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A polyoxometalate-encapsulated 3D porous metal–organic pseudo-*rotaxane* framework†

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A novel compound, $[Cu(bimb)]_2(HPW_{12}O_{40})\cdot 3H_2O$ (bimb = 1,4-bis(imidazol-1-ylmethyl)biphenyl) with a polyoxometalate-encapsulated 3D metal–organic pseudo-*rotaxane* framework that can be described as a 2-fold dianet topology showing well-defined 1D nano-scale tunnels, has been synthesized hydrothermally, and its de-/rehydration behavior has been investigated.

Porous coordination polymers (PCPs)[1a] have received considerable attention because of their diverse topologies and potential applications, such as for storage and separation of chemical matter.[1] Polyoxometalates (POMs), as a large family of metal–oxygen clusters, have been extensively studied due to their intriguing properties in chemistry, physics, catalysis, and materials science.[2–4] However, POM bulk crystals generally possess small surface areas (< 10 m^2 g^{-1}), which limits the effect of active sites and therefore their catalytic applications as solid catalysts. To overcome these drawbacks, immobilization of POMs on solid substrates is an effective strategy.[5] On the other hand, inorganic chemists have paid great attention to the rational design and synthesis of POM-based porous crystalline solids (POMPCS). These efforts have achieved significant results, which can be roughly divided into three types according to the style of the hollow skeletons: type I, POMPCS packed by macrocations and POMs, leaving some voids between them;[6] type II, POMPCS with POMs as templates in which other guest components are trapped;[7] type III, POMPCS whose opening skeletons are constructed by both metal coordination polymers and POMs, leaving some voids to accommodate guest components.[8] Unfortunately, most of the POMPCS reported did not have effective porous function, due to either the full occupation of the void spaces by irremovable guest components such as POM clusters or the collapse of the porous skeletons after treatment of guest removal. Up to now, only few examples[7a–d] of POMPCS with extra vacant space available have been obtained. Creation of POM-based molecular materials with functional cavity reversibility is still a challengeable endeavor.

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Poly-*rotaxanes* (and polypseudo-*rotaxanes*) are a particular species of entangle system characterized by "loops" that are threaded by "strings". Apart from their intrinsic aesthetic appeal, they have potential applications ranging from drug-delivery vehicles to sensor devices.[9] Kim and Loeb have constructed and discussed at length poly-*rotaxanes* (and polypseudo-*rotaxanes*) in comprehensive reviews.[10] However, among rapidly increasing coordination polymers, those that have poly-*rotaxane* (and polypseudo-*rotaxane*) structures are seldom observed, and porous metal–organic (pseudo-) *rotaxane* frameworks (MO*R*Fs) are even more rare.[11] An interesting question arising from this is whether the complicated species of POMs could be encapsulated into complicated 3D MO*R*F hosts, as there is generally a correlation between the complexity of the structure of a material and the functionality that it displays, as predicted early by Zubieta *et al.*[7a] If so, such materials should be able to combine the features of POMs, *rotaxanes* and PCPs and have virtues of the robustness of the porous frameworks and adjustment of porous sizes, broadening applications of POMs in materials science and industrial catalysis. Our primary investigation in the reaction system of Keggin POM, transition metal Cu and bimb (bimb = 1,4-bis(imidazol-1-ylmethyl)biphenyl) shows that this is feasible.
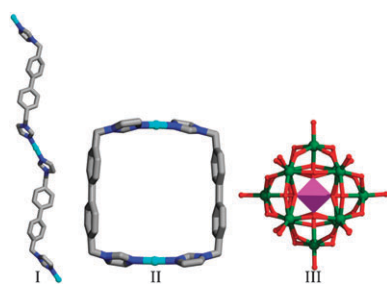
Herein, we communicate the preparation and structure of a new compound based on the three species mentioned above, $[Cu(bimb)]_2(HPW_{12}O_{40})\cdot 3H_2O$ (**1**), which is after the compound $[Cu^{II}(L)_2(H_2O)_2][Cu^I_2(L)_2]PMo_{12}O_{40}$ reported by Wang *et al*,[12] but has well-defined tunnels after occupation by the Keggin anions.

Compound **1**‡ was synthesized hydrothermally with a mixture of $H_3[PW_{12}O_{40}]\cdot 12H_2O$, $Cu(CH_3COO)_2\cdot H_2O$, and bimb in water at 170 °C (5 days). Single-crystal X-ray diffraction analysis§ reveals that **1** consists of three crystallographically distinct motifs: a 1D chain $[Cu(bimb)]^+$ (**I**), a 34-membered macrocycle $[Cu_2(bimb)_2]^{2+}$ (**II**) and a Keggin cluster $[PW_{12}O_{40}]^{3-}$ (PW$_{12}$) (**III**) (Fig. 1). In motif **I**, Cu^I atoms with a linear coordination geometry (Cu–N = 1.87(3) Å, ∠ N–Cu–N = 180(2)°) are bridged alternately by bimb ligands in the "*Z*"-type conformation (torsion angle of C–C–N–C = 67(2)°), resulting in a wavelike chain $[Cu(bimb)]^+$ with adjacent Cu⋯Cu distances of 17.796 Å (Fig. 1 left). The Cu^I atoms in motif **II** (Fig. 1, middle) are also in a linear coordination environment (Cu–N = 1.865(13) Å, ∠ N–Cu–N = 178.7(10)°), but conversely they are bridged by two "*U*"-type conformation bimb ligands (torsion angle of C–C–N–C is 106(2)°), to form a 34-membered macrocycle with edges at 0.550 and 9.699 Å,

