

Young Researcher Seminar
of
EPSRC-JSPS Core-to-Core Collaboration in Advanced Materials
International Network on Polyoxometalate Science
for Advanced Energy Materials
and
NANOXCAT French-Japan International Associate Laboratory

Date: 16th July, 2019

International Conference Center Hiroshima, Hiroshima, Japan

<http://www.pcf.city.hiroshima.jp/icch/english.html>

12:00 –	Registration	
12:50 – 13:00	Opening remarks	
13:00 – 13:12	Dr. Zhenxin Zhang	Ningbo University Zeolitic transition metal oxides for molecule adsorption and separation
13:12 – 13:24	Kentaro Yonesato	The University of Tokyo Precise Accumulation of Multiple Transition Metal Cations within Ring-Shaped Phosphotungstates
13:24 – 13:36	Chifeng Li	The University of Tokyo Polyoxometalate–Organic Architectures Based on Self-Assembly of Lacunary Phosphomolybdates and Pyridyl Ligands
13:36 – 13:48	Tsukasa Iwano	The University of Tokyo High Proton Conduction in Crystalline Composites Based on Preyssler-Type Polyoxometalates and Poly(allylamine)s
13:48 – 14:00	Tomoki Okunaga	The University of Tokyo Rapid Formation of Small Mixed-Valence Silver Clusters via Electron Transfer in a Porous Ionic Crystal Based on Polyoxometalate
14:00 – 14:12	Karen Silva Vargas	Ecole Centrale de Lille Deoxydehydration (DODH) of glycerol catalyzed ReO_3
14:12 – 14:24	Dr. Zhongling Lang	Northeast Normal University Polyoxometalate-mediated Electron Transfer Modulation for Application in Electrocatalytic CO_2 Reduction
14:24 – 14:36	Hiroyuki Gi	Hiroshima University Catalysis and reactivation of Nb_2O_5 for hydrogen desorption/absorption in MgH_2

- 14:36 – 14:50 **Coffee Break**
- 14:50 – 15:02 **Tomoyuki Hirano** Hiroshima University
Evaluation of cesium doped tungsten oxide nanoparticles made in diffusion flames for near-infrared shielding applications
- 15:02 – 15:14 **Singh Pankaj Kumar** Hiroshima University
Improved hydrogen release from MgH_2 by various Nb and Ta gel oxides
- 15:14 – 15:26 **Manuel Lechner** Ulm University
Aerobic oxidation catalysis with molecular polyoxometalates
- 15:26 – 15:38 **Yu Watari** Yamaguchi University
Cation dependence of the thermal molecular deformation of basket-type polyoxometalate
- 15:38 – 15:50 **Yuichiro Miyazaki** Yamaguchi University
Exploring macroscopic electrical properties of mixed valence POM
- 15:50 – 16:02 **Keita Kuge** Kyushu University
Photochemical Hydrogen Evolution in Biphasic Systems Consisting of Aqueous and Ionic-liquid Solutions
- 16:02 – 16:14 **Koichi Yatsuzuka** Kyushu University
Photochemical Hydrogen Evolution from Water Catalyzed by a Platinum(II) Complex Bearing Nindigo as a Redox-active Ligand
- 16:14 – 16:26 **Dr. Takeshi Shimizu** Kwansai Gakuin University
Research on the correlation between the structures and battery performances of MOFs with disulfide moiety-containing ligands
- 16:26 - 16:40 **Coffee Break**

- 16:40 – 16:52 **Dr. Joshua Karlsson** Newcastle University
Intramolecular Singlet Exciton Fission in an Elongated Bis-Pentacene Derivative
- 16: 52 – 17:04 **Kate A. Phipps** Newcastle University
Towards Super-Reduction: an Investigation of Polyoxometalate Redox Properties for Energy Storage
- 17:04 – 17:16 **Dr. Jamie Cameron** Nottingham University
Integration of Polyoxometalates into Functional Hybrid Soft Materials
- 17:16 – 17:28 **Catherine Peake** Nottingham University
Non-Aqueous Polyoxometalate Electrolytes for High Energy Density Redox Flow Batteries
- 17:28 – 17:40 **Elizabeth Hampson** Nottingham University
Asymmetric multi-functional redox-active hybrid polyoxometalates
- 17:40 – 17:52 **Dr. Masaru Fujibayashi** Hiroshima University
The Single-Molecular Electret (SME) Behaviors of Preyssler-Type Polyoxometalate
- 17:52 – 18:04 **Richard James** Newcastle University
- 18:04 – 18:16 **Dr. Conrad Holc** Nottingham University
Using polyoxometalates as redox mediators in Li-air batteries
- 19:00 - **Social mixer** Miyabi Sogo Hiroshima
<http://www.okonomi.co.jp/miyabi.html>

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Research keywords: zeolitic transition metal oxides, adsorption, separation, redox, catalysis

Zeolitic transition metal oxides for molecule adsorption and separation


Design of the structure and composition of crystalline microporous inorganic oxides is of great importance in fundamental science and practical applications. Zeolite is a typical material towards this design because of the tunable pore system and high thermal stability, while zeolite is limited to main group elements, which limits its applications. Another promising material is zeolitic transition metal oxide, which has both advantages of zeolite and transition metal oxide. However, the examples of zeolitic transition metal oxide are rare. Self-assembly of POM units and metal ions is a good approach to obtain zeolitic transition metal oxide. We have been studying on this field and find several typical zeolitic transition metal oxides.

One example is the ϵ -Keggin POM based zeolitic transition metal oxides. The materials are constructed by ϵ -Keggin POM units ($\text{XM}_{12}\text{O}_{40}$, $\text{X} = \text{Zn, Mn, Fe, Co, Ni}$, $\text{M} = \text{Mo, V, W}$) and metal ions as linkers with high elemental diversity.^[1,2] The micropores of the materials can be opened, which are accessible to small molecules, such as CO_2 , CH_4 , C_2H_6 , and C_2H_4 . We find the materials can be used as effective separation materials for CH_4/CO_2 and $\text{C}_2\text{H}_6/\text{C}_2\text{H}_4$. Furthermore, the materials show redox properties, which can be used catalysts for selective oxidations of methacrolein to methacrylic acid and ethyl lactate to ethyl pyruvate.

Another example is the cubane unit based zeolitic vanadotungstates.^[3] We report a new class of zeolitic vanadotungstates with tunable frameworks exhibiting a large porosity and redox activity. The assembly of $[\text{W}_4\text{O}_{16}]^{8-}$ units with VO^{2+} forms two isomeric porous frameworks. Owing to the complex redox properties and open porosity, the vanadotungstates efficiently catalyze the selective reduction of NO by NH_3 . This finding provides an opportunity for design and synthesis of inorganic multifunctional materials for future catalytic applications.

Reference.

