

Supporting Information

A 3D porous metal-organic framework containing nanotubes based on the multiple helices

Lei Hou,* Li-Na Jia, Wen-Juan Shi, Li-Yun Du, Jiang Li, Yao-Yu Wang* 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: lhou2009@nwu.edu.cn; wyaoyu@nwu.edu.cn, Tel: 86 29 88302604

Experimental

Materials and Measurements

All solvents and starting materials for synthesis were purchased commercially. Infrared spectra were obtained in KBr discs on a Nicolet Avatar 360 FTIR 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 STA 449C equipment at a heating rate of 10 $^{\circ}\text{C}/\text{min}$. Powder X-ray diffraction (PXRD) data were recorded on a Bruker D8 ADVANCE X-ray powder diffractometer (Cu $K\alpha$, 1.5418 Å).

Synthesis of Complex $[\text{Co}_2(\text{bpdc})_{1.5}(\text{Hbpz})]\cdot(\text{DMF})\cdot(\text{CH}_3\text{CN})\cdot(\text{H}_2\text{O})$ (1**).** a mixture of $\text{Co}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$ (0.050 g, 0.20 mmol), H_2bpdc (0.072 g, 0.30 mmol) and H_2bpz (0.038g, 0.20 mmol) in DMF (5mL) and CH_3CN (5mL) was placed in a Teflon-lined stainless steel vessel (15 mL), which was heated at 160 $^{\circ}\text{C}$ for 72 h, then cooled to room temperature at a rate of 5 $^{\circ}\text{C}/\text{h}$. Finally, prism purple crystals of **1** were obtained, which were isolated by

washing with DMF, and dried in vacuo (Yield: about 10 mg). Anal. Calcd for C₃₆H₃₇Co₂N₆O₈: C, 50.08; H, 4.66; N, 10.51%. Found: C, 50.14; H, 4.59; N, 10.46%. IR (KBr, cm⁻¹): 3426(vs), 2930(m), 2214(w), 1658(s), 1608(s), 1540(s), 1400(vs), 1259(w), 1172(w), 1039(m), 843(m), 768(m), 681(m).

Sorption Measurements

The sorption isotherms were measured using a Micrometrics ASAP 2020M instrument at different temperatures. The samples were activated in a quartz tube and dried under vacuum at 120 °C for 5 h to remove the solvent molecules prior to measurements.

Crystallography

Diffraction data were collected with a Mo K α radiation ($\lambda = 0.71073$ Å) on a Bruker-AXS SMART CCD area detector diffractometer. Absorption corrections were carried out utilizing SADABS routine.¹ The structure was solved by the direct methods and refined by full-matrix least-squares refinements based on F^2 .² All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were added to their geometrically ideal positions. **1** contains highly disordered solvent molecules, which can not be identified from the difference Fourier map. So the SQUEEZE routine³ was applied to remove the contributions to the scattering from the solvents. The reported refinement is of the guest-free structure using the *.hkp file produced by the SQUEEZE routine. The final formula was determined by combining single-crystal structures, elemental microanalyses and TGA. Relevant crystallographic data is listed in Table S1. Selected bond lengths and angles are given in Table S2.

References

- 1 Bruker. *SADABS, SMART and SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA, 2002.
- 2 G. M. Sheldrick, *SHELXL-97, program for the refinement of the crystal structures*. University of Göttingen, Germany, 1997.
- 3 A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7.

Table 1. Crystallographic Data and Structural Refinements for **1**^a

complex	1
formula	C ₃₁ H ₂₅ Co ₂ N ₄ O ₆
formula weight	667.41
<i>T</i> (K)	296(2)
crystal system	tetragonal
space group	<i>I</i> 4 ₁ / <i>a</i>
<i>a</i> (Å)	43.939(10)
<i>c</i> (Å)	8.5387(19)
<i>V</i> (Å ³)	16485(6)
<i>Z</i>	16
<i>D</i> _c (g cm ⁻³)	1.076
<i>μ</i> (mm ⁻¹)	0.841
reflns collected/unique	42861/8089
<i>R</i> _{int}	0.0503
<i>R</i> ₁ ^a (>2σ/all data)	0.0345 / 0.0492
<i>wR</i> ₂ ^a (>2σ/all data)	0.0930 / 0.0977
GOF	1.002

$$^aR_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}; wR_2 = \left[\frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2} \right]^{1/2}.$$

