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Confinement Effects of Coordination Cages on the Synthesis and Application of Polyoxometalates

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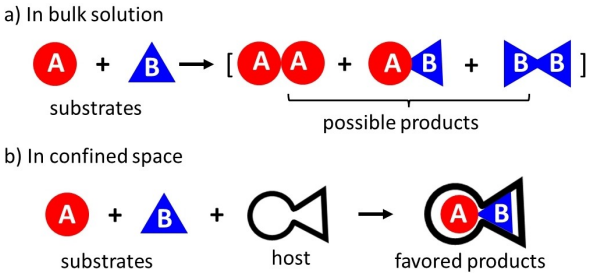
The confinement effects within coordination cages present powerful tools in modern chemistry, particularly for the synthesis and manipulation of complex molecules. This concept article reviews the use of coordination cages to stabilize and tune the properties of polyoxometalates (POMs), a class of nano-sized metallic clusters, expanding the focus beyond traditional organic reactions. The article provides a brief overview of coordination cages, POM chemistry and discusses the encapsulation of POMs in coordination cages, highlighting how these cages provide a confinement effect that enhances the stability and reactivity of POMs. Additionally, the concept of cavity-directed synthesis is explored as a method for creating labile POMs, which are often unstable in aqueous conditions, underlining its implications for supramolecular catalysis. Future research will focus on expanding the structures and applications of encapsulated POMs, as well as improving cage designs to unlock new cluster architectures.

Introduction

Enzymes have well-defined pockets in which chemical transformations occur, and this has been an inspiration for chemists for decades. This has resulted in a research field that is focused on the generation of hollow structures that can host smaller molecules. In the confined spaces of the host molecule, typically the properties of guest molecules are different, sometimes referred to as confinement effects.[1] In the context of chemical reactivity, these confinement effects can have different origins but usually arise from the restricted environments within host structures. For example, confinement could result in the pre-organization of the substrate in a conformation that is favorable for the reaction, resulting in rate enhancements.[2] In addition, the pre-organization of organic molecules that need to react can already result in rate enhancements, for example in Diels-Alder-type reactions.[3] As many of the cages reported have a preference for binding cationic guest molecules, reactions that proceed via positively charged intermediates or transition states are facilitated by the cage, making the cage act as a catalyst beyond just the organization of substrate molecules. An alternative strategy involves the encapsulation of transition metal complexes in cages as the reactive site, where the reactivity and selectivity are modulated by the confined space.[4]

The most simple form of inducing selectivity is for reactions in which a statistical mixture is formed, as shown in the cartoon figure where A and B are coupled (Scheme 1a). When substrates are isolated from the bulk solution and oriented in confined spaces in such a manner that only A can couple with B, the AB product can be obtained selectively (Scheme 1b). Co-encapsulation of two different guests for selective coupling has been explored, mostly using light for otherwise spin-forbidden coupling reactions.[5] Other factors such as spatial orientation, conformation sampling, and molecular interactions between host and guest can facilitate challenging and selective transformations that are difficult or impossible to achieve in bulk solutions.[6]



Scheme 1. A cartoon example of chemical reactions in a) bulk solution leads to a mixture, and b) confined space within host structures leads to selective A–B products, highlighting the confinement effects that promote the formation of the product that best fits the size and shape of the host.

Early research on confinement effects has been centered around hosts with a small cavity, including polycyclic ethers, cucurbiturils, calixarenes, cavitands, and cyclodextrins.[7] Particularly cucurbiturils and cyclodextrin hosts have hydrophobic cavities, while they are typically soluble in the aqueous phase and therefore are suitable for encapsulating hydrophobic guests. Although they can vary in cavity size and shape, they have been used as hosts for different chemical conversions. Among various other molecular hosts and porous materials, such as hydrogen-bonded molecular capsules,[8] metal-organic frameworks (MOFs),[9] and covalent organic frameworks (COFs),[10] the self-assembled coordination cages have drawn significant interest as an efficient bottom-up strategy for creating discrete hosts with nanometer-sized confined spaces.[11] These cages and porous frameworks (e.g., MOFs,

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COFs) provide nano-sized cavities for encapsulating guests, which enhances stability and improves chemical and physical performance.[9–11] However, porous frameworks, with their high surface areas, can accommodate a wider range of guests but have some drawbacks, such as limited control over the loading and distribution of guests, as well as restricted use of solid host-guest complexes in solution.[12] Self-assembled discrete cages, with precise molecular composition, exhibit high solubility in solution and provide cavities with well-defined sizes and geometries that allow for more controlled and precise encapsulation of guests. For example, they can precisely accommodate target polyoxometalates (POMs) within coordination cages for catalysis in water.[13]

