

Supporting Information

Stepwise and hysteretic sorption of CO₂ in a polycatenated Metal– Organic Framework

Di-Ming Chen* and Xue-Jing Zhang

*Henan Provincial Key Laboratory of Surface & Interface Science, Zhengzhou
University of Light Industry, Zhengzhou 450002, P. R. China.*

E-mail: cdm700@sina.com

Experimental Section

Materials and Methods. The ligand bpydbH₂ were prepared by a modified literature method¹, and the other chemicals purchased were of reagent grade and used without further purification. Powder X-ray diffraction measurements were recorded on a Rigaku D/Max-2500 X-ray diffractometer using Cu K α radiation. Gas adsorption experiments were performed on a gas adsorption analyzer Autosorb-IQ2 or Autosorb-IQ (Quantachrome Instruments). Ultrahigh purity N₂, CH₄, and CO₂ were used in the adsorption study. Before measurements, the samples were soaked in methanol for 3 days to remove the solvents of high boiling point, and then filtrated and dried at room temperature. The samples were loaded in sample tubes and activated under high vacuum at 80 °C. About 140 mg of degassed samples was used for gas sorption measurements, and the weight of each sample was recorded before and after outgassing to confirm the removal of guest molecules.

Synthesis of {[Zn₂(bpydb)₂(bpy)(EtOH)₂](DMF)(EtOH)}_n (1). A mixture of Zn(NO₃)₂·6H₂O (0.045 g, 0.15 mmol), bpydbH₂ (0.032 g, 0.075 mmol), bpy (0.015 g, 0.1 mmol), DMF (2 mL), H₂O (1 mL) and EtOH (1 mL) was added to a 5 mL glass bottle, and then heated at 80 °C for 3 days under autogenous pressure. After cooling to room temperature, yellow block crystals were obtained by filtration and washed with DMF and EtOH in sequence, and dried in air. The yield was 75% for **1** (based on based on bpydbH₂). Elemental analysis calcd (%) for **1** (C₆₇H₆₁N₇O₁₂Zn₂): C 62.62, H 4.63, N 7.63; found: C 62.41, H 4.78, N 7.59.

Synthesis of {[Cd₂(bpydb)₂(bpy)(MeOH)₂](DMA)(MeOH)}_n (2). A mixture of Cd(NO₃)₂·4H₂O (0.047 g, 0.15 mmol), bpydbH₂ (0.032 g, 0.075 mmol), bpy (0.015 g, 0.1 mmol), DMA (4 mL), H₂O (2 mL) and MeOH (4 mL) was added to a 20 mL glass bottle, and then heated at 80 °C for 3 days under autogenous pressure. After cooling to room temperature, yellow block crystals were obtained by filtration and washed with DMF and EtOH in sequence, and dried in air. The yield was 35% for **2** (based on based on bpydbH₂). Elemental analysis calcd (%) for **2** (C₆₅H₆₁Cd₂N₇O₁₂): C, 57.53; H, 4.53; N, 7.23; found: C 57.69, H 4.35, N 7.68.

X-ray Single Crystal Analysis. Data was collected on an Agilent Technologies SuperNova Single Crystal Diffractometer at different temperatures equipped with graphite-monochromatic Mo K α radiation ($\lambda = 0.71073$ Å). The structures were solved by SHELXS (direct methods) and refined by SHELXL (full matrix least-squares techniques) in the Olex2 package.² All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms attached to carbon were placed in geometrically idealized positions and refined using a riding model. For the highly disordered nature of the solvents, they could not be finely made out in the refinement, so the SQUEEZE³ routine of PLATON⁴ was applied to remove the diffraction contributed from the highly disordered guest molecules. The chemical formulas were determined by the combination of the crystal data, TGA, and elemental analysis.

