

Hybrid Organic–Inorganic Polyoxometalate Compounds: From Structural Diversity to Applications

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1. Introduction

Polyoxometalates (POMs) are discrete anionic metal–oxygen clusters which can be regarded as soluble oxide fragments. They exhibit a great diversity of sizes, nuclearities, and shapes. They are built from the connection of $\{MO_x\}$ polyhedra, M being a d-block element in high oxidation state, usually $V^{IV,V}$, Mo^{VI} , or W^{VI} .¹ While these species have been known for almost two centuries, they still attract much interest partly based on their large domains of applications. They play a great role in various areas ranging from catalysis,² medicine,³ electrochemistry,⁴ photochromism,⁵ to magnetism.⁶ This palette of applications is intrinsically due to the combination of their added value properties (redox properties, large sizes, high negative charges, nucleophilicity...). Parallel to this domain, the organic–inorganic hybrids area has followed a similar expansion during the last 10 years. The concept of organic–inorganic hybrid materials

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has exploded and been applied either to noncrystalline materials isolated under mild synthetic conditions following the method of ‘Chimie Douce’⁷ or to crystalline materials synthesized at room temperature or under hydrothermal conditions.⁸ The structure and properties that can be obtained for such materials depend on the nature of both components, and the search of multifunctional devices is often evoked as a motivation for their synthesis. In the field of catalysis, the study of organic–inorganic hybrids with POMs can help to understand the interactions between organic molecules and the surface of oxides and lead to more efficient recyclable multifunctional catalysts. In materials chemistry hybrid POMs can be linked together, they can also be incorporated into polymers, and they can interact with metallic surfaces or nanoparticles.

Since the development of organic–inorganic hybrids two classes of composites have emerged. These two classes have been defined according to the nature of the interaction



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between the organic and inorganic components.⁹ The first class (class I) gathers all the systems where no covalent bonds are shared between the organic and the inorganic parts. Only electrostatic interactions, hydrogen bonds, or van der Waals interactions are involved. In the second class (class II), the organic and inorganic moieties are linked via strong covalent or ionic–covalent bonds (Figure 1). The anionic character of POMs naturally allows their association with organic counter cations into class I hybrids. Considering class II hybrids, the organic ligand can substitute an oxo group of the POM and be directly linked to the metallic center. The nucleophilic character of the oxygen atoms localized on the surface of the POMs can also lead to covalent interactions with electrophilic groups bearing organic groups.

A special issue of *Chemical Reviews* in 1998¹⁰ was devoted to the field of POMs with, in particular, a state of the art review on main-group element, organic, and organometallic derivatives.¹¹ Since then several reviews have

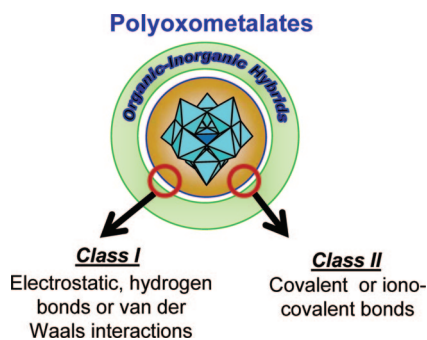


Figure 1. Definition of the two classes (I and II) of organic/inorganic hybrid POMs as defined in the present review.

been published on specific topics of class I hybrids, such as hybrid organic–inorganic nanocomposites with POMs,¹² molecular conductors,¹³ and organic–inorganic hybrid assemblies of POM crown-ether complexes,¹⁴ and class II hybrids, such as organonitrogen, organosilyl, and organophosphonyl derivatives,¹⁵ chirality in POM chemistry.¹⁶ Stabilization and immobilization of POMs in porous coordination polymers through host–guest interactions has also been recently reviewed.¹⁷ The present review is aimed to give a larger overview on recent developments of class I and class II hybrid organic inorganic materials. We will divide the description of these hybrid POMs in four parts. The first section will discuss class II hybrids where organic groups are covalently linked to POM units via p-block elements. Inside this part, we will give an exhaustive list of the various p-elements that can be linked to the POM. The second part will describe class II hybrids where the organic ligand is bound to d- and f-block elements grafted to the surface or encapsulated in the vacancy of a POM. Organometallic derivatives will also be described. The third section will focus on the reactivity and applications of covalently functionalized POMs, while the fourth one will be devoted to class I hybrids. Due to the numerous papers in this field, we will focus our attention only on POMs with targeted properties and emergent applications such as photochromic materials and nanomaterials. In all the sections we will only consider POMs with nuclearities greater than 2. The role of organic ligands in the family of spectacular objects developed by Müller¹⁸ will not be evoked in this review.

2. Organic Groups Covalently Linked to Polyoxometalate Units via p-Block Elements

2.1. Presentation and Generalities on the Functionalization of POMs

2.1.1. Importance of the Anchorage Point

Grafting an organic fragment onto an inorganic system requires an anchorage point ensuring the link between the two components. This link is closely dependent on the chemical nature and electronic properties of the inorganic entity. For example, the presence of the negative charge borne by the POMs is an important point that needs to be considered for the grafting of the organic fragment. Neutral or negatively charged organic systems will be chosen in order to favor covalent grafting over electrostatic interactions. Indeed, functionalization of POMs through oxygen atoms located at the periphery of the POM structure (M–O–X, X being a p-block element) is the most conventional route. Nevertheless, this link is not the only alternative, and a

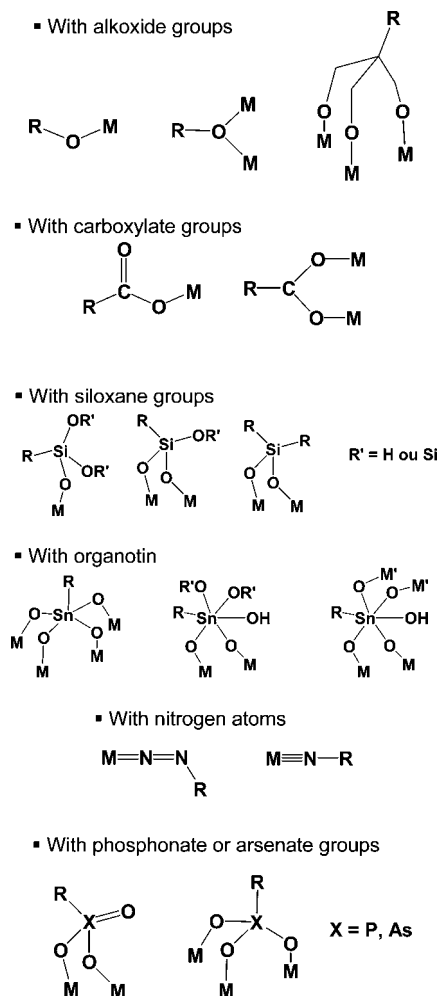


Figure 2. Main coordination modes of organic groups covalently linked to POM units via p-block elements.

variety of POMs has been functionalized using nitrogen atoms to generate single (or multiple) metal–nitrogen bond(s). Sections 2.2 and 2.3 have been written using an, at least partial, arbitrary classification in which the p-element considered is either the nitrogen atom when this atom is directly bound to the metal center of the POM or the X element (X = C, P, As, Sn, Ge...) when this one is connected to the oxygen atom bound to the metal center (Figure 2).

2.1.2. Nature, Degree, and Localization of the Functionalization

A large variety of organic fragments has been considered for the functionalization of POMs. Recently, many efforts have been devoted to induce and/or increase a synergy between the two components, namely, the organic moiety and the POM. The idea is indeed to benefit from the intrinsic physicochemical properties of the POMs. For example, it is possible to use fully conjugated organic fragments to favor electronic transfer or to insert an alkyl chain of variable length to bring flexibility.

The degree of functionalization corresponds to the number of organic molecules grafted onto the surface of the POM. It is a key feature for the design of organic/inorganic hybrids. For example, only one polymerizable organic group must be grafted onto POM to prepare nonreticulated hybrid polymers, while at least two polymerizable functions will be needed to generate reticulated polymers. Maatta et al. and

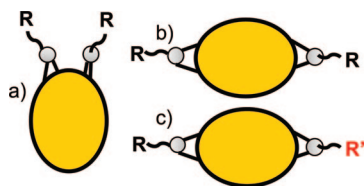


Figure 3. Schematic representation of the different hybrid organic/inorganic difunctionalized polyoxometalate systems.

Peng et al. designed hybrid organic/inorganic polymers bearing POMs as pendant groups using monosubstituted organoimido derivatives of the isopolyanion $[\text{Mo}_6\text{O}_{19}]^{2-}$.^{19,20} Lalot et al. synthesized a hybrid hydrogel with peculiar swelling properties from acrylamide and a tetrafunctionalized polymerizable heteropolyoxotungstate as cross-linker.²¹

POMs are also very attractive building blocks because of their remarkable structural diversity and well-documented reactivity. Consequently, they offer a perfectly adapted platform for a controlled localization of the functionalization by organic groups. This is illustrated in Figure 3 for the difunctionalization. The two organic fragments can be grafted either near one another (Figure 3a) or opposite one another (Figure 3b). A challenging aim is also to be able to form unsymmetrically functionalized structures in which two different organic groups are selectively grafted on various parts of the POM (Figure 3c). Examples of such functionalization are described below.

2.1.3. Influence of the Nature of the POM

The family of POMs can be divided in two main subclasses, namely, isopolyoxometalates and heteropolyoxometalates. These two subclasses and their specific properties will be used to illustrate the tremendous potentialities of POMs in terms of functionalization by organic groups.

2.1.3.1. Functionalization of Isopolyoxometalates. The versatility of the reactivity of isopolyoxometalates is perfectly illustrated by the Lindqvist organoimido derivatives family of general formula $[\text{M}_6\text{O}_{19-x}(\text{NR})_x]^{2-}$ with $\text{M} = \text{Mo}, \text{W}$ and $x = 1-6$ (Figure 4). This family, mostly developed with the hexamolybdate POM, is generated by the formal substitution of one or more $\text{Mo}=\text{O}_{\text{term}}$ bond(s) by one or more $\text{Mo}\equiv\text{NR}$ bond(s). Monosubstituted derivatives have been obtained with a variety of organoimido ligands using the hexamolybdate anion $[\text{Mo}_6\text{O}_{19}]^{2-}$ in a direct metathetical synthesis or starting from the octamolybdate anion $[\text{Mo}_8\text{O}_{26}]^{4-}$ in the presence of the *N,N'*-dicyclohexylcarbodiimide (DCC) dehydrating agent. When considering exclusively steric repulsion, the trans structure of the disubstituted hexamolybdate is expected to be easier to form compared with the cis isomer. However, the cis isomer is by far the most common structure among the disubstituted species even if the kinetically controlled trans isomer has been recently isolated.²²

2.1.3.2. Functionalization of Heteropolyoxometalates. Three main subclasses can be identified among heteropolyoxometalates: Anderson, Keggin, and Dawson families. In the Anderson structure, the heteroelement is octahedrally coordinated, while in the Keggin and Dawson structures, the heteroelement is tetrahedrally coordinated.

In the case of the Anderson family, covalent functionalization on both sides of the structure has been achieved using, for example, tris-alkoxo ligands. An original unsymmetrical functionalization of the Mn-Anderson POM has been recently described by Cronin et al. (Figure 5).²³

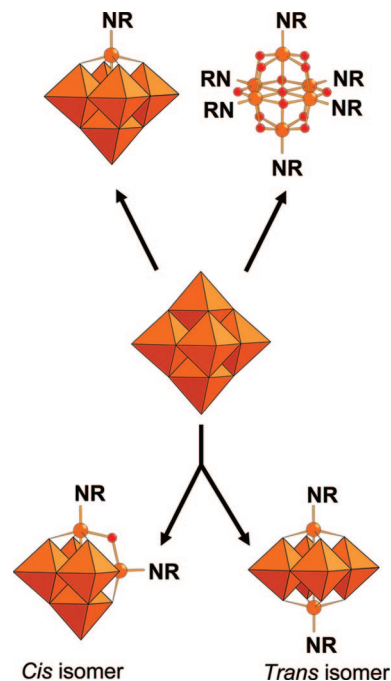


Figure 4. Polyhedral and ball-and-stick representations of four typical examples of Lindqvist organoimido derivatives $[\text{Mo}_6\text{O}_{19-x}(\text{NR})_x]^{2-}$ ($x = 0-6$). Orange octahedra, $\{\text{MoO}_6\}$; orange spheres, Mo; red spheres, O. The nature of the R groups is listed in Table 3.

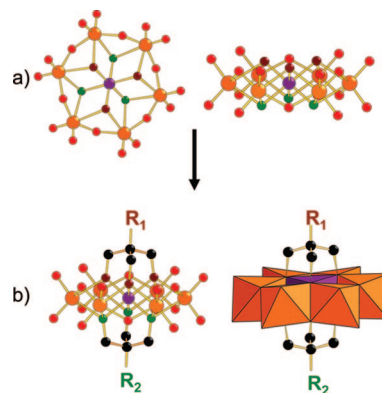


Figure 5. (a) Ball-and-stick representations of the nonfunctionalized $\{\text{MnMo}_6\text{O}_{24}\}$ Anderson POM, and (b) ball-and-stick and polyhedral representations of the unsymmetrically functionalized $[\text{MnMo}_6\text{O}_{18}(\text{C}_4\text{H}_6\text{O}_3\text{R}_1)(\text{C}_4\text{H}_6\text{O}_3\text{R}_2)]^{3-}$ POM ($\text{R}_1 = \text{NO}_2$; $\text{R}_2 = \text{NH}_2$ or NHCHR'_2 , where R'_2 is an aromatic group) (ref 23). Orange spheres, Mo; purple spheres, Mn; black spheres, C; red, brown or green spheres, O.

Functionalization of heteropolyoxometalates is mainly achieved after the formal removal of one or several metal “octahedra” from the original POM in order to generate so-called lacunary species. In nonlacunary heteropolyoxometalates the negative charge is delocalized over the entire structure. In lacunary heteropolyoxometalates, the nucleophilic properties of the oxygen atoms localized at the surface of the lacuna are increased and therefore make these oxygen atoms more reactive toward electrophilic groups such as organophosphonates, organoarsonates, organotin, etc. The variety of electrophilic groups available combined with the various topologies observed in lacunary heteropolyoxometalates explains the recent development of such organic/inorganic hybrids. The structure of the lacuna and the structural organization of the functionalizing agents are key parameters that need to be considered for the synthesis of

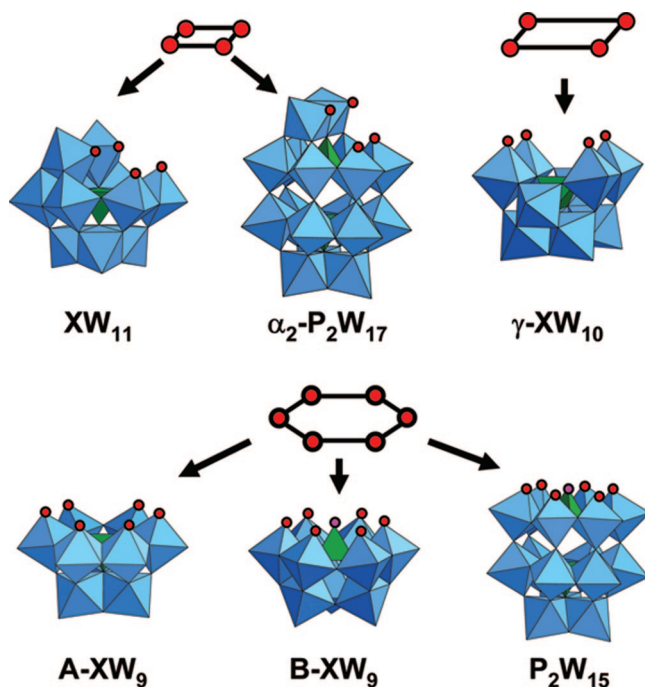


Figure 6. Representation of different lacunary POMs highlighting the geometry adopted by the oxygen atoms of the lacuna.

functionalized heteropolyoxometalates. It has to be noticed that, aside from few exceptions, functionalization of heteropolyoxometalates of Keggin and Dawson families is mainly observed with tungsten lacunary species. Molybdenum lacunary species such as $[\text{PMo}_9\text{O}_{34}]^{9-}$ are metastable and rapidly form the parent ‘saturated’ Keggin POM $[\text{PMo}_{12}\text{O}_{40}]^{3-}$.²⁴

Topology of Lacunary Heteropolyoxometalates. The structures of the lacuna obtained with the Keggin and Dawson families are generally similar and mainly depend on the number of vacancies generated in the parent ‘saturated’ structure. Examples of geometries observed in lacunary heteropolyoxometalates are shown in Figure 6. In monovacant species, four oxygen atoms are accessible at the surface of the lacuna for further reaction with an organic fragment. These four oxygen atoms present a slightly distorted square geometry. In divacant species such as $\gamma\text{-}[\text{XW}_{10}\text{O}_{36}]^{n-}$, the four nearly coplanar oxygen atoms of the lacuna define a rectangular geometry. In trivacant heteropolyoxometalates such as $[\text{XW}_9\text{O}_{34}]^{n-}$ or $[\text{X}_2\text{W}_{15}\text{O}_{59}]^{n-}$ six nearly coplanar oxygen atoms defining a distorted hexagon are available to react with organic fragments. For trivacant species, the nature of the isomer (A- or B- $[\text{XW}_9\text{O}_{34}]^{n-}$) and the nature of the heteroelement are crucial parameters that will influence the type of functionalization. In A- $[\text{XW}_9\text{O}_{34}]^{n-}$ a void space is present in the middle of the hexagon, while an oxygen atom of the central XO_4 tetrahedron points toward the middle of the hexagon in B- $[\text{XW}_9\text{O}_{34}]^{n-}$ and in $[\text{X}_2\text{W}_{15}\text{O}_{59}]^{n-}$. In the same way, the use of a central heteroatom possessing an electronic lone pair (As^{III} , Sb^{III} , ...) pointing toward the center of the hexagon will indeed affect the spatial arrangement of the organic fragments in the lacuna.

Topology of the Functionalizing Fragments. The different degrees of functionalization of vacant POMs together with the main coordination modes of organic substrate grafted via p-block elements are represented in Figure 7. We briefly illustrate the different topologies adopted by giving some typical examples.

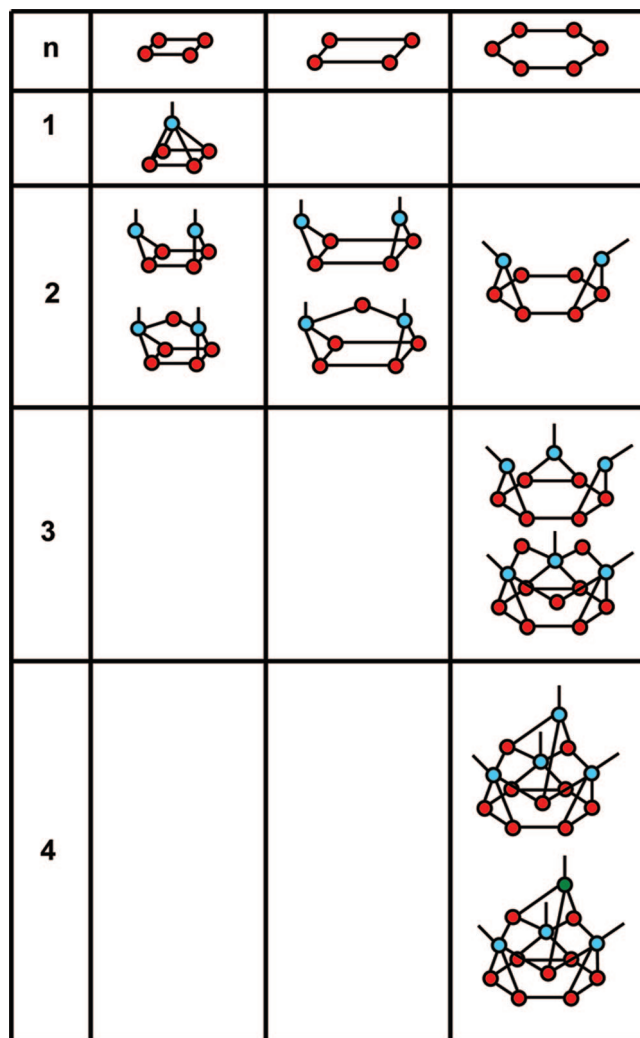


Figure 7. Different topologies adopted by monomeric lacunary heteropolytungstates functionalized by p-block element(s) bearing organic groups. *n* indicates the degree of functionalization.

Monofunctionalization is achieved using monovacant heteropolyoxometalates such as $[\text{XW}_{11}\text{O}_{39}]^{n-}$ or $[\text{X}_2\text{W}_{17}\text{O}_{61}]^{n-}$. The coordination of the p-block element to the four oxygen atoms of the lacuna and to an organic fragment necessarily implies that this p-block element is able to accommodate such a high coordination. Organotin has been extensively used to obtain monofunctionalized organic/inorganic hybrids.

Difunctionalization has been observed with mono- and multivacant heteropolyoxometalates. In these systems, the organic fragment is connected to two oxygen atoms of the lacuna through the p-block element. In the case of organosilanes, for example, the two silicon atoms can be directly connected via an oxo bridge.²⁵ Difunctionalization has also been achieved by reacting organophosphonates with trivacant POMs such as $[\text{PW}_9\text{O}_{34}]^{9-}$,²⁶ leaving two oxygen atoms of the lacuna potentially available to further react with other electrophilic groups.

Trifunctionalization and higher degrees of functionalization have also been obtained. For example, two very distinct types of tetrafunctionalization have been described. Either the four functionalizing fragments are directly connected to the oxygen atoms of the lacuna or three of these fragments are directly bound to the heteropolyoxometalate while the fourth one caps the first three fragments in order to generate a capping tetrahedron.

2.2. p-Elements from Column IV

In the first two sections are included all the ligands ensuring direct C–O–M bonds in the organic/inorganic hybrid polyoxometalates. We therefore gathered here alkoxo ligands and oxocarbon ligands such as carboxylates bound according to the schemes in Figure 2.

2.2.1. Direct C–O–M (M = Mo, W, V) Bonds with Alkoxo Ligands

2.2.1.1. Monodentate Alkoxides. The richness of the coordination modes of alkoxo ligands is exemplified in the well-known $[\text{Mo}_4\text{O}_{10}(\text{OCH}_3)_6]^{2-}$ anion, recently isolated as counterion of the bimetallic complex $[(\text{L}^{\text{Me}})\text{Co}_2(\text{MoO}_3(\text{OMe}))]^+$, where L^{Me} is a macrocyclic octadentate ligand.²⁷ In this fully oxidized tetramolybdenum cluster, the methoxides are either terminal or in a bridging position between two or three molybdenum centers.²⁸ Monomethylated $[\text{IMo}_6\text{O}_{23}(\text{OMe})]^{4-}$ and dimethylated $[\text{IMo}_6\text{O}_{22}(\text{OMe})_2]^{3-}$ anions with an Anderson-type structure have been recently isolated.²⁹ The anions can be synthesized from the mono-protonated $[\text{IMo}_6\text{O}_{23}(\text{OH})]^{4-}$ and diprotonated $[\text{IMo}_6\text{O}_{22}(\text{OH})_2]^{3-}$ anions by addition of methanol but cannot be obtained starting from the nonprotonated $[\text{IMo}_6\text{O}_{24}]^{5-}$ anion. Protonation of the polyoxometalate is therefore a prerequisite for the formation of methylated Anderson-type anions.

Modéc et al. developed a rich family of reduced polyoxoalkoxometalates based on the dinuclear $\{\text{Mo}_2\text{O}_4\}^{2+}$ fragment in which the two molybdenum centers are connected by a single metal–metal bond. Starting from pyridinium oxohalomolybdates(V), a series of di-, tetra-, hexa-, octa-, deca-, and dodecanuclear compounds was structurally characterized.³⁰ Remarkable features have been observed in this family of compounds such as the variety of connections between the dinuclear fragments or the presence of terminal alcohol ligands.³⁰

While the presence of terminal or bridging alkoxo ligands is indeed a key parameter for the final structure, most of the polyoxoalkoxometalates will be described or cited in the heading relevant with the other organic functions present in the structure, such as pyridine or pyridine derivatives, oxalate, carboxylates....

2.2.1.2. Trisalkoxides. Trisalkoxo ligands have been mainly used for the functionalization of Anderson-type polyoxomolybdates. The structures, of general formula $[\text{H}_x\text{M}\text{Mo}_6\text{O}_{18}\{(\text{OCH}_2)_3\text{CR}\}_2]^{y-}$ (with M = Mn^{III} , Fe^{III} , $x = 0$, $y = 3$; M = Ni^{II} , Zn^{II} , $x = 2$, $y = 2$; R = CH_3 , CH_2CH_3 , CH_2OH , $\text{CH}_2\text{OC}(\text{O})(4\text{-C}_5\text{H}_4\text{N})$, NH_2 , NO_2 , $\text{N}=\text{C}(2\text{-C}_5\text{H}_4\text{N})$, $\text{N}=\text{C}(4\text{-C}_5\text{H}_4\text{N})$, $\text{NHCO}(4\text{-C}_5\text{H}_4\text{N})$, $\text{NHCO}(\text{CH}_2)_n\text{CH}_3$ ($n = 4, 14, 16$), $\text{NHCH}_2\text{-pyrene}$), are obtained by treatment of $\alpha\text{-}[\text{Mo}_8\text{O}_{26}]^{4-}$ with the appropriate metal precursor and the designed trisalkoxo ligand in refluxing acetonitrile.³¹ The trisalkoxo ligand is either preformed and then grafted on the polyoxometalate or grafted on the polyoxometalate with a pendant reactive group such as an amino group that is further involved in an imination or an amidation reaction.^{31b,f} Two types of isomers containing organic ligands on both sides of the plane defined by the metal atoms have been structurally characterized: in the isomer δ , named after its idealized D_{3d} symmetry, the trisalkoxo ligand caps the two opposites triangular faces of the central $\{\text{MO}_6\}$ octahedron, while in the isomer χ , named after its symmetry close to C_{2h} , the organic ligand caps one triangular cavity on both sides of the polyoxometalate (Figure 8). To our knowledge,

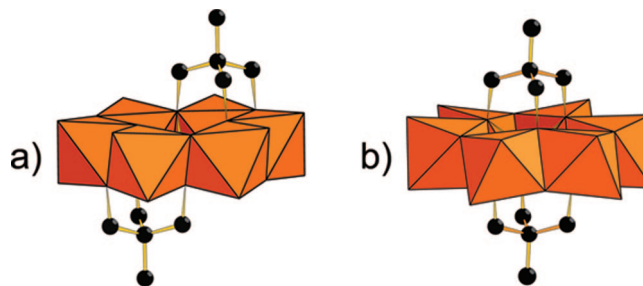


Figure 8. Polyhedral and ball-and-stick representations of Anderson-type $\{\text{MMo}_6\text{O}_{24}\}$ POMs functionalized by a trisalkoxo ligand: (a) χ isomer and (b) δ isomer (ref 31a). Orange octahedra, $\{\text{MoO}_6\}$; black spheres, C.

only one example of the χ isomer has been obtained, the $[\text{H}_2\text{ZnMo}_6\text{O}_{18}\{(\text{OCH}_2)_3\text{CCH}_3\}_2]^{2-}$ compound.^{31a} Heteroditopic trisalkoxo ligands have been also used to design organic/inorganic hybrid Anderson structures bearing mono- and bidentate pendant metal binding sites. These building blocks have been reacted with Ru^{II} and Zn^{II} tetraphenylporphyrins (TPPs) to form complexes with unique electrochemical properties^{31g} or with $[\text{PdCl}_2(\text{PhCN})_2]$ to form an anisotropic gel.^{31c} The unsymmetrically functionalized polyanion $[\text{MnMo}_6\text{O}_{18}\{(\text{OCH}_2)_3\text{CNO}_2\}\{(\text{OCH}_2)_3\text{CNH}_2\}]^{3-}$ was obtained from a one-pot reaction of $(\text{HOCH}_2)_3\text{CNO}_2$, $(\text{HOCH}_2)_3\text{CNH}_2$, $(\text{NBu}_4)_4[\text{Mo}_8\text{O}_{26}]$, and $\text{Mn}(\text{O}_2\text{CCH}_3)_3$ in refluxing acetonitrile (Figure 5).²³ The unsymmetrical polyanion was separated from the two symmetrical ones $[\text{MnMo}_6\text{O}_{18}\{(\text{OCH}_2)_3\text{CNO}_2\}_2]^{3-}$ and $[\text{MnMo}_6\text{O}_{18}\{(\text{OCH}_2)_3\text{CNH}_2\}_2]^{3-}$ by a series of crystallization–filtration steps from the mother solution. Reaction of the pendant amino group with various aromatic aldehydes led to a family of unsymmetrical polyanions of general formula $[\text{MnMo}_6\text{O}_{18}\{(\text{OCH}_2)_3\text{CNO}_2\}\{(\text{OCH}_2)_3\text{CN}=\text{CH-R}\}]^{3-}$. The purity of the initial unsymmetrical polyanion and the composition of the different species were established by chemical analysis and mass spectrometry.

The same approach has also been used to synthesize organic/inorganic building blocks bearing metal binding sites on opposite sides of a central Lindqvist polyoxovanadate. $[\text{V}_6\text{O}_{13}\{(\text{OCH}_2)_3\text{CCH}_2\text{OC}(\text{O})(4\text{-C}_5\text{H}_4\text{N})\}_2]^{2-}$ and $[\text{V}_6\text{O}_{13}\{(\text{OCH}_2)_3\text{CNHCO}(4\text{-C}_5\text{H}_4\text{N})\}_2]^{2-}$ have been reacted with $[\text{Ru}(\text{CO})(\text{TPP})]^{2+}$ to form molecular hybrid organic/inorganic porphyrin/polyoxovanadates complexes,^{31g} while $[\text{V}_6\text{O}_{13}\{(\text{OCH}_2)_3\text{CNHCO}(4\text{-C}_5\text{H}_4\text{N})\}_2]^{2-}$ has been associated with a variety of divalent metal cations to form coordination polymers reversibly reduced by chemical reductants.³² A similar approach has been recently used by Hill et al. to synthesize a three-dimensional coordination network by reacting Tb^{III} ions and the linking agent 4,4'-bis(pyridine-*N*-oxide) with the preformed $[\text{V}_6\text{O}_{13}\{(\text{OCH}_2)_3\text{C}(\text{NHCH}_2\text{C}_6\text{H}_4\text{-4-CO}_2)\}_2]^{4-}$ hybrid polyanion bearing two pendant carboxylate groups.³³ The coordination polymer with an open-framework structure was used to catalyze the aerobic oxidation of PrSH.

Two types of dendrimers bearing four terminal tris(hydroxymethyl) groups have been reacted with the Dawson polyoxometalate $[\text{H}_4\text{P}_2\text{V}_3\text{W}_{15}\text{O}_{62}]^{5-}$ in dry polar aprotic organic solvents to generate tetra(polyoxometalate) terminated dendrimers.³⁴ Each trisalkoxo ligand caps the $\{\text{V}_3\}$ ring on the top of the Dawson structure. Using the same Dawson structure, a series of trisalkoxopolyoxometalates $[(\text{RC}(\text{CH}_2\text{O})_3)\text{-P}_2\text{V}_3\text{W}_{15}\text{O}_{59}]^{6-}$, with R = CH_3 , NH_2 , NO_2 , has been recently synthesized and structurally characterized (Figure 9).³⁵

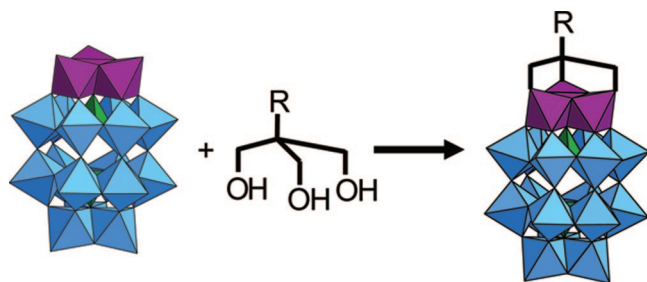


Figure 9. Polyhedral representation of $[(RC(CH_2O)_3)_2P_2V_3W_{15}O_{59}]^{6-}$ ($R = CH_3, NH_2, NO_2$), obtained from the parent $[H_4P_2V_3W_{15}O_{62}]^{5-}$ Dawson-type POM and the adapted triol (ref 35). Blue octahedra, $\{WO_6\}$; purple octahedra, $\{VO_6\}$; green tetrahedra, $\{PO_4\}$.

Depending on the nature of the pendant group R, supramolecular assemblies through H-bonding interactions have been observed in solid, solution, and the gas phase leading to the formation of tetramers or chain structures. Reaction of $[H_4P_2V_3W_{15}O_{62}]^{5-}$ in refluxing dry acetonitrile with two linear bis(tris(hydroxymethyl)) ligands afforded the dimeric hybrid structures $[(P_2V_3W_{15}O_{59}(OCH_2)_3CNHCO)_2]^{12-}$ and $[(P_2V_3W_{15}O_{59}(OCH_2)_3CCH_2)_2O]^{12-}$.³⁶ The structure of the first one was determined using single-crystal X-ray diffraction, and C–H···O hydrogen bonds have been observed between the tetrabutylammonium (TBA) counteranion and oxygen atoms of the dimeric polyanion leading to the formation of one-dimensional channels in the crystal lattice. Static and dynamic light scattering studies of mixed water/acetone solutions of the later polyanion showed the formation of remarkable supramolecular vesicle structures with diameters up to 120 nm. The same Dawson polyoxometalate was also reacted with a series of diols.³⁷ Even if they are not obtained from trisalkoxo ligands, the compounds are described here owing to the similarities with the structures described above. In the series of hybrids of general formula $[P_2V_3W_{15}O_{59}\{(OCH_2)_2C(Et)NHC(O)R\}]^{5-}$ ($R = CH_3, C_6H_4-p-NO_2, C_6H_5, C_6H_4-p-OMe, C_6H_4-p-NEt_2$), the carbonyl oxygen of the amide function replaces one oxygen atom of the $[P_2V_3W_{15}O_{62}]^{5-}$ polyanion. Electrochemical measurements showed the reciprocal influence of the redox properties of the organic ligand on the redox properties of the polyoxometalate.

