POLYOXOMETALATES

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Fluorescence-active nanorod-like triads assembled from organically-derivatized polyoxometalates

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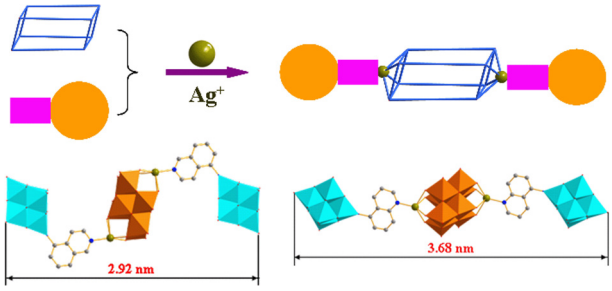
ABSTRACT: Two monosubstituted organoimido hexamolybdates containing isoquinoline or quinoline were successfully synthesized. Through the coordination driving of silver(I) ions, the obtained organoimido-derivatized hexamolybdates can assemble with β-octamolybdate in a controlled manner to form nanorod-like triads. Unlike the isolated polyoxometalates before assembly, nanosized polyoxometalate assemblies can exhibit interesting fluorescence activities.



KEYWORDS: polyoxometalate, nanorod-like triads, fluorescence, coordination, self-assembly

Coordination-driven self-assembly [1–5] has been extensively investigated as a means to construct supramolecules that vary in size and topology, including discrete nanostructures—such as rods, squares, rings, tetrahedrons, cubes [5], and cages [6–9]—polymers [10], two-dimensional (2D) nanosheets [11, 12], and metal-organic frameworks (MOFs) [13–15]. This is because the resulting multicomponent complexes have potential applications in materials science [16–19], catalysis [20, 21], molecular recognition [22], and biomedicine [23, 24]. The incorporation of high-nuclearity metal clusters into metallosupramolecular structures for developing multifunctional organic–inorganic hybrid materials has become a research hotspot [25]. Polyoxometalates (POMs), which represent a rich class of metal-oxygen clusters with diverse structures [26, 27] and fascinating photonic, electronic, and magnetic properties [27], have attracted considerable attention in this regard. A striking feature of POMs is the nucleophilicity of outer oxygen atoms, which can be directly coordinated with some metal ions to build up supramolecular structures [28, 29]. In particular, lacunary POMs are effective coordinators because of the strong chelating properties of multiple nearly planar oxygens with increased negative charge density [30–33].

The introduction of remote reactive groups into POMs via covalent methods can yield diverse metal–organic ligands that can be used as novel building blocks to construct sophisticated structures [34–40]. Several coordination polymers based on functionalized POMs and various metal ions have been obtained in the past decades [34–36]. For example, Peng et al. [36] and Hasenknopf et al. [37] reported a coordination-linked molecular dumbbell containing two hexamolybdate clusters and a coordinated triangle based on organically-derivatized hexavanadate derivatives, respectively. Moreover, our group [38] reported a paddle-wheel tetrapolyoxometalate derived from organoimido hexamolybdate containing carboxylic acid. Further, Yang et al. [39, 40] reported an octamer and two MOFs based on organically-derivatized Anderson-type POMs. However, to the best of our knowledge, controlled coordination-driven self-assembly of different POMs into discrete supramolecular structures, which not only affords nanomolecules but also combines the properties of different POM clusters for functional demands, has been rarely reported.

In this study, we report a coordination-driven self-assembly of Lindqvist-type organoimido hexamolybdates containing remote coordination groups with octamolybdate clusters to form nanorod-like POM triads (Scheme 1) with interesting fluorescence activities.

POM-based ligands $[Mo_6O_{18}(NC_9H_6\text{-}2\text{-}N)][N(C_4H_9)_4]_2$ (**Mo_6-iQ**) and $[Mo_6O_{18}(NC_9H_6\text{-}1\text{-}N)][N(C_4H_9)_4]_2$ (**Mo_6-Q**) were easily obtained by the N,N'-dicyclohexylcarbodiimide (DCC) protocol [41]. As shown in Fig. 1, **Mo_6-iQ** and **Mo_6-Q** exhibit the common structural feature of monosubstituted organoimido hexamolybdates [42–44], in which one terminal oxo is substituted by one organoimido ligand (being isoquinolimido in **Mo_6-iQ** and quinolimido in **Mo_6-Q**). The major difference between **Mo_6-iQ** and **Mo_6-Q**, which are structural isomers, is the heterocyclic nitrogen position, which is at the 2-site and 1-site in **Mo_6-iQ** and **Mo_6-Q**, respectively. These rationally designed ligands are expected to