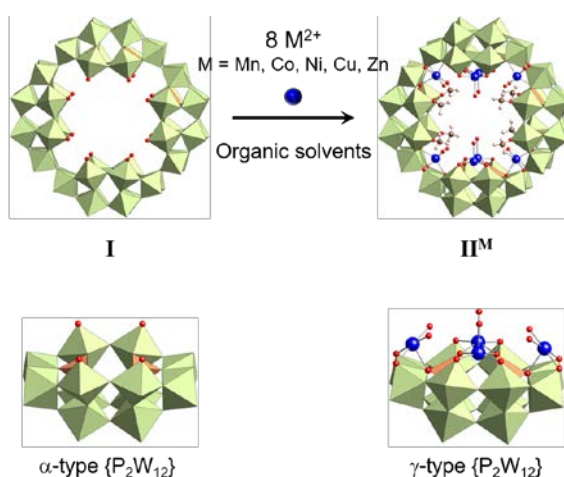
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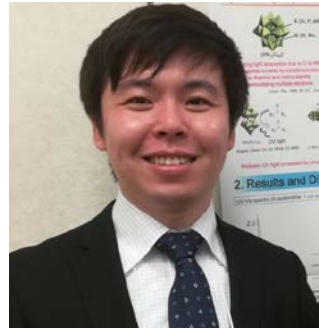
Research keywords: lacunary polyoxometalate, metal substitution

Precise Accumulation of Multiple Transition Metal Cations within Ring-Shaped Phosphotungstates

The precise syntheses of multinuclear metal structures such as metal-oxo cores and metal nanocluster have attracted extensive interests. We have synthesized metal-oxo clusters using lacunary polyoxometalates (POMs) as structurally well-defined multidentate ligands in organic solvent.^[1] The ring-shaped $[P_8W_{48}O_{184}]^{40-}$ (**P8W48**) is an attractive superlacunary compound for accumulating metal atoms within their cavity (approximately 10 Å in diameter). Herein, we report a synthesis of metal-containing **P8W48** by employing an organic-solvent soluble salt of **P8W48** ($[(n-C_4H_9)_4N]_{12}H_{28}[P_8W_{48}O_{184}] \cdot 30H_2O$, **I**).^[2] Based on X-ray crystallographic and elemental analyses, we first successfully synthesized K^+/Li^+ -free **P8W48** by cation exchange reaction of K^+/Li^+ salt of $[P_8W_{48}O_{184}]^{40-}$ and $(n-C_4H_9)_4NBr$ in dilute nitric acid. Bond valence sum (BVS) values of oxygen atoms indicated that reactive oxygen atoms ($W-OH$, $W-OH_2$) were accumulated inside its cavity. Therefore, metal cations could be site-selectively introduced into the cavity of **P8W48**. By the reaction of **I** and cobalt acetylacetonate, the $\{Co_8\}$ -possessing **P8W48** (**II^{Co}**) was successfully synthesized. **II^{Co}** possessed dicobalt centers $\{(Co-OH_2)(\mu_3-O)_2(Co-OH_2)\}$ on γ -type $\{P_2W_{12}\}$ units, whose $\{PO_4\}$ units were inverted from α -type $\{P_2W_{12}\}$ units, and $\{Co(OH_2)_2\}$ between α -type $\{P_2W_{12}\}$ unit and γ -type $\{P_2W_{12}\}$ unit. Methoxo groups coordinated to reactive sites of α -type $\{P_2W_{12}\}$ units and suppressed disordering of cobalt cations. We also successfully synthesized other **II^M** ($M = Mn^{2+}$, Ni^{2+} , Cu^{2+} , Zn^{2+}) structures.



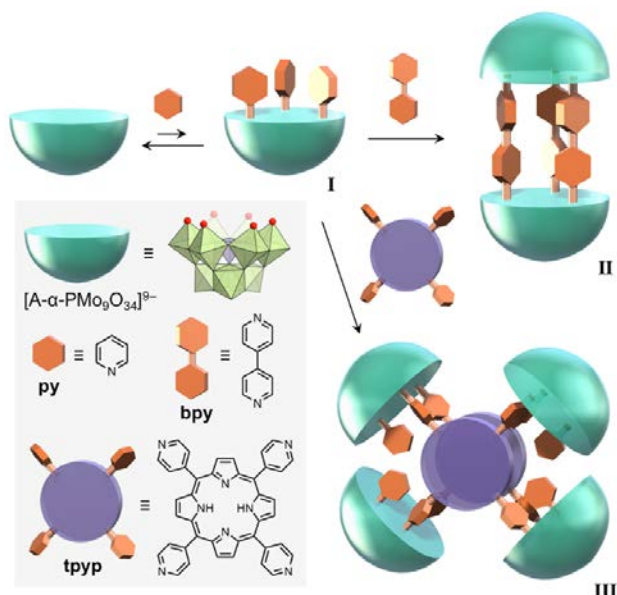
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Research keywords: Phosphomolybdate, Organic-Inorganic Hybrid, Pyridyl Ligand

Polyoxometalate–Organic Architectures Based on Self-Assembly of Lacunary Phosphomolybdates and Pyridyl Ligands

The development of novel systems for metal–organic architectures is an attractive research field because they are fascinating materials with unexplored functions. Lacunary polyoxometalates (POMs) offer structurally well-defined coordination sites with various coordination directions and numbers. By using them as precursors, we have designed metal-oxo clusters possessing unique catalytic and magnetic properties.^[1] Here, we report the successful self-assembly of POM–organic architectures comprising multivacant lacunary POMs and pyridyl ligands.^[2] We chose a Keggin-type trivacant lacunary phosphomolybdate $[A-\alpha\text{-PMo}_9\text{O}_{34}]^{9-}$ as a lacunary POM building block, because of (i) the unique properties of phosphomolybdates and (ii) the strong Lewis acidity of their vacant sites. However, the low hydrolytic stability of lacunary phosphomolybdates makes it extremely difficult to isolate and utilize them. Consequently, the introduction of organic ligands and/or metal species into their vacant sites has not been successfully achieved to date. We revealed that by introducing pyridine moieties to its vacant sites, the lacunary phosphomolybdate is significantly stabilized in organic solvents. Furthermore, the resultant structure can be utilized as a reactive building block to synthesize a dimer pillared by 4,4'-bipyridyl and a tetramer bridged by two cofacial porphyrin ligands, which can intercalate aromatic molecules.



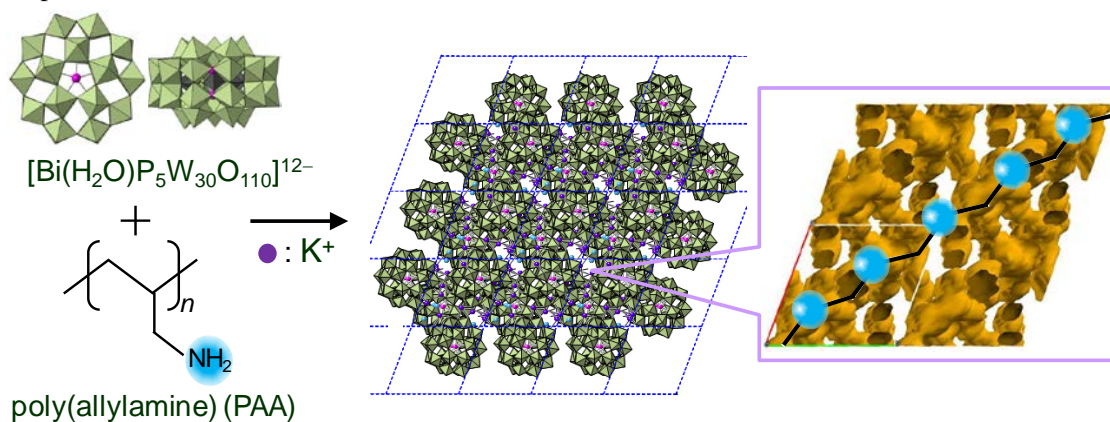
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Research keywords: Ionic crystals, Preyssler-type POMs, Hydrogen bonding network, Proton conduction

