M. Aureliano, A. Rompel, "Polyoxometalates as Potential Next-Generation Metallodrugs in the Combat Against Cancer" *Angew. Chem. Int. Ed.* **2019**, 58, 2980–2999.
[2] M. B. Čolović, M. Lacković, J. Lalatović, A. S. Mougharbel, U. Kortz, D. Z. Krstić, "Polyoxometalates in Biomedicine: Update and Overview" *Curr. Med. Chem.* **2020**, *27*, 362–379.
[3] A. Bijelic, M. Aureliano, A. Rompel, "The antibacterial activity of polyoxometalates: structures, antibiotic effects and future perspectives" *Chem. Commun.* **2018**, *54*, 1153–1169.
[4] L. S. van Rompuy, T. N. Parac-Vogt, "Interactions between polyoxometalates and biological systems: from drug design to artificial enzymes" *Curr. Opin. Biotechnol.* **2019**, *58*, 92–99.
[5] N. I. Gumerova, A. Rompel, "Synthesis, structures and applications of electron-rich polyoxometalates" *Nat. Rev. Chem.* **2018**, 2.
[6] S. Lentink, D. E. Salazar Marcano, M. A. Moussawi, T. N. Parac-Vogt, "Exploiting Interactions between Polyoxometalates and Proteins for Applications in (Bio)chemistry and Medicine" *Angew. Chem. Int. Ed.* **2023**, *62*, e202303817.
[7] G. Geisberger, S. Paulus, M. Carraro, M. Bonchio, G. R. Patzke, "Synthesis, Characterisation and Cytotoxicity of Polyoxometalate/Carboxymethyl Chitosan Nanocomposites" *Chem. - A Eur. J.* **2011**, *17*, 4619–4625.
[8] M. Croce, S. Conti, C. Maake, G. R. Patzke, "Nanocomposites of Polyoxometalates and Chitosan-Based Polymers as Tuneable Anticancer Agents" *Eur. J. Inorg. Chem.* **2019**, 348–356.

'Click' Chemistry as an Universal Tool for New Discoveries in the Chemistry of Polyoxovanadates

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The post-functionalization of polyoxometalate (POM) based organo-inorganic structures offers excellent opportunities for tailoring their structure and composition, allowing for the fine-tuning of physicochemical characteristics, solubility, redox behavior, and compatibility with organic or biological systems.[1] Among other methods, 'click' chemistry is considered a particulary useful and reliable approach, enabling the modular assembly of the hybrid POM-organic structures under mild conditions with high yields.

In our studies, we focus on modifications of hexavanadate clusters ($\{V_6\}$) that combine good stability, synthetic availability, and a relatively low price with attractive (photo)redox and catalitic properties. The starting point for developments of the 'click' strategy is the synthetic availability of the initial azido-functionalized hexavanadate platform. Against this backdrop, the original method[2] for its synthesis has been significantly optimized.

The synthetic availability of numerous terminal acetylenes has enabled the synthesis of numerous covalent conjugates, including those with chromophores, organometallic moieties, and reactive functional groups. These reactions have generally been shown to proceed particularly efficiently under microwave irradiation. In some cases, the route of these reactions could be precisely controlled by exploiting coordination chemistry and the solubility factor,[3] leading to selective asymmetric functionalizations.

In special cases, when the reaction is to be carried out *in vivo* or with sensitive biomolecules, the use of a Cu(I) catalyst is undesirable, i.e. the copper(I)-assisted azide-alkyne cycloaddition (CuAAC) must be replaced by a copper-free one.[4] The use of strain-promoted 'click' chemistry proved to be an excellent method for the conjugation of $\{V_6\}$ with oligonucleotide pendant groups, providing access to a series of building blocks for DNA origami.[5] This method could be considered the first published example of POM bioorthogonal chemistry *in vitro*.

[1] A. V. Anyushin, A. Kondinski, T. N. Parac-Vogt, *Chem. Soc. Rev.* **2020**, *49*, 382-432.
[2] H. Jia, Q. Li, A. Bayaguud, Y. Huang, S. She, K. Chen, Y. Wei, *Dalton Transactions* **2018**, *47*, 577-584.
[3] S. K. Petrovskii, M. Moors, D. Fuhrmann, J. Lorenz, K. Y. Monakhov, *Inorg. Chem.* **2024**, *63*, 13785-13792.
[4] S. K. Petrovskii, E. V. Grachova, K. Y. Monakhov, *Chem. Sci.* **2024**, *15*, 4202-4221.
[5] E. Vogelsberg, M. Moors, A. S. Sorokina, D. A. Ryndyk, S. Schmitz, J. S. Freitag, A. V. Subbotina, T. Heine, B. Abel, K. Y. Monakhov, *Chemistry of Materials* **2023**, *35*, 5447-5457.

Photoinitiated Single-Crystal to Single-Crystal Redox Transformations of Titanium-Oxo Clusters

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Metal-oxo clusters can undergo photochemical redox transformations with importance in photocatalysis.[1] It can be challenging to characterise the precise photoproduct directly following the photoredox reaction due to rapid structural changes in the solution phase, including ligand loss or exchange. Therefore, our research group have studied photoreactivity directly in the single crystal phase by following irreversible single crystal to single crystal (SC-SC) transformations under light. This presentation will highlight our findings in the photoredox reactivity of Ti-oxo-alkoxide clusters, including characterisation of the direct photoproduct after excitation by UV light.[2] Studies in the single crystal phase also provide additional mechanistic insight, due to site selective reactivity induced by the orientation of ligands within the crystal lattice. This allows us to understand a mechanisitic pathway that does not involve free organic-radicals, and differentiates between bridging and terminal alkoxide sites on the clusters. We believe the experimental setup, developed at the Diamond Light Source (UK), could be widely applicable to the study of the photochemistry of many different clusters and hope it is of interest to the FMOCs community.

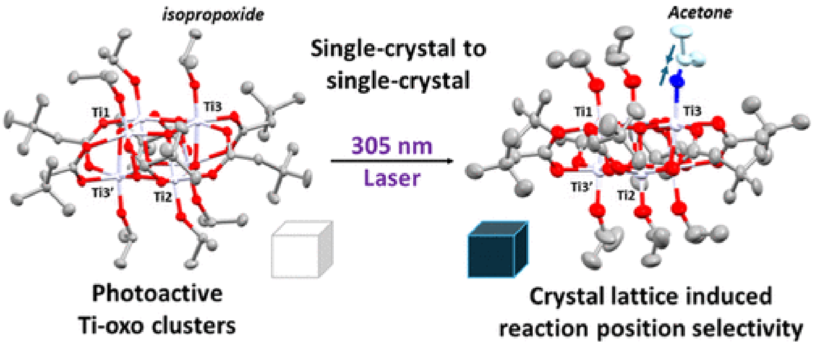

Figure: SC-SC transformation of a Ti-oxo-alkoxide-carboxylate cluster under UV light to a photoproduct with a coordinated acetone ligand and a two-electron reduced Ti core.

[1] a) T. Krämer, F. Tuna, S. D. Pike, *Chem. Sci.* **2019**, *10*, 6886-6898; b) S. E. Brown, I. Mantaloufa, R. T. Andrews, T. J. Barnes, M. R. Lees, F. De Proft, A. V. Cunha, S. D. Pike, *Chem. Sci.* **2023**, *14*, 675-683.
[2] S. E. Brown, M. R. Warren, D. J. Kubicki, A. Fitzpatrick, S. D. Pike, *J. Am. Chem. Soc.* **2024**, *146*, 17325-17333.

Redox-Active Polyoxometalates for Water Splitting and CO_2 Reduction: Mechanistic Insights from Theory

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Polyoxometalates (POMs) are a class of molecular metal-oxo clusters, typically composed of early transition metals such as W, Mo, and V in high oxidation states. Their exceptional redox activity, structural diversity, and functional tunability make them highly attractive for electrocatalytic applications in energy conversion processes—particularly water oxidation, carbon dioxide reduction (CO_2RR), and nitrogen fixation (N_2RR). Incorporation of redox-active metals such as Co, Mn, Ni, or Fe into the POM framework can significantly enhance their performance, especially in the oxygen evolution reaction (OER), which is the oxidative half-reaction of water splitting. POMs offer strong performance under acidic and neutral conditions, high structural precision, and excellent molecular-level control, making them ideal for mechanistic studies. Among them, cobalt-based POMs are among the most widely studied for OER due to their notable catalytic activity and ability to facilitate multi-electron, protoncoupled electron transfer (PCET) processes—crucial for the conversion of water to molecular oxygen (O_2).

In this talk, we will present some of our theoretical studies aimed at unraveling the key mechanistic steps involved in O_2 evolution from water.[1,2] Using a relatively simple but effective computational approach, we demonstrate that theoretical modeling can provide valuable insights and predictive power in rationalizing the reactivity of POM-based systems. We also discuss some examples of CO2 reduction using Cu and heterometal-substituted polyoxometalates.[3,4]

[1] J. Soriano-López, D. G. Musaev, C. L. Hill, J. R. Galán-Mascarós, J. J. Carbó, J. M. Poblet , *Journal of Catalysis*, **2017**, 350, 56–63
[2] K. Azmani, M. Besora, J. Soriano-López, M. Landolsi, A.-L. Teillout, P. de Oliveira, I.-M. Mbomekallé, J. M. Poblet, J.-R. Galán-Mascarós *Chemical Science*, **2021**, 12, 8755–8766.
[3] D. Azaiza-Dabbah, C. Vogt, F. Wang, A. Masip-Sánchez, C. de Graaf, J. M. Poblet, E. Haviv, R. Neumann *Angewandte Chemie*, *International Edition* **2023**, 62, e202305260
[4] D. Azaiza-Dabbah, F. Wang, E. Haddad, A. Solé-Daura, R. Carmieli, J. M. Poblet, C. Vogt, R. Neumann *Journal of the American Chemical Society*, **2024**, 146, 27871–27885

Proving photoactive Polyoxometalates as potent prosthetic groups for a novel class of artificial metalloenzymes.

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Boosting the catalytic activity of natural enzymes under conditions relevant to fine chemical synthesis remains an ongoing challenge.[1], [2] Introducing non-natural metal cofactors into proteins has already proven to be a powerful strategy to overcome some of the limitations in reactivity typically associated with natural enzymes.[3] The resulting biohybrid catalysts, also known as artificial metalloenzymes (ArMs), enable many new-to-nature reactions to be carried out under the strict control of the protein environment. ArMs active under visible light offer an exciting prospect for achieving mild and selective reaction conditions, however they remain extremely rare.[4] Polyoxometalates (POMs) hold great promise as cofactors in the design of such photoactive ArMs because they (a) bind regioselectively to proteins [5] and (b) exhibit good photoactivity in some cases, though mostly under UV light.[6] To date, no POM@protein complexes have been reported as active hybrid photocatalysts.

We herein report the for the first time the visible light photocatalytic activity of two transition metal substituted POMs with Keggin and Wells-Dawson structure, M-Kg and M-WD, in the oxidative C-C cleavage of hydrobenzoin. We further found that the activity of M-Kg improves by a factor of 3 in presence of some albumin proteins (SAs) for specific diasteomers of the substrate. ^{1}H NMR investigations confirmed a strong interaction between M-Kg and the diol substrate exclusively in the presence of SA protein, supporting the in situ formation of a reactive M-Kg@SA complex. In contrast, the presence of other commercially available proteins dimished the yield obtaind with M-Kg significantly. Also, the bigger Wells-Dawson analogue (M-WD) with the same transitions metal center only marginally improved the yield compared to its protein free counter part. To the authors' knowledge, this represents the first example of a photoactive ArM constructed from a POM and a protein.

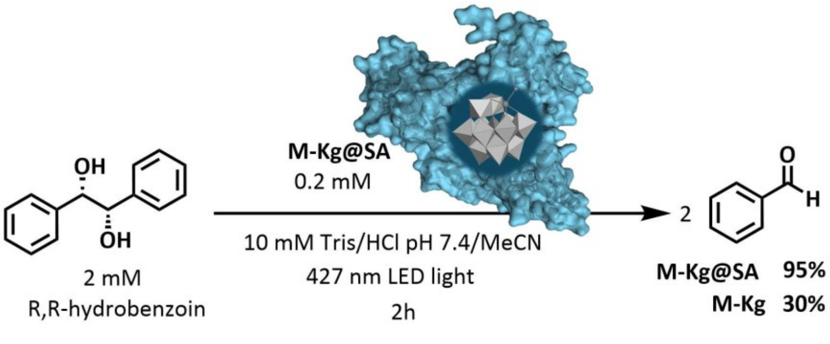

Figure 1: Photo-oxidative C-C cleavage using M-Kg@SA as catalyst.

[1] Renata, H. et al. *Angew. Chem. Int. Ed*. **2015**, 54 (11), 3351–3367.
[2] Zhou, L., et al., *Biotechnol. Adv*. **2024**, 73, 108376.
[3] Schwizer, F. et al., *Chem. Rev*. **2018**, 118 (1), 142–231.
[4] Emmanuel, M. A., et al. *Chem. Rev*. **2023**, 123 (9), 5459–5520.
[5] Salazar Marcano, D. E. et al. (Parac-Vogt, T.N.) *JACS Au* **2023**, 3 (4), 978–990.
[6] Suzuki, K. et al. *ACS Catal*. **2018**, 8 (11), 10809–10825.

Photoactive platform based on polyoxometalates and (iso)porphyrins

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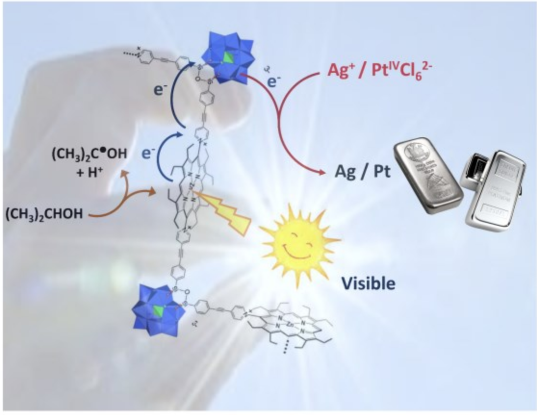
The development of hybrid materials incorporating polyoxometalates (POMs) is a promising approach to elaborate new functional materials. To expand the practical applications, their association to a visible- or NIR-light photosensitizer is needed and has been explored. In particular, the development of hybrid polymers incorporating POMs is a promising approach to elaborate new functional materials. Different strategies have been developed and explored. One approach consists in electropolymerization of POMs based on nucleophilic attack onto the electrogenerated porphyrin radical cation or dications. The formation of hybrid POM-porphyrin copolymeric films can be obtained by the electro-oxidation of porphyrin in the presence of the POM bearing two pyridyl groups (Nu-POM-Nu where Nu = Py, -NH_2 or -CH_2-OH).[1] This process is feasible for various type of POMs [2-4] or cluster [5] such as Dawson, Lindqvist, Anderson or Keggin type POMs. The photovoltaic performances of these hybrid materials have been investigated under visible-light or even NIR illumination [6-8] given by now good efficiency. In order to increase the efficiency, 3D mesoporous ITO electrodes (nanofiber formed by electrospun or porous ITO electrode obtained using a colloidal coassembly approach) have been also used and will be discussed. Furthermore, the photocatalytic recovery of noble metal such as Ag, Au, Pd and Pt under visible or even NIR light using such copolymeric films has been studied. In these films, (iso)porphyrin subunits can be excited under visible-NIR or only NIR illumination, acting as photosensitizers that transfer electrons to the polyoxometalate catalysts. Notably, such films demonstrated high efficiency in Pt(IV) photoreduction over repeated cycles without catalyst degradation.[9] Photocatalysis of the reduction of NO_x NO_3^-, HNO_2/NO_2^-, etc.) has been also tested with success under illumination where the volatile products of the photocatalysis has been detected using *in situ* DEMS (Differential Electrochemical Mass Spectroscopy).



1. D. Schaming, L. Ruhlmann et al, *Langmuir*, **2010**, 26, 5101.
2. I. Azcarate, I. Ahmed, R. Farha, M. Goldmann, X. Wang, H. Xu, B. Hasenknopf, E. Lacôte, L. Ruhlmann, *Dalton Trans.* **2013**, 42, 12688.
3. Z. Huo, D. Zang, S. Yang, R. Farha, M. Goldmann, B. Hasenknopf, H. Xu, L. Ruhlmann, *Electrochimica Acta*, **2015**, 179, 326.
4. Z. Huo, S. Yang, D. Zang, R. Farha, M. Goldmann, H. Xu, B. Antoine, G. Izzet, A. Proust, L. Ruhlmann *Electrochimica Acta,* **2021**, 368, 137635.
5. Y. Liang, M. N. Sokolov, M. A. Mikhaylov, H. Ibrahim, M. Goldmann, S. Choua, N. Le Breton, C. Boudon, V. Badets, A. Bonnefont, L. Ruhlmann, *Electrochimica Acta*, **2021**, 388, 138493.
6. Z. Huo, Y. Liang, Y. Lv, F. Melin, P. Hellwig, H. Ibrahim, M. Goldmann, C. Boudon, V. Badets, A. Bonnefont, L. Ruhlmann, *Chem. Comm.* **2021**, 57, 1482-1485.
7. I. Ahmed, R. Farha, M. Goldmann, L. Ruhlmann, *Chem. Comm.* **2013**, 49, 496.
8. I. Azcarate, Z. Huo, R. Farha, M. Goldmann, H. Xu, B. Hasenknopf, E. Lacôte, L. Ruhlmann, *Chem. Eur. J.* **2015**, 21, 8271.
9. Z. Huo, B. Akhsassi, J. Yu, M. Zheng, L. Mingxiu, T. Lan, Q. He, C. Boudon, G. Xu, Guojun; A. Proust, G. Izzet, L. Ruhlmann *Inorg. Chem*. **2025**, 64, 7, 3371–3383.

Heteropolyacid-Organic (Ether or Amide) Composites

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I am interested in heteropolyacid-oranic composites as heterogeneous acid-catalysts and proton-conducting materials in aqueous solution. The interaction of $H_3PW_{12}O_{40}$ with diethyl ether or amides have been utilized to isolate $H_3PW_{12}O_{40}$ from water and staining for microscopy, respectively. Interation of dimethyl acetoamide with proton of $H_3PMo_{12}O_{40}$ was reported by Hill group [1].

I present crystal structure analysis of heteropolyacids containing ethylene glycol derivatives or amide derivatives. Crystal structures with amides indicate that oxygen atoms of ethers or amides interact with protons of heteropolyacids (Figure 1). Using this interaction, we could immobilized $H_3PW_{12}O_{40}$ in tri(ethyleneglycol) containing polymer gel which did not leach $H_3PW_{12}O_{40}$ at room temperature for several days (Figure 2).

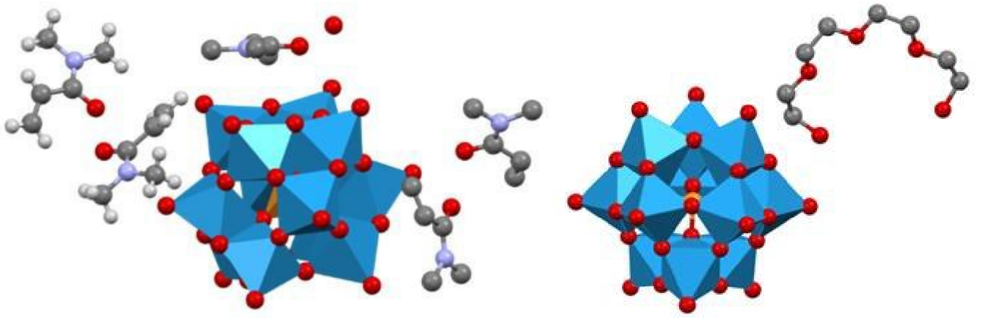

Figure 1: Crystal structure of (left) dimethylacrylamide- $H_3PW_{12}O_{40}$ and (right) PEG400-- $H_3PW_{12}O_{40}$

Figure 2: Polyethylene glycol hydrogel as a carrier of $H_3PW_{12}O_{40}$.

[1] M. M. Williamson, D. A. Bouchard, C. L. Hill, *Inorg. Chem*. **1987**, *26*, 1436.
[2] J. Zhu, T. Goto, S. Nakai, N. Tsunoji, M. Sadakane, *Mater. Adv*. **2021**, *2*, 3556.

X-ray Emission Spectroscopy to Investigate Electron Transfer Oxygen Transfer Reactions of Polyoxometalate

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Phosphovanadomolybdic acid, $H_5PV_xMo_{12-x}O_{40}.nH_2O$ is best known for its electron transfer-oxygen transfer behaviour towards organic molecules that are susceptible to oxidize. Khenkin et.al has shown that $H_5PV_xMo_{12-x}O_{40}.nH_2O$ is able to take electron from aromatic molecule such as anthracene, xanthene at 50oC and oxidize to anthraquinione, xanthone respectively.[1] Even it catalyses C-C bond cleavage for primary alcohols[2] and secondary alcohols present in molecules like glucose under mild conditions.[3] Most importantly, driving force for all these reactions can be tuned by choice of the reaction medium. For example, toluene was unable to react when the same reaction conditions like for anthracene or xanthene was applied. Upon changing the solvent from acetonitrile to 50% H_2SO_4 – H_2O mixture, $H_5PV_xMo_{12-x}O_{40}.nH_2O$ reacted with toluene to produce benzaldehyde.[4] Moreover, on reaction with benzene and $H_5PV_2Mo_{10}O_{40}$ in 50% H_2SO_4, a benzene radical was observed via Electron Paramagnetic Resonance (EPR) spectroscopy, which explains that an ion pair stage between the catalyst and the benzene radical was achieved and it was quite stable.[5] However, the question is how the octaherally coordinated vanadium is active for such reaction. In order to track the changes around the V-center, we applied, for the first time X-ray emission spectroscopy(XES)[6] at synchtrotron light source (ID26 beamline of ESRF, France). The results showed that the vanadium is distorted in the polyoxometalate framework and there are significant changes in the vanadium $K\beta_{2,5}$ and Kβ” line during the course of a reaction with xanthene or anthracene at room temperature for a period of of 6h as shown in fig.1.

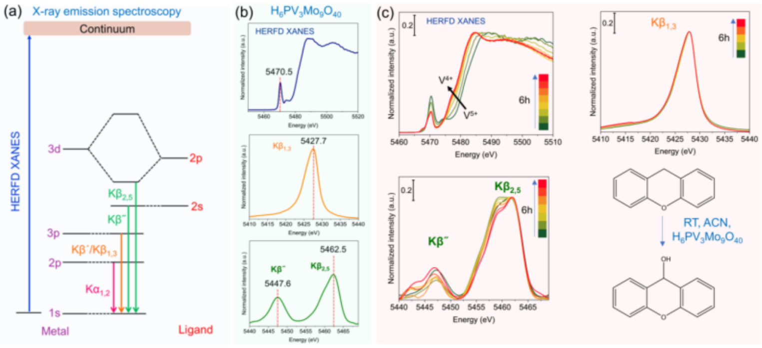

Figure 1: (a) Schematics representation of X-ray emission spectroscopy, (b) High energy resolution fluorescence detected X-ray absorption near edge structure (HERFD-XANES) analysis and Kβ XES spectra of $H_6PV_3Mo_9O_{40}$ and (c) time dependent spectra during the reaction of $H_6PV_3Mo_9O_{40}$ with xanthene at RT for 6h.

These findings are very new (unpublished) and it will open up a new avenue for the polyoxometalate chemistry and tracking their reaction pathways which is otherwise challenging.

[1] A. M. Khenkin, L. Weiner, Y. Wang, R. Neumann, *J. Am. Chem. Soc.* **2001**, *123*, 8531-8542. [2] A. M. Khenkin, R. Neumann, *J. Am. Chem Soc.* **2008**, *130*, 14474-14476. [3] **B. B. Sarma**, R. Neumann, *Nat. Commun.* **2014**, *5*, 4621. [4] **B. B. Sarma**, I. Efremenko, R. Neumann, *J Am. Chem. Soc.* **2015**, *137*, 5916-5922. [5] **B. B. Sarma**, R. Carmieli, A. Collauto, I. Efremenko, J. M. L. Martin, R. Neumann, *ACS Catal.* **2016**, *6*, 6403-6407. [6] **B. B. Sarma**, F. Maurer, D. E. Doronkin, J.-D. Grunwaldt, *Chem. Rev.* **2023**, *123*, 379-444.

Decoding Multi-Step Water Oxidation at Lacunary-POM-Modified Anodes via Hybrid Microkinetic Modeling

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Lacunary transition metal-substituted polyoxometalates (TM-POMs) are especially promising electrocatalysts due to their ability to undergo redox transformations without significant structural changes, maintaining high stability under harsh conditions. This study investigates water oxidation electrocatalysis using carbon paste electrodes modified with earth-abundant, Fe-containing POMs, which exhibit notable catalytic activity and robustness in both acidic and neutral environments [1].

We present a **hybrid microkinetic modeling approach** that integrates experimental linear sweep voltammetry (LSV) data with mechanistic insights derived from density functional theory (DFT). This strategy enables the development and parameterization of detailed microkinetic models [2], shedding light on the complex, multi-step water oxidation mechanism. In particular, it allows us to disentangle the **relative contributions of chemical and electrochemical steps to concentration changes, current generation, and overpotential**. Our findings demonstrate that overpotentials are governed not only by electrochemical transitions but also by key chemical steps within the catalytic cycle. This underlines the necessity of considering not only electrochemical steps when evaluating electrochemical parameters.

By connecting theoretical predictions with experimental observations, this work highlights **fundamental electrokinetic principles** and reaffirms the high potential of **TM-POMs as efficient electrocatalysts** for sustainable oxygen evolution.

[1] K. Azmani, M. Besora*, J. Soriano-López*, M. Landolsi, A. Teillout, P. Oliveira, I. Mbomekallé, J. M. Poblet and J.R Galán-Mascarós, *Chemical Science*, **2021**, *12*, 8755-8766.
[2] M. Besora, F. Maseras, *WIREs Comput. Mol. Sci.*, **2018**, *8*, 1759-0876.

Synthesis and Modification of Polyoxometalates under Non-Aqueous Conditions

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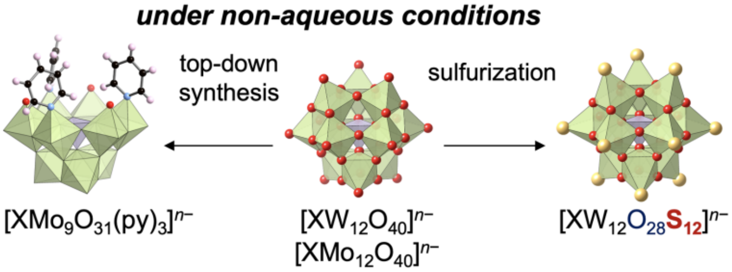
Polyoxometalates (POMs) exhibit diverse physical properties and applications, closely linked to their structures and elemental compositions. Therefore, precise control over their synthesis is this crucial for the rational design of functional materials. Although POMs are typically synthesized in aqueous media, controlling hydrolysis and condensation equilibria in such environments remains challenging. To address this, we have developed functional materials by utilizing lacunary POMs in organic solvents,combined with metal ions and organic ligands.[1] In this presentation, we report recent advances in the synthesis and molecular-level modification of POMs under non-aqueous conditions.[2,3]

In particular, we have addressed the persistent instability associated with the synthesis and utilization of lacunary polyoxomolybdates.[2] By employing pyridine-based ligands in organic solvents, we successfully synthesized tri-lacunary polyoxomolybdates via both top-down and bottom-up approaches. This strategy enhances their stability and enables the rational design of POM-based hybrid materials. Furthermore, we achieved site-selective substitution of surface oxygen atoms in POM frameworks with chalcogen atoms in organic solvents, providing a new strategy for tuning their electronic structures and functional properties.[3] These results provide the way for the development of next-generation POMbased catalysts and functional materials.



[1] a) M. Yamaguchi, K. Shioya, C. Li, K. Yonesato, K. Murata, K. Ishii, K. Yamaguchi, K. Suzuki, *J. Am. Chem. Soc.* **2024**, 146, 4549; b) M. Kamachi, K. Yonesato, T. Okazaki, D. Yanai, S. Kikkawa, S. Yamazoe, R. Ishikawa, N. Shibata, Y. Ikuhara, K. Yamaguchi, K. Suzuki, *Angew. Chem. Int. Ed.* **2024**, 63, e202408358.; c) K. Yonesato, D. Yanai, S. Yamazoe, D. Yokogawa, T. Kikuchi, K. Yamaguchi, K. Suzuki, *Nat. Chem.* **2023**, 15, 940; d) T. Minato, D. Salley, N. Mizuno, K. Yamaguchi, L. Cronin, K. Suzuki, *J. Am. Chem. Soc.* **2021**, 143, 12809.

[2] a) A. Jimbo, C. Li, K. Yonesato, K. Yamaguchi, K. Suzuki, *Dalton Trans.* **2025**, DOI: 10.1039/D5DT00252D;b) A. Jimbo, C. Li, K. Yonesato, K. Yamaguchi, K. Suzuki, *Chem. Lett*. **2025**, 54, upaf072; c) H. Sun, A. Jimbo, C. Li, K. Yonesato, K. Yamaguchi, K. Suzuki, *Chem. Sci.* **2024**, 15, 9281; d) C. Li, K. Yamaguchi, K. Suzuki, *Angew. Chem. Int. Ed.* **2021**, 60, 6960.

[3] a) K. Yonesato, K. Yamaguchi, K. Suzuki, *Chem. Sci.* **2024**, 15, 11267; b) Y. Watanabe, K. Yonesato, D.Yokogawa, K. Yamaguchi, K. Suzuki, *Inorg. Chem.* **2024**, 63, 23388.

Polyoxometalate-Based Solid-State Functional Materials

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Polyoxometalates (POMs) are nano-sized metal-oxide molecular anions with unique catalytic, electrochemical, magnetic, and luminescent properties, which have stimulated research across a broad range of scientific fields. We have reported that the complexation of POMs with molecular cations containing appropriate elements, charges, sizes, symmetry, ligands, etc. forms solid-state functional materials.[1-10] The properties of these POM-based materials can be summarized as follows: (i) POMs exhibit reversible redox properties, which can lead to the formation of "redox-active" frameworks. (ii) Guest binding and catalytically active sites can be incorporated in advance into the ionic components. These functions can be maintained and utilized in the solid state because the ionic components remain as discrete molecules within the crystal lattice. (iii) POMs can efficiently transport protons as counter cations because their negative charge is delocalized over the external oxygen atoms, reducing the effective surface charge density.

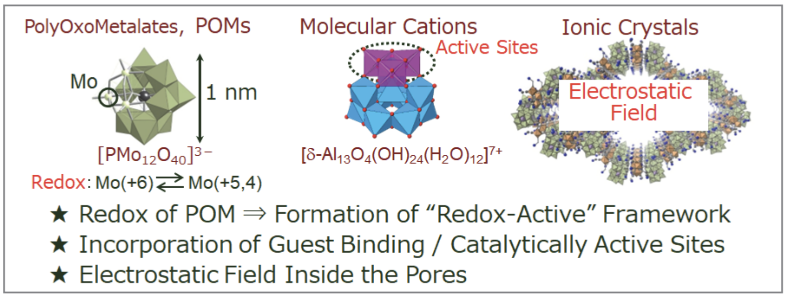

Figure 1: Characteristics of POM-based solid-state materials..

Recent original papers:
[1] Tuning Proton Conduction by Staggered Arrays of Polar Preyssler-Type Oxoclusters, *J. Am. Chem. Soc.* **2024**, 146, 26113.
[2] Enhanced Proton Conduction via Proton-Coupled Electron Transfer Reaction by a Keplerate-Type Polyoxometalate Capsule, *Inorg. Chem*. **2024**, 63, 24054.
[3] A Redox-Active Inorganic Crown Ether based on a Polyoxometalate Capsule, Chem. Sci. **2023**, 14, 5453.
[4] Size-Controlled Synthesis of Luminescent Few-Atom Silver Clusters via Electron Transfer in Isostructural Redox-Active Porous Ionic Crystals, *Small* **2023**, 19, 2300743.
[5] Vanadium-Substituted Polycationic Al-oxo clusters in a Porous Ionic Crystal Exhibiting Lewis Acidity, *Chem.Commun*. **2022**, 58, 12548.
[6] Polyoxocationic Antimony Oxide Cluster with Acidic Protons, *Sci. Adv*. **2022**, 8, eabm5379.
[7] Proton Conduction in Ionic Crystals Based on Polyoxometalates, *Coord. Chem. Rev*. **2022**, 462, 214524.
[8] Oxygen Evolution Reaction Driven by Charge Transfer from a Cr Complex to Co-ContainingPolyoxometalate in a Porous Ionic Crystal, *J. Am. Chem. Soc*. **2022**, 144, 2980.
Recent review papers:
[9] Polyoxometalates (POMs) as Proton Conductors, *ACS Enegy Lett*. **2025**, 10, 1958.
[10] Emerging Functionalized Lindqvist-Type Polyoxometalate-Based Compounds: Design, Synthesis, and Applications *ChemCatChem*, **2025**, 17, e202500066.

Exploring the Role of explicit Counter-Cations in Simulations and Beyond

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Since 2019, we have been incorporating explicit counter cations in our computational calculations to better understand an account of the effects they may have on our results.[1-3] This approach has allowed us to refine the accuracy of our models and provide a more comprehensive analysis. In this presentation, we will showcase our latest findings and evaluate the impact of including these counter cations. We will also discuss whether their inclusion remains necessary for future calculations or if alternative methods might be just as effective in achieving the desired outcomes.

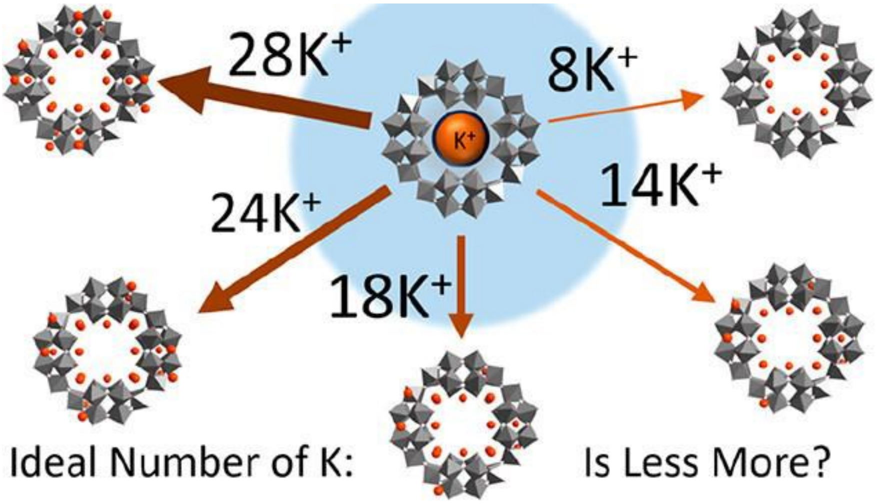

Figure 1: An example of our efforts in modeling $[P_8W_{48}O_{184}]^{40-}$ is shown when different numbers of explicit counter cations are incorporated into our model.[3]

[1] Jake, Jacobs, Maria Jose Aliaga-Gosalvez, Vihar P. Georgiev, and Laia Vilà-Nadal. "Advanced Modelling of Polyoxometalate Counter-Cations: Bridging Explicit Counter-Cation Inclusion and Solvent Effects for Electronic Applications." *ChemRxiv*, **2024**. Doi:10.26434/chemrxiv-2024-z45x9. This content is a preprint and has not been peer-reviewed.
[2] Jake Thompson and Laia Vilà-Nadal. "Computation of 31P NMR chemical shifts in Keggin−based lacunary polyoxotungstates." *Dalton Trans*., **2024**, 53, 564-571. Doi: 10.1039/D3DT02694A
[3] Daniel Malcolm and Laia Vilà-Nadal, "Computational Study into the Effects of Countercations on the [P8W48O184]40– Polyoxometalate Wheel" *ACS Organic & Inorganic Au*, **2023** 3 (5), 274-282 Doi: 10.1021/acsorginorgau.3c00014

Polyoxometalate-Ligation Mediated Assembly of Metal-Oxide Nanocrystals

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Metal-oxide nanocrystals (NCs) are a uniquely reactive class of nanostructures at the interface between molecular complexes and solid-state oxides. Until recently, two general types have been available: Electrostatically stabilized NCs typical of traditional colloid science and organic-ligand protected NCs. Neither type, however, has provided a pathway towards developing the solution-state chemistry of these reactive materials. We have addressed this by using polyoxometalate (POM) cluster anions to form soluble macroanion-like complexes of an unexpectedly wide variety of oxide-based NCs that, in turn, catalyze a correspondingly diverse range of reactions, while in many cases serving as building blocks for the rationally controlled assembly of soluble suprastructures such as the first examples of soluble metal-oxide NC superlattices. While these findings bring the science of metal-oxide NCs into the flexible realm of solution-state chemistry, we recently discovered that POM complexed metal-oxide NCs spontaneously and reversibly form an entirely new type of self-healing, cation-exhangeable gels, featuring unprecedented options for finely tuned pre- or post-synthetic modifications that directly determine structure, composition and reactivity. Preliminary results include more than 10 different gels, whose equilibrum-controlled formation is understand to arise from the self-limiting assembly of negatively-charged walls that establish a percolated network of water-filled nanocavities. These structural features are documented by—to our knowedge—the first cryo-SEM images of metal-oxide NC gels and high-resolution cryo-TEM tomographic revelation of NC organization inside the gel-wall itself. These organic-ligand-free metal-oxide NC gels represent a new class of porous materials that takes full advantage of the high reactivities inherent to exposed surfaces of nanometric-scale oxides. More generally, their self-limiting assembly establishes a new design principle for use in engineering functional-nanoparticle suprastructures.

