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Kirill Yu. Monakhov, Stanislav, K. Petrovskii, De-Liang Long, May Nyman, Axel Kahnt, et al.. Polyoxometalates for Health, Electronics, Energy, and the Environment: Challenges, Opportunities, and Future Horizons. 2026. <hal-05572083>

HAL Id: hal-05572083

<https://hal.science/hal-05572083v1>

Preprint submitted on 30 Mar 2026

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Polyoxometalates for Health, Electronics, Energy, and the Environment: Challenges, Opportunities, and Future Horizons

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ABSTRACT:

Polyoxometalates (POMs) – molecular metal–oxide clusters composed of charged metal–oxygen polyhedra formed via solution self-assembly processes – exhibit diverse and highly useful structure–property–reactivity relationships in the various states of matter. Found in both mineral phases and biological systems, POM motifs have played supporting roles in research areas recognized by Nobel Prizes, including structural biology and porous framework chemistry. Although their translation into real-world technologies still requires higher levels of technological readiness, POMs are currently being explored across a wide range of interdisciplinary fields. This work builds on the collective efforts of the global POM research community, which continues to generate both fundamental insights and innovative applications. Here, we present a comprehensive survey of POM research and outline future horizons in synthesis and characterization, with particular emphasis on recent breakthroughs and emerging directions. Four thematic domains – Health, Electronics, Energy, and the Environment – are used as an organizing framework to identify key shared principles and cross-disciplinary opportunities in POM research. The goal of this work is to consolidate international efforts, foster cross-disciplinary collaboration, and accelerate the development of application-ready POM materials.

1. INTRODUCTION

1.1 POMs – Scientific Relevance

Addressing today's urgent global challenges in health, energy, climate, communication, and transport requires transformative breakthroughs in materials science. This transformation must prioritize sustainability, cost-efficiency, and molecular-level tunability. POMs are ideally positioned to meet this need. With their unique combination of structural flexibility, redox activity, and tunable solution behavior,^[1-2] POMs provide a powerful and modular platform for next-generation molecular technologies. They hold great potential to serve as active functional units or efficiency enhancers in diverse processes, including technical catalysis, energy conversion, and hybrid electronic and sensing devices.

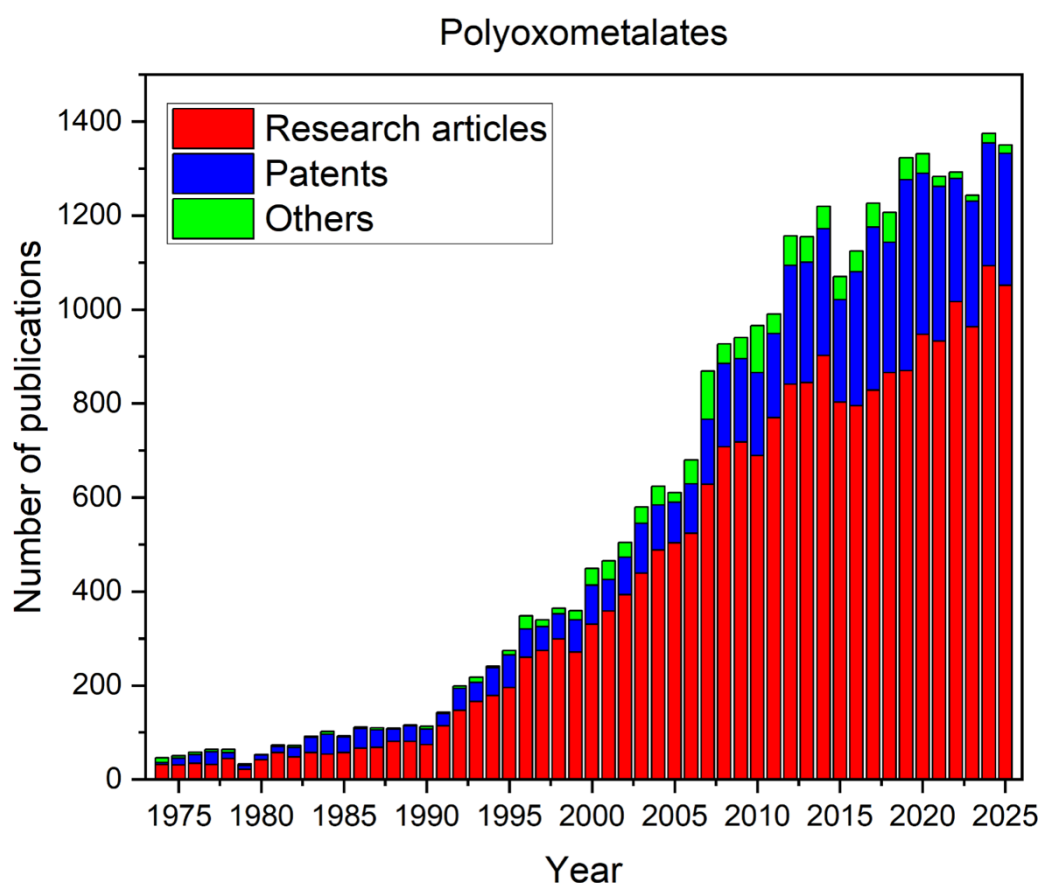


Figure 1. Histogram showing the number of research articles (red), patents (blue), and other types of publications (green) *per year* for the topic 'Polyoxometalates'. The search was performed using SciFinder[®]. The total number of hits for the research topic, as entered, was 29770. As of December 20th, 2025.

Over the past five decades, interest in POMs has grown exponentially, as seen in the rising number of scientific publications and patents (Figure 1). This momentum reflects their unique chemical

diversity and multifunctionality across the periodic table. POMs span a wide array of d-block and f-block elements, including W, Mo, V, Nb, Ta, Cu, Au, Pd, Zr, Hf, and U.^[3-4] Whereas most POMs synthesized in the laboratory do not typically replicate the motifs found in nature – from mineral phases^[5] to metalloproteins^[6-7] – some do, thereby highlighting their geological and biological relevance (Figure 2).^[8]

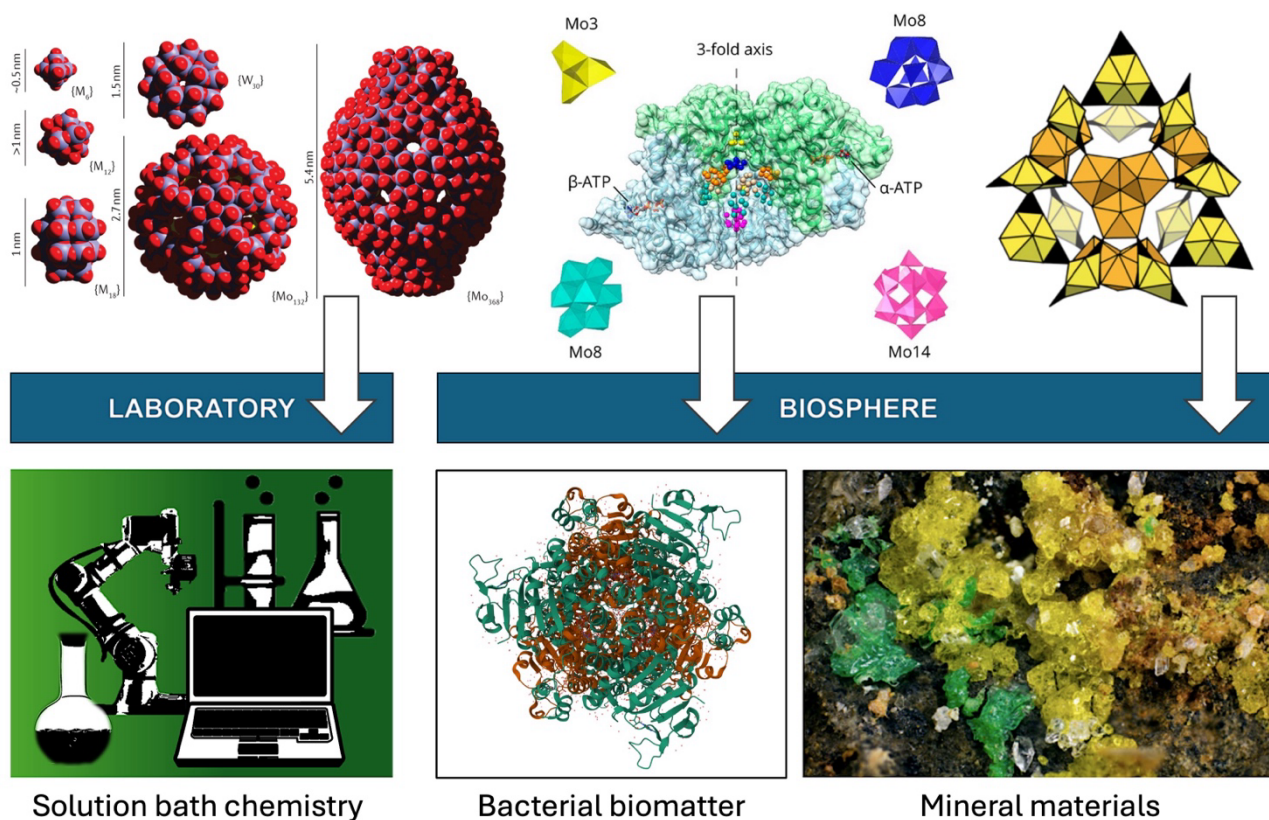


Figure 2. Comparison of structural and compositional characteristics among systems governed by solution bath chemistry, bacterial biomatter, and mineral materials. **Top left:** Synthetically accessible different dimensions of POMs. Reproduced from ref. [9] (copyright Spinger Nature). **Top middle / bottom middle:** POMs with molybdenum centers in the $(\alpha\beta)_3$ hexameric structure of the cage-like molybdenum storage protein (MoSto) [reproduced from ref. [10] copyright PNAS], and the MoSto containing the core POM clusters^[11] from the RCSB Protein Data Bank (RCSB PDB). **Top right / bottom right:** $[(UO_2)_{24}(CO_3)_{30}O_4(OH)_{12}(H_2O)_8]^{32-}$ in the mineral ewingite and the photograph of its crystals from a mine in the Czech Republic. Reproduced from ref. [12] (copyright The Geological Society of America). Color code: uranyl = yellow/orange pentagonal and hexagonal bipyramids, carbonate = black triangles.

In addition to the numerous representatives of polyoxoanions, the POM structural family also expands to their cationic analogues such as the Keggin- Al_{13} , $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ (aq),^[13] related chromium-based cations, Al/Cr mixed structures, and newly discovered aluminum frameworks.^[14-15] These have recently been complemented by Zr/Hf oxo-clusters^[16] and uranyl peroxide polyanions,^[17]

which are a rare example of POMs consisting exclusively of f-elements, thus expanding the scope of applications for actinide chemistry and nuclear applications.

POMs are commonly obtained as salts or hybrid compounds, in which the charged POM core is balanced by small or bulky counterions.^[18] These counterions do more than balance charge: they influence solubility, mediate redox processes,^[19] contribute to intermolecular charge transport, modulate the electronic properties of devices,^[20] affect hydrophobic interactions^[21] in the host–guest chemistry of POMs, and assist the formation of POM-based coordination frameworks.^[22] The incorporation of POMs into metal–organic frameworks (MOFs) has further expanded their structural diversity, giving rise to POM-based MOFs (POMOFs)^[23] that integrate porous architectures with the catalytic and electronic properties of molecular metal–oxide clusters. In particular, the redox activity of POMs is one of their strongest attributes.

In aqueous and organic media, POMs exhibit high speciation flexibility, assembling into capsules, micelles, and supramolecular architectures in response to pH, solvent, and hydrophilic (POM)–hydrophobic (ligand, cations) interactions. Their self-assembling behavior, including chaotropic properties,^[24] further distinguishes them from classical cluster compounds.

Their electrochemical^[25-26] properties can be precisely tuned through atomic substitution, organic ligation, post-functionalization or counterion exchange. These features allow POMs to function as responsive molecular modules across a wide range of fields, including biochemistry, molecular electronics, optics, catalysis, separation, energy storage, and green chemistry. Their polyoxoanion nature facilitates electrostatic interactions with proteins,^[27] while their countercations often play a non-innocent role in acid catalysis and supramolecular assembly.^[28]

POMs have already demonstrated a range of biological activities,^[29] including antimicrobial, antitumor, and antiviral properties, as well as the ability to function as capacitors and memristors^[30] at room temperature for alternative data storage, and their role as electrocatalysts in energy conversion.^[30] Their ability to selectively bind to the radioactive element americium^[31] has shaped global discussions on new strategies to process nuclear waste.^[32]

Overall, POMs can be viewed as an inorganic link between biological clusters and functional materials, representing a molecular technology with enormous untapped potential. Their fundamental properties – such redox activity, structural tunability, self-assembly behavior, and electronic functionality – are shared across diverse application areas. Building on the recent perspective and review articles,^[33-36] this work examines POM research and development across four interconnected domains: Health, Electronics, Energy, and the Environment. By identifying cross-

disciplinary challenges and opportunities, we aim to bridge global efforts, accelerate Technology Readiness Levels (TRLs), and establish POM science as a cornerstone for sustainable materials innovation.

1.2 The Global POM Community

Advancing POM science into real-world technologies requires not only materials innovations but also strategic coordination across disciplines and geographies. Over the past two decades, the international POM community has evolved into a decentralized yet highly active network. While each region contributes unique strengths, from synthesis and theory to application-driven research, a common theme is emerging: the push toward functionalization, integration, and translation of POMs into deployable technologies. This section offers a global snapshot of this dynamic landscape.

In Europe, long-standing coordination through the COST Action CM1203 “Polyoxometalate Chemistry for Molecular Nanoscience” (PoCheMoN) and the ongoing CNRS-led IRN network “Smart Molecular Oxides” has successfully fostered academic collaboration; however, closer engagement with industry remains both necessary and highly sought after. European researchers have advanced fundamental POM cluster chemistry, while aligning with application-driven initiatives in data storage, catalysis, and sustainable energy. Notably, Germany’s inclusion of POMs in the DFG priority program SPP 2262 “Memristive Devices Toward Smart Technical Systems” (MemrisTec) underscores European ambitions to explore molecular systems for future computing technologies.

China now hosts the largest and most rapidly growing POM community, with an emphasis on application-oriented research. Annual national meetings and the launch of the dedicated journal “Polyoxometalates” have created a strong internal ecosystem, while also offering an increasingly open platform for international engagement. Research themes range from catalysis and energy storage to biomedical applications – areas well aligned with China’s broader innovation agenda.

Japan maintains a focused, high-output POM community marked by strong academic–industrial ties. Biannual conferences and international joint efforts, such as the International Network on Polyoxometalate Science for Advanced Functional Energy Materials, exemplify Japan’s commitment to targeted collaboration. Japanese groups are particularly active in catalysis, photochemistry, materials integration, and electronic applications of POMs.

