

Nanoscale Polyoxometalate-Based
Inorganic/Organic HybridsYU-FEI SONG,^{1*} DE-LIANG LONG,² CHRIS RITCHIE,³ LEROY CRONIN^{2*}¹State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, No. 15 Beisanhuan East Road, Beijing 100029, P.R. China

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ABSTRACT: The latest advances in the area of polyoxometalate (POM)-based inorganic/organic hybrid materials prepared by self-assembly, covalent modification, and supramolecular interactions are presented. This Review is composed of five sections and documents the effect of organic cations on the formation of novel POMs, surfactant encapsulated POM-based hybrids, polymeric POM/organic hybrid materials, POMs-containing ionic crystals, and covalently functionalized POMs. In addition to their role in the charge-balancing, of anionic POMs, the crucial role of organic cations in the formation and functionalization of POM-based hybrid materials is discussed.

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1. Introduction

The development of functional molecular assemblies across multiple length scales represents one of the greatest challenges in the study of materials,¹ such as ultra-high capacity information storage materials,² molecular electronics,³ sensors,⁴ and so on. However, the rational design of systems that can be synthesized or self-assembled in a pre-determined manner to form highly complex architectures remains problematical. Hence, it is appealing to examine a unique class of discrete nanoscale metal-oxide clusters known as polyoxometalates (POMs)⁵ as potential modular building blocks for the construction of multifunctional materials.

Polyoxometalates constitute to a diverse range of metal-oxide clusters of early transition metals (V, Nb, Ta, Mo, W, and

so forth) that are typically observed in their highest oxidation states. Mostly prepared using “one-pot” reaction conditions, POMs cover an enormous size range with an unrivalled structural diversity. Owing to the rapid increase in computing power, the productivity of single-crystal X-ray crystallography (a key tool in elucidating POM structure) has advanced greatly. Consequently, the field of polyoxometalate chemistry has experienced a revolution since the 1990s, as exemplified by the synthesis and structural characterization of ultra-large species with metal nuclearities as high as 368 in a single molecule.^{6,7} Apart from structural characterization, a wide range of physical properties of POM-based materials have been investigated such as catalytic activity, photochemical activity, ionic conductivity,

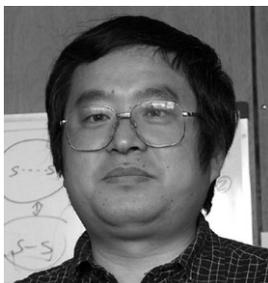
reversible redox behavior, bistability, and cooperative electronic phenomena.^{8–12,13}

Inorganic/organic hybrids represent the interface between two worlds of chemistry with significant contributions to and from the field of material science. Such hybrid materials may provide additional and/or enhanced functions and properties as a result of synergistic interactions between the inorganic and

organic components. Indeed, many recent efforts have centered on functional inorganic/organic hybrid materials that can combine the chemical activity of their components. One of the simplest classifications of inorganic/organic hybrids is according to the chemical interactions between the inorganic and organic components.¹⁴ *Type I* inorganic/organic hybrids refer to the situation where weak interactions (e.g., non-covalent



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interactions such as electrostatic, hydrogen bonding, and so on) are the dominant interactions between two components; whereas the hybrids are categorized as *Type II* when stronger interactions (such as covalent bonds) dominate.

POM-based inorganic/organic hybrids have drawn enormous attention in the past decades as exciting applications of these materials have been discovered in such diverse areas as light-emitting diodes,¹⁵ field-effect transistors,¹⁶ and solid-state lasers,¹⁷ to name just a few. The recent development of POM-based functional hybrids has focused on the controllability and functionality of the hybrid materials with improved applications-driven performance and/or other useful physical properties. In this paper, we describe the recent progress of POM-based inorganic/organic hybrids, and particularly the studies concerning rationally assembled POM-based multifunctional materials.

2. Effects of Organic Cations on the Formation of Novel POM Hybrids

A few years ago, it was discovered that protonated organic amines with hydroxyl groups could be utilized as cations and pH buffers in the preparation of new POMs. In contrast to the “template” role,¹⁸ used in the formation of certain aluminosilicates and aluminophosphates, organo-amines could be regarded as inverse templates.

In this respect, we reported the isolation of quasi-stable clusters including $[\text{H}_2\text{Mo}_{16}\text{O}_{52}]^{10-}$ by using protonated hexamethylenetetramine (HMTAH^+) in the synthesis of polyoxomolybdates.¹⁹ In contrast to known polyoxomolybdates of similar nuclearity, the characteristics of $[\text{H}_2\text{Mo}_{16}\text{O}_{52}]^{10-}$ include: 1) it has a flat form, with four of the sixteen molybdenum centers being one electron reduced (with respect to their highest

accessible oxidation states) to give the molecular formula of $[\text{H}_2\text{Mo}_4^{\text{V}}\text{Mo}_{12}^{\text{VI}}\text{O}_{52}]^{10-}$; 2) the shape of the cluster resembles that of a bat with its “body” consisting of a central unit with twelve molybdenum centers and the two wings each having two molybdenum centers; 3) this anion is diamagnetic owing to the strong antiferromagnetic exchange coupling within each of the two pairs of Mo^{V} units. By extending the synthetic strategy to a tungsten system with protonated triethanolamine (TEAH^+), a new isopolyoxotungstate of $[\text{H}_{12}\text{W}_{36}\text{O}_{120}]^{12-}$ was isolated with an alkali or alkaline earth metal ion to form metal complexes of the type $\{\text{M}\subset\text{W}_{36}\}$ ($\text{M} = \text{K}^+, \text{Rb}^+, \text{Cs}^+, \text{NH}_4^+, \text{Sr}^{2+}, \text{and Ba}^{2+}$).^{20,21} The resulting clusters are C_{3v} symmetric with a celtic-ring like shape and comprise three $\{\text{W}_{11}\}$ cluster subunits linked together by three $\{\text{W}_1\}$ bridges.

A new family of isopolyoxotungstates, $[\text{H}_4\text{W}_{19}\text{O}_{62}]^{6-}$ was isolated in a similar way to that of the $\{\text{W}_{36}\}$ clusters by utilizing TEAH^+ as cations with a slightly lower solution pH and longer refluxing time.²² Two isomers of α - (Figure 1a) and γ^* - $[\text{H}_4\text{W}_{19}\text{O}_{62}]^{6-}$ (Figure 1b) were obtained and characterized, in which the former (α form) shows D_{3h} symmetry and the latter (γ^* form), D_{3d} symmetry. The α - $[\text{H}_4\text{W}_{19}\text{O}_{62}]^{6-}$ cluster has the $\{\text{W}_{18}\text{O}_{54}\}$ cage and interior oxo ligand positions of the conventional Dawson cluster anion α - $[\text{W}_{18}\text{O}_{54}(\text{XO}_4)_2]^{6-}$ (Figure 1c), with the exception that the two tetrahedral heteroanions are replaced by a triangular-prismatic $\{\text{WO}_6\}$ unit, but this is now positioned in the center of the cluster and two μ_3 -oxo ligands. Above each of the oxo ligands, a tetrahedral “void” is identified in the positions that are typically occupied by the heteroatoms in conventional Dawson cluster anions of α - $[\text{W}_{18}\text{O}_{54}(\text{XO}_4)_2]^{6-}$.

