Supporting Information

A rod packing microporous metal-organic framework: unprecedented *ukv* topology, high sorption selectivity and affinity for CO_2

Lei Hou, Wen-Juan Shi, Yao-Yu Wang,* Ying Guo, Chen Jin and Qi-Zhen Shi

Key Laboratory of Synthetic and Natural Functional Molecule Chemistry of the Ministry of Education, Shaanxi Key Laboratory of Physico-Inorganic Chemistry, College of Chemistry & Materials Science, Northwest University. Xi'an 710069 (P. R. China).
Email: wyaoyu@nwu.edu.cn, Tel: 86 29 88302604

Materials and Measurements. All solvents and starting materials for synthesis were purchased commercially and were used as received. Infrared spectra were obtained from KBr pellets on a Bruker TENSOR 27 Fourier Transform Infrared spectrometer in the 400-4000 cm^{-1} region. Elemental analyses of C, H and N were determined with a Perkin-Elmer 2400C Elemental Analyzer. Thermalgravimetric analyses (TGA) were carried out in nitrogen stream using a Netzsch TG209F3 equipment at a heating rate of 5 °C/min. Powder X-ray diffraction (PXRD) data were recorded on a Bruker D8 ADVANCE X-ray powder diffractometer (Cu Kα, 1.5418 Å).

Synthesis of $[Cd_2L(H_2O)]_2\cdot 5(H_2O)$ (1). A mixture of 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (0.05 mmol, 0.022 g) and $Cd(NO_3)_2\cdot 4H_2O$ (0.031 g, 0.10 mmol) in water (10 mL) or water-ethanol (5 mL, 5 mL) was placed in a Teflon-lined stainless steel vessel (15 mL) and heated at 165 °C for 72 h, and then cooled to room temperature at a rate of 0.1 °C/min. The colorless rod-like crystals of **1** were isolated by washing with ethanol, and dried in vacuo. The yield was ~33 mg (86.4%). Anal. Calc. for $C_{38}H_{26}Cd_4F_{12}O_{23}$: C, 29.87; H, 1.71. Found: C, 29.93; H, 1.68%. IR (KBr, cm^{-1}): 3436s, 2928w, 1614m, 1552s, 1384s, 1255m, 1183m, 1083m, 794w.

Sorption Measurements. All the gas sorption isotherms were measured by using a ASAP 2020M adsorption equipment. The as-synthesized samples were treated by heating at 160 ºC for 6 h and subsequent 250 ºC for 1 h in a quartz tube under vacuum to remove the solvent molecules prior to measurements.

Crystallography. The diffraction data were collected at 295(2) K with a Bruker-AXS SMART CCD area detector diffractometer at 295(2) K using ω rotation scans with a scan width of 0.3° and Mo Kα radiation (λ = 0.71073 Å). Absorption corrections were carried out utilizing SADABS routine.[2] The structure was solved by the direct methods and refined by full-matrix least-squares refinements based on F^2.[3] All non-hydrogen atoms were refined anisotropically with the hydrogen atoms added to their geometrically ideal positions and refined isotropically except that the hydrogen atoms on the coordinated water molecules were located from the electron density and then refined using a riding model. However, the hydrogen atoms of the water solvates can not be located from the difference Fourier maps. Crystal data of **1**: $C_{38}H_{26}Cd_4F_{12}O_{23}$, $M = 1528.19$, 295(2) K, trigonal R-3 (No. 148), $a = b = 39.918(4)$ Å, $c = 7.7112(8)$ Å, $V = 10641.4(19)$ Å^3, $Z = 9$, $D_c = 2.146$ g cm^{-3}, $\mu = 0.954$ mm^{-1}, $R_{\text{int}} = 0.0501$, final $R_1 = 0.0385$, $wR_2 = 0.0901$ for 4657 unique reflections ($I \geq 2\sigma$), $S = 1.046$. CCDC-808236 contains the crystallographic data for this paper.