In the United States, the number of research groups specializing in POMs has decreased slightly, but significant contributions continue to be made, particularly in the areas of actinide-POM chemistry,^{[37-}

^{39]} POMs based on the group VII elements technetium (Tc) and rhenium (Re),^[40] and polyoxovanadate–alkoxide clusters.^[41]

The POM communities in Australia and New Zealand are smaller but increasingly integrated into global initiatives. Works on POM-based theranostics, electrocatalysts, and hybrid materials reflects a shift toward translational goals,^[42] supported by national programs such as the ARC Industrial Transformation Centre.

Altogether, these communities form a globally distributed but intellectually cohesive engine driving POM science forward. Despite regional differences in research focus, the translation of POM chemistry from fundamental molecular science toward functional materials and deployable technologies is a shared objective. In the following sections, recent advances in POM-based systems across the domains of Health, Electronics, Energy, and the Environment are discussed. We describe key molecular design strategies, materials integration approaches, and opportunities for future technological implementation.

2. FROM EMPIRICAL DISCOVERY TO KINETIC CONTROL IN SYNTHESIS

Since the first observation of Molybdenum Blue (MB) by Scheele in 1778, the synthesis of ammonium phosphomolybdate $(\text{NH}_4)_3[\text{PMo}_{12}\text{O}_{40}]\cdot\text{H}_2\text{O}$ by Berzelius in 1826, and the determination of the first crystal structure of 12-phosphotungstic acid $\text{H}_3[\text{PW}_{12}\text{O}_{40}]\cdot 5\text{H}_2\text{O}$ by Keggin in 1933,^[43] the synthetic landscape of POMs has expanded into a vast, modular, and chemically diverse domain. Their complex behavior in solution and functional complexity today require a shift toward a mechanistic understanding that connects molecular design with technological functions. The realization of POMs for specific applications will depend on the precision of their synthesis, environmentally friendly processing methods, and scalable production.

2.1 All-Inorganic POM Archetypes

Archetypal POM structures, including all-inorganic Lindqvist-type isopolyanions $[\text{M}_6\text{O}_{19}]^{q-}$, as well as Anderson-Evans $[\text{M}'\text{M}_6\text{O}_{24}]^{q-}$, Keggin $[\text{XM}_{12}\text{O}_{40}]^{q-}$, and Wells-Dawson $[\text{X}_2\text{M}_{18}\text{O}_{62}]^{q-}$ heteropolyanions (Figure 3), are typically formed through the solvent-based self-assembly of metal–oxygen polyhedra, which is governed by parameters such as pH, temperature, ionic strength, and precursor concentration.^[44-45]

Their lacunary derivatives^[4] are formed via stepwise or one-pot syntheses through the selective removal of metal–oxygen polyhedra, generating reactive, undercoordinated sites (Figure 4) that serve

as versatile platforms for the incorporation of additional metal centers. Such lacunary POMs readily coordinate late transition and noble metals^[46] as well as lanthanides,^[47] giving rise to heterometallic assemblies with tailored electronic, magnetic, and catalytic properties. These are particularly valuable for applications, where controlled local site substitution and environments are key to functionality.

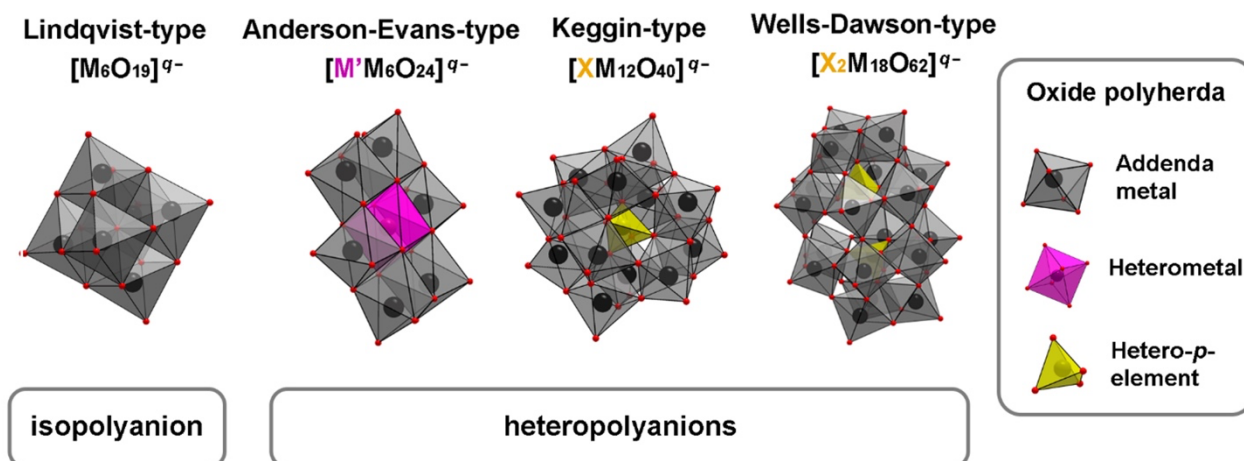


Figure 3. The most common structural archetypes of all-inorganic POMs.

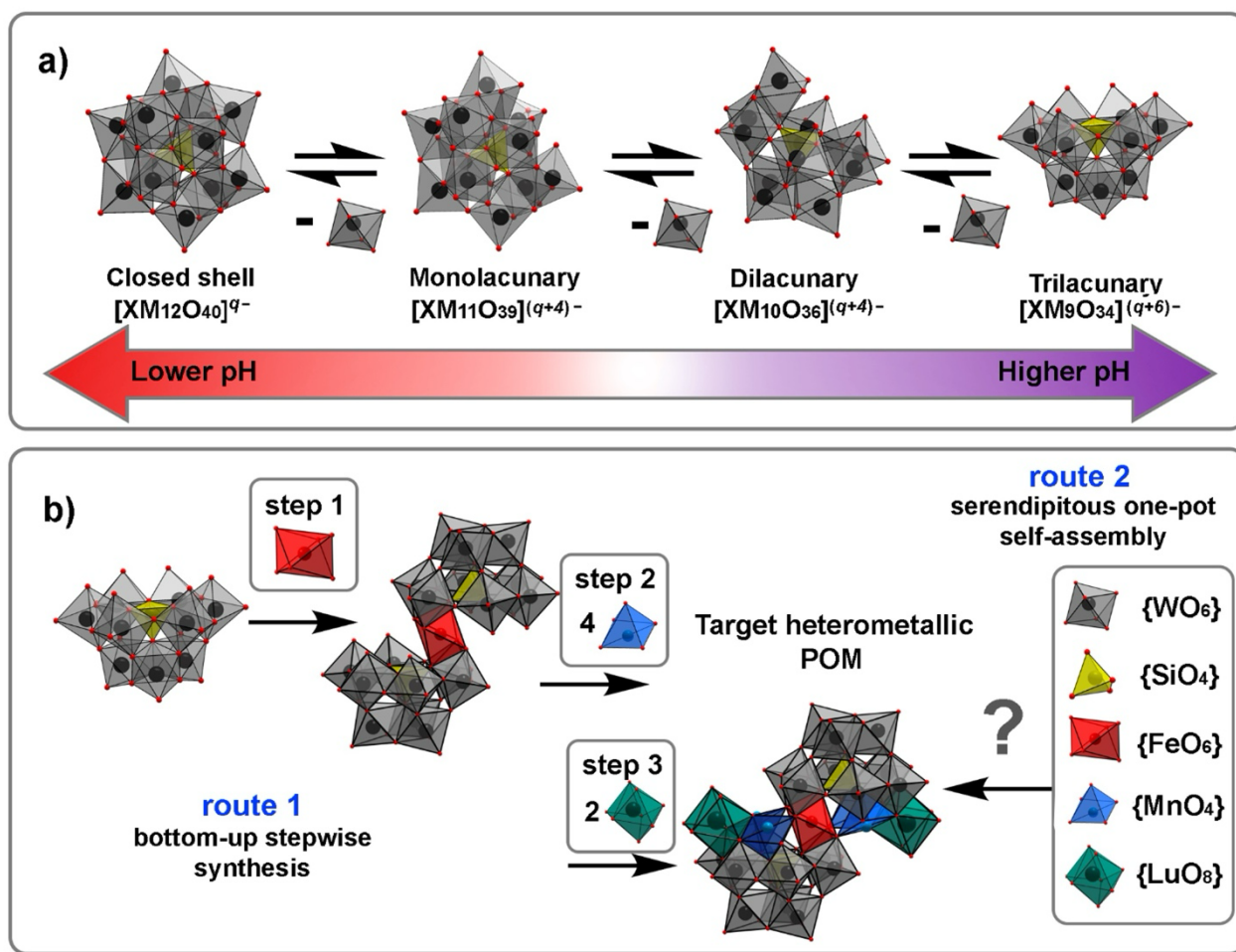


Figure 4. a) Generation of lacunary Keggin-type POM species by removal of addenda atom polyhedra (example: Keggin-type POM). b) Scheme of the stepwise (route 1) and one-pot assembly of complex heterometallic POM structures using the example of the compound $(Bu_4N)_7[(A-\alpha-SiW_9O_{34})_2FeMn_4O_2(Lu(acac)_2)_2]$ (*acac* = acetylacetonate). Only anionic POM structures are shown for clarity.^[48]

Today, synthetic kinetic control over the reactivity of all-inorganic POMs remains, however, challenging. This limitation arises from the intrinsic thermodynamic complexity of POM formation and the coexistence of multicomponent equilibria in solution,^[49-50] which becomes even more complex in the presence of many other reaction additives.

Recent progress in computational modeling of POM speciation^[50-53] is beginning to address these challenges by mapping nucleation pathways and the energetic landscape of POM formation, thus enabling the design of reaction conditions with predictive accuracy. However, current computational approaches are limited to thermodynamically equilibrated systems, and cannot yet account for the dynamic, out-of-equilibrium assembly pathways that often govern kinetically controlled POM structures.

2.2 POM–Organic Hybrids and Post-Functionalization

When POMs are ligated with organic groups and synthesized in organic or mixed aqueous-organic media, additional parameters such as solvent polarity, dielectric constant, and the effects of counterions or surfactants strongly influence their condensation dynamics, solubility, and resulting nuclearity. The challenge of synthetic kinetic control is further amplified, when these inorganic-organic hybrids are further post-functionalized (Figure 5).^[54-55]

Key post-functionalization strategies include: *i*) nucleophilic substitutions (e.g., halide exchange on activated alkyl linkers),^[56] *ii*) transition metal-catalyzed cross-couplings (e.g., Suzuki, Sonogashira),^[57] *iii*) click reactions such as Cu(I)-catalyzed azide–alkyne cycloaddition (CuAAC) and strain-promoted azide–alkyne cycloaddition (SPAAC),^[55, 58] *iv*) dehydrative condensation,^[59] *v*) coordination-driven self-assembly,^[60] enabling the construction of higher-order architectures.

One of the most critical next steps in the development of POMs with organic ligands is the systematic expansion of the toolbox for selective *asymmetric* ligation and post-functionalization, which remains rare but is essential. Such asymmetry is crucial for directional material assembly, molecular recognition and host–guest chemistry, and bioorthogonal labeling and targeting in biological systems. Currently, this type of functionalization is largely restricted to Anderson–Evans^[61] and Wells–Dawson POMs,^[62] with only very recent examples reported for Lindqvist-type structures.^[63] Addressing this gap will significantly expand the design space for functionally diverse POM-based materials, advancing chemical affinity and selectivity for specific substrates (e.g., solid-state supports,^[64-65] or biomolecular targets^[66-67]).

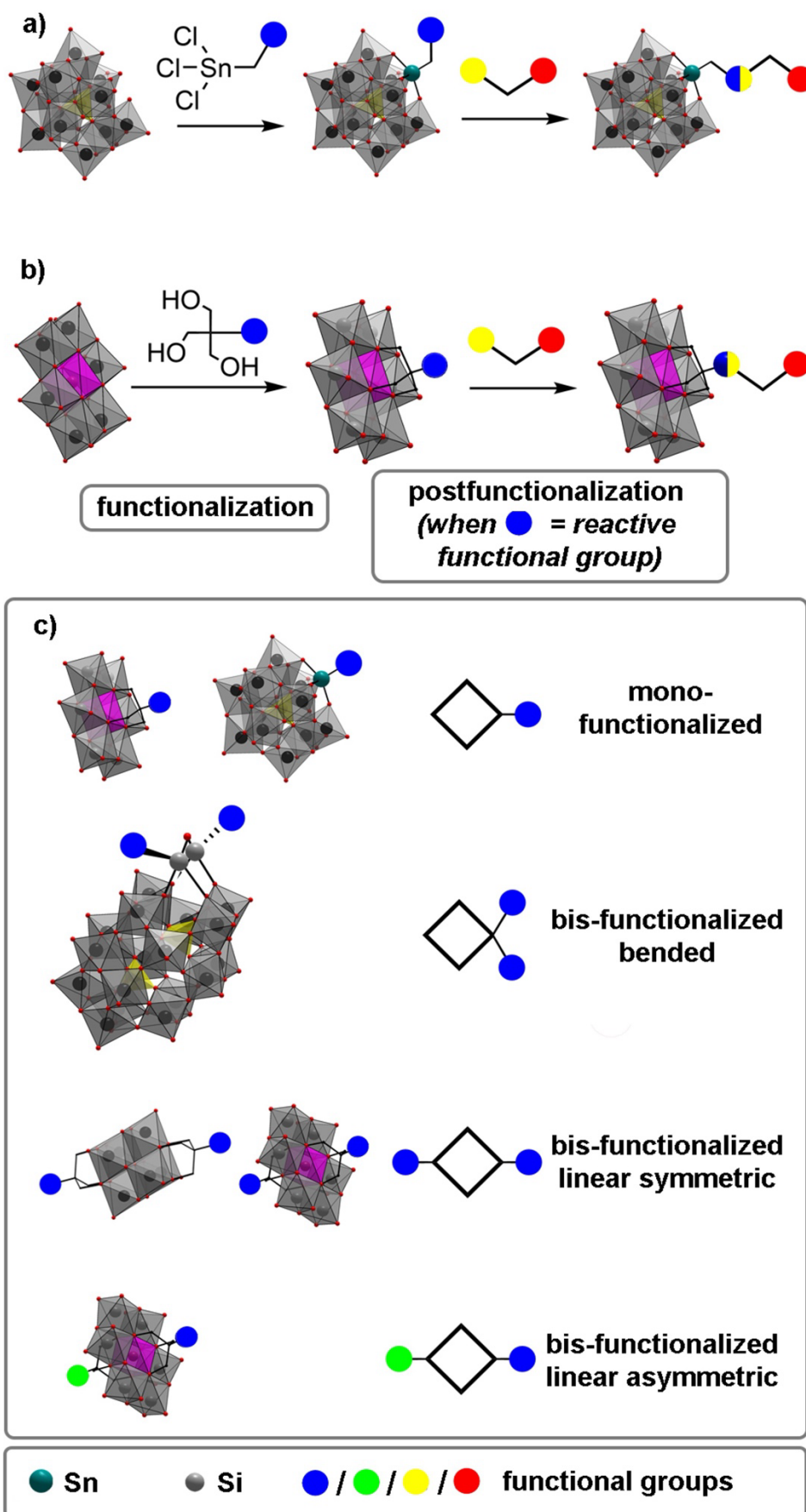


Figure 5. Functionalization of all-inorganic POMs through formal substitution of addenda metals (a) and through reaction of trisalkoxo ligands at the bridging oxygen atoms (b), followed by post-functionalization of the inorganic-organic hybrids. General topologies of covalent hybrids (c).

