



POM-BASICS :
Summer School in

“Polyoxometalates Chemistry for Fundamentals and Applications”

13th-15th June 2022



BOOK of Abstract

Spotlight and poster (alphabetical order)

- 1- Frédéric Avignon, “Hybrids cobalt based polyoxometalates and g-C₃N₄ for the catalytic oxydation of water into dioxygene”, Université Paris Cité (France)
- 2- Emilie Gérrouville Southampton, “Polyoxometalate-based Nanoscale Electronic Devices”, University of Southampton (UK)
- 3- Claire Jones, “Strategies for the arylimidio functionalisation of tungsten polyoxometalates”, University of east Anglia (UK)
- 4- Alisa Ranscht, “ Building Porous Organic Polymers from self-assembled Polyoxometalate – Cation systems”, Univesity Claude Bernard (Lyon, France)
- 5- Nada D. Savic, “Tuning the Proteolytic Activity of Metal Substituted Polyoxometalates by Surfactants Solutions”, KU Leuven (Belgium)
- 6- Jake A. Thompson, “Structural and Electronic Properties of Mono-Substituted Polyoxotungstates”, University of Glasgow (UK)

**“Polyoxometalates Chemistry for
Fundamentals and Applications”**

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Poster (alphabetical order):

- 7- Jordi Buils, “ On the use of the POMsimulator to understand the formation mechanism of metal oxide nanoclusters: the Keggin anion”, ICIQ, Universtat Rovira i Virgili, Tarragonan, (Spain)
- 8- Jake Castle, “Water Oxidation Electrocatalysis Using POM/CNT Hybrid Materials”, Nottingham (UK)
- 9- Zengfan Chen, “ The Application of Sulfate-templated Dawson-type Polyoxometalate in the Non-aqueous Redox Flow Battery”, University of Mainz (Germany).
- 10- Kieran Jones, “The Synthesis & Post-modification of Class II Organic-Inorganic Hybrid Heteropolyoxometalates”, Jubilee Campus, Nottingham, (UK)
- 11- Daniel Macolm, “Computationally based Predictions of New POM Species”, University of Glasgow (UK)
- 12- David Salazar, “Design and Synthesis of Mixed Polyoxometalate Hybrid Structures via a Modular Post-Functionalisation Strategy”, KU-Leuven (Belgium).
- 13- Nicole Tsang “Heteropolyoxometalates as Photocatalysts for Organic Synthesis”, Jubilee Campus, Nottingham (UK).
- 14- Jingjing Wang, “Investigation towards photoactive covalent hybrids based on (iso)porphyrin polyoxometalate assemblies”, University of Strasbourg (France).
- 15- Fangshun Yang, “Soft-Landed Host-Guest Complexes of Cyclodextrins and Polyoxovanadates as Single Molecule Memory Units on Surfaces” Leibniz-Institut (Germany).
- 16- Yulin Zhou, “Differential electrochemical mass spectrometry studies of nitrite reduction catalyzed by Keggin polyoxometalates” Universté de Stasbourg (France).



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Hybrids cobalt based polyoxometalates and g-C₃N₄ for the catalytic oxydation of water into dioxygene

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With the continuous intensification of human activities, the global energy consumption raised significantly for some years. Thus, providing more and more energy, mostly coming from fossil fuels, leads to the emission of greenhouse gases (mainly carbon dioxide) and to global warming. Dihydrogen showed to be a good alternative to fossil fuel, it is an energetic vector that could come from green processes. For instance, water can electrochemically be splitted into dioxygen and dihydrogen.

The oxidation process is more challenging due to requirement of high potentials and the simultaneous exchange of 4 electrons. The best catalysts for this process are noble metal oxides (RuO₂, IrO₂...) ¹ but they are expensive and rare. The challenge is to develop materials based on transition metal like cobalt, iron, nickel, with good efficiency and high stability. This process can be light-assisted with the use of semiconductors. One of the most used is TiO₂ which band gap is around 3.2 eV, unable to absorb visible light. So new materials able to use visible light must be developed. For example, C₃N₄ is a carbon-based semiconductor with 2.7 eV band gap ².

Here we show the positive effect of carbon nitride (C₃N₄), on the catalytic activity of a cobalt-based polyoxometalate (Co-POM) for electrocatalytic water splitting. Electrocatalysis of water is carried out at neutral pH. Carbon nitride alone shows no activity toward water splitting. In presence of Co-POM, the current obtained is much higher, showing a positive effect when associated to Co-POM (Fig.1). Moreover, experiments were done with light irradiation, using UV filter. Cyclic voltammetry shows that currents increase when irradiated, suggesting an electronic transfer under irradiation (Fig.2).

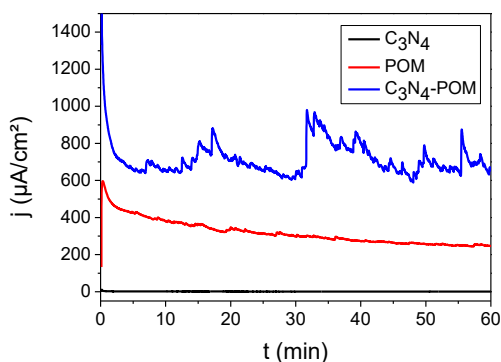


Figure 2. Chronoamperometry performed at 1.2 V vs ECS in a pH 7.2 KPi buffer, with carbon paste electrodes : 5%C₃N₄-14%POM

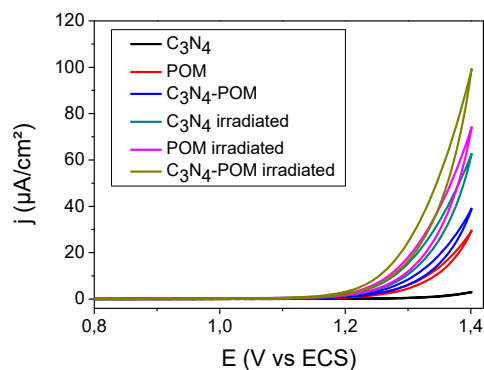
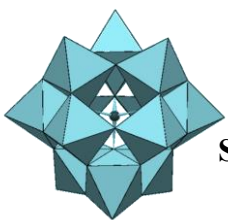


Figure 1. Cyclic voltammetry performed in a 7.2 KPi buffer on ITO with Nafion ink : 5%C₃N₄-14%POM

Association of C₃N₄ with Co-POM provides a green process toward water splitting, using the visible part of solar light, which is the principal limitation for the photo-catalytic process.

