Electronic Supplementary Information

A novel metal-organic coordination polymer for selective adsorption of CO_2 over CH_4

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Contents

1. Synthesis: All the reagents and solvents were purchased from commercial sources and used without further purification. Solvothermal reactions were carried out in digestion bomb reactors. Exact amounts of $Cu(NO_3)_2.3H_2O$ (0.2g) and 1,3,5-Tris(4-carboxyphenyl)benzene acid (0.1g) were dissolved in a 50mL digestion bomb reactor using (1:1) water-ethanol (15mL:15mL). The mixture solution was heated at 110℃ for 16 hours. Then the green diamond-shaped crystal $[Cu_2(HBTB)_2(H_2O)(EtOH)]\cdot H_2O\cdot EtOH$ (**1)** was obtained. The as-synthesized sample was obtained by filtration, washed with ethanol and then dried in air. Activated samples for gas adsorption measurements were prepared by heating the as-synthesized compound at 200℃ for 12 hrs in vacuum oven.

2. Single-crystal X-ray crystallography: Single-crystal XRD data of compound **1** (CCDC 708312) was collected on a Bruker SMART APEX CCD single crystal diffraction system with MoKα radiation (λ= 0.71073 Å). The structures were solved by direct methods with the help of SHELX-97 and refined by full-matrix least-squares techniques using SHELXL-97.

Empirical formula	C_{456} H_{308} $Cu_{16}O_{142}$
Molecular weight	9075.84
Temperature (K)	100(2)
Crystal system	Orthorhombic
Space group	Pbcm
a(Å)	28.0524(17)
b(Å)	14.8658(9)
c(Å)	28.7818(18)
α(º)	90
β(º)	90
γ(º)	90
V(A^3)	12002.6(13)
Z	1
D_{calcd}(g cm^{-3})	1.255
F(000)	4608
μ (mm^{-1})	0.774
Reflection (collected/unique)	104053/ 12040
R_{int}	0.0891
Goodness-of-fit on F^2	1.012
Final *R* indices [I>2σ(*I*)]	R_1 = 0.0468, wR_2 = 0.1425
R indices (all data)	R_1 = 0.1021, wR_2 = 0.1536
Max, min Δρ (e $Å^{-3}$)	1.629, -1.653

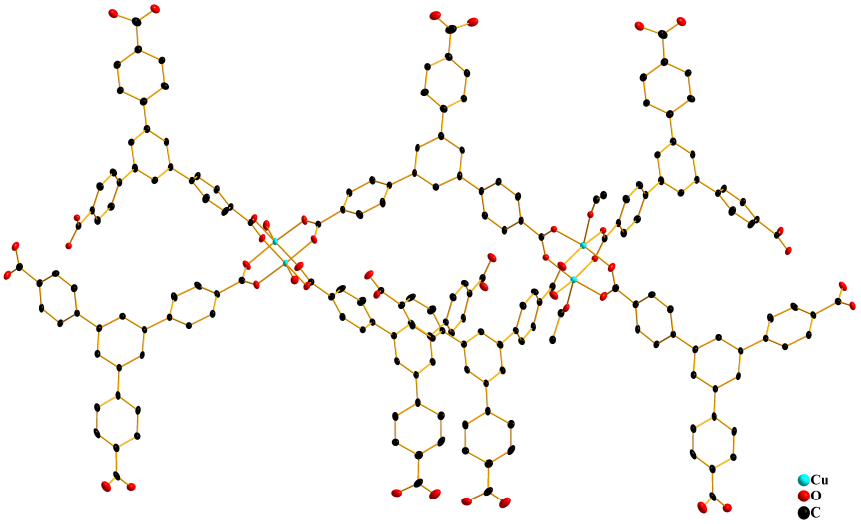

Fig. S1 ORTEP diagram of compound **1**
(All solvent molecules and hydrogen atoms are omitted for clarity)