The integration of POM units into peptide synthesis, exemplified by the automated incorporation of inorganic amino acid based on $[\text{Mn}^{\text{III}}\text{Mo}^{\text{VI}}_6\text{O}_{24}]$ Mn-Anderson POM unit into synthetic peptide chains showcases the feasibility of embedding POMs in sequence-defined bioconjugates with high precision.^[68-69] Although, these systems generate large volumes of reaction data, they form the foundation for machine learning (ML) models that can optimize future syntheses via AI-guided algorithms.

2.3 Supramolecular and Templated POM Architectures

The supramolecular organization of POMs illustrates how preorganized scaffolds and noncovalent forces can drive the selective formation of otherwise elusive topologies:

- i) Transition metal-coordination driven self-assemblies of POM building blocks^[70] enable the design of POM-scaffolding MOFs (POMOFs),^[71] cluster organic frameworks,^[72] metal-organic cages,^[73] and other dynamic architectures.^[60, 74]
- ii) Ionic surfactants^[75-76] and biomolecules^[77-78] act as structure-directing agents through electrostatic and hydrophobic effects, providing POM assembly in both solution and solid phases.
- iii) Chaotropic-effect-driven interactions assemble POMs into large-scale supramolecular frameworks,^[79-80] with potential implications for understanding POM adsorption on biological interfaces.
- iv) Coordination cages, such as the water-soluble $\text{Pt}_6\text{L}_4(\text{NO}_3)_{12}$ octahedral coordination cage, guide the cavity-directed synthesis of Lindqvist $[\text{Mo}_6\text{O}_{19}]^{2-}$ POMs in an aqueous medium, significantly improving the control of POM speciation.^[81]

2.4 Advanced Methods for the Controlled Synthesis of POMs

As the structural and functional complexity of POMs and POM-based materials grows rapidly, integrating rational experimental design with high-throughput, automated synthesis^[82] or advanced methods with kinetic–thermodynamic control becomes increasingly critical (Figure 6). Such approaches can enable efficient exploration of the immense multidimensional chemical space of POMs, especially that of giant clusters,^[83-85] and uncover hidden correlations between composition, structure, and function, and guiding the accelerated discovery of application-ready POM systems. Examples of these approaches are described below:

2.4.1 – Solvent-free mechanochemical synthesis exploits mechanically induced redox and condensation reactions under mild conditions, enabling the rapid, high-yield formation of reduced, electron-rich, and/or intermediate POM species with in-situ control.^[86] Beyond their synthetic utility, mechanochemical methods inherently adhere to green chemistry principles, minimizing solvent use and waste.^[87-88]

2.4.2 – Continuous-flow, microfluidic, modular reactor^[89] platforms and automated synthesis^[82, 90] provide access to precisely controlled (in-line/on-line) reaction environments, enabling rapid screening, fine-tuning of reaction parameters, and scalable synthesis of POMs.

2.4.3 – Microwave-assisted and solvothermal techniques enhance reaction kinetics and product selectivity in the synthesis of POMs^[91-93], POM-based nanomaterials,^[94] as well as in the hierarchical self-assembly^[95] of materials, where POMs serve as templating agents.

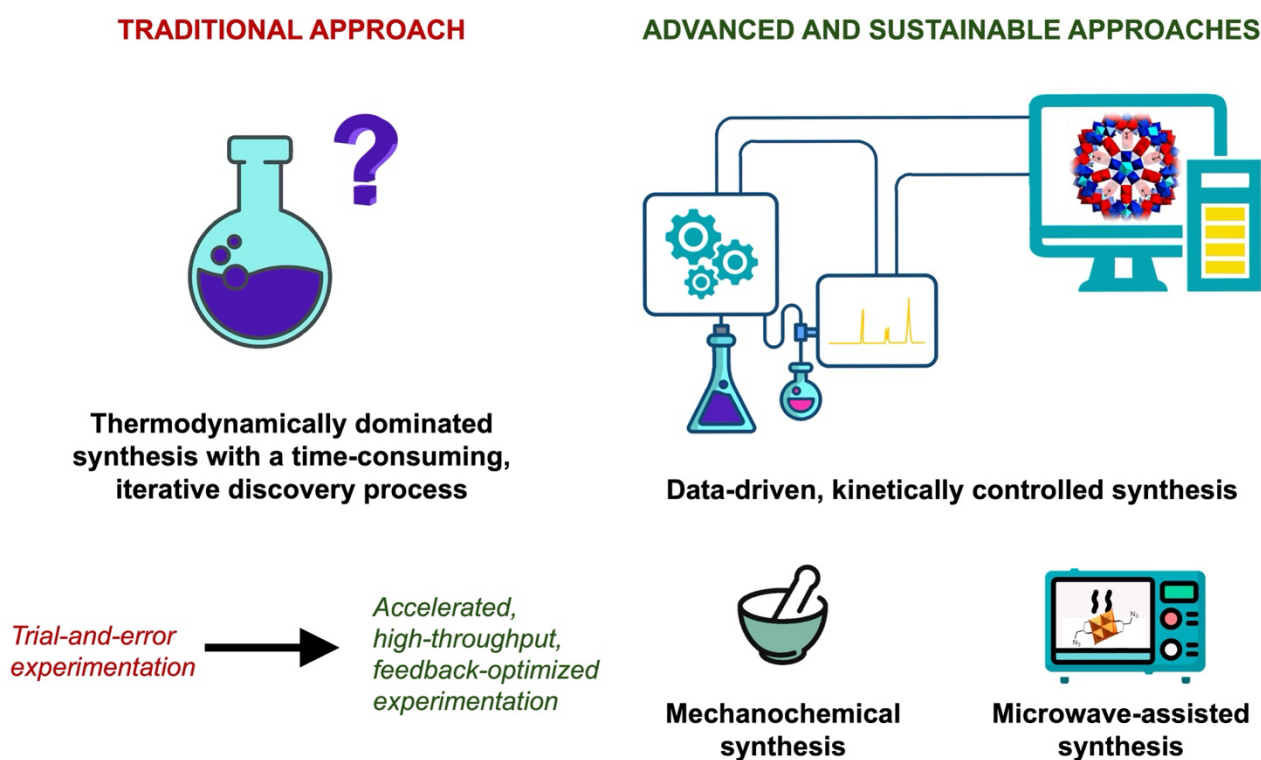


Figure 6. Evolution of POM synthesis: from empirical discovery to data-driven, reproducible, and scalable design.

Future Horizons: Synthesis of POMs

- 1) Achieve precise kinetic control over POM nucleation and growth beyond the constraints of thermodynamic equilibria.
- 2) Expand the library of asymmetrically functionalized POMs.
- 3) Achieve programmable, sequence-defined assembly of POM clusters, analogous to peptide synthesis or metal–organic framework (MOF) design.

3. METHODS OF STRUCTURAL AND CHEMICAL CHARACTERIZATION

In addition to classical analytical methods such as NMR, UV/Vis, IR spectroscopy, and single-crystal X-ray diffraction, a variety of emerging techniques have recently been employed, individually or in tandem, to broaden the understanding of POM properties across different states of matter (liquid, gaseous, and solid; Figure 7).

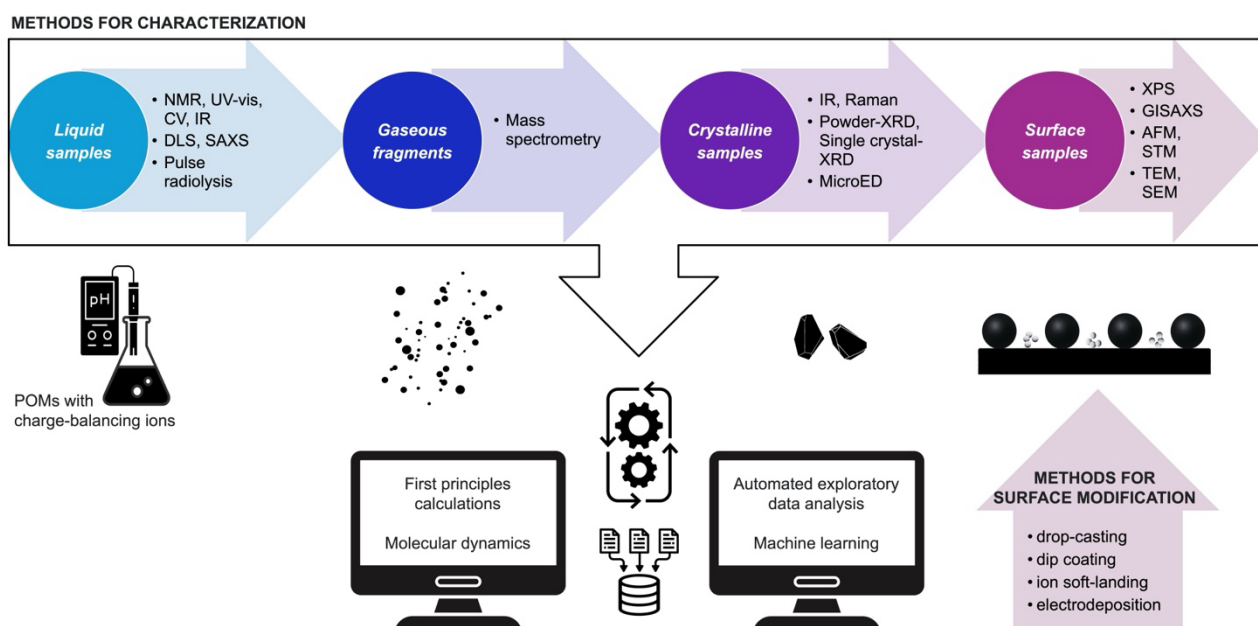


Figure 7. Application-oriented basic research platform for hybrid or multimodal studies and interoperable data infrastructures for POMs, emphasizing examples of methods for characterizing POMs and methods for modifying surfaces by POMs.

3.1 Crystallography

3.1.1 Single crystal X-ray diffraction (SCXRD)

Crystallography techniques, in particular single crystal X-ray diffraction (SCXRD), remain one of the most essential and powerful tools for elucidating the structures of chemical compounds across many sub-disciplines of chemistry, including POM research. Recent innovations, such as laboratory micro-focus X-ray sources or high-flux synchrotron facilities, high-resolution detectors, and advanced computational tools have enabled the structural characterization of super-large POM architectures, including those incorporating peptide ligands.^[96-97] SCXRD has become indispensable for deciphering the architectures of increasingly large, complex, and disordered POMs, and plays a central role in rationalizing their assembly processes.

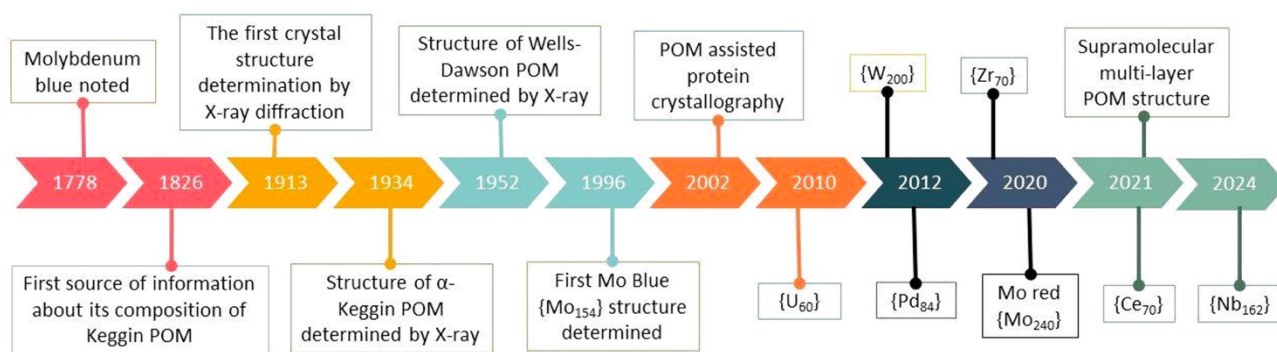


Figure 8. Milestones in discoveries and structural determination of POMs.

Figure 8 presents a timeline of major discoveries in POM crystallography. Although Scheele first mentioned the mysterious “molybdenum blue” in 1778, POMs were not structurally described until much later. Berzelius offered early compositional insights in 1826, while Pauling proposed the α -Keggin structure in 1928. Keggin employed X-ray diffraction in 1933 to determine the α -Keggin anion structure.^[43] In 1953, Dawson reported the Wells-Dawson structure.^[98] A major breakthrough came in 1996, when Müller resolved the crystal structure of the giant molybdenum blue cluster $\{Mo_{154}\}$.^[99] Since then, this family has expanded to include various other structures: ball-shaped $\{Mo_{102}\}$ ^[100] and $\{Mo_{132}\}$,^[101] wheel-shaped $\{Mo_{176}\}$,^[102-103] capped wheel $\{Mo_{248}\}$,^[104] lemon-shaped $\{Mo_{368}\}$,^[105] and further complex species like $\{Mo_{186}\}$,^[106-107] $\{Mo_{180}\}$,^[108] $\{Mo_{240}\}$,^[109] and the lantern-shaped L- $\{Mo_{132}\}$ ^[83] and capped wheel C- $\{Mo_{132}\}$.^[110] Recent studies continue to expand the structural and functional diversity of POMs, including mixed-valence polyoxovanadates such as $\{V_{15}\}$ with biologically relevant enzyme inhibition activity and new hybrid Dawson- and Lindqvist-type POM derivatives investigated for their structural and biochemical properties.^[111-112]

Interestingly, the crystallographic resolution of polyoxotungstates preceded that of polyoxomolybdates, likely due to tungsten’s stronger X-ray scattering and the higher stability of tungstates. Early examples include the Keggin and Wells-Dawson types, followed by discoveries of $\{P_5W_{30}\}$,^[113] $\{P_8W_{48}\}$,^[114] $\{W_{148}\}$,^[115] $\{W_{200}\}$,^[116] and the largest known isopolytungstates.^[117] Mixed Mo/W POMs such as $\{Mo_{126}W_{30}\}$ have also been characterized.^[118]

Polyoxoniobates, another important POM subclass, possess unique structural and chemical features that differ significantly from Mo and W analogues.^[119] Although challenging to stabilize and crystallize, Nb-based POMs have seen remarkable advances: from $\{Nb_6\}$ (1953)^[120] to the large $\{Nb_{288}\}$ cluster,^[121] with intermediate milestones including $\{XNb_{12}\}$,^[122] $\{Nb_{24}\}$,^[123] $\{Nb_{27}\}$,^[124] and transition-metal-supported $\{Nb_{128}\}$ ^[125] and $\{Nb_{162}\}$.^[126]

POM chemistry has further expanded to include less conventional metal oxides. Noteworthy examples are large polyoxopalladates^[127] and uranium-based clusters such as $\{U_{60}\}$ ^[128] and $\{U_{70}\}$ ^[129], and others.^[130] Also remarkable are the ring-shaped $\{Pd_{84}\}$,^[131] and isostructural $\{Zr_{70}\}$ ^[132] and $\{Ce_{70}\}$ ^[133] clusters.

