

# Controlling the Molecular Assembly of Polyoxometalates from the Nano to the Micron Scale: Molecules to Materials

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**Abstract:** Polyoxometalates (POMs) represent a class of metal-oxide units based upon oxides of Mo, W, V, and Nb. Such cluster building blocks can also be subsequently self-organized in complex 1D, 2D, and 3D frameworks leading to functional materials with diverse properties that span size ranges from 1 to 7 nm in terms of the size of the largest molecular units/clusters. However, since the cluster building blocks have great structural flexibility, the design of architectures is non-trivial due to the sensitive dependence on reaction parameters such as pH, cation type, temperature, templating and linking units, ionic strength, redox agents. Therefore, the ability to control the aggregation or

linking of the building blocks to give pre-defined structure-types as well as engineering the physical properties — for example, optical, electronic, catalytic activity/reactivity — is a tremendous challenge. In this review we survey our work from the control/design point of view and show how it is becoming possible to control the assembly of POM-based architectures. We also describe the polyoxometalate-based molecules-to-material transformations that can be seen as an osmotically driven crystal morphogenesis producing tubular architectures. This can be described as a new type of emergent phenomenon.

**Keywords:** device · framework · molecular design · polyoxometalate · redox

## 1. Introduction

Polyoxometalates (POMs) are the discrete assemblies of early-transition metal oxide  $\{MO_x\}$ , where  $x = 4-7$  and M is most frequently Mo, W, V, and Nb.<sup>[1]</sup> These subunits can be better understood when the metal-oxo building blocks are represented as polyhedral units, where the oxygen atoms are positioned on the vertices. The polyhedra can hence be connected by the edge and/or by the corner sharing modes, leading to anionic clusters having an impressive range of structural diversity following “one-pot” syntheses. Despite the apparent simplicity of the procedure, many synthetic parameters (e.g., counterion, pH, solvent, temperature, time of reaction, ionic strength, concentration) can act as decisive structural parameters. Indeed, a small deviation of one of these factors can lead to totally different cluster architectures that can inhibit the ability to reliably control or design the POM framework. A solution to this problem is desired, since POMs are nanoscale molecules with an extraordinary range of functions. The ability to design at the level of the molecular structures (in the 1–10 nm size range) would open up avenues that could only be accessed using molecular approaches to nanoscience.

In this respect we have recently described phenomenologically the control that can be exerted by the charge-balancing cation on the structure of polyoxometalate clusters during the self-assembly process.<sup>[2]</sup> In general, POMs are anionic and are hence associated with charge-balanc-

ing cations, although these are sometimes omitted from structural analysis as being “innocent”. However, depending on its size, charge, symmetry, solubility, the cation can be found to influence the framework assembly as well as to modulate the packing of the crystal lattice, the size of the framework, and if applicable the dimensionality of the network. In particular, we have demonstrated that the use of bulky cations such as protonated organic amines (hexamethylene tetramine, triethanol amine, morpholine,...) can direct the assembly of polyoxometalates via association in solution (we tentatively described this as a kind of shrink-wrapping process). Further, we have shown that it is possible to influence the symmetry of the cluster by changing the symmetry of the organo-cation.<sup>[3]</sup>

An elegant extension of this strategy has been recently reported.<sup>[4]</sup> It consists of trapping a cluster using a bulky ammonium cation, followed by the cation exchange with a second bulky ammonium cation, leading to a structure that would not have been obtained using the second ammonium in the direct one-pot synthesis. As represented in

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Figure 1, when triethylammonium (TEAH) is present in the reaction of  $\text{Na}_2\text{WO}_4$  with  $\text{Na}_2\text{S}_2\text{O}_4$  in an aqueous solution at pH 1.7, a Dawson-like cluster  $[\text{H}_2\text{W}_{18}\text{O}_{57}(\text{SO}_3)]^{6-}$  is obtained. Under the same conditions, using dimethylammonium (DMAH) instead of TEAH, another Dawson-like POM  $[\text{W}_{18}\text{O}_{54}(\text{SO}_3)_2(\text{H}_2\text{O})_2]^{8-}$  is produced in the solid

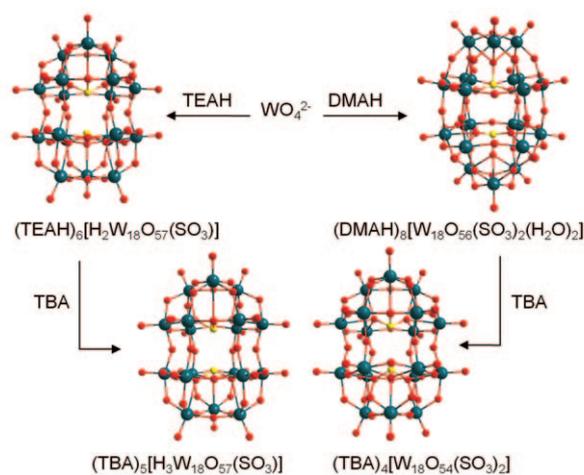
After her M.Sc. in 2003 at the University Louis Pasteur, Strasbourg, Marie Hutin moved to Geneva to work with Dr. J. R. Nitschke on the synthesis of dynamic Copper(I) complexes. After receiving her Ph.D. in 2007 she obtained a Swiss National Science Foundation fellowship in 2008 to study the cooperativity and residual dipolar couplings in self-assembled porphyrin oligomers in Oxford with Professor H. L. Anderson. In 2009, she took a post-doctoral fellowship with Professor E. W. Meijer at the Eindhoven University of Technology to study the crystallization of bis-(UPy-urea) polymers. Since October 2010, she has been the research coordinator of the group of Professor Lee Cronin. Her research currently focuses on photo-switchable POM-based materials.



De-Liang Long gained his B.Sc. and M.Sc. Degrees in chemistry from Wuhan University and completed his Ph.D. under the direction of Prof. Xin-Quan Xin at Nanjing University in 1996. After a post-doctoral appointment at Fujian Institute of Research on Structure of Matter, Chinese Academy of Sciences, in 1999 he held the Royal Society K. C. Wong Fellowship working with Prof. Martin Schröder at the University of Nottingham. He is currently a Reader in Inorganic Chemistry at the University of Glasgow, jointly running the Cronin group with Professor Lee Cronin. His interests are in inorganic synthesis, coordination chemistry, crystallography, and cluster based materials.