A family of reduced V^{IV} or mixed-valent V^{IV}/V^V polyoxotrisalkoxovanadates has been obtained using pentaerythritol $C(CH_2OH)_4$ in aqueous solution.³⁸ The same trinuclear building unit $\{V_3O_{13}\}$ or $\{V_3O_{12}F\}$ has been identified in all the structures. In $[H_4V^{IV}_6P_4O_{24}\{(OCH_2)_3CCH_2OH\}_2]^{6-}$ (Figure 10a), $[H_7V^{IV}_{12}V^V_7O_{47}\{(OCH_2)_3CCH_2OH\}]^{7-}$ (Figure 10b), $[V^{IV}_3V^V_4O_{16}F\{(OCH_2)_3CCH_2OH\}]^{4-}$, and $[V^{IV}_{10}V^V_2O_{26}F_2\{(OCH_2)_3CCH_2OH\}_2]^{6-}$ the trisalkoxo ligand caps the tetrahedral cavity of the trinuclear fragment in a $\mu_3\text{-}\kappa^2\text{:}\kappa^2\text{:}\kappa^2$ coordination mode, while the same trisalkoxo ligand adopts a $\mu_4\text{-}\kappa^2\text{:}\kappa^2\text{:}\kappa^2$ coordination mode in $[V^{IV}_2V^V_8O_{22}F_2\{(OCH_2)_3CCH_2OH\}_2]^{4-}$ bridging two $\{VO_5F\}$ octahedra of a trinuclear fragment $\{V_3O_{12}F\}$ and two $\{V^VO_5\}$ square pyramids. Magnetic measurements have been undertaken in order to study the magnetic interactions of the trinuclear unit with the other metal centers constituting the structure. The functionalization of a $\{V_6O_{19}\}$ Lindqvist POM by a calixarene fragment has also been reported.³⁹ The mixed-valent species $[V^{III}V^{IV}_5O_6(OCH_3)_8(\text{calix})(CH_3OH)]^-$ (calix = *p*-tert-butylcalix[4]arene) has been synthesized by solvothermal synthesis in methanol under anaerobic conditions. In this complex, the macrocycle caps the $\{V_6O_{19}\}$ fragment (Figure

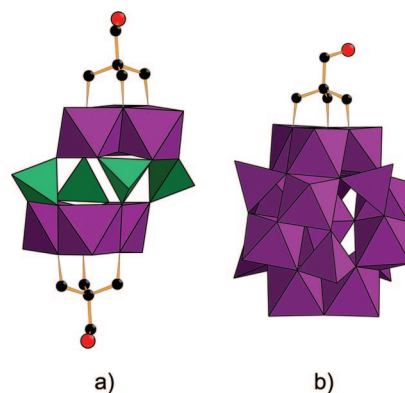


Figure 10. Polyhedral and ball-and-stick representations of the pentaerythritol-substituted polyoxovanadates (a) $[H_4V^{IV}_6P_4O_{24}\{(OCH_2)_3CCH_2OH\}_2]^{6-}$ and (b) $[H_7V^{IV}_{12}V^V_7O_{47}\{(OCH_2)_3CCH_2OH\}]^{7-}$ (ref 38). Purple octahedra, $\{VO_6\}$; green tetrahedra, $\{PO_4\}$; black spheres, C; red spheres, O.

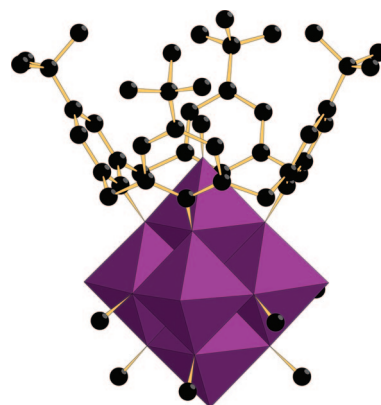


Figure 11. Polyhedral and ball-and-stick representation of the $[V^{III}V^{IV}_5O_6(OCH_3)_8(\text{calix})(CH_3OH)]^-$ anion (ref 39). Purple octahedra, $\{VO_6\}$; black spheres, C.

11). Gouzerh et al. characterized di-, tetra-, octa-, and one tetradecanuclear polyoxotrisalkoxomolybdates but also the rare tetranuclear polyoxotrisalkoxotungstates $[W_4O_{10}\{(OCH_2)_3CCH_3\}_2]^{2-}$.⁴⁰ The same group also prepared a family of organometallic polyoxometalates of variable nuclearity such as $[Mo_6O_{16}(OCH_3)_2\{(OCH_2)_3CCH_3\}_2\{Mn(CO)_3\}_2]^{2-}$ and $[Mo_6O_{18}\{(OCH_2)_3CCH_3\}_2\{Ru(\eta^6-C_6Me_6)\}_2]^{2-}$ in which the trisalkoxo ligands adopt various coordination modes.⁴¹

2.2.2. Other C–O–M Bonds

Carboxylate groups can bind to molybdates in different ways. Monodentate coordination has been observed in the octamolybdate derivatives $[Mo_8O_{26}(L)_2]^{4-}$ ($L = \text{glycine},^{42}$ nicotinic acid,⁴³ alanine,⁴⁴ glycylglycine,⁴⁴ proline⁴⁵) in which two ligands are attached symmetrically to two Mo^{VI} ions. Note that this family of functionalized octamolybdates was first evidenced by Yamase et al. in 1995.⁴⁶ The antitumoral activity of some of these compounds has been investigated.^{44,45}

Each oxygen atom of the carboxylate group can also bind to two different metal ions of the POM framework. This situation is found in the crown-shaped polyoxovanadium(V) cluster cation $[V_6O_{12}(OH)_3(O_2CCH_2CH_2NH_3)_3(SO_4)]^+$,⁴⁷ in Mo^V complexes where $\{Mo_2O_4\}^{2+}$ units are bridged by malonic or succinic acids,⁴⁸ or in the mixed-valence compound $[Mo_6O_{13}(Hsal)_2(\text{sal})_2(\text{acac})_2]$ ($Hsal = \text{salicylic acid}$, $\text{acac} = \text{acetylacetonate}$).⁴⁹ This bridging mode of $RCOO^-$ groups has also been observed in $[Mo_{10}O_{30}(CH_3COO)_4]^{8-}$,⁵⁰ $[Mo_{18}O_{52}(OH)_4(CH_3COO)_2]^{10-}$,⁵¹ and $[Mo_{46}O_{134}(OH)_{10-}$

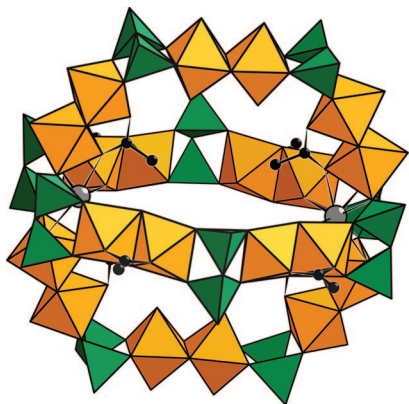


Figure 12. Polyhedral and ball-and-stick representation of the double wheel-shaped POM $[(\text{Mo}_2\text{O}_4)_{10}(\text{P}_2\text{O}_6\text{X})_{10}(\text{CH}_3\text{COO})_8(\text{H}_2\text{O})_4]^{28-}$ ($\text{X} = \text{O}$, ref 53; $\text{X} = \text{CH}_2$, ref 152a). Orange octahedra, $\{\text{MoO}_6\}$; green tetrahedra, $\{\text{PO}_3\text{X}\}$; gray spheres, Na; black spheres, C.

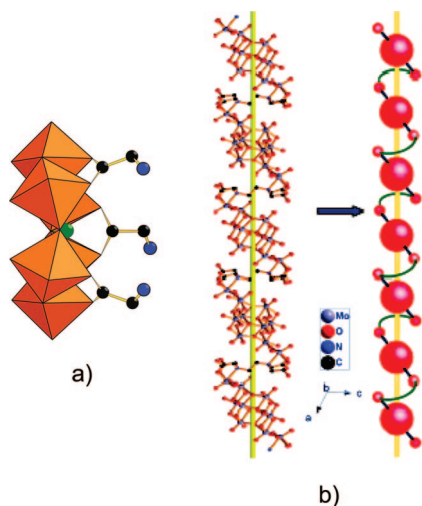


Figure 13. (a) Polyhedral and ball-and-stick representation of the $[\text{SeMo}_6\text{O}_{21}(\text{O}_2\text{CCH}_2\text{NH}_3)_3]^{2-}$ POM (ref 56). Orange octahedra, $\{\text{MoO}_6\}$; green sphere, Se; black spheres, C; blue spheres, N. (b) Representation of the meso-helical chain structure of compound $[\text{Na}_8\{\text{Mo}^{\text{VI}}_{10}\text{O}_{32}(\text{EDTA})\}(\text{H}_2\text{O})_{35}]_n$ (Reprinted with permission from ref 68. Copyright 2008 American Chemical Society).

$(\text{CH}_3\text{COO})_4]^{26-52}$ molybdates. Additionally, the fully reduced complex $[(\text{Mo}_2\text{O}_4)_{10}(\text{P}_2\text{O}_7)_{10}(\text{CH}_3\text{COO})_8(\text{H}_2\text{O})_4]^{28-}$ which possesses a unique double-wheel topology has been described (Figure 12),⁵³ and the polyoxomolybdate complex $[\text{Mo}_4\text{O}_{12}(\text{glycylglycylglycine})_2]^{54}$ with tripeptide ligands has also been characterized.

In the three families of crown-shaped hexamolybdate POMs $[\text{HM}_6\text{VO}_{22}(\text{NH}_3\text{CH}_2\text{COO})_3]^{55}$ $[\text{XM}_6\text{O}_{21}(\text{O}_2\text{CR-NH}_3)_3]^{n-}$ ($\text{X} = \text{Bi}^{\text{III}}$, Sb^{III} , As^{III} , $n = 3$; $\text{X} = \text{Se}^{\text{IV}}$ or Te^{IV} , $n = 2$; $\text{R} = \text{CH}_2$, C_2H_4 , C_3H_6 , CHCH_3 , $\text{CH}[(\text{CH}_2)_4\text{NH}_2]$)⁵⁶ (Figure 13a), and $[\text{RPM}_6\text{O}_{21}(\text{O}_2\text{CCH}_2\text{NH}_3)_3]^{2-}$ ($\text{R} = \text{OH}$, CH_3 , C_2H_5 , H)⁵⁷ the carboxylate groups connect two by two to the metallic ions. Note also that the synthesis under solvothermal conditions of reduced polyoxo(alkoxo)vanadium(III/IV) cages has been realized, leading to compounds which contain numerous bridging carboxylate ligands.⁵⁸ Besides, Modéc et al. studied the reactivity of dicarboxylate^{48,59} and trimesate ligands^{59b} with Mo^{V} precursors. In these complexes, the organic ligand bridges $\{\text{Mo}_2\text{O}_4\}^{2+}$ units.

Chelating ligands can connect via two C–O–M bonds to the same metallic atom of the POM. For example, bidentate oxalato ligands are bound to vanadium ions in the molyb-

dovanadates $[\text{Mo}_6\text{V}_2\text{O}_{24}(\text{C}_2\text{O}_4)_2]^{6-}$ and $[\text{H}_2\text{Mo}_2\text{V}_2\text{O}_{12}(\text{C}_2\text{O}_4)_2]^{4-}$.⁶⁰ acac ligands coming from the $[\text{VO}(\text{acac})_2]$ precursor connect vanadyl moieties attached to an hexavanadate core.⁶¹ Similarly, ligands arising from the $[\text{MoO}_2(\text{acac})_2]$ precursor chelate molybdenum(VI) ions in the tetranuclear $[\text{Mo}_4\text{O}_{10}(\text{acac})_4]$ complex.⁴⁹ They are also present in oxovanadium(IV) and oxovanadium(V) complexes with aminoalcohol ligands⁶² and vanadium(V) alkoxide clusters.⁶³ Chelating and bridging glycolato ligands are observed in the octanuclear POM $[(\text{MoO}_2)_8(\text{glyc})_6(\text{Hglyc})_2]^{64}$ and in the molybdenum(V) POM $[\text{Mo}_4\text{O}_8\text{Cl}_4(\text{glyc})_2]^{4-}$.⁶⁵ A series of crystalline vanadium(V) complexes have also been isolated with bridging and chelating tartrate ligands.⁶⁶ Homocitrate ligands have been found to coordinate molybdenum(VI) ions to form tetranuclear units in $[(\text{MoO}_2)_4\text{O}_3(\text{Hhomocit})_2]^{4-}$ complexes.⁶⁷

Besides these molecular compounds, a few 1D compounds have been described in which the organic ligand connects POM units. For example, chelating and bridging EDTA ($\text{EDTA} = 1,2\text{-diaminoethanetetraacetate}$) ligands bound to capping $\{\text{MoO}_4\}$ tetrahedra allow connection of decamolybdate units to form meso-helical chains (Figure 13b).⁶⁸ Another example is given by the $\{\text{Mo}_2\text{O}_4(\text{C}_2\text{O}_4)\text{Cl}_2\}_n$ polymer where the bischelating oxalate ligands connect $\{\text{Mo}_2\text{O}_4\}^{2+}$ units in zigzag chains.⁶⁹

Finally, besides these numerous families of carboxylate POMs, two squarate systems have been isolated since 1998. In $[\text{Mo}_4\text{O}_8(\text{C}_4\text{O}_4)_4]^{4-}$ ⁷⁰ and $[\text{Mo}_4\text{O}_8(\text{OH})_2(\text{H}_2\text{O})_2(\text{C}_4\text{O}_4)_2]^{2-}$,⁷¹ squarate ligands bridge $\{\text{Mo}_2\text{O}_4\}^{2+}$ units.

2.2.3. Oxothiomolybdenum(V) Wheels

Cadot, Sécheresse et al. discovered in 1998 a new family of cyclic oxothiomolybdate compounds based on the $\{\text{Mo}_2\text{O}_2\text{S}_2\}^{2+}$ building unit.⁷² The nuclearity and geometry of the neutral inorganic ring of general formula $\{\text{Mo}_{2n}\text{O}_{2n}\text{S}_{2n}(\text{OH})_{2n}\}^{2-}$ depend on the nature of the guest organic ligand (Table 1).⁷³ In most cases only one organic ligand is encapsulated in the molybdenum(V) framework but two ligands are sometimes present in the cavity. In this latter case mono- and bitemplated species are in equilibrium and formation of the bitemplated wheel is entropically governed.^{73c} Structures other than rings have been isolated with the oxalate ligand only.⁷⁴ ¹H NMR studies have evidenced dynamic processes for these host–guest systems, favored by the versatility of the Mo^{V} coordination which can be either octahedral or square pyramidal. NMR studies

Table 1. Cyclic Oxothiomolybdate Compounds

	abbreviated formula	ligand/POM ratio	ref
Linear Aiphatic Dicarboxylates			
oxalate ($\text{C}_2\text{O}_4^{2-}$)	$[\text{Mo}_8(\text{ox})]^{2-}$	1:1	73b
succinate ($\text{H}_4\text{C}_4\text{O}_4^{2-}$)	$[\text{Mo}_{12}(\text{succ})_2]^{4-}$	2:1	73c
glutarate ($\text{H}_6\text{C}_5\text{O}_4^{2-}$)	$[\text{Mo}_{10}(\text{glu})]^{2-}$	1:1	73b
	$[\text{W}_{16}(\text{glu})_2]^{4-}$	2:1	75
adipate ($\text{H}_8\text{C}_6\text{O}_4^{2-}$)	$[\text{Mo}_{12}(\text{adip})]^{2-}$	1:1	73d
pimelate ($\text{H}_{10}\text{C}_7\text{O}_4^{2-}$)	$[\text{Mo}_{12}(\text{pim})]^{2-}$	1:1	73b
suberate ($\text{H}_{12}\text{C}_8\text{O}_4^{2-}$)	$[\text{Mo}_{12}(\text{sub})]^{2-}$	1:1	73d
azelaate ($\text{H}_{14}\text{C}_9\text{O}_4^{2-}$)	$[\text{Mo}_{14}(\text{azel})]^{2-}$	1:1	73d
Nonsaturated and Aromatic Carboxylates			
fumarate ($\text{H}_2\text{C}_4\text{O}_4^{2-}$)	$[\text{Mo}_{12}(\text{fum})]^{2-}$	1:1	73c
muconate ($\text{H}_4\text{C}_6\text{O}_4^{2-}$)	$[\text{Mo}_{12}(\text{muco})]^{2-}$	1:1	73f
isophthalate ($\text{H}_4\text{C}_8\text{O}_4^{2-}$)	$[\text{Mo}_{16}(\text{isop})_2]^{4-}$	2:1	73e
terephthalate ($\text{H}_4\text{C}_8\text{O}_4^{2-}$)	$[\text{Mo}_{12}(\text{tere})]^{2-}$	1:1	73e
trimesate ($\text{H}_3\text{C}_6\text{O}_6^{3-}$)	$[\text{Mo}_{12}(\text{trim})]^{3-}$	1:1	73a
phenylenediacetate ($\text{H}_8\text{C}_{10}\text{O}_4^{2-}$)	$[\text{Mo}_{16}(\text{PDA})_2]^{4-}$	2:1	73e
tetramethylterephthalate ($\text{H}_{12}\text{C}_{10}\text{O}_4^{2-}$)	$[\text{Mo}_{12}(\text{TMT})]^{2-}$	1:1	73f

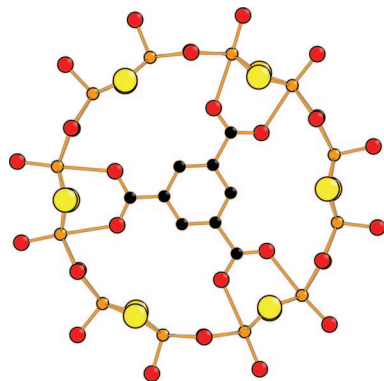


Figure 14. Ball-and-stick representation of the cyclic oxothiomolybdate $[\text{Mo}_{12}\text{S}_{12}\text{O}_{12}(\text{OH})_{12}\{\text{C}_6\text{H}_3(\text{COO})_3\}]^{3-}$ (ref 73f). Orange spheres, Mo; yellow spheres, S; black spheres, C; red spheres, O.

have also allowed determining the relative stabilities of these cyclic species. For example, for $\{\text{Mo}_{12}\}$ species, it has been shown that the $[\text{Mo}_{12}\text{S}_{12}\text{O}_{12}(\text{OH})_{12}\{\text{C}_6\text{H}_3(\text{COO})_3\}]^{3-}$ wheel (Figure 14) was by far the most stable one and that, in general, the encapsulation of rigid ligands leads to the most stable host–guest cyclic architectures. This experimental study was confronted to DFT calculations which have highlighted the important role of encapsulated water molecules.^{73f} Only one tungstate analogue has been successfully isolated, a probable consequence of the instability of the $\{\text{W}_2\text{O}_2\text{S}_2\}^{2+}$ oxothiocation in aqueous solution.⁷⁵ Floquet, Cadot et al. have shown that diffusion-correlated NMR (¹H DOSY) spectroscopy can be a powerful tool for the characterization and speciation of template molybdenum rings in solution.^{73d,e,76} Note also the recent demonstration of the electrocatalytic properties of this class of compounds which have proved to be efficient electrocatalysts for the reduction of protons into hydrogen.⁷⁷

2.2.4. Organosilyl Derivatives

The vast majority of hybrid polyoxometalates containing organosilyl derivatives has been obtained from reactions between lacunary heteropolyoxometalates (Keggin or Dawson lacunary structures) and the appropriate organosilane. The reactivity indeed relies on the nucleophilic properties of the oxygen atoms of the lacuna and the electrophilic properties of the RSi^{3+} group. Two main approaches have been used for the synthesis of these hybrids, depending on the pH-dependent stability of the lacunary heteropolyoxometalate. In the first synthetic strategy, the lacunary heteropolyoxometalate is phase transferred in a suitable organic solvent such as acetonitrile or dmf and is then reacted with an organotrichlorosilane. In the second approach, the lacunary heteropolyoxometalate and the appropriate organotrialkoxosilane are reacted in a mixed solvent such as $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ or $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ in the presence of hydrochloric acid to control the hydrolysis and condensation of the organosilane groups in the lacuna. Of course, this second method necessarily implies the stability of the lacunary heteropolyoxometalate in acidic medium.

As already mentioned in this review, the number and arrangement of the organosilyl groups filling the lacuna of the heteropolyoxometalate are largely related to the topology of this lacuna (Figure 7). The first organosilyl derivative of a lacunary polyoxometalate was described by Knoth in 1979. Reaction of organotrichlorosilanes with $[\alpha\text{-SiW}_{11}\text{O}_{39}]^{8-}$ afforded the anions $[\alpha\text{-SiW}_{11}\text{O}_{39}\{\text{O}(\text{SiR})_2\}]^{4-}$ ($\text{R} = \text{C}_2\text{H}_5$,

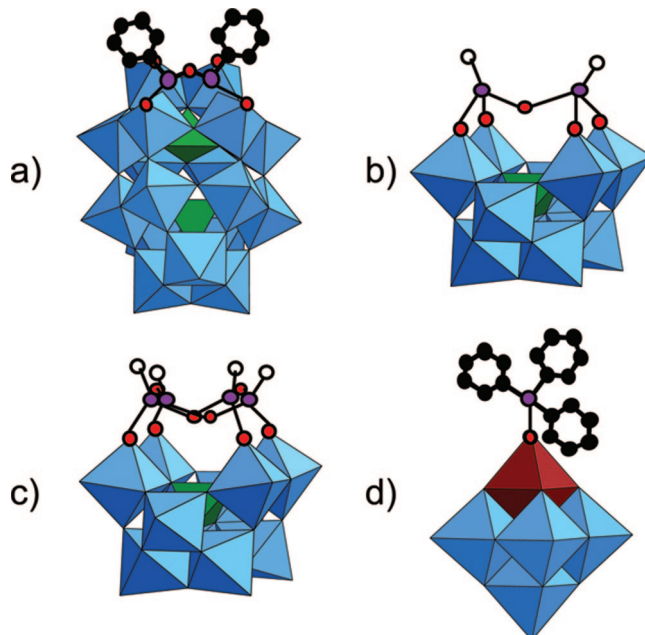


Figure 15. Polyhedral and ball-and-stick representations of the POMs (a) $[\text{P}_2\text{W}_{17}\text{O}_{61}(\text{PhSi})_2\text{O}]^{6-}$ (ref 83a), (b) $[\gamma\text{-SiW}_{10}\text{O}_{36}(\text{HSi})_2\text{O}]^{4-}$ (ref 84b), (c) $[\gamma\text{-SiW}_{10}\text{O}_{36}(\text{HSiO})_4]^{4-}$ (ref 84b), and (d) $[\text{NbW}_5\text{O}_{19}(\text{Ph}_3\text{Si})]^{2-}$ (ref 90). Blue octahedra, $\{\text{WO}_6\}$; green tetrahedra, $\{\text{XO}_4\}$ ($\text{X} = \text{P}$ or Si); brown octahedron, $\{\text{NbO}_6\}$; purple spheres, Si; black spheres, C; red spheres, O; white spheres, H.

C_6H_5 , $\text{NC}(\text{CH}_2)_3$, C_3H_5).⁷⁸ Until recently, only organosilyl derivatives of monovacant Keggin structures had been described and more specifically organosilyl derivatives of $[\text{XW}_{11}\text{O}_{39}]^{y-}$ ($\text{X} = \text{Si}$, $y = 8$; $\text{X} = \text{P}$, $y = 7$). Organosilyl fragments are either preformed and inserted in the lacunary polyanion⁷⁹ or an organosilyl fragment bearing a reactive pendant group is first inserted in the lacuna and the reactive pendant group is then further postfunctionalized, leading to families of functionalized polyoxometalates. The hybrid $[\text{PW}_{11}\text{O}_{39}\{\text{O}(\text{SiCH}=\text{CH}_2)_2\}]^{3-}$ has been used in hydrosilylation reactions to form $[\text{PW}_{11}\text{O}_{39}\{\text{O}(\text{SiCH}_2\text{CH}_2\text{SiR}'_2\text{R}')\}]^{3-}$ ($\text{R} = \text{R}' = \text{Et}$ or $\text{R} = \text{Me}$, $\text{R}' = \text{Ph}$),^{79b} while $[\text{PW}_{11}\text{O}_{39}\{\text{O}(\text{SiPh})_2\}]^{3-}$ has been involved in a coupling reaction under microwave irradiation, affording $[\text{PW}_{11}\text{O}_{39}\{\text{O}(\text{SiPhC}\equiv\text{CR})_2\}]^{3-}$ (with $\text{R} = \text{SiMe}_3$, Ph-tpy).²⁵ Metallosalen/polyoxometalate hybrids have been synthesized in three steps.⁸⁰ $[\text{SiW}_{11}\text{O}_{39}\{\text{O}(\text{Si}(\text{CH}_2)_3\text{NH}_2)_2\}]^{4-}$ was first synthesized and then reacted with salicylaldehyde to yield $[\text{SiW}_{11}\text{O}_{39}\{\text{O}(\text{Si}(\text{CH}_2)_3\text{N}=\text{CH}(2\text{-OHPh})_2\}]^{4-}$. The later anion was finally reacted with various metal ions, affording a family of metallosalen/polyoxometalate hybrids (salen = N,N' -bis(salicylidene)ethylenediamine).^{80,81} Bar-Nahum and Neumann also described the two-step synthesis of the Wilkinson's-type hybrid polyoxometalate $[\text{SiW}_{11}\text{O}_{39}\{\text{O}(\text{Si}(\text{CH}_2)_2\text{PPh}_2)_2\text{Rh}(\text{Cl})\text{PPh}_3\}]^{4-}$.⁸² The functionalization of monovacant heteropolyoxometalates has been lately extended to the Dawson polyoxometalate $[\text{P}_2\text{W}_{17}\text{O}_{61}]^{10-}$.⁸³ In all these organosilyl hybrid structures, the lacuna defined by four oxygen atoms of the polyoxometalate are filled by a dimeric μ -oxo-bridged $(\text{RSi})_2\text{O}$ group (Figure 15a). The tetrahedral environment of each silicon atom is provided by two oxygen atoms of the polyoxometalate, the bridging oxygen atom and the organic unit R.

Alternatively, divacant polyoxometalates $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$ and $[\gamma\text{-PW}_{10}\text{O}_{36}]^{7-}$ have proven to be much more versatile platforms to accommodate organosilane groups with a variety of structural arrangements. The 'classical' dimeric μ -oxo-

bridged (RSi)₂O group has been found in several hybrids derived from the [γ -SiW₁₀O₃₆]⁸⁻ polyanion (Figure 15b).⁸⁴ By using [γ -SiW₁₀O₃₆]⁸⁻ and organotrialkoxysilane in stoichiometric proportions, Thouvenot et al. isolated a series of hybrids containing either the dimeric μ -oxo-bridged (RSi)₂O group or the cyclotetrasiloxane (RSiO)₄ group (Figure 15b and 15c) capping the lacuna of the Keggin structure.^{84b} The tetrafunctionalized polyanions of general formula [γ -SiW₁₀O₃₆(OSiR)₄]⁴⁻ have then been used to generate hydrogels or ordered macroporous silica materials.^{21,85} In the [γ -PW₁₀O₃₆(*t*-BuSiOH)₂]³⁻ hybrid polyanion, the two organosilyl groups are connected to the Keggin backbone but are not directly connected together, except through an intramolecular hydrogen bond.⁸⁶ The absence of direct bonding usually observed in the dimeric μ -oxo-bridged (RSi)₂O group may be explained by the presence of a bulky organic unit. Reaction of [γ -PW₁₀O₃₆(*t*-BuSiOH)₂]³⁻ with an excess of Me₂SiCl₂ in deaerated dmf led to the new [γ -PW₁₀O₃₆(*t*-BuSiO)₂(SiMe₂)]³⁻ polyanion in which the two *t*-BuSiO groups are connected by the SiMe₂ fragment. The structure has been inferred from multinuclear NMR and infrared spectroscopies.⁸⁶

The same type of strategy has been used for the functionalization of the trivacant [PW₉O₃₄]⁹⁻ polyanion. In [PW₉O₃₄(*t*-BuSiOH)₃]³⁻ the three organosilyl groups are not directly connected but the functionalized polyanion further reacts with a 3-fold excess of RSiCl₃ in dmf to yield a series of complexes of general formula [PW₉O₃₄(*t*-BuSiO)₃(SiR)]³⁻ in which the lacunary Keggin structure is filled by a tetrameric heterosilyl group.⁸⁷ As for the isostructural homosilylated hybrids of general formula [PW₉O₃₄(RSiO)₃(SiR)]³⁻, they have been obtained from the direct reaction of the appropriate organotrichlorosilane with [β -A-PW₉O₃₄]⁹⁻ in acetonitrile.⁸⁸ Structures of the complexes [PW₉O₃₄(*t*-BuSiOH)₂{*t*-BuSi(OH)₂}]⁴⁻ and [PW₉O₃₄(*t*-BuSiOH)₂]⁵⁻, obtained from the controlled alkaline hydrolysis of [PW₉O₃₄(*t*-BuSiOH)₃]³⁻, have been inferred from multinuclear (²⁹Si, ³¹P, ¹⁸³W) NMR studies.²⁶

Two niobium-containing polyoxotungstates have been functionalized by organosilyl groups. In both cases the silicon atom is connected to the polyoxometalate backbone through a Si–O–Nb junction. [PW₁₁O₃₉NbO(SiMe₃)]³⁻ was obtained from reaction of [PW₁₁O₃₉NbO]⁴⁻ with Me₃SiOTf in acetonitrile,⁸⁹ while reaction of [(NbW₅O₁₈)₂O]⁴⁻ with RR'₂SiOH in dichloromethane or acetonitrile led to the family of polyanions [NbW₅O₁₉(SiRR'₂)₃]²⁻ (R = R' = Et, *i*-Pr, *o*-t-Bu, Ph; R = *t*-Bu, R' = Me) (Figure 15d).⁹⁰

2.2.5. Organotin Derivatives

Organotins have been extensively used in the past few years to synthesize organic/inorganic hybrid polyoxometalates. The use of organotin species is of specific interest for several reasons: (i) the relatively high stability of the Sn–C bond toward hydrolysis, (ii) the similar size of Sn^{IV} and W^{VI} and therefore the facile inclusion of organotin fragments in lacunary polyoxotungstates to ‘simply’ fill the lacuna or act as cationic linkers between polyoxometalates, (iii) the possibility to use mono- or diorganotin with various organic pendant groups, (iv) the different coordination numbers of Sn which range from 5 to 7, and (v) the ability to characterize the species in solution using multinuclear NMR spectroscopy such as ¹¹⁹Sn NMR. The syntheses of the organotin derivatives are essentially performed in water by reaction of organotrichlorotin reagents with preformed lacunary poly-

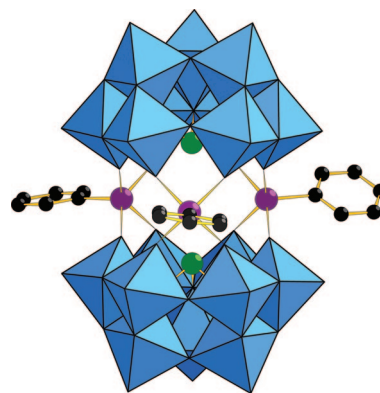


Figure 16. Polyhedral and ball-and-stick representation of [(PhSn)₃-Na₃(α -SbW₉O₃₃)₂]⁶⁻ (ref 93). Blue octahedra, {WO₆}; purple spheres, Sn; green spheres, Sb; black spheres, C.

oxometalates. This approach has been occasionally modified, for example, to avoid isomerization of the lacunary polyoxometalate.⁹¹

Four groups have mainly contributed to the development of the chemistry of organotin derivatives of polyoxometalates since 1998. The group of Liu studied the reactivity of monoorganotin moieties with mono-, di-, and trivacant Keggin or monovacant Dawson heteropolyoxotungstates.⁹² They used four different organotin fragments, {SnPh}³⁺,^{92a} {Sn(CH₂)₂CN}³⁺,^{92b,c} {Sn(CH₂)₂C(O)OCH₃}³⁺, and {CH₂-CH(CH₃)C(O)OCH₃}³⁺^{92b-d} and studied the antitumoral activity of these hybrids to Hela and SSMC-7721 tumor cells.^{92b-d}

The group of Pope synthesized two dimers of the trivacant polyoxometalates [α -XW₉O₃₃]⁹⁻ (X = As^{III}, Sb^{III}). The two tungstoantimonates are connected by three phenyltin fragments and three sodium ions, forming a central ring in [(PhSn)₃Na₃(α -SbW₉O₃₃)₂]⁶⁻ (Figure 16), while four phenyltin fragments are sandwiched between the two polyoxometalates in [{(PhSn)₂O}H(α -SbW₉O₃₃)₂]⁹⁻.⁹³ The same group used a different and original approach to form dimers of trivacant polyoxometalates by displacement of metal centers from preformed heteropolyoxometallic structures. The reaction of transmetalation between [WM₃(H₂O)₂(MW₉-O₃₄)₂]¹²⁻ and the appropriate organotin trichloride in aqueous solution led to the family of hybrids of general formula [WM(RSn)₂(MW₉O₃₄)₂]¹⁰⁻ (M = Co, Zn; R = CH₃, C₂H₅, *n*-C₄H₉).⁹⁴ Using the same approach, displacement of cerium by {SnCH₃}³⁺ afforded [CH₃SnW₅O₁₈]³⁻ in moderate yield. In the same article, dimers of the monovacant [SiW₁₁O₃₉]⁸⁻ polyanion and linear oligomers of the trivacant [WZn₃(H₂O)₂(ZnW₉O₃₄)₂]¹²⁻ polyanion have been synthesized by reaction with the ditin linker Cl₃Sn(CH₂)₄SnCl₃ in dmf.

