

Supplementary Information

One Non-interpenetrated Chiral Porous Multifunctional Metal–Organic Framework and Its Applications for Sensing Small Solvent Molecules and Adsorption

Ling Qin, Meng-Xi Zheng, Zi-Jian Guo, He-Gen Zheng,* Yan Xu*

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1. Experimental Section.

Materials and Measurements. Reagents and solvents employed were commercially available. IR absorption spectra of the compound **1** were recorded in the range of 400–4000 cm^{-1} on a Nicolet (Impact 410) spectrometer with KBr pellets. C, H and N analyses were carried out with a Perkin Elmer 240C elemental analyzer. Powder X-ray diffraction (PXRD) measurements were performed on a Bruker D8 Advance X-ray diffractometer using Mo- K_{α} radiation ($\lambda = 0.71073 \text{ \AA}$), in which the X-ray tube was operated at 40 kV and 40 mA. The as-synthesized samples were characterized by thermogravimetric analysis (TGA) on a Perkin Elmer thermogravimetric analyzer Pyris 1 TGA up to 973 K using a heating rate of 10 K min^{-1} under N_2 atmosphere. Luminescent spectra were recorded with a SHIMAZU VF-320 X-ray fluorescence spectrophotometer at room temperature. The gas sorption isotherms were measured by Micromeritics ASAP 2020 M+C surface area analyzer.

Gas Sorption Measurements

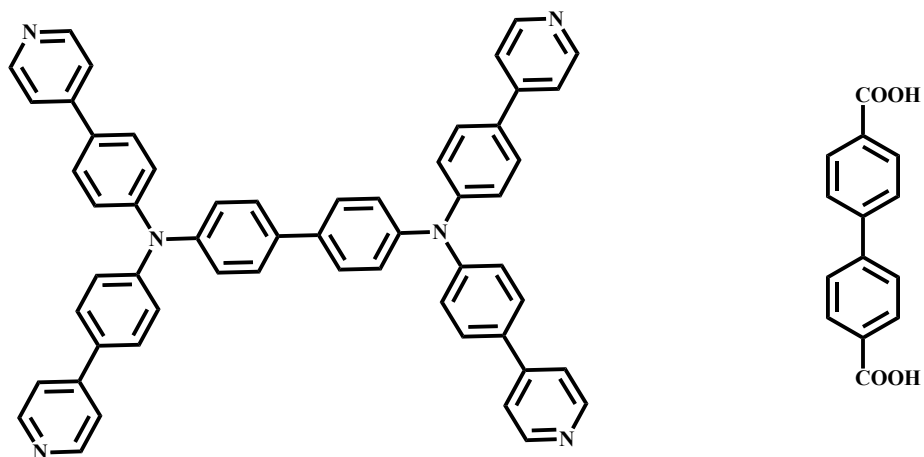
In the gas sorption measurement, Ultra-high-purity grade, N_2 , CO_2 and CH_4 (>99.999%) were used throughout the adsorption experiments. All of the measured sorption isotherms have been repeated several times to confirm the reproducibility within experimental error. Adsorption measurements (up to 1 bar) were performed on Micromeritics ASAP 2020 M+C surface area analyzer. About 90 mg of samples **1** were activated at 80 $^{\circ}\text{C}$ for 10 hours by using the “outgas” function of the surface area analyzer. Helium was used for the estimation of the dead volume, assuming that it is not adsorbed at any of the studied temperatures. The CO_2 and CH_4 isotherms were measured at 273 K.

Synthesis of compound 1: A mixture of $\text{H}_2\text{O}/\text{DMF}/\text{CH}_3\text{CN}$ containing the TPPBDA (0.1 mmol), H_2bpdc (0.2 mmol) and $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.1 mmol) was mixed in a Teflon vessel within the autoclave. The vessel was heated at 85 $^{\circ}\text{C}$ for 72 h and then cooled to room temperature. The yellow block crystals were obtained. The IR spectrum of the corresponding compound **1** is shown in the Fig. S3. The final formula

$\{[\text{Cd}_2(\text{TPPBDA})(\text{bpdC})_{3/2}(\text{H}_2\text{O})_2] \cdot 1/2\text{CO}_3 \cdot 5\text{DMF} \cdot 9\text{H}_2\text{O}\}$ was determined by elemental analysis and the basic composition and guest molecular of the compound **1** were obtained. The elemental analysis results are as follows: Calcd. for $\text{Cd}_4\text{C}_{185}\text{H}_{218}\text{N}_{22}\text{O}_{47}$ (**1**): C, 56.23; H, 5.56; N, 7.80, Found: C, 56.27; H, 5.58; N, 7.76.