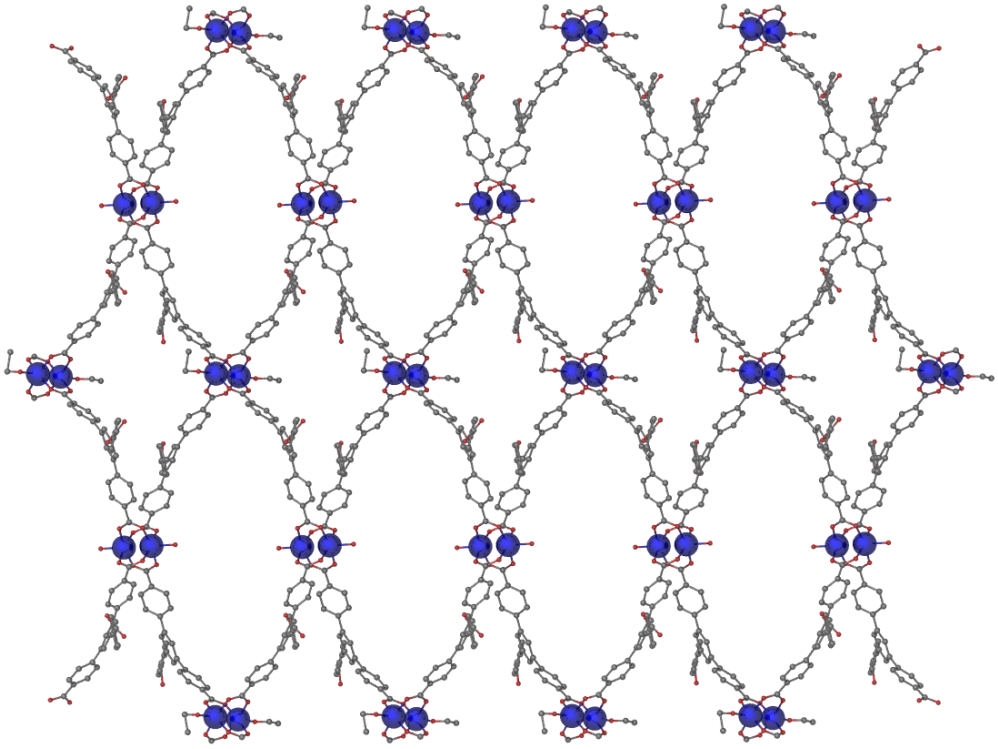

Fig. S2 (4, 4) 2D network composed of copper paddle-wheel clusters and $HBTB^{2-}$ ligands at the [100] plane.
(All solvent molecules and hydrogen atoms are omitted for clarity)