Over the past few years, the group of Kortz has been one of the main contributors to the development of the chemistry of organotin-containing polyoxometalates.⁹⁵⁻¹⁰¹ They used only two different organotin fragments, namely, the monophenyltin {SnPh}³⁺ and the dimethyltin {Sn(CH₃)₂}²⁺, which have been reacted with different preformed polyoxometalates to generate a variety of unprecedented structures ranging from monomeric, dimeric, trimeric, tetrameric, and dodecameric molecular systems to three-dimensional assemblies. The reactivity of dimethyltin moiety was initially developed to obtain structures of large size or higher dimensionality compared with monoorganotin fragments that lead mainly to monomeric or dimeric structures. For example, the tetrameric [{Sn(CH₃)₂(H₂O)}₂{Sn(CH₃)₂}As₃(α -AsW₉O₃₃)₄]²¹⁻ (Figure 17)⁹⁶ and

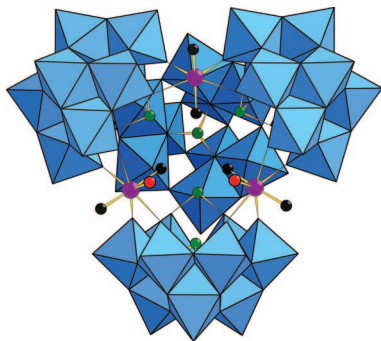


Figure 17. Polyhedral and ball-and-stick representation of $[\{\text{Sn}(\text{CH}_3)_2(\text{H}_2\text{O})\}_2\{\text{Sn}(\text{CH}_3)_2\}\text{As}_3(\alpha\text{-AsW}_9\text{O}_{33})_4]^{21-}$ (ref 96). Blue octahedra, $\{\text{WO}_6\}$; purple spheres, Sn; green spheres, As; red spheres, O; black spheres, C.

the dodecameric $[\{\text{Sn}(\text{CH}_3)_2(\text{H}_2\text{O})\}_{24}\{\text{Sn}(\text{CH}_3)_2\}_{12}(\text{A-XW}_9\text{O}_{34})_{12}]^{36-}$ ($\text{X} = \text{P}^{\text{V}}, \text{As}^{\text{V}}$)⁹⁷ polyanions illustrate the remarkable diversity of architectures available using the linking properties of the dimethyltin fragment. Kortz et al. also recently showed the crucial role of the guanidinium counterion to selectively crystallize hybrid polyanions present as minor species in solution⁹⁸ or to act as template agent for the synthesis of the isostructural three-dimensional series of polyanions $[\{(\text{CH}_3)_2\text{Sn}(\text{H}_2\text{O})\}_3(\text{A-}\alpha\text{-XW}_9\text{O}_{34})]^{n-}$ ($\text{X} = \text{P}^{\text{V}}, \text{As}^{\text{V}}; n = 3; \text{X} = \text{Si}^{\text{IV}}; n = 4$)⁹⁹. The list of compounds is given in Table 2. These compounds have been studied in the solid state using single-crystal X-ray diffraction, but their stability in solution was also studied using multinuclear NMR spectroscopy. Apart from hybrids derived from lacunary polyoxometalates, Kortz et al. also described the structure of a hexatungstate fragment stabilized by two dimethyltin groups in $[\{(\text{CH}_3)_2\text{Sn}\}_2(\text{W}_6\text{O}_{22})]^{4-}$ and a series of two-dimensional, $[\{(\text{CH}_3)_2\text{Sn}\}_4\text{O}_2(\text{MoO}_4)_2]$ and $[\{(\text{CH}_3)_2\text{Sn}\}\{\text{Mo}_2\text{O}_7(\text{H}_2\text{O})_2\}]$, - and three-dimensional, $[\{(\text{CH}_3)_2\text{Sn}\}(\text{MoO}_4)]$, molybdate hybrids.^{100,101}

Hasenkopf, Thorimbert, Lacôte et al. mainly focused on the reactivity of lacunary Dawson polyoxometalates with monoorganotin trichloride.^{91,102} The aim of the studies was to attach a pendant reactive group such as carboxylic acid, alkyne, or azide and further react these pendant groups through amide bond formation or click chemistry in order to graft a large variety of organic functions onto polyoxometalates. Mono-organotin derivatives of the monovacant $[\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61}]^{10-}$ isomer were successfully synthesized using ‘classical’ aqueous synthesis. The same approach with the chiral $[\alpha_1\text{-P}_2\text{W}_{17}\text{O}_{61}]^{10-}$ isomer led to its isomerization to the α_2 isomer. Therefore, monoorganotin derivatives of the $[\alpha_1\text{-P}_2\text{W}_{17}\text{O}_{61}]^{10-}$ isomer have been eventually obtained using

a phase-transfer approach and performing the reaction in acetonitrile. Among the monoorganotin derivatives, the two functionalized polyoxometalate isomers containing a pendant carboxylic group $\alpha_1\text{-}$ and $\alpha_2\text{-}[\text{P}_2\text{W}_{17}\text{O}_{61}\{\text{Sn}(\text{CH}_2)_2\text{CO}_2\text{H}\}]^{7-}$ have been reacted in acetonitrile with a large variety of organic molecules to generate an extended family of hybrids. This coupling technique allowed, among others, the first direct observation of the two pure $\alpha_1\text{-}$ stereoisomers using multinuclear NMR spectroscopy.⁹¹

Other groups contributed to the chemistry of tin-containing polyoxometalates. Neumann et al. described the synthesis of tin-centered adducts of general formula $[\text{PW}_{11}\text{O}_{39}\{\text{SnCl}\}]^{4-}$ -amine or -phosphine by reaction of the tetrahexyl ammonium salt of $[\text{PW}_{11}\text{O}_{39}\{\text{SnCl}\}]^{4-}$ with primary, secondary, and tertiary amines or a tertiary phosphine in THF.¹⁰³ Adducts were characterized by multinuclear NMR, ESI-MS, and elemental analyses. Formation of a covalent Sn–N bond in $[\text{PW}_{11}\text{O}_{39}\{\text{SnN}[\text{CH}(\text{CH}_3)_2]_2\}]^{4-}$ has been also evidenced from NMR measurements. The same approach has been successfully applied for the synthesis of polyoxometalate–amino acid complexes. A novel organotin-containing polyoxomolybdate with 34 molybdenum atoms and four $\{\text{BuSn}\}^{3+}$ fragments has been recently synthesized using a one-pot procedure.¹⁰⁴ The structure of this polyanion indeed is reminiscent of those of the well-known giant architectures reported by Müller et al.¹⁸ Finally, recent time-dependent DFT calculations showed that the trisubstituted polyanions of general formula $[\beta\text{-XW}_9\text{O}_{37}\{\text{SnR}_3\}]^{n-}$ ($\text{X} = \text{P}, \text{Si}, \text{Ge}, \text{R} = \text{Ph}; \text{X} = \text{Si}, \text{R} = \text{PhNO}_2, \text{PhC}\equiv\text{CPh}$) form a promising family of hybrids for second-order nonlinear optical properties.¹⁰⁵

2.2.6. Organogermyl Derivatives

Contrary to organosilyl and organotin derivatives, very few papers describe the functionalization of polyoxometalates by organogermyl groups. $[\text{PW}_{11}\text{O}_{39}\text{NbO}(\text{EMe}_3)]^{3-}$ ($\text{E} = \text{Ge}, \text{Sn}, \text{Pb}$) were obtained from the reaction of in-situ-generated Me_3EOTf and $[\text{PW}_{11}\text{O}_{39}\text{NbO}]^{4-}$ in acetonitrile.⁸⁹ The X-ray structure of the organogermyl derivative confirmed the connection of the $\{\text{Me}_3\text{Ge}\}^+$ group to the polyoxometalate via a Ge–O–Nb bridge, while multinuclear NMR spectroscopy supports a similar structure for the Si, Sn, and Pb derivatives. These hybrids react stoichiometrically with the weak acids $n\text{-Bu}_4\text{NX}$ ($\text{X} = \text{O}_2\text{CCH}_3, \text{F}, \text{Cl}, \text{Br}, \text{I}$) to form the polyanion $[\text{PW}_{11}\text{O}_{39}\text{NbO}]^{4-}$ and Me_3EX ($\text{E} = \text{Ge}, \text{Sn}, \text{Pb}$).

A family of organogermyl and organotin derivatives of Keggin anions has been recently described by Pope et al.¹⁰⁶

Table 2. Organotin Compounds

formula	dimensionality	ref
$[\{(\text{C}_6\text{H}_5)\text{Sn}(\text{OH})\}_3(\text{A-}\alpha\text{-GeW}_9\text{O}_{34})]^{4-}$, $[\{(\text{C}_6\text{H}_5)\text{Sn}(\text{OH})\}_3(\text{A-}\alpha\text{-HGeW}_9\text{O}_{34})]^{3-}$, $[\{(\text{C}_6\text{H}_5)\text{Sn}(\text{OH})\}_3(\text{A-}\alpha\text{-SiW}_9\text{O}_{34})]^{4-}$	0D, monomer	95f
$[(\text{PhSn})_2\text{As}_2\text{W}_{19}\text{O}_{67}(\text{H}_2\text{O})]^{8-}$	0D, dimer	95b
$[\{\text{Sn}(\text{CH}_3)_2\}_4(\text{H}_2\text{P}_4\text{W}_{24}\text{O}_{92})]^{28-}$	0D, dimer	95c
$[\{\text{Sn}(\text{CH}_3)_2\}_6(\text{OH})_2\text{O}_2(\text{H}_2\text{BW}_{13}\text{O}_{46})]^{12-}$	0D, dimer	95e
$[\{\text{PhSn}(\text{OH})\}_3(\text{A-}\alpha\text{-H}_3\text{SiW}_9\text{O}_{34})]^{8-}$	0D, dimer	95f
$[\{(\text{CH}_3)_2\text{Sn}(\text{H}_2\text{O})\}_4\{(\text{CH}_3)_2\text{Sn}\}(\text{B-}\beta\text{-XW}_9\text{O}_{33})_2]^{8-}$ ($\text{X} = \text{As}^{\text{III}}, \text{Sb}^{\text{III}}$)	0D, dimer	98
$[\{\text{Sn}(\text{CH}_3)_2\}(\text{Sn}(\text{CH}_3)_2\text{O})(\text{A-PW}_9\text{O}_{34})_3]^{21-}$	0D, trimer	95d
$[\{\text{Sn}(\text{CH}_3)_2(\text{H}_2\text{O})\}_2\{\text{Sn}(\text{CH}_3)_2\}\text{As}_3(\alpha\text{-AsW}_9\text{O}_{33})_4]^{21-}$	0D, tetramer	96
$[\{\text{Sn}(\text{CH}_3)_2(\text{H}_2\text{O})\}_{24}\{\text{Sn}(\text{CH}_3)_2\}_{12}(\text{A-XW}_9\text{O}_{34})_{12}]^{36-}$ ($\text{X} = \text{P}^{\text{V}}, \text{As}^{\text{V}}$)	0D, dodecamer	97
$[\{\text{Sn}(\text{CH}_3)_2\}_3(\text{H}_2\text{O})_4(\beta\text{-XW}_9\text{O}_{33})]^{3-}$ ($\text{X} = \text{As}^{\text{III}}, \text{Sb}^{\text{III}}$)	2D	95a
$[\{(\text{CH}_3)_2\text{Sn}(\text{H}_2\text{O})\}_3(\text{A-}\alpha\text{-XW}_9\text{O}_{34})]^{n-}$ ($\text{X} = \text{P}^{\text{V}}, \text{As}^{\text{V}}; n = 3; \text{X} = \text{Si}^{\text{IV}}; n = 4$)	3D	99

Table 3. Crystal Structures of Organonitrogen Derivatives of Lindqvist POMs Reported After 1998

formula	ref
monomeric organoimido	
(a) monofunctionalized $[\text{MoW}_5\text{O}_{18}(\text{NAr})]^{2-}$ anions	
Ar = $\text{C}_6\text{H}_3\text{-2,6-(CH}_3)_2$; $\text{C}_6\text{H}_2\text{-2,6-(CH}_3)_2\text{-4-I}$	113
(b) monofunctionalized $[\text{Mo}_6\text{O}_{18}(\text{NR})]^{2-}$ and $[\text{Mo}_6\text{O}_{18}(\text{NAr})]^{2-}$ anions	
R = Bu; Cy (Cy = cyclohexyl)	110
R = Me, Et; <i>n</i> -Pr; <i>i</i> -Pr; <i>n</i> -Bu; <i>t</i> -Bu; Cy; Hex; Ode (Ode = octadecyl)	121f
R = $\text{C}_6\text{H}_{10}\text{-1-(CH}_3)_4\text{-OH}$	121g
Ar = $\text{C}_6\text{H}_4\text{-2-CH}_3$	116g, 117
Ar = $\text{C}_6\text{H}_4\text{-2-CF}_3$; $\text{C}_6\text{H}_4\text{-4-OCF}_3$	124b
Ar = $\text{C}_6\text{H}_4\text{-2-F}$; $\text{C}_6\text{H}_4\text{-4-F}$; $\text{C}_6\text{H}_3\text{-2-(CH}_3)_4\text{-F}$; $\text{C}_6\text{H}_3\text{-3-(CH}_3)_4\text{-F}$	124a
Ar = $\text{C}_6\text{H}_4\text{-3-Cl}$	121e
Ar = $\text{C}_6\text{H}_4\text{-3-NO}_2$; $\text{C}_6\text{H}_3\text{-2-(CH}_3)_4\text{-NO}_2$; $\text{C}_6\text{H}_3\text{-2-(CH}_3)_5\text{-NO}_2$	123
Ar = $\text{C}_6\text{H}_4\text{-4-Cl}$	117, 121e
Ar = $\text{C}_6\text{H}_4\text{-4-Br}$	121b
Ar = $\text{C}_6\text{H}_4\text{-4-OH}$; $\text{C}_6\text{H}_3\text{-1-(CH}_3)_4\text{-OH}$; $\text{C}_{10}\text{H}_6\text{-6-OH}$	121g
Ar = $\text{C}_6\text{H}_4\text{-4-(CH=CH}_2)$	19
Ar = $\text{C}_6\text{H}_4\text{-4-OCH}_3$	116b
Ar = $\text{C}_6\text{H}_4\text{-4-CN}$	111
Ar = $\text{C}_6\text{H}_4\text{-4-[N(CH}_3)_2]$	121c
Ar = $\text{C}_6\text{H}_4\text{-4-COOMe}$; $\text{C}_6\text{H}_4\text{-4-COOEt}$	116q
Ar = $\text{C}_6\text{H}_3\text{-2,6-(CH}_3)_2$; $\text{C}_6\text{H}_2\text{-2,6-(CH}_3)_2\text{-4-I}$; $\text{C}_6\text{H}_2\text{-2,6-(CH}_3)_2\text{-4-C}\equiv\text{CH}$	112
Ar = $\text{C}_6\text{H}_3\text{-2,6-(i-Pr)}_2$	110
Ar = $\text{C}_6\text{H}_3\text{-2-(CH}_3)_4\text{-OH}$; $\text{C}_6\text{H}_3\text{-2-(CH}_3)_4\text{-OCOR}$ with R = CH ₃ , CH=CH ₂ , $\text{C}_6\text{H}_4\text{-4-Cl}$	116p
Ar = $\text{C}_6\text{H}_3\text{-2-(CH}_3)_4\text{-Br}$; $\text{C}_6\text{H}_2\text{-2,6-(CH}_3)_2\text{-4-Br}$	121d
Ar = $\text{C}_6\text{H}_2\text{-2,6-(CH}_3)_2\text{-4-[C}\equiv\text{C-C}_6\text{H}_4\text{-4-(CH}_3)_3]$	121a
Ar = $\text{C}_6\text{H}_2\text{-2,6-(CH}_3)_2\text{-4-CH=CR}^1\text{R}^2$ with R ¹ = H, R ² = C_6H_5 , CO ₂ Et, CN; R ¹ = CH ₃ , R ² = CO ₂ Me	121h
Ar = $\text{C}_6\text{H}_2\text{-2,6-(CH}_3)_2\text{-4-[C}\equiv\text{C-C}_6\text{H}_3\text{-2,5-(C}\equiv\text{CH)]}$	20
Ar = $\text{C}_6\text{H}_2\text{-2,6-(CH}_3)_2\text{-4-(C}\equiv\text{C-Fc)}$ with Fc = ferrocene	116e
Ar = $\text{C}_6\text{H}_2\text{-2,6-(CH}_3)_2\text{-4-C}\equiv\text{C-tpy}$	114
Ar = naphthalene	120a
Ar = 2-methylnaphthalene	120b
(c) difunctionalized $[\text{Mo}_6\text{O}_{17}(\text{NAr})_2]^{2-}$ anions	
cis	
Ar = $\text{C}_6\text{H}_4\text{-2-CH}_3$	116d,g
Ar = $\text{C}_6\text{H}_4\text{-2-CF}_3$	116f
Ar = $\text{C}_6\text{H}_4\text{-2-OCH}_3$	116m
Ar = $\text{C}_6\text{H}_4\text{-4-OH}$; $\text{C}_6\text{H}_3\text{-1-(CH}_3)_4\text{-OH}$	121g
Ar = $\text{C}_6\text{H}_3\text{-2,4-(OCH}_3)_2$	116h
Ar = $\text{C}_6\text{H}_3\text{-2,6-(CH}_3)_2$	116n
Ar = $\text{C}_6\text{H}_3\text{-2,6-(i-Pr)}_2$	110
Ar = $\text{C}_6\text{H}_2\text{-2,6-(i-Pr)}_2\text{-4-I}$	115
Ar = $\text{C}_6\text{H}_2\text{-2,6-(i-Pr)}_2\text{-4-C}\equiv\text{CH}$	116i
Ar = $\text{C}_6\text{H}_2\text{-2,6-(i-Pr)}_2\text{-4-C}\equiv\text{C-tpy}$	116j
trans	
Ar = $\text{C}_6\text{H}_3\text{-2,4-(CH}_3)_2$	118
Ar = $\text{C}_6\text{H}_3\text{-2,6-(CH}_3)_2$	22
(d) multifunctionalized $[\text{Mo}_6\text{O}_{19-x}(\text{NAr})_x]^{2-}$ anions ($x > 2$)	
Ar = $\text{C}_6\text{H}_3\text{-2,6-(i-Pr)}_2$	110
Ar = $\text{C}_6\text{H}_3\text{-2,6-(CH}_3)_2$	122
$[\text{O}_{18}\text{Mo}_6\text{N(R)NMo}_6\text{O}_{18}]^{4-}$ dimers	
R = $(\text{C}_2\text{H}_5)_3\text{C}\equiv\text{C}(\text{C}_2\text{H}_5)$	116o
R = $\text{C}(\text{OCH}_2)_3\text{MMo}_6\text{O}_{18}(\text{OCH}_2)_3\text{C}$ with M = Mn ^{III} , Fe ^{III}	116s
R = $\text{C}_6\text{H}_4\text{-C}_6\text{H}_4$; $2\text{-(CH}_3)_2\text{-C}_6\text{H}_3\text{-C}_6\text{H}_3\text{-2-(CH}_3)_2$	116r
R = $\text{C}_6\text{H}_4\text{-4-(phen)-4-C}_6\text{H}_4$ with phen = 1,10-phenanthroline	116k
R = $2,6\text{-(i-Pr)}_2\text{-C}_6\text{H}_2\text{-4-(3,3'-diethynyl-2,2'-diethoxyl-1,1'-binaphthalene)-4-C}_6\text{H}_2\text{-2,6-(i-Pr)}_2$	116l
R = $2,6\text{-(i-Pr)}_2\text{-C}_6\text{H}_2\text{-4-(6,6'-diethynyl-2,2'-diethoxyl-1,1'-binaphthalene)-4-C}_6\text{H}_2\text{-2,6-(i-Pr)}_2$	116l
R = $2,6\text{-(CH}_3)_2\text{-C}_6\text{H}_2\text{-4-C}\equiv\text{C-4-C}_6\text{H}_2\text{-2,6-(CH}_3)_2$	116a

Organogermyl derivatives of general formula $[\text{TW}_{11}\text{O}_{39}\{\text{Ge}(\text{CH}_2)_2\text{X}\}]^{n-}$ (T = Si, $n = 5$; Ga, $n = 6$; X = COOH, COOCH₃, CONH₂) have been obtained by reaction of the trichlorogermanes $\text{Cl}_3\text{Ge}(\text{CH}_2)_2\text{X}$ with the monovacant polyoxotungstate and characterized by multinuclear NMR spectroscopy. Esterification and amidation of the carboxylate derivatives led to hybrids $[\text{SiW}_{11}\text{O}_{39}\{\text{Ge}(\text{CH}_2)_2\text{COOC}_2\text{H}_5\}]^{5-}$ and $[\text{SiW}_{11}\text{O}_{39}\{\text{Ge}(\text{CH}_2)_2\text{CONHCH}_2\text{COOCH}_3\}]^{5-}$, respectively. Finally, the preformed tetra(trichlorogermane) derived from pentaerythritol tetraacrylate ($\text{Cl}_3\text{Ge}(\text{CH}_2)_2\text{COOCH}_2)_4\text{C}$ has been reacted in a mixed solvent $\text{H}_2\text{O}/\text{dmf}$ with 4 equiv of $[\text{SiW}_{11}\text{O}_{39}]^{8-}$ to yield the tetrameric polyoxometalate $[\{\text{SiW}_{11}\text{O}_{39}\text{Ge}(\text{CH}_2)_2\text{COOCH}_2\}_4\text{C}]^{20-}$.¹⁰⁶

2.3. p-Elements from Column V

2.3.1. Organoimido Derivatives

The great majority of organoimido derivatives POMs are based on Lindqvist-type polyoxomolybdates. The first description of an organoimido derivative was published by Zubieta et al. in 1988 from the reaction of $[\text{Mo}(\text{NR})\text{Cl}_4(\text{thf})]$ and $[\text{Mo}_2\text{O}_7]^{2-}$ to yield $[\text{Mo}_6\text{O}_{18}(\text{NR})]^{2-}$.¹⁰⁷ Maatta et al. then prepared in 1992 the tolylimido derivative $[\text{Mo}_6\text{O}_{18}(\text{Ntol})]^{2-}$ by reaction of $[\text{Mo}_6\text{O}_{19}]^{2-}$ with $\text{Ph}_3\text{P}=\text{Ntol}$ and reported the first X-ray characterization of an organoimido derivative,¹⁰⁸ thus opening the way to a large and still growing family of derivatives. As for the previous parts of this review, we will

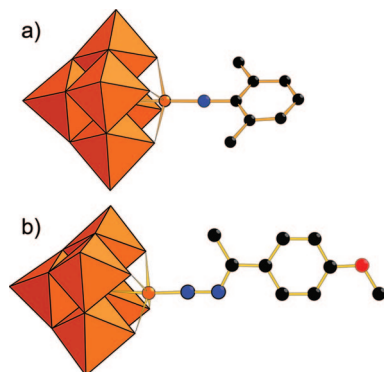


Figure 18. Polyhedral and ball-and-stick representations of (a) the organoimido derivative $[\text{Mo}_6\text{O}_{18}\{\text{N}(\text{C}_6\text{H}_3(\text{CH}_3)_2)\}]^{2-}$ (ref 112); (b) the organodiazenido derivative $[\text{Mo}_6\text{O}_{18}\{\text{N}_2\text{C}(\text{C}_6\text{H}_4\text{OCH}_3)\text{CH}_3\}]^{2-}$ (ref 127). Orange octahedra, $\{\text{Mo}_6\text{O}_6\}$; orange spheres, Mo; black spheres, C; red sphere, O; blue spheres, N.

only cite here compounds described after 1998. These compounds are gathered in Table 3. In 2000, a full study from Maatta et al. has shown the efficient approach based on the reaction of various organic isocyanates RNCO ($\text{R} = n$ -butyl, cyclohexyl, 2,6-diisopropylphenyl) with $[\text{Mo}_6\text{O}_{19}]^{2-}$ in pyridine by a modification of a protocol previously described by Errington et al.¹⁰⁹ By refluxing the Lindqvist precursor in pyridine with multiple equivalents of 2,6-(diisopropyl)phenylisocyanate, hybrids have been isolated with different degrees of functionalization with the general formula $[\text{Mo}_6\text{O}_{(19-x)}(\text{N}-2,6-(i\text{-Pr})_2\text{C}_6\text{H}_3)_x]^{2-}$.¹¹⁰ Cyclic voltammetry studies have shown that the $[\text{Mo}_6\text{O}_{18}(\text{NR})]^{2-}$ complexes are more difficult to reduce than the $[\text{Mo}_6\text{O}_{19}]^{2-}$ parent anion. Maatta et al. also described the synthesis of a styrylimido–hexamolybdate complex which can be copolymerized with 4-methyl-styrene¹⁹ and a *p*-cyanophenylimido derivative.¹¹¹ A major impulse in the field of organoimido-substituted POMs was then given in 2001 by Peng et al., who described an efficient process based on the use of dicyclohexylcarbodiimide (DCC) in acetonitrile.¹¹² DCC acts as a dehydrating agent and activates the terminal Mo–O bond. As an example, the structure of the organoimido derivative $[\text{Mo}_6\text{O}_{18}\{\text{N}(\text{C}_6\text{H}_3(\text{CH}_3)_2)\}]^{2-}$ is shown in Figure 18a. Using the same protocol mixed-polyoxotungstomolybdates $[\text{MoW}_5\text{O}_{18}(\text{NAr})]^{2-}$ have been isolated¹¹³ as well as a terpyridine-functionalized POM.¹¹⁴ Peng et al. have also shown that the use of $[\alpha\text{-Mo}_8\text{O}_{26}]^{4-}$ as a molybdate precursor instead of $[\text{Mo}_6\text{O}_{19}]^{2-}$ can lead to the synthesis of cis isomers of the difunctionalized $[\text{Mo}_6\text{O}_{17}(\text{NAr})_2]^{2-}$ POMs (Figure 4).¹¹⁵ Since this date, dehydration of a hexamolybdate precursor with DCC has become the conventional method to functionalize hexamolybdate POMs.^{20,116} In 2004, Guo and Wei slightly modified this method by the use of the corresponding arylammonium chloride salt $[\text{ArNH}_3^+\text{Cl}^-]$ of the aryl amine.¹¹⁷ They also described the synthesis of *trans*-difunctionalized $[\text{Mo}_6\text{O}_{17}(\text{NAr})_2]^{2-}$ organoimido derivatives of the Lindqvist polyoxomolybdate by kinetic control (Figure 4).^{22,118} Wang et al. performed DFT calculations and discussed the localization of the second substitution on hexamolybdate POMs.¹¹⁹ Bulkier aromatic groups such as naphthalene derivatives have been introduced to induce supramolecular assemblies and optical properties,¹²⁰ and a large number of crystal structures of monofunctionalized POMs continue to be reported in the literature.¹²¹ A recent study has demonstrated that bridging and not only terminal oxo ligands can also be replaced by organic imido ligands.¹²² Interestingly, antitumoral¹²³ and herbicidal^{116f,124} activities

have been investigated. Finally, the static first hyperpolarizabilities and the origin of the nonlinear optical activity of these mono- and diarylimido Lindqvist POMs have been investigated by Su et al. using density functional theory.¹²⁵

2.3.2. Organodiazenido Derivatives

Organodiazenido derivatives have been comparatively far less studied than organoimido derivatives. The first paper describing an organodiazenido-functionalized POM was published by the group of Zubieta. This system can be exemplified by the anion $[\text{Mo}_4\text{O}_8(\text{OCH}_3)_2(\text{NNC}_6\text{H}_5)_4]^{2-}$.¹²⁶ Since 1998, Maatta et al. synthesized the first diazoalkane–Lindqvist POM, $[\text{Mo}_6\text{O}_{18}(\text{N}_2\text{C}(\text{C}_6\text{H}_4\text{OCH}_3)\text{CH}_3)]^{2-}$ (Figure 18b), by reacting a phosphazine precursor directly with (*n*-NBu₄)₂[Mo₆O₁₉].¹²⁷ The analogous polyoxotungstic compound has been obtained using similar conditions.¹²⁸ A systematic study has been then performed by Gouzerh et al., who reported the synthesis of (*n*-NBu₄)₃[Mo₆O₁₈(N₂Ar)] (Ar = Ph, C₆H₄-*p*-CH₃, C₆H₄-*p*-F, C₆H₄-*p*-CN, C₆H₄-*p*-CF₃, C₆H₄-*p*-OCH₃, C₆H₄-*o*-Cl, C₆F₅, C₆H₄-*m*-NO₂, C₆H₄-*o*-NO₂, C₆H₄-*p*-NO₂, C₆H₃-*o,p*-(NO₂)₂, C₆H₄-*p*-CO₂H).¹²⁹ DFT calculations on functionalized $[\text{Mo}_6\text{O}_{18}\text{R}]^{n-}$ ($\text{R} = \text{O}, \text{NO}, \text{NAr}, \text{NNAr}, \text{NNAr}_2$; $n = 2, 3$) POMs showed that the functionalization produces a distortion in the cage geometry, leading to a change in the Mo–O–Mo vibrational pattern. The most reactive POMs are those substituted by π -acceptor ligands, inducing an increase in physical parameters such as chemical potentials and electrophilicity.¹³⁰ The DFT method has also been used to calculate the second-order polarizabilities of aryldiazenido hexamolybdates.¹³¹ The authors report that modification of the aryldiazenido fragment can drastically change the NLO response of the hybrid system in which the polyanion acts as an electron acceptor and the aryldiazenido ligand acts as an electron donor. Introduction of an electron donor enhances the second-order polarizabilities of the system. Unexpectedly, the authors also report that insertion of a second aromatic ring in the aryldiazenido fragment leads to an inversion of the direction of the charge transfer and a maximum NLO response. In this later case, the polyanion would act as a donor while the aryldiazenido ligand acts as an acceptor.

2.3.3. Pyridine and Dinitrogen Heterocyclic Ligands

Modéc et al. extensively studied the reactivity of $[\text{MoOCl}_5]^{2-}$ with pyridine and alcohols (mostly methanol).³⁰ A large family of compounds containing the $\{\text{Mo}_2\text{O}_4\}^{2+}$ structural unit with different nuclearities has been isolated and characterized as, for example, from the smallest to the largest POM frameworks: $[\text{Mo}_4\text{O}_8(\text{OR})_2\text{X}_2\text{Py}_4]$ ($\text{R} = \text{Me}, \text{X} = \text{Cl}; \text{R} = \text{Et}, \text{X} = \text{Br}$) (Figure 19),^{132,133} $[\text{Mo}_4\text{O}_8(\text{OCH}_3)_4(4\text{-MePy})_4]$,¹³² $[\text{Mo}_4\text{O}_8(\text{OOCCH}_3)_3(\text{OH})\text{Py}_4]$,¹³⁴ $[\text{Mo}_5\text{O}_{11}(\text{OCH}_3)_4\text{Py}_4]$,¹³⁵ $[\text{Mo}_6\text{O}_{12}(\text{OCH}_3)_6(\text{Py})_4]$,¹³² $[\text{Mo}_8\text{O}_{16}(\text{OCH}_3)_8(\text{Py})_4]$,¹³⁶ $[\text{Mo}_8\text{O}_{16}(\text{OCH}_3)_8(\text{R-Py})_4]$ ($\text{R} = \text{H}, 3\text{-Me}, 4\text{-Me}$),^{136–138} and $[\text{Mo}_{10}\text{O}_{26}\text{Py}_8]$.¹³² The highest nuclearity observed so far is 12 in $[\text{Mo}_{12}\text{O}_{28}(\text{OCH}_3)_2\text{Cl}_2(4\text{-EtPy})_8]$, $[\text{Mo}_{12}\text{O}_{28}(\text{OCH}_3)_2\text{Cl}_2(3\text{-MePy})_8]$,¹³⁹ and $[\text{Mo}_{12}\text{O}_{28}(\text{OC}_2\text{H}_5)_4(4\text{-MePy})_8]$.¹⁴⁰ Except in the case of the pentanuclear species, the terminal positions of the Mo^V centers are occupied by, at the most, one pyridine ligand. The reactivity of other nitrogen heterocyclic compounds such as pyrazine or imidazole has been studied, leading to an edge-sharing tetramolybdenum complex¹⁴¹ and the $[\text{Mo}_{16}\text{O}_{42}(\text{OH})_2(3-(i\text{-Pr})\text{C}_3\text{H}_3\text{N}_2)_{12}]$ POM,¹⁴² respectively. The reaction of a series of bidentate nitrogen donor ligands

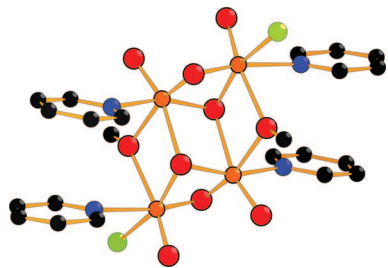


Figure 19. Ball-and-stick representation of the pyridine-substituted POM $[\text{Mo}_4\text{O}_8(\text{OCH}_3)_2\text{Cl}_2\text{Py}_4]$ (refs 132 and 133). Orange spheres, Mo; black spheres, C; red spheres, O; blue spheres, N; green spheres, Cl.

