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CRITICAL REVIEW

Functionalization and post-functionalization: a step towards polyoxometalate-based materials†

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Polyoxometalates (POMs) have remarkable properties and a great deal of potential to meet contemporary societal demands regarding health, environment, energy and information technologies. However, implementation of POMs in various functional architectures, devices or materials requires a processing step. Most developments have considered the exchange of POM counterions in an electrostatically driven approach: immobilization of POMs on electrodes and other surfaces including oxides, embedding in polymers, incorporation into Layer-by-Layer assemblies or Langmuir–Blodgett films and hierarchical self-assembly of surfactant-encapsulated POMs have thus been thoroughly investigated. Meanwhile, the field of organic–inorganic POM hybrids has expanded and offers the opportunity to explore the covalent approach for the organization or immobilization of POMs. In this critical review, we focus on the use of POM hybrids in selected fields of applications such as catalysis, energy conversion and molecular nanosciences and we endeavor to discuss the impact of the covalent approach compared to the electrostatic one. The synthesis of organic–inorganic POM hybrids starting from bare POMs, that is the direct functionalization of POMs, is well documented and reliable and efficient synthetic procedures are available. However, as the complexity of the targeted functional system increases a multi-step strategy relying on the post-functionalization of preformed hybrid POM platforms could prove more appealing. In the second part of this review, we thus survey the synthetic methodologies of post-functionalization of POMs and critically discuss the opportunities it offers compared to direct functionalization.

1. Introduction

The field of polyoxometalates (POMs) is an old one,¹ which has received tremendous impetus from the incisive review by Pope and Müller in 1991² and has accordingly witnessed considerable progress in the last two decades. One spectacular development refers to giant POMs,³ which are highlighted in another contribution to this issue. Generally speaking, the most attractive properties of POMs refer to their thermal and oxidative stability, to their structural analogy with metal oxides allowing to consider them as (soluble) molecular oxides, to their remarkable redox characteristics that make them good electron reservoirs, to the unique ligand properties of lacunary POMs and to the Brønsted acidity of the heteropolyacids, that is



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Anna Proust was born in 1967. She is a graduate of the Ecole Normale Supérieure and of the University Pierre et Marie Curie-Paris 06. She received her PhD degree in 1992 under the supervision of Professor P. Gouzerh. Her doctoral work dealt with nitrosyl derivatives of polyoxomolybdates. After a post-doctoral stay at the University of Bielefeld with Professor A. Müller, she returned to U.P.M.C. as assistant professor, then associate professor. She has been a full professor of inorganic chemistry since 2000 and a junior member of the Institut Universitaire de France (IUF) since 2006. Her research interests are focused on organometallic oxides, noble metal-substituted POMs and on the covalent functionalization of POMs, in particular with multiple metal–nitrogen bonds, organosilyl or organophosphonyl functions, with the prospect of applications in catalysis and materials science.

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maintained in the solid state. This unique combination of properties is the basis of many effective or potential applications in various areas ranging from medicine to catalysis and materials science. POMs allow tackling various important contemporary societal issues regarding health, environment, energy and information technologies. Related early work was reviewed in 1998⁴ and later developments can be found in recent reviews by Cronin and co-workers.^{5,6} Besides the above-mentioned giant POMs, other recent notable developments refer to POM-based water splitting catalysts^{7–17} and to magnetic polyoxometalates, especially single-molecule magnets (SMM).^{18–23} At the same time, a lot of work has been directed towards POM processing. In this context it is worth remembering that unmodified POMs are crystalline solids that are hard to process while organic–inorganic POM hybrids provide various options for easier integration of POMs into functional architectures and devices.

Since POMs are negatively charged, the first strategy to organize them relies on the exchange of their counterions. Selected examples refer to Layer-by-Layer (LbL) assemblies of POMs with positively charged polyelectrolytes as photo- or electro-chromic materials,²⁴ Langmuir–Blodgett films incorporating magnetic POMs,²⁵ surfactant-encapsulated POMs as optical or catalytic materials^{26,27} and electrostatic embedding of POMs into polymers. These topics have been nicely reviewed recently.²⁸ Immobilization of POMs on supports can be classified according to the type of support. A first group of studies deals with the immobilization of POMs on graphite and metal surfaces. Examples include the deposition of POMs on HOPG,^{29–31} Au^{32,33} and, to a lesser extent, Ag,³⁴ for microscopy imaging, the modification of nanoparticles^{35–37} and electrodes^{38,39} for electro-assisted catalysis and sensing, and the immobilization of functional POMs on carbon nanotubes (CNTs) for subsequent interfacing in devices.^{14,21} A second group of studies focuses on the immobilization of POMs onto oxide surfaces, *e.g.* silica and alumina, and their incorporation into polymeric matrices *via* organic copolymerization or sol–gel techniques, mainly with the aim to improve POM-based catalytic systems *via* their heterogenization.

In most cases, the immobilization of POMs relies on non-covalent interactions with the support. Only a few examples of covalent linking have been reported so far. Compared to the electrostatic approach, progress in the covalent approach has been up to now held back by the comparably small number of suitable organic–inorganic POM hybrids available. The covalent approach indeed requires the functionalization of POMs and their post-functionalization to be mastered, but it offers indisputable assets: (i) fine control of the interaction between the different components, which might result in enhancing synergistic effects, (ii) rational design of extended molecular assemblies, (iii) better dispersion of POMs in matrices, (iv) improvement of the long-term stability of the assembly. As the main routes for the functionalization of POMs have been discussed in several reviews,^{40–42} they will not be described again here. Rather we will focus on novel options provided by the post-functionalization of organically-derivatized POM hybrids regarding the elaboration of POM-based materials and devices (in this review the term “hybrid” will refer to covalently assembled species).

The scope of this review is to demonstrate how POM hybrids, taken as building blocks or modules, are affording an additional tool for the construction of POM-based materials or devices, following a bottom-up approach. In a first part, we will survey the use of functionalized POMs in catalysis, which is the traditional domain of application of POMs, but also in the emerging field of molecular nanosciences. Beyond the immobilization of POM catalysts on various surfaces, or the organization of POMs in complex media, systems consisting of supported organometallic catalysts or supported photosensitizers have been considered. Wherever possible, we will compare both the advantages and shortcomings of the electrostatic and covalent approaches. In one of the very first reports on organically-derivatized POMs the authors claim “*Such complexes would represent an entirely new class of compounds that would be expected to display novel combinations of properties, having applications in areas as diverse as organic synthesis, polymer chemistry, X-ray and electron microscope labelling and catalysis.*”⁴³ Indeed specially designed organosilyl derivatives of Keggin-type monovacant tungstophosphate⁴⁴ and cyclopentadienyl-titanium Wells-Dawson-type tungstophosphates^{45–47} could be used as labels for transmission electron microscopy. It was also soon recognized that water soluble salts of polyoxotungstates with covalently attached organic groups provide novel options for pharmaceutical applications of polyoxotungstates,^{48–50} *e.g.* they could improve biocompatibility and allow selective targeting of proteins as well as tuning bioactivity and cytotoxicity. While the topic remains of considerable interest (see *e.g.* ref. 50) it will not be covered further in this review.

In the second part of the review, we will analyze the synthetic methodologies and critically discuss the two complementary strategies: direct functionalization *versus* post-functionalization of already functionalized POMs (Fig. 1). Because different assets and limitations are inevitably associated to each approach, neither appears unquestionable. However, it is appealing to rely on a limited number of well-defined POM hybrids acting as molecular building blocks, prepared at a large scale and easily involved in various optimized post-functionalization reactions.

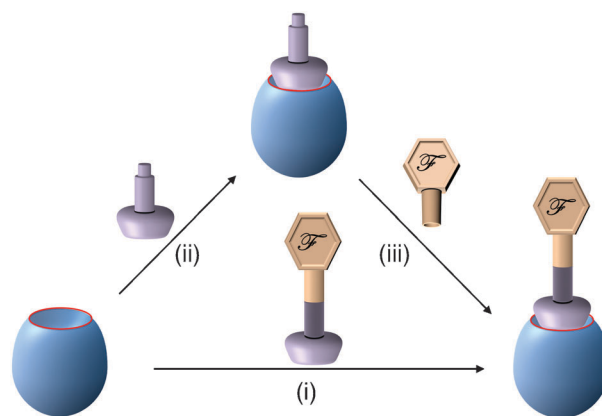


Fig. 1 Schematic representation of the different synthetic routes for the design of covalent POM-based organic–inorganic hybrids. Path (i): direct functionalization, paths (ii, iii): post-functionalization. The lacunary POM is represented in blue, while the anchoring tether is lilac and the added functional moiety (F) is beige.

2. Functionalized POMs in molecular and extended systems

2.1 Immobilization of catalysts

2.1.1 Immobilization of POMs on surfaces. POMs are versatile catalysts^{51–54} and electrocatalysts^{38,39} that can be used both in homogeneous and heterogeneous conditions. Generally speaking, heterogeneous catalytic processes are preferred for applications in industry as they provide better thermal stability and allow easier catalyst recovery and recycling. However, they are often less selective than homogeneous processes. The immobilization of POMs onto a support or into a matrix can be achieved in various ways, succinctly summarized in the introduction, while leading to catalytic systems that combine the advantages of both homogeneous and heterogeneous catalysts. Most of them refer to non-covalent interactions between POMs and supports. Indeed, self-assembled functional monolayers are produced by irreversible adsorption of POMs on metal surfaces and high-performance anchored homogeneous catalysts have been obtained by using heteropolyacids supported on silica or alumina, acting themselves as supports for anchoring different catalytic species, *e.g.* [Rh(diphosphine)(COD)]⁺.⁵⁵ POMs have also been adsorbed on various oxide supports possibly through interactions with protonated hydroxyl groups of the surface or electrostatically grafted to alkyl ammonium^{56–61} or imidazolium^{62,63}-functionalized mesoporous oxides, metal-oxide nanoparticles and polymeric membranes. Related examples refer to MOF-like iminium catalysts obtained by reacting multidentate chiral primary amines with heteropolyacids,⁶⁴ and to materials formed by combining heteropolyacids with amine-functionalized ionic liquids.⁶⁵