Further extension of the above strategy by utilizing other organic cations in the formation of new POM assemblies has been explored in the Cronin group, with some interesting examples being obtained.²³ Reaction of the divacant lacunary



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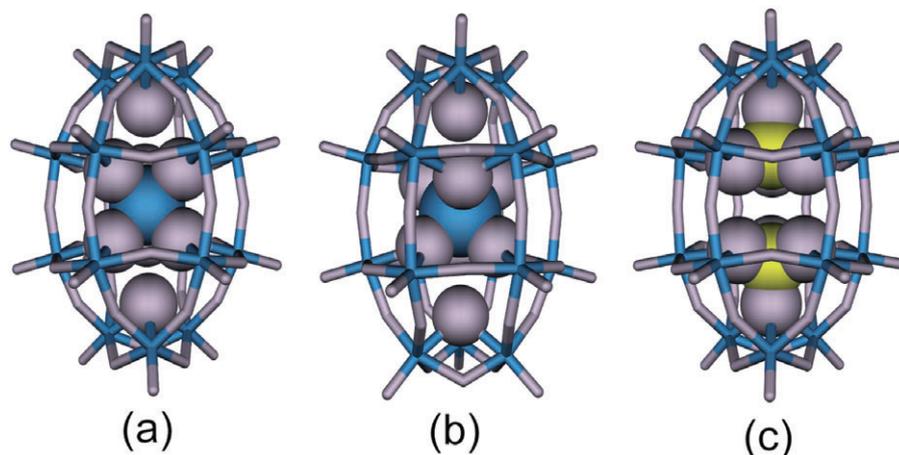


Fig. 1. X-ray single-crystal structure of a) α -[H₄W₁₉O₆₂]⁶⁻, b) γ^* -[H₄W₁₉O₆₂]⁶⁻, and c) the classical {W₁₈} Dawson system.

polyoxometalate [γ -SiW₁₀O₃₆]⁸⁻ with manganese(II) in the presence of morpholinium cations and potassium permanganate yields compounds with a new class of inorganic framework called the KegginNET with the composition $\{[(C_4H_{10}NO)_{40}(W_{72}Mn^{III}_{12}O_{268}Si_7)] \cdot 48H_2O\}_n$ (see Figure 2).^{23a} It has been shown that all the manganese(III) centers can be “switched” to manganese(II) using a suitable reducing agent to give the fully reduced framework, and this redox process occurs with retention of long-range order by cooperative structural changes within the W-O-Mn linkages that connect the Keggin units. The KegginNET can also be repeatedly disassembled into its building blocks by dissolution in hot water with subsequent recrystallization resulting in the reassembly of otherwise unmodified compound. These unique properties indicate that this compound defines a new class of materials that bridges the gap between coordination compounds, metal-organic frameworks, and solid-state oxides.

3. Surfactant Encapsulated POM Clusters

POM assemblies with surfactants as cations have shown great potential in the development of rationally assembled POM-based multifunctional materials. One example is the terbium-substituted heteropolyoxotungstate complex [surfactant]₁₃[Tb(SiW₁₁O₃₉)₂] \cdot 30H₂O (Figure 3).²⁴ This compound was prepared by the ionic self-assembly route and shows characteristic thermotropic liquid-crystalline (LC) behavior. The importance of this work²⁴ lies in the fact that it provides a general and facile method for fabrication of POM-based LC hybrid materials by using mesogroup-containing surfactants to encapsulate POMs.

Self-assembly of the cationic surfactant dimethyl dioctadecylammonium (DODA) with [Eu(H₂O)₂SiW₁₁O₃₉]⁵⁻ results

in the formation of a surfactant encapsulated cluster, (DODA)₄H[Eu(H₂O)₂SiW₁₁O₃₉],²⁵ which aggregates into vesicles in chloroform. These POM-based vesicles have a honeycomb architecture and provide great opportunities for the development of new materials, for example, semiconducting devices, separation membranes, and so forth. The study suggests that the combination of inorganic chemistry and colloidal surface chemistry may allow us to generate micro-sized patterns of inorganic functional units through stepwise self-assembly of preorganized building blocks.

Recently, tuning the meso-phase of ammonium amphiphile-encapsulated polyoxometalate complexes has been achieved by changing the structure of each component. Hydrogen-bonding-induced supramolecular POM-based liquid crystals and luminescent properties of europium-substituted polyoxometalate hybrids have also been investigated.²⁶ By controlling the solvent polarity, a stable assembly of (DODA)₄[SiW₁₂O₄₀] was obtained as onion-like spheres.²⁷ Such an onion-like structure can provide a similar microenvironment to vesicles, which makes these assemblies suitable carriers to perform novel catalytic and pharmacological functions. The above strategy has been extended to other POMs and cationic surfactants. For example, di(11-hydroxyundecyl)dimethylammonium bromide (DOHDA) was utilized as a bridging unit to obtain a stable, POM-based, silica-sol-gel hybrid material.²⁸ By using functional surfactants as encapsulating components, novel surfactant encapsulated clusters (SECs) combining the functionalities of both the POM and the surfactants have been created. It was found that SECs could be assembled into spherical aggregates in organic solvents, a feature which was attributed to the organization of the surfactants on the exterior of the polyoxometalate.