Leroy (Lee) Cronin graduated with a first class honour degree in Chemistry in 1994, and obtained a D.Phil. in 1997 at York University under Prof. P. H. Walton. After a post-doctoral research at Edinburgh University with Neil Robertson and at Bielefeld University, Germany, with Prof. A. Muller, he returned to the UK as a lecturer at Birmingham University in 2000. In 2002 he moved to Glasgow, was promoted to Reader in 2005, Professor in 2006, and was appointed to the Gardiner Chair of Chemistry in 2009. His research interests include synthetic chemistry, ligand design, hybrid materials, self-assembling and self organization/emergent systems, chemical evolution, and development of new methods to study nanomolecular systems.



**Figure 1.** Illustration of the shrink-wrapping synthesis approach using organo amines as cations. The POM structures shown are experimentally determined crystal structures. Green spheres: W; red spheres: O; yellow spheres: S.

state, exhibiting different structural and electronic features, though very similar in terms of cage nuclearity.

Once these clusters have been formed, the counterion can be exchanged by tetrabutylammonium (TBA). It is then possible, upon cation metathesis and crystallization, to transform the clusters again; this means that by step-wise cation metathesis the structure of the clusters can be changed from that of the parent clusters, and demonstrates the influence of the so called shrink-wrapping effect in solution. In most of the cases heteroatoms/heteroanions are present inside the cavity of the POM, like the sulfite in the example described here. These act as templates during the synthesis of the cluster, from which results the heteropolyanionic nature of most of the POMs. The examples of clusters with empty cavities, that is, they do not need any anionic templation to be formed, are relatively limited. These are called isopolyoxometalates.<sup>[1]</sup>

Once these clusters have been characterized and isolated, they can be connected within a discrete assembly (framework) or in a polymeric structure (network) via M–O–M bridges, organometallic complexes, or organic linkers. This can be defined as a type of “building block” approach to materials based upon POM cluster “nodes”. While the templating action of heteroanions leads to the formation of POMs, the cationic species (other heterometallic species such as silver or as potassium cations) can act as a template to link POMs together into frameworks.

We will discuss here the different frameworks that can be obtained with these linkers, and the new properties that can be engineered as a function of the linkers. One of the greatest challenges in this field is to reach a level of prediction that will allow reliable materials to be designed from the new types of molecular structures generated using shrink-wrapping cations; this could also allow the designed assembly of large networks with pre-defined

topologies and function reached by embedding the known clusters into the linked network architecture. Success here will result in the development of materials with exciting sought-after properties for application in a range of fields from biomaterials to electronic devices.

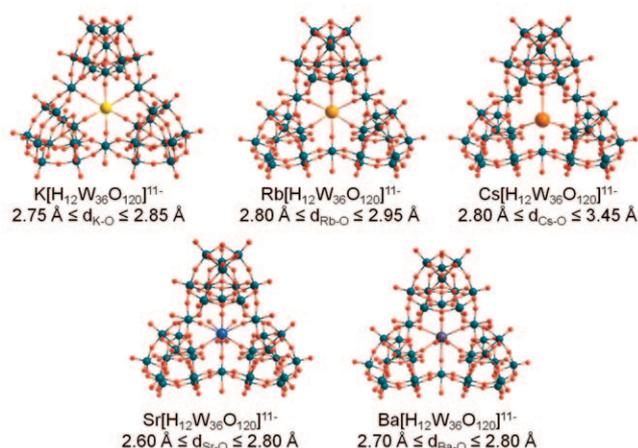
## 2. Polyoxometalate Structures

### 2.1. Architectures Obtained by Templatation

#### 2.1.1. Alkali and Alkaline Earth Metal Templates

Crown ethers are a well-known class of macrocyclic polyethers, widely used in supramolecular chemistry since their introduction in the 1960s by Pedersen.<sup>[5]</sup> One of their main properties is their ability to selectively bind metals from groups 1 and 2 of the periodic table, particularly  $K^+$  and  $Rb^+$ . Since the molecular binding unit is also pre-organized into a macrocycle, the chelate effect acts in favor of the formation of entropically highly stable cation–crown ether complexes. This design idea is also possible for polyoxometalate clusters due to their ability to form highly structured and well-organized metal-oxo frameworks. As such, a number of examples of POMs clusters are known whereby a crown-ether type moiety is embedded into the structure.<sup>[6]</sup> One of the most relevant examples is the anion  $[NaP_5W_{30}O_{110}]^{14-}$ .<sup>[7]</sup> Here, the presence of the central sodium cation is crucial to link the  $\{PW_6\}$  units in a cluster with a  $D_{5h}$  symmetry. Perhaps even more important is that recently we have shown that the use of trace amounts of  $K^+$  cation can be used to isolate or trap a new class of  $\{W_{36}\}$ -based clusters, leading to the isopolyoxotungstate with the highest nuclearity reported so far.<sup>[3b]</sup> This new cluster,  $[H_{12}W_{36}O_{120}]^{12-}$ , is obtained following the reaction of  $Na_2WO_4$  with TEA (triethanolamine) in acidic aqueous solution and after crystallization of the mixture. The overall cluster molecule has a  $C_{3v}$  symmetry with a Celtic-ring shape and a  $K^+$  encapsulated in the central  $\{W_6O_6\}$  ring (see Figure 2).