Table S2. Selected Bond Lengths (Å) and Bond Angles (°) for **1**^a

Co(1)-O(1)	1.9669(17)	O(1)-Co(1)-O(3) ^{#1}	101.85(8)
Co(1)-O(3) ^{#1}	1.9705(16)	O(5)-Co(1)-N(1)	115.22(8)
Co(1)-O(5)	1.9207(17)	O(1)-Co(1)-N(1)	108.65(8)
Co(1)-N(1)	1.9890(17)	O(3) ^{#1} -Co(1)-N(1)	114.72(7)
Co(2)-O(2)	1.9419(16)	O(2)-Co(2)-O(4) ^{#1}	103.62(7)
Co(2)-O(4) ^{#1}	1.9660(16)	O(2)-Co(2)-N(2)	117.19(8)
Co(2)-N(2)	1.9933(17)	O(4) ^{#1} -Co(2)-N(2)	111.64(7)
Co(2)-N(3) ^{#2}	2.0223(18)	O(2)-Co(2)-N(3) ^{#2}	107.63(8)
O(5)-Co(1)-O(1)	102.22(9)	O(4) ^{#1} -Co(2)-N(3) ^{#2}	106.67(7)
O(5)-Co(1)-O(3) ^{#1}	112.38(8)	N(2)-Co(2)-N(3) ^{#2}	109.47(7)

^aSymmetry codes: #1 *y*-3/4, -*x*+5/4, *z*-3/4; #2 -*y*+5/4, *x*+1/4, -*z*+5/4.

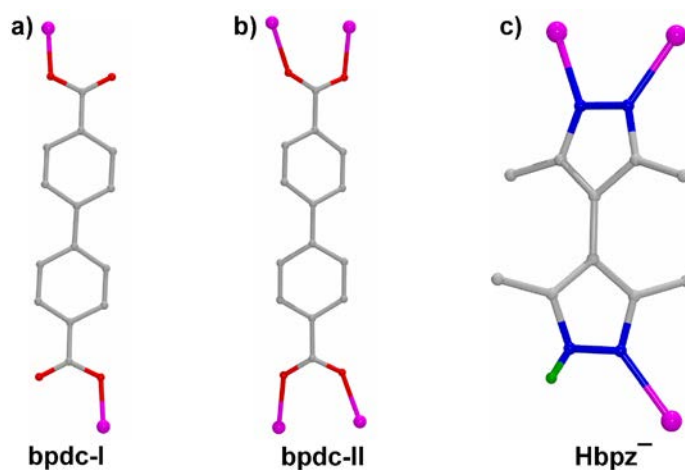


Fig. S1 Coordination fashions of bpdc^{2-} and Hbpz^- ligands.