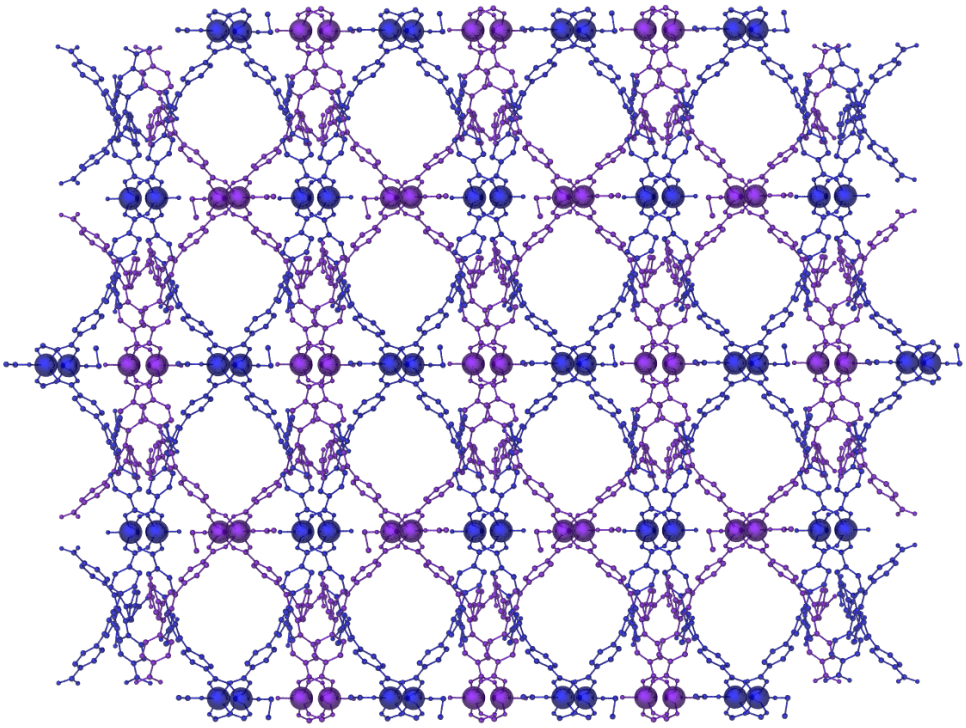

Fig. S3 Interpenetrating (4, 4) 2D networks.
(All solvent molecules and hydrogen atoms are omitted for clarity)

3. Powder X-ray diffraction: The powder-XRD pattern of samples were collected on a Bruker D8 powder diffraction system with Cu radiation (λ= 1.5406 Å).

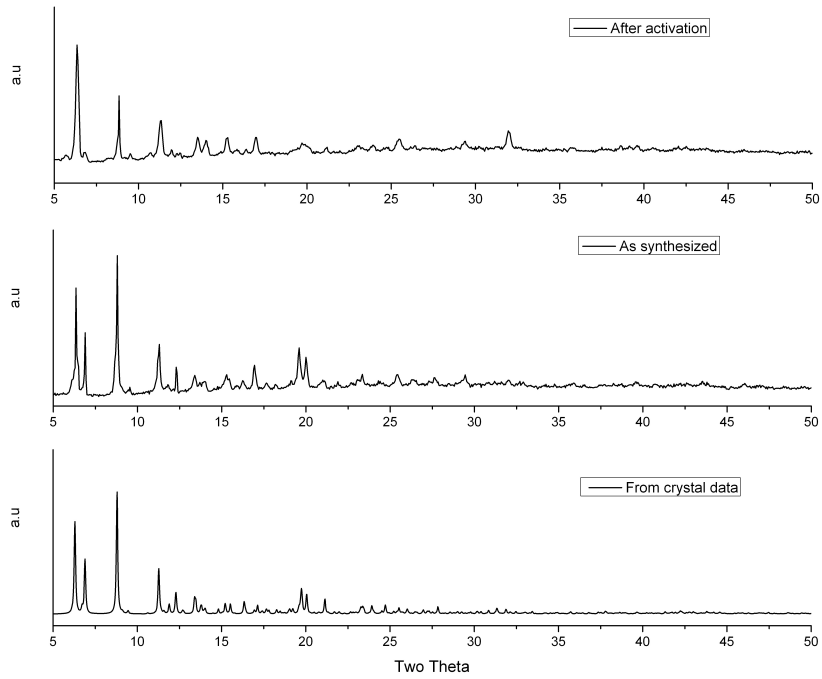

Fig. S4 A comparison of experimental powder-XRD pattern of **1** after activations to remove guest molecules (top), as synthesized (middle) and theoretical pattern from the single crystal data (bottom).

4. Elemental analysis: Elemental analyses were carried out on an Elementar Vario EL III analyzer. Calculated for $C_{456}Cu_{16}O_{142}H_{308}$: C, 60.29%; Cu, 11.28%; O, 25.03%; H, 3.39%. Found: C, 60.18%; Cu, 11.25%; O, 25.10%; H, 3.47%.

5. TGA analysis: Thermogravimetric analyses were carried out with a NETZSCH STA 449C unit at a heating rate of 10 ^{o}C/min under nitrogen.

