Polyoxometalate-Soft Matter Composite Materials: Design Strategies, Applications, and Future Directions

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Molecular metal oxides or polyoxometalates (POMs) offer unrivaled properties in areas ranging from catalysis and energy conversion through to molecular electronics, biomimetics, and theranostics. While POMs are ubiquitous metal oxide model systems studied in most areas of chemistry and materials science, their technological deployment is often hampered by their molecular nature, as this leads to increased degradation, leaching, and loss of reactivity, particularly when harsh applications, such as water electrolysis, thermal catalysis or highly basic/acidic reaction solutions are targeted. Therefore, immobilization of POMs on heterogeneous substrates has recently become a central theme in POM research. While early studies focused mainly on metal oxide and semiconductor supports, more recently, POM integration in soft matter matrices including polymers, conductive polymers, hydrogels, and stimuli-responsive matrices leads to breakthroughs in multifunctional composite design. This Review summarizes pioneering experimental and theoretical progress in this emerging field over the last decade, highlighting current challenges that need to be overcome to allow a more widespread technological deployment and providing the authors' view of some of the most promising future directions of the research field. In addition, the current understanding of correlations between structure (on the molecular, nano- and microscale) and reactivity in POM polymer composites is summarized, so that rational materials design can be further developed.

1. Introduction

The combination of hard and soft matter—often thought of as inorganic and organic components—can yield functional composites with unique and otherwise inaccessible properties. Prime examples are found in Nature, where biomineralization forms bones in vertebrates or shells in mollusks. These composites combine mechanical strength with flexibility and offer structural stabilization and protection. These materials are composed of hard inorganic components, e.g., calcium carbonate, $CaCO_3$ or hydroxy apatite, $Ca_5[OH(PO_4)_3]$, and polymeric soft matter, e.g., collagens, which are combined to give new structures and unique function.[1] In this Review, we will explore the combination of polymeric soft matter matrices with molecular metal oxides—polyoxometalates (POMs)—as a unique class of composites where structure, reactivity, and function can be controlled on the molecular level, while giving macroscopic materials suitable for technological device integration, e.g., as membranes, films, or gels.

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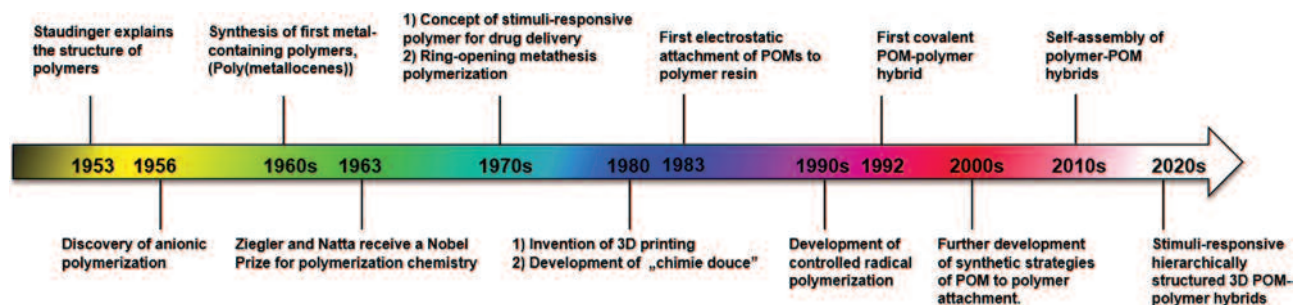Philosophenweg 7 07743, Jena, Germany

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Figure 1. Historic overview of POM-polymer hybrid materials.

1.1. The Relevance of Embedding Molecular Metal Oxide Species in Soft Matter

1.1.1. Soft Matter

The 21st century may rightfully be called the era of soft matter.[2,3] The term "soft matter" was officially introduced in science by Pierre-Gilles de Gennes in his Nobel Prize lecture in 1991.[4] In contrast to hard matter, which is characterized by structural rigidity and strong (e.g., covalent or ionic) interactions, soft matter possesses properties in between solids and liquids and is dominated by weaker, intermolecular interactions (e.g., dipolar or hydrogen bonding interactions) between the constituents. These systems are flexible and are responsive to external forces or stimuli. Further, soft matter features structuring on different length scales from nano- to micrometers, and the macroscopic behavior of soft matter is dictated by noncovalent, intermolecular interactions. Based on these characteristics, polymers, colloids, surfactants, liquid crystals, vesicles, biological objects etc., are all examples of soft matter.[5]

Among those, polymers represent a thriving and promising field that was established about 100 years ago by Staudinger.[6] Later on, the discovery of living anionic polymerization in 1956[7] and stereo-regular polyolefins[8] provided facile access to materials on a large scale. The interest in polymers as industrial materials was also driven by the invention of 3D printing in the 1980s, which provided access to hierarchically complex architectures, which were not achievable by conventional manufacturing technologies.[2] In addition, the discovery of controlled polymerization techniques in the 1990s significantly increased the portfolio of accessible materials and functionalities.[9] Another break-through in soft matter was the development of block copolymers that chemically link two or more polymer-chains into one compound, resulting in unusual structure and new function.[10] In the last three decades the focus of polymer chemistry has shifted to stimuli-responsive or "smart" materials, which adapt to environmental changes by changes of structure or reactivity, enabling application in sensing, drug delivery, self-healing coatings, or tuneable catalyst supports.[11,12]

With the development of polymer chemistry, the interest to incorporate inorganic materials into polymers also emerged. Significant influence on development of such polymer–inorganic nanocomposites can be linked to the discovery of "chimie douce" in 1980s.[13] With that, sol–gel-based approaches were established as an alternative to traditional high-temperature "shake and bake" chemistry and the resulting composites often featured extended organic–inorganic interfaces. The combination of complementary properties of organic (soft) and inorganic (hard) matter opened up the way for materials with unique, sometimes even synergistic, characteristics.[14] This led to extensive applications in fields like sensing, bio-imaging, photovoltaics, or in catalysis (**Figure 1**).[3]

1.1.2. Hard and Soft Matter Composites

In the classical approach of catalytically active hybrid materials, a catalyst is often grafted or anchored on the surface of an inorganic support (e.g., silica, titania, or alumina). The obtained heterogeneous catalyst (hard matter composite) typically shows high thermal stability and good performance, and can be easily recycled.[15] The reverse approach, where inorganic catalytic species are attached to a (structured) polymeric surface (soft matter composite) is less common, presumably due to a (perceived) lower stability of soft matter. However, polymer-supported catalysts open avenues that would not be possible with classical inorganic supports. Soft matter offers superior local control of the catalyst environment, e.g., by careful selection of building blocks for nanostructured polymer matrices. This can even enable approaches where polymers model the well-defined reaction-spaces of biological systems, e.g. ,enzymes.[16] In consequence, enhanced control over morphology, chain folding, and the presence of functional groups at the molecular level is possible, which could even result in the formation of artificial enzymes.[17] In addition, selection of a stimuli-responsive block allows to obtain smart catalytic materials in which the catalytic function can be controlled by external stimuli such as changes in pH, temperature, or light.[18] The selectivity and activity of the material can also be tuned by variation of local polarity in the vicinity of the catalytic center.[19] Currently, various inorganic materials have been used to design polymer–inorganic composites, however in this Review we focus only on hybrids based on polymers and molecular metal oxide clusters, so-called polyoxometalates (POMs).

1.1.3. Polyoxometalates

POMs are ideal molecular components for integration into soft matter matrices, based on their structural versatility combined with an enormous range of applications: POMs are molecular metal-oxide anions, typically based on early transition metals
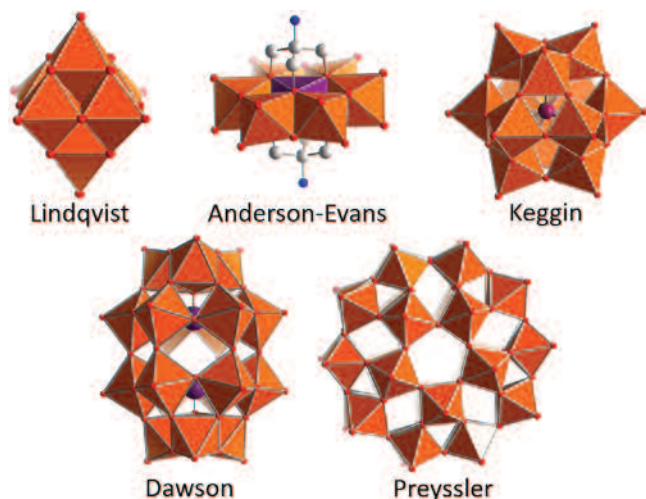
Figure 2. Prototype POM structures discussed in this review.