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Polyoxometalate-based Nanoscale Electronic Devices

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Polyoxometalates (POMs) are a class of inorganic, ionic (usually anionic), nanometer-sized molecular oxide compounds. They present many attractive inherent properties, such as chemical stability in temperatures ranging from -150°C to 320°C, ease of processing using non-toxic water-based solvents, chemical diversity (many possible structures through functionalisation), and ability to exchange reversibly multiple electrons without much structural change (rich redox properties)¹. POMs can therefore be used to create molecular memories.² As POMs can accept electrons, they support oxygen vacancy migration. This can be used to form/disrupt conductive filaments between two electrodes, a common operation of resistive memories.

Herein, we demonstrate resistive switching behaviour at low voltages in POM-based devices ($\text{H}_3\text{PW}_{12}\text{O}_{40}$, $\text{Na}_3\text{PW}_{12}\text{O}_{40}$, $\text{H}_3\text{PMo}_{12}\text{O}_{40}$, $(\text{NH}_4)_3\text{PW}_{12}\text{O}_{40}$). Since only a few electrons are needed to operate, these devices are expected to operate at high speeds and with low power consumption. To fabricate these devices, we patterned coplanar electrodes separated by a nanogap (10-15 nm) using adhesion lithography, a low-cost, high-throughput, large area fabrication technique.³ We deposited the POMs in this nanogap using a self-assembly approach, which allowed better control of the resistive switching at the nanoscale. When applying pulsed electrical stimuli to the devices, we observed behaviour similar to synaptic activity. These devices hold promise for application in bidirectional artificial synapses.⁴

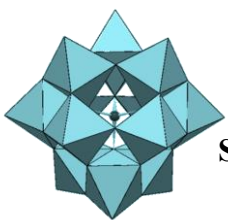
With molecular memories being increasingly studied owing to their potential to solve issues with traditional electronic devices, such as severe leakage current caused by the reduction in cell dimensions and inhomogeneous doping, POM-based memories research is very timely.

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Strategies for the arylimido functionalisation of tungsten polyoxometalates

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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 (Fig. 1), which is prerequisite for the hybrid to be a good NLO chromophore.

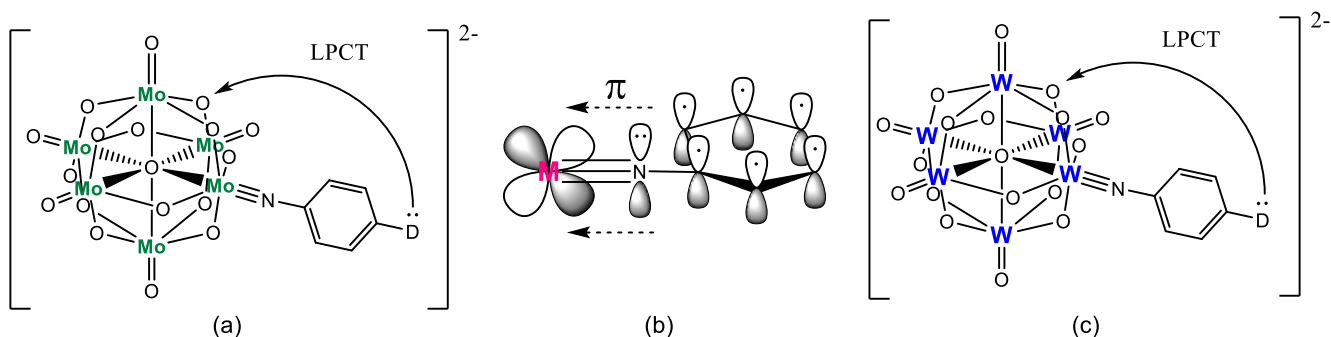


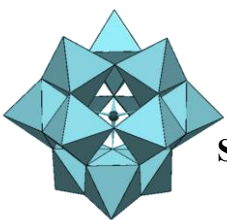
Fig. 1 (a) Generic a-POM chromophore showing ligand to POM charge transfer electronic coupling, (b) bonding between POM metal atom and an arylimido functional group showing the good π -orbital overlap, (c) analogous generic a-POT chromophore – the synthetic target.

Polyoxotungstates (POTs) are more stable than polyoxomolybdates and more transparent; advantages that are expected to improve their viability as NLO materials. However, imido functionalisation of hexatungstates (and even $\text{MoW}_5\text{O}_{19}[\text{NBu}_4]_2$) unlike hexamolybdates is very difficult to achieve and there is no synthetic route to these compounds. The terminal $\text{W}=\text{O}$ bond is much less reactive than the $\text{Mo}=\text{O}$ bond due to the W(VI) cation having a much higher charge density. Multiple established POM functionalization techniques have been trialed unsuccessfully including DCC-mediated coupling of anilines, isocyanates and triphenylphosphine imides.^{1,2}

Here we outline the results of synthetic work addressing the problem of arylimido functionalization of POTs. Arylimido functionalization of monotungstate complexes is relatively facile so our strategy starts from $[\text{ArNW}(\text{OMe})_4]_2$ dimers. Using this strategy, a single tungsten atom is pre-functionalised and POMs are synthesised by methods synonymous to the synthesis of heterometallic POMs.³

Tungsten Keggin have been isolated as functionalized/non-functionalised co-crystalline mixtures from insertion of ArNWCl_4 but the HCl released by the reaction appears to hydrolyse the $\text{W}=\text{N}$ bond and/or cause speciation.⁴ The advantage of our route is that the byproduct is methanol which can be removed if needed using sieves.

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Building Porous Organic Polymers from self-assembled Polyoxometalate – Cation systems.

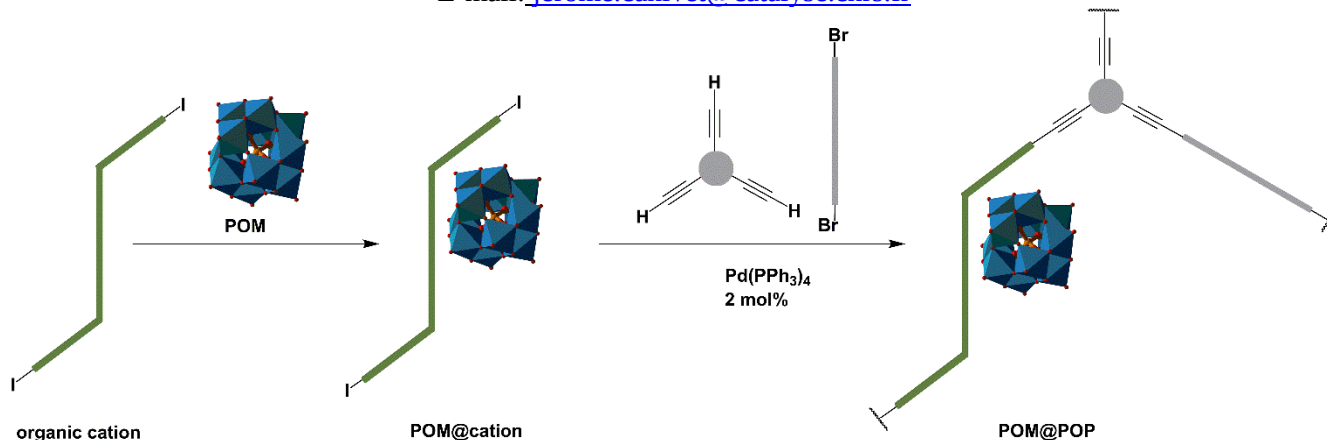
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Scheme. 1: General strategy to POM@POP from a POM@cation assembly.