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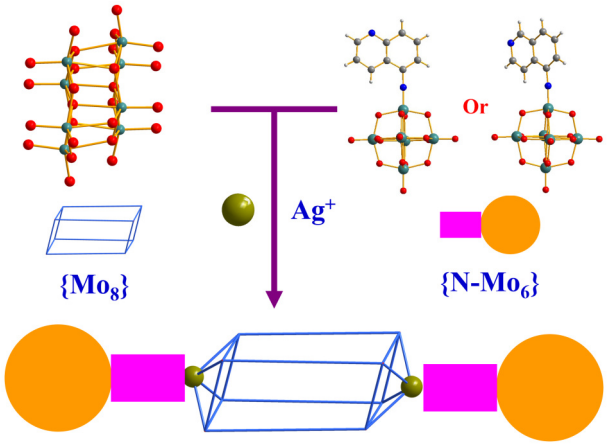

Scheme 1 Pictorial illustration of coordination driven assembly of isoquinolimido or quinolimido hexamolybdates with β-octamolybdate into nanorod-like triads.

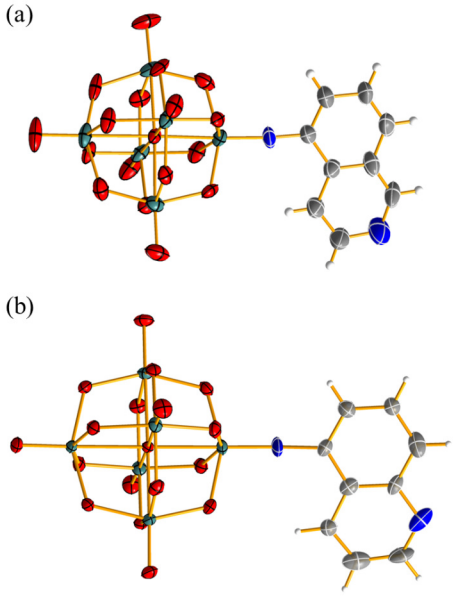

Figure 1 ORTEP drawing of cluster anions of (a) **Mo_6-iQ** and (b) **Mo_6-Q**. Mo teal, O red, N blue, C gray, H white. $[N(C_4H_9)_4]^+$ cations are omitted for clarity.

exhibit diverse structural behaviors during assembly with metal ions.

The silver(I) ion, which shows high affinity not only to O donor ligands [45–47] but also to N donor ligands [5], is chosen as the coordination linker. The coordination-driven self-assembly occurred when an acetonitrile solution of silver nitrate was added to the acetonitrile solution of equimolar **Mo_6-iQ** or **Mo_6-Q** and β-octamolybdate, giving rise to the corresponding nanorod-like POM triad $\{[Mo_6O_{18}(NC_9H_6\text{-}2\text{-}N)Ag]_2Mo_8O_{26}\}[N(C_4H_9)_4]_6$ (**(Mo_6-iQ-Ag)$_2$-Mo_8**) or $\{[Mo_6O_{18}(NC_9H_6\text{-}1\text{-}N)Ag]_2Mo_8O_{26}\}[N(C_4H_9)_4]_6$ (**(Mo_6-Q-Ag)$_2$-Mo_8**), respectively (Fig. 2).

The assembly products were characterized using infrared spectra; characteristic absorption bands of monosubstituted organoimido hexamolybdates and octamolybdate are clearly present (Figs. S1 and S2 in the Electronic Supplementary Material (ESM)). Strong peaks located at 953 and 794 cm^{-1} for **(Mo_6-iQ-Ag)$_2$-Mo_8** and at 952 and 796 cm^{-1} for **(Mo_6-Q-Ag)$_2$-Mo_8** are assigned to the stretching vibrations of Mo–O_t bonds and Mo–O_b–Mo in Lindqvist-type