The final formula for the complex was determined by combining single-crystal structure, elemental microanalysis and TGA.

References

1 Bruker. *SADABS*, *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconson, USA, 2002.

2 G. M. Sheldrick, SHELXL-97, program for the refinement of the crystal structures. University of Göttingen, Germany, 1997.

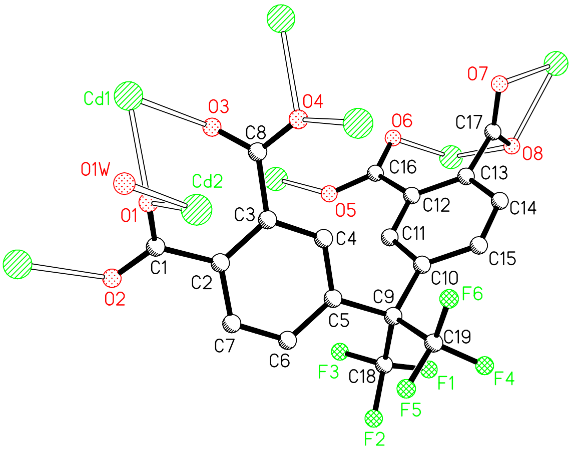

Fig. S1 The ball-and-stick drawing of the asymmetric unit in **1**, the hydrogen atoms and solvent molecules are omitted, and the atoms in the asymmetric unit are labeled.

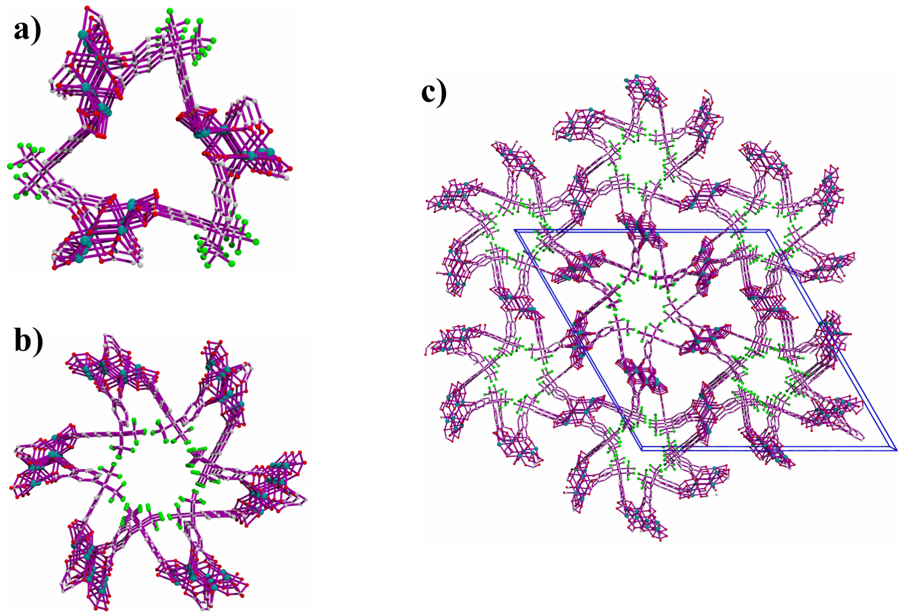

Fig. S2 a) The trigonal and b) hexagonal channels, and c) three-dimensional projection view of **1** along the *c*-axis.