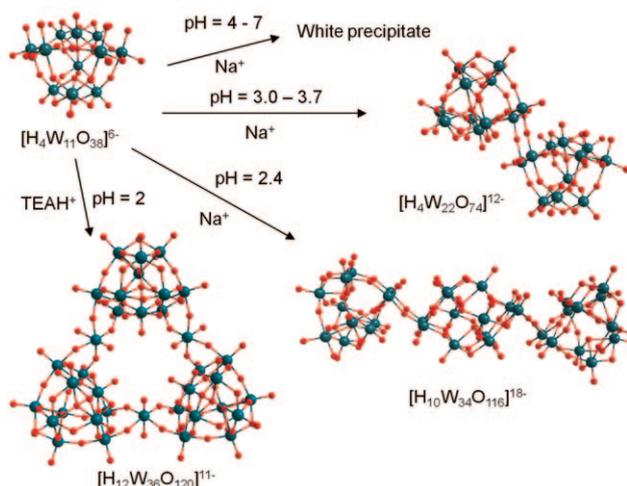
More specifically, the cluster is built from three  $\{W_{11}\}$  units similar to those reported by Lehmann et al.,<sup>[8]</sup> linked in a cyclic fashion with three  $\{W_1\}$  bridges around a  $K^+$  center. This inclusion of potassium is very similar to the inclusion of potassium in the motifs  $\{Mo_6O_6\}$  present in the spherical  $K_{20}\{Mo_{80}V_{22}\}$  cluster reported by Muller et al.<sup>[9]</sup> When larger quantities of potassium salt are added to the solution, a linear 1D chain is obtained,  $\{[K(TEAH)_4][K(H_2W_{12}O_{40})]\}_\infty$ , where  $K^+$  links the  $\{W_{12}\}$  units to each other. In extending these studies we wanted to see if it was possible to produce clusters with a range of cations and we have shown that, by preventing unwanted metal ion contamination (e.g. trace potassium) and by using very specific reaction conditions (e.g. pH, ionic strength, concentration of tungsten and TEA), it is possible to place other metals such as  $Rb^+$ ,  $Cs^+$ ,  $Sr^{2+}$ , and  $Ba^{2+}$  inside the  $\{W_{36}\}$  cavity.<sup>[10]</sup> As expected, the distance



**Figure 2.** Celtic-ring shaped  $\{W_{36}\}$  cluster complexing different cations. Green spheres: W; red spheres: O; yellow sphere: K; dark yellow sphere: Rb; orange sphere: Cs; blue sphere: Sr; dark blue sphere: Ba.  $Sr^{2+}$  and  $Ba^{2+}$  are disordered in the crystal structure.

between the cation and the oxygen atoms of the crown-ether-like ring within the POM  $d_{M-O}$  increase when going from  $K^+\{W_{36}\}$  to  $Cs^+\{W_{36}\}$ , with  $Cs^+$  positioned outside the cavity.  $Sr^{2+}$  and  $Ba^{2+}$ , however, fit well in the ring but are disordered in the crystal structure. Furthermore it should be stated that, besides the effect of the cationic template, the presence of the TEAH cation is necessary to form the Celtic-rings, and the fact that the omission of the TEAH results in the formation of a  $\delta$ -shaped cluster  $\{W_{34}\}$  (see Figure 3), nicely shows the real effect of the cation control (shrink-wrapping approach).

Notably, different structures appear depending on the pH. At pH 4–7, a white precipitate is formed.<sup>[11]</sup> When this is acidified between 3.0–3.7, the precipitate dissolves, followed by the slow growth of hexagonal crystals, corre-



**Figure 3.** Formation of the S-shaped  $\{W_{22}\}$ , the  $\delta$ -shaped clusters  $\{W_{34}\}$ , and the celtic-ring like cluster  $\{W_{36}\}$ , in function of the pH and the cation present. Green spheres: W; red spheres: O.

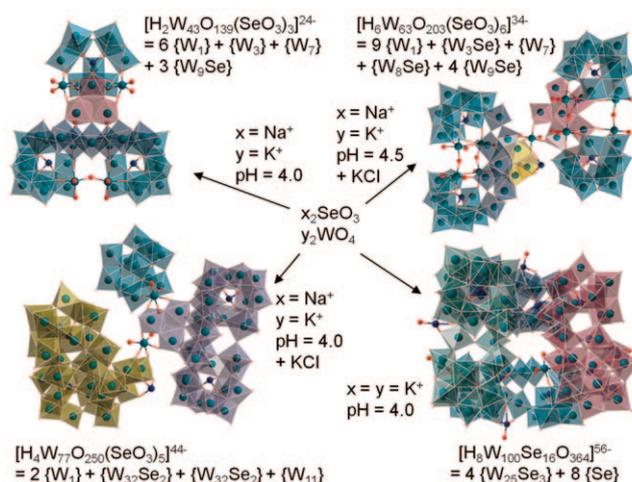
sponding to the S-shaped cluster  $\{W_{22}\}$  shown in Figure 3. The best yield for this structure has been obtained at pH 3.4. When the pH is lowered to 2.4, the §-shaped cluster is formed. This example illustrates the importance of the pH, and the possibility of linking building blocks through M–O–M bridges.

It has to be emphasized that the synthesis or discovery of new isopolyoxometalates is not that common, and these  $\{W_{36}\}$  isopolyoxotungstate clusters have the highest nuclearity to date. Similarly, we reported very recently the largest polyoxoniobate clusters containing a complexed potassium ion in  $\{Nb_6O_6\}$  crown-ether-like cycles.<sup>[12]</sup>  $K_{13}Na_3[HnNb_{27}O_{76}]$  and  $K_{19}Na_4[H_{10}Nb_{31}O_{93}(CO_3)]^{23-}$  have been obtained after crystallization of a mixture of  $K_7HnNb_6O_{19} \cdot 13H_2O$  and sodium dibenzylthiocarbamate. The cluster  $\{Nb_{27}\}$  is of  $C_{3v}$  symmetry incorporating three unusual  $\{(Nb)Nb_5\}$  units. The central Nb is coordinated to 7 oxo ligands. The cluster  $\{Nb_{31}\}$  is built from one  $\{Nb(CO_3)(Nb_5)_2\}$  unit, and two  $\{Nb(Nb)_5\}$  units that share one Nb center that coordinates to  $CO_3^{2-}$ . This Nb is involved in the structure of the crown-ether-like metallacycle  $\{Nb_6O_6\}$ . The unusual presence of pentagonal building blocks opens the way to the development of larger and more spherical clusters.