(phenanthroline and bipyridine derivatives) with V^{IV} precursors in methanol has also been investigated and hexameric and tetrameric oxoalkoxovanadates isolated.¹⁴³

2.3.4. Organophosphonate Derivatives

2.3.4.1. Polyoxomolybdate Hybrids. The interaction of monophosphonate as well as diphosphonate ligands with POMs has been investigated. The synthesis of the first heteropolyanions with organophosphonates was described in 1975 by Pope et al.¹⁴⁴ and the first structure reported in 1976.¹⁴⁵ These hybrid POMs of general formula $[(\text{RP})_2\text{Mo}_5\text{O}_{21}]^{4-}$ ($\text{R} = \text{H}, \text{Me}, \text{Et}, \text{Ph}, \text{C}_2\text{H}_4\text{NH}_3^+, p\text{-CH}_2\text{C}_6\text{H}_4\text{NH}_3^+$) have a pentanuclear Mo^{VI} core which incorporates two monophosphonate ligands bound on opposite sides of the metallic ring. Various $[(\text{RP})_2\text{Mo}_5\text{O}_{21}]^{4-}$ derivatives have been reported, functionalized by phosphonocarboxylate groups ($\text{R} = \text{C}_2\text{H}_4\text{CO}_2$)¹⁴⁶ and aminobenzylphosphonate groups ($\text{R} = \text{CH}_2\text{C}_6\text{H}_4\text{NH}_3$) to induce crystallographic assemblies by π - π -stacking interactions¹⁴⁷ or by enantiopure aminoalkylphosphonates ($\text{R} = \text{CH}_3\text{CH}(\text{NH}_3), \text{CH}_3\text{CH}(\text{CH}_3)\text{CH}(\text{NH}_3)$) to generate self-assembled fibrillar nanostructures with enhanced optical activity.¹⁴⁸ Hexanuclear architectures can also be isolated such as $[(\text{C}_6\text{H}_5\text{P})\text{Mo}_6\text{O}_{21}(\text{H}_2\text{O})_3]^{2-}$ ¹⁴⁹ and the $[\text{RPMo}_6\text{O}_{21}(\text{O}_2\text{CCH}_2\text{NH}_3)_3]^{2-}$ ($\text{R} = \text{OH}, \text{CH}_3, \text{C}_2\text{H}_5, \text{H}$) anions.⁵⁷ These last POMs contain only one organophosphonate group, encapsulated by the oxomolybdenum framework, which structures the molybdc wheel. The dodecanuclear heteropolyoxomolybdates $[(\text{RPO}_3)_4\text{Mo}_{12}\text{O}_{34}]^{4-}$ ($\text{R} = \text{Me}, \text{Et}$) contain four methyl- or ethyl-phosphonate groups and have the so-called inverted-Keggin structure.¹⁵⁰ The structures of POMs incorporating diphosphonate ligands are quite different. The reactivity of $\text{Mo}(\text{VI})$ and $\text{W}(\text{VI})$ ions with methylenediphosphonate $(\text{O}_3\text{PCH}_2\text{PO}_3)^{4-}$ and etidronate $(\text{O}_3\text{PC}(\text{CH}_3)(\text{OH})\text{PO}_3)^{4-}$ was first explored independently by Pope and Kortz^{151a,b} and Sergienko et al.^{151c} Later, reaction of the Mo^{V} synthon $[\text{Mo}_2\text{O}_4]^{2+}$ with methylenediphosphonate in aqueous solution and in the presence of a variety of structuring agents led to the formation of cyclic compounds with the general formula $\{(\text{Mo}^{\text{V}}_2\text{O}_4)(\text{O}_3\text{PCH}_2\text{PO}_3)\}_n$ ($n = 3, 4$) encapsulating the additional ligand ($\text{MoO}_4^{2-}, \text{SO}_3^{2-}, \text{CO}_3^{2-}, \text{O}_3\text{PCH}_2\text{PO}_3^{4-}, \text{CH}_3\text{AsO}_3^{2-}$).¹⁵² The wheels are built from the alternating connection of $\{\text{Mo}^{\text{V}}_2\text{O}_4\}$ units and bisphosphonate ligands, and their geometry depends not only on the nature of the guest but also on the nature of the counterions ($\text{NH}_4^+, \text{Na}^+, \text{Li}^+$).^{152b} Three POM architectures differ from the typical $\{(\text{Mo}^{\text{V}}_2\text{O}_4)(\text{O}_3\text{PCH}_2\text{PO}_3)\}_n$ framework: (i) a double wheel, crystallized in acetate buffer, built from the interconnection of octa- and dodecanuclear wheels via two sodium ions (Figure 12),^{152a} (ii) a rectangular anion formed in the presence of Mo^{VI} ions and ammonium counterions,^{152b} and (iii) a cyclohexane-like ring in a chair

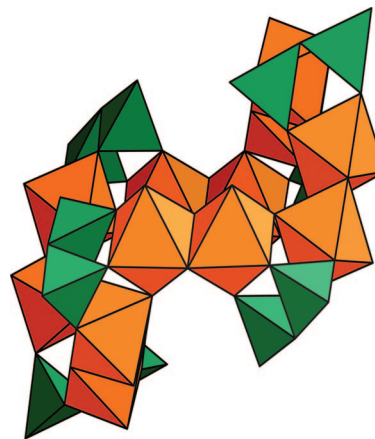


Figure 20. Polyhedral representation of the diphosphonate cyclohexane-like POM $[(\text{Mo}_2\text{O}_4)_6(\text{OH})_6(\text{O}_3\text{PCH}_2\text{PO}_3)_6]^{18-}$ (ref 152c). Orange octahedra, $\{\text{MoO}_6\}$; green tetrahedra, $\{\text{PO}_3\text{C}\}$.

conformation isolated in the absence of additional ligand and with ammonium counterions (Figure 20).^{152c} These reduced anions have been used as reductants and stabilizing agents for the synthesis in one step of metallic (Pt, Pd, Ag) nanoparticles in water and at room temperature.^{152c,153} This family of hybrid POMs is now currently extended to $(\text{O}_3\text{PC}(\text{R}_1)(\text{R}_2)\text{PO}_3)^{4-}$ derivatives, starting with $\text{R}_1 = \text{OH}, \text{R}_2 = \text{CH}_3$.¹⁵⁴

Besides these complexes synthesized under atmospheric pressure, hydrothermal processes have also allowed the isolation of numerous organophosphonate hybrids of polyoxomolybdates. For example, Zubieta et al. synthesized one- and two-dimensional networks based on the pentanuclear cluster $\{\text{Mo}_5\text{O}_{15}(\text{O}_3\text{P}(\text{CH}_2)_4\text{PO}_3)\}$ and coordination complexes bricks, like $\{\text{Cu}(2,2'\text{-bpy})_2\}$ and $\{\text{Cu}_2(\text{tpyz})(\text{H}_2\text{O})_2\}$ ¹⁵⁵ or $\{\text{Ni}_4(\text{tpyz})_3\}$ (tpyz = tetra(2-pyridyl)pyrazine).¹⁵⁶ In both cases, the organophosphonate derivatives are generated in situ during the reaction from MoO_3 and $\text{H}_2\text{O}_3\text{P}(\text{CH}_2)_4\text{PO}_3\text{H}_2$ precursors. Moreover, Sevov et al. described the hydrothermal synthesis of two mixed-valent polyoxomolybdenum diphosphonate anions $[\text{Mo}^{\text{V}}_6\text{Mo}^{\text{VI}}\text{O}_{16}(\text{O}_3\text{PCH}_2\text{PO}_3)_3]^{8-}$ ¹⁵⁷ and $[\text{Mo}^{\text{V}}_7\text{Mo}^{\text{VI}}\text{O}_{16}(\text{O}_3\text{PPhPO}_3\text{H})_4]^{3-}$.¹⁵⁸

2.3.4.2. Polyoxotungstate Hybrids. The first organophosphonate derivatives of polyoxotungstates $[\{\text{C}_6\text{H}_5\text{P}(\text{O})\}_2\text{X}^{n+}\text{W}_{11}\text{O}_{39}]^{(8-n)-}$ ($\text{X}^{n+} = \text{P}^{5+}$ or Si^{4+}) with two $\{\text{C}_6\text{H}_5\text{-P}(\text{O})\}_2^{2+}$ bridging groups were isolated by Hill et al.¹⁵⁹ In the presence of NBu_4Br , acting as a phase-transfer reagent, a series of organophosphoryl polyoxotungstates $[\{\text{RP}(\text{O})\}_2\text{X}^{n+}\text{W}_{11}\text{O}_{39}]^{(8-n)-}$ ($\text{X}^{n+} = \text{Si}^{4+}, \text{R} = \text{C}_6\text{H}_{11}, \text{PhCH}_2, \text{PhCH}_2\text{CH}_2, \text{H}_2\text{NCH}(n\text{-Pr}), \text{C}_6\text{H}_{11}$; $\text{X}^{n+} = \text{P}^{5+}, \text{B}^{3+}, \text{Ga}^{3+}, \text{R} = \text{C}_6\text{H}_{11}$) has been synthesized.¹⁶⁰ This study has been extended to organothiophosphoryl derivatives.¹⁶¹

Two organic ligands can also be grafted on the divacant polyoxotungstate precursor $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$ to form $[\gamma\text{-}\{\text{RP}(\text{O})_2\}\text{SiW}_{10}\text{O}_{36}]^{4-}$ ($\text{R} = \text{H}, \text{Et}, n\text{-Bu}, t\text{-Bu}, \text{C}_2\text{H}_4\text{COOH}, \text{Ph}$) anions.^{162a} Functionalization of $[\gamma\text{-XW}_{10}\text{O}_{36}]^{8-}$ ($\text{X} = \text{Si}, \text{Ge}$) has also been achieved using chiral phosphoryl groups.^{162b} The family of hybrids of general formula $[(\text{RPO})_2(\gamma\text{-XW}_{10}\text{O}_{36})]^{4-}$ ($\text{R} = N$ -protected aminoalkyl groups or O -protected amino acid derivatives) has been characterized using multinuclear NMR spectroscopy, electrospray ionization mass spectrometry, UV-vis spectroscopy, and circular dichroism (CD). Chirality transfer from the organic moiety to the POM has been confirmed from CD studies. Grafting of the organic pendant arm was achieved by direct reaction in acetonitrile, under phase-transfer conditions, of the N -

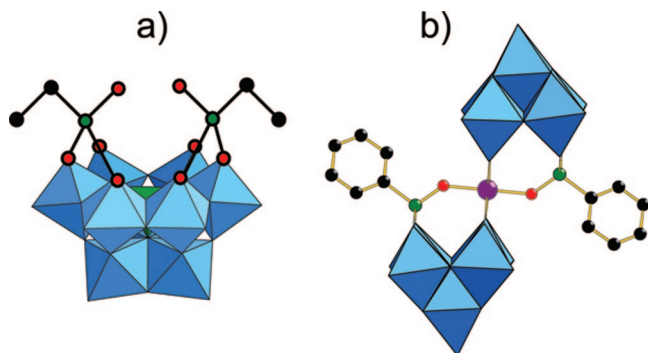


Figure 21. Polyhedral and ball-and-stick representations of the POMs (a) $[(\text{EtPO})_2\text{PW}_9\text{O}_{34}]^{5-}$ (ref 164) and (b) $[\text{NbW}_{10}\text{O}_{38}(\text{PPh})_2]^{3-}$ (ref 167). Blue octahedra, $\{\text{WO}_6\}$; green tetrahedron, $\{\text{PO}_4\}$; green spheres, P; purple sphere, Nb; black spheres, C; red spheres, O.

protected aminophosphonate with the dilacunary POM or by the sequential amino acid coupling on the preformed phosphonoacetic-substituted POM $[(\text{HOC}(\text{O})\text{CH}_2\text{PO})_2(\gamma\text{-XW}_{10}\text{O}_{36})]^{4-}$ ($\text{X} = \text{Si}, \text{Ge}$). The stability of the hybrids allowed their use in catalytic oxidation. Bisphosphonates such as $[\text{O}_3\text{PCH}_2(\text{C}_6\text{H}_4)_n\text{CH}_2\text{PO}_3]^{4-}$ ($n = 1, 2$) can also connect two divacant $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$ POMs to form hybrid cyclic dimers.¹⁶³

The reactivity of the trivacant $[\text{PW}_9\text{O}_{34}]^{9-}$ anion has also been studied. Only two electrophilic groups and not three, as could be expected, are grafted on the lacunary surface of the POM. This new family has the general formula $[\{\text{RP}(\text{O})\}_2\text{PW}_9\text{O}_{34}]^{5-}$ ($\text{R} = \text{Et}, n\text{-Bu}, t\text{-Bu}, \text{All}, \text{Ph}$) (Figure 21a).¹⁶⁴ Similarly, $[\{\text{RP}(\text{S})\}_2\text{PW}_9\text{O}_{34}]^{5-}$ ($\text{R} = \text{C}_6\text{H}_5, \text{C}_6\text{H}_{11}$) compounds have been obtained with organothiophosphoryl ligands.¹⁶⁵

The reactivity of organophosphoryl compounds has been also tested with the same success on monovacant Dawson POMs.^{83h,i,166} One recent study has compared the redox properties of hybrid Dawson POMs disubstituted with organophosphoryl and organosilyl compounds and shown that it is possible to tune the reduction potential of the POM through the choice of electrophilic groups.^{83f}

Finally, a new family of organophosphonate derivatives of Lindqvist niobiotungstates $[\text{NbW}_{10}\text{O}_{38}(\text{PR})_2]^{3-}$ ($\text{R} = \text{Me}, \text{Et}, \text{Pr}, n\text{-Bu}, \text{Hex}, \text{Hep}, \text{Cy}, \text{Ph}, \text{All}$) has been reported (Figure 21b). These POMs are built from the connection, via a niobium octahedron, of two lacunary isopolyoxometalate $\{\text{W}_5\text{O}_{18}\}$ moieties with a grafted electrophilic group.¹⁶⁷

2.3.4.3. Polyoxovanadate Hybrids. The chemistry of spherical and bowl-shaped molecular organophosphonate derivatives of polyoxovanadates was first developed by Müller et al.¹⁶⁸ and Zubieta et al.¹⁶⁹ The spherical potassium-capped vanadium methylphosphonate $[\text{H}_6\text{V}_{12}\text{O}_{27}(\text{VO}_4)(\text{PO}_3\text{CH}_3)_3]^{5-}$ has been synthesized by Yamase et al.¹⁷⁰ Schmitt et al. developed an approach to functionalize polyoxovanadates through partial reduction of V^{V} salts in the presence of organophosphonates and isolated hybrid capsules like the $[\text{H}_2\text{V}_{10}\text{O}_{18}(\text{O}_3\text{PC}_{12}\text{H}_8\text{PO}_3)_4]^{8-}$ anion (Figure 22).¹⁷¹ Fluoride-templated mixed-valence $\text{V}^{\text{IV}}/\text{V}^{\text{V}}$ tetranuclear vanadium phosphonate cage compounds $[(\text{V}_2\text{O}_3)_2(\text{RPO}_3)_4\text{-CF}]^-$ ($\text{R} = \text{H}, \text{Me}, t\text{-Bu}, \text{Ph}$) have been isolated from the reaction of dioxodichlorovanadate with phosphonic acids in CH_3CN in the presence of KF .¹⁷² Two oxovanadium phosphonate cage compounds, a neutral mixed-valent $\text{V}^{\text{IV}}/\text{V}^{\text{V}}$ $[(\text{V}_{12}\text{O}_{20})(\text{H}_2\text{O})_{12}(\text{Ph}_2\text{CHPO}_3)_8]$ cluster encapsulating two

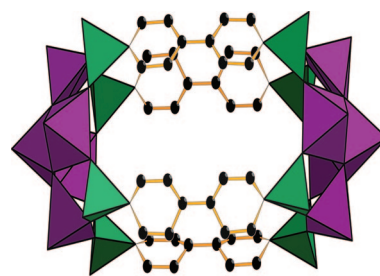


Figure 22. Polyhedral and ball-and-stick representation of the $[\text{H}_2\text{V}_{10}\text{O}_{18}(\text{O}_3\text{PC}_{12}\text{H}_8\text{PO}_3)_4]^{8-}$ POM (ref 171). Purple square pyramids, $\{\text{VO}_5\}$; green tetrahedra, $\{\text{PO}_4\}$; black spheres, C.

chloride anions and a neutral bowl-shaped $[\text{V}^{\text{V}}_6\text{O}_{12}(\text{H}_2\text{O})_3\text{-}(\text{Ph}_2\text{CHPO}_3)_3]$ cage, have also been synthesized in organic solvent.¹⁷³

2.3.5. Organoarsonate and Organoantimony Derivatives

Reaction of organoarsenate ligands with POM derivatives has been far less explored, although organoarsenate compounds have a reactivity close to that of organophosphonates. Two families of organoarsenates are known, the $[(\text{RASO}_3)_2\text{-M}_6\text{O}_{18}]^{6-}$ ($\text{M} = \text{Mo}$ or W)¹⁷⁴ and $[(\text{RASO}_3)_4\text{Mo}_{12}\text{O}_{34}]^{4-}$ ($\text{R} = \text{Me}, \text{Ph}, p\text{-C}_6\text{H}_4\text{NH}_3^+, \text{C}_2\text{H}_4\text{OH}$) POMs.¹⁷⁵ These latter species have an inverted-Keggin core and are analogous to the organophosphonate derivatives.¹⁵⁰ Both families of compounds can be synthesized under hydrothermal conditions and used as coordination complexes to get 2D and 3D hybrid networks.¹⁷⁶ The cyanophenylarsonate derivative $[(p\text{-NC-C}_6\text{H}_4\text{AsO}_3)_4\text{Mo}_{12}\text{O}_{34}]^{4-}$ has been structurally characterized.¹⁷⁷ Stein et al. also studied the formation of coordination networks using these organoarsenate derivatives as building blocks.¹⁷⁸ The formation of $\text{V}^{\text{IV}}/\text{V}^{\text{V}}$ polyoxometalates in the presence of organoarsenate ligands has also been studied and the structures of the $[\text{V}_5\text{O}_9(\text{O}_3\text{AsC}_6\text{H}_4\text{-4-NH}_2)_4]^{5-}$ compound reported by Schmitt et al.¹⁷¹

As far as organoantimony derivatives of POMs are concerned, there has been only the recent report of $[\{\text{Ph-SbOH}\}_3(\text{A-}\alpha\text{-PW}_9\text{O}_{34})_2]^{9-}$ which contains two POM units linked by three phenylantimony groups.¹⁷⁹ This anion is very similar to the organotin derivatives $[\{\text{RSnOH}\}_3(\text{A-}\beta\text{-PW}_9\text{O}_{34})_2]^{12-}$ ($\text{R} = \text{Ph}, \text{Bu}$) with a difference in the nature of the lacunary Keggin isomer present in the hybrids.¹⁸⁰

3. Organic Groups Linked to Polyoxometalates via d- and f-Block Elements

As a huge and still increasing number of compounds isolated under hydrothermal conditions have been reported this past decade, besides the compounds synthesized under mild conditions, only representative examples of the numerous structures obtained at higher temperature and pressure will be given in this part.

3.1. d-Block Elements Incorporated in Vacant POMs

The incorporation of d-block elements in vacant POM matrices is one of the oldest and most studied reactions in POM chemistry. More recently, introduction of organic ligands in such inorganic systems has been developed by several groups. The motivations of the introduction of an organic ligand in transition-metal clusters bound to POMs are multiple: (i) magnetic properties are highly dependent

on the nature of the bridging ligands, (ii) organic ligands can connect two or several POMs, and (iii) a synergetic effect between the properties of the POM and those of the ligand is also sometimes evoked. There are two main approaches to achieve the functionalization of the POM. In the first one a transition-metal-substituted POM precursor with labile ligands (most often a water molecule) is reacted with an organic ligand. The second is the bottom-up or self-assembly approach in which all the reactants, i.e., a vacant POM, or even sodium tungstate and a heteroelement, transition-metal ions, and an organic ligand are mixed together. The first approach is the less used one due to the difficulty to find stable POM precursors with exchangeable ligands.

3.1.1. Monomeric POMs

Historically this study was initiated on the monosubstituted Keggin derivative. Reaction of the lacunary $\{XW_{11}O_{39}\}$ anion with transition-metal cations M in aqueous solution leads to the transition-metal-substituted POM $\{XW_{11}O_{39}M(H_2O)\}$. In this complex, the metal center M is in a pseudoporphyrin environment; it is pentacoordinated by the POM, and its octahedral coordination sphere is completed by a water ligand. In 1970, Baker and Figgis¹⁸¹ studied the replacement of the coordinated water molecule and isolated the pyridine derivatives $[SiW_{11}O_{39}Co^X(py)]^{n-}$ ($X = II, n = 6$; $X = III, n = 5$). Following this work, Weakley prepared the pyridinium salt $(pyH)_5[PW_{11}O_{39}Co^{II}(py)]$.¹⁸² The exchange of the water molecule by various inorganic groups ($[Fe(CN)_6]^{4-}$, SCN^- , SO_3^{2-}) has also been studied by Zonnevijlle and Tourné.¹⁸³ Pope has shown that $[PW_{11}O_{39}Ru^{II}(H_2O)]^{5-}$ reacts with pyridine, sulfoxides, dialkyl sulfides, and active alkenes L ($L =$ maleic, fumaric, crotonic acids, 1-4-dihydroxybut-2-ene) to form $[PW_{11}O_{39}Ru^{II}L]^{5-}$ species, characterized by electronic absorption spectroscopy and ^{31}P and ^{183}W NMR spectroscopy for some of them.^{184a} These 11-phosphotungstosilicates can be oxidized, and the EPR spectra of three of them, $[PW_{11}O_{39}Ru^{III}L]^{4-}$ ($L = H_2O, dmsO, py$), have been analyzed. This study suggests, among other results, that the dmsO ligand is S bonded to the Ru^{III} center.^{184b} Bonchio et al. also characterized the dmsO derivative,¹⁸⁵ synthesized by microwave techniques. It is only recently that these monofunctionalized species have been characterized by single-crystal X-ray diffraction. The crystal structures of three monovacant silicotungstate derivatives have been reported: (i) $[SiW_{11}O_{39}Ru^{III}(dmsO)]^{5-}$, isolated by heating the aquo derivative with a large excess of dmsO,¹⁸⁶ (ii) $[SiW_{11}O_{39}M^{II}(im)]^{6-}$ ($M = Mn, Co$; $im =$ imidazole),¹⁸⁷ cocrystallizing with the aquo derivative, and (iii) $[SiW_{11}O_{39}Co^{II}(4,4'-bpy)]^{6-}$.¹⁸⁸ Hydrothermal conditions have also been used to crystallize insoluble salts with $[PW_{11}O_{39}Co^{II}(pbpy)]^{5-}$ ($pbpy = 5$ -phenyl-2-(4-pyridinyl)pyridine)¹⁸⁹ or $[PMo_{11}O_{39}Co^{II}(4,4'-bipy)]^{5-}$ POMs.¹⁹⁰ The Keggin-type organoimido derivative $[PW_{11}O_{39}\{Re^VNC_6H_5\}]^{4-}$ ¹⁹¹ and the ruthenium-phosphinimino derivative $[PW_{11}O_{39}\{Ru^VNPPH_3\}]^{3-}$ ¹⁹² have also been characterized. The reaction of the latter species with hydroxide has been investigated.¹⁹³ Note also that the three water molecules in $[(H_2O)_3M^{IV}(P_2W_{17}O_{61})]^{6-}$ ($M = Zr, Hf$) have been replaced by the chiral L-malic acid under hydrothermal conditions.¹⁹⁴

Unlike the compounds described above, the monolacunary $[\alpha-PW_{11}O_{39}]^{7-}$ anion accommodates two Ti^{IV} ions each coordinated to one oxalate ligand to form $\{[Ti^{IV}(OH)(ox)]_2(\mu-O)\}(\alpha-PW_{11}O_{39})^{7-}$.¹⁹⁵ ^{31}P NMR solution studies suggest a dissociation equilibrium to the monotitanium-

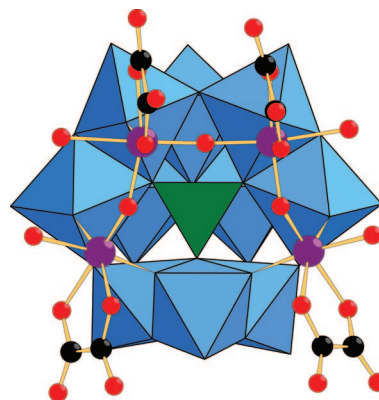


Figure 23. Polyhedral and ball-and-stick representation of the $\{[Ti^{IV}(ox)(H_2O)_4(\mu-O)_3(\alpha-PW_{10}O_{37})]^{7-}$ polyanion (ref 196). Blue octahedra, $\{WO_6\}$; green tetrahedron, $\{PO_4\}$; purple spheres, Ti; red spheres, O; black spheres, C.

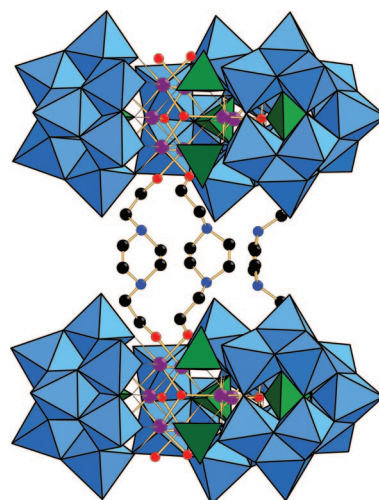


Figure 24. Polyhedral and ball-and-stick representation of the $\{[Co_9(OH)_5(H_2O)_3(HPO_4)_2(B-\alpha-PW_9O_{34})_3]_2(bhep)_3\}^{32-}$ polyanion (ref 198). Blue octahedra, $\{WO_6\}$; green tetrahedra, $\{PO_4\}$; purple spheres, Co; red spheres, O; black spheres, C; blue spheres, N.

substituted dimeric species $[(PW_{11}Ti^{IV}O_{39})_2OH]^{7-}$. An extension of this study is the preparation of $\{[Ti^{IV}(ox)(H_2O)_4(\mu-O)_3](\alpha-PW_{10}O_{37})\}^{7-}$, which contains a tetranuclear Ti^{IV} complex incorporated into a dilacunary Keggin POM (Figure 23).¹⁹⁶ The bis(acetate)dirhodium-11-tungstophosphate $[PW_{11}O_{39}\{Rh^{II}_2(OAc)_2(dmsO)_2\}]^{5-}$ synthesized under hydrothermal conditions constitutes another example of a monolacunary POM accommodating two transition-metal cations with bridging acetate ligands and S-bonded dmsO molecules.¹⁹⁷

The recently reported cluster $[PW_{10}Co^{II}_2O_{38}\{Hbhep\}_2]^{5-}$ ($bhep = N,N'$ -bis(2-hydroxyethyl)piperazine), synthesized by a one-pot procedure, can be described as a disubstituted α -Keggin cluster anion decorated by two bhep ligands.¹⁹⁸ By slightly changing the synthetic conditions the $\{[Co_9(OH)_3(H_2O)_3(HPO_4)_2(B-\alpha-PW_9O_{34})_3]_2(bhep)_3\}^{32-}$ cluster, which represents the largest Co^{II} POM isolated to date, has also been obtained. This compound contains two $\{Co_9\}$ units, each encapsulated by three trivacant POMs, which are connected via three bhep ligands (Figure 24).

Finally, in comparison with Keggin and Dawson ions, Lindqvist-type POMs have been far less studied. We mention that Errington et al. developed a two-step procedure to

synthesize $\{LCoW_5O_{18}\}$ (L = organic ligand) tungstates and published the crystal structure of the $[(py)CoW_5O_{18}H]^-$ anion.¹⁹⁹

3.1.2. Sandwich-type POMs

Sandwich-type structures encapsulate transition-metal clusters with exchangeable water molecules. Substitution of the two water molecules coordinated to the metal atoms in the sandwich-type $[M^II_4(H_2O)_2(B-\alpha-AsW_9O_{34})_2]^{10-}$ (M = Cd, Co, Cu, Fe, Mn, Ni, Zn)²⁰⁰ and $[M^II_4(H_2O)_2(B-\alpha-As_2W_{15}O_{56})_2]^{16-}$ (M = Cu, Mn, Co, Ni, Zn, Cd)²⁰¹ anions was first studied by Wang et al. under conventional bench conditions, but no crystal structure was reported to support the authors' assumptions. Besides, replacement of the two water molecules of the tetranuclear metal cluster of the Weakley-type sandwiches has been observed recently under hydrothermal conditions. Pending or bridging diamine ligands can thus bind to Zn^{II} ,²⁰² Cu^{II} ,²⁰³ Ni^{II} ,²⁰⁴ or Fe^{II} ²⁰⁵ centers. dmf molecules can also replace water ligands on $\{Mn_4\}$ sandwiches under solvothermal conditions.²⁰⁶ However, the report of the structures of imidazole- and pyridine-coordinated sandwich-type compounds $[\{Co^{II}(im)\}_3(B-\alpha-BiW_9O_{33})_2]^{12-}$,²⁰⁷ $[\{M^{II}(im)\}_3(B-\alpha-SbW_9O_{33})_2]^{12-}$ (M = Ni, Co, Zn, Mn),²⁰⁸ and $[\{Ni^{II}(py)\}_3(B-\alpha-AsW_9O_{33})_2]^{12-}$ ²⁰⁹ shows that functionalized sandwich-type POMs can also be prepared under mild conditions. The Cu^{II} analogues $[\{Cu^{II}_3(im)_2(H_2O)(B-\alpha-XW_9O_{33})_2\}]^{12-}$ (X = Bi, Sb) have been recently described.²¹⁰ Unlike the other members of this family of compounds, one Cu^{II} ion still bears a water molecule. Furthermore, the POMs are linked by $[Cu^{II}(im)]^{2+}$ cations to display an anionic chain.

Ethylenediamine-chelated Co^{III} centers have been inserted in polyoxotungstates to form the sandwich-type compounds $[K\{Co(en)WO_4\}\{WO(H_2O)\}(PW_9O_{34})_2]^{12-}$ and $[\{Co(en)(\mu-OH)_2Co(en)\}\{PW_{10}O_{37}Co(en)\}_2]^{8-}$.^{211a} They represent the first examples of POMs that incorporate embedded chelated heteroatoms. Both compounds were obtained from reaction between the cobalt precursor $K[Co(en)(CO_3)_2]$ and the trivalent POM $[A-PW_9O_{34}]^{9-}$ after careful acidification to release CO_2 . The same approach has been used to synthesize the polyoxomolybdates $[\{Co^{III}(en)\}_4Mo_{10}O_{38}]^{4-}$ and $[\{Co^{II}(H_2O)_2\}\{Co^{III}(en)\}_8\{Mo_{20}O_{76}\}]^{16-}$.^{211b}

Alternatively, bridging ligands can allow the formation of extended systems by connecting directly the metal centers inserted in the POM matrix. The use of acetate buffer as a reaction medium has led to the formation of the sinusoidal chain $\{Mn^{II}_3(OAc)_2(B-\alpha-SbW_9O_{33})_2\}$ (OAc = acetate) in which the sandwich-type anions are linked by bridging acetate ligands.²¹² It should be noted also that in these sandwich-type structures three $\{Na(H_2O)_2\}^+$ groups alternate with the three $\{M(OAc)\}$ groups in the central belt, as usually found in sandwich-type complexes made of $[X^{III}W_9O_{33}]^{9-}$ (X = As, Sb, Bi) subunits.²¹³ Substitution of the water molecules bound to the four transition-metal ions of the Krebs-type sandwich $\{M_4(H_2O)_{10}(B-\beta-XW_9O_{33})_2\}$ has been less studied despite the fact that this precursor contains 10 accessible water molecules. To our knowledge, $[Fe^{III}_4(ox)_4(H_2O)_2(XW_9O_{33})_2]^{14-}$ (X = As^{III} , Sb^{III} ; ox = oxalate) represent the only examples of functionalized molecular Krebs-type sandwich POMs. They have been prepared by reaction of the iron precursor with an excess of oxalic acid under mild conditions.²⁰⁵ The same reaction in the presence of ethylenediamine molecules at 130 °C has led to condensation of the POM units by removal of the two remaining water

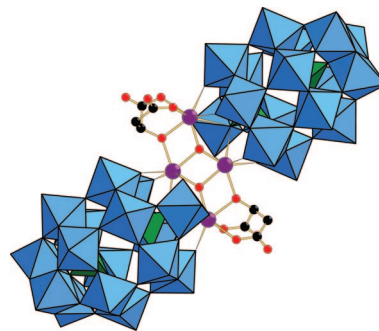


Figure 25. Polyhedral and ball-and-stick representation of the $[(\alpha-P_2W_{16}O_{59})Zr_2(\mu_3-O)(mal)]_2^{18-}$ polyanion (ref 216). Blue octahedra, $\{WO_6\}$; green tetrahedra, $\{PO_4\}$; purple spheres, Zr; red spheres, O; black spheres, C.

