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## Bio-inspired Oxyanion Reduction with Iron

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Oxyanions, potent groundwater contaminants, have long been regarded as chemically inert due to their nature as non-complexing anions, poor nucleophiles, and their resistance to both oxidation and reduction. These properties, coupled with their multi-electron and multi-proton reactivity, make the catalytic reduction of oxyanions a significant challenge. Biological systems employ metalloenzymes with highly specialized coordination spheres to catalyze the efficient reduction of kinetically inert oxyanions under mild conditions.<sup>1</sup> Inspired by these natural systems, we have developed homogeneous metal-based complexes to achieve oxyanion reduction. Our group focuses on designing transition metal complexes—particularly those based on iron—that can facilitate these difficult transformations. By leveraging ligand design, through secondary coordination sphere interactions, we aim to enhance the reactivity of iron centers and promote the reduction of a wide variety of oxyanions under mild conditions.<sup>2-6</sup> This presentation will highlight our recent advances in developing iron-based catalysts capable of selectively reducing oxyanions, offering insight into both the mechanistic challenges and the strategies employed to overcome them.

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# Scalable Routes to Functional Materials: Photocatalytic, TCO and Anti-Soiling Coatings

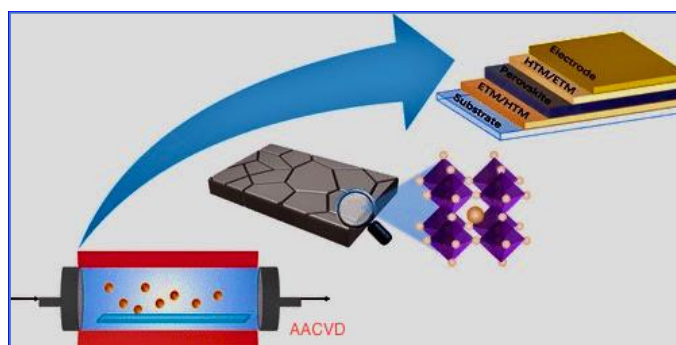
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The search for efficient materials for sustainable infrastructure is a key challenge to address the global environmental crisis. Sunlight-activated coatings, particularly those produced from scalable technologies, are sought in the glass industry for applications in self-cleaning windows. Current research involves developing processes towards sustainable and inexpensive functional materials including photocatalysts, anti-soiling coatings, transparent conducting oxides (TCOs) and photoelectrochemical films on glass. These find application as low-emissivity windows, photovoltaics, optoelectronic devices and self-cleaning windows, as well as anti-soiling coatings for solar modules.

Our method uses aerosol assisted chemical vapour deposition (AACVD) to develop scalable coatings. Chemical vapour deposition (CVD) is a film deposition method which involves a series of chemical reactions in the vapour phase. Due to its low cost, scalability and reliability, CVD has been industrially utilized in many optoelectrical fields, particularly glass coating and semiconductors. Compared to conventional CVD, the AACVD method is a solution-based process which uses aerosol droplets to transport precursors, with the aid of an inert carrier gases. Therefore, in AACVD volatility is no longer crucial and this allows for a wider choice of precursors being available for use and can lead to high quality films at low cost. AACVD can result in the formation of highly textured coatings which can enhance the functional properties. We have investigated the AACVD of a range functional thin films including perovskites, TCOs, photocatalyst, heterojunctions and low-emissivity coatings.



**Figure 1.** AACVD process for film deposition and device preparation.

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# Molecular redox reactivity of s-block elements

