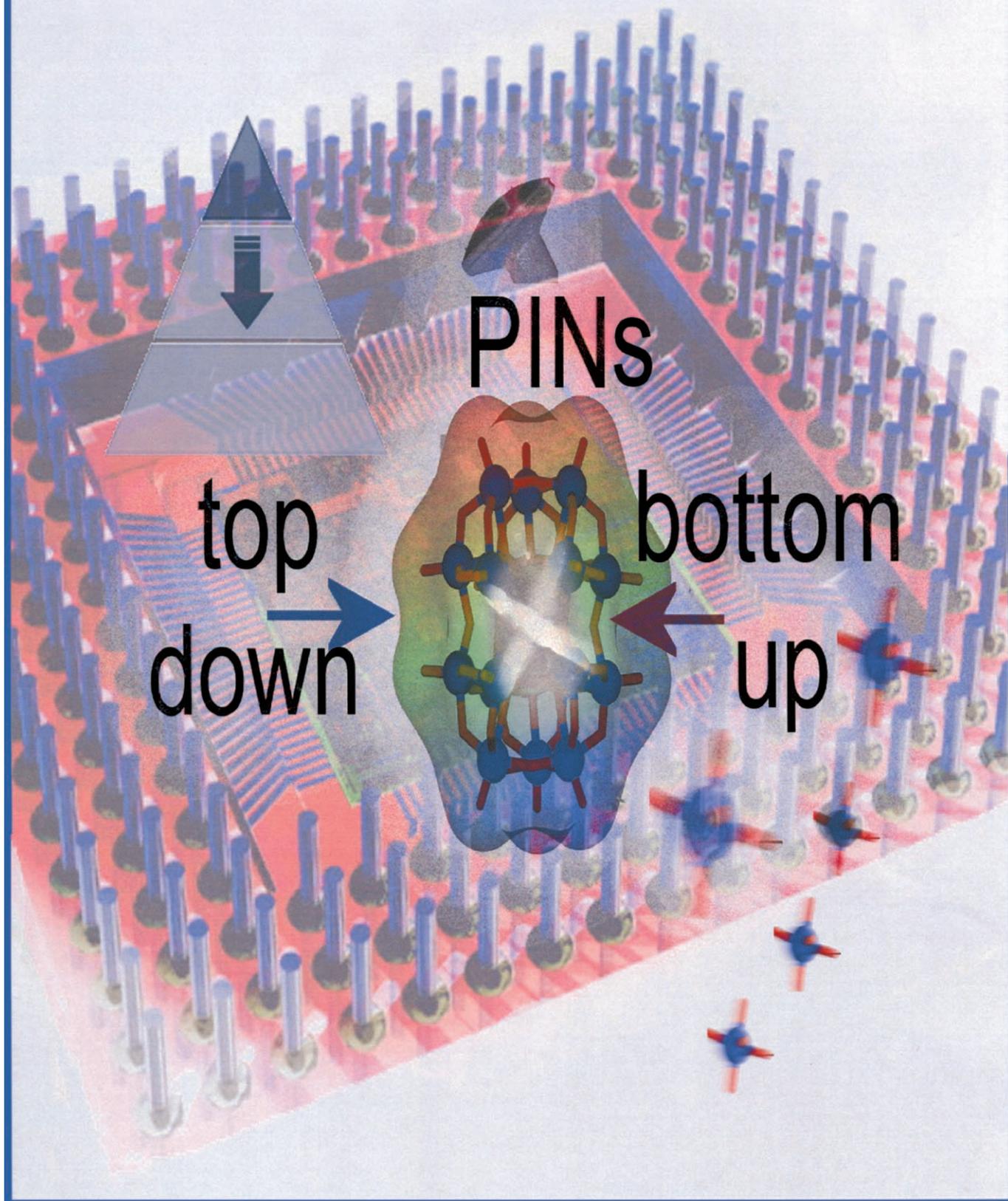


# Towards Polyoxometalate-Integrated Nanosystems



## Towards Polyoxometalate-Integrated Nanosystems

De-Liang Long and Leroy Cronin\*<sup>[a]</sup>

**Abstract:** Polyoxometalates represent a diverse range of molecular clusters with an almost unmatched range of physical properties and the ability to form structures that can bridge several length scales. The new building block principles that have been discovered are beginning to allow the design of complex clusters with desired properties and structures; several structural types and novel physical properties are examined herein. The overall message that is presented throughout is the possibility that polyoxometalate clusters could be excellent candidates to be exploited in the development of functional nanosystems or nanodevices. The concepts that underpin the development of nanoscale devices are discussed briefly, as are the considerable challenges that must be overcome to realise polyoxometalate-based functional nanosystems.

**Keywords:** molecular devices • nanostructures • polyoxometalates • redox chemistry • self-assembly

### Introduction

The controlled and designed manipulation of chemical systems over multiple-length scales from the molecular to the macroscale represents one of the greatest challenges in contemporary science. In particular the ability to understand, control and design molecular organisation is pivotal in realising the concept of functional nanosystems and nanomachines, the development of ultra-high capacity information storage materials,<sup>[1]</sup> molecular electronics<sup>[2]</sup> and sensors.<sup>[3]</sup> However, the problem faced by the chemist in the selection of systems that can be synthesised or self-assembled in a

pre-determined manner to form highly complex architectures which can organise different subunits with different properties is vast.