Table S1. Crystallographic data and structure refinement details for **1** and **2**.

compound	1	2
formula	C ₆₇ H ₆₁ N ₇ O ₁₂ Zn ₂	C ₆₅ H ₆₁ Cd ₂ N ₇ O ₁₂
fw	1287.00	1359.24
temp, K	129(2)	273.15
crystal syst	monoclinic	monoclinic
space group	<i>C2/c</i>	<i>Cc</i>
<i>a</i> , (Å)	25.1240(12)	25.864(5)
<i>b</i> , (Å)	17.0584(5)	17.137(3)
<i>c</i> , (Å)	30.6102(13)	15.838(3)
α , (deg)	90.00	90.00
β , (deg)	113.725(5)	118.80(3)
γ , (deg)	90.00	90.00
<i>V</i> , (Å ³)	12010.1(8)	6151(2)
<i>Z</i>	8	4
<i>D_c</i> (g/cm ³)	1.292	1.330
μ (mm ⁻¹)	0.860	0.749
<i>R_{int}</i>	0.0475	0.0302
reflections collected/unique	22446/10540	8488/508
GOF on <i>F</i> ²	1.066	1.032
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0603, 0.1589	0.0483, 0.1174
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0844, 0.1710	0.0539, 0.1209
largest peak, hole (e Å ⁻³)	0.89/-0.50	0.98/-0.43

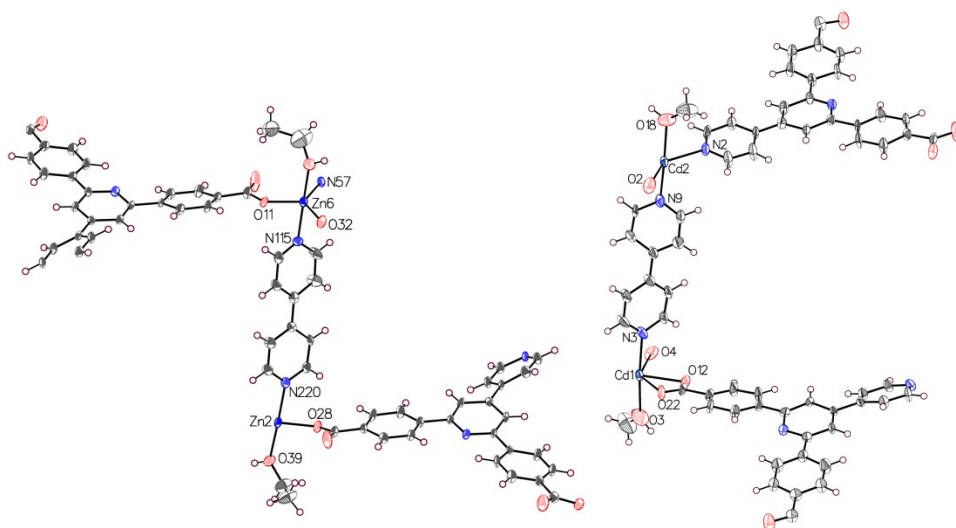


Fig. S1 A comparison for the asymmetric units of complex **1** (left) and **2** (right).

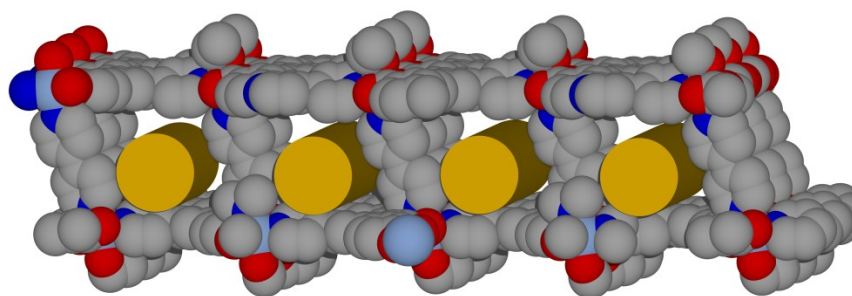
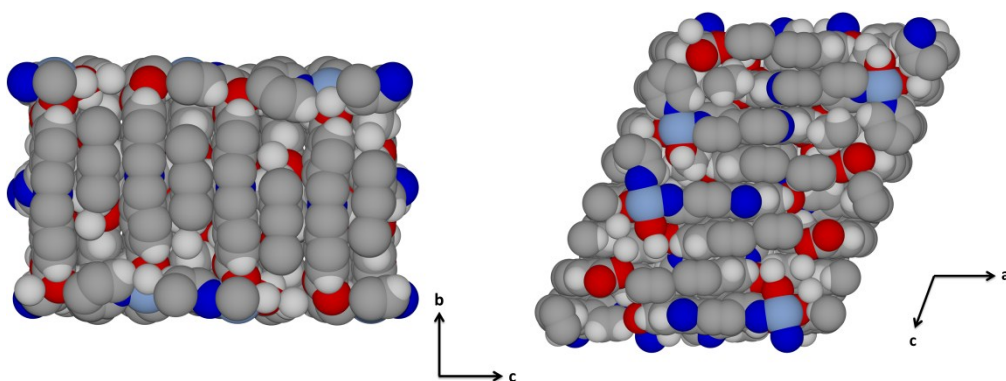