(group 5, 6) in their highest oxidation states (**Figure 2**).[20–22] POMs self-assemble spontaneously in solution by oligo-condensation reactions of oxometalate precursors (e.g., MoO_4^{2-}, WO_4^{2-}), sometimes in the presence of templating anions (e.g., halides, oxo-anions, etc.).[23] POMs contain between 2 and 368 metal centers are typically in the 1–5 nm size range and can feature several tens of negative charges.[20–22] POM structure formation is difficult to predict, but can be influenced by secondary reaction parameters including solvent, pH-value, temperature, pressure and others .[20] To-date, POM chemistry is dominated by W-, Mo- and V-based POMs, as these metals feature the ideal combination of high oxidation states, suitable ionic radius and availability of empty d-orbitals to stabilize terminal oxo ligands by d-p π-bonding.[20–22]

Over the last decades, advances in synthesis, characterization and mechanistic understanding have led to breakthroughs in POM applications ranging from (photo-)catalysis,[24,25] energy conversion/storage,[26] molecular magnetism and electronics[27,28] through to bio-medicine,[29–31] and artificial enzymes.[30] Of particular interest over the last decade was the development of POMs covalently functionalized with organic groups to merge the fields of metal oxide and organic chemistry.[32,33] Also, the redox-activity of POMs renders them ideal components for charge-transfer and storage as well as (photo-) redox catalysis. In addition, surface protonation of POMs makes them intriguing Brønsted acid catalysts.[34] Metal functionalization of the POM cluster shell can be used to further tune structure and reactivity.[23,35,36] The most commonly used POM structure types are summarized in Figure 2. Due to their molecular nature, POMs can easily be dissolved in various solvents, and solubility can be controlled by the type of counter-cation used.[37] This feature makes POMs amenable for solution-processing, so that incorporation in a wide variety of organic, bio-organic and inorganic heterogeneous matrices (including polymers, proteins, solid oxides) becomes possible.[38] Note that due to their facile synthesis, high stability under many typical operating conditions and ease of functionalization, Keggin- and Dawson-anions are the most widely used POMs in application-driven research.[23] However, care must be taken

when deploying these systems to ensure their structural integrity, as POMs can degrade and form colloids or nanostructured metal oxides that might still show some of the targeted properties (e.g., redox-reactivity or catalytic activity).[39] Careful analysis as outlined below is therefore required to distinguish function derived from POM versus function derived from POM degradation products.[40]

2. POM-Soft Matter Embedding Strategies

2.1. General Deposition Strategies

Two general approaches can be identified for the integration of POMs in soft matter matrices, that is the use of covalent (so-called Class I hybrids) or non-covalent linkages (so-called Class II hybrids).[14] For POMs, non-covalent materials integration is synthetically more straight-forward. Thus, early studies focused in Class II POM-polymer hybrids. In 1983, Parmon and co-workers reported the first example of electrostatic POM integration in soft matter. The group immobilized $H_4[SiW_{12}O_{40}]$ or $H_3[PW_{12}O_{40}]$ on a poly(2-vinyl pyridine) anion exchange resin. However, the resulting composite did not show the proposed light-driven hydrogen evolution activity, possibly due to the absence of mobile protons in close proximity to the POM.[41] In contrast, the catalytic activity of POMs can also increase upon immobilization. For example, Wang and co-workers prepared $H_3[PW_{12}O_{40}]$-based polymers with different degrees of polymerization. The authors reported a dependence of the POM-catalyzed tetrahydrothiophene oxidation on the size of the polymer; the polymer featuring ten repeating units showed the highest catalytic activity, which was 2.5 times higher than unsupported POM cluster.[42]

2.1.1. Class I Hybrids

In class I POM-polymer hybrids, the components are linked covalently, which can have benefits in terms of stability of the POM-polymer linkage.[43] However, due to synthetic challenges in covalently linking POM and polymer, this materials class is still in its infancy. First, organo-functionalized POMs suitable for covalent linkage to polymers are required, which limits the number of suitable candidates, mainly to Keggin, Dawson, Anderson and Lindqvist ion derivatives.[32,33,44] These species can be modified by organic anchoring groups, typically using multidentate tethering groups such as phosphonate or silyl moieties.[33] Note that these linkages can be chemically labile and result in a lower overall stability of the cluster. In addition, given the large number of polymers available, no generalized strategies for POM-to-polymer attachment exist, and each system needs to be carefully tuned for optimum POM covalent attachment.[45] We also note that often, covalent modification of polymers with POMs significantly affects the resulting composite properties, often leading to decreased solubility in general,[46] which causes challenges for materials processing and application. However, when developed successfully, this approach gives access to new materials with synergistic and often unexpected properties. The covalently
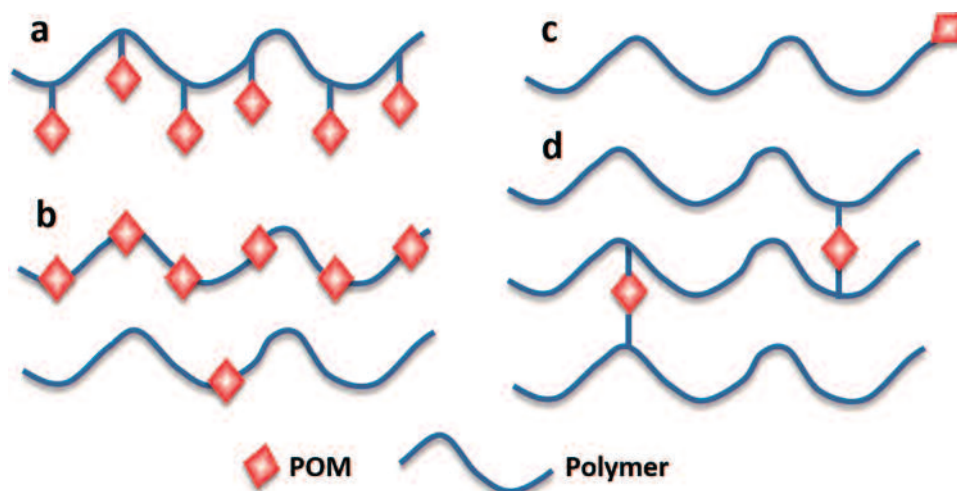
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Figure 3. Main classes of POM-polymer hybrids based on their chain configuration: a) side-chain, b) backbone, c) head-tail POM-polymer hybrids, d) cross-linked networks. The red symbols represent the POM clusters.

linked POM-polymer hybrid materials can be separated into five main classes, based on the location of the POM (**Figure 3**). The POM can be incorporated a) into the polymer side-chain, b) into the polymer backbone, c) as chain end group, (so called head – tail hybrids), d) as crosslinking agent, and e) in dendrimeric structures.

Based on the synthetic method, covalently linked POM-polymer hybrids can be produced directly by polymerization of POM-modified monomers or by post-polymerization modification. The first covalently linked POM-polymer hybrid was obtained by P. Judeinstein and co-workers in 1992 by direct polymerization of organofunctionalized Keggin-type POMs $[(RSi)_2SiW_{11}O_{40}]^{4-}$ (R = vinyl, allyl, methacryl, styryl) using free radical polymerization. The reactivity of the POM-containing monomer increased in the order vinyl << allyl < methacryl < styryl, suggesting that the proximity of the cluster to the polymerizable group decreases the polymerization rate. Due to the presence of two polymerizable groups in one POM cluster, a mixture of branched and linear polymers was obtained, where the POM was located along the polymer backbone.[47]

POM-polymer hybrids where the POM is incorporated along the backbone are usually synthesized by step-growth polymerizations, e.g. polyaddition and polycondensation. One particularly interesting example of polyaddition was reported by Song and colleagues who performed photo-induced [2+2] cycloaddition of *bis*-coumarin modified Anderson POMs. The success of polymerization can be visually monitored by change of the color of polymer from colorless to red due to an increase of the chromophore system. Upon 90 min of irradiation, polymers with molar masses of 337 kDa and a dispersity of 1.60 were obtained.[48] Also, the use of CLICK chemistry (Cu-catalyzed alkyne-azide coupling) has been reported by Cronin and co-workers to access POM-oligomers based on suitably functionalized Anderson-POMs.[49] Here, the authors first designed POM-based "monomers" featuring terminal amine groups at either end of the POM molecule. Chain growth was then enabled by functionalizing the terminal groups with alkyne moieties that could then undergo further CLICK-linkage. This route can be repeated, leading to well-defined Mn-Anderson hybrids ranging

from dimers to pentamers. Despite unprecedented control over the polymerization process, the proposed strategy is still limited due to the difficulties in synthesizing unsymmetrically functionalized POMs.

