

## Supporting Information

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

**Xin-Long Wang, Chao Qin, En-Bo Wang\* and Zhong-Min Su\***

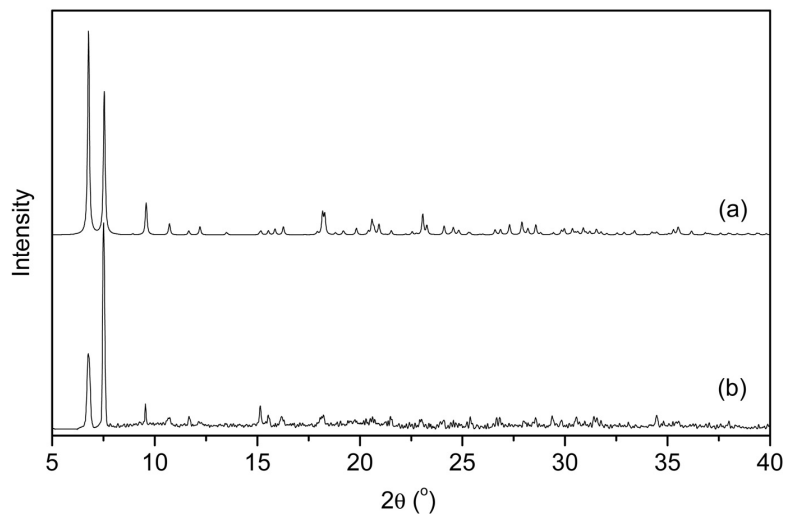
*Key Laboratory of Polyoxometalates Science of Ministry of Education, College of Chemistry, Northeast Normal University, Changchun 130024, China. Email: [wangenbo@public.cc.jl.cn](mailto:wangenbo@public.cc.jl.cn), [zmsu@nenu.edu.cn](mailto:zmsu@nenu.edu.cn)*

## Experimental section

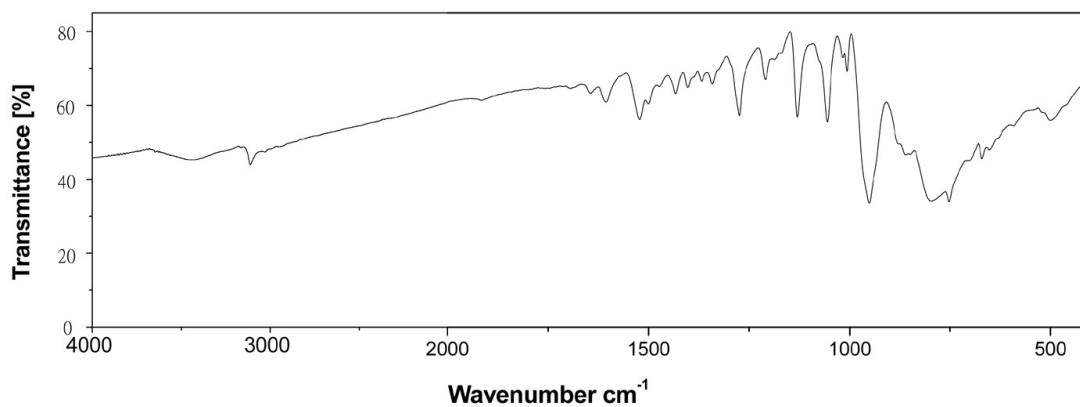
**Materials and general methods.** The organic ligand, 4,4'-bis(1,2,4-triazol-1-ylmethyl)biphenyl (**L**), was synthesized by the general method described in the literature.<sup>1</sup> Other reagents were purchased from commercial sources and used as received. Elemental analyses (P, Mo, and Cu) were determined by a Leaman inductively coupled plasma (ICP) spectrometer. FTIR spectra were recorded in the range 400–4000  $\text{cm}^{-1}$  on an Alpha Centaur FTIR spectrophotometer using a KBr pellet. TG analysis was performed on a Perkin–Elmer TGA7 instrument in flowing  $\text{N}_2$  with a heating rate of  $10^\circ\text{C min}^{-1}$ . A diffuse reflectance UV-vis spectrum (BaSO<sub>4</sub> pellet) was obtained from the solid state with a Varian Cary 500 UV-vis-NIR spectrometer. The X-ray powder diffraction patterns (XRPD) were recorded on a Rigaku D/Max-2500 diffractometer.

(1) X. R. Meng, Y. L. Song, H. W. Hou, H. Y. Han, B. Xiao, Y. T. Fan and Y. Zhu, *Inorg. Chem.* 2004, **43**, 3528.