In this respect it is interesting to examine the potential of a class of inorganic clusters known as polyoxometalates (POMs) as building blocks for functional nanoscale devices. This is because nanoscale polyoxometalate clusters provide an arguably unrivalled structural diversity of molecules displaying a wide range of important physical properties and nuclearities; these cover the range from 6 to 368 metal ions in a single molecule and are assembled under “one-pot” reaction conditions.<sup>[4]</sup> At the extreme, these cluster molecules are truly macromolecular, rivalling the size of proteins, and are formed by self-assembly processes, see Figure 1.<sup>[5]</sup>

The clusters are mostly anionic in nature, being based upon metal oxide building blocks with a general formula of  $\text{MO}_x$ , (in which M is Mo, W, V and sometimes Nb and  $x$  can be 4, 5, 6 or 7). POM-based materials have many interesting physical properties<sup>[6–10]</sup> that result from their versatile structures, the ability to delocalise electrons over the surface of the clusters, the ability to incorporate heteroanions, electrophiles and ligands, and to encapsulate guest molecules within a metal oxide based cage. POM clusters have been shown to exhibit superacidity,<sup>[6]</sup> catalytic activity,<sup>[6]</sup> photochemical activity,<sup>[7]</sup> ionic conductivity,<sup>[7]</sup> reversible redox behaviour,<sup>[8]</sup> bistability,<sup>[7]</sup> cooperative electronic phenomena,<sup>[7]</sup> the ability to stabilise highly reactive species<sup>[9]</sup> and extensive host–guest chemistry.<sup>[10]</sup>

The large number of structural types in polyoxometalate chemistry<sup>[11]</sup> can be broadly split into three classes.

- 1) Heteropolyanions: these are metal oxide clusters that include heteroions, such as  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ . These represent by far the most explored subset of POM clusters, with over 5000 papers being published on these compounds during the last four years alone. There is a great emphasis on catalysis in this literature, of which the Keggin  $[\text{XM}_{12}\text{O}_{40}]$  and the Wells–Dawson  $[\text{X}_2\text{M}_{18}\text{O}_{54}]$  (in which M = W or Mo) anions are fundamental examples. In particular W-based POMs are robust and this fact has been exploited to develop W-based Keggin ions with vacancies

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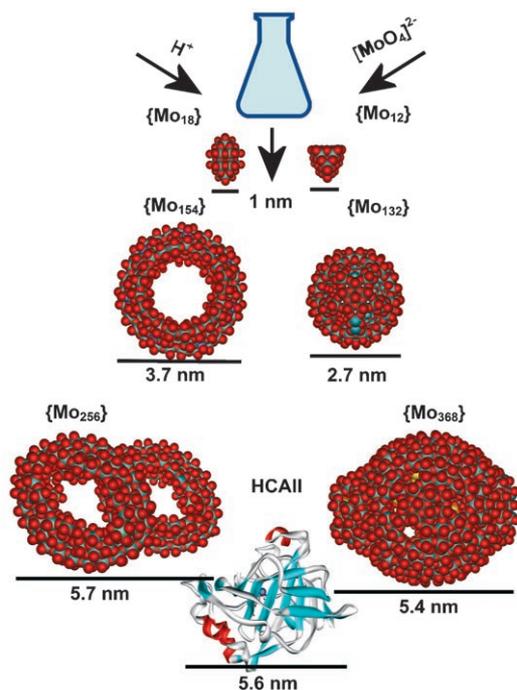


Figure 1. Representations of the structures of some Mo-based POM clusters (nuclearity given in subscript), all synthesised under “one-pot”–“one-step” acidic reaction conditions (space filling models: Mo green, O red) from the known and studied  $[M_{12}]/[M_{18}]$  Keggin/Dawson ions to the  $\{Mo_{154}\}/\{Mo_{132}\}$  and  $\{Mo_{256}\}/\{Mo_{368}\}$  clusters. These clusters are compared (to scale) with the protein Human Carbonic Anhydrase II (a medium-sized protein with 260 residues, MW 29.6 kD) to demonstrate their macromolecular dimensions.<sup>[4,5]</sup>

that can be systematically linked using electrophiles to larger aggregates.<sup>[4,11]</sup>

- 2) Isopolyanions: these are composed of a metal oxide framework, but without the internal heteroatom/heteroanion. As a result, they can be more unstable than their heteropolyanion counterparts. However they also have interesting physical properties, such as high charges and strongly basic oxygen surfaces; this means that they are attractive units for use as building blocks.
- 3) Mo-blue and Mo-brown reduced Mo-based POM clusters: these are related to molybdenum blue type species, which were first reported by Scheele in 1783.<sup>[12]</sup> Their composition was largely unknown until Müller et al. reported, in 1995, the synthesis and structural characterisation of a very high nuclearity cluster  $Mo_{154}$  crystallised from a solution of Mo-blue; this cluster has a ring topology.<sup>[13]</sup>

In this concept article we start to examine the pivotal role that polyoxometalate clusters can play in the development of nanoscale devices that utilise POM components.<sup>[14]</sup> This is because such functional nanosystems can exploit the building block principle already established in this area of chemistry, coupled with the range of physical properties, and the fact that POM systems can really be seen as molecular metal oxides.<sup>[15]</sup> To demonstrate this point a number of ex-

amples have been selected across the area of POM chemistry, including our contributions, to help highlight new directions and concepts. It should also be noted that metal oxides already play a massive role in the electronics and semiconductor industry today and their solid-state properties have been extensively studied,<sup>[16,17]</sup> however, we will examine possibilities from a molecular perspective. Many of these concepts are not new in isolation, but the possibility of using molecular design in metal oxides to produce functional systems that exploit size effects, ligand/hetero ion modification, switchable properties and cooperative electronic effects will undoubtedly be significant in the quest for functional nanosystems that start to bridge the gap between bottom-up and top-down assembly.<sup>[18]</sup> This is because POMs can be constructed that bridge large-length scales and lithographic techniques (top-down) can be used to direct the positioning of clusters, which can be built by using self-assembly processes (bottom-up).

