



FMOCS VII **FRONTIERS IN METAL OXIDE** **CLUSTER SCIENCE**

April 11th – 14th, 2023
Tarragona (Spain)

 UNIVERSITAT
ROVIRA I VIRGILI

 ICIQ ^{CS}
Institute of Chemical
Research of Catalonia

BOOK OF ABSTRACTS

FMOCS VII **2023**

FMOCS VII FRONTIERS IN METAL OXIDE CLUSTER SCIENCE

April 11th – 14th, 2023
Tarragona (Spain)



Organized By



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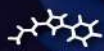
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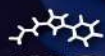
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	Tuesday 11 th	Wednesday 12 th	Thursday 13 th	Friday 14 th	
8:00	REGISTRATION DESK				
Chairperson	<i>Josep M. Poblet</i>	<i>Lixin Wu</i>	<i>Anna Proust</i>	<i>J.R. Galán-Mascarós</i>	
9:00	K1- Anna Proust	K8- Eugenio Coronado	K14- Ronny Neumann	K19- Emmanuel Cadot	9:00
9:30	K2- Graham Newton	K9- Tomoji Ozeki	K15- Mark Symes	K20- Masahiro Sadakane	9:30
10:00	I1- Xavier López	I7- Geoffroy Guillemot	I13- Andrea Sartorel	I21- Joaquin Soriano	10:00
10:20	I2- Scott Mitchell	I8- Enric Petrus	I14- Magda Pascual	I22- Clément Falaise	
10:40	F1-F3	F11-F13	F20-F23	I23- Bahareh Khezri	
10:50					
11:00	Coffee-Break	Coffee-Break	Coffee-Break	Coffee-Break	11:00
Chairperson	<i>Ronny Neumann</i>	<i>Dominique Vuillaume</i>	<i>Pere Miró</i>	<i>Carles Bo</i>	
11:30	K3-Carsten Streb	K10- Yang-Guang Li	K16- Sayaka Uchida	K21- Guillaume Izzet	11:30
12:00	K4-Kirill Monakhov	K11- Jorge J. Carbó	I15- Nadiia Gumerova	K22- Pierre Mialane	12:00
12:30	I3-Pere Miró	I9- Laia Vilà-Nadal	I16- Albert Solé	I24- Helena Nogueira	12:30
12:50	F4-F5	F14-F15	F24-F25	I25- Dominique Vuillaume	12:50
				Bus to Restaurant	13:30
13:15	Lunch (Hotel)	Lunch (Hotel)	Lunch (rest. Palau del Baró)	Lunch (Calçotada)	14:00
Chairperson	<i>Maria Besora</i>	<i>Emmanuel Cadot</i>	<i>John Errington</i>		
15:00	K5- Craig Hill			Rest. Ca Vidal, Perafort	
15:30	K6- Laurent Ruhlmann	K12- Lee Cronin	K17- Ulrich Kortz		
16:00	I4- Pierre Bauduin	I10- John Fielden	I17- Kosuke Suzuki		
16:20	I5- Eynat Haviv	I11-Jonathan De Roo	I18- Sébastien Floquet	Closing conference	17:00
16:40	I6- Israël Mbomekallé	I12-Mireia Segado	I19- Mhamad A. Moussawi		
17:00	Coffee-Break	Coffee-Break	Coffee-Break		
Chairperson	<i>Alexander Khenkin</i>	<i>Jordi Carbó</i>	<i>Scott Mitchell</i>		
17:30	K7- John Errington	K13- Tianbo Liu	K18- Lixin Wu		
18:00	F6-F10	F16-F19	I20- Santiago Reinoso		
18:30			F26-F27		

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F2- Claire Jones	F12- Maria Luisa Casasin	F21- Avra Tzaguy
F3- Abigail Seddon	F13- Francesc Penas	F22- Albert Masip
F4- Kilian Declerck	F14- Amar Mohammed	F23- Anusree Sundar
F5- Beatriz Rosales	F15- Estibaliz Ruiz	F24- Jiayao Zhang
F6- Alexander Kibler	F16- Iván Gómez	F25- Guillaume Bensoussan
F7- Dominic Shiels	F17- Jordi Puiggalí	F26- Kieran Jone
F8- Zhiwei Cai	F18- Ning Jiang	F27- Dima Azaiza
F9- Thomas Auvray	F19- Khalid Azmani	
F10- Marcel Langer		

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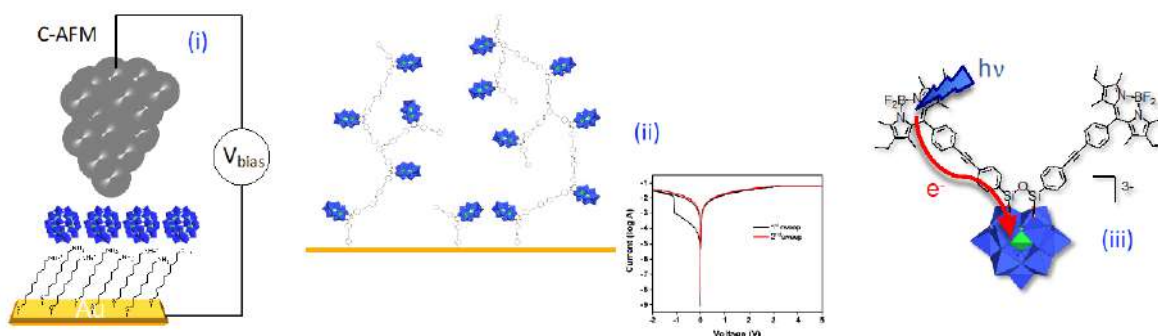
Polyoxometalates and electron transfers: thermodynamic and environmental effects

A. Proust, F. Volatron, G. Izzet

IPCM, Sorbonne Université, 4 place Jussieu, 75005 Paris anna.proust@sorbonne-universite.fr

Abstract

Polyoxometalates (POMs) are endowed with remarkable redox properties which pave the way to numerous applications in energy-related fields. The high tunability of redox potentials is the first lever to improve the efficiency of POM-based systems and materials. However, environmental effects such as the reorganization of the counter ions accompanying the electron transfers are also to take into account. From selected examples we will show: (i) how the redox behavior of POMs as known in solution translates in solid POM-based molecular junctions and how the nature of the counter cations also impact the electron transport;[1] (ii) how bulky tetrabutylammonium cations probably hinder the reversibility of the resistive switching in POM-based film; (iii) that the photo-induced electron transfer from a bodipy sensitizer to the POMs can be triggered both by the thermodynamics and the environment.[2]



(i) Electron transport in POM-based nano junctions (ii) WORM type memory ;
(iii) photo-induced electron transfer in POM-bodipy hybrids

1. (a) Laurans, M.; Dalla Francesca, K.; Volatron, F.; Izzet, G.; Guerin, D.; Vuillaume, D.; Lenfant, S.; Proust, A. *Nanoscale* **2018**, 10 (36), 17156–17165; (b) Laurans, M.; Trinh, K.; Dalla Francesca, K.; Izzet, G.; Alves, S.; Derat, E.; Humblot, V.; Pluchery, O.; Vuillaume, D.; Lenfant, S.; Volatron, F.; Proust, A. *ACS Appl. Mater. Interfaces* **2020**, 12 (42), 48109–48123.

2. (a) Toupalas, G.; Karlsson, J.; Black, F. A.; Masip-Sánchez, A.; López, X.; Ben M'Barek, Y.; Blanchard, S.; Proust, A.; Alves, S.; Chabera, P.; Clark, I. P.; Pullerits, T.; Poblet, J. M.; Gibson, E. A.; Izzet, G. *Angew. Chem. Int. Ed.* **2021**, 60 (12), 6518–6525; (b) Benazzi, E.; Karlsson, J.; Ben M'Barek, Y.; Chabera, P.; Blanchard, S.; Alves, S.; Proust, A.; Pullerits, T.; Izzet, G.; Gibson, E. A. *Inorg. Chem. Front.* **2021**, 8 (6), 1610–1618

Dynamic Supramolecular Assembly of Redox-active Superstructures based on Organofunctionalised Hybrid Polyoxotungstates

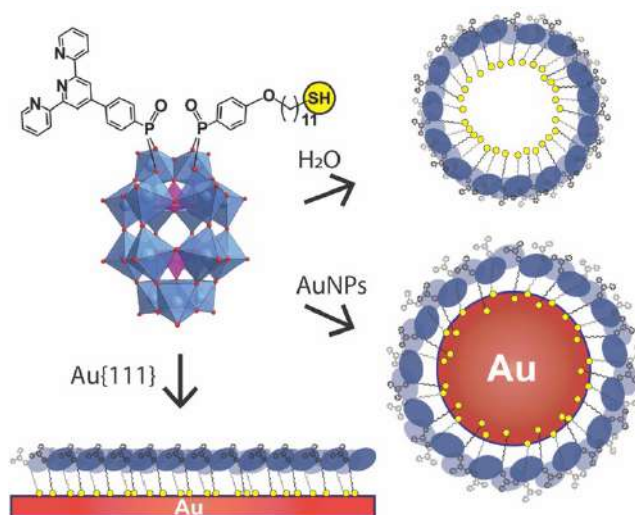
Graham Newton

Carbon Neutral Laboratories for Sustainable Chemistry, School of Chemistry, University of Nottingham, Nottingham, NG7 2TU, UK

Abstract

The direct organofunctionalisation of polyoxometalates is an accessible, modular approach to prepare molecular metal oxide clusters with bespoke structural, electronic and photochemical properties. Preparation of such ‘hybrid POMs’ with long hydrophobic alkyl chain pendant groups allows the isolation of amphiphilic systems that can undergo spontaneously self-assembly into solvent environment-dependent superstructures.[1] Controlling this process, and understanding how the physical properties of the molecular building blocks can be translated to the supramolecular material are key challenges in the field.

Our group has recently explored the synthesis, physical properties and supramolecular chemistry of symmetric and asymmetrically functionalised organophosphonate hybrid POMs.[2][3] Here, we present our findings on the controlled self-assembly of redox-active superstructures based on hybrid POMs and consider the opportunities offered by such systems.



An asymmetric hybrid POM bearing two different organic moieties and its self-assembly.

1. Cameron, J. M. *et al Chem. Soc. Rev.* **2022**, 51, 293-328; 2. Hampson, E. *et al Angew. Chem. Int. Ed.* **2019**, 58, 18281-18285; 3. Martin, C. *et al Angew. Chem. Int. Ed.* **2020**, 59, 14331-14335

Self-assembly, supramolecular chemistry and reactivity of metal-functionalized polyoxovanadates

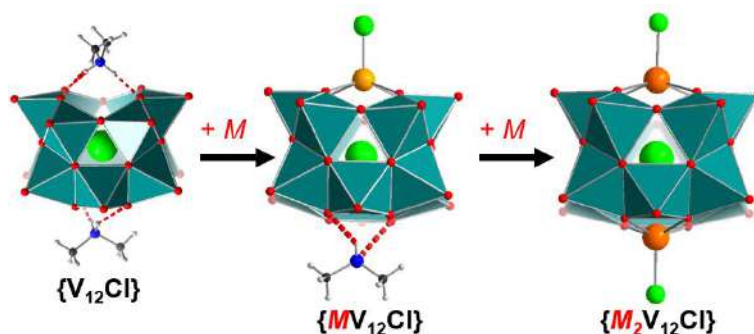
Carsten Streb

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Abstract

Polyoxovanadates are a molecular metal oxides with unique structure and reactivity.^[1] Groundbreaking studies were focused on structure and magnetism, while current research is focused on understanding correlations between polyoxovanadate structure and function, *e.g.*, in the fields of catalysis or energy storage.^[2]

Over the last decade, systematic studies have focused on functionalization of polyoxovanadates with organic ligands or metal cations to tune stability and reactivity.^[3] In this contribution, the structural and reactivity consequences of metal-functionalization of polyoxovanadates will be discussed. Predetermined cluster functionalization – similar to lacunary chemistry known for polyoxomolybdates and -tungstates – will be reported,^[4] and electrochemical and photochemical consequences of metal introduction will be described. Finally, an unusual synthetic approach using a highly reactive “universal” polyoxovanadate precursor will be described.^[5]



Controlled metal-functionalization of dodecavanadate clusters.

- [1] W. G. Klemperer, T. A. Marquart, O. M. Yaghi, *Angew. Chem. Int. Ed.* **1992**, *31*, 49–51.
- [2] M. Anjass, G. A. Lowe, C. Streb, *Angew. Chem. Int. Ed.* **2021**, *60*, 7522–7532.
- [3] S. Chakraborty, B. E. Petel, E. Schreiber, E. M. Matson, *Nanoscale Adv.* **2021**, *3*, 1293–1318.
- [4] K. Kastner, J. Forster, H. Ida, G. N. Newton, H. Oshio, C. Streb, *Chem. Eur. J.* **2015**, *21*, 7686–7689.
- [5] S. Greiner, J. Hettig, A. Laws, K. Baumgärtner, J. Bustos, A.-C. Pöppler, A. H. Clark, M. Nyman, C. Streb, M. Anjass, *Angew. Chem. Int. Ed.* **2022**, *61*, e202114548.

Surface-Confined Multi-Bit Polyoxometalates for Data Storage and Computer Processing

Kirill Yu. Monakhov*

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Abstract

Polyoxometalates (POMs) have emerged as a highly promising class of molecular memristors [1]. The POM structures containing vanadium centers as electron charge and spin carriers can be transferred as memristive single particles directly from solution [2] or via the gas phase using electrospray [3] on technologically relevant surfaces. For example, Lindqvist-type POM with a redox-active, diamagnetic $\{V_6O_{19}\}$ core stores 2 bits of information for its 4 electrically generated logic states at room temperature and low potentials below 2 volts [1,3]. POM charge-balancing cations can mediate electron transfer between the POM anions that act as physical multi-state switches [4,5]. The charge stabilization of the latter on conducting surfaces can be enabled by their supramolecular self-assembly with macrocyclic ligands such as cyclodextrins [3]. Integration into gold/DNA-origami hybrid assemblies allows spatially controlled positioning of these POM memristors with sub-nm-level precision into biologically relevant environments [6].

Our POM-based technology is based on a spatially controlled and dimensionally up-scalable molecular nanoengineering approach that is reconfigurable and biocompatible. POMs containing vanadium are able to store multiple different, potential-induced logic states at room temperature [7]. The external electrical contacting of POM-functionalized heterostructures remains a challenge that opens up exciting possibilities for studying surface-confined POMs in neuromorphic and in-memory computing applications.

Acknowledgments

The author acknowledges the support from the Deutsche Forschungsgemeinschaft through the Emmy Noether programme, the Leibniz Association through the Leibniz Collaborative Excellence funding programme, and the Boehringer Ingelheim Foundation through the Exploration Grant programme.

References

- [1] Linnenberg, O.; et al. *J. Am. Chem. Soc.* **2018**, *140*, 16635–16640.
- [2] Glöß, M.; et al. *Adv. Mater. Interfaces* **2022**, *9*, 2200461.
- [3] Yang, F.; et al. *ACS Appl. Nano Mater.* **2022**, *5*, 14216–14220.
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- [6] Vogelsberg, E.; et al. *manuscript under consideration*.
- [7] Moors, M.; et al. *Acc. Chem. Res.* **2021**, *54*, 3377–3389.

Counterion-dependence and surface characterization of POM water oxidation catalysts

Meilin Liu, Ben Yin, Ting Cheng, Fengyi Zhao, Xinlin Lu, Djamaladdin G. Musaev, Lianquan Lin, Craig L. Hill

Department of Chemistry, Emory University, Atlanta, GA 30322 U.S.A.

Abstract

3d-Metal-substituted POMs are promising as catalysts for the multi-electron processes needed in solar fuel production but also as homogeneous, modifiable models for metal oxide surfaces that are used as both photosensitizers and catalysts.¹ We have made and structurally characterized several different cation-derivatives of the Co-containing and Co-based POM water oxidation catalysts (WOCs), including 4 different salts of the acid-compatible and fast WOC, $[\text{Co}_9(\text{H}_2\text{O})_6(\text{OH})_3(\text{HPO}_4)_2(\text{PW}_9\text{O}_{34})_3]^{16-}$ (**C09**). The structures and catalytic water oxidation activities of these different **C09** derivatives have been correlated with the nature of counter-cations and their locations. We will also report results on development of needed methods to characterize POM WOCs on semiconductor surfaces. While an ensemble of methods that convincingly characterize small molecules on POM surfaces have been developed, additional methods to characterize POM catalysts on semiconductor surfaces, particularly methods that facilitate correlation of POM properties with WOC activity, are needed. We will present findings in the latter area.

¹ Yin, Q.; Geletii, Y. V.; Lian, T.; Musaev, D. G.; Hill, C. L. "Polyoxometalate Systems to Probe Catalyst Environment and Structure in Water Oxidation Catalysis" *Advances in Inorganic Chemistry*, **2022**, 79, 351-372 <https://doi.org/10.1016/bs.adioch.2021.12.009>

(Iso)porphyrins and Polyoxometalate Scaffolds

Laurent Ruhlmann

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Abstract

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-light photosensitizer is needed. The combination of porphyrins or isoporphyrins with POMs has greatly enlarged its field of applications over the last decades. In particular, the

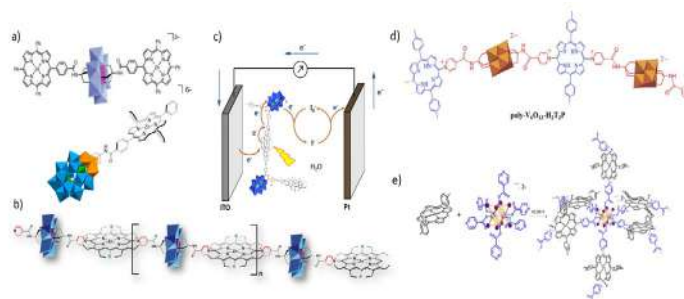


Figure 1 Various type of porphyrin-POM systems.

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 the entrapment of POMs in polymeric networks or the sandwiching of POMs between cationic polymers in layer-by-layer assemblies. In a second approach, coordination polymers were formed from polyoxometalates and organic ligands to yield new oxide materials with various structures, such as 1D chains, 2D networks, and 3D frameworks. In the third approach, we have developed a method of electropolymerization of POMs based on nucleophilic attack onto the electrogenerated porphyrin radical cation or dications [1]. The formation of hybrid POM-porphyrin copolymeric films (Fig. 1bd) can be obtained by the electro-oxidation of porphyrin in the presence of the POM bearing two pyridyl groups (Py-POM-Py) [2]. This process is feasible for various type of POMs [3-6] or cluster [7] such as Dawson, Lindqvist, Anderson or Keggin type POMs. Stable isoporphyrin – POM copolymers have been also developed recently showing interesting efficiency even upon the NIR illumination. Such materials will be compared with other porphyrin-POM compounds using various type of POMs (Fig. 1a). A second methodology is also proposed to form hybrid POM-porphyrin films: first the formation of cationic polyporphyrin electropolymer. Then, by metathesis reaction, the (partial) exchange onto the surface of the initial counter ions by the POM^{n-} [8] or by the nanoparticles stabilized with POM^{n-} [9]. The photovoltaic performances of these hybrid materials have been investigated under visible-light illumination [9-11] given by now good efficiency. The impedance as well as photochemical properties of such hybrid material under visible or NIR illumination will be also discussed. Finally, the photocatalytic properties of these films for the reduction of noble metallic ions as well as the generation of the $^1\text{O}_2$ singlet oxygen will be also presented.

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Non-Aqueous and Solvent-Free POM Chemistry: Recent Insights, New Paradigms.

R. John Errington

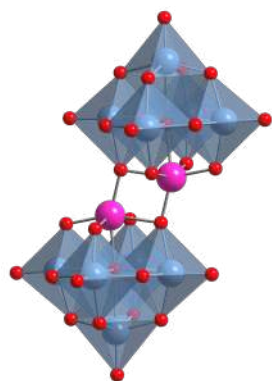
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Newcastle University, NE1 7RU, UK

Abstract

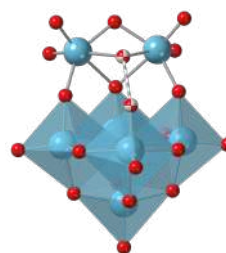
Recent refinements to our non-aqueous methods for the synthesis of reactive POMs¹ enable large-scale synthesis of ¹⁷O-enriched {MW₅} Lindqvist-type derivatives. For example, (TBA)₃[(ⁱPrO)TiW₅O₁₈] can be prepared in batches of > 20 g, which provides ready access to a range of derivatives, including dimeric [(TiW₅O₁₈)₂]⁴⁻ with the structure shown below. A series of analogous protonated structures [(MW₅O₁₈H)₂]⁶⁻ has been obtained from (TBA)₂[W₆O₁₉] for the first row M²⁺ transition metals, where M = Mn, Fe, Co,² Ni and Zn, and some indicative reactivity of these dimeric species will be described.

Detailed ¹⁸³W NMR investigations have provided a deeper understanding of tungstate speciation and structural dynamics during non-aqueous base degradation of (TBA)₂[W₆O₁₉] and revealed the structure of [W₇O₂₄H]⁵⁻, which has evaded structural characterisation since our first report of its ¹⁸³W NMR spectrum in 1993.³

We are exploring solvent-free, mechanochemical POM synthesis and reactivity to avoid limitations due to solvent reactivities. Some initial observations will be reported, including super-reduction with Li metal.



[(TiW₅O₁₈)₂]⁴⁻



[W₇O₂₄H]⁵⁻

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Magnetic polyoxometalates for quantum technologies

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ICMol. Univ. Valencia

Abstract

Spins provide one of the simplest platforms to encode a quantum bit (qubit), the elementary unit of future quantum computers. A challenge in this topic is to control the quantum decoherence in these spin qubits by minimizing the sources of decoherence (dipolar spin-spin interactions, hyperfine interactions and spin-phonon interactions). This loss of quantum information by interaction with the environment can be quantified by the phase memory time T_2 . Here, Here, I will show that magnetic polyoxometalates can provide an ideal platform to design robust molecular quantum spin systems [1, 2] showing enhanced decoherence, allowing to manipulate the spin state through an external electric field [3], or hosting more than one spin qubit in order to implement quantum logic gates [4].

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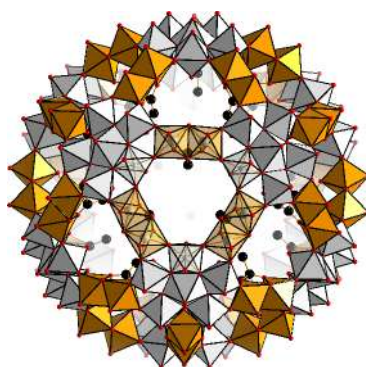
What is the fate of the Keplerate {Mo₁₃₂}?