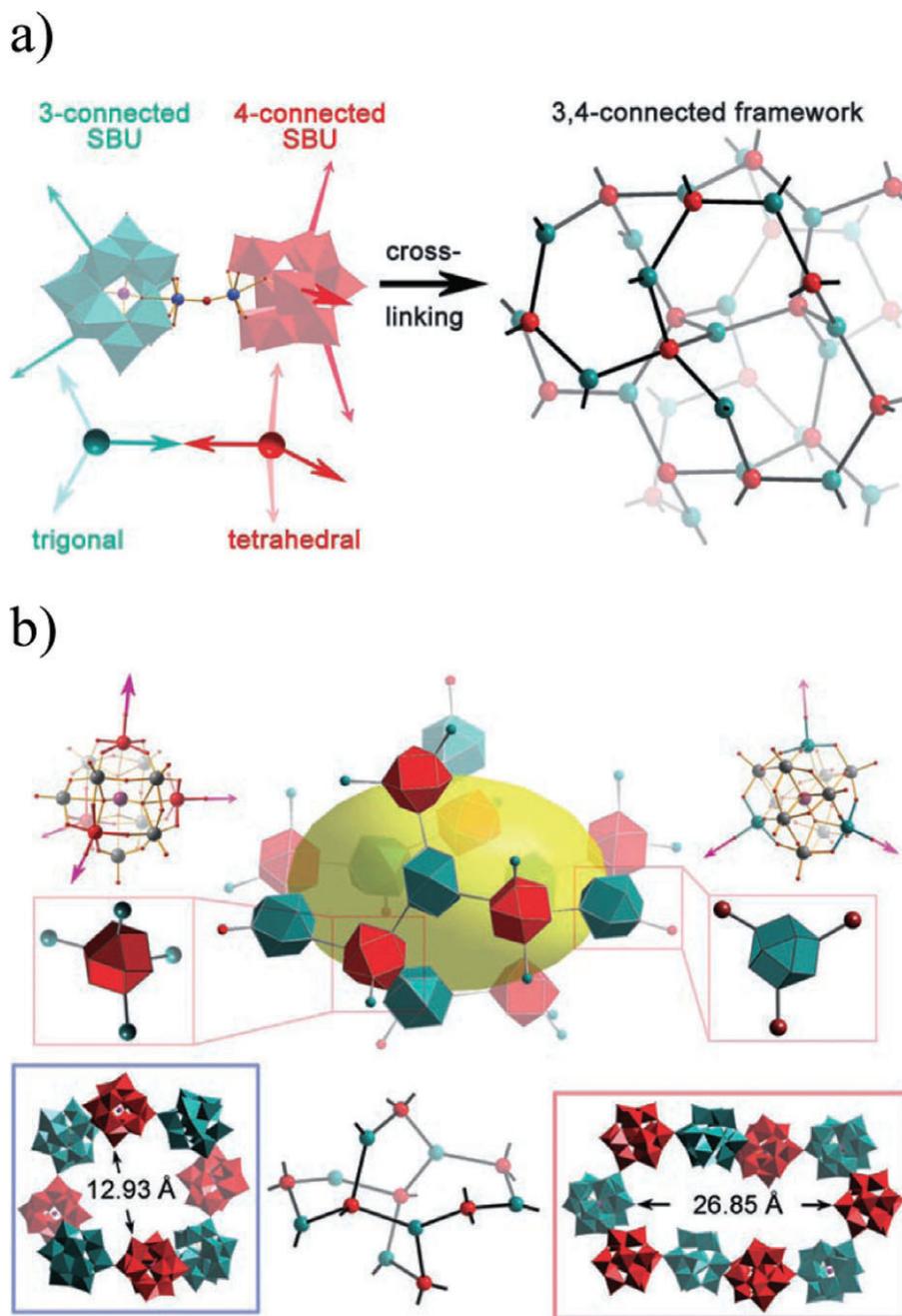


Fig. 2. a) Schematic rationalization of the KegginNET framework.²³ The network is built from two types of lacunary Keggin clusters which act as either 3-connected (green) or 4-connected nodes (red). The polyhedral representation of the clusters more clearly shows how the secondary building units (SBUs) are linked into an infinite 3D framework based upon 3-connected and 4-connected clusters. b) Illustration of the nanosized pockets in the KegginNET (top center) highlighted by the yellow ellipsoid (dimensions: $2.7 \times 2.4 \times 1.3$ nm). The 3- and 4-connected Keggin clusters (green and red, respectively) demonstrate the connectivity of each unit. Purple arrows highlight the connecting modes. A schematic view of the internal pocket is illustrated at the bottom center. The polyhedral representation of the eight-membered ring and of the ten-membered ring illustrates the smallest and largest dimensions of the pocket.

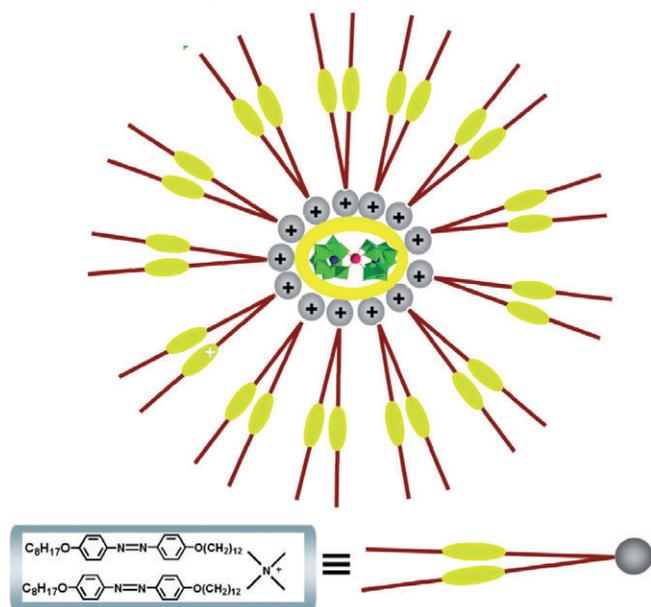


Fig. 3. The schematic and chemical structures of the surfactant encapsulated cluster (SEC-1), in which the POM cluster is $[\text{Tb}(\text{SiW}_{11}\text{O}_{39})_2]^{13-}$ and surfactant is an azobenzene-containing surfactant.

4. POM/Organic Polymer Hybrid Materials

Organic polymers are very easy to process owing to their excellent toughness and durability, making them suitable candidates for application as matrices for controlled assembly of POMs. Typical strategies utilized for the fabrication of POM/polymer hybrids include physical blending, electrostatic interactions, covalent bonding, and supramolecular and in-situ modifications.²⁹ Physical blending is a very convenient way to fabricate POM/polymer hybrids. Normally, a homogeneous solution can be obtained by mixing POMs with polymers in water, and this solution is then used for the preparation of composite films by dip- or spin-coating methods. However, the stability of these hybrid materials is relatively low owing to the lack of interactions between the POMs and the polymer matrix, thus limiting the practical application of the resulting POM-based inorganic/organic hybrids.

Anchoring of POMs onto polymer matrices through electrostatic interactions is an alternative approach giving increased stability. For example, POMs and ammonium-bridged diblock copolymers can be assembled through electrostatic interactions. The resulting amphiphilic hybrids assemble into rod-like grains with hexagonal mesostructures.

POMs can also be assembled with cationic polyelectrolytes using the layer-by-layer (LBL) technique. In this way, Dong and co-workers fabricated ultrathin films composed of POMs and quaternized poly(4-vinylpyridine) using the LBL method, allowing monolayer or multilayer films to be deposited on the

surface of gold electrodes.³⁰ Most importantly this LBL technique enables the tailoring of the material's composition, thickness, and physicochemical properties at the molecular level.