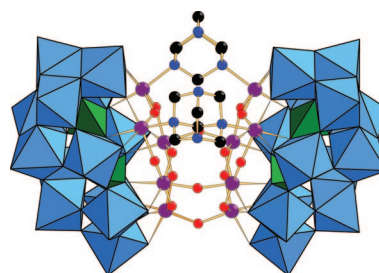


Figure 26. Polyhedral and ball-and-stick representation of the $[\{Fe_{10}(OH)_{15}(hmta)_2\}(P_2W_{13}O_{51})_2]^{13-}$ POM (ref 217). Blue octahedra, $\{WO_6\}$; green tetrahedra, $\{PO_4\}$; purple spheres, Fe; red spheres, O; black spheres, C; blue spheres, N.

molecules on the iron centers and formation of a 1D chain with protonated ethylenediamine counterions.^{205a}

Hill et al. described the synthesis of the enantiomerically pure polyoxotungstate $[\{\alpha-P_2W_{15}O_{55}(H_2O)\}Zr^{IV}_3(\mu_3-O)(H_2O)(L-tarH)\{\alpha-P_2W_{16}O_{59}\}]^{15-}$ ($tarH$ = tartaric acid), in which three Zr^{IV} ions and one W^{VI} center connect two trivalent POMs, and its enantiomer incorporating the D- $tarH$ ligand.²¹⁴ An interesting application of the functionalization of the POM is the chirality transfer from the enantiopure organic molecule L-tartrate to the achiral $[\alpha-P_2W_{15}O_{56}]^{12-}$ POM via the positively charged Zr^{IV} ions. The advantages of the Zr^{IV} ions are their high charge density and coordination flexibility. Note that the stereoselective interaction of amino acids with enantiomers of $[\alpha_1-P_2W_{17}O_{61}Ce^{III}(H_2O)_x]^{7-}$ was first evidenced by Pope et al. using ^{31}P NMR spectroscopy.²¹⁵ Following their work on the tartrate derivative, Hill et al. reported the crystal structures of two enantiomers of the polyoxotungstate cluster $[(\alpha-P_2W_{16}O_{59})Zr^{IV}_2(\mu_3-O)(mal)]_2^{18-}$ (mal = malate) (Figure 25).²¹⁶ ^{31}P NMR experiments show that the malate ligand is labile in solution. Finally, Wang et al. have recently shown that N-donor ligands such as hexamethylenetetramine are potential linkers for the assembly of transition-metal clusters embedded within POMs. They described a decanuclear Fe^{III} cluster sandwiched by two previously unknown $\{P_2W_{13}\}$ anions (Figure 26), disorder being found between one Fe^{III} center and one tungsten atom.²¹⁷

3.1.3. Acetate Ligand

An example of a structure with bridging acetate ligands has already been mentioned above.²¹² Besides this unique 1D structure, few examples of molecular POMs where acetate ions connect transition-metal centers have been reported, although a lot of syntheses are performed in acetate

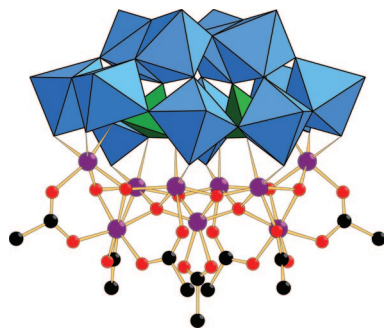


Figure 27. Polyhedral and ball-and-stick representation of the $[\text{H}_4\text{P}_2\text{W}_{12}\text{Fe}^{\text{III}}_9\text{O}_{56}(\text{OAc})_7]^{6-}$ polyanion (ref 219). Blue octahedra, $\{\text{WO}_6\}$; green tetrahedra, $\{\text{PO}_4\}$; purple spheres, Fe; red spheres, O; black spheres, C.

buffer solutions. The first one is the $[\gamma\text{-SiW}_{10}\text{O}_{36}(\text{OH})\text{Cr}^{\text{III}}_2(\text{OAc})_2(\text{OH}_2)_2]^{5-}$ anion prepared by the reaction of $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$ with $[\text{Cr}(\text{OH}_2)_6]^{3+}$ in acetate buffer solution.²¹⁸ In this complex two corner-linked CrO_6 octahedra encapsulated in the divacant POM are bridged by two acetate groups. Considering now the $[\text{H}_4\text{P}_2\text{W}_{12}\text{Fe}^{\text{III}}_9\text{O}_{56}(\text{OAc})_7]^{6-}$ POM isolated by Gouzerh et al., six of the seven acetate ligands act as bridging ligands between two iron centers while the seventh one is a chelating one, being coordinated to only one Fe^{III} center (Figure 27).²¹⁹ In the dimeric $[\{\text{Fe}^{\text{III}}(\text{OH})(\text{OAc})\}_4(\gamma\text{-SiW}_{10}\text{O}_{36})_2]^{12-}$ anion, two divacant units are connected by a hydroxo/acetato-bridged Fe^{III} core.²²⁰ This unstable anion is converted in water to the trimeric polyanion $[\{\text{Fe}^{\text{III}}_6(\text{OH})_9(\text{H}_2\text{O})_2(\text{OAc})_2\}(\gamma\text{-SiW}_{10}\text{O}_{36})_3]^{17-}$. The influence of acetate concentration on the formation of such iron silicotungstate derivatives has been studied. It has been shown that an increase of the concentration of the $\text{CH}_3\text{COOH}/\text{CH}_3\text{COOK}$ buffer (1 M versus 0.5 M) favors the formation of the acetate-free asymmetric dimeric $[(\beta\text{-SiW}_{10}\text{O}_{36})_2(\text{OH})](\gamma\text{-SiW}_{10}\text{O}_{36})]^{13-}$ POM.²²¹ Moreover, the demetalation of $[\{\text{Fe}^{\text{III}}(\text{OH})(\text{OAc})\}_4(\gamma\text{-SiW}_{10}\text{O}_{36})_2]^{12-}$ to form an asymmetric anion in which two Keggin units are stabilized by a bidentate acetate group is observed in 1 M acetate buffer.²²² Concerning now Co^{II} complexes, in $[\text{A-}\alpha\text{-SiW}_9\text{O}_{34}\text{Co}^{\text{II}}_4(\text{OH})_3(\text{OAc})_3]^{8-}$, acetate ligands bridge the capping Co^{II} center and the three Co^{II} ions incorporated into the vacancy of the $[\text{A-}\alpha\text{-SiW}_9\text{O}_{34}]^{10-}$ anion.²²³ In this complex the three hydroxo ligands can be partially substituted by N_3^- ligands. The analogous Ni^{II} species have also been characterized.²²⁴ Finally, in order to increase the nuclearity of the transition-metal clusters, Kögerler et al. recently explored the reactivity of preformed transition-metal clusters toward POMs. The $[\{\alpha\text{-P}_2\text{W}_{16}\text{O}_{57}(\text{OH})_2\}\{\text{Ce}^{\text{IV}}\text{Mn}^{\text{IV}}_6\text{O}_9(\text{OAc})_8\}]^{8-}$ POM represents the first example of compounds isolated following this strategy (Figure 28).²²⁵ This polyoxometalate-based manganese carboxylate cluster was synthesized from the reaction of $[\text{Ce}^{\text{IV}}\text{Mn}^{\text{IV}}_6\text{O}_9(\text{OAc})_9(\text{NO}_3)(\text{H}_2\text{O})_2]^{226}$ and the unstable trivacant $[\alpha\text{-P}_2\text{W}_{15}\text{O}_{56}]^{12-}$ POM in a $\text{CH}_3\text{COOH}:\text{H}_2\text{O}$ (1:3) mixture.

3.1.4. Concluding Remarks

Replacement of water molecules coordinated to transition-metal ions is obviously not favored in aqueous medium because of the competition between water molecules present in large amounts and the organic ligand. Note also that negatively charged and bulky ligands will react less favorably than small neutral ligands. For example, imidazole and pyridine are good candidates to bind to transition-metal ions embedded in POMs. A way to drive the reaction toward

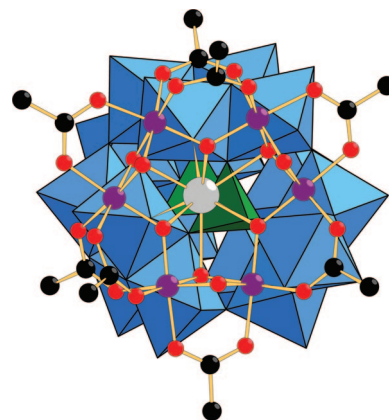


Figure 28. Polyhedral and ball-and-stick representation of the $[\{\alpha\text{-P}_2\text{W}_{16}\text{O}_{57}(\text{OH})_2\}\{\text{Ce}^{\text{IV}}\text{Mn}^{\text{IV}}_6\text{O}_9(\text{OAc})_8\}]^{8-}$ polyanion (ref 225). Blue octahedra, $\{\text{WO}_6\}$; green tetrahedra, $\{\text{PO}_4\}$; purple spheres, Mn; gray sphere, Ce; red spheres, O; black spheres, C; blue spheres, N.

substitution is to use a large excess of ligand, as illustrated by the obtaining of acetate POMs in buffered solutions. One must be cautious however that a large excess of ligand can favor formation of transition-metal complexes nonsupported on POMs due to a high affinity of the transition-metal ions toward some organic ligands.^{221,222} Another way to enhance the reactivity of the ligand is to exploit the hydrothermal conditions. These methods can favor formation of previously unknown transition-metal clusters architectures. Yang et al. thus successfully prepared in a couple of years a large family of transition-metal clusters stabilized by lacunary POMs and amines.²²⁷ The synthesis of functionalized 3d-substituted POMs performed in organic solvent has been comparatively much less studied^{206,228} than those performed in aqueous medium, and most of the time no crystal structures have been reported, probably because of the difficulty to find soluble POM precursors and also to crystallize POM compounds in organic solvents. Two noticeable examples concern (i) the work developed by Errington et al., who successfully synthesized Lindqvist-type hexametalate structures $[(\text{MeO})\text{MW}_5\text{O}_{18}]^{3-}$ ($\text{M} = \text{Ti}, \text{Zr}$), which provide systematic access to a wide range of derivatives via ligand substitution (Figure 29a),²²⁹ and (ii) the nice ternary porphyrinato Hf^{IV} and Zr^{IV} POM complexes obtained by reaction of the TBA salt of $[\text{H}_3\text{PW}_{11}\text{O}_{39}]^{4-}$ and $(\text{tpyp})\text{M}^{\text{IV}}(\text{OAc})_2$ ($\text{tpyp} = \text{meso-tetra}(4\text{-pyridil})\text{porphyrin}$; $\text{M} = \text{Hf}, \text{Zr}$) (Figure 29b).²³⁰

3.2. Transition-Metal Complexes Grafted at the Surface of the POM

In the previous section, the transition-metal ions M were coordinated to vacant polyoxotungstates via $\text{M}-\text{O}$ bonds with the nucleophilic oxygen atoms delimiting the lacuna, but these electrophilic groups can also be attached more weakly to saturated POM structures via terminal or bridging oxygen atoms. As the metal center is bound only to one or two oxygen atoms of the POM, several positions on M remain available to coordinate to an organic ligand. This approach thus allows the association of more sophisticated organic ligands with POMs. The connection of the POMs and formation of 1D, 2D, or even 3D structures when multidentate ligands are used is also possible, but the linking of POMs generally results from the direct connection via the metal center M , with “decorating” ligands. These structures are often described as organic–inorganic hybrid

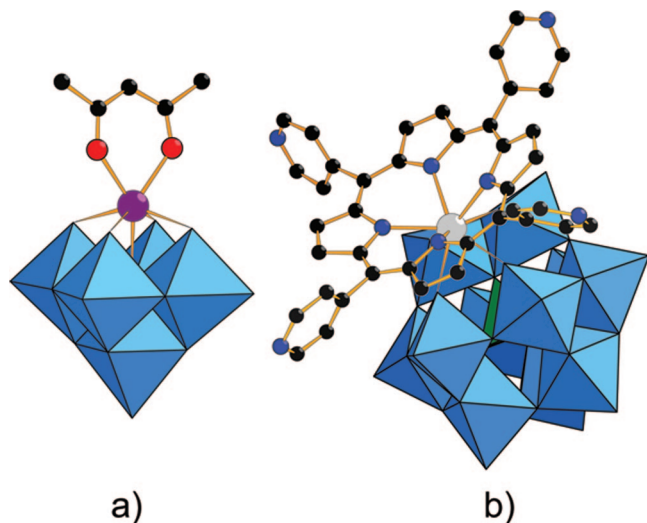


Figure 29. Polyhedral and ball-and-stick representations of (a) the Lindqvist POM $[(\text{acac})\text{Zr}(\text{W}_5\text{O}_{18})]^{3-}$ (ref 229) and (b) the $[(\text{tppy})\text{Hf}(\text{PW}_{11}\text{O}_{39})]^{5-}$ porphyrinato POM (ref 230). Blue octahedra, $\{\text{WO}_6\}$; green tetrahedron, $\{\text{PO}_4\}$; purple sphere, Zr; gray sphere, Hf; black spheres, C; red spheres, O; blue spheres, N.

materials and sometimes named coordination polymers. Examples of POM-based materials synthesized under usual bench conditions will be given below. In the field of hydrothermal synthesis a huge number of structures have been reported. This work has been initiated by Haushalter and Zubieta on polyoxomolybdates^{176,231} and polyoxovanadates²³² and extended to polyoxotungstates more recently.²³³ As already mentioned, it is beyond the scope of this review to list the increasing amount of such systems isolated under hydrothermal conditions, and only arbitrary chosen examples will be given.

3.2.1. Molecular Complexes

Gutiérrez-Zorrilla et al. studied the reactivity of the in-situ-generated $[\text{SiW}_{11}\text{O}_{39}\text{Cu}^{\text{II}}(\text{H}_2\text{O})]^{6-}$ monosubstituted anion with the dinuclear Cu^{II} -bridging carboxylate cationic complexes $[\{\text{Cu}^{\text{II}}(\text{phen})(\text{H}_2\text{O})_2(\text{OAc})_2\}^{2+}]$, $[\{\text{Cu}^{\text{II}}(\text{phen})(\text{H}_2\text{O})_2(\text{ox})\}^{2+}]$, and $[\{\text{Cu}^{\text{II}}(2,2'\text{-bpy})(\text{H}_2\text{O})_2(\text{ox})\}^{2+}]$ (phen = 1,10-phenanthroline).²³⁴ They have thus been able to determine the influence of the nature of the counterion of the acetate buffer solutions HOAc/MOAc ($M = \text{Na}, \text{K}, \text{Rb}, \text{NH}_4$) used for the synthesis process over the final products. With Rb^+ or NH_4^+ counterions the discrete $[\{\text{SiW}_{11}\text{O}_{39}\text{Cu}^{\text{II}}(\text{H}_2\text{O})\}_2\{\text{Cu}^{\text{II}}(\text{phen})_2(\mu\text{-ox})\}]^{10-}$ POM, in which the dinuclear copper-oxalate complex is sandwiched by two copper monosubstituted POMs, crystallizes with copper-phenanthroline species.²³⁴ One bimolecular POM decorated with dinuclear copper-phenanthroline complexes was also synthesized in potassium buffer solutions,^{235a} and the germanium analogue was reported.^{235b} The discrete $[\text{SiW}_{11}\text{O}_{39}\text{Cu}^{\text{II}}(\text{H}_2\text{O})]^{6-}$ POM decorated with dinuclear copper-bipyridine-oxalate complexes was isolated in sodium acetate buffer solutions.²³⁶ In $[\{\text{Cu}^{\text{II}}(\beta\text{-Ala})_2(\text{H}_2\text{O})_2\}_2\{\text{Cu}^{\text{II}}_4(\text{H}_2\text{O})_2(\text{AsW}_9\text{O}_{34})_2\}]^{6-}$, two copper complexes are linked to the sandwich-type POM via a terminal oxygen atom.²³⁷

The striking structure of the metalloporphyrin-POM aggregate $[\{\text{Mo}^{\text{V}}(\text{ddp})(\text{O})\}_2(\text{H}_2\text{SiW}_{12}\text{O}_{40})]$ (H_2ddp = dodecaphenylporphyrin), named “porphyrin hamburger” by the authors, has been reported recently (Figure 30).²³⁸ This molecule was obtained by reaction of the saddle-distorted Mo^{V} -dodecaphenylporphyrin complex and the Keggin POM

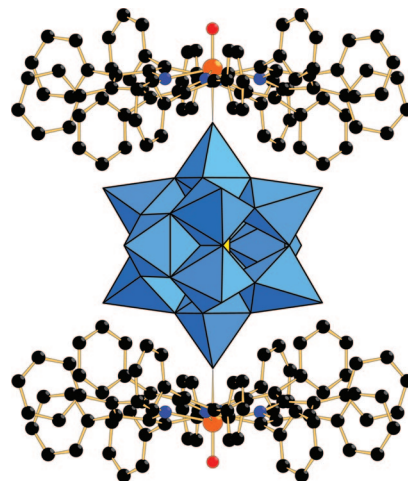


Figure 30. Polyhedral and ball-and-stick representation of the $[\{\text{Mo}^{\text{V}}(\text{ddp})(\text{O})\}_2(\text{H}_2\text{SiW}_{12}\text{O}_{40})]$ sandwich-type porphyrinato POM (ref 238). Blue octahedra, $\{\text{WO}_6\}$; yellow tetrahedra, $\{\text{SiO}_4\}$; orange spheres, Mo; red spheres, O; black spheres, C; blue spheres, N.

in organic solvent. In this large molecule, the POM is sandwiched by two $[\text{Mo}(\text{ddp})(\text{O})]^+$ units, directly linked to the inorganic anion via a Mo–O bond with a terminal oxo ligand. Besides, the spectacular structures of compounds where $[\text{V}_{10}\text{O}_{28}]^{6-}$ and $[\text{Mo}_6\text{O}_{22}]^{8-}$ units are encapsulated in silver(I)-alkynyl frameworks demonstrate the efficient use of CF_3COOH as an acid source in organic solvent for the synthesis of soluble neutral POM-based silver alkynyl cluster complexes of various sizes.²³⁹ Additionally, coordination of the functionalized Anderson-type anion $[\text{MnMo}_6\text{O}_{18}\{(\text{OCH}_2)_3\text{-CNHCO}(4\text{-C}_5\text{H}_4\text{N})\}_2]^{3-}$ to the metal ion in $[\text{Ru}(\text{CO})\text{TPP}]$ (TPP = tetraphenylporphyrin) and $[\text{Zn}(\text{TPP})]$ has been evidenced in solution by ^1H NMR, cyclic voltammetry, and fluorescence spectroscopy. Nevertheless, the association between the two fragments is weak.^{31g}

The grafting of $\{\text{Ru}^{\text{II}}(\text{dmsO})_3\}$ fragments has allowed the synthesis of several Ru^{II} -supported POMs, some with previously unknown structures. The $[\text{HW}_9\text{O}_{33}\text{Ru}^{\text{II}}_2(\text{dmsO})_6]^{7-}$,²⁴⁰ $[\text{M}(\text{dmsO})_3\text{Mo}_7\text{O}_{24}]^{4-}$ ($M = \text{Ru}^{\text{II}}, \text{Os}^{\text{II}}$),²⁴¹ $[\text{Ru}^{\text{II}}(\text{dmsO})_3(\text{H}_2\text{O})\text{-XW}_{11}\text{O}_{39}]^{6-}$ ($X = \text{Ge}, \text{Si}$),²⁴² $[\text{HXW}_7\text{O}_{28}\text{Ru}^{\text{II}}(\text{dmsO})_3]^{6-}$,²⁴³ and $[\{\text{Ru}^{\text{III}}_3(\text{dmsO})_9\text{PV}^{\text{V}}_{11}\text{V}^{\text{IV}}\text{Ru}^{\text{III}}\text{O}_{37}(\text{OH})_3\}_2]^{8-}$ POMs have been isolated.²⁴⁴ The dimeric complex $[\text{Ru}^{\text{II}}(\text{dmsO})_2\text{-}(\text{P}_2\text{W}_{17}\text{O}_{61})_2]^{18-}$ has also been obtained by Nomiya et al.²⁴⁵ This increasing number of structurally characterized ruthenium-substituted POMs is due to the use of the well-characterized, air-stable, and water-soluble precursor $\text{cis-Ru}^{\text{II}}(\text{dmsO})_4\text{Cl}_2$.²⁴⁶ Recently, Bi et al. have shown that the dmsO molecules can be coordinated through its oxygen atom to the metal centers inserted in the POM.²⁴⁷

Finally, very few hybrid polyoxovanadate molecular compounds have been isolated. $[\{\text{V}^{\text{IV}}\text{O}(\text{bmimpm})(\text{acac})\}_2\text{-}\{\text{V}^{\text{V}}\text{O}_{13}(\text{OCH}_3)_6\}]$ (bmimpm = bis(1-methylimidazol-2-yl)-4-methoxyphen-1-ylmethanol, acac = acetylacetonate) has been synthesized in methanolic solution by adding $[\text{V}^{\text{IV}}\text{O}(\text{acac})_2]$ to bmimpm.⁶¹ In this centrosymmetric molecule, two vanadyl moieties are linked to the $\{\text{V}_6\text{O}_{19}\}$ core via bridging oxygen atoms. The four remaining positions on the vanadium ion of the vanadyl group are occupied by two nitrogen atoms of the bmimpm ligand and two oxygen atoms of the acac group, these four atoms being located in the equatorial plane. Note also that solvothermal conditions have allowed isolation of the polyoxovanadates $[\text{V}_{16}\text{O}_{38}(\text{Cl})]^{12-}$ and $[\text{V}_{16}\text{Sb}_4\text{O}_{42}\text{-}(\text{H}_2\text{O})]^{8-}$ decorated with $\text{Cu}(\text{II})$ and $\text{V}(\text{IV})$ complexes, respectively.²⁴⁸

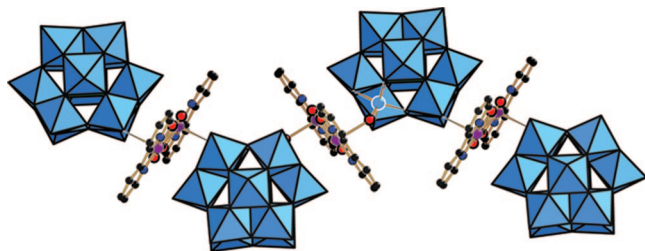


Figure 31. Polyhedral and ball-and-stick representation of the 1D $[\{Cu_2(2,2'-bpy)_2(\mu-ox)\}\{SiW_{11}O_{39}Cu(H_2O)\}]^{4-}$ compound (refs 236 and). Blue octahedra, $\{WO_6\}$; purple spheres, Cu; red spheres, O; black spheres, C; blue spheres, N.^{236,249}

3.2.2. Chain Coordination Polymers

Among extended systems, one-dimensional structures are the most common and copper ions are the most often encountered transition-metal ions in this type of compounds, probably because long Cu–O axial bonds (Jahn–Teller distortion) allow the connections between the rigid POM and the transition-metal complex. Typical examples are the 1D materials obtained by Gutiérrez-Zorrilla et al. in ammonium or rubidium acetate buffer solutions in which copper–bipyridine–oxalate dimers are linking $[SiW_{11}O_{39}Cu^{II}(H_2O)]^{6-}$ units (Figure 31).^{236,249} The related $[\{Ln^{III}(PW_{11}O_{39})_2\}\{Cu^{II}_2(2,2'-bpy)_2(\mu-ox)\}]$ ($Ln = La, Pr, Eu, Gd, Yb$)²⁵⁰ and $[Cu^{II}_2(2,2'-bpy)_2(\mu-ox)] [M^{III}(OH)_7Mo_6O_{17}]$ ($M = Al, Cr$)²⁵¹ 1D materials have been synthesized by reaction of copper–bipyridine–oxalate complexes with $[Ln^{III}(PW_{11}O_{39})_2]^{11-}$ or Anderson-type POMs.

$[Cu^{II}_2P_2Mo_5O_{23}(H_2O)_2(Hcyt)_4]^{252}$ ($cyt = cytosine$) and $\{[Cu^{II}(2,2'-bpy)(H_2O)_2]_5[Cu^{II}(2,2'-bpy)(H_2O)]\}[P_2Mo_5O_{23}]_2^{253}$ are also rare examples of hybrid materials synthesized at room temperature. They are obtained from reaction of Na_2MoO_4 , Cu^{2+} , H_3PO_4 , cytosine, or 2,2'-bipyridine. In these structures the $\{P_2Mo_5O_{23}\}$ units are linked to generate a chain via copper ions, which are also weakly bonded to the oxygen

atom of a cytosine ligand. Functionalized $[(O_2CCH_2PO_3)_2-Mo_5O_{15}]^{6-}$ POMs linked by Cu^{2+} centers to form 1D hybrid chains have also been obtained.²⁵⁴ Finally, a polymeric inorganic–organic compound with decavanadate ions bridged by $[Cu^{II}_2(Hcyt)_4]^{4+}$ ions has also been recently described.²⁵⁵

3.2.3. Layered and 3D Coordination Polymers

The $[\{SiW_{12}O_{40}\}\{Cu^{II}_2(2,2'-bpy)_2(H_2O)(ox)\}_2]$ compound, isolated at room temperature, shows a 2D arrangement of Keggin POMs linked by one of the copper ions of the oxalate cationic dimers.²⁵⁶ Peng et al. synthesized a 2D compound with $[SiW_{12}O_{40}]^{4-}$ anions linked by $\{Cu^{II}_2(phen)_2(OH)_2(H_2O)\}$ units.²⁵⁷ Anderson-type anions have also been connected to copper complexes to generate a 2D framework.²⁵⁸

Two enantiomerically pure 3D POM-based frameworks have been synthesized by Wang et al. by the reaction of $[BW_{12}O_{40}]^{5-}$, Cu^{II} , and D- or L-proline in water.²⁵⁹ Like what was observed in the tartrate and malate derivatives of Zr^{IV} -substituted POMs,^{214,216} the chiral proline ligand transfers chirality to the achiral Keggin POM via the Cu^{II} ions.

In comparison with copper ions, the reactivity of silver ions toward POMs in the presence of organic ligands has been far less studied but already afforded a few extended frameworks.²⁶⁰ Silver ions offer two main advantages: (i) they can adopt various coordination numbers (from 2 to 6) allowing flexibility as linking agents and (ii) a synergetic effect between Ag^I and POMs ions has been postulated and is expected to improve the catalytic selectivity of the POM.²⁶¹ Cronin et al. also reported that the 3D framework built from the covalent interaction of α -metatungstate ions and dimeric $[Ag^I(CH_3CN)_2]^{2+}$ bridging units can sorb and desorb acetonitrile molecules.²⁶² A gradual blockage of the solvent-accessible pore volume is however observed.

Table 4. POMs with Rare-Earth Complexes Synthesized under Mild Conditions

POM building unit	formula	dimensionality	ref
$[Cr^{III}Mo_6H_6O_{24}]^{3-}$	$(C_6H_6NO_2)_2[La^{III}(H_2O)_7][Cr^{III}Mo_6H_6O_{24}]$ $C_6H_6NO_2 = pyridine-4-carboxylic acid$	0D, monomer	278a
$[\beta-Mo_8O_{26}]^{4-}$	$[Ln^{III}(dmf)_7(\beta-Mo_8O_{26})]^-$ ($Ln = Gd, La$)	0D, monomer	276
$[AsW_9O_{33}]^{9-}$	$[Gd^{III}_6As_6W_{65}O_{229}(OH)_4(H_2O)_{12}(OAc)_2]^{38-}$	0D, hexamer	269
$[AsW_9O_{33}]^{9-}$	$[Yb^{III}_{10}As_{10}W_{88}O_{308}(OH)_8(H_2O)_{28}(OAc)_4]^{40-}$	0D, octamer	269
$[SiW_{11}O_{39}]^{8-}$	$[(SiW_{11}O_{39}Ln^{III})_2(\mu-OAc)_2]^{12-}$ ($Ln = Gd, Yb$)	0D, dimer	266a
$[P_2W_{18}O_{62}]^{6-}$	$[Ce^{III}(nmp)_3(H_2O)_5][Ce^{III}(nmp)_3(H_2O)_4][P_2W_{18}O_{62}]$ $nmp = N\text{-methyl-2-pyrrolidone}$	0D, monomer	280b
$[\alpha_2-P_2W_{17}O_{61}]^{10-}$	$[\{Yb^{III}(P_2W_{17}O_{61})_4(C_2O_4)_3(H_2O)_4\}]^{34-}$	0D, tetramer	267
$[SiMo_{12}O_{40}]^{4-}$	$[\{Ba^{II}(dmsO)_5(H_2O)\}_2(SiMo_{12}O_{40})]$	1D	279a
$\{\epsilon-PMo^V_8Mo^VI_4O_{40}\}$	$[\epsilon-PMo_{12}O_{37}(OH)_3\{La^{III}(H_2O)_4(C_5H_6O_4)_{0.5}\}_4]$ $C_5H_8O_4 = glutaric acid$ $[\epsilon-PMo_{12}O_{39}(OH)\{La^{III}(H_2O)_6\}_2\{La^{III}(H_2O)_5(C_4O_4)_{0.5}\}_2]$ $C_4H_2O_4 = squaric acid$	1D	272
$[P_2W_{18}O_{62}]^{6-}$	$[\{Ce^{III}(dmf)_4(H_2O)_3\}\{Ce^{III}(dmf)_4(H_2O)_4\}(P_2W_{18}O_{62})]$	1D	280a
$[P_2W_{18}O_{62}]^{6-}$	$[\{La^{III}(dmf)_6(H_2O)_3\}\{La^{III}(dmf)_4.5(H_2O)_{2.5}\}(P_2W_{18}O_{62})]$	1D	280b
$[PMo_{12}O_{40}]^{3-}$	$[\{Gd(dmf)_6\}\{Gd(dmf)_7\}(P_2W_{18}O_{62})]$ $[\{Ln^{III}(nmp)_6\}(PMo_{12}O_{40})]$ ($Ln = La, Ce, Pr$) $nmp = N\text{-methyl-2-pyrrolidone}$	1D	279b
$[CrMo_6H_6O_{24}]^{3-}$	$[Ce^{III}(dipic)(H_2O)_5][Cr^{III}Mo_6H_6O_{24}]^-$ $H_2dipic = pyridine-2,6-dicarboxylic acid$	1D	278b
$[W_{10}O_{32}]^{4-}$	$[Ce^{III}(H_2O)(dmf)_6(W_{10}O_{32})]$	1D	277
$[GeMo_{12}O_{40}]^{4-}$	$[\{Ba^{II}(dmsO)_5(H_2O)_3\}\{Ba^{II}(dmsO)_5(H_2O)\}(GeMo_{12}O_{40})]$	2D	279a
$\{\epsilon-Mo_{22}O_{52}(OH)_{18}\}$	$[Mo_{22}O_{52}(OH)_{18}\{La^{III}(H_2O)_4\}_2\{La^{III}(OAc)_2\}_4]$	2D	272
$[GeW_{11}O_{39}]^{8-}$	$[Sm^{III}_2(GeW_{11}O_{39})(dmsO)_3(H_2O)_6]^{2-}$	2D	279c
$[H_2W_{12}O_{40}]^{6-}$	$[(C_6H_5NO_2)Ln^{III}(H_2O)_5]_2[H_2W_{12}O_{40}]$ ($Ln = Ce, Pr, Nd$) $C_6H_6NO_2 = pyridine-4-carboxylic acid$	2D	279d
$\{\epsilon-PMo^V_8Mo^VI_4O_{40}\}$	$[\epsilon-PMo^V_8Mo^VI_4O_{35}(OH)_5\{La^{III}(H_2O)_3(C_9H_5O_6)_{0.5}\}_4]$ $C_9H_6O_6 = trimesic acid$ $[\epsilon-PMo^V_8Mo^VI_4O_{35}(OH)_5\{La^{III}(H_2O)_3\}_4(C_{10}H_2O_8)]$ $C_{10}H_6O_8 = terephthalic acid$	3D	273

Finally, the coordination polymer $[\text{Cd}^{\text{II}}(\text{bpe})(\alpha\text{-Mo}_8\text{O}_{26})]$ - $[\text{Cd}^{\text{II}}(\text{bpe})(\text{dmf})_4]$ ($\text{bpe} = 1,2\text{-bis}(4\text{-pyridyl})\text{ethane}$), in which cationic 1D $[\text{Cd}(\text{bpe})(\text{dmf})_4]_n^{2n+}$ chains penetrate anionic $[\text{Cd}^{\text{II}}(\text{bpe})(\alpha\text{-Mo}_8\text{O}_{26})]_n^{2n-}$ 2D frameworks, has been synthesized from reaction of the TBA salt of $[\text{Mo}_6\text{O}_{19}]^{2-}$, Cd^{2+} ions, and bpe ligands in dmf.²⁶³

3.3. Rare-Earth Complexes

Examples of POMs functionalized by rare earth complexes are far less numerous (Table 4). The interactions of organic ligands with the 1:1 complex of Ce^{III} with $[\alpha_1\text{-P}_2\text{W}_{17}\text{O}_{61}]^{10-}$ was first studied by Pope et al. on the basis of ^{31}P NMR.²¹⁵ The use of a paramagnetic lanthanide cation which magnifies the chemical shift differences between the diastereoisomers has allowed evidencing the interactions of the cerium ions encapsulated in the vacancy of the POM with chiral amino acids. A detailed study has also been performed on the Yb derivative.²⁶⁴ Only a handful of crystal structures of rare-earth-substituted POMs functionalized by organic ligands have then been reported. First, we mention the dimeric $[\{\text{La}^{\text{III}}(\text{OAc})(\text{H}_2\text{O})_2(\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61})\}_2]^{16-}$ ²⁶⁵ and $[\{\text{SiW}_{11}\text{O}_{39}\text{Ln}^{\text{III}}\}_2(\mu\text{-OAc})_2]^{12-}$ ($\text{Ln} = \text{Gd}, \text{Yb}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Ho}$ and Er)²⁶⁶ anions and the tetrameric $[\{\text{Yb}^{\text{III}}(\text{P}_2\text{W}_{17}\text{O}_{61})\}_4(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})_4]^{34-}$ ²⁶⁷ and $[\text{Ce}^{\text{IV}}_4\text{As}_4\text{W}_{44}\text{O}_{151}(\text{ala})_4(\text{OH})_2(\text{H}_2\text{O})_{10}]^{12-}$ ($\text{ala} = \alpha\text{-alanine}$)²⁶⁸ complexes. The recently described $[\text{Gd}^{\text{III}}_6\text{As}_6\text{W}_{65}\text{O}_{229}(\text{OH})_4(\text{H}_2\text{O})_{12}(\text{OAc})_2]^{38-}$ (Figure 32) and $[\text{Yb}^{\text{III}}_{10}\text{As}_{10}\text{W}_{88}\text{O}_{308}(\text{OH})_8(\text{H}_2\text{O})_{28}(\text{OAc})_4]^{40-}$ anions have been obtained from one-pot reactions of the trivacant $[\text{B-}\alpha\text{-AsW}_9\text{O}_{33}]^{9-}$ precursor, $\text{Gd}(\text{NO}_3)_3$, or YbCl_3 in 1 M sodium acetate buffer.²⁶⁹ The striking feature of the ytterbium complex is the incorporation of acetate ligands which are able to bridge both Ln and W centers. Reaction of the unstable $[\text{P}_2\text{W}_{12}\text{O}_{48}]^{12-}$ precursor with $\text{Gd}(\text{NO}_3)_3$, MnCl_2 , and sodium tartrate has allowed isolation of a crown-type POM shell $\{\text{P}_6\text{W}_{39}\}$ which encapsulates extra W^{VI} , Gd^{III} , and Mn^{II} ions linked by tartrate ligands.²⁷⁰ In order to improve the reactivity of POMs toward negatively charged ligands, the positively charged tetracapped $[\epsilon\text{-PMo}^{\text{V}}_8\text{Mo}^{\text{VI}}_4\text{O}_{35}(\text{OH})_5\{\text{La}(\text{H}_2\text{O})_3\}_4(\text{trim})_2]^{5+}$ cation²⁷¹ has been used as a precursor for the synthesis of 1D²⁷² to 3D²⁷³ coordination polymers. These organic–inorganic hybrid materials are synthesized at room temperature by replacement of water molecules bound to the lanthanum ions by oxygen atoms of carboxylate ligands. For example, in the $[\epsilon\text{-PMo}^{\text{V}}_8\text{Mo}^{\text{VI}}_4\text{O}_{35}(\text{OH})_5\{\text{La}(\text{H}_2\text{O})_3\}_4(\text{trim})_2]$ ($\text{trim} = \text{trimesate}$) 3D system, trimesate ligands connect the POM building units via La–O bonds, leading to a neutral open framework with only water molecules in the channels

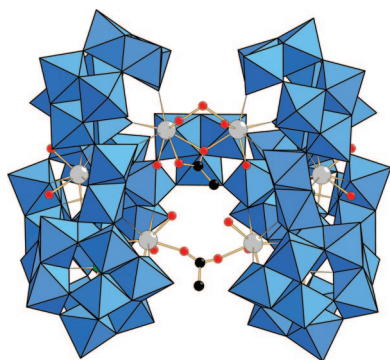


Figure 32. Polyhedral and ball-and-stick representation of the $[\text{Gd}_6\text{As}_6\text{W}_{65}\text{O}_{229}(\text{OH})_4(\text{H}_2\text{O})_{12}(\text{OAc})_2]^{38-}$ polyanion (ref 269). Blue octahedra, $\{\text{WO}_6\}$; green spheres, As; gray spheres, Gd; red spheres, O; black spheres, C.