### 2.1.2. Anionic Templates

The Keggin clusters have the general formula  $[XM_{12}O_{40}]^{n-}$ , where X is generally a tetrahedral template anion. If the template is replaced by an anion with a different geometry, the structure of the final cluster is changed. For example, if the template is the  $SeO_3^{2-}$  anion, which is trigonal and accepts only three bonds with oxygen (with a presumably stereochemically directing lone pair based on the Se center), the cluster obtained is only half-formed and open, leading to very interesting building blocks that are able to be linked into gigantic structures.<sup>[13]</sup> In these cases, by carefully choosing the molar ratio of W:Se, the pH of the solution, and the counter ions of the salts, we have been able to synthesize the clusters  $[H_2W_{43}O_{139}(SeO_3)_3]^{24-}$ ,  $[H_6W_{63}O_{203}(SeO_3)_6]^{34-}$ ,  $[H_4W_{77}O_{250}(SeO_3)_5]^{44-}$  and  $[H_8W_{100}Se_{16}O_{364}]^{56-}$  (see Figure 4).

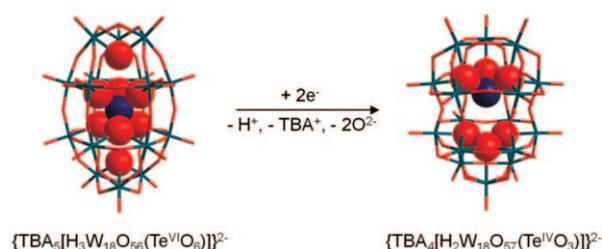
These clusters can be seen as an assembly of “sub-clusters”, connected either via  $\{WO_6\}$  or  $SeO_3^{2-}$  linkers. Their structural analysis, in combination with the experimental conditions, leads to a set of rules allowing a certain degree of predictability on the way the subunits self-assemble. Further, the potassium cation ligates at the surface of the cluster; therefore, its presence is very important for the formation of the POM. By increasing the concentration of  $SeO_3^{2-}$ , non-centrosymmetric subunits are formed, giving clusters of lower symmetry. In addition to this template effect, this anion acts as linker. Also, the addition of acid buffer avoids the formation of the subunit  $\{W_{11}\}$ , so that the chosen type of acid and pH is crucial. A



**Figure 4.** The different crystal structures obtained using  $SeO_3^{2-}$  as a template. In case of  $\{W_{43}\}$ ,  $\{W_{63}\}$ , and  $\{W_{77}\}$ , the different types of subunits are highlighted using different colors. In case of  $\{W_{100}\}$ , each of the four  $\{W_{25}\}$  subunits has a different color. Green spheres: W; blue spheres: Se; red spheres: O.

direct application of these rules, increasing the Se:W ratio to 3:2 in the presence of acetic acid, led to the cluster  $\{W_{100}\}$ , the biggest heteropolyoxotungstate reported so far.

The incorporation of tellurium in polyoxometalate clusters is known, however the number of published works relating to this remains relatively modest.<sup>[14]</sup> We have recently reported the first examples of Dawson-like clusters templated by tellurite and tellurate.<sup>[15]</sup> The tellurate in the Dawson-like cluster  $\gamma^*-[H_3W_{18}O_{56}(Te^{VI}O_6)]^{7-}$  can be selectively reduced to produce the structurally modified tellurite cluster  $[H_3W_{18}Te^{IV}O_{60}]^{5-}$  where the geometry of the Te cation was changed from octahedral to pyramidal, with the breaking of 6 W–O bonds. The reduction was followed by mass spectrometry, which revealed that the cage was not decomposed, see Figure 5. During the reduction, the Te ions moves from the center of the cluster towards the other end, resulting in a lowering of symmetry and a polarization of the cluster, which is potentially interesting for the design of polar material.

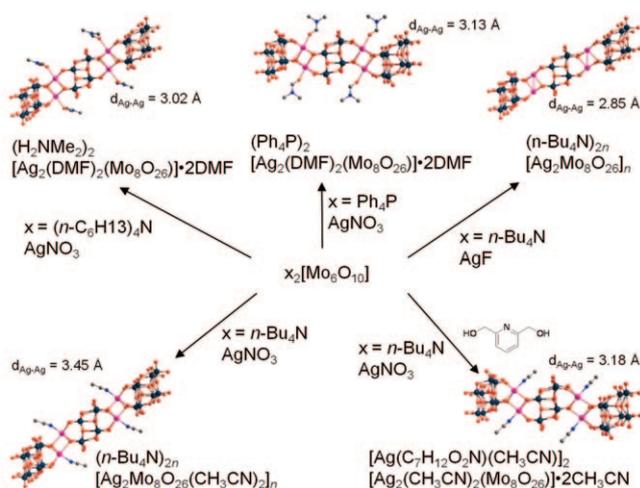


**Figure 5.** LEFT:  $Te^{VI}$  centered cluster. RIGHT:  $Te^{IV}$  cluster. This reaction was followed in situ using electrospray mass spectrometry. Green lines: W; red lines: O; red spheres: O; blue spheres: Te.

## 2.2. Architectures Obtained Using Linkers

### 2.2.1. Metal Complex Linkers

In 1998, Gouzerh et al. described the first Ag–Mo-based POM, where two  $\{\text{Mo}_5\text{O}_{13}\}$  building blocks are linked via dimeric  $\{\text{Ag}_2\}$  units with short Ag–Ag connections.<sup>[16]</sup> Since then, the versatility and geometrical features of silver have been widely used to connect POMs, building complex 3D framework materials, 2D networks, 1D chains, and monomeric units.<sup>[17]</sup> For instance we have recently reported the transformation of the Lindqvist cluster into the  $\beta$ -octamolybdate anion ( $\beta$ - $[\text{Mo}_8\text{O}_{26}]^{4-}$ ), which can bind different transition metals such as silver. Two different types of coordination sites are available: two tetradentate  $\{\text{O}_4\}$  sites which are preferred due to the weaker nucleophilicity of the oxygens and allow polymeric chains and 2D structures to be grown, and two  $\mu_2$ -oxygens sites, that allow the formation of 2D and 3D structures when involved in a coordination process; see Figure 6. Based on our recent work and CSI-MS results,



**Figure 6.** 1D chains based on the motif  $\text{Ag}\{\text{Mo}_8\}\text{Ag}$ , depending on the counterion of the Lindqvist cluster and the silver ion used. Dark blue spheres: Mo; light blue spheres: N; pink spheres: Ag; red spheres: O; grey spheres: C.