Although the preparation of POM/organic polymer hybrid materials through electrostatic interactions results in relatively stable products, this method is only suitable for polyelectrolyte matrices, whereas in the case of neutral POM/polymer hybrid materials, this approach cannot be used. Alternatively, covalent bonding can be used. Covalent bonding is a very useful way to fabricate POMs in polymer matrices, with the resulting hybrid materials obtained displaying the stability that is required for real world applications. For example, Maatta and co-workers reacted the terminal oxygen of the Lindqvist cluster with various imidazoles.³¹ The unsaturated double bond of the styrylimido-hexamolybdate complex allowed further modification through conventional free radical-induced copolymerization. Similarly, Peng and co-workers reported bifunctionalization of the Lindqvist cluster with two organic groups terminated with $\text{C}=\text{C}$,³² which provides a good opportunity for the polymerization of these molecules. As a result, the POM/organic polymer hybrid could form films easily with excellent photovoltaic behavior.

Interestingly, Wu and his co-workers reported a universal fabrication method for POMs,³³ in which the POMs were encapsulated in a cationic surfactant bearing an unsaturated organic group. As such, polymerizable surfactant encapsulated polyoxometalates (SEPs) could be prepared easily. These supramolecular modifications and in-situ polymerization methods have proven to be a powerful and effective way to modify the surface properties of POMs. As shown in Figure 4, the DMDA-encapsulated POMs (SEC-1) are terminated with polymerizable groups, and these groups can be copolymerized with polymer chains. In addition, the SECs prepared from europium-substituted POMs exhibit intense red emission and are expected to be promising luminescent materials;^{34–36} $\text{Na}_9[\text{EuW}_{10}\text{O}_{36}] \cdot 32\text{H}_2\text{O}$ (POM-1), for example, which possesses the highest luminescent quantum yield among the known luminescent POMs.³⁷ As for the polymer matrix, poly(methyl methacrylate) (PMMA) has been a popular choice on account of its high transparency. The resulting hybrid combines not only the high luminescence of POM-1, but also the transparency and good processing capability of PMMA. This approach is commonly used to build multifunctional POM-based polymer materials for various purposes.

An additional study into the synthesis of imido-derivatized Lindqvist clusters was made by Peng's group, reporting a POM-based polymer onto which terpyridine ligands were covalently grafted. The terpyridine ligands thus installed are useful coordination sites for further extension of the material to form coordination polymers.^{38,39} POMs can also be linked through direct condensation or through

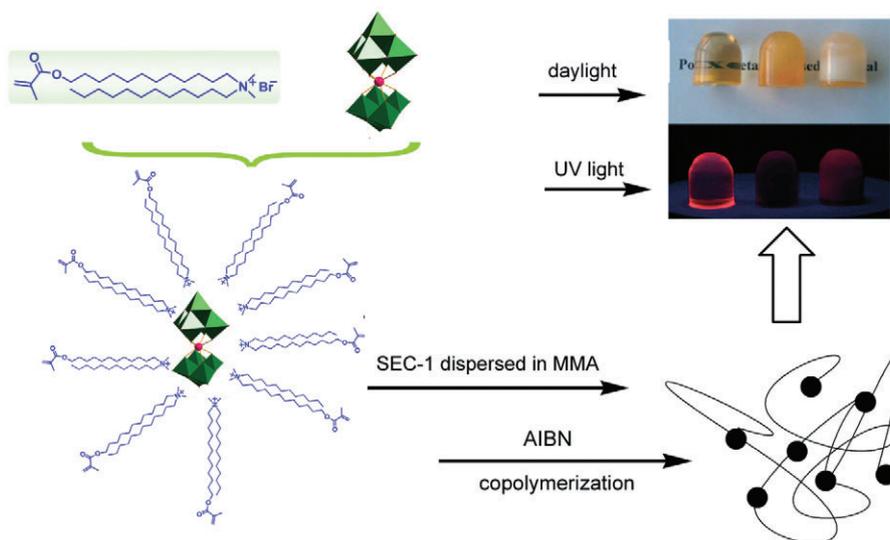


Fig. 4. Scheme shows the procedure for the preparation of a POM/PMMA hybrid,³³ including surfactant encapsulation, transfer into organic monomer solution, and the final copolymerization and the digital photographs of the hybrids in daylight and in ultraviolet light.

secondary metal ligand coordination complexes.^{40,41} Covalent hybrid materials based on nanolatex particles and Dawson clusters has been reported,⁴² and coordination polymers with controllable growth of chains and grids from polyoxomolybdate building blocks linked by silver(I) dimers (see Figure 5) were demonstrated too.⁴³

5. POM-containing Ionic Crystals

Owing to the great potential of 3D porous structures for guest-inclusion and catalytic applications, much attention has been paid to porous materials including inorganic zeolites (covalent bonding), metal organic frameworks (MOFs) or coordination polymers (coordination bonding) and layered compounds, and ionic crystals (hydrogen bonding and/or ionic bonding). Since POMs are extremely versatile in terms of their structure, size, and redox chemistry, their list of applications is very impressive including photochemistry, catalysis, molecular magnetism, and medicine. Furthermore, a new area of interest is the preparation of POM-containing ionic crystals and investigation of their physical properties. Ionic crystals can be prepared by self-assembly of the POMs and macrocations^{44–47} and most importantly, it is possible to predetermine their arrangement by the control of the shape, size, and charge of the macroions and thereby to create spaces in the crystal lattice. Furthermore, a better understanding of the synergistic interaction between POMs (macroanions) and large molecular cations (macroanions) will be very helpful for the development of novel ionic crystals with specific properties. In this respect,

Mizuno's group has made a great contribution to the design and synthesis of POM-containing ionic crystals with hydrophilic/hydrophobic channels and their selective sorption properties.^{48–56}

5.1 Ionic Crystals based on Aluminum-Oxygen Macrocations and POMs

In 2000, Kwon and co-workers reported the first aluminum-oxygen-based ionic crystals of POMs^{44a} with the molecular formula of $[\text{AlO}_4\text{Al}_{12}(\text{OH})_{12}(\text{H}_2\text{O})_{23}][\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}]_2(\text{OH})\cdot 29.5\text{H}_2\text{O}$. The crystal structure (Figure 6a) shows that $\{\text{Al}_{13}\}$ and $\{\text{AlMo}_6\}$ form a 2D aggregate in the crystal lattice. Guest-adsorption measurements show that this compound can undergo several desorption and adsorption cycles. A vacuum-dried sample at room temperature showed only a residual 2 % weight loss below 150 °C, indicating that most of the lattice water was lost under vacuum. When the dried sample was exposed to atmospheric humidity at room temperature overnight, water was adsorbed, as evinced by a gain of 14 % in mass. This weight-gain was found to be reversible upon a second thermal treatment at 150 °C. Although vacuum-drying collapses the lattice, the original crystal structure is essentially recovered upon rehydration with some loss of crystallinity, as indicated by XRD results.