Although such electrostatically immobilized POM-based materials often display appreciable stability, catalyst leaching may remain a problem. Besides, some coordinatively-linked hybrids have been formed by reaction between transition metal-substituted POMs, *e.g.* [PW₁₁O₃₉{M(H₂O)}]^{5–} (M = Co, Ni)^{66–68} (Fig. 2), β-[SiW₉O₃₇{Co(H₂O)}₃]^{10–},⁶⁶ and [Ln(PW₁₁O₃₉)₂]^{11–}^{67,68} and nitrogen atoms of alkylamine-functionalized porous materials. A few examples of covalently-linked hybrids have also been reported. The latter include polymer composites obtained by copolymerization of acrylic monomers with POMs bearing a

polymerizable function, although no application in catalysis has been mentioned yet,^{69–71} coordination networks,⁷² and porous silica materials with covalently grafted POMs obtained by co-condensation of lacunary POMs with tetraethylorthosilicate (TEOS) in various conditions. Thus the reaction of γ-[SiW₁₀O₃₆]^{8–} with TEOS, with or without addition of a polyfunctional linking group, followed by condensation around polystyrene colloidal crystals produces – after removal of the template – ordered macroporous hybrid materials (Fig. 2) that exhibit high catalytic activity for the epoxidation of cyclooctene.⁷³ Similarly, mesoporous hybrid materials with SBA-15 architecture and covalently-grafted Keggin-type POMs have been obtained by co-condensation of α-[SiW₁₁O₃₉]^{8–} and α-[PW₁₁O₃₉]^{7–} with TEOS around block copolymer Pluronic P123 and subsequent removing of the template.^{74,75} These materials have the potential for applications in catalysis. Another example refers to covalent grafting – *via* the diazonium route⁷⁶ – of amine-functionalized POMs obtained by condensation of *p*-aminotriethoxysilane with monovacant Keggin-type polyoxomolybdates. Interestingly, compared to adsorption, the covalent approach improves the catalytic performance for the oxygen reduction reaction (ORR) on PEMFC (Proton Exchange Membrane Fuel Cell) cathodes.⁷⁷ Although the amount of data is still limited, covalently-linked hybrid catalysts show, as expected, enhanced stability towards catalyst leaching and might also show improved performance compared to impregnated catalytic systems.

2.1.2 Organometallic catalysts tethered to POMs. Despite their net anionic charge, the charge surface density of complete POMs is rather low. The nucleophilicity of the oxo ligands can be increased by substituting vanadium(v) or niobium(v) for molybdenum(vi) or tungsten(vi), and the resulting mixed addenda polyanions show enhanced reactivity towards organometallic fragments, which is exemplified by the grafting of various d⁶-*fac*-{ML₃} units ({M(CO)₃}⁺, M = Mn, Re; {Ru(η⁶-arene)}²⁺; {Rh(η⁵-Cp*)}²⁺). The reactivity of (multi)-vacant POMs towards organometallic electrophiles has also been largely investigated.^{40,78,79} The impact of these systems in catalysis, and targeted bifunctional catalysis, was finally rather low. The main achievement was probably the discovery that POM-stabilized Ir nanoclusters are formed under reduction of POM-supported [(1,5-COD)Ir]⁺ complexes.^{80,81}

As hybrid POMs gained interest, Neumann and co-workers, then Bonchio and co-workers, developed new catalytic systems based on the covalent linkage of well-established organometallic catalysts to POM scaffolds: examples include tethering of metallo-salen,⁸² Wilkinson-type rhodium,⁸³ and Pd-NHC⁸⁴ units among others. These are illustrated in Fig. 3. They, respectively, involve the [SiW₁₁O₃₉]^{8–} and γ-[SiW₁₀O₃₆]^{8–} scaffolds functionalized with silyl groups and will be referred to as SiW₁₁-Msalen, SiW₁₁-Rh and SiW₁₀-Pd(NHC). The first two have been obtained after post-functionalization, while the last one results from direct functionalization.

These hybrids are generally described as being more active and/or selective than the related organometallic precursor complexes. The main role of the POM is to tune the steric and electronic properties of the catalyst. In the case of the SiW₁₁-Msalen complexes (M = Mn, Co, Ni, Pd), charge

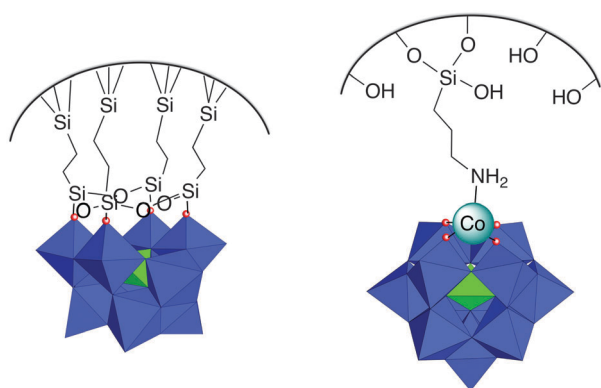


Fig. 2 Schematic representation of the grafting of γ-[SiW₁₀O₃₆]^{8–}⁷³ (left) and [PW₁₁O₃₉Co]^{5–}⁶⁶ (right) to mesoporous silica. Blue octahedra, {WO₆}; green tetrahedra, {SiO₄} (left), {PO₄} (right).

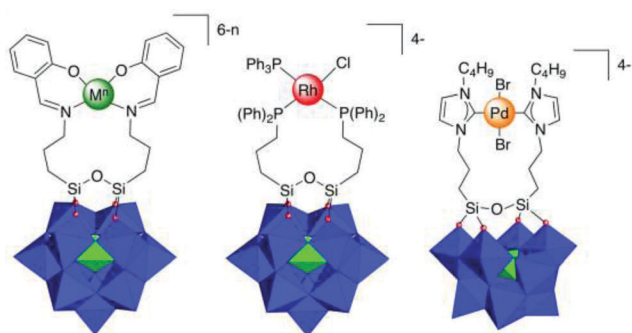


Fig. 3 Representation of the $\text{SiW}_{11}\text{-Msalen}$ ⁸² (left), $\text{SiW}_{11}\text{-Rh}$ ⁸³ (middle) and $\text{SiW}_{10}\text{-Pd(NHC)}$ ⁸⁴ (right) hybrids. Blue octahedra, $\{\text{WO}_6\}$; green tetrahedral, $\{\text{SiO}_4\}$.

transfer between the metallo-salen donor and the POM acceptor has been observed, with stabilization of unusual oxidation state of the appended metal M and/or oxidation of the salen ligand. Interestingly, this is an intramolecular phenomenon, not observed for mechanical mixtures of the parent POM and metallo-salen complexes. This underlines the beneficial effect of covalent tethering compared to an electrostatic association. Improved stabilization of intermediate Rh(III) was proposed to account for the increased reactivity of the $\text{SiW}_{11}\text{-Rh}$ hybrid.⁸³

Another expected role of the POM is to bring robustness to the whole hybrid and thus to increase its stability and performance. This is especially the case for the $\text{SiW}_{10}\text{-Pd(NHC)}$ system, whose activity in Suzuki–Miyaura C–C cross coupling has been investigated under harsh catalytic conditions under microwave irradiation. The POM, due to its charge, also allows uptake into ionic liquid media.⁸⁵

Finally, the presence of the POM facilitates the removal of the catalyst. The catalysis has been carried out under biphasic conditions using a water-soluble lithium salt of the $\text{SiW}_{11}\text{-Rh}$ or in organic solvent, from which the tetrabutylammonium salt of the catalyst was easily recoverable through ether induced precipitation. Nanofiltration has also been proposed.⁸⁶

We will not detail here the systems where cationic Pd- or Pt-based catalysts have been associated to the highly active $[\text{PMo}_{10}\text{V}_2\text{O}_{39}]^{5-}$ anion,⁸⁷ for tandem pinacol coupling rearrangement, Wacker-type catalysis or aerobic alkane oxidation, for which the POM was claimed to mediate the oxidation of Pt(II) to Pt(IV) . Disadvantages of the electrostatic approach are the lack of control over the stoichiometry of the adduct and the possible formation of insoluble salts. These difficulties may be overcome by appropriate ligand design. (For one example referring to the incorporation of photoactive $\{\text{Re}(\text{CO})_3(\text{bipy})\}^+$ units in POM hybrids for the purpose of performing the reduction of CO_2 , see Section 2.3.2).

2.2 Organization of POMs in complex media: POM-surfactant materials

Hydrophilic POMs of different sizes and shapes interact with hydrophobic cationic surfactants to produce core-shell like assemblies, called Surfactant-Encapsulated Clusters (SECs) or Surfactant-Encapsulated-POMs (SEPs), which can further self-assemble to give a variety of nanostructures on various surfaces/interfaces. This field has been mainly developed by

the groups of Kurth and Wu.^{26,88–91} The physico-chemical, catalytic and optical properties of such hierarchical assemblies have been reported and synergistic effects between $[\text{EuW}_{10}\text{O}_{36}]^{9-}$ anions and surfactants have even led to the design of a luminescent logic gate.⁹² This has been recently reviewed by Liu and Tang.²⁸ It is also worth mentioning that some assemblies have been built from non-ionic surfactants and POMs.⁹³

The alternate approach, namely the covalent linkage of hydrophobic tails to hydrophilic POMs leading to anionic amphiphiles with large polar heads, that we will call amphiphilic POMs, is more recent but is a rapidly growing area of research. It relies on a very few types of directly functionalized POMs: bis(silyl) derivatives of monovacant Keggin anions $[\text{XW}_{11}\text{O}_{39}\{\text{O}(\text{SiR})_2\}]^{p-}$ and post-modified bis(trisalkoxo) derivatives of the Mn-Anderson anion, $[\text{MnMo}_6\text{O}_{18}\{(\text{OCH}_2)_3\text{CNHCOR}\}_2]^{3-}$ ⁹⁴ and of the hexavanadate (R = large alkyl chain).^{72,95,96} These amphiphilic POMs differ on the relative orientation of the two hydrophobic chains, on the same side of the POM for the bis(silyl) derivatives, or on either side for the others. One may also cite bola-amphiphiles with V_3 -capped Wells-Dawson tungstophosphate⁹⁷ or organo-imido derivatized hexamolybdate polar heads (Fig. 4).⁹⁸

Chambers and co-workers were the first to report the ability of $[\text{XW}_{11}\text{O}_{39}\{\text{O}(\text{SiR})_2\}]^{p-}$ to form LB films at the air/water interface,⁹⁹ and more recently, Polarz and co-workers postulated that the organization of these amphiphilic POMs in the LB films is directed by the self-assembly of the polar heads in an hexagonal lattice.¹⁰⁰ More recently, Cronin, Liu and co-workers have greatly contributed to the emergence of this amphiphilic POM family and to the study of their self-organization in highly ordered structures: they have thus observed the formation of vesicles or reversed vesicles in mixed solvents, starting from $[\text{MnMo}_6\text{O}_{18}\{(\text{OCH}_2)_3\text{CNHCO}(\text{CH}_2)_n\text{CH}_3\}_2]^{3-}$ tectons,^{101,102} or recently from bola-amphiphilic-POMs constructed by linking two hydrophilic $[\text{P}_2\text{V}_3\text{W}_{15}\text{O}_{62}]^{9-}$ anions at both ends of various