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Abstract

Dark-brown aqueous solution of the Keplerate {Mo₁₃₂} anion, [Mo^{VI}₇₂Mo^V₆₀O₃₇₂(CH₃COO)₃₀(H₂O)₇₂]⁴²⁻,¹ loses its color upon standing in ambient conditions. This phenomenon can naturally be interpreted as the air oxidation of the mixed-valent (+5 and +6) species into fully oxidized oxomolybdate(s). It indicates that the Keplerate {Mo₁₃₂} is unstable in the presence of O₂, but its behavior in the absence of oxidizing reagents is unknown. Based on the time-dependent UV-vis measurements under N₂, we revealed that the Keplerate {Mo₁₃₂} transforms into a blue {Mo_{102+x}} Keplerate via an undetermined intermediate. It is noteworthy that the average oxidation state of the resultant blue {Mo_{102+x}} Keplerate is approximately the same as the starting {Mo₁₃₂} Keplerate.



Polyhedral representation of the Keplerate [Mo^{VI}₇₂Mo^V₆₀O₃₇₂(CH₃COO)₃₀(H₂O)₇₂]⁴²⁻ anion.

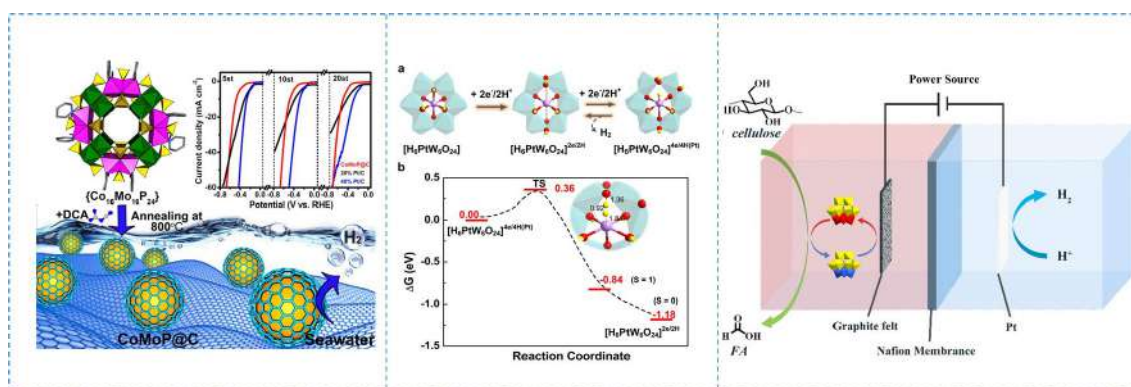
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POMs-Mediated Electrocatalysts for Hydrogen Evolution Reaction

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Abstract

A hot topic in the field of hydrogen energy development is to explore efficient and inexpensive electrocatalysts for hydrogen evolution reaction (HER) and reveal its electrocatalytic reaction mechanism. Polyoxometalates (POMs), as one of unique inorganic metal-oxo clusters with abundant elemental composition and defined structural feature, exhibit special advantages in the design of new HER electrocatalysts. On the one hand, POMs can be used as an ideal molecular pre-assembly platform to construct multi-interfacial nano-composite electrocatalysts to improve the HER performance. On the other hand, POMs provide an available metal/metal-oxide structural model to explore the mechanism of hydrogen evolution at the molecular level. The most important of all, POMs can be employed to develop co-generation hydrogen production technology, providing a feasible and practical path for hydrogen energy development^[1-6].



Electrocatalytic hydrogen evolution reaction based on POMs

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Atomistic Insight into the Supramolecular Assembly and Catalysis of Polyoxometalates in Solution via Dynamic Simulations

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Abstract

Polyoxometalates (POMs) have been widely applied in catalysis due to their tunable Brønsted/Lewis acidity and redox properties, combined with their ability to accommodate other transition metals. In addition, they give rise to unusual solution behavior that have found applications in biotechnology and supramolecular chemistry. This behavior has been recently conceptualized as a chaotropic effect that becomes more effective for large ions and can be referred as superchaotropic effect (an extension beyond the classical Hofmeister scale).¹ Low charge density anions are weakly hydrated and consequently have propensity to assemble with organic moieties and biomolecules.

The supramolecular assembly of POMs and their catalytic properties are not only dependent on POM nature, but also on macroscopic properties such as the solvent, pH, ionic force, concentration, or the counter-ions. We have approached to the atomistic modeling of those collective properties via classical Molecular Dynamics (MD) and Car-Parrinello (CPMD) simulations.² Also we are developing machine-learned reactive force fields, which fill the gap between the static description of POM structures by MD (no bond forming/breaking), and the low-scale systems available in CPMD simulations. Here we present the insight obtained from atomistic dynamic simulations on selected examples of POM self-assembly and aggregation with biomolecules that have implications in catalysis.

¹ Assaf, K. I.; Werner M. Nau, W. N. *Angew. Chem. Int. Ed.* **2018**, 57, 13968.

² See for example: *Nat. Chem.* **2017**, 9, 369; b) *Inorg. Chem.* **2017**, 56, 4148; c) *Chem. Eur. J.* **2020**, 26, 5799; d) *J. Am. Chem. Soc.* **2022**, 144, 8951.

Discovering the Origin of Life and Aliens using POMS

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We have theorised that living things are unified by the ability to produce ‘unnatural’ or complex objects from molecules to space craft. By applying a new mathematical approach to finding complex systems, we are able to show that complex molecules cannot be formed by chance, and must be made by a living process or machine. In this talk I will explain how we have validated the method by monitoring existing efforts to make life in the laboratory in Glasgow and looking at the change in complexity of the molecules from the bottom up (chemicals to biology) as well as by going from the top down (biological cells to chemicals), see Figure1. I will also explain how this approach can be used to find life in the solar system and beyond.

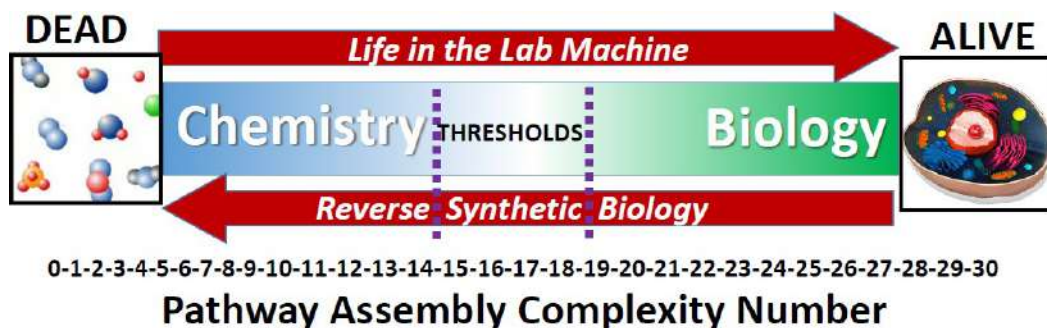


Figure 1. Graph showing pathway assembly complexity number spanning dead chemistry to living biology and the bottom up (life in the lab) and top down (reverse synthetic biology) approaches to developing our measurement system.

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Identify gel and coacervate phases and their critical transition conditions in dilute aqueous solutions of molecular clusters

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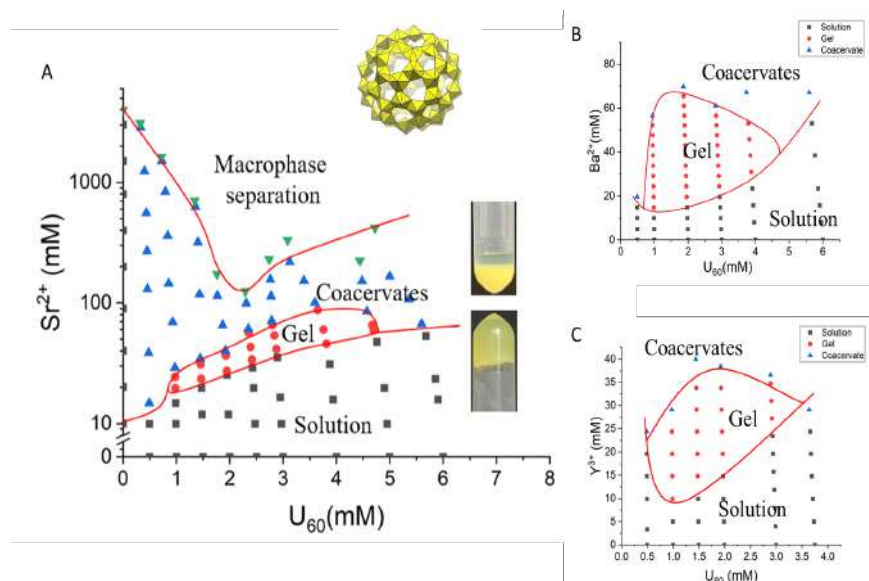
Abstract

It is our common understanding that inorganic salts demonstrate two major states in dilute aqueous solution: soluble and insoluble (precipitation/crystallization). 1-5 nm-size macroions represented by metal oxide molecular clusters are found to have more complex behaviors due to the noticeable counterion association and the consequent counterion-mediated attraction.

Collaborated with Burns' and Zang's groups separately, we identified two other phases in the aqueous solutions of nanoscale anionic clusters: gel and coacervate. The gel phase was observed in both highly charged macroions, e.g., uranyl peroxides $\{U_{60}\}^{60-}$ and $\{U_{24}P_{12}\}^{48-}$, and weakly charged $\{Mo_7O_{24}\}^{6-}$, in the presence of multivalent counteranions. In the first case, the counterion-mediated attraction leads to their formation of 2-D sheets (high charge cluster case). Due to the strong attraction from the multivalent cations, the 2-D sheets cannot bend and enclose to form the well-studied blackberry type structures, but stay as standalone sheets in solution. Their large excluded volume leads to the gelation in low concentrations (0.5 mg/mL), similar to the graphene gelation mechanism. In the second case, electrostatic interaction leads to 1-D linear chains and form gels similar to the gelation of polymer chains.

Coacervate phase has been broadly identified and covers a broad range in the phase diagrams. It is also highly fascinating because its formation mechanism is different from the commonly known coacervates formed by the strong interaction between positively and negatively charged polyelectrolytes. Positively charged macroions are missing from the current system. A new model is presented to explain their formation and features. The amount and the type of counterions are critical for such transitions. From our experimental data, we can identify multiple critical conditions required for the solution-gel, gel-coacervate, coacervate-precipitation transitions. Those rules are applicable for several different types of clusters.

Overall, we demonstrate that when soluble ions reach the scale of nanometer scale, they would possess very unique and complex features such as multiple macrophase transitions in dilute aqueous solution.



Trimetal Substituted Polyoxometalates and Guest-Host Keplerate Supramolecules as Inorganic Functional Mimics of Redox Metalloenzymes

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Abstract

The activation of small molecules will play an important role towards more sustainable chemical transformations. Furthermore, renewable solar and wind resources can provide the energetic driving for such reactions, leading to electrocatalytic transformations. In this talk, first I will present our research on the cathodic, reductive activation of O₂, N₂ and CO₂ trimetal substituted polyoxometalates as active site functional mimics of redox metalloenzymes. Second, I will present our ideas on the use of metal guest-Keplerate host supramolecules as inorganic analogs of redox metalloenzyme assemblies.

Cathodic activation of O₂: Paradoxically, nature's monooxygenase enzymes activate O₂ typically via a two-electron reductive pathway. Both Fe and Cu-based catalysis using reducing agents under protic conditions is known, but surprisingly, cathodic electrocatalysis using H₂O as a proton and electron source is almost unreported. Recently, we found that iron Keplerates, {Fe₃₀W₇₂} can be used as electrocatalysts for the oxidation of light alkanes and alkenes in water. Mechanistic studies have revealed that reaction intermediates have reactivity profiles similar to those observed for Compound I of cytochrome P-450. More recently, we have also found that tetra-Cu Weakley polyoxometalates are also very efficient electrocatalysts for the cathodic activation of O₂ and show reactivity profiles similar to those of the iron Keplerates.

Reduction of CO₂ to CO: The removal of CO₂ from the atmosphere through its capture or sequestration is a feasible technology, however, is not sustainable due to the high cost of the process and the low value of captured CO₂ requiring the transformation of CO₂ to a higher valued products. Therefore, we have prepared a series of trimetallo substituted polyoxometalates that on the one hand can catalyze the reversible reduction of CO₂ and oxidation of CO, and on the other hand can be tuned to reduce CO₂ with very low overpotentials.

Reduction of N₂ to NH₃: The electrification of ammonia synthesis is a key target for its decentralization and toward lowering the impact of chemical processes on atmospheric carbon dioxide concentrations. Using catalyst a tri-iron substituted polyoxotungstate, {SiFe₃W₉} in the presence of either Li⁺ or Na⁺ cations as promoters through their binding to {SiFe₃W₉} we show that in an undivided cell electrolyzer, rates of NH₃ formation was at up to 1.15 nmol sec⁻¹ cm⁻² with moderate faradaic efficiencies of ~25%. Based on an assumption of arbitrary 10% catalyst coverage on a Cu foil cathode, a TOF of 64 sec⁻¹ was calculated.

Iron-nickel guest-{Mo₆₀W₇₂} host supramolecules as an inorganic functional mimic of a hydrogenase enzyme: Can soluble inorganic metal oxides and the related guest-host complexes with encapsulated transition metals incorporated through assembly reactions, act as functional analogues of redox metalloenzymes that carry out multielectron transformations of small molecules? Here we show, that Fe-Ni assemblies bound to mercaptopropionate ligands within {Mo₆₀W₇₂} acts as a hydrogenase enzyme complex electro- and photoelectrochemically (PEC) forming hydrogen from protons and electrons. Reaction rate comparable to those found in the wild type enzyme are observed with very high faradaic efficiency under PEC conditions.

Decoupled Electrolysis with Soluble Redox Mediators for Energy Storage and Beyond

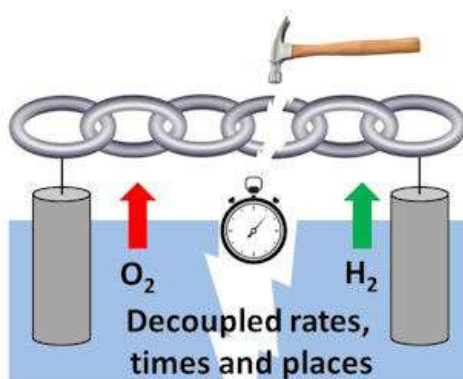
Mark D. Symes

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Abstract

There has been much interest recently in electrocatalytic water splitting for storing intermittent, renewably-generated power (e.g. solar) as chemical fuels such as hydrogen.[1] Conventional electrolyzers usually require stable power inputs in order to operate effectively and safely and so may be unsuited to harnessing renewable power, which is often intermittent and diffuse. Decoupled electrolysis [2] using suitable redox mediators [3] allows oxygen and hydrogen production to be separated in both space and time (see Figure). The advantages of this approach for harnessing intermittent power sources will be explained, with a special focus on the use of soluble redox mediators. Advantages include the production of ultra-pure product gases [4,5] and the potential to use such a system in a more diffuse, solar-driven hydrogen production platform.[6,7] The application of this technology to redox flow batteries with remarkably high energy densities [8,9] and to the electrochemical production of key feedstock chemicals [10-12] will also be discussed.

Schematic representation of decoupled electrolysis



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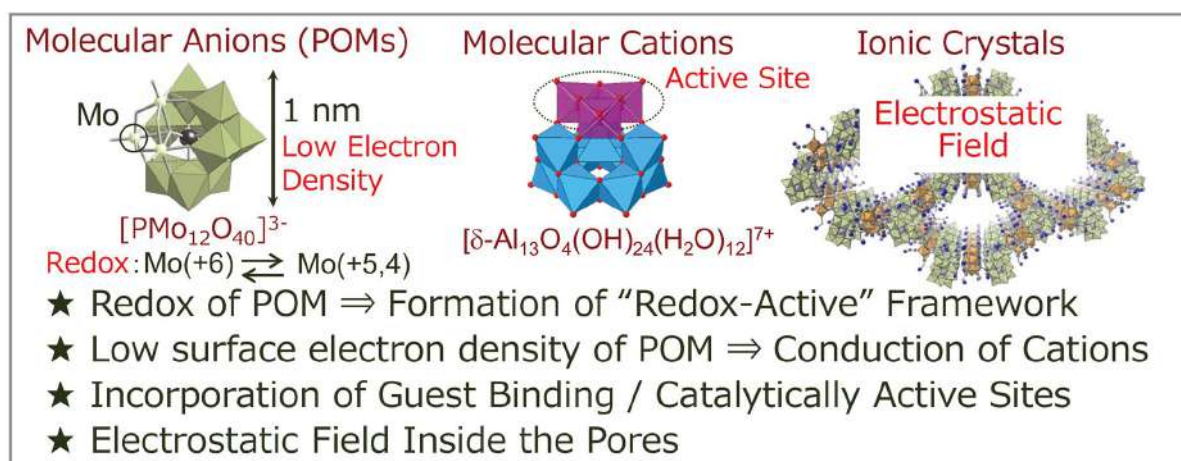
Porous Ionic Crystals Based on Metal-Oxo Clusters as a Tunable Platform for Functional Solid-State Materials

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Abstract

Porous crystalline materials such as zeolites and metal-organic frameworks (MOFs) have attracted wide attention due to their well-defined porous structures and high surface area, which are useful in gas storage and separation, ion exchange and conduction, and heterogeneous catalysis. Metal-oxo clusters are defined as inorganic multi-metal molecular complexes with water (H_2O), hydroxide (OH^-), or oxide (O^{2-}) ligands and possess unique catalytic, electrochemical, magnetic, and luminescent properties stimulating research in broad fields of science. We have reported that the complexation of metal-oxo clusters with counter ions of appropriate elements, charges, sizes, symmetry, ligands, etc., results in the formation of porous ionic crystals (PICs) with voids and channels in the crystal lattice. The properties of PICs can be summarized as follows. (a) Reversible redox properties of the metal-oxo clusters lead to the formation of “redox-active” PICs. (b) Guest binding and catalytically active sites can be incorporated beforehand into the ionic components. These functions can be maintained and utilized in the PICs since the ionic components still exist as discrete molecules in the crystal lattice. (c) metal-oxo cluster anions (polyoxometalates, POMs) can transport protons as counter cations efficiently because the negative charge of POMs is smeared over the external oxygen atoms decreasing the effective surface charge density. These properties lead to interesting functions in selective ion-uptake/exchange, proton conduction, heterogeneous catalysis, formation of luminescent mixed-valence metal clusters, etc., which are unique to PICs.^[1–10]



Ion-exchange: 1) *ACIE*, **2016**, 55, 3987. 2) *Chem. Mater.*, **2015**, 27, 2092. **Proton conduction:** 3) *Nanoscale*, **2021**, 13, 8049. 4) *ACS Appl. Mater. Interfaces*, **2021**, 13, 19138. 5) *Commun. Chem.* **2019**, 2, 9. **Catalysis:** 6) *JACS*, **2022**, 144, 2980. 7) *Nanoscale*, **2021**, 13, 18451. 8) *Chem. Commun.*, **2021**, 57, 8893. 9) *ChemCatChem* **2019**, 11, 3745. **Metal clusters:** 10) *Small*, **2023**, in press.

Recent Developments in Noble Metal-Oxo Cluster Chemistry: Synthesis, Structure and Catalysis

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Polyoxometalates (POMs) based exclusively on Pd^{II} ions (polyoxopalladates, POPs) were discovered in 2008.^[1] The area of POP chemistry has developed rapidly ever since due to the fundamentally novel structural and compositional features of POPs resulting in unprecedented electronic, spectroscopic, magnetic, and catalytic properties.^[2] In recent years efforts were made to modulate the POP structures along with their associated charges in order to try and control the structure-property relationship. This pursuit has led to the discovery of neutral palladium(II)-oxo clusters (POCs).^[3] Recently the synthesis of the first examples of cationic POCs has been reported.^[4] Besides the synthesis and structural characterization of POPs and POCs in the solid state and in solution their catalytic properties were also investigated. Here we report on some recent developments in noble metal-oxo cluster chemistry.^[5]

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Near-infrared photothermally enhanced catalysis of polyoxometalate complexes

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Abstract

Near infrared (NIR) absorption and photothermal conversion of inorganic metal nanoparticles, metal oxides and sulfides, are generated from non-radiative relaxation of plasmon resonance transition during returning to the ground state. Similarly, those reductive polymetallic oxygen clusters also show the near infrared absorption in the long wavelength region and have a good photothermal conversion ability. Therefore, we envisage that the near infrared light absorption and its conversion to the heat from polyoxometalates and other nanomaterials are possible to be used in enhancing catalytic properties. In addition, although photothermal catalysis of metal nanoparticles has been reported, such a process has not been realized in the system of polyanionic clusters. Apparently, this combination will be more conducive to the catalytic characteristics of polyoxometalate clusters. In targeting this purpose, we selected a series of POM complexes bearing NIR center including the cluster itself, graphene oxide, charge transfer complex, metal nanoparticles. The systematic investigations confirmed the practicability of the strategy in enhancing the performance of POMs.¹⁻³ The oxidation conversion in the presence of oxygen or hydroperoxide under the NIR photothermal conditions can be found to increase doubly or even higher with respect to the case without the use of NIR radiation. The catalytic center and photothermal center can be either integrated or separated while the catalytic efficiency enhancement of POMs did not show apparent difference. The mechanism study indicated that it is the locally raised temperature rather than that photo induced electron transfer contribute mostly to the enhanced catalysis. We believe that this strategy can be easily extended to develop other catalytic types of POMs with more efficient conversions and selectivity.

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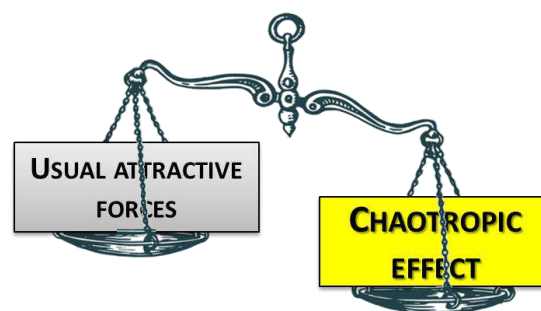
CHAOTROPIC EFFECT AS AN ASSEMBLY MOTIF IN POLYOXOMETALATE SUPRAMOLECULAR CHEMISTRY

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Abstract. The ability of biochemical substances such as phospholipids, glycans, or proteins to interact with discrete inorganic species is essential for some biological functions.^[1] Then, designing supramolecular hybrid architectures including dynamics and responsive behavior requires a fine balance



between the conglomerate of weak forces such as electrostatic, ion-dipole, dipole-dipole, hydrogen-bonding, dispersion, etc., that drives the aggregation processes. Recent reports highlight the intriguing properties of certain inorganic polynuclear anions, such as polyoxometalates (POMs) or polynuclear clusters for their extremely high propensity to interact strongly in aqueous solution with non-ionic organic components such as macrocycles or surfactants.^[2,3,4] This striking driving force has been identified as a strong solvent effect arising from chaotropic nature of the polyoxometalates in aqueous solution. In this communication, we will highlight the origin of this effect by proposing a classification of the chaotropic character of a large series of polyoxometalates, ranging from the Keggin type ions to the large nanoscopic ring-shape molybdenum blue. However, we will give some relevant examples showing how the chaotropic effect can be used to monitor supramolecular hybrid assemblies such as molecular core-shell, supramolecular MOFs or POM-containing bilayer type membrane.