Importantly, the nano-sized cavities of coordination cages open up significant opportunities for various applications, such as sensing, catalysis, drug delivery, gas separation, storage, and biological activity.[14] In catalysis, the confinement effect provided by coordination cages resulted in altered reactivity, selectivity, and/or stability.[15] For example, Fujita and colleagues reported that thermal [4 + 2] cycloaddition reactions (Diels-Alder reactions) are significantly accelerated (by 21-fold) within water-soluble Pd_6L_4 octahedral cages (Figure 1a), and also regioselective reactions were obtained for Diels Alder reactions on anthracene derivatives.[16] Raymond and co-workers used an anionic cage in water for selective organic transformations.[17] They also reported the same cage for the encapsulation of metal complexes and demonstrated the control of the selectivity in isomerization reactions by the second coordination sphere. Encapsulation of such metal complexes also resulted in increased stability of the catalysts.[18] These concepts of confinement-controlled metal catalysis can be extended to larger systems, in which multiple catalysts (and substrates) can be hosted.[19] For example, Reek and colleagues reported $M_{12}L_{24}$ spheres functionalized with 24-fold endohedral guanidinium hydrogen bonding motifs, to which catalysts with complementary hydrogen bonding units can be bound. Sulfonate functionalized gold complexes bound with much higher affinity (10^5 M^{-1}) compared to carboxylate analog (10^3 M^{-1}) (Figure 1b).

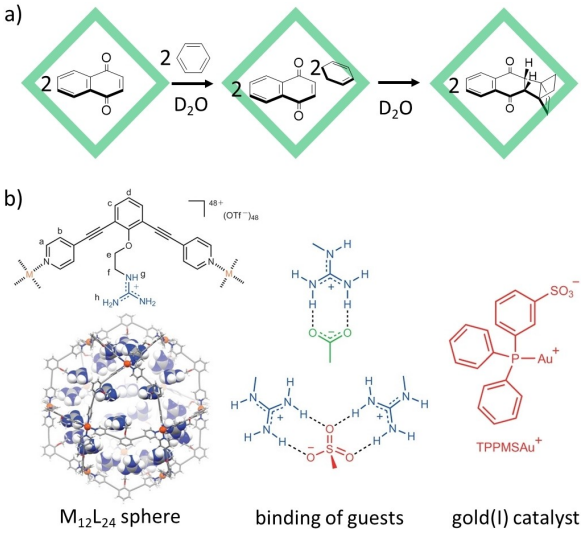
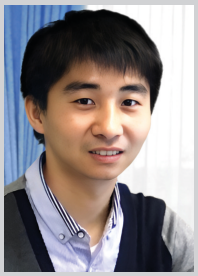


Figure 1. a) The water-soluble Pd_6L_4 octahedral cages provide an isolated space that promotes the Diels–Alder reaction between 1,4-naphthoquinone and 1,3-cyclohexadiene. b) $M_{12}L_{24}$ spheres with endohedral guanidinium-binding motifs that show different binding to sulfonate and carboxylate guests. Reprinted (adapted) with permission from ref. [19a]; Copyright: 2016 Springer Nature.



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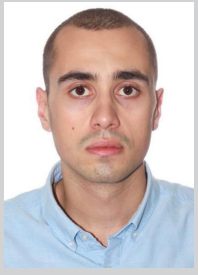

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Joost Reek obtained his PhD at the University of Nijmegen with Prof. Nolte (Supramolecular Chemistry). After a postdoc at the University of Sydney, he continued at the University of Amsterdam where he was promoted to Full Professor in 2006 and to Distinguished Faculty Professor in 2017. He is an elected member of the KNAW, the Royal Holland Society of Sciences and Humanities (KHMW), and the European Academy of Science. He is exploring new concepts in supramolecular transition metal catalysis, has a research program on catalysis for green energy applications, and explores supramolecular chemistry and catalysis for health-related applications.

Tatjana N. Parac-Vogt is a full Professor of Chemistry at KU Leuven. She is leading an interdisciplinary team performing research at the interface of inorganic chemistry, biochemistry, materials science and catalysis. Tatjana is the recipient of IUPAC 2023 Distinguished Women in Chemistry/Chemical Engineering award. She is a Fellow of the Royal Society of Chemistry and has been elected as a Chemistry Europe Fellow (Class 2020/2021), the highest award given by an association of European chemical societies.