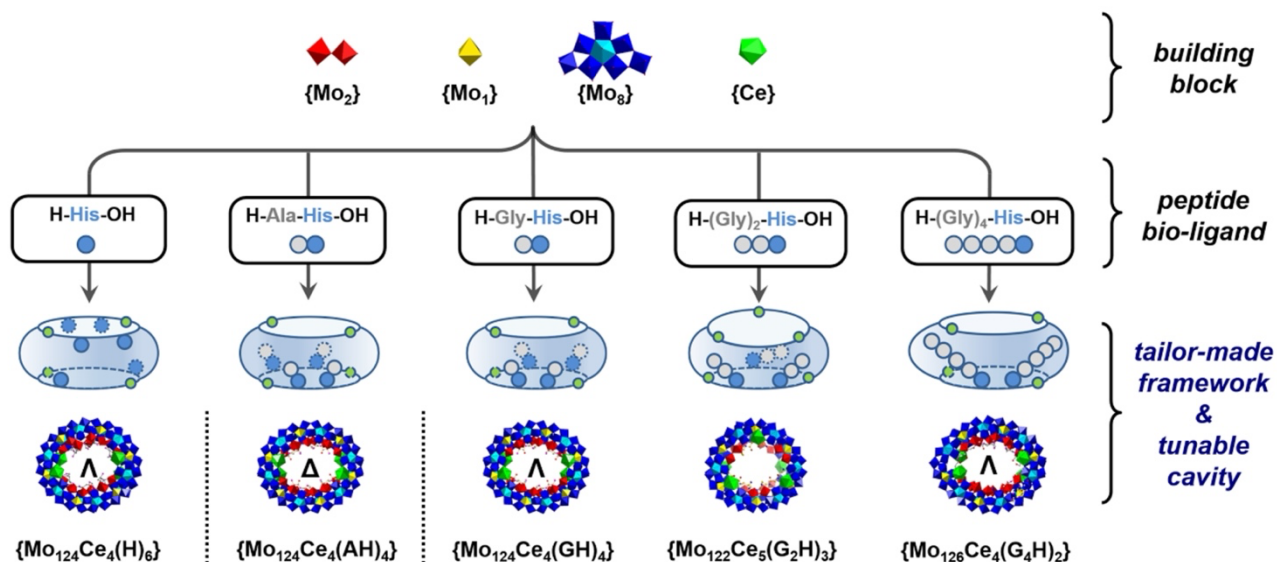


Figure 9. Schematic of peptide sequence-mediated self-assembly for biohybrid molybdenum blue nanowheels. Barrels represent peptide binding sites and helical Ce(III) arrangements that induce chirality.^[97]

SCXRD is critical for distinguishing POM isomers. For example, $\{H_4W_{19}O_{62}\}^{6-}$ theoretically has six isomers. In water, co-crystallization allows all six isomers to coexist in one crystal due to the solvent's high polarity. Switching to acetonitrile, i.e. a less polar solvent, enables separation and structural resolution of individual isomers via cation exchange and crystallization.^[134]

This technique is also key to detecting POM chirality. While molybdenum blue (MB) wheels are typically centrosymmetric, incorporating lanthanide ions breaks symmetry due to their helical arrangements. Although these syntheses typically yield racemic mixtures, the use of chiral amino acids and peptide ligands facilitates the selective formation and isolation of enantiomerically pure Ln-functionalized MB wheels.^[96-97] For example, MB compounds based on $\{Mo_{124}Ce_4\}$ frameworks form intrinsically chiral Λ or Δ configurations, dictated by the chirality of the peptide ligands (Figure 9).

SCXRD also provides insight into the construction of supramolecular POM assemblies. For instance, the $\{(Mo_6O_{19}@\gamma\text{-CD})_2@Mo_{154}\}$ nanocomposite is built hierarchically from five components via noncovalent interactions. Structural determination reveals encapsulation of $[Mo_6O_{19}]^{2-}$ anions by γ -

cyclodextrin (CD) units, forming a host–guest system with the Mo₁₅₄ wheel (Figure 10).^[135] Similar onion-like three-layered structures include {P₂W₁₈O₆₂@(γ-CD)₂@Mo₁₅₄}^[136] and {Re₆Te₈(CN)₆@(γ-CD)₂@Mo₁₅₄}^[135] highlighting the strong binding affinity between γ-CD and POM surfaces. These structures provide valuable insights into supramolecular self-assembly, offering templates for the rational design of complex multicomponent materials via non-covalent strategies.

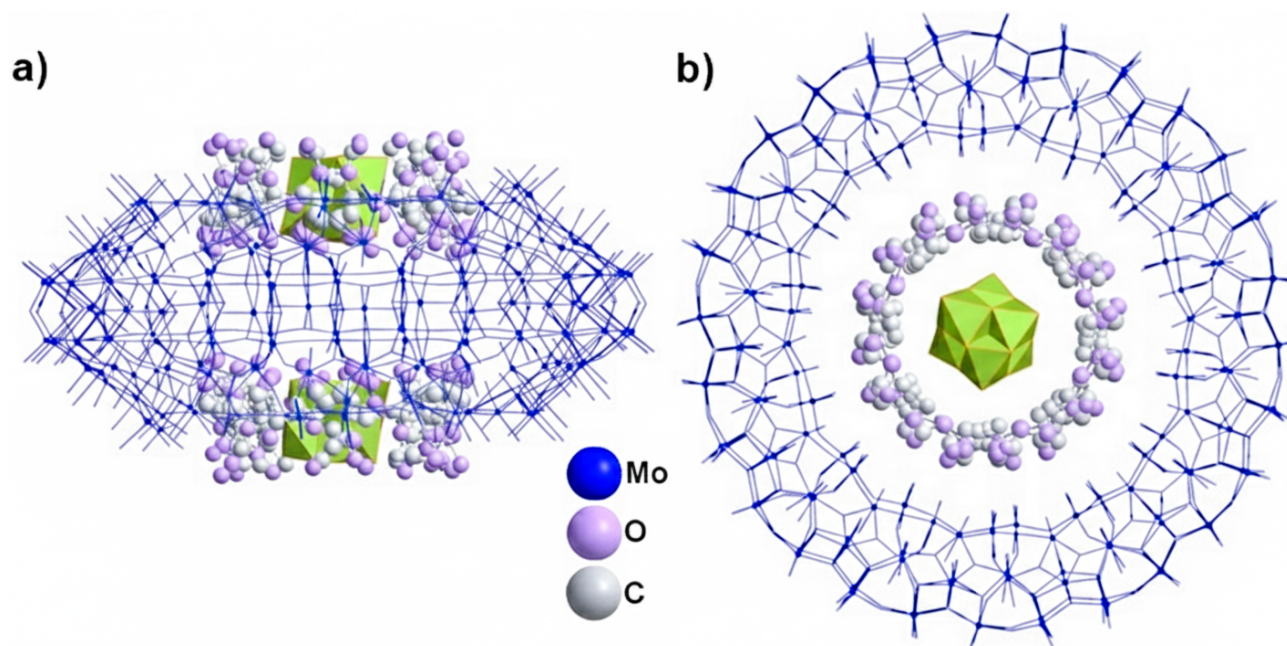


Figure 10. a) Side and b) top views of the multi-layer supramolecular structure {(Mo₆O₁₉@γ-CD)₂@Mo₁₅₄}, showing Mo₁₅₄ in blue wireframe, γ-CD in ball-stick, and Mo₆O₁₉ in green polyhedra. Taken from ref ^[135]

More complex systems involve POM–protein co-crystallization.^[137] POMs have proven valuable as phasing agents in protein crystallography due to their strong X-ray scattering properties, crucial for solving the phase problem in structural biology. For example, K₆[P₂W₁₈O₆₂]^[138] was instrumental in early ribosome crystallization efforts, recognized with the 2009 Nobel Prize in Chemistry.^[139] Today, the Protein Data Bank (PDB) includes over 50 entries involving POM–protein complexes. Beyond phasing, POMs aid protein crystal formation, helping address a key bottleneck in macromolecular crystallography. Their ability to promote crystallization and assist in structural elucidation underscores their growing role as powerful additives in structural biology.^[140-141]

3.1.2 Microcrystal electron diffraction (MicroED)

While SCXRD remains the gold standard for structural determination, its applicability is often limited by the need for large, high-quality crystals, requirements that are not always met in POM chemistry.

Recent rapid advancements in three-dimensional (3D) electron diffraction (ED) techniques have opened new pathways for solving structures of nano- and submicron-sized crystals.

Among the recent breakthroughs is MicroED, a technique that allows structure determination of crystals only tens to hundreds of nanometers in size. Originally developed for niche applications, MicroED is now transitioning into mainstream structural chemistry, thanks to innovations in hardware and software that streamline data acquisition and analysis. MicroED has gained traction in fields such as MOFs, COFs, zeolites, and protein crystallography, where the formation of sub-micron-sized crystals is common and often limits SCXRD-based analysis.^[142] Similar limitations are frequently encountered in POM chemistry, where solution equilibria and the tendency for multiple phases or isostructural mixtures to co-crystallize present significant challenges. In such cases, ED enables screening of heterogeneous or multiphasic samples that would otherwise be inaccessible.

Another key advantage of electron diffraction is its high sensitivity to light elements, such as lithium.^[143] This makes ED particularly attractive for studying POM-based ionic conductors, where the accurate determination of light cation positions and their occupancies is crucial for understanding conductivity pathways and optimizing performance.

POMs are known for their ability to undergo multi-electron reduction,^[144-145] with the distribution of additional electrons within the polyanion framework being highly dependent on its structure and composition. A unique advantage of ED is the potential to dose nanocrystallites with electrons in a controlled manner during measurements. This opens the door to in situ observation of structural changes related to reduction processes, including ion mobility within the crystal lattice. Such capabilities are particularly relevant for investigating POMs as electron transport materials, providing structural insights into charge compensation mechanisms and redox-induced phase transformations.

3.2 Small-Angle X-Ray Scattering (SAXS)

Small-angle X-ray scattering (SAXS) has become an increasingly powerful technique for elucidating the solution-phase behavior of POMs and related polynuclear oxoclusters. Traditionally applied to biomolecules,^[146] nanoparticles,^[147-148] and colloids, SAXS is now being adapted to systems at the molecular–nanoscale interface, where even small clusters (*ca.* 1 nm diameter) can produce meaningful scattering signals due to their high electron density, topological rigidity, and monodispersity.^[149-150]

Although POMs were once considered too small for conventional SAXS analysis, early studies demonstrated their suitability, particularly for high-Z systems like uranyl peroxide nanospheres.^[151]

In these systems, SAXS enabled the monitoring of long-term self-assembly processes, capturing the evolution of nanospheres over months. The unique structural features of these hollow, spherical clusters, coupled with uranium's high scattering power, yield intense oscillatory features that facilitate detailed structural interpretation.

Since then, SAXS has been employed to investigate a wide range of POM-related phenomena, including capsule assembly and interconversion,^[152-153] heterometal encapsulation,^[154] and the formation of supramolecular "blackberry" aggregates.^[155] High-charge clusters such as polyoxoniobates have also been studied, where SAXS provided the first direct structural evidence for contact ion-pairing in solution under conditions inaccessible to crystallography or spectroscopy.^[156-159]

The accessibility of SAXS has increased with the development of benchtop systems (some coupled with wide-angle X-ray scattering (WAXS)) and improved synchrotron beamlines, enabling routine analysis of smaller, more weakly scattering clusters. These advances have catalyzed diverse studies across multiple POM subclasses, including: *i*) super-reduced and redox-active POMs, often with open-shell configurations or delocalized electrons;^[145] *ii*) mixed d-f metal oxoclusters with complex topologies and electron-transfer properties;^[160] *iii*) tin-based clusters relevant for nanolithographic applications;^[161] *iv*) POM-based water oxidation catalysts, studied in both isolated and hybrid material contexts.^[162-163]

To support these studies, tailored data analysis and fitting protocols have been developed to accurately model scattering from small, dense clusters in solution, expanding the utility of SAXS across more complex and heterogeneous systems.^[164-166] This is particularly impactful for hybrid or supramolecular POM assemblies, where interactions with cyclodextrins and other large organic molecules guide the formation of defined host-guest structures.^[80, 135, 167]

Computational approaches, such as DFT modeling and SAXS curve simulation, have been used in conjunction with experimental data to predict and confirm supramolecular architectures, enabling structural assignments that are often elusive by other methods.^[168] SAXS has also been extended to the analysis of self-assembled soft hybrid materials and hydrophobic POM interactions, shedding light on superchaotropic effects and complex fluid-phase behavior.^[169-170]

The integration of SAXS with surface-sensitive techniques, such as grazing incidence SAXS (GISAXS), has enabled exploration of POM self-assembly upon deposition, revealing solvent- and hydrogen-bond-directed ordering on surfaces.^[171-172]

SAXS and GISAXS are now well-established as essential tools for the characterization of POMs in non-crystalline environments. They provide access to hierarchical structure, solvation-driven dynamics, and assembly behavior that complements single-crystal diffraction and spectroscopy. As techniques evolve and become more accessible, they are poised to further deepen our understanding of functional POM systems in solution and at interfaces, while also fostering collaborative, cross-disciplinary innovation across synthetic chemistry, soft matter, and materials science.

It is noteworthy that it has recently been shown that *in situ* X-ray total scattering experiments combined with pair distribution function analysis and computer-aided predictions provide a systematic framework for elucidating the pH-dependent speciation and formation pathways of molecular metal oxide nanoclusters under hydrothermal conditions.^[173-174]

3.3 Pulse Radiolysis Transient Absorption Spectroscopy

POMs are well-known for their ability to undergo reversible, multielectron redox transformations^[175] with minimal structural reorganization – properties that are critical for applications e.g. in photocatalysis, electrocatalysis, and photochemical energy conversion.^[176-177] However, despite these appealing redox characteristics, the use of pulse radiolysis and related radiation chemical methods (e.g., electron beam or gamma radiolysis) to investigate POM reactivity remains limited, largely due to the restricted availability of suitable infrastructure such as linear electron accelerators.

Among these techniques, pulse radiolysis transient absorption spectroscopy offers unique advantages. It enables real-time observation of elementary reactions between POMs and highly reactive short-lived species, making it a valuable complement to electrochemical and photochemical studies. Importantly, pulse radiolysis can selectively generate reductive or oxidative intermediates, allowing targeted investigation of specific mechanistic steps in redox-driven POM processes.

