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Cubic Polyoxometalate−Organic Molecular Cage

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Abstract: Tris(hydroxymethyl)aminomethane (Tris) was successfully grafted onto the surface of a Ni_6-substituted polyoxotungstate formed in situ to further generate a three-connected polyoxometalate building block. The cooperative assembly of Tris functionalized three-connected building blocks and rigid 1,3,5-benzenetricarboxylate gave rise to an unprecedented cubic polyoxometalate−organic molecular cage with high thermal and hydrothermal stability.

Cage molecules are of great interest because of their remarkable structural characteristics and well-defined cavities that (1) can incorporate various guest species for chemical reactivity;[1] (2) can be used for gas separation and storage;[2] and (3) may exhibit unusual spectroscopic, magnetic, and catalytic properties.[3] During the past few decades, the work on self-assembly of coordination complexes has produced many elaborate metal−organic cages with various sizes and shapes, such as tetrahedral,[4] octahedral,[5] cubic,[6] dodecahedral,[7] truncated tetrahedral,[8] cuboctahedral coordination cages,[9] and so on.[10] Most of those coordination cages are based on metal ions as vertexes. Using molecular secondary building blocks (SBUs) as large vertexes to construct coordination cages is particularly interesting.[11] At present, the SBUs in the reported coordination cages are mainly focused on metal carboxylate clusters.[11,12]

Polyoxometalates (POMs) are attractive inorganic building blocks owing to their nanosize and tunable acid/base, redox, magnetic, catalytic, and photochemical properties.[13] The design and synthesis of POM−organic cages might merge POM's merits to generate extra-large nanosized cages with special properties. Up to now, though many large POM aggregates were known, nearly all of them are built up from POMs joined together via oxygen−metal−oxygen bonds. Recently, Schmitt *et al.* studied the formation of POMs in the presence of organicarsonic and phosphonic acids and obtained several novel POM capsules.[14] Additionally, Cronin and Liu *et al.* have tethered tris(hydroxy-methyl)aminomethane (Tris) ligands onto the surface of Anderson-type and V_3-capped Wells−Dawson-type POMs to make a new class of POM-based inorganic−organic amphiphiles for constructing a series of supermolecular vesicles.[15] Furthermore, it is notable that Dolbecq *et al.* successfully made a series of rare POM−organic frameworks (POMOFs[16]) based on metal capped $\{PMo_{12}O_{40}\}$ ions as SBUs.[17] Nevertheless, as POMs have high negative charges and oxygen-rich compositions, the construction of POM−organic cages remains unknown to our knowledge. So the synthesis of POM−organic cages is an attractive but challenging topic.

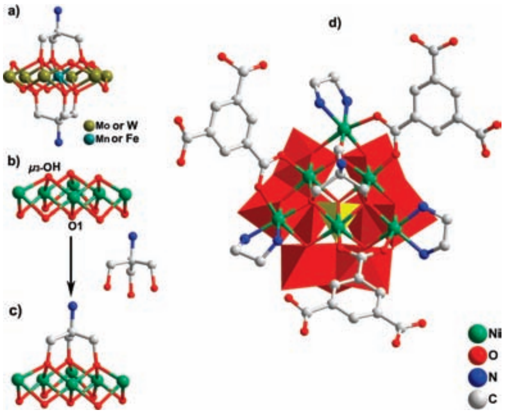

Figure 1. (a) Tris-grafted Anderson-type POMs. (b) **Ni_6** core. (c) Tris-grafted **Ni_6** core. (d) Coordination mode between Tris-grafted **Ni_6PW_9** and BTCs in **1**. WO_6 octahedron, red; PO_4 tetrahedron, yellow.

During the past two years, a kind of novel Ni_6-substituted POMs $[Ni_6(\mu_3\text{-}OH)_3(H_2O)_6(L)_3(B\text{-}\alpha\text{-}PW_9O_{34})]$ (**Ni_6PW_9**, L = en/enMe) was made by us, and they were used as SBUs to construct a series of POMOFs by replacing the terminal water ligands of **Ni_6PW_9** with different carboxylates.[18] Now, inspired by the above-mentioned work of Cronin and Liu, we are aware that **Ni_6PW_9** might be further covalently functionalized by a Tris ligand. This is because the flat arrangement of the Ni_6 core on **Ni_6PW_9** is similar to that of Anderson-type POMs, which are geometrically well-suited to be grafted by Tris (Figure 1a−c). It is well-known that the development of organic−inorganic hybrid POMs via covalent functionalization has attracted extensive interest.[15] Therefore, we aim at covalently anchoring Tris to **Ni_6PW_9** in an attempt to modulate the structures and properties of the obtained POMOFs. Further experimental efforts enabled the successful grafting of Tris onto the surface of **Ni_6PW_9** and production of an unprecedented cubic POM−organic molecular cage $[Ni(en)_2(H_2O)_2]_6\{Ni_6(Tris)(en)_3\ (BTC)_{1.5}(B\text{-}\alpha\text{-}PW_9O_{34})\}_8\cdot 12en\cdot 54H_2O$ (**1**, en = ethylenediamine, BTC = 1,3,5-benzenetricarboxylate).