The large cavities and the selective binding of the nanosphere enable efficient pre-organization of both the substrate and catalyst, with gold-based catalysts firmly anchored while the remaining binding sites are available to pre-organize the substrates. This pre-organization, combined with base-controlled substrate access to the catalysts, resulted in much higher (40-fold) reaction rates and substrate-selectivity in the cyclization reaction of acetylenic acid to enol lactone. The same $M_{12}L_{24}$ sphere can be used for controlled synthesis of iridium nanoparticles, which remain stable during catalysis.

These examples show that confinement effects imposed by coordination cages represent a powerful tool in modern chemistry, enabling molecular recognition, manipulation, and the synthesis of complex molecules.[2,6] For chemical conversions the coordination cages have been shown to facilitate reactivity and control selectivity, while for encapsulation of metal complexes, they can provide stabilizing effects. However, the extension of these phenomena to larger and more complex metallic clusters, such as polyoxometalates (POMs) has only recently been explored, yet it may hold a large potential. In this concept article, we focus on confinement effects induced by coordination cages on chemical phenomena, where the confinement of POM guests or multiple guests leads to new properties compared to those observed in bulk solutions. This article summarizes the current progress and challenges in supramolecular approaches based on the confinement effects of coordination cages for the encapsulation, synthesis, and applications of POMs. The article gives an introduction to coordination cages and POM chemistry, followed by a discussion of host-guest encapsulation of POMs within coordination cages. It then elaborates on the cavity-directed synthesis of labile POMs, and finally, it offers a summary and perspectives on future developments in this field.

Coordination Cages

Coordination cages are supramolecular metal-organic structures formed through the self-assembly of metal ions and multidentate organic ligands, resulting in well-defined three-dimensional structures with internal cavities.[20] For example, Fujita and co-workers reported water-soluble M_6L_4 octahedral cages with an internal cavity of approximately 900 $Å^3$.[21] These cages were formed in water through the self-assembly of four triangular ligands, 2,4,6-tris(4-pyridyl)-1,3,5-triazine, and six cis-protected palladium(II) or platinum(II) as building blocks (Figure 2a). Such coordination-driven self-assembly strategy features many advantages over traditional covalent synthesis, such as facile reaction conditions, self-correcting and defect-free assembly of the final thermodynamically most stable products.

Several methodologies for the design and preparation of coordination cages have been developed by the groups of Fujita, Stang, Raymond, Mirkin, Newkome, Nitschke and others.[20,22] The various design principles include the directional bonding method, the molecular paneling approach, the symmetry interaction strategy, subcomponent self-assembly, and the weak link strategy, and these have been well

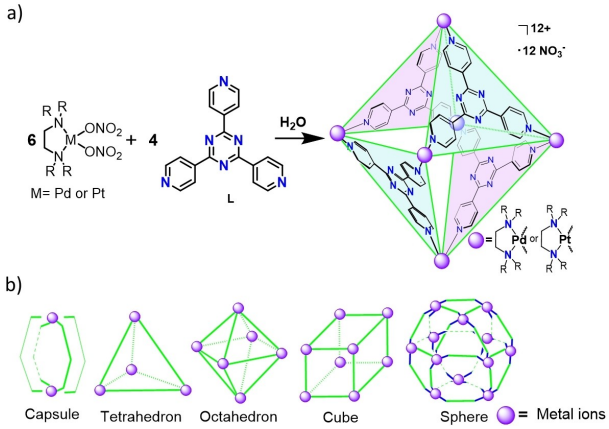

Figure 2. a) Self-assembly of M_6L_4 coordination cages reported by Fujita and b) common configurations of metal ions and organic ligands forming coordination cages.

summarized in review articles.[22] Generally, the shape and size of these structures and cavities are primarily determined by the geometric preferences of the metal ions and the shape of the multidentate organic ligands. The rapid development of coordination-driven self-assembly in the past decades resulted in a rich library of coordination hosts with different cavities, and different shapes such as capsules, tetrahedrons, octahedrons, cubes, and spheres (Figure 2b). Despite their complex structures, these coordination cages can be readily prepared through coordination-driven self-assembly. By modification of the organic ligands, the host cavity can be tuned, for example, to better accommodate target POM guests.