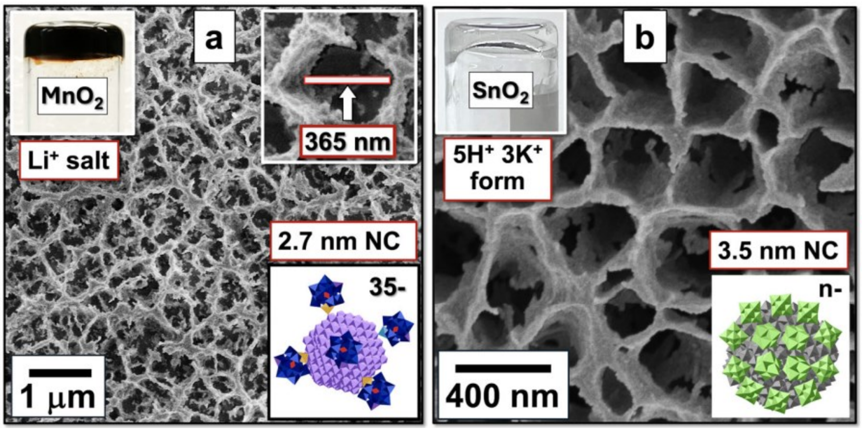

Figure: Cryo-SEM images of gels formed by Keggin-ligated MnO_2 (a) and hexaniobate-ligated SnO_2 (b) nanocrystals.

Supramolecular Polymerization of Polyoxometalates via Self-Sorting Nucleation-Growth for Enantiomeric Separations

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Supramolecular polymerization of large-scale spherical nanoparticles and nanorods has been studied extensively, but the current literature shows that it mainly follows an isochain growth mechanism similar to that of supramolecular polymerization of small organic molecules [1,2]. While exploring different polymerization modes in the construction of supramolecular polymers with multi-level structures and cochirality of small-scale nanoparticles (<10 nm), the intuitive visualization of the process and precise cross-scale chiral modulation are still challenging. To this end, we proposed a synergistic self-assembly strategy based on the previous research results [3,4], and developed a class of ionic complexes with homogeneous chemical composition as monomers for supramolecular polymerization by covering the surface of the rigid nuclei of polyoxometalates with organic chiral cationic organic components, and obtained single helix polymer chains with a core-shell structure with a maximum length of more than 20 μm and showed flexibility similar to that of covalent polymers. The polymerization mechanism was studied, and it was found that the composite nanoparticles adopted a different nucleation-growth mode from the known supramolecular polymerization process of nanoparticles, and confirmed that this process was accompanied by chiral self-classification. Permeable membranes prepared by simple aspiration of this supramolecular polymer show high enantiomeric separation selectivity. When used for histidine derivatives separation, the selectivity can reach 98% after 4 cycles[5]. The results not only reveal a new polymerization method for nanocluster supramolecular polymerization, but also verify the structure-induced functionalization potential of helical chirality in efficient racemate separation using the obtained macroscopic supramolecular polymer membranes comprising of polyoxometalates.

Keywords: polyoxometalate; supramolecular polymerization; self-classifying single strand; permeable membranes; enantiomeric separation

[1] Hashim, P.K.; Bergueiro, J.; Meijer, E.W.; Aida, T. Prog. *Polym. Sci.* **2020**, 105, 101250.
[2] Qin, B.; Yin, Z.H.; Tang, X. Y.; Zhang, S.; Wu, Y.H.; Xu, J.-F.; Zhang, X. *Prog. Polym. Sci.* **2020**, 100, 101167.
[3] Guan, W.M.; Wang, G.X.; Li, B.; Wu, L.X. *Coord. Chem. Rev.* **2023**, 481, 215039.
[4] Guan, W.M.; Li, B.; Wu, L.X. *J. Organomet. Chem.* **2023**, 998, 122801.
[5] Zhu, Z. X.; Zhang, G.H.; Li, B.; Liu, M. H.; Wu, L.X. *Nat. Commun.* **2024**, 15, 8033

Assembly of High-nulclearity Polyoxometalates and Their Derived Frameworks

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Polyoxometalates constitute an archetypal class of anionic metal-oxo aggregates, characterized by multiple metal centers and an abundance of surface oxygen atoms. These features not only confer unique catalytic and ion conductivity properties but also enable the construction of crystalline frameworks.[1] Herein, we describe the rational synthesis of a series of high-nuclearity polyoxometalates achieved by employing structure directing agents capable of inducing the generation of novel building blocks or modulating the connection modes of existing building blocks. This has resulted in the discovery of giant clusters such as $\{Mo_{74}\}$, $\{Mo_{85}\}$, $\{Mo_{158}\}$, $\{Mo_{172}\}$, $\{Mo_{200}\}$, and $\{Mo_{120}Ce_6\}_2$.[2] Moreover, we further demonstrate that these giant species can act as functional building blocks for constructing both all-inorganic frameworks and hybrid inorganic-organic frameworks.[3] Based on the synergistic effect from rational combination of all the components and the dimensionality evolution from 0D discrete clusters to 1D-3D networks, the high-nulclearity derived frameworks generally exhibit enhanced performance in proton conduction and photocatalysis. As a demonstration, 1D-$\{Mo_{200}\}$ displays superior proton conductivity of 1.32×10^{-1} S cm^{-1}, much higher than 8.28×10^{-2} S cm^{-1} for $\{Mo_{200}\}$ cluster.

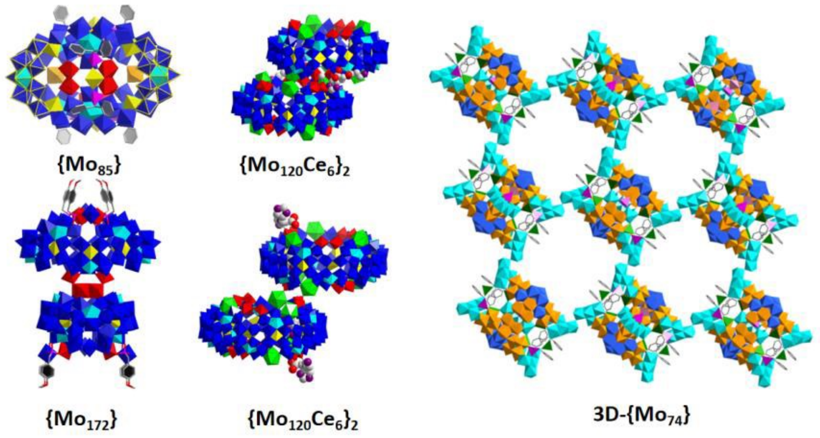

Figure: Crystal structures of $\{Mo_{85}\}$, $\{Mo_{172}\}$, $\{Mo_{100}Ce_6\}_2$ and 3D-$\{Mo_{74}\}$

[1] L. Cronin, A. Müller, *Chem. Soc. Rev.* **2012**, *41*, 7325–7648.
[2] M. Cheng, D. Zhang, Y. Liu, Z. Chen, Y. Ma, R. Tang, K. Wang, H. Wang, D.-L. Long, L. Cronin, W, Xuan, *CCS Chem.* **2025**, doi.org/10.31635/ccschem.025.202405353.
[3] Q. Zhao, Y. Zeng, Z. Jiang, Z. Huang, D.-L. Long, L. Cronin, W, Xuan, *Angew. Chem. Int. Ed.* **2025**, *64*, e202421132.

Molecular Design of Electron-Rich Polyoxometalates based Clusters Enabling Intelligent Energy Storage

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The construction of a molecular cluster-based intelligent energy storage system presents significant challenges due to the complexity of deep multifunctional integration[1,2].We have encapsulated low-valent metal atoms within ε-type Keggin structures, yielding a novel cluster denoted as $CuMo_{16}$. The central atoms in the ε-type Keggin structure exhibited lower oxidation states and larger ionic radii, necessitating the incorporation of four $\{Mo^{VI}O_3\}$ units to stabilize the resulting architecture. This unique structure displayed the characteristic "molybdenum red" coloration, with a high reduction degree of 76.47%. The specialized configuration significantly enhanced multi-proton-coupled electron transfer kinetics, enabling the rapid storage and release of thirteen electrons per molecule. The cluster can be assembled with polymers to construct intelegent flexible, wearable, rechargeable devices. The flexible electronics demonstrated real-time human motion detection capabilities alongside exceptional energy storage performance, achieving a specific capacity of 194.19 mAh g^{-1} at 0.1 A g^{-1} and maintaining 68.2% stability after 2,500 charge-discharge cycles. Molecular Dynamics (MD) simulations further confirmed the strong affinities between MA and $CuMo_{16}$ anions and cationic H_3O^+ ions, facilitated by electrostatic interactions with the $CuMo_{16}$ cluster.

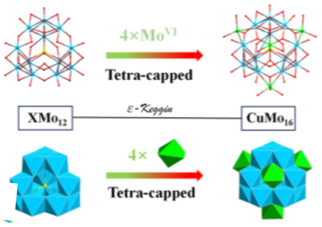

Figure 1 Structural representation between $CuMo_{16}$ and ε-Keggin structure (X = P, Si, et al)

[1] B. Li, X.-Z. Duan, H.-Y. Zang *et al*. *Angew. Chem. Int. Ed*. **2024**, 63, e202408096.
[2] R. Sekine, P. Ravat, H. Yanagisawa,*et al*., J. *Am. Chem. Soc*. **2021**,143, 2822.

High-Efficiency Electromagnetic Wave Absorption Materials Using Metal-Oxo Cluster Precursors

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The rapid evolution of wireless technology has intensified concerns regarding the environmental and health impacts of electromagnetic wave (EMW) radiation. Electromagnetic wave (EMW) absorbers, which convert microwaves into thermal energy, offer a promising solution to mitigate these challenges [1]. Conventional single-component absorbers (e.g., carbon or metal-based systems) suffer from impedance mismatch due to extreme dielectric/magnetic properties, limiting attenuation efficiency. Multi-component composites with engineered heterointerfaces enhance performance by synergizing dielectric/magnetic losses and interfacial mechanisms such as conductive loss and dipole polarization.However, precise control of interfacial defects and compositions remains a critical challenge, impeding systematic optimization.

Herein, we employ metal-oxo clusters (MOCs) with atomic-scale precision to regulate compositions, defects, and phase transitions at heterointerfaces. For instance, Anderson-type POMs {XMo$_6$} enable tailored MoS$_2$ _phases through sulfur vacancy-induced phase transitions, achieving permittivity control and excellent microwave absorption, in which the minimum reflection loss (RL$_{min}$) achieves −51.82 dB at 1.72 mm [2]. Extending this strategy, organic ligand-coated Fe$_{15}$-nanoclusters create hierarchical magnetic architectures, enabling efficient and broadband absorption across low-/middle frequencies [3]. This MOC precursor strategy establishes a paradigm for designing high-efficiency EMW absorbers, advancing the frontier of EM functional material engineering through atomic-scale precision control.

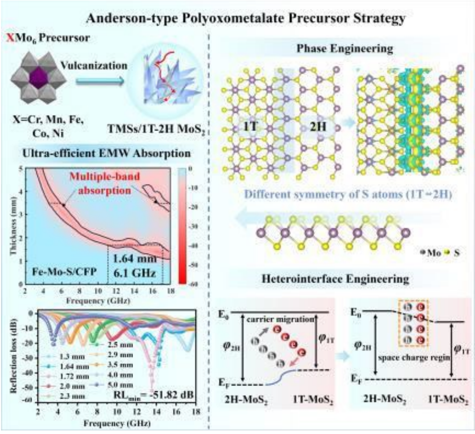

Figure 1: Phase engineering of MoS$_2$ via Anderson-type POM precursor for efficient electromagnetic wave absorption

[1] L. Liang, W. Gu, Y. Wu, B. Zhang, G. Wang, Y.Yang, G. Ji, *Adv. Mater.* **2022**, 34, 2106195
[2] X. Wang, Q. Zheng, L. Wang, W. Jiang, *Adv. Funct. Mater.* **2025**, 2501720
[3] X. Wang, P. Ou, Q. Zheng, L. Wang, W. Jiang, *Small* **2023**, 2307473

Heterometallic 3d-4f Cluster Cages: Anion-Guided Assembly and Applications as Nanoreactors

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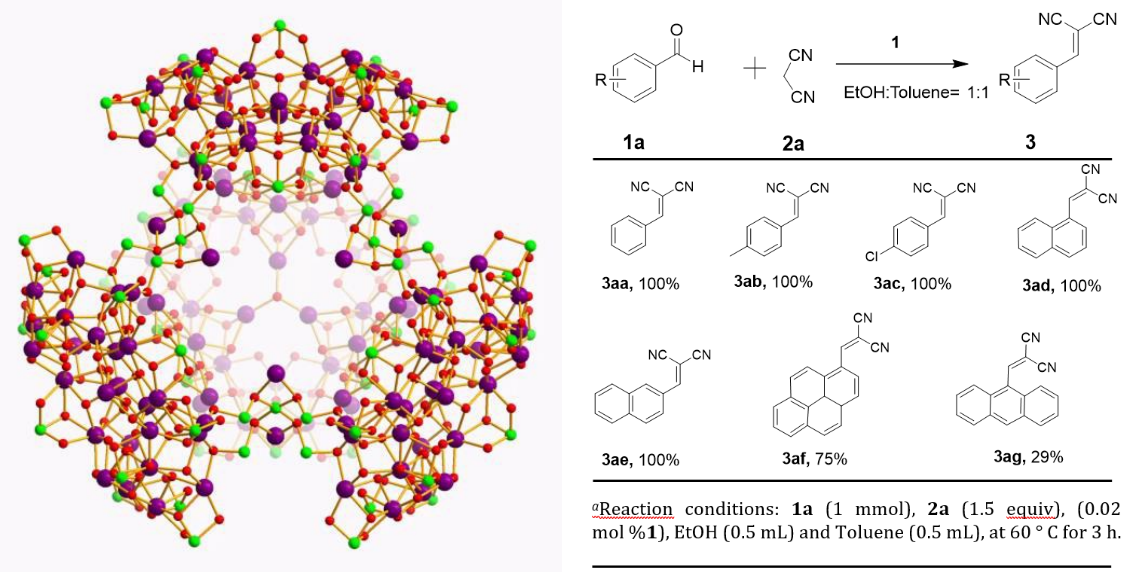
In this talk, anion-templated assembly of heterometallic 3d-4f clusters will be presented [1-3]. Obtained by base-promoted cohydrolysis of lanthanide and transition metal ions in the presence of certain organic ligands, some of these clusters display nanometer-sized cage-like structures with accessible internal void space (Figure 1) potentially useful for size-controlled chemical transformation, including catalysis. Selected examples will be used to demonstrate the use of such cluster cages as nanoreactors for catalytic Knoevenagel condensation [4] and conversion of CO_2 into cyclic carbonates. Our findings extend the use of lanthanide-containing clusters to go beyond their most-studied applications as luminescent and magnetic materials.



[a]Reaction conditions: **1a** (1 mmol), **2a** (1.5 equiv), (0.02 mol %**1**), EtOH (0.5 mL) and Toluene (0.5 mL), at 60 ° C for 3 h.

Figure 1: A hollowed-out heterometallic cluster for catalytic Knoevenagel condensation (Gd, purple; Ni, green; red, O) [4].

[1] W. Huang, Q. Yang, W. Chen, Z. Zheng, *J. Am. Chem. Soc.* **2025**. DOI: 10.1021/jacs.4c16564.
[2] N. Xu, N.; W. Chen, Y. Ding, Z. Zheng, *J. Am. Chem. Soc.* **2024**, *146*, 9506.
[3] N. Xu, N.; W. Chen, J. Miao, Y. Ding, Z. Zheng, *Angew. Chem. Int. Ed.* **2024**, *63*, e202409109.
[4] W. Chen, N. Xu, L. Qin, Y. Deng, G. Zhuang, Z. Zhang, T. Xie, P. Wang, Z. Zheng, *Angew. Chem. Int. Ed.* **2024**, e202420770.

1: Mild Hydrogenation of 4-(trifluoromethyl)benzaldehyde Using Silicotungstic Acid as a Redox Mediator

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Decoupled electrolysis offers a promising way to address key challenges in hydrogen production by allowing the separate and controlled generation of oxygen and hydrogen. This makes the process more flexible and better suited for integration with renewable energy sources.[1–3] It also enables the sustainable generation of redox mediators, such as reduced silicotungstic acid, which can store and transfer hydrogen equivalents in the form of an aqueous solution. Such reduced mediator solutions offer a safer and more practical alternative to the use of hydrogen gas for hydrogenation reactions. Reduced silicotungstic acid has demonstrated strong hydrogenation performance in various organic transformations especially with nitroarene derivatives, making it a valuable tool for sustainable synthesis.[2]

In this work, we used an electrochemical process to reduce silicotungstic acid. The 2-electron and 4-electron forms of the reduced mediator were then reacted with 4-(trifluoromethyl)benzaldehyde at room temperature and pressure, converting the aldehyde group into a hydroxymethyl group without the need for any additional catalysts. This process is illustrated in Figure 1, which shows the two key steps: electrochemical reduction followed by direct hydrogenation. The reaction products were analyzed using both ÅH NMR and GC-MS. This straightforward method provides a greener alternative to traditional approaches by avoiding the use of hydrogen gas, high temperatures, and sacrificial reagents during the production of target compounds.

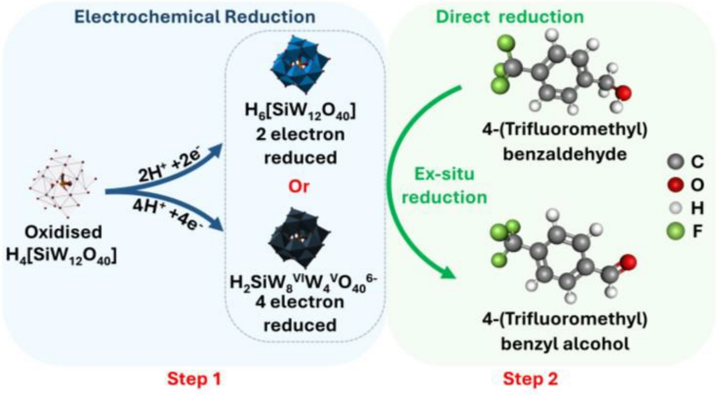

Figure 1: Schematic of the reaction pathway. Step 1: Electrochemical reduction of silicotungstic acid. Step 2: Direct hydrogenation, where the reduced silicotungstic acid reacts with 4-(trifluoromethyl) benzaldehyde to form the hydroxymethyl product.

[1] A. D. Stergiou, D. H. Broadhurst, M. D. Symes, *ACS Organic & Inorganic Au* **2023**, 3, 51–58.
[2] A. D. Stergiou, D. H. Broadhurst, M. D. Symes, *STAR Protoc* **2022**, 3, 101817.
[3] M. D. Symes, L. Cronin, *Nat Chem* **2013**, 5, 403–409.

2: Hybrids Based on Polyoxometalates and Carbon Nanomaterials (POM@Nanocarbon): Synthesis and Applications in Electrocatalysis

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Polyoxometalates (POMs) are discrete anionic metal-oxide clusters known for their structural diversity, rich redox chemistry, and tunable properties, making them ideal candidates for applications in catalysis and materials science[1,2]. Among them, Sandwich-Type POMs (STPs) offer promising opportunities due to their unique architecture and capacity to incorporate multiple redox-active centres[3].

Our work explores the synthesis, physicochemical characterization, and electrocatalytic applications of a new series of homo-atomic and mixed STPs incorporating nickel and/or copper. A novel synthetic protocol was developed to produce efficiently bimetallic STPs, $[(NiOH_2)_2Cu_2(As_2W_{15}O_{56})_2]^{16-}$ and $[(CuOH_2)_2Ni_2(As_2W_{15}O_{56})_2]^{16-}$, which were characterized by a wide range of techniques. Their electrochemical behaviour was investigated extensively in acidic media (pH 1–6), using Cyclic Voltammetry and Electrochemical Quartz Crystal Microbalance.

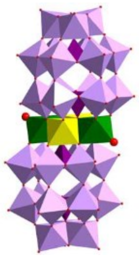

Figure 1: Mixed STP structure

Beyond molecular POMs, this research also focuses on the design and the characterization of hybrid materials combining STPs with carbon-based matrices derived from biomass (biochar)[4]. The electrocatalytic properties of both molecular STPs and hybrid materials (POM@Nanocarbon) were assessed towards the reduction of key environmental substrates, including O_2, H_2O_2, NO_3^-, and NO_2^-, in various pH conditions. The electrocatalytic reduction of O_2 by the hybrid materials exhibits enhanced activity compared to their individual components, both in acidic and in alkaline media.

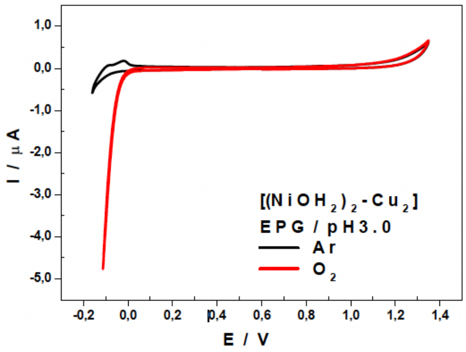

Figure 2: CVs of $[(NiOH_2)_2Cu_2(As_2W_{15}O_{56})_2]^{16-}$ in Ar (black) and in O_2 (red) atmosphere at a scan rate of 10 mV.s^{-1} in 0.2 M Li_2SO_4 + H_2SO_4 / pH 3.0.

[1] Y. Jiao, Y. Zheng, M. Jaroniec, S. Z. Qiao, *Chem. Soc. Rev.* **2015**, 44, 2060–2086.
[2] D. Jana, H. K. Kolli, S. Sabnam, S. K. Das, *Chem. Commun.* **2021**, 57, 9910–9913.
[3] F. Doungmene, C. S. Ayingone Mezui, P. De Oliveira, A.-L. Teillout, I.-M. Mbomekalle, *Curr. Inorg. Chem.* **2017**, 7, 28–38.
[4] I. S. Marques, B. Jarrais, I.-M. Mbomekallé, A.-L. Teillout, P. de Oliveira, C. Freire, D. M. Fernandes, *Catalysts* **2022**, 12, 440.

3: Metal Extraction And Recovery Using Lacunary Polyoxometalate-Ionic Liquids (POM-ILs)

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Modern electronic technology requires a large number of different functional materials, which often include rare and expensive elements. For example, smartphones contain around 15 percent copper, two percent tin and one percent of gallium, indium and different rare earth metals like lanthanum and neodymium. Noble metals like gold silver and palladium are also used in smaller, but still significant amounts[1]. Not only are these metals expensive, the large-scale mining of metal-containing minerals is harmful for the enviroment, as it causes pollution, deforestation and depletion of water reserves. The working conditions for miners in third-world countries are also often dangerous and unhealthy[2]. On top of that, the dependence on imports of rare earth metals from foreign countries is a current political issue. However, large amounts of these valuable materials are already circualting the economy as parts of various electronic devices. Because of the mentioned reasons, it is important to efficiently recycle electronic waste. One important step of the recycling process is the separation of the desired metal compounds from other waste components. It is already known that certain ionic liquids are able to extract metal ions from the aqueous phase into the organic phase[3].

In this project, polyoxometalate-ionic liquids (POM-ILs) are used to perform the extraction of different metal ions. POM-ILs are ionic liquids which consist of organic, lipophilic cations and polyoxometalate (POM) cluster-anions. These POM clusters can also be lacunary, containing a vacancy. Coordination of heteroatoms into these vacancies leads to substituted polyoxometalates[4]. The central idea of this project is that an organic solution containing a lacunary POM-IL should be able to extract different metal ions from an aqueous solution by forming substituted polyoxometalate ions.

In this project the extraction of different metals of interest like copper, indium, lanthanum and neodymium using lacunary POM-ILs is examined. By variation of both the organic cation and the polyoxometalate anion different POM-ILs are synthesized and their extraction efficiencies compared. The influence of experimental conditions like the concentrations of POM-IL and metal salt, pH value and volume ratio is also investigated to find the optimal set of parameters.

Future parts of the project will focus on the reconvery of the ectracted metals using electrochemical reduction and the subsquent use of the POM-IL for multiple extraction cycles.

[1]: https://goldrechner24.de/so-viel-edelmetall-steckt-in-ihrem-smartphone/
[2]: https://utopia.de/ratgeber/konfliktrohstoffe-smartphone-probleme_596230/
[3]: S. Herrmann, M. Kostrzewa, A. Wierschem, C. Streb, *Angew. Chem Int. Ed.* **2014**, *53*, 1-5.
[4]: R. Zarrougui, R. Mdimagh N. Raouafi, *Separation and Purification Technology* **2017**, *175*, 87-98.

4: Asymmetric Organic Inorganic Hybrid Wells Dawson Polyoxometalates

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Asymmetric organic-inorganic hybrid Wells Dawson polyoxometalates are phosphotungstates in which two different organic moieties are covalently bound to the cluster core.[1] The choice of the organic components plays a crucial role in tuning their electrochemical and physical properties.[2] By changing the organic component and bridging heteroatom (Sn, Si, P, As, etc), different functions and structural features can be achieved.

This poster describes the synthesis and characterisation of asymmetric hybrid polyoxometalates, bearing 3-phosphonopropionic acid (PPA) and 2,2′:6′,2′′-terpyridine (TPY). The electro- and photo-chemical properties of these hybrid POMs were assessed by cyclic voltammetry and UV-Vis spectroscopy, respectively, and compared to those of the plenary parent POMs.

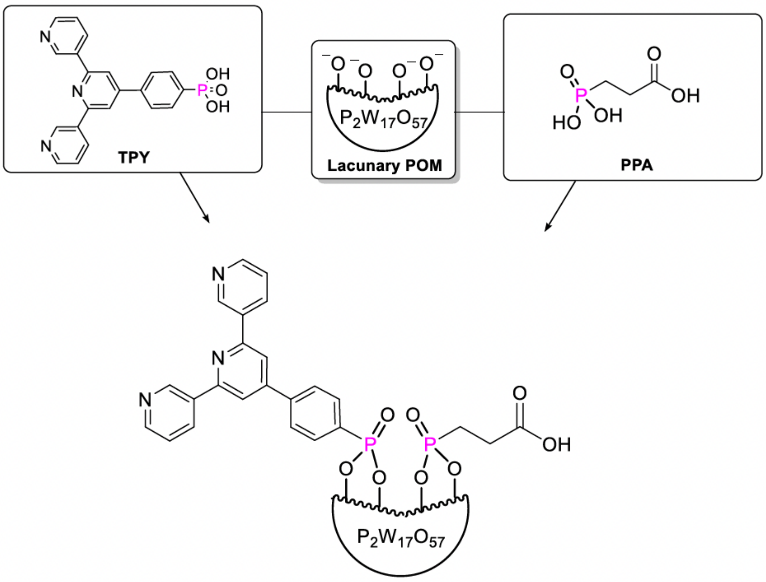

Figure 1: Synthesis of asymmetric hybrid polyoxometalates.

(1) Hampson, E.; Cameron, J. M.; Amin, S.; Kyo, J.; Watts, J. A.; Oshio, H.; Newton, G. N. Asymmetric Hybrid Polyoxometalates: A Platform for Multifunctional Redox-Active Nanomaterials. *Angew Chem Int Ed* **2019**, *58* (50), 18281–18285. https://doi.org/10.1002/anie.201912046.
(2) Martin, C.; Kastner, K.; Cameron, J. M.; Hampson, E.; Alves Fernandes, J.; Gibson, E. K.; Walsh, D. A.; Sans, V.; Newton, G. N. Redox-Active Hybrid Polyoxometalate-Stabilised Gold Nanoparticles. *Angew Chem Int Ed Engl* **2020**, *59* (34), 14331–14335. https://doi.org/10.1002/anie.202005629.

5: Electrocatalytic Reduction of Activated or Captured CO2 using Polyoxometalates

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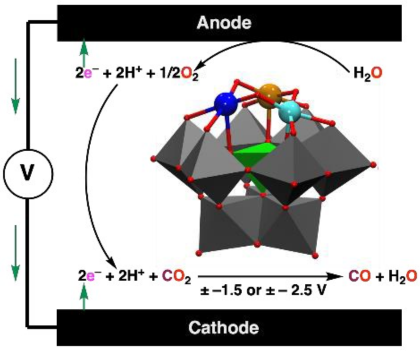
One of the most versatile CO_2 mitigation reactions is the reduction of CO_2 to CO as a platform chemical; a reaction that mimics the carbon monoxide dehydrogenase (CODHase) enzymes.[1,2] In this research, we have demonstrated new approaches for the electrochemical reduction of CO_2 by polyoxometalate electrocatalysts. Trimetallo-substituted polyanions are shown to be electrocatalysts for CO_2 reduction – CO oxidation.[3] A catalytic Tafel plot showed that $\{SiCu_{II3}W_9\}$ was the most reactive for CO_2 reduction and electrolysis yielded significant amounts of CO with 98% faradaic efficiency. In contrast, Fe-Ni compounds e.g. $\{SiFeNi_2W_9\}$ catalyzed the oxidation of CO to CO_2. Operaƒƒndo Raman spectroscopy in the presence of CO_2 showed different stable intermediates for $\{SiCu_{II3}W_9\}$ and $\{SiFe_{III}Ni_{II2}W_9\}$.[3] Electrocatalytic CO_2 reduction, CO_2RR to CO, is replete with challenges including the need to carry out the CO_2RR at low overpotentials. Previously, it was shown that a tricopper substituted polyoxometalate, $\{SiCu_{II3}W_9\}$, reduced CO_2 to CO with very high faradaic efficiency albeit at -2.5V versus Fc/Fc_+.[3] It is now demonstrated that introducing a non-redox metal Lewis acid, preferably Ga_{III}, as a binding site for CO_2 in the first coordination sphere of the polyoxometalate, forming heterometallic polyoxometalates such as $\{SiCu_{II}Fe_{III}Ga_{III}W_9\}$, leads to bimodal activity optimal both at -2.5 V and -1.5 V versus Fc/Fc_+; reactivity at -1.5V being at an overpotential of only ~200 mV.[4] These results were observed by cyclic voltammetry measurements and quantitative controlled potential electrolysis in undivided cells, where high faradic efficiency and chemoselectivity were obtained at -2.5V and -1.5V. IR spectroscopy showed that CO_2 binds to $\{SiCu_{II}Fe_{III}Ga_{III}W_9\}$before reduction. In-situ electrochemical attenuated total reflection surface-enhanced infrared absorption spectroscopy (ATR-SEIRAS) with pulsed potential modulated excitation revealed different observable intermediate species at -2.5V and -1.5 V. Using purified CO_2 as a starting material increases the overall cost of the process. The developed method includes chemically capturing CO_2, effectively isolating or separating it from other gases without releasing it. This captured CO_2, in the form of respective ammonium carbamate compound, is then electrochemically reduced at the cathode to produce carbon monoxide, possibly along with hydrogen by using catalysts.[5] Constant potential electrolysis of -0.9V vs. Ag/AgCl was carried out for 15 h at room temperature containing 2mM $\{SiCu_2GaW_9\}$ dissolved in 6 ml of the aqueous ammonium carbamate, yielding significant amounts of CO and H_2 as products comparing to $\{SiCuFeGaW_9\}$ and other polyoxometalates that yielding significant amounts of CO and H_2 as products at a more negative potential (-1.5V vs. Ag/AgCl). This catalyst was active in homogeneous and heterogeneous reaction setups at less negative potential yielding significant amounts of CO and H_2 as products. Overall, our research pioneers novel electrocatalysts for CO_2 reduction and presents a promising approach for sustainable and economically viable carbon utilization.



References:
[1] L. Xu, Y. Xiu, F. Liu, Y. Liang, S. Wang, *Molecules* **2020**, *25*, DOI 10.3390/molecules25163653.
[2] T. I. Doukov, T. M. Iverson, J. Seravalli, S. W. Ragsdale, C. L. Drennan, *Science (80-.).* **2002**, *298*, 567–572.
[3] D. Azaiza-Dabbah, C. Vogt, F. Wang, A. Masip-Sánchez, C. de Graaf, J. M. Poblet, E. Haviv, R. Neumann, *Angew. Chemie* **2022**, *134*, DOI 10.1002/ange.202112915.
[4] D. Azaiza-Dabbah, F. Wang, E. Haddad, A. Solé-Daura, R. Carmieli, J. M. Poblet, C. Vogt, R. Neumann, *J. Am. Chem. Soc.* **2024**, *146*, 27871–27885.
[5] G. Lee, Y. C. Li, J.-Y. Kim, T. Peng, D.-H. Nam, A. Sedighian Rasouli, F. Li, M. Luo, A. H. Ip, Y.-C. Joo, E. H. Sargent, *Nat. Energy* **2020**, *6*, 46–53.

6: Exploring The Quantum Confinement Effects And Photochemistry Of Iron(III)-oxo Clusters

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To address the current energy crisis, new technologies need to be developed, and water splitting is an important process to generate green hydrogen. A photocatalyst is required for this process that can promote both proton reduction as well as water oxidation.[1] Hematite (α-Fe_2O_3) is a promising material for this process due to its high natural abundance, low toxicity, and ideal band gap of ~2.2 ev.[2] However, the large-scale realisation of this material remains a challenge due to short charge carrier distances (~2-6 nm)[3] and the need for an external bias of ~0.6 V to drive the overall water splitting process.[4] Quantum confinement effects in ultrasmall systems could be utilised to effectively tune the band gap of the clusters based on their size, potentially removing the need for a potential bias. However, the effect of size upon the electronic structure of strongly correlated materials such a hematite is not widely explored in the literature. Iron-oxo clusters are atomically defined analogues of bulk oxide materials,[5,6] and in this poster the electronic structure and photochemistry of iron–oxo clusters will be explored using UV-Vis, electrochemistry, XPS and ultrafast spectroscopy.

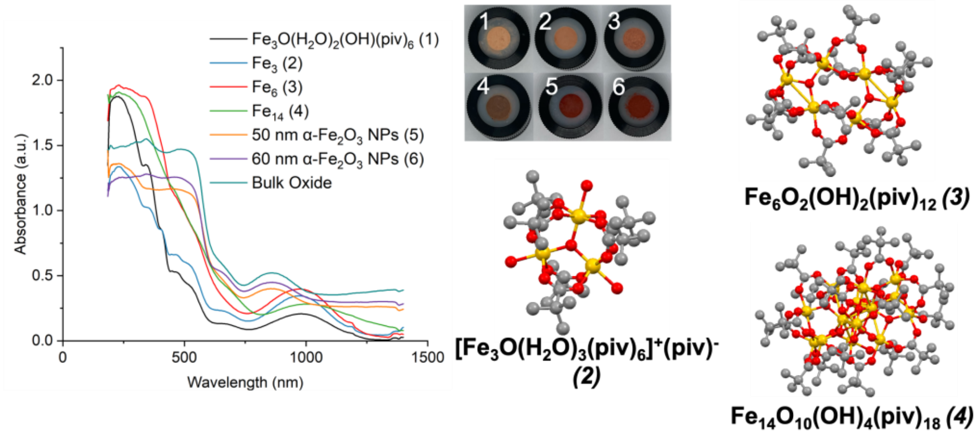

Figure 1: Solid-state UV-Vis spectra and crystal structures of clusters and nanoparticles of different sizes showing a blue shifing effect of the charge transfer onset with smaller sizes, consistent with quantum confinement effects.

1. F. Wang, L. Song, H. Zhang, L. Luo, D. Wang and J. Tang, *J Electron Mater*, 2017, **46**, 4716–4724.
2. P. S. Bassi, Gurudayal, L. H. Wong and J. Barber, *Physical Chemistry Chemical Physics*, 2014, **16**, 11834–11842.
3. S. Shen, S. A. Lindley, X. Chen and J. Z. Zhang, *Energy Environ Sci*, 2016, 9, 2744–2775.
4. H. Pan, X. Meng and G. Qin, *Phys Chem Chem Phys*, 2014, **16**, 25442–25448.
5. S. G. Baca, M. Speldrich, J. Van Leusen, A. Ellern and P. Kögerler, *Dalton Transactions*, 2015, **44**, 7777–7780.
6. S. G. Baca, M. Speldrich, A. Ellern and P. Kögerler, *Materials*, 2010, **4**, 300–310.