In 2003, Kwon's group reported another two $\{\text{Al}_{13}\}$ - $\{\text{W}_{12}\}$ -based ionic crystals with the formula $[\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}][\text{H}_2\text{W}_{12}\text{O}_{40}(\text{OH})\cdot 20\text{H}_2\text{O}]$ (Figure 6a) and $[\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}][\text{CoW}_{12}\text{O}_{40}(\text{OH})\cdot 20\text{H}_2\text{O}]$, which have almost

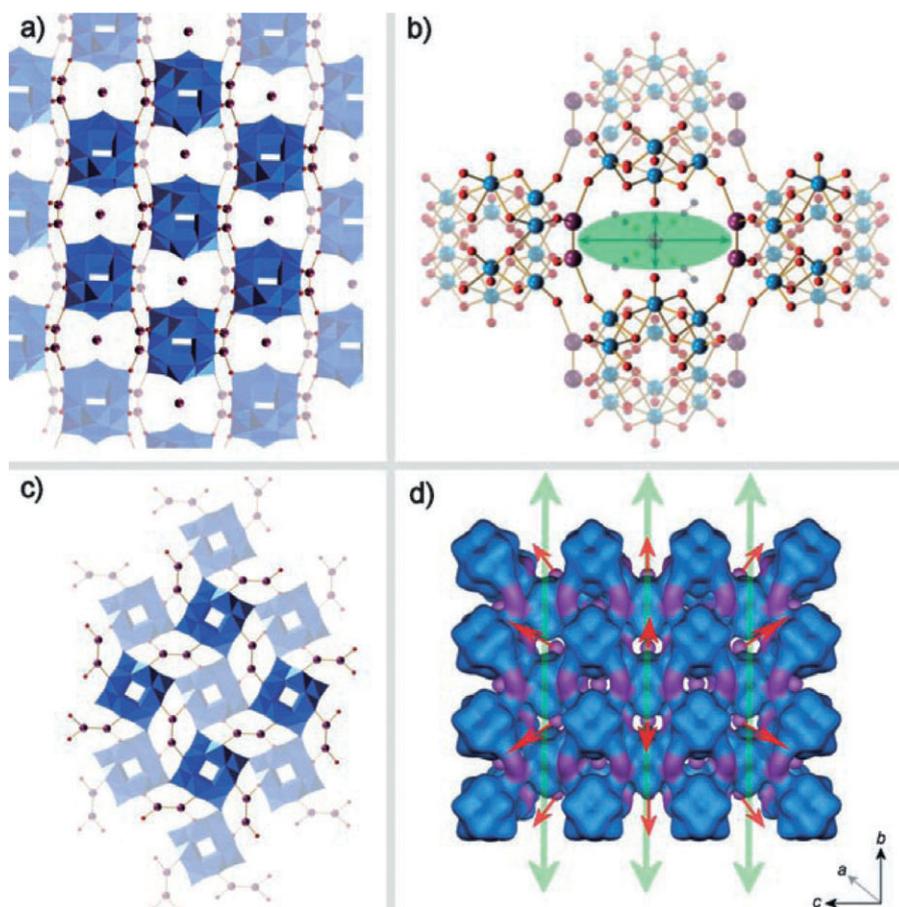


Fig. 5. Illustration of the $\{Ag_2\}$ - $\{W_{12}\}$ framework. a) View along the crystallographic a -axis, showing the spatial arrangement of the $\{W_{12}\}^{43b}$ units (blue) and $\{Ag_2\}^{2+}$ dimers (purple) to form channels in which the $[Ag(CH_3CN)_4]^+$ counterions are located. b) Detailed illustration of the channels; the pore dimensions are highlighted by a green ellipsoid. c) View along the crystallographic c -axis, illustrating the bridging mode of the $\{Ag_2\}^{2+}$ dimers. d) Space-filling representation of this framework, indicating the propagation of the channels along the crystallographic a -axis (red arrows) and the crystallographic b -axis (green arrows). Solvent molecules are omitted for clarity.

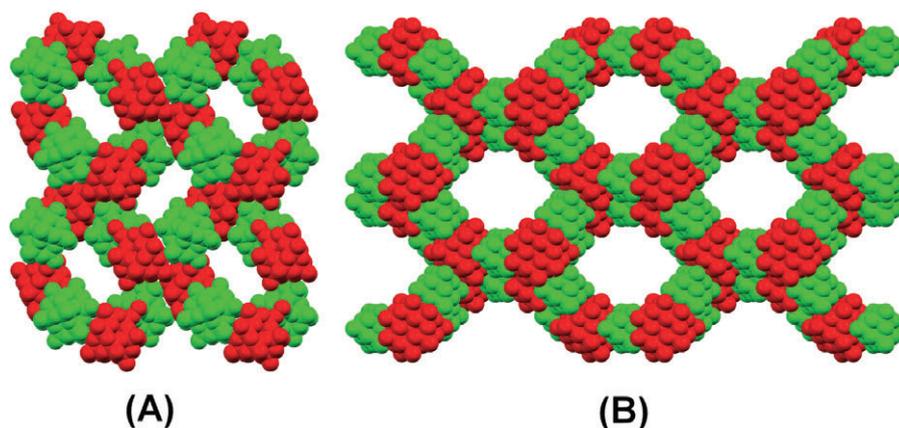


Fig. 6. The structure in “space-filling” form shows the aggregate of $\{W_{12}\}$ and $\{Al_{13}\}$ in the crystal lattice of $[Al_{13}O_4(OH)_{24}(H_2O)_{12}][H_2W_{12}O_{40}](OH) \cdot 20H_2O$. The green areas represent $\{W_{12}\}$ and the red areas are $\{Al_{13}\}$ and (A) shows the structure along the crystallographic b -direction, and (B) along the crystallographic c -direction.

identical structures except for the substitution of W_{12} for CoW_{12} .^{44b} Additionally, the $\{Al_{13}\}$ and $\{W_{12}\}$ in the structure are arranged alternately to form distorted eight-membered rings with channels running along the crystallographic *b*-direction. The channel's dimensions are calculated to be $12.8 \times 7.4 \text{ \AA}^2$, with water molecules and charge balancing OH^- ions filling the void volume between the cluster ions, which is calculated to be 43.8 % of the total volume by using the ionic radii of the atoms in the clusters. The crystal structures show that the macrocations and the POMs are packed mainly by face-to-face interactions through hydrogen bonds and electrostatic interactions.

By changing to a Lindqvist-type cluster, a new material with the molecular formula of $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]_2 [V_2W_4O_{19}]_3(OH)_{2 \cdot 27}H_2O$ ^{44c} was obtained by reaction of the octahedral Lindqvist-type polyoxometalate $[V_2W_4O_{19}]^{4-}$ and a truncated tetrahedral Keggin-type cluster, $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$. The crystal structure (Figure 6b) shows that the macrocations and POM anions are arranged alternately and have their contacting faces parallel to each other for maximum interaction through electrostatic and hydrogen bonding interactions, resulting in the formation of large extended one-dimensional channels with a cross-sectional area of $14.17 \times 13.88 \text{ \AA}^2$ that are filled with water and OH^- for charge balance.