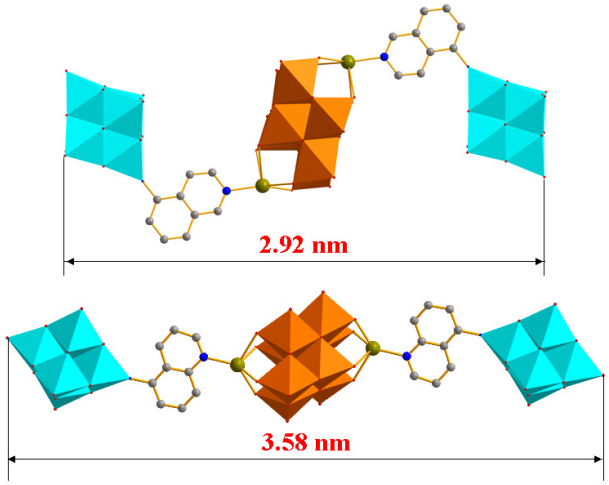

Figure 2 Combined polyhedral and ball-and-stick representation of nanorod-like POM triads **(Mo_6-iQ-Ag)$_2$-Mo_8** (top) and **(Mo_6-Q-Ag)$_2$-Mo_8** (bottom). The blue octahedron represents imido hexamolybdates ($Mo_6O_{18}N$), while the orange polyhedron represents β-octamolybdate (Mo_8O_{26}). $[N(C_4H_9)_4]^+$ cations, H atoms of isoquinoline and quinoline, as well as lattice solvent molecules are omitted for clarity.

clusters, respectively. Moreover, obvious strong shoulder peaks around 981 cm^{-1} for **(Mo_6-iQ-Ag)$_2$-Mo_8** and 978 cm^{-1} for **(Mo_6-Q-Ag)$_2$-Mo_8** are attributed to the typical absorption for mono-organoimido substitution, which has a slightly hypsochromic shift compared with that in **Mo_6-iQ** and **Mo_6-Q**, resulting from the isoquinoline and quinoline group coordination effect. Concomitantly, some new peaks appeared at 934 and 904 cm^{-1} in **(Mo_6-iQ-Ag)$_2$-Mo_8** and at 928 and 900 cm^{-1} in **(Mo_6-Q-Ag)$_2$-Mo_8**, attributable to Mo–O_t stretching vibrations in octamolybdate. Ultraviolet–visible (UV–Vis) absorption spectra (Fig. S3 in the ESM) show that the lowest energy electronic transition absorption bands have bathochromic shift to 378.5 and 375 nm for **(Mo_6-iQ-Ag)$_2$-Mo_8** and **(Mo_6-Q-Ag)$_2$-Mo_8**, respectively. In addition, the electrospray ionization mass spectrometry (ESI-MS) spectra of **(Mo_6-iQ-Ag)$_2$-Mo_8** and **(Mo_6-Q-Ag)$_2$-Mo_8** are almost identical because they are isomers with the same molecular weight and explicitly exhibit peaks corresponding to $[Mo_6O_{18}(NC_9H_6N)]^{2-}$ (calcd. 502.9 *m/z*), $[Mo_6O_{18}(NC_9H_6N)H]^-$ (calcd. 1006.8 *m/z*), $[Mo_6O_{18}(NC_9H_6N)NBu_4]^-$ (calcd. 1248.3 *m/z*), $[Mo_4O_{13}NBu_4]^-$ (calcd. 834.2 *m/z*), and $[Mo_4O_{13}Ag]^-$ (calcd. 699.6 *m/z*) (Figs. S4 and S5 in the ESM). The ^1H nuclear magnetic resonance (NMR) spectra of **(Mo_6-iQ-Ag)$_2$-Mo_8** and **(Mo_6-Q-Ag)$_2$-Mo_8** display resolved signals, attributable to quinoline and isoquinoline ligands and Bu_4N^+ (Figs. S6 and S7 in the ESM). Notably, the integration ratio of the ligands and Bu_4N^+ is 1:3, indicating that the stoichiometry among the organoimido hexamolybdates, β-octamolybdate, and silver ions is 2:1:2 in **(Mo_6-iQ-Ag)$_2$-Mo_8** and **(Mo_6-Q-Ag)$_2$-Mo_8**.