X-ray Crystallography. X-ray crystallographic data of **1** were collected at room temperature by way of sealing the better single crystals in a quartz tube with mother liquor. Crystallographic data were collected on a Bruker Apex Smart CCD diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) using the ω -scan technique. The intensity data were integrated by using the SAINT program. An empirical absorption correction was applied using the SADABS program. The structures were solved by direct method and the nonhydrogen atoms were located from the trial structures and then refined anisotropically with SHELXTL using full-matrix least-squares procedures based on F^2 values. The positions of the non-hydrogen atoms were refined with anisotropic displacement factors. The hydrogen atoms were positioned geometrically by using a riding model. The distribution of peaks in the channels was chemically featureless to refine, using conventional discrete-atom models. To resolve these issues, the contribution of the electron density by the remaining solvent molecules was removed by the SQUEEZE routine in PLATON.

Crystal data: for **1** after squeezed: $[\text{C}_{155}\text{H}_{112}\text{Cd}_4\text{N}_{12}\text{O}_{19}]$, $M_r = 2896.17$, Monoclinic, space group $C2$, $a = 28.950(2)$, $b = 39.508(3)$, $c = 10.2785(8) \text{ \AA}$, $V = 11697.2(15) \text{ \AA}^3$, $Z = 2$, $D_c = 0.822 \text{ g}\cdot\text{cm}^{-3}$, $\mu(\text{Mo-K}\alpha) = 0.401 \text{ mm}^{-1}$, $T = 293(2) \text{ K}$, 42952 reflections measured, 18400 independent reflections ($R_{\text{int}} = 0.0474$), final $R_1 [I > 2\sigma(I)] = 0.0375$ and final $wR_2 = 0.0977$.



Scheme 1. H₂bpdca carboxylate acid and TPPBDA ligand.