### Building Blocks and Structural Hierarchies in POM Chemistry—A Route to Bridge the Subnano with the Micron Scale?

One remarkable feature of POM cluster chemistry is that the building blocks are conserved between structures and it appears that they have intrinsic properties (high and variable charge and flexible ligand coordination modes) that facilitate the self-assembly of clusters containing many thousands of atoms in solution. In mixed valence Mo POM systems, the use of pentagonal-type building groups, with different symmetries, play a key role in the synthesis of these systems and the construction of nanoscale architectures.<sup>[5]</sup> This can be taken further by considering that edge-sharing (condensed) pentagons cannot be used to tile an infinite plane, whereas exactly 12 pentagons are required, in connection with well-defined sets of hexagons, to construct spherical systems such as that observed in the truncated icosahedron (the most spherical Archimedean solid), in polyhedral viruses or in the geodesic Fuller domes.<sup>[19]</sup> Indeed, the seminal work of Müller et al.<sup>[13,20–22]</sup> has demonstrated that Mo-based pentagonal building blocks allow the generation of very large clusters with nuclearities between 36 and 368 metal atoms in a single cluster molecule, see Figure 2. These clusters are built by using a range of conserved building blocks. For instance the spherical Keplerate cluster<sup>[20]</sup> can be considered in geometrical terms to be composed of  $(\text{pentagon})_{12}(\text{linker})_{30}$ ;  $\text{pentagon} = \{Mo(Mo)_5\}$  and  $\text{linker} = \{Mo^V_2O_4(OOR)^+\}$ ,  $\{OMo^V(H_2O)\}^{3+}$ ,  $\{Fe^{III}(H_2O)_2\}^{3+}$ ; that is, in the case of the cluster in which the linkers are  $\{Mo^V_2O_4(OAc)^+\}$  the overall formula is:  $[Mo^{VI}_{72}Mo^{V}_{60}O_{372}(MeCO_2)_{30}(H_2O)_{72}]^{42-}$ . In the case of the  $\{Mo_{256}Eu_8\} \equiv [\{Mo^{VI}_{104}Mo^{V}_{24}Eu^{III}_4O_{388}H_{10}(H_2O)_{81}\}_2]^{20-}$  system, which is composed of two elliptical  $\{Mo_{128}Eu_4\}$  rings, each ring is composed of 12 pentagonal units. However, the elliptical ring has a more complicated set of building blocks than the Keplerate cluster and is formally composed of

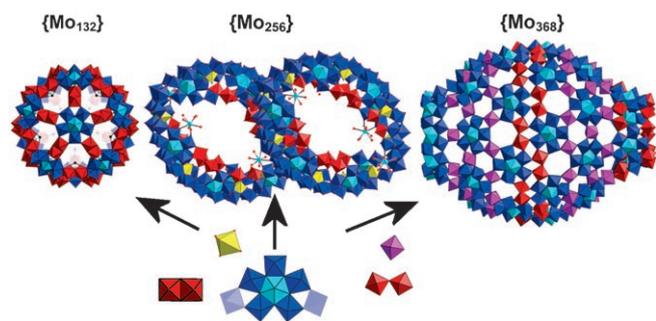


Figure 2. Structures of the  $\{\text{Mo}_{132}\}^{20-} \equiv [\text{Mo}_{72}^{\text{VI}}\text{Mo}_{60}^{\text{V}}\text{O}_{372}(\text{MeCO}_2)_{30}(\text{H}_2\text{O})_{72}]^{42-}$ ,  $\{\text{Mo}_{256}\}^{21-} \equiv [\text{Mo}_{256}\text{Eu}_8\text{O}_{776}\text{H}_{20}(\text{H}_2\text{O})_{162}]^{20-}$ , and  $\{\text{Mo}_{368}\}^{22-} \equiv [\text{H}_x\text{Mo}_{368}\text{O}_{1032}(\text{H}_2\text{O})_{240}(\text{SO}_4)_{48}]^{48-}$  clusters shown with polyhedral plots. The transferable building blocks found in these clusters are shown below, including the additional two units fused to the  $\{\text{Mo}_6\}$  building block, to make the  $\{\text{Mo}_8\}$  unit, in light blue.

$[\{\text{Mo}_1\}_6\{\text{Mo}_2\}_4\{\text{Mo}_8\}_2\{\text{Mo}_7\}_2\{\text{Mo}_9\}_2]$ , similar to the building blocks found in the archetypal “big-wheel” clusters.<sup>[13]</sup> More specifically the wheel clusters also incorporate a  $\{\text{Mo}_2\}$  unit in which the polyhedra are corner- rather than edge-sharing units (red polyhedra in Figure 2). Also, the pentagonal-centred units in the  $\{\text{Mo}_{132}\}/\{\text{Mo}_{368}\}$  spherical clusters are  $\{\text{Mo}_6\}$  type units (central pentagonal unit with five octahedra attached preserving the fivefold symmetry), whereas the pentagonal centre unit in the  $\{\text{Mo}_{256}\}$  and other wheel clusters has two additional  $\{\text{Mo}\}$  units fused to the bottom of the  $\{\text{Mo}_6\}$  unit to make a  $\{\text{Mo}_8\}$  type unit, see Figure 2.

The  $\{\text{Mo}_{368}\} \equiv [\text{H}_x\text{Mo}_{368}\text{O}_{1032}(\text{H}_2\text{O})_{240}(\text{SO}_4)_{48}]^{48-}$  system is even more complex, since it combines both negative and positive curvature. The building blocks can be represented as  $\{\text{Mo}(\text{Mo}_5)\}_8\{\text{Mo}(\text{Mo}_5)\}'_{32}\{\text{Mo}_2\}_{16}\{\text{Mo}_2'\}_8\{\text{Mo}_2''\}_8\{\text{Mo}_1\}_{64}$ , with 40 pentagonal units being required to complete the structure and can be considered to be a hybrid between the wheel and ball clusters.