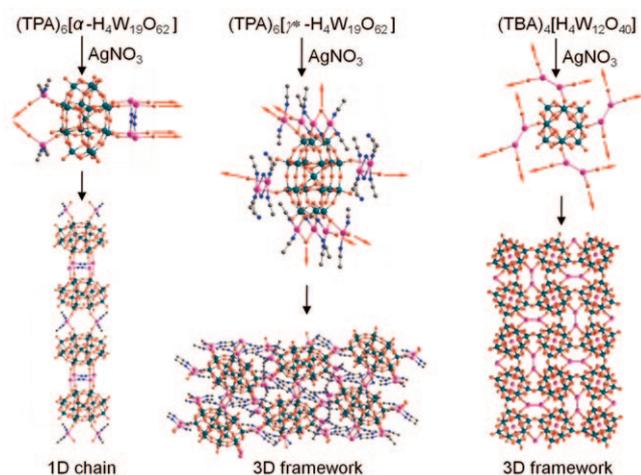
we noticed that it is very unlikely that the  $\{\text{Ag}_2\}$  and  $\{\text{Mo}_8\}$  units can act as separate building blocks, but that the structures' growths result from the association of ( $\text{Ag}\{\text{Mo}_8\}\text{Ag}$ ) building blocks in solution.<sup>[18]</sup>

This unit is very versatile, and we have developed the chemistry discovering a wide variety of structures which strongly depend on the reaction conditions, such as the solvent. This is shown by the fact we obtained different monomeric units  $(\text{Ph}_4\text{P})_2[\text{Ag}_2(\text{DMSO})_4\text{Mo}_8\text{O}_{26}]$ ,  $(\text{Ph}_4\text{P})_2[\text{Ag}_2(\text{CH}_3\text{CN})_2\text{Mo}_8\text{O}_{26}]$ , chains  $(\text{nBu}_4\text{N})_{2n}[\text{Ag}_2\text{Mo}_8\text{O}_{26}]_n$ ,  $(\text{nBu}_4\text{N})_{2n}[\text{Ag}_2\text{Mo}_8\text{O}_{26}(\text{CH}_3\text{CN})_2]_n$ ,  $[\text{Ag}(\text{C}_7\text{H}_{12}\text{O}_2\text{N})(\text{CH}_3\text{CN})]_2[\text{Ag}_2(\text{CH}_3\text{CN})_2(\text{Mo}_8\text{O}_{26})] \cdot 2\text{CH}_3\text{CN}$ ,  $(\text{Ph}_4\text{P})_2[\text{Ag}_2(\text{DMF})_2(\text{Mo}_8\text{O}_{26})] \cdot 2\text{DMF}$  and  $(\text{H}_2\text{NMe}_2)_2[\text{Ag}_2$

$(\text{DMF})_2(\text{Mo}_8\text{O}_{26})] \cdot 2\text{DMF}$ , grids,  $([\text{Ag}(\text{DMF})]_2[\text{Ag}(\text{DMF})_2]_2\text{Mo}_8\text{O}_{26}]_n$  and  $(\text{nBu}_4\text{N})_{2n}[\text{Ag}_2\text{Mo}_8\text{O}_{26}(\text{DMSO})_2]_n$ , and 2D networks  $(\text{HDMF})_n[\text{Ag}_3(\text{Mo}_8\text{O}_{26})(\text{DMF})_4]_n$  via simple manipulation of the reaction conditions.<sup>[18]</sup> The striking structures of the chains that can be obtained is highlighted in Figure 6. The shape of the octamolybdate sub-component cluster being structurally conserved, only the coordination of the silver is changed. The most common case is where the unit is comprised of a heptacoordinated cluster (6 Ag–O bonds and 1 ligand–silver interaction, the Ag–O distance being from 2.2 to 2.9 Å). The only exceptions are in the case without any solvent coordinated to the silver (1 Ag–Ag interaction and 5 O–Ag), and in the case of  $(\text{nBu}_4\text{N})_{2n}[\text{Ag}_2\text{Mo}_8\text{O}_{26}(\text{CH}_3\text{CN})_2]_n$  (1 Ag–L and 5 Ag–O interactions, the 6th Ag–O distance being 3.7 Å). Only the chain without any solvents coordinated to the Ag exhibits an Ag–Ag interaction ( $d = 2.85$  Å).

Initially the fact that silver cations could be coordinated to the oxo-ligands of polyoxometalates so easily seemed surprising, but we were able to show generally speaking that if the system is devoid of good electron donors (e.g., coordinating solvent) then the direct coordination of silver cations to POM frameworks can be encouraged and even controlled. For instance it is possible to directly coordinate silver cations to tungsten-based POMs and we have recently reported the synthesis of Dawson-like POMs  $[\text{H}_4\text{W}_{19}\text{O}_{62}]^{6-}$  using the organic template TEAH.<sup>[3a]</sup> Two different isomers have been isolated by precipitation with *n*-tetrapropylammonium (TPA),<sup>[19]</sup> and these isomers appear to be controlled or directed by the nature of the atom located inside the cavity. Unlike traditional Dawson-like clusters, as highlighted in Figure 1, these  $\{\text{W}_{19}\}$  clusters are templated by a central W unit. In the isomer  $\{\alpha\text{-W}_{19}\}$ , it is coordinated by six oxo ligands in a trigonal prismatic mode, while in the isomer  $\{\gamma^*\text{-W}_{19}\}$  it is in an octahedral environment (see in Figure 7, left and middle). These isomers can be classified to be fully in the class of isopolyanions, together with the most common Keggin-type isopolyoxotungstate or metatungstate  $[\text{H}_4\text{W}_{12}\text{O}_{40}]^{4-}$ ,<sup>[20]</sup> where the cavity is occupied by the protons. These three clusters react in similar conditions in acetonitrile with  $\text{AgNO}_3$  to form frameworks with different dimensionalities (Figure 7).