In one example, the integration of POMs into polymeric side-chains has been achieved by ring-opening polymerization of norbornene monomers modified with Dawson-POMs. The polymerization occurred nearly quantitatively and resulted in POM-polymer hybrids where $[H_4P_2V_3W_{15}O_{62}]^{5-}$ POM clusters are attached to well-defined polynorbornene backbones (**Figure 4**a). Molar masses up to 600 kDa and a low dispersity (PDI = 1.2) were reported, which corresponds to 100 POM-norbornene repeating units. The resulting composite showed catalytic activity for the oxidation of tetrahydrothiophene and could also be processed into thin films.[42] The same Dawson-type POM has also been used for the formation of head to tail type POM-polymer hybrids by ATRP (Figure 4b). Here, the macroinitiator was synthesized at first by ligand exchange between POM and bromofunctionalized tris-(hydroxymethyl)methane. This macroinitiator was then used in polymerization reactions, giving polystyrene-based head-to-tail hybrids with molar masses up to 119 kDa. Exchange of lipophilic NBu_4^+ cations with hydrophilic H^+ resulted in the formation of giant amphiphiles with hydrophilic POM headgroups and long hydrophobic tails, forming vesicles via self-assembly in aqueous media.[50] RAFT polymerization techniques have been used to access poly(N,N-diethylacrylamide) composites using trithiocarbonate-functionalized Dawson-type phosphotungstates as chain transfer agent and AIBN as initiator. Here, chain transfer agent (CTA) synthesis was performed through the formation of a lacunary POM with the next tin modification followed by azide-alkyne coupling (Figure 4c). This led to head to tail hybrid polymers with molecular weights in the range of 10 to 100 kDa and dispersities <1.5.

The covalent attachment of POMs to pre-formed dendrimers has been possible by post-polymerization modification. For example, $[H_4P_2V_3W_{15}O_{62}]^{5-}$ Dawson POMs have been directly attached to dendrimers featuring terminal tris(hydroxymethyl) groups through transesterification. The material obtained was
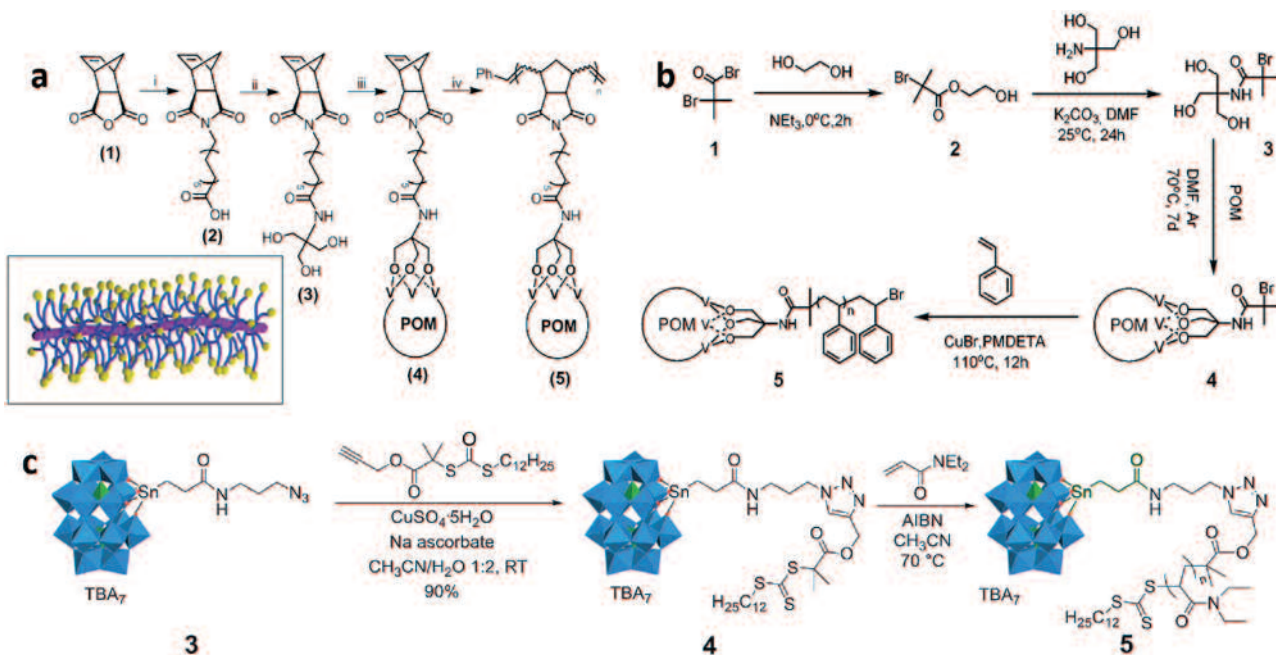
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Figure 4. Selected examples for the utilization of controlled polymerization techniques: a) ROP. Reproduced with permission.[42] Copyright 2009, American Chemical Society. b) ATRP. Reproduced with permission.[50] Copyright 2014, American Chemical Society. c) RAFT for the formation of covalently linked POM-polymer hybrids. Reproduced with permission.[51] Copyright 2014, Wiley-VCH GmbH.

used as a catalyst for the tetrahydrothiophene oxidation using tBuOOH or H_2O_2 as oxidant. Catalyst recycling and reuse by precipitation and filtration-recovery has also been demonstrated.[52] Also, for Keggin-POMs, dendrimer attachment has been achieved by reaction of dendrimer-based amino groups with tin chloride-modified POM clusters.[53]

2.1.2. Class II Hybrids

The simplicity of electrostatic attachment of anionic POMs to cationic polymers has made it the most used approach for POM-in-polymer integration, and various polymers have been used, including quaternized poly(vinylpyridine), polyimidazole, polyaniline, protonated polylysine, polypyrrole, poly(vinylchloride), polyethylene-*block*-polydimethyl aminoethyl methacrylate, or polystyrene-*block*-poly(2-dimethylaminoethyl methacrylate).[54] Despite the facile composite preparation, non-covalent attachment can often lead to POM leakage under operation, particularly upon pH changes. Especially in case of electrostatic attachment, drastic changes in pH can lead to weakening of the interaction and removal of POM from the polymer matrix (e.g., by POM protonation). Nevertheless, reversible attachment upon changes in pH could be potentially used for metal recovery and polymer recycling. In addition, electrostatic attachment is the method of choice for the formation of hierarchically structured 1D–3D POM-polymer hybrid materials. Particularly, when block-copolymers with chemically different "blocks" (e.g., a hydrophilic and a hydrophobic block) are used, then access to POM-functionalized hierarchical structures including micelles, vesicles, thin films, membranes, fibers, or porous solids becomes possible (**Figure 5**). In addition to direct mixing of

POM and polymer during the preparation, electrostatic POM-anchoring is also possible as a post-functionalization method of the pre-formed polymer. So far the direct mixing of POM with polymer is rather difficult as in this case all components should be well soluble in one solvent.[55] More often the attachment of POM is realized due to the electrostatic attachment of POM to polymers bearing an amino function, that also could be introduced in the commercial polymer network like poly(vinylidene difluoride) (PVDF) by plasma treatment.[56]

2.2. Challenges in Characterizing Molecular Species Embedded in Heterogeneous Matrices. Key (In Situ/"Operando") Techniques to Assess Reactivity, Stability, and Structural Integrity

The structural analysis of POM integrity within the soft matter matrix is most often performed using surface spectroscopic and microscopic techniques. In the following chapter, key techniques are presented, and their relevance is demonstrated by appropriate literature examples.

2.2.1. Fourier-Transform and Attenuated Total Reflectance Infrared Spectroscopy (FT-/ATR-IR)

FT-/ATR-IR are suitable solid-state methods to study materials such as powders, (hydro)gels,[57] films,[58] membranes,[59] etc., and to verify POM presence and integrity in a polymer matrix.[60,61] Note that ATR typically probes the sample surface, while FT-IR targets the sample bulk. POMs exhibit intense, characteristic metal-oxygen vibrational modes in the fingerprint region of 1000—500 cm⁻¹, which are highly sensitive to
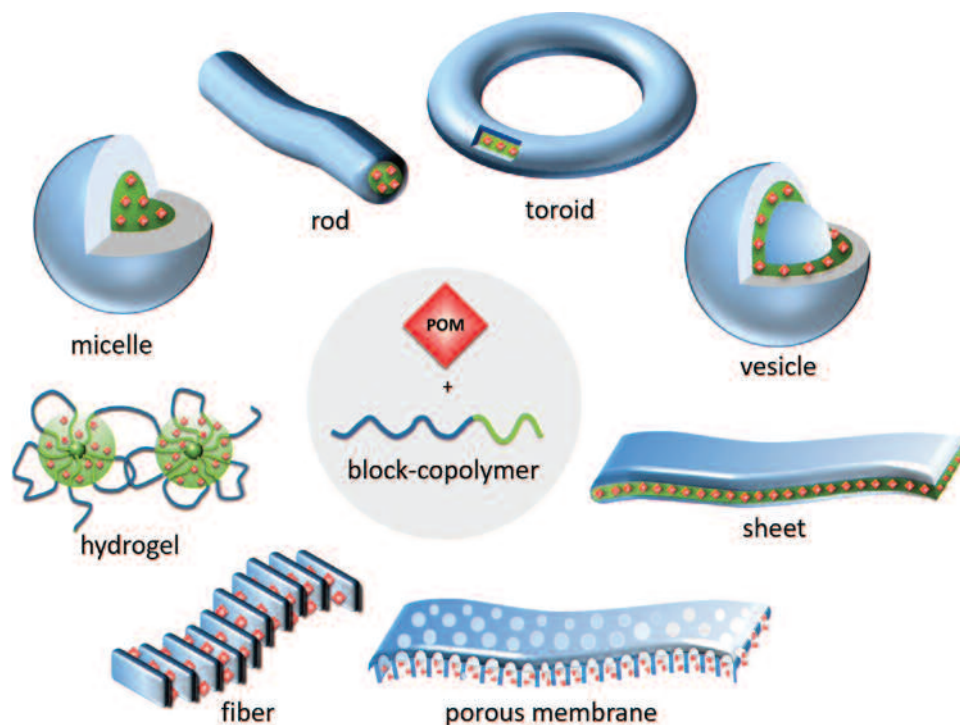
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Figure 5. Overview of 1D, 2D, and 3D POM-polymer hybrid structures obtained using block copolymer self-assembly.