In tungstate-based POMs the building block principle is guided by the ability to link lacunary fragments; this is often achieved with electrophilic building blocks such as lanthanide ions. One excellent example is the dodecamer of the  $\{\text{XW}_9\}$  units, a  $\{\text{W}_{148}\} \equiv [\text{Ln}_{16}\text{As}_{12}\text{W}_{148}\text{O}_{524}(\text{H}_2\text{O})_{36}]^{76-}$  system.<sup>[23]</sup> The 12  $\{\text{XW}_9\}$  units are linked by  $\text{Ln}^{\text{III}}$  cations and additional tungsten atoms to produce a folded cyclic cluster with  $D_{2d}$  symmetry.

The anion is completed by the four  $\{\text{W}_5\text{O}_{18}\}$  lacunary fragments and the structure is shown in Figure 3 (left). The degradation of the  $\alpha$ -Dawson anion forms lacunary derivatives, which link to give a cyclic  $\{\text{W}_{48}\}$  cluster  $\equiv [\text{K}_{28}\text{Li}_5\text{H}_7\text{P}_8\text{W}_{48}\text{O}_{184}]$ , see Figure 3 (right).<sup>[24]</sup> The  $D_{4h}$  structure of the  $\{\text{P}_8\text{W}_{48}\}$  anion can be seen as a tetramer of  $\{\text{P}_2\text{W}_{12}\}$  groups.

The major problem with this approach lies in establishing routes to produce reactive building blocks present in solution in significant concentrations and that can be reliably utilised in the formation of larger architectures without reorganising to other unknown fragments. Access to such building blocks has been the major limitation in stepwise

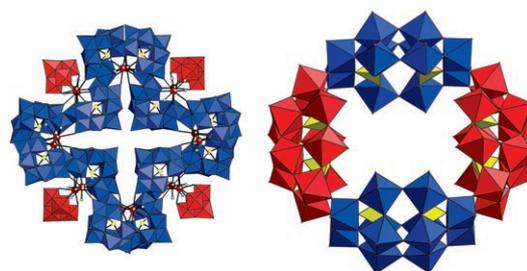


Figure 3. Structure of the  $\{\text{W}_{148}\}^{23-}$  and the  $\{\text{W}_{48}\}^{24-}$  clusters are shown as polyhedral plots on the left and right, respectively (not to scale).  $\{\text{W}_{148}\}$ : The  $\{\text{XW}_9\}$  units are shown in blue, the  $\{\text{W}_5\}$  units in red and the  $\text{Ce}^{\text{III}}$  ions in dark red, and the As atoms in yellow.  $\{\text{W}_{48}\}$ : The  $\{\text{W}_{12}\}$  hexavacant building blocks are shown in blue and red and the P-centred anions are shown in yellow.

growth of Mo-based POM clusters with respect to the more kinetically inert W-based clusters, which have shown a degree of control as illustrated by the isolation of the  $\{\text{W}_{148}\}$  cluster, see Figure 3.<sup>[23]</sup> Such limitations may be circumvented by adopting an approach that kinetically stabilises the building block in solution, thereby effectively preventing its reorganisation to other structure types.

In our work, whilst developing strategies towards this goal, we have found a new family of polyoxomolybdates<sup>[25,26]</sup> based on the  $[\text{H}_2\text{Mo}_{16}\text{O}_{52}]^{10-}$  framework, which appears to achieve the first part of this goal and allows the isolation of a new structure type by virtue of the cations used to “encapsulate” this unit, thereby limiting its reorganisation to a simpler structure. Furthermore the building block character of this anion is demonstrated when electrophilic transition-metal ions  $\text{M}^{2+}$  ( $\text{M} = \text{Fe}, \text{Mn}, \text{Co}$ ) are added to solutions of this cluster, resulting in  $[\text{H}_2\text{Mo}_{16}\text{M}_2\text{O}_{52}]^{6-}$  species that can undergo further condensation reactions.

These clusters were trapped by bulky organic cations during the self-assembly process; the cations appear to have restrained the clusters from reorganising into other well-known structure types. This yields a family of POMs with a range of symmetries, nuclearities and, most importantly, the potential to really “tailor” the physical properties by changing the cluster framework. This approach relies on trapping and stabilising nonspherical polyanions of low nuclearity and symmetry before their aggregation and re-arrangement to more uniform and stable structures. See Figure 4 for an example of a cluster trapped using this approach to yield a  $\{\text{Mo}_{16}\} \equiv [\text{H}_2\text{Mo}_{16}\text{O}_{52}]^{10-}$ .<sup>[25,26]</sup>

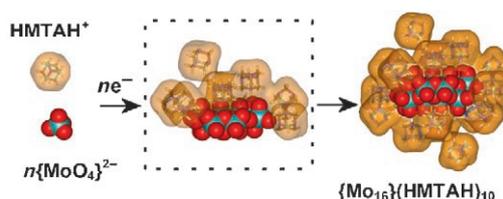


Figure 4. A schematic showing the “encapsulation” of the cluster units during the cluster assembly process in the presence of the bulky organic cation HMTA (hexamethyltetramine).