Polyoxometalates (POMs) with organic counter cations in strong Coulomb interactions with each other have proven interesting for a wide range of catalytic applications (CO₂ reduction, epoxidation reactions, desulfurization, degradation of cellulose, photocatalytic C-H activation). [1]-[3]

Porous organic polymers (POP) have been chemically stable and have been reported to efficiently heterogenize molecular catalytic systems. [4]-[6] To bring POM into close connection with the cationic charges within the POP, a two-step approach has been adopted in the literature, in which polymers with cationic backbones are synthesized and secondly the anions balancing the cationic polymer backbone are exchanged by POM. [7] With this only POMs smaller than the pore diameter can penetrate, larger POMs could block the pores' entrance, and the position of the POM cannot be precisely controlled.

Here we will present an alternative route: Building a network around POM@cation units. We will demonstrate the potential of this methodology by immobilizing phosphotungstic acid as a model compound in a cationic porous organic polymer. Therefore, the organic cations of the POM@cation assembly are functionalized with polymerizable end-groups. Thus, the POM@cation assembly could be covalently incorporated in a co-polymer. The obtained POM@POP composite contains up to 26 wt% of phosphododecatungstate resulting in an apparent surface area of up to 380 m²/g. The accessibility of the POM inside the POM@POP composite will be demonstrated combining water physisorption experiments with results from ³¹P solid-state NMR, recorded under controlled humidity. Molecular dynamic simulations highlight the position of the POM in close association with the backbone cations. We will demonstrate the benefit of their close proximity for proton relay under catalytically relevant conditions.

This original strategy of installing POM in close association with cations during polymer synthesis opens the possibility of permanently trapping reactive {POM@cations}_n assemblies in a material while controlling the environment around the active POM.

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Tuning the Proteolytic Activity of Metal Substituted Polyoxometalates by Surfactants Solutions

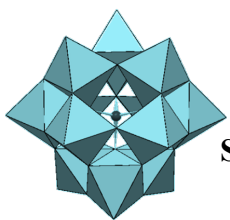
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The structural investigation of proteins is of crucial importance in the field of proteomics, and it typically relies on the use of mass spectrometry as an indispensable tool.^{1,2} Bearing in mind the complex and large structure of proteins, their cleavage into smaller peptide fragments by the natural enzymes is required to facilitate their analysis by mass spectrometry. However, considering that natural enzymes suffer from several shortcomings, our group has been developing a new class of artificial peptidases based on the polyoxometalates (POMs) as ligands for Lewis acid active metal ions.³ Due to their specific three-dimensional structure and negative charge, the controlled selectivity of peptide bond hydrolysis can be achieved through interactions of the POM with positively charged region of the proteins.³ Furthermore, it is well known that surfactants can alter protein structure by interacting with specific regions of proteins.^{4,5} Therefore, in this study we aim to explore the influence of surfactants on both the protein structure as well as the catalytic activity and selectivity of the POMs as catalysts for peptide bond hydrolysis. Hence, hydrolysis of horse heart myoglobin (Mb) was investigated in the presence of a Zr(IV)-substituted Keggin polyoxometalate – $(\text{Et}_2\text{NH}_2)_8[\{\alpha\text{-PW}_{11}\text{O}_{39}\text{Zr}(\mu\text{-OH})(\text{H}_2\text{O})\}_2] \cdot 7\text{H}_2\text{O}$ (Zr-K 2:2) – and three surfactants which differ in structure and polarity: the ionic surfactant sodium dodecyl sulphate (SDS), as well as the zwitterionic surfactants N-dodecyl-N,N-dimethyl-3-ammonio-1-propanesulfonate (Zw3-12) and 3-[(3-cholamidopropyl)dimethylammonio]-1-propanesulfonate (CHAPS). Hydrolytic reactions were monitored by sodium dodecyl sulphate polyacrylamide gel electrophoresis (SDS-PAGE). The interactions of Mb with investigated surfactants and POM were explored by different techniques: Trp-fluorescence, circular dichroism, and UV-Vis spectroscopy as well as cyclic voltammetry (CV), while the characterization of micellar superstructure formation between ternary system protein/surfactant/catalyst were explored using dynamic light scattering and electrical conductivity. The speciation of the catalyst in surfactant solutions was also followed by ³¹P Nuclear Magnetic Resonance Spectroscopy providing insight into its stability under reaction conditions.

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Structural and Electronic Properties of Mono-Substituted Polyoxotungstates

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Modern society depends on the efficient and consistent generation of ammonia (NH₃) in the industrial sector. The Haber–Bosch method, which runs at 350–500°C and 100–200 times atmospheric pressure (15–20 MPa), has been used to manufacture NH₃ since the early twentieth century.¹ Our suggestion is a well-informed design of the polyoxometalate based on research into the catabolic routes used by cyanobacteria in nature to fix N₂, which differ from the Haber–Bosch process.² Meanwhile, the industrial technique is a "brute force" approach to breaking the triple bond N–N, requiring high pressure and high temperature to speed up the reaction. In contrast, nature first attaches the protons to the N₂, allowing for simpler triple bond breaking at ambient temperature and pressure. Data from computational chemistry on the stability of various polyoxometalates will help us choose the optimum catalyst design. The reaction intermediates of such reactions have proven challenging to isolate experimentally. This work employs Density Functional Theory (DFT) calculations to elucidate the structural and electronic properties of transition-metal-substituted Keggin [M^{II/III}-PW₁₁O₃₉]^{5-/4-} and [M^{II/III}-P₂W₁₈O₆₁]^{8-/7-} anions to provide a valuable guideline for predicting the experimental feasibility of such species. Our results highlight the significance of frontier molecular orbitals of M^{II/III} to stabilization in both [PW₁₁O₃₉]⁷⁻ and [P₂W₁₈O₆₁]¹⁰⁻ frameworks. Our results indicate the d_{yz}, d_{xz}, d_{xy} molecular orbitals of [M^{II/III}-PW₁₁O₃₉]^{5-/4-} and [M^{II/III}-P₂W₁₈O₆₁]^{8-/7-} anions are non-bonding in character. Whilst the occupation of the σ_z² and σ_x²-y² molecular orbitals, which contain significant σ*(M–O) antibonding character, are consistent with poor metal–oxygen stabilization.