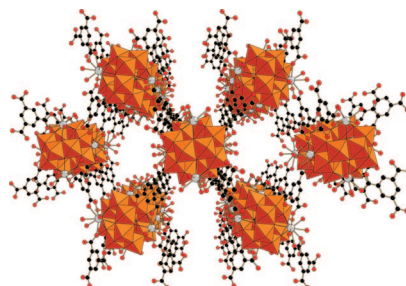


Figure 33. Polyhedral and ball-and-stick representation of the $[\epsilon\text{-PMo}^{\text{V}}_8\text{Mo}^{\text{VI}}_4\text{O}_{35}(\text{OH})_5\{\text{La}(\text{H}_2\text{O})_3\}_4(\text{trim})_2]$ 3D framework (ref 273). Orange octahedra, $\{\text{MoO}_6\}$; green tetrahedra, $\{\text{PO}_4\}$; gray spheres, La; red spheres, O; black spheres, C.

(Figure 33). Alternatively, hydrothermal conditions can be used to generate in situ the ϵ -Keggin isomer bound to organic ligands.^{273,274} Using the analogy between the silicon ion in silicates and the ϵ -Keggin isomer, simulation has allowed generating virtual 3D frameworks based on zeolitic and dense silicates structures, the so-called Z-POMOF structures, with large pores, motivating further experimental investigations on this class of materials.²⁷⁵ Interestingly, the experimental material with ϵ -Keggin POMs capped by Zn(II) ions linked by terephthalate ligands adopts a cristobalite-like structure which was predicted to be the most stable structure. The last category of POM-supported rare-earth complexes gathers several structures where rare-earth centers bound to organic ligands (dmf, dmsO, pyridine-4-carboxylic acid, *N*-methyl-2-pyrrolidone, pyridine-2,6-dicarboxylic acid, 3-hydroxypicolinic acid) are grafted on β -octamolybdate,²⁷⁶ decatungstate,²⁷⁷ Anderson,^{260c,278} Keggin,²⁷⁹ or Dawson²⁸⁰ type POMs.

3.4. Organometallic Complexes

Organometallic derivatives of POMs¹¹ have been studied for more than two decades, the $[(\text{C}_5\text{H}_5)\text{Ti}^{\text{IV}}\text{PW}_{11}\text{O}_{39}]^{4-}$ POM reported in 1978²⁸¹ being considered as the first one, and continue to attract interest because of their applications as homogeneous catalysts for oxidation reactions. They are also studied as models for solid oxide-supported organometallic compounds. In this section we will consider only POMs reported after 1998, containing more than 2 Mo or W atoms, and with a metal–carbon bond, the metal being mainly Ru but Rh- and Pt-substituted POMs have also been investigated; this excludes the dmsO derivatives, already described in the previous section. A distinction is usually made between POM-incorporated organometallic complexes where the organometallic moiety is incorporated into the vacancy of a POM and POM-supported organometallic complexes. We also distinguished here heteropolyoxometalates and isopolyoxometalates. These compounds are gathered in Tables 5 and 6, respectively.

3.4.1. Hetero-POM-Incorporated and Supported Organometallic Complexes

Pope et al. isolated the $[\text{XW}_{11}\text{O}_{39}\text{RhCH}_2\text{COOH}]^{n-}$ ($\text{X} = \text{P}, n = 5; \text{X} = \text{Si}, n = 6$) anions under hydrothermal conditions.²⁸² They have shown that further derivatization can be achieved by reaction of the terminal carboxylic group with 1-methylpiperidine. Proust et al. reported the reaction of $[\text{Ru}^{\text{II}}(\text{arene})\text{Cl}_2]_2$ ($\text{arene} = \text{benzene}, \text{toluene}, p\text{-cymene}, \text{hexamethylbenzene}$) with $[\text{PW}_{11}\text{O}_{39}]^{7-}$ leading to monomeric or dimeric compounds²⁸³ and the self-assembly reaction of

Table 5. Polyoxometalate-Incorporated and Supported Organometallic Complexes

POM building unit	formula	POM:M ratio (M = Ru, Rh, Pt)	ref
vacant polyoxometalates			
[PW ₁₁ O ₃₉] ⁷⁻	[PW ₁₁ O ₃₉ {Ru ^{II} (arene)(H ₂ O)}] ⁵⁻ [(PW ₁₁ O ₃₉ {Ru ^{II} (arene)}) ₂ (WO ₂)] ⁸⁻ (arene = benzene, toluene, <i>p</i> -cymene, hexamethylbenzene)	1:1 2:2	283a
	[PW ₁₁ O ₃₉ {Os ^{II} (<i>p</i> -cymene)(H ₂ O)}] ⁵⁻ [Ru ^{II} (arene)(H ₂ O)}(PW ₁₁ O ₃₉)] ⁵⁻ [Ru ^{II} (arene)}(PW ₁₁ O ₃₉) ₂ (WO ₂)] ⁸⁻ (arene = benzene, toluene, <i>p</i> -cymene, hexamethylbenzene)	1:1 1:1 2:2	283b 292
[γ -XW ₁₀ O ₃₆] ⁸⁻ (X = Si, Ge)	[Ru ^{II} (Cp)(H ₂ O)}{Ru ^{II} (Cp)}(XW ₁₀ O ₃₆)] ⁴⁻	1:2	287
[XW ₉ O ₃₄] ¹⁰⁻ (X = Si, Ge)	[Ru ^{II} (Cp) ₂](XW ₉ O ₃₄) ⁶⁻	1:2	286
[XW ₉ O ₃₄] ⁹⁻ (X = P, As)	[Ru ^{II} (C ₆ H ₆)(XW ₉ O ₃₄)] ⁷⁻	1:1	285
[PW ₉ O ₃₄] ⁹⁻	[(PW ₉ O ₃₄) ₂ (<i>cis</i> -WO ₂)(<i>cis</i> -Ru ^{III} L ^{Me}) ₂] ¹³⁻ (L ^{Me} = 1,3-dimethylimidazolidine-2-ylidene)	1:1	295
[AsW ₉ O ₃₃] ⁹⁻	[AsW ₉ O ₃₄]{AsW ₈ O ₃₁ }{Zn ₄ (OH) ₂ (H ₂ O) ₂ }{Ru(C ₆ H ₆) ₃ }] ⁶⁻	2:3	289
[SbW ₉ O ₃₃] ⁹⁻	[Sb ₂ W ₂₀ O ₇₀ {Ru ^{II} (<i>p</i> -cymene)} ₂] ¹⁰⁻	2:2	284
[XW ₉ O ₃₃] ⁹⁻ (X = Sb ^{III} , Bi ^{III})	[X ₂ W ₂₀ O ₇₀ (RuC ₆ H ₆) ₂] ¹⁰⁻ , [X ₂ W ₂₀ O ₇₀ (RuC ₁₀ H ₁₄) ₂] ¹⁰⁻	2:2	290
[α -P ₂ W ₁₇ O ₆₁] ¹⁰⁻	[Ru ^{II} (arene)(H ₂ O)}(α -P ₂ W ₁₇ O ₆₁)] ⁸⁻ (arene = benzene, <i>p</i> -cymene)	1:1	291
[P ₈ W ₄₈ O ₁₈₄] ⁴⁰⁻	[K(H ₂ O)] ₃ {Ru ^{II} (<i>p</i> -cymene)(H ₂ O)} ₄ P ₈ W ₄₉ O ₁₈₆ (H ₂ O) ₂] ²⁷⁻	1:4	288
substituted polyoxotungstates			
[PW ₉ V ₃ O ₄₀] ⁶⁻	[(Rh ^{II} Cp*)(α -1,4,9-PW ₉ V ₃ O ₄₀)] ⁴⁻	1:1	296b
[α -1,2,3-P ₂ W ₁₅ V ₃ O ₆₂] ⁹⁻	[(Rh ^{II} Cp*) ₂ P ₂ W ₁₅ V ₃ O ₆₂] ⁵⁻	1:1	296a
[α -1,2,3-P ₂ W ₁₅ V ₃ O ₆₂] ⁹⁻	[Pt ^{II} (cod)}(P ₂ W ₁₅ V ₃ O ₆₂)] ⁷⁻ (cod = 1,5-cyclooctadiene)	1:1	297
	[Ru ^{II} (C ₆ H ₆)}(P ₂ W ₁₅ V ₃ O ₆₂)] ⁷⁻	1:1	298
[α -1,2-P ₂ W ₁₆ V ₂ O ₆₂] ⁸⁻	[(Rh ^{II} Cp*)(α -1,2-P ₂ W ₁₆ V ₂ O ₆₂)] ⁶⁻	1:1	296c

Table 6. Organometallic Isopolyoxometalates

complexes	ref
niobates	
[Nb ₆ O ₁₉ {Ru ^{II} (<i>p</i> -cymene)}] ⁶⁻ , [Nb ₆ O ₁₉ {Ru ^{II} (<i>p</i> -cymene)} ₂] ⁴⁻	299b 299b
vanadates	
[(Ru ^{II} Cp*) ₄ V ₆ O ₁₉]	300
[Ru ^{II} (<i>p</i> -cymene)} ₄ V ₆ O ₁₉]	300
molybdates	
[Ru ^{II} (<i>p</i> -cymene)}{Rh ^{II} Cp*} ₃ Mo ₄ O ₁₆]	300
[Ru ^{II} (<i>p</i> -cymene)} ₂ {Rh ^{II} Cp*} ₂ Mo ₄ O ₁₆]	300
[Ru ^{II} (arene)} ₄ Mo ₄ O ₁₆] (arene = C ₆ H ₅ CH ₃ , <i>p</i> -cymene, 1,3,5-C ₆ H ₃ (CH ₃) ₃ , 1,2,4,5-C ₆ H ₂ (CH ₃) ₄)	299a, 300, 301
[Cp* ⁺ Rh ^{II} (H ₂ O)}Mo ₅ O ₁₃ (OMe) ₄ (NO)] ⁻	302
[Cp* ⁺ Rh ^{II} (μ -X)}Mo ₅ O ₁₃ (OMe) ₄ (NO)] ⁻ (X = Cl, Br)	302
[Ru ^{II} (C ₆ Me ₆) ₂ Mo ₅ O ₁₈ {Ru ^{II} (C ₆ Me ₆)(H ₂ O)}]	299a
[Ru ^{II} (arene)} ₂ Mo ₆ O ₁₈ {MeC(CH ₂ O) ₃ }] ²⁻ (arene = C ₆ H ₅ Me, C ₆ Me ₆)	41b
[Ru ^{II} (arene)} ₂ Mo ₆ O ₂₀ (OMe) ₂] ²⁻ (arene = C ₆ H ₅ Me, C ₆ Me ₆)	41b
[Cp* ⁺ Mo ₆ O ₁₈] ⁻	304
Cp* ⁺ Mo _x W _{6-x} O ₁₇ (x = 0, 2, 4, 6)	303
tungstates	
[Ru ^{II} (C ₆ Me ₆) ₄ W ₄ O ₁₆]	299a
[Ru ^{II} (C ₆ Me ₆) ₂ W ₅ O ₁₈ {Ru ^{II} (C ₆ Me ₆)(H ₂ O)}]	299a
[Ru ^{II} (<i>p</i> -MeC ₆ H ₄ <i>i</i> -Pr)} ₂ (OH) ₃] ₂][Ru ^{II} (<i>p</i> -MeC ₆ H ₄ <i>i</i> -Pr)} ₂ W ₈ O ₂₈ (OH) ₂ {Ru ^{II} (<i>p</i> -MeC ₆ H ₄ <i>i</i> -Pr)(H ₂ O)} ₂]	299a

the [Sb₂W₂₀O₇₀{Ru^{II}(*p*-cymene)}₂]¹⁰⁻ anion.²⁸⁴ In these organometallic derivatives, cationic {(arene)Ru(H₂O)}²⁺ groups are covalently bound to the nucleophilic oxygen atoms which delimit the lacuna of the POMs. Similarly, following the same strategy they have used for the grafting of {Ru^{II}(dmsO)₃} groups (see above), Kortz et al. studied the reaction of [Ru^{II}(arene)Cl₂]₂ (arene = benzene, *p*-cymene) with the POMs [XW₉O₃₄]⁹⁻ (X = P, As),²⁸⁵ [XW₉O₃₄]¹⁰⁻ (X = Si, Ge),²⁸⁶ [γ -XW₁₀O₃₆]⁸⁻ (X = Si, Ge),²⁸⁷ [H₇P₈W₄₈O₁₈₄]³³⁻²⁸⁸, [AsW₉O₃₄]⁹⁻ in the presence of Zn^{II} ions,²⁸⁹ and [X₂W₂₂O₇₄(OH)₂]¹²⁻ (X = Sb^{III}, Bi^{III}).²⁹⁰ Nomiyama et al. studied the reactivity of the monovacant [α -P₂W₁₇O₆₁]¹⁰⁻²⁹¹ and [PW₁₁O₃₉]⁷⁻²⁹² POMs with the same Ru^{II} precursor. Considering the monovacant Keggin-type POM, they have shown that the proportion of the monomeric [{(arene)Ru(H₂O)}PW₁₁O₃₉]⁵⁻ and dimeric [({(arene)Ru}PW₁₁O₃₉)₂(μ -WO₂)]⁸⁻ species was strongly dependent on the pH of the solution. These complexes are water soluble, and their study

as oxidation catalysts²⁹³ attracts interest in the context of the search of environmentally friendly reactions. Computational studies on the Ru derivatives of the monolacunary [XW₁₁O₃₉]^{m-} (X = P, m = 7; X = Si, m = 8) anions have recently been reported and evidenced the influence of the nature of the central heteroelement and the influence of the grafted cations.²⁹⁴ Additionally, the first carbene derivative [(PW₉O₃₄)₂(*cis*-WO₂)(*cis*-Ru^{III}L^{Me})₂]¹³⁻ (L^{Me} = 1,3-dimethylimidazolidine-2-ylidene) was obtained by the reaction of [Ru^{II}L^{Me}₄Cl₂]₂ with [PW₁₁O₃₉]⁷⁻ (Figure 34).²⁹⁵

An approach to increase the nucleophilicity of the oxygen atoms is to increase the negative charge of the POM by replacement of one or several M^{VI} centers (M = Mo, W) by cations with a lower charge (V^V, Nb^V, Ti^{IV}, ...). This strategy was successfully used by Nomiyama et al. for the synthesis of V^V-substituted POMs functionalized by {Cp*⁺Rh^{II}},²⁹⁶ {Pt^{II}(cod)} (cod = 1,5-cyclooctadiene),²⁹⁷ or {(C₆H₆)Ru^{II}}²⁹⁸ groups.

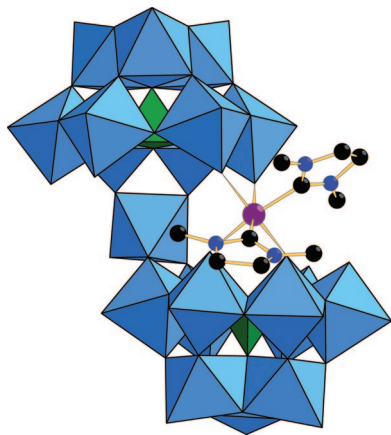


Figure 34. Polyhedral and ball-and-stick representation of the $[(PW_9O_{34})_2(cis-WO_2)(cis-Ru^{III}Me_2)]^{13-}$ polyanion (ref 295). Blue octahedra, $\{WO_6\}$; green tetrahedra, $\{PO_4\}$; purple sphere, Ru; black spheres, C; blue spheres, N.

3.4.2. $(\eta^6\text{-Arene})$ ruthenium and -Rhodium Oxomolybdenum and Oxotungsten Clusters

The synthesis of $(\eta^6\text{-arene})$ ruthenium and -rhodium oxomolybdenum and oxotungsten clusters has been developed by the groups of Isobe and Süss-Fink in the 1990s.¹¹ Several POMs incorporating $\{Ru(\text{arene})\}^{2+}$ groups have been then synthesized by Proust et al. by the condensation reaction of tungstate, molybdates, or $K_7H[Nb_6O_{19}]$ in the presence of organometallic precursors.²⁹⁹ *p*-Cymene ruthenium dichloride dimer reacts in aqueous solution with sodium molybdate or sodium vanadate to give the neutral amphiphilic cluster $[\{Ru^{II}(p\text{-cymene})\}_4Mo_4O_{16}]$ and $[\{Ru^{II}(p\text{-cymene})\}_4V_6O_{19}]$, respectively.³⁰⁰ The mixed-metal clusters $[\{Ru^{II}(p\text{-cymene})\}_2\{Rh(Cp^*)\}_3Mo_4O_{16}]$ and $[\{Ru^{II}(p\text{-cymene})\}_2\{Rh^{II}(Cp^*)\}_2Mo_4O_{16}]$ have also been synthesized.³⁰⁰ Proust et al. studied the equilibrium in solution between the windmill-like and the triple-cubane forms of $[\{Ru^{II}(\text{arene})\}_4Mo_4O_{16}]$.³⁰¹ The reactivity of the arene ruthenium dichloride dimer with $(n\text{-Bu}_4N)_2[Mo_2O_7]$ has been investigated in methanol and acetonitrile, forming derivatives of known oxoalkoxopoly-molybdates.^{41b} The $[Mo_5O_{13}(OMe)_4(NO)]^{3-}$ anion has also been used as a molybdenum precursor.³⁰² Finally, organometallic complexes $Cp^*Mo_xW_{6-x}O_{17}$ ($x = 0, 2, 4, 6$) have been synthesized from the reaction of $Cp^*M_2O_5$ with $Na_2M'O_4$ ($M, M' = Mo, W$) in aqueous medium,³⁰³ while the synthesis of the $[Cp^*Mo_6O_{18}]^-$ anion has been performed in methanol.³⁰⁴

4. Reactivity and Applications of Covalently Functionalized POMs

In this section we will give an overview, which is not aimed to be exhaustive, of the reactivity and various applications of covalently functionalized hybrid organic–inorganic POMs.

4.1. Postfunctionalization of Hybrid POMs

Keana et al. initiated in 1985 the study of the reactivity of an organic function supported by a POM, a Dawson-type anion monofunctionalized by a Ti^{IV} ion bearing a substituted cyclopentadienyl (Cp) group,³⁰⁵ and further exploited the chemistry of the organic ligand attached to the Cp group.³⁰⁶ However, most of the work on the modification of a covalent hybrid POM was reported this past decade. This postfunc-

ionalization allows introduction of sophisticated organic functions, which are difficult to introduce in one step, and also the linking of POM entities. A synergistic effect between the organic function and the inorganic POM is often much sought after. As organic chemistry in pure water is not much developed, the required condition is to have a stable, organic-soluble precursor which can be synthesized in good yield. Therefore, few hybrid POMs are suitable as precursors for the classical organic reactions described below.

4.1.1. “Click Chemistry”

Huisgen 1,3-dipolar cycloaddition of azides and alkynes catalyzed by copper(I) is an efficient reaction for the formation of 1,3-triazole derivatives.³⁰⁷ Recently, this chemical coupling has been extended to material³⁰⁸ and nanomaterial chemistry.³⁰⁹ Taking advantage of the feasibility of this reaction in polar medium, Hasenknopf, Lacôte, Thorimbert, and co-workers described the first synthesis using the click chemistry strategy involving POMs. Such reactions have been performed successfully on different POMs monofunctionalized by an organotin group ($[\alpha_1\text{-P}_2W_{17}O_{61}SnR]^{7-}$, $[\alpha_2\text{-P}_2W_{17}O_{61}SnR]^{7-}$, and $[PW_{11}O_{39}SnR]^{4-}$). Whatever the reactive organic group (azide or alkyne) carried by these POMs, the cycloaddition was performed in a CH_3CN/H_2O (1:2) mixture with very efficient yield and allowed introduction of a great variety of lipophilic and hydrophilic ligands.^{102b} Recently, Odobel et al. used this methodology for the grafting of two perylene groups,^{83h} metalloporphyrins,⁸³ⁱ or dendritic metalloporphyrins³¹⁰ onto the bis-organosilyl derivatives $[\alpha_2\text{-P}_2W_{17}O_{61}(SiR)_2]^{7-}$ ($R = Ph-CH_2-N_3$, $(CH_2)_2N_3$) Dawson POMs. Electron-transfer reactions have been evidenced within these perylene–POM conjugates (Figure 35a).

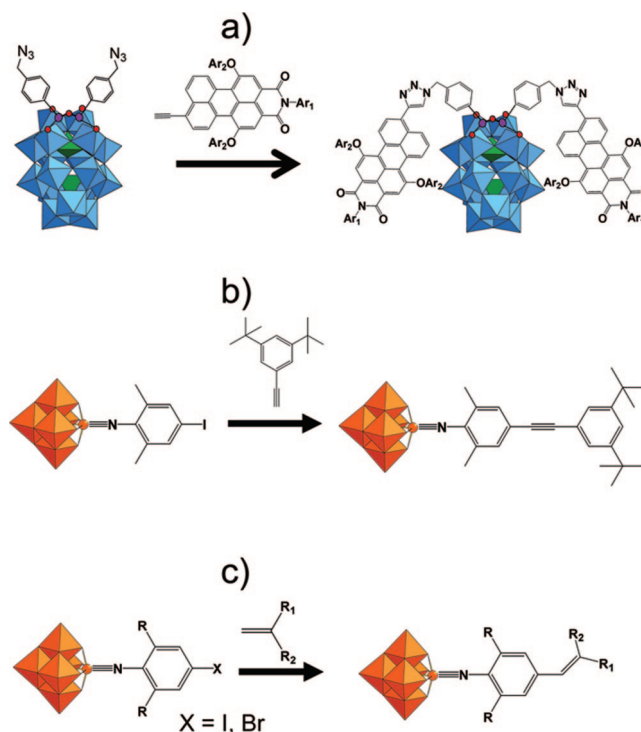


Figure 35. Illustration of different organic reactions performed in the presence of prefunctionalized POMs: (a) click chemistry (ref 83h), (b) Sonogashira reaction (ref 121a), and (c) Heck reaction (ref 121h). Blue octahedra, $\{WO_6\}$; orange octahedra, $\{MoO_6\}$; green tetrahedra, $\{PO_4\}$; orange spheres, Mo; purple spheres, Si; red spheres, O.

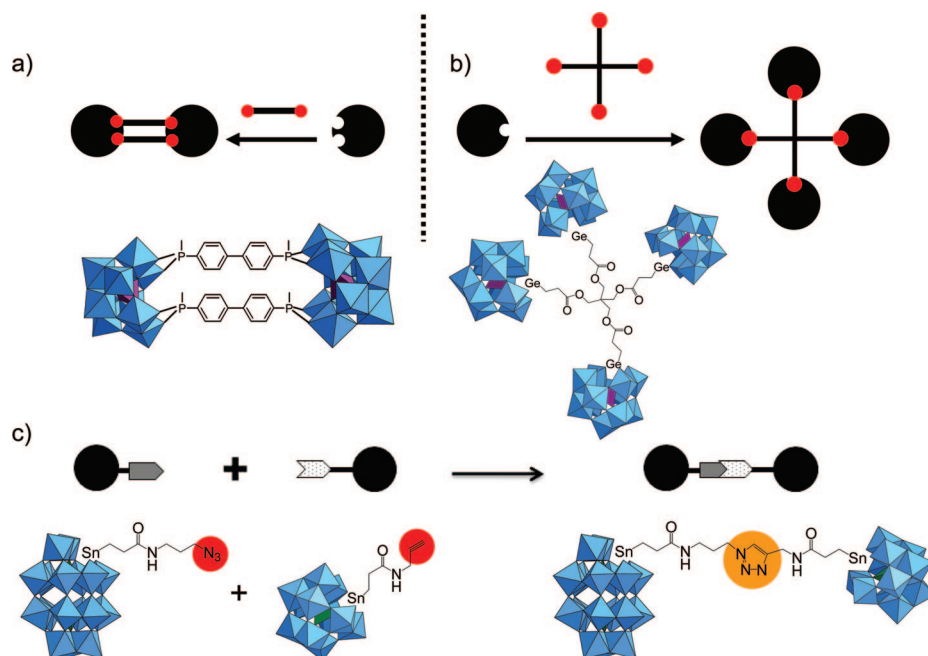


Figure 36. Two routes for the design of hybrid oligomers: (a and b) by reaction with polyelectrophilic groups (refs 106 and 163) or (c) by coupling of different prefunctionalized POMs (ref 102b). Blue octahedra, $\{\text{WO}_6\}$; green tetrahedra, $\{\text{PO}_4\}$; purple tetrahedra, $\{\text{SiO}_4\}$; green spheres, P; black spheres, C; red spheres, O.

4.1.2. Sonogashira and Heck Coupling

The Sonogashira coupling is a Pd-catalyzed coupling reaction between aryl halides and ethynyl groups.³¹¹ It occurs generally under mild conditions and has also been applied to coordination complexes.³¹² Peng et al. first performed successfully this cross-coupling reaction on $[\text{Mo}_6\text{O}_{18}(\text{NAr})]^{2-}$ (Ar = 2,6-dimethyl-4-iodophenyl) (Figure 35b).^{121a} Sonogashira coupling reactions have been then widely exploited on a variety of functionalized Lindqvist POMs with the aim to synthesize charge-transfer hybrids with one or two ferrocenyl units covalently attached,^{116e} hybrid molecular dumbbells,^{116a} hybrid polymers,^{20,115,116f} or for the direct covalent grafting on Si surfaces.³¹³ Recently, Sonogashira coupling was also applied for the covalent attachment of $\text{R}-\text{C}\equiv\text{C}-$ (R = SiMe_3 , Phtpy) groups on the difunctionalized organosilyl derivative $[\text{PW}_{11}\text{O}_{40}\{\text{SiPh}\}_2]^{3-}$.²⁵ Finally, Pd-catalyzed Heck coupling reaction of bromo- and iodo-functionalized aryl derivatives of hexamolybdates with alkenes also allowed access to a variety of hybrid POMs with organic conjugated segments covalently attached (Figure 35c).^{121h}

4.1.3. Other Types of Organic Reactions

The feasibility of many classical organic reactions such as Diels–Alder reactions, esterification, oxidation of an alcohol group, or reduction of an aldehyde group on monofunctionalized Keggin- or Dawson-type POMs has been demonstrated by Keana et al.^{306b} Pope et al. showed later that Keggin-type POMs monofunctionalized by a carboxylic acid terminated ligand, bound to a rhodium or a germanium ion inserted in the vacancy, can react with an alcohol or an amine.^{106,282} Formation of a peptide bond from the organotin derivative $\alpha_2\text{-}[\text{P}_2\text{W}_{17}\text{O}_{61}\{\text{Sn}(\text{CH}_2\text{CH}_2\text{COOH})\}]^{7-}$ Dawson POM with amino ligands was then later achieved.^{102a} Similarly, alcohols can be attached via esterification reactions.⁹¹ The regioselective mono-oxoacylation of $\alpha_1\text{-}$ and $\alpha_2\text{-}[\text{P}_2\text{W}_{17}\text{O}_{61}\{\text{Sn}(\text{CH}_2\text{CH}_2\text{COOH})\}]^{7-}$ has been investigated experimentally and also by DFT calculations.^{102c} Acylation

of the oxo ligand gives exalted electrophilicity to the acyl moiety and allows access to functionalized amides and thioesters. The kinetic resolution of an α_1 -substituted Dawson POM has been successfully performed by using this type of reaction.^{102d} The hydrosilylation of $[\text{PW}_{11}\text{O}_{39}(\text{Si}-\text{CH}=\text{CH}_2)_2\text{O}]^{3-}$ was achieved with Et_3SiH and PhSiMe_2H .^{79b}

Anderson- and Lindqvist-type POMs can also be post-functionalized via imine, amide, or ester bond formation. Reaction of the free amino group of the functionalized Anderson derivative $[\text{MnMo}_6\text{O}_{18}\{(\text{OCH}_2)_3\text{CNH}_2\}_2]^{3-}$ with various aldehydes, to give an imine derivative, has allowed introduction of binding functionalities.^{31b,j} Long alkyl chains have been grafted on Mn–Anderson anions through covalent amide bond formation.^{31f} Wei et al. developed esterification reactions on the phenolic hydroxyl-functionalized organoimido-substituted hexamolybdate $[\text{Mo}_6\text{O}_{18}(\text{NAr})]^{2-}$ (Ar = *p*-hydroxyl-*o*-tolyl) with various carboxylic acids (acetic, *p*-methylbenzoic, *p*-chlorobenzoic, propanoic, acrylic). This reaction is assisted by DCC as a dehydrating agent.^{116p}

4.2. Oligomers of Hybrids POMs

4.2.1. Heteropolyoxometalate Oligomers

Two approaches have been described. The first one consists of the reaction of heteropolyoxometalates with polyelectrophilic groups. Reaction of hydroxylated dendrimers with $[\text{H}_4\text{P}_2\text{V}_3\text{W}_{15}\text{O}_{62}]^{5-}$ anions has thus led to formation of dendritic tetranuclear POM molecules.³⁴ Following the same strategy, the first hybrid dumbbells with Dawson-type anions have been built from the connection of two $[\text{P}_2\text{V}_3\text{W}_{15}\text{O}_{62}]^{9-}$ POMs via linear bis(Tris) ligands (Tris = tris(hydroxymethyl)aminomethane).³⁶ Cyclic dimers have been built by reaction of the divacant POM $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$ with different bisphosphonates groups to yield $[\text{H}_2(\gamma\text{-SiW}_{10}\text{O}_{36})\{(\text{O})\text{PCH}_2(\text{C}_6\text{H}_4)_n\text{CH}_2\text{P}(\text{O})\}_2]^{6-}$ (Figure 36a).¹⁶³ Pope et al. linked four $[\text{SiW}_{11}\text{O}_{39}]^{8-}$ units with one tetrakis-

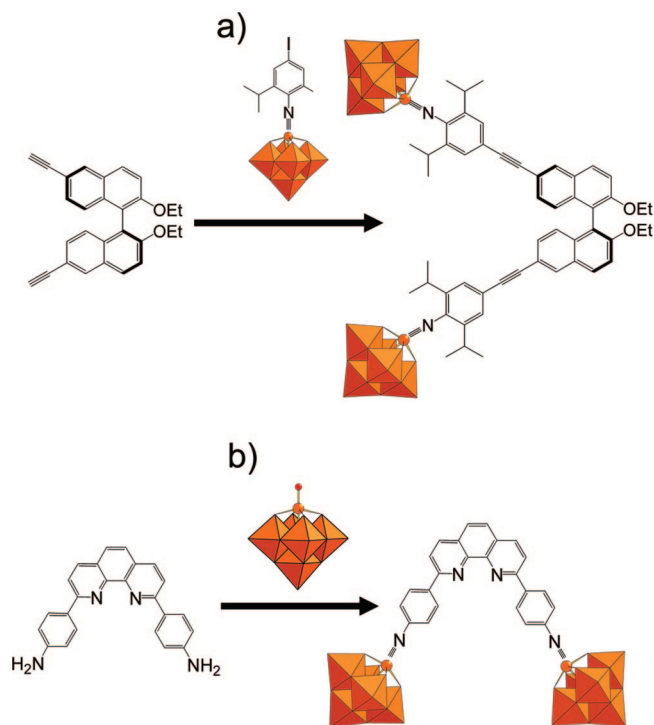


Figure 37. Two routes leading to dimeric hybrid POMs based on Lindqvist $[\text{Mo}_6\text{O}_{19}]^{2-}$ units (refs 116k and 116l). Orange octahedra, $\{\text{MoO}_6\}$; orange spheres, Mo.

trichlorogermaneester group, leading to the tetrameric $[(\text{SiW}_{11}\text{O}_{39}\text{GeCH}_2\text{CH}_2\text{COOCH}_2)_4\text{C}]^{20-}$ POM (Figure 36b).¹⁰⁶

The second approach consists of the coupling of prefunctionalized heteropolyphosphotungstates with azides and alkynes groups via click-chemistry reactions. This method offers the great advantage of formation of dissymmetrical structures. For example, click chemistry between the alkyne-terminated Dawson hybrid $[\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61}\{\text{Sn}(\text{CH}_2)_2\text{C}(\text{O})\text{NHCH}_2\text{C}\equiv\text{CH}\}]^{7-}$ and the azide-terminated Keggin hybrid $[\text{PW}_{11}\text{O}_{39}\text{Sn}(\text{CH}_2)_2\text{C}(\text{O})\text{NH}(\text{CH}_2)_3\text{N}_3]^{4-}$ has led to the synthesis of an original dissymmetric polyoxometalate dimer (Figure 36c).^{102b} Using prefunctionalized POMs, remarkable chiral molecular triads have been obtained from achiral POMs.^{116s} Anderson-type POMs $[\text{MMo}_6\text{O}_{18}\{(\text{OCH}_2)_3\text{CNH}_2\}_2]^{3-}$ ($\text{M} = \text{Mn}^{\text{III}}, \text{Fe}^{\text{III}}$) bearing pendant amino groups have been reacted with the Lindqvist-type POM $[\text{Mo}_6\text{O}_{19}]^{2-}$ using DCC as a dehydrating agent. Enantiopure crystals of the triads $[\text{Mo}_6\text{O}_{18}\text{NC}(\text{OCH}_2)_3\text{MMo}_6\text{O}_{18}(\text{OCH}_2)_3\text{CNMo}_6\text{O}_{18}]^{7-}$ ($\text{M} = \text{Mn}^{\text{III}}, \text{Fe}^{\text{III}}$) have been isolated by spontaneous resolution on crystallization.