To date, the application of pulse radiolysis to POMs has focused almost exclusively on one-electron reduction pathways. Initial studies employed radicals derived from alcohols (e.g., $\bullet\text{CH}_2(\text{OH})$, $\text{CH}_3\bullet\text{CH}(\text{OH})$, and $(\text{CH}_3)_2\bullet\text{C}(\text{OH})$) generated via radiolysis of aqueous N_2O -containing solutions to reduce archetypal Keggin and substituted POMs, including $[\text{PW}_{12}\text{O}_{40}]^{3-}$, $[\text{SiW}_{12}\text{O}_{40}]^{4-}$, $[\text{FeW}_{12}\text{O}_{40}]^{5-}$, and $[\text{H}_2\text{W}_{12}\text{O}_{40}]^{6-}$.^[178] The spectra of the corresponding one-electron-reduced species were first identified under gamma radiolysis conditions.^[179] These studies provided key rate constants for electron transfer reactions and revealed the persistence of structural motifs during reduction, reinforcing the robustness of POM frameworks.

Additional work has expanded these insights to less conventional POM systems. For instance, the one-electron reduction of $[W_{10}O_{32}]^{4-}$ using acetonitrile radical anions ($CH_3CN^{\bullet-}$) formed under anaerobic radiolysis conditions enabled both spectroscopic characterization of the transient $[W_{10}O_{32}]^{5-}$ species and determination of bimolecular rate constants relevant to its photocatalytic activity.^[180] Similarly, high-nuclearity transition metal-substituted POMs have been investigated, revealing intermediate mixed-valent species with Fe(II)/Fe(III) distributions, inferred from transient absorption data and postulated reaction pathways.^[181]

Recent investigations have extended this methodology to vanadium-based POMs, such as a tubular, dodecavanadate cage $[HV_{12}O_{32}Cl]^{4-}$ and Lindqvist-type hexavanadates. The one-electron reduction of these species with solvated electrons or organic radicals provided new transient absorption signatures and kinetic parameters for electron transfer.^[182-183] These efforts help map the electronic landscape of reduced vanadates, which are highly relevant for small-molecule activation and energy conversion applications.

Notably, all reported studies so far have focused exclusively on reductive processes. The use of oxidizing radicals, such as $SO_4^{\bullet-}$ or $Cl_2^{\bullet-}$, accessible via radiolysis of aqueous solutions, remains entirely unexplored in POM chemistry, despite their potential to drive reduced vanadates or transition metal-substituted POM derivatives (TMSPs)^[184] into unusual high oxidation states, as recently demonstrated in coordination chemistry with iron.^[185] Likewise, non-redox active radicals such as $\bullet CH_3$, obtainable from radiolysis of N_2O -saturated aqueous-DMSO systems, represent a promising frontier for understanding POM-catalyzed transformations involving radical intermediates.

Pulse radiolysis, particularly when combined with time-resolved transient absorption spectroscopy, provides a uniquely powerful platform to probe elementary redox steps, reaction kinetics, and transient intermediates in solution-phase POM chemistry. While infrastructure limitations have historically restricted widespread use, recent facility development (e.g. in Leipzig, Germany) has re-energized interest in this technique. Future opportunities include systematic exploration of both oxidative and non-redox radical processes, more complex multi-electron systems, and applications in small-molecule activation, photocatalytic cycles, and radical-mediated transformations.

Future Horizons: Structural and Chemical Characterization of POMs

- 1) Unify multimodal methods (SCXRD, MicroED, SAXS/GISAXS, cryo-TEM, time-resolved spectroscopies) into pipelines for resolving POM structures across phases and interfaces.
- 2) Enable true in situ/operando tracking of POM nucleation, redox behavior, ion transport, and supramolecular assembly with high temporal–spatial resolution.
- 3) Advance micro-/nanocrystal analysis using automated MicroED, nanobeam crystallography, and data-driven refinement to overcome size and disorder limitations.
- 4) Expand radiation-chemical tools to generate and probe out-of-equilibrium POM states and transient intermediates.

4. SURFACE ENGINEERING WITH MASS-SELECTED MOLECULAR IONS

The controlled and clean deposition of multiply charged POMs on substrates is a crucial step toward realizing their potential in diverse applications from catalysis to biomedicine. Traditional solution-based deposition methods often face limitations arising from the intrinsic polyanionic nature of POMs. Co-deposition of counteranions and subsequent formation of small crystallites or aggregates on surfaces are common issues that compromise surface uniformity and functionality. Ion soft-landing has emerged as a powerful technique to overcome these challenges by enabling the precise deposition of mass-selected, intact POM anions from the gas phase.^[186-188] In this approach, a solution of a POM salt is electrospayed, producing charged droplets that yield gaseous ions upon solvent evaporation. Anions are transported through a differential pumping system and filtered in a quadrupole to isolate species of defined mass-to-charge ratio. The resulting beam of selected ions is directed onto a substrate surface. Low kinetic energies of the ions ensure that structural integrity is preserved during deposition (Figure 11).

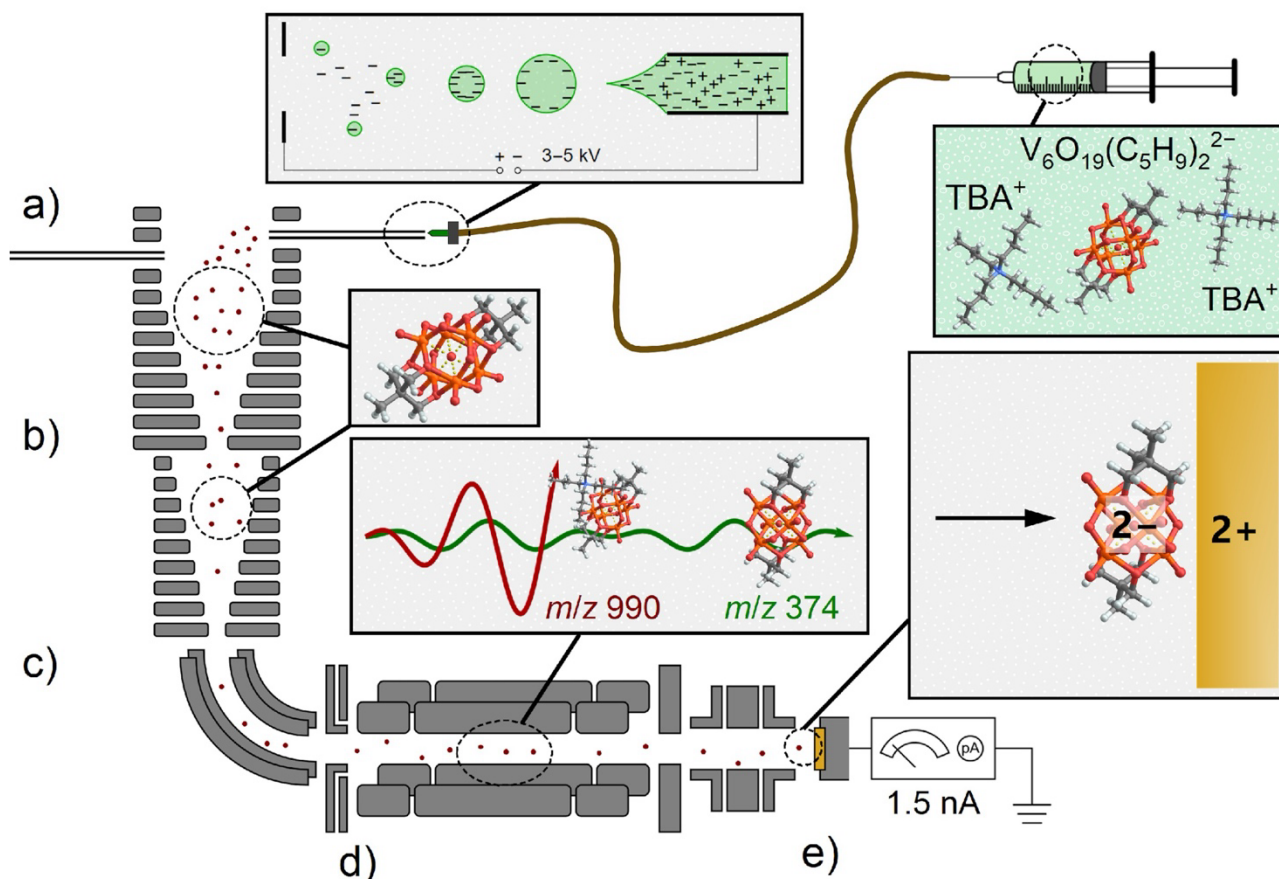


Figure 11. Schematic illustration of the ion soft-landing setup used for the deposition of Lindqvist-type POM dianions. A solution of the POM salt containing tetrabutylammonium (TBA) counterions is electrospayed (a), generating charged droplets that pass through a heated capillary to form gaseous ions. These ions are guided by a tandem ion funnel (b) into a 90°-bent ion guide (c), which separates ions from neutral species. The beam enters a quadrupole mass filter (d), where only dianionic POMs

with the selected m/z ratio are transmitted; mixed species such as $[\text{POM}]^{2-}[\text{TBA}]^+$ are excluded. The mass-selected ion beam is then focused via ion optics (e.g., einzel lenses) and the ions are softly deposited onto a grounded conducting Au substrate (e). Due to the intrinsic negative charge of POMs, charge balancing at the grounded surface is assumed to occur via electrostatic induction (surface dipole, here indicated by image charge within the surface).^[189] The ion current is monitored with a picoammeter to quantify the number of deposited ions.

High-resolution electron microscopy has demonstrated that aggregation, which frequently occurs in solution-processed films, can be effectively avoided using ion soft-landing.^[190-191] This paves the way for harnessing the properties of individual POM anions on surfaces in applications. Mass-selected, cyclodextrin-supported Lindqvist-type hexavanadate host-guest complexes were deposited on gold surfaces and scanning tunneling microscopy and spectroscopy (STM/STS) of the observed particles in the nm-size range revealed multilevel resistive switching behavior.^[192] These findings provide key insights for the design of POM-based memory devices and molecular-scale electronics.

Using ion soft-landing and STM studies of Lindqvist hexavanadates, the surface interactions and the role of various substituents at the periphery of ligand scaffolds in modulating the redox properties and resistive switching behavior of POMs have also been investigated.^[193] In addition, influences of surface and POM-to-POM interactions on the vibrational bands of soft-landed V-doped Keggin-type POMs were investigated.^[194]

The method has also proven valuable in electrochemical interface engineering. Soft-landing of Keggin-type POMs onto carbon nanotube electrodes improved both the stability and performance of the electrode-electrolyte interface.^[190] Coupling soft-landing with in situ cyclic voltammetry and IR spectroscopy allowed real-time monitoring of structural changes during redox cycling.^[195] Moreover, "atom-by-atom" metal substitution such as replacing Mo atoms in Keggin-type structures or V atoms in Lindqvist-type polyoxovanadate-alkoxide structures with W was disclosed through precise, mass-selected deposition of each individual species, enabling systematic studies of redox tuning.^[196-198]

The development of electrospray-coupled soft-landing instruments with advanced ion currents has enabled the generation of multilayer POM assemblies on surfaces using mass-selected ions. However, understanding charge balancing in these layers remains a significant challenge, especially when depositing stable anions without countercations. Studies with other anionic systems suggest that surface layers may attract contaminants or undergo potential driven chemistry generating H^+ within such layers.^[199] A solution involves dual-polarity soft-landing, where alternating deposition of anions and cations provides charge-balanced material layers.^[200]

Fragment ion soft-landing is a promising frontier,^[201] expanding the accessible chemical space of surface-engineered POMs. Given the rich gas-phase fragmentation chemistry of POM anions,^[193, 202-203] mass-selected fragment ions can be deposited to probe their electrochemical properties or to investigate their behavior as substrate-bound species for resistive switching or catalysis.^[204] This approach also enables access to previously unattainable POM structures via gas-phase recombination or on-surface reactions, as shown in studies of other anionic fragments.^[205-207]

To meet the demands of scalable surface modification, benchtop electrospray deposition setups have gained attention. These systems, although lacking high-vacuum and mass-selection capabilities, offer rapid, low-cost deposition with sufficient precision for many device applications. A dry ion localization and locomotion (DRILL) interface, combining multiple electrospray emitters with ambient ion optics, has been successfully employed to prepare POM-coated electrodes with performance comparable to vacuum-deposited materials.^[208] Benchtop deposition of $[\text{PW}_{12}\text{O}_{40}]^{3-}$ onto a cathode of a photoelectrochemical cell enhanced the device power output more than threefold, demonstrating the technique's utility in solar energy conversion.^[209] In energy storage applications, benchtop deposition of POM anions on porous carbon electrodes with surface, positively charged, functional groups achieved a threefold increase in capacitance, highlighting its promise for supercapacitor technologies.^[210]

Future Horizons: Mass-Selected Ion Deposition for POM Surface Engineering

- 1) Develop robust charge-compensation strategies and ultraclean deposition protocols to enable the preparation of stable mono- and multilayer POM films with molecular precision.
- 2) Expand ion deposition to complex architectures and fragment ions, integrating *in situ* spectro-electrochemical probes to directly correlate structure and function at interfaces.
- 3) Translate precision deposition into scalable device fabrication through dual-polarity and benchtop methods, advancing POM-enabled electronics, catalysis, and energy-storage/conversion technologies.

