An unusual polyoxometalate-encapsulating 3D polyrotaxane framework formed by molecular squares threading on a twofold interpenetrated diamondoid skeleton†

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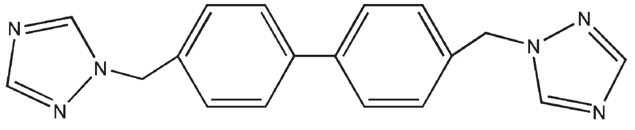
Received (in Cambridge, UK) 26th June 2007, Accepted 20th July 2007
First published as an Advance Article on the web 8th August 2007
DOI: 10.1039/b709563e

Threading molecular square "beads" on a twofold interpenetrated diamondoid skeleton gives a new type of 3D metal–organic polyrotaxane framework with large channels, in which nanosized Keggin anions as guests are encapsulated for the first time.

Entanglements are common in biology as seen in catenanes, rotaxanes and molecular knots,[1] and have attracted considerable attention due to their aesthetic and often complicated architectures and topologies.[2] Among these, polyrotaxanes represent an intriguing subset, in which many molecular "beads" are threaded on a long molecular "string". Apart from their intrinsic aesthetic appeal, interest in these compounds has been heightened by the fact that their unique mechanically interlocked structures are more flexible than the usual networks entirely based on coordination bonds, and therefore can be set in motion but stay together thanks to the rotaxane nature of the system—a functional property that has potential applications, ranging from drug delivery vehicles to sensor devices.[3]

Since the pioneering work by Sauvage and Stoddart, admirable synthetic strategies initiated by Kim and Loeb have been developed to assemble rotaxanes (or pseudorotaxanes) into polyrotaxanes with highly ordered structures in the solid state.[4] Nevertheless, the construction of 3D metal-based porous polyrotaxanes remains a challenging issue in synthetic chemistry. On the other hand, polyoxometalates (POMs),[5] exemplified by the ubiquitous spherical Keggin structure,[6] constitute a fascinating class of inorganic systems that is incomparable in structural diversity[7] as well as wide-ranging applications, such as in catalysis, medicine, and materials science.[8] In particular, recent results have indicated that these large non-coordinating POM anions (generally nanoscale in diameter) can be incorporated into the void space of conventional coordination frameworks,[9] thereby offering a new opportunity for carrying out chemical reactions within the intercrystalline voids. We thus envision that it would be possible to construct POM-encapsulating metal–organic *rotaxane* frameworks (MO*R*Fs defined by Loeb[4b]). Such materials should be able to combine the flexible structure feature of polyrotaxanes with the unique physical and chemical properties of POMs, and may find broader applications in the materials science field.

With this aim in mind, we chose a long, flexible N-containing ligand 4,4′-bis(1,2,4-triazol-1-ylmethyl)biphenyl (**L**), synthesized according to the literature method,[10] and the readily available Keggin-type heteropolyanion $PMo_{12}O_{40}^{3-}$ in our synthetic strategy, based on the following considerations: (i) long flexible ligands, when coordinated with transition-metal ions, have shown the ability to produce unique metal–ligand entangled nets, such as polycatenanes,[11] polyrotaxanes,[12] and other uncommon species,[13] and (ii) due to the steric hindrance of POMs, bridging of subunits by relatively large ligands is unlikely; this thus ensures that the polyanion may exist in the form of the isolated state. Fortunately, this effort has led to the isolation of the first Keggin-encapsulating 3D metal–organic polyrotaxane network, namely $[Cu^{II}(\mathbf{L})_2(H_2O)_2][Cu^{I}_2(\mathbf{L})_2]PMo_{12}O_{40}$ (**1**), which, to our surprise, is constructed by threading molecular square 'beads' on a twofold interpenetrated diamondoid skeleton. This work is our first step toward bridging two important but distinct areas of research: polyrotaxane and POM chemistry.



