Cations in control: crystal engineering polyoxometalate clusters using cation directed self-assembly

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The synthetic engineering of anionic polyoxometalate (POM) clusters with predefined properties tailored to specific applications is a great challenge using routine "one-pot" POM syntheses. Under such conditions, difficulties often arise from the multitude of complex reaction pathways and self-assembly processes occurring in solution. In this respect the major role of the charge balancing cations cannot be ignored, in fact such cations are crucial, both in the assembly of the building blocks, linkage to the overall cluster, and then assembly into the bulk material. Further, the role of the cation facilitating the selective crystallization of a particular cluster type cannot be divorced from the reaction process since the crystallization process itself can help pull "virtual" building blocks into being. This perspective briefly outlines our efforts towards engineering novel POM based materials, highlighting the use of large organic cations as "Shrink-wrapping" agents to isolate new POM clusters, frameworks and cage compounds. Central to this perspective is the hypothesis that, in the case of POM cluster assembly, the mechanism and various equilibria which define the clusters can be controlled by the selective crystallisation using cation control. Consequently, this indicates that the process of crystallisation can have a profound effect on self-assembly at the molecular level. We therefore propose that the crystallization process itself may define the molecular structure of the cluster leading to the conundrum, which came first, the cluster or the crystal of the cluster?

1. Introduction

Polyoxometalates (POMs) are discrete, anionic metal-oxide clusters of early transition metals (most frequently Mo, W, V and Nb) representing a large and important class of inorganic materials,[1] whose relevance is being highlighted in a number of review articles, with an extraordinary reach in terms of applications, physical and chemical properties.[2,3]

One of the most interesting aspects of POM chemistry is the underlying deceptively simple synthetic procedures.[4] This is because the majority of the complex POM clusters isolated so far are synthesized by a range of surprisingly straightforward synthetic procedures, which often involve a "one-pot" synthesis step. Frequently, in the "one-pot" process, acidification of the precursor metal salts in aqueous solutions in the presence of chosen ingredients such as reducing agents, hetero-elements, counterions

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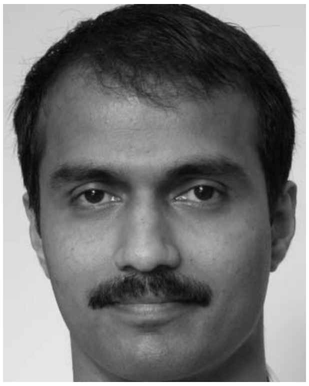

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etc. leads to the formation of a variety of combinatorially linkable polyoxometalate building blocks in solution.[5] These small building blocks, formed by the edge- and corner-sharing of $\{MO_x\}$ units (where M = Mo, W; $x = 4$–7), then self-assemble to form various cluster anions depending on the reaction conditions. In fact, these "one-pot" reactions can hide very complex solution speciation processes arising from the presence of a multi-equilibrium situation, that depends on a multitude of factors such as pH, ionic strength, reaction time, temperature, counterions, concentration of starting materials, presence of electron donors and their redox potential. What makes understanding, not to mention control of the synthesis of POM clusters so difficult, is because of the sensitive dependence of the cluster architectures assembled with the reaction *and* crystallization conditions. This means that a barely detectable change in any given parameter can alter the solution speciation affecting the outcome of the reaction.[1] This fact is exemplified in the assembly of reduced Mo clusters; ring shaped "Mo-Blues" and spherical shaped "Mo-browns", in which the building blocks *viz.* $\{Mo_1\}$, $\{Mo_2\}$, $\{(Mo)Mo_5\}$, $\{Mo_8\}$, that are formed in the reaction medium self-assemble to form very large molecular clusters of varying structural diversity ranging from balls, wheels, capped wheels and large "lemon" shaped clusters depending upon the specific reaction conditions.[6] However the common aspect in these clusters is the "closed" nature of the structures being of spherical or torriodal in topology, and this aspect has been the subject of much discussion.[5]

From a crystal engineering point of view, one important factor that affects the formation of one particular POM species out of vast library of candidates relates to the crystallisation process itself. This point is brought into sharp focus when one realises that, although many researchers focus on the POM framework exclusively, these POMs are poly-anions and cannot exist without the charge balancing cations, which often define the network into which the anion is "complexed" and electroneutrality is achieved. In this way the cations themselves appear to be able to re-route or control the complex, since almost an infinite number of species and equilibria are available in solution that are removed from solution to the solid state, see Fig. 1. Since the properties of the cations such as size, charge, symmetry, solubility *etc.* are found to modulate the reactivity of POM building blocks, these cations can affect the nature of the product obtained from a POM synthesis.[7] A proper match between the cations and anionic POM species is needed for effective crystallization, hence most often the product isolated in crystalline form may not necessarily be the one with highest abundance in solution.[1b] Fig. 2 depicts the distribution of cations, anionic POM clusters and their combined lattice arrangement in a true POM crystal structure, which highlights the vast number of counter cations that are present in the structure.

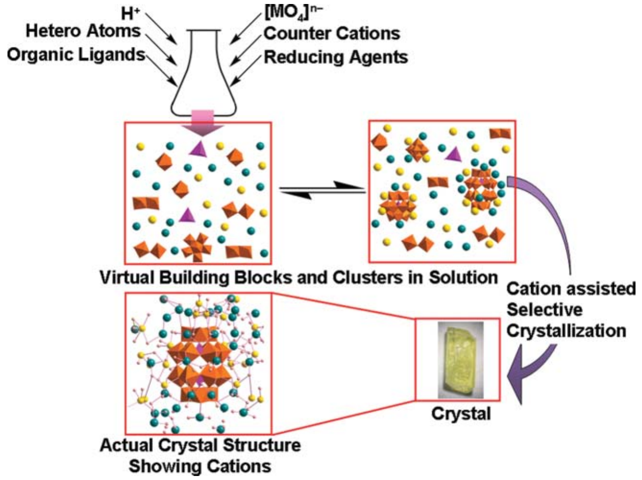

Fig. 1 Schematic representation of the traditional "one-pot" synthesis of POM clusters leading to the formation of various structural archetypes in solution highlighting the role of cations in selective crystallization of a particular product. Yellow and green spheres represents different cations. The top left shows a range of "virtual" geometrically possible units and the top right shows the cations complexing the clusters and pulling certain structures out of solution.

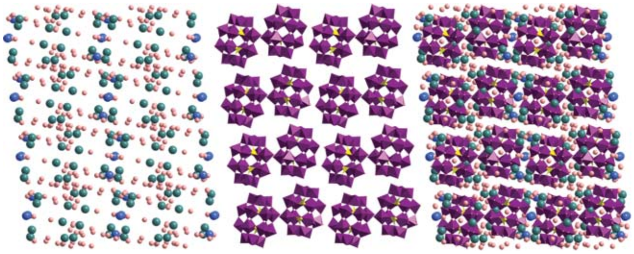

Fig. 2 Packing diagrams depicting the separate and combined arrangements of cations and POM cluster anions in a crystal lattice. Left: only cations (blue and green spheres) and solvent water molecules (rose spheres); middle: only POM clusters (violet and yellow polyhedra) and right: POM cluster anions, counter cations and solvent water molecules together in a crystal lattice.

Modern crystal engineering is a hybrid of supramolecular chemistry and materials chemistry, dealing with the design and synthesis of crystalline materials having the desired solid state properties.[8] As POM chemistry is now very well established after several decades of research including intense underpinning structural studies, the initial structural and topological curiosity has been replaced by the quest for new tuneable and functional

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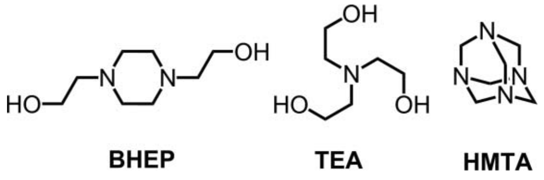
clusters capable of exhibiting novel, and controllable physical properties.[4] This means that the crystal engineering of POM-based materials should be directed towards the incorporation of well conceived functionalities into such systems in order to develop the materials aspects of POM chemistry. For example POM synthesis, employing solution processing methods, has great potential to allow the assembly of new solid state materials using a molecular design approach.[9–12]

This perspective briefly outlines our recent efforts to control the self-assembly of POM-based nanoscale molecules, and their assembly into nanostructures and solid state materials. Given that POMs are gigantic polyanions, the manipulation of the self-assembly process using cations is vital, and perhaps could provide the basis to design, using a crystal engineering type approach, pre-defined POM-based materials.[9] We reasoned that two things are most important here – first, the discovery of novel POM building blocks and second, the direction of their self-assembly in a controlled way to form useful materials. To achieve these targets, we are using a simple strategy, which is based on the use of bulky organic amine cations as counter-ions in POM synthesis.[9–12] The use of such bulky cations helps to isolate self-assembled POM species in one-pot reaction systems thus preventing their rapid aggregation into clusters having stable uniform spherical topology. Also such cations together with other linker units are found to be capable of directing the self-assembly of POM building blocks into extended structures. We termed this approach as "Shrink-wrapping"[9–12] and involves mainly the use of organic amines such as hexamethylene tetramine (HMTA), triethanol amine (TEA), *N*,*N*-bis-(2-hydroxyethyl)-piperazine (BHEP), morpholine *etc.* which are capable of acting as well defined (encapsulating) cations, as well as ligands (although at low pH it is unlikely these amines act as ligands), buffers, and even as redox reagents in some cases, see Scheme 1. Further, we were able to produce a number of discrete iso and heteropolyoxo clusters as well as many extended architectures using this simple but efficient concept, described briefly in the following sections.