5.2 Ionic Crystals based on the Chromium-Oxygen Macrocations and POMs

By utilizing $[Cr_3O(OOCH)_6(H_2O)_3]^+$ and $[Cr_3O(OOCC_2H_5)_6(H_2O)_3]^+$, Mizuno's group has developed a series of "molecular sieve" type ionic crystals.^{48–54} It is found that slight adjustment of just one of the components (the macrocations, POM anions, and the metal cations (for charge balance)) has significant effect on the channel size and the adsorption properties of the resulting ionic crystals.

The assembly of $[Cr_3O(OOCH)_6(H_2O)_3]^+$ and Keggin $\{W_{12}\}$ clusters lead to a number of POM-based ionic crystals including $Na_2[Cr_3O(OOCH)_6(H_2O)_3][\alpha-PW_{12}O_{40}] \cdot 16H_2O$ (**1**), $K_3[Cr_3O(OOCH)_6(H_2O)_3][\alpha-SiW_{12}O_{40}] \cdot 16H_2O$ (**2**), $Rb_4[Cr_3O(OOCH)_6(H_2O)_3][\alpha-BW_{12}O_{40}] \cdot 16H_2O$ (**3**) and $Cs_5[Cr_3O(OOCH)_6(H_2O)_3][\alpha-CoW_{12}O_{40}] \cdot 7.5H_2O$ (**4**), in which the macrocations and $\{W_{12}\}$ are arranged alternately to form columns with **1** and **2** to give honeycomb structures, with **3** to give a layered structure, or with **4** to give a densely packed structure. The spaces between the columns are occupied by water molecules and the space volumes correspond to 36 %, 36 %, 32 %, and 17 % of the crystal lattices for the above ionic crystals of **1–4**, respectively. For example, in the case of $K_3[Cr_3O(OOCH)_6(H_2O)_3][\alpha-SiW_{12}O_{40}] \cdot 16H_2O$,⁴⁸ the amount of alcohols and nitriles absorbed decreased in the order of methanol > ethanol > 1-propanol \approx 1-butanol = 0

and acetonitrile > propionitrile > butylnitrile = 0. The same order was observed for the hydrophilicity. Experimental results indicate that the sorption properties of this compound are chiefly associated with the hydrogen-bonding interactions between the polar regions and oxygen atoms of $[Cr_3O(OOCH)_6(H_2O)_3]^+$ and $\{W_{12}\}$. The inclusion properties were explained quantitatively by the change in the lattice energy associated with the structural change of the host during the guest sorption-desorption. Another example of POM-macrocation ionic crystals, $Cs_5[Cr_3O(OOCH)_6(H_2O)_3][\alpha-CoW_{12}O_{40}] \cdot 7.5H_2O$, shows the shape-selective adsorption of water molecules and selective separation of water from an ethanol/water azeotropic mixture.

The complexation of Dawson-type POMs with the macrocation $[Cr_3O(OOCH)_6(H_2O)_3]^+$ gives the ionic crystals⁵¹ $(NH_4)_4[Cr_3O(OOCH)_6(H_2O)_3]_2[\alpha-P_2W_{18}O_{62}] \cdot 15H_2O$ (**5**), $(NH_4)_5[Cr_3O(OOCH)_6(H_2O)_3]_2[\alpha-P_2W_{17}VO_{62}] \cdot 15H_2O$ (**6**), and $(NH_4)_7[Cr_3O(OOCH)_6(H_2O)_3]_2[\alpha-P_2W_{15}V_3O_{62}] \cdot 15H_2O$ (**7**). These compounds and their guest-free phases showed that their honeycomb packing crystal structures, water sorption kinetics, and alcohol sorption properties were influenced by the anion charges of the Dawson-type polyoxometalates.

When $[Cr_3O(OOCC_2H_5)_6(H_2O)_3]^+$ is used, another microstructured ionic crystal of $K_2[Cr_3O(OOCC_2H_5)_6(H_2O)_3]_2[\alpha-SiW_{12}O_{40}] \cdot 3H_2O$, containing both hydrophilic and hydrophobic channels, was formed.⁵² The water resided in the hydrophilic channel and was removed by evacuation at 303 K to form the guest-free phase, which adsorbed various kinds of polar hydrogen-bonding organic molecules, and the amounts of C3 alcohols taken up were comparable to or larger than that of water, showing an amphiphilic sorption property. The polar non-hydrogen-bonding chlorocarbons and non-polar molecules were excluded. These studies showed that the ethanol molecules were mainly absorbed into the hydrophilic channel below $P/P_{0-0.5}$, while the sorption into the hydrophobic channel was dominant above $P/P_{0-0.5}$. As a result, channel-selective sorption and collection of hydrophilic and hydrophobic molecules by $Cs_2[Cr_3O(OOCC_2H_5)_6(H_2O)_3]_2[\alpha-SiW_{12}O_{40}]$ was accomplished.

It has been demonstrated that 1) the assembly of Keggin-type POMs of $[\alpha-XW_{12}O_{40}]^{n-}$ ($n = 3-6$) with a macrocation of $[Cr_3O(OOCH)_6(H_2O)_3]^+$ and alkali metal ions forms ionic crystals with hydrophilic channels; 2) the channel size of ionic crystals of Dawson-type polyoxometalates of $[\alpha-P_2V_xW_{18-x}O_{62}]^{(6+x)-}$ increases with a decrease in x and can be controlled; 3) while the use of a $[Cr_3O(OOCH)_6(H_2O)_3]^+$ macrocation forms only hydrophilic channels, the use of $[Cr_3O(OOCC_2H_5)_6(H_2O)_3]^+$ forms both hydrophobic and hydrophilic channels in the crystal lattice.

In general, the properties of ionic crystals based on the chromium-oxygen macrocations and POMs have been summarized as follows:⁵⁵ 1) the use of macrocations reduces the

Coulombic interaction between the cationic and anionic components in the ionic crystals, which reduces the possibility of forming densely packed ionic crystal structures and thereby provides a good opportunity to form porous crystal lattices; 2) the ionic crystals composed of POMs and organic macrocations show pore-surface and guest sorption properties different from inorganic zeolites, metal organic frameworks (MOFs), and coordination polymers; 3) incorporation of catalytically active POMs will enable heterogeneous catalysis in the corresponding ionic crystals.

Recently, an interesting inorganic/organic porous ionic crystal $K_{1.5}[Cr_3O(OOCH)_6(C_5H_5N)_3]_2[Cr_3O(OOCH)_6(C_5H_5N)(CH_3OH)_2]_{0.5}[\alpha-SiW_{12}O_{40}]$ was reported with winding pseudo-one-dimensional channels.⁵⁶ The channel volume and cross-sectional area of the opening were estimated to be $4.1 \times 10^{-2} \text{ cm}^3 \text{ g}^{-1}$ (310 \AA^3 per formula) and 30 \AA^2 , respectively. At 298 K, this compound absorbed molecules with cross-sectional areas smaller than around 30 \AA^2 , such as ethane, ethylene, water, ethanol, and 1,2-dichloroethane, while the larger *n*-butane, 1-pentene, 1-butanol, and 1,2-dichloropropane molecules were excluded. These results showed the size-selective absorption of industrially important small organic molecules at room temperature could be realized on some specific POM-based ionic crystals.

