

Electronic Supplementary Information for MS:

**An Unprecedented (5,12)-Connected 3D Self-penetrating
Metal-Organic Framework Based on Dinuclear Barium Clusters as
Building Blocks**

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Experimental section

Materials and general methods. All chemicals were commercially purchased and used without further purification. The organic ligand 1,4-bis(1,2,4-triazol-1-yl)butane (btb), was synthesized by the general method described in the literature.¹ Elemental analyses (C, H and N) were performed on a Perkin-Elmer 2400 CHN Elemental Analyzer. Elemental analysis Ba was determined by a tps-7000 Plasma-Spec(I) inductively coupled plasma atomic emission spectrometer (ICP-AES). IR spectrum was recorded in the range 400-4000 cm^{-1} on a Bio-Rad FTS-185 FT/IR Spectrophotometer using KBr pellets. TG analysis was performed on a NETZSCH STA 449C instrument in flowing N_2 with a heating rate of 10 $^\circ\text{C}\cdot\text{min}^{-1}$. Fluorescence measurements were performed on an F-4500 FL fluorescence spectrophotometer equipped with a 150 W xenon lamp as the excitation source. XRPD data were recorded on a XD-3 diffractometer using $\text{Cu K}\alpha$ radiation.

Synthesis of $[\text{Ba}(\mu_2\text{-OH}_2)(\text{SDBA})(\text{btb})_{0.5}]$ (1**).** A mixture of $\text{Ba}(\text{OH})_2\cdot 8\text{H}_2\text{O}$ (0.126g, 0.4 mmol), H_2SDBA (0.061g, 0.2 mmol), btb (0.076g, 0.4 mmol), NH_4F (0.030g, 0.8 mmol) and distilled water (10 mL) in 18mL Teflon reactor under autogenous pressure was heated at 150 $^\circ\text{C}$ for 3 days and then cooled to room temperature naturally. Colorless block crystals of **1** were obtained (yield: 57% based on Ba). The XRPD pattern of the bulk product of **1** was in agreement with the simulated pattern from single-crystal X-ray diffraction data, demonstrating the phase purity of the product (Fig. S11). Elemental analysis (%) calcd for $\text{C}_{18}\text{H}_{16}\text{BaN}_3\text{O}_7\text{S}$: C, 38.90, H, 2.90, Ba, 24.71, N, 7.56%. Found: C, 39.12, H, 3.09, Ba, 24.48, N, 7.31%.

IR (KBr pellet): 3787(w), 3157(m), 3097(m), 3068(m), 3039(m), 2954(m), 1960(w), 1606(s), 1560(s), 1511(m), 1441(w), 1375(s), 1323(m), 1301(s), 1273(m), 1169(s), 1149(m), 1130(m), 1101(m), 1070(w), 1014(s), 991(w), 963(w), 872(m), 786(s), 742(m), 712(s), 697(m), 679(m), 664(w), 646(w), 612(s), 578(m), 538(w), 478(w), 459(m), 425(w).

Crystallographic Data Collection and Refinement

Single-crystal X-ray diffraction data for compound **1** were collected on a Bruker Smart Apex CCD diffractometer with Mo K α monochromated radiation ($\lambda = 0.71073 \text{ \AA}$) at 293(2) K. Absorption corrections were applied using the multiscan technique. The structures were solved by the direct method and refined by the full-matrix least-squares method on F^2 using the SHELXL-97 software.² All of the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were generated geometrically. The aqua hydrogen atoms were located from difference Fourier maps. During the refinement, a restrained refinement comment "ISOR" is used to restraint the Non-H atoms with the ADP problems, these atoms are as follows: N1, C16, N3, N2, C15, N2A, C15A. The triazolyl group (N1-C16-N3-N2-C15) is disordered in two positions (Fig. S1) with the occupancies of 50%, respectively. The triazolyl ring (N1-C16-N3-N2-C15) is refined with restrained comments "DELU" and "SIMU" to be sure that all the atoms have the similar environment.

CCDC 783475 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> (or from the Cambridge

Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033).

Reference

- (1) J. Torres, J. L. Lavandera, P. Cabildo, R. M. Claramunt and J. Elguero, *J. Heterocyclic. Chem.*, 1988, **25**, 771.
- (2) (a) G. M. Sheldrick, *SHELXS 97, Program for Crystal Structure Solution*, University of Göttingen, Germany, 1997; (b) G. M. Sheldrick, *SHELXL 97, Program for Crystal Structure Refinement*, University of Göttingen, Germany, 1997.