Scheme 1 The various shrink-wrapping cationic precursors used in our studies.[9–12]

2. Background

The effective control over the self-assembly of $\{MO_x\}$ units in the traditional "one-pot" synthesis has always been the main aim for researchers looking for new POM clusters. In the case of reduced Mo-based clusters often called "Mo-blues", the work of Müller *et al.* showed that it was possible to generate and control the self-assembly of some building units in solution by varying the synthetic conditions.[5] One of such building block is the pentagonal $\{Mo(Mo)_5\}$ unit which is pivotal in the effective tiling of many spherical Archimedean solid structures. These $\{Mo(Mo)_5\}$ building blocks, in the presence of suitable linkers, such as doubly bridging $\{Mo^V{}_2O_4(\text{ligand})\}$ units, where "ligand" can be acetate, sulfate *etc.*, leads to giant mixed-valence clusters with diverse topologies such as the spherical icosahedral $\{Mo_{132}\}$, big wheel $\{Mo_{154}\}/\{Mo_{176}\}$, capped cyclic $\{Mo_{248}\}$ and basket shaped $\{Mo_{116}\}$ architectures[5,6] (Fig. 3). One other important achievement with Mo-based clusters, in the context of cluster engineering, is the ability to manipulate the structure, pore size and interior properties of the spherical Keplerate capsules by changing the bidentate ligands of the $\{Mo^V{}_2O_4(\text{ligand})\}$ linker.[13] In parallel with these studies in "Mo-blue" chemistry, Pope and co-workers have achieved interesting W-based clusters including the largest tungstate cluster reported so far, by using hetero-transition metal ions as linkers.[14] Apart from Mo and W, which are the two main metals explored in POM chemistry, the engineering of novel cluster types based on other metals like vanadium,[15] tantalum,[16] niobium,[17] uranium[18] and palladium[19] is also being explored with great vigour since these represent possible new routes in the search for new metal-oxide based materials. Further, the pentagonal $\{M(M_5)\}$ building block necessary for the tiling of large Archimedean structures, was recently discovered in the case of W and Nb clusters (rather than just Mo),[20] pointing to the prospect of the isolation of large clusters similar to "Mo-blues" in the case of these metals as well.

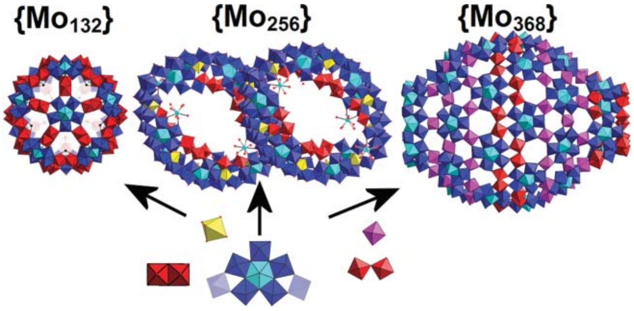


Fig. 3 $\{Mo_1\}$, $\{Mo_2\}$, $\{(Mo)Mo_5\}$ *etc.* building blocks self-assemble according to the reaction conditions leading to various structurally diverse Mo-blue clusters.[5,6]

The often serendipitous nature of the "one-pot" reactions has prompted researchers to utilize a better defined "building block approach", which utilizes preformed POM clusters as building blocks for the generation of networks or aggregates.[1,4] In this way, POM building blocks are assembled either through M–O–M oxo bridges or by the use of metal–organic complexes as linkers. In fact an almost bewildering number of molybdenum- and tungsten oxide-based organic–inorganic hybrid materials are reported by various groups using metal–organic complexes/coordination polymers as linkers between POM clusters, and the number of examples is expanding seemingly at an exponential rate.[21] The metal–organic units used as linkers can also act as charge balancing counterions, templates and covalently linked network constituents in these compounds. The most widely used organic ligands in these studies involve 4,4′-bipy, 2,2′-bipy and ethylene diamine. However, the multiplicity of coordination sites on POM building blocks often makes the product prediction difficult in "building-block approach" as well similar to the "one-pot" synthetic approach. Further, most of these studies exploit well known clusters and have not led to profoundly new or highly functional materials with new properties. However many of the reaction systems in this class have used hydrothermal reaction conditions, which has led to some interesting results and new materials that appear to cause a shift in their reactivity from the kinetic to the thermodynamic domain compared to traditional aqueous reactions, such that the equilibrium phases are replaced by more complex metastable phases.[22] Therefore, the hydrothermal method is now commonly employed for the engineering of organic–inorganic hybrid POM materials as a modification of "one-pot" synthesis. Many interesting architectures and frameworks are engineered through hydrothermal synthesis by the careful selection of the metal organic and POM building blocks.[23]

Functionalization of POM clusters with organic units, *via* ion exchange or direct covalent functionalisation, is yet another strategy towards the development of functional materials as it will enhance the synergistic combination of properties of polyoxometalates and organic units. By tailoring the organic and/or inorganic part properly, one could design interesting hybrid systems with unique functional properties.[24]

3. Isopolyoxometalates and their derivatives

Isopolyoxometalates (iso-POMs) are a sub-class of polyoxometalates, which are composed of a metal-oxide framework, but without an internal heteroatom/heteroanion template. As the POM clusters are synthesized by the condensation of $\{MO_x\}$ units (where M = Mo, W; $x = 4$–7) at low pH, a number of possible edge- and corner-shared $\{MO_x\}$ intermediates are possible, which can then serve as structural components of large polyoxometalates assembled by conservative self-organizing processes. However, it is observed that the self-organization of these building blocks to large structures often requires a template to assemble the cage around, such as a heteroanion, *e.g.* PO_4^{3-}, thus leading to the formation of heteropolyanions. Because of this, the number of POM structures formed without the templating effect of an heteroanion/heteroatoms is surprisingly limited. For example, compared to the vast class of known heteropolytungstates, only a limited number of isopolytungstates have been reported thus far.[4] It is noted that, solution control by the manipulation of pH as well as cations are very important in the synthesis of iso-POMs, and perhaps define an even more interesting target than the heteropolyanions for the use of crystal engineering techniques to control the cluster and crystal architectures.

The use of bulky organic cations to control the self-assembly of building blocks in the synthesis of iso-POMs was successfully leading to the development of a new family of Mo-based iso-POMs. By utilising protonated hexamethylenetetraamine (HMTAH, $C_6H_{13}N_4^+$) as counterion, the cluster compound $(HMTAH)_{10}[H_2Mo_{16}O_{52}]\cdot 34H_2O$, $\{Mo_{16}\}$, was isolated as crystalline precipitate from an acidified molybdate solution (pH 4) in the presence of a reducing agent in 20–30% yield.[9] This cluster has a "flat" geometry and four of the sixteen Mo centres are one-electron reduced. The main body of this "bat-shaped" cluster consists of a central unit with twelve molybdenum atoms and two "wings" each with two molybdenum atoms (giving the formulation $[\{Mo_{12}\} + 2\{Mo_2\}]$). The role of the "Shrink-wrapping" cation in the encapsulation of this rare non-spherical POM can be understood from the very close interaction between surface oxo ligands of the cluster anion and the HMTAH cations. There are 18 short hydrogen-bonded cluster surface oxygen-to-cation interactions for the anion, which are in the range $2.581(7) \leq d[E(\text{–}H)\cdots O(Mo)] \leq 3.140(5)$ Å, where E = N, C; there are also a number of additional longer contacts in the range $3.157(5) \leq d[E(\text{–}H)\cdots O(Mo)] \leq 3.296(3)$ Å. This shows that the clusters are extensively linked to the HTMAH cations *via* hydrogen bonds. Also, the anion layers in this compound are effectively separated from each other by HMTAH cation layers. Fig. 4 clearly illustrates that the cluster anions are effectively covered, or "shrink-wrapped" by the HTMAH cations in the solid state. Although cation–anion association will be present in solution, encouraged by both electrostatic and hydrogen-bonding effects, the extent of the interactions seen in the present compound in solid state appears to play a crucial role in solution as well. This is because experiments attempting to synthesize the $\{Mo_{16}\}$ cluster under similar reaction conditions (by altering pH value, concentrations, ionic strength, and temperature), but with different large cations (for example $[HN(CH_2CH_2OH)_3]^+$), resulted in the formation of the well-known Dawson-type cluster. Also attempts to dissolve this compound in the presence of other cations appear to result in the decomposition of the cluster anions. These observations strongly support the "Shrink-wrapping" effect of the bulky organic cation HMTAH in the formation of this iso-POM.

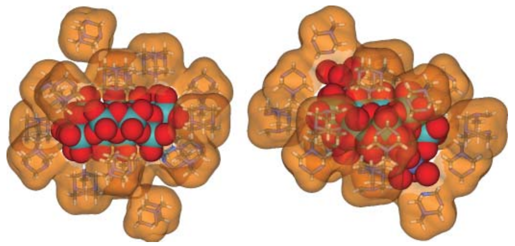


Fig. 4 Model for an actual crystal structure of a POM. The $\{Mo_{16}\}$ isopolyoxometalate cluster anion is closely surrounded by HMTAH cations, effectively "Shrink-wrapping" around it.

This $\{Mo_{16}\}$ cluster anion possesses high nucleophilicity and hence can bind two divalent transition-metal ions (such as Fe^{II}, Mn^{II}, Co^{II}, Ni^{II}, or Zn^{II}) to its framework. This led to a family of isostructural complexes exhibiting the basic topology found for the parent $\{Mo_{16}\}$ cluster with the addition of two $[M^{II}(H_2O)_4]$ moieties yielding a complex of the composition: $[M^{II}_2(H_2O)_8H_2Mo^{V}_4Mo^{VI}_{12}O_{52}]^{6-}$ (M = Mn, Fe, Co). The encapsulating effect of the "Shrink-wrapping" cations is found to prevent any significant inter-cluster magnetic exchange interactions in these compounds.[25]

Extension of the "Shrink-wrapping" organic cation strategy to tungsten-based systems has resulted in the trapping and isolation of an interesting isopolytungstate $(TEAH)_9Na_2\{(H_2O)_4K\subset[H_{12}W_{36}O_{120}]\}\cdot 17H_2O$, which is the largest isopolyoxotungstate reported so far in the literature.[26] This cluster compound was isolated from a reaction mixture comprising Na_2WO_4, $Na_2S_2O_4$ and protonated triethanolamine (TEAH) as organic cation, in water at pH 2. Subsequent experiments have shown that the addition of $Na_2S_2O_4$ is not necessary for the synthesis of this compound. The 3-fold symmetric cluster anion $[H_{12}W_{36}O_{120}]^{12-}$, $\{W_{36}\}$, is comprised of three $[H_4W_{11}O_{38}]^{6-}$, $\{W_{11}\}$, cluster subunits linked together by three $\{WO_6\}$ bridges. The centre of this "Celtic-ring" cluster has a $\{W_6O_6\}$ ring, that maps extremely well onto the structure of the crown ether 18-crown-6 and holds a K^+ ion at its centre.