7: Selective Gas Sorption in a Microporous Octamolybdate-Metalorganic Hybrid

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The extended open framework $[\{Cu(cyclam)\}_3\{\kappa\text{-}Mo_8O_{27}\}]\cdot 14H_2O$ (**1**, cyclam = 1,4,8,11-tetraazacyclotetradecane) undergoes two sequential single-crystal-to-single-crystal transformations upon thermal dehydration to afford two anhydrous phases with permanent microporosity: $[Cu(cyclam)][\{Cu(cyclam)\}_2(\lambda\text{-}Mo_8O_{27})]$ (**2a**) and $[\{Cu(cyclam)\}_3(\mu\text{-}Mo_8O_{27})]$ (**3a**) [1]. Surprisingly, solid-phase transitions imply not only modifications in the crystal packing, but also the isomerization of octamolybdate anions, leading to three octamolybdate clusters which have never been observed before (Figure 1A). The thermally activated phases display accessible empty channels which have proved to adsorb C1 and C2 gases at high temperatures (273 and 298 K). Further investigations in the adsorption capacity of these compounds by using ideal adsorbed solution theory (IAST) revealed that **3a** showed significant potential for selective separation of gas mixtures (Figure 1B-1C), specially; i) the ability to preferentially adsorb C_2H_2 over C_2H_4 ($S_{C_2H_2/C_2H_4} = 3.0$) even at very low concentration of acetylene (1:99), with values comparable to those for commercial sorbents [2], and ii) the selective uptake of C_2H_6 over C_2H_4 ($S_{C_2H_6/C_2H_4} = 1.4$), which makes this compound compound one of the scarce materials exhibiting this behaviour as most of the adsorbents reported in literature share the opposite trend [3]. These features make **3a** a promising molecular separator with interesting sensing ability. Breakthrough experiments demonstrate that this behaviour can be extended to a real gas flow.

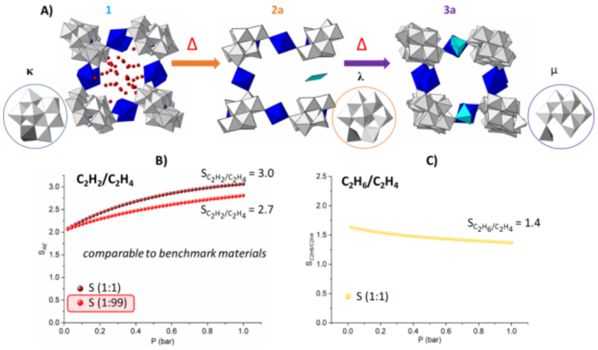

Figure 1: A) Schematic representation of the SCSC transformations of 1, together with sorption selectivity of different C2 gas mixtures on 3a predicted by IAST calculation for B) C_2H_2/C_2H_4 and C) C_2H_6/C_2H_4.

[1] E. Ruiz-Bilbao, A. Iturrospe, S. Reinoso, B. Artetxe, G. Beobide, L. San Felices, L. Lezama, J. M. Gutiérrez-Zorrilla, S. Darwish, D. Sensharma, M. J. Zaworotko, *Angew. Chem. Int. Ed.* **2023**, *62,* e202307436.

[2] T.-L. Hu, H. Wang, B. Li, R. Krishna, H. Wu, W. Zhou, Y. Zhao, Y. Han, X. Wang, W. Zhu, Z. Yao, S. Xiang, B. Chen, *Nat. Commun.* **2015**, *6*, 7328.

[3] L. Li, R.-B. Lin, R. Krishna, H. Li, S. Xiang, H. Wu, J. Li , W. Zhou, B. Chen, *Science* **2018**, *362*, 443.

8: Data-driven strategies for the study of the aqueous speciation of polyoxometalates using POMSimulator

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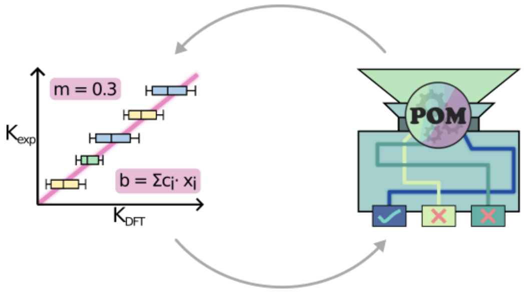
For the past 5 years, our group has been developing a novel computational methodology called POMSimulator[1–4] aimed at simulating complex Chemical Reaction Networks (CRNs) that take place in the self-assembly of polyoxometalates. From DFT calculations this methodology can automatically generate and solve millions of CRNs for isopolyoxometalates (IPA). More recently we have expanded the use of POMSimulator to heteropolyoxometalates (HPA).[5]

The huge amount of data generated in the POMSimulator framework has encouraged us to the development of a new data-driven approach for the prediction of the scaling parameters of formation constants derived from DFT calculations.[6] Additionally, to reduce the computational cost of DFT calculations, we have developed a new GNN model based on AABBA autocorrelations[7] for the prediction of thermodynamical properties. In this communication, these new data-driven strategies will be discussed.



[1] E. Petrus, M. Segado, C. Bo, *Chemical Science* **2020**, *11*, 8448–8456.
[2] E. Petrus, C. Bo, *Journal of Physical Chemistry A* **2021**, *125*, 5212–5219.
[3] E. Petrus, M. Segado-Centellas, C. Bo, *Inorg. Chem.* **2022**, *61*, 13708–13718.
[4] E. Petrus, J. Buils, D. Garay-Ruiz, M. Segado-Centellas, C. Bo, *J Comput Chem* **2024**, *45*, 2242–2250.
[5] J. Buils, D. Garay-Ruiz, M. Segado-Centellas, E. Petrus, C. Bo, *Chem. Sci.* **2024**, 10.1039.D4SC03282A.
[6] J. Buils, D. Garay-Ruiz, E. Petrus, M. Segado-Centellas, C. Bo, *Digital Discovery* **2025**, 10.1039.D4DD00358F.
[7] L. Morán-González, J. E. Betten, H. Kneiding, D. Balcells, *J. Chem. Inf. Model.* **2024**, *64*, 8756–8769.

9: Advanced Optical and Magnetic Properties In 2D Hybrid Systems Featuring Lanthanide-Polyoxometalates

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Lanthanide complexes that exhibit both single-molecule magnet (SMM) behavior and optical properties are particularly attractive for advanced quantum and spintronic applications. The combination of slow magnetic relaxation and luminescence enables multifunctional materials that can be used for quantum information storage, optically addressable spin qubits, and magneto-optical devices.[1] However, to fully exploit their potential, it is crucial to assemble these molecular units into well-ordered architectures that preserve and enhance their intrinsic properties. Metal-organic frameworks (MOFs) provide an ideal platform for this purpose, as their tunable structures allow for precise control over the spatial arrangement of the lanthanide clusters. By carefully selecting linkers and metal centers, it is possible to modulate magnetic coupling between the paramagnetic atoms, enhance coherence properties, and optimize luminescence and magnetic behavior for targeted applications.[2]

Given all of the above, when $[Ln(W_5O_{18})_2]^{9-}$ Peacock-Weakley-type polyoxometalate anions that show interesting optical and magnetic properties[1,3] and $\{X(cyclam)\}^{2+}$ -linkers (X = Cu, Zn) are used, novel 2D metal-organic frameworks are designed. When Cu(II) is used, nine isostructural compounds with the general formula $K[\{Ln_{III}(W_5O_{18})_2\}\{Cu(cyclam)(H_2O)\}_4]\cdot 12H_2O$ (**CuLn**, Ln = Ce – Ho) are obtained. However, when Zn(II) is used as transition metal source, new derivatives with the general formula $Na_3[\{Ln_{III}((W_5O_{18})_2\}\{Zn(cyclam)\}_2\{Zn(cyclam)(H_2O)_2\}\cdot 18H_2O$ (**ZnLn**, Ln = La – Tb) are formed. Zn derivatives show enhanced luminescence properties in comparison to the Cu derivatives. These latter compounds do not exhibit solid-state photoluminescence, while their SMM properties show a slight improvement compared to their precursors.

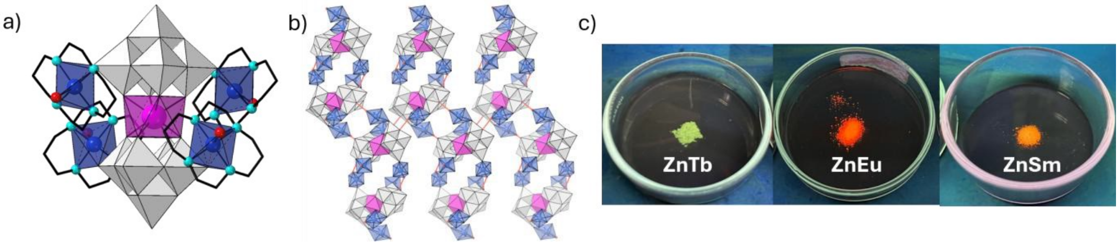

Figure 1.- a) Molecular structure of CuEu; b) projection of the supramolecular hybrid sheet parallel to the $[11\bar{1}]$ plane and c) ZnLn compounds under UV light. Color code: {WO6}, grey; {EuO8}, pink; Cu, dark blue; N, light blue; Owater, red; C, black. K and H atoms and solvent water molecules are omitted for clarity. H bonds are represented as red lines.

[1] Shiddiq, M.; Komijani, D.; Duan, Y.; Gaita-Ariño, A.; Coronado E.; Hill, S. *Nature*. **2016**, *531*, 348–351.
[2] Cardona-Serra, S.; Clemente-Juan, J. M.; Coronado, E.; Martí-Gastaldo, C.; Navarro-Moratalla, E. *Eur. J. Inorg. Chem.* **2013**, *2013* (10-11), 1903–1909.
[3] Sugeta, M.; Yamase, T. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 444–449.

10: Data-driven Approches in Polyoxometalate Catalysis: The Water Oxidation Case

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Traditional computational catalysis relies on the description of elementary reaction steps through the characterization of minima and transition states on the potential energy surface (PES) using quantum mechanics (commonly DFT) methods. An alternative, computational strategy consists of deriving mathematical models with parameters (descriptors) that could be fit to reproduce data.

Metal-oxo clusters have been extensively used to design oxidation catalysts in a variety of reactions, including selective, green oxidation of organic substrates and the nowadays ubiquitous water oxidation catalysis (WOC).[1] These clusters can serve as a template for larger catalysts architectures, incorporate other catalytically active transition metals (TMs) generating complexes soluble in polar solvents or tractable molecular models of single-site heterogeneous catalysts. Computationally, the mechanism of WOC by TM-substituted polyoxometalates has been stablished,[2] and Linear Scaling Relationships (LSRs) between Proton-Coupled Electron-Transfer (PCET) steps were constructed.[3] Here, we will present our attempts to employed statistical data-driven approaches to predict the catalytic outcome of large sets of clusters and inspire the design of novel catalysts.

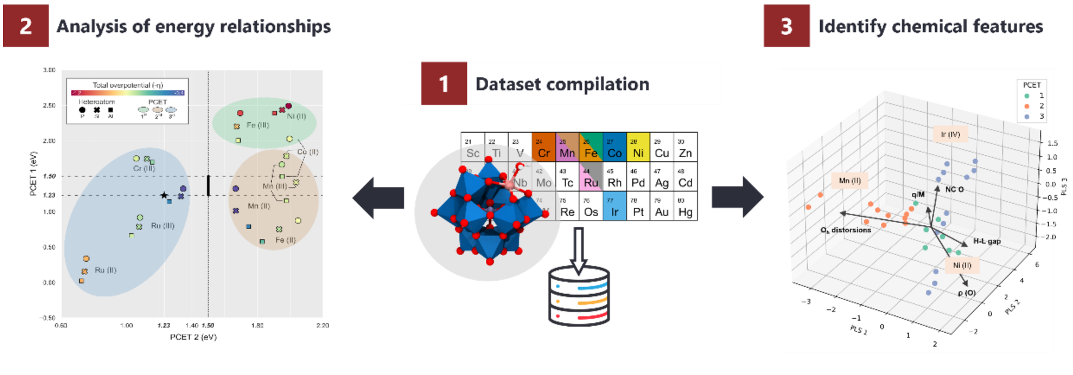

Figure 1: Schematic representation of the data-driven workflow.

[1] S. J. Folkman, J. Soriano-Lopez, J. R. Galán-Mascarós, R. G. Finke. *J. Am. Chem. Soc.*, **2018**, *140*, 24910-24916.
[2] (a) J. Soriano-López, D. G. Musaev, C. L. Hill, J. Ramón Galán-Mascarós, J. J. Carbó, J. M. Poblet, *J. Catal.* **2017**, *350*, 56-63; (b) K. Azmani, M. Besora, J. Soriano-López, M. Landolsi, A.-L. Teillout, P. de Oliveira, I.-M. Mbomekallé, J. M. Poblet, J.-R. Galán-Mascarós, *Chem. Sci.* **2021**, *12*, 8755-8766.
[3] M. J. Craig, R. Barda-Chatain, M. García-Melchor. *J. Catal.*, **2021**. *393*, 202-206.

11: Dye-sensitized photocathodes based on photosensitizer-polyoxometalate hybrid assemblies

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In artificial photosynthesis, the goal is to integrate light harvesting and the catalysis of water electrolysis (or carbon dioxide reduction) into a single photoelectrochemical (PEC) device. Polyoxometalates (POMs), known for their exceptional electron-storage capacity and redox stability, have attracted significant attention in artificial photosynthetic devices as redox mediators, electron shuttles, and electron/proton reservoirs. Association of a photosensitizer (PS) to a POM brings about visible light-induced electron transfer leading to a charge-separated (CS) state with the hole on the PS and an electron in the POM. This efficient CS state formation in PS-POM hybrids is key in their implementation in PEC photocathodes.

We have developed PS-POM hybrids based on a push-pull dye (**T1**) covalently attached onto Keggin (**K**)- and Dawson (**D**)-type polyoxotungstates [1]. A combination of electrochemistry and steady-state spectroscopy confirmed an efficient charge separation between the dye and the POM units (*i.e.*, up to 83% quenching in **K-T1**). The hybrids were grafted onto a mesoporous NiO film, a *p*-type photocathode, and photocurrent densities, *j*, were measured using $[Co(NH_3)_5Cl]^{2+}$ as sacrificial electron acceptor (*vide infra*). Indeed, this assembly exhibited *j* that is seven times higher than the reported **POM** and **T1** co-grafted (*i.e.,* non-covalent) onto nanoporous ITO emphasizing the important role of covalent attachement and the nature of the substrate [2]. Moreover, the presence of POM enhanced the *j* generated (per mole of dye) by 2-fold compared to having the **T1** dye alone. Post-mortem surface analysis of the films by wavelength dispersive X-ray spectroscopy (WDS) showed that the hybrids remained stable on the substrate throughout the measurement. Overall, the findings highlight the potential of PS-POM hybrids in their integration in PEC devices.

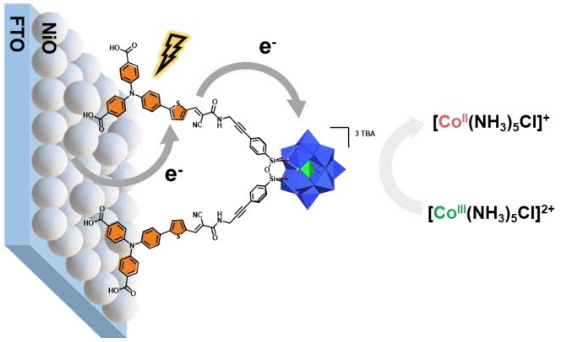

Figure: Scheme of the electron transfer pathway during the the photocurrent measurements of POM-T1 hybrids on mesoporous NiO.

[1] A. Moinel, M. Brochnow, C. Aumaître, E. Giannoudis, J. Fize, C. Saint-Pierre, J. Pécaut, P. Maldivi, V. Artero, R. Demadrille, M. Chavarot-Kerlidou, *Sustainable Energy Fuels* **2022**, *6*, 3565–3572.
[2] Y. Ben M'Barek, T. Rosser, J. Sum, S. Blanchard, F. Volatron, G. Izzet, R. Salles, J. Fize, M. Koepf, M. Chavarot-Kerlidou, V. Artero, A. Proust, *ACS Appl. Energy Mater.* **2020**, *3*, 163–169.

12: Weaving Coordination Polymers Into Dynamic Supramolecular Gels

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Incontrovertibly, building up intelligent supramolecular nanomaterials in a bottom-up fashion is the utmost achievement of the molecular switches and machines community. But even more appealing is the possibility of moving these materials from the bottom spheres, exerting an external control at each level, from the nanoscopic to macroscopic one, thanks to multiresponsive building blocks.[1,2] Here we report supramolecular coordination polymers formed between metal ions and polyoxometalate hybrids bearing two terpyridine ligands in a linear geometry (Figure 1).[3,5] Upon complexation, the polymeric chains self-assemble in fibers, on account of the electrostatic forces between the negatively charged polyoxometalate cores and the positively charged metal nodes. Eventually, the fibers physically cross-link and confer to the material a gel structure. Through SAXS and electron microscopy experiments, supported by molecular dynamics, we were able to infer the molecular-level arrangement of the polymers in the fibers. Thanks to their intrinsically dynamic nature, these gels exhibit not only interesting mechano- and thermo-responsive properties, such as birefringence or self-healing after breaking, but most interestingly the capability of yielding long-range effects by responding to minor inputs addressing the different building blocks, at the molecular, supramolecular or macromolecular level.[6]

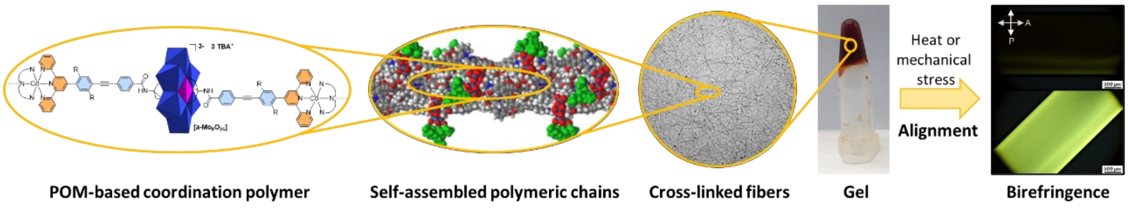

Figure 1: Self-organization from the molecular to the material level.

[1] M.-O. M. Piepenbrock, G. O. Lloyd, N. Clarke, J. W. Steed, *Chem. Rev.* **2010**, *110*, 1960–2004.
[2] C. D. Jones, J. W. Steed, *Chem. Soc. Rev.* **2016**, *45*, 6546–6596.
[3] M. S. Centellas, M. Piot, R. Salles, *et al.*, *Chem. Sci.* **2020**, *11*, 11072–11080.
[4] M. Piot, B. Abécassis, D. Brouri, *et al.*, *Proc. Natl. Acad. Sci. U.S.A.* **2018**, *115*, 8895–8900.
[5] G. Izzet, B. Abécassis, D. Brouri, *et al.*, *J. Am. Chem. Soc.* **2016**, *138*, 5093–5099.
[6] L. Casimiro, F. Volatron, G. Boivin, *et al.*, *JACS Au* **2024**, *4*, 12, 4948-4956.

13: Mixed-Valent Redox-Equilibrated Polyoxovanadates for Symmetric Non-Aqueous Redox-Flow Batteries

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Redox flow batteries (RFBs) are considered promising energy storage systems for stationary and large-scle application due to a simple and scalable design, high robustness as well as high safety and low costs.[1] The unique configuration of RFBs makes them uniquely flexible and results in decoupled energy storage and power delivery, which provides operational flexibility in different scenarios. However, conventional aqueous RFBs suffer from low energy density due to limited battery voltage, as well as significant self-discharging.[2]

Herein, we report the development of a symmetric non-aqueous RFB using the polyoxovanadate cluster [3] **$\{MV_{13}\}$** (= $(n\mathrm{Bu}_4\mathrm{N})_4$ $[\mathrm{MV}_{13}\mathrm{O}_{33}\mathrm{Cl}]$ (M= VO_2^+ or MgOH^+))) as redox active species in an acetonitrile electrolyte.[4] The **$\{MV_{13}\}$** cluster demonstrates remarkable electrochemical properties showing multiple reversible redox processes, enabling the reversible storage and release of sixteen electrons. The RFBs were assembled, and battery performances were investigated systematically, the batteries demonstrated a high specific capacity with an impressive coulombic efficiency of 93% at the current density of 0.6 mA cm^{-2}.

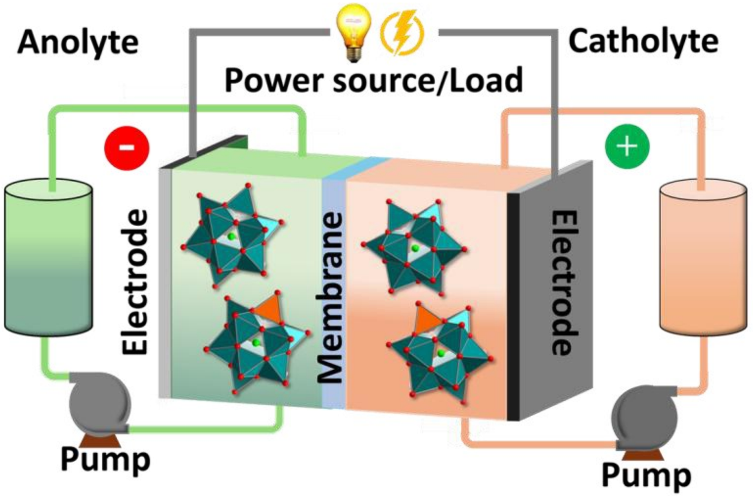

Figure 1: Schematic illustration of the symmetric $\{MV_{13}\}$-based nonaqueous redox flow battery

[1] B. Dunn, H. Kamath, J.-M. Tarascon, *Science* **2011**, *334*, 928 – 935.
[2] J. Friedl, M. V. Holland-Cunz, F. Cording, F. L. Pfanschilling, C. Wills, W. McFarlane, B. Schricker, R. Fleck, H. Wolfschmidt, U. Stimming, *Energy Environ. Sci.* **2018**, *11*, 3010 – 3018.
[3] M. Remmers, B. Mashtakov, S. Repp, S. J. Rein, K. Wang, M. Anjass, Z. Chen, L. M. Carrella, E. Rentschler, C. Streb. Redox, *Angew. Chem. Int. Ed* **2024**, e202418864.
[4] L. E. VanGelder, E. Schreiber, E. M. Matson, *J. Mater. Chem. A* **2019**, 7, 4893 – 4902.

14: Design And Synthesis Of Pyridyl Phosphonate-Functionalised Polyoxometalates

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The organofunctionalisation of polyoxometalates (POMs) offers a route towards designing organic-inorganic hybrid materials with modular structures and tunable physical properties.[1] Recent studies have shown that integrating redox-active POMs with transition metal-based coordination complexes can enhance catalytic performance through synergistic effects.[2] Such hybrid systems hold great promise for applications in electrocatalysis, energy conversion, and small-molecule activation.

In this work, we present the synthesis of novel pyridyl phosphonate-functionalised POMs as versatile building blocks for multi-component electrocatalytic assemblies. The pyridyl groups provide well-defined coordination sites for metal complexes, allowing precise control over the electronic and structural properties of the hybrid system. Our synthetic approach involves functionalising lacunary POM precursors with pyridyl phosphonate linkers, facilitating their integration with molecular electrocatalysts. Spectroscopic and electrochemical characterisation highlights their potential for modulating electron transfer properties and catalytic activity.

Future research will focus on conjugating molecular electrocatalysts to these pyridyl-modified POMs to construct structured multi-component systems.[3] By systematically tuning the electronic interactions between the POM core and the attached catalytic units, we aim to develop efficient and selective electrocatalytic systems for sustainable energy conversion and small-molecule transformations.

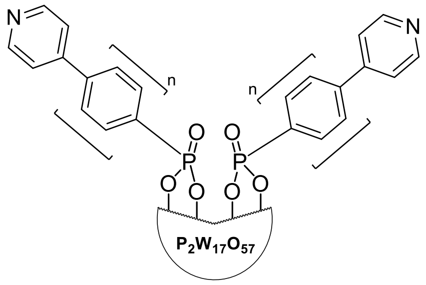

Figure 1: Proposed molecular structure of a pyridyl phosphonate-functionalised hybrid POM

[1] S. S. Amin, K. D. Jones, A. J. Kibler, H. A. Damian, J. M. Cameron, K. S. Butler, S. P. Argent, M. Winslow, D. Robinson, N. J. Mitchell, H. W. Lam and G. N. Newton, *Angewandte Chemie International Edition*, DOI:https://doi.org/10.1002/anie.202302446.
[2] E. Hampson, J. M. Cameron, J. A. Watts and G. N. Newton, *Chemical Communications*, 2020, **56**, 8237–8240.
[3] D. Basu, S. Mazumder, J. Niklas, H. Baydoun, D. Wanniarachchi, X. Shi, R. J. Staples, O. Poluektov, H. Bernhard Schlegel and C. N. Verani, *Chemical Science*, 2016, **7**, 3264–3278.

15: Proton-Coupled Electron Transfert To And From Polyoxometalates

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Polyoxometalates (POMs) are nano-sized molecular oxides that are well-known photocatalysts, able to promote Hydrogen Atom Transfer (HAT) from an organic substrate. Due to their ability to behave as multi-electron acceptors, polyoxometalates are ideal candidates to address environmental and energy challenges, particularly photocatalyzed hydrogen production[1–3]. Keggin and Wells-Dawson POMs based on W and Mo have been widely studied, but the mechanism of hydrogen evolution is still unclear. Early studies showed that silox POMs can store electrons and react with protons to eventually promote the release of H_2. We sought to understand how protons trigger electron release from our reduced SiloxPOM hybrids (Fig. 1)[4]. We also aim at achieving the reduction of O_2 into H_2O_2 with decatungstate- and Dawson-type POMs, in order to use it subsequently as a green epoxidizing agent[5].

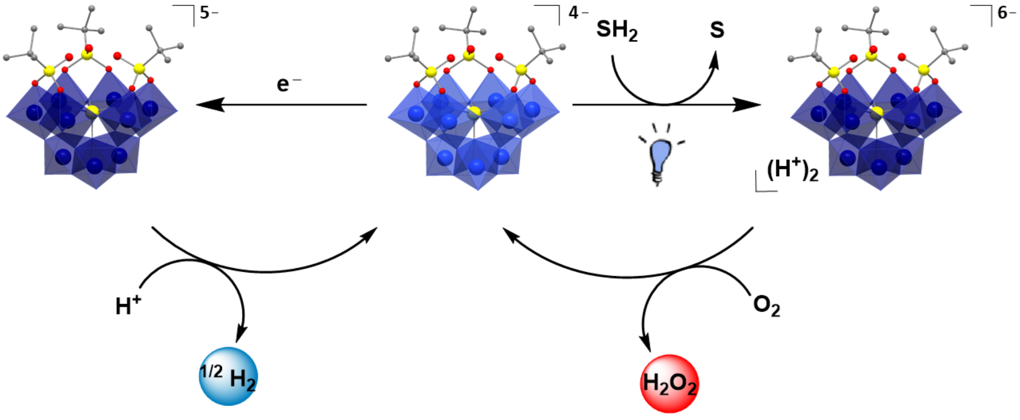

Figure 1 - (left) spontaneous hydrogen release from reduced *Silox*POM upon protonation, and (right) hydrogen peroxide formation from aerobic solution of protonated/ reduced cluster obtained by photo-oxidation of a suitable substrate SH_2.

[1] L. Hammarström, *Acc. Chem. Res.* **2015**, *48*, 840–850.
[2] B. Matt, J. Fize, J. Moussa, H. Amouri, A. Pereira, V. Artero, G. Izzet, A. Proust, *Energy Environ. Sci.* **2013**, *6*, 1504.
[3] S. Amthor, S. Knoll, M. Heiland, L. Zedler, C. Li, D. Nauroozi, W. Tobaschus, A. K. Mengele, M. Anjass, U. S. Schubert, B. Dietzek-Ivanšić, S. Rau, C. Streb, *Nat. Chem.* **2022**, *14*, 321–327.
[4] T. Zhang, A. Solé-Daura, S. Hostachy, S. Blanchard, C. Paris, Y. Li, J. J. Carbó, J. M. Poblet, A. Proust, G. Guillemot, *J. Am. Chem. Soc.* **2018**, *140*, 14903–14914.
[5] T. Zhang, L. Mazaud, L.-M. Chamoreau, C. Paris, A. Proust, G. Guillemot, *ACS Catal.* **2018**, *8*, 2330–2342.

16: Oxygen-dependent Organic Photooxidations by Polyoxometalate-functionalized Membranes

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Visible light-driven organic transformations represent a key strategy towards sustainable energy and chemical processes. Amongst various photocatalysts, polyoxometalates (POMs), owing to their well-defined redox properties and robust catalytic behavior, provides an ideal environment for such applications.

In this work, we report the fabrication of catalytically active porous block copolymer membrane via non-solvent induced phase separation (NIPS) of amphiphilic block copolymers.[1] The photocatalytic water oxidation-active POM, $(Na_{10}[Co_4(H_2O)_2(VW_9O_{34})_2]\cdot 35H_2O)$[2] $\{Co_4V_2\}$ was successfully immobilized onto the membrane via electrostatic interactions between the POM anions and the cationic charges of hydrophilic poly (amino methacrylate) units. The resulting POM immobilized membrane catalyzes photo-oxidation of 1, 5-dihydroxynapthalene (1,5-DHN), yielding juglone as the primary product under ambient conditions using air as terminal oxidant. The catalytic system exhibits an excellent regeneration and reusability over multiple cycles without any structural degradation. Furthermore, the photocatalytic oxidative homocoupling of benzylamine and photo-oxidation of benzyl alcohol shows the oxidative versatility of the heterogenous matrix.

Overall, the results highlight the potential of POM-integrated membrane as a robust and scalable platform for heterogenous photocatalysis, with promising implications for industrial oxidation processes.

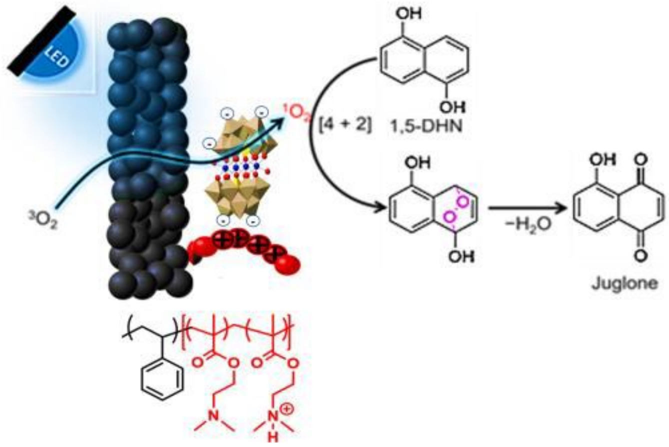

Figure : Oxygen-mediated photo-oxidation of 1,5- DHN to juglone via POM-functionalized membranes

[1] I. Romanenko, M. Lechner, F. Wendler, C. Hörenz, C. Streb, F. H. Schacher, *J. Mater. Chem. A*, 2017,**5**, 15789-15796.
[2] H. Lv, J. Song, Y. V. Geletii, J. W. Vickers, J. M. Sumliner, D. G. Musaev, P. Kögerler, P. F. Zhuk, J. Bacsa, G. Zhu, C. L. Hill, *J. Am. Chem. Soc*. 2014, 136, **26**, 9268–9271.

17: Non-aqueous Superbasic Polyoxoniobates

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Polyoxometalates (POMs) are valued catalysts due to their high stability, tuneable redox behaviour and photoelectric behaviours.[1] While traditionally used as acid and oxidation catalysts, more highly charged POMs have recently shown promise as strong base catalysts.[2-4] In this regard, the highly charged Group 5 POMs are the main focus of attention.[5] Polyoxoniobate (PON) research has largely focused on aqueous-soluble derivatives and there have been limited studies in organic media, although these will provide opportunities to expand the systematic chemistry of basic PONs.

We are exploring organic-soluble superbasic hexaniobates with the Lindqvist stuctre with a view to developing new superbase catalysts, including their use in the ALPHA process for methyl methacrylate production. Key factors such as charge density and degree of protonation are being probed using FTIR, elemental analysis, and O_{17} spectroscopy while basicity is being accessed using indicators and model organic reactions. A range of tetra-alkylammonium cations is being explored in order to establish factors necessary to minimise cation decomposition during synthesis and reactivity studies. Stratagies are also being investigated to immobilise the $\{Nb_6\}$ PONs on silica supports for catalytic testing at Mitsubishi Chemical UK, where the ALPHA process was developed.

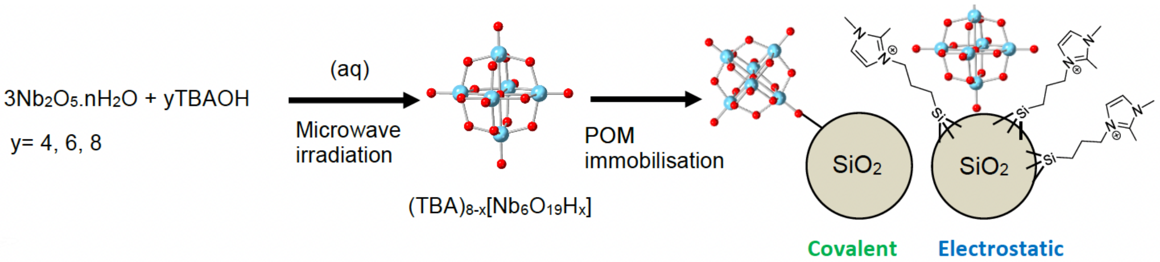

Figure 1: Project outline

POMs immobilized to trial with ALPHA process

1. S. Wang, G, Yang, *Chem. Rev.*, 2015, **115**, 11, 4893–4962
2. C. Sun, S. Liu, D. Liang, K. Shao, Y. Ren, Z. Su, *J. Am. Chem. Soc.*, 2009, **131**, 5, 1883–1888.
3. H. Lv, Y. V. Geletii, C. Zhao, J. W. Vickers, G. Zhu, Z. Luo, J. Song, T. Lian, D. G. Musaevb, C. L. Hill, *Chem. Soc. Rev.*, 2012, **41**, 7572-7589.
4. K. Kamata, K. Sugahara, *Catalysts*, 2017, **7**, 345.
5. S. Hayashi, N. Sasaki, S. Yamazoe, T. Tsukuda, *J. Phys. Chem. C*, 2018, **122**, 51, 29398–29404.

18: Polyoxometalate-Based Covalent Organic Frameworks for Targeted Pollutant Separation

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Strategically integrating polyoxometalates (POMs) into covalent organic frameworks (COFs) is an innovative approach to developing advanced materials for environmental remediation.[1] In this study, we present the design and synthesis of a robust cationic COF formed by the Schiff base condensation of triaminoguanidinium chloride (TAG$_{Cl}$) and 1,3,5-triformylphloroglucinol (TP).[2] This is the first successful implementation of a guanidinium-based cationic framework for fabricating POM-COF hybrids via ion-exchange strategies. These exchangeable framework ions provide an exceptional opportunity to adjust the COF's porosity and pore dimensions at the nanoscale. Incorporating the Keggin-type polyoxometalate $[PW_{12}O_{40}]^{3-}$ into the cationic COF matrix notably enhances its ability to capture toxic oxoanionic pollutants from aqueous environments.[3] The resulting POM–COF composite exhibits remarkable stability, rapid adsorption kinetics, and a high affinity for hazardous anionic species. This performance is attributed to synergistic interactions, including electrostatic attraction, hydrogen bonding, and redox activity, between the COF host and POM guests. Our findings underscore the potential of cluster-based hybrid materials in addressing critical environmental challenges. We provide a thorough overview of this novel material's synthesis, structural characterization, and pollutant removal efficiency, demonstrating its potential in advanced water purification technologies.

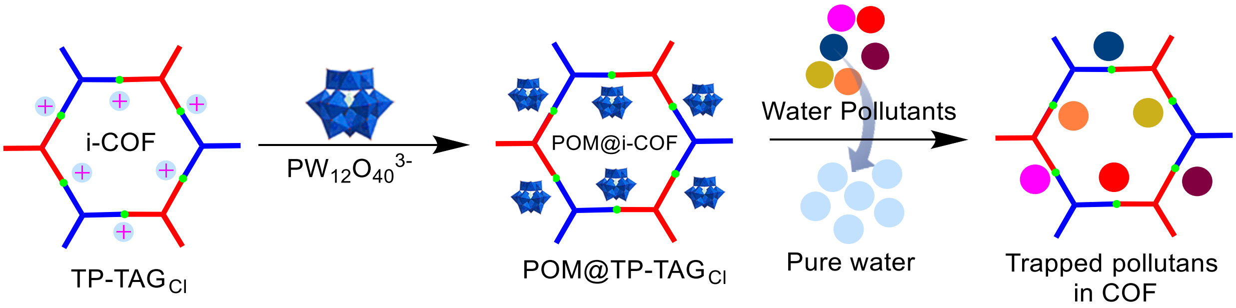

Figure: Representation POM based COF for oxoanionic pollutant capture

[1] M. Lu, M. Zhang, J. Liu, T.-Y. Yu, J.-N. Chang, L.-J. Shang, S.-L. Li and Y.-Q. Lan, *Journal of the American Chemical Society* **2022**, *144*, 1861-1871.
[2] M. Liu, Q. Xu and G. Zeng, *Angewandte Chemie International Edition* **2024**, *63*, e202404886.
[3] N. I. Gumerova and A. Rompel, *Nature Reviews Chemistry* **2018**, *2*, 0112.

19: Guest Transition Metals in Host Keplerate Nanocapsules as Inorganic Functional Mimics of Monooxygenase Enzymes

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Keplerate type Polyoxometalate nanocapsules are known host compounds. It was often demonstrated to host many types of organic molecules and inorganic cations.[1] We showed in previous research the possibility to stabilize transition metals guests inside a {Mo132} Keplerate nanocapsule with phosphate lignds, in organic solution.[2] Since then, we have modified the encapsulation process and used different ligands that contain functional groups that coordinate transition metals, so the encapsulation can be carried out in aqueous solution.