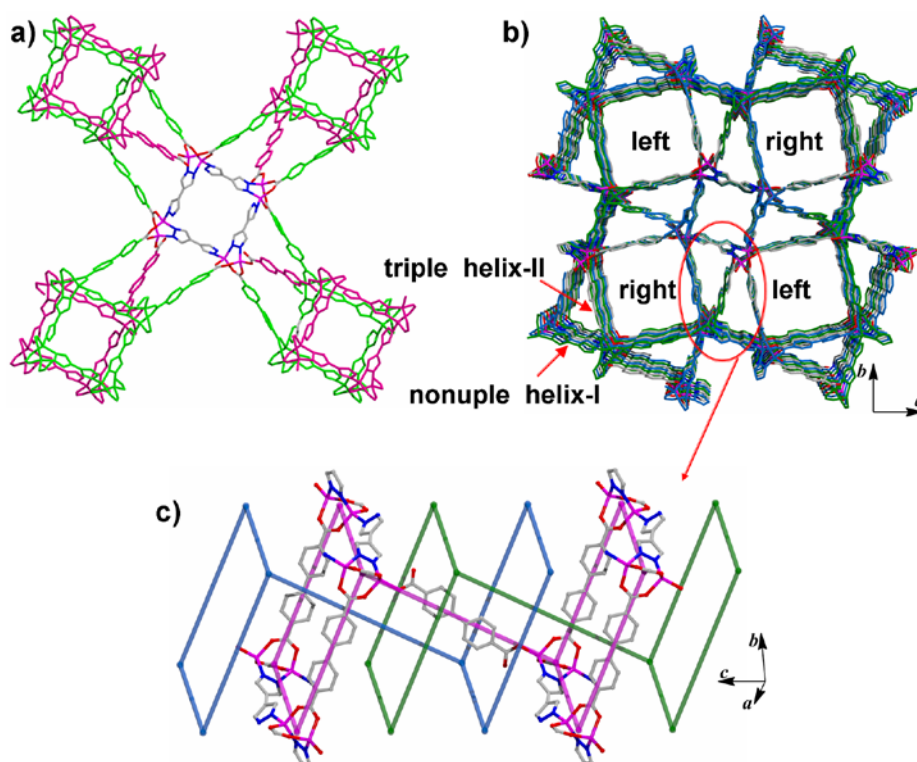


Fig. S2 a) Each $[\text{Co}_2(\text{CO}_2)_2(\text{Hbpz})]_4$ molecular building block (MBB) connecting adjacent eight MBBs through twelve bpdc^{2-} linkers. b) The 3-fold interpenetrated 3D structure of **1** along the c axis, featuring the superposed stacks, and adjacent nanotubes exhibiting opposite chirality. c) A coplanar square ring comprised of four Co_2 clusters, two bpdc-II , and two Hbpz^- , which has a large windows (sizes ca. $11.5 \times 7.5 \text{ \AA}^2$), and enables two bpdc-I from other two frameworks to traverse.

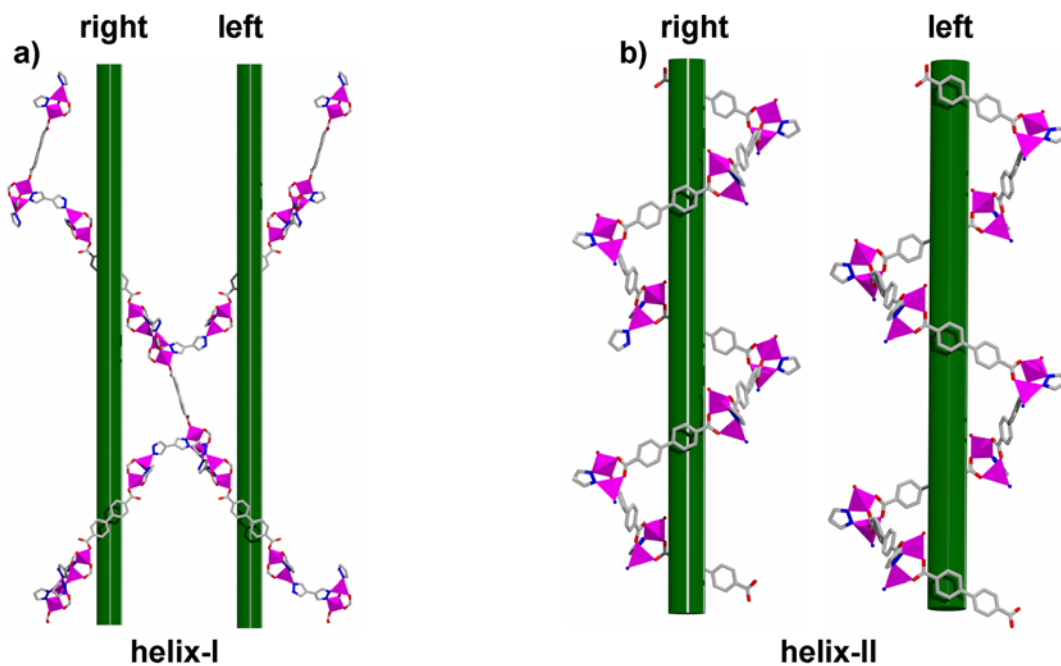


Fig. S3 a) Right- and left-handed helix-I generated through the linkage of Co_2 clusters with bpdc-I and Hbpz⁻ ligands, possessing the shared bpdc-I ligands between two helices. b) Right- and left-handed helix-II based on Co_2 clusters and bpdc-II.