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Solid-State Heat-promoted Synthesis and Acid-promoted Synthesis of Polyoxomolybdate from Methylammonium Monomolybdate

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We are interested in synthesis of isopolyoxomolybdates because their structure and counteraction are important as precursor of Mo-based oxides[1] and staining reagents for TEM (transmission electron microscopy) virus observation[2].

Acid-addition to monomolybdate is a most common method to produce polyoxomolybdates by dehydrative condensation [3]. We would like to present solid-state heating of methylammonium monomolybdate ($(\text{CH}_3\text{NH}_3)_2[\text{MoO}_4]$) produces several polyoxomolybdates depend on the heating temperature (Fig. 1) [4]. In some cases, structures made by solid-state heating are different from those made by acid-addition.

Furthermore, we present applications of these polyoxomolybdates as Mo-precursor of Mo-V based metal oxides and negative staining reagents for SARS-CoV-2 observation.

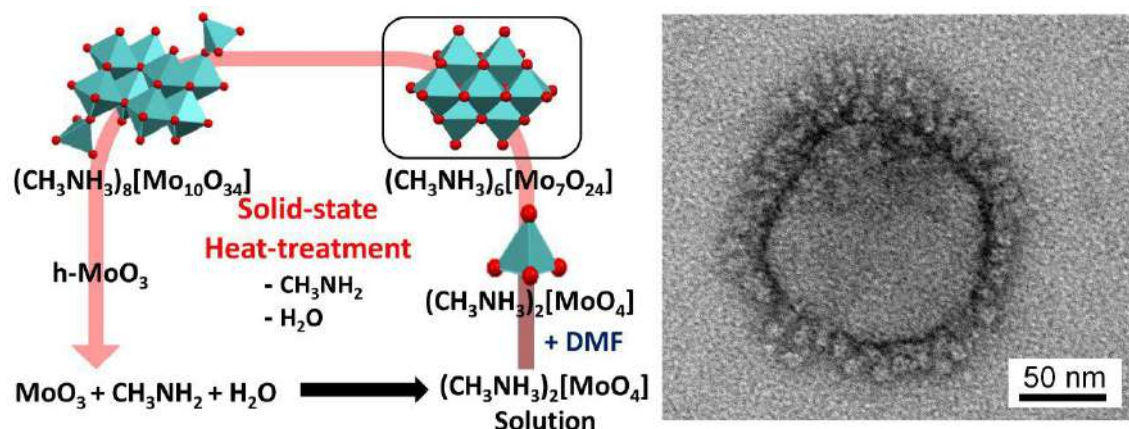


Fig. 1 Polyoxomolybdates prepared by solid-state heating of methylammonium monomolybdate, $(\text{CH}_3\text{NH}_3)_2[\text{MoO}_4]$, and TEM image of SARS-CoV-2 using $(\text{CH}_3\text{NH}_3)_6[\text{Mo}_7\text{O}_{24}]$.

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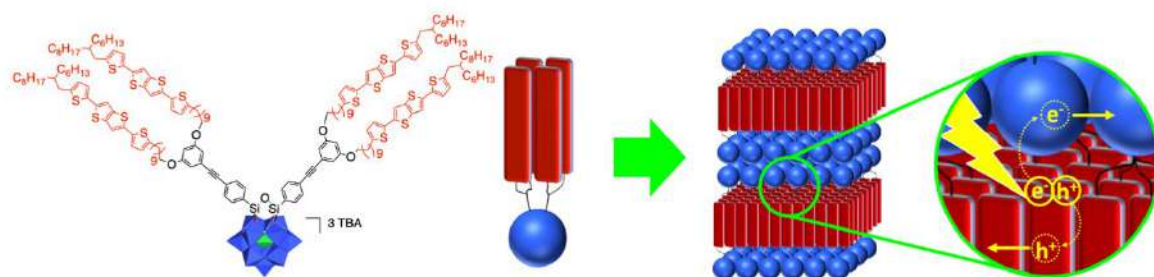
Covalent hybrid polyoxometalates, versatile platforms for the elaboration of self-assembled nano-architectures.

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Abstract

Owing to their nanoscale size, their structural complexity, their sensitivity to various types of interactions and their electron accepting properties, POMs are attractive molecular building units for the elaboration of complex molecular assemblies with synergistic or even emergent or properties.¹ In this context, we are interested in synthesizing supramolecular assemblies of organo-functionalized hybrid polyoxometalates.² The approach relies on the synthesis of POM-based building blocks bearing remote self-assembling functions. Selected examples will be herein presented including hierarchical nanostructures formed by coordination driven self-assembly^{3–5} and photoactive mesomorphic materials.⁶ An important emphasis will be devoted to the control of the shape of the hierarchical nano-organization.



Photoactive mesogen hybrid and its self-assembled nanoorganization in the solid state
intermingling electron and hole conduction channels.

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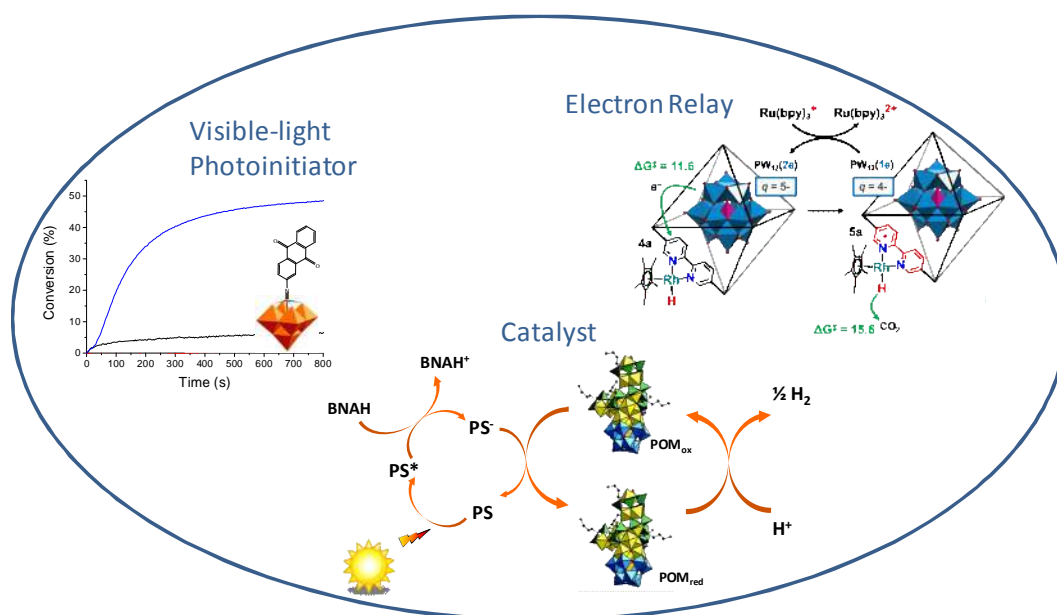
Three different roles of polyoxometalates in photocatalytic events

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Due to their high tunability, stability and optical and redox properties, POMs can be used in a very wide range of photocatalytic reactions (oxidation of organic substrates, HER (Hydrogen Evolution Reaction), OER (Oxygen Evolution Reaction), etc.).[1] In this type of process, POMs act as catalysts in the vast majority of cases, but they can also play other roles.

In this presentation, we will first present a classical case where a Keggin-type POM capped by fourteen nickel centers acts as catalyst for the HER.[2] In a second part, we will show that Lindqvist POMs can be used for switching from UV to visible the polymerization activity of organic photoinitiators.[3] Finally, we will evidence that POMs can be efficiently used as electron relay in the photocatalytic carbon dioxide reduction reaction (CO₂RR).[4]



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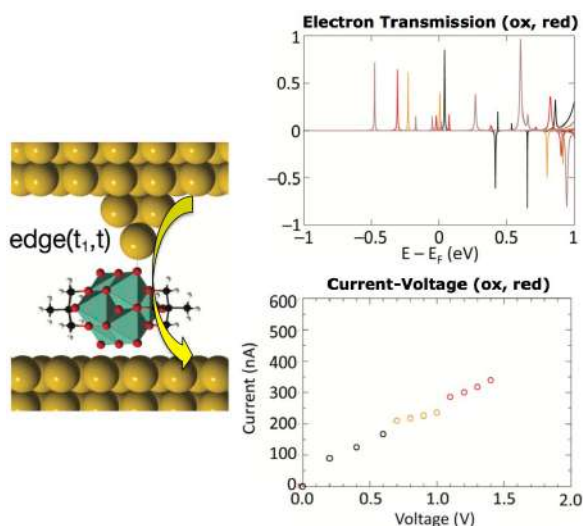
Computational Study of the Staircase Molecular Conductivity of Polyoxovanadates Adsorbed on Au(111)

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Abstract

Continuing with the research on POM systems with multiple resistive states,[1] this computational study presents the molecular conduction properties for derivatives of V_6O_{19} and $V_{18}O_{42}$ frameworks,[2] which were targeted as possible successors of the materials that are currently used in complementary metal–oxide semiconductor technology. Conductivity calculations on the Lindqvist-type adsorbed on Au(111) shows a staircase conductivity vs. a bias voltage, which depends directly on the oxidation state of the POM. After these proof-of-principle calculations we explored $V_{18}O_{42}$, a larger system featuring many more easily accessible redox states —hence, supposedly more interesting from the multiple-state resistive (memristive) viewpoint. Calculations suggest that the latter molecule does not possess staircase conductivity due to the large number of unpaired electrons in the resting state.



Model system in the conductivity calculations (left), electronic transmission and current-voltage behavior (right) for the functionalized V_6O_{19} derivative.

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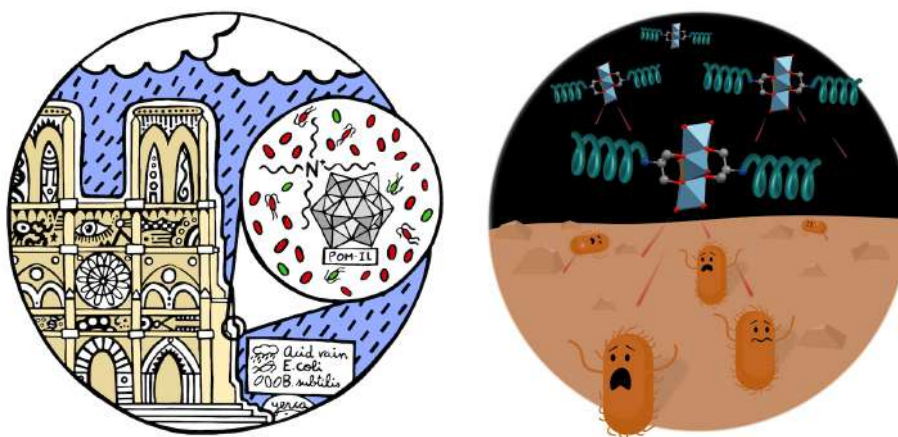
Using polyoxometalates as multifunctional coatings, scaffolds, and supramolecular self-assembly tools

Scott G. Mitchell

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Abstract

Organo-functionalisation of polyoxometalates represents an effective approach to obtain diverse structures and arrays of practical materials with tailored surface chemistry, charge, polarity, and redox properties. POMs also possess excellent biological activity: they can cross lipid membranes, interact with proteins and are producers of reactive oxygen species. Together, this combination of physical properties with biological activity makes them suitable for a variety of end uses. I will show how we use POMs as multifunctional coatings, scaffolds, and supramolecular self-assembly tools that can be used for catalytic, biomedical, and environmental applications. I will discuss the preparation of POM-peptide hybrids for catalytic, adhesive, and biomedical applications,[1-3] POM-IL composites for universal pollutant removal[4,5] and multifunctional surface coatings,[6,7] with a particular focus on the activity of these materials against model microorganisms, including algae, bacteria, and moulds.[8,9]



Modular POM-IL materials act as precision biocides with anticorrosive properties that meet the requirements of heritage conservation (left); “on-POM polymerization” of N-carboxyanhydrides as a platform to design antimicrobial POMlymer materials (right).

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Nucleation Mechanisms and Redox Profiles of Polyoxovanadate-Alkoxides Clusters

Pere Miró

Polyoxovanadate-alkoxide (POV-alkoxide) clusters are a class of electroactive species with redox properties that can be tuned via heterometallic functionalization during their synthesis. However, their formation mechanism and structure-redox relationships remain largely unknown, thus limiting the rational design of new clusters with the desired redox properties. Here, we present a computational study on the nucleation pathways of two POV-alkoxides, one containing only vanadium centers, $[(V^V_{6-n}V^{IV}_nO_6)(O)(O-CH_3)_{12}]^{(4-n)+}$ and another including an heterometallic iron $[(V^V_{5-n}V^{IV}_nO_5)(OCH_3)_{12}(O)(Fe^{III}Cl)]^{(3-n)+}$. We also studied the structure-redox relationships in the redox profiles of POV-alkoxides functionalized with one or more early first row transition metals. These studies will bring us closer to understanding the structure-redox relationships of POV-alkoxides and identifying new synthetic targets with improved redox properties.

The superchaotropic property of polyoxometalates as an opportunity in polymer, surfactant and colloid science

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Abstract

In 2015, the chaotropic nature of nanometer sized ions (nano-ions) with low charge density, such as some polyoxometalates and ionic boron clusters, has been identified.[1] The chaotropicity of nano-ions is evidenced by their strong binding with non-ionic organic matter, such as surfactants, macrocycles and co-solvents, in water. In the present contribution, recent findings on the effect of Keggin polyoxometalates on water soluble polymers will be presented.[2,3] A focus will also be made on the effect of POM counterions on hybrid organic-inorganic molecular assembly.[4] We will show that the superchaotropic property of POMs offers many opportunities to tailor of polymer/surfactants properties in solution, such as their gelation,[2] molecular assembly[3,4] and foaming behavior.[5]

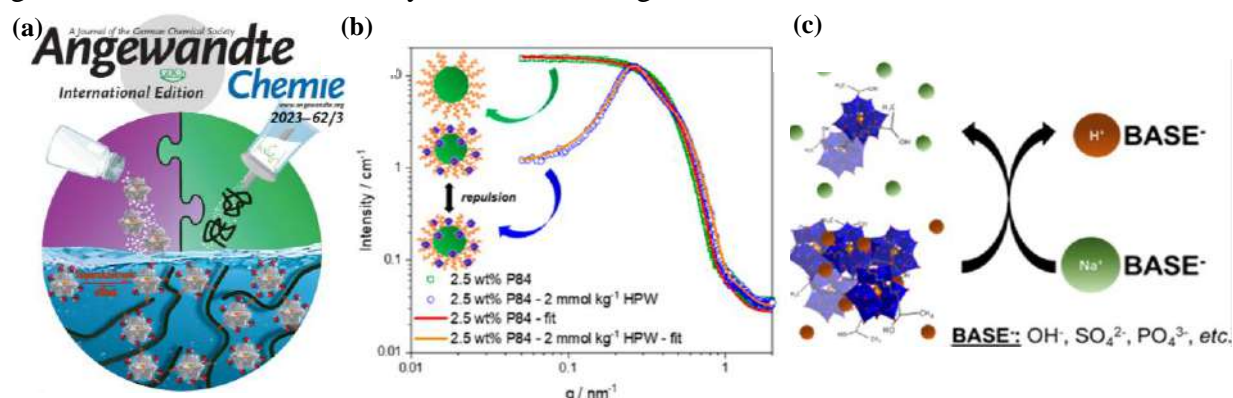


Figure 1 (a) Keggin POMs induce the cross-linking and hydrogel formation of polymeric cellulose ethers [2] (b) Small angle neutron scattering spectra of polyethoxy-polypropoxy-polyethoxy polymer (Pluronic P84[®]) showing strong adsorption of POM at the surface P84 micelles. (c) Sketch of the effect of POM counterion on the POM-di-propoxypropylether (C₃P₂) co-assembly.

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Guest Transition Metals in Host Keplerate Nanocapsules- Towards Inorganic Functional Mimics of Redox Metalloenzymes?

Eynat Haviv, Bo Chen, Raanan Carmieli, Lothar Houben, Hagai Cohen, Gregory Leitus, Liat Avram, and Ronny Neumann

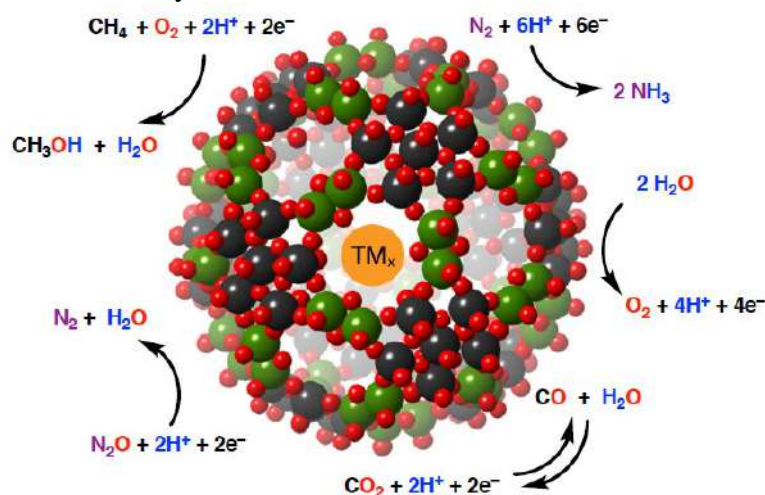
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Abstract

Host-guest solution chemistry with wide range of organic and organometallic hosts is an important and established research area, while the use of inorganic hosts is a more nascent area of research. In the recent past in a few cases, Keplerate-type molybdenum-oxide based porous, spherical clusters, shorthand notation $\{\text{Mo}_{132}\}$, have been used as hosts for organic guests. In a previous publication¹ we demonstrated a procedure to encapsulate transition metal cations, from an organic solvent, by design into a Keplerate capsule. By this methodology three first row transition metal cations ($\text{M}^{2+} = \text{Mn}^{2+}, \text{Fe}^{2+}, \text{Co}^{2+}$) were encapsulated as guests into a porous Keplerate inorganic host, $\{\text{Mo}_{132}\}$ containing phosphate ligands. Different from previous research², the methodology allows control by design of the average number of guest cations introduced into the capsule, in the range of 1-10 guests cations per capsule.

An additional development of our methodology was recently achieved, and allows the encapsulation process from aqueous solution based on the affinity of transition metal cations to different functional groups, such as thiols and carboxylic acids. Thus, by changing the ligands inside the capsule we can achieve variety of host guest systems with different properties.

Here, we will present the preparation and characterization of Keplerate guest host complexes based on $\{\text{Mo}_{132}\}$ and $(\text{W}^{\text{VI}}_{72}\text{Mo}^{\text{V}}_{60})$ inorganic capsules and demonstrate early results of their application as a functional enzyme model.



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Parameter affecting the mass transport of polyoxometallates through vertically oriented mesoporous silica films

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Abstract

Diffusion of polyoxometallate (POM) units through vertically-aligned mesoporous silica films (MSFs) with monodisperse size (2.1 -2.9 nm) prepared by the electrochemically assisted self-assembly (EASA) method has been studied in aqueous media. [1] As expected, a strong resistance to mass transport of the bulky POM anions was observed, due to electrostatic repulsions arising from the negatively-charged silica surface. [2] Ionic strength and pH are key parameters allowing to modulate and enhance the mass transport properties of POMs through MSFs. Thus, the presence of MSFs onto an ITO electrode greatly influenced the voltammetric response of POMs in acidic media. In particular, at pH 0.3 the silica surface is positively-charged and thus more suitable to accumulate POM anions favoring their ingress through the mesochannels, considerably enhances their electrochemical response with respect to the less acidic medium (Fig. 1). Overall, the main experimental parameters that affected voltammetric currents, determined from our studies are: (a) the membrane pore size, (b) the POM probe charge and size, (c) the solution pH influencing the surface density of charge of silica and the corresponding accumulation of POM via electrostatic interactions, and (d) the ionic strength of the solution.

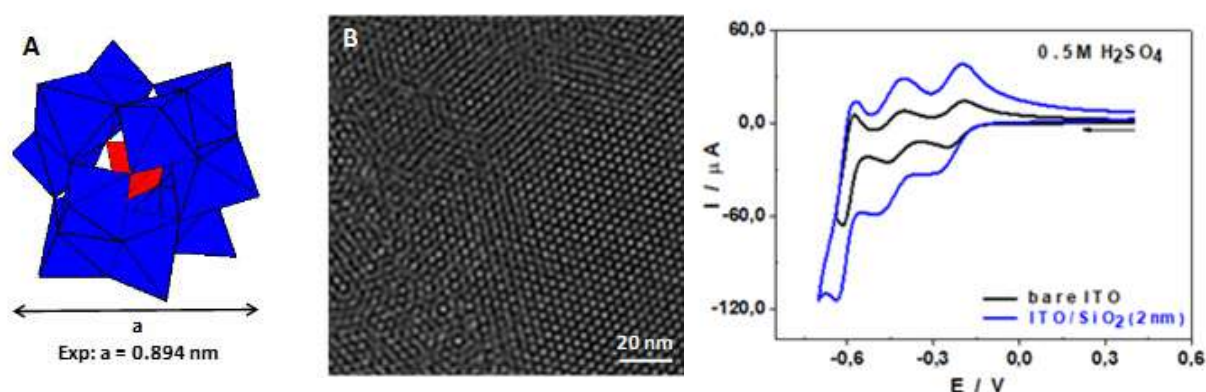


Fig. 1. (A) Polyhedral representation of the KEGGIN structure. (B) Typical TEM imaging of an oriented mesoporous silica film generated by EASA (top view). (C) Cyclic voltammograms of $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ recorded on ITO bare electrode and on MSF onto ITO electrode.

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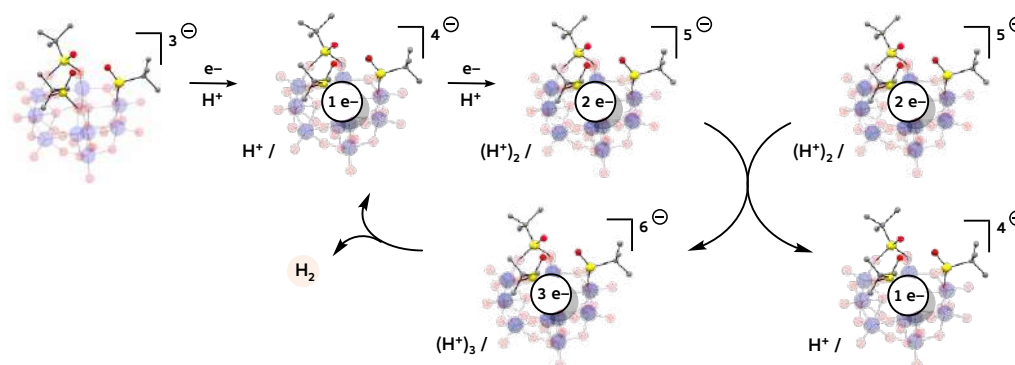
Protonation of reduced polyoxotungstates : towards the understanding of H₂ release onto a hybrid *SiloxPOM*

Ludivine K/Bidi, Alix Desjonquères, Geoffroy Guillemot

Sorbonne Université, CNRS, Institut Parisien de Chimie Moléculaire, F-75005 Paris, France

Abstract

The accumulation of multiple reduction equivalents at a single site remains a key step towards the development of innovative catalytic materials capable of addressing environmental and energy challenges.[1] Due to their ability to behave as electron and proton acceptors, polyoxometalates are ideal candidates in these areas, particularly in photocatalyzed hydrogen production.[2] Despite numerous works over the years, the mechanism leading to hydrogen evolution onto polyoxometalates is rather undefined. We thus came interested in studying the reaction of protons on reduced species of polyoxotungstates and in particular on hybrids that we synthesize in our group.[3,4] Our results and perspectives will be presented in this communication.[5]



A possible scenario for the release of hydrogen onto reduced *SiloxPOM* derivatives.