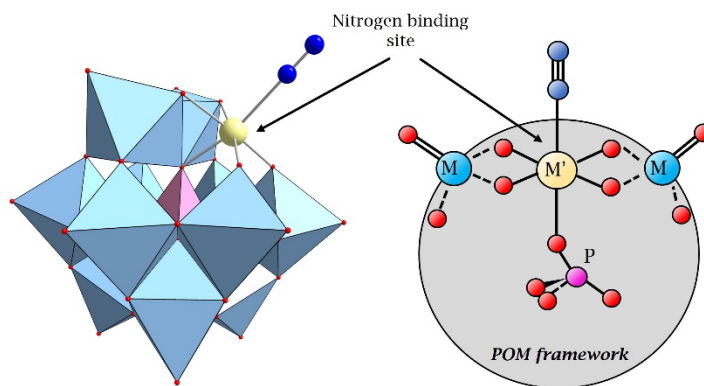


Figure 1. Polyhedral (**top-left**) representation of mono-substituted heteropolyanion. The nitrogen molecule adsorbs onto the transition metal site through the η¹ (end-on) binding mode. The schematic depiction (**top-right**) shows the mono-substituted heteropolyanion in the nitrogen-bound state.

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ON THE USE OF THE POMSIMULATOR TO UNDERSTAND THE FORMATION MECHANISMS OF METAL OXIDE NANOCCLUSERS: THE KEGGIN ANION

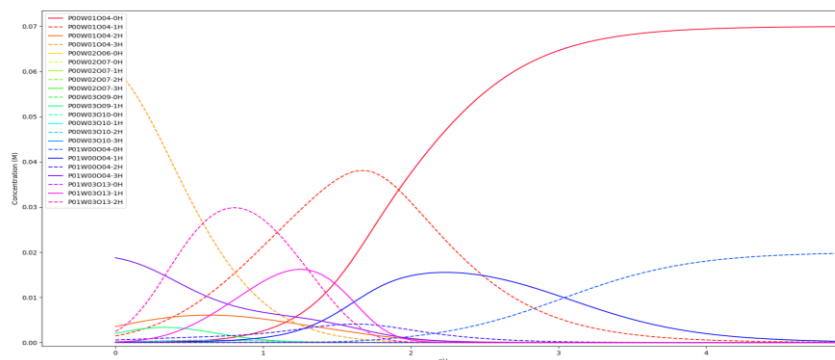
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In recent times we introduced the POMSimulator,^[1-3] which is new computer code that allows dealing with polyoxometalates in a unique manner by computing speciation phase diagrams (Conc. vs pH). This is achieved in an almost automatic manner making use of advanced graphs libraries. We presented results for the formation of octamolybdate^[1], as also for bigger clusters for Mo and W^[2]. Also, isopolyanions of V, Nb and Ta were recently studied^[3] and results obtained by the simulations were found in excellent agreement with experiments. Our method revealed the large differences between the metals and enabled identifying the reaction mechanisms for growing large clusters. Interestingly. Finally, we found very good linear relationships between experimental and computed formation constants.

In this communication we will present new results on the Keggin $[XM_{12}O_{40}]^{n-}$ anion as treated by the POMSimulator. Introducing an heteroatom in the simulator implies a high increase on the number of species in solution and of possible reactions, so additional strategies need to be implemented to make the simulations feasible. We found that the high stability of some neutral building blocks, such as M_3O_9 , and their acid/base properties, are instrumental for the growing of larger clusters.

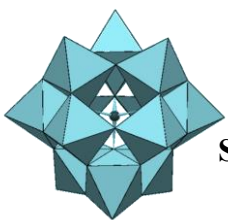


• Acknowledgements (optional)

This work was supported by the Spanish Ministerio de Ciencia e Innovación through project PID2020-112806RB-I00 and through the Severo Ochoa Excellence Accreditation 2020-2023 (CEX2019-000925-S, MCI/AEI), the ICIQ Foundation and the CERCA Program of the Generalitat de Catalunya.

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- [3] E. Petrus, M. Segado and C. Bo, Prediction of Aqueous Speciation and Self-Assembly Mechanism of Vanadium, Niobium and Tantalum Polyoxometalates, <https://doi.org/10.26434/chemrxiv-2022-2pt95>.



Water Oxidation Electrocatalysis Using POM/CNT Hybrid Materials

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Polyoxometalates (POMs) are polyanionic metal oxide clusters of group five or six transition metals in their highest oxidation states. They possess remarkable physical, chemical and electronic properties owing to a wide range of uses in catalysis, particularly photocatalysis and electrocatalysis.^{1,2} Currently, there is a large focus on achieving efficient water splitting as an important step in the global shift away from non-renewable fuels, however, it is currently held back by the poor kinetics and thermodynamics of the water oxidation reaction (WOR). Commonly used WOR catalysts are noble metals or transition-metal oxides however neither are ideal, with noble metals being considered limited and expensive resources and metal oxides being uncompetitive in acidic media. As a result, there is a necessity for sustainable materials that can be used in both acidic and basic media whilst also being capable of sufficient catalytic performance.

When looking at POMs as electrocatalysts it is important to consider their stability across the pH range. Optimal WOR activity is observed in basic conditions whereas POMs will disassemble at high pH. Via the encapsulation/combination of POMs and single-walled carbon nanotubes (SWNT), we can prevent HO⁻ anions from interacting with the POM directly thus protecting the redox properties of the POM through the conductive SWNT wall. The protection of POMs in usually unfavourable media will allow for the development and analysis of typically unavailable materials for the basic WOR.

In this work, we evaluate the electrochemical properties of [Co₄(H₂O)₂(PW₁₁O₃₄)₂] (**Co₄P₂**) through cyclic voltammetry in acidic and basic media. The work will then focus on the methods of ensuring encapsulation of **Co₄P₂** in SWNT with the Co₄P₂@SWNT being assessed as a WOR catalyst in comparison to other carbon materials.