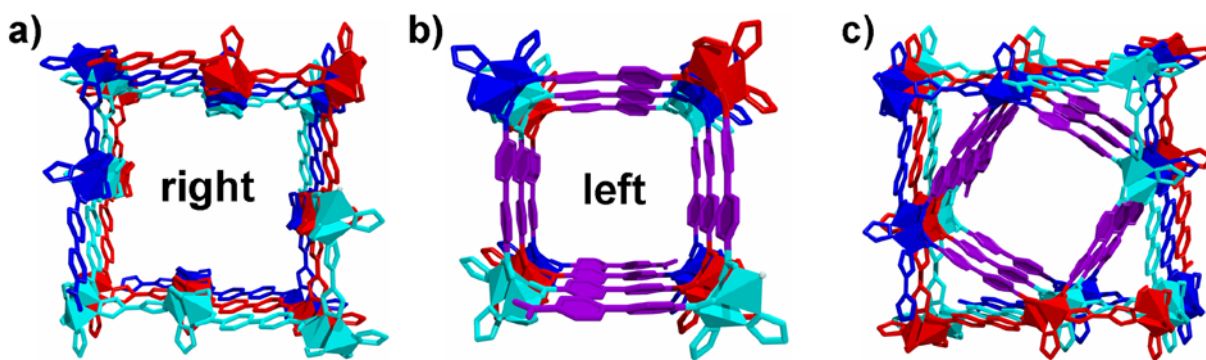


Fig. S4 a) 3-fold right-handed nanotubular helix-I and b) left-handed nanotubular helix-II in a single framework, and c) three helix-I cycling one helix-II by sharing Co_2 dimers to generate a “3+1” type quadruple helices.

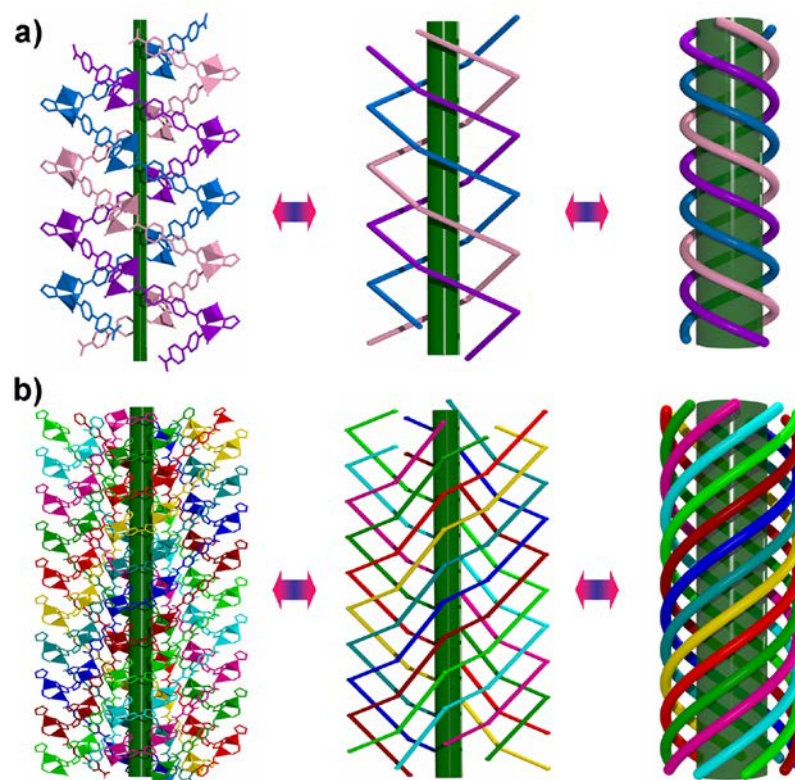


Fig. S5 The nanotubular architectures in **1** generated through the parallel associations of triple left-handed (a) and nonuple right-handed helical chains, respectively.