Supporting Figures

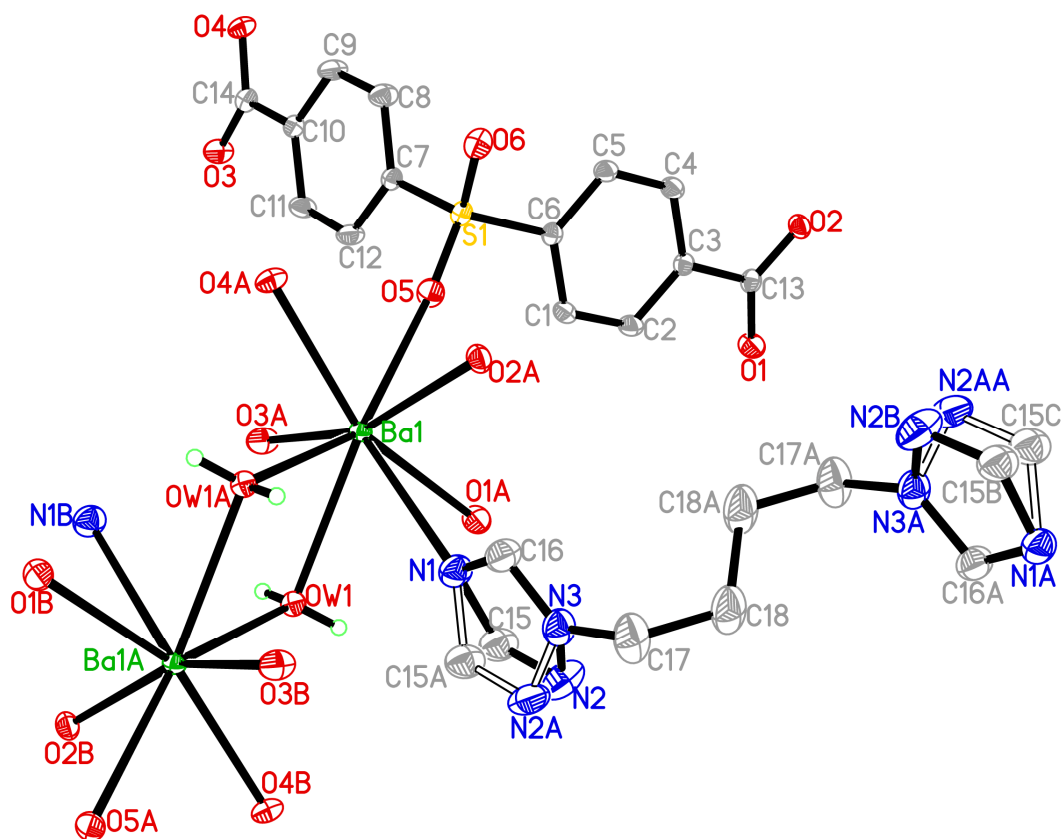


Fig. S1 ORTEP diagram showing the coordination environment for the Ba atom in 1.

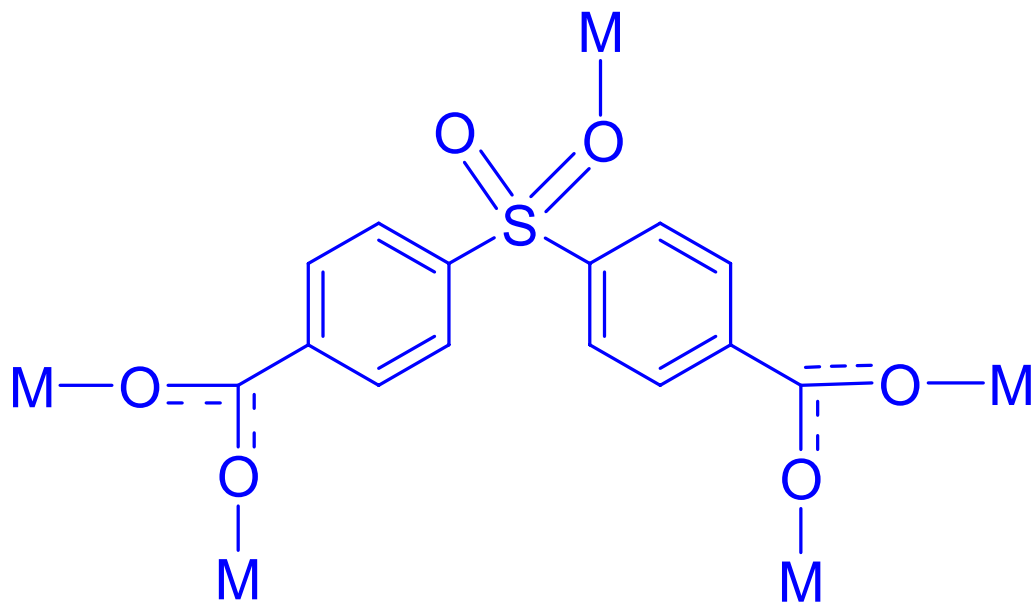


Fig. S2 The coordination mode of SDBA ligand in 1.