High Proton Conduction in Crystalline Composites Based on Preyssler-Type Polyoxometalates and Poly(allylamine)s

Abstract: Polyoxometalate based solids are promising candidates of proton-conducting solid electrolytes. In this work, a Preyssler-type polyoxometalate is crystallized with K^+ and poly(allylamine), which is also a good proton conductor, from aqueous solutions. Here we show that the low durability of polyoxometalate and poly(allylamine) due to hygroscopicity is overcome by the electrostatic interaction between the polyoxometalate and protonated amine moieties in the solid state. Crystalline compounds are synthesized with poly(allylamine) of different average molecular weights, and all compounds achieve proton conductivities of $10^{-2} \text{ S cm}^{-1}$ under mild relative humidity and low-temperature conditions. Spectroscopic studies have revealed that the side-chain mobility of poly(allylamine) and rearrangement of hydrogen-bonding network contribute to the proton conduction in compounds with poly(allylamine) of low and high average molecular weights, respectively. While numbers of proton-conducting amorphous polyoxometalate-polymer composites have been reported, these results show both structure-property relationship and high functionality in crystalline composites.¹⁾



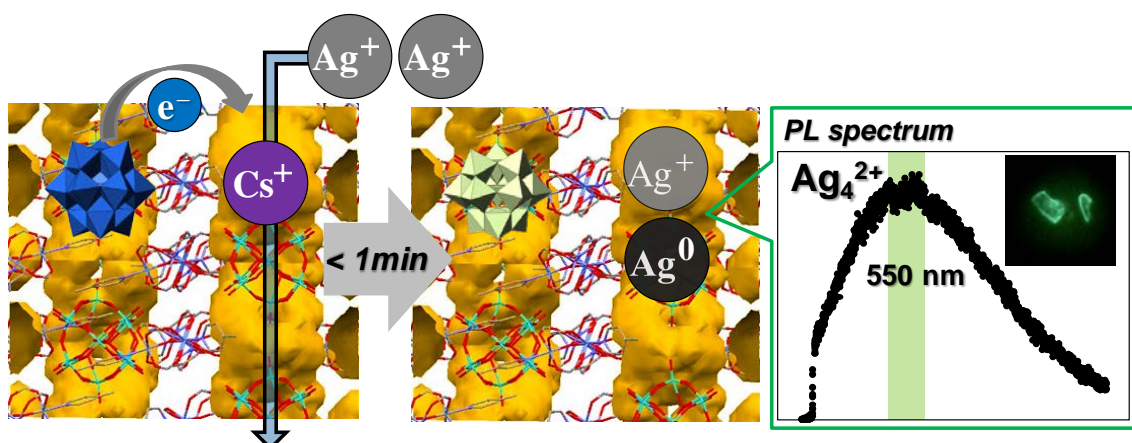
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Research keywords: Ionic crystals, Redox Chemistry, Cation-Exchange and Uptake

Rapid Formation of Small Mixed-Valence Silver Clusters via Electron Transfer in a Porous Ionic Crystal Based on Polyoxometalate

Abstract: Reversible redox property is one of the keys to further functionalize porous crystalline materials. We have previously synthesized a redox-active porous ionic crystal with dodecamolybdophosphate $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ and $[\text{Cr}_3\text{O}(\text{OOCH})_6(\text{mepy})_3]^+$ (mepy = 4-methylpyridine) as building blocks. The crystal showed cooperative migration of electrons with alkali metal ions in the 1-D channel.¹⁾ Besides, it has been well known that silver ions (Ag^+) and clusters (e.g., Ag_3^+) can selectively adsorb unsaturated hydrocarbons via σ and π -bonds.^{2,3)} Based on these considerations, we utilized a redox-active porous ionic crystals of $\text{Cs}_2[\text{Cr}_3\text{O}(\text{OOCH})_6(\text{mepy})_3]_2 [\text{PMo}^{\text{V}}\text{Mo}^{\text{VI}}_{11}\text{O}_{40}]$ to form silver clusters (mainly Ag_4^{2+}), and this ion-exchange ($\text{Cs}^+ \rightarrow \text{Ag}_4^{2+}$) took less than 1 min, while the ion-exchange ($\text{Cs}^+ \rightarrow \text{Ag}^+$) of $\text{Cs}[\text{Cr}_3\text{O}(\text{OOCH})_6(\text{mepy})_3]_2 [\text{PMo}^{\text{VI}}_{12}\text{O}_{40}]$ took more than 24 h. Photoemission spectra of the compound showed this reaction consisted of two steps: electron transfer from reduced POM to Ag^+ and the subsequent formation of a silver cluster, and diffusion of the silver cluster and exchange with Cs^+ . In addition, the compound containing the silver cluster showed high affinity toward unsaturated hydrocarbon guests.⁴⁾



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Research keywords: (Glycerol, Deoxydehydration, Allyl alcohol, Separation process)

Deoxydehydration (DODH) of glycerol catalyzed ReO₃

Summary: Allyl alcohol is a platform molecule with high potential as a starting material for various large-scale chemical intermediates such as acrylonitrile and acrylic acid ^{[1][2]}. Today, the main bottleneck for these applications lies in the sourcing of allyl alcohol. As a renewable source, glycerol is a promising starting material for the synthesis of allyl alcohol ^{[3][4][5]}. We have recently developed a heterogeneous catalyst based on rhenium oxide for the deoxydehydration (DODH) reaction of glycerol to allyl alcohol, obtaining a maximum yield of 85% using 2-Hexanol as hydrogen donor at 175°C and high reusability. With this in mind, in order to approach a viable separation process, the distillation process of allyl alcohol was studied as the first stage of separation (Figure 1). Simulation process (Aspen plus V9 software) was carried out using the binary coefficients of NRTL, WILSON and UNIQUAC as thermodynamic models. The corresponding binary coefficients were obtained from the experimental equilibrium phase diagram liquid-vapor at atmospheric pressure of the possible mixtures downstream from the reactor. On the other hand, Taking into account the formation of 2-hexanone as co-product during DODH reaction (Figure 2), the regeneration of 2-hexanol was carried out *via* catalytic hydrogenation of 2-hexanone using different catalysts, obtaining a maximum yield of >99%

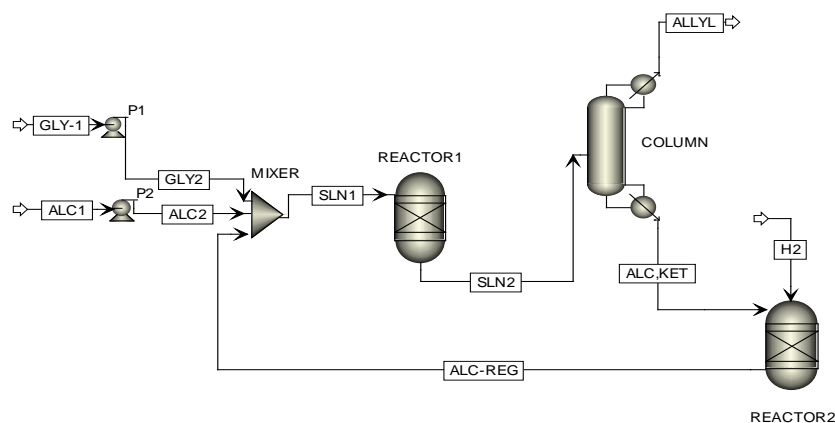


Fig. 1 Separation process of allyl alcohol obtained from deoxydehydration of glycerol.