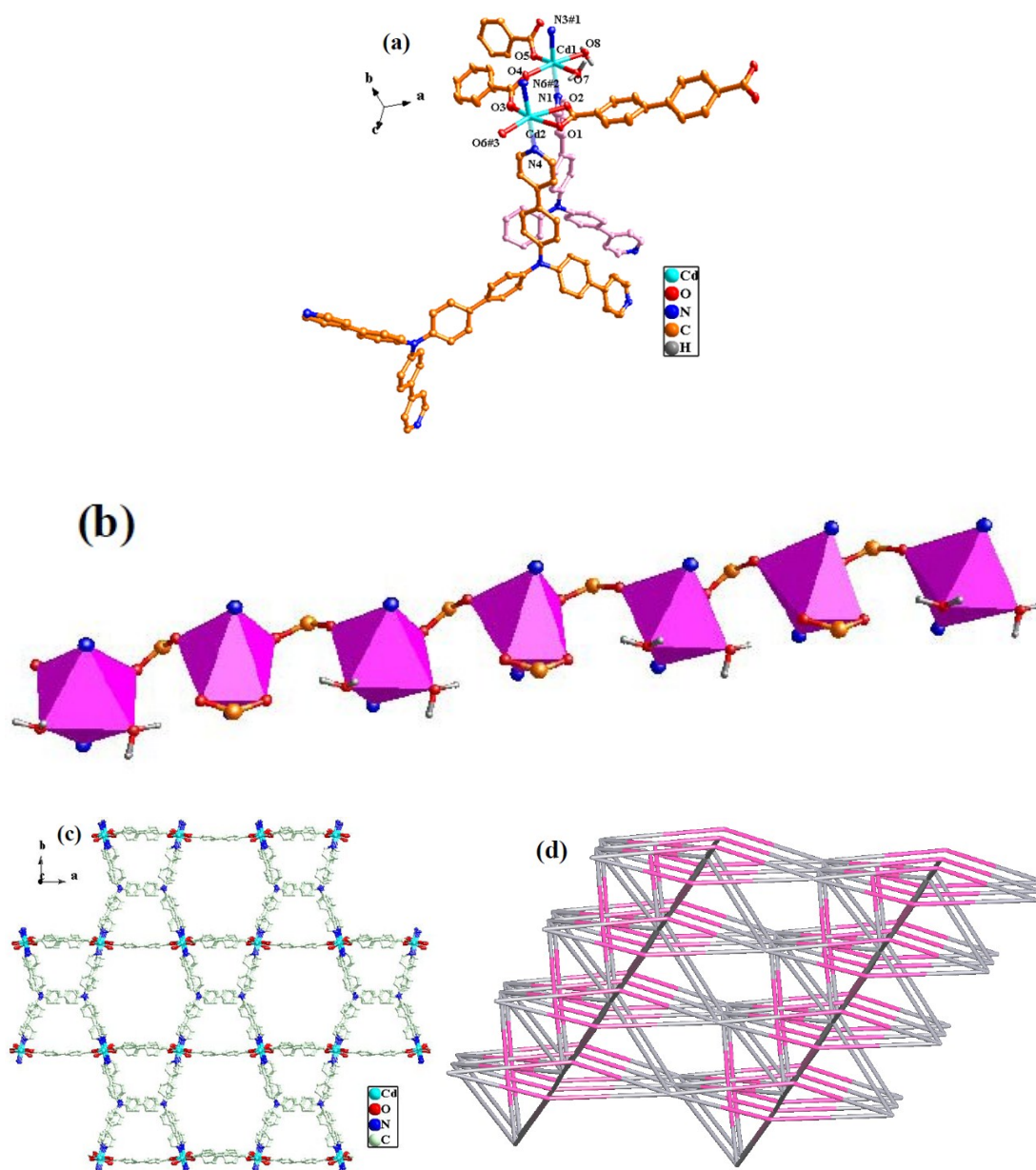


Fig. S1. (a) Coordination environment of compound **1** with 30% ellipsoid probability (hydrogen atoms and carbonate anions (decomposed from the dimethylamine) are omitted for clarity). Symmetry code: #1 = $0.5 - x, 0.5 + y, -z$. #2 = $0.5 - x, 0.5 + y, 1 - z$. #3 = $x, y, 1 + z$; (b) Ball and stick and polyhedral representation of rod-shaped SBUs; (c) A perspective of 3D framework along the c axis; (d) A view of 3D topology framework formed by Cd cations and mixed-ligand.

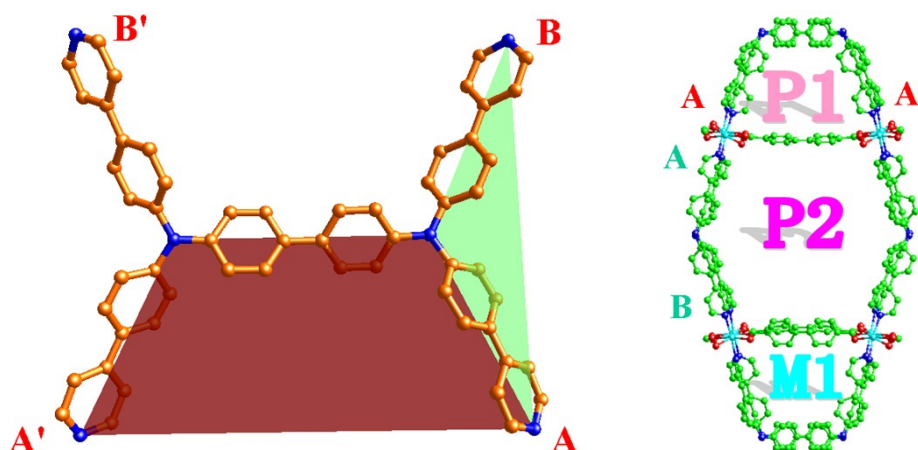


Fig. S2. Three types of 2_1 helices are bridged by the bpdc^{2-} ligand and nitrogen donors of the half of TPPBDA (mode AA' represents the upper or lower half part of the ligand and mode AB represents the left or right half part of the ligand).