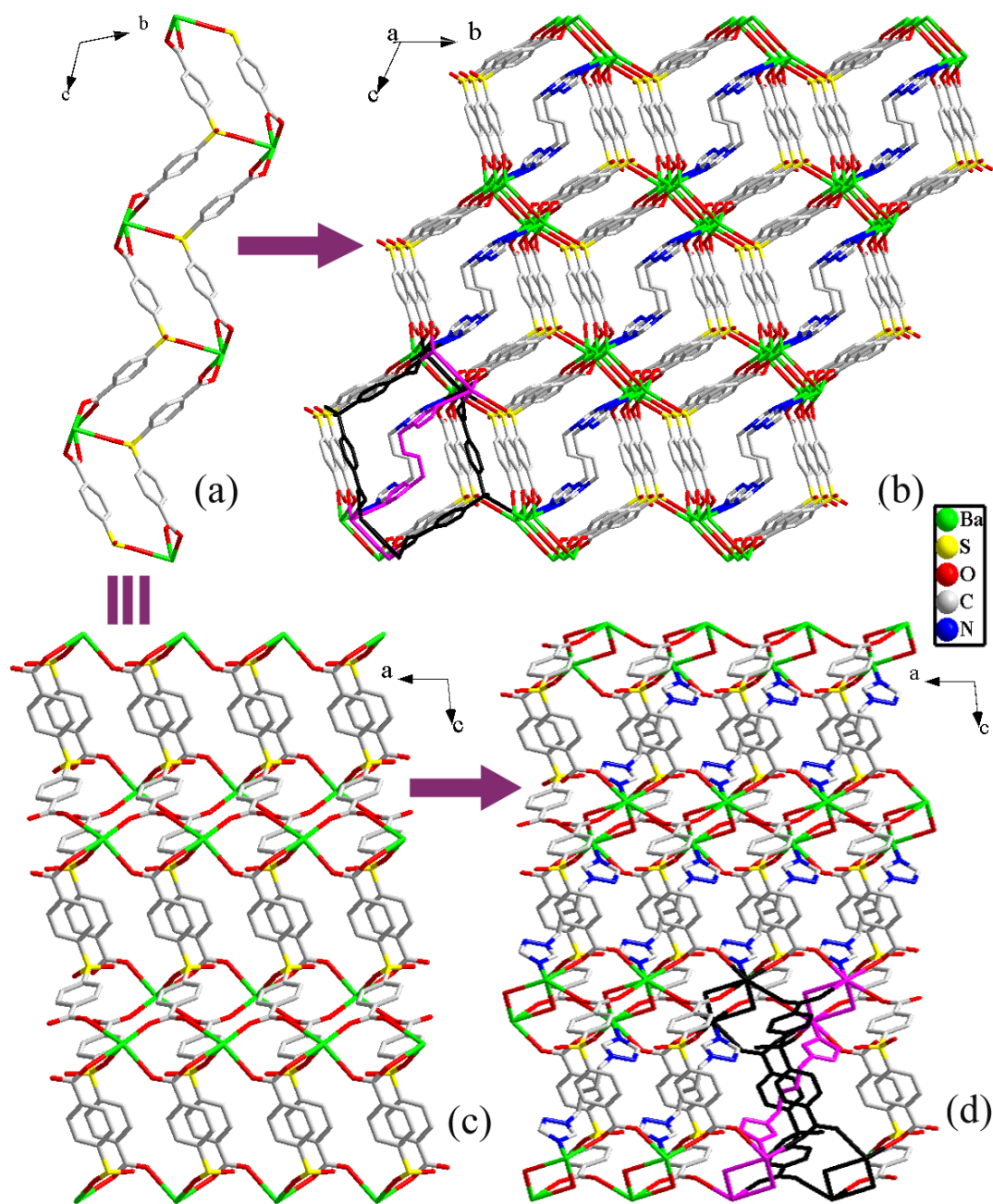


Fig. S3 Perspective views of the 2D molecular “double-floor” (a, c) and the 3D self-penetrating framework of **1** (b, d). The self-penetrating shortest circuit and rod are highlighted by black and purple.