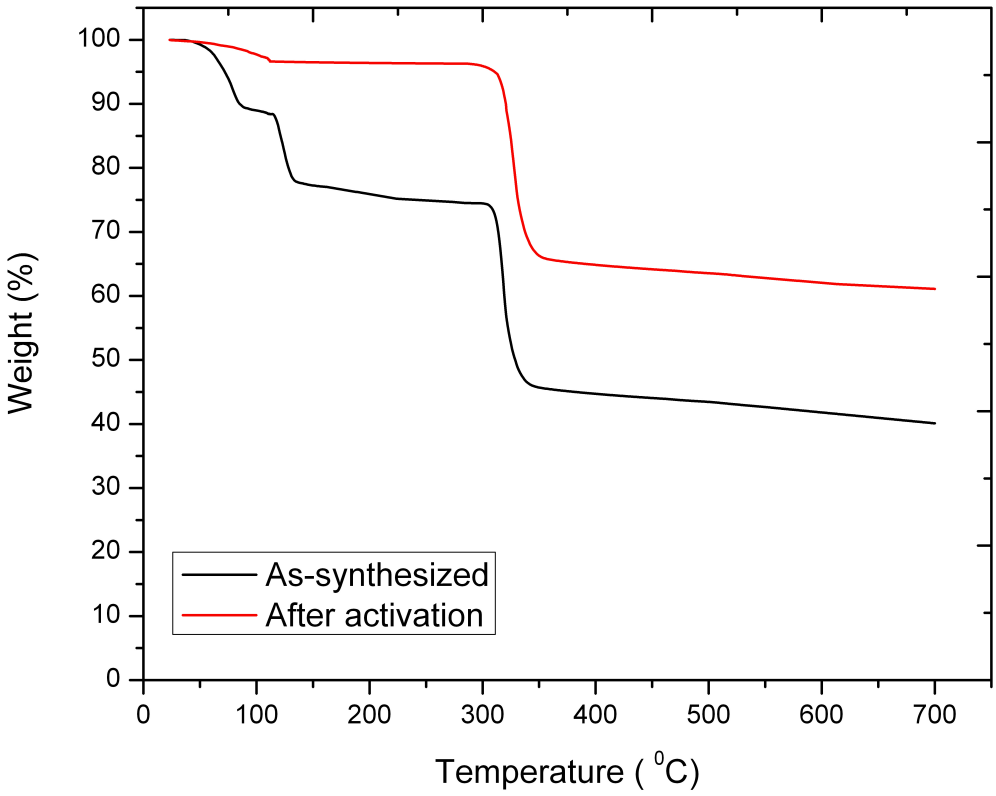

Fig.S5 TGA trace of compound **1**.

6. Specific surface area: Nitrogen adsorption isotherm of activated product at 77 K was measured with Autosorb-1 from Quantachrome Corporation to calculate the surface area. The BET surface area is calculated to be 600m^2/g. The Langmuir surface area is calculated to be 900m^2/g. However, it should be noted that these surface areas should be considered with some caution because low measurements at low relative pressures could not be obtained. Thus, the BET analysis was performed near the saturation point.

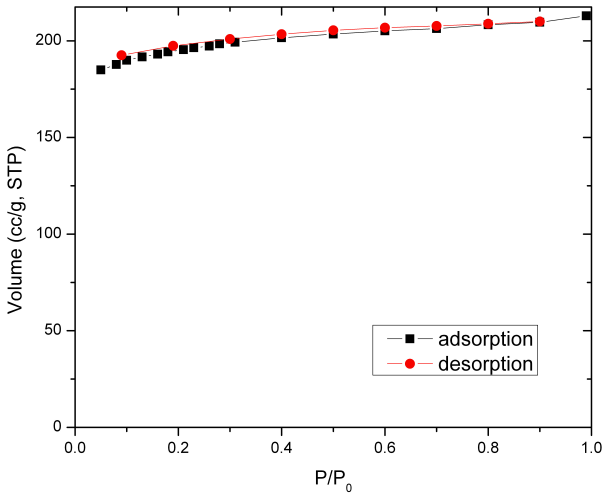

Fig. S6 N_2 isotherm of activated samples of **1** at 77K

7. FTIR: Infrared (IR) spectra were recorded with PerkinElmer Spectrum One as KBr pellets in the range 4000 - 400cm^{-1}.