4.2.2. Lindqvist Dimers

Hexamolybdate $\text{Mo}_6\text{O}_{19}^{2-}$ clusters can be easily mono-functionalized through formation of a $\text{Mo}\equiv\text{N}-\text{R}$ bond (see above). This functionalization allows the linking of two POM units by an organic bridge, following a one-step or two-step procedure. In the one-step procedure formation of the dimer is obtained directly by reaction of the molybdate precursor with a diaminoligand. Maatta et al. have thus shown that 1,4-diaminocyclohexane allows one to obtain diimido-bridged hexamolybdates.³¹⁴ More or less rigid bridges were then used such as alkylene-bis(phenoxy-4-amine),^{116b} bis-2,9-di(4-aminophenyl)-1,10-phenanthroline (Figure 37a),^{116k} phenyl, or biphenyl groups.^{116r} Intramolecular charge transfer has been evidenced in the later hybrid dimer. Note also that the dimeric $[\text{Mo}_6\text{O}_{18}\text{NC}(\text{C}_2\text{H}_5)=$

$\text{C}(\text{C}_2\text{H}_5)\text{NMo}_6\text{O}_{18}]^{4-}$ anion has been formed by the direct linking of two hexamolybdate units by an unexpected $\text{C}\equiv\text{C}$ bond.^{116o} This bond results from the doubly dehydrogenative coupling of two saturated sp^3 C–H bonds of the *n*-alkylamine hydrochloride precursor.

The first study based on a two-step procedure was described by Peng et al. The hybrid precursor, an organoimido-derivative of $\text{Mo}_6\text{O}_{19}^{2-}$ functionalized by one iodide–aryl group, has been reacted with its ethynyl-substituted analogue, following a Sonogashira coupling method.^{116a} In this hybrid molecular dumbbell the two POMs units are linked through an extended π -conjugated organic bridge. Similarly, two Lindqvist POMs have been connected by an enantiopure 1,1'-binaphthyl group (Figure 37b).^{116l}

4.3. Micellar Structures, Hybrid Polymers, and Hybrid Gels

The hybrid compounds described so far are mainly isolated as solid crystalline materials which can be characterized most of the time by single-crystal X-ray diffraction, but noncrystalline hybrid materials such as micellar structures, polymers, and gels can also be formed from the assembly of functionalized POMs.

4.3.1. Micellar Structures

Amphiphilic surfactants are constituted by a polar headgroup and a long apolar chain and have found applications in many domains from biology to nanomaterials and to ionic liquids. Polar headgroups are inorganic entities which vary from coordination complexes³¹⁵ including porphyrins³¹⁶ to oxide nanoparticles.³¹⁷ The use of POMs as polar headgroups linked to long alkyl chains was first achieved by Chambers, Atkinson, and co-workers.^{79a} The amphiphilic compound is the monovacant POM functionalized by two organosilyl groups $[\text{SiW}_{11}\text{O}_{39}\{\text{Si}(\text{CH}_2)_{11}\text{CH}_3\}_2\text{O}]^{4-}$. Monolayer and multilayer thin films have been prepared by Langmuir–Blodgett techniques. Since this date, Cronin and co-workers described the covalent functionalization of Anderson POMs by long hydrophobic alkyl chains linked to the hydrophilic $\{\text{MnMo}_6\text{O}_{24}\}$ core by tris-alkoxo groups.^{31f} Exchange of the TBA^+ cations with dimethyldioctadecyl ammonium (DMDOA) results in formation of new POM assemblies in which the functionalized POMs are encapsulated by surfactant of DMDOABr. The Mn–Anderson– C_{16} surfactants form vesicular structures in $\text{CH}_3\text{CN}/\text{water}$ mixed solvents (Figure 38a).³¹ⁱ Besides, hybrid dimers built from the connection of two $[\text{P}_2\text{V}_3\text{W}_{15}\text{O}_{62}]^{9-}$ POMs via linear bis(Tris) ligands (Tris = tris(hydroxymethyl)aminomethane) and possessing very large polar headgroups have been characterized. They also self-assemble into hollow vesicles, with a size from 60 to 120 nm, according to the concentration and the composition of the water/acetone solutions (Figure 38b).³⁶

4.3.2. Hybrid Polymers and Gels

In this section, the term ‘polymer’ will be taken in the large sense and will be used for the classical organic polymers with covalently attached POMs as well as noncrystalline 1D coordination networks with POM building units. Different approaches can be followed for the synthesis of hybrid polymers.³¹⁸ The first way corresponds to the polycondensation of two difunctional precursors (Figure 39a). The second one consists in polymerizing one hybrid mono-

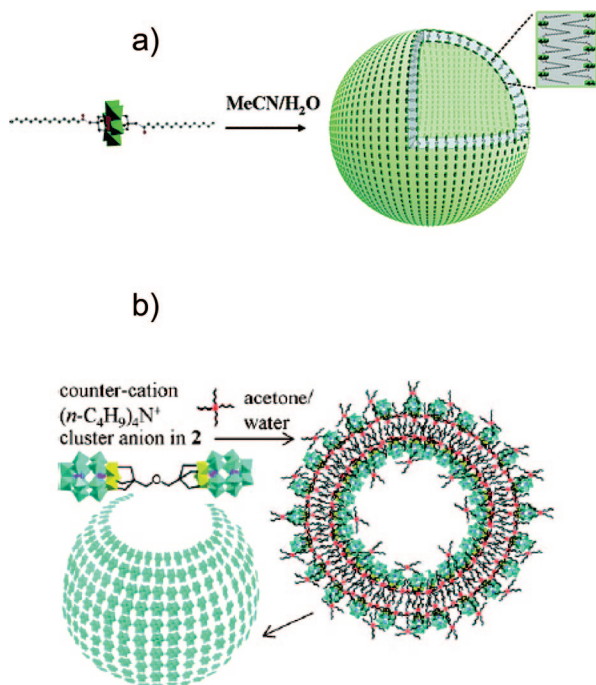


Figure 38. Two self-assembly reactions leading to vesicles made of (a) Mn-Anderson- C_{16} POMs (Reprinted with permission from ref 31i. Copyright 2009 American Chemical Society) and (b) dimeric Dawson POMs (Reprinted with permission from ref 36. Copyright 2009 Wiley).

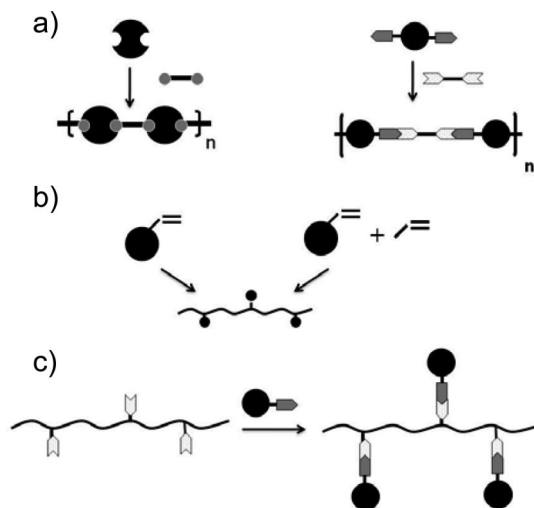


Figure 39. Schematic representation of different approaches for the design of hybrid polymers: (a) by polycondensation of two difunctionalized precursors (organic linkers and inorganic moieties), (b) by homopolymerization or copolymerization of a hybrid monofunctionalized POM, and (c) by grafting of hybrid monofunctionalized POMs on a preformed polymer.

mer itself or copolymerizing it with an organic monomer (Figure 39b). The third way concerns the grafting of hybrid entities on a preformed polymer (Figure 39c). In the two later methods, the hybrid entity must be monofunctionalized. As a consequence, hybrid polymers reported so far in the literature are quasi-exclusively based on Lindqvist-type POMs on which introduction of only one functional group is easy.

Considering the polycondensation pathway, Peng et al. succeeded in condensing *cis*-difunctionalized $[Mo_6O_{17}(NArC)_2]^{2-}$ POMs by Sonogashira coupling with an aromatic-dialkyne group.¹¹⁵ The number of repeating units in

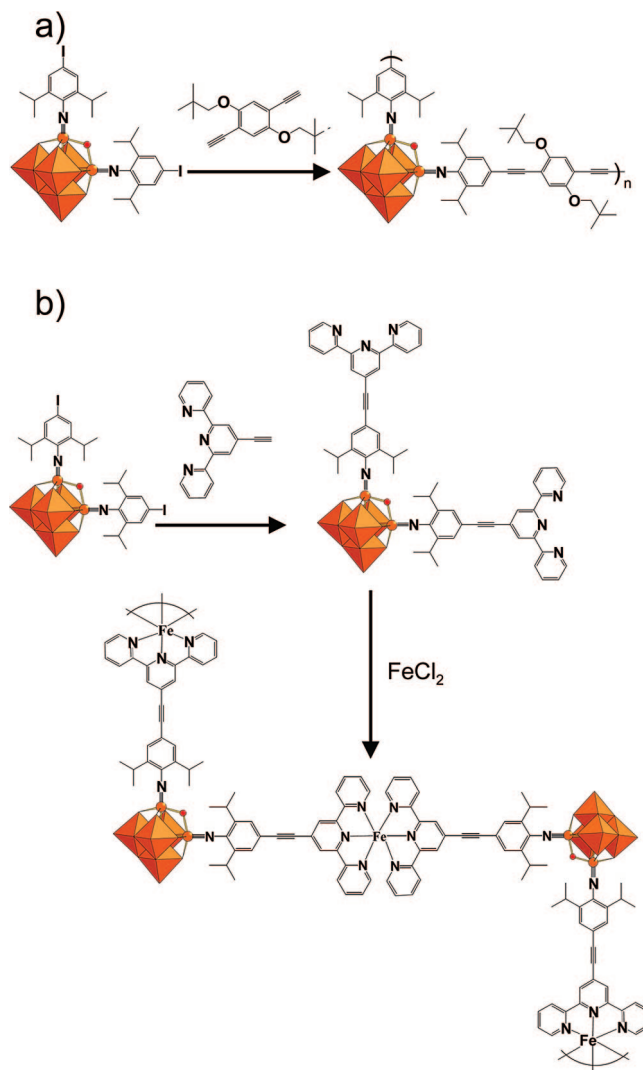


Figure 40. Formation of (a) a hybrid polymer based on Lindqvist POMs (ref 116i) and (b) a metallohybrid polymer based on Lindqvist POMs (ref 116j). Orange octahedra, $\{MoO_6\}$; orange spheres, Mo; red spheres, O.

the polymer was estimated to be about 18. These hybrid polymers are soluble in dmf and dmsO, and films can be spin coated from solutions (Figure 40a).¹¹⁶ⁱ These materials could find applications in photovoltaic cells. The difunctionalized bisterpyridine derivative $[Mo_6O_{17}(NArC\equiv Ctpy)_2]^{2-}$ was used as precursor and polycondensed by complexation of Fe^{II} ions by the terpyridine groups (Figure 40b).^{116j} Using a similar strategy, Hasenkopf et al. studied the complexation of the difunctionalized Anderson POM $[MnMo_6O_{18}\{(OCH_2)_3CNHCO(4-C_5H_4N)\}_2]^{3-}$, which can be viewed as a 4,4'-bipyridine ligand with a large spacer between the pyridine rings, with Pd^{II} ions. Interestingly, this self-assembly reaction leads to the formation of a transparent and birefringent gel.^{31c}

Formation of hybrid polymers by copolymerization has been comparatively less investigated. To our knowledge, only the study described by Maatta et al. illustrates this approach. The precursor is the organoimido derivative monofunctionalized by a styrene group $[Mo_6O_{18}(NC_6H_4CH=CH_2)]^{2-}$. The hybrid copolymer with POM pendant units has been obtained by copolymerization with 4-methylstyrene monomers.¹⁹

Considering now the third way, monofunctionalized hexamolybdate clusters have been covalently attached to the side

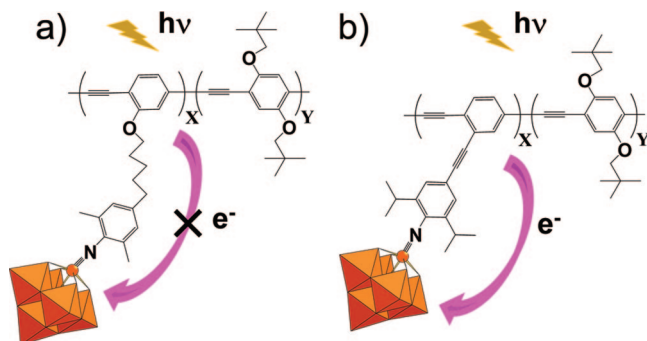


Figure 41. Schematic representations of two rigid conjugated polymers bearing Lindqvist POMs grafted via (a) a flexible alkyl chain (no photoinduced electron transfer allowed) or (b) a rigid and conjugated bridge (photoinduced electron transfer allowed) (ref 20). Orange octahedra, $\{\text{MoO}_6\}$; orange spheres, Mo.

chains of conjugated polymers through a rigid conjugated bridge or through flexible alkyl chains (Figure 41).²⁰ A photoinduced electron transfer between the polymer and the POM can be observed if the linker connecting the two components is a rigid, conjugated organic ligand. This system can be potentially interesting for applications in photovoltaic cells.

Finally, a last type of hybrids has been formed with organosilyl derivatives. In these polymers the POMs act as reticulating agents for the polymerization of an organic monomer. The first study was performed by Judenstein in 1992.³¹⁹ The radical copolymerization of the difunctionalized $[\text{SiW}_{11}\text{O}_{39}(\text{SiR})_2\text{O}]^{4-}$ ($\text{R} = \text{vinyl, allyl, styryl, acrylate}$) POMs with an organic monomer such as methacrylate or styrene was performed in dmf. Two kinds of POMs, $[\gamma\text{-SiW}_{10}\text{O}_{36}(\text{SiMethacryloyl})_2\text{O}]^{4-}$ (HPOM-1) and $[\gamma\text{-SiW}_{10}\text{O}_{36}(\text{SiMethacryloylO})_4]^{4-}$ (HPOM-2), have been used as reticulating agents to get an organic polymethacrylate gel with HPOM-1 and a polyacrylamide hydrogel with HPOM-2.^{21,84a} High swelling rates have been observed with the two types of gel, particularly with HPOM-2 in aqueous medium. In this last case, the high rate of swelling is due to the presence of HPOM-2 covalent aggregates in solution. These hydrogels have been used to confine magnetic nanoparticles.^{85a} This study has shown that the trapping of magnetic NPs is increased compared to purely organic ferrogels. Indeed, with HPOM-2, the high swelling rate obtained leads to a better mobility of NPs inside these networks (Figure 42).^{85b}

4.4. Grafting of Hybrid POMs on Surfaces

Three types of surfaces will be considered in this part: surfaces inside macroporous silica, planar surfaces such as gold or silicon, and nanoparticle surfaces.

4.4.1. Macroporous Silica

Incorporation of POMs in macroporous silica has been achieved by Stein et al.^{85c} Two approaches have been used in order to get high loadings of POMs, both incorporating POMs during the formation of macroporous silica. In the first one, the dilacunary $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$ POM has been directly reacted with tetraethoxysilane (TEOS), while in the second one, $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$ was first reacted with the bifunctional bridging ligand 1,2-bis(triethoxysilyl)ethane, acting as covalent linker between the POM and the macroporous silica, prior to reaction with TEOS. Removal of the polystyrene colloidal crystal template proved to be a

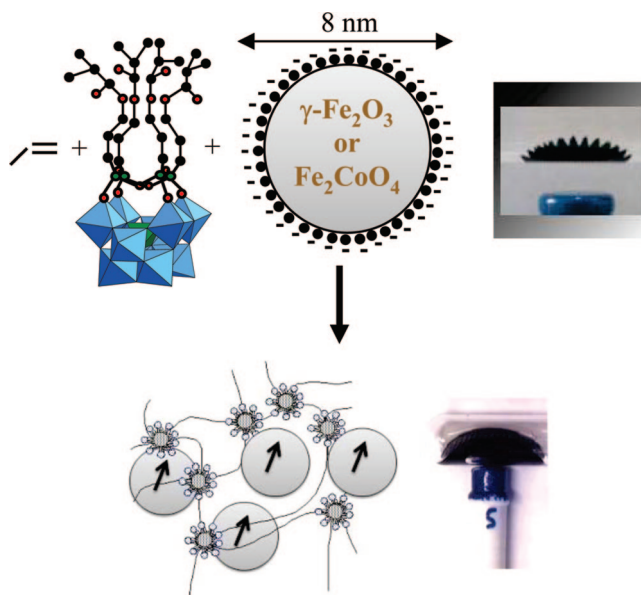


Figure 42. Schematic representation of the formation of ferrogels from the $[\gamma\text{-SiW}_{10}\text{O}_{36}(\text{SiMethacryloylO})_4]^{4-}$ tetrafunctionalized POM. Blue octahedra, $\{\text{WO}_6\}$; green octahedra, $\{\text{SiO}_4\}$; green spheres, Si; black spheres, C; red spheres, O.

key step to maintain the integrity of the POM structure and to obtain high incorporation of POMs within the silica wall structures. These materials have been designed to study their catalytic activities for the epoxidation of cyclooctene with anhydrous $\text{H}_2\text{O}_2/t\text{-BuOH}$ solutions at room temperature.

4.4.2. Planar Surfaces

Functionalization of Si^0 or Au^0 surfaces and chemical control of monolayer or multilayer assemblies is a great challenge for biomedical, electronic, or optical applications. Two types of POM precursors have been used: monofunctionalized Lindqvist and difunctionalized Mn–Anderson POMs. Errington et al. described the covalent attachment of $\{\text{TiW}_5\}$ units on silicon surfaces, through covalent Ti–O–C alkoxide bonds, by alcoholysis of the Ti–OMe bond in $[(\text{MeO})\text{TiW}_5\text{O}_{18}]^{3-}$.³²⁰ Tour et al. prepared a monofunctionalized hexamolybdate cluster bearing a conjugated bridge with one diazonium end group. Diazonium chemistry has ensured a strong grafting of the POMs onto the surface through C–Si bonds whatever the crystalline face (Si(111) or Si(100)). Electronic interactions have been evidenced through the organic conjugated bridge leading to potential applications in semiconductor electronic devices (Figure 43a).³¹³ Cronin et al. covalently attached, through an amide bond, the difunctionalized Mn–Anderson POM $[\text{MnMo}_6\text{O}_{18}\text{-}\{(\text{OCH}_2)_3\text{CNH}_2\}_2]^{3-}$ on gold surfaces modified by 16-mercaptohexadecanoic acid moieties (Figure 43b). The free amine group on the attached POM allows further postsynthetic covalent modification on these self-assembled monolayers (SAMs), and introduction of a pyrene group has thus been performed.^{31h} These SAM–POM–pyrene systems show specific cell adhesion behavior on the patterned area which is not observed in the absence of the inorganic unit, but to date the role of the POM cluster in this process is not clearly understood.

4.4.3. Nanoparticles

While the electrostatic interaction of POMs with metallic nanoparticles has been widely documented,³²¹ showing their

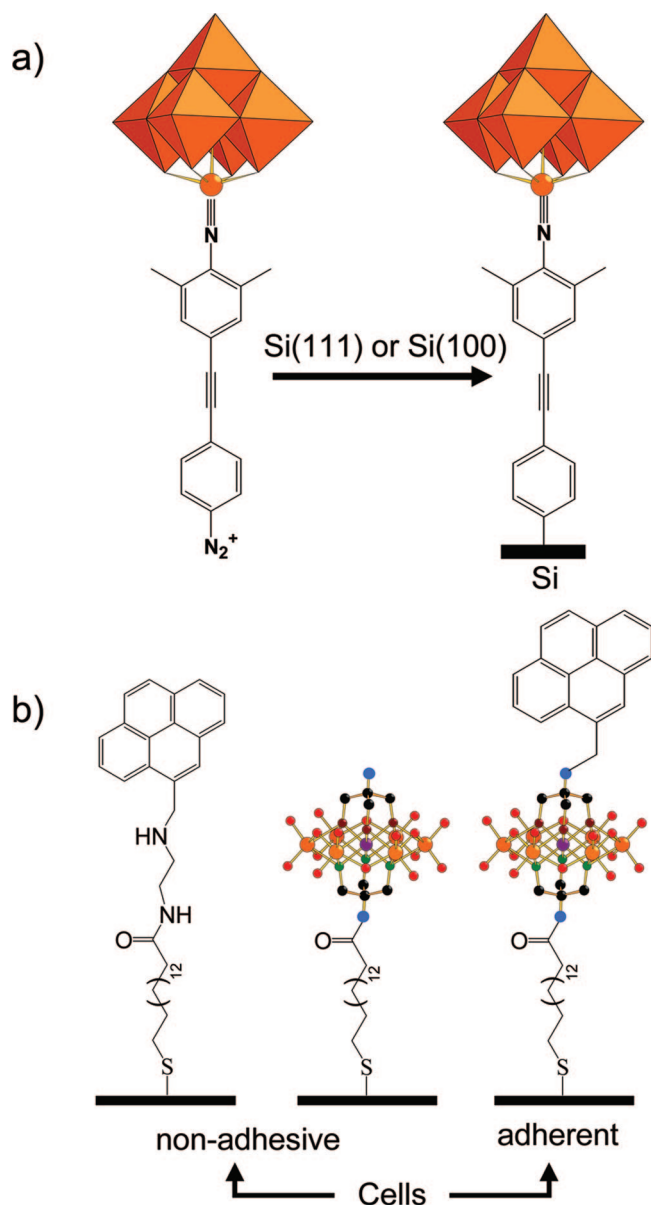


Figure 43. Schematic representations of two types of grafting of POMs on surfaces: (a) the grafting of hybrid Lindqvist POMs on silicon surface (ref 313) and (b) the grafting of functionalized Anderson POMs on gold surface (ref 31h). Orange octahedra, $\{\text{MoO}_6\}$; orange spheres, Mo; purple spheres, Mn; black spheres, C; red, brown or green spheres, O; blue spheres, N.

protecting-ligand shell role, there are very few examples of direct covalent grafting. One of the first descriptions has been given by Keana et al. A Keggin-type POM with a pendant diene function has been covalently attached to silica particles with a dienophile function via a Diels–Alder reaction.^{306a} More recently, introduction of an alkylthiol group in the difunctionalized $[\text{SiW}_{10}\text{O}_{36}(\text{SiC}_3\text{H}_6\text{SH})_2\text{O}]^{4-}$ anion allowed the covalent grafting of hybrid POMs on the surface of gold NPs via S–Au bridges.^{84c} The presence of the protective layer of POMs induces formation of well-separated NPs. Following a similar strategy, Pd nanoparticles have been stabilized by $[\text{SiW}_{11}\text{O}_{40}(\text{SiC}_3\text{H}_6\text{SH})_2]^{4-}$ POMs.^{79c} Nanolatex particles can also be functionalized by hybrid POMs. The covalent attachment of $[\text{P}_2\text{W}_{17}\text{O}_{61}(\text{SiC}_3\text{H}_6\text{SH})_2\text{O}]^{6-}$ POMs to nanolatex NL- CH_2Cl particles is thus ensured by the aqueous reaction between the mercaptopropyl groups on the POM and the benzyl chloride functions carried by the nanolatex.^{83b}

4.5. Catalytic Activity of Hybrid POMs

Polyoxometalates have been extensively studied in homogeneous or heterogeneous catalysis, as photocatalysts or electrocatalysts. They have been mainly involved in acid and oxidation catalysis.³²² Hybrid polyoxometalates have been essentially studied as oxidation catalysts. The catalytic properties of metalosalen–polyoxometalates ($\text{M}(\text{salen})\text{--POM}$), consisting of a monolacunary $[\text{SiW}_{11}\text{O}_{39}]^{8-}$ functionalized by an organosilyl group bearing a pendant metalosalen moiety, have been studied in various oxidation reactions with hydrogen peroxide as an oxygen source. In particular, $\text{Fe}(\text{salen})\text{--POM}$, $\text{Ni}(\text{salen})\text{--POM}$, and $\text{Co}(\text{salen})\text{--POM}$ systems have been studied in the epoxidation of olefins.⁸¹ Higher yields have been obtained with $\text{M}(\text{salen})\text{--POM}$ compared with the parent $\text{M}(\text{salen})$ complex. $\text{Fe}(\text{salen})\text{--POM}$ and $\text{Co}(\text{salen})\text{--POM}$ have also been studied for the oxidation of alkanes or primary and secondary benzyl halides.^{81c,d}

A series of POM-supported organometallic complexes of general formula $\{m(\text{CH}_3\text{CN})_x\text{M}^{n+}/\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}^{9-}\}$ ($\text{M}^{n+} = \text{Mn}^{2+}$, Fe^{2+} , Co^{2+} , $m = 1, 2$; $\text{M}^{n+} = \text{Cu}^{2+}$, $m = 2, 3$; $\text{M}^{n+} = \text{Ni}^{2+}$, Zn^{2+} , Cu^+ , $m = 2$) has been used by Finke et al. as precatalysts for norbornene and cyclohexene oxygenation using $[\text{PhIO}]_n$ as the oxidant.³²³ Similar precatalysts $[(\text{CH}_3\text{CN})_x\text{Fe}\cdot\text{SiW}_9\text{V}_3\text{O}_{40}]^{5-}$ and $[(\text{CH}_3\text{CN})_x\text{Fe}\cdot\text{P}_2\text{W}_{15}\text{V}_3\text{O}_{62}]^{5-}$ showed record catalytic lifetime 3,5-di-*tert*-butylcatechol dioxygenase activity using molecular oxygen.³²⁴ Nevertheless, the authors recently indicated that only the vanadium seems to be essential and that the true catalyst does not involve the intact polyanion or even Fe^{n+} .³²⁵ Autoxidation of cyclohexene by POM-supported organometallic complexes such as $[(\text{cod})\text{Ir}^{\text{I}}\cdot\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}]^{8-}$, $[(\text{C}_6\text{H}_6)\text{Ru}^{\text{II}}\cdot\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}]^{7-}$, and $[(\text{OC})_3\text{Re}^{\text{I}}\cdot\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}]^{8-}$ has also been thoroughly studied by Finke et al.^{325,326} This study showed, among other significant results, that when $[(\text{cod})\text{Ir}\cdot\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}]^{8-}$ is used as the precatalyst for the autoxidation of cyclohexene the true catalyst is polyoxoanion supported. The catalytic activity of $[\text{Pt}(\text{cod})\cdot\text{P}_2\text{W}_{15}\text{V}_3\text{O}_{62}]^{7-}$ has also been measured for oxidation of cyclohexanol with H_2O_2 .²⁷⁶

Various organometallic-supported on POMs, and mainly organoruthenium-supported on POMs, have been indeed studied as oxidation catalysts.^{287,290,293,327} For example, $[\{\text{Ru}(\text{C}_6\text{H}_6)(\text{H}_2\text{O})\}\{\text{Ru}(\text{C}_6\text{H}_6)(\gamma\text{-XW}_{10}\text{O}_{36})\}]^{4-}$ ($\text{X} = \text{Si}, \text{Ge}$) have been tested for the electrocatalytic oxidation of dmsO,²⁸⁷ while $[\text{X}_2\text{W}_{20}\text{O}_{70}\{\text{Ru}(\text{C}_6\text{H}_6)\}_2]^{10-}$ and $[\text{X}_2\text{W}_{20}\text{O}_{70}\{\text{Ru}(\text{C}_{10}\text{H}_{14})\}_2]^{10-}$ ($\text{X} = \text{Sb}, \text{Bi}$) have been tested for the oxidation of *n*-hexadecane and *p*-xylene.²⁹⁰ Bonchio et al. studied the selective hydroxylation of adamantane by $[\{\text{Ru}^{\text{II}}(\text{C}_6\text{Me}_6)\}_3\text{M}_5\text{O}_{18}]$ ($\text{M} = \text{Mo}, \text{W}$) using 2,6-dichloropyridine *N*-oxide as primary oxidant.³²⁷ Nomiya et al. compared the catalytic properties of the water-soluble $[\{\text{LRu}^{\text{II}}(\text{H}_2\text{O})\}(\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61})]^{8-}$ ($\text{L} = \text{C}_6\text{H}_6$, *p*-cymene) precatalysts with other water-soluble ruthenium(II)-supported Dawson-type POMs for the selective oxidation of alcohols with 1 atm of molecular oxygen.²⁹³

Other hybrid polyoxometalates have been used in oxidation catalysis with molecular O_2 , H_2O_2 , or *t*BuOOH. The 3D coordination network $\{\text{Tb}(\text{bpdo})_2[\text{V}_6\text{O}_{13}\{(\text{OCH}_2)_3\text{C}(\text{NHCH}_2\text{C}_6\text{H}_4\text{-4-CO}_2)\}_2]\}$ (bpdo = 4,4'-bis(pyridine-*N*-oxide)) was used as heterogeneous catalyst for the oxidation of PrSH into PrSSPr using only ambient air as the oxidant (Figure 44).³³ $[\text{M}(\text{dmsO})_3\text{Mo}_7\text{O}_{24}]^{4-}$ ($\text{M} = \text{Ru}^{\text{II}}, \text{Os}^{\text{II}}$) have been used as catalysts for the aerobic oxidation of alcohols. Two alternative mechanisms for oxidation of benzylic alcohols have been proposed depending on the electronic properties of the

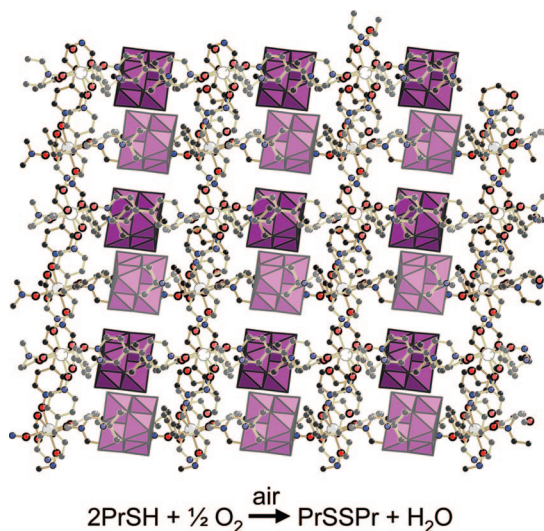


Figure 44. Polyhedral and ball-and-stick representation of the $\{\text{Tb}(\text{bpdo})_2[\text{V}_6\text{O}_{13}\{(\text{OCH}_2)_3\text{C}(\text{NHCH}_2\text{C}_6\text{H}_4-4-\text{CO}_2)\}_2]\}_n$ 3D network, a heterogeneous catalyst for the oxidation of PrSH into PrSSPr using air as the oxidant (ref 33). Purple octahedra, $\{\text{VO}_6\}$; gray spheres, Tb; black spheres, C; red spheres, O; blue spheres, N.