The next step in this research direction is to investigate the catalytic properties of such an assembly. As the Keplerate nanocapsules hosts are redox active cages that contain pores for substrate insersion and the transition metal guests can be used as catalytic centers in confined space, we are using this assembly as a functional mimic of metaloenzymes. In the research presented here, we encapsulated Fe(II) and Cu(II) inside a {W72Mo60} Keplerate POM, that contain imidazole acetate ligands. Using electrochemistry, we used this assembly to demonstrate monooxygenase type activity. Upon reduction of the encapsulated iron or copper cations, oxygen is activated and used to oxygenate alkanes, alkenes and aromatic compounds.

Here, we will present the investigation of the catalytic activity of the new assembly, with emphasis on substrate encapsulation and it’s influence on the catalytic parameters. We will show how using a unique NMR technique, GEST,[3] can help with the kinetic investigation of substrate encapsulation, and how we can easily modify the assembly to control this parameter.

[1] (a) S. Kopilevich, H. Gottlieb, K. Keinan-Adamsky, A. Müller, I. A. Weinstock, Angew. *Chem., Int. Ed.* 2016, **55**, 4476−4481. (b) B. B. Sarma, L. Avram, R. Neumann, *Chem. - Eur. J.* 2016*,* **22**, 15231−15236. (c) R. Pow, W. Xuan, D.L. Long, N. Bell, L. Cronin, *Chem. Sci.* 2020*,* **11**, 2388−2393. (d) S. Chakraborty, A. Shaniderman-Grego, S. Garai, M. Baranov, A. Müller, I. A. Weinstock, J. *Am. Chem. Soc.* 2019*,* **141**, 9170−9174. (e) A. Müller, S. K. Das, S. Talismanov, S. Roy, E. Beckmann, H. Bogge, M. Schmidtmann, A. Merca, A. Berkle, L. Allouche, Y. Zhou, L. Zhang, *Angew. Chem. Int. Ed*. 2003, **42**, 5039 –5044
[2] E. Haviv, B. Chen, R. Carmieli, L. Houben, H. Cohen, G. Leitus, L. Avram, R. Neumann, *J. Am. Chem. Soc.* 2020, **142,** 34, 14504-14512.
[3] L. Avram, M. Iron, A. Bar-Shir, *Chem. Sci.* ,2016*,* **7**, 12, 6905-6909.

20: Electrocatalytic CO_2 Reduction Coupled with Alkene Oxidation

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With the increasing amount of CO_2 gas in the atmosphere, there is scientific effort to find a way to convert the CO_2 into valuable chemicals. One of the methods which being studied is electrochemical reduction of CO_2 to CO using transition metals containing catalysts.[1] The CO_2 reduction rection (CO_2RR) occurs on the cathode while on the anode, usually, there is water oxidation reaction to form O_2 (OER). Two major challenges with this process are first, the O_2 that being formed in the anode is released without being used and second, the thermodynamic potential of OER is high (1.23 V) which leads to high cell potential (low energy efficiency).[2]

Here, the electrochemical reduction of CO_2 was coupled to the electrochemical activation of water, while using the 'activated water' specie for alkene oxidation. In this way, the oxygen atom is transferred to high value product instead of being released as O_2 gas.

Polyoxometalates (POMs) were used as catalysts for those reactions. Copper substituted POM, $[SiW_9Cu_3O_{37}]^{10-}$, was used for CO_2 reduction reaction[3] and cobalt substituted POM, $[Co_9(H_2O)_6(OH)_3(HPO_4)_2(PW_9O_{34})_3]^{16-}$, for water activation reaction.[4] We showed that we can couple the two reactions and form CO in the cathode and epoxide in the anode. In addition, we showed that by using the cobalt catalyst in the anode we can decrease the potential on the anode, which leads to higher yields and faradaic efficiency.

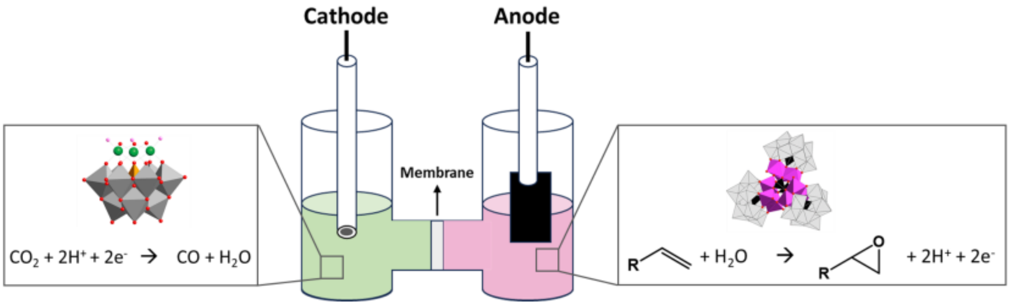

Figure 1: Electrochemical cell for CO_2 reduction coupled to alkene oxidation.

[1] M. Mikkelsen, M. Jørgensen, F. C. Krebs, *Energy Environ. Sci.* **2010**, *3*, 43–81.
[2]J. Na, B. Seo, J. Kim, C. W. Lee, H. Lee, Y. J. Hwang, B. K. Min, D. K. Lee, H.-S. Oh, U. Lee, *Nat. Comm.* **2019**, *10*, DOI 10.1038/s41467-019-12744-y.
[3] D. Azaiza-Dabbah, C. Vogt, F. Wang, A. Masip-Sánchez, C. de Graaf, J. M. Poblet, E. Haviv, R. Neumann, *Ange. Chem. Int. Ed.* **2021**, 61, DOI 10.1002/anie.202112915.
[4] J. Soriano-López, S. Goberna-Ferrón, L. Vigara, J. J. Carbó, J. M. Poblet, J. R. Galán-Mascarós, *Inorg. Chem.* **2013**, *52*, 4753–4755.

21: Superchaotropic polyoxometalate binding as a switchable crosslinking motif in polymer solutions and gels

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α-Keggin poyloxometalates (POMs) with low charge density, such as $SiW_{12}O_{40}^{4-}$ (SiW, Fig.1a) interact strongly with non-ionic hydrated interfaces driven by a water-mediate driving force, called the chaotropic effect.[1] In solution of a non-ionic polymer, hydroxypropylcellulose (HPC), this binding results in more than 100-fold increase in viscosity at millimolar HSiW-concentrations, see Fig.1b, and even induces gelation at higher HSiW-concentration at c(HSiW) > 30 mM.[2] These effects even exceed those of the ionic surfactant SDS, which has been widely studied for its thickening effects on non-ionic polymers. For HSiW, these rheological effects appear because the POMs bind tightly to the polymer with K_A= 200 mM^{-1} and act as physical crosslinks between adjacent polymer chains forming a network as found by Small Angle Neutron Scattering. As the Keggin POM is a photocatalyst, photoredox reactions can be employed to reduce the POM, increase its charge density and thus diminish its binding to HPC. Photoredox cycles with ascorbic acid as a sacrificial reducing agent and atmospheric O_2 as an oxidizing agent were then used to generate switchable HPC-solutions and gels, see Fig.1c. This concept of switchable chaotropicity for POMs enables a unique and novel strategy to make non-ionic polymers addressable through UV-light for soft material applications.

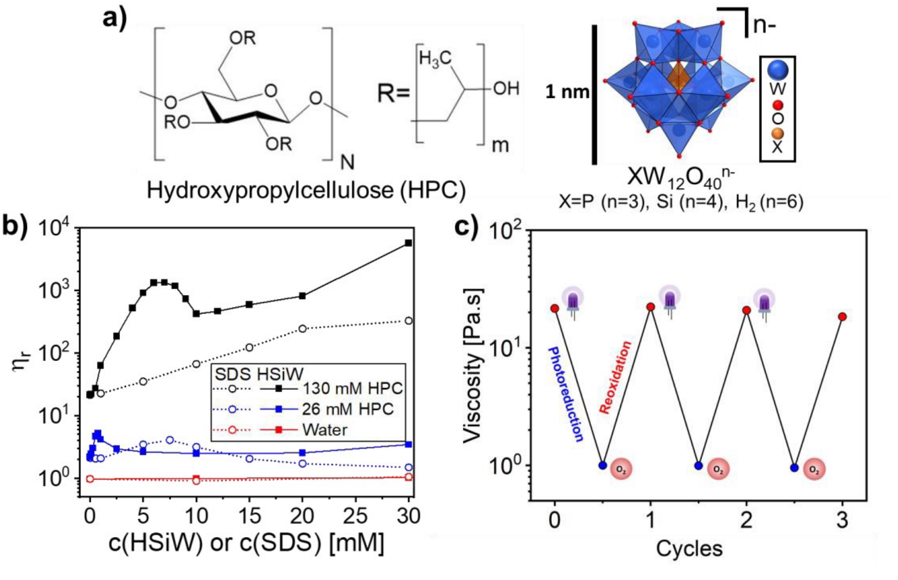

Figure 1: a) Chemical structure of hydroxypropylcellulose and the Keggin POMs. b) Viscosity of HPC solution as a function of concentration $H_4SiW_{12}O_{40}$ (HSiW) and Sodium Dodecylsulfate (SDS), c) Reversible viscosity of 130 mM HPC with 5 mM $H_3PW_{12}O_{40}$ + 250 mM ascorbic acid.

[1] K. I. Assaf, W. M. Nau, *Angew. Chem. Int. Ed.* **2018**, 57, 13968–13981

[2] M. Hohenschutz, P. Bauduin, C.G. Lopez, B. Förster, W. Richtering *Angew. Chem. Int. Ed.* **2023**, 62, e202210208

22: Insights Into The Structure Of New Tc Based Polyoxometalates: Which Is The Oxidation State?

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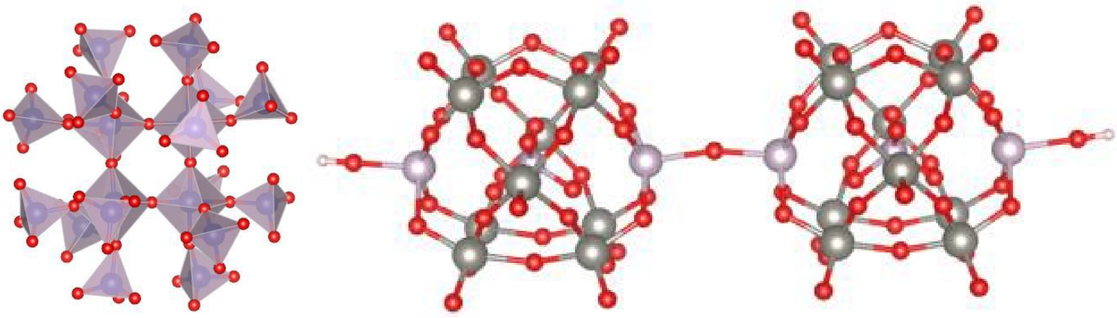
Polyoxometalates (POMs) are a class of metal-oxygen cluster anions composed primarily of early transition metals (such as Mo, W, or V) in high oxidation states. The study of complementing the experimental findings by applying computational techniques to POM-based Tc has gathered attention from our point of view.

Recently, we analyzed Tc(V) metal-oxo cyclic tetramers and discussed their relative stability, and of those Re(V) counterparts [1]. In this communication, we will also present new computational studies on the behavior of dimeric species like POM-Tc-O-Tc-POM. The bonding pattern has been investigated considering different oxidation states, such Tc3+ and Tc 4+. Through geometrical comparisons between crystal structures and DFT-optimized structures, we aim at discussing the most plausible Tc oxidation state in new Tc-based Keggin structures.



[1] J. Bustos, M. Shohel, A. G. Buzanich, L. Zakharov, J. Buils, M. Segado-Centellas, C. Bo, M. Nyman, Chem. Eur. J. 2025, 31, e202404144

23: Enhanced Proton Conduction via Proton-Coupled Electron Transfer Reaction by a Keplerate-Type Polyoxometalate Capsule

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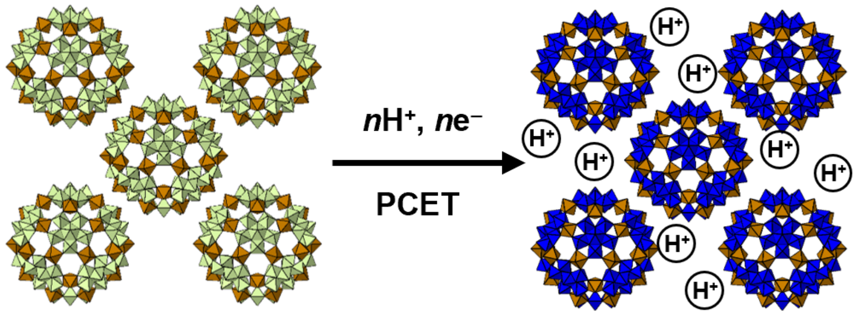
Polyoxometalates (POMs), anionic metal-oxide clusters, are actively studied for their versatile structural designs and element selectivity. A series of Keplerate-type POMs with core–shell structures, known as POM capsules, that feature a Keggin-type POM core, has been reported. These POM capsules, with their neutral to negative charge and large molecular surface area, can serve as platforms for proton (H^+) conduction. In this study, we aimed to introduce proton carriers into the POM capsule through a proton-coupled electron transfer (PCET) reaction. It is crucial to avoid excessive reduction, as it increases electrostatic interaction between the proton and the POM capsule, hindering proton conduction. The number of incorporated electrons was varied from 0 to 11, and the POM capsule containing 3 electrons exhibited proton conductivity an order of magnitude higher than that of pristine or highly reduced POM capsules. This study serves as a proof of concept, demonstrating that PCET, combined with the core–shell structure, can effectively enhance the proton conductivity without being limited by the choice of constituent elements.



POM capsule for enhanced proton conduction

Figure Proton uptake through PCET reaction in Keplerate-type POM

24: Organic Functionalization Of Thiomolybdates for HER – Enabling The Design Of Photocatalytic Dyads

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Thiomolybdates are a promising class of molecular catalysts for photocatalytic or electrocatalytic hydrogen evolution reaction (HER). [1] The prototype cluster $[Mo_3S_{13}]^{2-}$ has been studied for HER catalysis under both homogeneous and heterogeneous conditions, providing a noble metal free alternative to commonly used platinum catalysts. [2,3] Although thiomolybdates have received increasing attention in recent years, their structural diversity remains limited. [4,5] This work focuses on establishing structural modifications of thiomolybdate clusters by functionalization with organic ligands, therefore accessing more structural diversity and investigating in the photocatalytic HER activity of these new compounds. Structural modifications allow to gain further insights into the mechanism of catalytic hydrogen evolution. Furthermore, organic functionalization can be utilized to design dyads containing both, ruthenium-based photosensitizers or organic dyes respectively.

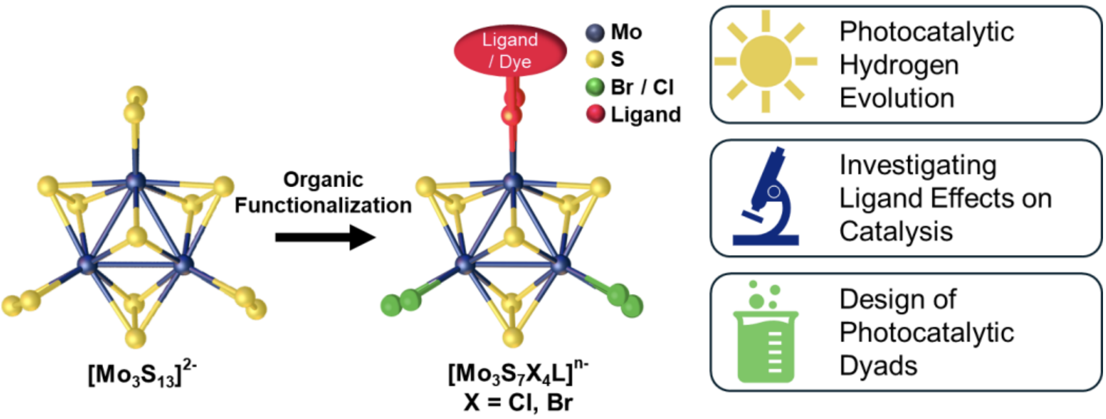

Figure 1: Simplified reaction scheme on the functionalization of $[Mo_3S_{13}]^{2-}$ with organic ligands / dye molecules and overview of main objectives.

[1] A. Müller, R. G. Bhattacharyya, B. Pfefferkorn, *Chem. Ber.* **1979**, *112*, 778–780.
[2] M.-L. Grutzka, A. Rajagopal, C. Streb, P. Kurz, *Sustain. Energy. Fuels,* **2018**, *2,* 1893-1904.
[3] M. Dave, A. Rajagopal, M. Damm-Ruttensperger, B. Schwarz, F. Nägele, L. Daccache, D. Fantauzzi, T. Jacob, C. Streb, S*ustain Energy. Fuels,* **2018**, *2,* 1020.
[4] S. Batool, M. Langer, S. N. Myakala, M. Heiland, D. Eder, C. Streb, A. Cherevan, *Advanced Materials* **2023**, 2305730.
[5] V. P. Fedin, M. N. Sokolov, Y. V. Mironov, B. A. Kolesov, S. V. Tkachev, V. Y. Fedorov, Inorganica Chim Acta **1990**, *167*, 39–45.

25: Tetris in a Tube: Exploring the Self-assembly of Polyoxometalates in Organic Media Using Multinuclear Chemical Shift Imaging NMR

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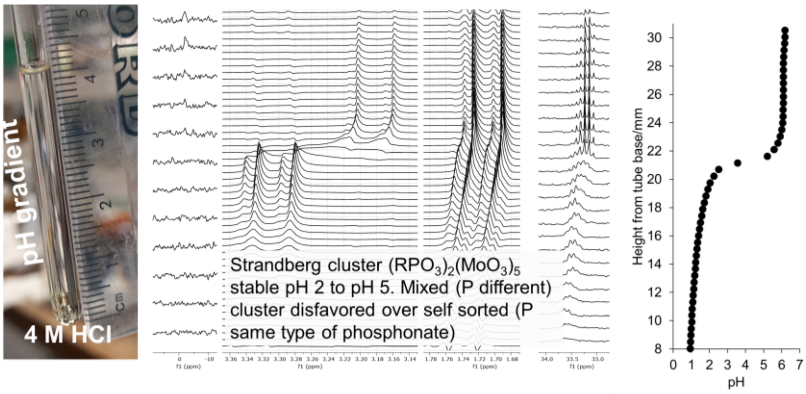
We demonstrate a high throughput technique that permits the in-situ study of the pH-sensitive self-assembly of polyoxometalates (POMs) and their speciation in a range of solvents. POM speciation is well studied using 1D-NMR [1] and computationally modelled [2] in aqueous solution, however, for solubility/stability reasons almost all synthesis of *functionalised* POMs is conducted in organic solvents. The gaps in our understanding of POM self-assembly in these solvents [3] hugely restrict POM functionalisation to top-down approaches [4] and limit our ability to design POMs to fully exploit form and function. As part of unrelated work, we have developed highly efficient methods to determine the acid dissociation constants (pK_a) of pharmaceutical ingredients in organic media.[5,6]. We create pH gradients in standard 5 mm NMR tubes and record NMR spectra at different spatial positions along the gradient using chemical shift imaging (CSI) techniques, thereby studying a system across a wide pH range simultaneously in one sample; a highly efficient approach that can nowadays be applied on any modern spectrometer. As a first study with POMs, we have followed the self-assembly of phosphates and phosphonates with sodium molybdate to give Strandberg [7] and other polyoxometalate clusters, reproducing known speciation in H_2O and enabling the rapid testing of other solvents including DMSO/water, DMF/MeCN and methanol. Our technique promises to be a highly efficient tool to address important questions regarding the behaviour of polyoxometalate clusters in organic media.



Strandberg cluster $(RPO_3)_2(MoO_3)_5$ stable pH 2 to pH 5. Mixed (P different) cluster disfavored over self sorted (P same type of phosphonate)

1 N. Gumerova and A. Rompel, *Chem. Soc. Rev.*, **2020**, *49*, 7568
2 J. Buils, D. G-Ruiz, M. S-Centellas, E. Petrus, C. Bo, *Chem. Sci.*, **2024**, *15*, 14218
3 D. Shiels, M. Pascual-Borras, P. Waddell, C. Wills, J-M. Poblet, R. J. Errington, *Chem. Comm.*, **2023**,*59*, 7919
4 J. C. Duhacek, D.C. Duncan, *Inorg. Chem.*, **2007**, *46*, 7253
5 M. Wallace, N. Abiama and M. Chipembere, *Anal. Chem.*, **2023**, *95*, 15628
6 G. Schenck, K. Baj, J. A. Iggo and M. Wallace, *Anal. Chem.*, **2021**, *94*, 8115
7 D. E. J. Packiam and K. Vidyasagar, *Dalton Trans.*, **2017**, *46*, 16102

26 Self-Limiting Assembly of a Keggin-Ion Complexed Metal-Oxide Nanocrystal Gel

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The design of functional materials via supramolecular or nanoparticle gelation is a growing frontier in nanochemistry.[1-3] Metal-oxide nanocrystals (NCs) offer unique optical, electronic, and catalytic properties, but conventional sol-gel approaches typically compromise these attributes through irreversible metal speciation and amorphous phase formation. Herein, we report a new type of gel formed by $[PSnW_{11}O_{39}]^{3-}$-O_2– ($PSnW_{11}$)-complexed SnO_2 NCs, synthesized in aqueous media without organic ligands. Unlike conventional sol-gel methods, this approach yields dynamic, reversible gels that retain the phase and properties of the constituent NCs. Cryo-SEM imaging reveals a percolated structure composed of self-limiting, negatively charged gel walls enclosing interconnected aqueous nanocavities. The gels exhibit self-healing and cation-exchange behavior, as demonstrated by solution-state NMR spectroscopy and confocal microscopy, confirming dynamic ion mobility within the network. The $PSnW_{11}$–SnO_2 gel exemplifies a new class of functional, porous nanomaterials based on POM-mediated assembly.

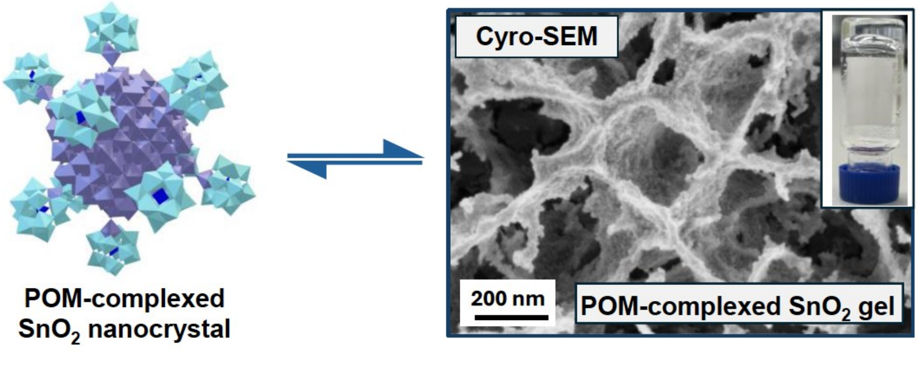

Figure 1: Representation of a $[PSnW_{11}O_{39}]^{3-}$-O_2– ligated SnO_2 NC. The SnO_2 core is in light-violet, and the $[PSnW_{11}O_{39}]^{3-}$-O_2– oxo-donor ligands are in teal blue color. The cryo-SEM image at right shows gel walls that surround water-filled cavities..

[1] Zhang, S.; Shi, W.; Wang, X., Locking volatile organic molecules by subnanometer inorganic nanowire-based organogels. *Science* **2022,** *377*, 100-104.
[2] Yeom, J.; Santos, U. S.; Chekini, M.; Cha, M.; de Moura, A. F.; Kotov, N. A., Chiromagnetic nanoparticles and gels. *Science* **2018,** *359*, 309-314.
[3] Saez Cabezas, C. A.; Ong, G. K.; Jadrich, R. B.; Lindquist, B. A.; Agrawal, A.; Truskett, T. M.; Milliron, D. J., Gelation of plasmonic metal oxide nanocrystals by polymer-induced depletion attractions. *Proc. Nat. Acad. Sci.* **2018,** *115*, 8925-8930.

27: Light-Induced Oxidation Of Benzyl Alcohol By Titanium Substituted Keggin-Type Polyoxotungstate Via Excited State PCET

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PCET processes at metal oxide surfaces are invaluable in the field of organic redox transformations, and precise understanding and control of the PCET mechanism directs the kinetics, thermodynamics and product distributions.[1] To conduct detailed mechanistic studies polyoxometalates featuring transition-metal oxide sites can be used as molecular models for the analogous solid state metaloxides.[2] In this study, a titanium substituted polyoxotungstate is investigated in the visible light driven oxidation of benzyl alcohol to benzaldehyde enabled by prior substrate coordination. The substrate precoordination was investigated using NMR, ESI-MS and absorption spectroscopy. To identify the underlying PCET processes an electrochemical investigation was performed using Pourbaix analysis and Randles-Sevcik analysis. The structure of the coordination compound was calculated using DFT and based on this structure the reduction potentials were calculated to rationalize experimental data.

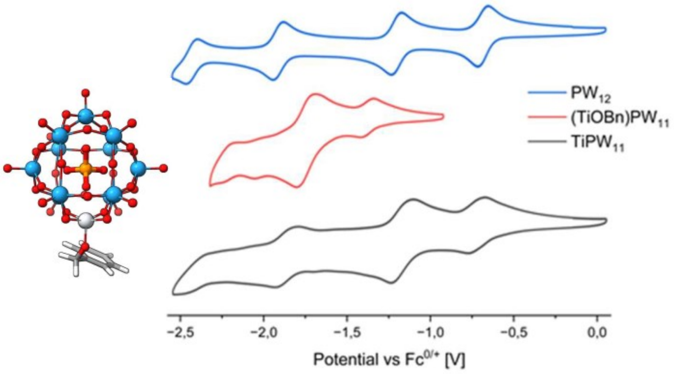

Figure 1: Calculated structure of $[(TiOBn)PW_{11}O_{39}]^{4-}$ and the CVs of $TBA_3[PW_{12}O_{40}]$ (blue), $TBA_4[(TiOH)PW_{11}O_{39}]$ (grey) and $TBA_4[(TiOBn)PW_{11}O_{39}]$ (red).

[1] J. Castillo-Lora, M. F. Delley, S. M. Laga, J. M. Mayer, *Journal of Physical Chemistry Letters* **2020**, 11, 7687–7691.
[2] Z. Lu, S. E. Cooney, J. R. McKone, E. M. Matson, *JACS Au* **2024**, 4, 1310–1314.

28: Synthesis and Characterization of Palladium(II)-Containing Tungstophosphate

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Polyoxometalates (POMs) are discrete, anionic *d*-block metal-oxo clusters which are usually formed in aqueous medium.[1] POMs are known for their ability to form an enormously large number of shapes, sizes, and compositions, covering a broad range of properties. Frequently it is possible to incorporate a variety of guest metal ions into lacunary POM derivatives.[2] Examples of noble metal-containing POMs exist but are a bit scarce due to the lower reactivity of these elements as compared to most 3d metal ions.[3] In particular several examples of Pd^{2+}-containing polyoxotungstates have been reported, the first one being the palladium(II)-containing isopolyoxotungstate $[Pd_2W_{10}O_{36}]^{8-}$.[4] Since then several more examples of palladium-containing POMs have been reported.[5]

Herein, a novel palladium(II)-containing tungstophosphate has been synthesized via a one-pot aqueous route and comprehensively characterized using single-crystal XRD, NMR spectroscopy, ESI-mass spectrometry and catalytic studies.

[1] (a) P. Yang, U. Kortz, In *Comprehensive Coordination Chemistry III*; E. Constable, G. Parkin, L. Que Jr, Eds, Vol. 7, Elsevier, **2021**, pp 4–28; (b) M. T. Pope, *Heteropoly and Isopoly Oxometalates*, Springer-Verlag, 1983.
[2] L.-L. Liu, L. Wang, X.-Y. Xiao, P. Yang, J. Zhao, U. Kortz, *Coord. Chem. Rev.* **2024**, *506*, 215687-125715.
[3] N. V. Izarova, M. T. Pope, U. Kortz, *Angew. Chem. Int. Ed.* **2012***, 51*, 9492-9510.
[4] S. J. Angus-Dunne, R. C. Burns, D. C. Craig, G. A. Lawrance, *J. Chem. Soc., Chem. Commun*. **1994**, *4*, 523-524.
[5] (a) L.-H. Bi, M. Reicke, U. Kortz, B. Keita, L. Nadjo, R. J. Clark, *Inorg. Chem.* **2004**, *43*, 3915-3920; (b) L.-H. Bi, U. Kortz, B. Keita, L. Nadjo, H. Borrmann, *Inorg. Chem.* **2004**, *43*, 8367-8372; (c) L.-H. Bi, U. Kortz, B. Keita, L. Nadjo, L. Daniels, *Eur. J. Inorg. Chem.* **2005**, 3034-3041; (d) L.-H. Bi, M. H. Dickman, U. Kortz, *CrystEngComm* **2009**, *11*, 965-966; (e) N. V. Izarova, A. Banerjee, U. Kortz, *Inorg. Chem.* **2011**, *50*, 10379-10386; (f) A. Rajan, A. S. Mougharbel, S. Bhattacharya, T. Nisar, V. Wagner, U. Kortz, *Inorg. Chem.* **2020**, *59*, 13042-13049.

29: Elaboration and Characterization of {Mo_3S_x}-based Electrocatalysts for Hydrogen Evolution Reaction

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Releasing new "green" energy sources with low carbon footprint is the actual driving force for numerous studies. Besides renewables, hydrogen is a clean energy vector that can be obtained through different processes. Water Electrolysis, namely Proton Exchange Membrane Water Electrolysis (PEMWE), is the most efficient technique for green hydrogen production since it can easily be coupled to renewable source of electricity. However, using expensive and scarce Platinum Group Metals (PGMs)-based electrocatalysts represents an important drawback [1]. In this communication, we will reveal a new class of PGM-free electrocatalyst for Hydrogen Evolution Reaction (HER). These electrocatalysts were obtained through two different approaches (Figure) while maintaining the main principle: coupling the molecular catalyst {Mo_3S_x} to polyoxometalates (POM), leading to WO_n-Mo_3S_x materials. This is considered a successful extrapolation of molecular approaches developing high performing POM-{Mo_3S_4} electrocatalysts [2,3]. In addition to their synthesis and thorough physico-chemical characterizations, these electrocatalysts were studied in a three-electrode cell through Linear Sweep Voltammetry, Cyclic Voltammetry and Electrochemical Impedance Spectroscopy. Further investigations at the active site scale through Atomic Force Microscopy (AFM) or AFM coupled to Scanning Electrochemical Microscopy were conducted. Implementing the best performing catalysts in real operating conditions PEM cell is the final aim of this study.

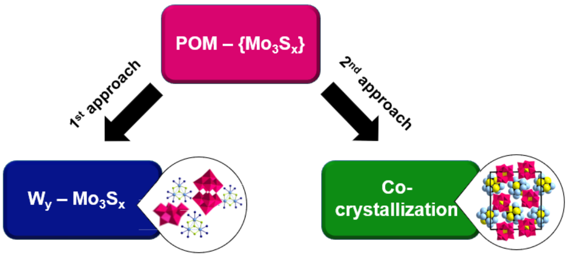

Figure 1: Schematic illustration of the synthesis approaches leading to {Mo_3S_x}-based electrocatalysts

[1] M. Chatenet, B. G. Pollet, D. R. Dekel, F. Dionigi, J. Deseure, P. Millet, R. D. Braatz, M. Z. Bazant, M. Eikerling, I. Staffell, P. Balcombe, Y. Shao-Horn, H. Schäfer, *Chem. Soc. Rev.* **2022**, *51*, 4583–4762.
[2] J. Al Cheikh, R. Zakari, A. C. Bhosale, A. Villagra, N. Leclerc, S. Floquet, P. C. Ghosh, A. Ranjbari, E. Cadot, P. Millet, L. Assaud, *Mater. Adv.* **2020**, *1*, 430–440.
[3] J. Tourneur, B. Fabre, G. Loget, A. Vacher, C. Mériadec, S. Ababou-Girard, F. Gouttefangeas, L. Joanny, E. Cadot, M. Haouas, N. Leclerc-Laronze, C. Falaise, E. Guillon, *J. Am. Chem. Soc.* **2019**, *141*, 11954–11962.

30: Polyoxometalate-based Artificial Photosynthesis

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Energy policies in developed nations are pressing. Solar energy, abundant on Earth, could meet global demands if efficiently harnessed. Storing intermittent solar energy is a challenge. An attractive option, however challenging, is to store this energy into chemical bonds, for example (photo)reducing proton into H_2 or carbon dioxide. Due to the intrinsic photoreactivity of the POM, mixed V-W Dawson derivatives functionalized with a Cu-complex could store up to three electrons, and the latter have been used for reductive catalytic applications. In a follow up of our previous work on CO_2 (photo)electroreduction with POM derivatives, the aim of this project is to activate by light the catalytic properties of the grafted complex by replacing the Cu-Dipyridyl moiety by a Co-complex and its Fe- or Ni-analogues, known for their ability to electro-reduce protons or CO_2, and to test the photo-/electro-catalytic properties of these new hybrids.

31: Host-guest chemistry in electrocatalysis: reduction of nitrate and nitrous oxide utilizing $W_{72}Mo_{60}$ keplerate-type polyoxometalates

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Polyoxometalates (POMs) play a significant role in lowering the activation energy of chemical reactions as electrocatalysts. The Keplerate-type POM, $W_{72}Mo_{60}$, can function as a confined space for catalytic activity. When combined with 4-imidazole acetic acid ligands, it facilitates the encapsulation of transition metal cations in specific oxidation states. This confined environment effectively mimics the active site of metalloenzymes. The confined space acts as a catalytic site, promoting the reduction of small substrate molecules, such as nitrogen oxides (NO_3^- and N_2O), within the principles of green chemistry. By applying a reduction potential, the transition metals can undergo repeated reductions after catalyzing the reduction of substrate molecules.

Nitrate reduction occurs via two primary pathways: denitrification and Dissimilatory Nitrate Reduction to Ammonium (DNRA), both catalysed by N_XO_Y reductase enzymes in nature. In the denitrification pathway, nitrate is reduced to nitrous oxide (N_2O), which is further reduced to nitrogen gas (N_2). In the DNRA pathway, nitrate is reduced to ammonia (NH_3). The electrocatalytic process using Keplerate type POM mimics these enzyme-catalyzed reactions. Additionally, the confined space within the POM structure closely resembles that of nitrous oxide reductase, facilitating the study of these catalytic processes. In this context, the two-electron reduction of nitrous oxide to nitrogen gas was examined separately.

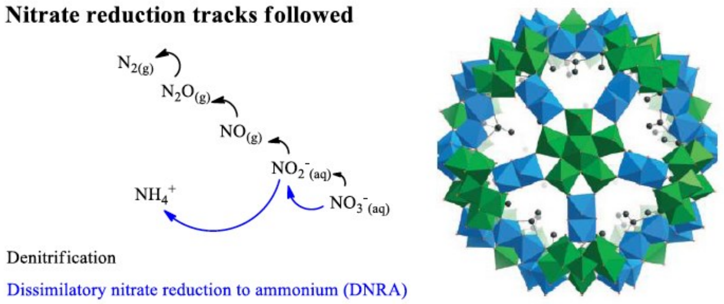

Figure 1: Denitrification and dissimilatory nitrate reduction to ammonium (DNRA) electrocatalyzed by $W_{72}Mo_{60}$ Keplerate-type polyoxometalates (POM)[2].

[1] Haviv, E. et al. Guest Transition Metals in Host Inorganic Nanocapsules: Single Sites, Discrete Electron Transfer, and Atomic Scale Structure. J Am Chem Soc 142, 14504–14512 (2020).
[2] Schäffer, C. et al. Unprecedented and Differently Applicable Pentagonal Units in a Dynamic Library: A Keplerate of the Type $\{(W)W_5\}_{12}\{Mo_2\}_{30}$. Angewandte Chemie 121, 155–159 (2009).

32: Palladium(IV)-Containing Polyoxotungstate

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Polyoxometalates (POMs) are discrete, anionic, polynuclear transition metal-oxo complexes of early *d*-block elements in high oxidation states, such as W^{VI} or V^{V}.[1] POMs exhibit a large variety of shapes, sizes, and compositions, with potential applications ranging from materials science to catalysis and biomedicine.[2] The incorporation of palladium(II) in lacunary heteropolytungstates has resulted in several polyanions, such as $[Pd_2(PW_{11}O_{39}H_{0.5})_2]^{9-}$, $[Pd_2(P_2W_{17}O_{61}H_{0.5})_2]^{15-}$, and $[Pd_3(H_2O)_9Bi_2W_{22}O_{76}]^{8-}$.[3] More recently, the tetra-Pd^{II}-containing 30-tungsto-4-arsenate(V) $[Pd^{II}_4(As_2W_{15}O_{56})_2]^{16-}$ has been reported including some catalytic studies.[4]

Here, we report on the first example of a palladium(IV)-containing polyoxotungstate, which was characterized by single-crystal X-ray diffraction, FT-IR, XPS, and mass-spectrometry.