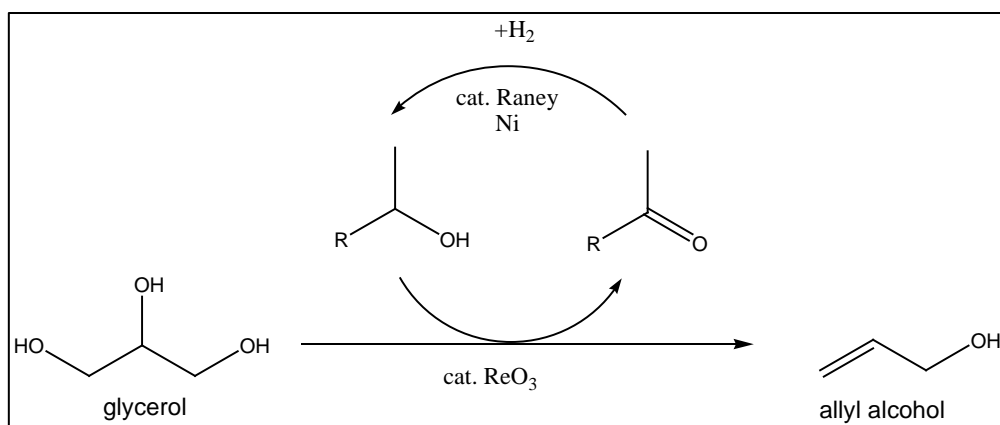


Fig. 2 Deoxydehydration (DODH) of glycerol into allyl alcohol with a sacrificial secondary alcohol^[6].


Collaborations:

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Research keywords: Polyoxometalates; Density functional theory; Electronic structure; Catalytic mechanism

Polyoxometalate-mediated Electron Transfer Modulation for Application in Electrocatalytic CO₂ Reduction

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Electrocatalytic CO₂ reduction reaction (CO₂RR) to produce high value-added chemicals for example CO is a potential solution to meet future energy requirements. In this project, we construct a series of polyoxometalate (POM)-based manganese carbonyl (MnL) electrocatalysts (POM-MnL: SiW₁₂-MnL, PW₁₂-MnL and PMo₁₂-MnL) toward CO₂RR, which demonstrates an effective electron-transfer-modulation strategy to improve the efficiency and selectivity of CO₂RR. Through the comprehensive analysis by combination of experiment and DFT calculations, we have addressed the role of POMs in the CO₂RR process. This work highlights the significance of electron-transfer modulation to promote CO₂RR and may provide new inspiration for the design of efficient and high-selective catalysts for electrocatalytic CO₂RR.

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Research keywords: hydrogen storage materials, magnesium hydride, catalyst, reactivation

Catalysis and reactivation of Nb₂O₅ for hydrogen desorption/absorption in MgH₂

Magnesium hydride (MgH₂) is one of attractive hydrogen storage materials because of its high gravimetric hydrogenation capacity, 7.6 wt.%. However, the hydrogen absorption reaction is kinetically slow and generally requires higher temperature than 300 °C as thermal activation. Niobium oxide (Nb₂O₅) is an excellent catalyst to drastically improve the reaction kinetics of Mg^[1,2]. In this work, catalysis and reactivation of the Nb-oxide are investigated.

Amorphous-Nb₂O₅ were dispersed on MgH₂ by ball-milling for 2 h. Then, the sample were kept for 6 months in the globe box filled with purified Ar gas. The hydrogen desorption (HD) and absorption (HA) properties were investigated by thermogravimetry-differential thermal analysis (TG-DTA) under Ar and H₂ flow conditions. The surface chemical state were analyzed by X-ray photoelectron spectroscopy (XPS).

Amorphous-Nb₂O₅ shows superior catalysis as same as the best activated MgH₂ by Nb₂O₅ reported in previous work even though the ball milling time is ten times shorter^[2] (Fig.1 a). After 6 months, the HD temperature increased over 100 °C because the chemical state of Nb oxide was degraded. The degraded catalyst was reactivated by dehydrogenation and rehydrogenation treatments (Fig.1 b.c). Thus, the catalysis of Nb oxide is intelligently preserved under the reactions with H₂.

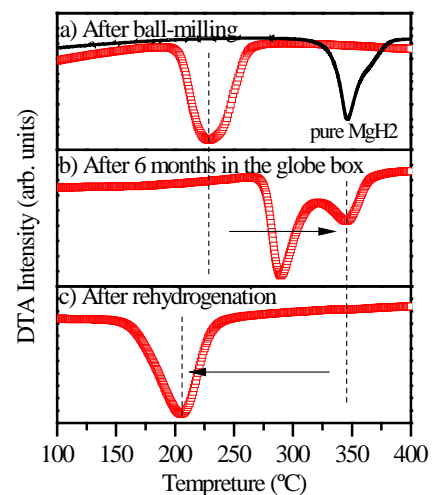



Fig. 1 H₂ desorption properties of pristine MgH₂, as-synthesized, degraded, and rehydrogenated MgH₂ with Nb₂O₅

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Research keywords: Particle technology, Flame synthesis, nanoparticle, Aerosol, $\text{Cs}_{0.32}\text{WO}_3$


Evaluation of cesium doped tungsten oxide nanoparticles made in diffusion flames for near-infrared shielding applications

Cesium doped tungsten oxide ($\text{Cs}_{0.32}\text{WO}_3$) nanoparticles has been regarded as highly promising near-infrared (NIR) shielding material. Until now, $\text{Cs}_{0.32}\text{WO}_3$ nanoparticles have been synthesized via solid state, hydrothermal, water controlled-release solvothermal, and thermal plasma synthesis methods that need high energy, costs, or long time. Thus, it is necessary to synthesize $\text{Cs}_{0.32}\text{WO}_3$ nanoparticles using a rapid and energy effective method to make it feasible for large-scale and practical applications.

In this work, highly crystalline and hexagonal single-phase $\text{Cs}_{0.32}\text{WO}_3$ nanoparticles were successfully synthesized by flame-assisted spray pyrolysis (FASP) followed by annealing under a reducing gas atmosphere [1]. The as-synthesized nanoparticles from FASP indicated multiple phases of hexagonal $\text{Cs}_{0.32}\text{WO}_3$ and cubic $\text{CsW}_{1.6}\text{O}_6$. However, after annealing at 650°C for 1 h under a reducing gas atmosphere, the crystal structure of the $\text{Cs}_{0.32}\text{WO}_3$ nanoparticles changed completely to a single hexagonal $\text{Cs}_{0.32}\text{WO}_3$ phase. In addition, the $\text{Cs}_{0.32}\text{WO}_3$ nanoparticles prepared in this research showed a remarkable near-infrared shielding ability with a 97.7% cut-off at 1500 nm. Unlike conventional methods, the proposed process in this research has several advantages, including a short reaction time and the ability to yield products with high purity and good energy efficiency, in particular the use of a grinding process was avoided. In conclusion, FASP shows great promise as a new method for rapid and energy effective production of $\text{Cs}_{0.32}\text{WO}_3$ nanoparticles that exhibit absorption in the near-infrared region without the need for a grinding process.