structural changes, degradation or interactions with the environment. Hence, IR-spectroscopy can be used, e.g., to assess POM stability or leaching in reactivity studies by analysis of POM-characteristic signals in the fingerprint region <1000 cm^{-1}.[62–64] In addition, POM-polymer interactions can be experimentally studied, including hydrogen bonding,[61] π-stacking,[65] electrostatic,[57,58] ionic[61] and covalent attachment[66,67] by analysis of the specific vibrational features.[61,65,68] IR spectroscopy (in combination with other methods) also allows to track the progress of a reaction by evaluating changes in vibrational intensities, as demonstrated by Judeinstein and co-workers for a (POM-methacrylate) polymerization reaction, where the intensity decrease of the polymer-based C=C-vibration is used as spectroscopic probe.[47]

2.2.2. Raman Spectroscopy

Raman spectroscopy is a vibrational spectroscopy method to characterize POM-polymer composites that offers higher signal resolution compared with conventional IR spectroscopy. However, it typically operates at high excitation laser power, which can cause damage to sensitive samples. In one example, Luis Vilas, Gutiérrez–Zorrilla and colleagues[69] used confocal Raman microscopy (CRM) to access depth profiles/cross sections of composite films containing POMs. The study highlighted that POM-identification within the films is possible at high spatial resolution, enabling the observation of homogeneous POM distribution. In another example, Jacob, Travaš-Sejdić, Streb and co-workers used "operando" Raman-spectro-electrochemistry to explore reversible redox-cycling of POM-conductive polymer composites.[70] Yang and colleagues

used in situ Raman spectroscopy to assess structural changes, degradation, and substrate binding in a mesoporous POM-soft matter hybrid.[62]

2.2.3. X-Ray Photoelectron Spectroscopy (XPS)

XPS is a surface sensitive (top few nm) technique to quantify the elemental composition of solids under ultra-high vacuum. The technique can also be used to study POM or polymer surface-processes including structure changes, degradation, diffusion, or leaching.[71] In addition to the detection of characteristic binding energies and the assignment of metal oxidation states, changes in signal intensity ratios can be used to gain insights into chemical changes before and after specific reactions.[63,72]

2.2.4. Nuclear Magnetic Resonance (NMR) Spectroscopy

NMR spectroscopy can be used to probe the structural integrity of POMs and their interaction with polymers in solution and the solid state. In one example, Ikegami and co-workers studied a Keggin-phosphotungstate embedded in a copolymer matrix.[73] The authors used ^{31}P-NMR to verify cluster integrity and to explore the reactivity loss during recycling. Hill and colleagues[66] used the solid-state method Cross-Polarization Magic Angle Spinning (CP-MAS) ^{13}C-NMR to examine the presence of covalent bonds between polymer-anchored 1,3,5-benzenetricarboxamide linkers and polyoxovanadate clusters. The presence and integrity of the vanadate cluster itself was confirmed by solid-state MAS-^{51}V-NMR and solution ^{51}V-NMR.

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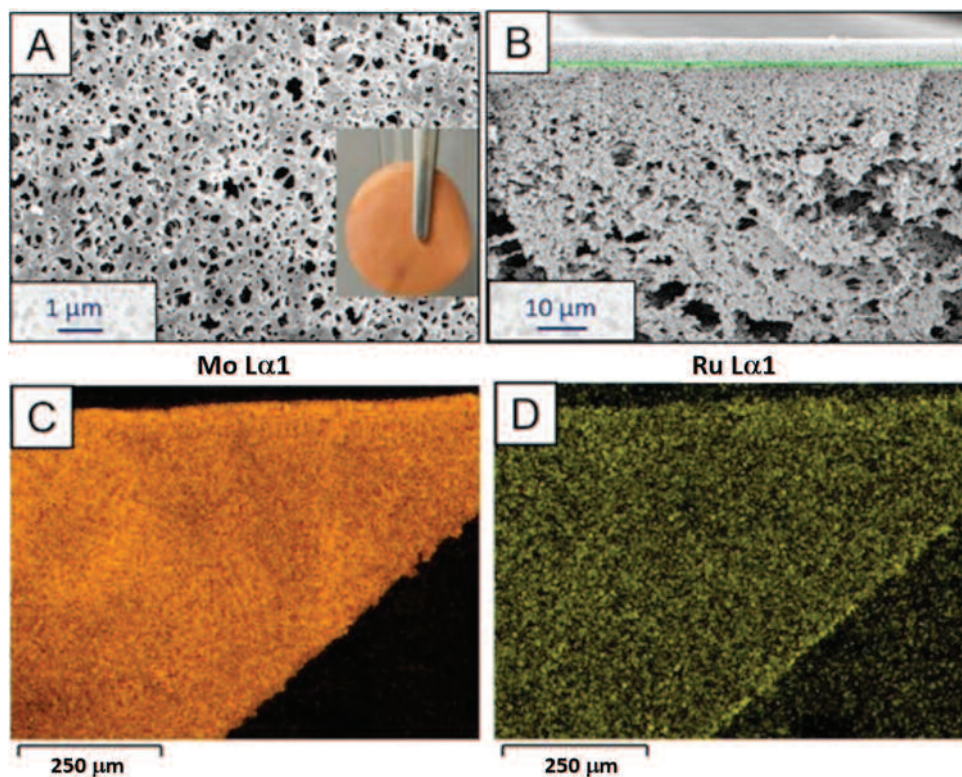MATERIALS**

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Figure 6. a,b) Top view and cross sectional SEM micrographs of a non-functionalized block copolymer membrane. Inset A: photograph of the functionalized membrane showing the characteristic color of the immobilized molecular species. c,d) EDX elemental mapping (Mo/Ru) mapping of functionalized membrane. Reproduced with permission.[79] Copyright 2020, RSC Publishing.

2.2.5. UV–vis Absorption and Emission Spectroscopies

UV–vis absorption and emission spectroscopies can be used to probe the presence and reactivity of POMs in soft matter.[64] In one example, Oms, Dessapt, Roger and co-workers[74] designed a polymer containing Anderson-type POM and organic spiropyran. The materials showed strong solid-state photochromism that was tuned by the POM loading amount. In another example, Zhang, Wan and colleagues[75] reported a pH-responsive POM-soft matter hydrogel unusual, POM-dependent luminescence properties.

2.2.6. Elemental Analysis

Elemental analysis allows the determination of metals and most non-metals in composite materials by CHN elemental analysis (EA) and inductively coupled plasma optical/atomic emission spectroscopy (ICP-OES/AES). This enables validation of elemental compositions,[76] determine POM- and organic contents,[63] and assess POM stability and leaching resistance.[63]

2.2.7. Scanning Electron Microscopy (SEM) and Energy-Dispersive X-Ray Spectroscopy (EDX)

SEM provides nanometer-resolution information of the morphology,[57] micro- and nanostructure of POM-soft matter systems. When combined with EDX, structural and elemental information can be obtained, e.g. to, study POM incorporation and distribution in soft matter matrices.[56,63,77] Bonchio, Carraro and co-workers used SEM-EDX to investigate the surface and cross-sectional morphology of a photocatalytically active POM-polymer membrane, and provide information on membrane changes during catalysis.[78] Streb, Schacher and colleagues reported light-driven hydrogen evolving nanoporous block copolymer membranes functionalized with a molecular photosensitizer ($[Ru(bpy)_3]^{2+}$) and a HER-active catalyst ($[Mo_3S_{13}]^{2-}$).[79] SEM-EDX was used to explore the distribution of the molecular components on the membrane surface (**Figure 6**).

2.2.8. High-Resolution Transmission Electron Microscopy (HR-TEM)

HR-TEM provides down-to atomic resolution analysis of thin samples. Due to the large difference in electron density, HR-TEM is particularly suitable for studying POM distributions in organic soft matter. In one example, Breu, Kamperman and co-workers showed that different nanostructures (micelles, networks, and vesicles) can be accessed in POM ($H_3[PMo_{12}O_{40}]$)/PB-b-PDMEAMA hybrids, depending on the POM-to-polymer ratio.[55]

2.2.9. Atomic Force Microscopy (AFM)

AFM can be performed under ambient conditions on non-pretreated (e.g., dried) samples. AFM gives access to surface topology

and roughness of POM-polymer hybrids. For example, Luis Vilas, Gutiérrez–Zorrilla and colleagues[69] used AFM to show that POMs of different size feature distinct distributions at polymer interfaces.