[1] M. T. Pope, Heteropoly and Isopoly Oxometalates, Springer-Verlag, 1983.
[2] (a) A. Sundar, N. V. Maksimchuk, I. D. Ivanchikova, O. V. Zalomaeva, D. Bajuk-Bogdanović, O. A. Kholdeeva, G. Ćirić-Marjanović, B. S. Bassil, U. Kortz, Chem. Eur. 2024, 2, e202300066; (b) T. Ma, X. Ma, Z. Lin, J. Zhang, P. Yang, T. Csupász, I. Tóth, S. Misirlic-Dencic, A. M. Isakovic, D. Lembo, M. Donalisio, U. Kortz, Inorg. Chem. 2023, 62, 13195-13204.
[3] (a) N. V. Izarova, A. Banerjee, U. Kortz, Inorg. Chem. 2011, 50, 10379-10386; (b) L.-H. Bi, M. H. Dickman, U. Kortz, CrystEngComm 2009, 11, 965-966.
[4] A. Rajan, A. S. Mougharbel, S. Bhattacharya, T. Nisar, V. Wagner, U. Kortz, Inorg. Chem. 2020, 59, 13042-13049.

33: Photocatalytic Tandems Based on Polyoxothiometalates and Metallic Clusters for the Production of Dihydrogen

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The photocatalytic hydrogen evolution reaction (HER) involves cascade reactions starting with light excitation of a photosensitizer to transfer an electron to a proton reduction catalyst and ending with regeneration of the photocatalytic system through a sacrificial electron acceptor/donor agent, as illustrated in Figure. Nobel metal coordination complexes are the most effective molecular photosensitizers known to date for homogeneous catalysis. In this study, we investigate the potential of luminescent octahedral metal clusters and thio-polyoxometalates (ThioPOMs) as nobel metal-free photocatalytic tandem in homogeneous HER. The ThioPOMs,[1-3] which combine a lacunary polyoxometalate and the aquo cluster $[Mo_3S_4(H_2O)_9]^{4+}$, are known to be efficient catalysts for proton reduction.[4] Our ambition is to use ThioPOMs in conjunction with octahedral molybdenum clusters of the $M_6X_8L_6$ variety to act as economically viable photosensitizers[4] to replace the much more expensive iridium or ruthenium-based photosensitizers. Here, we report the synthesis, characterization, and HER photocatalytic activity of ThioPOMs $[\{AsW_{15}O_{53}\}\{Mo_3S_4(H_2O)_3\}]^{9-}$ and $[\{PW_{11}O_{39}\}\{Mo_3S_4(H_2O)_3(OH)\}]^{28-}$ in organic solutions and organic-water mixtures using different clusters. The results are compared with previous work on equivalent systems and discussed in terms of the hydrolytic stability effects of the clusters and ThioPOM catalysts in the media studied. Finally, the crystal structures of new CLUSPOM compounds, combining cationic octahedral metal clusters and anionic POMs, are also obtained and can serve as models[5] for cluster-ThioPOM catalyst tandems.

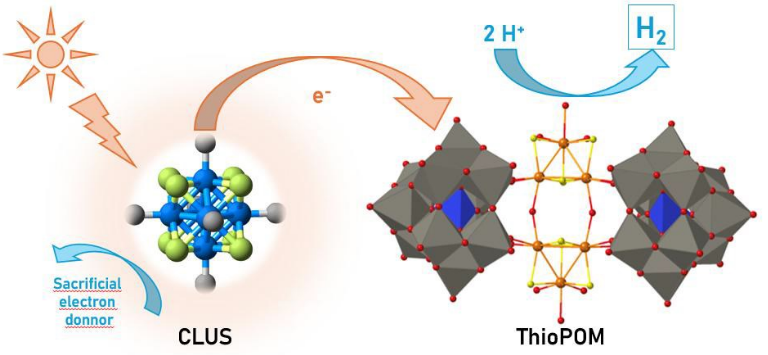

Figure: CLUSThioPOM induced electron transfer process for HER

[1] E. Cadot, M. N. Sokolov, V. P. Fedin, C. Simonnet-Jegat, et al. *Chem. Soc. Rev.*, **2012**, *41*, 7335.
[2] A. Müller, V. P. Fedin, C. Kuhlmann, H. Bögge, B. Hauptfleisch, et al. *Chem. Commun.*, **1999**, 1189.
[3] M. N. Sokolov, I. V. Kalinina, E. V. Peresypkina, et al. *Angew. Chem. Int. Ed.*, **2008**, *47*, 1465.
[4] Y. Smortsova, C. Falaise, A. Fatima, M.-H. Ha-Thi, et al. *Chem.-Eur. J.*, **2021**, *27*, 17094.
[5] A. Fatima, Y. Smortsova, C. Falaise, N. Leclerc, et al. *Chem. Commun.*, **2023**, *59*, 10988.

34: Polyoxometalate/Polymer Composites for the Photodegradation of Organic Dyes

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The textile industry generates large volumes of wastewater that presents serious risks to both human health and to the environment. [1] This industry releases textile effluents often containing high concentrations of dyes and other persistent organic pollutants.

Polyoxometalates (POMs) are good candidates to overcome such environmental challenges thanks to their well-known and diverse catalytic and photocatalytic properties. Recent work by Dumur, Lalevée, and coworkers have demonstrated the effective use of POMs embedded in a polymer (poly-trimethylol propanetriacrylate) for the photodegradation of pharmaceutical contaminants. [2]

In this context, our work investigates the photodegradation under visible light of various dyes, Rose Bengal (RB), Methyl Orange (MO), and Methylene Blue (MB). This poster focuses on the study of the RB photodegradation by two POM@polyurethane (POM@PU) composites : $[TBA]_4Li_2[PMo_{11}Li]$@PU and $[NMe_2(C_{10}H_{22})(C_2H_5OH)]_4Li_2[PMo_{11}Li]$@PU. [3]

The POM/polymer composites were thoroughly characterized using Scanning Electron Microscopy (SEM), Energy-dispersive X-ray (EDX) analysis, UV-Visible spectroscopy, Contact Angles and X-ray Photoemission Spectroscopy (XPS). Their characterization brought out their exceptional stability, enabling their reuse up to 8 cycles as effective pollutant removal. Deep investigation of their structure presents noticeable differences that relate to their catalytic activity difference.

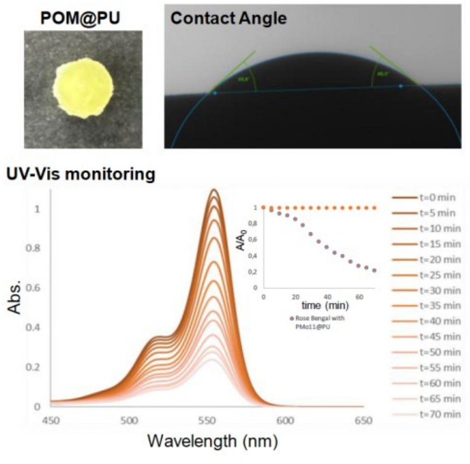

Figure 1-POM@PUpellet, contact angle measurementand UV-Vis monitoring of Rose Bengal Photodegradation byPOM@PU.

[1] Trabelsi-Souissi, S., Oturan, N., Bellakhal, N., & Oturan, M. A. (2011). Desalination and Water Treat., 25(1– 3), 210–215

[2] Brahmi, C., Benltifa, M., Ghali, M., Dumur, F., Simonnet-Jégat, C., Valérie, M., Morlet-Savary, F., Bousselmi, L., & Lalevée, J. (2021). J. Environ. Chem. Eng., 9(5), 106015

[3] Li, H., Qi, W., Li, W., Sun, H., Bu, W., & Wu, L. (2005). Adv. Mater., 17(22), 2688–2692

35: Construction of Oxidative High-valent Metal Centers Stabilized by Polyoxometalate Ligands for Oxidation Catalysis

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Transition metal centers with unusually high oxidation states are known to be catalytically active sites in various redox reactions.[1] Polyoxometalates (POMs) are excellent inorganic ligands with rich surface coordination oxygen atoms and superior structural flexibility,[2] but their stabilization ability towards strongly oxidative high-valent transition metal centers remains to be investigated in details.

Herein, we report a new method to construct high-valent metal centers embedded in POM frameworks, namely silver-assisted peroxysulfate oxidation method. By adding Ag(I) salts as the catalyst, we have successfully constructed various novel POM species containing unusual high-valent Cu^{3+} and Ni^{3+} with exotic structural and chemical properties[3,4], as revealed by comprehensive theoretical and experimental studies. It is found that POM is capable of stabilizing the high-valent Ag^{2+} and Ag^{3+} oxidation intermediates by forming different POM-Ag^{2+}/$^{3+}$ complexes in a "self-adaptive" fashion depending on the reaction conditions used. The promising catalytic activities of these POMs in electrochemical oxidation reactions (e.g. water oxidation) are explored, highlighting the value of the strategy for further development of potential POM-based electrochemical catalysts.

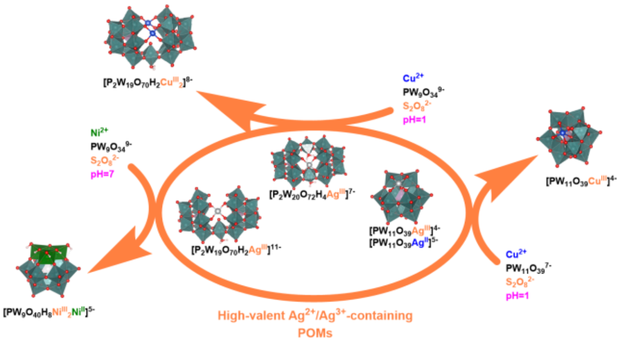

Figure 1. Schematic illustration on the construction of various high-valent metal-substituted POMs by silver-assisted peroxysulfate oxidation method.

[1] K. Ray, F. Heims, M. Schwalbe, *et al. Curr. Opin. Chem. Biol.*, **2015**, 25, 159-171.
[2] S. S. Wang, G. Y. Yang, *Chem. Rev.*, **2015**, 115(11), 4893-4962.
[3] X. Li, Y. Ren, Z. Weng, *et al. Chem. Commun.*, **2020**, 56, 2324–2327.
[4] X. Li, B. K. Y. Ng, P.-L. Ho, *et al. Chem. Sci.*, **2024**, 15, 9201–9215.

36: Cobalt-Based Polyoxometalate on Titanium Dioxide: An Efficient Photocatalyst for Nitrogen Fixation in the Gas Phase

Rongji Liu,[1] Abdelkarim Zaim,[2] Jacqueline Patzsch,[2] Tobias Rios-Studer,[1] Sarra Rahali,[1]
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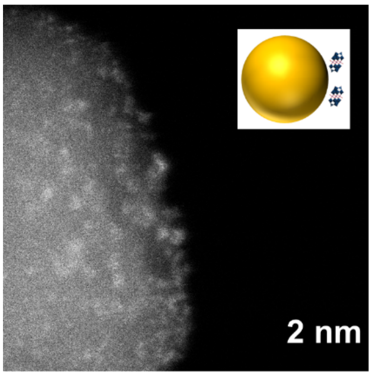
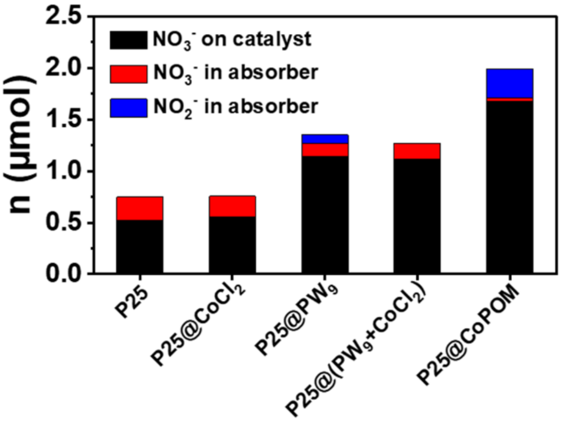
Industrial nitric acid production involves a two-step process: the Haber-Bosch method for ammonia synthesis, followed by Ostwald oxidation of ammonia under high-temperature and high-pressure conditions. In contrast, photocatalysis provides a promising alternative for directly converting nitrogen molecules into nitrogen-containing compounds under ambient conditions. However, this approach still faces challenges such as limited visible-light utilization and insufficient product selectivity. Herein, we construct a photocatalytic system for gas-phase nitrogen conversion by depositing a cobalt-containing polyoxometalate (POM), $Na_{10}[Co_4(H_2O)_2(PW_9O_{34})_2]$ (CoPOM), on commercial P25 nanoparticles. STEM, XPS, and XAS et al. analyses confirm that the molecular CoPOM is uniformly dispersed on the P25 surface without valence state alteration. Control experiments demonstrate the critical role of POM in enhancing nitrogen conversion efficiency: P25@$Na_8H[PW_9O_{34}]$ (PW9) exhibits a 60% higher activity than pristine P25, whereas P25@CoPOM achieves the highest performance with a 280% increase in NO_2^-/NO_3^- yield. More interestingly, P25@CoPOM demonstrates bifunctional activity for reductive and oxidative nitrogen fixation, producing 0.8 μmol NH_4^+ and 2.0 μmol NO_2^-/NO_3^- over 18 h. Post-catalytic characterization confirms the structural integrity of P25@CoPOM, highlighting its robustness for gas-phase photocatalytic nitrogen conversion.





[1] Yuan, S. J. *et al.* Nitrate formation from atmospheric nitrogen and oxygen photocatalysed by nano-sized titanium dioxide. *Nat. Commun.* **4**, (2013)
[2] Gong, R. *et al.* Self-Activation of a Polyoxometalate-Derived Composite Electrocatalyst for the Oxygen Evolution Reaction. *ACS Appl. Energy Mater.* **4**, 12671–12676 (2021).

37: Substrate-Controlled Self-Organization of Polyoxovanadates into Hysteretic Switchable Materials

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Within the broad class of polyoxometalates (POMs), Lindqvist-type polyoxovanadates (POVs) occupy a unique position by combining compact architectures with high stability, ligand post-functionalisation, and redox flexibility. When integrated into device-like architectures, these POVs demonstrate resistive switching behaviour, showing reversible transitions between distinct conductive states in response to electrical stimuli.[1,2] The multiresistive switching observed in scanning tunnelling spectroscopy (STS) investigations demonstrates their potential application as active elements in alternative memory and neuromorphic computing systems. The controlled immobilisation of these clusters onto technologically relevant substrates remains one of the key challenges for the development of real-world molecular-based electronics. Here, we present the results on the surface modification of three different conducting substrates (Au(111), HOPG and SiO_2/Si(100)) with solution-processed, carboxylic acid-terminated Lindqvist-type POVs (**V6-COOH**). The materials were characterised using various surface-sensitive microscopy and spectroscopy methods and the experimental results were supported by density functional theory (DFT) calculations.

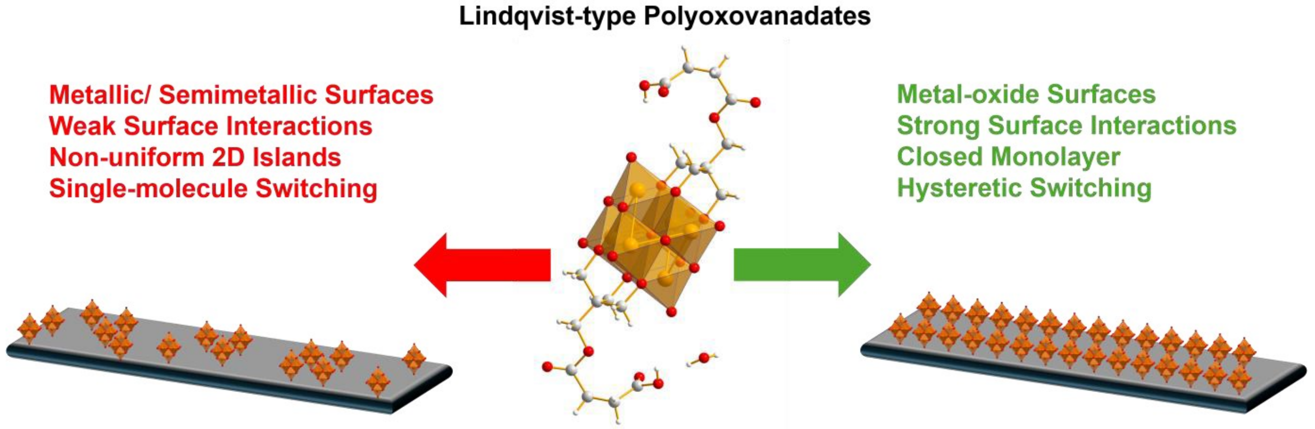

Figure 1. Schematic representation of the behaviour of polyoxovanadate (V6-COOH) on different substrate surfaces.

[1] O. Linnenberg, M. Moors, A. Notario-Estévez, X. López, C. de Graaf, S. Peter, C. Baeumer, R. Waser, K. Yu. Monakhov, *J. Am. Chem. Soc.* **2018**, *140*, 48, 16635 – 16640.
[2] S. K. Petrovskii, M. Moors, S. Schmitz, E. V. Grachova, K.Yu. Monakhov *Chem. Commun.* **2023**,*59*, 9517 – 9520.

38: The Development Of Bifunctional Metallosalen-Type Polyoxometalate Compounds For Catalysis

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Metallosalen complexes are well-known catalysts for the formation of polycarbonates through CO_2/epoxide copolymerization. CO_2/epoxide copolymerization promises to convert waste CO_2 _into useful biodegradable polycarbonates, promoting sustainability and a circular carbon economy.[1] However, challenges such as recyclability and reactivity towards bio-based epoxides hamper their use in industrial processes. One strategy to address this issue is to dock typically homogeneous catalysts onto polyoxometalates (POMs), resulting in organic-inorganic hybrid POMs,[2] which can facilitate catalyst recovery and recycling.[3] Metallosalen-type hybrids based on the monolacunary Keggin-POM are known,[4] showing increased catalytic performance compared to the salen alone.[5] Herein, we present the state-of-the-art bifunctional metallosalen-type POM-complex $\{MSiW_{11}O_{39}[O(SiR)_2]\}$, (R-$(CH_2)_3N{=}CH\text{-}C_6H_2O(p\text{-}(CH_2)_4NBu_3\text{-}o\text{-}{}^tBu)$). Here, ‘bifunctional’ refers to the fact that the required co-catalyst is already attached to the catalyst backbone. Co-catalysts are reported to be essential for the ring opening of the epoxide.[6] In this work, we have synthesized salicylaldehyde-based ligands with the NBu_3X^- co-catalyst attached to the backbone, which was subsequently attached to the POM, before the metal was inserted. Catalytic studies are ongoing.

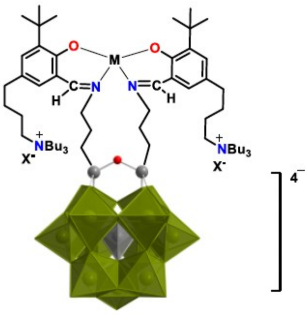

Figure 1: X-Cl, Br, NO_3 etc. Molecular structure of the bifunctional metallosalen-type POM. Color code: $\{WO_6\}$ olive-green octahedra, $\{SiO_4\}$ grey tetrahedra, {Si} grey, {C} black, {N} blue and {O} red.

[1] S. J. Poland, D. J. Darensbourg, *Green Chem.* **2017**, *19*, 4990–5011. [2] T. Iftikhar, M. H. Rosnes, *Front. Chem.* **2024**, *12*, 1447623. [3] X. Xin, Z. Li, M. Chi, M. Zhang, Y. Dong, H. Lv, G.-Y. Yang, *Green Chem.* **2023**, *25*, 2815–2824. [4] I. Bar-Nahum, H. Cohen, R. Neumann, *Inorg. Chem.* **2003**, *42*, 3677–3684. [5] V. Mirkhani, M. Moghadam, S. Tangestaninejad, I. Mohammadpoor-Baltork, N. Rasouli, *Inorganic Chemistry Communications* **2007**, *10*, 1537–1540. [6] S. S, J. K. Min, J. E. Seong, S. J. Na, B. Y. Lee, *Angew Chem Int Ed* **2008**, *47*, 7306–7309.

39: Exploring Electrochemical Properties of Novel Mixed-Valent {V_{18}}-Polyoxovanadates in Non-Aqueous Environments

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Polyoxovanadates, molecular vanadium oxide cluster anions, are attractive molecular species for charge transfer and storage. Here, a cation metathesis route was used to transfer the literature-known {V_{18}} clusters[1] from the aqueous to the organic phase, resulting in a group of highly redox-active species. In this contribution a deeper analysis of the electrochemical behavior of the compounds will be presented. Currently, the influence of various solvents as well as quaternary ammonium salts as supporting electrolyte on electron transfer kinetics of the {V_{18}} family is being studied. Finally, mixed-valent {V_{18}}-type POVs are being explored for their application in non-aqueous redox-flow batteries in symmetric configuration.

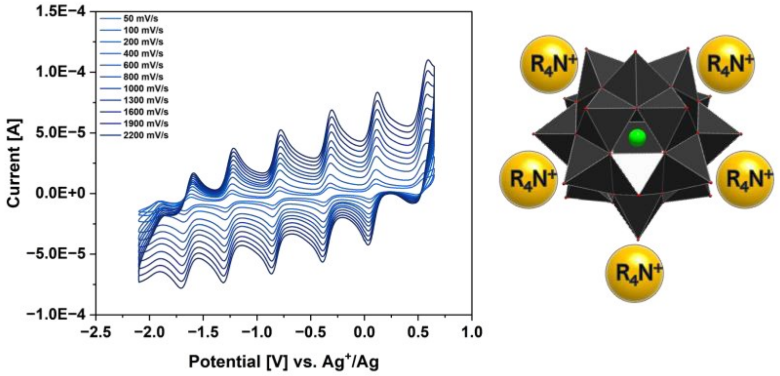

Figure 1: Electrochemical profile of mixed-valent {V_{18}} at different scan rates & proposed structure in polyhedral representation.

[1] A. Müller, R. Sessoli, E. Krickemeyer, H. Bögge, J. Meyer, D. Gatteschi, L. Pardi, J. Westphal, K. Hovemeier, R. Rohlfing, J. Döring, F. Hellweg, C. Beugholt, M. Schmidtmann, *Inorg Chem* 1997, *36*, 5239–5250.

40: Polyoxometalates in Motion: A Molecular Dynamics View into Their Solution Behavior

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Polyoxometalates (POMs) are a versatile class of metal-oxide clusters whose structural diversity and rich redox chemistry have established them as key players in catalysis, energy storage, and materials science, among other areas. Despite their widespread use, a detailed understanding of their behaviour in solution (the medium where they are most frequently applied) remains limited.[1] In this talk, we examine the solvation structure, dynamics, and intermolecular interactions of POMs through several examples of atomistic molecular dynamics simulations. These studies provide insight into how the complex charge distribution and geometry of POMs govern their mobility and stability in liquid environments,[1] and reveal the profound influence that counterion identity can exert on their electronic properties. The examples discussed cover a wide range of topics and systems, including the aggregation of hybrid polyoxometalates,[2] the ion-pairing behaviour of various R_4N^+ cations and its impact on the redox properties of the POM,[3] the influence of solvent mixing on the properties of a Keggin-type POM,[4,5] and the structural and electronic features required for a POM to associate with a nanotube, among others.

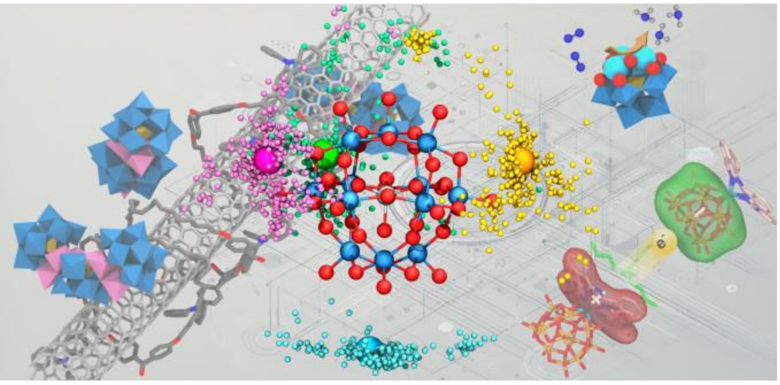

Figure: Representative examples highlighting the critical role of explicit environment description in POM-related systems: ion-pairing, POM···CNT nanocomposites, electrochemical N_2 reduction, and electron transfer processes, among others.

[1] X. López, J. J. Carbó, C. Bo, J. M. Poblet, *Chem. Soc. Rev.* **2012**, *41*, 7537–7571.
[2] I. Werner, J. Griebel, A. Masip-Sánchez, X. López, K. Załeski, P. Kozłowski, A. Kahnt, M. Boerner, Z. Warneke, J. Warneke, et al., *Inorg. Chem.* **2022**, *62*, 3761–3775.
[3] G. Toupalas, J. Karlsson, F. A. Black, A. Masip-Sánchez, X. López, Y. Ben M'Barek, S. Blanchard, A. Proust, S. Alves, P. Chabera, I. P. Clark, T. Pullerits, J. M. Poblet, E. A. Gibson, G. Izzet, *Angew. Chem. Int. Ed.* 2021, 60, 6518–6525.
[4] V. A. Grigoriev, C. L. Hill, I. A. Weinstock, *J. Am. Chem. Soc.* **2000**, *122*, 3544–3545.
[5] D. Azaiza-Dabbah, C. Vogt, F. Wang, A. Masip-Sánchez, C. de Graaf, J. M. Poblet, E. Haviv, R. Neumann, *Angew. Chem. Int. Ed.* **2022**, *61*, e202112915.

41: One-step Synthesis of {$Mn_{10}Ce_4$} Oxo Cluster within Polyoxometalates and Stepwise Synthesis of Intermediates

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Understanding the reaction mechanisms of one-step multielement inorganic synthesis is crucial for advanced material design. However, isolating and characterizing intermediate structures remains challenging, even for molecular multielement inorganic compounds. To address this challenge, we developed stepwise synthesis methods for constructing high-nuclearity multielement anionic molecular metal oxides (polyoxometalates, POMs) in organic solvents.[1-3] Applying this stepwise synthesis method to the one-step synthesis of large multielement POMs enables the elucidation of complicated formation processes to the final product. In this study, we first produced a new large multielement POM possessing {$Mn_{10}Ce_4$} oxo cluster via one-step synthesis (Figure 1). Given the unclear formation process of this POM, a stepwise synthesis method was employed to elucidate the reaction mechanisms. Through single-crystal X-ray crystallography and mass spectrometry, three intermediate structures were successfully revealed. Remarkably, the unusual repositioning reaction of Ce cations was discovered. This unusual formation process can be used to develop synthetic strategies for designing and constructing new inorganic materials.

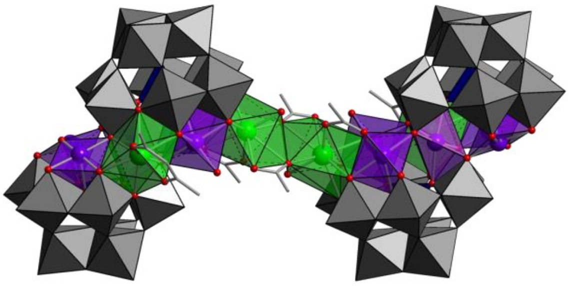

Figure 1: Polyhedral representation of a large multielement POM possessing {$Mn_{10}Ce_4$} oxo cluster. The atoms are represented by polyhedra and spheres: Mn, purple; Ce, green; O, red; Si, blue; and W, gray. The acetate and acac ligands are represented by gray sticks.

[1] T. Minato, K. Suzuki, Y. Ohata, K. Yamaguchi, N. Mizuno, “A modular synthesis approach to multinuclear heterometallic oxo clusters in polyoxometalates” *Chem. Commun.* **2017**, *53*, 7533.
[2] T. Minato, D. Salley, N. Mizuno, K. Yamaguchi, L. Cronin, K. Suzuki, “Robotic stepwise synthesis of hetero-multinuclear metal oxo clusters as single-molecule magnets” *J. Am. Chem. Soc.* **2021**, *143*, 12809.
[3] T. Minato, M. Sadakane, “A Cationic Metal Glue Strategy for Expanding Paramagnetic Hetero-Multinuclear Metal-Oxo Clusters within Polyoxometalate Ligands” *Angew. Chem. Int. Ed.* **2023**, *62*, e202309469.

42: Incorporation and Physical Confinement of Bulky Molecules within $\{Mo_{132}\}$ Caged Cluster

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It is well known that molecules confined within an internal space exhibit unique behaviors different from those in the conventional open environments. Keplerate-type polyoxometalate $[Mo_{132}O_{372}(OCOCH_3)_{30}]^{42-}$ ($\{Mo_{132}\}$) is an attractive candidate because the inorganic caged framework offers an inner void space that can communicate with the outside through the surface pores.[1] Although $\{Mo_{132}\}$ is polyanionic and highly hydrophilic, its interior surface is mostly covered by methyl groups derived from acetate ligands, creating a hydrophobic inner space. This allows the uptake of various organic guests driven by hydrophobic effects.[2] Thus, upon simply mixing with $\{Mo1_{132}\}$ in water, lipophilic guests such as benzene are effectively trapped within the host. However, hindered guests such as benzophenone are hardly trapped by this method due to the size limitation of surface pores. In this study, we demonstrate that solid-state grinding of the host-guest mixture can be used to encapsulate hindered guests. Typically, a powdery mixture of $\{Mo_{132}\}$ and benzophenone was ground in a mortar for 15 min at room temperature and then treated with D_2O. After removal of insoluble materials, the resulting D_2O solution showed a characteristic 1H NMR signal at 5.8 ppm, which was assignable to the encapsulated benzophenone. DOSY measurement showed that the diffusion coefficient of the new peak was comparable to that of the inner acetate ligands. It should be noted that the host–guest complex encapsulating benzophenone was very tough. No guest elimination was observed even when the complex was treated with chloroform. In contrast, small guest molecules encapsulated by $\{Mo_{132}\}$ were smoothly released when treated under similar conditions. These results indicate that hindered guest molecules once trapped within $\{Mo_{132}\}$ are nearly irreversibly confined.

[1] A. Müller, P. Gouzerh, Chem. Soc. Rev. 2012, 41, 7431.
[2] R. W. Pow, W. Xuan, D. L. Long, N. L. Bell, L. Cronin, Chem. Sci., 2020, 11, 2388; B. B. Sarma, L. Avram, R. Neumann, Chem. Eur. J. 2016, 22, 15231; C. Murata, J. Shin, Y. Shichibu, K. Konishi, Chem. Commun. 2023, 59, 2441; C.Murata, A. Nakashuku, Y. Shichibu, K. Konishi, Chem. Eur. J. 2023, 30, e20230232.

43: Porous Ionic Crystals based on Polyoxometalates for efficient CO_2 photoreduction and H_2 production in aqueous media

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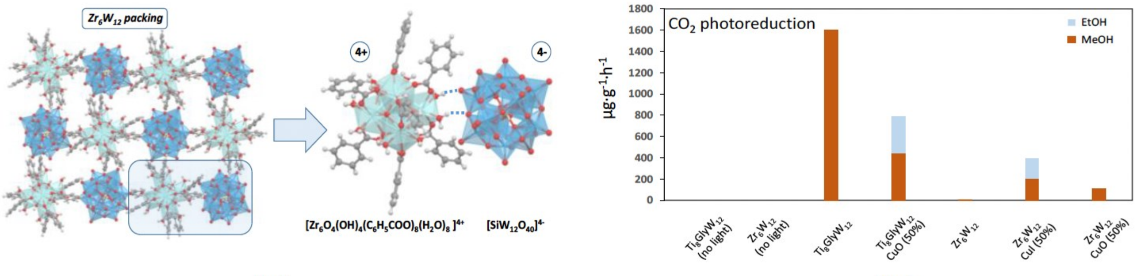
In this work, we report the synthesis of Porous Ionic Crystals (PIC) that merge cationic metal-organic clusters with polyoxometalate anions. The study encompasses the design of ionic hybrid materials constructed from titanium(IV) zirconium(IV) or hafnium(IV) oxo clusters coordinated with monocarboxylic ligands $[M_6O_4(OH)_4(L)_8(H_2O)_8]^{4+}$ or $[M_8O_8(L)_6(H_2O)_{12}]^{4+}$ (M: Ti, Zr, Hf; L: carboxylic ligand) and a Keggin type polyoxometalate anions of the formula $[SiM_{12}O_{40}]^{4-}$ (M: Mo, W).[1] This combination creates stable, multifunctional materials through the integration of cationic clusters with robust polyoxometalate units.

The photocatalytic evaluation of these systems under UV irradiation shows their ability to drive both CO_2 photoreduction and water splitting in aqueous media. In most of the hybrid compounds, the use of cocatalysts is required to enhance electron transfer toward CO_2 molecules and improve catalytic performance. However, the best results were obtained with the titanium-based Ti_8GlyW_{12} system, which exhibits intrinsic activity without the need for cocatalysts. This behavior is attributed to an efficient Z-scheme charge separation between the titanium-oxo cluster and the polyoxometalate for UV light driven CO_2 conversion to methanol in aqueous media (methanol at a rate of 1600 $\mu g \cdot g^{-1} \cdot h^{-1}$) , while also promoting hydrogen generation via water splitting of 75 $\mu mol \cdot g^{-1} \cdot h^{-1}$ all without the need for sacrificial reagents (Figure 1). Together, these dual function catalysts demonstrate a promising route towards energy conversion and environmental remediation, paving the way for next generation photocatalytic systems.



(a) (b)

Figure 1: (a) Crystal packing of Zr_6W_{12} together with a detail of the two constituent clusters. [1] (b) Together with the experimental results for CO_2 conversion to valuable alcohols in aqueous media..

[1] Napal, J.; Pascual-Colino, J.; Perfecto-Irigaray, M.; Beobide, G.; Castillo, O.; Luque, A.; Pérez-Yáñez, S. Artetxe, B.; Inorg. Chem. Front. 2022, 9, 935-940.

44: Bioinspired Hybrid Architectures: Enhancing the Antimicrobial Activity of POM-Peptide Materials

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Biofilm environments exhibit strong resistance to conventional antibiotic treatments,[1] highlighting the urgent need for novel antimicrobial agents to combat resistant bacteria and inhibit biofilm formation. Our team investigates hybrid-based materials that integrate multiple mechanisms of action within a single agent, enhancing synergistic effects and minimizing the risk of antimicrobial resistance

Among the organic molecules that can be combined with POMs, peptides have garnered increasing interest due to their diverse secondary structures and broad chemical versatility. Recently, we introduced POMlymers, a class of covalent POM-polypeptide hybrids synthesized via the ring-opening polymerization (ROP) of amino acid N-carboxyanhydrides, initiated by an amino group on the POM. By incorporating apolar and positively charged amino acids, we designed these hybrids to mimic key structural features of antimicrobial peptides.[2][3] We have also investigated the self-assembly properties of POMlymers in aqueous solutions, demonstrating that nanoscale assemblies of covalent POMlymers exhibit peroxidase-like activity, surpassing that of the free POM anion. In contrast, ionic assembly negatively impacts catalytic efficiency.[4] Building on these findings, here I will discuss our exploration of conjugating various peptide architectures to POM scaffolds to determine how peptide chain length, conjugation mode, and self-assembly influence the corresponding biological activity of POM-peptide hybrids.

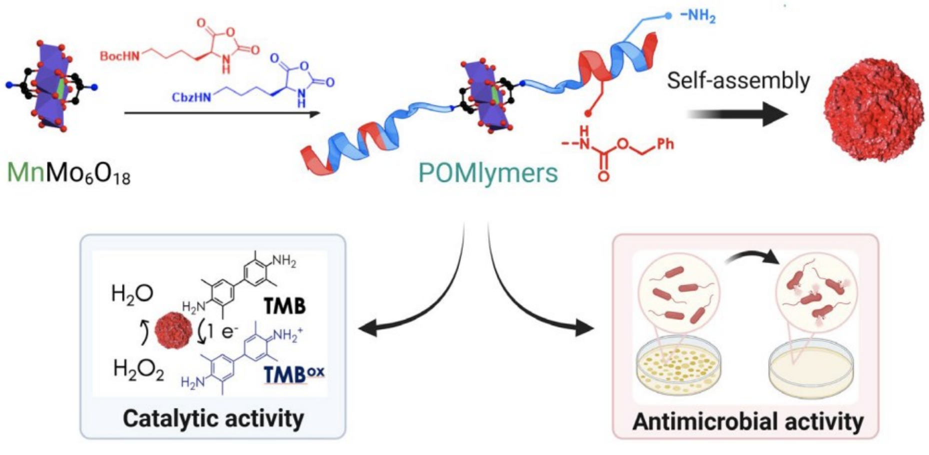

Figure 1: Overview of the POMlymers synthesis, self-assembly, and bio-applications.

[1] L. Kumar et al. *ACS Omega* **2023**, *8*, 21391–21409.
[2] H. Soria-Carrera et al. *Chem. Sci.* **2023**,*14*, 10-28.
[3] H. Soria-Carrera et al. *Angew. Chem. Int. Ed.* **2021**, *60*, 3449–3453.
[4] H. Soria-Carrera et al. *Nanoscale* **2022**, *14*, 5999–6006.