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Development of a Method for Predicting the Aqueous Speciation and Self-Assembly of Polyoxometalates

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Abstract

The self-assembly of polyoxometalates (POMs) is governed by several parameters: pH, ionic force, temperature, and total concentration. Despite that POMs have successfully been applied to catalysis and materials, the formation mechanism of these molecular clusters still is rather unclear.¹ To tackle this issue, we have developed POMSimulator, a method which not only identifies the reaction mechanism, but also provides speciation models. The method has its foundations on three major theories: quantum mechanics (QC), graph theory, and chemical equilibria.² Hitherto, we have applied it successfully to five isopolyoxometalates: -molybdates, -tungstates, -vanadates, -niobates, and -tantalates.³⁻⁴ Figure 1A shows a chemical reaction network that has been generated automatically for describing the self-assembly process. Additionally, Figure 1B shows a speciation phase diagram for polyoxoniobates. The plot shows the potential of the method, as it allows the characterization of formation constants that have been elusive so far. Finally, we have found that it exists an excellent linear scaling between theoretical and experimental data. This evidence can potentially unlock the determination of several hundreds of unreported formation constants. Recent kinetic results of the self-assembly process will be presented as well.

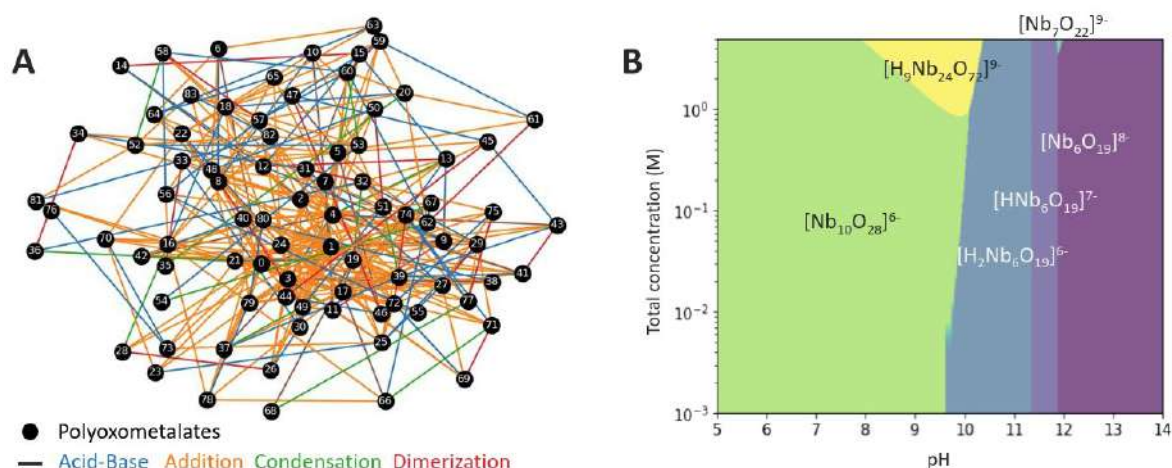


Figure 1. (A) Chemical reaction network for the self-assembly mechanism (B) Speciation phase diagram for polyoxoniobates.

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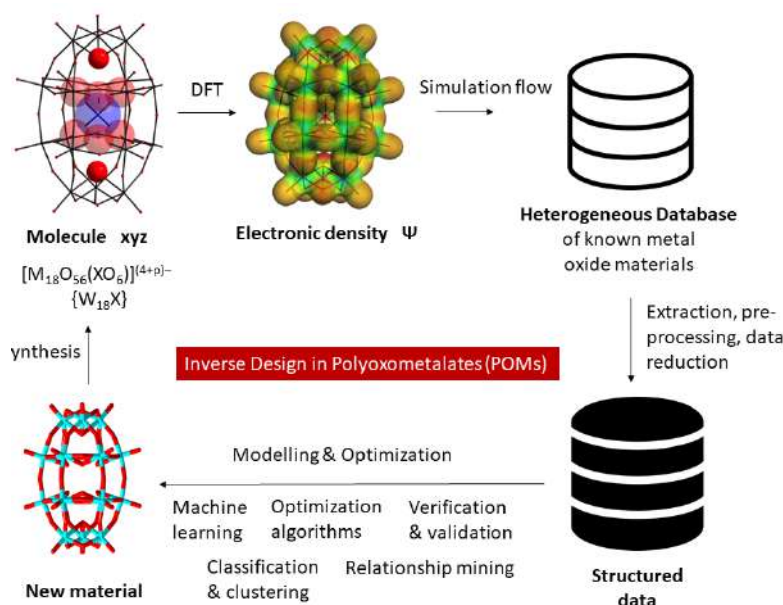
POM synthetic chemists benefit from computational chemistry

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Abstract

For over 20 years, Density Functional Theory (DFT) calculations have been critical in understanding the properties of polyoxometalates (POMs) based on their electronic structure. Together with my team we propose to go one step further and computationally explore the space generated by the self-assembly of known molecular metal oxides to predict new structures.^[1] Material scarcity and rising energy costs demands better planning and a more focused search strategy to find new materials. Inverse design can aid in the discovery of: a specific catalyst for a zero-carbon fertiliser fuel,^[2] a new porous materials based in POMs building-blocks,^[3] and polyoxometalate based single atom catalysts (SACs).^[4]



Proposed workflow for achieving inverse design in metal oxides is described. The known molecules' coordinates are used to generate their ground-state electron density using density functional theory (DFT) methods.

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Aryl-Imido Polyoxometalates for Photonics: Towards Switchable Devices

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Abstract

Arylimido polyoxometalate (POM) hybrid materials show strong electronic coupling between POMs and organic subunits. This has enabled synthesis of POM-based charge-transfer chromophores with high non-linear optical (NLO) activity, high transparency, and in some cases reversibly redox-switchable NLO responses (Figure 1a).[1,2]

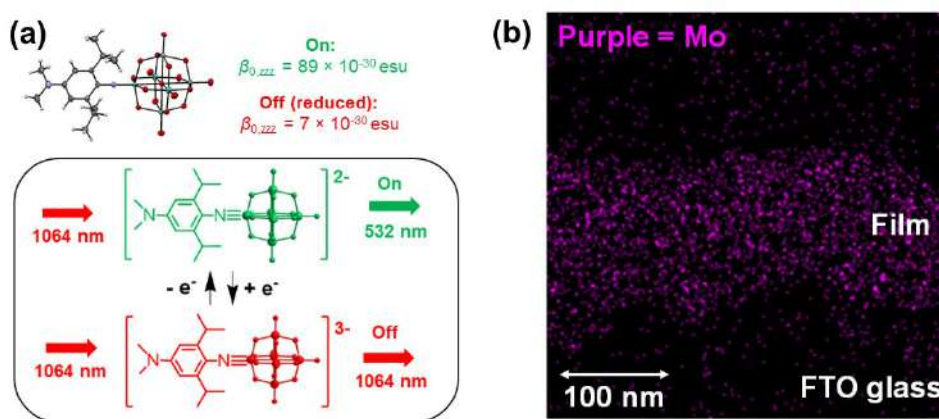


Figure 1 (a) Electrochemically switched NLO response in an arylimido POMophore. (b) Elemental map of an arylimido-POM/polypyrrole film.

This talk will discuss the development of redox switchable POMophores based on the hexamolybdate, extension of the work to polyoxotungstates, and approaches to surface functionalization with imido-POMs [3] (Figure 1b) – a challenging and critical step for application in devices.

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Fatty acid capped, metal oxo clusters as the smallest conceivable nanocrystal prototypes

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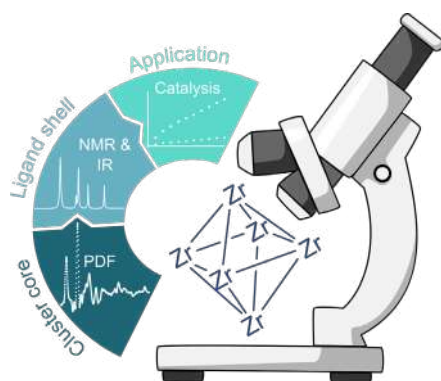
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Abstract

Metal oxo clusters of the type $M_6O_4(OH)_4(OOCR)_{12}$ ($M = \text{Zr}$ or Hf) are valuable building blocks for materials science.

Here,[1] we synthesize a series of zirconium and hafnium oxo clusters with ligands that are typically used to stabilize oxide nanocrystals (fatty acids with long and/or branched chains). The fatty acid capped oxo clusters have a high solubility but do not crystallize, precluding traditional purification and single-crystal XRD analysis. We thus develop alternative purification strategies and we use X-ray total scattering and Pair Distribution Function (PDF) analysis as our main method to elucidate the structure of the cluster core. We identify the correct structure from a series of possible clusters (Zr_3 , Zr_4 , Zr_6 , Zr_{12} , Zr_{10} , and Zr_{26}). Excellent refinements are only obtained when the ligands are part of the structure model. Further evidence for the cluster composition is provided by nuclear magnetic resonance (NMR), infrared spectroscopy (FTIR), thermogravimetry analysis (TGA), and mass spectrometry (MS). We find that hydrogen bonded carboxylic acid is an intrinsic part of the oxo cluster. Using our analytical tools, we elucidate the conversion from a Zr_6 monomer to a Zr_{12} dimer (and vice versa), induced by carboxylate ligand exchange. Finally, we compare the catalytic performance of Zr_{12} -oleate clusters with oleate capped, 5.5 nm zirconium oxide nanocrystals in the esterification of oleic acid with ethanol. The oxo clusters present a five times higher reaction rate, due to their higher surface area.

Since the oxo clusters are the lower limit of downscaling oxide nanocrystals, we present them as appealing catalytic materials, and as atomically precise model systems. In addition, the lessons learned regarding PDF analysis are applicable to other areas of cluster science as well, from semiconductor and metal clusters, to polyoxometalates.



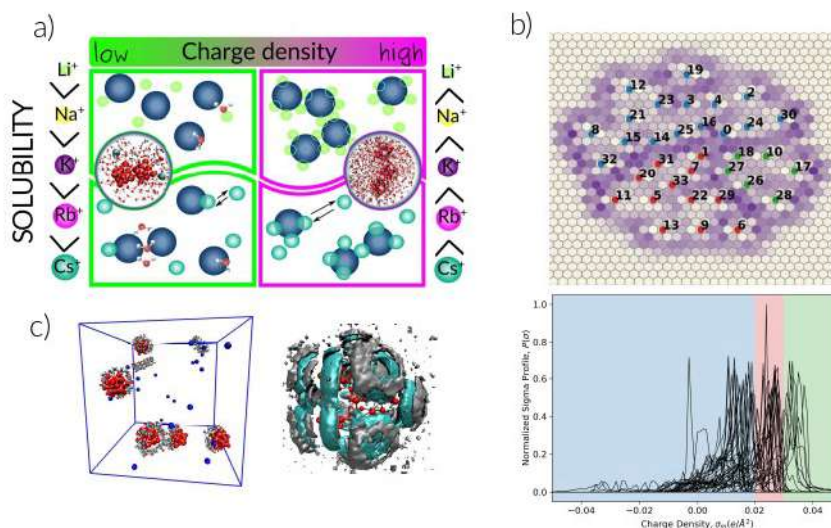
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Unlocking the role of anion solvation sphere in supramolecular chemistry of metal-oxo clusters

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The anionic character of polyoxometalates combined with their size gives them unique properties when interacting with cations and neutral molecules. These properties make POMs ideal systems for building multi-functional materials with applications in catalysis, electronics, and biology. The solubility of POMs with alkali cations shows opposing trends based on the size and charge of the anion. By means of molecular dynamics simulations, we were able to define two different aggregation patterns for high- and low-charge density POMs (Fig. a). Aggregation depends on the strength of the ionic interaction, the ability of the POM to destabilize the cation's solvation sphere, and the POM's solvation sphere.¹ We expanded this study by combining quantum descriptors with machine learning (ML) methods to develop a predictive solubility trend model that is applicable to a wide range of POMs and inorganic salts (Fig. b), and we discovered a new amphoteric behavior.² On the other hand, the supramolecular chemistry of POMs with neutral molecules, such as γ -cyclodextrin, also strongly depends on the POM's charge density.³ Simulation results show a correlation between the structure of the POM's solvation sphere and what is called the chaotropic effect (Fig. c).



a) Normal Solubility (low-charge POMs) and Anomalous (high charge POMs). b) Neural network and sigma-profiles: normal (blue), amphoteric (red) i anomalous (green). c) Snapshot of a molecular dynamics simulation of Keggin-cyclodextrine; SDF isosurfaces plot of water molècules in the first solvation shell.

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² T. Rahman, E. Petrus, M. Segado, N. P. Martin, L. N. Palys, M. A. Rambaran, C. Andre Ohlin, C. Bo and M. Nyman, *Angew. Chem. Int. Ed.* **2022**, 61, e202117839.

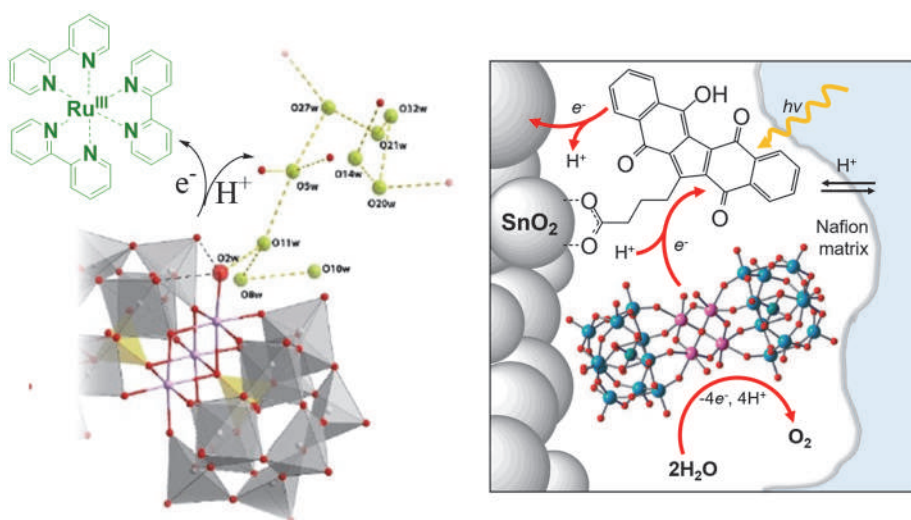
³ S. Yao, C. Falaise, A. A. Ivanov, N. Leclerc, M. Hohenschutz, M. Haouas, D. Landy, M.A. Shestopalov, P. Bauduin, E. Cadot. *Inorg. Chem. Front.*, **2021**, 8, 12-25.

Moving electrons AND protons in photosynthetic systems for oxygen evolution

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The reactivity in natural and artificial photosynthetic schemes occurs through the exchange of electrons AND protons.[1,2] The mechanistic comprehension of these processes is pivotal in maximizing the efficiency of charge separation, ultimately feeding the synthetic catalytic routines. In this contribution, the proton-coupled electron transfer (PCET) reactivity of metal-aquo sites embedded in polyoxometalates within light activated systems for oxygen evolution will be presented.[3,4] The role of both the photogenerated oxidant and of the base will be discussed, in particular for systems embedded onto regenerative photoelectrode surfaces.[3,4]



PCET events in photosynthetic systems dealing with transition metal substituted polyoxometalates.[3,4]

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Mechanochemical Approach to Super-reduced Polyoxometalates

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Abstract

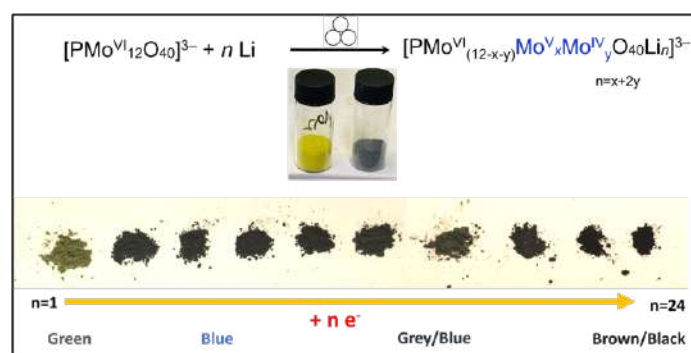
The constantly growing demand in renewable energy sources brings the need of new methods to store this energy that can be released when demand exceeds generating capacity. Storage of energy as electrical charge in batteries and storage of energy via the conversion into chemical fuels are the two most promising solutions to this challenge. Polyoxometalates (POMs) often called ‘electron/ion sponges’ are ideal candidates in this regard due to their ability to reversibly accept multiple electrons with no change in their structure, making them excellent models to study mechanisms of electrochemical nature.

Although a various number of works have reported charge storage and conversion materials based on electron-rich POMs,¹ the formation of ‘super-reduced’ POMs by chemical reduction has hardly been investigated.

This prompted us to explore the step-wise mechanochemical reduction of the Keggin-type POM, TBA₃[PMo₁₂O₄₀], in order to provide better fundamental understanding of the reactivity and the electronic properties of the resulting electron-rich nanoscale metal oxides.

The resulting products of the reductions have been analysed by NMR, FTIR, XPS, XAS and electrochemoelectrochemical methods in order to investigate the formation of ‘super-reduced’ POMs.

The results have demonstrated that is possible to inject electrons mechanochemically into TBA₃[PMo₁₂O₄₀], confirming the reduction from Mo^{VI} up to Mo^{IV}. Moreover, when higher amounts of reducing agent are used the formation of an extra Mo chemical environment is observed, which is proposed to be Mo₂C.



Visual representation of the chemical reduction of Keggin-type POM, [PMo₁₂O₄₀]³⁻

¹ Wang H.; Hamanaka, S.; Nishimoto, Y.; Irlle, S.; Yokoyama, T.; Yoshikawa, H.; and Awaga, K. *J. Am. Chem. Soc.*, **2012**, 134, 4918.

Speciation of polyoxometalates in aqueous solutions

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Polyoxometalates (POMs) are generally characterized in the solid state prior to dissolution, and this structural information is used as the framework on which the solution chemistry is developed. After dissolution in aqueous media, POM anions, like many other compounds can be protonated, hydrolyzed, and sometimes even undergo redox processes, all of which affect the presence of the active species [1]. With the growing number of successful and promising applications of POMs in aqueous solutions, understanding speciation in solution based on pH, temperature, incubation time, the type of buffer solution, the presence of a reducing or chelating agent, and the effect of ionic strength is of paramount importance and attributes the activity to the POM species actually present in solution.

In this contribution, the speciation atlas of POMs commonly used in catalytic and biological applications in aqueous solutions will be discussed. Each of the ten POMs is described under 54 conditions characterized using a quantitative NMR spectroscopy-based approach, the most readily available method for understanding processes in solution. The speciation atlas of polyoxometalates sets a new benchmark in the study of metal oxides in solution.

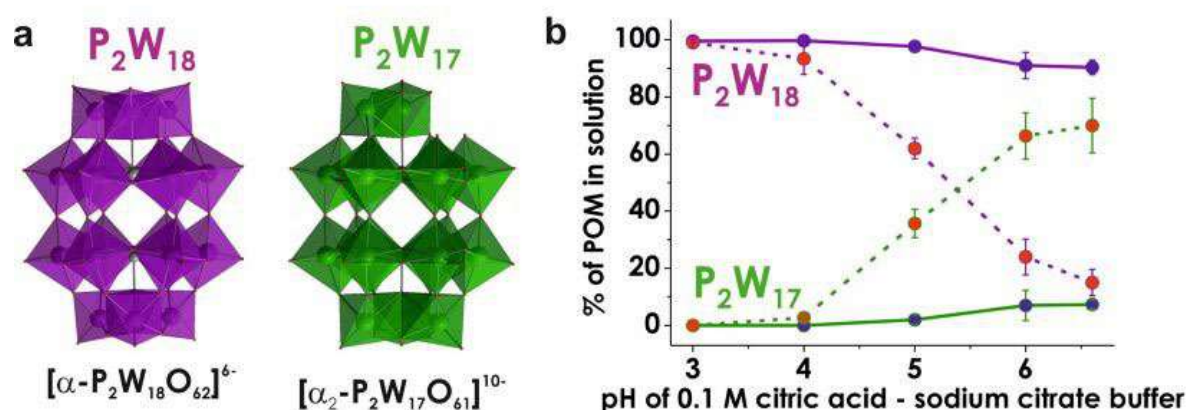


Fig. 1. a. Polyhedral representation of Wells-Dawson $[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ ($\{\text{WO}_6\}$, purple) and $[\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61}]^{10-}$ ($\{\text{WO}_6\}$, green). b. Concentration curves of P_2W_{18} (purple) and P_2W_{17} (green) before (solid line, blue dot in the middle) and after incubation for 24 h at 37 °C (dash line, red dot in the middle) in $\text{K}_6[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}]$ (10 mM) 0.1 M citric acid – sodium citrate solutions in the pH range from 3 to 6.

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Exploring the application of Path Metadynamics to determine acidity constants of polyoxometalates

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Abstract

The protonation of polyoxometalates (POMs) has a strong impact on their electronic structure, influencing in turn their redox properties and reactivity. Thus, determining the protonation states that prevail under experimental conditions is essential to attain an accurate description of POMs' properties using computational methods. However, static DFT calculations with implicit solvation models usually fail at predicting acidity constants of POMs in a quantitative manner because they cannot capture neither the variations in the hydrogen bonding network around the POM during the acid-base process, nor the dynamic nature of the proton in solution that describes the deprotonated state.

In this talk, I will discuss the potential of first-principles molecular dynamics (MD) simulations (DFT-based MD) in combination with the Path Metadynamics (PMD) enhanced sampling technique^[1] to accurately predict acidity constants of POMs using explicitly solvated systems. Then, I will cover preliminary results obtained thus far regarding the application of DFT-MD and PMD methods to two different POM systems of increasing complexity, which aim to unveil the nature of the protonation sites and to reproduce (and predict) the pK_a values of their protonated counterparts (see Figure).