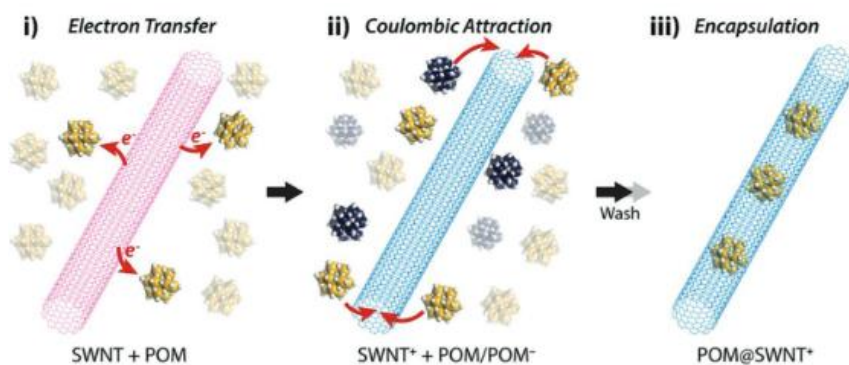
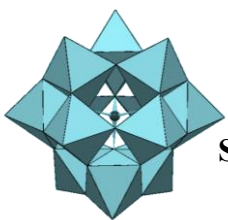


Figure 1 - Schematic of the proposed mechanism of encapsulation³



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13th-15th June 2022

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The Application of Sulfate-templated Dawson-type Polyoxometalate in the Non-aqueous Redox Flow Battery

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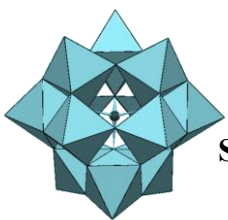
➤ General Contest

To utilize the stable and reliable renewable energy supply, it is under great urgency to develop technologies of energy storage, transmission and conversion. Among the deployed battery technologies, redox flow batteries (RFBs) store energy in the form of charged, soluble, redox-active molecules in solution[1]. This functionality gives RFBs several advantages over traditional batteries, including longer cyclic lifespan and less loss of power capacity due to side reactions during the electro-chemical energy conversion[2,3]. Polyoxometalates (POMs) are considered as attractive candidates in RFBs for their capacity to store multi-electrons and achieve multi-electrons transformation, which grant them fast kinetics and high current densities. Besides, as early transition metal oxide clusters, POMs served as active species for RFBs also benefit from their nano-sized structure since their huge structure prevents them from permeating through the membranes easily during the cyclic tests[4]. However, majority of the related publications focused on symmetric RFBs, and this conventional method potentially restrict the RFBs' cell voltages, energy densities and cyclic life.

➤ My study

Herein, we designed and investigated two novel symmetric and asymmetric NRFBs with $[C_{16}H_{36}N]_4[S_2W_{18}O_{62}]$ and benzophenone as redox pairs. These two batteries both exhibited stable and reasonable energy storage capacities during the charge/discharge cyclic tests. In comparison with the symmetric batteries, the cyclic life and specific capacity of asymmetric ones were significantly improved, due to the increased solubility and enhanced number of transferred electrons per POM molecule in the electrode reactions. For the asymmetric NRFB, two diverse active species could cooperate well and delivered better performances. During the charge-discharge cyclic tests, it yielded impressive results with the coulombic efficiency more than 97%, and higher voltage efficiency and energy efficiency were delivered without reduction. Besides, the permeability of polyoxoanion $[S_2W_{18}O_{62}]^{4-}$ cross through AMI-7001 membrane was only $1.307 \times 10^{-7} \text{ cm}^2 \text{ min}^{-1}$ and less than 1% active species had crossed over after 3 d stationary tests. As an energy storage technology, the performances of POMs based NRFBs could be enhanced from different perspectives, such as decreasing the inner resistances, increasing the solubility of POMs, utilizing more electrons per molecules. POMs hold tremendous promises in energy storage systems, yet great challenges still remain to be addressed before the success for commercial utilizations in the future.

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The Synthesis & Post-modification of Class II Organic-Inorganic Hybrid Heteropolyoxometalates

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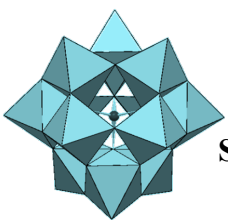
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Polyoxometalates (POMs) are polyanionic metal oxide clusters capable of forming diverse structures displaying unique and varied physical, chemical, and electronic properties. Such flexibility in their structure, composition, and modification enables POMs to be widely applicable in a broad range of fields; from nanoscopic materials to catalysis, and medicine, to name a few.^{1,2,3}

At the forefront of molecular metal oxide research is the sub-class of POMs known as organic–inorganic hybrid POMs. These hybrid materials can be defined as either class I hybrids, by which the organic fragment interacts with the POM cluster non-covalently, or as class II hybrids, covalently bound organic-inorganic clusters. Class II hybrid POMs are of particular interest to us due to the synergistic effects of the organic moieties and POM provided through their covalent hybridisation.^{4,5}

Here we will highlight our approach to the synthesis and/or post-modification of various class II hybrid heteropolyoxometalate clusters. The effects of hybridisation on the clusters overall properties will be discussed. Furthermore, the photocatalytic and supramolecular assembly behaviours of these materials have been explored to showcase the benefits of organic-inorganic hybridisation.

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Computationally based Predictions of New POM Species

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The discovery of tungsten light bulb filaments, penicillin, Velcro, Teflon, semiconductors, saccharine, has had a major influence on our civilization. Some of these breakthroughs came via goal-oriented lab work and trial-and-error study, while others came from a mix of intuition and chance.¹ Easy-to-find materials were discovered decades ago, and today we must delve deep into the materials universe to locate compounds with the desired qualities. We have started studying a family of all-inorganic porous materials,² POM frameworks named “POMzites”, composed of ring-shaped tungsten oxide $[P_8W_{48}O_{184}]^{40-}$ (abbreviated as $\{P_8W_{48}\}$) building blocks connected with transition metal linkers (TM-linkers) forming zero- to three-dimensional frameworks; see Fig. 1. Here we show the volume of results we have so far obtained and the most promising structures we believe to be synthesizable. These results can be used to roughly assess the viability of synthesizing more than two dozen $[X_2W_{18}O_{62}]^{6-}$ Wells-Dawson and complementary lacunary structures, as well as providing our database with the volume of results it requires to yield truly accurate results; the more information we give the network, the better it will become at predicting new structures, creating a positive feedback loop. We plan on attempting to synthesize at least several of these predicted structures in the lab, both theoretically favourable and unfavourable to achieve a true understanding of the data, to ensure our data is of a sufficient quality to be fed to the neural network. Neural network aside, we have demonstrated the untapped potential of DFT-level calculations for analyzing POMs and the current computational capabilities which now allow us to converge structures of this size at this level of accuracy.