Focusing on the crown ether like central cavity of $\{W_{36}\}$ cluster anion for host–guest chemistry with alkali and alkali-earth metal ions, complexes of the type $\{M{\subset}W_{36}\}$ ($M = K^+$, Rb^+, Cs^+, NH^{4+}, Sr^{2+} and Ba^{2+}) have been successfully synthesized.[27] These complexes demonstrate that, $\{W_{36}\}$ cluster anion can act like a type of inorganic "crown ether" with similar preferences to 18-crown-6, but with much greater rigidity, and therefore, having potential to distinguish between different cations. In a further extension of this work, a range of protonated aliphatic and aromatic guest cations such as 2-phenethylamine, 4-phenylbutylamine, *p*-xylylene diamine and 1,6-diaminohexane were successfully locked into the crown-ether like cavity of this iso-POM, and their structure-directing effects on the resulting framework arrangements are probed. It was found that parts of the organic guest cation protrude from the central binding cavity of the cluster and that the nature of this protruding organic "tail" has a directing ability and is in fact able to control the solid-state structure of the resulting compounds, Fig. 5.[28]

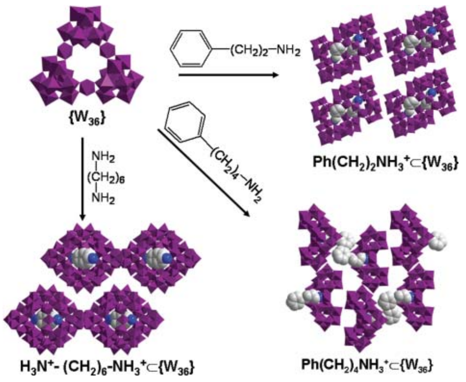


Fig. 5 Illustration of the framework arrangement of some host guest complexes prepared from inorganic crown ether analogue $\{W_{36}\}$ cluster and various amines. The effect of protruding amines in directing the self-assembly leading to various framework arrangements can be visualized from these figures. All the frameworks are viewed along crystallographic *a* axis.

The synthesis of $\{W_{36}\}$ cluster showed that, the presence of inorganic species such as $Na_2S_2O_4$ in the reaction medium could be crucial in the isolation of similar isopolytungstates. But unlike the polyoxomolybdates, the influence of such inorganic species on the assembly of polyoxotungstates has not been well-documented in the literature. In an attempt to discover radically new cluster architectures in the isopolyoxotungstate family, we have found that, acidification of a solutions of sodium tungstate to pH 3.4 in presence of $Na_2S_2O_4$ could lead to the isolation of a "S"-shaped $[H_4W_{22}O_{74}]^{12-}$ cluster anion, $\{W_{22}\}$, and on lowering the pH further (down to pH 2.4) could also lead to a related "§"-shaped $[H_{10}W_{34}O_{116}]^{18-}$cluster anion, $\{W_{34}\}$.[29] It is noteworthy that we have also observed that these new isopolytungstates could only be isolated in good yield in the presence of the inorganic species Na_2SO_3, even though it is not included in the crystal structure.

All of the above isopolytungstates $\{W_{36}\}$, $\{W_{34}\}$ and $\{W_{22}\}$ contain a basic building block: $\{W_{11}\}$ subunits ($[H_4W_{11}O_{38}]^{6-}$), having a fish-net structure, in which two fused half cubanes share one edge with another half cubane, and has two corner-shared dimeric tungsten-species bridging them together. In $\{W_{36}\}$ cluster, these $\{W_{11}\}$ subunits are linked together by three $\{WO_6\}$ units to give the celtic ring shaped cluster having a crown-ether type cavity at the centre. In the $\{W_{22}\}$ cluster, two $\{W_{11}\}$ building units are directly linked together to give the "S" shaped cluster, while in the $\{W_{34}\}$ cluster, two identical $\{W_{11}\}$ subunits are connected together in a *trans* fashion by a $[H_2W_{12}O_{42}]^{10-}$, $\{W_{12}\}$ unit through two μ_2-oxo bridges to give an expanded "§"-like architecture. The evolution of the clusters from $\{W_{11}\}$ to $\{W_{22}\}$, $\{W_{34}\}$ and $\{W_{36}\}$ is very important (Fig. 6), as it leads towards a new building block principle for developing new clusters of isopolytungstates. It should be noted here that, unlike the $\{W_{36}\}$ cluster, the $\{W_{22}\}$ and $\{W_{34}\}$ clusters are formed without the presence of any shrink wrapping cations. But it is intriguing to observe here that the approximately C_{3v} symmetric $\{W_{36}\}$ cluster anion is formed in the presence of shrink wrapping cation TEAH having approximately C_{3v} symmetry, the absence of which led to the formation of linear structures such as $\{W_{22}\}$ and $\{W_{34}\}$. This observation could be pointing to the structure directing role of the "Shrink-wrapping" cations in the synthesis of such iso-POM species.

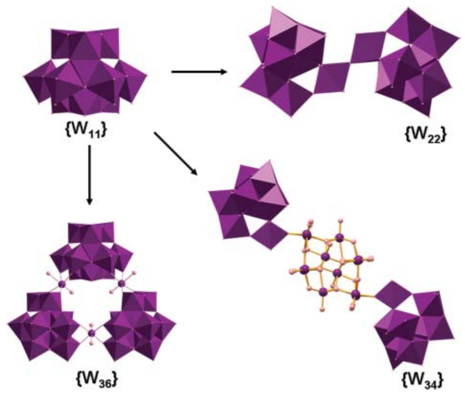


Fig. 6 Formation of three isopolyoxotungstate formed by the different linking mode of same basic building block $\{W_{11}\}$. $\{WO_6\}$ units (violet polyhedra), W, (violet spheres), O (rose spheres).

"Shrink-wrapping" cations could also lead to isopolyoxotungstates that are structural analogues of heteropoly acids. For example, a reaction system comprising of tungstates and TEAH cation at lower pH values (around 0.8) yielded a fundamentally new type of isopolyoxotungstate isolated as $(TEAH)_6[H_4W_{19}O_{62}]$, $\{W_{19}\}$.[30] This Dawson structural archetype incorporating a $[WO_6]^{6-}$ anion template is a rare and unprecedented cluster type. Furthermore, the stabilization of the $\{WO_6\}$ moiety in a trigonal prismatic coordination environment was new in polyoxotungstate chemistry. In the absence of the bulky organic TEAH cations, under otherwise identical reaction conditions, only the well-known $[W_{10}O_{32}]^{4-}$ cluster compound was formed, therefore implying the existence of a crucial cation effect on the formation of this new isopolytungstate.

4. Cage compounds and switchable POMs

Many POM clusters can be thought of as molecular cages enclosing some particular species at its centre. For instance the conventional Dawson archetype incorporates two tetrahedral anions such as PO_4^{3-}, AsO_4^{3-}, or SO_4^{2-} at the centre, while the

Keggin clusters incorporate only one such anion. Incorporation of a redox-active species inside a POM cage would be highly desirable in this respect, in view of the development of switchable POM molecules. In an attempt to develop a POM based switchable system, we targeted the incorporation of some non-conventional templating units, *e.g.* sulfite ions, inside a Dawson cage. The hypothesis for this investigation was that confinement of such species in a closed molecular cage could lead to properties arising from the intra-molecular electronic interactions between the encapsulated anions. Moreover, this could also lead to the manipulation of the physical properties of the $\{Mo_{18}\}$ Dawson-type POM cluster.

The incorporation of two sulfite ions as templating moieties inside a Dawson-like cluster is achieved from a reaction mixture at pH 4.0 containing metal salt, excess of protonated triethanolamine (TEAH) cation and $Na_2S_2O_4$ as a reducing agent as well as the source of SO_3^{2-}.[10] The product is crystallized as $(TEAH)_6[Mo_{18}O_{54}(SO_3)_2]\cdot 4H_2O$ which incorporates two pyramidal sulfite SO_3^{2-} ions as the central cluster templates.

This new cage compound represents the first Dawson-like $\{M_{18}\}$ cluster incorporating the pyramidal sulfite anion, and the first that includes two such pyramidal anions in the same $\{M_{18}\}$ cage. The two sulfite anions show a short S–S interaction inside the cluster cage and hence unusual electronic properties. This new "non-classical" Dawson-like cluster also shows interesting thermochromic behaviour between 77 K (pale yellow) and 500 K (deep red). In an extension of this approach, the first two examples of polyoxotungstate clusters incorporating two sulfite anions, $(TBA)_4[W^{VI}{}_{18}O_{54}(SO_3)_2]$ and $K_7Na[W^{VI}{}_{18}O_{56}(SO_3)_2(H_2O)_2]\cdot 20H_2O$ have been successfully synthesized, where TBA = tetrabutylammonium cation.[31] The cluster $K_7Na[W_{18}O_{56}(SO_3)_2(H_2O)_2]\cdot 20H_2O$ has a curious structure incorporating two terminal water ligands which was unknown for a closed-shell hetero-polyoxometalate cluster (HPOM clusters) of any type. Moreover, this compound demonstrated new electronic properties. The cluster anion, $[W_{18}O_{56}(SO_3)_2(H_2O)_2]^{8-}$, undergoes a unique electron-transfer reaction when heated, in which a structural re-arrangement allows the two embedded pyramidal sulfite (SO_3^{2-}) anions to release up to four electrons (analogous to the "soldiers" hidden inside the "Trojan Horse") to the surface of the cluster generating the sulfate-based, deep blue, mixed-valence cluster $[W_{18}O_{54}(SO_4)_2]^{8-}$. Although electron-transfer reactions and structural rearrangements are well-known for hetero-POMs, this is the first example of a coupled structural rearrangement and electron-transfer process, whereby the electrons are "released" from the core of the cluster. It is also the first example of a fully characterized unimolecular reaction involving an HPOM.