The structure of **Ni_6PW_9** can be described as a well-known trilacunary Keggin B-α-$[PW_9O_{34}]^{9-}$ unit capped by a hexanuclear nickel cluster (Ni_6) (Figure S1). The Ni_6 core of **Ni_6PW_9** is built from three truncated $\{Ni_3O_3(OH)\}$ cubanes *via* sharing one edge with each other (Figure 1b), with all sharing a common vertex (O1 atom), forming a flat triangle configuration with three μ_3-OH groups on one side. Similar to the flat arrangement of Anderson-type POMs (Figure 1a), the three μ_3-OH groups on Ni_6 are the potential reactive sites that might be substituted by the alkyls of Tris. Thus, we introduced the Tris into the well-defined hydrothermal reaction conditions for making **Ni_6PW_9**,[18] resulting in the formation of **1**.

X-ray analyses reveal that **1** crystallizes in the hexagonal space group $R\bar{3}$ and exhibits a POM−organic molecular cage constructed from 8 Tris-grafted **Ni_6PW_9** SBUs and 12 BTC linkers. The coordination mode of **Ni_6PW_9** with Tris and BTC is shown in

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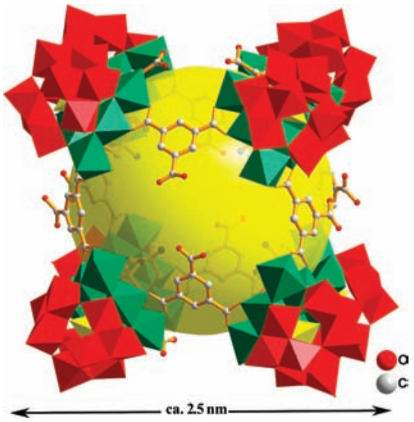

Figure 2. Structure of molecular cage in **1**. WO_6 octahedron, red; PO_4 tetrahedron, yellow; NiO_6/NiO_4N_2 octahedron, green. The chelated en ligands are omitted for clarity.

Figure 1c−d. The Tris is covalently capped onto the top of $\mathbf{Ni_6PW_9}$ through substituting the three OH groups on the surface of $\mathbf{Ni_6}$ core by three alkyls, while three BTC ligands each coordinate to one side of $\mathbf{Ni_6PW_9}$ by replacing two terminal water ligands on each side of the triangle Ni_6 core with one carboxyl group adopting an η^1:η^1:μ_2 coordination. Thus each $\mathbf{Ni_6PW_9}$ acts as a triangular three-connected SBU. Further, the most intriguing feature is that every 8 such triangular SBUs are joined together by 12 BTC linkers to form a large cubic POM−organic molecular cage with an inner spherical cavity diameter of approximately 1.7 nm and an overall edge length of roughly 2.5 nm (Figure 2), which is one of the largest molecular cage species ($M_r > 28\,000$). It is notable that though various kinds of molecular cages were known,[4−12] **1** represents the first molecular POM−organic coordination cage. The 3D packing diagram of **1** along the *c*-axis shows the cages enjoy a hexagonal close-packed structure (Figure S2). In addition to posessing a fascinating structure, **1** also exhibits high hydrothermal and thermal stability (Figure S3) as well as the reversible inclusion of crystallographic water as a guest (Figure S8).

In **1**, the Tris ligands play an important role in the formation of the cage. We have pointed out earlier that the geometrical arrangement of the Ni_6 core makes $\mathbf{Ni_6PW_9}$ an ideal three-connected SBU.[18] However, in fact, during the course of construction of extended structures, the $\mathbf{Ni_6PW_9}$ units are inclined to form aggregates or infinite chains as SBUs by sharing terminal oxo atoms with each other *via* W═O−Ni linkages. For example, the reaction of **1** without Tris ligands will produce a 2D POMOF $\{[Ni_6(OH)_3(en)_3(PW_9O_{34})](1,\ 3,5\text{-}HBTC)\}[Ni(en)(H_2O)_3]\cdot 2H_2O$ based on infinite $\mathbf{\{Ni_6PW_9\}_\infty}$ chains as SBUs.[18] So it is difficult to make $\mathbf{Ni_6PW_9}$ act as an independent three-connected SBU. Now, the incorporation of Tris causes the $\mathbf{Ni_6PW}$ to not easily be utilized in the formation of polymers because of the steric hindrance of the Tris ligand on the surface of the Ni_6 core. As a result, $\mathbf{Ni_6PW_9}$ can serve as independent three-connected SBUs and give rise to the cubic cage.

In summary, we have successfully incorporated a Tris ligand into a Ni_6-substituted POM. The assembly of such a functionalized POM generates an unprecedented cubic POM−organic molecular cage with an intriguing superlarge size. Further, the introduction of Tris ligands may derive new organic−organic hybrid POMs because (1) the free NH_2 group of Tris can be used to create a new coordination site for transition metal ions; (2) the Tris ligand can be modified by organic reactions;[19] and (3) Tris can be replaced by other Tris derivatives. We are currently exploring these possibilities.

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Supporting Information Available: Experimental details; TGA, PXRD, EDS, IR, and magnetic analysis; and figures for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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