Reference

[1] Tomoyuki Hirano, Shuhei Nakakura, Febrigia Ghana Rinaldi, Eishi Tanabe, Wei-Ning Wang, Takashi Ogi*, Synthesis of Highly Crystalline Hexagonal Cesium Tungsten Bronze Nanoparticles by Flame-assisted Spray Pyrolysis, *Advanced Powder Technology*, 29, 2512-2520 (2018).

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Research keywords: Catalysis, Kinetics, Thermodynamics, Activation Energy, Hydrogen Energy

Improved hydrogen release from MgH₂ by various Nb and Ta gel oxides

The catalytic properties of various Nb and Ta oxides for hydrogen desorption and absorption of magnesium (Mg) are investigated to improve the kinetics. 6 types of oxides are synthesized by solution method as additives, which are Nb₂O₅ gel, Nb₂O₅ gel with heat treatment (HT) at 500 °C, Ta₂O₅ gel, Ta₂O₅ gel with HT at 500 °C, Nb+Ta gel, and Nb+Ta gel with HT at 500 °C, where all the oxides are amorphous phase. MgH₂ with 1 mol% of various Nb and Ta oxides are ball milled to disperse additives on surface of Mg. The observation of morphology are performed by scanning electron microscopy (SEM). The hydrogen desorption and absorption properties are investigated by thermogravimetry (TG) under Ar and H₂ flow conditions, respectively.

Fig. 1 shows dehydrogenation curves of MgH₂ with various oxide additives. Although pristine MgH₂ desorb hydrogen more than 350 °C, the hydrogen desorption of all the samples were observed below 300 °C, suggesting that all the additives showed catalytic effects for the hydrogen desorption of MgH₂. Among them, Nb₂O₅ gel with HT revealed the highest catalytic effect. The desorption of hydrogen started around 200 °C, which is comparably lower than that of previous report^{1, 2)}. Other results are shown and discussed in the presentation.

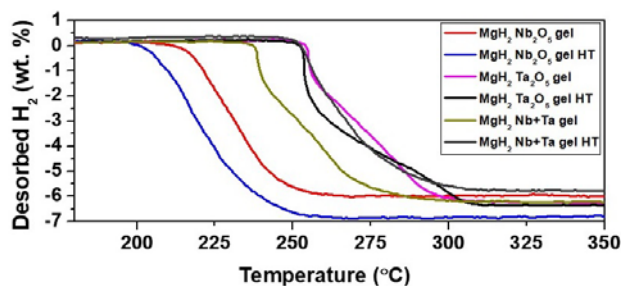



Fig. 1 Hydrogen desorption curve of MgH₂ with various oxides

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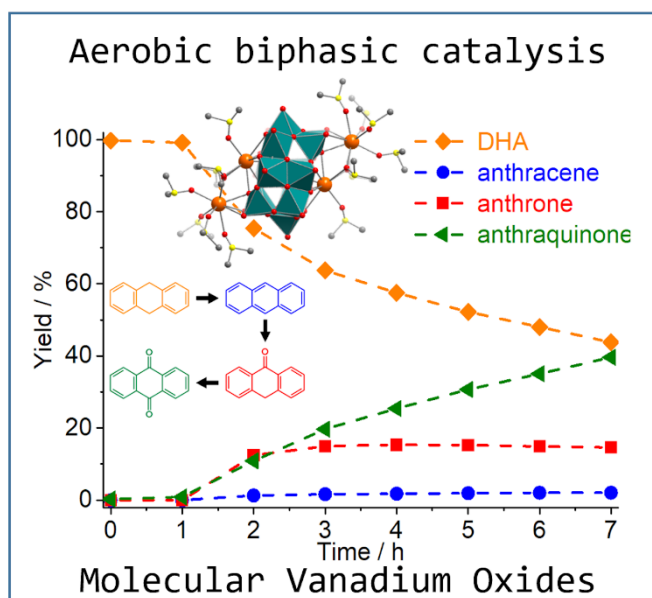
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Research keywords: catalysis, oxidation, polyoxometalate, polyoxovanadate, self-assembly

Aerobic oxidation catalysis with molecular polyoxometalates

Abstract: Aerobic catalytic oxidations are promising routes to replace environmentally harmful oxidants with O₂ in organic syntheses. Here, we report a molecular barium vanadium oxide, [Ba₄(dmsO)₁₄V₁₄O₃₈(NO₃)] (= {Ba₄V₁₄}) as viable homogeneous catalyst for a series of oxidation reactions in N,N-dimethyl formamide solution under oxygen (8 bar). Starting from the model compound 9,10-dihydroanthracene, we report initial dehydrogenation/ aromatization leading to anthracene formation; this intermediate is subsequently oxidized by stepwise oxygen transfer, first giving the mono-oxygenated anthrone and then the di-oxygenated target product, anthraquinone. Comparative reaction analyses using the Neumann catalyst [PV₂Mo₁₀O₄₀]⁵⁻ as reference show that oxygen diffusion into the reaction mixture is the rate-limiting step, resulting in accumulation of the reduced catalyst species. This allows us to propose improved reactor designs to overcome this fundamental challenge for aerobic oxidation catalysis.



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Research keywords: molecular deformation

Cation dependence of the thermal molecular deformation of basket-type polyoxometalate

【Abstract】

A polynuclear metal complex in which primary transition metal ions such as Mo and W are bridged by oxo ligand is known for polyoxometalate (POM). It is an inorganic molecule characterized by a molecular size of 1-6 nm, various molecular shapes, a stable mixed valence state, etc. In addition, it has been applied as a catalyst, electron and electrode material because of its multi-step redox activity^[1]. Moreover, it has been clarified that POM exhibits unique physical properties and functions that are different from each other by hybridizing with organic molecule. In our laboratory, we have been developed a new substance group of organic-inorganic hybrid POM using mixed valence basket type POM (Figure 1). The organic site (R) can be derived by designing a organic phosphonic acid^[2-3]. Herein, the influence of organic sites and counter cations on crystal structure and phase transition mechanism were investigated in depth.

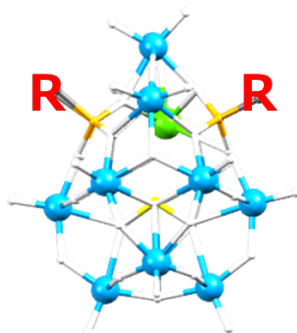



Figure 1. Structure of organic-inorganic hybrid type basket POM



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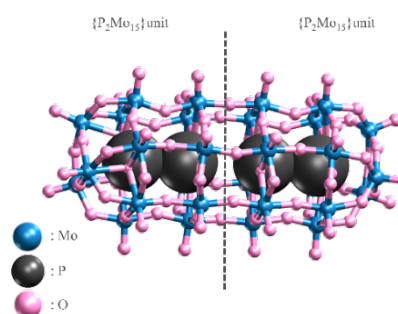
Research keywords: electrical properties

Exploring macroscopic electrical properties of mixed valence POM

Polyoxometalate (POM) is a polynuclear molecular cluster that is assembled by $\{Mo_x\}$ polyhedral building blocks ($x = 4-7$, $M =$ transition metals such as Mo, W, V, and Nb). POMs generally show high electron accepting ability due to the highest oxidation state such as +6 for Mo and W. Partially reduced mixed valence (MV) state of $M^{V/VI}$ is stabilized by the electron delocalization between several M sites. However, in different from bulk metal oxide that shows varieties of macroscopic electric properties of electric conduction and dielectric properties, POMs in the solids are almost silent for these properties. This is because of their structure isolated by counter cation. Long range ordering or charge transport are difficult.