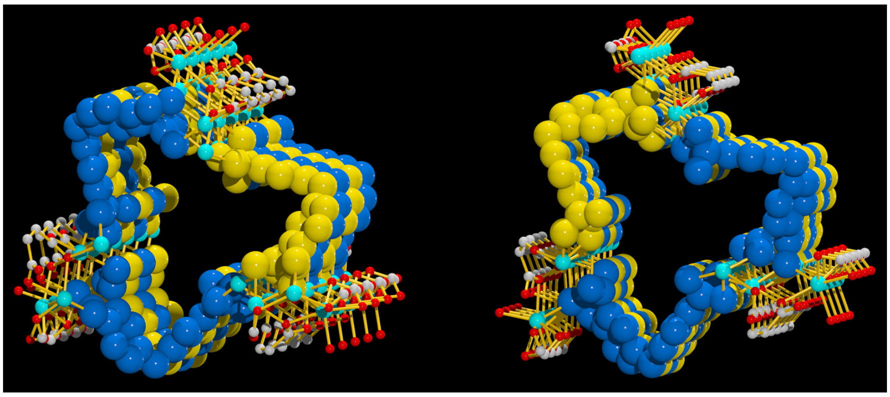

Fig. S3 The 3_1 left- and right-helical channels in **1** along the *c*-axis.

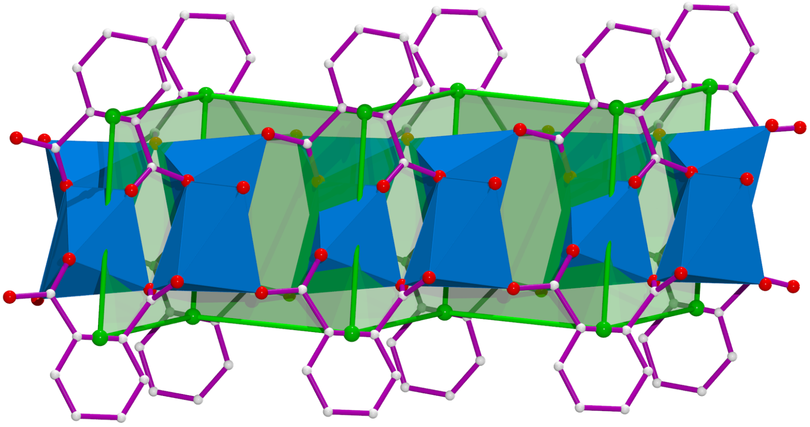

Fig. S4 A simplified zigzag rod-shaped SBU by considering the center of phenyl C=C bond as node.

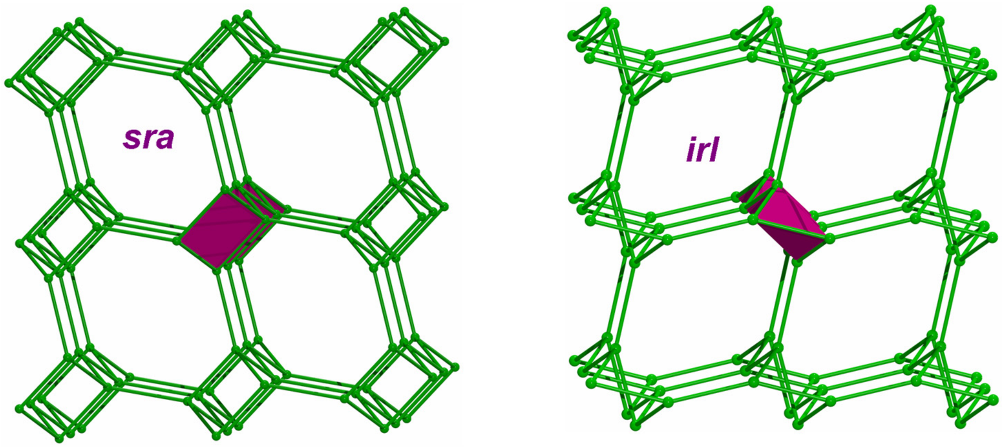

Fig. S5 The drawings of 4-connected *sra* and *irl* nets, with the same point symbol of $4^2 6^3 8$, however, different vertex symbols: *sra*, $4.6.4.6.6.8_2$; *irl*, $4.6.4.6.6.10_{12}$, analysed by Topos 4.0.