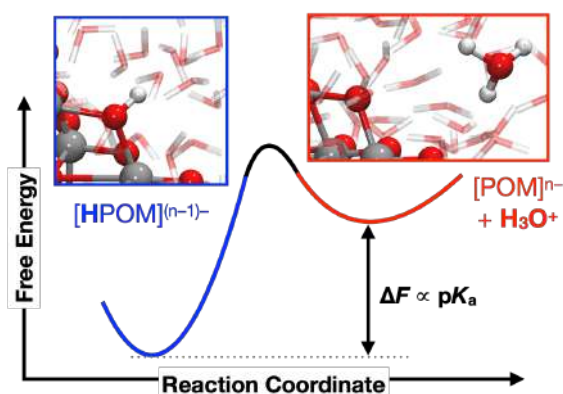


Figure. Pictorial representation of the free-energy landscape along a (de)protonation event.

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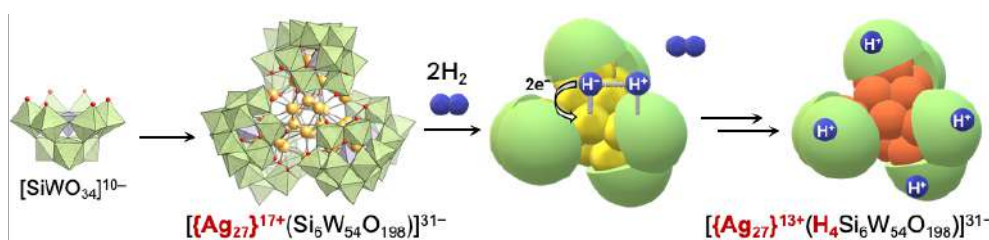
Synthesis and Catalytic Properties of Atomically Precise Silver Nanoclusters with Polyoxometalates

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Abstract

Atomically precise metal nanoclusters have attracted increasing interest in diverse fields owing to their diverse properties and applications that are strongly dependent on their structures, electronic states, and supporting ligands.^[1] Polyoxometalates (POMs) are bulky anionic metal-oxo clusters possessing unique structures and properties, such as acidity/basicity, electronic states, and redox properties. We have recently developed synthetic methods for metal-oxo clusters and inorganic–organic hybrids using lacunary POMs in organic solvents.^[2,3] Here, we present a new strategy for synthesizing atomically precise Ag nanoclusters using lacunary POMs as multidentate inorganic ligands.^[4–7] In particular, we envisaged that unique properties of POMs make them attractive ligands for Ag nanoclusters with the potential to impart novel catalytic, photocatalytic, and other properties. For example, $\{\text{Ag}_{27}\}^{17+}$ and $\{\text{Ag}_7\}^{5+}$ nanoclusters were synthesized by using a lacunary POM $[\text{SiW}_9\text{O}_{34}]^{10-}$. These molecular hybrids of Ag nanoclusters and POMs showed high stability, synergistic unique reactivity with H_2 , and catalytic properties, which differ from Ag nanoclusters synthesized using organic ligands.



Synthesis and reactivity of molecular hybrids of Ag nanoclusters and POMs.

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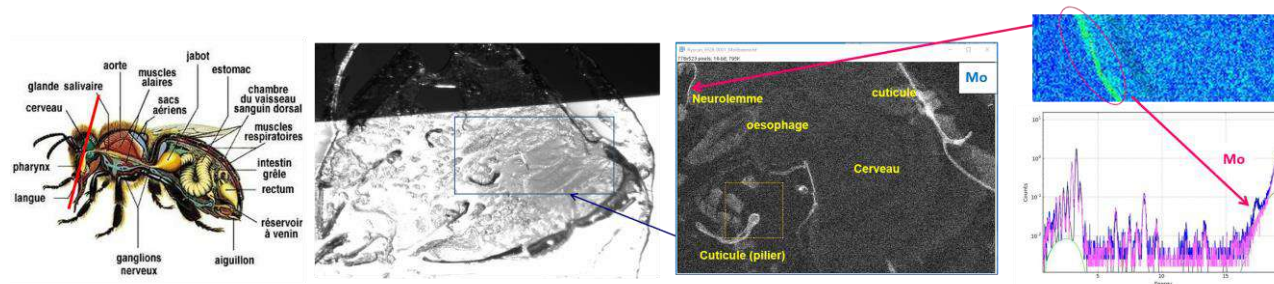
Serendipity in chemistry. When an “old” [Mo₂O₄]-based complex can contribute to the safeguard of the honeybees.

Arcadie FUIOR,^{a,b} Loic COLIN,^c Valentina CEBOTARI,^d Isabelle RIBAUD,^e Isabelle GERARD,^a Olga GARBUZ,^d Mathieu FREGNAUX,^a Aurelian GULEA,^b Ion TODERAS,^d Jean-Christophe SANDOZ,^{c,*} and Sébastien FLOQUET^{a,*}

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- b. State University of Moldova, Chisinau, Republic of Moldova.
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Bees are experiencing a worrying decline around the world. Beyond this decline, 20,000 species of plants are also affected by their disappearance and nearly 40% of our diet. Molybdenum is an essential trace element for life. Found in over fifty enzymes, Mo plays an important role in plants and in animals. For several years we are developing molecular complexes based on Mo for applications in biology.[1,2] In particular, very simple coordination complexes have proved to be very active in beekeeping. Non-toxic, these molecules seem to stimulate the immune system of bees, which become more resistant to temperature variations, parasites and bee diseases and therefore provoke a significant decrease of the colonies mortality. A first part of this talk will be focus on the choice of the complexes and their effects in beehives in different conditions and different countries.[3] A second part will be dedicated to understanding of the role played by these complexes within the bees' organism, thanks to many techniques such as ICP-MS, X-Ray Fluorescence experiments performed on Synchrotron SOLEIL or XPS studies.



Localization of molybdenum within the head of a bee fed with a Mo-complex

[1] A. Fuior, A. Hijazi, O. Garbuz, V. Bulimaga, L. Zosim, D. Cebotari, M. Haouas, I. Toderas, A. Gulea and S. Floquet, *Journal of Inorg. Biochem.*, **2022**, 226, 111627.

[2] A. Fuior, D. Cebotari, M. Haouas, J. Marrot, G. Minguez Espallargas, V. Guérineau, D. Touboul, R. Rusnac, A. Gulea and S. Floquet, *ACS Omega*, **2022**, <https://doi.org/10.1021/acsomega.2c00705>

[3] A. Fuior, S. Floquet, V. Cebotari, D. Cebotari, A. Gulea, I. Toderas. « Food supplement based on molybdenum for bees ». Patent deposited in France on 07/23/2020 (FR2007784). Extended PCT and Argentina on 07/19/2021 (WO2022/018009).

HARVESTING THE INTERACTIONS BETWEEN HYBRID-POMS AND PROTEINS

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Abstract

Oxidative modifications of proteins and the ability of these proteins to interact with organic/inorganic species are crucial for several applications in biotechnology. Thus, designing organic-inorganic hybrid species that can selectively bind and modify certain regions of proteins is a key in understanding the nature and effect of these interactions on the structure and function of target proteins. Polyoxometalates (POMs), an exceptional class of metal-oxo anionic clusters displaying outstanding physical and chemical properties combined with vast structural diversity that can be further expanded through the covalent attachment of organic moieties onto the cluster to form hybrid POMs (HPOMs).[1,2] Generally, POMs are renowned for their applications in numerous fields such as catalysis, sorbents, sensors... Moreover, POMs are known to interact with biological matter, such as proteins, resulting in promising antibacterial, antiviral and anticancer properties.[3] Although the exact mechanism behind this biological activity is not yet fully understood, our recent results highlight the nature of interactions between HPOMs and proteins. These interactions involve a conglomerate of weak non-specific interactions, mainly through a fine balance between electrostatic and hydrophobic effects, with hydrogen bonding or ion-dipole contacts ensuring a specific recognition process mediated by the nature of the organic ligand attached onto the inorganic POM core.[4] Therefore, a better understanding of these non-covalent interactions that govern the associations of HPOMs and proteins will provide invaluable insights for the development of HPOMs as possible therapeutic agents and for their use in the formation of novel biomaterials. For this purpose, the interaction between a series of POMs based on the derivatives of archetypal Anderson-Evans $[X\text{M}_6\text{O}_{24}]^{n-}$ and Lindqvist $[\text{M}_6\text{O}_{19}]^{n-}$ anions and proteins was investigated.

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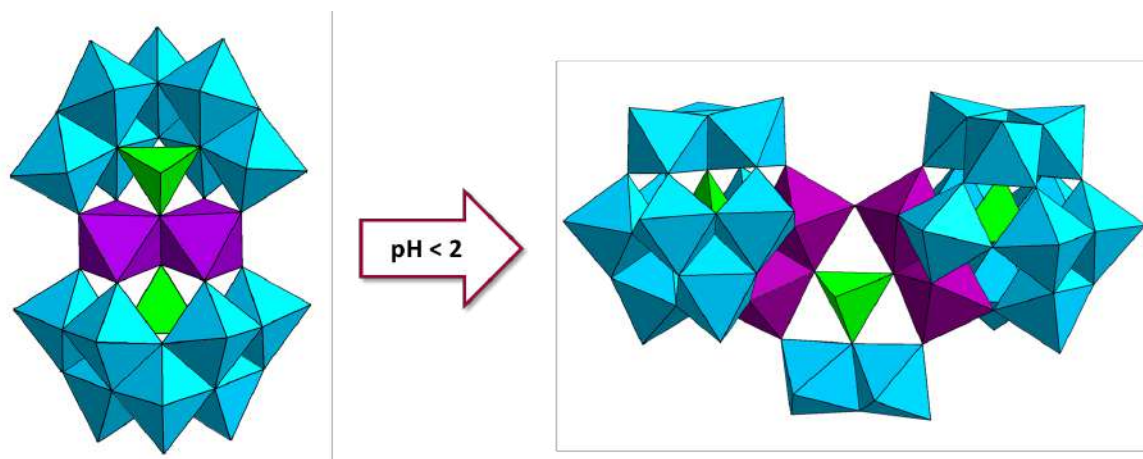
A Titanium(IV)-Containing Sandwich-Type Molybdo germanate

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Abstract

The current catalog of transition metal-substituted heteropolymolybdates is still very much underdeveloped compared to the vast number of heteropolytungstate counterparts reported to date. The new titanium(IV)-containing molybdo germanate $[\text{Ti}_2(\text{HGeMo}_7\text{O}_{28})_2]^{10-}$ has been obtained as different alkaline metal salts in moderate-to-high yield from simple one-pot synthetic procedures at mild bench conditions. Its structure comprises a central $\{\text{Ti}_2\text{O}_{10}\}$ edge-sharing fragment sandwiched between two $\{\text{MoO}_2\}$ -monocapped hexalacunary α -Keggin-type molybdo germanate moieties. This species represents the fourth example known to date of water-soluble titanium(IV)-containing heteropolymolybdates and, among those with sandwich-type structure, the first one in which the heteroatom does not show any lone pair [1]. The title anion is solution-stable at moderate acidic conditions but dismantles in solutions with pH values below 2, from which the peculiar $[\{(\text{GeMo}_{10}\text{Ti}_2\text{O}_{37})_2\text{O}\}\{\text{Mo}_2\text{O}_7(\text{OH}_2)_2\}(\text{GeO}_4)]^{12-}$ assembly comprising Ti(IV)-disubstituted Keggin subunits can be isolated [2].



Structures of $[\text{Ti}_2(\text{HGeMo}_7\text{O}_{28})_2]^{10-}$ and $[\{(\text{GeMo}_{10}\text{Ti}_2\text{O}_{37})_2\text{O}\}\{\text{Mo}_2\text{O}_7(\text{OH}_2)_2\}(\text{GeO}_4)]^{12-}$.

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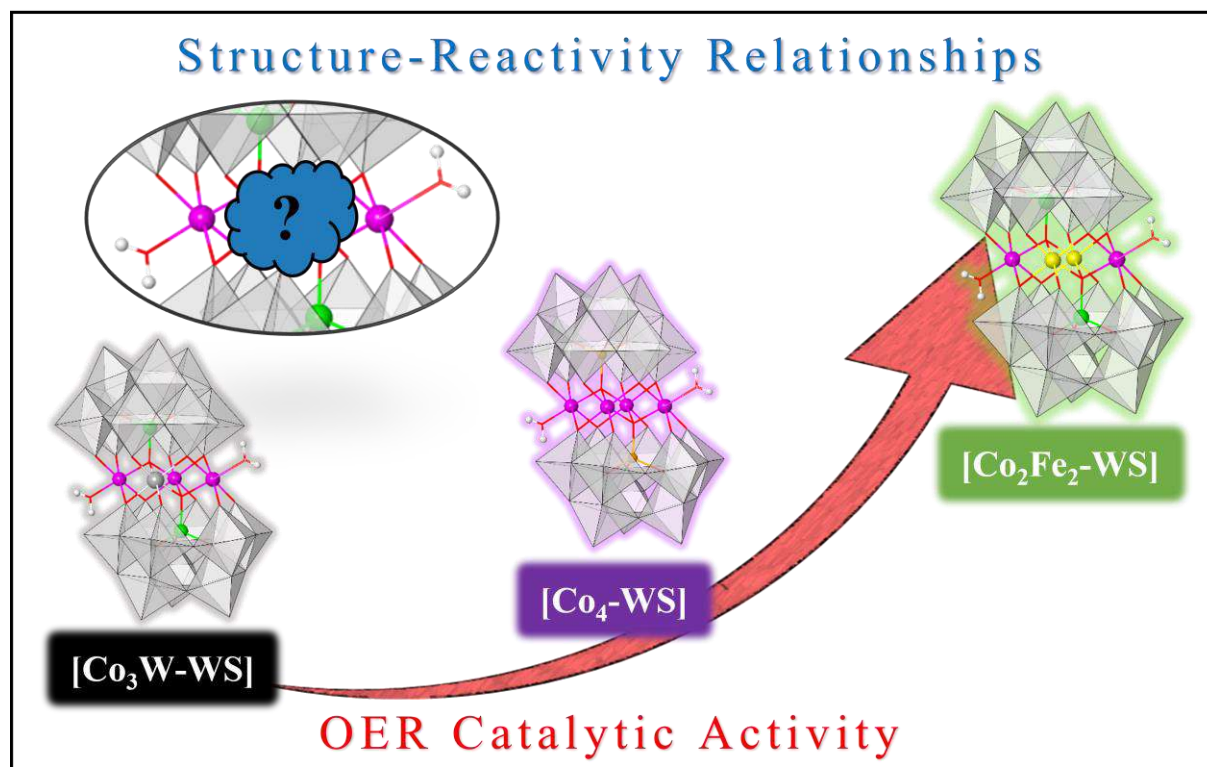
Tuning the Water Oxidation Catalytic Activity of Polyoxometalates via Molecular Engineering

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Abstract

Water is considered the ultimate energy vector from which we can obtain the necessary reducing equivalents for storing energy in the form of H₂ via the hydrogen evolution reaction (HER).[1] Within the water splitting scheme, the oxygen evolution reaction (OER) is a bottleneck that limits the development of this technology due to the high thermodynamic requirements and sluggish kinetics. Hence, the discovery of cost-effective, efficient, and durable OER catalytic materials with enhanced kinetics for oxygen production while alleviating the high energetic requirements is of utmost importance.[2] In this respect, polyoxometalates (POMs) have attracted significant interest during the last decade due to their intrinsic redox stability, synthetic molecular amenability, and processability.[3] Particularly cobalt-containing POMs (Co-POMs) are nowadays known to represent genuine molecular catalysts that display high catalytic activity and excellent stability characteristics in the solid state as part of modified working electrodes.[4] Efforts to improve the catalytic properties of Co-POMs systems through modification of their components facilitated unique insights into the mechanistic aspects that govern the water oxidation process. These structure-reactivity relationships highlight the impact of molecular modifications, leading to systems with improved performance characteristics.[5] In spite of these efforts, the relations between the POM structure and reactivity are yet to be comprehensively understood. Under this purview, it is somewhat surprising that the role of the inner, coordinatively saturated metal ions, located in the central oxo-belt of the Weakley sandwich, remains unclear; and their influence on the catalytic activity is yet to be fully understood.[6] In this talk, I will present the heterogeneous OER activity of a novel mixed-metal Co-Fe Weakley POM $[\text{Co}^{\text{II}}_2(\text{H}_2\text{O})_2\text{Fe}^{\text{III}}_2(\text{B}-\alpha\text{-Co}^{\text{II}}\text{W}_9\text{O}_{34})_2]^{14-}$ (**Co₂Fe₂-WS**). The strong influence of the coordinatively saturated metal ions in the central belt on the OER activity is demonstrated, where **Co₂Fe₂-WS** shows improved OER performance compared to that of the parent $[\text{Co}^{\text{II}}_4(\text{H}_2\text{O})_2(\text{B}-\alpha\text{-P}^{\text{V}}\text{W}_9\text{O}_{34})_2]^{10-}$ (**Co₄-WS**) system. The underlying principle is further exemplified by $[\text{Co}^{\text{II}}_2(\text{H}_2\text{O})_2\text{Co}^{\text{II}}\text{W}^{\text{VI}}(\text{B}-\alpha\text{-Co}^{\text{II}}\text{W}_9\text{O}_{34})_2]^{12-}$ (**Co₃W-WS**) containing a central W^{VI} ion and which drastically decreases the catalytic activity of the POM.



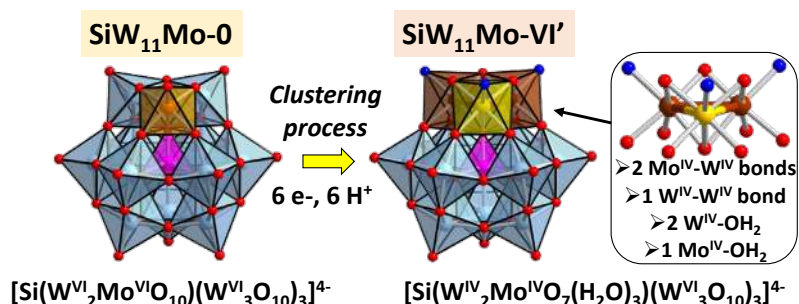
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Making Metal-Metal Bonds in Polyoxometalates by six-electron reduction process

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Abstract. Pioneering works of Launay, Hervé and Pope showed that the reduction of Keggin anions $[XW_{12}O_{40}]^{n-}$ with $X = H_2, B$ or Si can lead to six-electron reduced entities in which 5d-electrons are localized in three metal-metal bonds, forming a W^{IV} based trinuclear cluster. [1-3] Surprisingly, the chemistry of these Janus-like POMs containing an electron-rich clustered triad remains largely unexplored while these entities can be formed when POMs are used as molecular electron reservoirs in electrochemical energy-storage systems. In this communication, we will report our recent findings about the six-electron reduced POMs. First, we will present the electrochemical preparation of the first example of POM containing heterometallic metal-metal bonds between addenda centers. Its structure (see figure) has been elucidated using multinuclear NMR and X-ray diffraction studies. Then, we will show that the formation of metal-metal bonded triad in POMs is not limited to the Keggin-structure, but can be also extended to 18-tungstate hetero-polyanions. Finally, we will demonstrate that reduction-induced aquation of the POMs strongly affect their supramolecular behavior, cancelling their ability to interact with non-ionic organic moieties. This last point clearly demonstrates that superchaotropism of POMs is not only about a matter of the “shape, size and charge”.



Schematic representation showing the formation of **SiW₁₁Mo-VI'** induced by the six-electron reduction of molybdenum mono-substituted α -Keggin type silicotungstate **SiW₁₁Mo-0**.

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POM-Assisted MXenes for green sustainable energy

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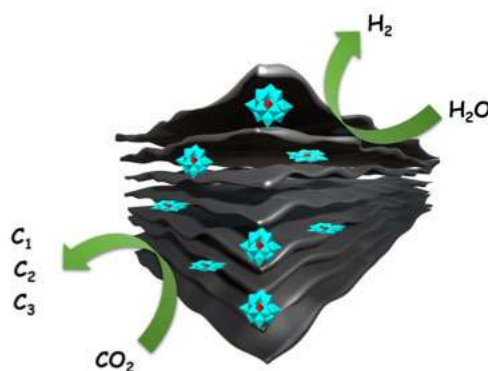
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Abstract

The need to reduce our carbon footprint has reached a critical point. This can be achieved either by switching from fossil to green fuels (H_2) or by carbon sequestration, involving both storage and utilization. As part of the utilization strategy, the photo/electrochemical reduction of CO_2 (PEC-R) is an attractive method because it not only mitigates greenhouse gas emissions but also provides CO_2 as a carbon source for generating value-added chemicals and fuels.[1] However, the use of PEC-R is currently limited because ‘state-of-the-art’ electrocatalysts lack stability, efficiency, and selectivity towards a single PEC-R product at low overpotentials. While 2D materials and their hybrids with polyoxometalates (POMs) have shown great potential in hydrogen generation and energy conversion reactions and some of them even as electrocatalysts for PEC devices, very little research has focused on POM-2D-material hybrids beyond graphene.[2, 3] We focused to synthesize novel POM-MXene hybrids as photo/electrocatalysts for hydrogen generation and CO_2 conversion. Characterization and analytical techniques have been provided a detailed understanding of the HER and CO_2 reduction mechanism and possible reaction intermediates, thereby enabling re-engineering, and thus enhancement of the photo/electrocatalyst activities.



POM-Assisted MXenes

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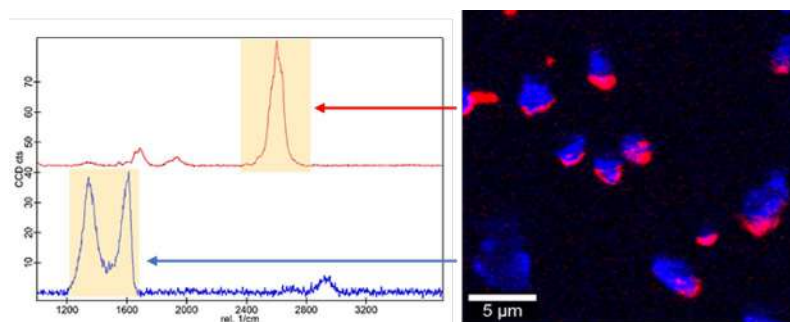
Lanthanopolyoxometalate functionalization of reduced graphene oxide mediated by surface-grafted ionic liquids

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Abstract

Polyoxometalates (POMs) show multi-advantages for photodriven applications, such as in photoluminescent materials or as photocatalysts [1]. The possibility of heterogenization without loss of properties, is a strong potential for the application of POM based nanocomposites. This work aims to prepare new nanostructured materials based on lanthanide containing polyoxometalate clusters supported in graphene. Graphene based substrates were prepared by chemical derivatisation of graphene oxide (GO), aiming to achieve a better insertion of POMs in terms of dispersion and chemical stability. The best method was by far, the functionalization of GO with an ionic liquid cation. The final substrate properties are consistent with a GO reduction in the process. Nanocomposites prepared by the insertion of $[\text{Ln}(\text{M}_5\text{O}_{18})_2]^{9-}$ ($\text{Ln} = \text{Eu}^{3+}, \text{Tb}^{3+}$; $\text{M} = \text{W}, \text{Mo}$) in the graphene based substrate (rGO-IL-LnM10 composites), show interesting luminescent properties, that depend on the graphene modification. Raman imaging and electron microscopy, show a very good distribution of POMS in the prepared substrates.