In contrast to the traditional POM-based salts, alternated packing structure of $[PMo^V Mo^{VI}_{11} O_{40}]^{4-}$ and a pyridine derivative tetrathiafulvalene (TTFPy) showed unique electrical conduction through the POMs.[1] Conductivity σ was 6.30×10^{-7} S/cm at room temperature, showing macroscopic electrical conductivity comparable to semiconductor Si. Furthermore, we developed the charge polarization type dielectrics using mixed valence $[PMo^V_2 Mo^{VI}_{12} O_{40}]^{4-}$. [2]

Herein we explored macroscopic electrical properties of rod-shaped POM of $\{P_4 Mo_{30}\}$. MV salt was newly prepared and investigated.



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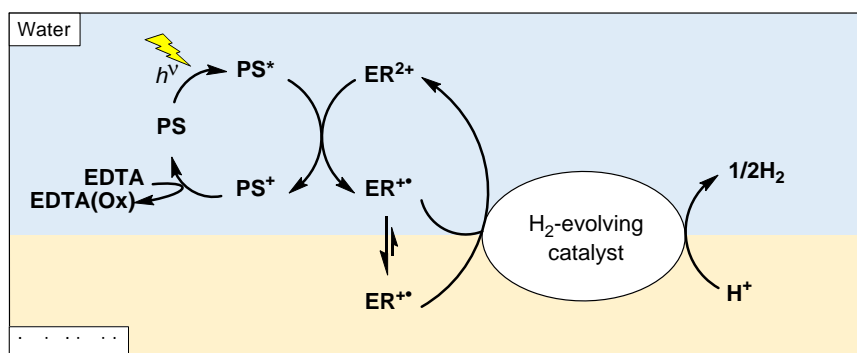
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Research keywords: Photochemical H₂ evolution, Biphasic system, Ionic liquid

Photochemical Hydrogen Evolution in Biphasic Systems Consisting of Aqueous and Ionic-liquid Solutions

Photochemical H₂ evolution has been intensively studied in order to solve energy and environmental problems. In this area, most studies focus on multi-component photochemical systems, which consist of a photosensitizer, an electron relay, a sacrificial electron donor and an H₂-evolving catalyst. However, these systems often suffer from the charge recombination among diffusing redox active species. On the other hand, ionic liquids (**ILs**) have attracted much attention for its unique characters, such as non-volatility and high chemical stability. In addition to these unique characters, properties of **ILs** could be controlled by changing the molecular structure and the combination of a cation and an anion.

In this study, we adopt **ILs** as a phase to carry out the H₂ evolution photocatalyzed by multi-component photochemical system (Scheme 1). Specifically, we have developed an aqueous-**IL** biphasic model, where **ILs** serve as a reservoir of reducing equivalents required for the catalytic H₂ evolution. We also demonstrated photochemical H₂ evolution proceeds in the presence of colloidal Pt as an H₂-evolving catalyst. In addition to this works, our recent studies on polyoxometalates, in which photochemical water oxidation catalysed by mono- and dicobalt polymolybdate, are also discussed in the presentation.



Scheme 1. Schematic diagram of a multi-component photochemical H₂ evolution in a biphasic system consisting of an aqueous solution and an **IL** solution.

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Research keywords: Photochemical hydrogen evolution, Platinum(II) complex, Redox-active ligand

Photochemical Hydrogen Evolution from Water Catalyzed by a Platinum(II) Complex Bearing Nindigo as a Redox-active Ligand

Some platinum(II) complexes^[1] together with macrocyclic *N*-heterocyclic carbene cobalt (Co-NHC) complexes^[2] have been shown to serve as molecular catalysts for hydrogen evolution reaction (HER) in a photochemical system consisting of EDTA, [Ru(bpy)₃]²⁺ and methylviologen (MV²⁺: electron relay). Remarkably, the driving force for HER driven by MV⁺ is only 150 meV (Figure 1). Nevertheless, these catalysts have been shown to promote HER via the unique catalytic pathways on the basis of the metal-centered proton-coupled electron transfer (PCET).

In order to further improve their catalytic activities, the authors attempted to finely tune the redox properties of electron relays.^[3] Consequently, we found that the tetramethyl-substituted methylviologen electron relay can achieve 30 times higher photocatalytic turnover frequency relative to that by the non-substitute methylviologen. We also find that a new water-soluble Nindigo Pt(II) complex can promote photocatalytic HER in the same photochemical system (Figure 1), where Nindigo is an iminated compound of indigo, and is expected serve as an electron reservoir site.^[4]

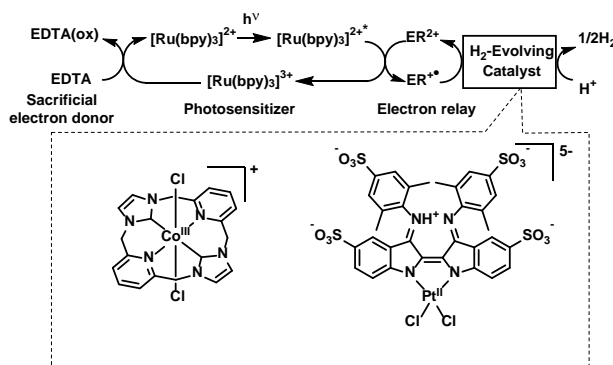


Figure 1. Photochemical H₂ evolution from water catalyzed by some molecular catalysts.


The kinetics of water oxidation catalyzed by a monocobalt polymolybdate (Co-POM), intensively studied so far in our group, will also be discussed as part of our approaches to the polyoxometalates. Reference.

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Research keywords: *Metal organic framework (MOF); rechargeable battery; disulfide; redox reaction, X-ray absorption fine structure (XAFS)*


Research on the correlation between the structures and battery performances of MOFs with disulfide moiety-containing ligands

Recently, we have realized improvement of battery performances of disulfide compounds by immobilizing them as a ligand in a MOF^[1]. In order to further advance this finding, we performed physical property and electrochemical measurements for disulfide-containing MOFs (DS-MOFs), and we investigated the correlation between their structures and battery performances.