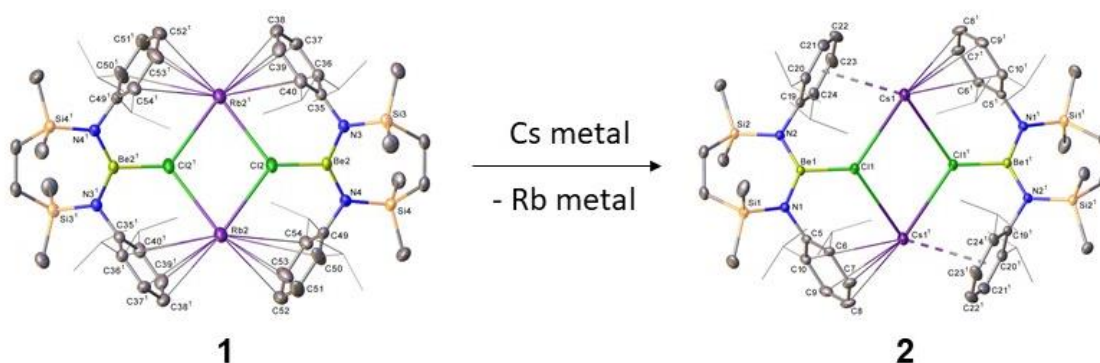
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Familiar to anybody who likes salt on their chips, a quintessential feature of alkali metal ( $M = \text{Li, Na, K, Rb, Cs}$ ) chemistry is the stability and resistance to reduction of the  $M^+$  cations. In such cases, as an article of chemical faith, the resultant  $M^+$  oxidation state is generally considered incorruptible, whether as a component of a stable side product or incorporated into the compound of interest.

This presentation will discuss the counterintuitive observation that alkali metal components of heterobimetallic s-block (e.g. the Be compounds, **1**  $\rightarrow$  **2**), p-block and d-block molecules are, at least in part, interconvertible and prone to an unprecedented range of group 1-based redox reactivity.<sup>1-4</sup> This behaviour provides a novel means with which to access regions of otherwise inaccessible chemical space and, more broadly, may carry significant implications for other areas of scientific and technological importance in which  $M^+$  mobility and ease of electrochemical cycling are a primary consideration.



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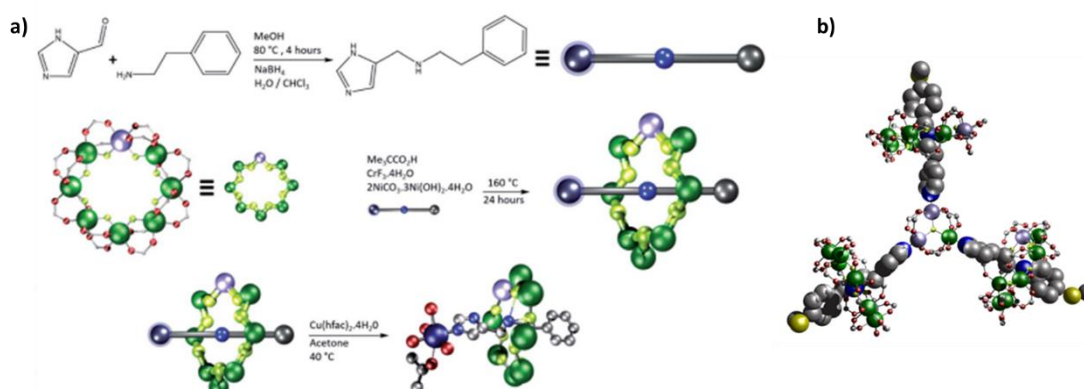
# Synthetic and Spectroscopic Studies of Molecular Magnets using Supramolecular Assemblies as Multi-Qubit Systems for Quantum Information Process

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Supramolecular chemistry enables complex arrays to be assembled that can bring together similar and dissimilar spin systems. Through careful design, *g*-engineering approaches can be used to tune multi spin systems that maintain the unique identity of each individual spin.<sup>1</sup> Investigating the interactions between such systems to exploit the electron spin can be done through various EPR techniques, showing larger more complex systems can be developed, without quenching individual qubit properties. This work is based on the anionic  $[\text{Cr}_7\text{NiF}_8(\text{O}_2\text{C}^t\text{Bu})_{16}]^-$  ring, which provides a spin with relatively low *g* value of  $\sim 1.78$ . This [2]rotaxane can be coordinated to many different spin systems by the adaption of a thread that sits within the centre of the ring.<sup>2,3</sup> The thread can be used to tune the exchange interaction or it can be modified to control the overall structure of the resulting supramolecular complex.