Fig. 1 The three crystallographically distinct motifs in **1**: **I**, $[Cu(bimb)]^+$ chain; **II**, $[Cu_2(bimb)_2]^{2+}$ macrocycle; **III**, $[PW_{12}O_{40}]^{3-}$ Keggin cluster.

and twisting angles of $120.18°$, indicating a distorted square geometry. The motif **III** (see Fig. 1, right and IR spectrum in Fig. S1, ESI†) shows the well-known α-Keggin type structure, consisting of central PO_4 tetrahedron corner-sharing four triad $\{W_3O_{13}\}$ clusters.

One structural feature of **1** is the unusual 3D MO*R*F connected by the 0D 34-membered macrocycles (motif **II**) acting as molecular "loops" and the 1D chain (motif **I**) serving as a long molecular "string". On one hand, each of the "strings" threads through the "loops" in an A–B–A–B model (Fig. S2 left and Fig. S3a–c, ESI†), on the other hand, each of the "loops" encircles two molecular strings (Fig. S2 right and Fig. S3d, ESI†). Consequently, a complicated 3D MO*R*F is formed by repeating this interesting entangled pattern (Fig. 2 and Fig. S4, ESI†). This entangled fashion is rare in the previous reports on pseudo-*rotaxane* structure,[11] namely, one "loop" encircles two "strings" rather than a single one (Fig. S2 right, ESI†). Also, **1** represents the first example of a 3D MO*R*F constructed of 0D + 1D subunits. Topological analysis shows that the MO*R*F can be described as a 2-fold **dia** net if we take as a node the two "strings" in one "loop" as illustrated in Fig. S5, ESI†.

Another fascinating structural feature of compound **1** is its highly opened 3D MO*R*F. The pseudo-*rotaxane* motifs composed of $[Cu(bimb)]^+$ chains, and $[Cu_2(bimb)_2]^{2+}$ macrocycles are hexagonally arranged to construct hexagonal cylinders with 3D channels: straight channels along the axes of the cylinders (*ca.* 20 × 13 Å, see **A** in Fig. 3); on the walls of the cylinders, channels made of elliptic pores are distributed (*ca.* 14 × 13 Å, see **B/C** in Fig. 3), which are so large that the Keggin PW_{12} anions are accommodated as charge-compensating guests (Fig. 3). More interestingly, after occupation of the PW_{12} clusters, the overall 3D MO*R*F still possesses significant
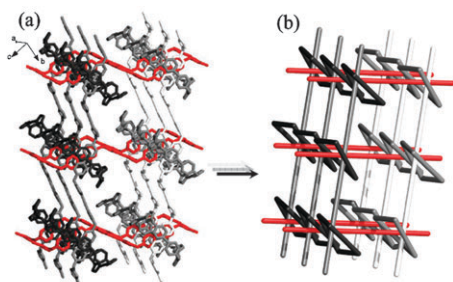
Fig. 2 View of the 3D pseudo-*rotaxane* structure (a), and schematic illustration of the pseudo-*rotaxane* structure (b).
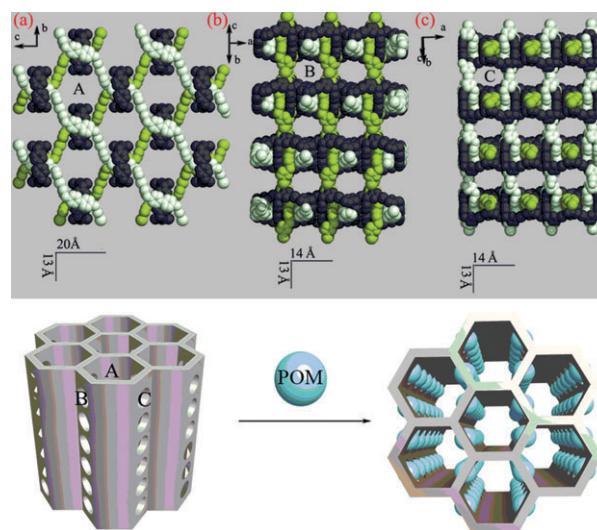
Fig. 3 Space-filling models showing the unusual MO*R*F with three-directional tunnels (top). Their schematic model and arrangement of POMs in the tunnels composed of **B** and **C** pores (bottom).

void space (the dimension of the windows of the channel is *ca.* 12 × 10 Å) (Fig. S6, ESI†). Calculations using *PLATON* reveal that the effective free volume is 2767.6 Å^3 after removal of the solvent-water molecules, equal to 31.0% of the crystal volume 8941.0 Å^3.