2.2.10. Thermogravimetric Analysis (TGA)

TGA can be used to quantify the POM-content in a POM-polymer hybrid by determining the amount of combustible components.[61] In addition, TGA provides information on the thermal stability[58] and degradation temperature[67] of the samples studied.

2.2.11. Dynamic Scanning Calorimetry (DSC)

DSC can further be used to identify melting/solidification behavior[65] and glass-transitions[76] in POM-soft matter composites, e.g., hydrogels.[57]

2.2.12. Electron Paramagnetic Resonance (EPR) Spectroscopy

EPR spectroscopy provides insights into the electronic states of POMs embedded in soft matter. In one example, Lalevée and co-workers[80] followed the catalytic performance and oxidative re-generation of POMs when embedded in a polymer matrix using EPR spectroscopy.

2.2.13. Electrochemical Analyses

Electrochemical analyses are ideal tools to study the redox-activity of POMs embedded in redox-active or conducting polymers. Voltammetric-, bulk electrolysis and related studies can provide critical information on the accessible oxidation states, changes in reversibility and electron storage/transfer capabilities of the materials studied.[67,76,81]

2.3. Computational Studies on Polyoxometalates-Soft Matter Hybrid Materials

Over the last two decades, the number of publications dedicated to computational studies of POMs has increased steadily. The rise on computational power alongside the appearance of novel theoretical methods has made possible to target transition metal compounds with high accuracy.[82] Recent reviews[83,84] have covered some of the applications of theory to POMs. However, the number of computational studies addressing POM-soft matter composites is far below those, which focus on computed properties of POMs. Here, we discuss computational studies of POM-soft matter hybrid materials, first pointing to the challenges associated with model POMs.

2.3.1. Computational Methods

Even though theory has been able to provide qualitative and quantitative descriptions of some of the properties of iso-lated POMs, this path has been far from straightforward and hindered by the many limitations of the available methods. Atomistic simulations can employ quantum mechanical (QM) methods (**Figure 7**, bottom), either based on ab initio wave function or density functional theory[85] (DFT). Whereas wave function methods quickly become unfeasible as the size of the molecular system increases, DFT has a better trade-off between cost and accuracy and is therefore more popular. DFT studies on POMs until 2012 can be found in the excellent review from Bo, Poblet and co-workers.[84] Recent examples, where DFT has aided the interpretation of experimental data or predicted POM properties include the calculation of redox potentials,[86–88] X-ray spectra,[89] reaction mechanisms,[88,90–92] and non-linear optical (NLO) properties.[93–95]

When studying the interactions of POMs and soft matter, the large dimensions of the global system requires the use of classical approximations. Most methods in this category involve molecular dynamics (MD) simulations based on parametrized force fields—also known as molecular mechanics (MM). In this fashion, atoms are considered as classical balls that follow Newton's equations in time. To recover QM effects and thus improve accuracy, hybrid QM/MM methods[96,97] divide the system in (at least) two regions, a small one that is treated quantum mechanically with high accuracy, and the rest that is described with a suitable force field. The different flavors of QM/MM methods depend on how the interaction between the QM and MM regions is described. The computational cost of QM/MM is roughly as expensive as that of the chosen QM method, and thus combined with MD, propagation time scales are shorter than those that can be achieved with MD only (see Figure 7). When the system is much larger than the computational feasibility of all-atom MD allows or propagations in the µs-ms regime are targeted, coarse-grained[98] modeling can reduce the number of degrees of freedom by defining a group of atoms in a so-called bead. Despite its lower resolution as compared with all-atom simulations, combined with MD coarse-grained modeling exhibits a computational speedup of the order of N^2, with N the number of particles.[99] To reach larger spatial and time scales, at the meso- or macroscale, supra coarse-grained MD strategies include one or more molecular units in one bead (see top of Figure 7). Furthermore, static information on the positioning or interaction modes between POMs and macromolecular systems can be addressed by means of molecular docking.[100]

2.3.2. Modeling POM Geometries

Before any molecular properties can be calculated, one requires an accurate prediction of the equilibrium geometry. If the system is flexible, one needs to sample and energetically rank all accessible conformers. Unlike for main group element-containing molecules, conformational energy benchmarks for transition metals are scarce and they lack the inclusion of POMs in their datasets.[102,103] It is worth noting that in recent times there have been major advances in the development of new density functionals that allow to routinely compute several hundreds of atoms, while conserving the accuracy of more computationally demanding counterparts.[104–108] Regarding
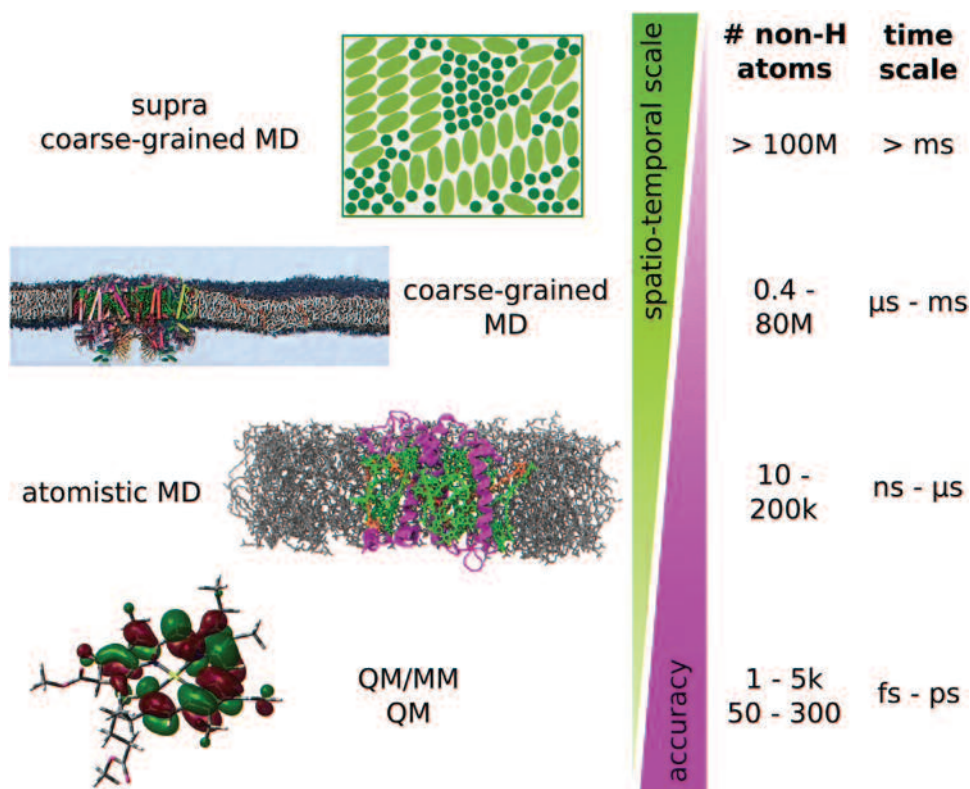
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Figure 7. A general hierarchical scheme of different modeling approaches, including approximate time-scales and system sizes that can be studied with each method. Reproduced with permission (http://creativecommons.org/licenses/by/4.0/).[101] Copyright 2020, the Authors, published by Springer.

flexibility, Jahn-Teller (JT) effects and redox isomerism should also be considered when describing the conformational landscape of POMs. For example, the DFT studies of López, Poblet and co-workers[109] found that intrinsic geometrical distortions present in molybdates are due to pseudo JT distortions. Likewise, Irlet and colleagues[110] attributed JT distortions as the driving force for the molecular and electronic structure changes during super-reduction of a α-Keggin POM cluster. Very recently, some of us[111,112] showed that the position of JT axes influences the local reactivity in a Mn-based POM,[113] which is a synthetic mimic of the oxygen evolving complex in natural photosynthesis.

2.3.3. Modeling POM Electronic Properties

As POMs are composed of transition metals, they inherit the associated computational challenges of dealing with such atoms. If calculating relative energies of different spin states can be a difficult task in a transition metal complex, to do so in a POM is considerably more challenging as the many metal atoms increase the number of oxidation and spin states. Ideally, such problems are best treated with QM methods[] able to deal with the multi-configurational situations that most likely such structures incur. However, multi-configurational QM methods are computationally very demanding and applications to POMs are scarce.[115,116] Alternatively, the relative stability of high and low-spin states is often calculated with the cheaper broken-symmetry DFT approach.[117,118] In this framework, the low-spin

manifold is accessed by a variational self-consistent-field optimization of a mono-configurational wave function, where the sign of the spin-density of an atomic center is inverted to represent a lower symmetry state compared to the high-spin state. One example of low-spin states calculated in this fashion is the computed redox potentials of a Mn-based POM,[88] but many more exist. Broken-symmetry DFT has also been employed to calculate magnetic properties of POMs.[119,120]

2.3.4. Modeling POMs Embedded in Polymers

Due to their large size, high conformational flexibility, and often amorphous structure, the choice of a computational technique to model polymers is far from trivial.[121] Particularly, for the study of POM-in-polymer integration, all-atom MD simulations and coarse-grained MD approaches are by far the most popular choices.