Polyoxometalates (POMs)

POMs are a diverse class of negatively charged inorganic clusters composed of metal-oxygen units, primarily involving transition metals like tungsten, molybdenum, and vanadium in their highest oxidation state.[23] POMs exhibit diverse features in terms of molecular composition, size, solubility, shape, charge density and redox potential. POMs are characterized by versatile and tunable compositions and the structure formed strongly depends on different conditions used during synthesis, such as stoichiometry of the components, solvent, pH, temperature, concentration and the type of countercations. The most common POM archetypes are shown in Figure 3, namely the Lindqvist $[M_6O_{19}]^{m-}$ (M = W or Mo), Anderson $[XM_6O_{24}]^{m-}$ (M =

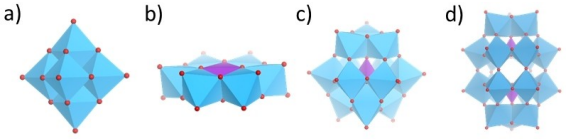

Figure 3. Most common POM archetypes: a) Lindqvist $[M_6O_{19}]^{m-}$ (M = W or Mo), b) Anderson $[XM_6O_{24}]^{m-}$ (M = Mo and X = Mn, Al or Te) c) Keggin $[XM_{12}O_{40}]^{m-}$ and d) Dawson $[X_2M_{18}O_{62}]^{m-}$ anions (M = W or Mo and X = P, Si or As).

Mo and X = Mn, Al or Te) Keggin $[XM_{12}O_{40}]^{m-}$ and Dawson $[X_2M_{18}O_{62}]^{m-}$ anions (M = W or Mo and X = P, Si or As). Moreover, further derivatization of POMs is possible by functionalizing with transition metals, lanthanides, and organic molecules.[24] For example, the hybrid macrocycles and cages combine POMs and carboxylate ligands, showcasing unique host-guest properties.[25] The structural diversity and associated variation in chemical properties make POMs interesting materials for various chemical and industrial applications.[26]

Due to their rich redox properties and Lewis acidity, POMs have found application as a catalyst in a range of organic transformations.[23e] They are also utilized in environmental remediation and industrial processes due to their catalytic efficiency.[26a] In the field of medicine, POMs exhibit potential as therapeutic agents due to their antibacterial and antiviral properties, and they are being explored as drug delivery systems.[26b–c] Additionally, POMs have been extensively used in materials science due to their electronic, optical, and magnetic properties, contributing to the development of advanced materials.[27]

Despite their promising applications, POMs still face several challenges that should be solved to fully harvest their potential. One significant challenge is the synthesis and stabilization of POMs with desired properties. The complex nature of POMs requires precise control over reaction conditions, and they can be sensitive to environmental factors, which affect their stability.[23c] Most POMs are characterized by high stability in solid-state, however, understanding their solution chemistry and extending their functions in solution are challenging tasks. Thus, stabilization and identification of POM species in solution are essential for their applications, especially in aqueous solutions. For instance, the Lindqvist $[Mo_6O_{19}]^{2-}$ POM tends to hydrolyze into its precursor (MoO_4^{2-}) in neutral aqueous solutions (Figure 4a). Strategies such as encapsulating POMs within coordination cages (Figure 4b) or incorporating them into robust matrices have been investigated as means to enhance their stability.[13] Furthermore, using POMs in practical applications on an industrial scale remains a challenge because of the complexities involved in scaling up their synthesis. Ensuring that POMs maintain their performance and stability under operational conditions is crucial for their use in applications. Additionally, the tuning of POM properties for specific applications requires a deep understanding of their structure-function relationships and meticulous control over their selective synthesis. With regard to this, developing supramolecular approaches for the templated synthesis, to stabilize and solubilize POMs provides an interesting alternative tool to solve these challenges. Furthermore, creating supramolecular POM assemblies might provide additional tools to tune the properties or might lead to dual-functional materials, resulting in systems with extended functions.

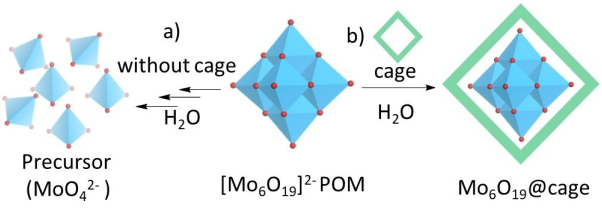

Figure 4. Hydrolysis of POMs and supramolecular host-guest stabilization: a) Lindqvist $[M_{O6}O_{19}]^{2-}$ POM hydrolyze into its precursor (MoO_4^{2-}) in neutral aqueous solutions, b) Lindqvist $[M_{O6}O_{19}]^{2-}$ POM stabilized in a coordination cage.