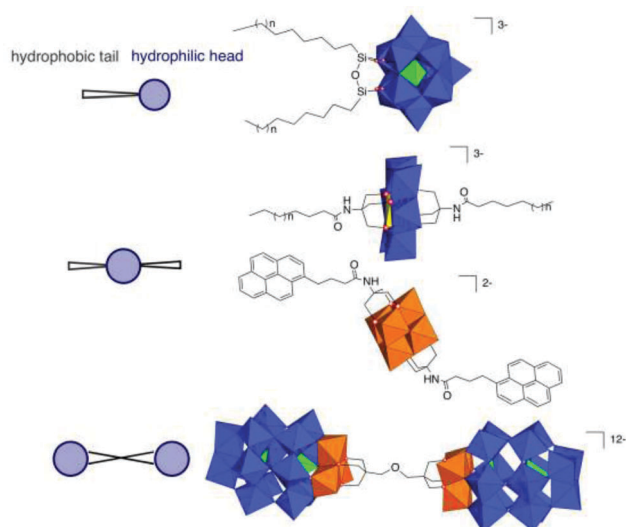


Fig. 4 Different types of amphiphilic POMs based on bis(silyl)derivatives (top), Mn-Anderson and Linqvist hexavanadate derivatives (middle), V_3 -capped Wells-Dawson derivatives (bottom). Blue octahedra, $\{\text{WO}_6\}$ or $\{\text{MoO}_6\}$ (Anderson); yellow octahedron, $\{\text{MnO}_6\}$; orange octahedra, $\{\text{VO}_6\}$; green tetrahedra, $\{\text{PO}_4\}$.

hydrophobic bis(trisalkoxo) linkers.^{103,104} Their amphiphilic properties, akin to those of conventional surfactants, were studied and LB films obtained at the air/water interface. Cronin and co-workers have also described a rare example of an unsymmetrically functionalized Anderson-type POM hybrid displaying two different trisalkoxo ligands that form nanofibrils of several microns in length at the solvent/air interface.¹⁰⁵

Up to now, most studies have been devoted to the physico-chemical characterization of these hybrid materials and this has been reviewed very recently by Liu and co-workers.¹⁰⁶ The effects of different parameters on the final architecture are discussed, another important factor being the kinetic of formation of the vesicles, which can take weeks to months. As now well recognized in the chemistry of POMs,¹⁰⁷ their counterions are very likely playing a crucial role, not only in screening the charge. Polarz and co-workers have thus described the formation of lyotropic liquid crystalline phases,¹⁰⁸ the structures of which depend on the alkyl chain lengths and counterions associated with the $[PW_{11}O_{39}\{O(SiR)_2\}]^{3-}$ amphiphiles: while an hexagonal phase of packed cylinders is obtained with sodium as counterions, the acid salt leads to a lamellar structure. At lower concentrations, micelles were observed and the ability of these amphiphiles as emulsifying agents was also demonstrated. Interestingly, use of the acid salt to prepare styrene emulsions in water leads, after heating, to the formation of polystyrene particles stabilized by POMs. Such studies pave the way for the development of catalytic applications of those self-assembled attractive hybrid architectures and forthcoming applications in electronic and photonic devices are expected. Hill and co-workers have thus described hybrid POMs with one or two pyrene groups linked to the hexavanadate core *via* trisalkoxo unit and the counterion-dependent formation of fluorescent vesicles has been observed in water–DMSO mixtures.¹⁰⁹ Another double-tailed fluorescent surfactant with a central hexavanadate polar core $[V_6O_{13}\{(OCH_2)_3CCH_2OCO(CH_2)_{16}CH_3\}_2]^{2-}$ exhibits strong blue luminescence, provided that protons or sodium are used as counterions in place of tetrabutylammonium.¹¹⁰

Relatively few amphiphilic POMs have been described so far. Varying the structure of the POM polar head as well as the number and the type of hydrophilic tails, *e.g.* by using dendritic synthons¹¹¹ and incorporating specific functionalities, like photo-isomerizable units,¹¹² should bring new perspectives and broaden the range of applications. This especially refers to the potential for forming thermotropic or lyotropic liquid-crystalline materials, as highlighted by Faul *et al.*¹¹³

2.3 Photosensitized POMs

POMs are photo-active species and their application in photo-chemically assisted catalysis has been thoroughly investigated. These studies mainly involved classical POMs of Lindqvist, Keggin, Wells–Dawson or decatungstate types.^{51,114–119} Hydrogen evolution has also been observed through photo-activation of Transition Metal-Substituted POMs (TMSPs) in the presence of protons and sacrificial reductants, which may be provided by waste water.¹²⁰ Since POMs are metal oxides with empty d orbitals, the photochemical events invariably correspond to LMCT processes, lying in the UV part of the spectrum.

However, in line with the depletion of fossil fuels and the need to increase the contribution from alternative energy resources, the conversion of solar energy (and especially its visible part) to chemical fuels is a challenging issue. Its storage through water splitting or conversion to other fuels *via* carbon dioxide reduction has renewed the interest in assembling POMs and photosensitizers. As fuel production is generally a multi-electron process, the ability of POMs to be reduced in several steps and to accommodate several electrons as electron reservoirs as well as the known activity of reduced POMs in electro-assisted catalysis make them attractive candidates to tackle such a scientific challenge.

More generally, many donor–acceptor systems based on organic donors, including dyes,¹²¹ and inorganic POM acceptors have been described, especially in the search for molecular conductors.^{122,123} Although this does not really fall under the scope of this section, it is worth mentioning a rare example of an electroactive donor covalently linked to a Lindqvist-type POM, recently reported by our group.¹²⁴ Intramolecular charge transfers have also been observed in ferrocenyl or phenanthroline imido derivatives of the hexamolybdate anion.^{125–127}

2.3.1 POM–chromophore dyads. The last decade has witnessed increased efforts in the design of covalent POM–photosensitizer dyads following seminal articles by Bond, Wedd, Keyes and co-workers reporting on the photophysical properties of electrostatic adducts between ruthenium polypyridyl complexes and POMs: $[Ru(bpy)_3]_2[\alpha-S_2M_{18}O_{62}]$ ($M = Mo, W$) salts display a new inter-ion charge transfer transition around 480 nm and enhanced quantum yield for visible photoreduction of the POM in the presence of benzyl alcohol or DMF.^{128–130} For these electrostatic adducts, the luminescence is retrieved by addition of excess of $LiClO_4$. Recently, Hill and co-workers described the formal replacement of bipyridine ligand in $[Re(CO)_3(bipy)X]$ chromophores by the all-inorganic oxidatively and hydrolytically stable $[P_2W_{17}O_{61}]^{10-}$ ligand.¹³¹ The resulting dark red rhenium-supported $[P_4W_{35}O_{124}\{Re(CO)_3\}_2]^{16-}$ chromophore displays an intense metal-to-POM charge transfer (MPCT), similar to that observed in the $[Ru(bpy)_3]_2[\alpha-S_2M_{18}O_{62}]$ systems, but enhanced, probably due to the presence of W–O–Re covalent bonds. Transient absorption spectroscopy demonstrates that the CT excited state is formed instantaneously, but is short lived and decays with a lifetime of 1.4 ps.

The covalent approach to the functionalization of POMs with a photosensitizer is supposed to bring some improvements like an increased solubility, a better control of the chromophore-to-POM ratio, a better stability to external variations of pH, ionic strength, temperature, and should allow to control the relative orientation of the chromophore and the POM. Odobel, Mayer and co-workers were the first to enter this field,^{132,133} closely followed by some of us. Huisgen 1,3-dipolar cycloadditions involving previously prepared bis(silyl) and bis(phosphonyl) derivatives of the $[P_2W_{17}O_{61}]^{10-}$ anion bearing pendant azides or alkynes afforded perylene and porphyrin conjugates (Fig. 5). Fluorescence quenching was observed and attributed to intramolecular electron transfer to the POM, although no charge-separated excited states could be observed through laser flash photolysis, probably because of a faster charge recombination process. As the more flexible tether leads to higher quenching of the fluorescence, a through-space

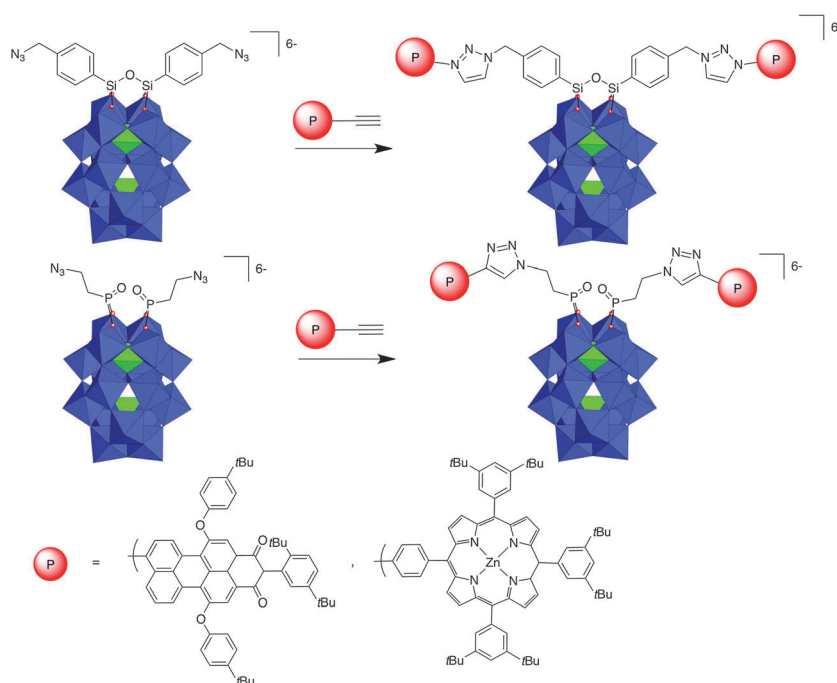


Fig. 5 Synthesis of photosensitized POM-based hybrids through Huisgen 1,3-dipolar cycloadditions.^{132,133} Blue octahedra, {WO₆}; green tetrahedra, {PO₄}.

interaction induced by a folded conformation of the POM hybrid is proposed to overcome the poor electronic conduction of the triazole linker.

Almost at the same time, we also undertook a long-term project on POM photosensitization relying on our expertise in the field of POM hybrids. As starting hybrid POM platforms, we chose silyl-derivatized Keggin- and Wells-Dawson-type POMs and used Sonogashira cross coupling for providing rigid linkers (Fig. 6).^{134,135} Our first objective was to anchor ruthenium(II) polypyridyl complexes and pyrene as model systems. The synthetic strategies will be discussed in Section 3.2.5.