The assembly structures of **(Mo_6-iQ-Ag)$_2$-Mo_8** and **(Mo_6-Q-Ag)$_2$-Mo_8** are determined by single-crystal X-ray diffraction analysis. As shown in Fig. 3, the β-octamolybdate anion can be regarded as a bi-lacunary decamolybdate, and four terminal oxo groups—almost arrayed as a plane—display the chelation effect. Indeed, two silver ions occupy the lacunary sites, and each is caught by four terminal oxo groups. The respective bond lengths of Ag–O are 2.322, 2.380, 2.789, and 2.660 Å in **(Mo_6-iQ-Ag)$_2$-Mo_8** (Fig. 3(c)) and 2.418 (2.325), 2.320 (2.426), 2.543 (2.830), and 2.768 (2.489) Å in **(Mo_6-Q-Ag)$_2$-Mo_8** (Fig. 3(d)); the bond lengths are much longer than those of Mo–O_b due to the weaker Ag–O coordination bond than the

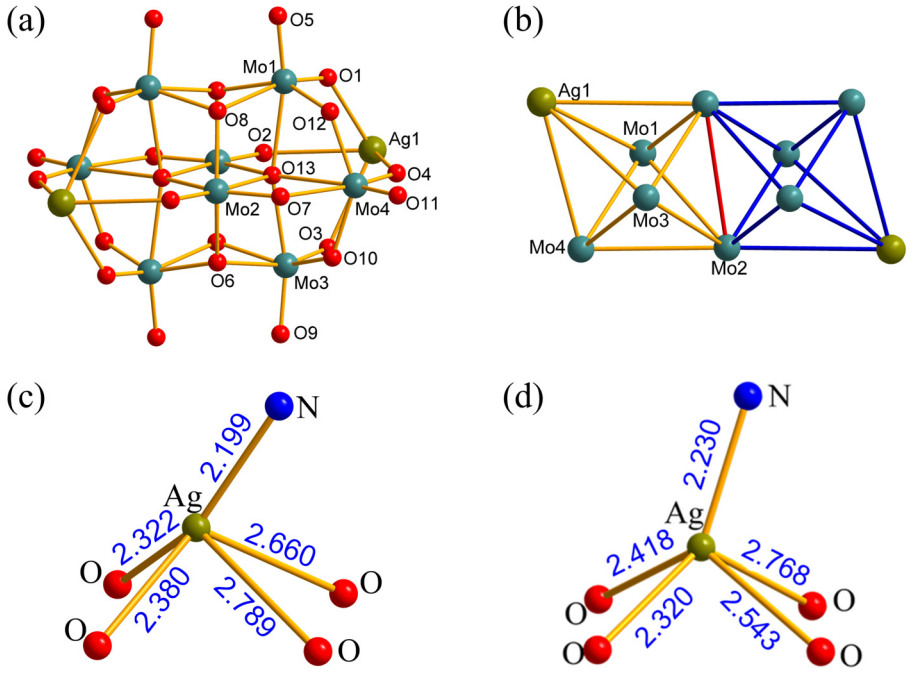

Figure 3 (a) The coordination structures of β-octamolybdate anion and two silver ions and (b) the forming decanuclear structure. The coordination environments of silver ions within compounds (c) $(Mo_6\text{-}iQ\text{-}Ag)_2\text{-}Mo_8$ and (d) $(Mo_6\text{-}Q\text{-}Ag)_2\text{-}Mo_8$.

Mo–O bond as well as the larger radii of silver than molybdenum. In addition, each silver ion coordinates with one heterocyclic nitrogen atom of the organoimido-substituted hexamolybdate, and the bond lengths of Ag–N are 2.199 and 2.230 (2.187) Å in $(Mo_6\text{-}iQ\text{-}Ag)_2\text{-}Mo_8$ and $(Mo_6\text{-}Q\text{-}Ag)_2\text{-}Mo_8$, respectively. Overall, the three POM clusters are nearly aligned in a straight line in both $(Mo_6\text{-}iQ\text{-}Ag)_2\text{-}Mo_8$ and $(Mo_6\text{-}Q\text{-}Ag)_2\text{-}Mo_8$. Further, these two triad assembly structures can be viewed as nanosized rods with lengths of ca. 2.92 and 3.58 nm for $(Mo_6\text{-}iQ\text{-}Ag)_2\text{-}Mo_8$ and $(Mo_6\text{-}Q\text{-}Ag)_2\text{-}Mo_8$, respectively.

In the packing diagram of $(Mo_6\text{-}iQ\text{-}Ag)_2\text{-}Mo_8$, each triad assembly is connected to the neighboring triads via hydrogen bonding interaction (C–H···O; Table S1 in the ESM), forming a supramolecular 1D chain (Fig. S8 in the ESM). In addition, a 2D-plane supramolecular structure is formed in the crystalline state of $(Mo_6\text{-}iQ\text{-}Ag)_2\text{-}Mo_8$ via the C–H···O hydrogen bonding (Fig. S9 in the ESM). In contrast, a dimer was formed in the crystal packing of $(Mo_6\text{-}Q\text{-}Ag)_2\text{-}Mo_8$ via the hydrogen bonding interaction (Table S2 and Fig. S10 in the ESM).