5. FROM FUNDAMENTALS TO THE REAL-WORLD APPLICATION

5.1. Health

Due to their versatile chemical properties, structural tunability and diversity, POMs have demonstrated great potential in biomedicine, including the field of nanomedicine.^[211] They have shown promising applications as anticancer, antibacterial, and antiviral agents, carriers for drug delivery, as well as coatings with biocidal properties.^[212-214] Furthermore, the non-covalent interactions between POMs and biomolecules such as proteins can be leveraged for a wide range of bioanalytical applications.^[78]

Beyond antimicrobial and anticancer applications, POMs have also attracted increasing attention as potential therapeutic agents for neurodegenerative diseases such as Alzheimer's disease. Several studies have shown that specific POM structures can interact with amyloid- β (A β) peptides, modulating or inhibiting their aggregation and thereby reducing associated neurotoxicity, highlighting their promise as metallodrug candidates for targeting amyloid-related pathological pathways.^[215-218]

To facilitate the use of POM agents in clinical practice, it is crucial to acquire a comprehensive understanding of their metabolic pathways in living organisms. Additionally, optimizing the delivery systems for POM agents, continuously developing new POM agents, and exploring their mode of action in complex organisms are essential. Furthermore, fundamental studies aimed at gaining insight into the conformational and structure-property relationships of active species at the molecular level are also necessary. Detailed mechanistic studies have begun to clarify how structural parameters of POMs including cluster size, charge, and topology govern their interactions with biological macromolecules and enzyme systems, thereby helping to establish fundamental structure-property relationships that underpin their potential therapeutic activity.^[219] As such, to realize the clinical application of POM agents, it is imperative to delve into the following issues:

Identifying the active species of POMs under biological conditions. Like many other metallotherapeutic agents, POMs can undergo hydrolysis, ligand exchange, and interaction with biomolecules^[77] during circulation and metabolism, resulting in a complex speciation chemistry.^[1, 45, 220] The generated species have different stability, pharmacokinetics, binding affinity, reactivity, and selectivity towards the target, all of which play a crucial role in determining the therapeutic efficacy of POMs. Therefore, elucidating the composition and structure of the active POM species under a given set of biological conditions is a fundamental prerequisite for optimizing their properties and carrying out effective bio-related applications. In this context, polyoxovanadates have served as

particularly informative model systems, as their speciation and biological activity have been extensively investigated. For instance, decavanadate $[V_{10}O_{28}]^{6-}$ is among the most studied POM species in biological environments and has been shown to interact with proteins, enzymes, and membranes, providing important insights into the relationship between POM structure, stability, and bioactivity.^[217] More recent studies have further demonstrated how the dynamic speciation of vanadium-based POMs under physiological conditions influences their interactions with biomolecules and cellular pathways, reinforcing the importance of identifying the active species responsible for biological effects.^[221-222]

Understanding the functional mechanism of POMs at the molecular level. Understanding the specific biotargets and mechanisms through which POMs exert their effects requires comprehensive investigations across various cellular systems and pathways. Many studies have focused on understanding the uptake,^[223] response and impact of POMs on multiple cellular processes, and found that POMs could interact with cell membranes or bacterial cell walls, influence enzyme activity, interfere with the cell signaling pathways, and induce other cellular responses.^[224] However, the exact functional mechanism or specific biotarget of POMs are still not well understood. At the molecular level, the functional mechanism of POMs can be attributed to several factors, including their ability to interact with biomolecules via electrostatic interactions, as well as to their redox chemistry,^[225] enzyme-like activity,^[226-227] and structural effects.^[228] These factors could lead to the diverse interactions with biomolecules (e.g., proteins,^[78] nucleic acids, and cell membranes), induce conformational changes^[229] and alter the function or stability of biomolecules, influence cellular redox processes, accelerate chemical reaction, and modulate biochemical pathways in biological systems. In this context, studies on polyoxovanadates have provided important mechanistic insights, showing that species such as decavanadate can bind to proteins and enzymes, modulate their activity, and induce structural rearrangements that affect catalytic function and cellular metabolism.^[217] Detailed biochemical and spectroscopic investigations have further demonstrated how POM binding to enzymes or protein assemblies can lead to changes in protein conformation and activity, illustrating how specific structural features of POM clusters govern their interaction with biological targets.^[230] Therefore, delving into the interaction between POMs and biological systems or biomolecules at the molecular level is crucial to gain insights into their functional mechanisms and to elucidate the conformational relationships of active species. In particular, recent studies have emphasized that key physicochemical parameters – such as POM size, topology, and especially overall charge and charge density – play a decisive role in governing their affinity for biological targets and their inhibitory or modulatory effects on proteins and enzymes, thereby establishing

important correlations between POM structure, electrostatic properties, and biological activity.^[111-112, 219]

Continuously developing POM-based agents to enrich the drug library and enhance the targetability. POM agents face several challenges that limit their targetability. One major obstacle is their lack of specificity in interacting with cells, tissues, or organisms. Like many other inorganic complexes, POM agents cannot differentiate between healthy and diseased cells, which result in off-target effects and potential harm to healthy tissues. Another challenge is the intricate and dynamic nature of the internal microenvironment. POM agents may struggle to effectively navigate and interact with the complex network of cells, biomolecules, and physiological processes within the body, impeding their ability to reach the intended target and exert the therapeutic effects. Furthermore, specific subpopulations of cells or tissues may have distinct characteristics. Selectively targeting the subpopulation by POMs pose a great challenge, limiting the precision therapy and individualized treatment. Nevertheless, numerous experimental studies have demonstrated that many POMs exhibit strong biological activity, with inhibitory concentrations (IC₅₀) that are often different from – and in many cases lower than – those of clinically approved drugs. For example, recent analyses of polyoxovanadates, polyoxomolybdates, polyoxotungstates, and polyoxoniobates across a wide range of cancer cell lines have shown distinct and frequently stronger cytotoxic effects than several established anticancer agents, highlighting the considerable therapeutic potential of these clusters.^[112, 231] To address these issues, future research could focus on the development of delivery systems^[232-233] that release POMs at specific site, the modification of POMs with targeted molecules^[234] that could specifically recognize cellular markers, and the design of self-assembled POM-peptide hybrids^[235] that protect and improve cellular interactions. Alternative methods include the construction of POM-based biorthogonal catalytic platforms^[58, 236] for pathologically activated therapeutics. The bioorthogonal chemical approach provides high selectivity of reagents towards specific substrates and confers an improved tolerance to the great variety of functional groups present in the biological environment.^[58] Developing hybrid organic–inorganic POMs that provide organic groups for conjugation to different biological molecules could pave the way forward towards targeted POM therapeutics. Currently, there are still no systematic studies and examples reporting true bioorthogonal processes involving POM building blocks. Developing bioorthogonal POM chemistry would be extremely useful for POM-based drug targeting, cell labelling, and *in vivo* imaging methods, among others. The bioorthogonal attachment of magnetic nanoparticles to cell membranes *via* supramolecular protection followed by strain-promoted “click” conjugation has

already been demonstrated,^[237] which indicates the viability of this approach for POMs and once which represents a veritable challenge for POM chemists.

In conclusion, considering the ever-growing interest in biomedical applications of POMs and the promising potential they have demonstrated so far, further research (Figure 12) should be developed along the following directions:

1) Precision therapy to improve the delivery and accumulation of POM agents within target cells, tissues, or organisms. This could be achieved by biofunctionalization of POMs for targeted delivery, followed by supramolecular assembly of the resulting hybrid POMs to protect them from the surrounding biological environment and improve their stability and transport. In addition, the redox activity of many POMs can lead to the generation or modulation of reactive oxygen species (ROS), often through Fenton-like catalytic processes. Because ROS levels strongly influence cellular signaling, oxidative stress, and cell viability, controlling POM-mediated ROS generation through targeted delivery strategies could enhance therapeutic selectivity, while minimizing damage to healthy tissues.^[238-239]

2) Individualized treatment by POM agents tailored to different cellular microenvironments and routes of administration to improve their efficacy and reduce their toxicity. This far-reaching target would require development of chemical protocols that would simultaneously protect POMs from biological environments and enhance their reactivity and selectivity towards specific bioorthogonal tags. Importantly, ROS modulation by POMs has been shown to depend strongly on the exposure conditions and biological context, with both pro-oxidant and antioxidant effects reported in vitro and in vivo. These time-dependent and environment-dependent responses further support the need for personalized strategies that account for cellular redox states and microenvironmental factors, when designing POM-based therapeutics.^[33]

3) Constructing POM-based theranostics platforms for biosensing and real-time monitoring of the targeted process. To achieve this, methods for chemically tailoring selective interactions of POMs towards complex biomolecules would need to be further developed to promote biosensing applications, including surface modification and other engineering challenges to detect target analytes or provide feedback on therapeutic efficacy. Specifically, the development of redox-active POMs functionalized with aptamer sequences^[240] should make these hybrid bioPOM structures suitable for selective and quantitative biomarker detection in modular lab-on-a-chip devices. These devices incorporating embedded POM–aptamer nanosensing components show strong potential for high-demand point-of-care applications in personalized health diagnostics.^[241] Beyond biomedical

sensing, the redox properties of POMs and their ability to generate ROS also underpin their catalytic role in environmental remediation, including the degradation of emerging pollutants through Fenton-like or photo-assisted oxidative pathways, highlighting an emerging conceptual link between POM applications in health and environmental technologies.^[242-243]

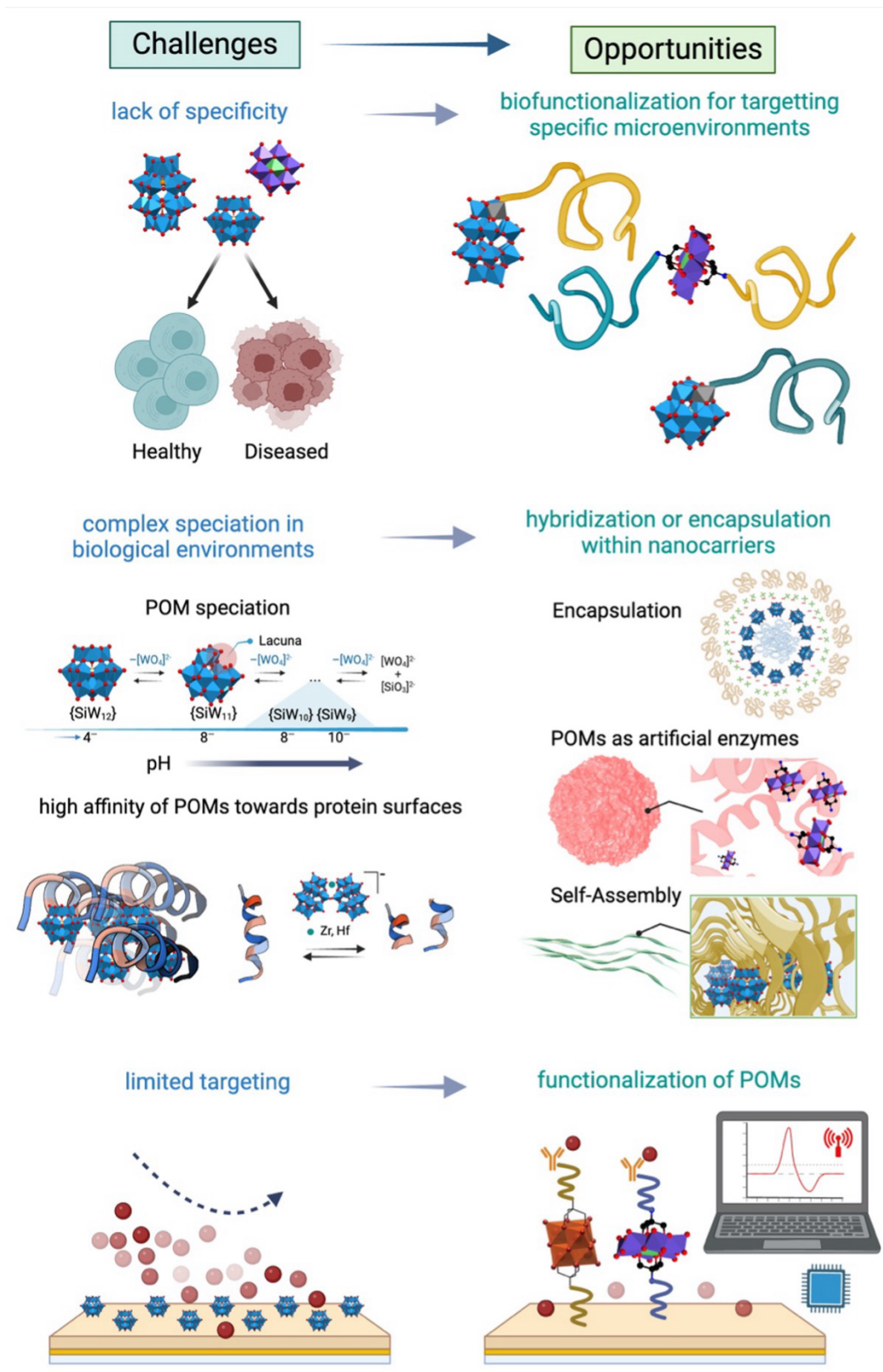


Figure 12. Challenges and opportunities for POM in bio-applications. Lack of specificity, when targeting diseased cells, can be countered through biofunctionalization for targeting specific microenvironments or cell membranes. Complex POM speciation in biological environments and the high affinity of POMs to protein surfaces can be answered by encapsulating/incorporating POMs into nanocarriers or hybridizing POMs with naturally occurring polymers or biomolecules. Biosensing challenges include the limited targeting of POMs, which can be remedied by conjugating functional groups and/or biomolecules that can help with detecting specific analytes using electrochemical approaches.

Future Horizons: POMs for Health

- 1) Resolve active POM species in biology through real-time speciation, single-cell uptake imaging, and in vivo reaction-path mapping.
- 2) Enable programmable POM therapeutics using bioorthogonal chemistry, adaptive supramolecular shielding, and microenvironment-responsive delivery systems.
- 3) Create integrated POM theranostics by combining redox-active POM probes with aptamer-based targeting for continuous sensing and feedback-guided treatment.

5.2. Electronics

The previously known efforts to implement purely organic compounds forming self-assembled monolayers (SAMs) as well as various types of metal complexes as active computing components into the working environment of prototypal electronic devices suffered from (i) high sensitivity of the structural integrity and switching potentials of molecular objects to the deposition parameters, (ii) their low selectivity towards different technical substrates, (iii) non-uniform layer formation, (iv) destructive electrical contacting by macroscopic electrodes due to mechanical sensitivity, (v) poor reproducibility of the conductivity data, and (vi) low applicability to neuromorphic mechanisms of electron transport and switching. Compared to metal oxide devices, organic devices usually show lower switching speeds and lower endurance due to their lower mechanical and electrical robustness.

We believe that these challenges can potentially be addressed by focusing on advanced chemical, electronic, and emerged room-temperature switching properties of new and revisited POMs that have been developed in recent years. However, their successful technological integration in form of single molecules or mono-/multilayers, capable of storing high charge capacity within their metal–oxygen or metal–metal bonds, into the working environment of solid-state electrodes, nanogaps, and surface interfaces will require further thorough investigation by the consolidated efforts of chemists, physicists, and engineers. Figure 13 illustrates these key challenges paving the way for POM-based electronics in the areas such as resistive switching and spin qubit materials and devices over the next 15 years.

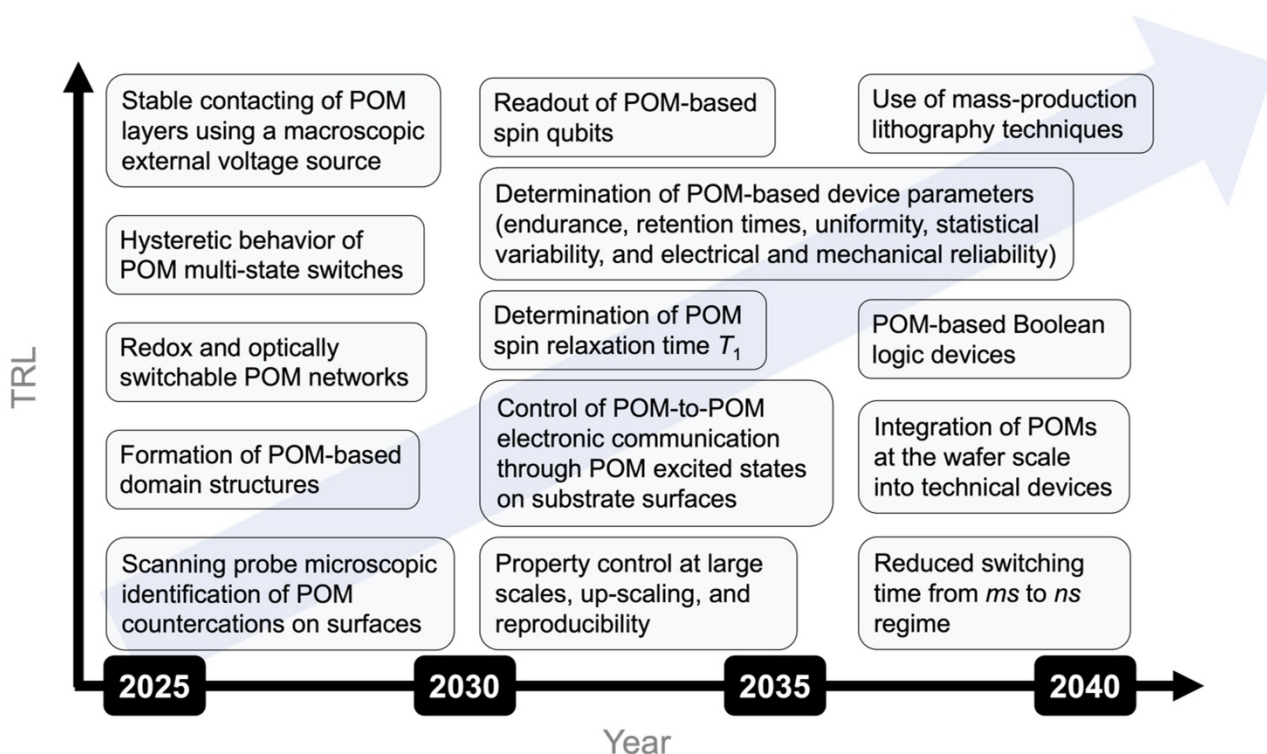


Figure 13. Challenging tasks that must be solved to bring POM-based electronics (including manipulation of charge and spin) to higher TRLs. The TRL increases within each group of specified challenges.