The photophysical properties were investigated for both systems. In the case of the POM–pyrene system, a total quenching of the chromophore luminescence was observed, while for the POM–ruthenium the quenching was partial (*ca.* 15 to 30%). The quenching was attributed to intramolecular electron transfer from the chromophore to the POM. Nevertheless, such excited states could not be observed. Several reasons were put forward: inadequate physical properties of the ruthenium chromophore (low quantum yield and short lived excited state), insulator character of the phenylpyridyl unit and/or possibly fast reverse process. However, in the POM–ruthenium system, a comparative study of the luminescence quenching showed that the electron transfer is still faster in the covalently bonded hybrids than in systems where the POM and the ruthenium complexes are assembled *via* electrostatic interactions, which underlines the beneficial effect of the covalent linkage. More recently, in collaboration with the team of Amouri we turned to cyclometalated iridium(III) conjugates showing better photochemical efficiency.¹³⁶

Meanwhile, Hasenknopf and co-workers described the synthesis of trisalkoxo derivatives of Lindqvist-, Keggin- and Wells-Dawson-type POMs decorated with a terminal terpyridine unit.¹³⁷ In some cases, the grafted terpyridines were coordinated

to {RuCl₃} moieties, however the photophysical properties of the resulting hybrids were not reported.

2.3.2 Photocatalysts. Additionally to Mayer and Odobel's work,^{133,138} other groups combined porphyrins with POMs. The first examples of covalent linkage between porphyrins and POMs were built through coordination of the metalloporphyrin core metal either to an oxygen of a Keggin anion¹³⁹ or to pyridyl moieties attached to the POM *via* organic linkers.¹⁴⁰ Nevertheless in such systems, the coordination link turned out to be too weak. More recently hybrid POM–porphyrin copolymeric films were obtained by electrochemical oxidation of zinc porphyrins in the presence of functionalized Anderson-type POMs bearing pyridine units.¹⁴¹ These films allow photocatalytic reduction of Ag(I) under visible light irradiation in air in the presence of propan-2-ol at the 2D interface between water and the copolymeric films.

Bonchio and co-workers described the synthesis and photocatalytic activity of POM–fullerene hybrids resulting from the direct functionalization of [γ-SiW₁₀O₃₆]⁸⁻ with organosilyl-fulleropyrrolidines.¹⁴² The resulting hybrids were found to be active in catalytic photooxygenation of phenol and L-methionine ester in water under heterogeneous conditions using visible light irradiation for wastewater treatment applications.

Finally, among the numerous coordination complexes tested for electro- or photo-assisted CO₂ reduction, polypyridyl complexes have played a crucial role and are still at the forefront of current research.^{143–145} Neumann and co-workers have proposed to replace the sacrificial amine or ethanolamine reducing agents commonly associated with [ReL(CO)₃S] (S = solvent) photocatalysts by H₂, that would be oxidized to two protons and two electrons by a POM, in the presence of Pt(0). This led them to design a 1,10-phenanthroline L ligand

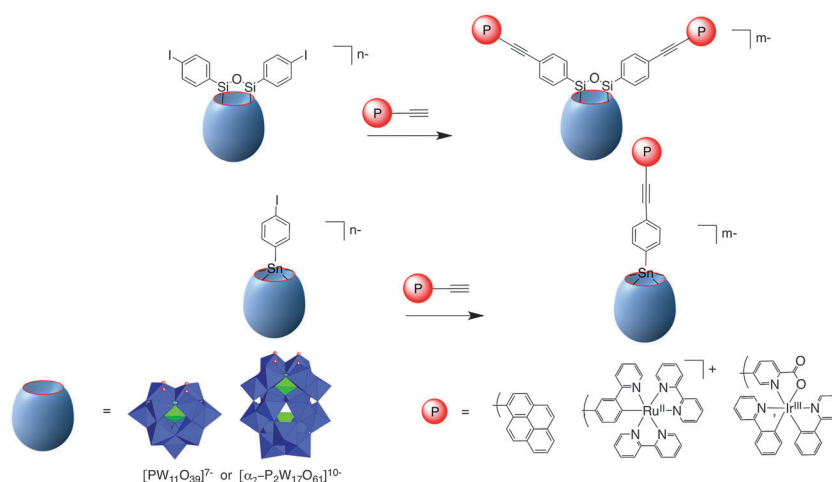


Fig. 6 Synthesis of photosensitized POM-based hybrids through Sonogashira coupling reactions.^{134–136}

decorated with a 15-crown-5 ether which was successively reacted with $[\text{Re}(\text{CO})_5\text{Cl}]$ and $\text{H}_3[\text{PMo}_{12}\text{O}_{40}]$, providing a supramolecular hybrid in which one sodium cation interacts with the crown ether as well as two POM units.¹⁴⁶ Irradiation of a suspension of the hybrid in dimethylacetamide under 1 bar of CO_2 and 2 bar of H_2 , at room temperature, in the presence of additional Pt/C indeed yielded CO with a small amount of CH_4 , albeit with low turnover frequency and quantum yield. Interestingly, no reduction products were detected in a control reaction carried out with a mixture of $[\text{Re}(\text{phen})(\text{CO})_3\text{Cl}]$ and $\text{H}_3[\text{PW}_{12}\text{O}_{40}]$, underlying the beneficial effect of linking the two components, even if not in a covalent way.

2.4 An emerging field: POMs and molecular nanosciences

2.4.1 POM hybrids in microelectronics/molecular electronics.

Taking advantage of ionic interactions between positively charged organic molecules or polymers and negatively charged POMs, many POM-based functional films displaying significant electrical and photo properties have been prepared. The unique redox properties of many POMs (reversible multi-step processes, limited structural rearrangement upon reduction, delocalization of added electrons), together with their size from subnanometer to a few nanometers make them attractive candidates for the elaboration of molecular electronic devices. They have often been presented as zero-dimensional n-type semi-conductors with low charging energies.^{117,147} Understanding charge transport phenomena occurring in POM-based molecular junctions is a prerequisite to their integration in memory devices. Argitis, Glezos and co-workers have a long-standing interest in such studies and have discussed the tunneling and percolation conduction mechanisms in single-layers and multilayers of alternating $\text{H}_3[\text{PW}_{12}\text{O}_{40}]$ and 1,12-diaminododecane self-assembled on 3-aminopropyl-triethoxysilane (APTES)-modified silicon surfaces.^{148,149} Taking another step towards the implementation of memories or storage devices, they have also reported on capacitance–voltage characteristics of a POM monolayer inserted in a vertical junction.¹⁴⁷

As part of a broad program on molecular electronics,¹⁵⁰ Tour and co-workers have investigated the possibility of modulating the conductance in silicon devices by monomolecular monolayer

grafting as an alternative to the control by impurity doping which becomes problematic when scaling to the sub-20 nm region. An electronically controlled series of diazonium salts from π -electron donors to π -electron acceptors, including an organo-imido hexamolybdate, have been covalently attached onto the oxide-free H-passivated *p*-silicon surface of the channel region of pseudo-MOSFETs (Metal-Oxide-Semiconductor Field-Effect Transistor). The observed variation of the drain current and threshold voltage was related to charge-transfer between the channel and the molecules and to their electron donor–acceptor ability.^{151,152}

Similarly, other groups interested in the development of molecular electronics have also chosen the CMOS (Complementary Metal Oxide Semiconductor) compatible processes, as an hybrid molecular/semiconductor transition technology, which is probably more pragmatic than the pure molecular approach on metals. Covalent grafting of a monolayer of molecules on silicon for the purpose of implementing DRAM (Dynamic Random Access Memory) or flash memory devices has thus been reported for ferrocene and porphyrins.^{153–156} In such systems, the information should be stored as an electric charge by using the discrete redox states of the molecules, provided that they are stable enough to fulfill the read/write/erase functions. The organic tether linking the silicon surface to the redox-active molecules has a threefold role: (i) it anchors the molecules to the surface; (ii) it acts as a dielectric to isolate the semiconductor from the possibly charged molecules; (iii) it allows fine tuning of the electronics characteristics depending on its length, rigidity, conjugated character, all parameters that affect charge transfer, charge retention properties and hysteresis behavior. Porphyrins and POMs display multiple accessible redox states in different potential ranges and could thus be promising for non-volatile multilevel memories, as recognized by Bidan and co-workers.¹⁵⁷ In a collaborative work we have described the anchorage of hybrid POMs on *n*-silicon wafers, by electrografting of an alkynyl- or diazonium-terminated hybrid POM (Fig. 7).¹⁵⁸ The redox behavior of the surface-confined POMs was recovered, using the silicon wafer as the working electrode, which was challenging by itself,¹⁵⁹ and the electrical characterization was completed by impedance measurements of a hybrid molecule/silicon capacitor.

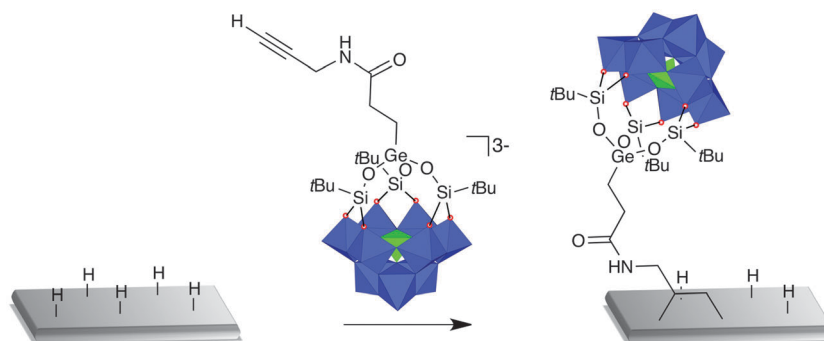


Fig. 7 Schematic representation of the anodic electrografting of $[PW_9O_{34}(tBuSiO)_3Ge(CH_2)_2CONHCH_2CCH]^{3-}$ on *n*-silicon wafers.¹⁵⁸ Blue octahedra, $\{WO_6\}$; green tetrahedra, $\{PO_4\}$.

It is worth recalling that the first attachment of a POM to a silicon substrate was achieved by Errington and co-workers, through an alcoholysis reaction between $[(RO)TiW_5O_{18}]^{3-}$ anions and a preassembled alkanol monolayer on silicon.¹⁶⁰

In all the above examples final integration into CMOS circuits remains to be done and the field of molecular electronic junctions is progressing.¹⁶¹ The covalent approach and the LbL method are complementary approaches to resistive and capacitive memories that pave the way to future applications of POMs but require a better control in the formation of the monolayer and its morphology.