The successful trapping of one $\{WO_6\}$ unit inside a Dawson-like cage leading to the formation of the iso-POM $(TEAH)_6[H_4W_{19}O_{62}]$ pointed to the possibility of replacing the central $\{WO_6\}$ moiety of this system with similar $\{XO_6\}$ species, for example X = Pt^{IV}, Sb^{V}, Te^{VI}, or I^{VII}. Encapsulation of such templates in very high or very low oxidation states should significantly affect the acidic, catalytic, and redox properties of the resulting cluster systems. Following a synthetic strategy the same as that of $\{W_{19}\}$ iso-POM, we were able to embed iodine(VII) into a Dawson-like $\{W_{18}O_{54}\}$ matrix as the periodate species IO_6^{5-} to yield a range of cluster salts, $K_6[H_3W_{18}O_{56}(IO_6)]\cdot 9H_2O$, $(TPA)_6[H_3W_{18}O_{56}(IO_6)]$, and $(TBA)_6[H_3W_{18}O_{56}(IO_6)]$, (TPA = tetrapropylammonium cation).[32]

The formation of $[H_3W_{18}O_{56}(IO_6)]^{6-}$ appears, at least empirically, to be induced by the IO_6^{5-} anion (which contains a three-fold symmetric axis), although the cluster is produced in a modest yield. Prompted by this observation, we undertook the synthesis of $[H_3W_{18}O_{56}(IO_6)]^{6-}$ in the presence of three-fold symmetrical TEAH cation, and obtained $(TEAH)_6[H_3W_{18}O_{56}(IO_6)]$ in higher yields. This result is in tune with our previous observations that the formation of 3-fold symmetrical $\{W_{19}\}$ cluster, $[H_4W_{19}O_{62}]^{6-}$, requires the presence of three-fold symmetrical TEAH cations (the well-known $[W_{10}O_{32}]^{4-}$ cluster is formed in the absence of TEAH)[30] and hence highlights the cation effect in the formation of these POM cage clusters.

Looking for other non-conventional switching systems, we also targeted the encapsulation of TeO_6^{6-} units within $\{W_{18}O_{54}\}$ cluster shells to give a tellurate-based Dawson-like anion.[33] Unlike our previous experiences, this did not appear to be straightforward, and necessitated the techniques such as cryospray mass spectroscopy (CSI-MS) to screen the reaction systems for suitable cations. Of the cations screened, dimethylammonium (DMAH) and tetrabutylammonium (TBA) were found to be successful, yielding the Te^{VI}-encapsulated Dawson-like cluster anion $[H_3W_{18}O_{56}(Te^{VI}O_6)]^{7-}$ as $Na(DMAH)_6[H_3W_{18}O_{56}(Te^{VI}O_6)]\cdot 14H_2O$ and $(TBA)_7[H_3W_{18}O_{56}(Te^{VI}O_6)]\cdot 4CH_3CN$ respectively. We also investigated the redox properties of $[H_3W_{18}O_{56}(Te^{VI}O_6)]^{7-}$ to see if it was possible to access a Te^{IV}-based species by reducing the inner hetero atom. On addition of solid $Na_2S_2O_4$ to the acidified solution of $[H_3W_{18}O_{56}(Te^{VI}O_6)]^{7-}$, the solution initially turned blue, owing to the reduction of the $\{W_{18}\}$ based cluster shell, and then became pale yellow within seconds. We postulated that the central Te was reduced in this process from Te^{VI} to Te^{IV}. This reduction was confirmed by the isolation of $[H_3W_{18}O_{57}(Te^{IV}O_3)]^{5-}$, by precipitation with TBA, and this material on crystallization from acetonitrile followed by single-crystal X-ray diffraction analysis revealed that the Te^{IV} centre shifts by 1.10 Å towards one end of the cluster to form a pyramidal tellurite ion, see Fig. 7. Hence, upon formal two-electron reduction, the central octahedral $\{Te^{VI}O_6\}^{6-}$ unit is transformed into a pyramidal $\{Te^{IV}O_3\}^{2-}$ unit with the breaking of three Te–O bonds. Two interior "capping" oxo ligands were also lost during this reduction process. This redox reaction can be monitored *in situ* by the use of CSI-MS analyses. Further, it was observed that the inclusion of the tellurium-based heteroanion activates the surface of the $\{W_{18}O_{54}\}$ cluster cage, facilitating the assembly of the clusters to nanoscale structures without the introduction of other transition metal electrophiles. The self-assembled nano structure thus isolated in the solid state, $Na_8(DMAH)_{18}[H_{10}Te^{VI}{}_2W_{58}O_{198}]\cdot 35H_2O$, contains two $\{W_{18}Te^{VI}\}$ anions linked together by two $\{W_{11}\}$ units.

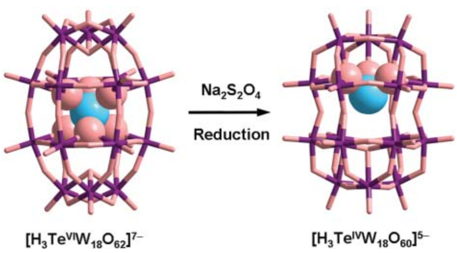


Fig. 7 Structural transformation as a result of the reduction of Te^{VI} to Te^{IV} inside a tungsten based molecular cage.

The role of cations is found to be important in the isolation of the above Te-based clusters as well. Na(DMAH)$_6$-[$H_3W_{18}O_{56}(Te^{VI}O_6)$]·14$H_2O$ is achieved from a reaction system containing Na_2WO_4 and $Te(OH)_6$ at pH 0.8 in the presence of DMAH. The presence of DMAH is crucial since its absence leads exclusively to the formation of the Anderson-type cluster $[TeW_6O_{24}]^{6-}$, which reiterates the pivotal role of organic cations for the assembly of new POMs.[33]

Inclusion of other transition metal based hetero anions as templates inside a Dawson-like cage has also been attempted. This has been achieved in the case of mixed metal (V/Mo and V/W) Dawson-like capsules having a unique composition $\{M_{17}V_3\}$.[34] A family of clusters which can be formulated as $V_2\subset\{M_{17}V_1\}$ having the α-Dawson cluster framework have been synthesized and the synthetic approach involves the aqueous reaction of $Na_2MO_4{\cdot}2H_2O$ (M = Mo or W) and NH_4VO_3 in presence of protonated triethanolamine (TEAH) as "shrink-wrapping" cation. A variety of experimental techniques have been tested to synthesize these compounds including hydrothermal synthesis. It is interesting to note that in all these cases, each of the $\{M_{17}V_3\}$ cluster anions obtained contain two $\{V^VO_4\}$ vanadate templates with one $\{V^{IV}O\}^{2+}$ vanadyl group integrated into the $\{M_{18}\}$ cluster framework. Fig. 8 shows a series of Daswon-like cluster cage compounds developed in our group so far incorporating various guest species.

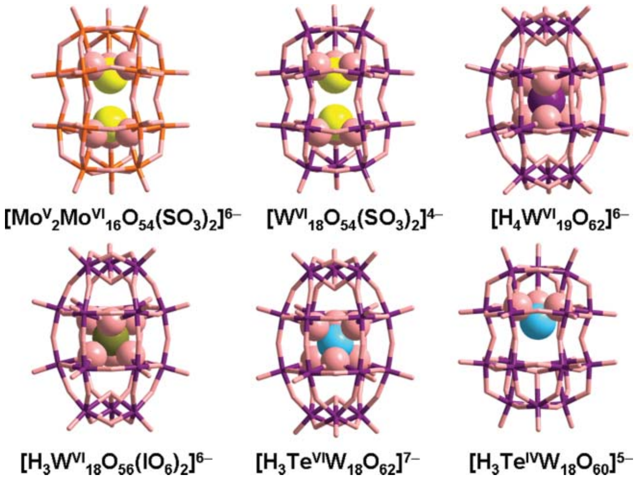


Fig. 8 Some of the Dawson-type cage compounds developed in the Cronin group incorporating various guest systems.

5. POM based architectures and framework materials

The last couple of decades have witnessed an enormous growth of open-framework inorganic materials. The majority of these include metal–organic frameworks containing discrete inorganic building blocks; the geometry and cavities of such frameworks mainly depending on the nature of the building units.[35] Often, POM clusters are used as large inorganic building blocks in an attempt to expand the lattice of such framework materials.[36] In this respect, we have successfully combined the "shrink-wrapping" strategy and "building block approach" with the help of suitable linker units resulting in diverse polymeric architectures and robust framework materials based on some well-known POM building blocks.

For instance, we have utilized silver(I) to act as a linker in POM chemistry due to its versatile range of geometries and bonding modes.[37] In this way, using β-octamolybdate as building unit and bulky TBA as cations, two 1D chain structures, $(TBA)_{2n}[Ag_2Mo_8O_{26}]_n$ and $(TBA)_{2n}[Ag_2Mo_8O_{26}(CH_3CN)_2]_n$ have been formed by the condensation with Ag^I salts.[11] In these 1D chains, the flexible TBA cations nearly completely wrap around the linear chain of linked $[Ag^IMo^{VI}_8O_{26}AgI]^{2-}$ units effectively isolating them from one another. The mode in which the $\{Ag(Mo_8)Ag\}$-type "units" assemble to create the overall solid-state architecture was also found to be critically dependent on the reaction conditions. On changing the cations from TBA to small cations, the steric shielding and/or "Shrink-wrapping" ability of organic cations is reduced leading to a partial disruption of the "insulation" and as a result, the electrophilic polyoxomolybdate chains could be interlinked. This leads to a grid-like structure $(TBA)_{2n}[Ag_2Mo_8O_{26}(DMSO)_2]_n$ and a 2D array, $(HDMF)_n[Ag_3(Mo_8O_{26})(DMF)_4]_n$, where DMSO = dimethylsulfoxide and HDMF = protonated dimethylformamide. In the latter, the relatively bulky TBA ions are exchanged for HDMF cations thereby allowing the chains to condense to a 2D array. Interestingly, the use of Ph_4P^+ ions instead of TBA cations led to a discrete cluster $(Ph_4P)_2[Ag_2Mo_8O_{26}(DMSO)_4]$. These compounds clearly demonstrate that suitable combination of linkers and bulky organic cations can effectively control the self-assembly of POM building blocks thereby resulting in interesting architectures, see Fig. 9.

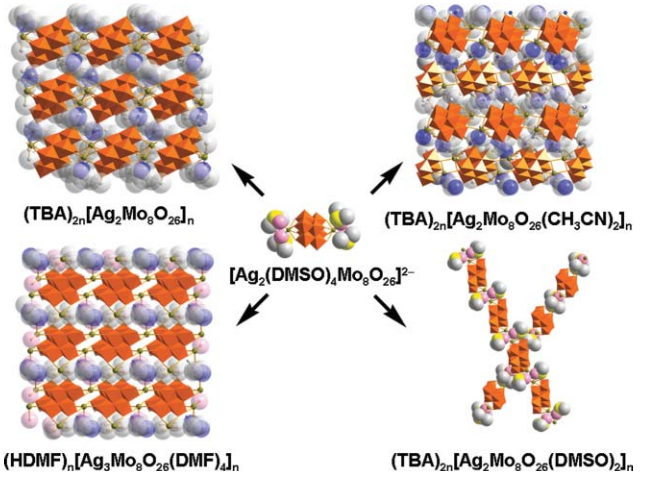


Fig. 9 Summary of the structures isolated from the silver-octamolybdate reaction system. The solvents and counterions are represented in space fill models to highlight their influence in determining the overall topologies achieved which include monomeric structures, 1D chains, grid and 2D network as shown. Color scheme: $\{Mo_8\}$ polyhedra orange, O (rose), C (grey), N (blue), S (yellow).