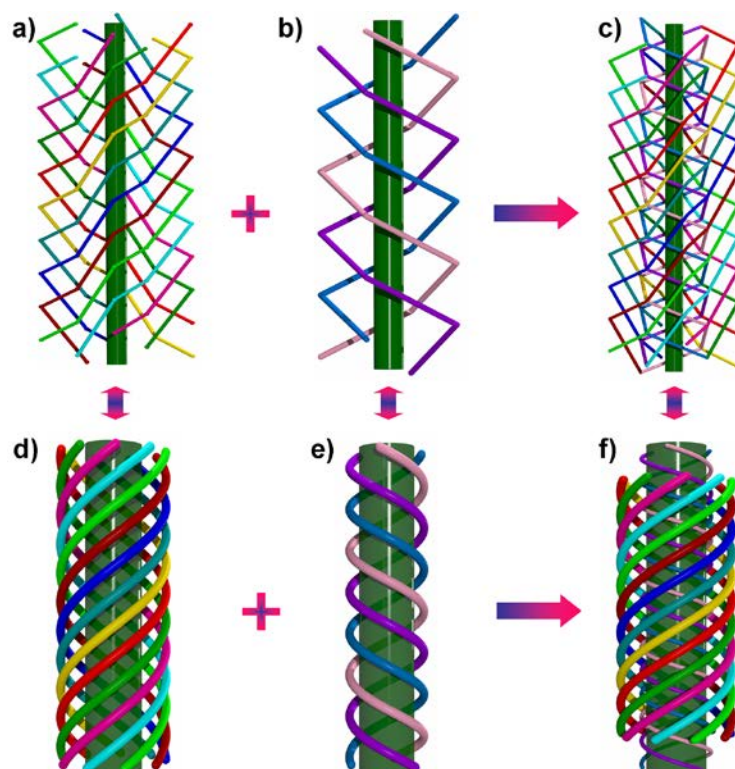


Fig. S6 The double-walled nanotube created through nonuple and triple helices with opposite chirality in **1**.

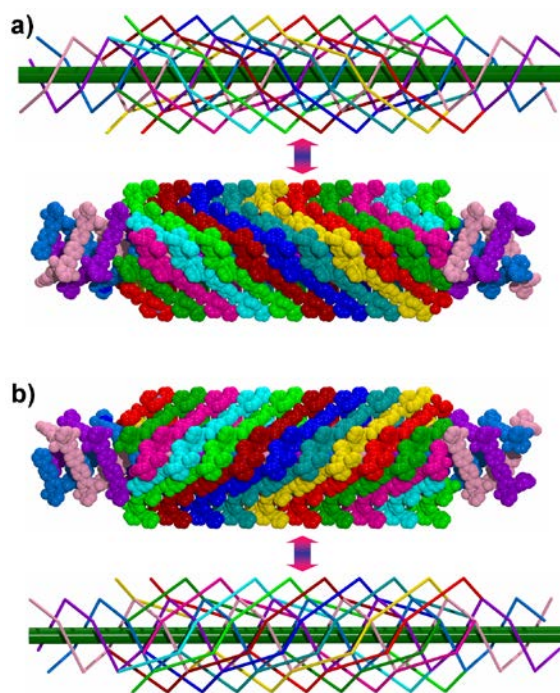


Fig. S7 Two opposite chiral double-walled nanotubes with twelvefold helices in **1**.