45: Temperature Sensors Based on Europium Polyoxometalate and Metal-Organic Frameworks

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In contrast to contact-type thermometers, luminescent thermometers allow remote and precise temperature measurement at the micrometer scale in a non-invasive manner.[1]

Herein, two new ratiometric luminescent thermometers containing lanthanide molecular species encapsulated in metal-organic frameworks (MOFs) will be presented. In EuW_{10}@Tb-TATB, the $[EuW_{10}O_{36}]^{9-}$ polyoxometalate (POM) is incorporated into the cavities of the mesoporous terbium MOF Tb-TATB.[2] The reported material acts as a temperature sensor at ambient temperature, exhibiting a high relative thermal sensitivity (Sr) of 2.68%.K−1. In a second time, luminescent carbon dots and $[EuW_{10}O_{36}]^{9-}$ have been combined with the Zn MOF ZIF-8.[3] EuW_{10}/Cdots@ZIF-8 material contains a very low rare-earth content (2.7 wt%) while exhibiting a high Sr value of 1.4%.K^{-1} at 353 K. This shows that cheap, easy to synthesize and highly sensitive POM-based temperature ratiometric sensors can be obtained.

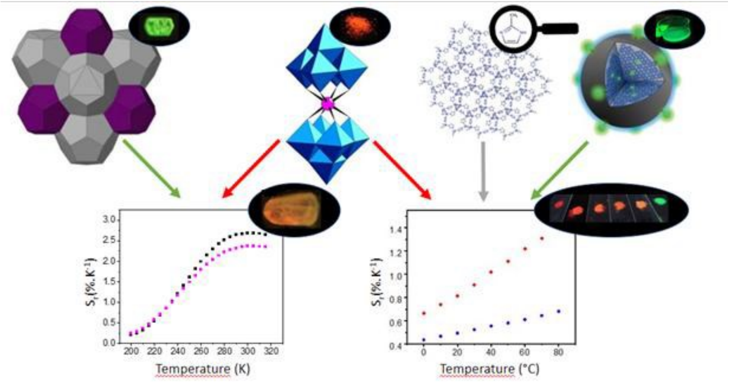

Figure: Representation of the two composites EuW_{10}@Tb-TATB and EuW_{10}/Cdots@ZIF-8, images of samples under irraditation at 254 nm and the relative thermal sensitivity of the two composites

[1] C. D. S. Brites, P. P. Lima, N. J. O. Silva, A. Millan, V. S. Amaral, F. Palacio, L. D. Carlos, *Nanoscale* **2012**, *4*, 4799–4829.
[2] C. Viravaux, O. Oms, A. Dolbecq, E. Nassar, L. Busson, C. Mellot-Draznieks, R. Dessapt, H. Serier-Brault, P. Mialane, *J. Mater. Chem. C* **2021**, *9*, 8323–8328.
[3] C. Viravaux, P. Mialane, A. Dolbecq, N. Ramsahye, C. Mellot-Draznieks, H. Serier-Brault, O. Oms, *J. Mater. Chem. C* **2024**, *12*, 15535-15540.

46: Fluorinated Arylarsonate-Containing Polyoxomolybdates: pH-Dependent Formation of Mo_6 *vs* Mo_{12} Species and Their Solution Properties

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Polyoxometalates are discrete, anionic metal-oxo clusters of early transition metals in high oxidation states. The class of polyoxomolybdates comprises isopolyanions and heteropolyanions.[1-2] Polyanions with covalently bound organic groups are potentially of interest for biomedical applications.[3] Here, we report on the synthesis and characterization of several novel fluorinated arylarsonate-containing heteropolymolybdates. The reaction of different fluoro-arylarsonates with sodium molybdate in aqueous acidic medium resulted in the formation of three polyoxo-6-molybdates and three polyoxo-12-molydates, which can be interconverted reversibly as a function of pH (Fig. 1).[4] All six polyanions have been characterized in the solid state by single-crystal and powder X-ray diffraction, infrared spectroscopy, elemental analysis, thermogravimetric analysis (TGA), and in solution by multinuclear NMR spectroscopy (^{1}H, ^{13}C, ^{19}F).

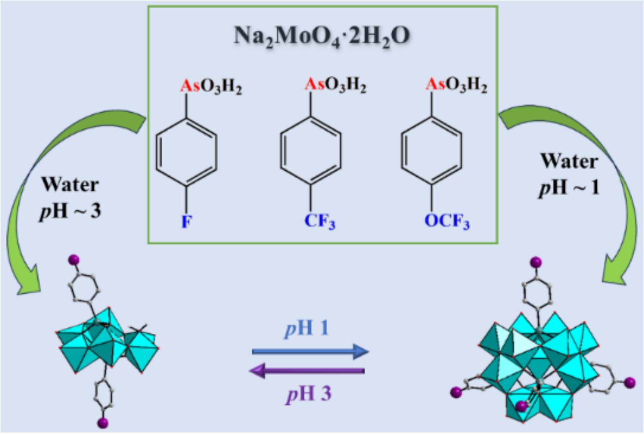

Figure: Representation of the synthetic scheme.

[1] M. T. Pope, *Heteropoly and Isopoly Oxometalates*; Springer: Berlin, 1983.
[2] P. Yang, U. Kortz, In Comprehensive Coordination Chemistry III; Constable, E. C., Parkin, G., Que Jr, L., Eds., Vol. 7, Elsevier, **2021**; pp 4-28.
[3] P. Manna, S. Bhattacharya, U. Kortz, *Inorg. Chem*. **2021**, *60*, 7161-7167.
[4] A. Pal, S. Bhattacharya, X. Ma, A. B. Kiran, C. Silvestru, U. Kortz, *Inorg. Chem*. **2024**, *63*, 18838-18846.

47: Photoactive Polyoxometalate-doped Nanofibers: Sustainable Solutions for Water Remediation

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The modern society is facing a number of challenges related to health, sustainability, and environmental protection described as sustainable development goals (SDGs) at Agenda 2030. In this context, advanced functional polymeric materials have proved to be great candidates for pollutant remediation (SDGs 6, 14 and 15), due to their low price, the ease of processing them into various shapes and the available catalogue of materials with a broad range of physical, mechanical, chemical, and thermal properties. One of the most promising strategies for water remediation involves the use of electrospun nanofibers that incorporate photocatalytically active compounds such as metal oxide semiconductors [1]. The large exposed surface displayed by the nanofibers allow not only the absorption of pollutants, but also a more efficient photooxidation process originating from the greater contact area. Encouraged by the interesting photocatalytic activity showed by some Keggin-type anions [2], especially those displaying cobalt(II) atoms at heteroatomic site or addenda metal position, herein we report on a series of electrospun hybrid membranes formed by the encapsulation of Keggin-type polyoxometalates (A[α-$XW_{12}O_{40}$] (A=H_4, X=Si; A=K_4H_2, X=Co)) and K_6[α-$SiW_{11}O_{39}Co(H_2O)$] in nylon-66. Polyamide-66 was selected because of its high chemical resistance under extreme conditions and its capacity for the adsorption of organic dye pollutants. Membranes were characterized by FT-IR spectroscopy, SEM microscopy, and EDX analyses and their thermal and mechanical properties were evaluated. Adsorption capacity as well as photodegradation activity under UV irradiation were quantified by UV-Vis spectroscopy and compared with reported results [3].

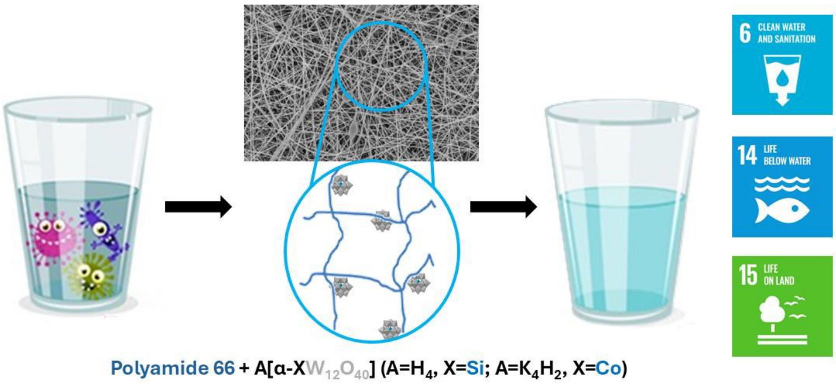

Figure 1: Schematic representation of how the hybrid POM-polymer fiber could carry out the sanitation of contaminated water.

[1] Pathak, D.; Sharma, A.; Sharma, D.P.; Kumar, V. *Appl. Surf. Sci. Adv.*, **2023**, *18*, 100471.
[2] Yang, F.; He, X.; Xin, T.; Yang, H.; Bai, L.; Gao, L.; Wang, Y. *Molecules*, **2023**, *28*, 3968.
[3] Snider, V.G.; Hill, C.L. *J. Hazard. Mater.*, **2023**, *442*, 130015

48: Black Titanium-oxo cluster as a photocatalyst for regioselective oxidative cleavage and modification of proteins

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A key challenge in redox proteomics is unraveling how oxidative modifications influence protein structure and function. Advancing this field requires highly selective and controlled methods for introducing oxidative changes, particularly those targeting backbone cleavage and side-chain modifications. Inspired by previous work in which a Zr-oxo cluster was used for protein editing of hen egg white lysozyme (HEWL) (Figure 1),[1] we report the synthesis, characterization, and application of a new black titanium-oxo cluster featuring a [Ti_6O_5] core structure. This cluster exhibits exceptional photophysical properties—including a very low band gap—and a strong photocurrent response, enabling its use as an efficient heterogeneous photocatalyst for the regioselective oxidative cleavage and modification of β-lactoglobulin under UV light. These results highlight the significant potential of insoluble titanium-oxo clusters for selective protein modification under mild, light-driven conditions, paving the way for new strategies in controlled protein editing within redox proteomics and related fields.

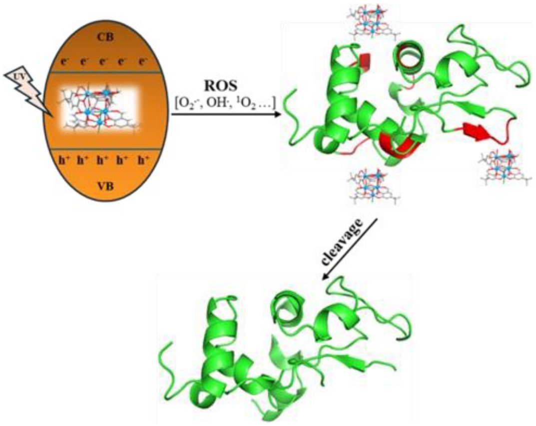

Figure 1: Proposed mechanism for photooxidative cleavage of HEWL induced by irradiation of the Zr5-oxo cluster.

[1] S. Xie, S. S. Passadis, M. Gray, N. A. G. Bandeira, H. N. Miras, T. N. Parac-Vogt. (to be published)

49: Revitalisation of group IV metal-oxo clusters: synthetic approaches, structural motifs and applications

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Group IV metal-oxo clusters (MOCs) represent a unique family of molecular species increasingly utilized in applications ranging from catalysis and materials chemistry to electronics and sensors.[1] The appropriate choice of the organic ligand can influence the hydrolysis process of metal ions, leading to novel structural motifs and modifications that facilitate the stabilization of new cores and the discovery of new phenomena. Oximes, as significant members of the mixed O/N-donor ligand family, act as hydrolysis-delaying agents while inducing structural diversity and significantly influencing the cluster's light-harvesting and photocurrent responses.[2] Catechol ligands, on the other hand, play a crucial role in the photoelectrochemical and photocatalytic properties of MOCs by facilitating charge transfer to the metal–O core, enhancing photocurrent conversion under visible-light irradiation.[3] This presentation will provide synthetic approaches and structural characteristics of oxime- and catechol-based MOCs, while also highlighting how combining both groups within a single organic ligand can enable the exploitation of their structural and electronic effects to modulate the properties of the MOCs.[4]

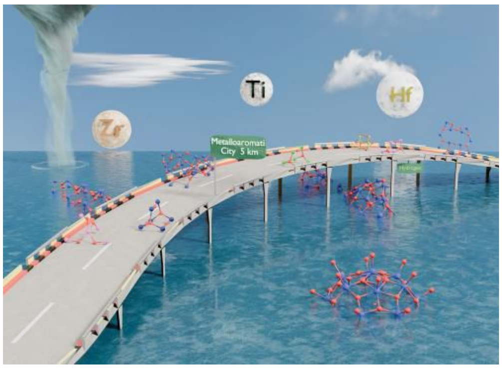

Figure 1: Structural motifs of group IV metal-oxo clusters

[1] Y. Zhang, F. de Azambuja, T. N. Parac-Vogt. *Coord. Chem. Rev.* **2021**, 438, 213886
[2] S. Chen, W. H. Fang, L. Zhang, J. Zhang. *Inorg. Chem.*, **2018**, 57, 8850–8856.
[3] J. Le Hou, P. Huo, Z. Z. Tang, L. N. Cui, Q. Y. Zhu, J. Dai. *Inorg. Chem.*, **2018**, 57, 7420–7427.
[4] S. S. Passadis, S. Hadjithoma, N. J. Fairbairn, G. J. Hedley, N. A. G. Bandeira, A. C. Tsipis, H. N. Miras, A. D. Keramidas, T. A. Kabanos. *Inorg. Chem.* **2022**, 61, 20253-20267.

50: Coordination Zr/Ce-oxoclusters with octahedral geometry as the basis for highly ordered mixed-metal oxide layers

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Oxide layers of transition metals play a central role in the production of memristive data storage devices, where changes in electrical conductivity — for example, due to local valence changes at the metal centers — are exploited for information storage under applied external potentials. These memory devices are distinguished by their high energy efficiency, scalability, and durability, rendering them a promising alternative to conventional charge-based memory technologies in numerous application domains.[1], [2] Mixed metal oxides, commonly synthesized via sputtering, pulsed laser deposition (PLD), or atomic layer deposition (ALD), are increasingly investigated to enhance switching performance. Nevertheless, these high-temperature fabrication techniques are associated with substantial energy demands and frequently result in an inhomogeneous distribution of metal constituents and their corresponding oxide phases within the deposited layers.

In this work, we present an alternative approach for the fabrication of technically relevant multimetallic oxide layers, based on the thermally or photochemically induced conversion of organically functionalized hexanuclear transition metal oxo clusters, which serve as neutral analogues of anionic Lindqvist-type polyoxometalates. The choice of zirconium- and cerium-based oxoclusters over the technically more common hafnium- and titanium-based systems was motivated by the higher stability of the resulting oxide phases, which exhibit comparable switching properties, as well as by cost advantages. Nevertheless, a transfer of the process to complexes containing hafnium or titanium is, in principle, feasible due to the chemical similarity of these metals. To this end, zirconium- and cerium-based oxoclusters are first synthesized as precursors incorporating various 3d, 4f and alkali metals and subsequently deposited onto SiO_2/Si substrates.[3] The well-defined stoichiometry of these polynuclear coordination compounds ensures optimal mixing of the distinct metal species. Subsequent removal of the organic ligands through thermal treatment and/or irradiation with high-energy photons yields phase-mixed metal oxide layers or nanoparticles.

[1]. M. Aono; R. Waser, *Nat. Mater.* **2007**, *6*, 833–840.
[2]. K. Szot, G. Staikov R. Dittmann, R. Waser, Adv. Mater. **2009**, *21*, 2632–2663.
[3]. M. Seiß, J. Lorenz, S. Schmitz, M. Moors, M. Börner, K.Monakhov, *Dalton Trans.*, **2024**, 53, 8454-8462.

51: Biomass valorization via POM catalysts (BioValCat): Influence of POM structure type for glucose oxidation to acetic acid

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The BioValCat (Enhanced Biomass Valorisation by Engineering of Polyoxometalate Catalysts) project (ERC CoG: Project 101086573) builds on groundbreaking discoveries in selective homogeneously catalyzed biomass utilization.[1] Based on the previous investigations of the Erlanger OxFA process, which have shown promising results in the bio-based production of formic acid with the help of polyoxometalate catalysts such as $H_8PV_5Mo_7O_{40}$,[2] the scope of BioValCat will be to expand the homogeneously catalyzed biomass utilization technology for more valuable products.

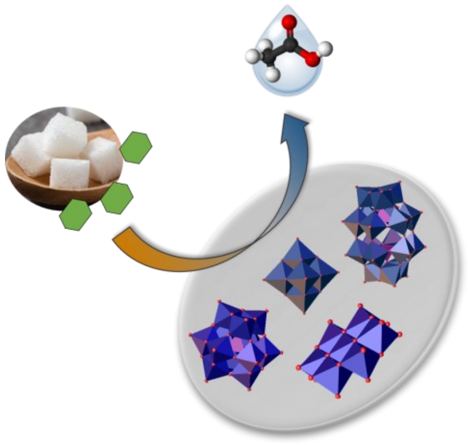

Figure:Glucose valorization to acetic acid via multi-structural polyoxometalate catalysts

In our initial investigation we selected highly active multifunctional Keggin-, Anderson-Evans-, Wells-Dawson-, and Lindqvist-type polyoxometalates for the selective oxidation of biomass. Using glucose as a model substrate for cellulosic biomass, we were able to obtain higher-chain monocarboxylic acids such as propionic acid, acetic acid, and dicarboxylic acids such as succinic acid by using V substituted polyoxotungstates under different oxidative conditions, compared to the classic OxFA-process. In addition, we discovered a relationship between the structure type and catalytic performance for acetic acid production. Based on these findings, we will continue to focus on further valorisation products by achieving the selective implementation through a targeted modification of the catalyst.

[1] J. Albert *et al.*, *Energy and Enviromental Science* **2015**, *8 (10)*, 2985-90
[2] J. Albert *et al.*, *ChemSusChem* **2023**, *16 (16), e202300072*

52: New Insights into the Role of Main-Group Elements in Polyoxometalates

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Main group elements as heteroatoms in polyoxometalate are well known features such as the Keggin-, Wells-Dawson, or Anderson-Evans structures. In a systematic study we have now investigated the influence of main group-elements, specifically group 15 elements, on the formation of POM structures. We have employed a combined experimental and computational approach to reveal the structure determining influence of group 15 elements in the formation of polyoxoemtalates.[1]

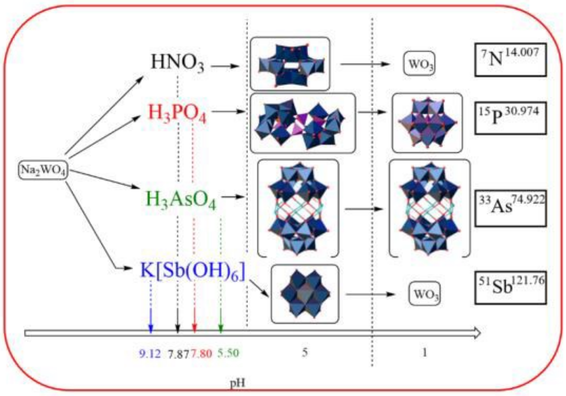

Figure: Formation of different POM structure types in dependence of the heteroelement and pH value.[1]

Since Keggin-type POMs, in which the framework element has been partially substituted by another transition metal, have gained increasing prominence in sustainable catalysis,[2-4] we also investigate the possibility to partially replace the framework metal with a main group element. Specifically, we study the partial replacement of W in the $[PW_{12}O_{40}]^{3-}$ anion with Al and Si, and are looking forward to presenting our first results.

[1]J.-C. Raabe, F. Jameel, M. Stein, J. Albert, M. J. Poller, *Dalt. Trans.* **2024**, *53*, 454–466.
[2] J. D. H. Krüger , M. J. Poller , C. Lyall, J. Lowe, U. Hintermair, J. Albert *ChemCatChem,* **2024**, DOI 10.1002/cctc.202400402.
[3]A. Wesner, J. Raabe, M. J. Poller, S. Meier, A. Riisager, J.Albert, *Chem. – A Eur. J.* **2024**, *30*, DOI 10.1002/chem.202402649.
[4] J.-C. Raabe, M. J. Poller, D. Voß, J. Albert, *ChemSusChem,* **2023**, 16, e202300072.

53: Post-functionalization of super-reduced polyoxometalates

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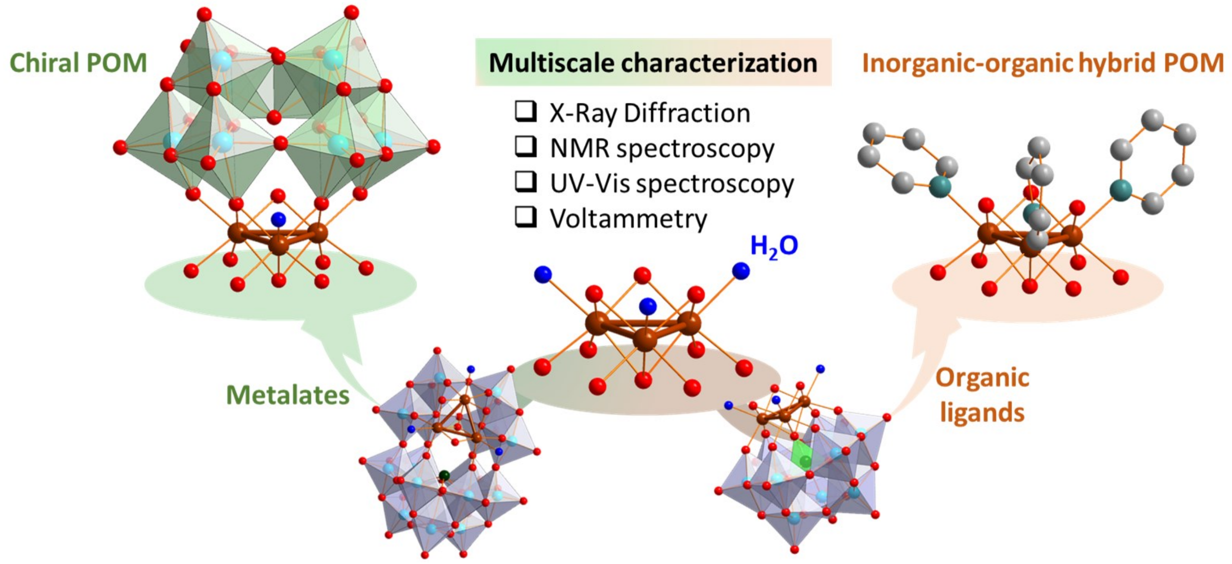
Polyoxometalates (POMs) are known to undergo numerous successive electron exchange processes, covering a wide range of redox potentials modulated by their chemical composition. This property paves the way to a variety of applications in energy conversion and storage, as demonstrated by Cronin et al. when they succeeded in storing 18 electrons on the Dawson anion.[1][2] Despite the promising performances of reduced POMs, fundamental investigations into their structure and reactivity are still in their early stages.

We have recently shown that the reduction of six-electron POMs is accompagned by the formation of coordinating water molecules on the super-reduced sites.[3][4] The lability of these aquo ligands opens up unique possibilities for the post-functionalization of these super-reduced POMs. In this communication, we report on the first functionalizations of super-reduced POMs with various N-donor ligands and metalate ions. The preparation, the structural characterizations, and the solution behaviour of these novel compounds will be discussed.



[1] Cronin, L. et al. *Nature Chem* **10**, 1042–1047 (2018)
[2] Cronin, L. et al. *J. Am. Chem. Soc.***144,** 8951-8960 (2022)
[3] Falaise, C. et al. *Inorg. Chem.* **62,** 2494–2502 (2023)
[4] Mpacko Priso, G. et al *Angew. Chem. Int. Ed.* **62**, e202312457 (2023)

54: Computational Insights into the Catalytic Properties and Solution Behaviour of Zirconium Oxo Clusters

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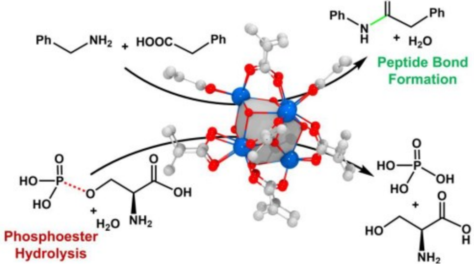
Zirconium oxo clusters (ZrOCs) are discrete molecular entities composed of zirconium atoms interconnected by oxo (O^{2-}) and hydroxo (OH^{-}) bridges incorporating carboxylate ligands[1] which stabilize their structure as for example $[Zr_6(OH)_4O_4(OOCCH_3)_{12}]$. These clusters serve as building blocks for zirconium-based metal–organic frameworks (Zr-MOFs) and have demonstrated significant potential as catalysts in various chemical transformations, particularly in the organic synthesis field.

Herein, we present a computational study into the reactivity and solution behavior of ZrOCs across a series of reactions including amide bond formation[2], dipeptide cyclization, peptide bond hydrolysis, and phosphoester bond hydrolysis[3] under different reaction conditions. Our results reveal detailed mechanistic insights into these catalytic pathways, emphasizing the role of Zr centers in promoting bond formation or hydrolysis with remarkable efficiency depending on their coordination enviroment. Other key factors such as the Zr Lewis acidity or the ZrOCs speciation have been found to be crucial for their catalytic activity. For example, partial substitutions of Zr atoms with Mg significantly enchances the cluster activity by generating under-coordinated Zr sites, which increases their Lewis acidity and consequently they have a higher hydrolytic activity. Additionally, we investigated the collective behaviour of ZrOCs in solution, focusing on their solvation sphere in different solvent environments which correlates with the observed reactivity trends[2]. These findings provide a comprehensive picture of ZrOC-based catalysts from computational tools, offering valuable insights into their reactivity and solution dynamics for improving the catalyst efficiency and robustness in different fields.



[1] Y. Zhang, F. de Azambuja, T. N. Parac-Vogt, *Coord. Chem. Rev.* **2021**, 438, 213886-213914.
[2] Y. Zhang, J. Puiggalí-Jou, A. Mullaliu, A. Solé-Daura, J. J. Carbó, T. N. Parac-Vogt, F. de Azambuja, *Inorg. Chem.* **2024**, 63, 20347–20360
[3] E. Luiz, F. de Azambuja, A. Solé-Daura, J. Puiggalí-Jou, A. Mullaliu, J. J. Carbó, F. R. Xavier, R. A. Peralta, T. N. Parac-Vogt, *Chem. Sci.* **2024**, 15, 18008–18021.

55: Selective Oxidative Cleavage of Diverse Proteins Using Cu-Substituted Polyoxometalates: Exploring Catalytic Behavior and Nuclearity Effects

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Selective cleavage of peptide bonds under physiologically relevant conditions remains a fundamental challenge in biomolecular catalysis. Here, we introduce a series of Cu(II)-substituted polyoxometalates (Cu-POMs) that act as artificial metalloprotease-like systems, catalyzing oxidative scission of peptide bonds in structurally diverse proteins. Systematic variation of Cu nuclearity within Keggin-type scaffolds reveals a clear correlation between multinuclear architecture and catalytic performance. Notably, the trinuclear CuIIKeg (3:1) complex exhibits superior cleavage efficiency, even at substoichiometric concentrations, emphasizing the functional advantage of multi-center redox systems. Cleavage across five distinct proteins—including HEWL, BSA, myoglobin, β-lactoglobulin, and hemoglobin—was shaped by surface charge distribution and local topology. Site-directed oxidation is mediated by POM-confined ROS generation, a feature absent in free Cu(II) systems [1,2]. These findings establish Cu-POMs as modular, redox-active platforms for selective peptide bond activation, expanding the toolkit of artificial protease design under mild, biocompatible conditions [3-7].

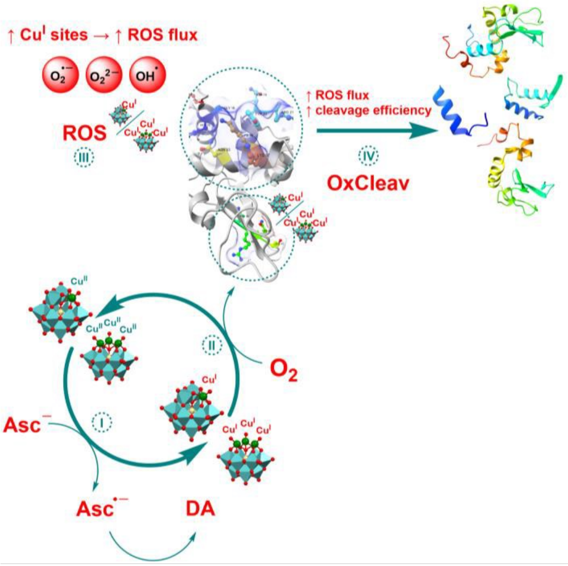

Figure: FMultinuclear Cu–POMs boost local ROS flux, enabling selective oxidative protein cleavage under mild conditions.

[1] T. N. Parac-Vogt, M. A. Moussawi, F. de Azambuja, Angew. Chem. Int. Ed. 2025, DOI: 10.1002/anie.202423078.
[2] S. A. M. Abdelhameed, F. de Azambuja, T. Vasović, N. D. Savić, T. Ćirković Veličković, T. N. Parac-Vogt, Nat. Commun. 2023, 14, DOI: 10.1038/s41467-023-36085-z.
[3] U. Törnvall, Anal. Methods 2010, 2, 1638–1650.
[4] J. M. Antos, M. B. Francis, Curr. Opin. Chem. Biol. 2006, 10, 253–262.
[5] J. O. Kang, P. C. Chan, L. Kesner, Peroxidation of Lysozyme Treated with Cu(II) and Hydrogen Peroxide, 1985.
[6] A. Sap, E. Dezitter, L. Vanmeervelt, T. N. Parac-Vogt, Chem. Eur. J. 2015, 21, 11692–11695.
[7] L. Vandebroek, Y. Mampaey, S. Antonyuk, L. Van Meervelt, T. N. Parac-Vogt, Eur. J. Inorg. Chem. 2019, 506–511.

56: Controlled Functionalisation and Conversion Reactions of Tube-Type Dodecavanadates

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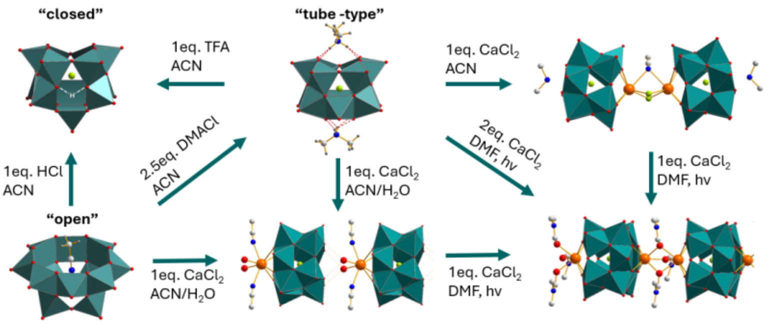
Polyoxovanadates synthesised from organic solvents have been described for their versatility as oxidation catalysts,[1] their shape recognition ability,[2] and their supramolecular aggregation into polymeric networks.[3] However, controlled structural transformation and functionalisation into the desired clusters often remains a challenge. One example to make functionalisation with heterometals more predictable is the placeholder strategy, in which dimethylammonium (DMA) stabilises two binding sites on the "tube-type" dodecavanadate and can be replaced in a further reaction step.[4]

In this work, we present different pathways for controlled functionalisation with heterometals and ligands as well as proton induced conversions of the alkylammonium stabilized “tube-type” dodecavanadate. We show how metal functionalisation via the placeholder strategy is applicable for all lanthanides as well as yttrium and calcium for crystallographic comparison of isostructural single crystals. The reaction was investigated via liquid IR and ^{51}V NMR as well as ^{139}La NMR and no side products were detected. The binding of a second heterometal was tested using calcium as a redox inactive ion, which has been used by our group to improve the electrochemical behaviour of the cluster.[3] The enhanced photoactivity similar to the magnesium functionalised dodecavanadate reported by our group leads to selectively difunctionalised clusters.[5] To control supramolecular aggregation different counter ions and solvents were investigated and various organic ligands were tested to potentially enable surface chemistry and the design of dissipative systems. Additionally, the influence of protons on the functionalised cluster was investigated to reveal a similar behaviour to the proton induced structural conversion between the “open”, “closed” and “tube-type” dodecavanadate first reported by Hayashi et al..[6]



Synthetic pathways for controlled functionalisations and structure conversions of dodecavanadates.

[1] Kikukawa Y, Ogihara K, Hayashi Y., *Inorganics.* 2015, 3(2), 295-308.
[2] Y. Kikukawa, H. Kitajima, Y. Hayashi, *Dalton Trans.* 2019, 48, 7138–7143.
[3] S. Greiner, B. Schwarz, M. Ringenberg, M. Dürr, I. Ivanovic-Burmazovic, M. Fichtner, M. Anjass, C. Streb, Chem. Sci. 2020, 11, 4450–4455.
[4] K. Kastner, J. T. Margraf, T. Clark, C. Streb, Chem. Eur. J. 2014, 20, 12269-12273.
[5] Repp, S., Remmers, M., Rein, A.S.J. et al., Nat Commun. 2023, 14, 5563.
[6] Inoue , Y. Kikukawa , S. Kuwajima and Y. Hayashi , *Dalton Trans.*, 2016, **45** , 7563 —7569.

57: Co-immobilization Of Polyoxometalates And Organic Cations Onto (Mesoporous) Silica For Supported CO2 Cycloaddition Onto Epoxides

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Cyclic carbonates are key compounds with a large scope of applications, such as plastics (including polycarbonates) or solvents in paints and batteries.[1] However, their industrial production still uses extremely toxic C(IV) sources such as phosgene and gives rise to HCl.[2] At the same time, CO2 is the most abundant greenhouse gas in the atmosphere and its mitigation remains one of the greatest environmental challenges of our time. Using this widely available, cheap and non-toxic resource as a carbonaceous feedstock in Carbon Capture and Utilization processes looks like an exciting opportunity.[3] In this context, the one-pot synthesis of cyclic carbonates from alkenes, using an oxidant and CO_2 is of obvious interest. This strategy, referred as oxidative carboxylation cascade reaction, requires the successive use of oxidation (OxCat) and CO_2 cycloaddition catalysts (CyCat).[4] Of all OxCat and CyCat catalysts described so far, we recently showed that first-row transition metalsubstituted polyoxometalates $[PW_{11}O_{39}M(H_2O)]_n^-$ (TMSP; M = Cr, Mn, Fe, Co, Ni, Zn) proved effective for each individual step,[5] ideally leading to auto-tandem catalysis processes. In addition, DFT calculations have suggested that an unexpected carbonic anhydrase-like mechanism occurred in the absence of halides (fig.1 c). In the whole sequence of reactions, we have also found that the catalytic efficiency was also increased by using quaternary ammonium counter-ion with long chains. While this behavior was known in the case of CyCat (fig.1 a), this was a more unexpected result for epoxidation reactions. This trend was also confirmed after immobilization of the catalysts on mesoporous silica. The catalytic materials with the highest turnover frequency were obtained using both NR_4^+ cations from TMSP and alkylammonium grafted onto silicas with the longest chains (fig.1 b).

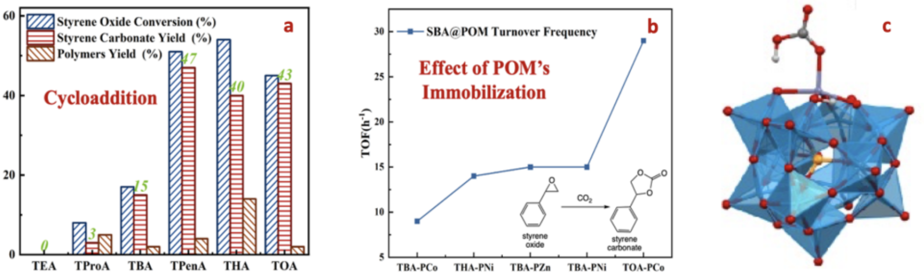

Figure 1: CO_2 cycloaddition on styrene oxide with $[PW_{11}O_{39}Co(H_2O)]^{5-}$ in homogeneous conditions (a); supported onto $SBA-CH_2CH_2CH_2NMe_3Cl$ (b) as a function of chain length of the $NR_4{}^+$ counter-ion and DFT calculation of TMSP with CO_2 (c)

[1] A. J. Kamphuis, F. Picchioni, P. P. Pescarmona, Green. Chem. 2019, 21, 406.
[2] S. Fujita, M. Arai, B.M. Bhanage, Direct Transformation of Carbon Dioxide to Value-Added Products over Heterogeneous Catalysts, in: B.M. Bhanage, M. Arai (Eds.), Transform. Util. Carbon Dioxide, Springer Berlin Heidelberg, 2014, pp. 39–5.
[3] M. Aresta, A. Dibenedetto, A. Angelini, J. CO2 Util. 2013, 3-4, 65; A.W. Kleij, M. North, A. Urakawa, Chemsuschem 2017, 10, 1036; M. Aresta, Coord. Chem. Rev. 2017, 334, 150. d) C. Chauvier, T. Cantat, ACS Catal. 2017, 7, 2107.
[4] X.D. Lang, L.N. He, Chem. Rec. 2016, 16, 1337; L. Wang, S. Que, Z. Ding, E. Vessally, RSC Adv. 10 (2020) 9103; M. Balas, R. Villanneau, F. Launay, J. CO2 Util, 2022, 65, 102215.
[5] J. Ren, A. Proust, F. Launay, R. Villanneau, Chem. Commun. 2024, 60, 4549.