2.4.2 POMs in optoelectronics and spintronics. Interestingly, one of the first reports on the use of POMs in photovoltaic cells relied on the covalent approach with the preparation of conjugated poly-(phenylene-ethynylene) polymers containing functionalized organo-imido hexamolybdates as main or side-chain pendants. Owing to their electron-accepting abilities, POMs were expected to successfully replace other electron acceptors like fullerenes introduced to promote charge separation from the photo-generated excitons. Single-layer photovoltaic cells based on a film of the polymer sandwiched between a transparent anode and a cathode have been fabricated. The power conversion efficiency of 0.15% compares well with other conjugated polymers in the same device configuration but remains low.^{162,163} To improve the charge transport, use of rod-coil diblock polymers (Fig. 8), with separate domains, was recently proposed but no photo-current measurements have been reported.¹⁶⁴

The view of POMs as electron-acceptors to rival fullerenes or other kind of acceptors, whilst valid, should probably be

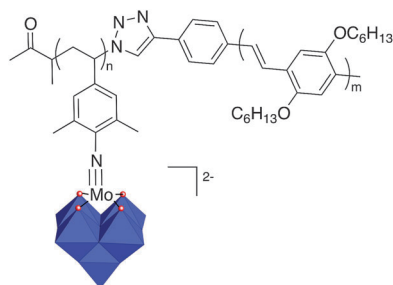


Fig. 8 Representation of a POM-based rod-coil diblock hybrid polymer.¹⁶⁴ Blue octahedra, $\{WO_6\}$; green tetrahedra, $\{PO_4\}$.

enlarged and future use of POMs in the field of optoelectronics offers more promise if they are simply considered to be electronic relays or redox mediators. Indeed a survey of the literature reveals that POMs have been used for modification of photo-anodes as well as counter electrodes. It is likely a matter of matching between the discrete energy levels of the POMs, those of the other components of the device, and the Fermi levels of the electrodes, data that require further accurate experimental determination and theoretical modeling. On the one hand, the photovoltaic response of a multilayer film ITO electrode sensitized by cobalt-phthalocyanines was improved by incorporation of a layer of $[P_2Mo_{18}O_{62}]^{6-}$ with a conversion efficiency increased from 0.29 to 0.36%, which remains very modest.¹⁶⁵ This was attributed to photo-induced electron transfers to the POMs, thus facilitating electron-hole pair separation. On the other hand, Su, Wang and co-workers have described a platinum counter electrode modified by multilayer electrochemical deposition of $K_3H_4[SiW_9Al_3O_{37}(H_2O)_3]$ and poly(diallyldimethylammonium chloride), which induces a 20% increase in the conversion efficiency of a DSSC (Dye Sensitized Solar Cell), due to an acceleration of the I_3^- reduction rate.¹⁶⁶ Similarly, performances of hybrid LEDs have been improved by modification with a thin layer of spin-cast $H_3[PW_{12}O_{40}]$ as an electron injection layer at the aluminium cathode,¹⁶⁷ while the same anion immobilized on the surface of boron-doped diamond (BDD) itself functionalized by pyridinium dyes was used to modulate the direction of the current flow from the functionalized BDD surface to methylviologen (MV): in the absence of the POM, electrons are transferred from the LUMO of the photoirradiated dye to MV^{2+} , while in the presence of POMs, electrons are transferred from MV^+ to the HOMO of the photoirradiated dye, through the POM, so acting as a molecular switch.¹⁶⁸

While self-organization of POMs on metallic or HOPG surfaces is documented, analogous studies on other types of electrodes are required to further support the development of optoelectronic devices using fabrication techniques other than LbL. Since classical vapor deposition methods are excluded because of the ionic character of POMs, spin-coating or drop casting methods will prevail. Cronin, Pignataro and co-workers have thus demonstrated how the nature of the POMs and their functionalization influence the morphology of the final architectures obtained on methylated or hydroxylated silicon surfaces.¹⁶⁹ Besides the covalent surface modification with hybrid POMs, the

effect of the nature of the functionalization on the surface organization of POMs is worth investigating further. Use of functionalized POMs could also help to improve contacts in multilayer devices, for example as an interfacial layer between an oxide electrode and an organic layer, interacting with both the organic and the inorganic components due to its modular hybrid character, engineering the morphology which in turn will impact the physical properties. While the last decade has witnessed the development of DSSCs,¹⁷⁰ LEDs and other molecular elements for photonics, because of their low cost of fabrication and easy processability, POMs as functional molecular oxide dopants or additives could help enhance performances that are still to be improved compared to inorganic materials.

POM hybrids are prospective materials for optoelectronics. While a relatively small number of nonlinear optically active POM-based materials have been experimentally studied,^{171–173} quantum chemical studies have been done, mainly by Su and co-workers, on a fairly large number of available^{41,42,174,175} as well as theoretically designed hybrids. Continued attention has been paid to organoimido and other derivatives of hexamolybdates for which remarkably large second-order nonlinear optical properties have been predicted in some cases.^{176–180} These theoretical studies provide insight into the electronic structure as well as in the origin of NLO properties of POM hybrids¹⁸¹ and they could help design high-performance materials.

Spin transport electronics, or spintronics, *i.e.* the detection and manipulation of electron spin in the solid state, is a relatively new research area, still dominated by conventional inorganic materials though molecular materials are now being actively considered. In this context, POMs have been put forward, mainly under the impulsion of Coronado and co-workers.^{182,183} The bi-capped mixed-valence anion $[\text{PMo}_{12}\text{O}_{40}(\text{VO})_2]^{9-}$ with two localized spins associated with the V(IV) caps, whose coupling should be triggered by the redox state of the central POM, has been proposed as a potential two-qubit gate. There is yet no example using POM hybrids and addressing an individual molecule is still very challenging. The deposition of POM-based SMMs on CNTs by Mialane and co-workers^{21,23,184} is also relevant to this topic.

2.4.3 POM hybrids and surface patterning. Surface nano-structuration is a key issue to improve the efficiency and sensitivity of sensors and biosensors. Due to their rigidity and anionic character, this could be addressed by POM hybrids. Surface patterning through covalent grafting of POMs onto mercaptoacid Self-Assembled Monolayers (SAMs) adsorbed on planar gold substrates has indeed been achieved.^{185,186} Both examples involve coupling reactions between terminal carboxylic acid functions of the SAM and amino-terminated hybrid POMs ($[\text{PW}_{11}\text{O}_{39}\{\text{O}(\text{SiC}_6\text{H}_4\text{NH}_2)_2\}]^{3-}$ ¹³⁵ or unsymmetrical (amino-trisalkoxo)(pyrene-trisalkoxo)-Anderson). In our system, only one of the two amino groups was grafted to the SAM, while the second allows the immobilization of proteins and the subsequent recognition of their specific biotargets.¹⁸⁶ Cronin and co-workers have observed fibroblast cell adhesion to area patterned with aromatic pyrenes. Interestingly, the adhesion is selective, since no such behavior was observed in the case of surface patterning with bis(amino-trisalkoxo)-Anderson or

pyrene groups alone, suggesting that the role of the POM, yet not identified, is not restricted to that of a cumbersome and charged platform.¹⁸⁵ Direct covalent grafting of POM hybrids on gold substrates is also possible, like in the case of the thiol derivative $[\gamma\text{-SiW}_{10}\text{O}_{36}\{\text{O}(\text{SiC}_3\text{H}_6\text{SH})_2\}]^{4-}$.¹⁸⁷

2.5 Other applications

In Sections 2.1 to 2.4 we referred to applications of POMs, especially POM hybrids, in various areas ranging from anchored heterogeneous catalysis and photocatalysis to solar energy conversion, micro- and opto-electronics. Some of the selected topics pertain to energy applications. Besides photovoltaics applications and modified counter electrodes for DSSCs, this is also the case of cathode catalysts for PEMFCs. We will briefly mention here a few other related cases where use of POM hybrids might provide some advantages, especially for energy storage. Thus POM-doped conductive polymers or POM-decorated CNT materials show potential as supercapacitor electrode materials.^{188–190} Their performance might be increased by strengthening the interaction between POMs and other electrode components. Although a very few conductive polymers containing POMs embedded through covalent bonds have been reported so far,¹⁶³ they might also be of interest for catalytically active electrodes. It is also worth mentioning that POM/SWCNTs (Single-Wall Carbon NanoTubes) materials have been recently tested as cathodes in molecular cluster batteries, their high efficiency being attributed to the electron sponge behavior of $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ and its ability to be reduced by 24 electrons in the course of the discharging process.^{191,192} Their performance might be enhanced by use of POM hybrids especially designed to strengthen the interaction between POMs and CNTs. Regarding PEMFCs, current attention is directed at use of heteropolyacids.^{193,194} Again it might be of interest to evaluate the performance of materials obtained from polymerizable organosilyl-functionalized POMs.^{69–71}

3. Direct functionalization versus post-functionalization: scope and methodologies

In the previous sections we have highlighted various types of functional nano-architectures based on POM hybrids in context of the development of new organometallic catalysts (Section 2.1.2.) and the conversion of solar energy (Section 2.3). Covalent functionalization of POMs provides – in principle – a robust link between the POM and the appended functional group. We have discussed the role(s) of the POM and whenever possible we have compared covalently-linked hybrids with similar electrostatically self-assembled hybrids. We have shown that functionalization provides an efficient tool for the self-organization of POMs in various phases (Section 2.2), their immobilization on surfaces and their embedment in polymer matrices (Sections 2.1.1 and 2.4.2), again making comparison with the electrostatic approach. While we described the type of linking involved in the assemblies, we have so far left aside the synthetic methodologies. The two basic strategies, respectively, rely on direct functionalization of POMs or post-functionalization of preformed hybrid POM platforms, which will now be discussed with special emphasis on the second,

3.1 Direct functionalization

While multiple functionalization of POMs is rather readily achieved as far as the appended functions are the same, hetero functionalization remains a challenging issue. For example the common protocol for the synthesis of (trisalkoxo)-functionalized Anderson-type POMs results in the formation of symmetrical hybrids $[\text{MMo}_6\text{O}_{18}\{(\text{OCH}_2)_3\text{CR}\}_2]^{n-}$ with the trisalkoxo groups grafted on each side of the platform.^{94,198} Only quite recently has a single-side functionalized hybrid been obtained by direct functionalization of the parent Anderson-type POM.¹⁹⁹ In principle, such a compound could provide access to unsymmetrical hybrids although ligand scrambling reactions cannot be excluded. Indeed by using an equimolar mixture of two different trisalkoxo ligands, Cronin and co-workers have obtained the two symmetric and the unsymmetrical hybrids in a one pot reaction and achieved their separation by fractional crystallization.^{105,200} Attempts to bring additional functionalities to the metal framework of organo-derivatized POMs usually result in the loss of the first function. In principle this could be avoided by suitable protection. This led us to study the complexation of the POM hybrid $[\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61}(\text{SnC}_6\text{H}_4\text{I})]^{7-}$ with cyclodextrins (CD) and to investigate whether the POM-CD adducts could be partially hydrolyzed without removal of the organotin function (Fig. 9). While this proved not to be the case, some protecting effect was nevertheless observed since the POM hybrid was fully restored after basic degradation and reacidification, which is otherwise not observed.²⁰¹