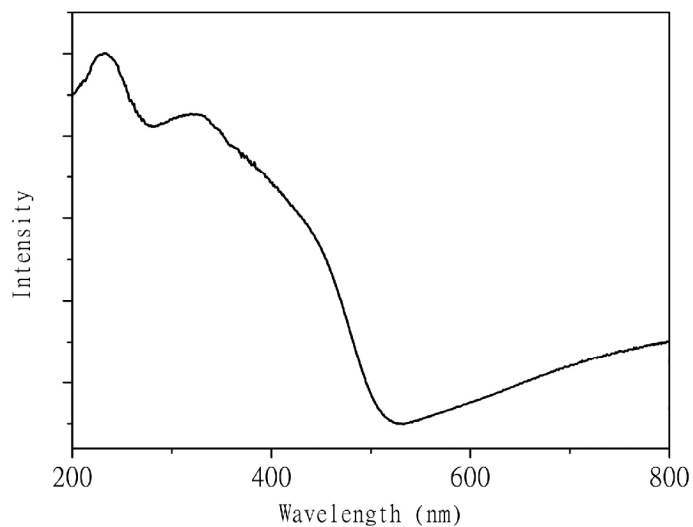
**Synthesis of the ligand 4,4'-bis(1,2,4-triazol-1-ylmethyl)biphenyl (L).** 1,2,4-triazole (1.38 g, 20 mmol) was dissolved in acetone (30mL), and then PEG-400 (2 g), anhydrous potassium carbonate (5g), and potassium iodide (0.5 g) were added to the above solution. After the solution was stirring for 30 min, 4,4'-bis(chloromethyl)biphenyl (2.5 g, 10 mmol) was added. The mixture was vigorously stirred and refluxed for 10 h. A white residue was obtained after filtering and distilling off the filtrate. The crude product was re-crystallized from hot water to give white crystalline product. Yield: 1.7 g (54%). Anal. Calcd for C<sub>18</sub>H<sub>16</sub>N<sub>6</sub>: C, 68.34; H, 5.10; N, 26.56. Found: C, 68.26; H, 5.02; N, 25.50. IR (KBr)/ $\text{cm}^{-1}$ : 3099 ( $\nu_s$  ArH), 1508s ( $\nu_s$  C=C, C=N), 1269 ( $\nu_s$ ), 1140 ( $\nu_s$ ), 1014 ( $\nu_s$  C–C, C–N), 751( $\nu_s$ ).



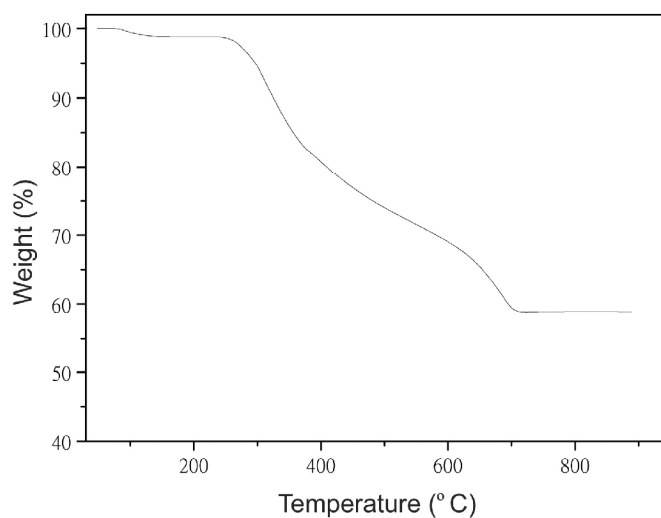
**SI-1** PXRD patterns: calculated from the X-ray single-crystal data (a) and observed for the as-synthesized solids (b).