Fig. S2 The schematic representation of the 1D channels of the 2D bilayers.



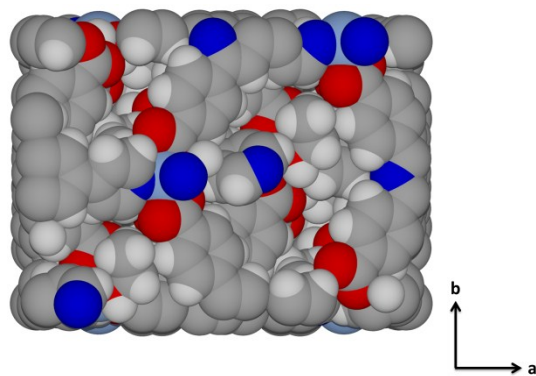


Fig. S3 The space filling mode views of **1** along *a*, *b*, *c* axis.

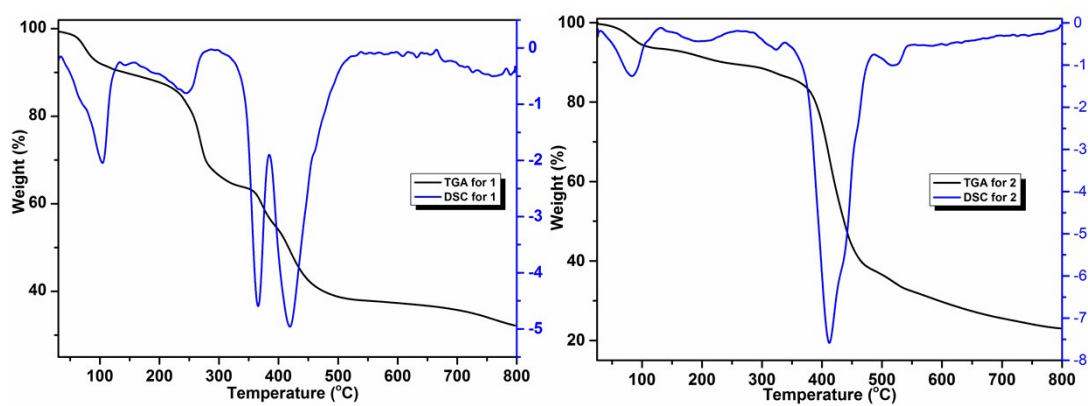


Fig. S4 TGA-DSC curves for complexes **1** and **2**.

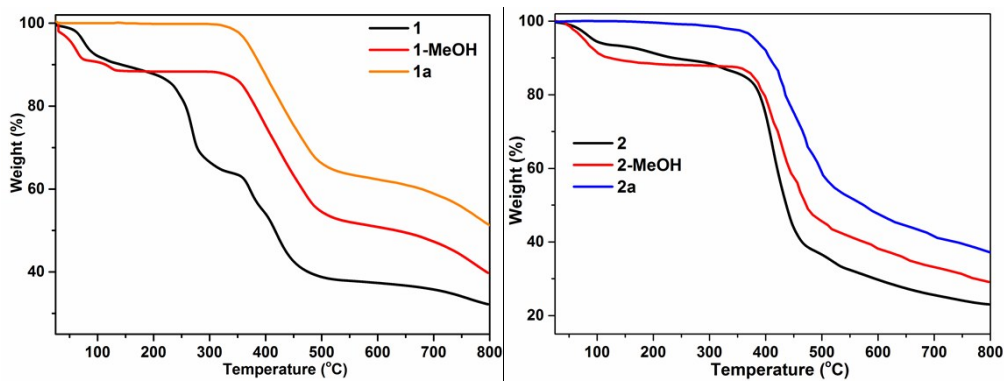


Fig. S5 TGA curves for **1** and **2** after different treatments.