Furthermore, the organic cations can also be used as structure directing moieties, not only at a molecular level, but also allowing the formation of polymers that allows large aggregates to assemble, see Figure 5.<sup>[27]</sup> The effect of

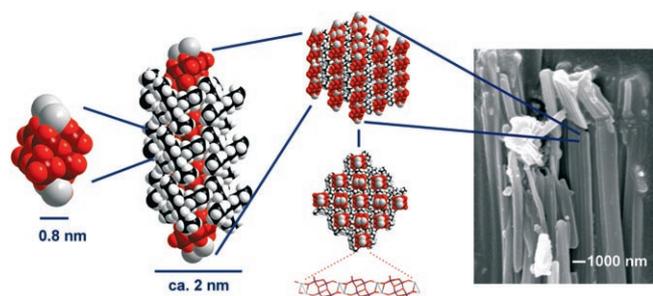


Figure 5. Space-filling representations of segments of the linear chain of linked  $[\text{Ag}^{\text{I}}\text{Mo}^{\text{VI}}_8\text{O}_{26}\text{Ag}^{\text{I}}]^{2-}$  showing the growth of the structure into linear chains encapsulated by the organic  $n\text{-Bu}_4\text{N}^+$  ions and the arrangement of the packed array of these chains, along with a stick representation of the chain framework (Mo: brown, O: red, Ag: grey, C: black, H: white). The organisation of the packed linear chains forming microcrystals of the compound are shown in the SEM image on the right with the crystallographic  $a$  axis parallel to the direction of the molecular chains.

the use of encapsulating cations, here the tetra- $n$ -butylammonium ion ( $n\text{Bu}_4\text{N}^+$ ), is demonstrated by the reaction of  $(\text{Bu}_4\text{N})_2[\text{Mo}_6\text{O}_{19}]$  with silver(I) fluoride in methanol; this reaction ultimately results in the formation of a unique one-dimensional chain structure of the composition:  $(n\text{Bu}_4\text{N})_{2n}[\text{Ag}_2\text{Mo}_8\text{O}_{26}]_n$ . Here, the flexible  $n\text{Bu}_4\text{N}^+$  ions almost completely wrap around the linear chain of linked  $[\text{Ag}^{\text{I}}\text{Mo}^{\text{VI}}_8\text{O}_{26}\text{Ag}^{\text{I}}]^{2-}$  units, see Figure 5. In the solid state these strands are packed to a network of collinear organic “tunnels” that accommodate the polymeric  $\{\text{Ag}_2\text{Mo}_8\}_\infty$  anions. The nature of the  $\{\text{Ag}_2\}$  linker groups and the Ag coordination environments, however, were found to depend on the reaction conditions, which suggests that the precursors in the reaction solution are not individual  $\{\text{Ag}_2\}$  and  $\{\text{Mo}_8\}$  groups but, most probably,  $\{\text{Ag}(\text{Mo}_8)\text{Ag}\}$ -type synths, see Figure 5.

In this section we have shown that POMs have an incredible structural hierarchy that allows the construction of complex molecules with a great deal of flexibility and structural variation. In the past, this structural variation has proved to be an Achilles heel when fully designed systems are desired, but a level of control is now available and the building block concept is becoming better understood.

### Functional POM Clusters—Prototype Devices?

There is little doubt that diverse physical properties common to polyoxometalates places them in an almost unmatched class of materials, which could be extremely useful as hybrid materials and nanocomposites.<sup>[28]</sup> In this section we will focus on POM systems with properties that could be exploited in the development of molecular-scale devices.

**Host-guest chemistry of POM-based superclusters:** The development of host-guest chemistry based on POM superstructures has been one of the most interesting developments and begins to show possibilities for POMs acting as sensors, storage capsules, and hosts that are able to respond to external stimuli. For instance molecular growth from a  $\{\text{Mo}_{176}\}$  ring to a  $\{\text{Mo}_{248}\}$  ring with the inner voids covered with “hub-caps” has been possible,<sup>[29]</sup> as well as the complexation of a metalloporphyrin within the cavity of the  $\{\text{Mo}_{176}\}$  wheel.<sup>[30]</sup> In W-based POMs the  $\{\text{W}_{48}\}$  cluster<sup>[24]</sup> has been used to complex approximately 20 Cu centres within the framework.<sup>[31]</sup>

The Keplerate  $\{\text{Mo}^{\text{VI}}_{72}\text{Mo}^{\text{V}}_{60}\text{L}_{30}\}^{n-}$  ( $n=42$  when  $\text{L}=\text{acetate}$ ,  $n=72$  when  $\text{L}=\text{sulfate}$ ) ball cluster provides an ideal framework to extend these ideas, as it is a spherical cluster with a high charge and accessible inner chamber with a large volume; the nature of the surface of the inner chamber and the pores can be tuned. Investigations of the uptake of various cations, such as lithium, by such clusters have given insight into basic principles of cation transport through “molecular pores”. This was investigated by using porous Keplerates with sulfate ligands on the inner surface; the cluster behaves as a semipermeable inorganic membrane open for  $\text{H}_2\text{O}$  and small cations.<sup>[32]</sup> Similar studies of the uptake/release of cations by a capsule in solution may be extended to investigate nanoscale reactions in solutions as well as a large variety of cation-transport phenomena, see Figure 6. The pores shown in the Keplerate have the form  $\{\text{Mo}_9\text{O}_9\}$ -ring and provide a structural motif rather similar to that of the classical crown ethers.

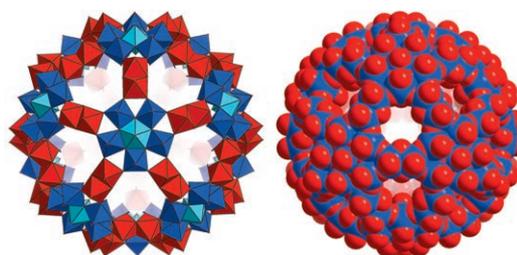


Figure 6. Polyhedral structure (left) and space-filling structure (right) of the  $\{\text{Mo}^{\text{VI}}_{72}\text{Mo}^{\text{V}}_{60}\text{L}_{30}\}^{n-}$  ball cluster. The space filling structure is looking directly down the one of the  $\{\text{Mo}_9\text{O}_9\}$ -ring pores.