In this study, we chose DS-MOFs with a large pore volume : [Co(NCS)₂(4dpds)₂]_n (1D-DS-Co-MOF)^[2], [Cu(C₂O₄)(4dpds)]_n (2D-DS-Cu-MOF)^[3], [Mn₂(6dtba)₂(H₂O)₂]_n (3D-DS-Mn-MOF 1)^[4] and MOFs with a small pore volume : [Cu₄(HCO₂)₆(OH)₂(4dpds)₂]_n (1D-DS-Cu-MOF)^[5], [Mn₅(2dtba)₄(OH)₂]_n (3D-DS-Mn-MOF 2)^[6] as cathode active materials of lithium metal batteries. Whereas three DS-MOFs with a large pore volume exhibited capacities close to their theoretical values based on the redox reactions of metal ions and disulfide bonds, two DS-MOFs with a small pore volume exhibited very small capacities. Powder X-ray diffraction and S and each metal *K*-edge XAFS analyses revealed that the reversible redox reactions of metal ions and disulfide bonds in the DS-MOFs with a large pore occurred. On the other hand, metal ions and disulfide ligands in the ones with a small pore volume did not show redox reaction at all. In conclusion, we found that the pore volume is one of the factors controlling the electrochemical properties of DS-MOFs.

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Research keywords: molecular photophysics, fluorescence, transient absorption spectroscopy, singlet exciton fission, solar fuels.

Intramolecular Singlet Exciton Fission in an Elongated Bis-Pentacene Derivative

Singlet exciton fission¹ has gained considerable interest over the past five years as a means by which the number of charge carriers per absorbed photon could be doubled in an organic solar cell. Singlet fission (SF) generates two triplets from the singlet excited state where a pair of coupled organic chromophores satisfying the energy requirement $E S_1 \geq 2 \times T_1$ interact. SF sensitizers have become a more practical proposition for solar cells as more singlet fission chromophores have emerged. First seen in crystals of acenes, SF has also been observed in concentrated solution for TIPS-pentacene². Recently intramolecular SF (iSF) in covalently linked SF bichromophores has been reported³.

Pentacene in particular is a well-studied SF chromophore both in crystals and in solution. Triplet quantum yields of up to 200 % have been seen in solution for pentacene derivatives³. Recent reports suggest SF sensitizers can be incorporated into existing organic solar cell designs⁴, but more work is required to understand the mechanism.

The study here presents a new bridged bispentacene chromophore (**BBP**)⁵ where two TIPS-pentacene units have been linked by a fluorene bridge, a

spatial separation of ~ 10 Å. A study of the photophysics of this system in solution has attempted to shed more light on how the rate of intersystem crossing is enhanced. Nano- and picosecond transient absorption spectroscopy suggests there is strong communication between pentacene moieties in the

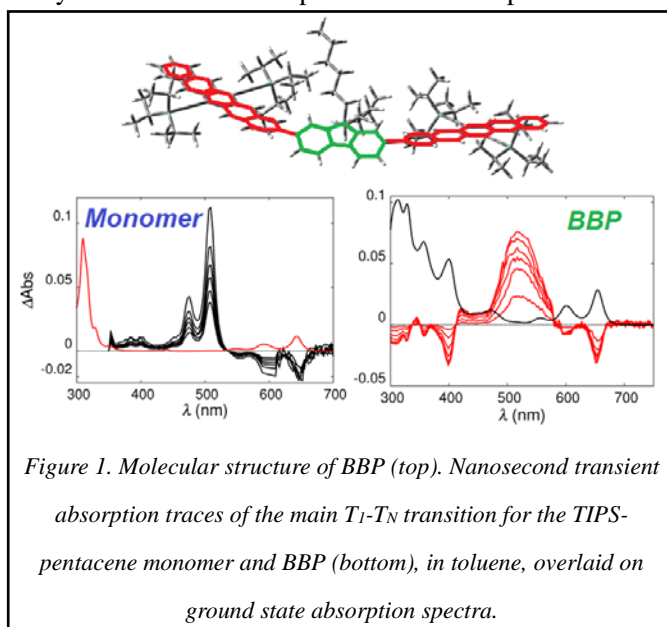



Figure 1. Molecular structure of BBP (top). Nanosecond transient absorption traces of the main T_1 - T_N transition for the TIPS-pentacene monomer and BBP (bottom), in toluene, overlaid on ground state absorption spectra.

bichromophore, showing an unusually long-lived delocalized triplet state. Pulse radiolysis measurements were used to confirm a triplet yield in excess of unity in the case of BBP, with a high level of confidence.

It has been shown that charge transfer may play a critical role in the SF mechanism⁶. Data for BBP suggest prevailing conformations between the TIPS-pentacene units may affect charge transfer, indeed molecular modelling shows a far from rigid structure for BBP. Molecular orbital calculations suggest super-exchange also plays a role in the communication between the pentacene units. Additional bands in the absorption spectrum of BBP compared to TIPS-pentacene might be attributed to charge transfer. The energy gap law predicts a short-lived triplet. For our system specifically we see a partitioning between single triplets and triplet exciton pairs (due to iSF) on a single BBP molecule.

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Research keywords: Polyoxometalate, energy storage, reduction

Towards Super-Reduction: an Investigation of Polyoxometalate Redox Properties for Energy Storage.

Polyoxometalates (POMs) are promising materials for energy storage, this is due to their ability to reversibly accept multiple electrons with no change to their structure. POMs have been investigated for applications in supercapacitors and Li-ion batteries.¹⁻³ The Keggin POM, $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ has been investigated for use in supercapacitors and more recently Li-ion batteries.^{1,3} The study by Awaga *et al.* focused on the tetrabutylammonium salt of $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ and suggested that it could be reversibly reduced by 24 electrons in a coin cell.³ This study set out to investigate the step-wise chemical reduction of $(\text{TBA})_3[\text{PMo}_{12}\text{O}_{40}]$ using metal-mercury amalgams (Li and Na) in acetonitrile and propylene carbonate. These reductions have been followed by multinuclear NMR and FTIR in order to investigate the formation of 'super-reduced' POMs by chemical reduction in solution. NMR spectra show comparatively narrow peaks when up to 12 electrons are added to the POM to give blue solutions but very broad peaks are observed for the brown solutions produced upon addition of 12 or 24 electrons. The dramatic colour change from dark blue to dark brown is indicative of a significant change in electronic properties.

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Research keywords: Polyoxometalates, Poly-ionic Liquids, 3D-Printing, Supramolecular Assembly, Advanced Soft Materials

Integration of Polyoxometalates into Functional Hybrid Soft Materials

Polyoxometalates (POMs) have long been targeted as attractive, bespoke molecular clusters in which their highly tuneable structure and composition allows their form to be tailored towards a desired functionality. This has led to an explosion in their proposed application across a wide range of fields, including catalysis, energy storage and molecular biology, to name but a very few.^[1] More recently, the community has begun to explore new approaches which combine the rational design of these functional molecular building blocks with novel self-assembly or compositing strategies in order to translate the attractive properties of POMs into new materials with well-defined morphologies over a wide range of possible length-scales (*e.g.* from nanometers to centimeters).^[2] Here, I will present a brief overview of our recent work in this area, encompassing both “bottom-up” and “top-down” design strategies for the incorporation of POM clusters into functional soft materials. This will include our work on redox-active inorganic-organic hybrid POM surfactants, which we have explored as a building block for a range of functional nano- and micro-scale supramolecular soft materials,^[3] and our work on POM/poly-ionic liquid (PIL) polymer composites, which can be 3D-printed into a range of custom-designed photochromic objects.^[4]

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Research keywords: Energy Storage, Redox Flow Batteries, Polyoxometalates


Non-Aqueous Polyoxometalate Electrolytes for High Energy Density Redox Flow Batteries

Redox flow batteries (RFBs) are rechargeable energy storage devices that can be readily scaled to meet various grid needs. RFBs differ from conventional batteries in that they store electrical energy in redox-active electrolytes. The electrolytes are stored in external reservoirs and are pumped into the electrochemical cell during charge/discharge. Traditional RFBs are composed of redox mediators, typically metals, dissolved in aqueous solvent at maximum concentrations of 3 mol dm^{-3} .¹

Polyoxometalates (POMs) are promising redox mediators for energy dense electrolytes, due to their highly reversible multi-electron redox activity. In this contribution, we investigate the use of organic-inorganic hybrid POMs in organic electrolytes, with the view to increase POM solubility and maximise cell voltage. In addition, we explore the use of electrolytes containing ionic liquids, salts that are liquids below $100 \text{ }^\circ\text{C}$. By dissolving the redox-active POMs in ionic liquids, we exploit the low volatility, thermal stability and wide electrochemical window of these solvents. We describe the synthesis of phosphotungstate-based POMs containing redox-active ferrous cations and discuss the effects of the ionic environment of ionic liquids on the electrochemical behaviour of the redox species.