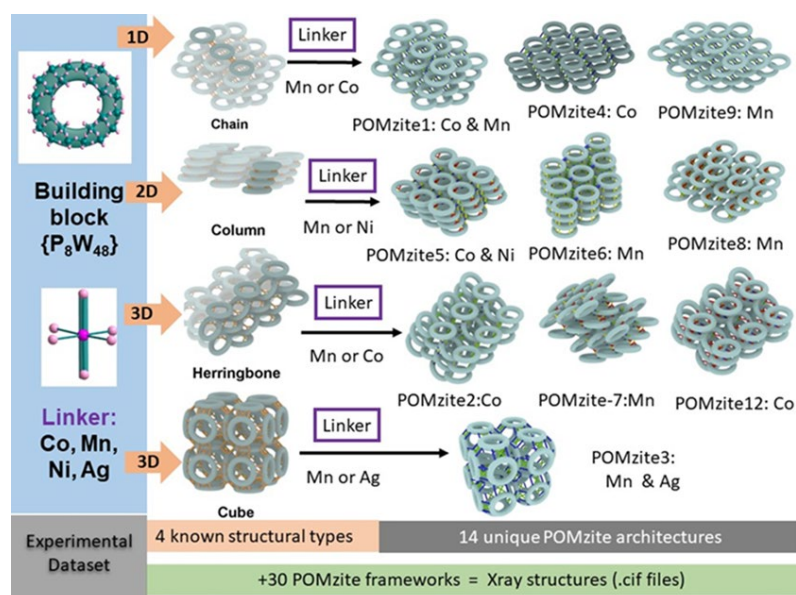
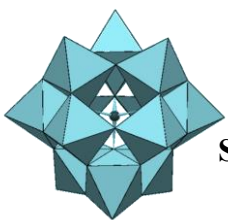


Figure 1. The minimal building block library of $[P_8W_{48}O_{184}]^{40-}$ (abbreviated as $\{P_8W_{48}\}$) nodes and transition metal linkers (Co, Mn, Ni, Ag) that forms a family of 14 POM-all-inorganic framework architectures (namely, “POMzites”).

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Design and Synthesis of Mixed Polyoxometalate Hybrid Structures via a Modular Post-Functionalisation Strategy

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In organic chemistry the wide range of possible functional groups available allows for the targeted design and synthesis of a vast number of different molecular structures, where the desired properties can be tuned through the careful choice of functional groups. Expanding such a modular approach to include inorganic “functional groups” further pushes the limits of synthetic chemistry towards the formation of novel organic-inorganic hybrid compounds with potential as functional materials. Polyoxometalates (POMs) are ideal building blocks for the formation of hybrid structures in this way due to the ability of several POMs to be covalently functionalized with a wide range of organic moieties.¹ Moreover, combining different POMs as inorganic “functional groups” within a single molecular structure could further diversify and enhance the properties of the resulting hybrids since each POM has distinct properties, depending on its composition and structure. Hence, a versatile strategy for combining the archetypal Lindqvist, Anderson-Evans and Wells-Dawson structures using polyol linkers was developed (**Figure 1**).² Using this strategy, hexavanadate (V_6) and chromium hexamolybdate ($CrMo_6$) POMs bis-functionalized with dipentaerythritol ($R-POM_1-R$; $R = (OCH_2)_3CCH_2OCH_2C(CH_2OH)_3$) were post-functionalized with aluminum hexamolybdate Anderson-Evans ($AlMo_6$) and Wells-Dawson $\{P_2V_3W_{15}\}$ POMs (POM_2) to form four novel mixed heterometallic POM-POM hybrid triads ($POM_2-R-POM_1-R-POM_2$). Their formation in high-yields was confirmed by a multi-technique approach while their redox properties were explored through cyclic voltammetry. Moreover, the straight-forward one-pot synthesis used to obtain the POM-POM hybrids could potentially be expanded to other metal-oxo clusters.

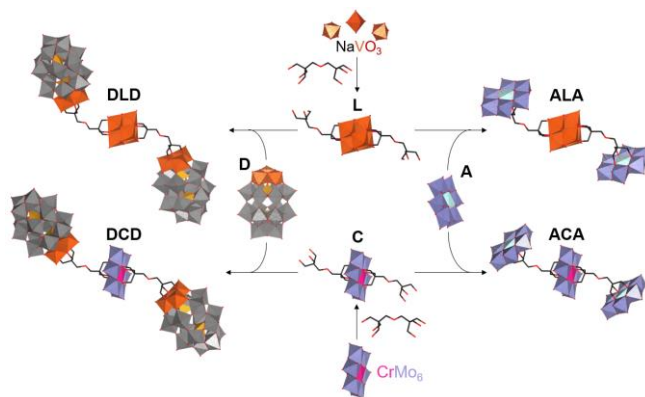
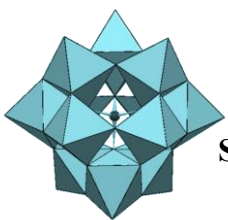


Figure 1. Synthesis of 4 novel POM-POM hybrids (**DLD**, **DCD**, **ALA**, **ACA**) from $[V_6O_{13}\{(OCH_2)_3C-R\}_2]^{2-}$ (**L**) and $[CrMo_6O_{18}\{(OCH_2)_3C-R\}_2]^{3-}$ (**C**) bis-functionalized with dipentaerythritol ($R = CH_2OCH_2C(CH_2OH)_3$) as building blocks that can be post-functionalized with $[P_2V_3W_{15}O_{62}]^{9-}$ (**D**) or $[Al(OH)_2Mo_6O_{13}]^{3-}$ (**A**).

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Heteropolyoxometalates as Photocatalysts for Organic Synthesis

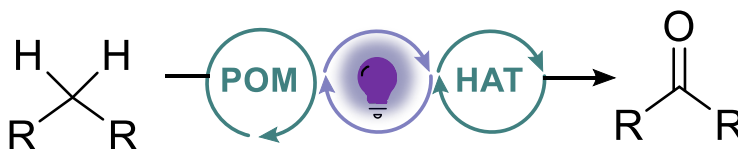
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Polyoxometalates (POMs) are highly attractive photocatalysts owing to their vast structural and compositional diversity, excellent thermal stability, and tuneable physical and chemical properties.^{1,2} They have been shown to promote a variety of organic hydrogen atom transfer (HAT) reactions and in particular the decatungstate anion ($[W_{10}O_{32}]^{4-}$; usually in its tetrabutylammonium salt (TBADT)) is one of the most widely used catalysts in the field.³

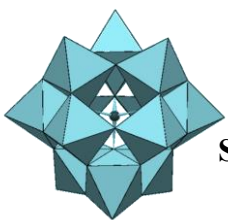
Paying particular attention to the area of POM photochemistry, limitations arise when using decatungstate as the catalyst. Firstly, TBADT exhibits limited regioselectivity and requires the use of high energy UV light (usually around 330 nm) - restricting substrate scope and functional group tolerance. Secondly, TBADT has limited application to single electron transfer (SET) photocatalysis, a key target in late-stage functionalisation chemistry. New tuneable catalysts that build on the strengths of TBADT while improving selectivity and substrate scope and opening the door to new catalytic processes will revolutionise this area of research.