Combined Raman images and spectra of the rGO-IL-EuW10 nanocomposite.

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Acknowledgments: Maria J. Martins thanks FCT for the PhD grant (SFRH/BD/131433/2017 and COVID/BD/151933/2021). This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020, UIDP/50011/2020 & LA/P/0006/2020, financed by national funds through the FCT/MEC (PIDDAC).

Polyoxometalate molecular junctions, influence of the redox states and the counterions.

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Abstract

Polyoxometalates (POMs) are nanometric molecular oxides with remarkable redox properties that can be explored in the context of advanced molecular devices (MDs). However, the precise relationship between the electrical conductance of the MDs, the redox state and the nature of the counterions remains to be clarified.¹ Here, we demonstrate the reversible in situ photoreduction of phosphomolybdate $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ monolayer self-assembled on Au electrodes. The conductance (C-AFM measurements) is increased by ~ 10 , and the analysis of large current-voltage (I-V) datasets by unsupervised machine learning and clustering algorithms allows us to correlate this increase with the evolution of the I-V shape (symmetric vs. rectifying) and the energy of the molecular orbitals in the MDs: LUMO at 0.6-0.7 eV above ε_{F} for $\text{PMo}_{12}(\text{O})$ vs. SUMO at ~ 0.3 eV for $\text{PMo}_{12}(\text{I})$.² We also synthesized a series of Preyssler POMs $[\text{Na} \subset \text{P}_5\text{W}_{30}\text{O}_{110}]^{14-}$ stabilized with four different counterions, H^+ , K^+ , NH_4^+ and tetrabutylammonium ($\text{N}(\text{C}_4\text{H}_9)^{4+}$ or TBA^+). The low-bias conductance gradually increases over two decades with changing the counterion in the order K^+ , NH_4^+ , H^+ and TBA^+ . Albeit the LUMO of the P_5W_{30} (with respect of Au ε_{F}) increases from ~ 0.4 eV to 0.7 eV, the electrode coupling energy evolves from ~ 0.05 to 1 meV depending on the nature of the counterion in the order K^+ , NH_4^+ , H^+ and TBA^+ in correlation with the MD conductance.³ Underlying possible physical reasons will be discussed.

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³ On the role of counterions in the electron transport properties of polyoxometalate nanodevices. C. Huez, F. Volatron, A. Proust & D. Vuillaume. In preparation

The Photoactivation of Borotungstate Keggin POMs

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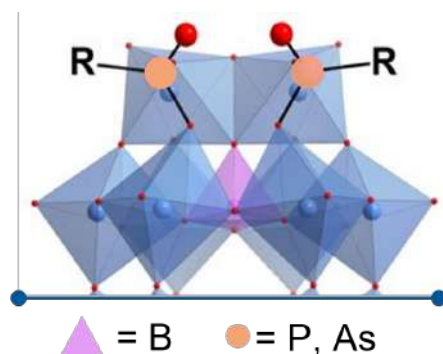
E-mail: pcynt@nottingham.ac.uk

Abstract

The design and synthesis of novel polyoxometalates (POMs) that exhibit vast compositional diversity and excellent thermal stability, while also possessing tunable physical and chemical properties, represents a significant and challenging endeavor in the field of inorganic material chemistry.¹ Through rigorous research efforts, a diverse array of POMs with potential applications in water oxidation, CO₂ reduction, and organic electro- and photocatalysis have been developed.^{2,3}

A particularly attractive feature of certain POM archetypes is the ability to modulate their properties through the incorporation of various chemical elements, thereby enabling the enhancement of functionality and the tuning of chemical properties. One such example of this is the incorporation of organic moieties through hybridization onto inorganic POM structures.⁴

Here we report on the development of a novel family of boron-centered hybrid POMs that exhibit photocatalytic activity in organic single electron transfer (SET) chemistry. The impact of organofunctionalization and hybridization on the photoactivation of these POMs will be discussed, with the performance trends being rationalized through an analysis of electronic structure, redox chemistry and photocatalytic efficiency.



Polyhedral representation of boron-centred hybrid POMs.

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Strategies for the arylimidio functionalisation of tungsten polyoxometalates

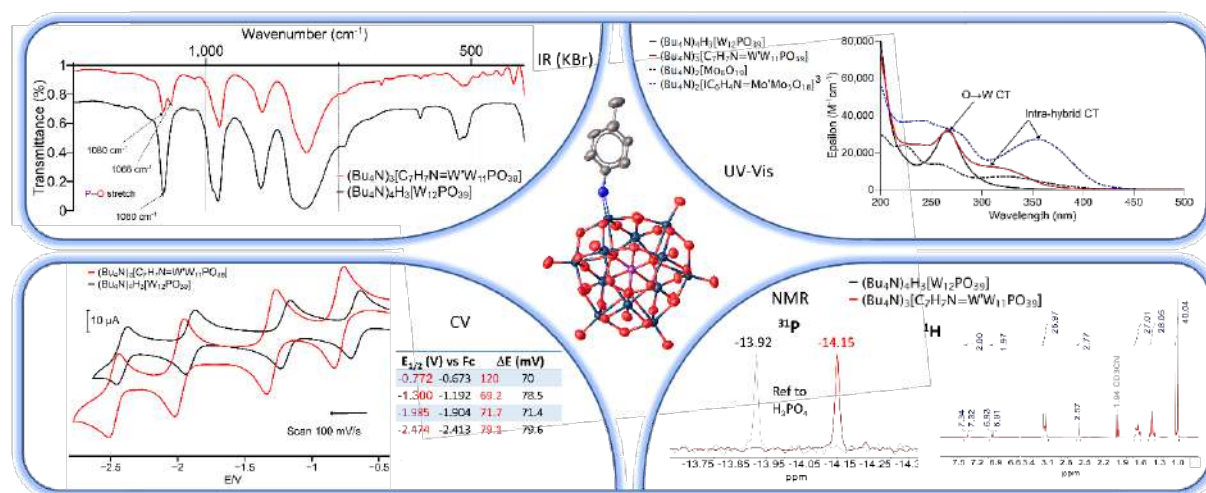
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Abstract

Arylimido functionalization of polyoxometalates gives rise to emergent properties not found in either standalone subunit, such as the non-linear optical (NLO) behaviour of arylimido-polyoxomolybdates (a-POMs) [1]. An arylimido organic group is chosen because imido functionalization achieves strong electronic communication between the POM and the organic group through the conjugated imido bond which is prerequisite for the hybrid to be a good NLO chromophore. Keggin anions are attractive targets for redox switchable NLO chromophores [2] due to their multiple stable redox states, as well as being more stable and more transparent than a-POMs.

Polyoxotungstates (POTs) (and even $\text{MoW}_5\text{O}_{19}[\text{NBu}_4]_2$) unlike hexamolybdates are very difficult to functionalise and there is no reliable synthetic route to these compounds. Here we outline the results of synthetic work addressing the problems of arylimido functionalisation of Keggin; building on the work of Duhacek and Duncan [3] who previously isolated $[\text{PW}_{12}\text{O}_{39}\text{NPh}]^{3-}$ as a cocrystal with $[\text{PW}_{12}\text{O}_{40}]^{3-}$, $[\text{PW}_{12}\text{O}_{39}\text{NTol}]^{3-}$ has been isolated, crystallised free of $[\text{PW}_{12}\text{O}_{40}]^{3-}$ and is fully characterised (see Figure). The synthesis of $[\text{PW}_{12}\text{O}_{39}\text{NC}_6\text{H}_4\text{I}]^{3-}$ and post-functionalisation by Songashira coupling will be discussed as this is the most promising route to N-donor NLO chromophores. The direct synthesis of N-donor functionalized aryl-imido W(+6) monotungstate complexes is problematic due to the nitrogen lone-pair. Results of a preliminary exploration of aryl-imido Keggin featuring alternative donor groups such as S-donors, O-donors and metal-donors will be presented.



Characterisation by IR, UV-Vis, NMR, CV and XRD of the $[\text{PW}_{12}\text{O}_{39}\text{NTol}]^{3-}$ anion

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Electrochemical investigations into non-aqueous carbon dioxide activation using metal-substituted Keggin polyoxometalates

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Abstract

Polyoxometalates (POMs) are famously tuneable allowing a wide reach of applications. Functionalisation of common structures through a variety of synthetic routes allows for easy specification of favourable properties such as size, redox capabilities, catalytic activity, and electron storage. CO₂ levels are ever-increasing, and the atmospheric level is already over 400 ppm.^[1] Therefore, its catalytic conversion is essential to the supply of renewable energy, chemicals, and the mitigation of global warming.

Previous reports demonstrate POMs facilitating electron transfer as a redox mediator in the electrocatalysis of CO₂ into reduced species.^[2] Limitations to small molecule activation via this route include requiring a catalytic species comprised of expensive or rare earth metals such as Au or Ag, or access to structures is limited by complex syntheses.^[3] Herein, we report a novel POM structure which allows the formation of reduced CO₂ products electrocatalytically via the coordination of CO₂ onto the surface of the POM studied by various methods including photoelectrocatalytic studies.

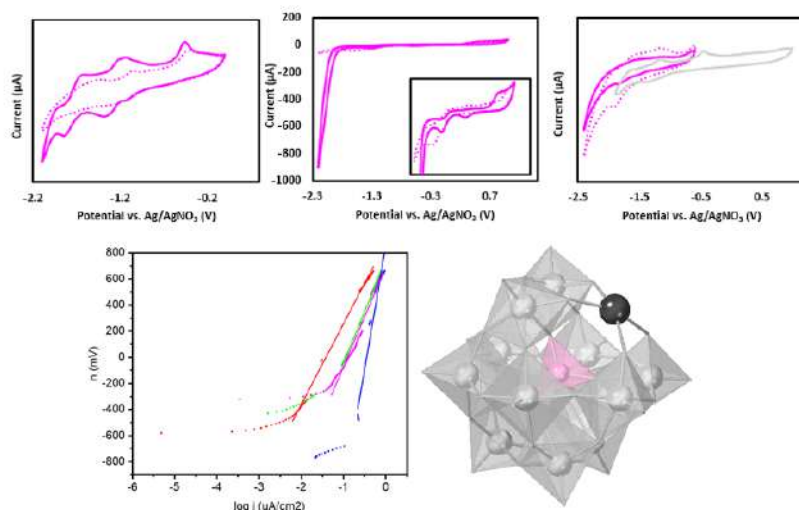


Figure 1. Electrochemical studies of a substituted Keggin POM - Pt wire counter electrode, GC working electrode, Ag/AgNO₃ reference with 0.1 M TBA PF₆ in MeCN. (a) CO₂ (solid line) argon (dotted). (b) Au W.E. (solid line), glassy carbon W.E. (dotted) all under CO₂. (c) CO₂ and glassy carbon electrode in argon (grey), under CO₂ 100 mVs⁻¹ (pink line), and under CO₂ at 200 mVs⁻¹ (pink dotted). (d) Tafel plot of Bi- (red), Sb- (green), Pb- (blue) substituted and Masa1a (magenta) POM. 3 mM concentration, 0.3M TBAP in MeCN. GC W.E., Ag/AgNO₃ R.E., and Pt wire C.E (e) lacunary Keggin POM structure where M = Bi, Sb, Pb.

The structure-activity relationship of POMs is exploited, demonstrating their ability to activate small molecules (CO₂) into desirable products to aid with low net carbon emissions. Their structures are based on a substituted lacunary Keggin structure, with varying substituents in the ‘free’ position.

Acknowledgements

Newcastle University & EPSRC, Professor Franti Hartl, Dr. Natalie Flores-Diaz, Dr Magda Pascual Borrás

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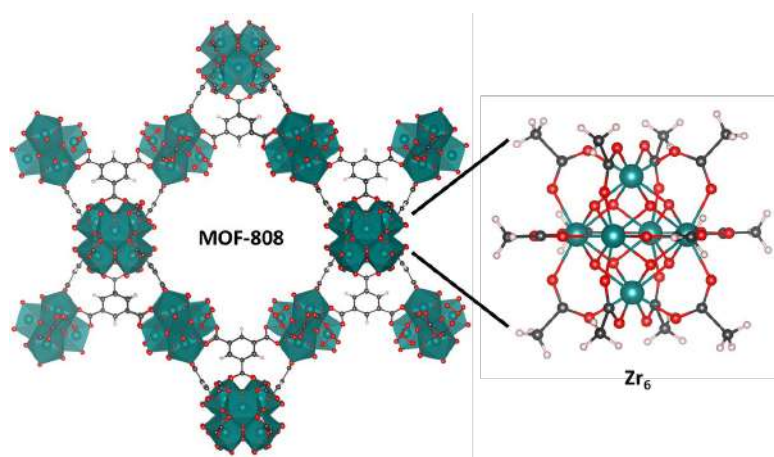
Metal-oxo clusters as new class of nanozymes toward protein hydrolysis

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Abstract

Nanozymes are nanomaterials with intrinsic enzyme-like properties, which have the ability to replace natural enzymes by mimicking their catalytically active centres. Compared to natural enzymes, nanozymes have shown unique advantages such as high catalytic activity, low cost, high stability, and tuneable activity.^[1] During the past decade, our group has developed an array of artificial metalloproteases, such as polyoxometalates (POMs) and metal-organic frameworks (MOFs) for protein hydrolysis.^[2,3] While POMs act as homogeneous catalysts, making their separation from the protein digest difficult, MOFs are heterogeneous catalysts, but adsorption of protein fragments hinders their recyclability. In this respect, Lewis-acidic metal-oxo clusters (MOCs) could offer a solution to these problems due to a tuneable solubility, small surface area, and high stability.^[4] In this study, the hydrolytic potential of $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{C}_2\text{H}_3\text{O}_2)_8(\text{H}_2\text{O})_2\text{Cl}_3$ (Zr_6)^[5], a water-soluble MOC previously used for the synthesis of MOF-808, was investigated through hydrolysis of equine skeletal muscle myoglobin, thereby providing both a comparison with the previously investigated MOF catalyst and a stepping-stone for the development of new, heterogeneous MOCs. The appearance of new fragments at lower molecular weight in sodium dodecyl sulphate-polyacrylamide gel electrophoresis (SDS-PAGE) serves as an indication to protein hydrolysis. Molecular interactions between the protein and the MOC were evaluated by different techniques including circular dichroism (CD), UV-Vis, and tryptophan fluorescence spectroscopy. Moreover, FT-IR spectroscopy, and a combination of ^1H , ^{13}C , and DOSY NMR spectroscopy were used to elucidate MOC stability under the investigated reaction conditions.



MOF-808 (left) consists of Zr_6 clusters (right) connected with trimesate organic linkers

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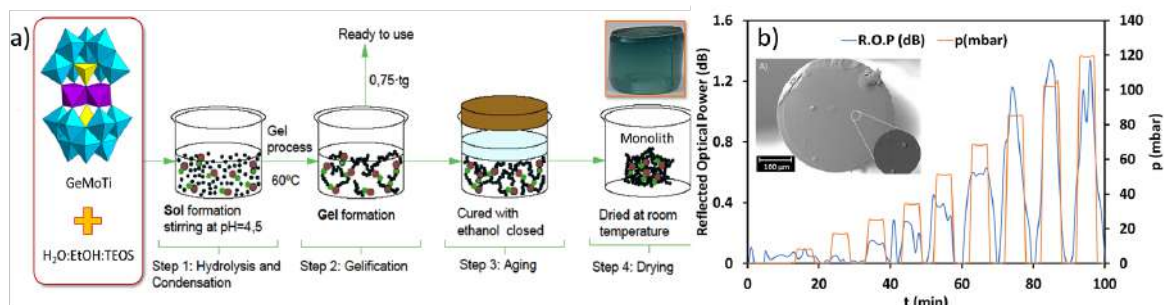
Development of Fiber Optic Chemical Sensors Based on Polyoxometalate-Doped Porous Xerogel Membranes

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Abstract

Porous siliceous xerogels show manifold properties suitable for development membrane sensing components for fiber-optic chemical sensors (FOCS), e.g. thermochemical stability, refractive index similar to that of the optical fiber, and transparency in a wide wavelength range. Their porous textures (specific surface area, average pore distribution) and surface chemistry can be precisely fine-tuned by including functional guests into the TEOS xerogel matrix (XG). This work aims at studying xerogel materials modified with embedded polyoxometalate guests (POM-XG). The novel $[\text{Ti}_2(\text{HGeMo}_7\text{O}_{28})_2]^{10}$ sandwich-type species has been incorporated into a XG matrix through a modification of literature sol-gel method^[1]. The resulting POM-XG material is transparent and photoactive, its color change from yellow to green under sunlight. The textural properties of the TEOS matrix are maintained upon POM incorporation, POM-XG being microporous with pore size centered at 1 nm ($\text{aBET}=700 \text{ m}^2\text{g}^{-1}$, $V=0.3 \text{ cm}^3\text{g}^{-1}$). The FOCS has been constructed by dip-coating and preliminary test against VOCs have afforded variations in the R.O.P signal when exposed to MetOH. Two factors could case these variations: surface VOC adsorption and changes originating from the photochromic species.



a) Synthesis of the (POM-XG) material and b) time-response of a POM-XG exposed to MetOH

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2. Financial support: MICINN-Government of Spain (project PID2020-113558RB-C42)

Polyoxometalates as electrolyte additives in Li-S batteries

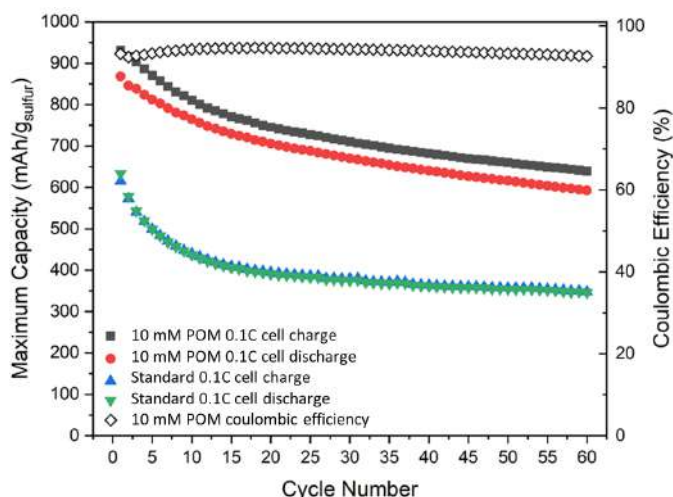
Alexander Kibler, Margaret Smith, Nathan Richardson, Darren Walsh, Lee Johnson,
Graham Newton

The GSK Carbon Neutral Laboratories for Sustainable Chemistry, School of Chemistry,
University of Nottingham, Jubilee Campus, Nottingham, NG7 2TU, U.K.

Abstract

Electrical Energy Storage (EES) systems will continue to play a crucial role in the evolution of the renewable energy landscape and the development of small-scale devices. For over 30 years, Li-ion batteries have dominated the commercial market due to their high energy density and cycling stability; however, they are approaching their theoretical cell specific energy of *ca.* 300 W h kg_{cell}⁻¹. Whilst this is sufficient for consumer electronics and short-range electric vehicles, new EES systems will be required to power larger, more energy intensive systems (*e.g.*, minimum of 500 W h kg_{pack}⁻¹ required for short-haul commercial flight).¹

Lithium-sulfur (Li-S) is one of the most promising next-generation battery technologies due to its impressive theoretical cell specific energies of 610 W h kg_{cell}⁻¹.² Unfortunately, their application has been hindered by key operational challenges due to complex polysulfide speciation in the electrolyte and terminal insulating phases generated during charge and discharge. These lead to electrode passivation, high overpotentials, low material utilization and therefore poor cycling performance. To tackle these issues, there has been a focus on electrolyte additives to improve the redox kinetics of rate-determining steps in the electrochemical pathway of these cells, either by acting as dissolved charge mediators or electrocatalysts. We present our recent findings in the utilisation of POMs as performance-enhancing electrolyte components in Li-S batteries.



Enhanced gravimetric capacity obtained from POM additive Li-S cell (10 mM) vs. standard cell over 60 cycles at 0.1C

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SYNTHESIS AND REACTIVITY OF HETEROMETAL-SUBSTITUTED LINDQVIST-TYPE POLYOXOMETALATES

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Abstract

Polyoxometalates containing one or more heterometal have been used as active components in environmentally important transformations, such as water-oxidation or carbon dioxide reduction.[1,2] Examples of such polyoxometalates are common in the literature for the more well-studied polyoxometalate structures, like those based on the Keggin or Wells-Dawson architecture.[3] However, examples based on the smaller Lindqvist unit are rarer. [4]

Herein, we describe a robust synthetic methodology for the synthesis of transition metal substituted (TBA)_n[X-MW₅O₁₈] Lindqvist-type polyoxometalates (TBA= tetrabutylammonium) (shown in **Figure 1**). We have applied a degradative reassembly approach to incorporate a variety of transition metals into the metal-oxide framework, which can act as well-defined models for catalytically active sites of extended metal oxide materials. Both the degradation and reassembly steps were probed using ¹⁷O NMR and ¹⁸³W NMR spectroscopy, giving insight into the reaction mechanism and potential intermediates.

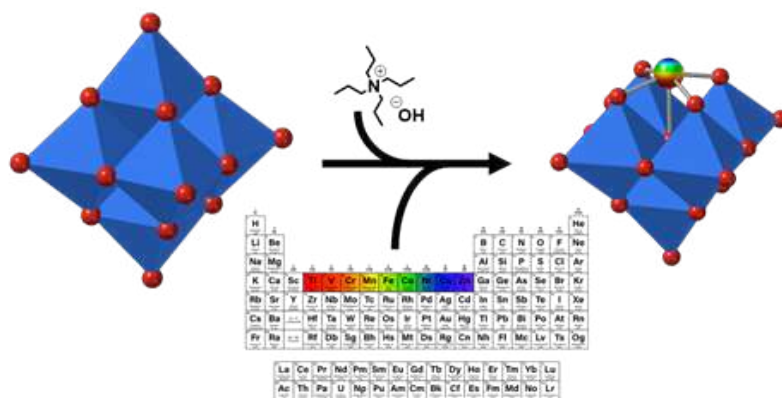


Figure 1: Synthesis of substituted Lindqvist-type polyoxometalates from hexatungstate.