Further studies on silver-octamolybdate system by varying solvents and counter ions led to a new set of interesting POM architectures.[38] In these structures, formation of $\{Ag_2\}$ linking units is realized and the fine-tuning of Ag–Ag distances in these linkers is achieved with the help of different coordinating solvents. Five compounds based on silver octamolybdate building blocks have been isolated, including an uncommon 0D $(Ph_4P)_2[Ag_2(CH_3CN)_2(Mo_8O_{26})]$, three 1D polymeric chains $([Ag(C_7H_{12}O_2N)(CH_3CN)]_{2n}$ $[Ag_2(CH_3CN)_2(Mo_8O_{26})]_n\cdot 2CH_3CN$, $(Ph_4P)_{2n}[Ag_2(DMF)_2(Mo_8O_{26})]_n\cdot 2DMF$, and $(DMAH)_{2n}[Ag_2(DMF)_2(Mo_8O_{26})]_n\cdot 2DMF$, and a 2D cross-linked network $[(Ag(DMF))_2(Ag(DMF)_2)_2Mo_8O_{26}]_n$. Fig. 10 depicts some of these architectures highlighting the crucial roles of counter ions and solvent molecules in the isolation of such architectures. Therefore, these studies on silver-octamolybdate system comprehensively describes the synthetic strategies that allow the formation of 0D, 1D and 2D structural assemblies starting from a single POM building block $\{Mo_8\}$, and the flexible silver(I) cation linker.

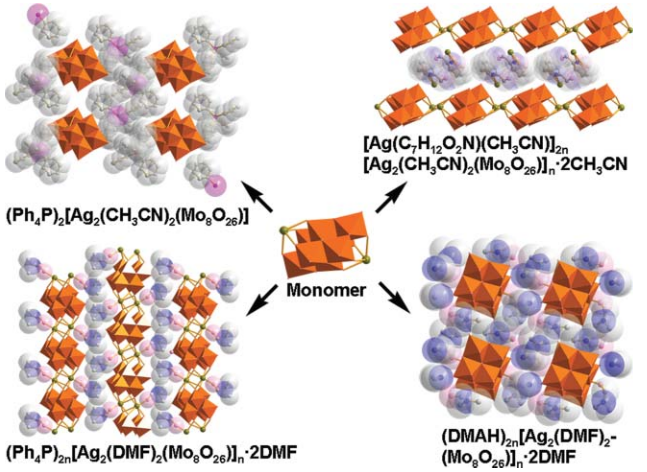


Fig. 10 More examples of silver-octamolybdate based architectures isolated as a result of solvent and counter ions influence self-assembly. Color scheme: $\{Mo_8\}$ polyhedra (orange), O (rose), C (grey), N (blue), P (pink).

The above studies on silver-octamolybdate system have also shown that, careful control over solvent and ligand system can result in the formation of structurally supporting $\{Ag_2\}^{2+}$ building blocks. Exploiting the potential of such silver(I) dimers to act as linkers between larger isopolyoxometalates, we were able to develop a purely inorganic 3D porous framework.[39] The resulting "POM based open framework" or "POMOF", $[Ag(CH_3CN)_4]\subset\{[Ag(CH_3CN)_2]_4[H_3W_{12}O_{40}]\}$, is made up of two principal SBUs, protonated α-metatungstate clusters $[H_3W_{12}O_{40}]^{5-}$ ($\{W_{12}\}^{5-}$) and dimeric $\{[Ag(CH_3CN)_2]_2\}^{2+}$ ($\{Ag_2\}^{2+}$) bridging units. These building units are assembled such as to enclose two sets of collinear channels in the crystal lattice. T_d-symmetric $[Ag(CH_3CN)_4]^+$ units are located in these channels and appear to act as templates in the self-assembly of this framework material. One important key to this framework formation is the ability of the Ag^+ to self-organize into $\{Ag_2\}^{2+}$ dimers with short silver–silver ($Ag^I\cdots Ag^I$) contacts which are stabilized by argentophilic metal–metal interactions. Each dimeric $\{Ag_2\}^{2+}$ motif cross-links four POM building blocks. It was observed here that, in order to encourage the formation of the $Ag\cdots Ag$ interactions, coordinating solvents must be avoided, because the use of such solvents resulted in the capping of Ag centres yielding low dimensional structures. This material shows reversible sorption capabilities allowing the sorption and desorption of small organic molecules. The assembly of such purely inorganic POM-based porous frameworks is highly desirable in materials science, because they are expected to combine the thermodynamic stability of zeolites and mesoporous silicas with the sophistication and versatility of metal–organic frameworks (MOFs).

The effect of the structural features of the organic cations on the supramolecular structure of the POM framework is examined in the case of polyoxomolybdenum(V) phosphate clusters $[CH_6N_3]_{12}[Mo_{12}O_{62}H_{11}NaP_8]\cdot 11H_2O$, $[C_4H_6N_3]_{14}[Mo_{12}O_{62}H_9NaP]\cdot 13H_2O$ and $[C_2H_{10}N_2]_6[Mo_{12}O_{62}H_9Na_3P_8]\cdot 18H_2O$ containing sodium-linked dimeric $\{Mo_6\}_2$ moieties as inorganic building blocks and guanidinium, 2-aminopyrimidinium or protonated ethylenediamine respectively as structure-directing amine cations.[40] It was found that in these compounds, the rigid amines guanidinium and 2-aminopyrimidinium induced the formation of layered arrangements, whereas structurally more flexible ethylenediamine resulted in the formation of polymeric chains, Fig. 11. This study is therefore one of the best examples which shows that the geometry, rigidity and hydrogen bonding ability of organic amine cations can influence the overall structure of the POM supramolecular framework.

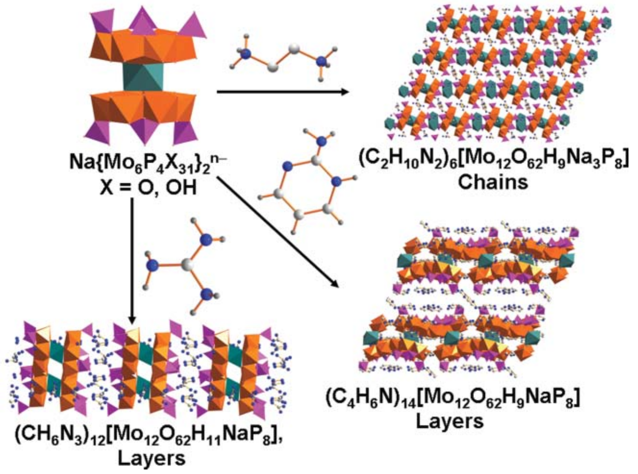


Fig. 11 Summary of the formation of layered or chain-like structures from $\{Mo_6\}_2$ moieties depending on the amine used in the synthesis.

The transfer of properties from small building blocks to the large POM cluster assemblies is an interesting aspect in POM chemistry that is ripe for expansion/concrete development. For example, Craig Hill and co-workers have achieved chirality transfer from smaller enantiopure organic molecules such as tartrate onto POM clusters leading to chiral, non-racemizing and enantiomerically pure polyoxotungstate clusters.[41] Extending this concept into large POM based supramolecular frameworks, we have successfully developed a chiral framework material having sorption capabilities. We used diprotonated (2)-sparteine as the chiral cation and the dimeric polyoxomolybdenum(V) phosphate anion $[H_{15}Mo_{12}NaO_{62}P_8]^{8-}$ as the POM building block, resulting in the porous chiral hybrid framework $(C_{15}H_{28}N_2)_4(C_9H_6O_6)_1[H_{15}Mo_{12}NaO_{62}P_8]\cdot 10H_2O$.[42] In this chiral framework, each dimeric $\{Mo_6\}$ POM cluster is shielded by four (2)-sparteine cations which form $N–H\cdots O$ hydrogen bonds to the cluster anion (minimum distance dN–H$\cdots$O = 2.67 Å). The structure is further reinforced by a complex network of hydrogen-bonded water molecules and incorporates chiral channels along the crystallographic *a* axis, capable of accommodating organic molecules like benzene tricarboxylic acid and water molecules. The porous nature of this compound is confirmed by reversible water sorption properties.

In our attempt to develop POM based chiral frameworks, we have also used large chiral metal–organic macrocation as one of the starting material. Fe-acrylate based chiral macrocation $[Fe_3(\mu_3\text{-}O)(CH_2{=}CHCOO)_6(H_2O)_3]^+$ is reacted with trilacunary Dawson cluster $[\alpha\text{-}P_2W_{15}O_{56}]^{12-}$, $\{P_2W_{15}\}$, under normal reaction conditions. This macrocation is found to decompose slowly in the presence of $\{P_2W_{15}\}$ and in doing so, helps to buffer the reaction medium leading to the formation of a nanosized tetrahedral polyoxotungstate molecule $K_{21}Na_8[KFe_{12}(OH)_{18}(\alpha\text{-}1,2,3\text{-}P_2W_{15}O_{56})_4]\cdot 70H_2O$.[43] This 21 kDa POM cluster is found to be water stable as was directly observed in solution/gas phase using electrospray mass spectrometry. In the crystal lattice, the tetrahedral anionic cluster units are inter-connected *via* external potassium ions to form an extended 3D network in the solid state with an accessible solvent volume of 6000 Å^3 per unit cell. This study was partly inspired by the works of Mizuno *et al.*, who have extensively used similar metal–organic macrocations for example: $[Cr_3O(OOCH)_6(H_2O)_3]^+$ with POM clusters resulting in interesting framework materials.[44]

Looking for new organic cations as shrink-wrapping agents, we used *N*,*N*′-bis(2-hydroxyethyl)piperazine (BHEP), which is found to act as a tri-functional species being a cation, ligand and buffer in POM synthesis. The ethanol arms attached to the nitrogen donors of the piperazine ring add flexibility to the ligand and form flexible coordination environment for the ligation of transition metals. BHEP can effectively buffer the pH range 4–8 allowing precise pH control. These properties make BHEP an interesting structure directing cation in POM synthesis. Two new POM architectures, the dimeric cluster unit $[\{PMnW_{11}O_{39}\}_2(PO_4)]^{13-}$ and a 2D network based on $[P_2Mn_4W_{18}O_{68}]^{10-}$ anions are isolated at pH 6.05 and 6.80 respectively using BHEP as buffer, encapsulating cation and as a ligand.[12] The dimeric cluster unit, formulated as $(H_2BHEP)_5(HBHEP)Na_2[(PMnW_{11}O_{39})_2\{PO_4\}]\cdot 18H_2O$ is composed of two $\alpha\text{-}[PMnW_{11}O_{39}]^{5-}$ clusters connected by a bridging phosphate unit that links the Mn^{2+} centres attached to the mono-vacant Keggin entity. This moiety is stabilized, in the solid state, by the surrounding four H_2BHEP ions. The 2D network, $(H_2BHEP)_3Na_4[P_2Mn_4W_{18}O_{68}]\cdot 15H_2O$, is synthesized using a slight increase of pH and temperature in comparison to the dimeric compound. However, the structure of this new compound was entirely different; consisting of two $\{B\text{–}PW_9O_{34}\}$ units sandwiching four manganese centres between them in a belt-like fashion. The synthesis of these compounds reiterates the multi-functionality of the BHEP ligand and the importance of solution pH in determining the nature of the resulting POM architectures under otherwise identical reaction conditions.