**Figure 1:** a) Scheme for rotaxane with coordinate to a second spin system, b) coordination of rotaxane to a triangle node producing the [4]rotaxane  $[\{\text{Cr}_7\text{Ni}\}_3\{\text{Ni}_2\text{Cr}\}]$ .

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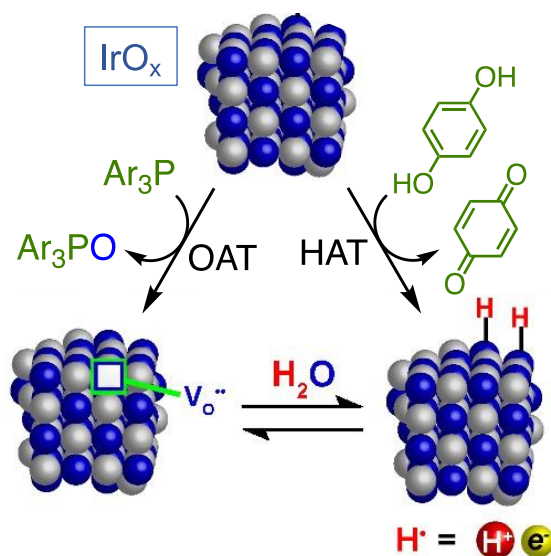
## Fundamental Redox Reactions at Metal-Oxide Interfaces

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Redox reactions of metal-oxido/hydroxido/aqua species often occur by proton-coupled electron transfer (PCET) or by oxygen atom transfer (OAT). What has been learned for molecular  $\text{MOH}_n$  complexes in solution provides a strong foundation for understanding the surface redox chemistry of metal-oxides.<sup>1,2</sup> However, the core issues of stoichiometry, thermochemistry, and reaction barriers are more challenging to measure at solid/solution interfaces, and they are often complicated to even define. Our laboratory is studying chemical and electrochemical reactions of the surfaces of  $\text{IrO}_x$ ,  $\text{NiO}$ ,  $\text{TiO}_2$ ,  $\text{WO}_3$ , and  $\text{CeO}_2$ , both as nanoparticles and thin films, and both with aqueous and aprotic organic solutions.<sup>3-5</sup> The transfer of electrons to or from these materials is tightly coupled to the transfer of protons or other cations. These often—but not always—occur in a 1:1  $e^-/\text{H}^+$  ratio, which is equivalent to a hydrogen atom transfer (HAT) process ( $\text{H}^\bullet = e^- + \text{H}^+$ ). As illustrated in the Scheme below, HAT reactions can be connected oxygen atom transfers (OAT) of the same material. The evolving understanding of reactions at solid/liquid interfaces should be relevant to heterogeneous catalysis, electrocatalysis, corrosion, and other processes from the environment to chemical synthesis.



Scheme connecting oxygen atom transfer (OAT) and hydrogen atom transfer (HAT) reactions of colloidal iridium oxide nanoparticles.

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## Latest Developments with Layered Double Hydroxides