In the search for bifunctional POM hybrids, it is also worth recalling that the reactions of organophosphonic acids $\text{RPO}(\text{OH})_2$ and organophosphonic dichlorides RPOCl_2 with trivacant POMs of the type $[\beta\text{-A-XW}_9\text{O}_{34}]^{n-}$ ($\text{X} = \text{P}$, $n = 9$; $\text{X} = \text{Si}$, $n = 10$) or $[\alpha\text{-B-XW}_9\text{O}_{33}]^{9-}$ ($\text{X} = \text{As}$, Sb) give, respectively, the hybrids $[\alpha\text{-A-XW}_9\text{O}_{34}(\text{RPO})_2]^{(n-4)-}$

Finally very few examples selected in Section 2 fall into this category of direct functionalization. They are encountered in the preparation of some amphiphilic POMs, like the bis(silyl) derivatives of the Keggin anions, and also some bola-amphiphilic POMs.^{98,103} Both strategies, direct and post-functionalization have been attempted for the preparation of SiW₁₀-Pd(NHC) (see Section 2.1.2) and this gives rise to an interesting discussion: the post-functionalization by coordination of various Pd(II) complexes, [Pd(OAc)₂] or [PdCl₂(CH₃CN)₂], to the preformed NHC-functionalized POM finally proved to be unsuccessful, possibly because of electrostatic interaction between the Pd(II) and the anionic POM. The target POM hybrid was thus prepared by direct reaction between a Pd(II) complex containing NHC ligands terminated with triethoxysilyl groups and the divacant [γ-SiW₁₀O₃₆]⁸⁻ anion.⁸⁴

As the complexity of the targeted functional system increases the post-functionalization strategy is expected to be more attractive. The methodologies used to further derivatize preformed hybrid POM platforms will be presented according to the type of covalent bond formed.

3.2.1 Metal coordination. Especially designed POM hybrids can coordinate to metal ions not only to provide additional (*e.g.* optical, catalytical, *etc.*) properties but also – on the basis of their structure-directing properties – the controlled building of various architectures (supramolecular assemblies, coordination networks, *etc.*). The Wilkinson-type hybrid POM, mentioned in Section 2.1.2 (Fig. 3c), is easily prepared by reaction between the phosphine derivatized platform $[\text{SiW}_{11}\text{O}_{39}\{\text{O}(\text{SiCH}_2\text{CH}_2\text{PPh}_2)_2\}]^{4-}$ and $[\text{RhCl}(\text{COD})_2]_2$ in the presence of triphenylphosphine.⁸³ Pyridine and terpyridine ligands have also been appended to POMs and their coordination chemistry towards various metallic cations shown to give monometallic species, oligomers or coordination polymers, depending on the number of the ligands grafted to the POM and the coordination sphere of the incoming cation. Accordingly, monometallic species have thus

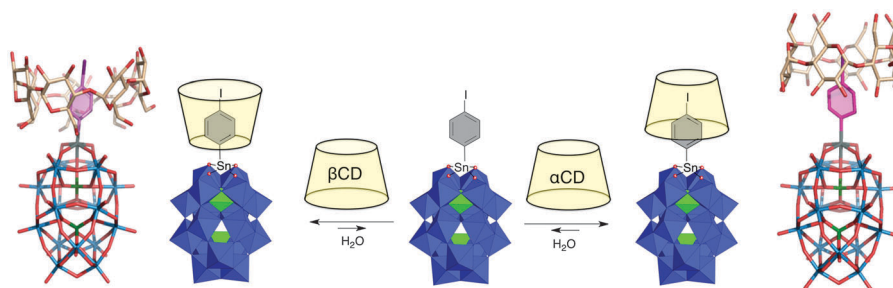


Fig. 9 Representation of host guest POM–cyclodextrin adducts.²⁰¹ Blue octahedra, {WO₆}; green tetrahedra, {PO₄}.

been obtained starting with mono-functionalized POMs, a terpyridine-trisalkoxo-Wells-Dawson type POM in the reaction with $[\text{RuCl}_3(\text{iPrSH})_2(\text{CH}_3\text{OH})]$,¹³⁷ and the terpyridine-imido-hexamolybdate with FeCl_2 ,²⁰⁴ while a bimetallic palladium complex has been formed in the reaction between a bis(terpyridine-trisalkoxo)-Anderson and $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$.¹³⁷ Interestingly, a similar reaction between a bis(pyridine-trisalkoxo)-Anderson and $[\text{PdCl}_2(\text{C}_6\text{H}_5\text{CN})_2]$ in acetonitrile, followed by addition of methanol, yielded a transparent and birefringent gel,²⁰⁵ while a coordination polymer was obtained in the reaction of bis(terpyridine-imido)-hexamolybdate with FeCl_2 ,²⁰⁴ or bis(pyridine-trisalkoxo)-hexavanadate with divalent first-row transition-metal cations.⁹⁶ By varying the coordination sphere of the incoming palladium and exploiting the concepts of supramolecular chemistry, Hasenknopf and co-workers have described a trimer built on a bis(pyridine-trisalkoxo)-hexavanadate and $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$ (Fig. 10).²⁰⁶

Coordination driven assemblies of POMs and porphyrins have been described starting from bis(pyridine-trisalkoxo)-Anderson-type POMs and metallic porphyrins ($\text{M} = \text{Zn}, \text{Ru}$)¹⁴⁰ or *via* the reverse approach from TMSPs ($\text{TM} = \text{Co}$ or Ni) and pyridine substituted porphyrins.²⁰⁷ The coordination of metallic derivatives of POMs has been presented above as a strategy to immobilize POMs on amine functionalized porous materials (see Section 2.1.1).

Owing to the large variety of coordination complexes and the reversibility of their transformations, coordination chemistry is a versatile and efficient tool for the elaboration of self-assembled systems. However, in cases of inert metals, coordination reactions might require harsh conditions, and lead to mixtures of compounds, which are often difficult to purify due to the lack of suitable separation methods in POM chemistry (see Section 3.3).

3.2.2 Peptide and related bonds. Formation of a peptide bond through the reaction of an amine with an activated carboxylic acid usually involves mild conditions. The efficiency of the reaction depends on the coupling agent, which has been thoroughly investigated by Lacôte and co-workers. Isobutylchloroformate in the presence of a base (*t*BuOK or NEt_3) gave the best results in the coupling of the tin derivatives α_1 - and α_2 - $[\text{P}_2\text{W}_{17}\text{O}_{61}(\text{SnCH}_2\text{CH}_2\text{COOH})]^{7-}$ or $[\text{PW}_{11}\text{O}_{39}(\text{SnCH}_2\text{CH}_2\text{COOH})]^{4-}$, as tetrabutylammonium salts in MeCN, with various

amines or thiols, while EDCC was preferred when reactions with alcohols are considered.²⁰⁸ In seeking a deeper insight into the mechanism of the reaction, the authors found that an acylated intermediate with an organic chain folded and inserted into the POM backbone is formed in the absence of nucleophile.²⁰⁹ This intermediate was isolated and involved in further reactions, notably with peptides, and led to chiral recognition and kinetic resolution of the starting material.²¹⁰

The use of the functionalized Anderson- or hexavanadate-type POMs with pendant pyridine ligands was presented above (see Section 3.2.1). In these cases, the peptide bond linking the pyridine to the trisalkoxo ligand is formed before incorporation into the POM (direct functionalization). Inspired by these results, Cronin and co-workers have devised a full family of amphiphilic Anderson-type POMs, obtained by post-functionalization of the initial hybrid Anderson platform $[\text{MnMo}_6\text{O}_{18}\{(\text{OCH}_2)_3\text{CNH}_2\}_2]^{3-}$ with acyl chloride in the presence of NEt_3 .^{101,102} A similar procedure was used by Wu and co-workers for the preparation of surfactant-encapsulated photoresponsive POM assemblies.¹¹² The hexavanadates functionalized with one or two pyrene fluorescent probes recently reported by Hill and co-workers were prepared by the reaction between $[\text{V}_6\text{O}_{13}\{(\text{OCH}_2)_3\text{CNH}_2\}_2]^{2-}$ and pyrene containing succinate ester.¹⁰⁹ Finally, esterification of $[\text{V}_6\text{O}_{13}\{(\text{OCH}_2)_3\text{CCH}_2\text{OH}\}_2]^{2-}$ with long-chain carboxylic acids, in the presence of DMAP and DCC as activating agents, gave the double-tailed fluorescent surfactants described by Wei and co-workers.¹¹⁰

Formation of amide bonds also allows the patterning of planar gold surfaces by linking carboxylic acid-terminated SAM on gold with amino-functionalized POMs (see Section 2.4.3).^{185,186} Very recently Bonchio and co-workers have described a fluorescent chemosensor devised by reaction between $[\gamma\text{-SiW}_{10}\text{O}_{36}\{\text{O}(\text{SiC}_3\text{H}_6\text{NH}_2)_2\}]^{4-}$ and a sulfonyl chloride (dansyl chloride).²¹¹

3.2.3 Imines as linkers. The formation of an imine bond by reaction between an amine and a carbonyl function is generally followed by its reduction by NaBH_4 to prevent its hydrolysis. This has been less exploited in the post-functionalization of POMs, although some examples have been quoted in Section 2. These include the formation of the metallosalen POM derivative (with no subsequent reduction, see Section 2.1.2)⁸² and the

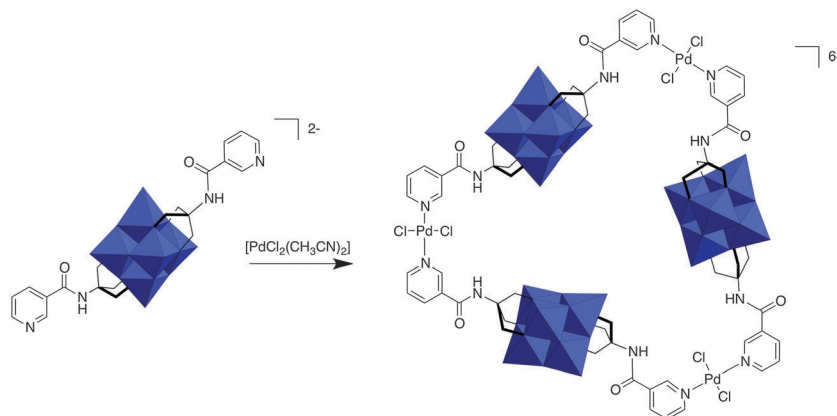


Fig. 10 Synthesis of a POM-based trimer from a bis(pyridine-trisalkoxo)-hexavanadate anion and $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$.²⁰⁶ Blue octahedra, $\{\text{VO}_6\}$.

formation of symmetrical and unsymmetrical bis(trisalkoxo)-Anderson-type derivatives.^{105,200}

3.2.4 Huisgen 1,3-dipolar cycloaddition. The copper catalyzed 1,3-dipolar cycloaddition of azides to alkynes is a well-documented procedure in organic synthesis,²¹² which has been used by Lacôte and co-workers in their investigations of organic-inorganic hybrid POMs.²¹³ It rapidly appeared that the conventional experimental conditions had to be modified to take into account the solubility of the tetrabutylammonium salts of the POMs and to bypass the pairing of copper cations and POMs. Finally full conversion could be obtained in acetonitrile with stoichiometric amounts of CuSO₄ (1 equivalent) and excess of sodium ascorbate (10 equivalents). The optimized procedure was applied by Mayer, Odobel and co-workers to couple bis(azidoethyl-phosphonate) or bis(azidoethyl-silyl) derivatives of the Wells-Dawson anion [P₂W₁₇O₆₁]¹⁰⁻ with perylene moniimide or porphyrins bearing an alkyne residue.^{132,133} The authors also reported the reverse reaction of bis(phenyl-ethynyl phosphonate) derivative of the POM with azide-derivatized porphyrins.