The isomer  $\{\alpha\text{-W}_{19}\}$  (linked to 6 silver(I)) led to the formation of a mono-dimensional chain, where the silver connectors exist with two different geometries: tetrahedral and linear. In contrast to the  $\{\gamma^*\text{-W}_{19}\}$  cluster (linked to 12 silver(I)), the trimeric caps are not coordinated to silver(I), and the chain is formed exclusively via silver bridges between the terminal oxygen on the central belt of the cluster. The second isomer is brought in a 3D framework via different silver coordination modes. Its central belt is linked to two dimeric  $\{\text{Ag}_2\}$  units, in which the  $\text{Ag}^{\text{I}}$  are 5-fold coordinated in a distorted trigonal bipyramidal geometry. Subsequently, four  $\{\text{Ag}_2\}$  dimers



**Figure 7.** W-based POMs linked by silver cations. The counterions are not shown and the molecules of solvent coordinated to the silver on the structure at right are hidden for clarity reasons. Green spheres: W; light blue spheres: N; pink spheres: Ag; red spheres: O; grey spheres: C.

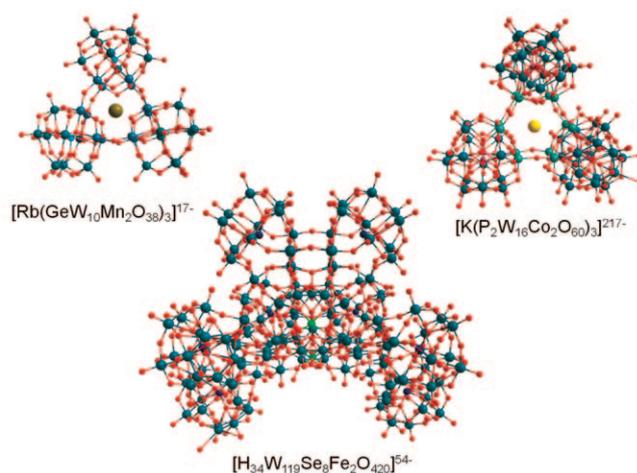
(with  $d_{\text{Ag-Ag}} = 3.41 \text{ \AA}$ ) connect the trimeric cap to the belt of further clusters. The Keggin-type POM  $\{W_{12}\}$ , directly linked to 8 silver(I) from dimeric units  $\{Ag_2\}$ , self-assemble in a porous 3D framework, the first in a series of polyoxometalate open frameworks (POM-OFs). In this structure,  $d_{\text{Ag-Ag}} = 2.91 \text{ \AA}$ , and each dimeric  $\{Ag_2\}$  unit cross-links four  $\{W_{12}\}$  clusters. It is believed that the absence of coordinating ligands such as DMSO or 4,4'-bipyridine favors the formation of Ag–Ag interactions and the latter structure is very interesting since the entire framework is “supported” by Ag–Ag interactions.

### 2.2.2. Combining Different Linkers and Templates

During the past decade we have reported a series of structures using different linkers or templates, as described above. Thanks to these studies, combined with the recent advances in mass spectrometry analysis of the POMs-based intermediates,<sup>[21]</sup> a deeper understanding in the formation of these architectures has been gained, and it is possible to predict their topology to a limited extent but it is likely that this will improve dramatically in years to come.

The cluster  $[Rb(GeW_{10}Mn_2O_{38})_3]^{17-}$  (see Figure 8) has been obtained by reacting the divalent lacunary decatungstogermanate  $[\gamma\text{-}GeW_{10}O_{36}]^{8-}$  with  $Mn(OAc)_2$  and  $KMnO_4$  in acidic aqueous solution.<sup>[22]</sup> This POM consists of three Keggin clusters linked together by M–O–M bridges. The structure is discrete and not polymeric, thanks to the Ge template, complexed by two heterometallic crown-ether-like nanorings  $\{Mn\text{-O}\text{-}W\}$ .

Similarly, the cluster  $[K(P_2W_{16}Co_2O_{60})_3]^{21-}$  is synthesized from the reaction of the POM  $[\alpha\text{-}P_2W_{18}O_{62}]^{6-}$  with  $CoCl_2$ . The initial Wells–Dawson cluster is substituted twice by



**Figure 8.** Illustration of the structural complexity that can be reached using different types of linkers. Green spheres: W; red sphere: O; olive sphere: Rb; light blue sphere: Ge; yellow sphere: K; blue spheres: Se; purple spheres: P; light green spheres: Fe.

$Co^{III}$  cation. Three of them are linked together via M–O–M bridges around a  $K^+$  template. The potassium is encapsulated within two  $\{Co\text{-O}\text{-}W\}$  anionic nanorings, forming the cyclic triangular cluster. These POMs are good candidates to be used as building blocks for the design and synthesis of larger structures. However, to try and produce building blocks that can be linked more effectively to even larger structures, it is important to see if the templating units can be used to form intrinsically more “divergent” building blocks. We were inspired to do this after our success using selenium-based heteroanions  $SeO_3^{2-}$  as a template leading to open structures that can be linked together.<sup>[23]</sup> In an extension to this work we were able to employ heteroanionic units not only as templates, but also as linkers, which has allowed the synthesis of the largest POM observed both in solution and the solid state,  $[H_{34}W_{119}Se_8Fe_2O_{420}]^{54-}$  (Figure 8, bottom). This gigantic molecule is obtained by the combination of Se and Fe templates and linkers and this saddle-shaped cluster is characterized by its massive dimensions:  $2.3 \times 2.8 \times 1.9 \text{ nm}$ , with a molecular mass of 30 kDa. While the Se units form the arms, the Fe core links the units and are found in pentagonal sub-units  $\{W(W_4Fe)\}$ , which direct the assembly.

## 3. POM Properties and Applications

The design of all-inorganic framework architectures with well-defined physical properties is one big dream in polyoxometalate chemistry. This is because the cluster building blocks in the POM family already show a great deal of potential in terms of catalysis, electronic properties, and so on. Therefore the controlled assembly of all-inorganic POM architectures could allow access to a field of

materials with the potential for design (c.f. MOFs) but with the stability and functionality of zeolites.