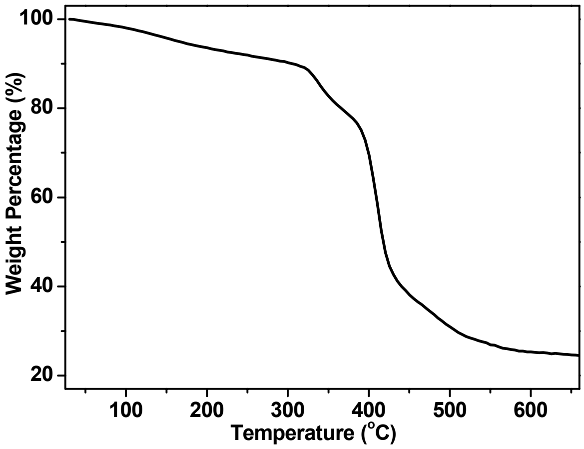

Fig. S6 TGA plot of **1** under N_2 atmosphere.

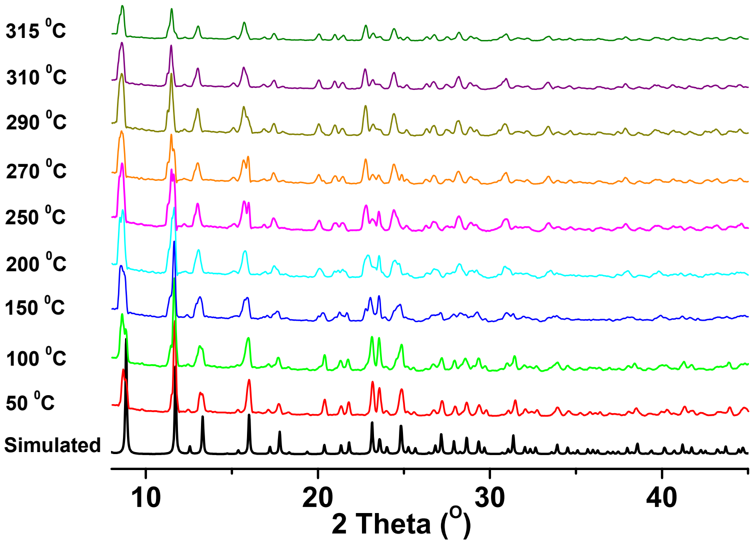

Fig. S7 The variable-temperature PXRD patterns of **1**.

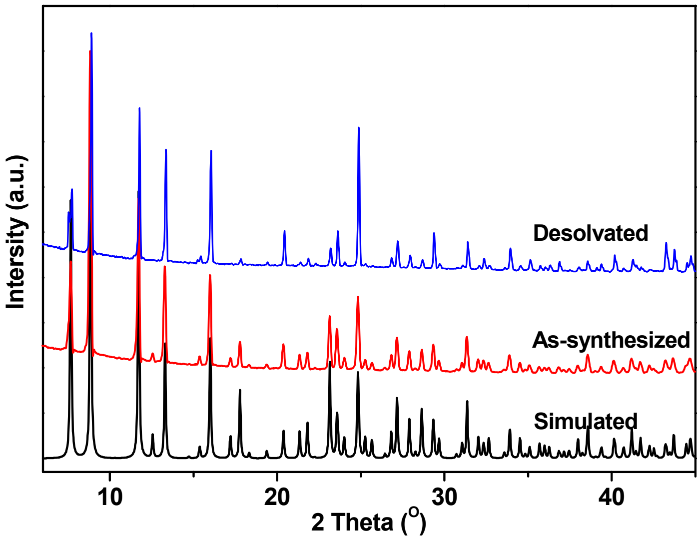

Fig. S8 PXRD patterns of **1** simulated from the X-ray single-crystal structure, as-synthesized and desolvated samples.