An example for a soft matter environment where POM-integration has been computationally studied are dendrimers. The POM@dendrimer systems are termed artificial dendrizymes,[122,123] as they are intended to have structural resemblance with natural metalloproteins and are to be applied as enhanced catalysts. Early studies by Volkmer, Kurth, Krebs and colleagues[123] on a heteropolytungstate cluster encapsulated in a shell of dendritically branching surfactants laid the foundations for later applications of all-atom MD simulations on POMs embedded in dendrimers.[124,125] Their study was mostly qualitative in nature, giving insights into the packing
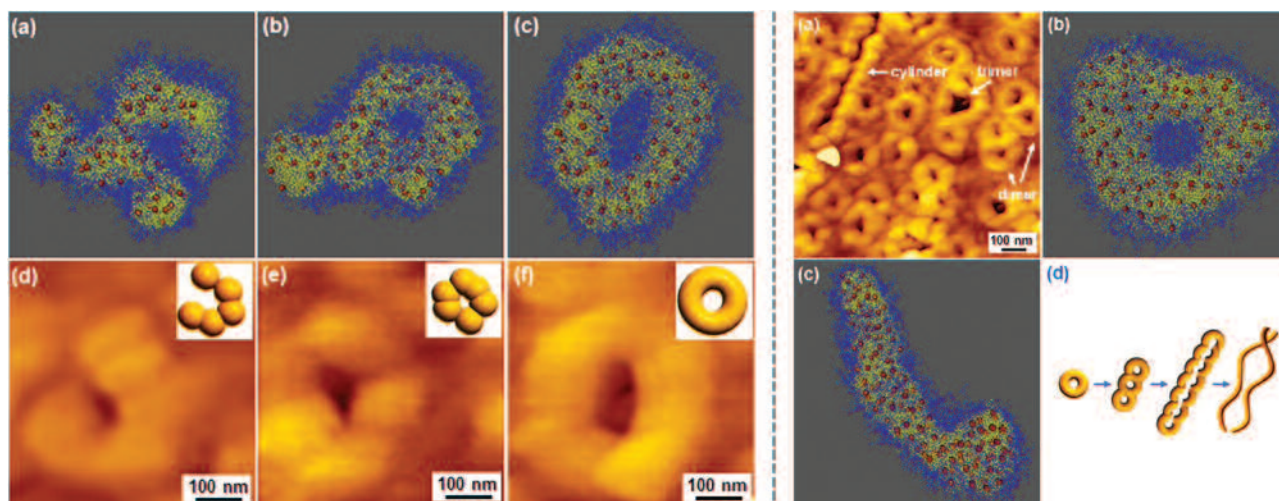
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Figure 8. Left: a–c) coarse-grained MD snapshots of the micelles. d–f) AFM images of intermediate states during the formation of toroids. Right: a) AFM image of the coexisting shapes of the micelles, b) snapshot from the simulated early stage formation of the toroidal micelle, c) snapshot from the simulated evolution of the toroidal micelle into cylinder shape.[60] Reproduced with permission.[60] Copyright 2015, American Chemical Society.

arrangement of dendrons over the anionic metal cluster. More recently, several studies combining theory and experiment have been carried out on perfluorosulfonic acid polymers (PFSA) doped with heteropoly acids (HPAs), which is a subset family of POMs.[126–129] PFSAs are able to form proton exchange membranes, which upon doping with HPAs should see an increase in the proton conductivity capabilities. Maupin, Herring and co-workers[126] combined experiment and theory to study the PFSA membranes doped with $[H_3PW_{12}O_{40}]$ and $[H_4SiW_{12}O_{40}]$ HPAs. All atom MD simulations assisted the understanding of the observed enhanced proton conducting capabilities of the membranes, by addressing the solvent distribution. From their calculations, they concluded that enhanced proton conductivity was due to a trapping mechanism of solvent water molecules around the HPAs, resulting in a hydrogen-bonding network.[126] A study by the same group[127] followed a very similar modeling protocol to provide additional information regarding the balance between the loading of HPAs and the resulting conductivity. Relying solely on computer simulations, Mosavian and co-workers[128] studied the doping of Nafion® 117 with $[H_3PW_{12}O_{40}]$, $[H_5IW_6O_{24}]$, $[H_9AlW_6O_{24}]$, and $[H_2W_6O_{19}]$. They applied MD simulations coupled with quantum mechanically derived proton hopping[130] to investigate the hydrogen bond network and structural diffusion of protons. This method allows to compute rate constants of proton hopping between water molecules, and to detect decreased activation energies in the proton migration between two adjacent water molecules when the POMs are integrated in the Nafion® 117. The same authors also employed all-atom MD simulations to investigate in more detail the creation of a change in the water network triggered by POMs through a detailed percolation analysis.[129]

Computational simulations of other mechanisms, such as co-assembly of POMs and polymers, requires accessing to time-scales much longer than those accessed by atomistic MD methods, e.g., using coarse-grained MD.[121] In this manner, Li, Quian, Wu and colleagues[60] showed the time evolution of a supramolecular star polymer with a Keggin-type POM cluster core ($[CoW_{12}O_{40}]^{5-}$) and blockcopolymers. The system was composed of a supramolecular star copolymer with the POM as a core and a solution of a block-copolymer. Their simulations showed the time evolution of the system going from the formation of toroidal micelles (**Figure 8**, left) to their assembly into cylindrical micelles (Figure 8, right), which nicely agreed with measured AFM images. Very recently, coarse-grained MD was also used to simulate the self-assembly mechanism of POM nanoparticles decorated with mobile polymer ligands (i.e., via electrostatic interactions),[131] providing designing rules for tailored self-assembly into lamellar, cylindrical, and spherical structures.

Complementary to the methods above, it is also possible to take truncated models of POM-polymer structures sufficiently small for QM calculations. For example, in a joint experimental and theoretical work, De Luca and co-workers[132] constructed a model system composed of: i) the Keggin POM $[PMo_{12}O_{40}]^{3-}$, ii) one and three acryloyloxyundecyltrimethyl ammonium bromide surfactant tails, and iii) 36 explicit water molecules, that was analyzed with DFT calculations, through a rather elaborate protocol. The computed non-covalent interaction energies among this Keggin POM, bromide ions, and the surfactant, as well as solvation energies provided insights into the bromide ion exchange process led by the POM. In another study, NLO properties were calculated in a POM cluster with attached polymeric chains as a pendant.[133] By creating a model system of one attached polymer chain with varying number of π-spacer units, time-dependent DFT calculations were performed to elucidate the structure/property relationship that leads to tuneable NLO properties.

2.3.5. Modeling POMs in Miscellaneous Soft Matter Environments

Although there are less examples, computational modeling has been also used to study the integration of POMs in lipid bilayer membranes and surfactants or to analyze self-aggregation processes. For example, a study from Aksimentiev and co-workers[134] made use of coarse-grained MD to propose a route

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for spontaneous self-assembly of a POM nanocapsule into a phospholipid membrane. Polarz and colleagues[135] fabricated a novel surfactant by self-assembly of a Keggin-type polyoxometalate functionalized with anthraquinone via a π-conjugated chain. The supramolecular composite showed promising capabilities as an electron reservoir and frontier molecular orbitals were computed at the DFT level of theory to understand the electron confinement properties. In a recent study,[136] a surfactant-encapsulated POM was integrated into a polymerizable bicontinuous microemulsion to create a novel smart material for wastewater treatment. By using DFT QM/MM calculations, non-covalent binding energies between the POM and the surfactant tails were evaluated in order to analyze the stability of the supramolecular system.[136] Bo, Izzet and co-workers[137] prepared soft nanostructured materials through aggregation of dumbbell-like POM units joined by hybrid organic–inorganic linkers and DFT calculations were used to analyze the electronic configuration of the metal centers at the linkers; additional all-atom MD simulations provided further insights into the assembly mechanism.

3. Application-Driven POM-Soft Matter Composite Design

3.1. Stimuli-Responsive Materials and Sensing Applications

As described above, polyoxometalates are versatile compounds and of interest for various applications. It can be beneficial to enhance selectivity or tune solubility by combining POMs with stimuli-responsive materials such as polymers or biomolecules. In that way, a variety of different triggers can be used to activate specific properties of the POM that are required in different environments. The most common triggers for responsive materials are pH, heat, light and electricity. Due to their versatility, POMs can be responsive to all these triggers under suitable circumstances. With these different triggers, applications of responsive POM/organic hybrid systems in various fields such as theranostics,[138] sensors,[139] catalysis,[140] or redox systems[141] are possible. Decisive for the application of POMs in different soft matter matrices are the controlled accessibility of the POM and at the same time the sensible enhancement of the POM's properties.