**SI-2** IR spectrum of compound **1**.

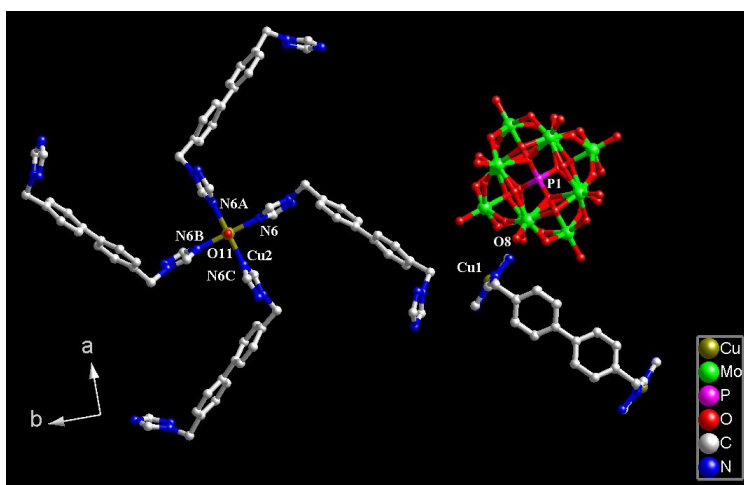


**SI-3** UV-vis spectrum of compound **1**.

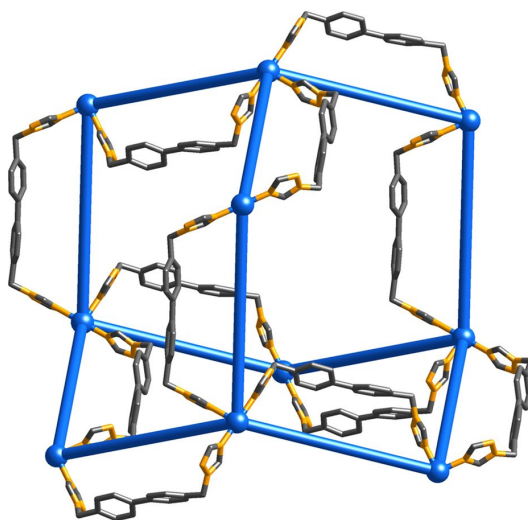


**SI-4** TG curve of compound **1**.

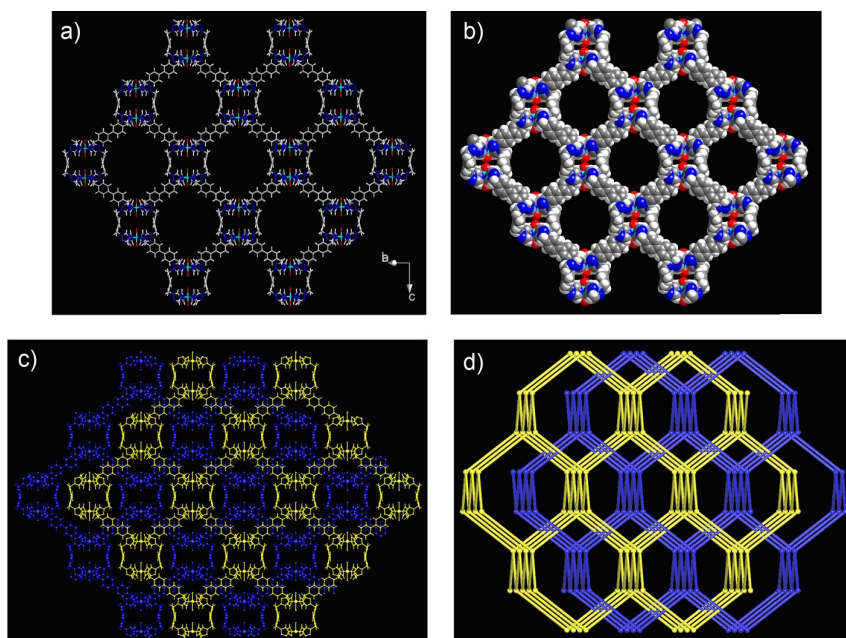
The TG curve of **1** shows the weight loss of 1.20% (calcd 1.09%) from 80 to 160°C corresponds to the release of coordinated water molecules. No weight losses were observed up to 250°C, at which the release of ligands starts to occur, indicating the collapse of polyrotaxane framework.



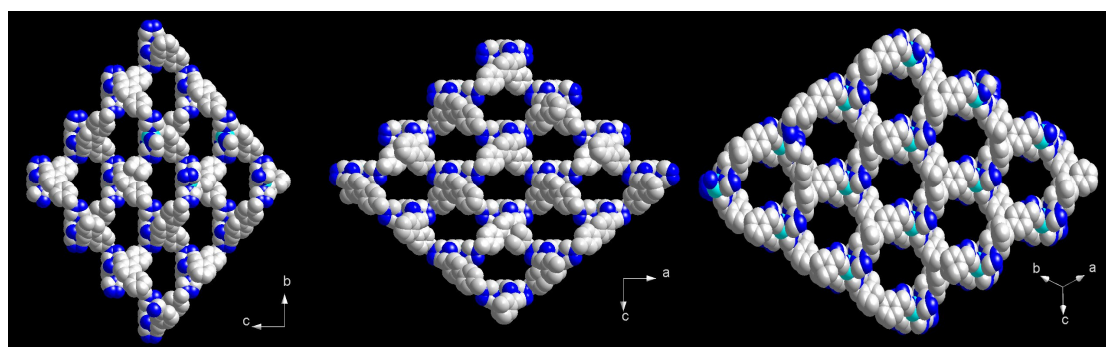
**SI-5** Three crystallographically distinct motifs in **1**, showing the coordination environments of copper centers.