The important pH buffering capacity of BHEP is revealed in the synthesis of three Co(II)-containing silicotungstates *viz.* $[Co_3(H_2O)(B\text{-}\beta\text{-}SiW_9O_{34})(B\text{-}\beta\text{-}SiW_8O_{29}(OH)_2)]^{12-}$, $[Co_3(H_2O)(B\text{-}\alpha\text{-}SiW_9O_{34})(B\text{-}\beta\text{-}SiW_8O_{31})]^{14-}$, and $[Co_9Cl_2(OH)_3(H_2O)_9(B\text{-}\beta\text{-}SiW_8O_{31})_3]^{17-}$ which have been observed before only as dimeric or higher nuclearity cluster complexes. The synthetic strategy employed involves the reaction of Co(II) ions, the dilacunary $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ polyanion and the bulky organic cation BHEP in basic media at pH 8.0–9.0.[45] Although the BHEP ligand is not incorporated in these structures, the fact that these clusters do not form in the absence of BHEP in the reaction medium, led to the conclusion that this amine ligand plays a vital role in the isolation of these intermediate clusters, by acting as a buffer at these high pH values.

A prototype of a 3D polyoxometalate framework based on pure metal oxides and constructed without the use of external linkers to connect the polyanionic framework nodes has been achieved by the reaction of the divacant lacunary polyoxometalate $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ with Mn(II) in the presence of morpholinium cations and potassium permanganate, under strict pH control. This extended modular framework made up of POM building blocks incorporates "active sites" capable of responding to guest inclusion.[46] The resulting pure metal oxide framework, $[(C_4H_{10}NO)_{40}(W_{72}M_{12}O_{268}X_7)_n]$ ($M = Mn^{III}$, $X = Si$), based upon Mn-substituted Keggin-type POM building blocks encloses elliptical pockets of 26.85 × 23.62 × 12.93 Å size and house solvent molecules and morpholinium cations in these pockets, Fig. 12. This material can undergo a reversible redox process that involves the simultaneous inclusion of the redox reagent with a concerted and spatially-ordered redox change of the framework. Importantly, this compound can be repeatedly disassembled and reassembled without any structural changes by dissolution in hot water followed by recrystallization. These unique properties define a new class of POM-based materials that bridge the gap between coordination compounds, metal–organic frameworks and solid-state oxides. Furthermore, it has been shown that all the Mn(III) centres in the oxidized form of this compound can be "switched" to Mn(II) using a suitable reducing agent to give the fully reduced framework. Moreover, the redox processes can be precisely followed by the single-crystal to single-crystal transformation between the oxidized and reduced states of the framework.

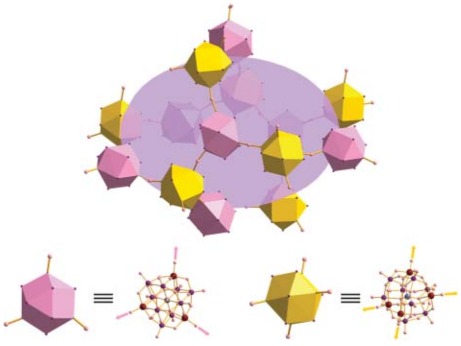


Fig. 12 Illustration of the nanosized pockets in $[(C_4H_{10}NO)_{40}(W_{72}Mn_{12}O_{268}Si_7)_n]$ highlighted by the purple ellipsoid (dimensions: ~ 2.7 × 2.4 × 1.3 nm). The trigonal (rose) and tetrahedral (yellow) building block connectors are shown at the bottom; rose and yellow arrows highlight the connecting modes.

Extending the building block approach further by using very large building blocks such as a superlacunary $[H_7P_8W_{48}O_{184}]^{33-}$, $\{P_8W_{48}\}$, polyoxoanion and transition metal ions such as Co(II) as linkers, two cyclic cobalt-substituted heteropolyoxometalate frameworks $K_{15}Li_5[Co_{10}(H_2O)_{34}(P_8W_{48}O_{184})]\cdot 54H_2O$ and $K_8Li_{12}[Co_{10}(H_2O)_{44}(P_8W_{48}O_{184})]\cdot 60H_2O$ have been synthesized under strict control of pH and buffer. In both these frameworks, the central crown cavity of $\{P_8W_{48}\}$ is functionalised by a total of six Co(II) ions and additional Co(II) ions are grafted onto the outer rings extending the Co(II)-$\{P_8W_{48}\}$ anions into 1D chains in the former and to a 3D networks in latter.[47]

As we have seen from the above examples, the combination of "building block approach" of POM synthesis with "Shrink-wrapping" cation technique has yielded several novel architectures and framework materials. It is to be noted here that, most of these materials are derived starting from simple POM building blocks such as lacunary Keggin or Dawson cluster derivatives. The most exciting aspect of this approach lies in the possibility of developing some true porous POM based materials starting from large, inherently porous POM clusters such as $\{P_8W_{48}\}$, $\{Mo_{154}\}$[5] *etc* having open cavities at the centre.[47]

6. POM based single molecule magnets (SMMs)

In POM chemistry, the development of novel magnetic materials such as single molecule magnets (SMMs) has been a synthetic target for a long time. The main approaches towards this goal include the magnetic functionalization of metal oxide fragment itself, the interlinking of POM building blocks or the use of lacunary POM fragments as multidentate ligands binding to polynuclear paramagnetic coordination clusters.[48] One of the major limitations in the development of such materials is that the underlying design strategies lie within the boundaries set by the serendipitous self-assembly of metal ions, bridging ligands and the POM building blocks. In short, control over the self-assembly is crucial in the design of magnetic POM materials.

Utilizing morpholine as the organic cations, we were successful in synthesizing the first two examples of MnII/III-based SMMs encapsulated within a polyoxometalate ligand system derived from the trivacant lacunary $\{\text{B-}\alpha\text{-}X^{IV}W^{VI}{}_9O_{34}\}^{10-}$ polyanion.[49] These clusters were isolated as $Na_4K(C_4H_{10}NO)_7\{[GeW_9O_{34}]_2[Mn^{III}{}_4Mn^{II}{}_2O_4(H_2O)_4]\}\cdot 15H_2O$ and $(C_4H_{10}NO)_{12}\{[SiW_9O_{34}]_2[Mn^{III}{}_4Mn^{II}{}_2O_4(H_2O)_4]\}\cdot 15H_2O$ and can be described as consisting of two $\{\text{B-}\alpha\text{-}XW_9O_{34}\}^{10-}$ (X = Ge, Si) polyanions that sandwich a mixed-valence cationic hexanuclear $[Mn^{III}{}_4(H_2O)_2Mn^{II}{}_2O_4(H_2O)_2]^{8+}$ cluster. The $\{[Mn^{III}{}_4Mn^{II}{}_2O_4(H_2O)_4]\}$ cluster is a *Ci*-symmetric double cubane, in which each cubane comprises three Mn^{III} and one Mn^{II} centre, with two of the Mn^{III} centres shared between the cubanes, see Fig. 13.

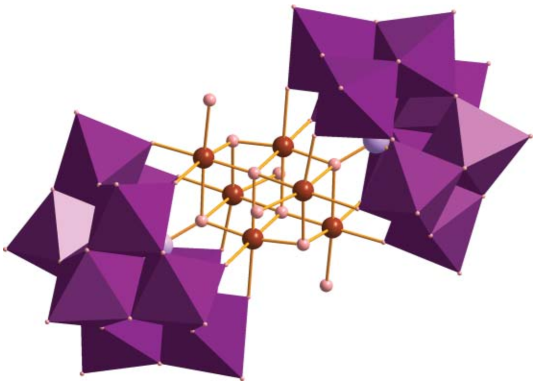


Fig. 13 Representation of the $[\{XW_9\}_2\{Mn_6\}]^{12-}$ polyanion, where X = Ge and Si. The polyoxotungstate fragments are shown as polyhedra, and the central $\{Mn_6O_4(OH_2)_4\}$ double-cubane cluster and the connecting heteroatoms are shown as ball-and-stick. Mn(III) (brown), Mn(II) (violet), X (purple), O (red), H_2O (pink), H omitted for clarity. The elongated Jahn–Teller axes of the Mn(III) ions are shown in black.