Host-Guest Encapsulation of POMs

Host-guest encapsulation offers a straightforward approach for enhancing the stability and functionality of POMs, in analogy to what has been observed for metal complexes. The use of coordination cages as hosts for anionic guests has received increasing attention, and binding strategies include the use of solvophobic effects, size and shape complementarity, as well as electrostatic interactions using the charge of the cage.[28] Given that POMs are negatively charged, possess a three-dimensional shape, and are highly polar, the positively charged coordination cages with a well-defined cavity could serve as ideal hosts for their encapsulation. To maximize host-guest binding in POMs@-cage complexes, a combination of multiple factors is typically explored. Once encapsulated, the local environment of the cage can play a key role in protecting POMs, improving their stability, and modulating their properties.

In 2007, Mizuno and colleagues reported the successful encapsulation of POMs within palladium-based molecular squares, $[(en^*)Pd(4,4'\text{-bpy})]_4(NO_3)_8$, (Figure 5).[13g] Their study demonstrated that the molecular square with a diameter of 1.2 nm was capable of completely encapsulating smaller POMs like $[W_6O_{19}]^{2-}$ and $[W_{10}O_{32}]^{4-}$ (small diameter about 1.0 nm) within the square. The cage could not accommodate the larger $[\alpha\text{-}SiW_{12}O_{40}]^{4-}$ (diameter of >1.2 nm) within its cavity, and as a result, a different geometry of the host-guest complex was formed. This shows that the encapsulation process is highly dependent on size compatibility between the guest POM and the cavity of the molecular square. In 2013, the same group investigated molecular hexagons formed by the ligand 3-bis(4-

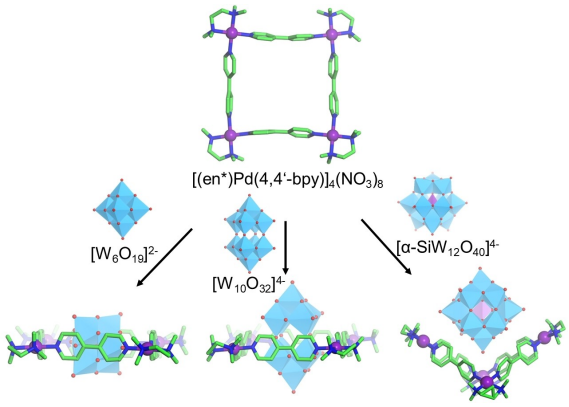

Figure 5. The crystal structure of coordination molecular square, $[(en^*)Pd(4,4'\text{-bpy})]_4(NO_3)_8$, where the smaller POMs, $[W_6O_{19}]^{2-}$ and $[W_{10}O_{32}]^{4-}$, are encapsulated within the cavity, while the larger POM, $[\alpha\text{-}SiW_{12}O_{40}]^{4-}$ is located outside the cavity. Reprinted (adapted) with permission from ref. [13g]; Copyright: 2012 American Chemical Society.

pyridylethynyl)benzene. The steric effects of supporting ligands on the corners of the structure, like ethylenediamine, tetramethylethylenediamine, and phosphinoethane, significantly influenced the structure that was formed, resulting in hexagonal (trimer), rhomboidal (dimer), and infinite-chain supramolecular complexes.[13d] The resulting structures also affected the size and shape of the cavities available for binding guests. The resulting molecular hexagons, with their expanded cavities, enabled the successful encapsulation of larger Keggin-type POMs such as $[\alpha\text{-}PW_{12}O_{40}]^{3-}$, demonstrating the potential of these coordination assemblies to host larger guest POM structures.

In 2012, Dai and colleagues reported a copper-based porous coordination polymer based on the tris(4-pyridyl)triazine ligand and a copper precursor. The porous structure contained squares in which Keggin-type POMs were encapsulated. The light-sensitizing properties of the tris(4-pyridyl)triazine ligand (Figure 6a)[13f] were used to make this an efficient heterogeneous photocatalyst for the degradation of methyl orange under near-neutral conditions. The approach capitalizes on the synergy between the photocatalytic properties of the copper-based coordination polymer and the catalytic efficiency of the electron-accepting Keggin POM.

Wang, Wu, and colleagues developed a strategy to create porous materials via electrostatic interactions, using discrete metallo-triangle as cation building blocks to accommodate anion POM (Figure 6b).[13b] They selected $[Mo_6O_{19}]^{2-}$ as the encapsulated POM, leveraging its suitable size (0.8 nm in diameter) and negative charge. This design aimed to harmonize the shape, size, and charge between the POM and the metallo-triangles. The resulting ionic complexes, $[Zn_3LC_3][Mo_6O_{19}]_3$, exhibited tunable vapor adsorption properties for organic molecules such as benzene and cyclohexane. By varying the length of the alkyl chains in the metallo-triangles, the adsorption properties could be tuned, showcasing the versatility in adsorption-based applications.