L

Crystals of **1** were obtained from heating a mixture of $Cu(NO_3)_2{\cdot}3H_2O$, **L**, and $H_3PMo_{12}O_{40}$ at 140 °C for 5 days.‡ The phase purity of bulk products was confirmed by powder X-ray diffraction (SI-1†). In the IR spectrum of **1** (SI-2†), strong peaks at 1130, 1055, 951, and 798 cm^{-1} are due to ν_{as}(P–O), ν_{as}(Mo=O$_d$), ν_{as}(Mo–O$_b$–Mo) and ν_{as}(Mo–O$_c$–Mo),[14] while bands at 3112, 1605, 1522, 1433, 1275, and 1209 cm^{-1} are ascribed to the **L** ligand. A broad band at 3443 is assigned to ν(OH) of the coordinated water. In the UV-vis spectrum (SI-3†), the oxide-to-molybdenum charge transfer absorption maxima are observed at 232 and 324 nm.[15] The TG curve of **1** (SI-4†) shows a weight loss of 1.20% (calcd 1.09%) from 80 to 160 °C, corresponding to the release of two coordinated water molecules per formula unit, further supporting the formula of **1**.

Single-crystal X-ray analysis§ has revealed that **1** crystallizes in the high-symmetry tetragonal space group $P\bar{4}n2$ (No. 118) and consists of three crystallographically distinct motifs: a 3D diamondoid network $[Cu^{II}(\mathbf{L})_2(H_2O)_2]^{2+}$ (**A**), a molecular square $[Cu^{I}_2(\mathbf{L})_2]^{2+}$ (**B**), and a ball-shaped Keggin anion $[PMo^{V}Mo^{VI}_{11}O_{40}]^{4-}$ (**C**).

The Cu center in the first motif (Fig. 1, left) has an oxidation state of +2, as confirmed from bond valence sum (BVS)

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† Electronic supplementary information (ESI) available: IR, TG, PXRD, UV-vis spectra and complementary drawings for crystal structure. See DOI: 10.1039/b709563e

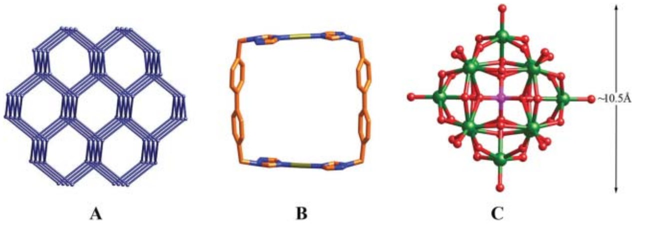

Fig. 1 The three crystallographically distinct motifs in **1**.

calculations[16] (1.749). The Cu2 center lies at a site with $\bar{4}$ symmetry and is coordinated by four nitrogen atoms from four individual **L** ligands (Cu–N 2.029(4) Å) and two coordinated water molecules (Cu–O11 2.223(6) Å) lying at a site with imposed twofold symmetry, forming an elongated (4 + 2) octahedron due to the Jahn–Teller effect (SI-5†). Each Cu^{II} center is bridged to four adjacent metal centers through **L** ligands in boat conformations (torsion angle of N–C–C–N is 50.78(2)°) to form a typically diamondoid framework containing large adamantanoid cages with equal Cu···Cu edges of 15.09 Å. Each cage, delimited by four cyclohexane-like windows in chair conformations, exhibits maximum dimensions (corresponding to the longest intracage Cu···Cu distances) of 30.33 × 36.87 × 36.87 Å (SI-6†).

In contrast to the Cu^{II} atom of the first motif, the Cu center in **B** (Fig. 1, middle) is univalent (the value of BVS for Cu1 center is 0.918) and assumes a typically linear coordination environment (Cu–N 1.898(6) Å, N–Cu–N 178.6(4)°), which lies at a site with imposed twofold symmetry. The partial reduction of Cu^{II} into Cu^{I} may be attributed to the excess of the N-containing ligand during the hydrothermal synthesis.[17] As depicted in Fig. 1, two Cu^{I} centers are linked by two **L** ligands to form a 34-membered macrocycle with the edge distances at 10.05 and 10.85 Å, and twisting angles at exactly 90°, indicating an approximately ideal square geometry.

