Supplemental Information

A *pcu*-Type Metal-organic Framework Based on Covalently Quadruple Cross-linked Supramolecular Building Blocks (SBBs): Structure and Adsorption Properties

Chuanqiang Li^a, Wenge Qiu^a*, Wei Shi^b, Haibin Song^b, Guangmei Bai^a, Hong He^a*, Jian Li^a, and Michael J. Zaworotko^c

Experimental Sections

Synthesis of ligand, H₄L:

Diethyl 5-hydroxyisophthalate (5.950g, 25mmol), dibromomethane (2.150g, 12.5mmol) and anhydrous K_2CO_3 (4.125g, 30.0mmol) were added to 50 mL of acetone and refluxed for 32h. Excess K_2CO_3 was filtered off. The solvent in the filtrate was removed under reduced pressure and the residue was washed with aqueous solution of NaOH (5%), then the product was extracted into chloroform (50mL×3). The chloroform solution was dried over anhydrous MgSO₄ and afforded the tetraester (2.75g, 45%) when the solvent was removed under reduced pressure. Hydrolysis of the tetraester (2.000g, 4.0mmol) to the tetraacid was achieved by refluxing for 24h in a solution comprised of 28.5mmol (1.600g, 28.5mmol) KOH dissolved in 60 mL of ethanol/H₂O (v/v 1:2). Partial solvent removal and acidification afforded a colorless precipitate, **H**₄L (1.39g, 90%). IR (KBr, cm⁻¹): 3375, 2987, 1700, 1598, 1456, 1402, 1269, 1128, 1103. 1024, 907, 759, 727, 687, 666, 609, 545, 449; ¹H-NMR (DMSO-d_6): 13.60-13.30(w, 4H), 8.58 (s, 2H), 8.26 (s, 4H), 6.51 (s, 2H).

Synthesis of 1:

H₄**L** (38mg, 0.1mmol) and CuCl₂•2H₂O (34.1mg, 0.2mmol) was dissolved in a mixture of dimethylformamide (DMF, 10mL), H₂O (2ml) and concentrated HCl (0.1mL). The obtained solution was divided into ten parts (1.2mL) in glass vials. The vials were capped and heated at 85°C for 48h to yield blue-green block crystals (yield = 60% based on H_4L).

X-ray structure determination of complex 1.

The X-ray diffraction data of complex **1** were collected on Oxford diffractometer SuperNova TM at 123K with a graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å) using the ω -scan technique. The structure was solved by direct method and refined by full-matrix least-squares on F² with anisotropic displacement parameters for non-H atoms using the SHELXS-97 and SHELXL-97 programs.^{1,2} The hydrogen atoms were placed in idealized positions and constrained to ride on their parent atoms. Crystallographic data and structural refinement parameters are listed in Table S1. The structure was treated with the Squeeze procedure implemented in Platon program.³

Characterization of chemical structure of ligand molecule and characterization

of physical and chemical properties of complex 1

¹H-NMR data were collected on a Bruker ARX-400 spectrameter with DMSO solution by using tetramethylsilane as an internal standard. IR spectrum was recorded on Brucker TENSOR 27 using KBr pellets. Elemental analyses (C, H and N) were performed on a Flash EA 1112 elemental analyzer. Thermogravimetric analysis (TGA) was performed on an EXTAR6000 TG/DTA6300 instrument under nitrogen atmosphere (200mL/min). The sample was heated at a constant rate of 10°C/min from 30°C to 600°C. Powder X-ray diffraction was performed on a Bruker D8 Advance using Cu-K α radiation (λ =1.5406Å) at room temperature with a scan speed of 0.5s per step and a step size of 0.02°.

Low-Pressure Sorption Measurements

The low-pressure nitrogen sorption isotherm measurement on compound **1** was performed at 77 K and 0-760 Torr on a Micromeritics ASAP 2020. A sample of approximately 70 mg was soaked with dry methanol for 12 hours, and separated from the mixture, and then the process was repeated four times to remove DMF and H_2O solvates. The sample was activated by drying under vacuum at room temperature overnight. Before the measurement, the sample was degassed at 120°C for 12 h. Nitrogen isotherm at 77 K was measured in liquid nitrogen baths using UHP-grade (99.999%) gas source.