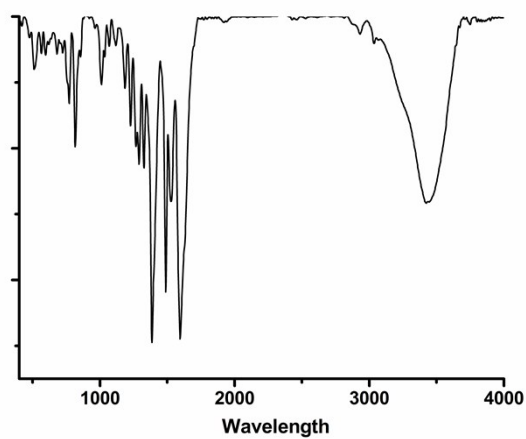


Fig. S3. IR spectra of compound **1**.

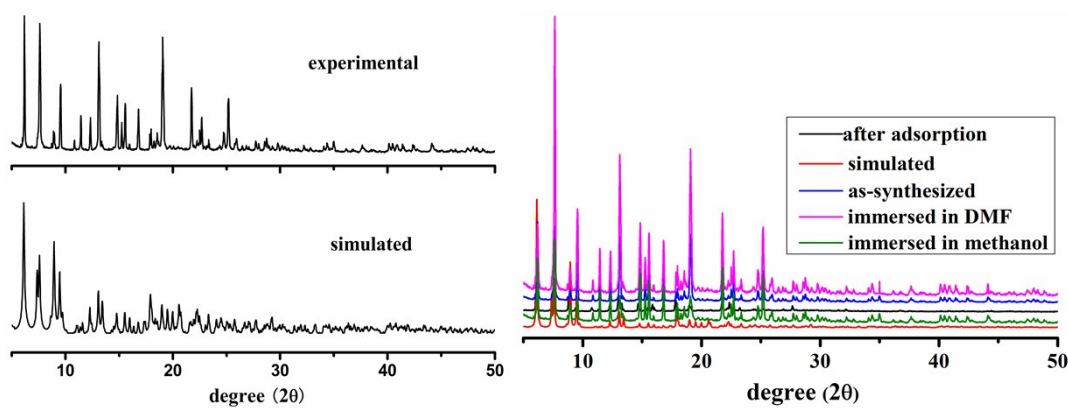


Fig. S4. Powder X-ray diffraction patterns of compound **1**.

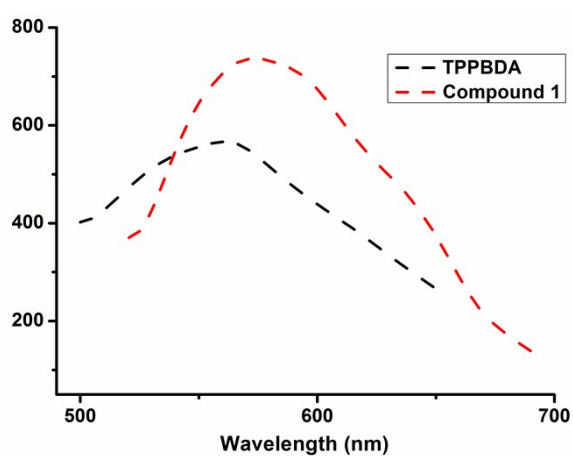


Fig. S5. Solid-state photoluminescent spectra of compound **1** and TPPBDA ligand at room temperature.

Thermal Analysis. For compound **1**, a gradually weight loss of 31.2% is observed from 30 to 260 °C, which is attributed to the loss of the lattice water, DMF molecules, CO_3^{2-} and coordinated water molecules (calcd 30.0%), of which the lattice water and DMF molecules were removed by the SQUEEZE routine in PLATON and were obtained by element analyses.