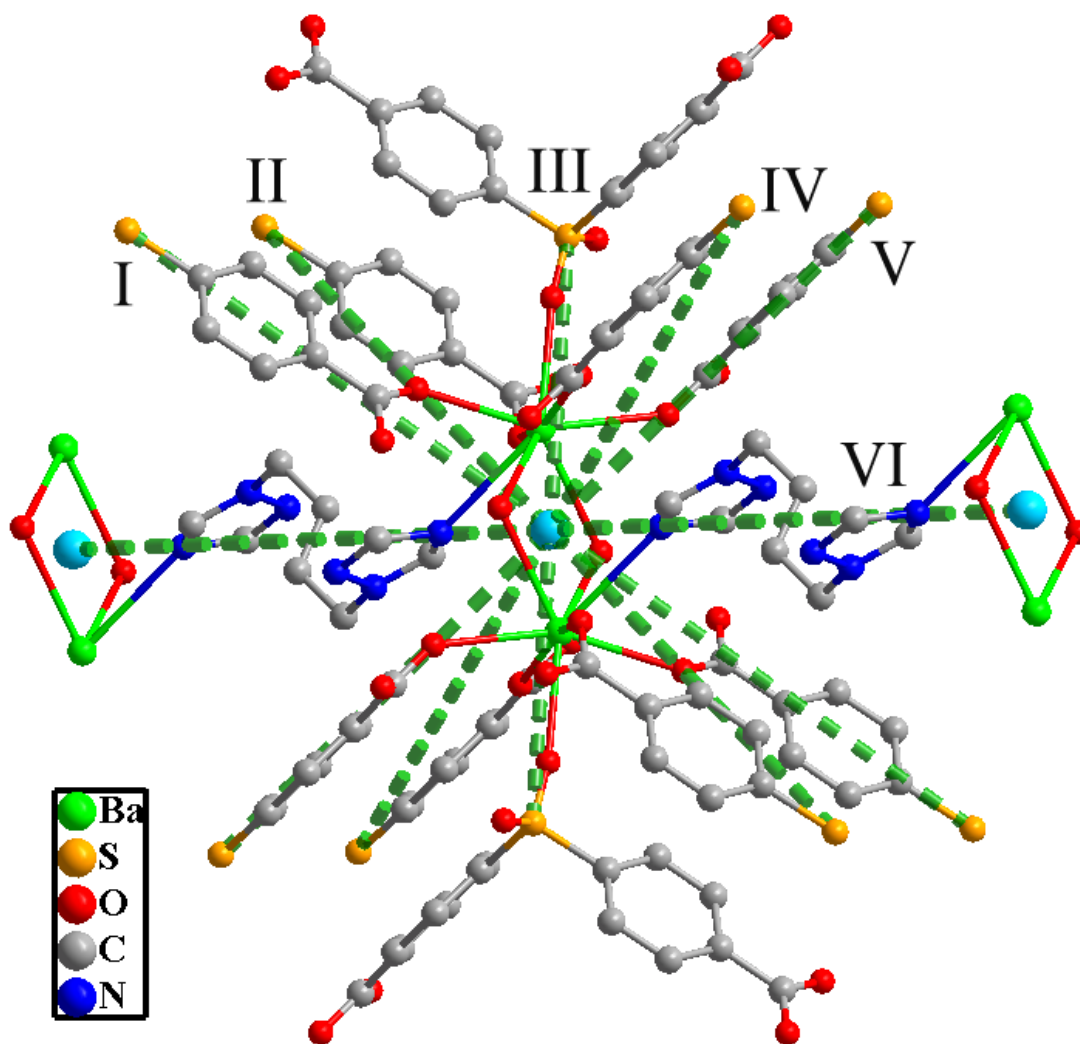


Fig. S4 Perspective view of the twelve-connected $[\text{Ba}_2(\mu_2\text{-OH}_2)_2]$ core in **1**. The symbols of six types of linkers are I (9.678 Å), II (9.355 Å), III (6.487 Å), IV (9.669 Å), V (10.443 Å) and VI (14.527 Å), respectively.

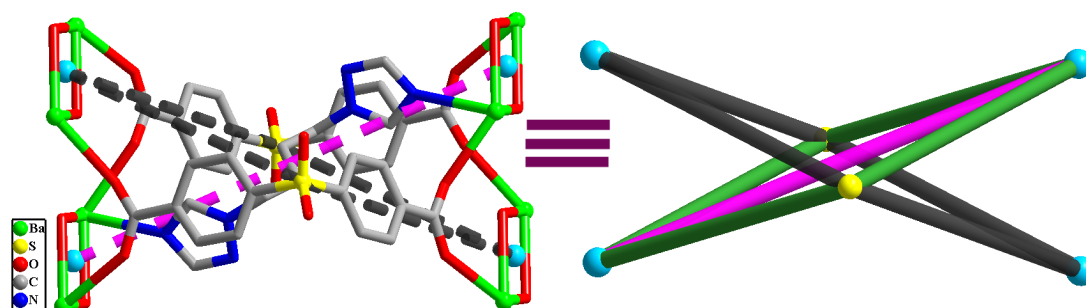


Fig. S5 The detail of the entanglement of four-membered ring (black) passed through by one btb ligand as a rod (purple) in the 3D self-penetrating framework of **1**.