5.3 Ionic Crystals based on Iron-Oxygen Macrocations and POMs

By reaction of $[Fe_3O(OOCH)_6(H_2O)_2]^{3+}$ and $[\alpha-SiW_{12}O_{40}]^{6-} \cdot 16H_2O$ at pH 1.8 in formic acid, an ionic crystal of $K_3[Fe_3O(OOCH)_6(H_2O)_2][\alpha-SiW_{12}O_{40}] \cdot 16H_2O$ ⁴⁹ was obtained, in which weak electrostatic and hydrogen bonding interactions could be observed in the crystal structure. As with the corresponding chromium-oxygen based ionic crystal, the resulting porous crystal lattice herein could reversibly absorb water and small organic molecules.

Izarova's group reported a slightly different method⁴⁵ to prepare such iron-oxo-based ionic crystals. Reaction of $FeCl_3$ with $[\alpha-SiW_{12}O_{40}]^{4-}$ or $[\alpha_2-P_2W_{17}O_{61}]^{10-}$ in a NaAc/HAc buffer led to the formation of $[Fe_3(\mu_3-O)(CH_3COO)_6(H_2O)_3]_4[\alpha-SiW_{12}O_{40}] \cdot 19H_2O$ and $KNa[Fe_3O(CH_3COO)_6(H_2O)_3]_3[\alpha_2-P_2W_{17}Fe(H_2O)O_{61}] \cdot 32.5H_2O$, respectively, and it should be noted that both the trinuclear iron-oxygen macrocations and the corresponding ionic crystals were formed in-situ, which is different from the other experiments where the macrocations were synthesized separately.

6. Functionalization of POMs by Organic Ligands and Transition Metal Complexes

Organo-modified POMs are a unique type of POM-containing inorganic/organic hybrid.⁵⁷ For example,

tris(organotin)-substituted Keggin and Dawson tungstophosphates have been prepared by reaction of organotin trichlorides with $[A-PW_9O_{34}]^{9-}$ and $[\alpha-P_2W_{15}O_{56}]^{12-}$ POMs to yield $[(PhSnOH)_3(PW_9O_{34})_2]^{12-}$ and $[(PhSn)_3(P_2W_{15}O_{59})_{12}]$.⁵⁸ Recently, POMs derivatized by organotin groups were subsequently used in the copper-catalyzed azide/alkyne cycloaddition reaction to generate novel hybrid assemblies.⁵⁹ The synthesis and characterization of organophosphonic acid-lacunary POM hybrids have been widely investigated since the late 1990s.⁶⁰ Organophosphonic acids of $RPO(OH)_2$ and organophosphonic dichlorides $RPOCl_2$ react with lacunary heteropolytungstates in homogeneous solution or under phase-transfer conditions.

Among many different transition metals likely to be incorporated into POMs, ruthenium appears to be particularly attractive because of the unique catalytic potential of this metal.⁶¹ As such, many ruthenium derivatives of polyoxoanions have been synthesized by reaction of $[Ru(\text{arene})Cl_2]$ and $[Ru(DMSO)_4Cl_2]$ precursors with oxomolybdates and oxotungstates. In addition to Ru-containing POM hybrids, high-valent metal nitrido fragments, including $[\alpha-PW_{11}O_{39}Re^{VI}N]^{4-}$, $[\alpha-PW_{11}O_{39}Os^{VI}N]^{4-}$, $[\alpha_1-P_2W_{17}O_{61}Os^{VI}N]^{7-}$, and $[\alpha_2-P_2W_{17}O_{61}Os^{VI}N]^{7-}$, have been successfully incorporated into POM clusters by reaction of the monovacant species of $[\alpha-PW_{11}O_{39}]^{7-}$, $[\alpha_1-P_2W_{17}O_{61}]^{10-}$, and $[\alpha_2-P_2W_{17}O_{61}]^{10-}$ with the nitride complexes of $[Re^{VI}NCl_4]^-$ and $[Os^{VI}NCl_4]^-$ in either aqueous solution or in acetonitrile.⁶² The most important feature of these POM hybrids is that apart from their potential utility in nitrogen-atom transfer reactions, the nitride-Keggin systems offer the possibility to access other nitrogenous heteropolyanions such as organoimido and phosphorane iminato species. Additionally, the reactivity of the above mentioned nitride derivatives of POMs towards nucleophilic and electrophilic reagents are under investigation.^{63,64}

In recent years, considerable attention has been paid to covalently bonded inorganic/organic hybrids because the covalent bond improves the stability of the hybrid assemblies and might enhance the interaction between the inorganic and organic components. This may also facilitate the construction of POM-based integrated nanosystems.⁵⁷ In addition, the functionalization of POM frameworks, by replacing/derivatizing the oxo ligands, is one of the most important steps in developing POMs for multifunctional materials since this will not only allow a much greater degree of control, but also facilitate stepwise syntheses to introduce a range of diverse pendant functionalities.

Hybrid materials based on covalently grafting organic species containing a delocalized π system onto POMs have drawn increasing attention in recent years, among which organoimido derivatives of Lindqvist clusters have attracted particular interest. The use of aromatic systems allows the possibility of extended conjugation between the organic π