### 3.1. Magnetic Frameworks

Anion lacunary POMs can be viewed not only as clusters, but as multidentate ligands for the formation of polynuclear metal complexes with other transition metals. Such cluster-cores, terminated or “protected” with POM building blocks, is appealing since novel cores could potentially be stabilized and new properties, for example, electronic and magnetic, could be accessed. Unsurprisingly, several POM-based single molecular magnet (SMM) clusters have been published just recently.<sup>[24]</sup> One of these examples comprises a Mn<sup>II/III</sup> cluster embedded within POM ligand capping groups,<sup>[25]</sup> whereby the SMM cluster is a mixed valence {Mn<sub>6</sub>} encapsulating two lacunary POMs [XW<sub>9</sub>O<sub>34</sub>]<sup>10-</sup>. Two analogous cluster POM-compounds were obtained, Na<sub>4</sub>K(C<sub>4</sub>H<sub>10</sub>NO)<sub>7</sub>-{[GeW<sub>9</sub>O<sub>34</sub>]<sub>2</sub>[Mn<sup>III</sup><sub>4</sub>Mn<sup>II</sup><sub>2</sub>O<sub>4</sub>(H<sub>2</sub>O)<sub>4</sub>]}·15H<sub>2</sub>O and (C<sub>4</sub>H<sub>10</sub>NO)<sub>12</sub>{[SiW<sub>9</sub>O<sub>34</sub>]<sub>2</sub>[Mn<sup>III</sup><sub>4</sub>Mn<sup>II</sup><sub>2</sub>O<sub>4</sub>(H<sub>2</sub>O)<sub>4</sub>]}·15H<sub>2</sub>O, which are both isostructural, but with different templating heteroanions. Magnetic χ<sub>m</sub>T measurements revealed that in both complexes, ferro- and antiferromagnetic exchange interactions within the {Mn<sub>6</sub>} core were present. Furthermore, it should be possible to tune these magnetic properties by reducing the {XW<sub>9</sub>} hetero-anion lacunary cluster “caps”.

### 3.2. Redox Switchable Frameworks

As described earlier, POMs can be connected with many different linkers to form a 3D framework. However, pure POM 3D frameworks are unusual. We have recently reported the synthesis of the first pure Keggin network  $[\{W_{72}M_{12}O_{268}X_7\}_n]^{y-}$ , where M = Mn<sup>III</sup>, X = Si.<sup>[26]</sup> The repeat unit consists of two types of building blocks; three connected and four connected Keggin clusters linked via Mn–O–W bridges (see Figure 9). One interesting aspect of this structure is that the Mn<sup>III</sup> can chemically be reduced in the solid state through single crystal to single crystal (SC–SC) transformation within 60 min. It is possible to follow the entire-crystal oxidation–reduction crystallographically and the crystal structure remains nearly intact, with only the distance d<sub>M–W</sub> between two clusters changing, resulting in the expansion of the unit cell by 5.48% in volume (for the reduction process), and therefore a switch-over of the electronic properties. The reverse reaction is also possible, both in solution (followed by subsequent recrystallization) and in the solid state. The change of oxidation state of the metal within the crystal can be monitored through the change of color of the crystals and further work has allowed the generalization of this new type of responsive materials.<sup>[27]</sup>

Not only have the crystal structures of the 3D Keggin framework with Si- or Ge-based heteroatoms and Mn-

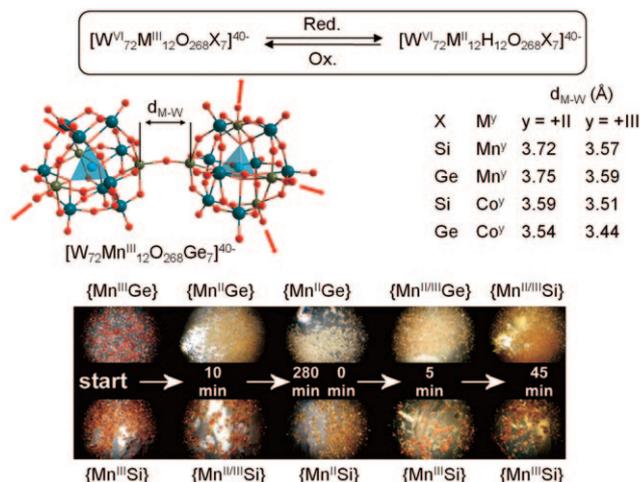


Figure 9. Redox-switchable Keggin networks.

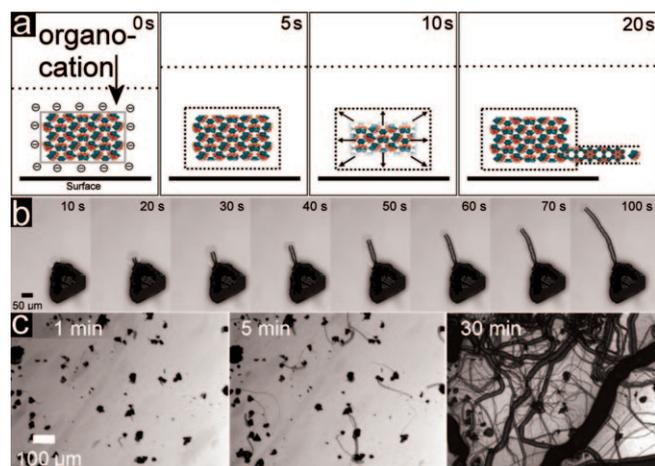
linkers been achieved, but it is also possible to change the Mn ions for Co and also show switching between the Co +II and +III oxidation states. In general, d<sub>M–W</sub> is smaller when M has the oxidation degree +III, and when M = Co. Surprisingly, the change of heteroatom has only a very small effect on d<sub>M–W</sub> when M = Mn +II and +III. However, the biggest change due to the heteroatom is reported between {Co<sup>III</sup>Ge} (see Figure 9) (with d<sub>M–W</sub> = 3.44 Å) and {Co<sup>III</sup>Si} (d<sub>M–W</sub> = 3.51 Å). The biggest difference in cell volume is noticed between {Mn<sup>II</sup>Ge} (V = 60652 Å<sup>3</sup>) and {Co<sup>III</sup>Ge} (V = 54955 Å<sup>3</sup>). Another consequence of the change of oxidation state is the change of color of the crystals. It can indeed be visually noticed that the reduction of {Mn<sup>III</sup>Ge} to {Mn<sup>II</sup>Ge} is faster than the oxidation reaction, as opposed to the reduction of {Mn<sup>III</sup>Si} to {Mn<sup>II</sup>Si}, which is slower than the corresponding oxidation reaction. This has been confirmed by the measured rate constants and shows nicely how the crystal-based oxidation and reduction reactions can have the kinetics tuned in either direction as a function of the embedded heteroanion.