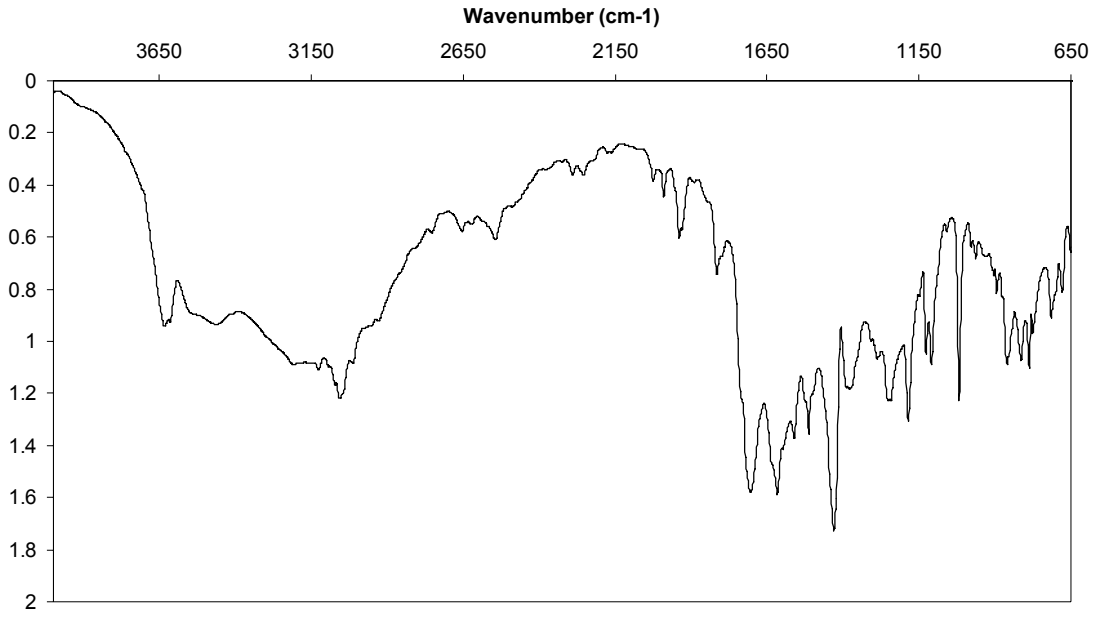

Fig. S7 FT-IR pattern of the compound **1**

8. Adsorption experiments: Gas adsorption isotherms were recorded with the GHP-100 gravimetric high pressure analyzer with C. I. microbalance from VTI Corporation.

Selectivities were calculated as $\alpha_{12} = \frac{q_1}{q_2}\frac{P_2}{P_1}$, where q is the loading of carbon dioxide (1) or methane (2), and P is the partial pressure.

Table S1 The selectivity of adsorption for CO_2/CH_4 in **1**

Total pressure (bar)	Selectivity
0.5	17
1	12.4
5	6.9
10	5.7
15	5.2
20	4.8

Table S2. Isotherm model parameters Dual-site Langmuir-Freundlich Equation

	CO_2	CH_4
q_1	5.77426	1.63253
q_2	45.98447	53.07639
b_1	0.24846	0.15266
b_2	2.90E-04	1.37E-03
n_1	1.29344	0.85358
n_2	0.61797	0.89407
R^2	0.99996	0.99998
Chi^2/DoF	0.00025	0.00005

$$q = q_1 \frac{b_1 P^{1/n_1}}{1 + b_1 P^{1/n_1}} + q_2 \frac{b_2 P^{1/n_2}}{1 + b_2 P^{1/n_2}} \quad (1)$$