58: Functionalised POMs: The DFT Part of Combined DFT and Experimental Studies

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POMs are widely studied for their catalytic and electrochemical abilities, with many proving highly successful for a range of applications. In this study, we consider different POM structures. The first comprises a set of POMs in which specific metals have been substituted. These are split between the interesting interactions of different additives in promoting high selectivity and reactivity versus “standard conditions”[1], in which binding of these additives at the “active” sites promotes high selectivity, while the other shows unusual electronic properties along with good (photo)catalytic promise [2]. In the second study, we demonstrate the deepening understanding of various molecular properties of hybrid inorganic-organic POMs on their photocatalytic ability, showing that conjugation alone is not the answer to reducing the HOMO-LUMO gap closer to the visible wavelength end of the spectrum.

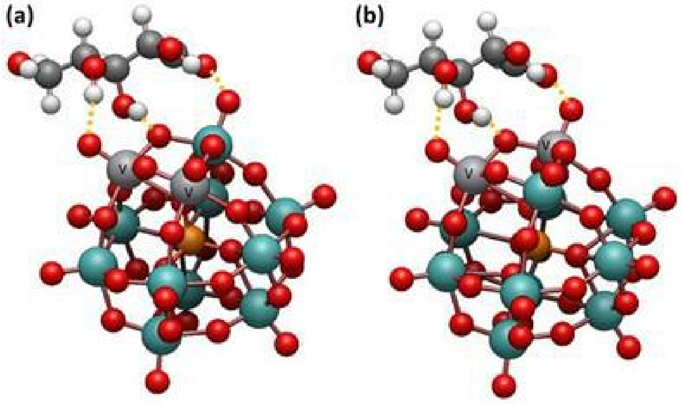

Figure 1: Binding of xylose at the (a) V-O-Mo site and (b) V-O-V sites of HPA-2.

[1] J.-D. H. Krueger, D. Sivarajah, M. J. Poller, D. Robinson and J. Albert, “Influence of Reactive Additives on the Polyoxometalate-Catalyzed Oxidation of Xylose to Formic Acid”, *CatChemCat* **2025**, e202500096 (in press).
[2] S. S. Amin, K. D. Jones, A. J. Kibler, H. A. Damian, J. M. Cameron, K. S. Butler, S. P. Argent, M. Winslow, D. Robinson, N. J. Mitchell, H. W. Lam, G. N. Newton, “Diphosphoryl-functionalized Polyoxometalates: Structurally and Electronically Tunable Hybrid Molecular Materials”, *Angew. Chem. Int. Ed.* **2023**, *62*, e202302446.

59: Synthesis and Reactivity of Soluble Cerium(IV)-oxo Clusters Towards Proton-Coupled Electron Transfer Reactions

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Cerium oxide (ceria) is a mixed-valence oxide containing both Ce^{4+} and Ce^{3+} ions, with its redox state (%Ce^{3+}) varying in response to redox reactions. This behaviour is particularly pronounced at the nanoscale, where increased surface-to-bulk ratios stabilize Ce^{3+} sites, enhancing its redox flexibility. These properties make ceria a valuable catalyst, cocatalyst, and reducible oxide support. Ceria's redox activity primarily involves hydrogen or oxygen atom transfer, with thermochemistry playing a key role in its reactivity. At near-ambient temperatures or in colloidal suspensions, charge balance can be maintained via hydrogen atom binding. Reduction typically occurs through hydrogen atom addition (H• → e$^-$ + H$^+$), converting Ce^{4+} to Ce^{3+} and protonating an oxide site.1,2

In this work, we synthesize solubilized cerium-oxo clusters, giving us the advantage of being able to use solution-based techniques, to probe the structure-reactivity relationships and kinetics of proton-coupled electron transfer reactions using various hydrogen-atom transfer reagents.

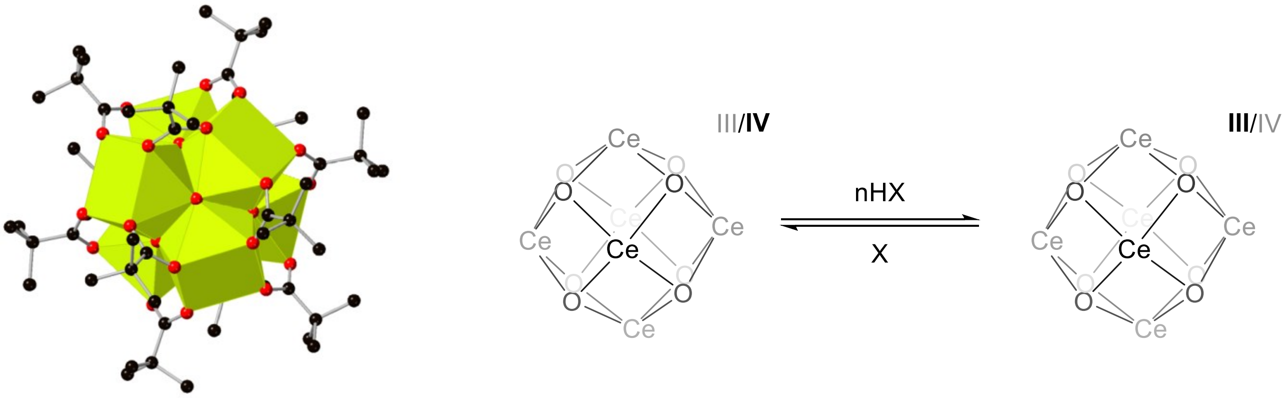

Figure 1.) (left) Single-crystal structure of a representative Cerium-Oxo Cluster ([Ce6(O2CtBu)12(O)4(OH)4]). (right) Proton-Coupled electron transfer reaction of cerium-oxo clusters.

[1] Shahed, S. M. F.; Hasegawa, T.; Sainoo, Y.; Watanabe, Y.; Isomura, N.; Beniya, A.; Hirata, H.; Komeda, T. *Surf. Sci*. 2014, **628**, 30– 35
[2] Rishi G. Agarwal, Hyun-Jo Kim and James M. Mayer, *J. Am. Chem. Soc. 2021, 143, 7, 2896–2907*.

60: Engineering Hybrid Polyoxometalates (HPOMs) with Multiple POMs: From Synthesis to Oxidation Catalysis

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Combining two or more distinct Polyoxometalate (POM) clusters with varying functional properties into a single covalently linked entity poses significant challenges and remains scarce in the literature.[1], [2] This approach enables us to navigate between two realms of chemistry, i.e., organic and inorganic, allowing us to manipulate the redox properties and self-assembly of Hybrid Polyoxometalates (HPOMs). In this study, we have strategically modified the catalytic properties of POMs through a stepwise process, beginning with covalent attachment and progressing to click chemistry, to synthesize a novel HPOM referred to as a POM-POM hybrid. This HPOM has been successfully characterized using ^{1}H NMR, ESI-MS, and FT-IR spectroscopic techniques. Additionally, we investigated the self-assembly behavior of this HPOM, resulting in an intriguing spindle morphology that has rarely been observed in HPOMs.[3] Finally, we examined the heterogeneous catalytic properties of the HPOM in the oxidation of sulfides. We found that it selectively catalyzed the conversion of sulfide to sulfoxide when compared to its individual building blocks.

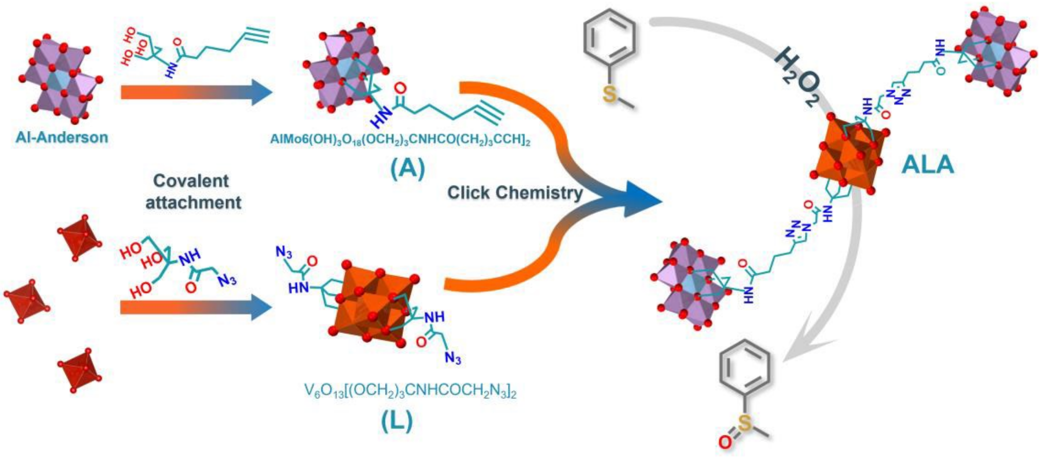

Figure: Immobilization of multiple POM in a single entity for selective oxidation of sulfide

[1] M. F. Misdrahi, M. Wang, C. P. Pradeep, F. Y. Li, C. Lydon, L. Xu, T. Liu**,** *Langmuir* **2011**, *27*, 9193–9202.
[2] D. E. S. Marcano, M. A. Moussawi, A. V. Anyushin, S. Lentink, L. Van Meervelt, I. Ivanović-Burmazović, T. N. Parac-Vogt, *Chem. Sci.* **2022**, *13*, 2891–2899.
[3] M. Wei, L. Wang, B. Li, L. Wu, *Chem. Commun.* **2024**, *60*, 11536–11539.

61: NMR Insights Into The Supramolecular Interaction Between The Polyoxoanion $[\alpha\text{-SiW}_{11}\text{O}_{39}]^{8-}$ And Amyloid Peptides

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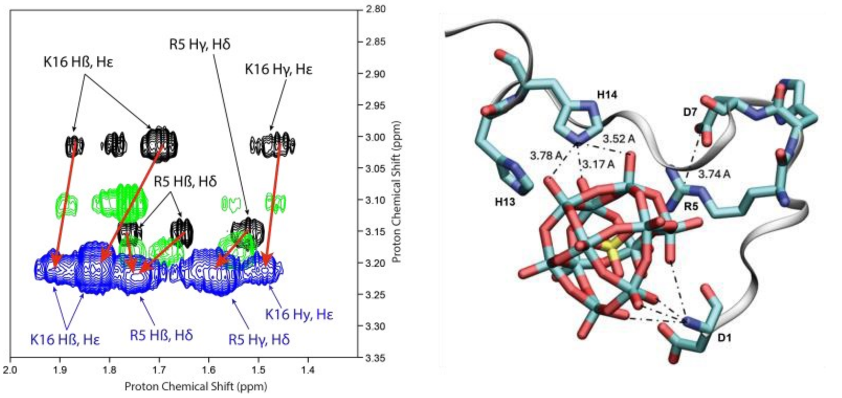
One of the hallmarks of Alzheimer's disease is the abnormally high presence of amyloid plaques in the brain. These plaques result from the still poorly understood aggregation of amyloid-β(Aβ) peptides, a process driven by supramolecular interactions between Aβ peptides. This aggregation leads to the formation of nuclei that evolve into soluble aggregates before ultimately precipitating as mature fibrils.[1] Our work, along with that of others, has shown that polyoxometalates (POMs), polyoxoanions of early transition metals in their highest oxidation states, can modulate this aggregation process.[2,3] Gaining a better understanding of the interactions between POMs and Aβ peptides could thus provide valuable insights into the aggregation mechanism itself.



We will describe the 1D and 2D NMR and MD studies of the interaction of the $[\alpha\text{-SiW11O39}]^{8-}$ anion with both $A\beta^{1-40}$ peptide and its truncated $A\beta^{1-16}$ fragment (Figure 1). These studies allowed us to calculate an affinity constant and map the interaction of the POM with the peptide.[4]

ANR-21-CE06-0030-03 is acknowledged for financial supports.

[1] Ke, P. C.; Mezzenga, R. et al. Chem. Soc. Rev. 2017, 46 (21), 6492–6531.
[2] Atrián-Blasco, E.; de Cremoux, L.; Lin, X.; Mitchell-Heggs, R.; Sabater, L.; Blanchard, S.; Hureau, C. Chem. Commun. 2022, 58 (14), 2367-2370.
[3] Gao, N.; Liu, Z.; Zhang, H.; Liu, C.; Yu, D.; Ren, J.; Qu, X. Angew. Chem. Int. Ed., 2022, 61 (16), e202115336.
[4] Roux, A.; Decremoux, L., Hureau, C., Blanchard. S., Giraud, N., in preparation

62: POM-Mediated Assembly of a Small-Ion Superlattice

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The assembly of charged nanoparticles (NPs) with much smaller, oppositely charged ions has recently emerged as a rational strategy for designing multidimensional nanostructured materials, including superlattices (SLs).[1,2] In this study, we demonstrate that negatively charged polyoxometalate (POM)-protected 4 nm gold (Au) NPs[3-5] can be reversibly assembled into SLs through electrostatic interactions with Co^{2+}_{aq} in water. Disassemmbly into individual Au NPs shows that electrostatically-stabilized POM protecting-ligand shells remain intact during SL formation, after which the small mobile ions may diffuse rapidly through the lattice. Additional insight into the criteria that must be met to obtain well-defined SL assemblies was provided by investigating the effects of POM charge and the nature and valence of countercations. The findings sum to a new strategy for using POM cluster anions to rationally design well-defined NP assemblies.

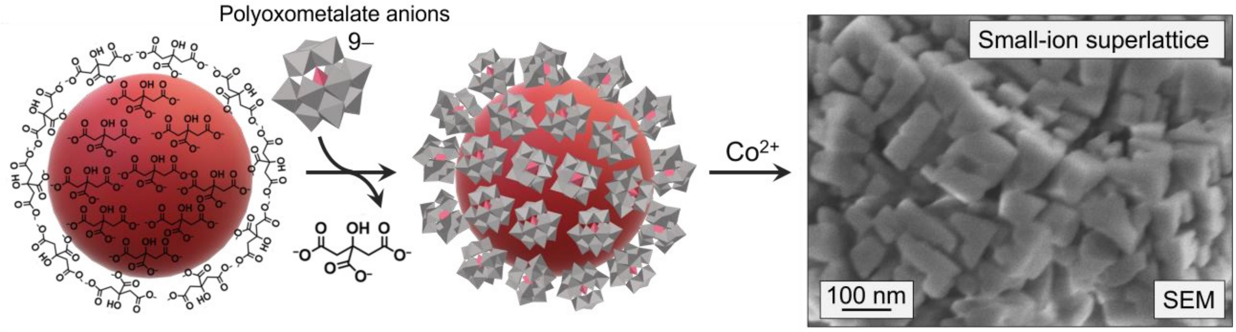

Figure: Replacement of citrate ligands on Au NPs by electrostatically-stabilized monolayers of $K_9[AlW_{11}O_{39}]$ (left and center), followed by the addition of Co^{2+}_{aq}, induces the formation of SLs (SEM image at right).

[1] T. Bian, A. Gardin, J. Gemen, L. Houben, C. Perego, B. Lee, N. Elad, Z. L. Chu, G. M. Pavan, R. Klajn, Nat. Chem. **2021**, *13*, 940– 949.
[2] I. Coropceanu, E. M. Janke, J. Portner, D. Haubold, T. D. Nguyen, A. Das, C. P. N. Tanner, J. K. Utterback, S. W. Teitelbaum, M. H. Hudson, N. A. Sarma, A. M. Hinkle, C. J. Tassone, A. Eychmuller, D. T. Limmer, M. Olvera de la Cruz, N. S. Ginsberg, D. V. Talapin, Science. **2022**, *375*, 1422– 1426.
[3] Y. Wang, A. Neyman, E. Arkhangelsky, V. Gitis, L. Meshi, I. A. Weinstock, J. Am. Chem. Soc. **2009**, *131*,
[4] Y. Wang, O. Zeiri, M. Raula, B. Le Ouay, F. Stellacci, I. A. Weinstock, Nat. Nanotechnol. **2017**, *12*, 170-176.
[5] S. Chakraborty, C. K. Tiwari, Y. Wang, G. Gan-Or, E. Gadot, I. A. Weinstock, J. Am. Chem. Soc. **2019**, *141*, 14078-14082.

63: Organofunctionalized Anderson Polyoxometalate-Based Aerogel

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Polyoxometalate-based aerogels, constructed by supramolecular interactions and metal coordination, have a prospect of expanding the smart materials field.[1,2] Here, we report the polyoxometalate organogel formed by the reaction of ZnCl2 with TRIS-functionalized Anderson polyoxometalate $[MnMo_6O_{18}\{(OCH_2)_3CNH_2\}_2]^{3-}$ in MeCN. The organogel was converted to aerogel by freeze-drying methodology. This poster will illustrate the use of various experimental techniques to follow the transformation of POM to organogel and aerogel. Initial insights into the role of solvent, POM used, and metal salt will also be discussed. Moreover, the resulting aerogel shows promising selective alcohol oxidation for benzyl alcohol and furfuryl alcohol.

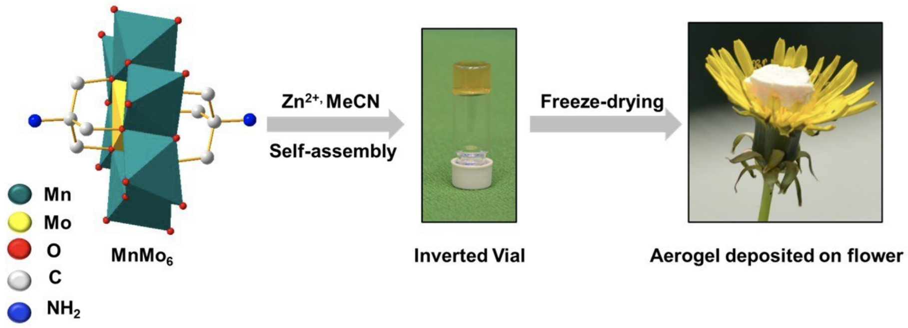

Figure1: Illustration of the formation of organogel and aerogel from TRIS-functionalized Anderson POM.

[1] C. Dong, X. Liu, Z. Li, K. Guo, C. Song, Y. Zhang, M. Zhang, F. Ma, F. Rosei, X. Zhang, X. Huang, *Adv Funct Mater* **2024**, *2418410*, 1–9.
[2] T. Liu, Y. Zhang, C. Wang, Y. Kang, M. Wang, F. Wu, W. Huang, *Small* **2024**, *20*, 1–11.

64: Polyoxo-Noble-Metalates into Polyoxo-Noble-Metalate Metal-Organic Frameworks

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Polyoxopalladates (POPs) are polyoxo-noble-metalates with Pd as the addenda atom and tetrahedral or tripodal oxoanions (e.g., PO_4^{3-}, AsO_4^{3-}, SeO_3^{2-}, and $PhAsO_3^{2-}$) or bidentate groups (e.g., acetate and dimethylarsinate).[1-4] On the other hand, metal-organic frameworks (MOFs) are formed by metal ions or clusters serving as building blocks, connected by organic ligands, resulting in a three-dimensional structure.[5] Both classes of materials possess an enormous diversity in composition and structure, associated with diverse properties and applications in molecular recognition, biosensing, catalysis, and magnetism.[1-6] In 2019, we showed that an externally functionalized Pd_{13} POP can form a three-dimensional MOF framework, representing the first POP-MOF, JUB-1.[7] In subsequent studies, novel JUB-1 derivatives with varied topologies, such as JUB-2, were synthesized by one-pot aqueous reactions and structurally characterized by a range of analytical techniques involving X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS), and cyclic voltammetry (CV), among others. These findings provide a deeper understanding of polyoxopalladate chemistry and serve as the basis for the rational design and assembly of novel polyoxopalladate-based metal-organic frameworks (MOFs).

[1] P. Yang, U. Kortz, *Acc. Chem. Res.* **2018**, *51*, 1599−1608.
[2] N. V. Izarova, M. T. Pope, U. Kortz, *Angew. Chem. Int. Ed.* **2012**, *51*, 9492.
[3] E. V. Chubarova, M. H. Dickman, B. Keita, L. Nadjo, F. Miserque, M. Mifsud, I. W. C. E. Arends, U. Kortz, *Angew. Chem., Int. Ed.* **2008**, *47*, 9542-9546.
[4] N. V. Izarova, M. H. Dickman, R. Ngo Biboum, B. Keita, L. Nadjo, V. Ramachandran, N. S. Dalal, U. Kortz, *Inorg. Chem.* **2009**, *48*, 7504-7506.
[5] G. Maurin, C. Serre, A. Cooper, G. Férey, *Chem. Soc. Rev.* **2017**, *46*, 3104-3107.
[6] P. Yang, M. E. Mahmoud, Y. Xiang, Z. Lin, X. Ma, J. H. Christian, J. K. Bindra, J. S. Kinyon, Y. Zhao, C. Chen, T. Nisar, V. Wagner, N. S. Dalal, U. Kortz, *Inorg. Chem.* **2022**, *61*, 18524-18535.
[7] S. Bhattacharya, W. W. Ayass, D. H. Taffa, A. Schneemann, A. L. Semrau, S. Wannapaiboon, P. J. Altmann, A. Pöthig, T. Nisar, T. Balster, N. C. Burtch, V. Wagner, R. A. Fischer, M. Wark, U. Kortz, *J. Am. Chem. Soc.* **2019**, *141*, 3385-3389.

65: From Lindqvist To Wells-Dawson: Mapping PCET Reactivity In Polyoxotungstates

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Proton-coupled electron transfer (PCET) is a fundamental mechanistic concept enabling a wide range of chemical and biochemical transformations, including energy conversion, catalysis, battery systems and material science.[1] A detailed understanding of PCET mechanisms on the molecular level is crucial for the rational design of efficient catalysts, particularly in key processes such as water splitting and fuel cell operation for green energy applications. Our research group investigates PCET mediators based on both metal-doped and unsubstituted polyoxotungstates (POT) as promising platforms for tunable redox behaviour.[2,3] In this study, we focus on ground-state (GS) PCET reactivity of a series of POT differing in the size of their tungsten oxide framework. Through electrochemical measurements, including determination of formal redox potentials, electron transfer kinetics and potential-pk$_a$ correlation analysis, we aim to elucidate the influence of cluster size and structure on PCET-behaviour and to contextualize the reactivity of transition-metal-functionalized POTs within this structure-PCET-reactivity relationship.

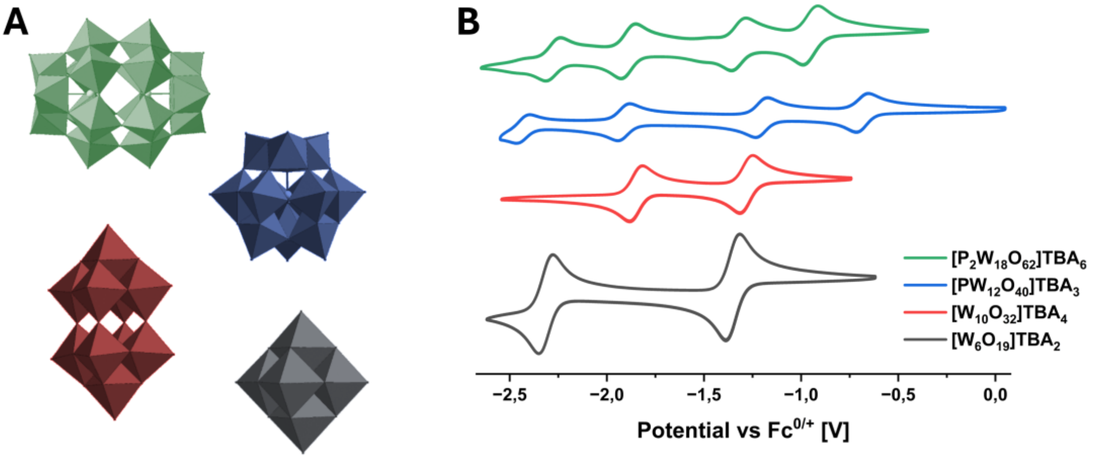

Figure 1: (A) Wells-Dawson- (green), Keggin- (blue), Lindqvist-Type (black) and Decatungstate (red) polyoxotungstates with WO$_6$ units displayed as polyhedra.[4] (B) Corresponding cyclic voltammograms.

[1] S. Hammes-Schiffer, *ACS Publications* **2010**, *12*, 110
[2] Z. Lu, S. E. Cooney, J. R. McKone, E. M. Matson, *JACS Au* **2024**, *4*, 1310.
[3] C. Streb, *Dalton Transactions* **2012**, *41*, 1651.
[4] N. I. Gumerova, A. Rompel, *Nature Reviews Chemistry* **2018**, *2*, 112.

66: Investigating multi-electron reduction processes from titanium-oxo clusters

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Photocatalysts are of great interest to chemists as they provide a greener way to activate challenging reactions. Titanium based catalysts are of particular interest due to the high natural abundance of titanium, low cost and its band gap of ~3.2 eV which is accessible by UV irradiation.[1, 2] The most famous titanium based photocatalyst is titanium dioxide (TiO_2) which is known for its use in suncream, white paint, self-cleaning windows and much more.[3] Studying Ti-oxo (TOCs) clusters as analogues of TiO_2 is a way of gaining more in-depth insight into the structure, chemical behaviour and reaction mechanisms of TiO_2. TOCs are large molecules comprised primarily of alternating titanium and oxygen atoms with the general formula $Ti_nO_m(OR/Cl)_x(L)_y$. Some TOCs are able to exhibit a mixed valent state with 3+ and 4+ titanium centres when the TOC is photoactivated resulting in TOCs that contain either high energy electrons or high energy electrons with associated protons which may be able to be harnessed for catalysis.[4] Manipulating the structure surrounding the Ti-oxo units allows the introduction of enhanced tunability of the excitation gap and therefore the electrons produced. This tunability allows TOCs to be designed with high selectivity for specific redox process such as the reduction of nitrous oxide. In this poster the synthesis of photoactivatable titanium-oxo clusters with varying ligands will be explored and the resultant changes to absorption abilities of the clusters will be analysed. Additionally, the potential applications of these clusters will be considered.

1. B. J. Watson and R. G. Eggert, *J. of Ind. Ecol.*, 2021, **25**, 890-899.
2. M. Pelaez, N. T. Nolan, S. C. Pillai, M. K. Seery, P. Falaras, A. G. Kontos, P. S. M. Dunlop, J. W. J. Hamilton, J. A. Byrne, K. O'Shea, M. H. Entezari and D. D. Dionysiou, *Appl. Catal. B.*, 2012, **125**, 331-349.
3. A. J. Haider, Z. N. Jameel and I. H. M. Al-Hussaini, *Energy Procedia*, 2019, **157**, 17-29.
4. S. E. Brown, I. Mantaloufa, R. T. Andrews, T. J. Barnes, M. R. Lees, F. De Proft, A. V. Cunha and S. D. Pike, *Chem. Sci.*, 2023, **14**, 675-683.

67: POM-BODIPY Hybrids for Enhanced Antibacterial Activity Under Visible Light

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The rapid rise of antimicrobial resistance (AMR) poses a significant global health threat by diminishing the efficacy of antibiotics, leading to persistent infections and elevated mortality rates[1]. According to the World Health Organization (WHO), AMR contributes to nearly 5 million deaths annually, surpassing the mortality rates of HIV/AIDS and malaria. Addressing this critical challenge requires innovative antibacterial strategies capable of overcoming conventional resistance mechanisms. Our approach focuses on developing polyoxometalate (POM)-based hybrid materials by covalently grafting inorganic $[Mo_6O_{19}]^{2-}$ _Lindqvist-type polyoxomolybdates with organic photosensitizers. Previous work in our group demonstrated the promising antibacterial activity of such hybrids incorporating UV-sensitive fragments (e.g., anthraquinone, benzophenone)[2]. Building on this foundation, we now introduce a novel class of visible-light-active POM-BODIPY hybrids designed for photodynamic therapy (PDT). These materials synergistically combine the unique electronic properties of polyoxometalates with the exceptional photophysical characteristics of BODIPY dyes, creating a system optimized for enhanced visible-light absorption and reactive oxygen species (ROS) generation. While POMs and BODIPY derivatives have been extensively studied individually, their integration into a single, conjugated, covalently linked hybrid for PDT applications remains unexplored. Our work bridges this gap, offering a platform that merges molecular design with biological functionality.

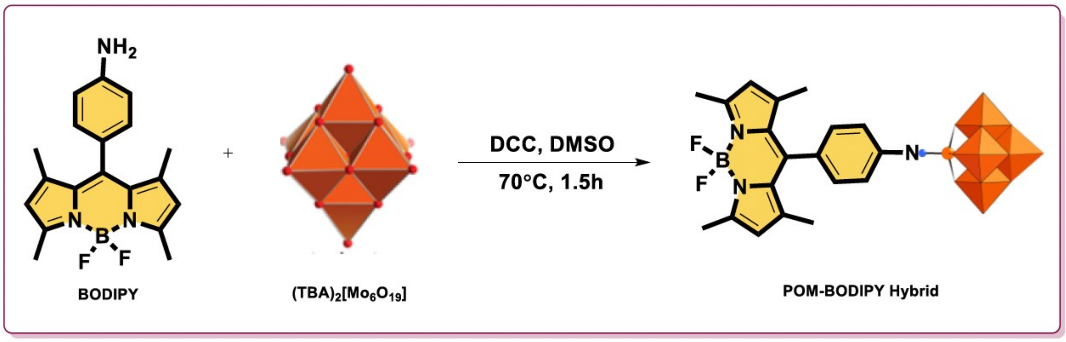

Figure Representation of the compound POM-BODIPY

[1] T. Li, Z. Wang, J. Guo, C. de la Fuente-Nunez, J. Wang, B. Han, H. Tao, J. Liu, X. Wang, *Sci. Total Environ.* **2023**, *860*, 160461.

[2] Z. El Hajj, L. Pierau, J.-P. Malval, J. Marrot, P.-E. Mazeran, D. Naoufal, M.-H. Ha-Thi, K. Steenkeste, A. Dolbecq, S. Floquet, O. Oms, D.-L. Versace, P. Mialane, *Macromolecules* **2023**, *56*, 6105–6116.

68: Developing Non-Aqueous Actinide-Polyoxometalate Chemistry

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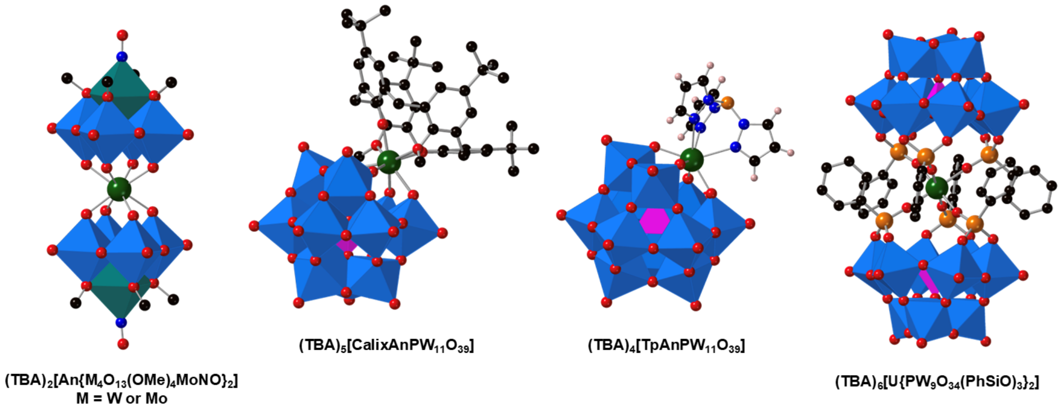
Polyoxometalates (POMs) have become a popular support for actinide centers [1,2]. Often crystallizing easily, they allow researchers to develop series of isostructural actinide, lanthanide, and transition metal-containing complexes and characterization by single crystal X-ray diffraction allows the co-ordination preferences of actinides to be probed [3]. However, a significant limitation of the use of POMs as "ligands" is that, until now, this has limited the solvent choice for synthesis and, more importantly, reactivity studies to water. This body of work investigates the use of preformed lacunary polyoxometalate species as supports for actinide centers in organic solvents. The properties of new actinide-containing structures (Figure 1) were studied in non-aqueous media give new insights into the expansive redox and optical properties of actinide-containing POMs. Combinations of different POM architectures (and/or organic ligands) with actinides were found to yield structures which behaved differently. Some structures favored higher actinide valencies, while others mediated intense actinide-POM charge transfer, exemplifying tuning the POM structure can be as a tool for tuning chemistry at the actinide center.



$(TBA)_2[An\{M_4O_{13}(OMe)_4MoNO\}_2]$
M = W or Mo

$(TBA)_5[CalixAnPW_{11}O_{39}]$

$(TBA)_4[TpAnPW_{11}O_{39}]$

$(TBA)_6[U\{PW_9O_{34}(PhSiO)_3\}_2]$

Figure 1: A series of new actinide-POM complexes synthesised using non-aqueous methods. Calix = 1,3-Dimethoxy-4-tert-butylcalix[4]arene, Tp = Tris(pyrazolyl)borate.

[1] M. Dufaye, S. Duval, T. Loiseau, *CrystEngComm* **2020**, *22*, 3549-3562.
[2] Auvray, T.; Matson, E. M. Polyoxometalate-based complexes as ligands for the study of actinide chemistry. *Dalton Trans.* **2020**, *49*, 13917-13927.
[3] I. Colliard, J. R. I. Lee, C. A. Colla, H. E. Mason, A. M. Sawvel, M. Zavarin, M. Nyman, G. T. P. Deblonde, *Nat. Chem.* **2022**, *14*, 1357-1366.

69: POM/2D Nanocomposites as Water Oxidation Electrocatalysts

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Polyoxometalates (POMs) have been thoroughly studied as oxygen evolution reaction (OER) materials, whereby structure/activity relationships have provided knowledge to rationally design POMs with increased catalytic capabilities.[1] Heterogenization of POMs is a promising strategy to increase their OER activity and to overcome stability issues seen under homogeneous conditions.[2] A common heterogenization approach is the deposition of POMs over the positively charged surface of bulk materials via electrostatic interactions. 2D materials offer an appealing platform to obtain hybrid nanocomposites with monodisperse POMs over the 2D surface. In this respect, layered double hydroxides (LDHs), formed by positively charged brucite-type inorganic layers stacked together with interlayer anions forming sandwich structures, are 2D materials with applications in different energy-related areas.[3] POMs, as polyanionic species, are excellent candidates to be combined with LDHs to obtain hybrid POM/LDH nanocomposites. These nanocomposites have been typically employed as catalysts for fine organic synthesis.[4] However, only few examples of their use as OER materials are reported in the literature, in which the fate of the POM counterpart under working conditions has not been properly established.[5] Here, I will present our most recent results on the OER activity and stability of hybrid POM/LDH nanocomposites.[6]

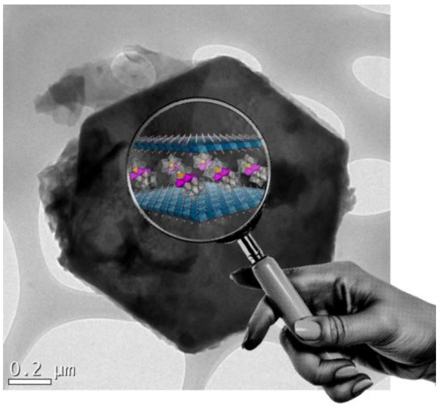

Figure: Elucidation of the OER activity and stability of POM/LDH nanocomposites

[1] J. Soriano-López et al., *Chem. Sci.* 2023, **14**, 13722-13733
[2] D. Gao et al., *Molecules* 2020, **25**, 157
[3] J. A. Carrasco et al., *Chem. Mater.* 2019, **31**, 6798-6807
[4] A.-E. Stamate et al., *Catalysts* 2020, **10**, 57.
[5] X. Xue et al., Int. J. Hydrogen Energy 2020, **45**, 1802-1809
[6] J. Soriano-López et al., *Inorg.Chem.* 2025, **64**, 3242-3255

70: POM-PS Dyads Based On Heteroleptic Cu(I) Complexes

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Organic–inorganic hybrid systems represent a fascinating class of materials due to their significant potential as next-generation functional materials. In particular, the field of polyoxometalate (POM) chemistry has seen increasing interest in the design of novel covalently organo-functionalized POMs which open new avenues for applications in energy conversion and storage technologies[1].

In this study, we investigated covalent POM–photosensitizer (POM–PS) dyads incorporating heteroleptic copper complexes. We further examined how the structural rigidity of the copper complexes and the resulting photophysical properties influence charge accumulation on the POM framework.

In addition, we explored the feasibility of productive photoreductive catalysis in N,N-dimethylformamide (DMF) employed here as a non-innocent solvent.