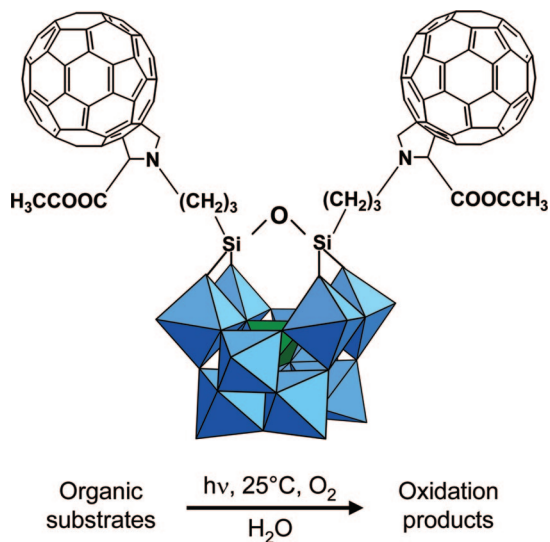


Figure 45. Schematic representation of the proposed structure of $\{\gamma\text{-SiW}_{10}\text{O}_{36}[\text{N}-(3\text{-silylpropyl})-2\text{-carboxy-3,4\text{-fulleropyrrolidine}]_2\text{-O}\}$, a catalyst for the photooxidation in water of phenol and L-methionine (ref 84d). Blue octahedra, $\{\text{WO}_6\}$; green tetrahedra, $\{\text{SiO}_4\}$.

substituent.²⁴¹ The lacunary polyoxotungstate $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$ functionalized with organosilylfulleropyrrolidines was investigated as a potential catalyst for wastewater treatment (Figure 45).^{84d} The hybrid POMs have been studied for the photooxidation in water of phenol and L-methionine. Preliminary mechanistic studies suggest a type II photooxidation mechanism. The TBA salt of $[\{\text{Ti}(\text{OH}_2)(\text{ox})\}_2(\mu\text{-O})(\alpha\text{-PW}_{11}\text{O}_{39})]^{5-}$ has been studied as precatalyst for the homogeneous epoxidation of alkenes with H_2O_2 .^{195b} It showed higher catalytic activity compared with the dimeric mono-, di-, and tri- Ti^{IV} -substituted polyoxotungstates $[(\alpha\text{-PTi}_x\text{W}_{12-x}\text{O}_{40-x})_2\text{O}]^{(6+2x)-}$. The poly(polyoxometalate) dendrimer described by Hill et al. bearing four Dawson-type POMs has been used for oxidation of the thioether tetrahydrothiophene by $t\text{BuOOH}$ and H_2O_2 .³⁴ The reaction was shown to be catalyzed by strong acids. The family of hybrid polyoxotungstates of general formula $[\text{G}_z\text{XW}_{12-n}\text{O}_{40-m}]^{k-}$ (G

$= (\text{RSi})_z\text{O}_{z-1}$, RSiOH , RPO ; $z = 2\text{--}4$; $\text{X} = \text{P}, \text{Si}$; $n = 1\text{--}3$; $m = 1\text{--}6$; $k = 3\text{--}5$) has been tested as microwave-assisted oxidation catalysts of a variety of organic species in the presence of H_2O_2 .³²⁸ A mechanism, involving formation of a transient η^1 -hydroperoxo intermediate, was proposed for the nucleophilic oxidation of aromatic sulfoxides. Olefin epoxidation by $[\gamma\text{-SiW}_{10}\text{O}_{36}(\text{PhPO})_2]^{4-}$ has also been studied in hydrophobic ionic liquids, under microwave irradiation, in the presence of H_2O_2 .³²⁹ Finally, optically active polyoxotungstates functionalized with chiral organophosphonates have been tested, with limited performances, for the enantioselective oxidation of methyl *p*-tolyl sulfide with H_2O_2 .^{162b}

Besides these studies dedicated to the oxidative catalytic properties of polyoxometalates, the catalytic properties of POM hybrids have also been investigated for a variety of other reactions. The Wilkinson's-type catalyst $[\text{SiW}_{11}\text{O}_{39}\text{-}\{\text{O}(\text{Si}(\text{CH}_2)_2\text{PPh}_2)\text{Rh}^{\text{I}}(\text{Cl})\text{PPh}_3\}]^{4-}$ has been studied for the hydrogenation of various alkenes.⁸² The catalytic activity was tested either in a single liquid organic phase reaction medium or in an aqueous biphasic liquid–liquid reaction. In the monophasic system and using 1-octene as substrate, the efficiency of the POM-functionalized catalyst was $\sim 50\%$ higher than with the classic $(\text{Ph}_3\text{P})_3\text{Rh}^{\text{I}}\text{Cl}$ Wilkinson catalyst. Catalytic hydrogenation of various substrates has been studied using organometallic catalysts anchored on Keggin-type heteropolyacids initially grafted on an alumina support.³³⁰ Catalytic results seem to point out a direct interaction between the heteropolyacid and the metal atom of the organometallic complex. $\{\text{M}(\eta^6\text{-arene})\}^{2+}$ ($\text{M} = \text{Ru}, \text{Os}$) derivatives of POMs have shown moderate catalytic activity for the racemization of (*S*)-1-phenylethanol.³³¹ The stability in aqueous electrolytes and the decomposition pathways of the ball-shaped hybrids $[\{\text{Sn}(\text{CH}_3)_2(\text{H}_2\text{O})\}_{24}\{\text{Sn}(\text{CH}_3)_2\}_{12}\text{-}(\text{A-XW}_9\text{O}_{34})_{12}]^{36-}$ ($\text{X} = \text{P}^{\text{V}}, \text{As}^{\text{V}}$) have been studied by Nadjo et al.^{97c} The electrocatalytic reduction properties of the phosphorus derivative toward NO_x has then been tested. These studies showed that the P-ball-shaped hybrid POM is one of the few examples of POMs that are able to electrocatalytically reduce nitrate and, in this specific case, to reduce nitrate beyond the state of nitrite. Preliminary studies also showed promising interaction between the P-ball-shaped hybrid POM and the biological relevant NO.

5. Organic–Inorganic Ionic Hybrid Materials with Targeted Properties

In organic–inorganic ionic hybrid materials the anionic POMs and organic cations are not covalently linked but interact via electrostatic forces. We will focus in this part on some families of ionic materials with specific physical properties. These properties result either from the inorganic component or the organic cations or from the synergy between both. We will first describe compounds with catalytic and sorption properties, then hybrid materials with nonlinear optical properties, and finally noncrystalline materials with electro- and/or photochromic properties.

5.1. Catalytic and Sorption Properties

Two families of POMs with sorption and catalytic applications can be distinguished. The first family involves hybrid materials with porous coordination polymer hosts and POM guests. In the second family both the anionic and the cationic components are 0D.

5.1.1. Coordination Polymers with POM Guests

As far as catalytic applications are concerned, POMs are well-known heterogeneous catalysts, for either acid or oxidation reactions (*vide supra*). However, the low surface area of most solid POMs is unfavorable. The immobilization of POMs within the pores of a coordination polymer can be seen as a way to obtain a well-defined solid with accessible catalytically active species. Structures of coordination polymer networks, mostly synthesized under hydrothermal conditions, with POMs immobilized through host–guest interactions have been recently reviewed.¹⁷ We mention a few materials isolated under mild conditions. For example, the $[\text{PM}_{12}\text{O}_{40}]^{3-}$ ($\text{M} = \text{Mo}, \text{W}$) anions have been used as noncoordinating anionic templates for construction of 3D Cu^{I} coordination polymers with 4,4'-bpy³³² or phenanthroline³³³ ligands. Similarly, $[\text{PM}_{12}\text{O}_{40}]^{3-}$ anions can play the role of guests for three-dimensional coordination polymer hosts with Co^{II} ions connected by 4,4'-bpy³³⁴ or Cu^{II} ions connected by the long flexible bpp ligands (bpp = 1,3-bis(4-pyridyl)propane).³³⁵ Electrocatalytic activity toward the reduction of nitrite has been reported for this last compound. In all of these materials the pores of the coordination polymers are totally blocked by the bulky POM anions. In this respect two hybrids recently described represent an exception and are very promising candidates for catalytic applications. The $[\text{Cu}^{\text{II}}_2(\text{btc})_{4/3}(\text{H}_2\text{O})_2]_6[\text{H}_n\text{X}\text{M}_{12}\text{O}_{40}] (\text{TMA})_2$ (btc = benzenetricarboxylate; TMA = tetramethylammonium; $\text{X} = \text{Si}, \text{Ge}, \text{P}, \text{As}$; $\text{M} = \text{W}, \text{Mo}$) materials possess two kinds of pores, the other being partially filled with water molecules and TMA⁺ cations (Figure 46).³³⁶ They consequently exhibit a high surface area ($460 \text{ m}^2 \text{ g}^{-1}$). The authors state that the heterogeneous acid catalytic properties of the POMs are enhanced by their incorporation into the pores of the Cu-btc-based MOF. Férey et al. first described the encapsulation of Keggin-type POMs within the pores of the chromium terephthalate MIL-101 MOF.³³⁷ A recent study has shown that incorporation of $[\text{PW}_{11}\text{Co}^{\text{II}}\text{H}_2\text{O}_{39}]^{5-}$ and $[\text{PW}_{11}\text{Ti}^{\text{IV}}\text{O}_{40}]^{5-}$ (~10% POM/MIL-101) makes this modified MOF a good heterogeneous selective oxidation catalyst.^{338a} Unlike all the other materials reported above, the synthesis follows a two-step procedure, MIL-101 being prepared before incorporation of the POMs. The one-pot synthesis of MIL-101(Cr) incorporating POMs has been also recently described.^{338b} The catalysts thus formed showed remarkable activity for the

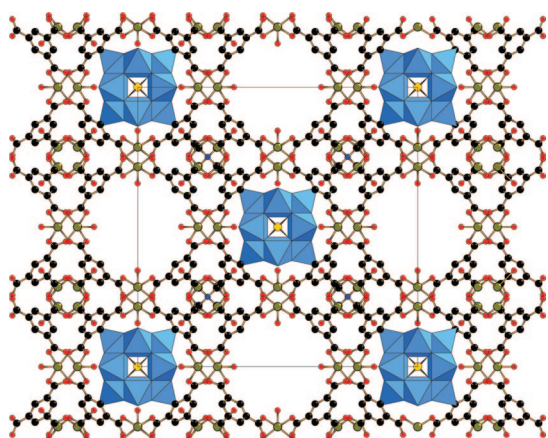


Figure 46. Polyhedral and ball-and-stick representation in the *bc* plane of the $[\text{Cu}^{\text{II}}_2(\text{btc})_{4/3}(\text{H}_2\text{O})_2]_6[\text{H}_n\text{X}\text{M}_{12}\text{O}_{40}](\text{C}_4\text{H}_{12}\text{N})_2$ 3D framework (ref 336). Blue octahedra, $\{\text{WO}_6\}$; green spheres, Cu; yellow spheres, Si; red spheres, O; black spheres, C; blue spheres, N.

Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate and for acid-catalyzed reactions.

5.1.2. 0D Anionic and Cationic Frameworks

A few examples of porous ionic solids with POMs and organic cations have been reported. For instance, the assembly of $[\text{PW}_{12}\text{O}_{40}]^{3-}$ anions and sodium ions trapped into calix[4]arene derivatives leads to microporous frameworks.³³⁹ In this material, channels with sizes of about $4 \times 8 \text{ \AA}$ are occupied by solvent molecules (CH_3OH and CHCl_3). These molecules can be desorbed at $100 \text{ }^\circ\text{C}$ without the framework collapsing, and the pretreated solid can then sorb efficiently some small alcohols. In the second example, the H-bonded assembly of $[\text{Mo}_{36}\text{O}_{112}(\text{OH}_2)_{16}]^{8-}$ POMs and $\text{H}_2\text{bpy}^{2+}$ cations delineates channels in which water molecules can be reversibly incorporated.³⁴⁰ However, the most efficient ionic materials with sorption properties are nanostructured ionic crystals with POMs (the macroanions) and chromium(III) transition-metal complexes (the macrocations).³⁴¹ The idea is based on the creation of molecular-sized spaces in the crystal lattice of these organic–inorganic hybrids, favored by the reduction of the Coulomb interaction between both macrocomponents. Mizuno et al. thus reported the formation of materials possessing hydrophilic channels built from the association of Keggin-type POMs such as $\{\text{XW}_{12}\text{O}_{40}\}$ ($\text{X} = \text{Si},^{342} \text{Co},^{343} \text{P},^{342c} \text{B}^{342c}$) with $[\text{Cr}^{\text{III}}_3\text{O}(\text{OOCH})_6(\text{H}_2\text{O})_3]^+$ clusters, while both hydrophilic and hydrophobic channels are observed when the $[\text{Cr}^{\text{III}}_3\text{O}(\text{OOC}_2\text{H}_5)_6(\text{H}_2\text{O})_3]^+$ complex is considered (Figure 47).³⁴⁴ Dawson-type POMs have also been incorporated,³⁴⁵ and recently the interaction of $[\text{Ru}^{\text{III}}_3\text{O}(\text{OOCCH}_3)_6(\text{H}_2\text{O})_3]^+$ with Keggin and Dawson anions has been investigated.³⁴⁶ The presence of alkali-metal cations, ammonium, or even silver ions which compensate for the anionic charge of the POMs has a strong influence on the structure and sorption properties.³⁴¹ Most of these solids reversibly sorb various kinds of polar organic molecules such as alcohols as well as water, several systems presenting good selectivities.³⁴¹ For example, $\text{Rb}_4[\text{Cr}_3\text{O}(\text{OOCH})_6(\text{H}_2\text{O})_3][\alpha\text{-BW}_{12}\text{O}_{40}]$ selectively sorbs methanol compared with ethanol and propanol.^{342c} The silver derivative $\text{Ag}_2[\text{Cr}_3\text{O}(\text{OOC}_2\text{H}_5)_6(\text{H}_2\text{O})_3]_2[\alpha\text{-SiW}_{12}\text{O}_{40}]$ can selectively sorb small unsaturated hydrocarbons such as ethylene or *n*-butene.³⁴⁷ In this case, the selectivity is explained by the π complexation of the unsaturated hydrocarbons with Ag^+ . These studies show that nonporous flexible frameworks can

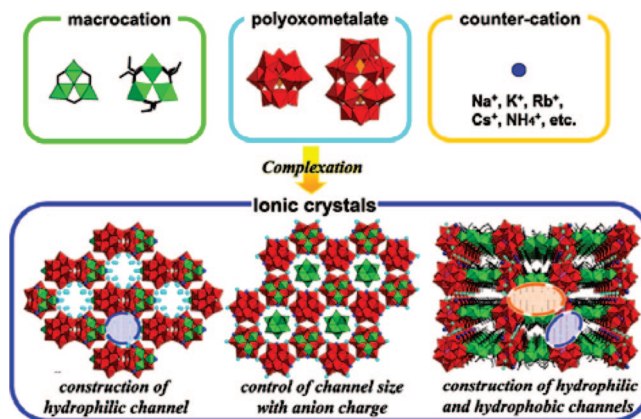


Figure 47. 0D anionic and cationic framework porous materials based on Dawson or Keggin POMs and $[\text{Cr}^{\text{III}}_3\text{O}(\text{OOR})_6(\text{H}_2\text{O})_3]^+$ ($\text{R} = \text{H}, \text{C}_2\text{H}_5$) clusters. Formation of compounds with hydrophilic channels or hydrophilic and hydrophobic channels is illustrated (Reprinted with permission from ref 341. Copyright 2007 Elsevier).

compete with the well-known MOF structures in terms of sorption properties.³⁴⁸ Furthermore, catalytic applications have also been described. Indeed, following the same approach, Mizuno et al. have also shown that fine particles of the hybrid ionic salt with the Keggin-type $[\gamma\text{-SiV}_2\text{W}_{10}\text{O}_{38}(\text{OH})_2]^{4-}$ POMs and cationic transition-metal complexes $[\text{Ni}(\text{tacn})_2]^{2+}$ (tacn = triazacyclononane) heterogeneously catalyze the epoxidation of olefins with H_2O_2 .³⁴⁹

Astruc, Nlate et al. developed a family of dendritic polyoxometalate complexes built through ionic bonding and studied their properties as recoverable and reusable oxidation catalysts.³⁵⁰ The common factor to all the complexes of this family is the peroxophosphotungstate $[\text{PO}_4\{\text{WO}(\text{O}_2)_2\}_4]^{3-}$. In their first report, the trianionic POM has been associated with tricationic tripods, namely, triammonium groups, to build mono-, di-, tri-, tetra-, and hexa-POM-triammonium salts.^{350a} These dendritic systems have been used as catalysts for the epoxidation of cyclooctene by H_2O_2 . In the following reports, the trianionic POM has been used as the core of the dendrimeric structures in which cationic quaternary ammonium dendrons are assembled with the central POM through ionic bonding.^{350b,c} 9- and 27-armed dendrimers have been synthesized, characterized, and used as recyclable catalysts for the oxidation of alkenes, sulfides, and alcohols using H_2O_2 . This study showed that the dendritic structures increase the stability of the POM and concomitantly decrease the reaction kinetic.^{350b,c} More recently, Nlate et al. synthesized enantiopure dendritic POMs.^{350d} Enantiopure dendritic quaternary ammonium ions and the achiral $[\text{PO}_4\{\text{WO}(\text{O}_2)_2\}_4]^{3-}$ POM have been assembled through electrostatic interactions, and the resultant original structures have been studied as catalysts for the oxidation of thioanisole to the corresponding sulfoxide with H_2O_2 and with modest enantiomeric excess.

5.2. NLO Properties

In the field of molecular materials, second-order nonlinear optical (NLO) compounds have been attracting continuous interest because of their potential applications in telecommunications, optical computing, optical data storage, and optical information processing.³⁵¹ At the molecular level, organic molecules which possess an electron acceptor linked to an electron donor group through a π -conjugated bridge exhibit large molecular hyperpolarizability (β). Organic molecules of the stilbazolium family,³⁵² such as DAMS^+ (*trans*-4-(4-dimethylaminostyryl)-1-(pyridinium)), are thus well-known molecular precursors of materials with NLO properties. Organometallic and coordination complexes also attract growing interest.³⁵³ However, not all the molecular materials crystallizing with these molecules exhibit solid-state NLO properties. Indeed, in order to get an observable bulk nonlinear susceptibility ($\chi^{(2)}$) the molecules which exhibit molecular hyperpolarizability must adopt a parallel alignment in the crystal. The required condition for a favorable crystal packing is then that the material crystallizes in a noncentrosymmetric space group. In this respect the counteranion plays an important role in achieving a noncentrosymmetric structure in ionic crystals. Experimental³⁵⁴ and theoretical^{125b,c,355} studies have shown that POMs themselves can possess molecular hyperpolarizabilities. These factors have motivated the search for hybrid ionic materials with POMs as counteranions. However, only a few NLO active molecular materials with POMs anions, namely, $\text{H}_4\text{SiW}_{12}\text{O}_{40} \cdot 4\text{HMPA} \cdot 2\text{H}_2\text{O}$ (HMPA = hexamethylphos-

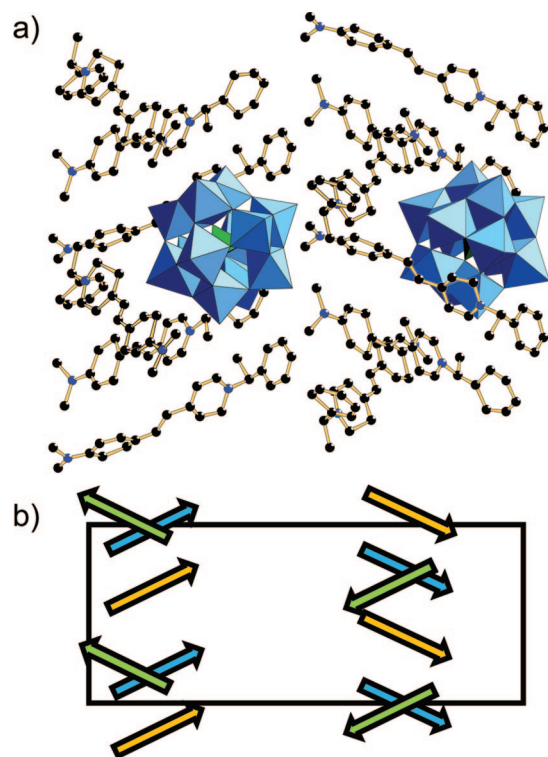


Figure 48. (a) View of the unit cell of $(\text{CHIDAMS})_3[\text{PW}_{12}\text{O}_{40}]$. (b) Schematic view of the arrangement of the CHIDAMS^+ cations highlighting that the total dipole moment is nonzero (ref 360). Blue octahedra, $\{\text{WO}_6\}$; green tetrahedra, $\{\text{PO}_4\}$; black spheres, C; blue spheres, N.

phoramide),³⁵⁶ $[\text{DAMS}][\text{NH}_2\text{Me}_2]_2\text{HSiFeMo}_{11}\text{O}_{40} \cdot 3\text{H}_2\text{O}$,³⁵⁷ $[(R)\text{-C}_5\text{H}_{14}\text{N}_2][(\text{MoO}_3)_3(\text{SO}_4)] \cdot \text{H}_2\text{O}$,³⁵⁸ and $[\text{H}_3\text{O}][3\text{-HPBIM}]_2\text{-}[\text{PW}_{12}\text{O}_{40}]$ (3-HPBIM = 2-(3-pyridyl)benzimidazolium),³⁵⁹ have been reported, probably because of the difficulty to crystallize materials in noncentrosymmetric space groups. One way to force the growth of molecular salts in such space groups is introduction of a chiral center on the organic molecules, although this method does not preclude formation of pseudocentrosymmetric arrangements. Two examples of ionic salts with a chiral DAMS^+ derivative have been recently described, the $(\text{CHIDAMS})_3[\text{PW}_{12}\text{O}_{40}]$ compound (CHIDAMS = *trans*-4-(4-dimethylaminostyryl)-1-(*S*)-(1-phenylethyl)pyridinium) being the most second-harmonic generation (SHG) efficient POM-based material reported so far (Figure 48).³⁶⁰ However, it should be noted that the SHG efficiency of this material remains far lower than that of the most efficient materials such as DAST, which associates DAMS^+ cations and tosylate anions.³⁶¹ Another interesting feature of the molecular materials with electron-rich aromatic organic molecules and POMs is the phenomenon of charge transfer between the organic molecules acting as electron donors and the POMs acting as an electron acceptors, as first reported by the group of Hill.³⁶² This interaction is evidenced by the dark color of the hybrid salts correlated to the apparition of an additional absorption band in the diffuse reflectance spectrum of the hybrid which is not present in the spectrum of the precursors.^{356,357,359,360} The charge-transfer character is related to the reduction potentials of the POMs acceptors³⁶³ and has been described only for Keggin $\{\text{XM}_{12}\text{O}_{40}\}$ and Lindquist $\{\text{M}_6\text{O}_{19}\}$ (M = Mo, W) POMs.

5.3. Photochromic and Electrochromic Materials

It has been known for a long time that a large number of POMs can act as electron reservoirs and be photochemically or electrochemically reduced to form colored mixed-valence species with no significant structural changes. Furthermore, reduction of POMs to the so-called heteropoly blues species is reversible. The study of these photo- or electrochemical reduction processes still attracts a lot of interest, particularly in the search of multifunctional materials. A review on the photochromic properties of hybrid ionic salts with POMs and organic molecules was published in 2006,⁵ following the previous review on photochromic POMs of Yamase,³⁶⁴ and therefore, only recent and representative examples will thus be described in this part. In photochromic hybrid materials POMs are associated with organic amines, π -conjugated molecules, or polymers. The mechanism usually admitted is based on the light-induced transfer of a proton from a hydrogen-bonded atom in the organic molecule to a bridging oxygen atom of the photoreducible site in the POM. The bleaching process is observed when the hybrid material is put in the dark and is accelerated by heat and the presence of O_2 . This mechanism has been specified recently by Dessapt and Jobic.³⁶⁵ Kinetic studies combined with theoretical calculations strongly suggest that the photochromism of organoammonium polyoxomolybdates is based on the homolytic cleavage of N^+-H bonds involved in the $N^+-H\cdots O$ hydrogen bond associated with the reducible Mo(VI) site. The following examples illustrate the various preparation modes of photochromic hybrids. Crystalline materials of photochromic hybrids based on isopolyoxomolybdates ($[Mo_7O_{24}]^{6-}$, $[Mo_3O_{10}]^{2-}$, $[Mo_8O_{27}]^{6-}$) and DABCO or piperazine-protonated amines (DABCO = 1,4-diazabicyclo[2.2.2]octane, piperazine) can be synthesized under usual bench or hydrothermal conditions.³⁶⁶ These compounds shift from white or pale yellow to pale pink, reddish brown, or purple under UV illumination depending on the chemical nature of the inorganic building unit, the organic component playing a role on the kinetics of the color change (Figure 49). Multilayer thin films of dye-polyoxometalates ($[BW_{12}O_{40}]^{5-}$, $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$) with heterocyclic planar and rigid

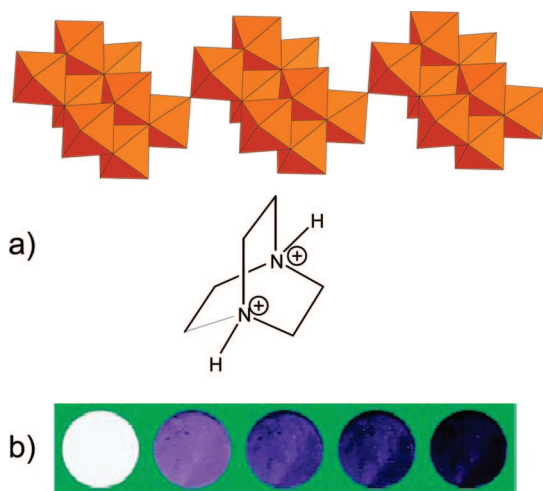


Figure 49. (a) Representation of the $1/\infty[Mo_8O_{27}]^{6-}$ chains and of the H_2DABCO^{2+} cation constituting the $(H_2DABCO)_3 \cdot (NH_2(CH_3)_2)_{0.5}Na_{0.75}(H_3O)_{0.75}[Mo_8O_{27}] \cdot$ ionic system. Orange octahedra, $\{MoO_6\}$. (b) Color of this compound after 0, 5, 20, 50, and 140 min irradiation (from left to right) at 365 nm (Reprinted with permission from ref 366. Copyright 2007 American Chemical Society).

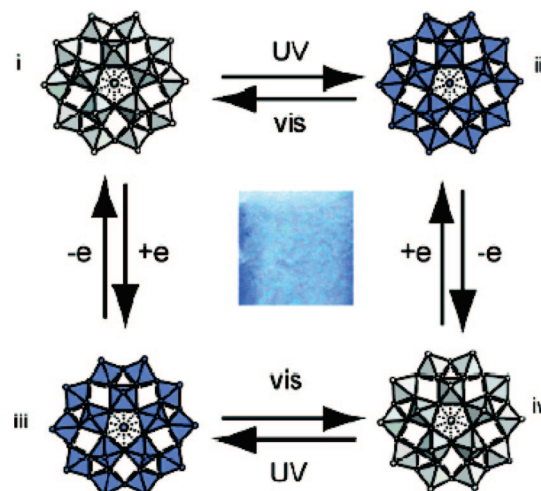


Figure 50. Illustration of the electrochromic and photochromic behavior of the film prepared from the $[NaP_5W_{30}O_{110}]^{14-}$ Preyssler POM and poly(4-vinylpyridine). Photoinduced coloration (i \rightarrow ii) can be followed by oxidation (ii \rightarrow iv), or electrochemically induced coloration (i \rightarrow iii) can be followed by bleaching with visible light (iii \rightarrow iv). The center of the figure shows a representative picture of the colored window (Reprinted with permission from ref 369. Copyright 2006 American Chemical Society).

phenothiazine and phenoxazine composite films have been prepared by electrostatic layer-by-layer (LbL) methods.³⁶⁷ Films with the Preyssler-type POM $[NaP_5W_{30}O_{110}]^{14-}$ and polyethyleneimine³⁶⁸ or poly(4-vinylpyridine)³⁶⁹ have been synthesized by an analogous technique. Interestingly, the color of the film with poly(4-vinylpyridine) reversibly changes from transparent to blue not only by photoinduced stimulation but also by electroinduced stimulation (Figure 50). The photochromic properties of films with the substituted Keggin $[PMo_{10}V_2O_{40}]^{5-}$ and 1,10-decanediamine³⁷⁰ have also been studied. In such reversible systems the speed of coloration is improved by the introduction of V ions in the POM matrix. Surfactant-encapsulated $[MP_5W_{30}O_{110}]^{n-}$ (M = Eu, Na) POM clusters have been dispersed in silica matrices by means of a sol-gel approach. The hybrid films exhibit stable and reversible photochromic properties, and the encapsulated POMs can be used as reductants for the in-situ synthesis of metal NPs.³⁷¹ Finally, photochromic hybrid liquid crystalline materials built from nonionic surfactants and $[PW_{12}O_{40}]^{3-}$ have been elaborated.³⁷² These hybrid systems are potential candidates for applications involving UV-light-sensitive coatings or liquid-crystal-based photochromic switches.

Electrochromic materials containing POMs have also been widely studied, mainly as films. For example, electrochromic devices have been built by LbL deposition of the Preyssler $[EuP_5W_{30}O_{110}]^{12-}$ anion, PAH (PAH = poly(allylamine hydrochloride)), and poly(styrenesulfonate) on ITO-coated glass slides (ITO = indium tin oxide).³⁷³ The same anion has been associated with functionalized surfactants using the ionic self-assembly route.³⁷⁴ All materials exhibit both thermotropic and lyotropic liquid-crystalline phase behavior. The influence of the functional groups on the electrochromic properties of these hybrid films has been studied, showing that ferrocene-containing complexes exhibit no electrochromic properties probably because of a charge transfer between the POM and the ferrocenyl group. Similarly, deposition of $[P_2W_{17}O_{61}Ni(H_2O)]^{8-}$ and PAH on quartz or ITO substrates has been realized. Such electrochromic films could be used as pH sensors.³⁷⁵ The color of electrochromic films with the

monovacant $[P_2W_{17}O_{61}]^{10-}$ Dawson-type POM can be tuned by the presence of copper or iron phenanthroline complexes.³⁷⁶ The presence of TiO_2 has been shown to increase the stability of electrochromic multilayer films of $[P_2W_{18}O_{62}]^{6-}$ and PAH.³⁷⁷ LbL films with Dawson anions $[P_2W_{18}O_{62}]^{6-}$ and poly(hexyl viologen) undergo a colorless to blue to violet transition over the potential range from 0.1 to -0.9 V.³⁷⁸ This device also shows a pH dependence of its electrochemical response.

5.4. Other Properties of Ionic Hybrid POMs

The description of the family of molecular conductors based on POMs and tetrathiafulvalene (TTF) derivatives or perylene would be pertinent in this part. However, as a review was published in 2005 by Coronado et al.¹³ and as very few recent examples of materials with organic donors and POMs have been reported since this date,³⁷⁹ these compounds are not presented here. Considering the luminescent properties of POMs, it must be recalled that $[EuW_{10}O_{36}]^{9-}$ is the best luminescent POM and the performances of its hybrid salts under several forms (surfactant encapsulated, Langmuir–Blodgett, or LbL films) with various organic counterions have been widely studied. A recent review of Binnemans on lanthanide-based luminescent hybrid materials includes a detailed chapter on hybrid POMs.³⁸⁰ It should be noted also that an increasing number of studies on the photocatalytic properties of POMs, and in particular of films of ionic hybrid POMs, have been reported. POMs seem very efficient for the photocatalytic degradation of environmental pollutants.³⁸¹ In the same respect an emerging topic is the study of the interaction between biological molecules and POMs.³⁸²

Finally, we also mention in this section that the use of electrostatic hybrid approaches allows not only making new materials but also reorganizing and stabilizing POMs to produce new clusters types.³⁸³ Extending this work, the same group has shown that, choosing appropriate POM units and organic counterions, spontaneous and rapid growth of hollow micrometer-scale tubes can be achieved. In the system characterized by Cronin et al., the membranes are composed of a 1D network of Keggin units connected via Mn–O–W bridges and polyaromatic counterions.³⁸⁴ The same group has also recently reported a pure inorganic POM framework synthesized from the reaction of divacant $[\gamma-SiW_{10}O_{36}]^{8-}$ anions with Mn^{II} in the presence of morpholinium cations and potassium permanganate.³⁸⁵ In the $(C_4H_{10}NO)_{40}[W_{72}Mn^{III}_{12}O_{268}Si_7]$ 3D material, Keggin units are connected through Mn–O–W linkages. This compound can undergo a reversible single-crystal to single-crystal redox transformation by chemical reduction of the Mn^{III} centers with simultaneous unit-cell expansion by 5.5 vol. %.

6. Concluding Remarks

The field of polyoxometalates has considerably evolved since the first study of the reactivity of monomeric anionic POM species and attracts increasingly growing interest as attested by the number of papers published in the past decade. The functionalization of POMs with covalently or noncovalently linked organic species is one way to increase this already huge family of compounds. There is no doubt that in the future hundreds of new compounds will be discovered. Although structural characterization is a very attractive and powerful tool, we can already envision that in the future the

focus will be not only on new structures as an objective on its own but also on applications, and POMs with their diversity of properties have a role to play to solve modern concerns in the field of environment, energy, and biology. Furthermore, as the complexity of the organic function increases, crystallization of hybrid species is more and more difficult and the use of other techniques of characterization such as mass spectroscopy, which has so far been limited to fully organic species, will become critical.

7. Abbreviations

acac	acetylacetonate
adip	adipate
ala	α -alanine
all	allyl
azel	azelaate
bhep	<i>N,N'</i> -bis(2-hydroxyethyl)piperazine
bmimp	bis(1-methylimidazol-2-yl)-4-methoxyphen-1-yl-methanol
bpdo	4,4'-bis(pyridine- <i>N</i> -oxide)
bpe	1,2-bis(4-pyridyl)ethane
bpp	1,3-bis(4-pyridyl)propane
bpy	bipyridine
btc	benzenetricarboxylate
Bu	butyl
calix	<i>p</i> - <i>tert</i> -butylcalix[4]arene
CD	circular dichroism
CHIDAMS	<i>trans</i> -4-(4-dimethylaminostyryl)-1-(<i>S</i>)-(1-phenylethyl)pyridinium
cod	1,5-cyclooctadiene
Cp	cyclopentadienyl
Cy	cyclohexyl
cyt	cytosine
DABCO	1,4-diazabicyclo[2.2.2]octane
DAMS	<i>trans</i> -4-(4-dimethylaminostyryl)-1-(pyridinium)
DCC	dicyclohexylcarbodiimide
DFT	density functional theory
DMDOA	dimethyldioctadecyl ammonium
dmf	<i>N,N</i> -dimethylformamide
dms	dimethyl sulfoxide
EDTA	1,2-diaminoethanetetraacetate
EPR	electron paramagnetic resonance
Et	ethyl
Fc	ferrocene
fum	fumarate
glu	glutarate
Hep	heptyl
Hex	hexyl
HMPA	hexamethylphosphoramide
Hsal	salicylic acid
H ₂ ddp	dodecaphenylporphyrin
H ₂ glyc	glycolic acid
H ₄ homocit	homocitric acid
3-HPBIM	2-(3-pyridyl)-benzimidazolium
im	imidazole
<i>i</i> -Pr	isopropyl
isop	isophthalate
ITO	indium tin oxide
LbL	layer-by-layer
mal	malate
Me	methyl
muco	muconate
NLO	nonlinear optical
OAc	acetate
Ode	octadecyl
ox	oxalate
PAH	poly(allylamine hydrochloride)
pbpy	5-phenyl-2-(4-pyridinyl)pyridine
PDA	phenylenediacetate

Ph	phenyl
phen	1,10-phenanthroline
pim	pimelate
pipz	piperazine
POM	polyoxometalate
Pr	propyl
py	pyridine
salen	<i>N,N'</i> -bis(salicylidene)ethylenediamine
sub	suberate
succ	succinate
tacn	triazacyclononane
tartH	tartaric acid
TBA	tetrabutylammonium
<i>t</i> -Bu	<i>tert</i> -butyl
TEOS	tetraethoxysilane
tere	terephthalate
thf	tetrahydrofuran
TMA	tetramethylammonium
TMT	tetramethylterephthalate
tol	tolyl
TPPs	tetraphenylporphyrins
tpy	2,2':6',6''-terpyridine
tpyp	<i>meso</i> -tetra(4-pyridyl)porphyrin
tpypy	tetra(2-pyridyl)pyrazine
trim	trimesate
Tris	tris(hydroxymethyl)aminomethane

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