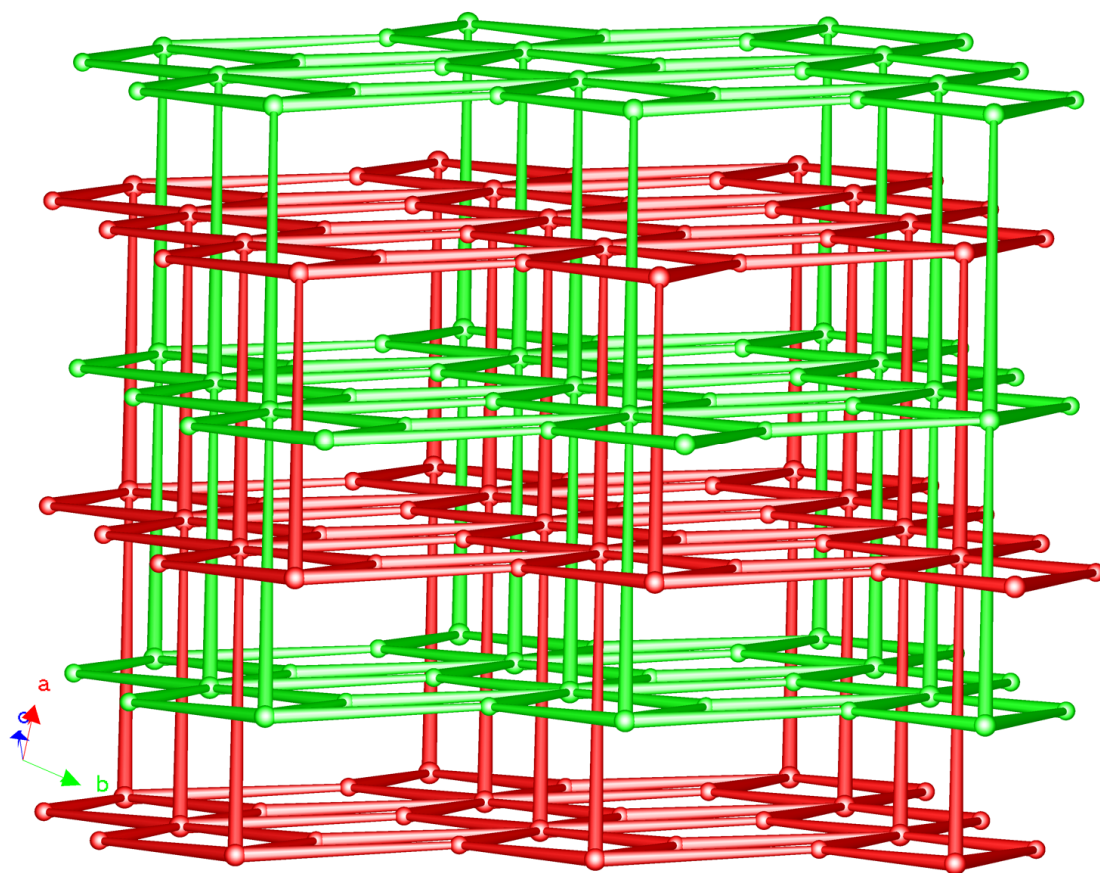


Fig. S6 Schematic view of twofold interpenetrating (3,8)-connected 3D $(4^3)_2(4^6.6^{18}.8^4)$ nets isolated by removing type I (9.678 Å) and type V (10.443 Å) links from **1**.