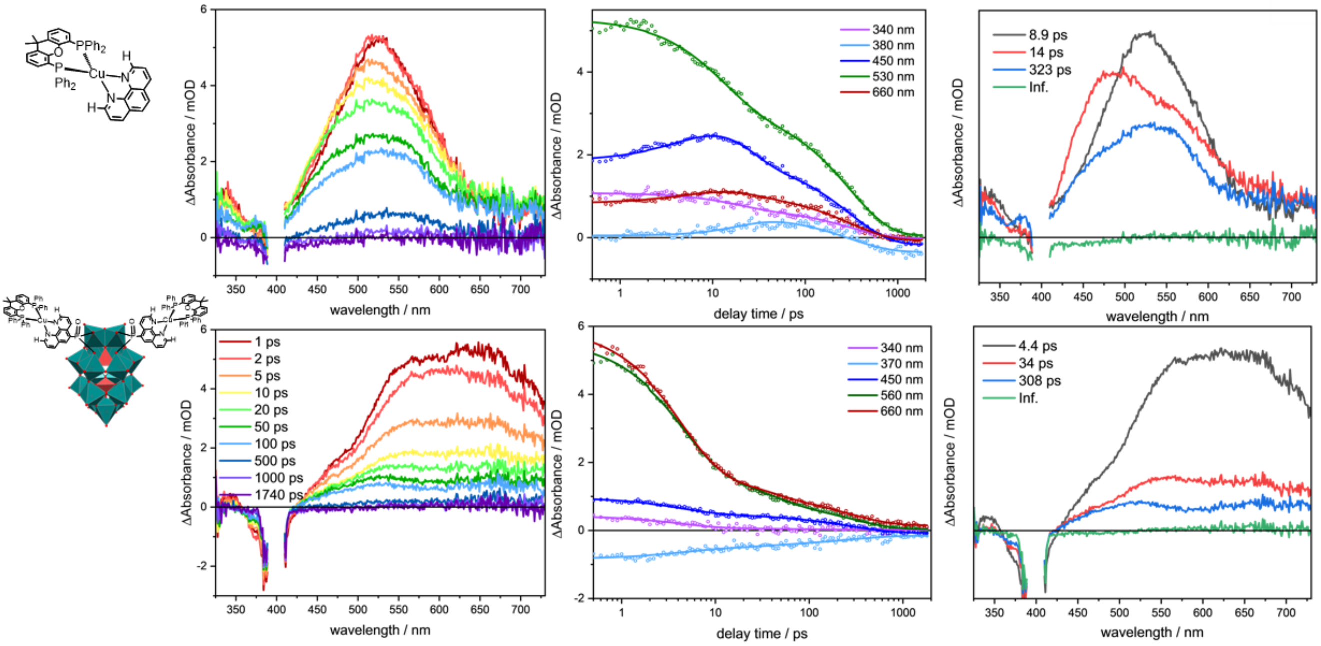

Figure 1: TA-Spectroscopy of the heteroleptic Cu(I) complex and the POM-PS dyads.

[1] S. Amthor, S. Knoll, M. Heiland, L. Zedler, C. Li, D. Nauroozi, W. Tobaschus, A. K. Mengele, M. Anjass, U. S. Schubert, B. Dietzek-Ivanšić, S. Rau, C. Streb, Nat Chem 2022, 14, 321–327.

71: Reactivity of an Organophosphonato Ligands-Introduced Hexavacant Lacunary Polyoxometalate

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Various types of lacunary polyoxometalates (POMs) can be synthesized by removing [M_xO_y] (M = W^{6+}, Mo^{6+}, etc.) units, and they have attracted considerable attention as precursors for preparing catalysts and magnetic materials because various types of metal cations and organic ligands can be introduced into their vacant sites. Therefore, it is important to select appropriate types of lacunary POMs in order to design molecular structures and control their properties.[1] Furthermore, lacunary POMs that are soluble in organic solvents are useful for introducing metal cations without undesired decomposition and isomerization reactions. Among the lacunary POMs, $[P_2W_{12}O_{48}]^{14-}$ ($\{P_2W_{12}\}$) is particularly important because $\{P_2W_{12}\}$ possesses the largest vacant sites among lacunary POMs and is expected to enable the synthesis of unique functional materials by introduction of multiple ligands, bulky ligands, and both ligands and metal cations.[2] However, isomerization and oligomerization reactions of $\{P_2W_{12}\}$ easily occur in water.[3]

We have previously reported the synthesis of an organophosphonato ligand-introduced $\{P_2W_{12}\}$ ($\{P_2W_{12}L_2\}$) by using ammonium salt of $\{P_2W_{12}\}$ without isomerization and oligomerization reactions, however {P2W12} framework was unstable in water.[4] Therefore, the tetrabutylammonium (TBA) salts of $\{P_2W_{12}L_2\}$ (TBA-$\{P_2W_{12}L_2\}$) was synthesized to stabilize $\{P_2W_{12}\}$ framework in solution states and to introduce metal cations in organic solvents . In this presentation, we report the stability of TBA-$\{P_2W_{12}L_2\}$ in the presence of acid or base in organic solvents (Figure 1).

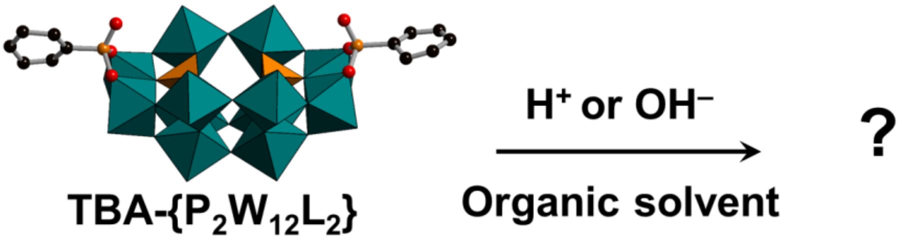

Figure 1. the stability of TBA-$\{P_2W_{12}L_2\}$ in the presence of acid or base in organic solvents.

[1] H. N. Miras, J. Yan, D.-L. Long, L. Cronin, Chem. Soc. Rev. 2012, 41,7403.
[2] J. M. Cameron, G. Guillemot, T. Galambos, S. S. Amin, E. Hampson, K. M. Haidaraly, G. N. Newton, G. Izzet, Chem. Soc. Rev. 2022, 51, 293.
[3] S. S. Mal, A. Banerjee, U. Kortz, Dalton Trans. 2025, 54, 5208.
[4] S. Take, T. Minato, M. Sadakane, Chem. Lett. 2024, 53, upae118.

72: Supramolecular Self-assembly Driven By Both Chaotropic Effect And Electrostatic Interactions Of A Three-component System Comprising Giant Polyoxometalate, Cyclodextrin And Cations

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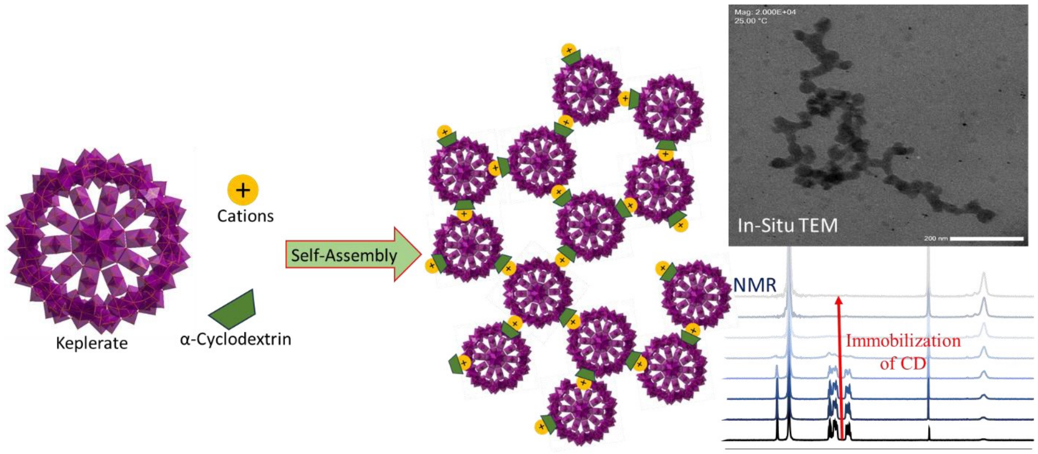
Polyoxometalates (POM) are a class of inorganic compounds well-known for their complexation ability of hydrophobic materials. These interactions are attributed to the chaotropic effect, a solvent effect driving supramolecular complexations in aqueous solutions.[1] Cyclodextrins (CD) are organic macrocycle widely studied for their inclusion/complexation properties due to their hydrophobic cavity and in this context, POM - CD systems were able to form a wide variety of supramolecular complexes.[2] So far complexation with POM mostly took place with γ-CD leading to highly stable supramolecular adducts. In this communication, we show how the smallest α-CD exhibit striking strong interactions with the giant spheroidal POM, the so-called Keplerate type ion, abbreviated Mo_{132}. Surprisingly, the interaction process, which can lead to large nano-aggregates appears precisely mediated by a third component, corresponding to cations such as NH_4^+, K^+, Ca^{2+}, Ba^{2+}. This three-component supramolecular system i.e. -CD / Mo_{132} / cation has been studied by NMR, 2D-NMR (DOSY), SAXS and in-situ TEM. Furthermore, some structural models involving POM, -CD and Ba^{2+} will be discussed.



[1]Assaf, K. I.; Nau, W. M. Angew. Chem. Int. Ed. 2018, 57 (43), 13968–13981.
[2] a) Yao, S.; Falaise, C.; Ivanov, A. A.; Leclerc, N.; Hohenschutz, M.; Haouas, M.; Landy, D.; Shestopalov, M. A.; Bauduin, P.; Cadot, E., Inorg. Chem. Front. 2021, 8; b) Ma, X.-Q.; Xiao, H.-P.; Chen, Y.; Lai, Q.-S.; Li, X.-X.; Zheng, S.-T. Polyoxometalate-Based Macrocycles and Their Assembly. Coord. Chem. Rev. 2024, 510, 215818

73: Electrode–Polyoxometalate Interactions: Adsorption-Driven Control of Redox Properties and Catalytic Function in Keggin-Type POMs.

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Polyoxometalates (POMs) are redox-active metal–oxide clusters with well-defined electron transfer properties that make them promising candidates for electrocatalysis and energy conversion. While their intrinsic redox behavior has been extensively studied, the role of interfacial interactions at electrode surfaces remains poorly understood. Herein, we investigate the electron transfer kinetics of Keggin-type POMs using rotating disk electrode (RDE) voltammetry to systematically decouple mass transport from interfacial kinetics. We demonstrate that both the redox thermodynamics and kinetics are sensitive to structural variables, including the identity of the central heteroatom (X = Al^{+3}, Si^{+4}, P^{+5}), the nature of the addenda metal (Mo vs W), and substitution with first-row transition metals (Cu^{+2}, Ni^{+2}, Fe^{+3}). Cu-substituted analogues exhibit quasi-reversible, multi-electron behavior marked by electrodeposition and higher charge transfer coefficients (α), while Fe and Ni substitutions preserve diffusion-limited kinetics. The influence of counterions was probed by pairing $[SiW_9CuFeGaO_{39}]^{-9}$ with a series of tetraalkylammonium cations of varying chain lengths. Longer-chain cations hindered surface adsorption and suppressed electrodeposition, with implications for CO_2 reduction selectivity and Faradaic efficiency. Our findings point out the critical role of the interfacial microenvironment—including electrode composition, POM–electrode affinity, and counter cation identity—in modulating redox behavior. This study provides a mechanistic basis for the rational tuning of POM-mediated electrocatalysis and enables clear differentiation between competing interfacial processes through RDE–LSV analysis.

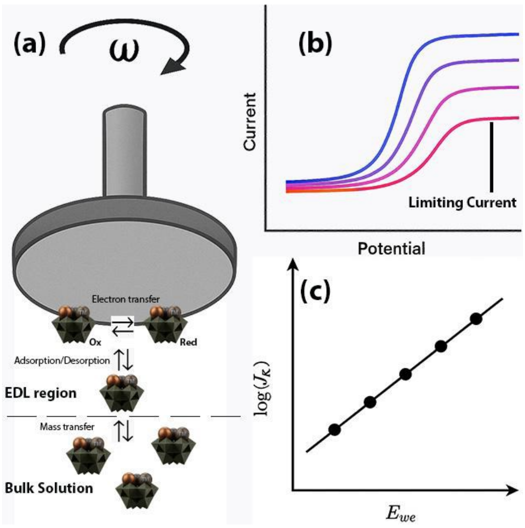

Figure 1: (a) Schematic illustration of a RDE setup, highlighting possible electrochemical reaction pathways. (b) Representative LSVs demonstrating increased current response with increasing electrode rotation rates. (c) Corresponding Tafel plot constructed from LSV data.

74: Catalysis of Al_{13} Oxo-Hydroxo Clusters in Organic Solvents

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Aluminum oxide (alumina) is widely used as a catalyst because of the thermodynamically stable structure and high specific surface area.[1] Bulk alumina can be utilized as a Lewis acid catalyst, while they are inactive as a Brønsted acid catalyst.[2]

Molecular alumina clusters are cationic aluminum oxo-hydroxo clusters and possess the similar surface structures to those of alumina. In contrast to the bulk alumina, molecular alumina clusters have proton-rich structures, and these protons are thought to act as Brønsted acid sites.[3] However, molecular aluminum clusters have not been studied as catalysts presumably because they tend to be gelatinized or isomerized in aqueous media. To develop efficient Brønsted acid catalysts, utilization of aprotic solvents instead of water has proven to be a key strategy.[4] Therefore, we envisaged that organic solvent-soluble molecular aluminum clusters would show unique Brønsted acid catalysis by using Al-OH_2 moieties.

In this study, we report on synthesis and catalysis of organic solvent-soluble molecular aluminum clusters. Organic solvent-soluble molecular aluminum clusters were synthesized by metathesis reaction of counter anions of molecular aluminum cluster from inorganic anions to organic anions. Then, the catalytic activity for pinacol rearrangement reaction was investigated using Al-containing compounds including various types of Al_{13} clusters and alumina.

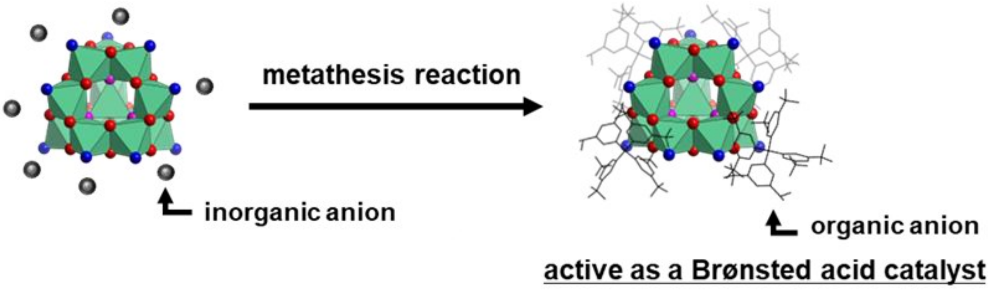

Figure 1: image description.

[1] I. Bezverkhy P. Afanasiev, C. Geantet, M. Lacroix, *J. Catal.* 2001, *204*, 495–497.
[2] R. M. Pearson, *J. Catal.* 1977, *46*, 279–288.
[3] L. Bergaoui, I. Mrad, J. F. Lambert, A. Ghorbel, *J. Phys. Chem. B* 1999, *103*, 2897–2902.
[4] M. A. Mellmer, C. Sener, J. M. R. Gallo, J. S. Luterbacher, D. M. Alonso, J. A. Dumesic, *Angew. Chem. Int. Ed.* 2014, *53*, 11872–11875.

75: Exploring the pH-dependent Self-assembly of Polyoxometalates in Organic Media Using Multinuclear Chemical Shift Imaging NMR

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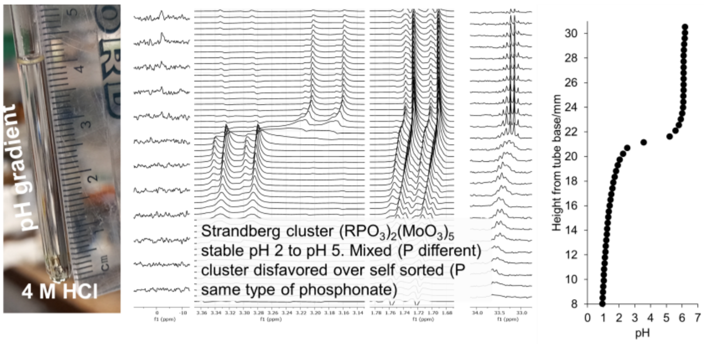
We demonstrate a high throughput technique that permits the in-situ study of the pH-sensitive self-assembly of polyoxometalates (POMs) and their speciation in a range of solvents. POM speciation is well studied[1] and computationally modelled[2] in aqueous solution, however, for solubility/stability reasons almost all synthesis of chemically functionalised POMs is conducted in organic solvents. The gaps in our understanding of POM self-assembly in these solvents hugely restrict POM functionalisation to top-down approaches and limit our ability to design POMs to fully exploit form and function. As part of unrelated work, we have developed highly efficient methods to determine the acid dissociation constants (pKa) of pharmaceutical ingredients in organic media.[4,5] We create pH gradients in standard 5 mm NMR tubes and record NMR spectra at different spatial positions along the gradient using chemical shift imaging (CSI) techniques, thereby studying a system across a wide pH range simultaneously in one sample; a highly efficient approach that can nowadays be applied on any modern spectrometer. As a first study with POMs, we have followed the self-assembly of phosphates[1] and phosphonates with sodium molybdate to give Strandberg[3] and other polyoxometalate clusters, reproducing known speciation in H_2O[1] and enabling the rapid testing of new systems. Our technique promises to be a highly efficient tool to address important questions regarding the behaviour of polyoxometalate clusters in organic media. We are also exploring the pH-dependent interaction of POMs with DNA and proteins.



Strandberg cluster $(RPO_3)_2(MoO_3)_5$ stable pH 2 to pH 5. Mixed (P different) cluster disfavored over self sorted (P same type of phosphonate)

1. N. Gumerova and A. Rompel, *Chem. Soc. Rev.*, 2020, **49**, 7568
2. J. Buils, D. G-Ruiz, M. S-Centellas, E. Petrus, C. Bo, *Chem. Sci.*, 2024,**15**, 14218
3. D. E. J. Packiam and K. Vidyasagar, *Dalton Trans.*, 2017,**46**, 16102
4. M. Wallace, N. Abiama and M. Chipembere, *Anal. Chem.*, 2023, **95**, 15628
5. G. Schenck, K. Baj, J. A. Iggo and M. Wallace, *Anal. Chem.*, 2021, **94**, 8115

76: Redox Mediating Polyoxometalates for Electrosynthetic Applications

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Polyoxometalates (POMs) are attractive molecular oxide clusters renowned for their rich multi-electron redox chemistry.[1] Their ability to reversibly store multiple electrons, combined with tunable solubility, makes them promising candidates for redox catalysis. In recent years, increasing attention has been given to their application as redox mediators in electrosynthetic processes.[2,3] The use of POMs in this context enables a broad range of solvents and reaction conditions. Moreover, their redox properties can be finely adjusted by exchanging metal centers, template ions, or counterions, allowing for precise control over selectivity and access to different reaction pathways.

In this contribution the influence of different Polyoxometalates and different electrode materials to the selectivity of the nitrobenzene reduction to aniline is studied. While the mixed phase reaction in water already gives the aniline product in high yields, the same reaction in acetonitrile may be used to further convert intermediates to other products.

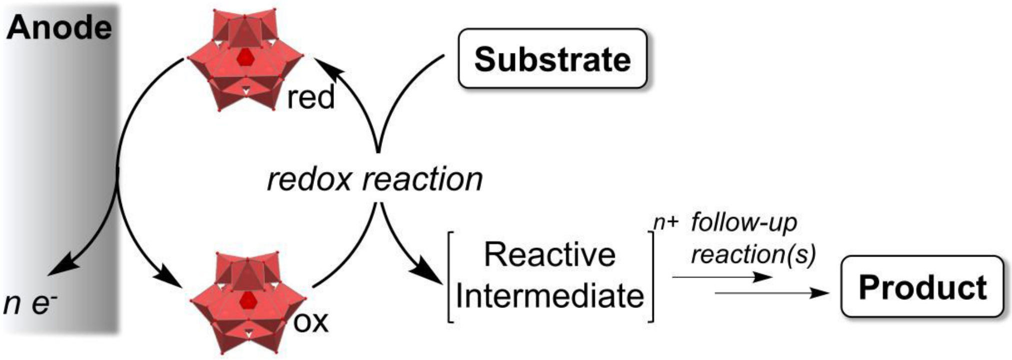

Figure: General Reaction Scheme of an electrosynthetic Reaction utilizing Polyoxometalates as Redox Mediators.

[1] S. S. Wang, G. Y. Yang, *Chem Rev* **2015**, *115*, 4893–4962.
[2] A. D. Stergiou, M. D. Symes, *Cell Rep Phys Sci* **2022**, *3*, 100914.
[3] A. D. Stergiou, M. D. Symes, *Catal Today* **2022**, *384–386*, 146–155.

77: Polyoxothiometalates as Molecular Mediators in Lithium-Sulfur Batteries

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Lithium-sulfur batteries are projected to surpass lithium-ion technology in gravimetric energy density, cost, and safety. They are particularly promising for the aerospace industry due to their lightweight and high-capacity characteristics. However, their practical implementation is hindered by sluggish reaction kinetics and poor cycle life, driven by the low conductivity of sulfur and lithium sulfide and high solubility of polysulfides. Overcoming these limitations is essential to making lithium-sulfur technology viable. Enhancing lithium-sulfur battery performance requires strategies to accelerate redox kinetics, with molecular mediators offering a promising solution by facilitating sulfur redox and polysulfide conversion.[1] Here, we explore polyoxothiometalates (POTMs) as a new class of molecular mediators in lithium-sulfur batteries. Combining the rich redox activity and tuneable structures of polyoxometalates (POMs) with the catalytic properties of metal sulfide compounds, POTMs provide a mobile metal sulfide surface to enhance sulfur utilization and rate performance. POTMs are synthesized through a facile post-synthetic modification of POMs, directly substituting oxygen sites with sulfur.[2] The resulting structures are characterized, and their electrochemical behaviour is investigated using cyclic voltammetry. POTMs offer a novel strategy to improve lithium-sulfur battery performance.

1 Y. Song, W. Cai, L. Kong, J. Cai, Q. Zhang and J. Sun, Advanced Energy Materials, 2020, 10, 1901075.
2 K. Yonesato, K. Yamaguchi and K. Suzuki, Chem. Sci., 2024, 15, 11267–112711 Y. Song, W. Cai, L. Kong, J. Cai, Q. Zhang and J. Sun, Advanced Energy Materials, 2020, 10, 1901075. 2 K. Yonesato, K. Yamaguchi and K. Suzuki, Chem. Sci., 2024, 15, 11267–11271

78: Development of metal nanoparticle-based catalysts protected with lacunary polyoxometalates

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Catalysis is crucial for advancing sustainable technologies, playing a key role in energy conversion and green chemistry.[1] Metal nanoparticles are at the forefront of the catalytic field due to their unique physical and chemical properties.[2] Specifically, their properties can be further tuned by modifying them with appropriate components, leading to promising new functionalities. Polyoxometalates (POMs), a class of molecular metal oxides, have been utilized in the preparation of metal nanoparticles.[3] However, the inherent stability issues of POM-modified metal nanoparticles have sometimes limited their catalytic applications. Here, we developed a facile approach to obtaining stable and reactive metal nanoparticle catalysts by utilizing lacunary POMs as modifying agents (Figure 1).[4] We confirmed the presence of strong interactions between metal nanoparticles and lacunary POMs, which modulated the electronic states and enabled activity control of the catalysts. The moderate steric effect of POMs not only enhanced stability but also preserved the catalytic activity of the metal nanoparticles. By applying this strategy to various catalytic systems, our work facilitates designing novel nanomaterials for environmentally benign reactions.

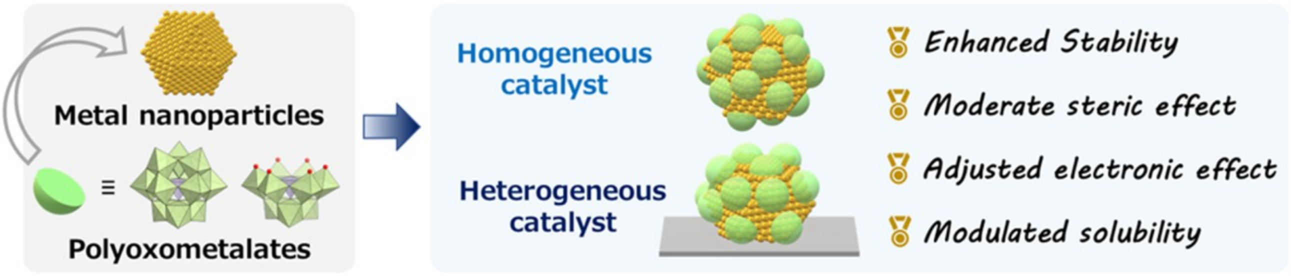

Figure 1: General design of metal nanoparticle catalysts by functional polyoxometalate modification

[1] a) C.-J. Li, B. M. Trost, Proc. Natl. Acad. Sci. U. S. A. 2008, 105, 13197; b) V. Polshettiwar, R. S. Varma, Green Chem. 2010, 12, 743.
[2] a) D. Astruc, Chem. Rev. 2020, 120, 461; b) R. Ciriminna, E. Falletta, C. D. Pina, J. H. Teles, M. Pagliaro, Angew. Chem. Int. Ed. 2016, 55, 14210.
[3] a) Y. Wang, I. A. Weinstock, Chem. Soc. Rev. 2012, 41, 7479; b) I. A. Weinstock, R. E. Schreiber, R. Neumann, Chem. Rev. 2018, 118, 2680; c) K. Xia, K. Yamaguchi, K. Suzuki, Angew. Chem. Int. Ed. 2023, 62, e202214506.
[4] a) K. Xia, T. Yatabe, K. Yonesato, T. Yabe, S. Kikkawa, S. Yamazoe, A. Nakata, K. Yamaguchi, K. Suzuki, Angew. Chem. Int. Ed. 2022, 61, e202205873; b) K. Xia, T. Yatabe, K. Yonesato, S. Kikkawa, S. Yamazoe, A. Nakata, R. Ishikawa, N. Shibata, Y. Ikuhara, K. Yamaguchi, K. Suzuki, Nat. Commun. 2024, 15, 851; c) K. Xia, T. Yatabe, K. Yamaguchi, K. Suzuki, Dalton Trans. 2024, 53, 11088.

79: Regioselective protein editing via a Zr_5 nanocluster

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Proteins are highly vulnerable to oxidative modifications due to the redox activity of amino acids, with damage arising from endogenous reactive oxygen species (ROS) or external stressors[1]. Such modifications, including amino acid side-chain oxidation and peptide backbone cleavage, are implicated in aging and various diseases. However, the structural and functional consequences of protein oxidation remain poorly understood. Redox proteomics seeks to address this gap, requiring methods that enable site-selective and controlled protein oxidation. Traditional oxidation techniques often lack selectivity or require harsh conditions result in the need for milder, more targeted approaches. Our recent work demonstrated that Cu(II)-substituted POMs can induce site-specific oxidative cleavage of hen egg white lysozyme (HEWL) in the presence of ascorbate[2]. Group IV metal-oxo clusters, especially Zr-based clusters, possess high stability and strong Lewis acidity which makes them suitable for applications in catalysis and bioconjugation. While Ti-oxo clusters dominate photocatalysis[3], Zr/Hf analogs remain underexplored. Hence, we developed a novel zirconium-oxo nanocluster, $[Zr^{IV}_5(\mu\text{-}OH)_2(\mu\text{-}O)_2(\mu_3\text{-}O)Cl_2(H_2O)_6(\mu\text{-}\eta^1,\eta^2,\eta^1\text{-tBu-dihyde-O,O',O''})_5]$ (Zr_5), which exhibits outstanding photophysical properties as an efficient heterogeneous photocatalyst for the regioselective oxidative cleavage of HEWL under UV irradiation. The reaction yields eight distinct fragments (12.9, 12.1, 10.3, 8.9, 7.2, 6.5, 5.7, and 4.1 kDa) and modifies methionine and tryptophan residues. Radical trapping experiments indicate that hydroxyl radicals play a dominant role in protein oxidation. Moreover, Zr_5 demonstrates excellent stability and selectivity, maintaining catalytic performance over three reaction cycles.

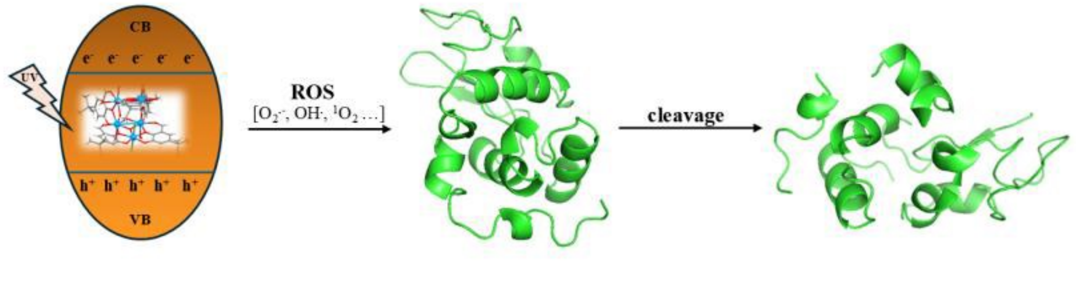

Figure 1: The photocatalytic mechanism for protein cleavage.

[1] S. Barelli, G. Canellini, L. Thadikkaran, D. Crettaz, M. Quadroni, J. S. Rossier, J. D. Tissot, N. Lion, Proteomics Clin Appl 2008, 2, 142-157.
[2] S. A. M. Abdelhameed, F. de Azambuja, T. Vasovic, N. D. Savic, T. Cirkovic Velickovic, T. N. Parac-Vogt, Nat Commun 2023, 14, 486.
[3] S. S. Passadis, M. Gray, T. N. Parac-Vogt, A. D. Keramidas, H. N. Miras, T. A. Kabanos, Dalton Trans 2024, 53, 18400-18419.

80: Synthesis and Catalysis of Nitrate-Incorporated Polyoxovanadate Derivaives

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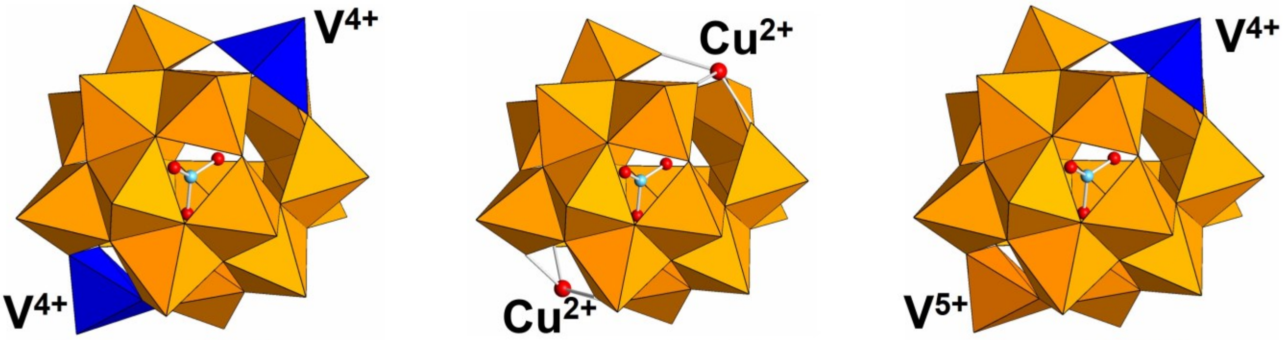
Polyoxovanadates are the family of vanadium-oxygen cluster anions with high molecularity. There are several chemical environments of vanadium atoms. In addition, most spherical polyoxovanadates possess both V^{4+} and V^{5+} and some of them are disordered. Therefore, it is difficult to determine the accurate active vanadium sites in a polyoxovanadate. The local structure control among the related polyoxovanadates leads to understand the reactivity of the specific sites.[1] Nitrate-incorporated polyoxovanadates of $[V_{18}O_{46}(NO_3)]^{5-}$ (V18) and their derivatives were synthesized (Figure). [2,3] The catalytic property was different among derivatives. With V18, epoxidation preferably proceeded. The metal-substituted one shows selective oxidation of alcohol. The oxidized V18 (V18ox) shows higher reactivity than the others.



$[V_{18}O_{46}(NO_3)]^{5-}$
(V18)

$[Cu_2V_{16}O_{46}(NO_3)]^{5-}$
(Cu2V16)

$[V_{18}O_{46}(NO_3)]^{4-}$
(V18ox)

Figure. Structures of nitrate-incorporated polyoxovanadate derivatives.

[1] Y. Kikukawa, Y. Sakamoto, H, Hirasawa, Y. Kurimoto, H. Iwai, Y. Hayashi, *Catal. Sci. Technol.*, **2022**, *12*, 2438-2445.
[2] I. Yoshida, R. Mitsuhashi, Y. Kikukawa, Y. Hayashi, *Inorganics*, **2024**, *12*, 61.
[3] I. Yoshida, Y. Kikukawa, R. Mitsuhashi, Y. Hayashi, *Nanoscale*, **2024**, *16*, 10584-10589.

81: Highly Ordered Cu Spacer Layers for Electroreduction of CO_2 to Dimethyl Carbonate

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Simultaneously activating CH_3OH and CO_2, subsequently asymmetrically coupling $*OCH_3$ and $*CO$ into dimethyl carbonate (DMC) industrial material pose a big challenge. Herein, we present highly ordered Cu spacer layers $\{\{Cu_6(\mu_3\text{-}OH)_3(en)_3(H_2O)_3\}(B\text{-}\alpha\text{-}PW_9O_{34})\}$ for simultaneously activating CH_3OH and CO_2, and fixation of the $*OCH_3$ and $*CO$ intermediates into DMC. During the electrocatalytic reaction process, the μ_3-OH in the hexa-muclear $\{Cu_6(\mu_3\text{-}OH)_3(en)_3(H_2O)_3\}$ (en = ethylenediamine) nanocluster is beneficial to dehydrogenate CH_3OH into $*OCH_3$. And the W element in Keggin-type $\{B\text{-}\alpha\text{-}PW_9\}$ can provide empty 5d obtrtal to form the unique feedback π bond with O 2p orbitals in CO_2, thereby enabling W elements to refill their own electrons back into the anti-bonding orbitals of CO_2, further facilitating the efficient conversion of CO_2 to $*CO$ intermediate. Under the help of the K^+ adsorbed layer around the catalyst, $*OCH_3$ is adsorbed on the surface of the whole structure and couple with $*CO$, resulting in 1.0 mol L^{-1} yield of DMC. The faraday efficiency of DMC is 85% under normal temperature. The successful fabrication of the catalyst is anticipated to provide a significant impetus for the green synthesis of DMC.

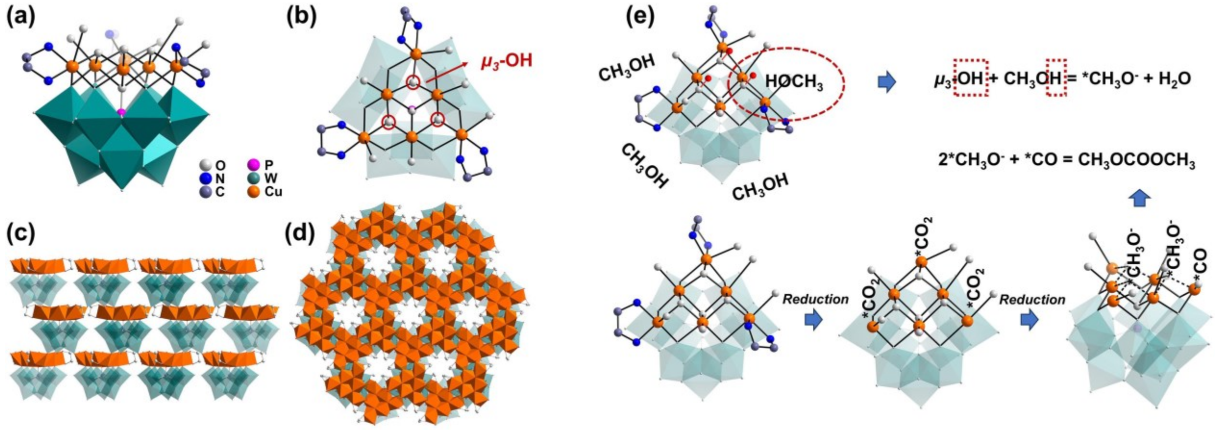

Figure 1. (a) Structure representation of $\{\{Cu_6(\mu_3\text{-}OH)_3(en)_3(H_2O)_3\}(B\text{-}\alpha\text{-}PW_9O_{34})\}$. (b) Structure illustration of $\{Cu_6(\mu_3\text{-}OH)_3(en)_3(H_2O)_3\}$. (c) The staggered arrangement of $\{\{Cu_6(\mu_3\text{-}OH)_3(en)_3(H_2O)_3\}(B\text{-}\alpha\text{-}PW_9O_{34})\}$ units along the *b* axis. (d) The staggered arrangement of $\{\{Cu_6(\mu_3\text{-}OH)_3(en)_3(H_2O)_3\}(B\text{-}\alpha\text{-}PW_9O_{34})\}$ units along the *c* axis.

[1] J.-W. Zhao, H.-P. Jia, J. Zhang, S.-T. Zheng, G.-Y. Yang, *Chem. Eur. J.* **2007**, *13*, 10030 – 10045.
[2] B. Xu, S. Luo, W. Hua, H. Xiao, B. Chong, G. Yan, H. Li, H. Ou, B. Lin, G. Yang, *J. Am. Chem. Soc.* **2025**, *147*, 200 – 210.