In 2012, Clever and colleagues reported the use of coordination cages with confined cavities for POM encapsulation. This represents an important example in the understanding of confinement effects between Pd_2L_4 coordination cages and POMs (Figure 7).[13e] They developed a self-assembled structure composed of four concave ligands and two Pd(II) ions in square-planar coordination, which could encapsulate the Lindqvist $[Mo_6O_{19}]^{2-}$ POM in solution with high specificity, forming a 1:1 host-guest complex as determined by an NMR spectroscopic titration study and electrospray ionization mass spectrometry. Upon crystallization, an unexpected structural transformation occurred, and X-ray diffraction revealed that the $[Mo_6O_{19}]^{2-}$ POM was no longer bound in a Pd(II) based cage. Instead, it was wrapped by a chiral, cyclic arrangement of three ligands, resulting in a species with the formula $[Mo_6O_{19}]^{2-}$@-$(ligand)_3 + 2H^+$. This transformation underscores that POMs can be stabilized in solution by the host architecture, while the crystallization of the cage with the POM may lead to a rearrangement of the structure with associated different properties. This is something important to be aware of when developing cages for POM encapsulation.

In 2018, Sun and colleagues developed a new water-soluble Pd_4L_2coordination cage that increased both the size and adaptability of the cavity compared to the M_6L_4 cages reported by Fujita, enabling it to host a broader range of guests, including polyaromatic molecules and multiple POMs such as $[Mo_6O_{19}]^{2-}$ or $[Mo_8O_{26}]^{4-}$ (Figure 8).[13c] The cage was self-

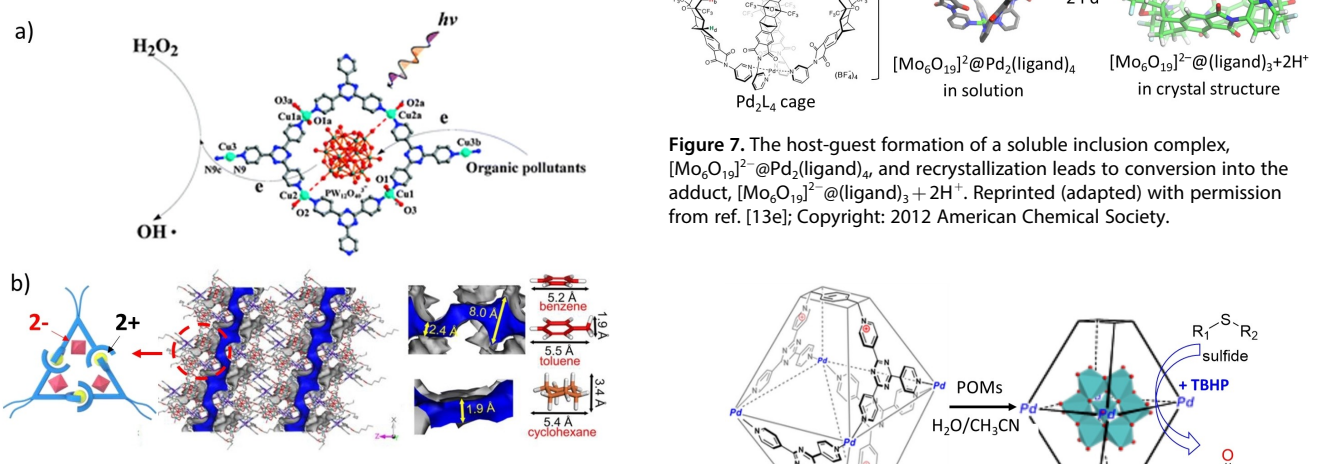

Figure 6. a) Encapsulation of Keggin-type POMs in a copper-based coordination polymer for photocatalytic degradation of methyl orange. Reprinted (adapted) with permission from ref.[13f]; Copyright: 1996 Royal Society of Chemistry. b) side view of packing diagram and channel of composite, $[Zn_3LC_3][Mo_6O_{19}]_3$ with a schematic of the simulated cross-section and VOCs. Reprinted (adapted) with permission from ref. [13b]; Copyright: 2022 Wiley-VCH.

