Electronic Supplementary Material (ESI) for Chemical Communications

Support Information

Chiral recognition of a 3D chiral nanoporous metal–organic framework

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1. Reagents and Materials: All chemicals were at least of analytical grade. Cadmium Nitrate Tetrahydrate ($Cd(NO_3)_2 \cdot 4H_2O$, 99%), 4,4´-biphenyldicarboxylic acid (H_2bpdc, 98%), and L-Leucine (99%) were purchased from Adamas. Hexane, dichloromethane (DCM), isopropanol and N,N-Dimethylacetamide (DMA) were from Tianjin Guangfu Fine Chemical Research Institute (Tianjin, China), and ethanol (HPLC grade) from TEDIA. 1,1'-bi-2-naphthol, 1,2-diphenyl-1,2-ethanediol, benzoin, and flavanone were obtained from Acros, 1-(4-chlorophenyl)ethanol from Alfa Aesar, furoin and troger's base from Aldrich, 3-benzyloxy-1,2-propanediol and 3,5-dinitro-N-(1-phenylethyl)benzamide from Fluka, and warfarin sodium from TCI.

2. Instrumentation. Stainless steel empty column (250 mm long × 2.0 mm i.d.) and 1/3 HP liquid pump were purchased from Alltech (USA). The HPLC system was equipped with a liquid delivery pump and UV-vis detector (LabTech LC600, USA). The Auto Science AT-330 column heater was used to control the column temperature during HPLC separation. The instrument control and data acquisition were carried out by the LabTech HPLC Workstation.

The powder X-ray diffraction (PXRD) patterns were obtained with a D/max-3B diffractometer (Rigaku, Japan) using Cu_{ka} radiation. The scanning electron microscopy (SEM) images were recorded on a Philip model XL30ESEMTMP scanning electron microscope at 30.0 kV. The TGA experiment was performed on a ZRY-1P Simultaneous Thermal Analyzer (Shanghai, China). The N_2 adsorption-desorption isotherms was measured by Quantachrome Nova 2000e Surface Area & Pore Size Analyzer at 77 K.

3. Synthesis of 1. 1 was synthesized according to the method of Xiang-Rong Hao et al.[S1] Typically, a DMA solution (5 mL) containing $Cd(NO_3)_2 \cdot 4H_2O$ (92mg, 0.3 mmol), H_2bpdc (60 mg, 0.25 mmol), and L-leucine (59 mg, 0.45 mmol) were stirred in N,N´-Dimethylacetamide (DMA) (5 mL). The obtained mixture was transferred to a Teflon-lined bomb. Then, the Teflon-lined bomb was heated at 140 °C for 2 days in an oven. After being cooled to room temperature, the resultant colorless rod-shaped crystals were washed thoroughly with DMA and dried at room temperature. The yield is 175 mg. Elemental analysis (%) calculated for **1**: C 53.72, H 5.53, N 6.06; found for **1:** C 53.61, H 5.36, N 6.24. This result is coincident to reference S1.

4. Column Packing Procedure for HPLC Measurement. In order to control the packing quality, a conventional high-pressure slurry packing procedure was adopted. Before the packing, the activating **1** was crushed in ethanol applying soft pressure. After crushing, the crystals were suspended in a mixture of hexane and dichloromethane. Then the suspension was packed into the empty column under 40~50 MPa with hexane/CH_2Cl_2 (9:1, v/v) as the slurry solvent. By changing the pressure to press the slurry into the column, the crystals could dispose slowly to get a better packing, then column **MOF** was obtained. Before chromatographic experiments, column **MOF** was rinsed and equilibrated with hexane/CH_2Cl_2 (9:l, v/v) until the baseline stabilized. After column use, the N_2 adsorption-desorption isotherms of sample gave a BET surface area of 43.081 m^2/g with a pore volume of 0.2263 cm^3/g. Probably because the MOF is the nanotubes assembled by the parallel

alignment, another possible reason is that some cation impurity exist in chiral anionic $[Cd(bpdc)_{1.5}]^-$ framework after column use, such as protonated dimethylamine, which affect N_2 adsorption. It also can indicate that the sample still keeps porous framework after HPLC measurement.