Due to their ability to form self-assembled and chemically engineered, covalently bound and supramolecular network structures, to exhibit redox-controlled conductance behavior, and to have electronic “crosstalk”, POMs can be developed in two promising directions in the field of computing memory:

- 1) Non-interference POM capacitors or memristors^[30] for creating alternative digital memory with minimal charge leakage and high information density in discrete states.
- 2) Artificial 3D neuron-like, analog networks consisting of interconnected memristive POM building blocks with electronic POM-to-POM communication for neuromorphic^[244] applications.

Although the potential of spin-active or spin-functionalized POMs in molecular quantum computing does need further exploration following the many far-reaching contributions of Coronado and colleagues,^[245-248] this is not the subject of detailed discussion in this section.

The key aspect in the development of POMs for directions 1 and 2 is the control and understanding of intermolecular interactions through electron tunneling processes between the individual POM units, their counteractions, and the substrate surface. It is important to study the formation of POM networks in which POM units are cross-linked by metal^[249] or redox-active cations, organic moieties,

and/or hydrogen bonds. While an intensive POM-to-POM communication will be typically not favorable in conventional data storage devices due to the problematic signal overspread in densely packed memory cells and, thus, should be minimized, it is crucial for the creation of functional neuromorphic networks. In this context, the still relatively unexplored role of counteractions in the liquid phase and especially within molecular layers or networks on surfaces is of enormous importance, as they could be of comparable importance for POM-to-POM communication. From a chemical point of view, this process can be described as artificial data processing in which the counteractions act as chemical transmitters in the “synaptic cleft” between the POMs as artificial biological neurons.^[250] Understanding the dynamics of cations in these processes is necessary, because these dynamics control the synaptic behavior of neuromimetic devices.

To implement POMs in various alternative computing devices with higher TRLs in the coming years and decades, further thorough study of the fundamental properties of POM-functionalized surface materials and their switching mechanisms, the technically oriented investigation of POM layers using macroscopic external voltage sources, as well as the adaptation of device manufacturing principles to the molecular level is necessary (Figure 14). To support and accelerate this implementation, the following fundamental aspects need to be explored:

Strain energy of surfaces and POMs. Atomic-scale strain engineering can be used as a tool to modify the nanophysics of devices. For example, the interface influence of strain energy potentials on the metal–insulator–transition was demonstrated for VO₂ thin films.^[251] It is currently unknown how strain-dependent changes in the lattice surface strain energy affect or can be used to tune the adsorption energy and surface-selective interaction of POMs, as well as the reactivity of POMs. In addition, the importance of molecular strain energy needs to be considered to understand whether it can have a good or bad effect on the switching properties, induce hysteresis in POM layers, and might thus be used as a selector for functional, responsive POM structural motifs.

Polarizability and dipole orientation at POM–substrate interfaces. Variations in polarizability, which is associated with the dielectric constant of POMs, were shown to determine the charge transport across molecular junctions based on POM hybrids anchored to the surface of Pt nanoparticles via remote terminal thiol groups.^[252] Such interfacial charge transfer dynamic was also observed in systems consisting of small molecules anchored to the surface of CdSe quantum dot nanoparticles.^[253] In addition to polarizability, the control of dipole (re)orientation^[254] along the switched POM-bearing junction needs to be studied in detail, as these factors can directly influence the current–voltage characteristics and the molecular orbital alignment at the interface between

POMs and an anchoring spacer layer on the electrode.^[255] On the other hand, it may be important to investigate whether the surface lattice deformation itself (expansion/contraction due to a decrease/increase in the orbital overlap between surface atoms) induced by ion doping effects, could be effectively exploited to influence polarizability of POM single molecules or layers immobilized on the surface electrodes, resulting in tunable charge separation and electron transfer at their interface.

Tailoring the molecular characteristics of ligands attached to POM. Ligands play an important role in POM-based molecular electronics. The influence of the electronic factors of ligands on the adsorption and switching stability of POMs, on the increase in POM's redox switching capability^[256-257] on the surface, as well as on the relative position of the electronic band structure of POMs with respect to the Fermi level of the surface was demonstrated on gold^[258] and silicon^[259] surfaces. Based on this knowledge, it is important to understand how ligand tuning can be used to optimize the POM interaction with technically relevant substrate surfaces such as Si (oxide coated or not), 2D materials (e.g., transition metal dichalcogenides),^[260] and metals to form stable and responsive, confined POM layers. In particular, the transfer of knowledge from perfectly ordered, monocrystalline model substrates, which are used in fundamental studies, to technically grown thin-film substrates with increased surface roughness and defect density is a challenge that should not be underestimated and for which ligand optimization is of great importance.

Blending of adlayer structures with POM properties. Adlayer materials such as DNA origami^[261] and carbon nanotubes placed between the electrode surface and the POM molecules were shown to provide a platform for spatially controlled positioning and stable switching of POMs, to induce synaptic-like behavior or to generate spontaneous spikes and noise, which are the crucial characteristics of molecular neuromorphic devices. The effects of cations^[262] (e.g., Na⁺ vs. TBA⁺ vs. ionic liquid cations (imidazolium, pyridinium, pyrrolidinium, phosphonium)), when interacting with the adlayer material on the topographic properties (formation of POM-based domains), stabilization of reduced states (formation of H-bonding interactions),^[263] switching resistance, and hysteretic behavior of POMs on surfaces, still need to be explored. It is already known that POM counteranions can affect the dynamics of charge transfer in POM layers, as well as the current–voltage characteristics of materials functionalized with POMs.^[19-20]

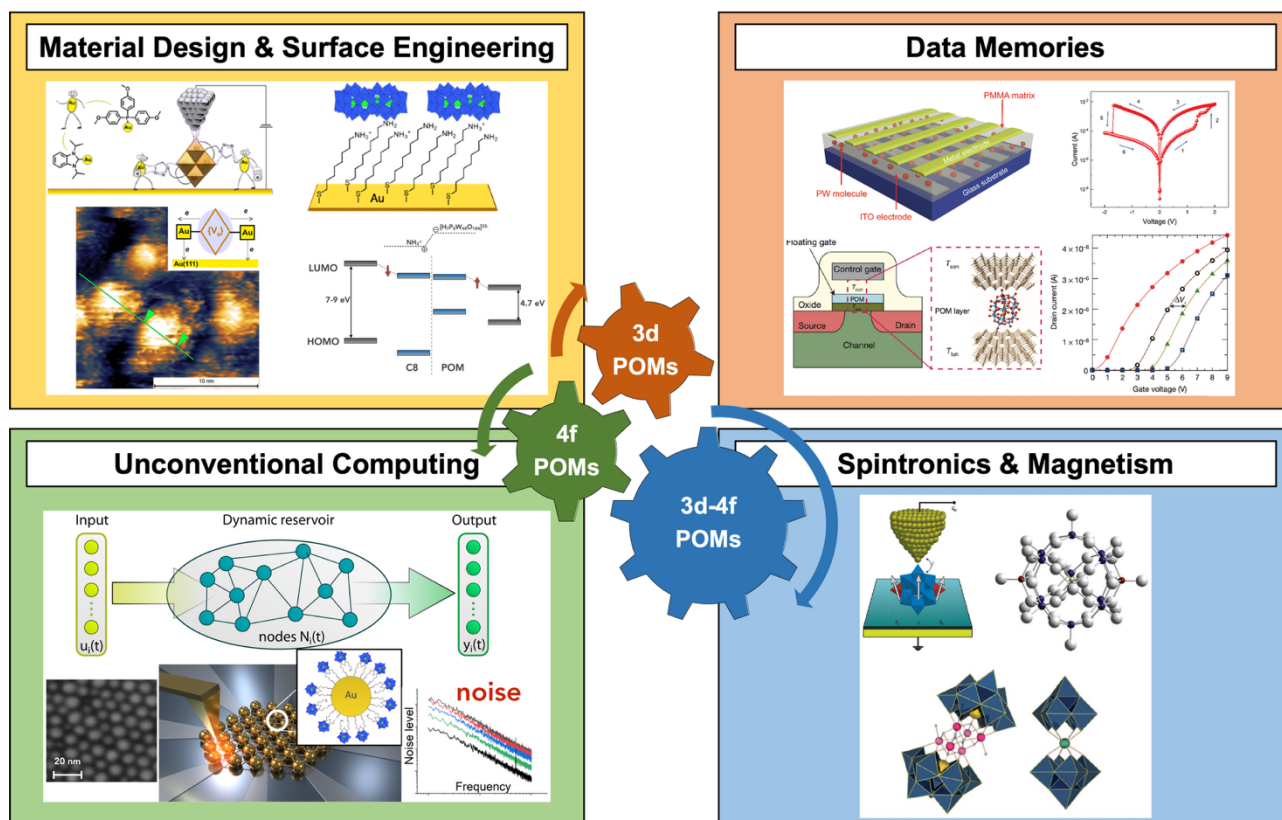


Figure 14. Main research directions of POM nanoscience towards technical devices. For this image the elements of graphics were adopted from original studies: top left,^[255-256] top right,^[264] bottom left,^[265] bottom right.^[248, 266]

Future Horizons: POMs for Electronics

- 1) Engineer POM–interface control through strain tuning, dipole orientation, and ligand design to achieve reliable adsorption, redox switching, and stability on device substrates.
- 2) Exploit ion-driven charge transport by mastering counterion dynamics and POM–POM tunneling to create durable molecular memristors and neuromorphic networks.
- 3) Build scalable hybrid architectures that integrate POMs with DNA origami, nanotubes, 2D materials, and polymers for manufacturable molecular electronic and quantum devices.

5.3. Energy and the Environment

Owing to their adaptable physicochemical characteristics (multi-electron transfer and acidity), structural flexibility, and variety, POMs have exhibited significant promise in catalysis, particularly in the activation of small molecules and the generation of sustainable fuels, and in energy storage materials.^[267] More specifically, they have revealed encouraging applications as catalysts^[268-270] for hydrogen evolution reactions (HER),^[271-272] CO₂ reduction,^[273-276] carbon capture technologies,^[277] molecular oxygen activation^[278] and oxygen evolution reactions (OER)^[279], organic reactions,^[77, 280] biomass valorization,^[281-282] and energy storage systems, including components for supercapacitors

(Figure 15).^[283–286] Advancing the use of POMs in energy and catalysis requires understanding their mechanisms and interactions in complex environments. Research into novel POMs and understanding of their nanoscale processes is essential to fully harness their potential.

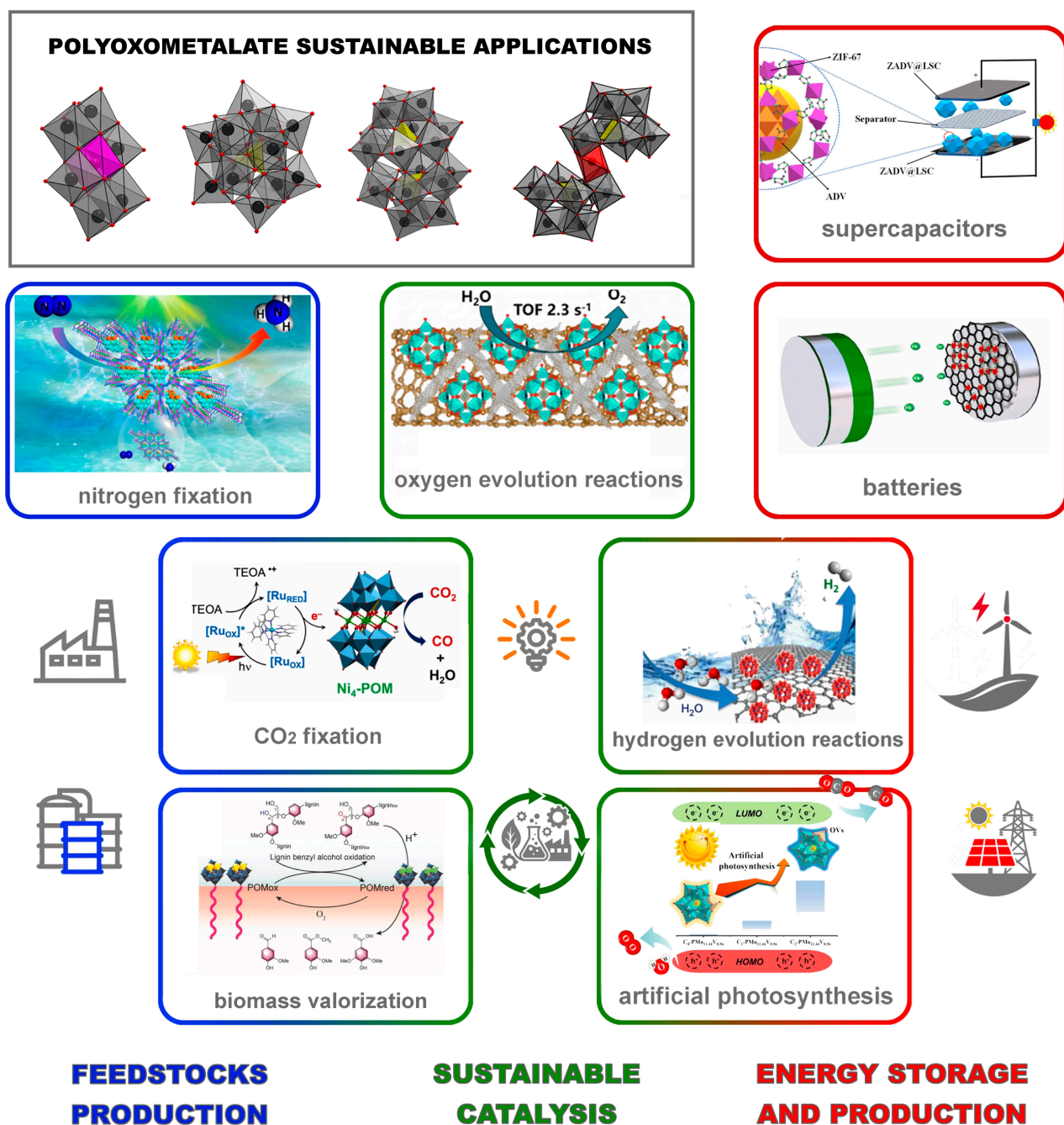


Figure 15. Main research directions of POM-based materials for sustainable applications. Images illustrating OER,^[279] HER,^[272] CO₂ fixation,^[276] biomass valorization,^[282] nitrogen fixation,^[287] artificial photosynthesis,^[288] POM-based batteries^[289] and supercapacitors^[290] are reproduced from the corresponding references with permission from the respective copyright holders.