Here we describe a range of heteropolyoxometalate clusters and their organofunctionalized analogues and assess their performance as HAT and SET catalysts in a range of organic reactions. Their performance is discussed based on their electronic structure and redox chemistry. We will demonstrate how careful design of POM catalysts can open new doors in organic photocatalysis.



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Investigation towards photoactive covalent hybrids based on (iso)porphyrin-polyoxometalate assemblies

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Polyoxometalates (POMs), are promising candidates for various photoelectrochemical applications due to their excellent photosensitivity, redox, and catalytic properties, as well as their relative stability.^[1,2] However, POM clusters in their ground state can be mainly excited mainly by UV light inducing a charge transfer from an oxygen atom to the d0 TM (transition metal). This limits the application of POMs in solar-driven catalysis.^[3] In order to deal with this problem, we hence have designed covalently (iso)porphyrin- polyoxometalate hybrid material, like Fe^{III}POM-ZnT₂isoP^{*} copolymer by electropolymerization, where the (iso)porphyrin subunit acts as electron donor and POMs building block acts as electron acceptor. This process was monitored by cyclic voltammetry as well as EQCM (Electrochemical Quartz Crystal Microbalance). Their electrical properties have been studied by electrochemical impedance spectroscopy and their photovoltaic performances have been investigated by photocurrent transient measurements under visible-NIR light irradiation. The photocurrent for the Fe^{III}POM-ZnT₂isoP^{*} copolymer can be up to -300 μA/cm². Finally, the morphology characterization was investigated by Atomic Force Microscope (AFM). But the application of the hybrid materials in energy conversion domain still needs further investigation.

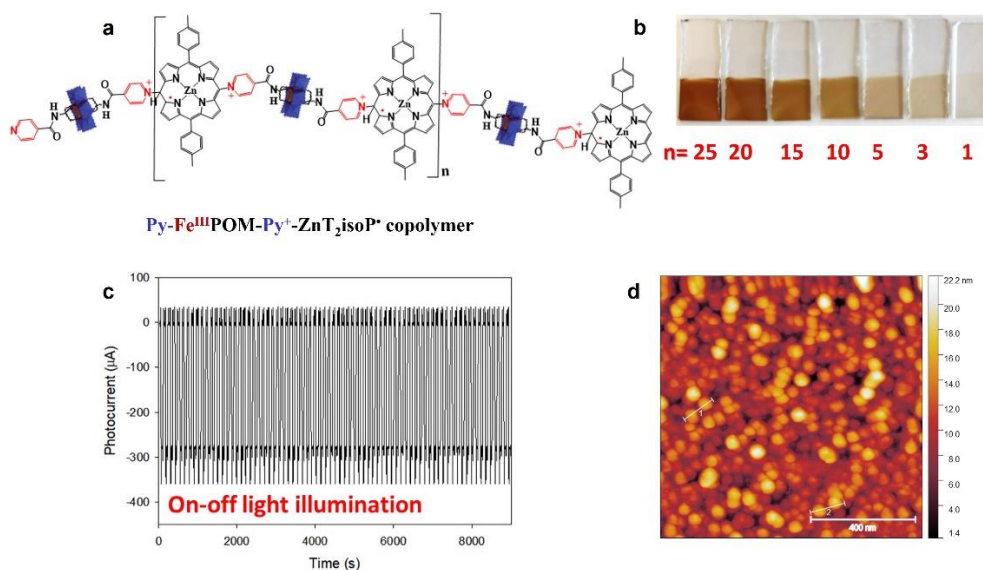
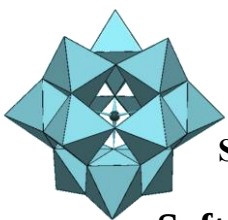


Figure 1. a) Electropolymerization process; b) Fe^{III}POM- ZnT₂isoP^{*} copolymer deposited on ITO with different scan numbers; c) Transient photocurrent test within 4 h; d) Morphology characterization by AFM.

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Soft-Landed Host-Guest Complexes of Cyclodextrins and Polyoxovanadates as Single Molecule Memory Units on Surfaces

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Polyoxometalates (POMs)¹ have emerged as highly promising active components for nano-electronic devices.² In our Laboratories, we focus on POMs with V(3d) states,³ which have been found to be excellent candidates for integration into multi-resistive memories.⁴ Their stabilization on substrate surfaces remains one of the challenging tasks that will allow solving the problem of controlled electronic modification at the single-molecule level as well as assessing the role of counterions in electron transport processes through POM-based junctions. Herein, we demonstrate how to address these challenges by employing cyclodextrins (CDs) as stabilizing macrocyclic agents and an advanced molecular deposition technique such as an ion soft landing (**Fig. 1**). This method enables to deposit mass-selected polyatomic ions with precisely controlled composition, charge state and kinetic energy on substrates.

We transferred the complex of β -cyclodextrin (β -CD) and $[V_6O_{13}\{(OCH_2)_3CCH_2OH\}_2]^{2-}$ (abbreviated $[V_6-(OH)_2]^{2-}$) from solution into the gas phase, mass selected a doubly charged ion $[\beta\text{-CD} + [V_6-(OH)_2]^{2-}]^{2-}$ and deposited it onto a gold surface with the desired kinetic energy. Photoelectron spectroscopy (PES) experiments and quantum mechanical calculations indicated the stability of the formed host-guest complex in the gas phase. Using Liquid Extraction Surface Analysis (LESA) (**Fig. 2**), we demonstrated that $[\beta\text{-CD} + [V_6-(OH)_2]^{2-}]^{2-}$ is soft-landed as intact molecule on the substrate surface. The adsorption and electronic characteristics of these molecules were then characterized by scanning tunneling microscopy (STM) (**Fig. 3**). We identified single host-guest complexes, each with a size of 2–3 nm, and probed their switching *via* scanning tunneling spectroscopy (STS). The obtained I - V curves show characteristic discrete conduction states of the hexavanadate component with a stepwise increase of the electrical conductance at different tip potentials.