Reference

[S1] Hao, X. R.; Wang, X. L.; Qin, C.; Su, Z. M.; Wang, E. B.; Lana, Y. Q.; and Shao, K. Z. *Chem. Commun.*, 2007, **44**, 4620-4622.

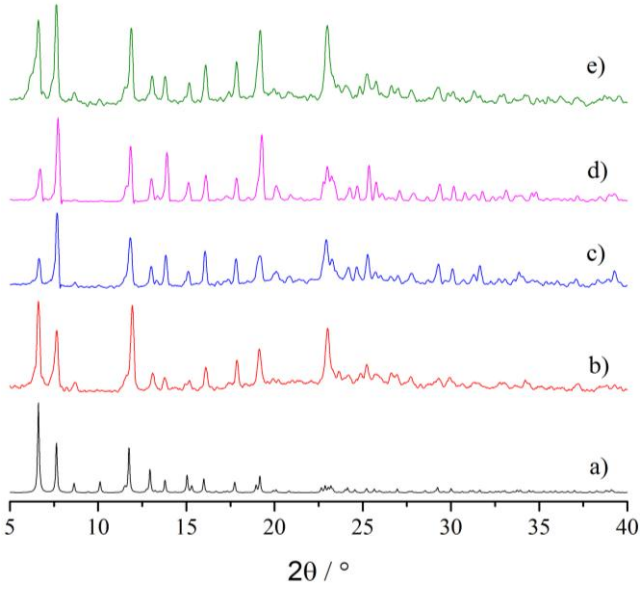

Fig. S1. PXRD patterns of **1**: (a) simulated from single-crystal X-ray diffraction data, (b) as-synthesized, c) after removal of guest solvent molecules, (d) after HPLC measurement, (e) after re-adsorption of solvent molecules.

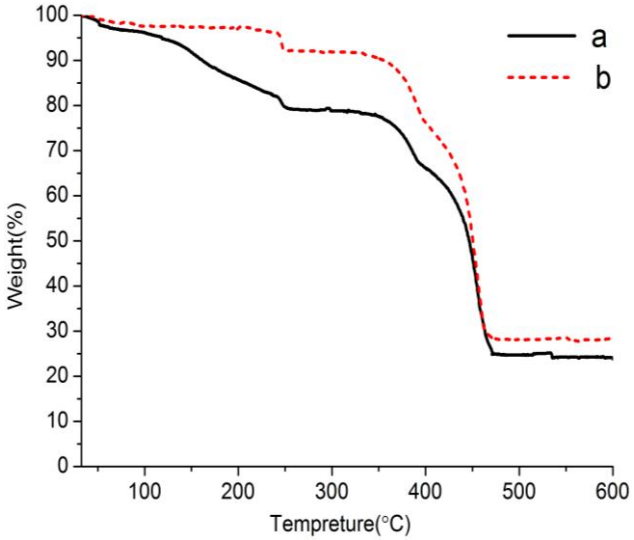

Fig S2. TG curve of 1: a) before removal of DMA guest Molecules., b) after removal of DMA guest Molecules.

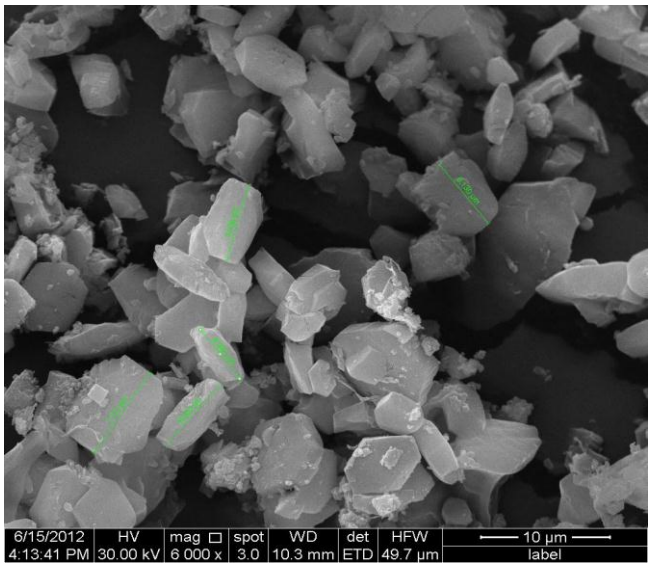

Fig. S3. SEM image of the prepared **1**.