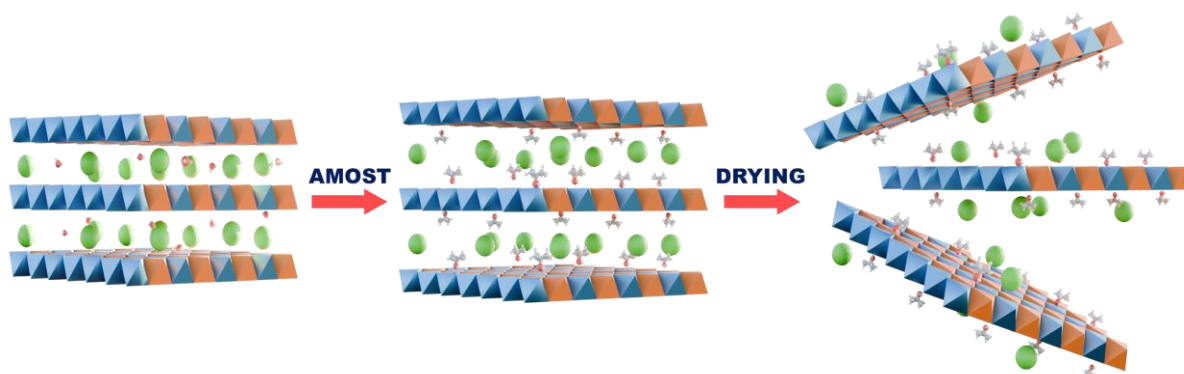
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Layered double hydroxides (LDHs) are a highly tunable class of inorganic materials with the general formula  $[M_{(1-x)}M'_x(OH)_2]^{a+} [A^{n-}]_{a/n}$  where M and M' are most commonly divalent and trivalent metal cations,  $A^{n-}$  is an anion and  $0 < x < 1$ . The metal hydroxides form a positively charged brucite-like layers, with the intercalated anions providing charge balance. However, agglomeration of the LDH platelets leads to low surface area dense "stone-like" agglomerates which limits their use in many applications.

We have developed both solvent dispersion and core@shell approaches to avoid the agglomeration of the LDH platelets. For example, our Aqueous Miscible Organic Solvent Treatment (AMOST) process can create highly dispersed LDH-based materials consisting of nanosheet dispersions. This process produces exposed active sites with high surface areas and porosity. It is now possible to tailor these materials to a wide range of novel applications such as solid CO<sub>2</sub> sorbents<sup>1</sup> and heterogeneous catalysis.<sup>2,3,4,5</sup>



Schematic illustration of the Aqueous Miscible Organic Solvent Treatment (AMOST) synthesis of highly dispersed layered double hydroxides (LDHs).

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# Organometallic Chemistry at the Edge: Installing Active Sites on Clusters and Nanosheets

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A central research goal in the Velian group is to create next-generation single-site catalysts poised to harness the cooperativity between the active site and chemically non-innocent supports. To emulate defect sites in inorganic heterogeneous catalysts in a controlled fashion, we embed well-defined active sites on the surface of clusters (i.e.,  $\text{Co}_6\text{Se}_8\text{L}_6$ ) and 2D nanosheets (i.e., black phosphorus).

The first part of this seminar will introduce a class of atomically precise nanoclusters distinguished by the presence of discrete active sites that engage dynamically with the non-innocent metal chalcogenide cluster support and with substrates. Structure-function studies provide unprecedented atom level insights into catalytic interfaces and the role of allostery and metal/support cooperativity in catalysis.<sup>1–3</sup>

The second part of the talk will introduce an top-down approach to active-site synthesis, in which the basic principles of organometallic chemistry are harnessed to anchor metal complexes on the surface of two-dimensional black phosphorus nanosheets.<sup>4–6</sup>

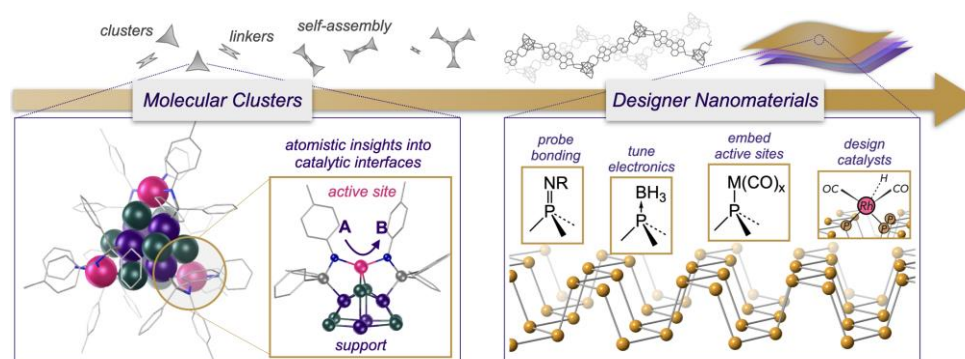


Figure 1. Installing Active Sites Across Lengthscales.

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