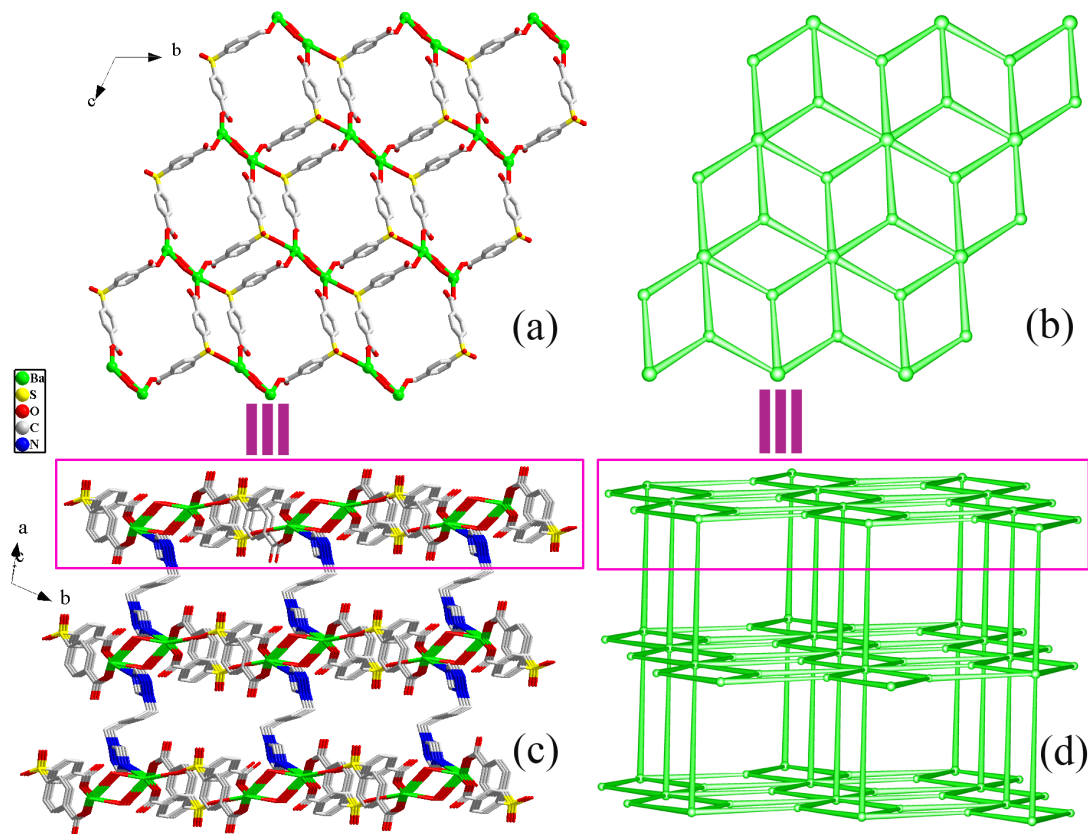


Fig. S7 View of the 2D network (a) corresponding a (3,6)-connected 2D **kgd** network of $(4^3)_2(4^6.6^6.8^3)$ topology (b). Perspective (c) and simplified (d) views of the single (3,8)-connected 3D net constructed from (3,6)-connected 2D layers and further connected by btb ligands as links.