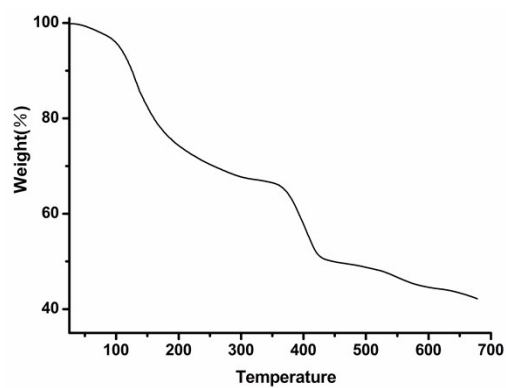


Fig. S6. The TGA diagrams of compound 1

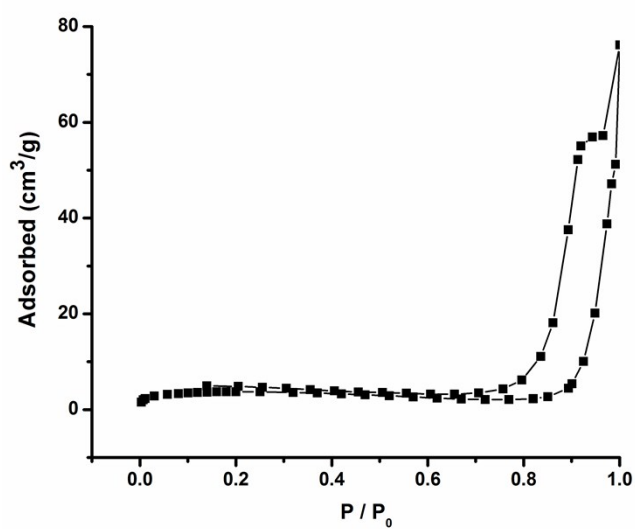


Fig. S7. Nitrogen isotherms measured at 77 K.

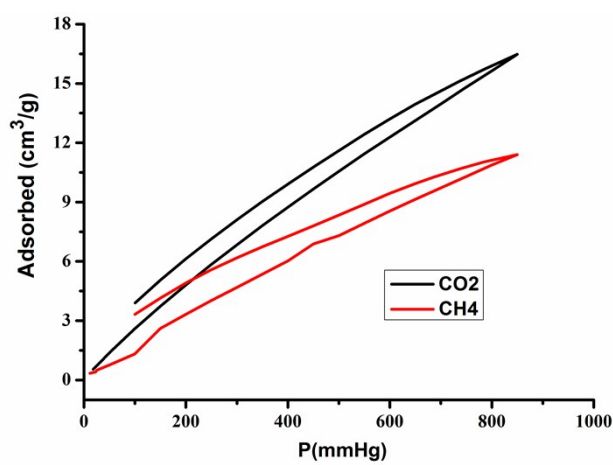


Fig. S8. Gas adsorption isotherms for CO₂ (black) and CH₄ (red) at 273 K.

Table S1. Dielectric constant values and maximum emission wavelength numbers of different organic solvents

solvent	dielectric constant	maximum emission wavelength numbers
hexane	2	406
acetic acid	4.1	557
toluene	2.4	423
chloroform	4.8	461
dichloromethane	9	481
ethanol	24	541
methanol	33	520
acetonitrile	37	541
dimethylformamide	38	512
water	80	510

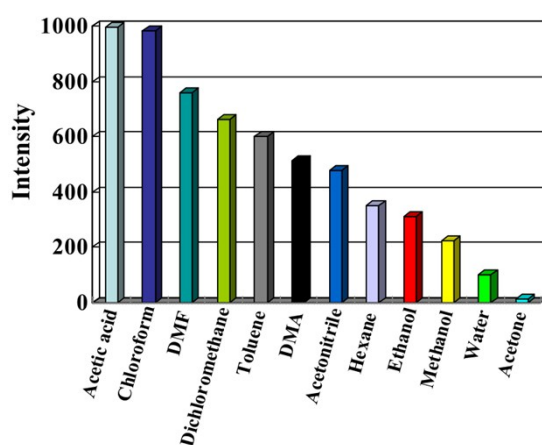


Fig. S9. The fluorescent intensities of compound 1 in suspension in various solvents.