This comparison is even more striking for the  $\{\text{W}_{36}\}$ -based cluster with the formula  $\{(\text{H}_2\text{O})_4\text{K}[\text{H}_{12}\text{W}_{36}\text{O}_{120}]\}^{11-}$  and includes the threefold symmetric cluster anion  $[\text{H}_{12}\text{W}_{36}\text{O}_{120}]^{12-}$ , see Figure 7. Interestingly the cluster anion complexes a potassium ion at the centre of the  $\{\text{W}_{36}\}$  cluster in an  $\text{O}_6$  coordination environment.<sup>[33]</sup> The  $\{\text{W}_{36}\}$  structure consists of three  $\{\text{W}_{11}\}$  subunits; these subunits contain a ring of six basal W positions, an additional W position in the centre of this ring, and four apical W positions in a butterfly configuration. Every W position around the cluster centre has a distorted  $\text{WO}_6$  octahedral coordination geometry with one terminal  $\text{W}=\text{O}$  moiety ( $d(\text{W}=\text{O})\sim 1.70 \text{ \AA}$ ) extending towards

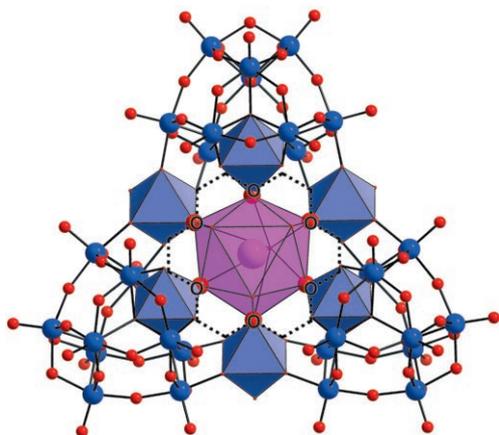


Figure 7. Representation of the  $\{(H_2O)_6K[H_{12}W_{36}O_{120}]\}^{11-}$  cluster with the central potassium ion shown in purple. The framework of [18]crown-6 is superimposed onto the central  $\{O_6\}$  moiety to scale and the six W groups, each of which donate oxygen ligands to coordinate to the potassium ion, are shown in polyhedral representation.

the cluster centre where the K ion is located; this arrangement maps extremely well onto the structure of the crown ether [18]crown-6. The implications for the development of this system in a similar fashion to the crown ethers is interesting, especially the possibilities for discrimination and sensing of metal ions using this cluster framework.<sup>[33]</sup>

**Magnetic and conducting POMs:** The development of POM-based clusters incorporating paramagnetic centres is an interesting goal, since it is possible to utilise existing building blocks/clusters to generate very large magnetic molecules. In fact it has been shown that it is possible to substitute the  $\{Mo_2\}$  “linker” groups present in the Keplerate  $\{Mo_{132}\}$ ,  $(pentagon)_{12}(linker)_{30}$  species with  $Fe^{III}$  to yield a  $\{Mo_{72}Fe_{30}\}$  cluster with the formula  $[Mo_{72}Fe_{30}O_{252}-(CH_3COO)_{10}\{Mo_2O_7(H_2O)\}\{H_2Mo_2O_8(H_2O)\}_3(H_2O)_{91}]^{34}$ . This cluster is smaller than the parent  $\{Mo_{132}\}$  structure with an outer diameter of approximately 25 Å and an inner diameter of about 18 Å, see Figure 8. Further, the  $\{Mo_{72}Fe_{30}\}$  cluster is composed of only  $Mo^{VI}$  atoms, whereas the  $\{Mo_{132}\}$  cluster contains 60 reduced  $Mo^V$  centres (the 30 linking

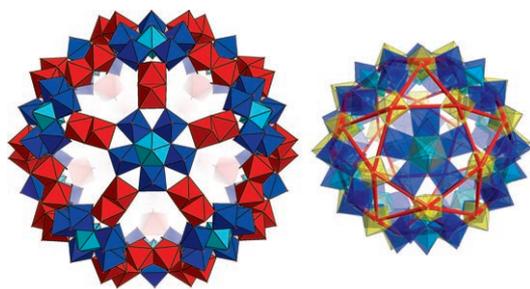


Figure 8. Polyhedral representations of the structures of the  $\{Mo_{132}\}$  and  $\{Mo_{72}Fe_{30}\}$  clusters to scale (left and right, respectively). The icosidodecahedron formed by connecting the 30 Fe centres is shown.