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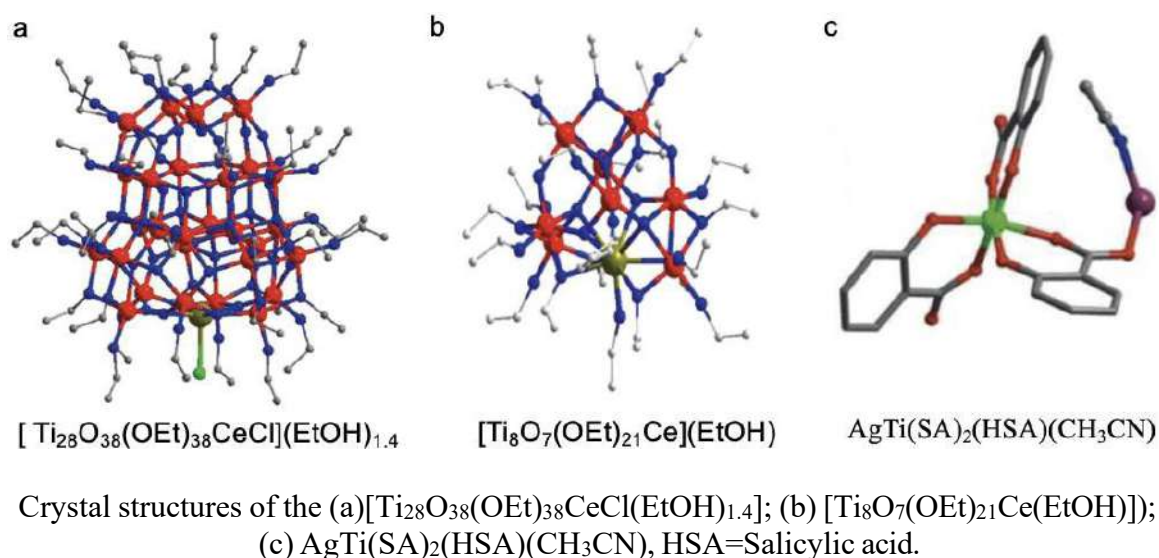
The applications of Ce and Ag doped polyoxotitanate

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Abstract

With the pursuit of higher quality drugs and food, the functionalization of their packaging materials is gradually gaining more attention. Polyoxotitanate clusters are attracting attention for their excellent performance. Novel Ce/TiO₂ were prepared based on two types of Ce(III)-doped polyoxotitanium cage ([Ti₂₈O₃₈(OEt)₃₈CeCl(EtOH)_{1.4}] and [Ti₈O₇(OEt)₂₁Ce(EtOH)]). Homogeneous CeO₂/TiO₂@PVDC/PVC film was formed from the PVDC emulsion mixed with CeO₂/TiO₂ coated on the PVC's surface. The film showed excellent UV absorption and water vapor barrier properties. Novel Ag/TiO₂ were prepared based on AgTi(SA)₂(HSA)(CH₃CN) and calcinated at different temperatures. As for the antibacterial testing of staphylococcus aureus, materials calcinated at low temperatures present highly bactericidal, destroying almost all bacteria. While high temperature significantly reduced the bactericidal ability.



Electron transfer kinetic in covalent dyads based on polyoxometalate and rhenium photosensitizer

Thomas Auvray,^{a,b} Georges Turner,^a Mirco Natali,^{c*} and Garry S. Hanan^{a*}

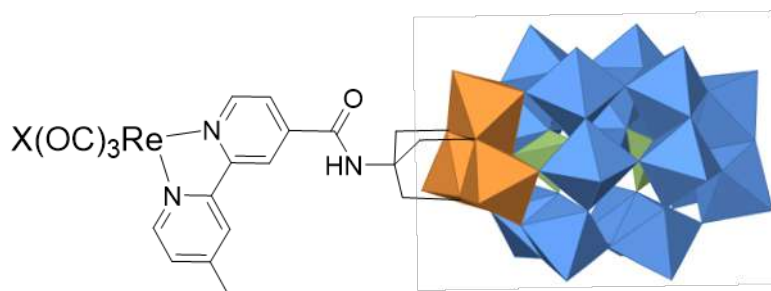
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Abstract

Covalent dyads combining Ir(III) photosensitizers (PSs) and POMs have been shown to outperformed the corresponding bimolecular system in photocatalytic hydrogen evolution both in term of activity and stability.[1,2] In this study, we applied our previously reported Re(I) complexes based on polypyridyl functionalized Dawson polyoxovanadotungstates for photocatalytic hydrogen evolution. [3,4] Opposite to the previously repoted systems, the dyads showed poor activity and are less efficient than the bimolecular systems. However, addition of a platinum co-catalyst to favour re-oxidation of the reduced POMs allows for significant enhancement of the activity which is sustained for a longer period using the dyads. The electron transfer dynamic within the dyads was investigated via transient absorption measurements revealing fast charge separation and recombination within the dyads, with the expected decrease in electron transfer rates when increasing the length of the organic bridge.



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Light-driven catalytic Water Splitting in Nanoporous Block Copolymer Membranes

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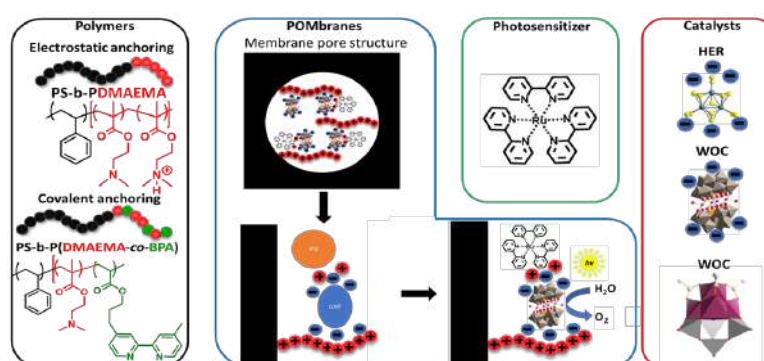
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Abstract

Sustainable energy conversion of solar radiation into chemical reactivity can be implemented by heterogeneous light-driven catalysis. Here, we will report the progress in developing hierarchically structured soft matter composites incorporating molecular light-driven catalytic units such as polyoxometalate catalysts for water oxidation catalysis (WOC) or thiomolybdate catalysts for hydrogen evolution reaction (HER) together with molecular photosensitizers (PS).^[1,2] We present different mechanisms for the immobilization of the required catalysts and photosensitizers on the membranes using the introduction of various functionalities and monomers. In general, the working principle is based on either electrostatic or covalent anchoring on asymmetrical block copolymers leading to three generations of membranes with improved stability and catalytic results from oxygen or hydrogen evolution experiments.



Overview of working principle and different anchoring techniques for catalysts and photosensitizers.

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Understanding the aqueous speciation of heteropolyoxometalates with POMSimulator: the Keggin anion

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Abstract

In recent times we introduced the POMSimulator,^[1,2,3] which is a new computer code that allows dealing with polyoxometalates systems. This new method has been applied successfully on 5 different isopolyoxometalates systems. The POMSimulator workflow is almost automatic, using graph theory as the main engine. POMSimulator also shows excellent agreement with experiments, presenting big differences between the different metals. By using this method, we also found great linear relationships between experimental and computed formation constants. In this communication, we will be presenting the new results on the Keggin anion treated by POMSimulator. As opposed to isopolyoxometalates, the introduction of a heteroatom in this program implies an exponential increase in the number of species and possible reactions. New strategies will have to be implemented in order to make simulations feasible. Otherwise, the amount of time used on calculations would grow factorially. So far, initial results show good agreement with the experimental speciation diagrams. ^[4,5,6]

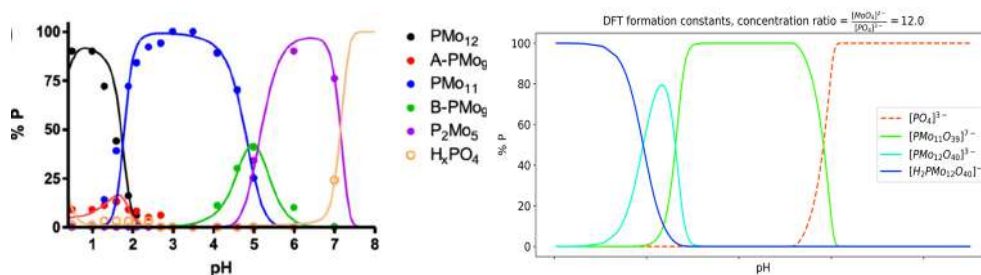


Fig 1. (Left) Experimental speciation diagram for phosphomolybdate Keggin^[4]. (Right) POMSimulator's speciation diagram for phosphomolybdate Keggin.

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– Polyoxometalate-ionic liquids (POM-ILs) and their application in tribology as lubricant additives–

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Abstract

Tribology is the branch of science and technology that deals with interacting moving surfaces, which can suffer from friction and wear. Efficient lubrication, as the main method to combat them, is therefore a key aspect for the success of many industries. Nowadays however, there is a pressing need for greener, more sustainable lubrication research, as defined by the UN sustainable goals and imposed by the current global energy crisis [1].

Optimal lubrication occurs through the efficient separation of the moving surfaces by a lubricant film. This results in the reduction of friction and wear that arise due to the contacting forces. Thoughtful formulation of the lubricating agents should lead to an optimal and targeted performance, but other key properties, such as oxidation ability, heat transfer capacity or anticorrosion properties can also be incorporated into the lubricant through the use of lubricant additives, which are chemical substances present in the lowest proportion (1-30% depending on the application).

In the field of tribology there is a growing demand for more environmentally conscious materials and waste management without a loss of performance. Highly polluting lubricant additives such as zinc dialkyldithiophosphates (ZDDPs), and many other, need to be replaced by more environmentally acceptable alternatives. Polyoxometalate based ionic liquids (POM-ILs) offer the advantage of a modular design where the cation and anion can be independently tuned through chemical design, thereby enabling the formation of multifunctional materials suitable for lubricants. The physical, rheological, and chemical properties of POM-ILs are useful for applications such as catalysis, petrochemical processing, water oxidation, and antimicrobial and anticorrosive coatings [2–4]. We believe that their properties can be used within the field of tribology.

In this work, the interaction of POM-ILs with metal surfaces has been studied to understand whether variations in the charge density and hydrophilic nature of the POM-ILs could affect their operation in a tribological setting. The selected POM-IL was a $[\text{SiW}_{11}\text{O}_{39}] [(\text{C}_6\text{H}_{13})_3(\text{C}_{14}\text{H}_{29})\text{N}]_8$, which has already shown good results as antimicrobial agent [2]. The results we have obtained so far provide an interesting starting point for further studies, and thus we would like to continue down this path, especially since the amount of literature in the field is very scarce. The results obtained so far have shown how the presence of POM-ILs in a lubricant has considerably improved the friction behavior and antiwear characteristics compared with a plain base oil (Figure 1).

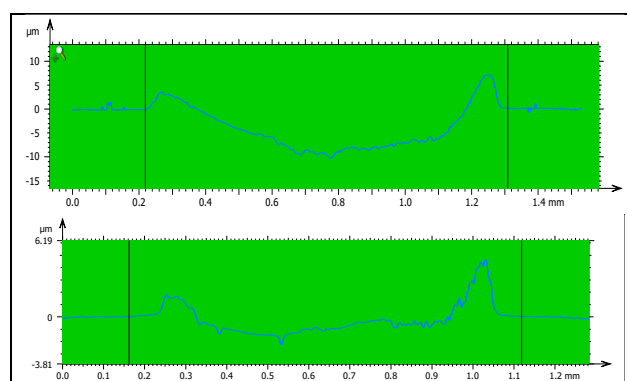


Figure 1. The wear scar was compared for both plain lubricant (top image) and lubricant with POM-IL (bottom image). Showing a reduction in wear scar depth (red area) in the case of POM-IL added lubricant.

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Mechanistic study of the photocatalytic CO₂ reduction catalyzed by Nickel-containing polyoxometalates

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While the catalytic proton reduction activity of POMs has been widely studied, there have been only scarce reports on CO₂ reduction.¹ Recently, a Ni-containing POM, $[\{\text{SiW}_9\text{Ni}_4\}_4(\text{L})_6]^{32-}$ (L= 2,5-furandicarboxylate), was reported to exhibit one of the highest CO production activities among POM catalysts.² This motivated our group to experimentally investigate the catalytic properties of a series of Ni-based POMs under photocatalytic conditions, using $[\text{Ru}(\text{bpy})_3]^{2+}$ and triethanolamine as photosensitizer and sacrificial donor, respectively. Amongst the analyzed Ni-POMs, the sandwich-type $[\text{Ni}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]^{10-}$ (Figure 1) was found to be the most active for CO₂ reduction into CO and was thus selected to investigate the reaction mechanism at an atomic level by means of DFT calculations. Interestingly, our results indicate that the protonation of the POM structure, which is favorable under the experimental conditions, is an essential requirement to allow the reduction of the POM-based catalyst and its subsequent CO₂ reduction activity. Further computational work is under way to rationalize the reactivity trends along the series of experimentally-tested POMs, which is expected to reveal the key factors that govern the catalytic activity and in turn, to prompt the rational design of more efficient CO₂ reduction catalysts.

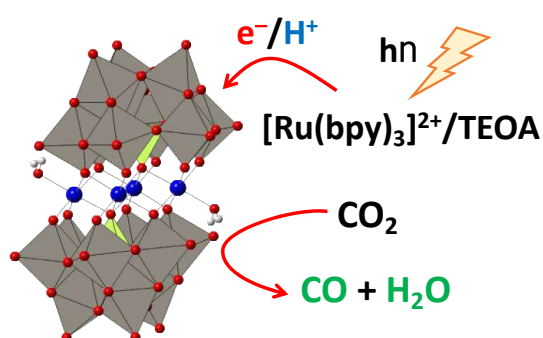


Figure 1: Schematic representation of the CO₂ photoreduction process catalyzed by $[\text{Ni}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]^{10-}$

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Notes

A versatile approach to reactive {MW₅} polyoxometalates

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Abstract

Investigations of heterometal-substituted POMs have mainly involved Keggin-type anions, due to their relative ease of handling and synthesis.[1,2] We are interested in the effects of the different coordination parameters imposed on sites within the Lindqvist structure, and our efforts to optimise the non-aqueous synthesis of substituted Lindqvist-type polyoxometalates (POMs) [MW₅O₁₈]ⁿ⁻ will be described.

Previous work in our group successfully produced cobalt-substituted Lindqvist POMs (TBA)₆[(CoW₅O₁₈H)₂] and (TBA)₃[(py)CoW₅O₁₈] via non-aqueous hydrolysis of (TBA)₂WO₄ and WO(OMe)₄. [3] A variation on the method involving base degradation of (TBA)₂[W₆O₁₉] has now led to the Mn- and Fe-substituted analogues, as confirmed by X-ray crystallography. Preliminary cyclic voltammetry experiments have been carried out on the {MnW₅} system and work is ongoing to explore access to higher oxidation state heterometals via reaction with suitable oxidizing agents. Initial results for M = Cr, Mn, Fe and Co will be reported.

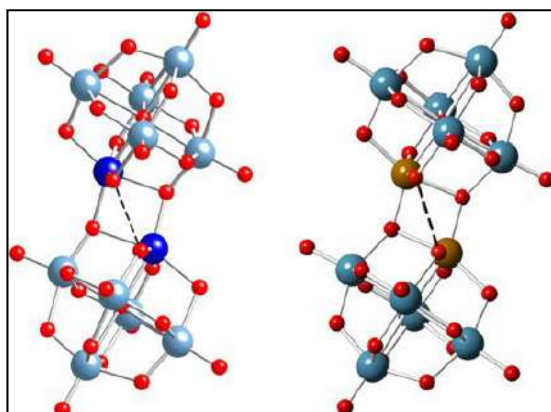


Figure 1 : Structures of [(MW₅O₁₈H)₂]⁶⁻ for M = Co (left) and Fe (right) showing hydrogen bonded interactions (dashed line).

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Selective sorption properties in a microporous POM-metalorganic hybrid that undergoes up to five transitions between single-crystalline states

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Abstract

The extended open framework $[\{\text{Cu}(\text{cyclam})\}_3(\kappa\text{-Mo}_8\text{O}_{27})] \cdot 14\text{H}_2\text{O}$ (**1**) (cyclam = 1,4,8,11-tetraazacyclotetradecane) undergoes two sequential single-crystal-to-single-crystal transformations upon thermal dehydration to afford two different anhydrous phases: $[\text{Cu}(\text{cyclam})][\{\text{Cu}(\text{cyclam})\}_2(\lambda\text{-Mo}_8\text{O}_{27})]$ (**2a**) and $[\{\text{Cu}(\text{cyclam})\}_3(\mu\text{-Mo}_8\text{O}_{27})]$ (**3a**). Solid-phase transitions imply modifications on the crystal packing, as well as the isomerization of octamolybdate anions. Compound **2a** rehydrates to yield $[\{\text{Cu}(\text{cyclam})\}_3(\kappa\text{-Mo}_8\text{O}_{27})] \cdot 13\text{H}_2\text{O}$ (**5**), whereas hydration of **3a** involves the condensation of one additional water molecule to the cluster, leading to the γ -isomer in $[\{\text{Cu}(\text{cyclam})\}_3\{\gamma\text{-Mo}_8\text{O}_{26}(\text{OH})_2\}] \cdot 11\text{H}_2\text{O}$ (**4**). The later can be fully dehydrated with no significant structural change to yield **6a**. It is worth highlighting that i) three of the octamolybdate clusters have never been observed before; and ii) up to three different microporous phases with accessible voids can be isolated from the parent compound, which in contrast to the behavior of classical MOFs, exhibit the capacity to selectively adsorb C_2H_6 over C_2H_4 . Results from water vapor sorption analyses show some of the highest uptake values reported to date for POM-based systems.

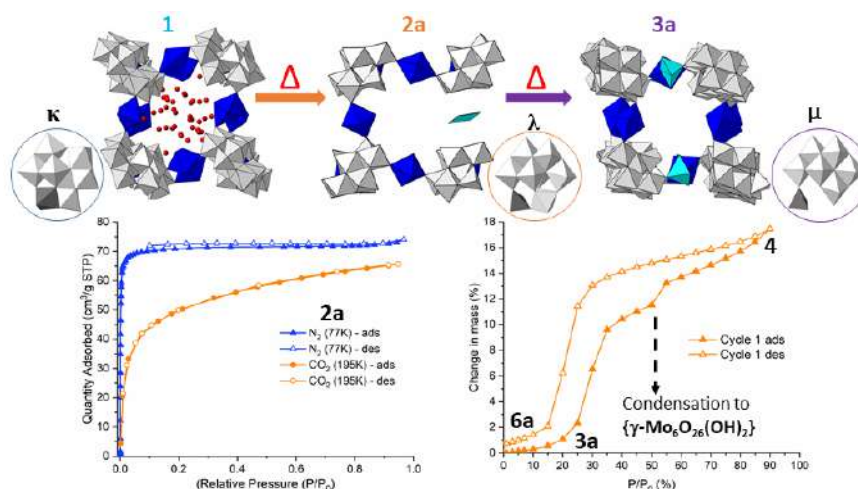


Figure 1. Schematic representation of the SCSC transformations of **1**, **2a** and **3a**, together with experimental gas sorption isotherm for **2a** and dynamic vapor sorption isotherm for **3a**.

Controlled crystallization of lanthanide-based Preyssler polyoxometalates in the presence of non-constituent additive ions

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Abstract

Preyssler polyoxometalates (POMs) containing lanthanide ions encapsulated in the cluster have shown exceptional results as single-molecule magnets and spin-qubits.^[1,2] However, the advances in this area are hindered by the size and quality of the crystals. In this work, we have studied how the presence of additive ions (*i.e.* Al^{3+} , Y^{3+} , and In^{3+}) affect the crystallization process of $\text{K}_{12}[\text{MP}_5\text{W}_{30}\text{O}_{110}]$ (where $\text{M} = \text{Gd}$ and Y). The results show that the concentration of these ions in the solution plays an important role in controlling the crystallization rate of the grown POM crystals leading to a significant increase in their size, while showing very little or no tendency to be incorporated into the structure. This has allowed us to obtain pure Gd- or Y-POM crystals, as well as diluted magnetic crystals formed by the diamagnetic Y^{3+} POM doped with the magnetic Gd^{3+} ion.

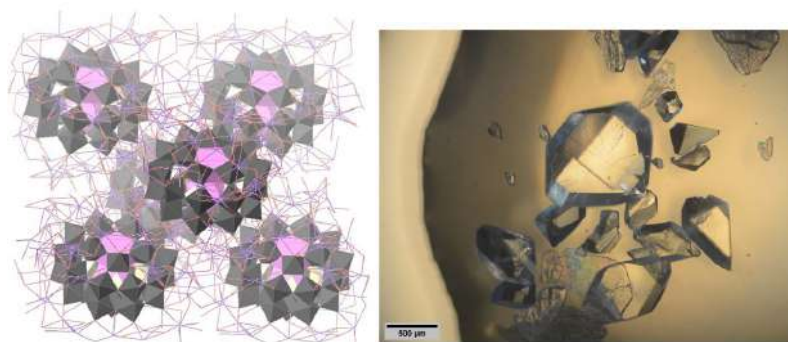


Figure: Crystal structure of $\text{K}_{12}[\text{GdP}_5\text{W}_{30}\text{O}_{110}]\cdot n\text{H}_2\text{O}$ (left). Images of YW_{30} crystals (right).

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Assessing the dynamic behavior of polyoxometalates in water solution by machine-learned reactive force fields

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Abstract

To fully understand polyoxometalate (POM) chemistry in solution is essential to identify their individual speciation profiles, assessing their protonation state, composition, and active structures at the operating experimental conditions.^[1] Atomistic modeling of these properties have relied on classical Molecular Dynamics (MD), which can't reproduce reactive events, or *ab initio* MD simulations, which are unpractical due to the high computational cost. Alternatively, reactive force field methods such as ReaxFF, are able to simulate bond forming/breaking processes at a similar computational spence to classical MD simulations.^[2] Musaev *et al.* have developed ReaxFF parameters for investigating the protonation state of niobates in water solution.^[3] Here, we extend the development of ReaxFF parameters for molybdates and tungstates in water solution, using conventional optimizers and an in-house implemented machine learning method, the Genetic Algorithm and Artificial Neural Network hybrid method (GA-ANN)^[4]. The developed force field has been applied to a varied set of structures (Mo₆, Mo₇, Mo₃₂, Mo₁₃₂) to further understand their properties at atomistic level.

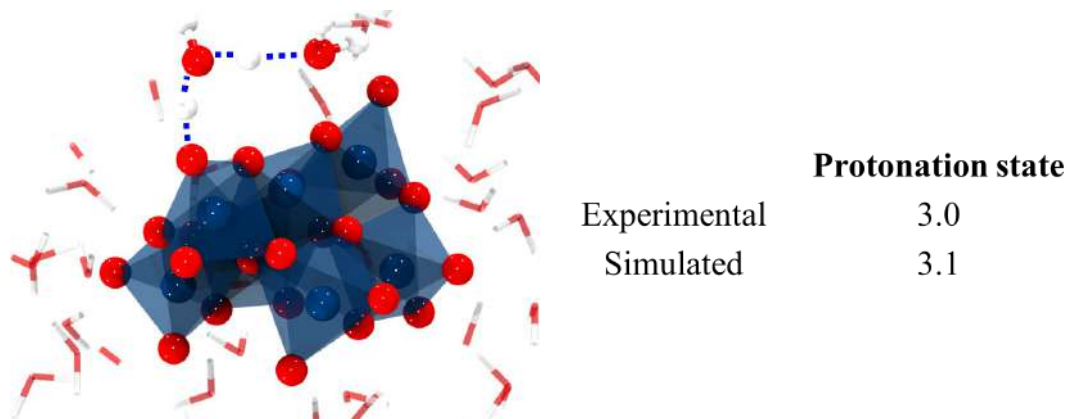


Figure 1. ReaxFF MD simulation of H₆[Mo₇O₂₄] in a water solution, snapshot illustrating a proton transfer process.