For many applications the embedding of POMs in organic thin films is a suitable method. This provides a high stability of the resulting systems and functional polymers enhance the properties of the POMs. Different thin film formation methods are employed, including Langmuir–Blodgett deposition, spin-coating, as well as layer-by-layer (LbL) methods, where cationic and anionic layers are deposited in an alternating fashion (**Figure 9**a).[142] These deposition methods are ideally suited for the deposition of POMs and subsequent application in sensing and stimuli-responsive materials.[142] When integrated into electrochemical devices, redox-active POMs can be coupled to external electrical stimuli to trigger changes of their physicochemical properties, such as their redox-states. In one example, Volkmer and co-workers used LbL assembly to fabricate thin films containing the polycation poly(allylamine hydrochloride) (PAH) as positively charged layer and anionic layers composed of the polyanion poly(styrenesulfonate) (PSS) and the Preyssler-

heteropolytungstate anion $[Eu(H_2O)P_5W_{30}O_{110}]^{12-}$.[143] Films with switchable electrochromism, short response times and high cyclic stability were reported.

Similar concepts have been used for the assembly of POM-based sensors, which often utilize the POM redox-activity to detect gases or toxins. In one example, Kurth and co-workers used LbL assembly to fabricate a POM-based sensor for nitrogen monoxide. To this end, alternating layers of the polyelectrolytes PSS and PAH were deposited on an ITO electrode, followed by the alternating adsorption of the cobalt containing Dawson based POM $[Co_4(H_2O)_2(P_2W_{15}O_{56})_2]^{16-}$ and PAH. The resulting multilayer assembly shows selective gas permeability and sensing selectivity. The deposition of a PSS/PAH/PSS surface layer was used to prevent anion (e.g., nitrite/nitrate) diffusion into the film, so as to prevent unwanted redox-reaction of the POM with these species. High sensitivity for NO detection (down to 1 nм) was reported.[147]

POMs can also be utilized in sensors by the embedding in thin films of conductive organic polymers. This allows substrates to access redox-active POMs that can be directly electrically addressed via the conductive polymer.[139] McCormac and colleagues prepared an electrochemical sensor for the detection of hydrogen peroxide based on a polypyrrole film with transition metal-substituted Dawson-POMs as dopant anions. These films were directly deposited on a glassy carbon electrode by electropolymerization from solutions containing pyrrole and the respective POM.[148]

Another approach to POM-based sensing materials is the use of lanthanide-functionalized POMs. These compounds can show excellent photoluminescent properties, such as long decay times and intense and sharp emission bands.[149] Wang and co-workers used the photoluminescent Preyssler anion $[EuP_5W_{30}O_{110}]^{12-}$ together with PAH for LbL film assembly.[150] Building on this principle, Ma, Yao, and colleagues immobilized Europium-containing polyoxometalates in agarose nanocomposite films to create photoluminescent sensors for gaseous acids and bases based on pH-dependent on/off switching of the europium-based red luminescence (Figure 9B).[145]

A related concept for the development of luminescent POM-polymer hybrids is the immobilization of POMs in hydrogels. This can lead to sensors with response mechanisms based on pH, light or humidity. Zhang, Wan, and co-workers used an ABA triblock copolymer and a $[Dy(W_5O_{18})_2]^{9-}$ POM for the reversible formation of a supramolecular hybrid hydrogel. The DMAEMA units of the hydrophilic $PDMAEMA_{35}$-b-PEO_{230}-b-$PDMAEMA_{35}$ triblock copolymer can be protonated. This has been used for the electrostatic co-assembly of protonated DMAEMA with anionic POMs. Notably, the emission behavior of the system changed significantly upon gelation, so that applications as smart, pH-sensitive materials can be envisaged.[75]

A similar approach has been established for carbon dioxide detection in solution using core-shell nanostructures based on PEO_{114}-b-$PDMAEMA_{16}$ diblock copolymers electrostatically functionalized with $Dy(W_5O_{18})_2^{9-}$ POM. Also, here the DMAEMA units of the block copolymer are protonated during changes in pH. In this case, the pH change is induced by the acidic reaction of CO_2 in water. Due to the missing third block in the block copolymer, however, the mechanism for the change of fluorescence is different. The block copolymer and
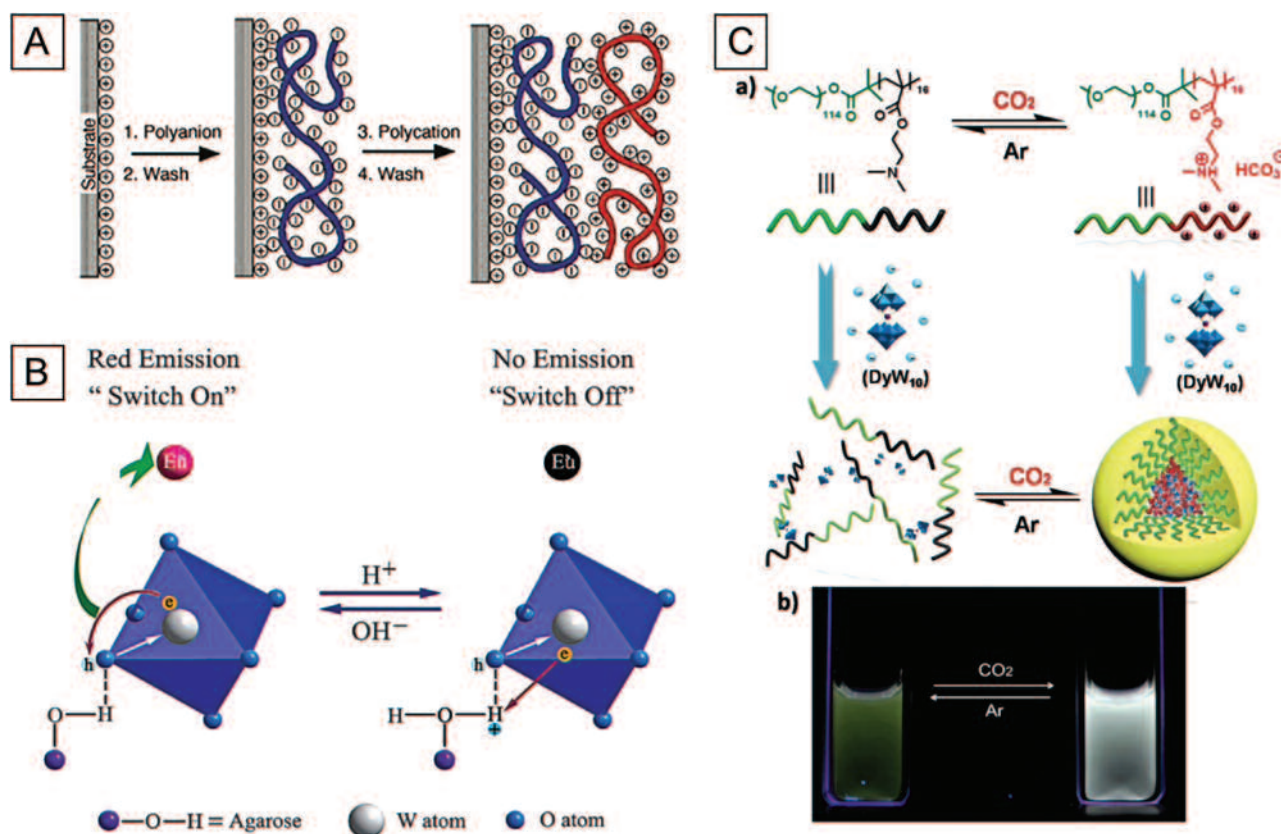
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Figure 9. A) Working principle of the layer-by-layer deposition method. Reproduced with permission.[144] Copyright 1997, American Association for the Advancement of Science. B) Luminescent switch, illustration of the nanocomposite film ("e", electrons; "h", holes). Reproduced with permission.[145] Copyright 2010, RSC Publishing. C) Structural change of the PEO-*b*-PDMAEMA block copolymer and schematic representation of the reversible formation of a hybrid micelle after the reaction with CO_2 in aqueous medium. Reproduced with permission.[146] Copyright 2015, RSC Publishing.

the POM do not form hydrogels but complexes. When the pH is decreased by dissolved CO_2, the charged DMAEMA units assemble around the negatively charged POMs. This leads again to a change of the fluorescence color from weakly green to white. When the solution is then purged with inert gases, the CO_2 is removed from the solution, which leads to the disassembly of the complexes and the sensor can be used again (Figure 9C).[146]

3.2. . Biomedical Applications

POMs have been employed in a range of biomedical settings including antiviral, antimicrobial and anticancer applications.[31,151] However, for in vivo applications it is crucial to mediate their toxicity and increase the selectivity as well as their mode of action. Linking POMs to biologically inspired soft matter matrices is a method of choice to achieve these goals.