$\{Mo_2\}$  units are reduced). The presence of the  $Fe^{III}$  centres, combined with the weak antiferromagnetic exchange between these centres, means that there are 30 mainly uncorrelated 5/2 spins at room temperature and the cluster therefore behaves like a paramagnet with 150 unpaired electrons. The  $Fe^{III}$  centres of the cluster span an icosidodecahedron and the extremely rich and interesting magnetic properties have been investigated by using a simple Heisenberg model.<sup>[35]</sup> In this respect the  $\{Mo_{72}Fe_{30}\}$  cluster has been termed as a mesoscopic paramagnet for which classical behaviour extends down to extraordinarily low temperatures.<sup>[35]</sup>

Rather than using self-assembly of pure POM building blocks, the ligand-directed assembly of magnetically interesting POM clusters can also be considered. For instance a  $\{V_8O_{14}\}$  cluster can be formed with two ligated 1,3,5-trideoxy-*cis*-inositol moieties, yielding a vandyl cluster with a large spin ground state arising from strong ferromagnetic interactions within the cluster.<sup>[36]</sup>

The formation of hybrid materials based on POMs with stacks of partially oxidised p-electron donor molecules of tetrathiafulvalene (TTF) has been accomplished to yield conducting POM-based materials. This is interesting because the inorganic POM anion can act as a structural spacer unit, incorporate additional functionality, such as a scaffold for paramagnetic ions, or can act as an electron acceptor.<sup>[28]</sup> This area is progressing rapidly with the compounds based on  $[BEDT-TTF]_5[H_3V_{10}O_{28}]^{37}$  and  $[BEDT-TTF]_6[Mo_8O_{26}]^{38}$  ( $BEDT-TTF$  = bis(ethylenedithio)tetrathiafulvalene), which behave as metals down to 50 and 60 K with room temperature conductivities of 360 and 3  $Scm^{-1}$ , respectively. In addition, a POM radical salt with metallic behaviour down to 2 K has been synthesised.<sup>[39]</sup> The compound is based on  $[BEDO-TTF]_6K_2[BW_{12}O_{40}]$  and is formed from  $[BW_{12}O_{40}]^{5-}$  and the organic radical bis(ethylenedioxy)tetrathiafulvalene ( $BEDO-TTF$ ). The realisation of POM–organic conducting hybrids means that devices incorporating both POM clusters and organic conductors and polymers are also accessible.

**Thermochromic and thermally switchable POM clusters:** In our attempts to design functional clusters we have focused on substitution of the heteroanions within the Wells–Dawson structure to create nonconventional Dawson clusters incorporating two pyramidal anions. Our design rationale was based on the idea that such clusters may exhibit unprecedented properties arising from the intramolecular electronic interactions between the encapsulated anions (in this case we aimed to engineer between S⋯S atoms of two encapsulated sulfite ions), thus providing a novel route to manipulate the physical properties of the  $\{Mo_{18}\}$  Dawson-type clusters. The synthesis of these clusters was accomplished by extending our previous work utilising organic cations and allowed the isolation of the  $\alpha-[Mo_{18}^{VI}O_{54}(SO_3)_2]^{4-}$  (type 1), which incorporates the targeted two pyramidal sulfite  $SO_3^{2-}$  ions as the central cluster templates. This compound showed thermochromic behaviour between 77 K (pale yellow) and 500 K (deep red), see Figure 9.<sup>[40]</sup>

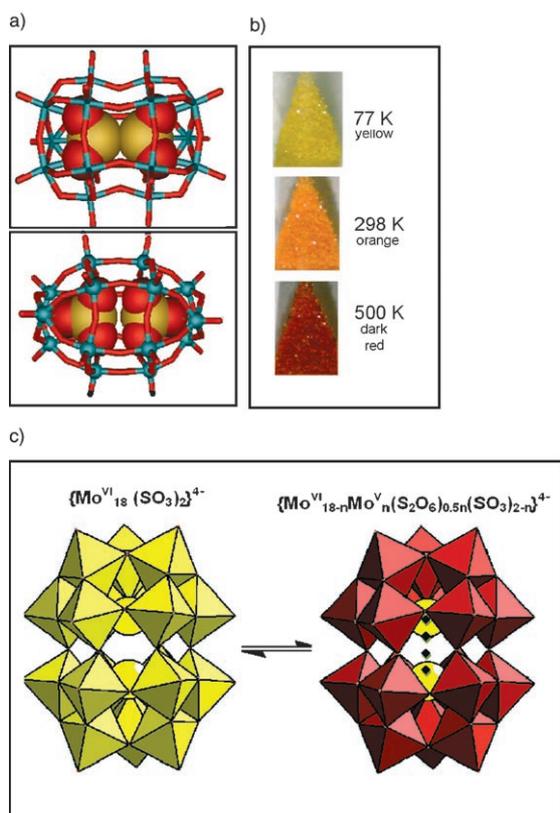


Figure 9. a) The crystal structure of the new type of sulfite Dawson structure above, compared to the known sulfate Dawson structure below, showing the S...S interaction. b) Photographs of the thermochromic material at 77, 298, and 500 K. c) Two polyhedral views of the yellow sulfite Dawson structure (on the left) at 77 K and the resulting red sulfite Dawson structure (on the right) at 500 K. A possible mechanism is also shown for the process resulting from the formation of a partial bond between the  $\text{SO}_3^{2-}$ , accompanied by electron release to the cluster shell (M atoms in green, O atoms in red, S atoms in yellow,  $\text{SO}_3$  groups in space-filling to show the S...S interaction).<sup>[40]</sup>

In an extension of this work to W-based Dawson-like clusters we succeeded in synthesising the analogous polyoxotungstate clusters incorporating the sulfite anion,<sup>[41]</sup>  $[\text{W}^{\text{VI}}_{18}\text{O}_{54}(\text{SO}_3)_2]^{4-}$  (type 1) the isostructural tungstate analogue to the  $\{\text{Mo}_{18}\}$  example, and  $[\text{W}^{\text{VI}}_{18}\text{O}_{56}(\text{SO}_3)_2(\text{H}_2\text{O})_2]^{8-}$  (type 2), see Figure 10.