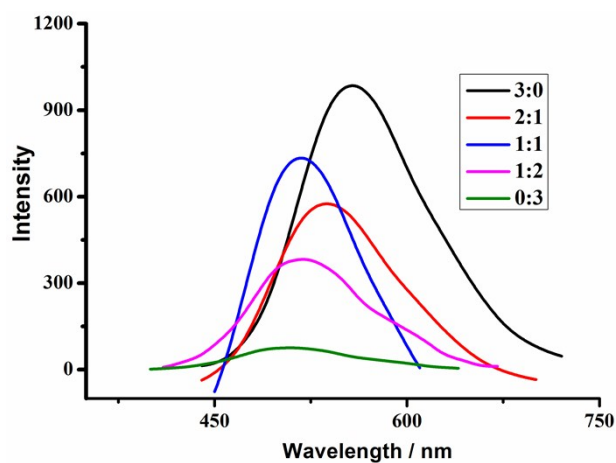


Fig. S10. The luminescent emission spectra of the sample **1**-acetic acid series immersed in sets of mixtures of solvents with increasing volumetric ratios of sample **1**-water.

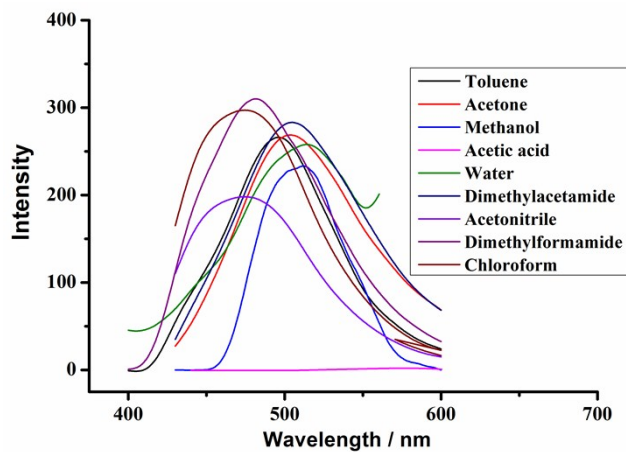


Fig. S11. The emission of TPPBDA in suspension in various organic solvents.

Table S2. Selected Bond Lengths (Å) and Angles (deg) for Compound **1**

Compound 1			
Cd1-N1	2.322(3)	Cd1-N3 ^a	2.294(3)
Cd1-O4	2.306(3)	Cd1-O5	2.264(2)
Cd1-O7	2.373(2)	Cd1-O8	2.326(3)
Cd2-N4	2.344(3)	Cd2-N6 ^b	2.298(3)
Cd2-O1	2.359(2)	Cd2-O2	2.415(2)
Cd2-O3	2.201(2)	Cd2-O6 ^c	2.267(3)
N1-Cd1- N3 ^a	170.35(12)	N1-Cd1-O4	88.38(12)
N1-Cd1-O5	88.32(12)	N1-Cd1-O7	85.54(12)
N1-Cd1-O8	89.43(11)	N3 ^a -Cd1-O4	89.39(12)
N3 ^a -Cd1-O5	101.25(12)	N3 ^a -Cd1-O7	85.00(12)
N3 ^a -Cd1-O8	90.81(12)	O4-Cd1-O5	95.97(9)
O4-Cd1-O7	87.97(9)	O4-Cd1-O8	167.95(10)
O5-Cd1-O7	172.61(15)	O5-Cd1-O8	95.81(11)
O7-Cd1-O8	80.04(10)	N4-Cd2- N6 ^b	178.36(12)
N4-Cd2-O1	89.59(11)	N4-Cd2-O2	90.78(11)
N4-Cd2-O3	84.96(14)	N4-Cd2- O6 ^c	91.29(11)
N6 ^b -Cd2-O1	92.04(12)	N6 ^b -Cd2-O2	89.99(12)
N6 ^b -Cd2-O3	93.42(15)	N6 ^b -Cd2- O6 ^c	88.79(12)
O1-Cd2-O2	54.25(8)	O1-Cd2-O3	161.09(12)
O1-Cd2- O6 ^c	94.83(9)	O2-Cd2-O3	107.63(10)

O2-Cd2- O6^c

149.00(9)

O3-Cd2- O6^c

103.36(10)

Symmetry Codes: for **1**: $a = 0.5 - x, 0.5 + y, -z$. $b = 0.5 - x, 0.5 + y, 1 - z$. $c = x, y, 1 + z$.