One approach has been reported by Wang and co-workers. The group combined POMs with lipids to generate liposome-encapsulated $[SiW_{11}TiO_{40}]^{6-}$. In these systems, the POMs were encapsulated in spherical lipid-bilayer vesicles (d = 15–60 snm), resulting in a significant drop in toxicity during in vivo anti-cancer studies. Further in vitro studies showed improved cell-membrane penetration and enhanced antitumor activity and

stability in comparison to the pure POM.[152] Similar effects have also been reported when POMs were covalently attached to lipids. Liu and colleagues functionalized a Preyssler-POM with a long-chain organoalkoxysilane lipid. The amphiphilic POM hybrids spontaneously assembled into vesicles and exhibit significantly increased antitumor activity in comparison to the pure POMs. According to the authors, this difference is due to the improved cell-membrane binding and cell uptake of the functionalized POM (**Figure 10**A).[153]

A similar approach is the encapsulation of POM in chitosan, a polysaccharide copolymer of β-(1,4)-2-acetamido-D-glucose and β-(1,4)-2-amino-D-glucose. Chitosan is known to enhance in vivo drug delivery whilst reducing undesired side-effects.[37] These benefits have been explored in the encapsulation of POMs in chitosan matrixes, targeting bio-medical applications.[38] In one example, Nair and co-workers used a POM/chitosan hybrid as potential anti-cancer treatments. The group designed stable, monodisperse hybrid nanoparticles with a diameter of $\approx$200 nm by encapsulating the europium POM $[Cs \subset Eu_6As_6W_{63}O_{218}(H_2O)_{14}(OH)_4]^{25-}$ by a simple ionotropic gelation method. The hybrid was tested against a range of cancer cell-lines in vitro and showed a slow and sustained POM release, so that significantly lower doses of the hybrid were required (based in IC_{50} values) compared with the pure POM reference.[155]

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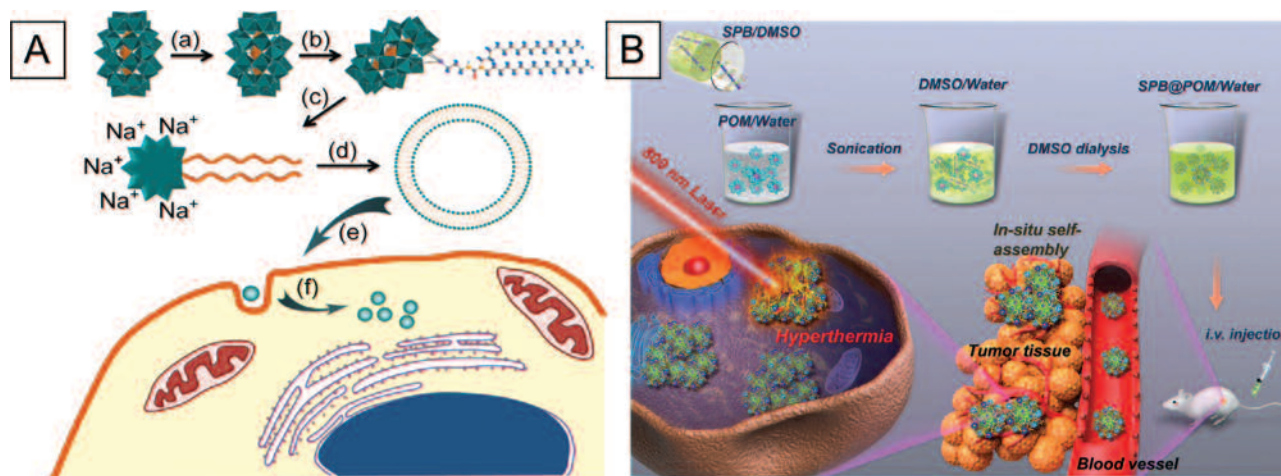FUNCTIONAL
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Figure 10. A: Illustration of the synthesis process of POM-based organic–inorganic hybrids, $[(C_{16}H_{33})_2NCONH(CH_2)_3SiNaP_5W_{29}O_{110}]^{14-}$ (Na-lipid-P_5W_{29}), and their vesicle formation in water/MeCN solution. The lacunary Preyssler-type ion, P_5W_{29}, is presented using a polyhedral model, and the organic part is presented using a ball and stick model (P, orange; W-O polyhedral, green; C, gray; N, yellow; H, blue; Si, purple). a) Synthesis of a lacunary Preyssler-type POM, b) covalent reaction between lacunary POM and organoalkoxysilane lipid, c) cation exchange, d) formation of micelles of Na-lipid-P_5W_{29}, e) entering the tumor cells, f) intracellular localization. Reproduced with permission[153] Copyright 2015, Wiley-VCH GmbH. B: Schematic of pH/GSH-responsive SPB@POM for tumor-specific self-assembly and phototheranostic enhancement. Reproduced with permission[154] Copyright 2018, Wiley-VCH GmbH.

A different approach to anti-tumor activity of POM-polymer hybrids has been reported by Wang, Chen and co-workers. The group used semiconducting polymer brushes and POM clusters that aggregated specifically to larger in the low pH, reducing microenvironment of a tumor. This led to enhanced retention of the particles in the tumor. Further, chemical reduction of the Mo-based POM resulted in enhanced NIR light absorption, enabling efficient use in hyperthermia-inducing photothermal therapy (Figure 10B).[154]

3.3. Molecular Electronics

The anchoring of electronically or magnetically active POMs[28,156,157] in functional polymers holds great promise for the design of unique composites, e.g., for molecular electronics, quantum computing, or spintronics. To-date, most studies in the field have focused on the deposition of POMs on metal or semiconductor surfaces, while POM-polymer composites have received little attention. This could in part be due to the challenging fabrication and processing of POM-polymer composites, particularly when sub-nanometer accuracy in the positioning of the POMs is required. For molecular electronics, this precision is needed, as electronic and magnetic interactions between neighboring POMs have major impact on their performance, e.g., in the context of the loss of information due to quantum decoherence effects.[28] In a pioneering example, Mallah, Wernsdorfer, Mialane, and co-workers embedded the single molecule magnet (SMM) POM $[Fe_4(H_2O)_2[FeW_9O_{34}]_2]^{10-}$ (= [Fe_6W_{18}]) into a gelatin biopolymer.[158] Magnetic analyses showed similar behavior between the pure POM compound, and the POM-gelatin-composite, highlighting that the sensitive magnetic properties of the POM were not affected by the (diamagnetic) gelatin matrix.

Redox-active POMs can also be used as reactive sites in molecular junctions, i.e., systems where molecules act as charge-transfer sites between two metal electrodes. Velessiotis, Glezos,

and co-workers[159,160] demonstrated that POM-polymer composites can be used as active materials in molecular junctions. The group fabricated a PMMA-[$H_3PW_{12}O_{40}$] composite and provided first insights into the electronic transport properties of the system. In particular, the authors report that POM-concentration as well as electrode geometry are two key factors for electron transport. Two distinct transport mechanisms (tunneling vs hopping) were reported depending on the electrode distances. The design of a POM-polymer composite for non-volatile, rewritable multilevel memories was reported by Zhang and colleagues.[161] The authors used Anderson-POMs covalently linked to the backbone of a PMMA polymer as active compound. The material showed three distinct redox states with long retention times. Resetting the material to enable re-writing was possible by careful choice of the redox potentials employed. Other POM-based applications in molecular electronics and related fields have recently been reviewed by Chen, Dong, and co-workers,[162] and Zhou, A. L. Roy, S.-T. Han, and co-workers.[163]

In summary, the use of POMs with controllable spin and/or redox states combined with the flexibility, processability and scalability of soft-matter polymers holds great promises to realize nanoscale devices for molecular electronics. Key for the further development is to understand how to control the POM distribution within such hybrid materials, ultimately tailoring the composite structure from nano- to microscale, as well as engineering robust and functional polymers that contribute to the device performance.

3.4. Solar and Electrochemical Energy Conversion, Catalysis

POM-polymer composites are key materials for energy conversion and storage, and have been used in batteries, supercapacitors, fuel cells, and electrocatalysis. The field has been reviewed recently, and is therefore not discussed in detail here.[139,164,165]

4. Outlook and Summary

POM-polymer composites are versatile materials merging the areas of organic and inorganic chemistry and overall benefit from improvements in both synthetic access to the respective building blocks as well as advances in analytical techniques. Over the last decades, they have opened new avenues to harness synergisms from these fields and develop applications in biomedicine, energy conversion/storage, molecular electronics, and other fields. Their characterization from the molecular to the macroscopic level is still challenging, and advanced methods are currently being developed to gain further understanding of the complex behavior of these systems, especially regarding a precise description of the surrounding of a single POM site within a given soft matter matrix, both from an experimental and a theoretical point of view. With that, it will be possible to address changes in reactivity or selectivity (e.g., in case of a catalytic process) upon matrix embedding of a given POM, or even to understand effects on long-term stability or cyclability if the soft matter environment provides local buffering, additional functional groups, or even competing ligands—the latter allowing for new and straightforward (covalent) anchoring strategies of suitable building blocks. In the future, the authors expect that combined experimental and theoretical studies will shed light on the correlation between structure, properties, and function, enabling the knowledge-based design of next-generation POM-polymer composites.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

organic–inorganic hybrids, polymers, polyoxometalates, self-assemblies

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