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Research keywords: synthesis, organic-inorganic hybrid, asymmetric, redox properties

Asymmetric multi-functional redox-active hybrid polyoxometalates


Covalently linked organic groups in organic-inorganic hybrid polyoxometalates (POMs) provide a means of fine-tuning both new and intrinsic properties in the hybrid system, through the design of the individual components, in order to tailor properties for function.¹ By tuning the electronic character of the POM in this way, photochemical systems can be developed with improved catalysis or photosensitivity.² Controlled design has potential also in materials chemistry, by achieving directed assembly onto surfaces and into various nanostructures.³

The grafting of two different organic ligands, to create an “asymmetric” hybrid”, introduces additional possibilities for tailoring properties and controlling assembly in a more complex system, but their isolation and purification remains a synthetic challenge. Here, we present our recent advances in the synthesis and characterisation of asymmetrically organophosphonate-functionalised Wells-Dawson-POM derivatives, using a simple and inexpensive purification method.

The unique properties and reactivity of this asymmetric system is explored by exploiting both postfunctionalisation by metal coordination at the binding site on one ligand, and, additionally, by solvent-dependent self-assembly into soft nanostructures facilitated by the second, aliphatic ligand. This capability of controllable self-assembly combined with metal complexation in an asymmetric structure is a step towards creating far-more advanced catalytic and switchable multi-component systems.

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Research keywords: preyssler-type polyoxometalate, single-molecule, ferroelectricity

The Single-Molecular Electret (SME) Behaviors of Preyssler-Type Polyoxometalate

Ferroelectric materials had been widely applied for electric/optical devices because of switchable electric polarization by external field. However, this property tends to disappear with decreasing size of materials approximately less than 10 nm due to superparaelectric state. Recently, our group newly established the mechanism of switchable electric polarization in single-molecule, single-molecular electret (SME), by using preyssler-type polyoxometalates (POMs) $[\text{Tb}^{3+}\text{cW}_{30}\text{O}_{110}]^{12-}$.^[1] In this work, details of dielectric properties and SME behavior were investigated.

Molecular structure of $[\text{Tb}^{3+}\text{cW}_{30}\text{O}_{110}]^{12-}$ was shown in figure 1. This type of POMs possesses two stable ion sites in W-O cage and encapsulated terbium ion moves randomly at high temperature. With decreasing temperature, it was localized at either site. Temperature- and frequency-dependent dielectric properties did not show ferroelectric phase transition behavior, but the wide frequency range of dielectric dispersions associated with displacement of terbium ion. Despite the loss of long-range dipole order, electric field dependence polarization and temperature-dependent polarization measurement clearly observed ferroelectric-like behavior. Maximum spontaneous polarization was estimated about $6 \mu\text{C cm}^{-2}$ at 290 K with $\pm 4.00 \text{ kV cm}^{-1}$ (figure 2).

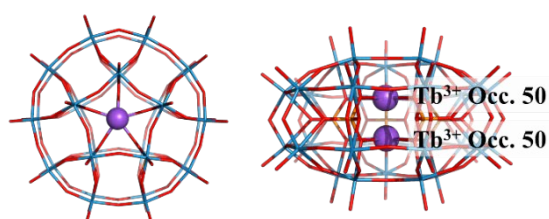


Fig. 1. Top and side views of $[\text{Tb}^{3+}\text{cW}_{30}\text{O}_{110}]^{12-}$.

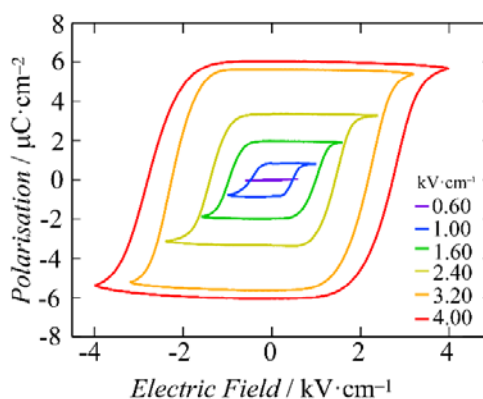



Fig. 2. Hysteresis loops depending on applied electric field at 290K.

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Research keywords: BODIPY, Organic synthesis, dye synthesis, BODIPY POMS

The design and synthesis of BODIPY dyes with carboxylic acid anchor groups for Sonogashira coupling to both Keggin and Dawson POMS. This is an expansion on previous work done in collaboration E-POM team from Sorbonne Université, where simple BODIPY dyes were coupled to both Keggin and Dawson POMS.¹ This project has wider aims to have the anchored BODIPY-POMS for both use in DSSC's as well as water splitting.

Future collaborations are open where custom BODIPY dyes are required to be made.

1 Rapid photoinduced charge injection into covalent polyoxometalate-bodipy conjugates
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Research keywords: Li-air batteries, homogeneous catalysis, Keggin-type POMs

Using polyoxometalates as redox mediators in Li-air batteries

Li-ion and related battery technologies will be important for years to come. However, society needs energy storage that exceeds the capacity of Li-ion batteries. We must explore alternatives to Li-ion if we are to have any hope of meeting the long-term needs for energy storage. One such alternative is the Li-air (O₂) battery; its theoretical specific energy exceeds that of Li-ion, but many hurdles face its realization.^[1-5] One of the major challenges for Li-air batteries is in obtaining efficient, reversible charging and discharging.

Recently, it has been demonstrated that redox mediators (RMs) can improve cell cycling by altering the electrochemical reactions occurring at the electrode and acting as homogeneous catalysts.^[6-8] However, these RMs are typically organic molecules and only possess one redox process within the Li-air potential window, making them suitable for either discharge or charge, not both. This has been overcome by the use of two mediators, one for discharge and the other charge.^[9]

Polyoxometalates have also been used as RM and, furthermore, have several advantages over organic RMs, one of which is that they undergo multi-electron redox processes.^[10] Therefore, POMs could act as RMs for both charge and discharge, i.e. bi-functional RMs. Here, we consider the requirements for a successful POM-based RM for Li-air batteries and discuss our recent work investigating Keggin-type POMs as RM candidates. POMs with varying degrees of metal ion substitution have been synthesized and characterized electrochemically in order to assess their suitability for Li-air batteries.

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