3.2.5 Carbon-carbon cross couplings. Palladium catalyzed C-C cross couplings are fundamental tools in the arsenal of the organic chemist.²¹⁴ The first Sonogashira-type couplings to be carried out on functionalized POMs were done by Peng and co-workers, following the preparation of the 2,4-alkyl-4-iodophenyl or 2,4-alkyl-4-ethynylphenyl imido derivatives of the hexamolybdate [Mo₆O₁₈(NArX)]²⁻ (X = I or CCH).^{215,216} Classical conditions using [PdCl₂(PPh₃)₂] catalyst and CuI co-catalyst, in the presence of NEt₃, have been successfully applied to the coupling of complementary alkyne or iodo derivatized functional units. Dumbells,²¹⁷ enantiopure 1,1'-binaphthyl derivative²¹⁸ of the hexamolybdate, have thus been described. Similarly a terpyridine ligand was linked to the POM and coordinated to various metallic cations.^{204,219}

The synthesis of conducting polymers containing hexamolybates as main- or side-chain pendants, as well as their incorporation in rod-coil diblock polymers for applications in photovoltaics, relies on the same protocol,¹⁶²⁻¹⁶⁴ which was also used by Tour and co-workers for the synthesis of a diazonium salt-derived organo-imido hexamolybdate especially designed for subsequent grafting onto silicon.¹⁵²

In the course of designing POM-based artificial photosynthetic devices, we recently synthesized new organosilyl^{134,135,220} and organotin^{136,201} POM-based platforms bearing, respectively, one or two iodo aryl moieties. Such hybrids were prepared both in the Keggin and Wells-Dawson series (Fig. 11).

These four POM hybrids, mainly isolated as tetrabutylammonium salts, display very distinct redox behaviour (principally due to their difference of charge) allowing fine-tuning of the redox properties of the resulting hybrid, which could be useful for electronic applications. All of them have been involved in Sonogashira coupling reactions in similar conditions than those reported by Peng. Nevertheless, we observed that microwave activation often considerably increases the reactivity, compared to simple heating. Still due to difference of charge, the purification methods have to be adapted to each hybrid. In a first synthetic approach, we synthesized the Keggin-based organosilyl hybrid with pendant terpyridine units.¹¹⁹ However we were not able to efficiently coordinate this hybrid to common photoactive heavy transition metal complexes (*e.g.* Ru(II) and Os(II) polypyridine complexes), as this requires harsh conditions. We thus decided to directly graft the chromophore onto the POM platform bearing the iodo-aryl moieties. Different photosensitizers were then attached to these POM hybrids by Sonogashira cross coupling reactions. While the resulting photoactive systems bearing organic chromophores or neutral organometallic complexes can be easily obtained,^{120,121} the coupling reaction between the POM hybrid and a charged complex is more challenging. Indeed, the charge of the complex both favours ion pair formation with the POM and inhibits the Sonogashira coupling reaction, possibly due to a lowering of the charge density of the alkynyl moiety. These difficulties can be bypassed by the use of complexes bearing carbocyclometalated ligands that not only activate the terminal alkyne but also reduce the overall charge of the organometallic complex, which lowers electrostatic interaction between the POM and the photoactive complex. Finally, when coupling a POM hybrid with a charged complex, ionic liquid can be used for the purification purpose as it may help dissociating the ion-pair.¹⁶³

The synthesis of POM hybrids bearing terminal alkynyl moieties was also performed, *either directly* or in a two-step reaction from the iodo-aryl POM hybrid precursors. It involves synthesis of the trimethylsilyl-protected alkyne hybrids, followed by deprotection of the trimethylsilyl group. For this last reaction, classical cleavage reaction conditions (*i.e.*, fluoride or base) have to be precluded, since they result in the partial cleavage of the organosilyl tether to the POM. However, we found that addition of Ag(I) salts selectively leads to the protidesylation reaction of the trimethylsilyl-alkyne group. Sonogashira coupling could then be performed with compounds displaying a halogeno-aryl moiety.²²¹ The side-products formed by decomposition of the alkynyl tether could not be entirely separated from the desired product, which necessitates adapting the reaction conditions

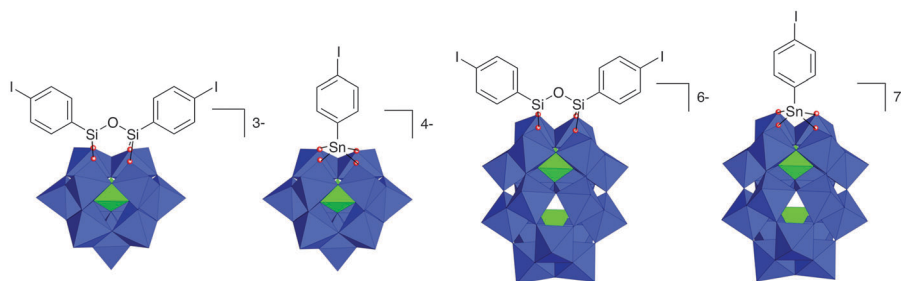


Fig. 11 Different POM-based platforms allowing easy post-functionalization reactions. Blue octahedra, {WO₆}; green tetrahedra, {PO₄}.^{135,220}

(notably the nature of the palladium catalyst) to minimize the formation of by-products. The reactivity of the alkyne function might also be lowered by its grafting to the electron withdrawing POM.

Curiously, there is only one other example Pd-catalyzed coupling reaction involving a hybrid POM platform reported in the literature, namely a Heck reaction performed by Wei and co-workers on the same imido functionalized hexamolybdate $[\text{Mo}_6\text{O}_{18}(\text{NArX})]^{2-}$ ($\text{X} = \text{Br}, \text{I}$) to add remote olefin units.²²² Once again, the experimental conditions had to be adjusted to take into account the POM features: as the POM precursor was found to decompose in hot solution of MeCN, DMF, NMP or pyridine containing various bases such as Cs_2CO_3 , K_3PO_4 , CH_3COOK , NaOH , $t\text{BuOK}$ and Et_3N , the reaction was carried out in a mixture of THF–NMP in the presence of PhNHMgBr as a base. It was also noticed that introduction of phosphine was not mandatory, at variance with the common protocol. Several Pd catalysts were tested, among which $[\text{Pd}_2(\text{dba})_3]$ gave the best results.

3.2.6 Other reactions. Other reactions have been performed in the synthesis of functional POM-based systems described in Section 2. Some of them rely on electro-assisted processes, like electropolymerization leading to POM–porphyrin films (see Section 2.3.2),¹⁴¹ electrografting of diazonium or alkynyl decorated POM hybrids to silicon substrates,^{151,158} while grafting of $[\text{W}_5\text{O}_{18}\text{Ti}(\text{OR})]^{3-}$ anions was achieved *via* alcoholysis (see Section 2.4.1).¹⁶⁰

Covalent incorporation of POMs in porous silica (see Section 2.1.1) involved condensation of silanol groups of pre-built

mesoporous SBA-15 and $[\text{SiW}_{11}\text{O}_{39}\{\text{O}(\text{SiOH})_2\}]^{4-}$ anions⁷⁵ or reaction of $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$ with 1,2-bis(triethoxysilyl)ethane followed by condensation with TEOS.⁷³

The different hybrid POM platforms involved in the post-functionalization reactions have been gathered in Table 1. We have not included the reactions driven by metal coordination because of their great diversity. From this table it appears that the number of reactions and related platforms are rather limited regarding the tremendous number of organic reactions available. Compared with direct functionalization of POMs which may involve alkaline salts of parent POMs, like in the preparation of silyl, phosphonyl or tin derivatives, the post-functionalization reactions reported to date have all been carried out in organic solvents, starting generally with tetra-butylammonium salts of the hybrid POM platforms. When anchorage of electroactive groups has been considered, it is worth mentioning that the redox properties of both the POMs and the electroactive groups were not altered, thus reflecting limited electronic interactions through the organic tether and allowing rational design of extended structures.¹³⁴

3.3 Direct or post-functionalization: a balanced picture

Although most examples described in Section 2 deal with post-functionalization of preformed hybrid POM platforms, rather than direct functionalization of the parent POMs, one might think it is a question of opportunity, depending on the available reagents and that both approaches would equally be relevant. It is probably not the case, although both approaches have rarely been compared in the same study.⁸⁴

Table 1 Main hybrid POM platforms involved in post-functionalization reactions (the metal-coordination route was not considered because of its versatility). \mathcal{F} refers to a functional group, to a polymer or a surface