As the change of heterometal or/and heteroatom affects the physical properties of the framework, the assembly of mixtures of the isostructural frameworks or “redox-analogs” was done leading to a series of mixed Co/Mn POMs network and to the first example of POMs alloys, and opened the way to new materials with emergent properties.

### 3.3. POM-Based Cation Exchange Reactions: Membranes and Microtubes

In this review we have explored how cation control can be used to manipulate the assembly of POM-based materials in a hierarchical sense. This means that the cations not only control the molecular assembly, but also the connectivity of the cluster nodes into a larger network struc-

ture. In addition, it is even possible to use cation-exchange reactions after the material has been formed into a crystalline array. For example, when crystals of POM-based material are submerged in water on a glass slide and then a bulky organic cation is added (in the first case, we added a cation called dihydroimidazolphenanthridinium, but  $[\text{Ru}(\text{bipy})_3\text{Cl}_2]$  is equally suitable, for instance) the crystal is transformed into an amorphous architecture comprising tubular growths, see Figure 10, and this process can easily be visualized under an optical microscope.



**Figure 10.** Scheme showing the transformation of crystals of POMs by cation exchange to tubular materials. (A) Cartoon showing how an organo-cation added to a crystal in water causes the formation of a tube. (B) Close-up of a single crystal over 100 s after addition of the cation. (C) A view of many crystals and their transformation over 30 min.

This process occurs via cation exchange; this dissolves the outer layer of the crystal, instantaneously forming a semi-permeable membrane around the crystal, due to cation-exchange reactions, that eventually ruptures under osmotic pressure. After this rupture event, tubes are observed to grow for many thousands of microns, the diameter can be controlled (between 10 and 100 microns, typically), and the growth rate controlled by the concentration of the added cation.<sup>[28]</sup>

Although we initially reported this tube formation using the Keggin networks with  $M = \text{Mn}$  and  $X = \text{Si}$ ,  $\text{Ge}$ , a wide range of POMs can be used, with the only limitations being the POM crystal having a low solubility in water and quite large organo-cations. The width of the microtubes is controlled by the added cation concentration, as noted above. A lower concentration of the added cation increases the diameter of the emerging tubes, but slows down the rate of growth. Additionally, the charge density/cation size also changes the size of the tube. The growth direction can also be controlled, by manually breaking the tubes, or by applying an electric field or a source of heat, changing the convection of the solution.

The key point is that the cation exchange modification is a type of post-synthetic modification and material reprocessing of the POM. This means that microtubes with applications in catalysis, sensing, or as configurable microfluidic arrays may be imagined.

#### 4. Summary and Outlook

In this review we focused on the inorganic linkers and templates that can be used to assemble POMs together, into 1D, 2D, and 3D solid state frameworks, with an emphasis on explaining molecular assembly using cation and linker/template control. The POMs themselves are very versatile and even organic-inorganic hybrids can be designed that can allow the development of new types of surfactants<sup>[29]</sup> or even hybrid surfaces that are recognized by living cells.<sup>[30]</sup> Since the hybrids based upon POMs can subsequently self-assemble to even larger length scale such as 10–100 nm, and also to microscale with the formation of tubes, it is evident that POM-based materials are able to link the nano- with the macro-world. This range of scales is impressive and it is likely that POMs will find applications in areas as diverse as imaging, catalysis, biology, molecular electronics, and energy devices. For example, it has recently been shown that a ruthenium-POM complex can catalyze the oxidation of water to oxygen,<sup>[31]</sup> and this is important for the development of new catalysts for energy solutions and also for understanding how biology efficiently harnesses the process of charge separation in photosynthesis. However the characterization of these molecules remains difficult and the development of new analytical tools for these new POM-based materials is one of the greatest challenges and necessities of this field.

Although tremendous progress has been made in the past decade to understand the self-assembly process of POMs, huge effort is still required in order to fully predict resultant structures. Several tools are becoming more and more essential in that regard, such as high-resolution electrospray mass spectrometry.<sup>[21]</sup> This technique is important since it allows the building blocks present in solution to be investigated directly. In the chemistry of polyoxometalates this is particularly interesting, since W and Mo have many isotopes which allow detailed analysis and fragmentation studies. Also, the use of low temperature “cryospray” techniques allows the investigation of weak, reversible, electrostatic interactions present in supramolecular systems. Traditionally, the discoveries of new POM-based clusters has been limited to those that can be crystallized, and this presents a fundamental limit to the discovery–design process, but we have shown that this does not have to be the case with the example of following the in-situ reduction of the heteroatom of a Dawson-like cluster,  $\text{Te}^{\text{VI}}$  in  $\text{Te}^{\text{IV}}$ .<sup>[15]</sup>

As described at the start of this article, one of the main difficulties in POM chemistry, apart from characteriza-

tion, is the controlled assembly of new structures by precise reaction control. So what have we learned until now, and are there any specific rules? In our work we have 4 key rules that we employ in the assembly of new POM frameworks: (i) screen the initial reaction conditions with different buffers to control the pH and ensure the buffers chosen give bulky organo-cations when protonated; (ii) use heteroanion templates that have stereochemically active lone-pairs to prevent closure of the architecture; (iii) screen the reaction solutions using high resolution electrospray mass spectrometry to characterize the building blocks present; (iv) control the pH, reduction potential, and ionic strength, allowing for oscillations in these parameters.

Finally, the manipulation of these conditions systematically represents a great step forward, but also the use of more highly controlled synthetic reactor systems, such as flow systems capable of performing several reactions in parallel where the reaction conditions can be precisely set and monitored, is a very important development. For instance, we have recently used such a flow system to precisely control the redox environment, thereby allowing the isolation of a cluster complete with its template.<sup>[32]</sup> Finally, it seems now that the simultaneous development of new analytical systems and new POM-based materials will provide an unprecedented insight into the process of molecular self-assembly. This is very exciting since the design of building blocks, large cluster molecules, linked-cluster materials, and functional materials with emergent properties will surely offer many surprises and bring us one step closer to taming the room at the bottom between 1 and 10 nm for real applications.

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