Building upon their intrinsic multielectron redox flexibility and structural tunability, POMs have become increasingly central to catalytic transformations relevant to sustainable energy. This

versatility is evident across key reaction families, from H₂- and O₂-evolving processes to CO₂ conversion and biomass upgrading.

POMs for energy storage

POMs as electrode materials in Li-ion batteries. Since the first report in 2012 on the use of the phosphomolybdate Keggin [PMo₁₂O₄₀]³⁻ as the positive electrode active material alongside a lithium metal negative electrode,^[291] POMs have also been explored extensively as negative electrode (anode) materials in Li-ion batteries. Thorough studies^[292-296] have investigated a large range of POM-based electrodes as a mean to access anode capacities that significantly exceed the lithium storage limit of graphite. Another opportunity is offered by POMs used as bulk metal oxide precursors, which can be controllably decomposed to yield cathode materials with specific characteristics, such as good rate performance or enhanced life cycles.^[297] In POM-based electrode systems the challenge remains how to improve the electrical conductivity of the electrodes while limiting potential leaching of POMs into the organic electrolyte and simultaneously maximizing the specific surface area. It is also critical that future POM-based anode systems will be designed to limit the effects of volume expansion and contraction upon lithium intercalation and deintercalation.

POMs as solution-phase charge carriers. Whereas Li-ion systems exploit POMs as solid-state active materials, redox-flow technologies leverage their solution-phase redox properties. This shift from solid to liquid formats illustrates the conceptual breadth of POM charge storage and emphasizes their potential in scalable, stationary energy applications. Redox Flow Batteries (RFBs) are a promising technology that use soluble redox-active molecules as charge carriers stored in external reservoirs, making RFBs ideal for scalable stationary energy storage.^[298] Today, the most advanced RFB is the all-vanadium system developed in the late 1980s.^[299] However, widespread commercialization of the technology is hindered by the relatively high cost of vanadium, and by the limited energy density of 25-35 WhL⁻¹ of the battery (an order of magnitude below that of Li-ion batteries), limiting its translation between sectors. POMs are appealing charge carriers for RFBs allowing access to high energy density due to their multiple accessible redox states, solution stability and tunable solubility. Examples of POM-based RFBs encompass both the so-called symmetrical RFBs, in which the same POMs provided both positive and negative redox couples,^[300-301] or RFBs using different POMs in the positive and negative electrolytes, allowing the tuning of the cell voltage.^[302] Leveraging on the high electron sponge character of POMs, a practical energy density of 225 WhL⁻¹ has been reported upon storing 18 electrons on Li₆[P₂W₁₈O₄₀] clusters in the negative electrolyte.^[303] Another promising direction is the use of organic electrolytes that offers higher voltages and energy densities.^[304]

Organofunctionalized POMs, which are soluble in non-aqueous systems, provide an opportunity to improve the charge carrier properties.^[305-306] This approach has also the potential to couple the multi-electron capacity of POMs with the solubility and tunability of organic redox molecules.^[307] POM RFBs have made key advances with future focus on high-energy-density applications. While unlikely to compete in low-cost micro-grid systems, POM multi-electron redox chemistry offers superior energy densities over all-vanadium RFBs.

POMs in next-generation battery technologies. The success of POMs in both solid-state and flow-cell platforms has naturally stimulated exploration in emerging battery chemistries beyond lithium. Their tunable redox potentials, ionic conductivities, and ability to stabilize reactive intermediates make them promising components in sodium-, zinc-, and sulfur-based systems. The redox properties and ionic conductivity of POMs also render them promising components in the so-called beyond lithium batteries.^[308] They are generally hoped to offer sustainable alternatives to existing technologies as they mature over the coming years.^[309] POMs have been deployed as electrode materials in aqueous zinc-ion batteries,^[310] sodium-ion batteries,^[311] and as components in Mg-S and Li-S systems, as additive in polymeric separators^[312] or as catalysts.^[313] POMs have also the potential to work as soluble redox mediators in next-generation batteries, as shown in Li-S and Li-air cells.^[314] There is significant scope to study the interplay between POM redox chemistry, addenda atom chemistry, and redox mediator performance in a range of next-generation battery technologies.

POMs in supercapacitors. Complementary to battery technologies, supercapacitors benefit from the fast, reversible electron transfer and proton activity intrinsic to many POMs. This places POMs at the interface between faradaic and non-faradaic storage mechanisms, enabling hybrid pseudocapacitive behavior. While batteries store more energy but have slower charge/discharge rates due to the electrode chemistry, supercapacitors store less energy but offer higher power densities due to ion movement in the electrolyte.^[315] Pseudocapacitors, another sub-class of supercapacitors, combine some characteristics of both classes.^[316] Since the report in 1998 of the use of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ as a pseudocapacitive electrode material,^[317] POMs have been extensively studied as the redox-active components of supercapacitor electrodes as recently reviewed.^[318] Future POM supercapacitor research will focus on immobilizing POMs on conductive substrates to enhance energy density and minimize POM dissolution. Strategies include covalent hybridization and nanoconfinement, alongside developing ultra-stable composite electrodes.

POMs in environmental catalysis

The same redox robustness and modularity that underpin POM performance in energy storage systems are equally valuable in environmental catalysis. Indeed, POMs provide a unified platform for both energy conversion and chemical remediation, enabling multielectron transformations central to pollutant degradation, oxidation chemistry, and sustainable synthesis. The same fundamental attributes that make POMs attractive for electrochemical energy storage also position them as highly effective catalysts in a range of chemical transformations, often providing superior performance due to their ability to mediate complex multi-electron processes. They also endow POMs with a distinctive versatility that underpins progress in sustainable chemistry, ranging from energy conversion to green synthesis. Overall, a unique set of their relevant properties includes:

- redox properties and protonic acidities designed at the molecular level by altering their composition, heteroatoms, and counteranions. Their ability to reversibly accept and release electrons allows for adjustable multi-step reduction potentials.^[184, 319-323] Combined with rapid electron-transfer kinetics and stability, this renders them exceptionally suitable candidates for electrochemical applications.^[324-325]
- the possibility of incorporating transition metals and lanthanoid metals into the POM framework, as additional redox centers or as Lewis acid centers for bespoke applications. An elegant example is the tetra-Ru core containing POM $[(\text{SiW}_{10}\text{O}_{36})_2\{\text{Ru}_4(\text{H}_2\text{O})_4\text{O}_4(\text{OH})_2\}]^{10-}$ that exhibits multi-redox behavior with wide range of applications in water^[267, 326-329] and alcohol oxidations.^[330] A promising approach is the stabilization of atomically precise metal nanoclusters by ring-shaped^[331-332] or lacunary POMs.^[333] Extending this hybrid approach, POMs can also be utilized to cap simple nanometric metals oxides.^[334-336] The POMs both enable solubility of functional materials and provide synergistic function, demonstrating CO_2 reduction^[334-335] promoted by solar light and water oxidation.
- tunable Brønsted acidity of protonated forms of POMs due to their low charge density. Acidic POMs are highly soluble in water and polar solvents, with solubility adjustable via counteranions. Their strong Brønsted acidity makes them effective catalysts for esterification, hydrolysis, alkylation, biomass valorization^[337-342] and the design of proton-conductive materials.^[343]

Given the above discussed distinctive properties, POMs hold great promise for small molecule activation in POM-based biomimetic processes. Transition metal-modified POMs promote N_2 ^[344-347] and CO_2 activation,^[348-351] by enabling efficient electron transfer processes. Incorporation of Lewis acidic metal centres is expected to facilitate CO_2 anchoring and to give efficient electrochemically-

assisted reduction at low overpotentials.^[274] Photochemically assisted CO₂ reduction should be further explored, utilizing alternative electron sources as sacrificial reductants, like hydrocarbons instead of amines.^[275] Moreover, organic ligand functionalization will potentially stabilize intermediates, while the integration of proton relays will facilitate the formation of ammonia or low molecular weight hydrocarbons. Nonetheless, challenges related to material recovery and scalability must be addressed to ensure their widespread implementation. Throughout these processes, POMs can mediate electron transfers and enable light-driven processes with semiconductors and consequently reducing the overall energy input. Researchers aim to optimize these bio-inspired POMs and their electronic structure to create efficient, selective, and sustainable catalysts for ambient catalytic processes. Ongoing progress in this area is expected to play a crucial role in tackling global challenges related to energy and food security by providing a greener substitute for the Haber-Bosch process, reducing climate effects caused by elevated concentrations of CO₂, while providing a sustainable route for the selective production of C1-C3 feedstocks. Despite this breadth of functionality, translating POM based systems into practical devices requires overcoming several persistent challenges. These include stability, conductivity, selectivity, and integration into scalable architectures, issues that must be addressed to fully exploit their potential.

In conclusion, POMs have emerged as valuable materials in the fields of energy, catalysis, photocatalysis, electrocatalysis, and environmental applications, owing to their distinctive redox properties, structural adaptability, and adjustable electronic features. Nevertheless, despite their considerable potential, various challenges impede their practical implementation, including issues related to stability, reusability, precise reactivity tuning, charge recombination, low conductivity, selectivity, scalability, and the integration into functional devices. Hence, it is essential to encourage the exploration efforts and foster synergies in the following domains:

Electronic structure engineering. POMs offer insights into structure-property relationships, enabling the design of compounds with tailored characteristics. To enhance visible-light activity in POM-based photocatalysts, new strategies like doping, heterostructure formation, and plasmonic enhancement should be explored. This approach advances both structural and chemical understanding that could act as a springboard for the development of new generation functional materials for energy applications.

Mechanistic insights and theoretical modelling. Advancements in computational chemistry and machine learning can play a crucial role in understanding POM-catalyzed reactions at the atomic level.^[352] Predictive modeling can guide the rational design of next-generation POM-based catalysts.

Rational design of hybrid POM materials for energy storage and conversion. Hybrid materials with MOFs, conductive polymers, carbon nanostructures or membranes^[353] can improve further the stability, charge transfer, and catalytic performance.^[354] Future research should focus on immobilizing POMs^[355] on conductive substrates to enhance energy density through pseudocapacitive behavior and minimize POM loss. Strategies like covalent hybridization and nanoconfinement, along with a better understanding of POM electrochemistry and the development of ultra-stable composite electrodes, are crucial for advancing integrated systems. These studies point toward a rapidly maturing field in which POMs serve as multifunctional platforms for energy and environmental technologies. Looking ahead, several strategic research directions are poised to accelerate the translation of molecular POM science into operational devices and industrially relevant processes.

Practical integration in energy and environmental applications. POMs are promising for energy and environmental applications like green hydrogen production, CO₂ reduction, N₂ conversion, pollutant degradation, and energy storage. They effectively break down complex organic molecules in water and remove heavy metals from wastewater, often outperforming conventional methods. However, bridging the gap between lab research and industrial application remains a key challenge requiring interdisciplinary collaboration.

Future Horizons: POMs for Energy and the Environment

- 1) Device-level translation: Moving beyond molecular and electrode-scale studies toward fully integrated POM-based batteries, flow cells, electrolyzers, and photoelectrochemical devices with long-term operational stability.
- 2) Operando and time-resolved characterization: Development of advanced spectroscopic and electrochemical tools to resolve transient redox states, ion-coupled electron transfer, and structural dynamics under realistic working conditions.
- 3) Defect, interface, and morphology engineering: Control of POM-support interfaces, defect chemistry, and mesoscale architectures to regulate charge transport, ion diffusion, and catalytic selectivity.
- 4) Electrolyte and membrane co-design: Tailoring electrolytes, separators, and ion-selective membranes specifically for POM redox chemistry to suppress crossover, improve cyclability, and enable high-voltage operation.
- 5) Closed-loop recycling and recovery: Design of POM systems that allow molecular-level regeneration, recovery, and reuse within circular energy and catalytic platforms.
- 6) Autonomous and AI-driven discovery: Integration of machine learning, robotic synthesis, and self-optimizing electrochemical platforms for accelerated identification of next-generation POM materials.

6. SUMMARY AND OUTLOOK

Here we have covered innovative and influential POM studies, delved into the latest groundbreaking developments, and built bridges between established, new, and required knowledge to accelerate and transform “still academic” multifunctional POM materials towards technological maturity. The coming decades will be marked by radically new directions and discoveries in the field of POMs, including POM-based microfluidics, 3D printing of reconfigurable and programmable materials using POMs as photoinitiators and stimuli-responsive constituents,^[356] POM-based neuromimetic networks,^[250] and POM chemistry under extreme conditions. The transferability and integrability of POM’s structure–property–reactivity relationships across the four titled grand application areas Health, Electronics, Energy, and the Environment is key to their outstanding functional behavior, which is currently at the basic research level and early TRLs 1-4. A pioneering example of this would be Electronics, where POM-based biomimetic processes using solution-processable ions and small molecules can, in principle, be combined with the catalytic activation of the latter on technical surfaces and at electrode interfaces to enable, e.g., radically new artificial information processing devices or next-gen molecular diagnostics on property-leveraged digital platforms. Scalability, commercialization from bench to production scale, and economic viability are the biggest challenges that POM-based materials and devices will face in order to impact these technological advances.

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Notes

The authors declare no competing financial interest.

Acknowledgements

K.M., S.K.P., A.K., and M.M. gratefully acknowledge funding by the DFG via project numbers 536022773 (2DPOMristor), 558671949 (CovPOMNet) and 495326276 (PhotOcellMatrix). J.W. is grateful to the Volkswagen Foundation for a Freigeist Fellowship and thanks Dr. Harald Knorke for his help with graphical material. M.N. acknowledges U.S. Department of Energy (DOE), Office of Basic Energy Sciences (BES), Division of Material Sciences and Engineering (MSE), under award DE SC0010802. T.N.P.-V. thanks KU Leuven (C14/23/088) and FWO (G025924N) for funding. M.S. thanks JSPS KAKENHI Grant-in-Aid for Transformative Research Area (A) "Supra-ceramics (JP22H05144)". S.G.M. acknowledges support through PID2022-141276OB-I00 and CEX2023-001286-S funded by MCIN/AEI/10.13039/501100011033 (Ministerio de Ciencia e Innovación/Agencia Estatal de Investigación, Spain) and the Antimicrobial Resistance (AMR) Connection of the Spanish National Research Council (CSIC).

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