Parallel to our report on first POM based SMM cluster, Coronado and co-workers have synthesized another POM based SMM cluster, $[ErW_{10}O_{36}]^{9-}$, which consist of two $[W_5O_{18}]^{6-}$ moieties sandwiching an Er^{3+} ion.[50] Following these compounds, more POM based SMMs are being reported recently, one of which includes a $\{Mn(III)_2\}$–POM composite material produced by the introduction of $[Mn(salen)(H_2O)]_2(ClO_4)_2\cdot H_2O$, $\{Mn(III)_2\}$, into the polyoxometalate systems $Na_3[XMo_6(OH)_6O_{18}]$ (X = Al and Cr).[51] Very recently nonairon(III) and hexairon(III) complexes, $Na_{14}(C_4H_{12}N)_5[(Fe_4W_9O_{34}(H_2O))_2(FeW_6O_{26})]\cdot 50H_2O$ and $Na_6(C_4H_{12}N)_4[Fe_4(H_2O)_2(FeW_9O_{34})_2]\cdot 45H_2O$, synthesized by hydrothermal method, have also been reported to exhibit SMM behaviour.[52]

7. Organic–inorganic hybrid POMs

An important step in POM chemistry towards functional materials is the development of organic–inorganic hybrid clusters by covalent functionalization of POMs with suitable organic groups. Covalent functionalization allows the synergistic combination of the properties of metal–oxo clusters and organic units, thereby allowing to fine tune the cluster properties such as solubility, redox properties, biological activities and so on.[24] Out of the various methods used for the covalent functionalization of POM clusters, grafting of tris(hydroxymethyl)aminomethane and its derivatives (denoted hereafter as TRIS) on to clusters is an important approach, as this group of molecules is geometrically well suited for grafting onto Anderson, Wells-Dawson and Lindqvist-type clusters.[53] Many POM hybrids containing TRIS as a linker between organic moieties and POM units are being developed for their potential applications as polymer support, POM based gels, and as light harvesting complexes.[54]

An interesting framework material, assembled purely through hydrogen bonding interactions, is achieved using an Anderson-based organic–inorganic hybrid cluster as the building block.[55] In the development of this framework material, a TRIS tethered pyrene moiety was covalently grafted onto a Mn-Anderson cluster, leading to the isolation of the hybrid cluster $TBA_3[MnMo_6O_{18}\{(OCH_2)_3CNH\text{–}CH_2\text{–}C_{16}H_9\}_2]\cdot 2DMF\cdot 3H_2O$ with properties different from that of pure building blocks. Furthermore, the self-assembly of this [Mn-Anderson(TRIS-pyrene)$_2$]$^{3-}$ building block together with TBA cations produces a nanoporous framework with nanoscale solvent-accessible 1D channels in the solid state. This material appears to be stable until 240 °C despite being constructed from very weak C–H···O═Mo hydrogen bonding interactions. The guest-uptake measurements revealed that the framework is nanoporous and is able to absorb up to 12% by weight of chlorobenzene.

Using TRIS-grafted Mn-Anderson clusters as the building block and Ag cations as linkers, the hybrid compounds $\{Ag_3[MnMo_6O_{18}\{(OCH_2)_3CNH_2\}_2(DMSO)_5]\cdot 3(DMSO)\}_n$; and $\{Ag_3[MnMo_6O_{18}\{(OCH_2)_3CNH_2\}_2(DMSO)_6(CH_3CN)_2]\cdot DMSO\}_n$ have been synthesized. These compounds having 1D chain structure form fibres on the Si surface >10 µm in length with a diameter of *ca.* 0.5 mm indicating that such hybrid clusters have potential for use in the self-assembly of functional materials.[56]

Using long alkyl chain cations, the hydrophobicity of certain POM clusters could be increased, thus imparting new materials properties to such clusters. In an attempt to develop amphiphilic hybrids, we have successfully attached long (C-16 and C-18) alkyl-chains onto TRIS grafted Mn-Anderson cluster by manipulating the reactivity of the free $–NH_2$ group of the TRIS moiety. Some of these long alkyl chain grafted hybrids indeed exhibited amphiphilicity forming supramolecular vesicles in solutions.[57] Further, cations are exchanged from TBA to dimethyldioctadecyl ammonium (DMDOA), inducing new properties to these hybrids such as increased hydrophobicity. It is found that, some of these new materials form interesting microstructures on surfaces and exhibit interesting physical properties including phase transition and nanoparticle formation.[58]

Moving on to larger clusters, we have developed a series of TRIS-grafted Dawson-like clusters to study their self-assembly in solid state and in solutions. TRIS derivatives containing free $–NH_2$, $–NO_2$ and $–CH_3$ functionalities $H_2N–C(CH_2OH)_3$, $O_2N–C(CH_2OH)_3$ and $H_3C–C(CH_2OH)_3$ were successfully grafted onto the V_3 capped Dawson-like cluster $[P_2V_3W_{15}O_{62}]^{9-}$, resulting in a series of hybrid POM cluster anions having the general formula $[X–C(CH_2O)_3P_2V_3W_{15}O_{59}]^{6-}$, where X = $–NH_2$, $–NO_2$ or $–CH_3$. It is found that these hybrid clusters are capable of acting as supramolecular building blocks and are capable of self-assembling into larger supramolecular structures through hydrogen bonding interactions between the grafted TRIS moiety and the cluster oxygen atoms in solid state and in solution. Most importantly, it is found that the formation of these supramolecular architectures is controlled by the nature of the grafted H-bonding organic cap and/or the solvent system employed. Crucially, the NH_2-capped cluster anion $[H_2NC(CH_2O)_3P_2V_3W_{15}O_{59}]^{6-}$ on crystallization from acetonitrile gave a fully H-bonded supramolecular assembly having a distorted tetrahedral structure, $(TBA)_{16}H_8[H_2NC(CH_2O)_3P_2V_3W_{15}O_{59}]_4 \cdot 8(CH_3CN)$; while crystallization from DMF led to $(TBA)_4H_2[H_2NC(CH_2O)_3P_2V_3W_{15}O_{59}] \cdot 3DMF$ in which H-bonding between cluster and solvent DMF molecules lead to the formation of an infinite hydrogen-bonded chain structure in the solid state, Fig. 14.

Fig. 14 Solvent dependant formation of different architectures from tris-grafted $\{P_2V_3W_{15}\}$ clusters.

The role of the H-bonding ability of the organic caps of these cluster hybrids $[X–C(CH_2O)_3P_2V_3W_{15}O_{59}]^{6-}$, where X = $–NH_2$, $–NO_2$ or $–CH_3$ in forming multiple aggregates in solution and gas phase was analyzed by comparing their cryospray mass spectra. The CSI-MS studies confirmed the formation of hydrogen-bonded nano-structures in the solution as well as revealed valuable information about the mechanism of this self-assembly process. For example, the formation of hydrogen bonded monomer, dimer, trimer and tetramers are detected in the solution and gas phase by CSI-MS studies in the case of $–NH_2$ and $–NO_2$ capped hybrid clusters; even higher aggregations such as pentamers and hexamers were detected in solution and gas phase in the case of $–NO_2$ capped cluster, see Fig. 15. The detection of these higher aggregates in solution and gas phase actually points to the formation of a number of virtual clusters in the solution before crystallisation of a particular cluster out of the solution phase takes place. Therefore, this study revealed that the covalent grafting of H-bonding organic caps onto POM clusters can precisely control the supramolecular self-assembly of cluster species in the solid state and in solutions and also shows the existence of cluster aggregates in solution other than the one that crystallized out ultimately.[59]

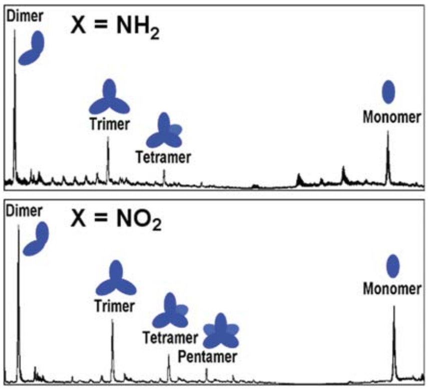


Fig. 15 CSI-MS spectra and supramolecular assemblies of $[X–C(CH_2O)_3P_2V_3W_{15}O_{59}]^{6-}$ clusters as a function of the different substituents (X) on the organic cap. Top X = $–NH_2$, bottom X = $–NO_2$.

In further extension of TRIS-Dawson hybrid cluster chemistry, we were successful in developing a class of POM-based "inorganic–organic–inorganic" hybrid clusters derived by grafting linear bis-(TRIS) ligands onto the V_3-capped Dawson-like cluster $[P_2V_3W_{15}O_{62}]^{9-}$. These inorganic–organic–inorganic "dumbbell" hybrids are approximately 3.4 nm long, representing the first examples of such dumbbells based on functional Dawson-like clusters.[60] Structural studies confirmed that these compounds contain two $\{P_2V_3W_{15}O_{62}\}$ cluster anions as dumb-bell heads, which are linked together by linear bis(tris) ligands. The TBA cations are found to play a crucial role in controlling the self-assembly of these clusters in the solid state. The TBA cations undergo extensive C–H···O hydrogen bonding interactions with the cluster heads of the dumb-bells, effectively wrapping around them, hence making the dumb-bell heads bulkier compared to their relatively thin middle part. This together with the peculiar zig-zag packing mode of these hybrids, lead to the formation of 1D channels along the crystallographic *b* axis in the crystal lattice. It is found that the diameter of these channels, ~1 nm, also correspond to the length of the organic linker unit, thus suggesting a possibility of controlling the void space in similar hybrid dumb-bell systems by changing the length of the linker unit, Fig. 16. Furthermore, these hybrids are shown to self-assemble in solutions forming vesicles as proved by light scattering and transmission electron microscopy (TEM) techniques.[60]

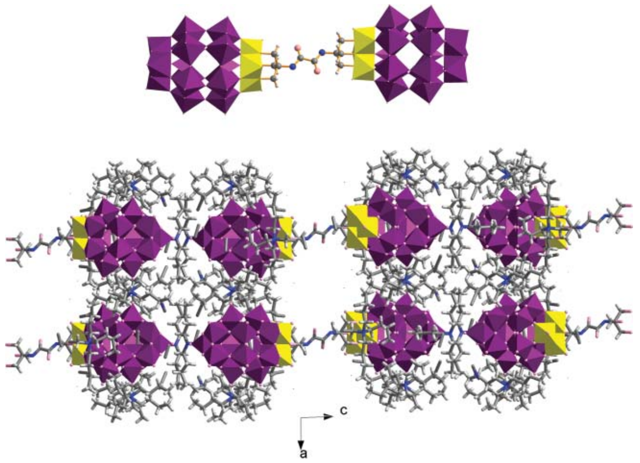


Fig. 16 Combined ball and stick and polyhedral representation of the "inorganic–organic–inorganic" hybrid cluster anion derived by grafting linear bis-(tris) ligands onto the V_3-capped Wells-Dawson-type cluster $TBA_5H_4[P_2V_3W_{15}O_{62}]$ (above) and the packing diagram (below) of the same compound showing the selective gathering of TBA cations around dumb-bell heads leading to voids in the crystal lattice. C (grey), H (white), N (blue), O (rose), W (violet polyhedra), V (yellow polyhedra), P (pink polyhedra).