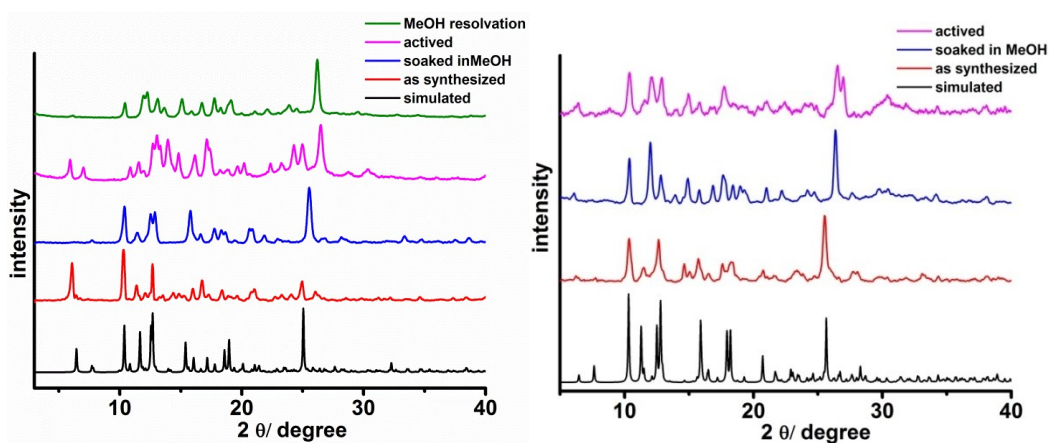


Fig. S6 PXR patterns for **1** and **2**.

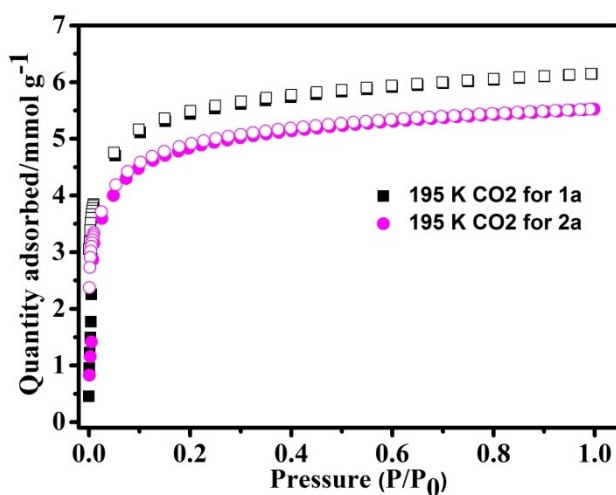


Fig. S7 195 K CO₂ sorption isotherms of **1a** and **1b** (closed symbols, adsorption; open symbols, desorption).

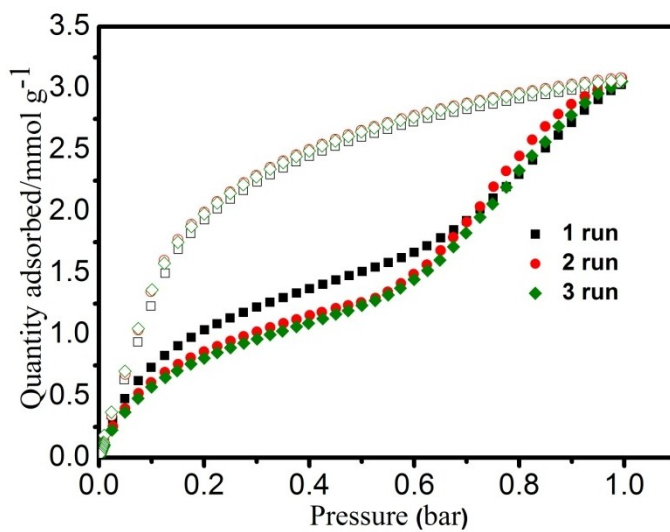


Fig. S8 273K CO₂ adsorption isotherms of **1a** in three runs.