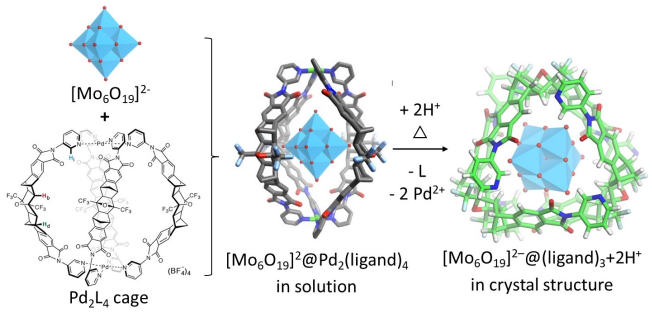

Figure 7. The host-guest formation of a soluble inclusion complex, $[Mo_6O_{19}]^{2-}$@$Pd_2(ligand)_4$, and recrystallization leads to conversion into the adduct, $[Mo_6O_{19}]^{2-}$@$(ligand)_3 + 2H^+$. Reprinted (adapted) with permission from ref. [13e]; Copyright: 2012 American Chemical Society.

Figure 8. Design of Pd_4L_2 cage: Featuring an enlarged cavity for hosting polyaromatic molecules and POMs. Reprinted (adapted) with permission from ref. [13c]; Copyright: 2018 American Chemical Society.

assembled using 2,4,6-tri(4-pyridyl)-1,3,5-triazine (TPT) ligands and p-xylene bridges, replacing two palladium corners compared to previously reported cages, such as the Pd_6L_4 cage. The encapsulation of POMs within the Pd_4L_2 coordination cage renders them soluble in a mixture of CH_3CN and H_2O, representing a significant advancement in the host-guest stabilization of POMs for applications in aqueous solutions. Notably, in selective desulfurization reactions, the encapsulation of POMs within the Pd_4L_2 cage showed a significant increase in conversion rates and selectivity compared to the free POM, leading to the formation of sulfoxides over sulfones. Recently, the same group extended the host to adaptive macrocycle-based coordination cages.[13h–i] This demonstrates the potential of these systems to improve POM catalysis through molecular confinement.

Cavity-Directed Synthesis of Labile POMs

The term "cavity-directed synthesis" refers to a synthetic strategy that utilizes the confined space within a molecular cage to influence the reactivity, stability, and selectivity of encapsulated guests. When reactions are carried out in self-assembled cages, the products will be steered to those that fit and are shaped complementary to the cavity, providing tools to control selective synthesis.[29] The tunable geometry, size, and functional groups of coordination cages make them versatile tools and allow a diversity of structures to be obtained. This approach is particularly effective in the synthesis of complex structures within coordination cages, including both organic and inorganic molecules, such as POMs.

In 2000, Kusukawa, Fujita, and colleagues reported a cavity-directed synthesis of cyclic siloxane trimers within a self-assembled M_6L_4 coordination cage, whereas such trimers are usually unstable (Figure 9a).[29a] The molding effect of the cage not only facilitated the formation of the cyclic trimers but also acted as a stabilizing shield, preventing their decomposition, which typically occurs in bulk solution. Later, work by the same group has shown that the synthesis could be directed to other structures by changing the shape of the directing cage.[29b] Recently, Takezawa, Fujita, and colleagues extended this concept to selectively synthesize a methylene-bridged arene trimer, where the confined cavity of the M_6L_4 cage prevents uncontrolled polymerization.[29c] These examples show that reactive species can be formed and isolated in a controlled, nanoscale environment in ways not feasible under typical conditions.

The cavity of a coordination cage can be also used to manipulate and stabilize reactive sulfur clusters. In 2017, Yoshizawa and colleagues demonstrated this by encapsulating sulfur clusters within an M_2L_4 polyaromatic capsule (Figure 9b).[30] This encapsulation enabled the precise formation and characterization of otherwise unstable sulfur allotropes, such as cyclic S_6 and S_8 clusters, using electrospray ionization time-of-flight mass spectrometry. Remarkably, this system also allowed the formation and stabilization of a rare cyclic S_{12} cluster, which forms upon light irradiation. These examples

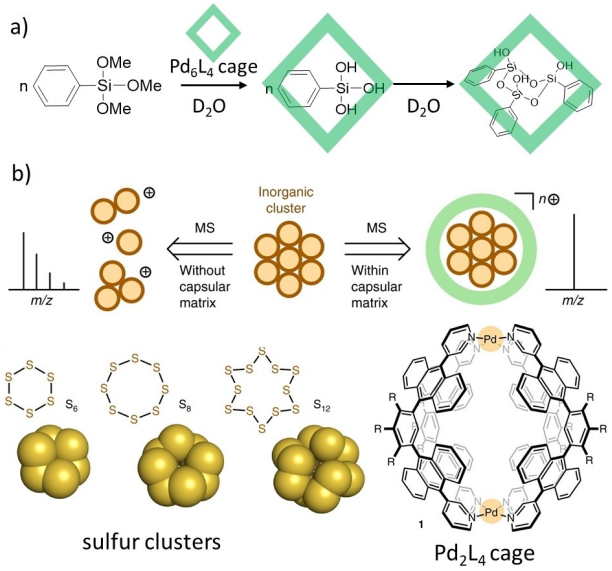

Figure 9. Cavity-directed synthesis in a) organic synthesis of poly-silanols and b) formation of sulfur clusters. Reprinted (adapted) with permission from ref. [29a]; Copyright: 2000 American Chemical Society. Reprinted (adapted) with permission from ref. [30]; Copyright: 2017 Springer Nature.