High-Pressure Sorption Measurements

High-pressure sorption isotherm measurements of N_2 , O_2 , CO_2 and CH_4 on compound **1** were performed on a Micromeritics ASAP 2050 volumetric adsorption analyzer at various temperatures and 0-6200mmHg. Compound **1** (about 200mg) was loaded in a sample tube with a known volume, and then was degassed at 120°C for 12h. The sample density was used to calculate free space volume. The temperature was controlled by ice/water or water bath. The methane adsorption isotherms of **1** at 273, 289 and 295K were used to derive the heat of CH_4 adsorption, using Clausius-Clapeyron equation.⁴ The pressure data were used to calculate Q_{st} at a given sorption amount with the best fit of Langmuir equation to the experimental data by using the Origin 8.0 program.

References

- 1 G. M. Sheldrick, *SHELXS 97, Program for the Solution of Crystal Structures*; Gottingen University: Gottingen, Germany, 1997.
- 2 G. M. Sheldrick, SHELXL 97, Program for the Refinement of Crystal Structures; Gottingen University: Gottingen, Germany, 1997.
- 3 A. L. Spek, Appl. J. Crystallogr. 2003, 36, 7.
- 4 F. Roquerol, J. Rouquerol and K. Sing, Adsorption by Powders and Solids: Principles, Methodology, and Applications; Academic Press: London, 1999.

Empirical formula	C ₅₄ H ₄₁ Cu ₆ NO ₃₆		
Formula weight	1661.2		
Temperature	123K		
Crystal System	tetragonal		
Space Group	P4/mcc		
Unit Cell Dimensions	a = b = 23.5670(6)Å		
	c = 46.997(2)		
	$\alpha = \beta = \gamma = 90^{\circ}$		
Volume	26102.3 (17) Å3		
Z	8		
Density	0.835 Mg/m ³		
Absorption coefficient	1.025 mm ⁻¹		
F(000)	8002		
Crystal Size	$0.2 \times 0.2 \times 0.2 \text{ mm}^3$		
Theta range for data collection	2.59 to 25.01 deg.		
Reflections collected	50904		
Independent reflections	11668 [R(int) = 0.0589]		
Absorption correction	Multi-scan		
Refinement method	Full-matrix least-squares on F ²		
Max. and min. transmission	1.00000 and 0.80173		
Data / restraints / parameters	11668 / 44 / 444		
GOF on F2	0.537		
Final R indices $[I \ge 2\sigma(I)]$	R1 = 0.0550, wR2 = 0.1588		
R indices (all data)	R1 = 0.0.768, wR2 = 0.1686		
Largest diff. peak and hole	1.179 /-0.539 eÅ3		

Table S1. Crystal data and structure refinement for complex 1

Table S2. Elemental analysis of the as-synthesized sample of complex 1

According to the elemental analysis and TGA data, the free solvent molecules in the framework channel of complex 1 were calculated. It was found that there were about nineteen DMF and eleven H₂O molecules.

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	Complex 1	С	Н	Ν	С	Н	Ν
	Found	41.11	6.00	8.67	40.98	6.03	8.68
		41.05	6.02	8.68			
	Calculated	41.06	6.08	8.63			

Formula: Cu₆[(C₁₇H₈O₁₀)₃(H₂O)₅(C₃H₇NO)] (C₃H₇NO)₁₉ (H₂O)₁₁

Temperature/K	$q_m/cm^3(STP)g^{-1}$	b	Adj R-Square
273	319.6	1.1×10^{-4}	0.99983
289	334.2	7.3×10 ⁻⁵	0.99999
295	341.5	5.9×10 ⁻⁵	0.99998

Table S3. Langmuir-type isotherms fitting parameters of CH_4 adsorption onto complex 1

Additional Figures

Figure S1. Schematic representation of the octahedral node from the assembly of SBBs via six square open windows in three orthogonal directions



Figure S2. The structure of the complex 1 with three types of cages





(Cage 3)

Figure S3. Space filling models of complex **1** viewed along **a** (1), **b** (2) and **c** (3) axes, respectively.



(1)





(3) **Figure S4**. The conformation of ligand molecule in complex **1**



Figure S5. X-ray diffraction patterns for complex **1** samples: the as-synthesized(b), activated under vacuum at 423K(c), re-adsorbed methanol of the activated sample(d) and treated under 523K(e), compared to the calculated data(a), indicating the phase purity and stability of **1**



Figure S6. TGA data for the as-synthesized, methanol exchanged and activated samples of complex 1



Figure S7. High-pressure absorption isotherms of **1** (CH₄, black squares; CO₂, purple triangles; O₂, red circles and N₂, blue triangles) at 295K.







Figure S9. Isosteric heats of adsorption of methane for complex **1** calculated from the corresponding isotherms at 273, 289 and 295 K.





Figure S10. FTIR spectrum of the as-synthesized sample of complex 1