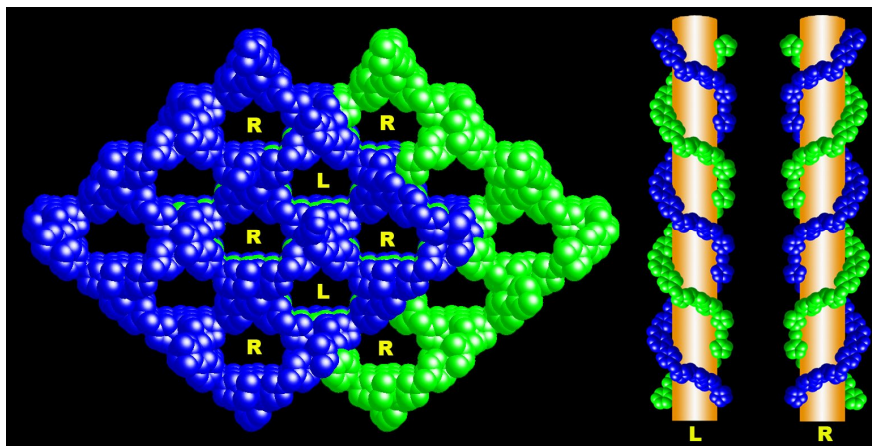
**SI-6** A single cage with the maximum dimensions (corresponding to the longest intracage Cu...Cu distances) of  $30.33 \times 36.87 \times 36.87$  Å.



**SI-7** Top: stick and space-filling views of a single diamondoid framework along the  $[1 -1 0]$  direction, showing the extra-large cavities; bottom: stick and schematic views of the twofold interpenetration along the  $[1 -1 0]$  direction.

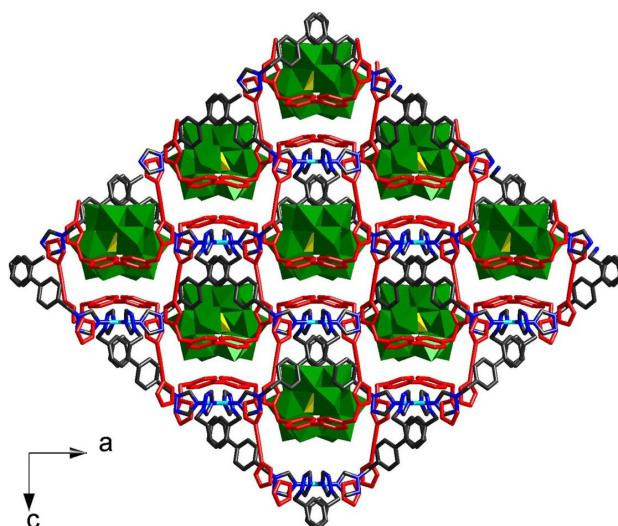


**SI-8** Views of the channels after interpenetration along the  $[100]$ ,  $[010]$  and the  $[332]$  directions.

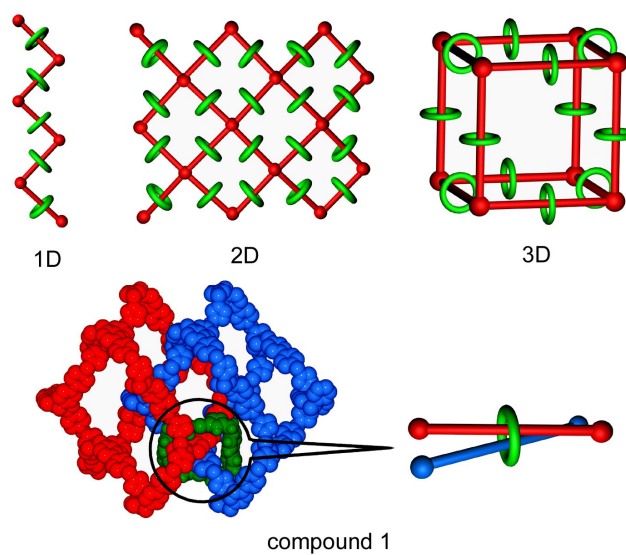


**SI-9** Views of the helical nanochannels after interpenetration along  $b$  axis (left) and the two intertwined helices that enclose the channel.

As shown in this figure, each channel is enclosed by two intertwined helices of the same handedness coming from two interpenetrating lattices, therefore as far as each nanochannel is concerned, it is chiral. However, note that the helical channels within one row are exclusively left-handed, whereas those within the neighboring rows are exclusively right-handed, in other words, the channels within the alternating rows are pairs of enantiomers, thus leading to the racemization of the whole framework.



**SI-10** View of the 3D framework encapsulating non-coordinating POM anions in the open channels along the  $b$  axis. Color code: yellow  $\text{PO}_4$ ; green  $\text{MoO}_6$ ; red molecular square; cyan Cu; blue N; black metal-ligand lattice.



**SI-11** Schematic representations of the known 1D, 2D, 3D polyrotaxanes and the peculiar 3D polyrotaxane reported herein.