Encouraged by the single-crystal X-ray diffraction result, which reveals large free spaces within the framework, we carried out PXRD experiments to investigate de-/rehydration abilities of compound **1**. Firstly, PXRD experiments proved the good phase purity of compound **1** as the diffraction peaks of both simulated and experimental patterns match well (see Fig. 4a,b and Fig. S7, ESI†). After heating of the powder sample at 200 °C in air for 1 h, the guest water molecules (1.6%) in compound **1** were lost, according to the TG analysis (see Fig. S8, ESI†), and a little change around 25° of 2θ in the PXRD pattern was observed, suggesting some subtle change occurred in the crystal structure. After the dehydrated sample was exposed to moisture at room temperature for 1 day, almost the same PXRD pattern as that of the as-synthesized one remained (see Fig. 4b–d), although there were slight shifts and splitting of some peaks attributable to the subtle change of the relative positions of some atoms in the crystal lattice.[13] This indicated that the same framework structure was recovered after rehydration.[7c] After heating of compound **1** at 300 °C in air for 1 h, the main diffraction peaks below 10° of 2θ in the PXRD pattern were maintained, whereas other peaks showed clear changes in breadth and intensity, indicating that the framework in compound **1** was at least partially decomposed at this temperature (see Fig. 4e). The electrochemical behavior of a **1**-modified carbon paste electrode (**1**-CPE) was investigated in 1 M H_2SO_4 aqueous solution at different scan rates (see Fig. S9 left, ESI†). In the potential range of +400 to −800 mV, three reversible redox peaks exist; II–II′, III–III′ and IV–IV′, attributable to the redox process of $W^{VI/V}$ in the PW_{12} polyanions.[14] In addition, the irreversible anodic peak I is assigned to the oxidation of the Cu(ɪ) centers. The peak currents of III are linearly proportional to the scan rates (see Fig. S9 right, ESI†), indicating a possible surface-controlled redox process.
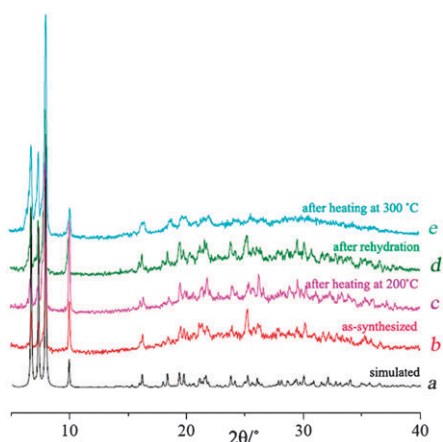
Fig. 4 PXRD patterns of compound **1**.

In summary, we have synthesized a new compound, which not only possesses a new type of 3D MO*R*F constructed by 0D + 1D subunits, but also represents a unique POM-encapsulated MO*R*F with nano-scale porous structure. Considering that the structure has the features of POMs, rotaxanes and PCPs, compound **1** may represent a new kind of material that combines the useful properties of these three chemical families. Compound **1** has potential in adsorption and catalysis applications. Study of these properties is underway.

Notes and references

‡ *Synthesis* of **1**: A mixture of $H_3[PW_{12}O_{40}] \cdot 12H_2O$ (300 mg, 0.1 mmol), $Cu(CH_3COO)_2 \cdot H_2O$ (159 mg, 0.8 mmol), bimb (160 mg, 0.5 mmol) and 10 mL H_2O was stirred for 1 h. The pH was adjusted to 4.6 with 1 M NaOH, and then the mixture was transferred to an 18 mL Teflon-lined reactor and kept under autogenous pressure at 170 °C for 5 days. After the reactor was slowly cooled to room temperature over a period of 10 °C h^{-1}, red crystals of **1** were obtained in a yield of 50% based on W. Elemental analysis: $C_{40}H_{43}Cu_2N_8O_{43}PW_{12}$ (**1**). Anal. Calcd for **1**: C, 13.03; H, 1.17; N, 3.04 (%). Found: C, 13.12; H, 1.21; N, 2.96 (%).

§ *Crystal data* for **1**: $M = 3687.94$, orthorhombic, space group *Pnnn*, $a = 14.172(5)$ Å, $b = 24.011(5)$ Å, $c = 26.274(5)$ Å, $V = 8941(4)$ Å^3, $Z = 4$, $T = 293(2)$ K, 73 762 reflections measured, 8084 unique ($R_{int} = 0.0956$) which were used in all calculations; $R_1 = 0.0466$ and w$R_2 = 0.1034$ for $I > 2\sigma(I)$. CCDC–764098. The water molecules were highly disordered and could not be modelled properly, thus *PLATON* was applied to remove the contributions to the scattering from the solvent molecules. The reported refinements are of the guest-free structures using the *.hkp files produced by using the *SQUEEZE* routine. The *R*factor before *SQUEEZE* 0.0622. The amount of water came from the TG experiment.

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