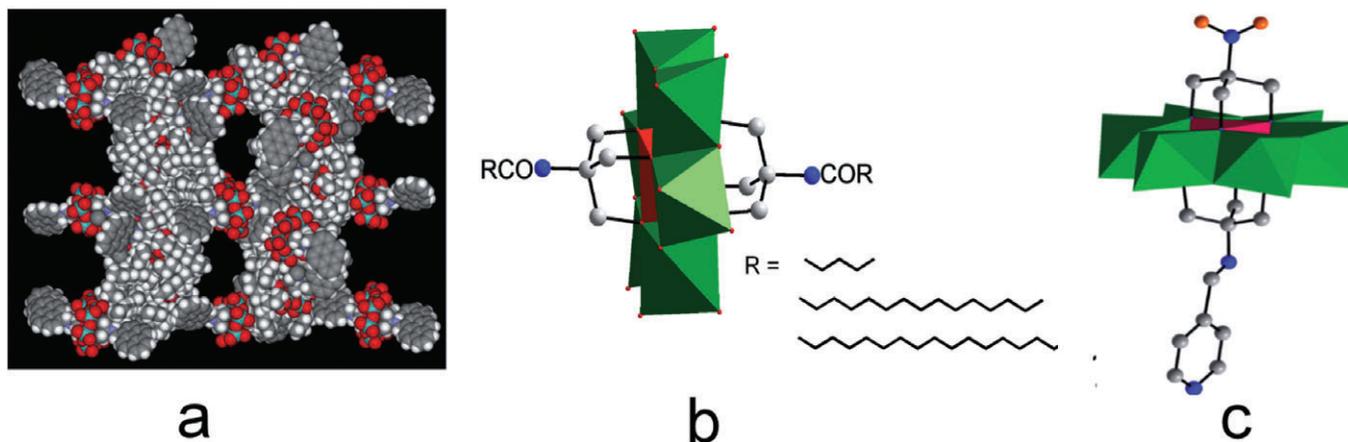


Fig. 7. a) A Pyrene group derivatised Mn-Anderson framework shown in space filling representation projected onto the crystallographic-*ac* plane, in which the butterfly shaped 1-D channels are clearly observed. O = red, Mo = green, C = black, H = white, N = blue. b) The POM-containing hydrophilic/hydrophobic molecular assemblies have been built up by covalently anchoring long alkyl chains onto the Anderson cluster. c) X-ray crystal structure of an unsymmetric Anderson-based cluster in “Polyhedron” form shows that a pyridine ring has been covalently tethered to the Mn-Anderson cluster (Mn pink, Mo green, N blue, C grey, O orange).

electrons and the inorganic framework, resulting in strong d- π interactions. Furthermore, organoimido derivatives of POMs with a remote organic functional group can be utilized as building blocks to construct more complicated and interesting POM-organic hybrids. This modular building block strategy brings both rational design and structure control into the synthesis of POM-containing inorganic/organic hybrids. Among the many hybrid materials, covalently linked organoimido POMs have attracted particular interest and have been widely investigated. In the case of the organoimido compound of Lindqvist-type (aryldiazenido)polyoxomolybdates, it has been shown that the six terminal oxygen ligands in the hexamolybdate anion can be partially or completely replaced with organoimido ligands to give compounds of the form $(n\text{Bu}_4\text{N})_3[\text{Mo}_6\text{O}_{18}(\text{NAr})_x]$ ($x = 1-6$) by carefully controlling the molar ratios of the isocyanate with respect to the cluster. However, the above reaction is greatly restricted by its nonselective nature, which results in a mixture of various multiply-functionalized products. In this regard, it was discovered that instead of using $[\text{Mo}_6\text{O}_{19}]^{2-}$ as the parent cluster, the reaction of $[\alpha\text{-Mo}_8\text{O}_{26}]^{4-}$ with aromatic amines gives the bisimido derivative selectively. It has been shown that the synthetic method for the preparation of such clusters was dramatically improved in the presence of dicyclohexylcarbodiimide (DCC). The reaction of aryl amines with $[\text{Mo}_2\text{O}_7]^{7-}$ and $[\text{Mo}_7\text{O}_{24}]^{6-}$ in the presence of DCC yielded imido derivatives of hexamolybdate with cluster rearrangement. Attempts to extend the synthetic strategy to other POM clusters have found only very limited success. Hexatungstate $[\text{W}_6\text{O}_{19}]^{2-}$ does not react with aromatic amines or isocyanates. However, the reaction of $[\text{MoW}_5\text{O}_{19}]^{2-}$ with aromatic amines does proceed and aryl

imido derivatives of the mixed metal $[\text{MoW}_5\text{O}_{19}]^{2-}$ cluster can be synthesized. With Keggin structures, the POMs' redox activities result in oxidation of aromatic amines, preventing functionalization by this method.

Recent investigations have shown that covalent functionalization of Anderson clusters can be achieved^{65,66} through a “tris” (tris(hydroxymethyl)aminomethane) linker with three pendant hydroxyl groups replacing the hydroxide groups on the surface of the Anderson. As a result, this has produced a variety of tripods that allow further derivatization through imine and peptide bonds. We have been working on the covalent functionalization of Anderson clusters during the past five years, with several systems being documented.⁶⁷ These include the controllable molecular assembly of Anderson clusters, Anderson-containing fluorescent materials, hydrophobic-hydrophilic materials, the supramolecular self-assembly process of Anderson-containing hydrophobic materials, asymmetric Anderson-based materials, Anderson-based biomaterials, and silver-connected supramolecular architectures (see Figure 7). For example, by tethering the highly delocalized aromatic pyrene moiety to the Anderson type cluster through the “tris” connector, we have been able to modify the physical properties of the Anderson cluster dramatically. Secondly, by covalently anchoring long alkyl-chains onto the Anderson cluster, POM-containing hydrophobic assemblies have been obtained with controlled morphologies and interesting physical properties. Thirdly, by utilizing dynamic and static light scattering techniques, coupled with SEM and TEM, we were able to gain an in-depth understanding of the self-assembly processes of a surfactant encapsulated Anderson-based hydrophobic/hydrophilic material for the first time. The particular POM used herein,

with its attached “tris” linker as a bridge, can be utilized as a building block to construct more complicated POM-organic hybrids. As such, this modular building block approach brings rational design and structural control into the synthesis of novel inorganic/organic POM-based hybrid materials. Such design can also be achieved using a mixture of first row transition metals and organic ligands⁶⁸ to produce a type of MOF system and a range of differently linked POM-based hybrids and hetero-metallic structures.⁶⁹

Since the controlled assembly of POM-based building blocks defines a crucial challenge in engineering POMs to assemble into novel architectures with functionality, an important extension to this building block concept is realized by the use of POMs to form inorganic/organic hybrids that comprise covalently connected POMs and organo fragments. It is apparent that the organic components can dramatically influence the microstructures of inorganic oxides, providing a way for the design of novel materials. However, the major problem is that the covalent functionalization of POMs in general is not straightforward. As such, only a few covalently bonded POM-organic molecular hybrids and polymeric hybrids have been prepared and studies of the physical properties of these systems have yet to be carried out systematically.

7. Conclusions and Perspectives

The area of POM chemistry has experienced an unprecedented development during the past five years as shown by the many novel POM clusters that have been structurally characterized by single crystal X-ray crystallography, and the development of POM-based multifunctional materials that have been fundamentally important (such as POM-containing single molecule magnets) and promising for applications (such as POM catalytic materials). It is clear that POM chemistry has exceptional scope for development in nanoscale science since POM clusters have been proven to be ideal candidates in the development of a new type of supramolecular chemistry based upon the “building-block” approach. It should be possible to design micro- and/or macromolecules of ever increasing size and complexity using these ideas. This is exciting since POMs have a vast range of interesting properties ranging from electronic, photochemical, catalytic, and those associated with their very high charge and size. Further, the investigation of POM-containing inorganic/organic hybrid materials could help exploit such properties by allowing the POMs to be more compatible in a range of material types, for example, in polymer blends or in organic materials. A full understanding of such a design concept will not only lead to new types of POM-based hybrid materials, such as redox switchable host-guest systems, that could be used in information storage or even in light harvesting systems, and could also find application as robust sequestration agents.

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