The third motif **C** (Fig. 1, right) exhibits a classic α-Keggin geometry in which four corner-sharing Mo_3O_{13} triad clusters that result from the association of three edge-sharing MoO_6 octahedra are arrayed around the center PO_4 tetrahedron in an ideal C_s symmetry. The central P atom lies at a site with $\bar{4}$ symmetry.

The most fascinating aspect of **1** is the unique combination fashion of these three structurally divergent motifs, whose rationalization can be described stepwise for the sake of understanding. First of all, the foregoing description for a single **A** net tells only half the story. Because of the spacious nature of a single network, it allows a second identical diamondoid network to penetrate it in a normal mode,[2a] thus giving a twofold interpenetrated structure (Fig. 2a and SI-7†). An analysis of the topology of interpenetration, according to a recent classification,[18] reveals that it belongs to Class **Ia** (the two identical interpenetrated nets are generated only by translation and the translating vector is [001] (15.17 Å)). Notably, even with this interpenetration, the framework is still highly open, containing three-directional helical channels of approximately 12.9 × 12.9 Å along the [100] and [010] directions and of 12.7 × 13.1 Å along the [332] direction, all of which are enclosed by two intertwined helices of the same handedness coming from two interpenetrating lattices (Fig. 2b, SI-8,9†). In consequence of mother nature's *horror vacui*, such a crystal structure with extra-large pores is unstable except by inclusion of suitable guests or by further interpenetration. Motif **B**, *i.e.* the molecular square described above, fulfils this need, however, not by the common interpenetration, but rather by the unusual [3]rotaxane mode. As illustrated in Fig. 2c, the unprecedented [3]rotaxane is composed of a molecular square "bead" threaded on two "strings" from two edges of two interpenetrated adamantane units. This unique interlocking pattern, when repeated over the twofold interpenetrated diamondoid network, results in a new type of 3D polyrotaxane involving [3]rotaxane components. Closer inspection reveals that each edge of an adamantane unit is encircled by one molecular square (Fig. 2d). More intriguingly, these molecular squares look like "hoops" encircling the aforementioned helical channels (Fig. 2e). The introduction of motif **B**, however, occupies only a small fraction of the available space in the crystal so that the overall 3D polyrotaxane network still possesses significant void space that exactly traps the reduced Keggin anions (*ca.* 10.5 Å in diameter) as charge-compensating guests in the helical nanochannels (Fig. 2a, 2e, and SI-10†). Notably, there exist weak interactions (Cu1···O8 2.936 Å) between Keggin ions and Cu1 atoms from the host framework, which stabilize the whole crystal structure. If considering these weak interactions, an approximate square-planar coordination configuration is formed at Cu1. While it is quite common to find small counter anions, organic ligands, or solvent molecules in the void space of coordination polymers, to our knowledge, inclusion of nanosized polyanions into the helical channels is still rare, which would be of significant relevance to applications in chemistry and materials science.