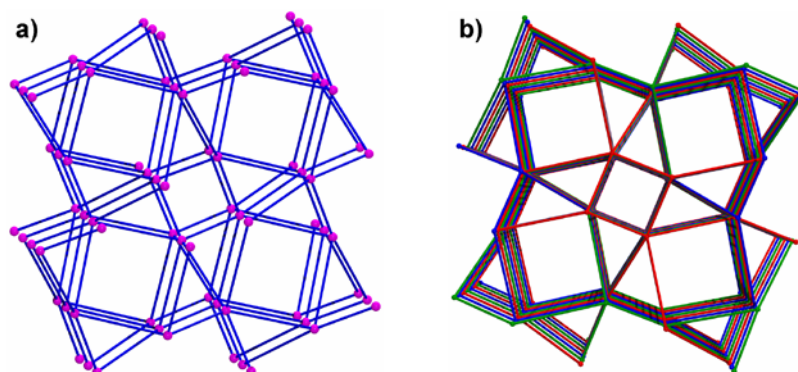


Fig. S8 a) The single 5-connected zfy topology net, and b) its 3-fold interpenetrated fashion in **1**.

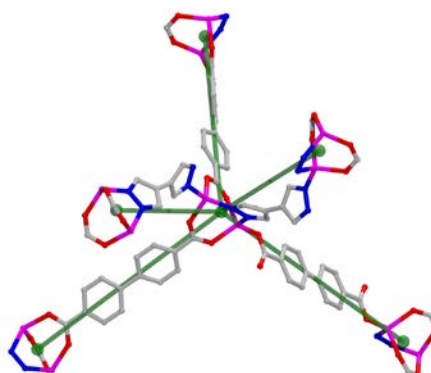


Fig. S9 The distorted pyramidal geometry of 5-connected Co_2 cluster in **1**, resulting from the significant torsion of Hbpz^- ligands.

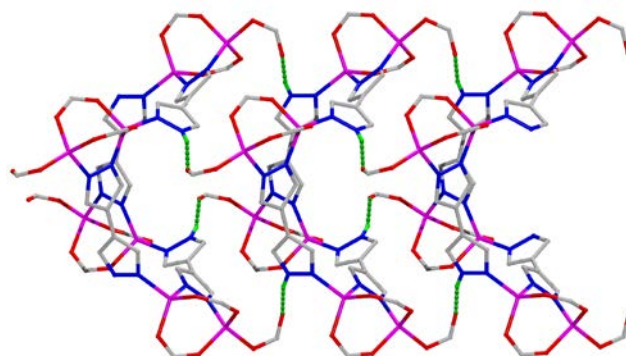


Fig. S10 The N–H···O hydrogen bonding interactions ($H\cdots O = 1.959 \text{ \AA}$, $N\cdots O = 2.795 \text{ \AA}$, $\angle N-H\cdots O = 153.15^\circ$) between pyrazole –NH groups and uncoordinated carboxylate O atoms in the $[Co_2(CO_2)_2(Hbpz)_4]$ MBBs from adjacent frameworks, which contribute to stabilize the framework of **1**.

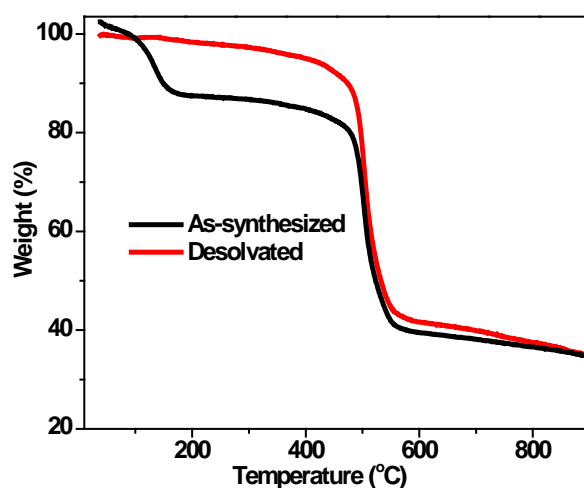


Fig. S11 TGA plots of the as-synthesized and desolvated **1** under N_2 atmosphere.