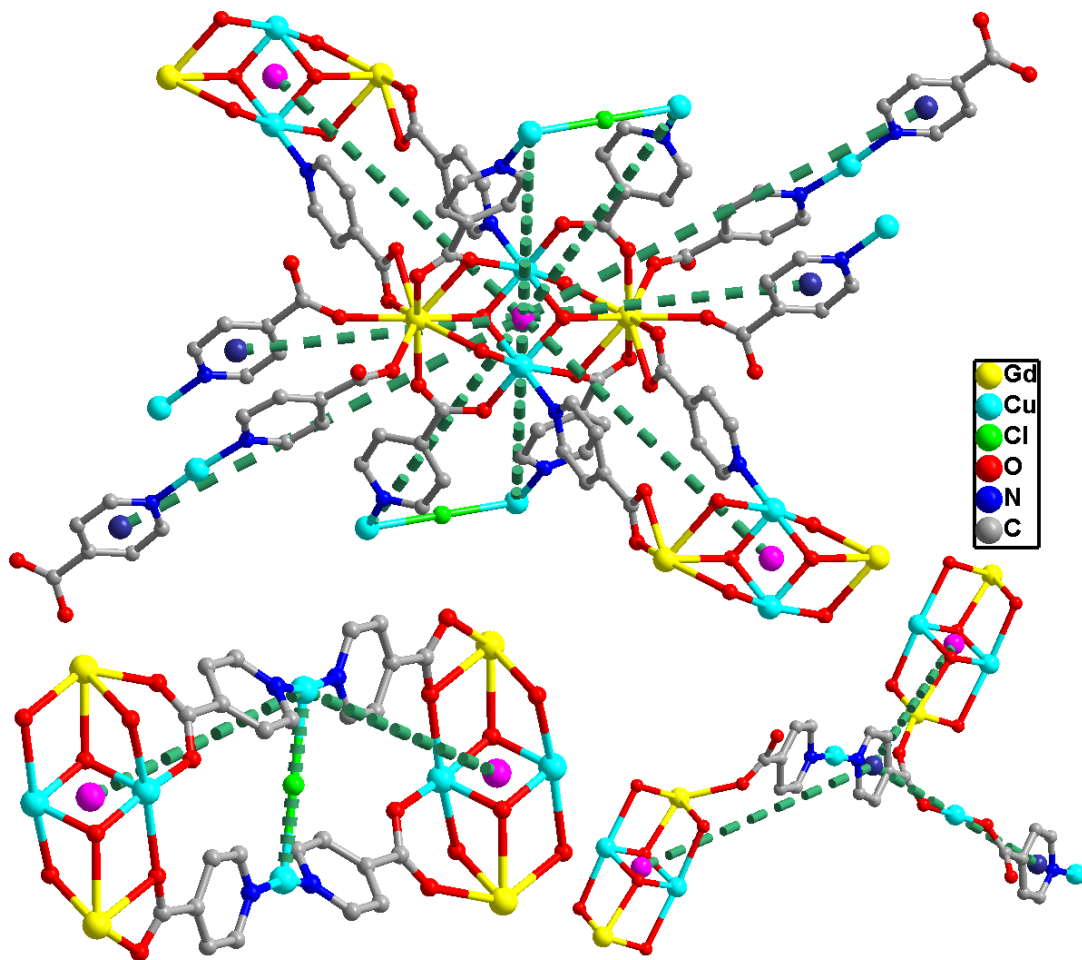


Fig. S8 View of the ten-connected node and two kind of three-connected nodes for the network reported in Ref. [12e]. The figure is generated from CIF data in Ref. [12e].

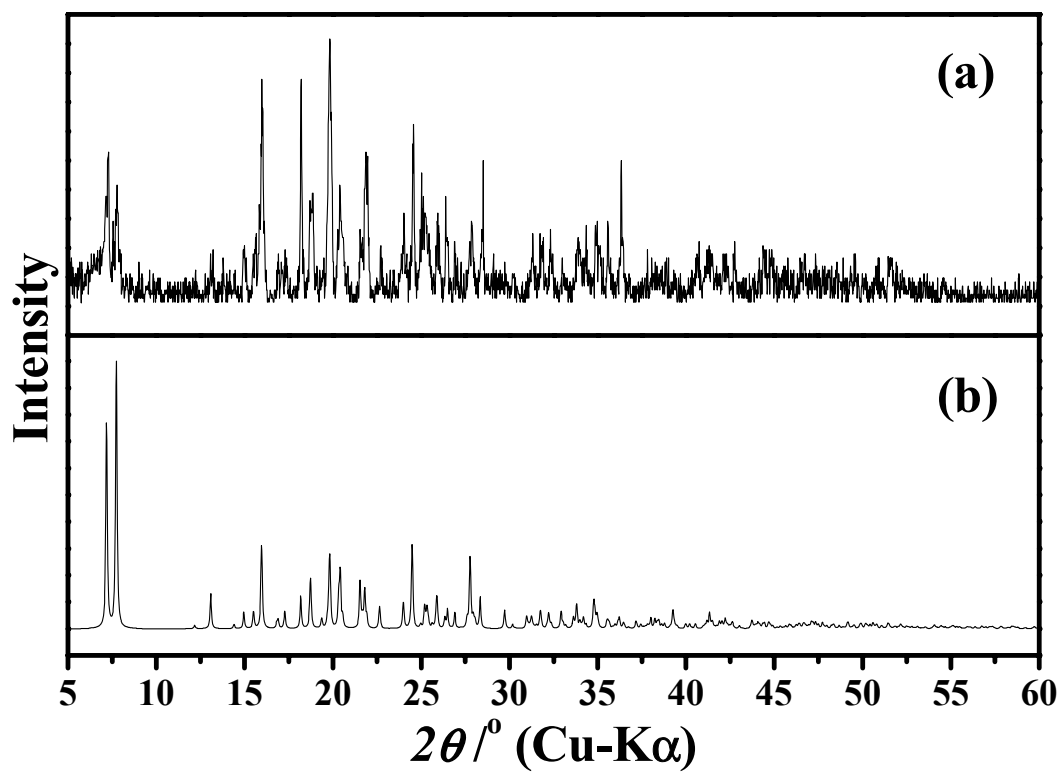


Fig. S9 The XRPD patterns for: (a) as-synthesized samples of **1**, and (b) simulated one based on the single-crystal structure of **1**.