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Diarylethene-polyoxometalate coordination complex: visible light-driven "on"/"off" photochromism

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Here, we report the photochromic polyoxometalate (POM)-based diarylethene (DAE, also written DTE) coordination complex [1]. The metastable trilacunary heteropolyoxomolybdate $[\text{PMo}_9\text{O}_{31}(\text{py})_3]^{3-}$ - $\{\text{PMo}_9\}$; py = pyridine) and the ditopic pyridyl-containing dithienylethene ($\text{C}_{25}\text{H}_{16}\text{N}_2\text{F}_6\text{S}_2$) self-assemble *via* a facile ligand replacement methodology allowed us to form the photo-active capsule $[(\text{PMo}_9\text{O}_{31})_2(\text{DAE})_3]^{6-}$ (Fig. 1) [2-3]. Electrocyclisation of the three DAEs occurs sequentially and has been investigated using a combination of steady-state and time-resolved spectroscopies with the discovery of a photochemical cascade whereby rapid photoinduced ring closure is followed by electron transfer from the ring-closed DAE to the POM in the latent donor-acceptor system on subsequent excitation. This interpretation is also

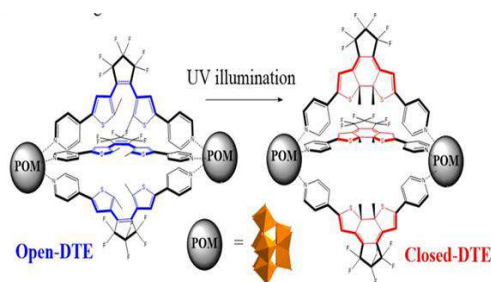


Figure 1. Photo-active DAE-POM capsule.

supported by computational and detailed (spectro)electrochemical analysis. Ring-closing quantum yields were also determined using a custom quantum yield determination setup (QYDS), providing insight into the impact of POM coordination on these processes. The effect of the complex environment on DAE photochromism was

also investigated. Additionally, we would modified the ET path length between POM and DAE subunits in order to modulate the electrocyclisation efficiency. Overall, this work extends our understanding of the synthesis and characterization of DAE-POM photosensitive complex and their potential applications, allowing us to better understand the electron transfer required for homogeneous photocatalysis.

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Understanding polyoxometalates as water oxidation catalysts through iron vs. cobalt reactivity

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Abstract

Cobalt polyoxometalates (Co-POMs) have emerged as promising water oxidation catalysts (WOCs), with the added advantage of their molecular nature despite being metal oxide fragments.¹⁻² In comparison with metal oxides, that do not offer well-defined active surfaces, POMs have a controlled, discrete structure that allows for precise correlations between experiment and computational analyses. Thus, beyond highly active WOCs, POMs are also model systems to gain deeper mechanistic understanding on the oxygen evolution reaction (OER). The tetracobalt Weakley sandwich $[\text{Co}^{\text{II}}_4(\text{H}_2\text{O})_2(\text{B}-\alpha\text{-PW}_9\text{O}_{34})_2]^{10-}$ (**Co4-WS**) has been one of the most extensively studied.³ We have compared its activity with that of the iron analogue $[\text{Fe}^{\text{III}}_4(\text{H}_2\text{O})_2(\text{B}-\alpha\text{-PW}_9\text{O}_{34})_2]^{6-}$ (**Fe4-WS**) looking for the electronic effects determining their activity. Furthermore, the effect of POM nuclearity was also investigated by comparison with the iron- and cobalt-monosubstituted Keggin clusters.

Electrocatalytic experiments employing solid state electrodes containing the POMs and the corresponding computational calculations demonstrate that Co^{II} -POMs display better WOC activity than the Fe^{III} derivatives. In good agreement with the experimental data, computational methods, including pK_a values, confirm that the resting state for Fe-POMs in neutral media corresponds to the **S**₁ ($\text{Fe}^{\text{III}}\text{-OH}$) species. Overall, the proposed reaction mechanism for **Fe4-WS** is analogous to that found for **Co4-WS**, despite their electronic differences. The potential limiting step is a proton-coupled electron transfer event yielding the active **S**₂ ($\text{Fe}^{\text{IV}}\text{=O}$) species, which receives a water nucleophilic attack to form the O–O bond. The latter has activation energies slightly higher than those computed for the Co-POMs, in good agreement with experimental observations. These results provide new insights for the accurate understanding of the structure–reactivity relationships of polyoxometalates in particular, and of metal oxides in general, which are of utmost importance for the development of new bottom-up synthetic approaches to design efficient, robust and non-expensive earth-abundant water oxidation catalysts.⁴

¹ J. Soriano, S. Goberna, L. Vigara, J. J. Carbó, J. M. Poble and J. R. Galán-Mascarós, *Inorg. Chem.*, **2013**, 52, 4753–4755

² M. Blasco, J. Soriano, J. J. Carbó, J. M. Poble and J. R. Galán-Mascarós, *Nat. Chem.*, **2017**, 10, 24

³ J. Soriano, D. G. Musaev, C. L. Hill, J. R. Galán-Mascarós, J. J. Carbó and J. M. Poble, *J. Catal.*, 2017, 350, 56–63

⁴ K. Azmani, M. Besora, J. Soriano, M. Landolsi, A. Teillout, P. Oliveira, I. M. Mbomekallé, J. M. Poble, J. R. Galán-Mascarós, *Chem. Sci.*, **2021**, 12, 8755–8766

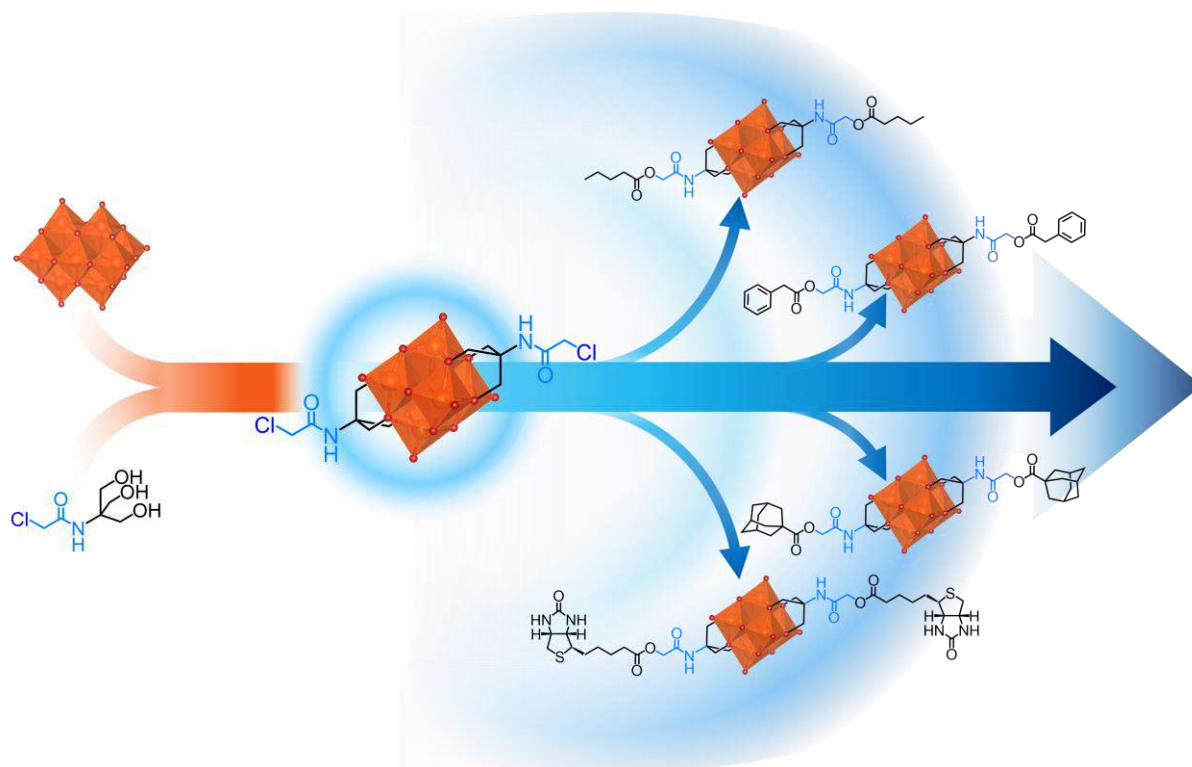
Rational Synthesis of Elusive Organic-Inorganic Hybrid Metal-oxo Clusters: Formation and Post-functionalization of Hexavanadates

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Abstract

Organic-inorganic hybrid compounds can help pave the way towards novel functional materials by being able to combine the properties of organic and inorganic components.¹ Attaching organic moieties onto hybrid metal-oxo nanoclusters are of special importance due to the possibilities that this opens in the fields of materials science, catalysis, and energy storage.²⁻⁴ The Lindqvist hexavanadate family of clusters ($[\text{V}_6\text{O}_{13}\{(\text{OCH}_2)_3\text{C-R}\}_2]^{2-}$; $\text{V}_6\text{-R}$) is particularly interesting due to the magnetic, redox, and catalytic properties that it exhibits.⁵⁻⁷ However, compared to other metal-oxo cluster types it has been less extensively explored due to poorly understood synthesis mechanism and the limited number of viable methods of post-functionalization.⁸ Considering this, an in-depth investigation of the factors that influence the formation hybrid hexavanadates ($\text{V}_6\text{-R}$ HPOMs) was conducted and the acquired knowledge was employed to develop $[\text{V}_6\text{O}_{13}\{(\text{OCH}_2)_3\text{CNHCOCH}_2\text{Cl}\}_2]^{2-}$ (**V₆-Cl**) as a new and tunable platform for the formation of complex hybrid structures based on metal-oxo clusters in high yields. Moreover, **V₆-Cl** platform was derivitized via nucleophilic substitution with various carboxylic acids of differing complexity to showcase its versatility and potential in the fields of supramolecular chemistry and biochemistry.



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Nitrogen Reduction to Ammonia Catalyzed by an Ironoxotungstate Promoted by an Alkali Metal Cation

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Abstract

Electrocatalytic ammonia synthesis is key for decentralization of the process and lowering the CO₂ emission ensuing from industrial ammonia synthesis. Recent advances on N₂ electrochemical reduction to NH₃ via the lithium mediated approach have shown some promising results, in spite of these advances the reaction still requires quite negative potentials, anhydrous conditions, alcohols as proton/electron donor and fairly rare lithium. While organometallic electrocatalysts using redox mediators have hardly been reported. Here, we present an alternative approach for N₂ to NH₃ electrocatalytic reduction at a metal cathode, using a soluble inorganic molecular catalyst and H₂O as proton/electron donor. The catalyst is a tri-iron substituted polyoxotungstate, {SiFe₃W₉} that in the presence of either Li⁺ or Na⁺ cations as promoters can reduce N₂ to NH₃. The alkali metal interaction with {SiFe₃W₉} was investigated using a combination of spectroscopic tools and theoretical means, the alkali metal cation was shown to enable, through decrease of the redox potential of {SiFe₃W₉}, the activation of N₂ at under ambient conditions. Controlled potential electrolysis experiments carried out with highly purified ¹⁴N₂ and ¹⁵N₂ ruled out NH₃ formation from contaminants. Importantly using Na⁺ cations, polyethylene glycol as solvent, the anodic oxidation of water can be used as proton and electron donor for the formation of NH₃. In an undivided electrolyzer, NH₃ formation rates were at up to 1.15 nmol sec⁻¹ cm⁻² with faradaic efficiencies of ~25%.

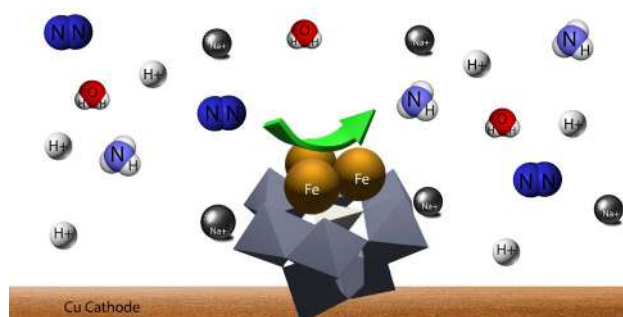


Figure 1. Schematic presentation of sustainable electrosynthesis of NH₃ from H₂O and N₂ using {SiFe₃W₉} as electrocatalyst and an alkali cation - Na⁺ as promotor.

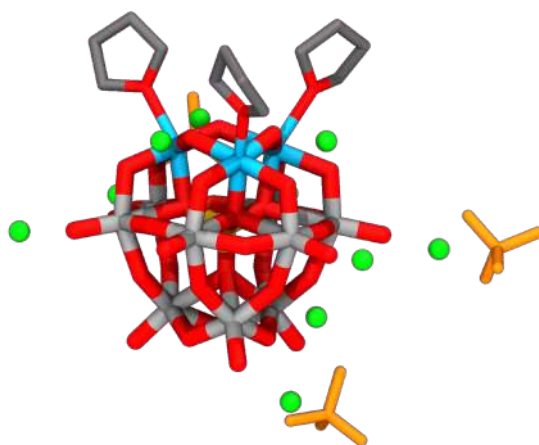
The magic role of lithium cations. Deeper understanding of alkali aggregation in electrocatalytic reduction of dinitrogen assisted by a tri-iron Keggin-type polyoxotungstate

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Abstract

The Haber-Bosch process, which now accounts for the majority of ammonia synthesis, is energetically demanding and a large contributor to CO₂ emissions. Recently, Prof. Ronny Neumann's group has synthesized an inorganic molecular catalyst, {SiFe₃W₉} which, by means of alkaline ions (Li⁺ or Na⁺), is capable of reducing at low potentials and activating N₂ under ambient conditions. Here, using Molecular Dynamics and DFT calculations, we demonstrate the impact of Li⁺ cations on the electronic structure of {SiFe₃W₉}, the need for them to activate N₂, and why they should be accounted for in theoretical calculations to reproduce electrochemical behavior of polyoxometalates.¹



Representative snapshots of the coordination sphere of {Fe₃W₉}. Three THF molecules remained at an average distance of 2.35 Å (2.13 Å upon DFT optimization). Light blue: Fe; red: O; blue: N; gray: W; silver: C; ClO₄⁻: orange and green: Li.

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Recent Developments in Peroxo-Cerium(IV)-Containing Polyoxometalates

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Peroxo-containing polyoxometalates (POMs) are attractive for applications in oxidation catalysis. This area was initiated in 1985 with the discovery of the so-called Venturello ion $[\text{PO}_4(\text{WO}(\text{O}_2)_2)_4]^{3-}$ and the following studies of its associated catalytic properties, in particular for the homogeneous epoxidation of olefins.^[1] In 2019 the first peroxo-cerium(IV)-containing polyanion, $[\text{Ce}^{\text{IV}}_6(\text{O}_2)_9(\text{GeW}_{10}\text{O}_{37})_3]^{24-}$, was prepared and used as a recyclable homogeneous oxidation catalyst.^[2] Here we present some recent developments in this area, including synthesis, structural and catalytic studies.

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Mixed Noble Metal-Oxo Clusters: Platinum(IV)-Gold(III) Oxoanion

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In 2004, the first discrete polyoxoplatinate(III) $[\text{Pt}^{\text{III}}_{12}\text{O}_8(\text{SO}_4)_{12}]^{4-}$ was reported which is composed of six dumbbell-shaped metal-metal bonded Pt^{III}_2 dimers coordinated by oxo and sulfato bridges.^[1] In 2010, the first discrete polyoxoaurate $[\text{Au}^{\text{III}}_4\text{As}_4\text{O}_{20}]^{8-}$ was prepared, comprising a bowl-shaped structure with four square-planar coordinated Au^{III} ions capped by four arsenato groups.^[2] Two years later the selenito-analogue $[\text{Au}^{\text{III}}_4\text{Se}_4\text{O}_{16}]^{4-}$ was prepared.^[3] Very recently, the polythioplantate(II) $[\text{Pt}_3\text{S}_2(\text{SO}_3)_6]^{10-}$ was discovered and its solution and catalytic properties evaluated.^[4]

Here we present the first discrete mixed platinum(IV)-gold(III) oxoanion and its structural characterization in the solid state, in solution and in the gas phase.

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Design and synthesis of Keplerates as inorganic enzymes and photoelectrocatalytic application to the Hydrogen Evolution Reaction

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Abstract

The synthesis or activation of small molecules such as O₂, NH₃, CO or H₂ is a determining issue at the heart of the great challenges posed to catalysis for the decades to come¹. If solutions may already exist, they often come at a high energetic cost, trigger waste and generate pollution. Though, millions of years of evolution have resulted in the development of enzymes that, in numerous cases, fantastically execute some of the reactions that chemists attempt at reproducing in the bulk solution. Why not rely exclusively on those catalysts to perform these tasks then ? Stability, reaction conditions, purification ; enzymes are not perfect, and these are a few examples of the bones of contention that come up, pushing us to seek and develop alternative chemical solutions. In our works, a spotlight is therefore put on the Hydrogen Evolution Reaction (HER), catalysed by a Keplerate-type polyoxometallate². The inorganic catalyst is specifically tailored towards HER by prior understanding of the key-features of (de)hydrogenase enzymes³. Hence the ‘inorganic enzyme’ label affixed onto this project. Presenting an internal cavity comparable to the active site, itself covered with thiol-terminated interior ligands and able to host Ni and Fe cation guests ; all the pre-requisites for the HER are gathered in one spot. Going farther, the use of appropriate light irradiation and applied potential in the framework of a 3 h constant potential electrolysis (CPE) allow to improve the catalytic profile of the system in terms of faradaic efficiency (FE), turnover number (TON) and turnover frequency (TOF). The Ni_nFe_m@Keplerate ($n, m \in \mathbb{N}$; $n+m \leq 10$) even allows to go past the 100 % FE threshold relative to the electrons supplied by the potentiostat. Enabled by a unique molecular architecture, these excellent results push us to envision multiple future outcomes for our ultra-modular system, whose preparation and features are entirely novel and will soon be the object of a publication.

¹ Burrows, C. J., Holy Grails in Chemistry, Part II. *Acc. Chem. Res.* **2017**, 50, 3, 445

² Müller, A.; Krickemeyer, E.; Bögge, H.; Schmidtman, M.; Peters, F. Organizational Forms of Matter: An Inorganic Super Fullerene and Keplerate Based on Molybdenum Oxide. *Angew. Chemie Int. Ed.* **1998**, 37 (24), 3359–3363.

³ Wolfgang Lubitz, Hideaki Ogata, Olaf Rüdiger, and Edward Reijerse, *Chem. Rev.* **2014**, 114, 8, 4081–4148

A New Class of Hybrid Diphosphoryl Polyoxometalate: Versatile Platforms for Structural and Electronic Optimization

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Abstract

The synthesis and characterization of a new class of hybrid polyoxometalate (POM) Wells-Dawson phosphotungstates of the general formula $[P_2W_{17}O_{61}(P_2O_2X)]^{6-}$ ($X = O, NH, \text{ or } CR_2$) will be discussed. Modifying the bridging unit X was found to impact the redox potentials of the POM. Notably, diphosphonate hybrid POMs ($X = CR_2$) offer further access to a range of pendant functionalized molecules that can be installed using the synthetical versatile diphosphonic acid precursor thereby enabling opportunities to explore new chemical space. Compared to existing monophosphonate ($RP=O$) hybrid Wells-Dawson POMs, diphosphoryl clusters offer a wider tunable redox window and enhanced hydrolytic stability. This study provides the basis for the rational design and synthesis of next-generation hybrid Wells-Dawson phosphotungstates.

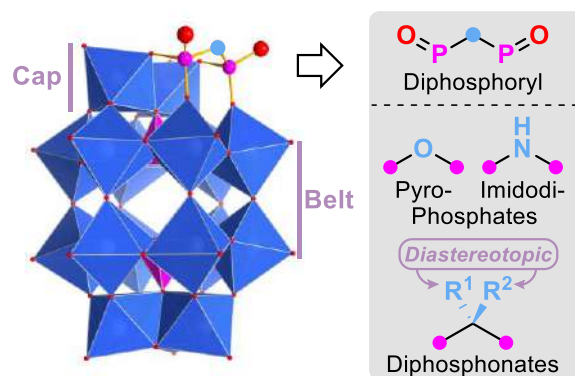


Figure 1. Class II hybrid diphosphoryl Wells–Dawson phosphotungstates. Molecule colour code: blue polyhedra = (WO₆), pink polyhedra = (PO₄), red spheres = O, pink spheres = P.

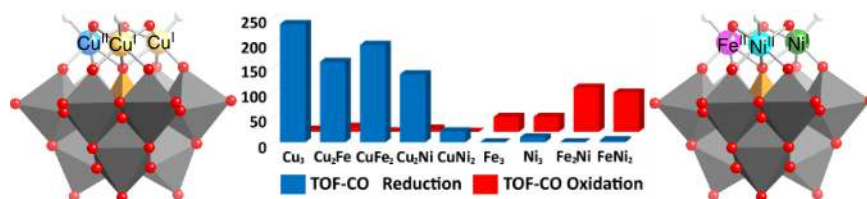
Molecular Transition Metal Oxide Electrocatalysts for the Reversible Carbon Dioxide-Carbon Monoxide Transformation¹

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It is known that the greenhouse effect is highly influenced by the concentration of CO₂ in the atmosphere. The sources of CO₂ are: power generation, public electricity and heat production from fossil fuel combustion. Previous research shows different ways to reduce CO₂ emission into the atmosphere, by reduction of the amount of CO₂ produced, use of CO₂, and storage of CO₂. Carbon monoxide dehydrogenase (CODH) enzymes are active for the reversible CO oxidation – CO₂ reduction reaction and are of interest in the context of CO₂ abatement and carbon neutral solar fuels. Bioinspired by the active site composition of the CODH's, polyoxometalates triply substituted with first row transition metals, were modularly synthesized. The polyanions, in short, {SiM₃W₉} and {SiM'₂M''W₉}, M, M', M'' = Cu(II), Ni(II), Fe(III) are shown to be electrocatalysts for reversible CO oxidation – CO₂ reduction. A catalytic Tafel plot showed that {SiCu₃W₉} was the most reactive for CO₂ reduction, and electrolysis reactions yielded significant amounts of CO with 98% faradaic efficiency. In contrast, Fe-Ni compounds such as {SiFeNi₂W₉} preferably catalyzed the oxidation of CO to CO₂ similar to what is observed for the [NiFe]-CODH enzyme. Compositional control of the heterometal complexes, now and in the future leads to control of reactivity and selectivity for CO₂ electrocatalytic reduction.



Reference:

[1] Azaiza-Dabbah, D.; Vogt, C.; Wang, F.; Masip-Sánchez, A.; de Graaf, C.; M. Poblet, J.; Haviv, E.; Neumann, R. *Angewandte Chemie*, **2021**.