highlight the ability of coordination cages to protect these delicate clusters not only during analysis but also in ambient conditions.

Liu, Parac-Vogt, and colleagues recently applied the concept of cavity-directed synthesis for the preparation of labile Lindqvist POMs, $[M_6O_{19}]^{2-}$ (M=Mo or W), using a water-soluble Pt_6L_4 coordination cage (Figure 10).[13a] These POMs are known to be hydrolytically unstable, and as a result, cannot exist in notable concentrations in pure aqueous solution.[23c] In bulk aqueous solution, their precursors, molybdate and tungstate anions, tend to self-condense into various POM structures across all pH ranges, but the formation of Lindqvist POMs is generally unfavorable. For decades, these POMs could only be synthesized in aqueous solutions containing a high percentage of organic solvents or in the presence of organic macrocycles, such as cyclodextrins.[31] Using cavity-directed synthesis, these elusive POMs were prepared by condensing molybdate or tungstate precursors at room temperature within the confined cavity of a water-soluble $Pt_6L_4(NO_3)_{12}$ coordination cage. This encapsulation not only stabilized the labile POMs in water but also enhanced their catalytic properties. The resulting POM@-

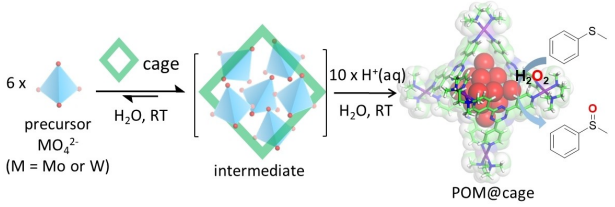

Figure 10. Cavity-directed synthesis of labile Lindqvist POMs, $[M_6O_{19}]^{2-}$ (M=Mo or W), using a water-soluble Pt_6L_4 coordination cage, and applied in selective sulfoxidation reactions. Reprinted (adapted) with permission from ref. [13a]; Copyright: 2024 Wiley-VCH.

cage complex demonstrated excellent catalytic efficiency for selective sulfoxidation reactions using H_2O_2 as a green oxidant in pure aqueous media. These results showcase the potential confinement effects of coordination cages in the synthesis of labile POMs, enhancing their applicability for environmentally friendly catalysis.

Summary and Outlook

In summary, confinement effects induced by coordination cages offer unique advantages for the synthesis and application of POMs. By providing a controlled nanometer-sized environment, POMs of specific dimensions can be bound in these cages, thereby significantly enhancing the stability of the POMs that are often prone to hydrolysis which leads to structural degradation in water. In addition, well-defined cavities of coordination cages can be used for cavity-directed synthesis of POMs, facilitating the synthesis of otherwise inaccessible POM structures. Potentially, this may lead to POMs with tailored properties in diverse application areas including catalysis. Although the initial examples show great promise, some challenges remain in advancing POM chemistry through the confinement effects of coordination cages. First, current research primarily focuses on symmetric POMs, such as Lindqvist and Keggin structures. Expanding this scope to include asymmetric or metal-substituted POMs could unlock novel behaviors, requiring more precise designs and deeper studies on supramolecular stabilization. Second, the modulation of POM properties within cages is underexplored, with most studies maintaining the intrinsic characteristics of POMs. Future work should investigate how cages can modify POM functionalities, such as inducing chirality or enhancing electronic properties. Third, the reliance on palladium and other noble metal-based coordination cages for POM encapsulation presents a limitation. Developing noble metal-free cages for POM encapsulation could provide more sustainable and cost-effective alternatives. Finally, expanding applications beyond catalysis, particularly in fields like optoelectronics, magnetism, and biomedicine, could lead to groundbreaking innovations. In conclusion, while the field has made great progress, future efforts must focus on expanding the diversity of POM structures, deepening our understanding of how cages influence POM behavior, and exploring applications beyond catalysis. This will drive further advancements in metal-oxo chemistry and open up new practical applications.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

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