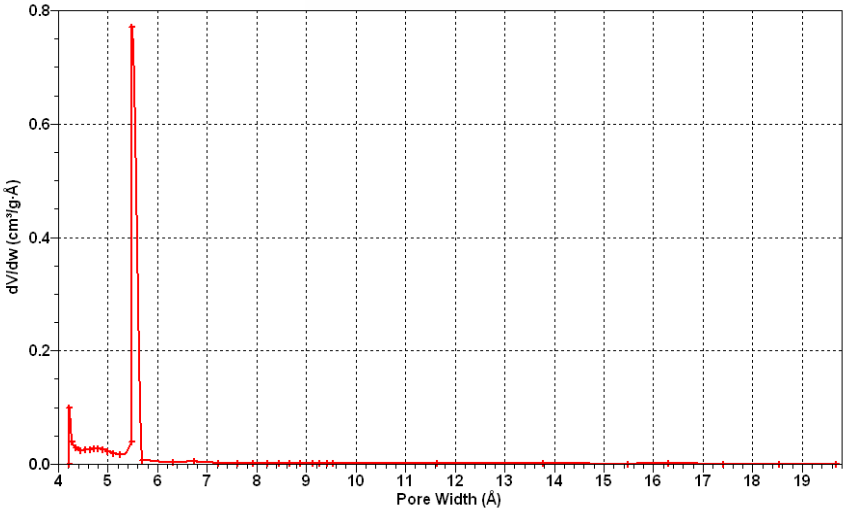

Fig. S9 Differential pore volume as a function of pore width calculated from the adsorption isotherm of N_2 at 77 K using the Horvath-Kawazoe model, median pore width of 5.2 Å.

Calculation of sorption heat for CO_2 uptake using Virial 2 model

$$\ln P = \ln N + 1/T\sum_{i=0}^{m} a_i N^i + \sum_{i=0}^{n} b_i N^i \qquad\qquad Q_{\mathrm{st}} = -R\sum_{i=0}^{m} a_i N^i$$

The above virial expression was used to fit the combined isotherm data for **1** at 273 and 293 K, where P is the pressure, N is the adsorbed amount, T is the temperature, a_i and b_i are virial coefficients, and m and N are the number of coefficients used to describe the isotherms. Q_{st} is the coverage-dependent enthalpy of adsorption and R is the universal gas constant.

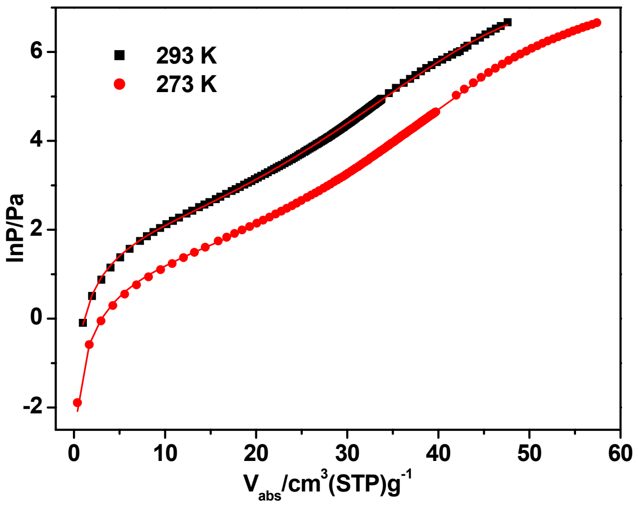

Fig. S10 CO_2 adsorption isotherms for **1** with fitting by Virial 2 model. Fitting results: a0 = -4438.01325 ± 84.69343, a1 = 74.33271 ± 12.95598, a2 = -7.34738 ± 0.57573, a3 = 0.14156 ± 0.00782, a4 = -0.00035 ± 0.00001, b0 = 15.18128 ± 0.30054, b1= -0.27887 ± 0.04551, b2 = 0.02601 ± 0.00198, b3 = -0.00041 ± 0.00003. Chi^2 = 0.00049, R^2 = 0.99975.