Parent POMs	Hybrid POM platforms	Post-functionalisation		Ref.
		Reagents	Reactions	
Anderson	$[\text{MnMo}_6\text{O}_{18}\{(\text{OCH}_2)_3\text{CNH}_2\}_2]^{3-}$	\mathcal{F} COCl, \mathcal{F} COOH	Peptide and related bonds	101, 102, 111, 112, 185
Lindqvist	$[\text{V}_6\text{O}_{13}\{(\text{OCH}_2)_3\text{CNH}_2\}_2]^{2-}$	\mathcal{F} C(O)H	Imine	105
	$[\text{V}_6\text{O}_{13}\{(\text{OCH}_2)_3\text{CCH}_2\text{OH}\}_2]^{2-}$	\mathcal{F} COOR	Peptide and related bonds	109
	$[\text{Mo}_6\text{O}_{18}(\text{NArI})]^{2-}$	\mathcal{F} COOH		110
	$[\text{Mo}_6\text{O}_{18}\{\text{NAr}(\text{CCH})\}]^{2-}$	\mathcal{F} CCH	Sonogashira cross coupling	162–164, 215, 216
Keggin	$[\text{Mo}_6\text{O}_{18}\{\text{NAr}(\text{CCH})\}]^{2-}$	\mathcal{F} I		
	$[\text{Mo}_6\text{O}_{18}(\text{NArX})]^{2-}$ ($\text{X} = \text{Br}, \text{I}$)	\mathcal{F} CHCH ₂	Heck cross coupling	222
	$[\text{W}_5\text{O}_{18}\text{Ti}(\text{OR})]^{3-}$	\mathcal{F} OH	Alcoholysis	160
	$[\text{PW}_{11}\text{O}_{39}(\text{SnCH}_2\text{CH}_2\text{COOH})]^{4-}$	\mathcal{F} NH ₂ , \mathcal{F} OH, \mathcal{F} SH	Peptide and related bonds	208
	$[\text{PW}_{11}\text{O}_{39}\{\text{O}(\text{SiC}_6\text{H}_4\text{NH}_2)_2\}]^{3-}$	\mathcal{F} COOH		186
	$[\gamma\text{-SiW}_{10}\text{O}_{36}\{\text{O}(\text{SiC}_3\text{H}_6\text{NH}_2)_2\}]^{4-}$	\mathcal{F} SO ₂ Cl		211
	$[\text{SiW}_{11}\text{O}_{39}\{\text{O}(\text{SiC}_3\text{H}_6\text{NH}_2)_2\}]^{3-}$	\mathcal{F} C(O)H	Imine	82
	$[\text{PW}_{11}\text{O}_{39}\{\text{SnCH}_2\text{CH}_2\text{C}(\text{O})\text{NH}(\text{CH}_2)_3\text{N}_3\}]^{4-}$	\mathcal{F} CCH	Huisgen 1,3-dipolar cycloaddition	213
	$[\text{PW}_{11}\text{O}_{39}\{\text{SnCH}_2\text{CH}_2\text{C}(\text{O})\text{NHCH}_2(\text{CCH})\}]^{4-}$	\mathcal{F} N ₃		134, 135
	$[\text{PW}_{11}\text{O}_{39}\{\text{O}(\text{SiC}_6\text{H}_4\text{I})_2\}]^{3-}$	\mathcal{F} CCH	Sonogashira cross coupling	
Wells-Dawson	$[\text{PW}_{11}\text{O}_{39}\{\text{O}(\text{SiC}_6\text{H}_4(\text{CCH}))_2\}]^{3-}$	\mathcal{F} I		134–136
	$[\text{PW}_{11}\text{O}_{39}(\text{SnC}_6\text{H}_4\text{I})]^{4-}$	\mathcal{F} CCH		
	$\alpha_1\text{- or } \alpha_2\text{-}[\text{P}_2\text{W}_{17}\text{O}_{61}(\text{SnCH}_2\text{CH}_2\text{COOH})]^{7-}$	\mathcal{F} NH ₂ , \mathcal{F} OH, \mathcal{F} SH	Peptide and related bonds	208
	$\alpha_1\text{- or } \alpha_2\text{-}[\text{P}_2\text{W}_{17}\text{O}_{61}\{\text{SnCH}_2\text{CH}_2\text{C}(\text{O})\text{NH}(\text{CH}_2)_3\text{N}_3\}]^{7-}$	\mathcal{F} CCH	Huisgen 1,3-dipolar cycloaddition	213
	$\alpha_1\text{- or } \alpha_2\text{-}[\text{P}_2\text{W}_{17}\text{O}_{61}\{\text{SnCH}_2\text{CH}_2\text{C}(\text{O})\text{NHCH}_2(\text{CCH})\}]^{7-}$	\mathcal{F} N ₃		
	$\alpha_2\text{-}[\text{P}_2\text{W}_{17}\text{O}_{61}\{\text{O}(\text{SiC}_6\text{H}_4\text{CH}_2\text{N}_3)_2\}]^{6-}$	\mathcal{F} CCH		132, 133
	$\alpha_2\text{-}[\text{P}_2\text{W}_{17}\text{O}_{61}\{\text{P}(\text{O})\text{CH}_2\text{CH}_2\text{N}_3\}_2]^{6-}$	\mathcal{F} CCH		
	$\alpha_2\text{-}[\text{P}_2\text{W}_{17}\text{O}_{61}\{\text{P}(\text{O})\text{C}_6\text{H}_4(\text{CCH})\}_2]^{6-}$	\mathcal{F} N ₃		
	$\alpha_2\text{-}[\text{P}_2\text{W}_{17}\text{O}_{61}\{\text{O}(\text{SiC}_6\text{H}_4\text{I})_2\}]^{6-}$	\mathcal{F} CCH	Sonogashira cross coupling	134, 135
	$\alpha_2\text{-}[\text{P}_2\text{W}_{17}\text{O}_{61}(\text{SnC}_6\text{H}_4\text{I})]^{7-}$	\mathcal{F} CCH		

The main concern should be the purity of the final system and this should dictate the choice of the synthetic approach. Besides recrystallization, purification methods suitable for anionic POMs are severely lacking: conventional silica or alumina chromatography is generally precluded because of strong adsorption, although we have successfully used it in some cases,^{223,224} and reverse phase chromatography could be more effective to separate a POM from non-POM compounds than to achieve the separation of a mixture of POMs. Use of size-exclusion gels has been occasionally mentioned.^{135,225,226} Nevertheless, regarding the continuous development of modified stationary phases for liquid phase chromatography, an important effort should be devoted to the identification of new chromatographic media that would lead to selective retention of POM hybrids. Gel and capillary electrophoresis have also been successfully applied to the separation of POM mixtures, albeit for analytical purposes only.^{227–230} Remarkably, as a promising proof of principle, Cronin and co-workers used gel electrophoresis to discriminate and isolate nanoscale clusters.²³¹ Still this methodology has to be adapted to perform separation of POMs on a preparative scale and to be operative in organic media to allow organic–inorganic purification of POM-based hybrids. In the current absence of efficient, adaptable and large-scale methods of purification of POM hybrids, it is thus crucial that their synthesis gives quantitative yields. Direct functionalization of a POM may lead to mixtures of POMs that are difficult to separate unless they have different charges, hence solubilities, in which case fractional crystallization can be used. On the other hand, post-functionalization relies mainly on organic reactions, which are often easier to be pushed to completion. If not, separation of hybrid POMs from non-oxide residues, possibly introduced in excess to improve the yield, is achievable. A peculiar attention must be paid to the purity of the POM based products, especially if they have to be engaged in catalysis or photophysical events, which are very sensitive to impurities. Therefore strict monitoring by NMR, electrochemistry and other suitable techniques is mandatory.

Well-proven protocols are generally available for the organic reactions or organometallic catalyzed reactions involved in the post-functionalization of hybrid POM platforms. However, the presence of POMs introduces a great change, so that the conventional protocols have to be adapted, beginning with the solvent choice. The integrity of hybrid POM platforms could be damaged by co-reactants, for example nucleophiles, both at the POM side or the initial functionalization site. Organic derivatives of POMs are often sensitive to the addition of hydroxide with loss of the organic moiety, and while this has been made reversible once in the presence of cyclodextrins,²⁰¹ applications in subsequent synthesis appear limited. In the case of organo-silyl derivatives of POMs bearing trimethylsilyl-protected alkyne functions, conventional fluoride-based deprotection cannot be used because of competitive breaking of the silicon to POM oxygen bonds. That is why we proposed to use silver salts.¹³⁵ The reactivity of added metallic cations may be inhibited by ion-pairing with the POM. This led Lacôte and co-workers to increase the amount of copper precatalyst in the Huisgen 1,3-dipolar cycloaddition.²¹³ Similarly, interaction between Pd-catalysts and POM platforms is possible,⁸⁴ which could explain why addition of phosphine is not required in Heck

reaction,²²² and surely accounts for altered reactivity of the catalysts. The above-mentioned limitations probably explain the relatively limited set of Pd-catalyzed C–C cross-coupling reactions achieved on hybrid POM platforms, whose expansion will thus resort on sound organometallic expertise. However, it makes no doubt that the catalog of reliable experimental procedures will expand with time, for the benefit of the post-functionalization approach, at variance with direct functionalization of POMs, which finally relies on a limited number of reactions.

Direct and post-functionalization do not involve the same reactions: direct functionalization relies on the now well-documented reactivity of silyl, phosphonyl, tin, amine or trisalkoxide precursors, which might however be less accessible or more difficult to purify, especially in the case of tin, as the intricacy of the targeted functional system increases. Once the difficulties discussed above overcome on a simple model reaction, a post-functionalization strategy has *in principle* no limitation. The use of preformed hybrid POM platforms that are available at a large scale is attractive. After some work-up, purity of the final materials could also prove to be higher following the post-functionalization approach.

4. General conclusions and outlooks

While the catalog of available procedures for the direct functionalization of POMs is not currently expanding and while hetero-functionalization of POMs still remains a challenge, the last ten years have witnessed a remarkable increase in the use of preformed organic–inorganic POM-based hybrid platforms for the rational design of functional architectures, assemblies and materials. In this review, we have selected the most relevant examples to illustrate the elaboration of POM-anchored (photo)-catalysts or photosensitizers, the organization of amphiphilic POMs in complex assemblies and the immobilization of POMs on various surfaces, for applications in catalysis, micro- or opto-electronics, *etc.* Whenever possible, we strived to highlight the strengths of the covalent approach by comparison with the electrostatic approach which still dominates the processing of POMs. The attractiveness of the covalent approach is manifold: (i) enhanced stability, overcoming external variation of pH (in the stability range of POMs), ionic strength, leaching (in the case of surfaces), *etc.*; (ii) enhanced control on the number and relative orientation of the components, tuning of the steric or electronic features of the tether and possible increase of synergistic effects; (iii) better dispersion in a polymer or on a surface. We are thus confident that beyond those currently developed new fields of applications of hybrid POM platforms are forthcoming. These could include new photochromic materials, since recently published results are based on electrostatic assemblies,^{232,233} and materials for NLO.^{171–173}

In the second part of this review, we have thus listed the available hybrid POM platforms and the synthetic routes to their implementation. There is no doubt that these will diversify in the near future. The role and the expertise of the molecular chemist are here essential to supply pure and reliable samples, a step that cannot be avoided.

The use of tailor-made hybrid POM platforms as so many building blocks opens new avenues for the stepwise, rational and scalable engineering of molecular-based materials, following

the so-called bottom-up strategy. The promises of POM-based materials have often been outlined, but ultimately real applications have been more hinted at than realized, even in the field of catalysis where few POMs are used at the industrial scale. There are thus plenty of room and challenges to meet.

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