8. Bridging the gap between solution and the solid state

Although single crystal X-ray crystallography gives unambiguous structural information on crystalline solid state materials, it does not give any information about the solution processes. In this respect, solution studies are extremely important to help understand the mechanism of cluster self assembly and crystallization of polyoxometalates. However it is a great challenge to understand the self-assembly since conventional spectroscopic techniques have significant drawbacks. For example, NMR is of limited use when the symmetry of the assembling architecture is high, when the structures are labile or paramagnetic, and for nuclei that have a poor receptivity. To address these issues we have recently employed high resolution time of flight (TOF) mass spectrometry to examine the structures and assembly/disassembly of high nuclearity polyoxometalates and coordination clusters, as well as dynamic light scattering (DLS) to probe the nucleation events in solution since we have found that these techniques are highly useful analytical tools in the probe of self-assembly processes involving nano-sized metal-oxide architectures.[61,62]

Recently, we were successful in following the pH dependant cluster disassembly process of a POM cluster for the first time in solution phase using DLS technique. In this study, a large phosphotungstate $K_{24}[P_4W_{52}O_{178}]\cdot 47H_2O$ ($\{P_4W_{52}\}$, 2.65 × 2.23 nm), is synthesized starting from Na_2WO_4 in a "one-pot" synthesis which is then subjected to pH dependant disassembly into smaller clusters. The parent cluster which is stable at pH ~ 2 disassembles into smaller clusters $K_{19}[P_3W_{39}O_{134}]\cdot 30H_2O$ ($\{P_3W_{39}\}$, 2.23 × 1.97 nm) at pH 2–3, $K_{20}[P_4W_{44}O_{152}]\cdot 48H_2O$ ($\{P_4W_{44}\}$, 2.3 × 1.93 nm) at pH 3–5 and finally into $K_{14}[P_2W_{19}O_{69}(OH_2)]\cdot 24H_2O$ ($\{P_2W_{19}\}$) at pH 6. This cluster disassembly is successfully followed by particle size measurements on solutions of $\{P_4W_{52}\}$ maintained at pH 2–6 using DLS instrument. It was found that the hydrodynamic diameter of the particles in these solutions showed a gradual decrease in size as the pH of the solution was increased from 2 to 6 (from 1.7 nm at pH 2 to 0.7 nm at pH 6; see Fig. 17), which is in accordance with the size of the clusters isolated at these pH values in solid state. Therefore, this study clearly shows that the DLS measurement gives a considerable amount of information regarding the particle sizes of the cluster species in solution and hence more insight into their self-assembly, disassembly processes, see Fig. 17.[63]

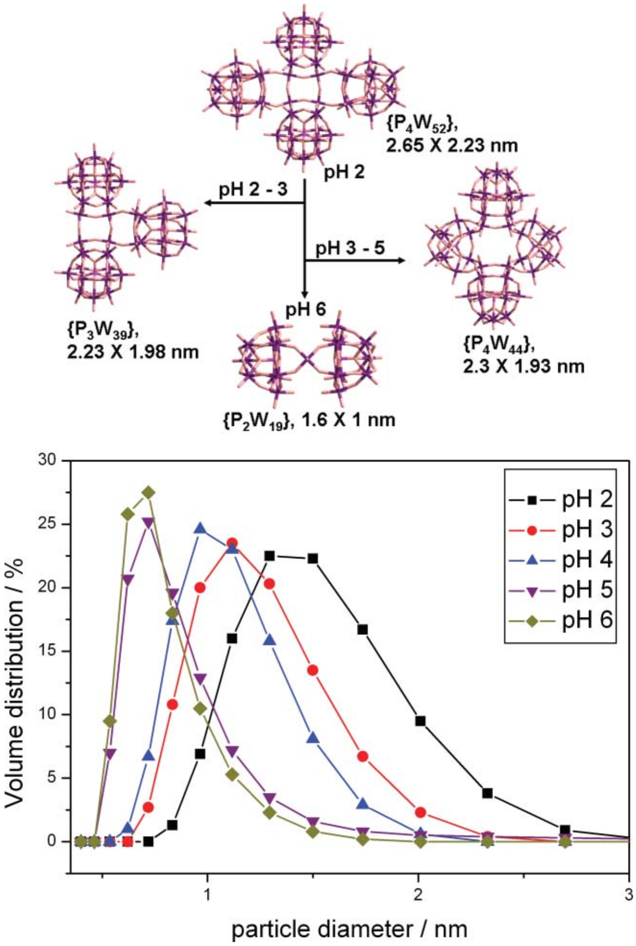


Fig. 17 Above: molecular structures of $\{P_4W_{52}\}$ cluster anion and its pH controlled decomposition products. Color scheme: W (violet), O (rose), P (purple). Below: volume size distribution of particles of $\{P_4W_{52}\}$ in solutions at different pH values using DLS measurements.

Another pertinent example involves the use of cyrospray ionisation-mass spectrometry (CSI-MS) which we used to shed light upon the mechanism of self-assembly of POM clusters in solution. By using CSI-MS in conjunction with electronic spectroscopy, it was possible to monitor the real-time re-arrangement of a Lindqvist $\{Mo_6\}$ cluster into β-octamolybdate anion $\{Mo_8\}$ and its subsequent self-assembly into the silver linked POM structures in unprecedented details. The role of Ag(I) ion in the solution state rearrangement of $\{Mo_6\}$ into $(TBA)_{2n}[Ag_2Mo_8O_{26}]_n$ is revealed as a result of this study. Also this study revealed the structure directing roles of the organic cations in POM growth in solution, as the rate of $\{Mo_6\}$ to $\{Mo_8\}$ interconversion was found to decrease on increasing the size of the counter cation.[64]

9. Conclusions and perspectives

The crystal engineering of POM materials is challenging because of the highly sensitive nature of the synthetic procedures. This means that the successful discovery and development of new cluster/synthesis approaches has previously relied upon an intuitive approach. Further, we have shown in this perspective that the structure of the clusters formed can also be dramatically influenced by the cations present in solution, and also subsequent cation exchange reactions on the POM cluster after isolation. What is perhaps until now not clear is that separate and successive cation exchange reactions can have a profound influence as follows: primary cation exchange reactions can be used to control the assembly of cluster building blocks from the most basic units; secondary cation exchange reactions can be used to control the linking of these cluster building blocks to larger fragments and tertiary exchange reactions can be used to define solid-state networks and cluster-of-cluster type assemblies.

These exchange reactions can be taken one step further, even transforming existing crystals. In recent work, we have been able to show that it is possible to even disassemble crystals of polyoxometalate clusters using a quaternary cation exchange reaction by adding organic cations to an aqueous solution in which the crystal of the polyoxometalate is immersed, see Fig. 18. This results in the near-instantaneous dissolution of the crystal, *via* the formation of a semi-permeable membrane around the crystal.[65] This membrane then gives birth to micron scale tubes that grow with vast aspect ratios at controllable rates along the surface on which the crystal is placed.

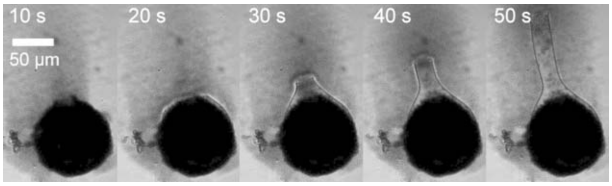


Fig. 18 Time lapse sequence showing the real time development of a membrane around a crystal of a polyoxometalate and the extension of the membrane away from the crystal.

The tubes are comprised of an amorphous mixture of polyoxometalate-based anions and organic cations. It is possible to flow liquid through the tubes, control the direction of growth and overall tube diameter,[66] and it has been shown that tube growth is driven by an osmotic pressure within the membrane sack around the crystal which ruptures to release the pressure. These robust, self-growing, micron-scale tubes offer opportunities in many areas, including the growth of micro-fluidic devices and self-assembly of metal oxide based semi-permeable membranes for many diverse applications.

Finally, it is worth commenting that the use of ion exchange reactions to modulate the redox conditions in flow system, controlling the crystallisation of gigantic clusters, has recently been used by us to unveil new mechanistic perspectives in assembly of gigantic polyoxometalate wheel shaped clusters, first characterised by Müller and co-workers in Bielefeld in 1995.[67] Not only did this approach allow a reactive intermediate host–guest complex to be isolated, $Na_{22}[Mo^{VI}_{36}O_{112}(H_2O)_{16}]\subset[Mo^{VI}_{130}Mo^{V}_{20}O_{442}(OH)_{10}(H_2O)_{61}]$, but also showed how the synthesis of the empty wheel could be improved, see Fig. 19.[68]

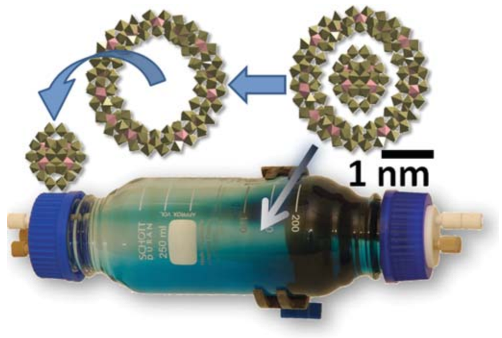


Fig. 19 A photograph of the flow systems with the blue "plume" from which the host–guest cluster crystallises (bottom). A schematic above is shown of the host–guest complex $\{[Mo^{VI}_{36}O_{112}(H_2O)_{16}]\subset[Mo^{VI}_{130}Mo^{V}_{20}O_{442}(OH)_{10}(H_2O)_{61}]\}^{22-}$ is shown in polyhedral plot (Mo centres shown in gold and pink with the pentagonal centres shown in pink. Also, the ejection of the $[Mo^{VI}_{36}O_{112}(H_2O)_{16}]^{8-}$ template, to give the empty wheel, $[Mo^{VI}_{130}Mo^{V}_{20}O_{442}(OH)_{10}(H_2O)_{66}]^{14-}$, is shown (top).

In general this approach could help define a new field of complex POM synthesis *via* cation exchange/redox modulation. Indeed, it appears that cation exchange reactions may be so critical that it will be possible to develop new approaches to the non-equilibrium structured polyoxometalate assembly of a range of new clusters, materials and devices. Furthermore, the investigation of dynamic systems that can be controlled effectively is vitally important for the development of new types of complex synthetic systems/inorganic systems chemistry.

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