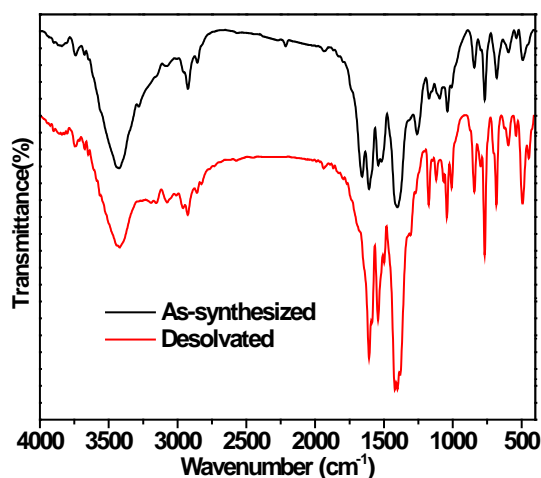


Fig. S12 FTIR spectra of the as-synthesized and desolvated **1**. In the spectrum of the as-synthesized **1**, the weak peak at 2214 cm^{-1} and strong peak at 1658 cm^{-1} are designated to

the C≡N and C=O characteristic stretching peaks of the solvent CH₃CN and DMF molecules, respectively. Heating the sample at 120 °C for 5 h under vacuum, the absence of peak at around 1660 cm⁻¹ in the IR spectrum of desolvated **1** indicates the complete removal of nonvolatile DMF solvents.

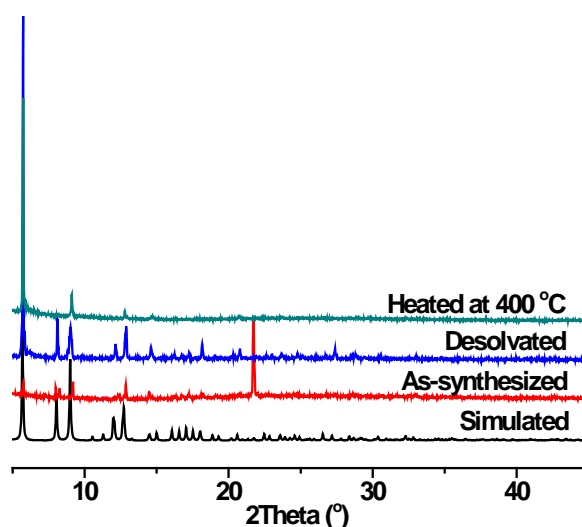


Fig. S13 PXR D patterns of **1** simulated from the X-ray single-crystal structure, as-synthesized, desolvated (120 °C) and heated (400 °C) samples, reflecting highly crystalline even heated at 400 °C.

Calculation of sorption heat for CO₂ uptake using Virial 2 model

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

The above equation was applied to fit the combined CO₂ isotherm data for **1** at 273.15 and 293.15 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.

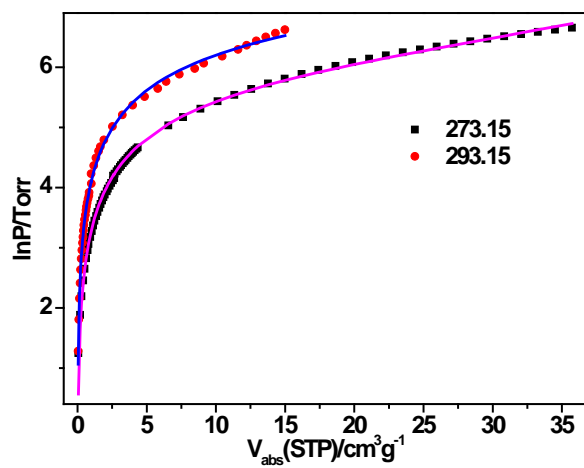


Fig. S14 CO₂ adsorption isotherms for **1** with fitting by Virial 2 model. Fitting results: $a_0 = -3316.04238$, $a_1 = 20.39141$, $a_2 = 0.14961$, $b_0 = 15.45207$, $b_1 = -0.0987$. $\chi^2 = 0.00788$, $R^2 = 0.99591$.