We further investigated the fluorescent properties of $(Mo_6\text{-}iQ\text{-}Ag)_2\text{-}Mo_8$ and $(Mo_6\text{-}Q\text{-}Ag)_2\text{-}Mo_8$. POMs are usually considered as fluorescence quenchers due to their special ability to store electrons [48]. We found that monosubstituted organoimido hexamolybdate containing a 6-nitroquinoline moiety exhibits no fluorescence [49]. Interestingly, we found that the assembled POM triads $(Mo_6\text{-}iQ\text{-}Ag)_2\text{-}Mo_8$ and $(Mo_6\text{-}Q\text{-}Ag)_2\text{-}Mo_8$ clearly display blue luminescence in N,N-dimethylformamide (DMF) solution with peaks at 455.4 and 480.6 nm, respectively (Fig. 4), although the building units of organoimido hexamolybdates, β-octamolybdate, and silver nitrate alone have no fluorescence in DMF solution. Previous studies [50, 51] have reported that organically-derivatized polyoxovanadates demonstrate luminescence properties by replacing tetrabutylammonium (TBA) counterions with protons and sodium ions. Therefore, the photoluminescence in this study may arise from an increase in the effective quinoline excimers, not only due to partial replacement of TBA by Ag^+ but also because the interferential effect of TBA is blocked off by β-octamolybdate.

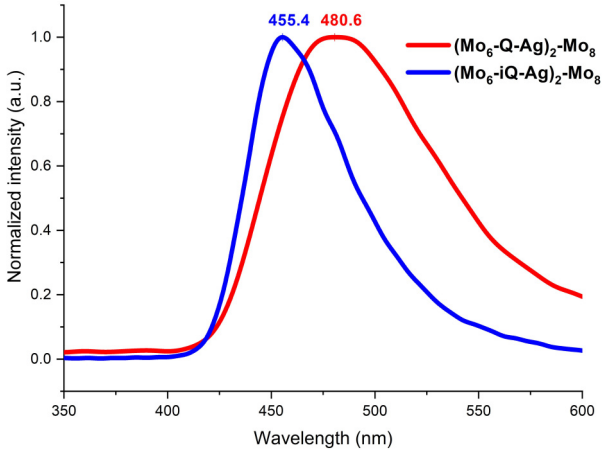

Figure 4 The fluorescence emission spectra of $(Mo_6\text{-}iQ\text{-}Ag)_2\text{-}Mo_8$ (in 2.0×10^{-4} mol/L DMF solution with excitation wavelength of 330 nm) and $(Mo_6\text{-}Q\text{-}Ag)_2\text{-}Mo_8$ (in 1.0×10^{-3} mol/L DMF solution with excited wavelength of 320 nm).

In summary, we successfully synthesized two fluorescence-active nanorod-like POM triads by the coordination-driven self-assembly of two POM types, i.e. Lindqvist-type organoimido hexamolybdate and β-octamolybdate. The length of the discrete assembly structures is tunable by varying the binding sites of POM-based ligands. This work offers a new approach to controllably assemble different POM types into discrete supramolecular architectures. Extension of this approach toward lacunary POMs and their potential applications in nanoscale assembly, fluorescence sensing and imaging, and catalysis are in progress in our laboratory.

Electronic Supplementary Material: Supplementary material (experimental details, IR, UV–Vis, ESI-MS, ^{1}H NMR spectra, packing diagrams, tables of hydrogen bonding, and CCDC Nos.

2517248 (**Mo_6-iQ**), 2514736 (**Mo_6-Q**), 2514833 ((**Mo_6-iQ-Ag)$_2$-Mo_8**), and 2514835 ((**Mo_6-Q-Ag)$_2$-Mo_8**)) is available in the online version of this article at https://doi.org/10.26599/POM.2025.9140106.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. Author Yongge Wei is the Editor-in-Chief of this journal, but he is not involved in the peer-review or decision of this article.

Author contribution statement

C.-L. L.: Data curation, project administration, validation, experimental design, writing – original draft. M.-Y. C.: Experiment, data curation, validation. J. H. and R. N. N. K.: Data curation, writing – review & editing. Y. G. W.: Project administration, funding acquisition, writing – review & editing. All the authors have approved the final manuscript.

Use of AI statement

None.

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