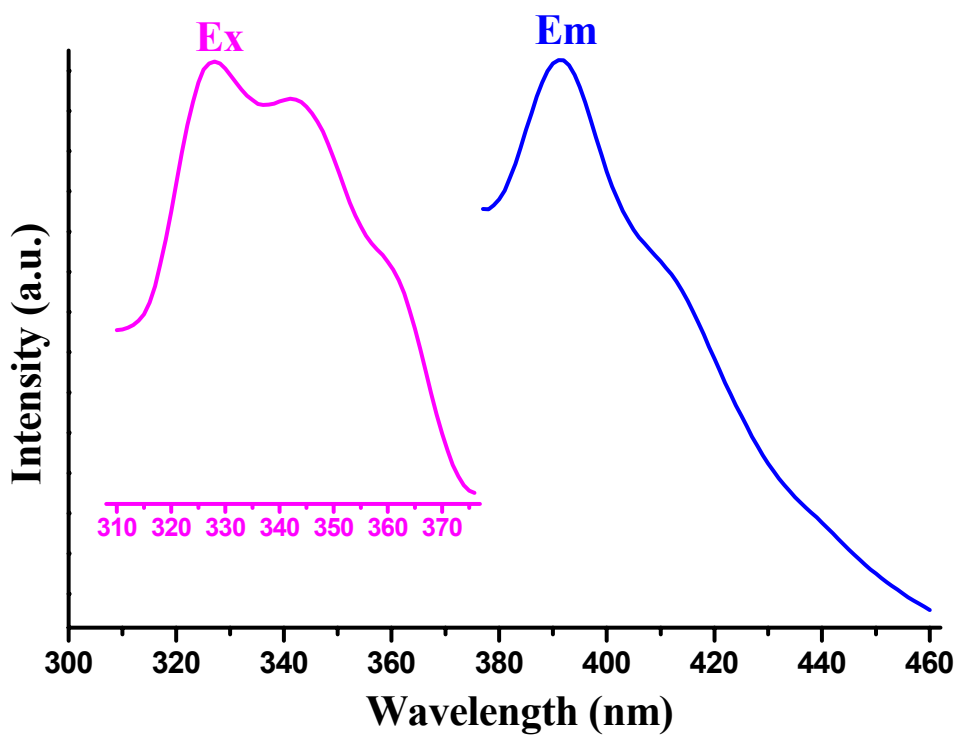


Fig. S10 Solid-state emission spectra of H₂sdba ligand at room temperature.

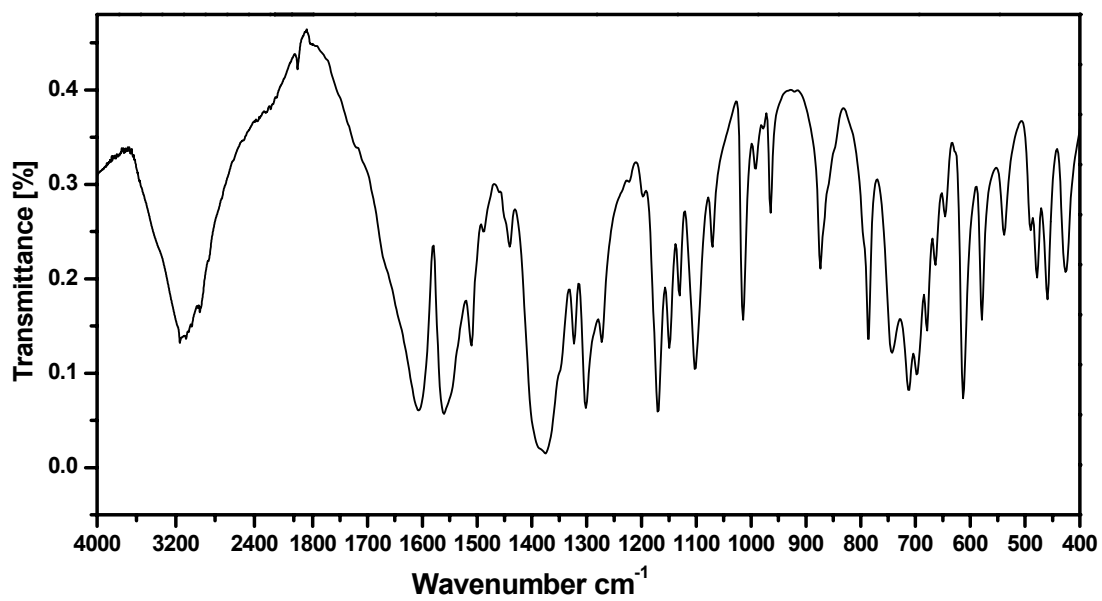


Fig. S11 The IR spectra for compound 1.