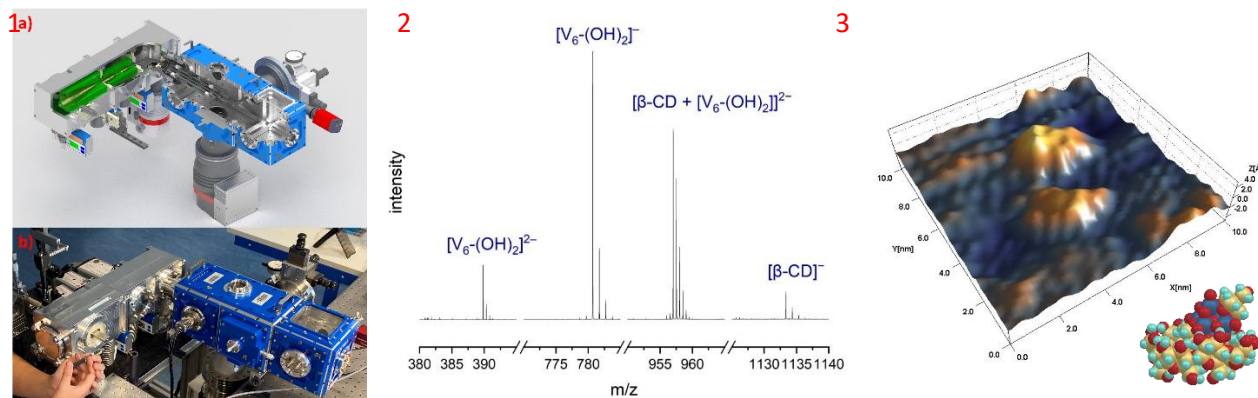


Fig. 1a) Technical drawing and **1b)** the corresponding original ion soft-landing apparatus.

Fig. 2 LESA mass spectrum of soft-landed $[\beta\text{-CD} + [V_6-(OH)_2]^{2-}]^{2-}$ on a gold surface.

Fig. 3 3D STM imaging of two single soft-landed supramolecular polyoxovanadate–cyclodextrin anions.

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Differential electrochemical mass spectrometry studies of nitrite reduction catalyzed by Keggin polyoxometalates

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Nitrite or nitrous acid electrochemical reduction is catalyzed, among others, by polyoxometalates (POMs). In most cases, studies are performed as a function of pH and the electrocatalytic performance is presented as the variation of catalytic current with nitrite or nitrous acid concentration.^[1-3] In this work, the reduction of nitrite catalyzed by a series of polyoxometalates (POMs) belonging to the Keggin family have been investigated. The POMs were selected due to the increase in their global charge and decrease of the redox potential, from $\text{PW}_{12}\text{O}_{40}^{3-}$, $\text{SiW}_{12}\text{O}_{40}^{4-}$, $\text{BW}_{12}\text{O}_{40}^{5-}$ to $\text{H}_2\text{W}_{12}\text{O}_{40}^{6-}$ respectively. DEMS (Differential electrochemical mass spectrometry) analysis was performed for these compounds for the first time to identify the gaseous products.

Main conclusion: DEMS-CV experiments provide real-time reaction product information shown in Fig 1. The found gaseous products were only ^{15}NO and $^{15}\text{N}_2\text{O}$. There is direct correlation between the redox potential of the POM and the production of NO. The consumption of NO is linked to the production of N_2O and the gaseous products are similar to the products obtained by catalytic reduction of nitrite by gold and silver.^[4] The probable catalytic redox processes are schematized in Fig. 2. Firstly, HNO_2 (pH 2) or NO_2^- (pH 5) are reduced to NO by POM^- . The next reaction step might involve the reduction of NO into HNO catalyzed by POM^{2-} . Finally, the production of N_2O from HNO might occur through a complex reaction.^[5] Further research will concern immobilization of POMs and study of the products issued from the heterogeneous catalysis.

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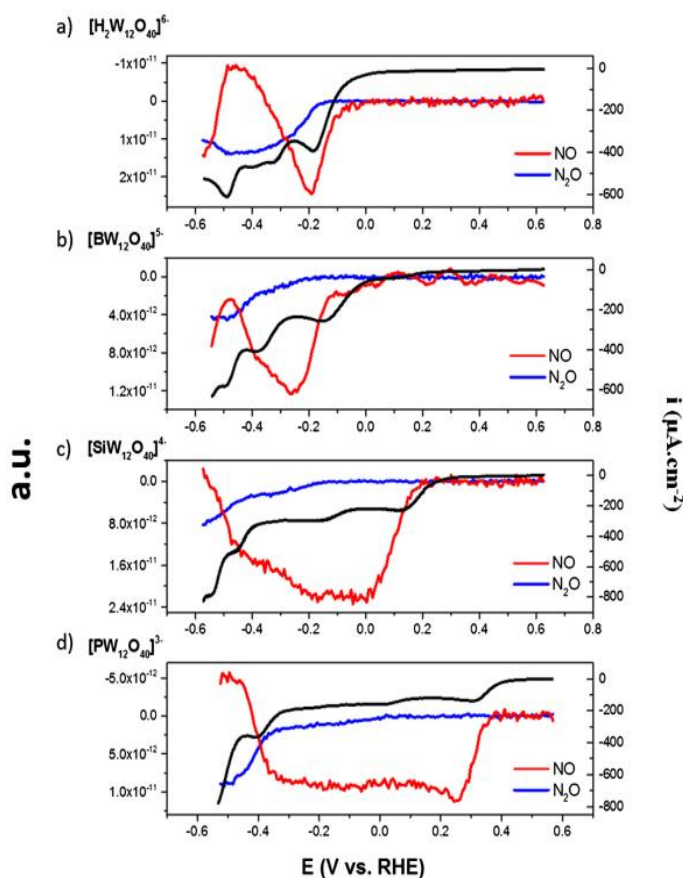


Fig 1. Cyclic voltammetry (black curve), DEMS signal of m/z 31 (^{15}NO , red curve) and m/z 46 ($^{15}\text{N}_2\text{O}$, blue curve) for the forward scan (from 0.8 V to -0.6 V vs. RHE, 0.5 mV.s^{-1}). Electrolyte: 0.5 M $\text{Na}_2\text{SO}_4/\text{H}_2\text{SO}_4$ at pH 2

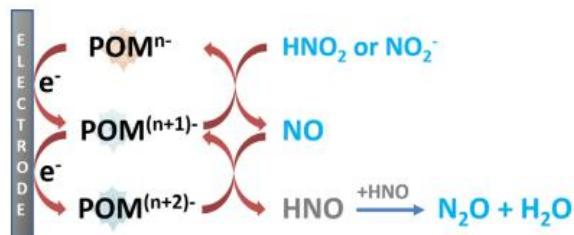


Fig 2. Catalytic redox processes of nitrite or nitrous acid electroreduction catalyzed by polyoxometalates.