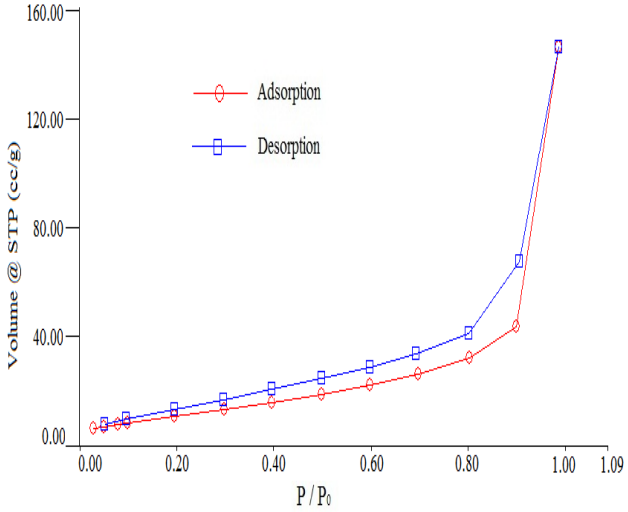

Fig. S4. N_2 adsorption-desorption isotherms of sample after column use.

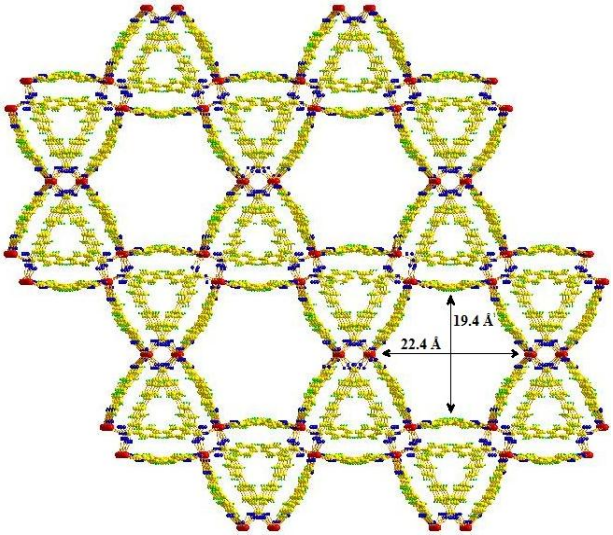

Fig. S5. Two types of channels (hexagonal and trigonal channels) exist in the 3D network. The hexagonal chiral nanotube with a 19.4 Å by 22.4 Å free aperture.

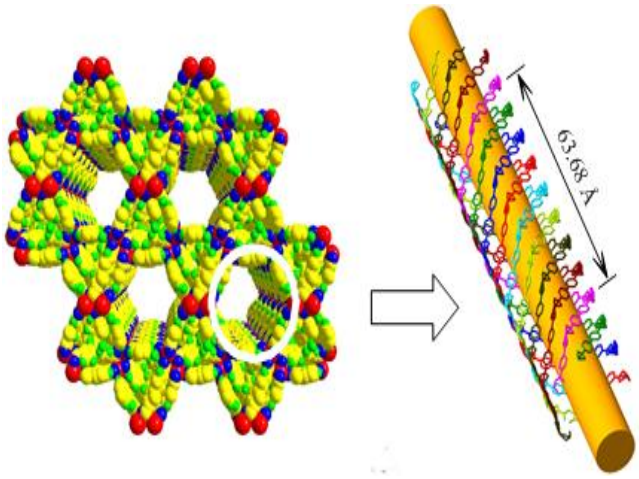

Fig. S6. (a) A space-filling diagram of crystal **1**. (b) Perspective view of a chiral nanotube, right-handed octuple helices with a helical pitch of 63.68 Å are displayed.