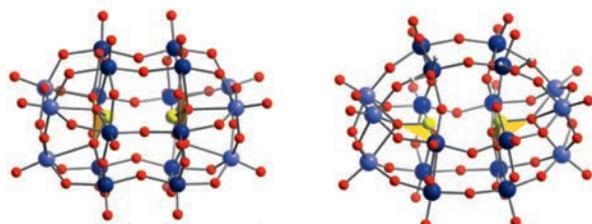


Figure 10. Ball-and-stick representations of the structures of the  $D_{3h}$ -symmetric  $\alpha$ - $[\text{W}_{18}\text{O}_{54}(\text{SO}_3)_2]^{4-}$  (type 1; left) and the  $C_{2v}$ -symmetric  $[\text{W}_{18}\text{O}_{56}(\text{SO}_3)_2(\text{H}_2\text{O})_2]^{8-}$  (type 2; right) cluster ions (W: equatorial  $\{\text{W}_6\}$  - dark blue, capping  $\{\text{W}_3\}$  - light blue; O: red; H: grey; S: yellow). Yellow polyhedra represent the pyramidal  $\text{SO}_3$  units.

Comparison of the types 1 and 2  $\{\text{W}_{18}\}$  Dawson structures shows that the  $[\text{W}^{\text{VI}}_{18}\text{O}_{54}(\text{SO}_3)_2]^{4-}$  also engineers the short S...S interaction, whereas the  $[\text{W}^{\text{VI}}_{18}\text{O}_{56}(\text{SO}_3)_2(\text{H}_2\text{O})_2]^{8-}$  cluster contains two sulfite anions that are locked into a different binding mode and appear to expand the upper part of the cage. This cluster also undergoes an interesting reaction when heated, whereby a structural rearrangement allows the two embedded pyramidal sulfite ( $\text{S}^{\text{IV}}\text{O}_3^{2-}$ ) anions to release up to four electrons to the surface of the cluster and results in the sulfate-based, deep blue, mixed-valence  $[\text{W}_{18}(\text{SO}_4)_2]^{8-}$  cluster. Thus the type 2 cluster appears to be surprisingly well prearranged for an internal reorganisation and a concurrent internal redox reaction, in which the encapsulated sulfite anions act as embedded reducing agents and are oxidised to sulfate when heated to over 400 °C, see Figure 11.

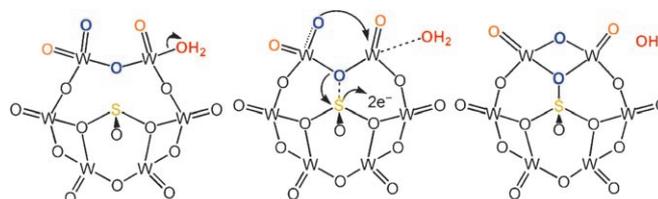
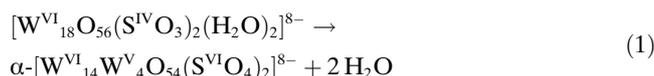


Figure 11. Mechanism of the internal sulfite-to-sulfate oxidation showing the movement of the oxygen atoms (shown in orange, blue and the waters in red). The equatorial cluster "belts" and the central sulfur position of a  $\{\text{W}_9(\text{SO}_3)\}$  fragment is illustrated.

In the course of this reaction a maximum of four electrons could be transferred to the metal oxide framework, causing a colour change from colourless ( $\{\text{W}^{\text{VI}}_{18}\}$ ) to blue ( $\{\text{W}^{\text{VI}}_{14}\text{W}^{\text{V}}_4\}$ ). The overall reaction is accompanied by the release of the two coordinated water ligands of the W centres so the following reaction occurs [Eq. (1)]:



In this cluster system the enclosure of sulfite anions with a "correct" orientation transforms the anions from "innocent" structural templates to electronically reactive, functional units. These can now release electrons to the cluster shell upon activation by heat; the sulfite groups in type 2 clusters are "activated" whereas those in type 1 appear more innocent.

### Outlook—Towards Polyoxometalate-Integrated Nanosystems?

The gap between concepts in molecular design to produce polyoxometalate-integrated nanosystems or molecular scale devices is vast due to the problem of fabrication and control of molecular orientation. Molecule-by-molecule assembly is clearly a great challenge, therefore the design of self-organ-

ising and self-assembling systems utilising ideas and inspiration from supramolecular chemistry to form functional molecular systems that can be connected from the molecule to the macroscale world is highly desirable.<sup>[42]</sup> However, the route to achieve such a grand aim is still unclear and many scientific fields are converging on the development of nanoscale and molecular electronics and interdisciplinary approaches are being developed to address the significant scientific and technical barriers. Clearly the design and synthetic approaches to polyoxometalates, and the fact these clusters can be constructed over multiple length scales, along with their almost unmatched range of physical properties means that they are great candidates to be used as both the scaffold, and the functional part of any nanodevice. Therefore there is great scope to investigate the self-assembly of functional POM systems on surfaces and in the crystalline state to produce architectures that can be fabricated to form a polyoxometalate-based device. Indeed recent work in the production of thin films of polyoxometalate clusters<sup>[43]</sup> and the use of POM clusters in “nanocasting”<sup>[44]</sup> are examples in which the cross disciplinary approach is beginning to utilise the potential of this class of clusters. One possible approach to the fabrication of POMs may, for instance, utilise lithographic techniques to prepare patterned substrates for the formation of “functional” polyoxometalate clusters, or even utilise the POM cluster in the growth of nanoscale moieties that can be directed to individual electrodes patterned by using lithography.<sup>[45]</sup>

The challenge now is to design individual POM cluster molecules that can interact both with each other, and with the macroscale, in a desired fashion in response to inputs and environmental effects, so a functioning molecular system is really constructed. In this respect recent advances in polyoxometalate chemistry<sup>[35,36,39,41,45]</sup> mean that all the components are available conceptually and synthetically to allow the design and realisation of polyoxometalate-based integrated nanosystems (PINs).

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