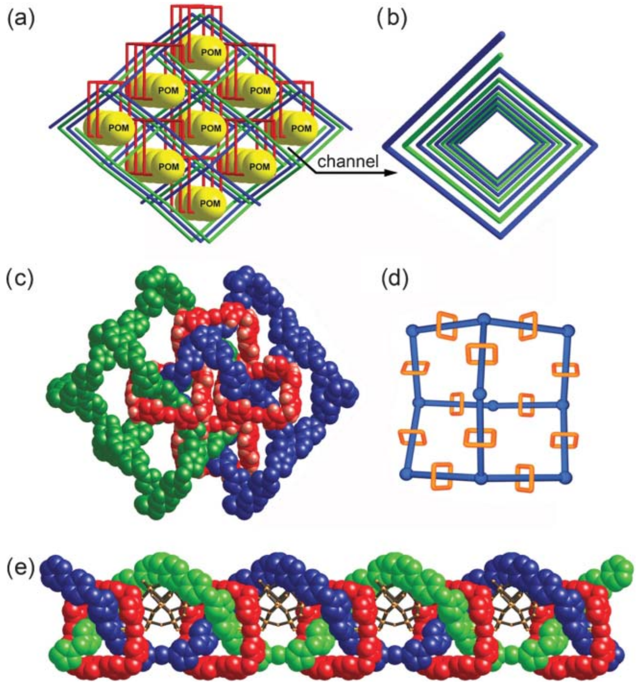

Fig. 2 (a) A schematic presentation of the overall 3D network. (b) Schematic view of the helical channel after interpenetration along the *a* axis. (c) A space-filling model showing two interpenetrating diamondoid units (green and blue) interlocked by molecular squares (red). (d) A schematic illustration of an adamantanoid cage locked by twelve molecular squares. (e) View of the helical nanochannel encapsulating Keggin anions.

As a whole, compound **1** is remarkable in that: (i) it is one of the rather few 3D polyrotaxanes characterized by single-crystal X-ray diffraction methods to date,[19] and to the best of our knowledge, is the only known rotaxane framework containing non-macrocyclic ligands (usually cyclodextrin and cucurbituril) as molecular "beads"; (ii) its entangled fashion is completely unprecedented in the area of coordination polymers; namely, molecular square "beads" lock two interpenetrating nets in this case rather than a single one (SI-11†),[19,20] and therefore compared with the prevalent [2]rotaxane, it is also the first time that the [3]rotaxane moiety is observed in polyrotaxanes with high structural regularity; and (iii) it represents the first example of encapsulating functional, nanosized POMs into open MO*R*Fs, bringing together the two fields of polyrotaxanes and polyoxometalates.

In conclusion, we have successfully incorporated nanosized Keggin polyanions into an unusual 3D MO*R*F. The framework of **1** has the common features of interpenetration, rotaxanes and POMs and may generate a new kind of material that combines the useful properties of these three areas. Considering that a large variety of POMs can be used in this synthetic strategy, further work is underway in our lab.

The authors thank the National Science Foundation of China (No. 20371011), Science and Technology Development Project Foundation of Jilin Province (No. 20060420), Testing Foundation of Northeast Normal University (No. 201586000/201372000), Ph.D Station Foundation of Ministry of Education (No. 20060200002), and Science Foundation for Young Teachers of Northeast Normal University (No. 20070303).

Notes and references

‡ Synthesis of **1**: a mixture of $Cu(NO_3)_2 \cdot 3H_2O$ (36 mg, 0.15 mmol), **L** (158 mg, 0.5 mmol), $H_3PMo_{12}O_{40}$ (91 mg, 0.05 mmol), and water (10 mL) was sealed in a 23 mL Teflon reactor under autogenous pressure at 140 °C for 5 days, and then cooled to room temperature at a rate of 10 $^\circ C\ h^{-1}$. Black crystals were obtained in 52% yield (86 mg, based on Mo). Elemental analysis calcd (%) for $C_{72}H_{68}Cu_3Mo_{12}N_{24}O_{42}P$: P 0.93, Mo 34.74, Cu 5.75; found: P 0.76, Mo 34.32, Cu 5.46. IR (cm^{-1}): 3443 br, 3112 m, 1645 w, 1605 m, 1522 m, 1433 w, 1402 w, 1369 w, 1342 w, 1275 s, 1209 m, 1130 s, 1055 s, 1006 m, 951 s, 861 w, 798 s, 753 m, 671 m, 501 m.

§ Crystal data for **1**, $C_{72}H_{68}Cu_3Mo_{12}N_{24}O_{42}P$: $M_r = 3314.37$, tetragonal, space group $P\bar{4}n2$, $a = 18.443(3)$, $b = 18.443(3)$, $c = 15.166(3)$ Å, $\alpha = \beta = \gamma = 90^\circ$, $V = 5158.5(14)$ Å^3, $Z = 2$, $\rho_{calcd} = 2.134$ g cm^{-3}, $T = 293$ K, $S = 1.068$, $R1 = 0.0337$ for 5891 independent reflections [$I > 2\sigma(I)$]. CCDC 298626. For crystallographic data in CIF or other electronic format, see DOI: 10.1039/b709563e

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