Calculation of sorption heat for CO₂ uptake using Virial model:

$$\ln p = \ln N + \frac{1}{T} \sum_{i=0}^m a_i N_i + \sum_{i=0}^n b_i N_i \quad Q_{st} = -R \sum_{i=0}^m a_i N_i$$

The above equation was applied to fit the combined CO₂ isotherm data for **1a** at 273 and 298 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.

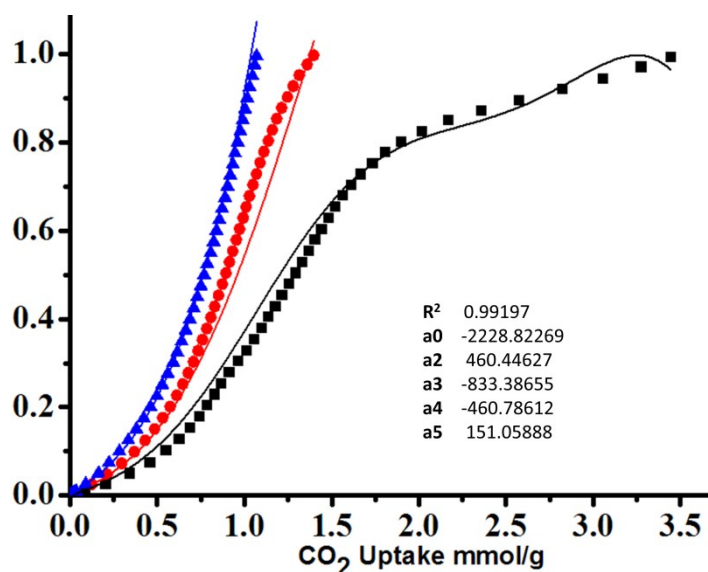


Fig. S9 CO₂ adsorption isotherms for **1a** with fitting by Virial model.

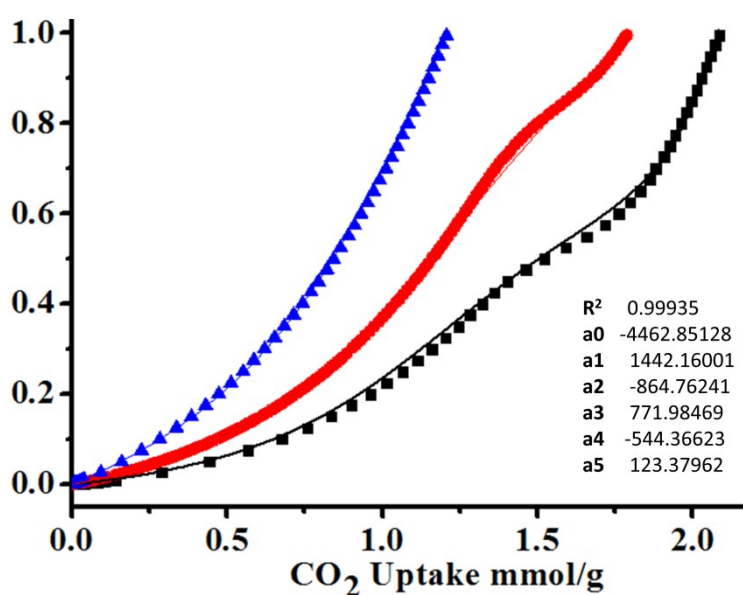


Fig. S10 CO₂ adsorption isotherms for **2a** with fitting by Virial model.

IAST Adsorption Selectivity Calculation

The ideal adsorbed solution theory (IAST) was adopted based upon the experimental single gas adsorption measurements as described in the main text, including carbon dioxide and nitrogen at 273 K and 298 K, which is commonly used to predict binary mixture adsorption selectivity. Using the pure component isotherm fits, the adsorption selectivity is defined by:

$$S_{ads} = (q_1/q_2)/(p_1/p_2),$$

Where q_i is the amount of i adsorbed and p_i is the partial pressure of i in the mixture fits.

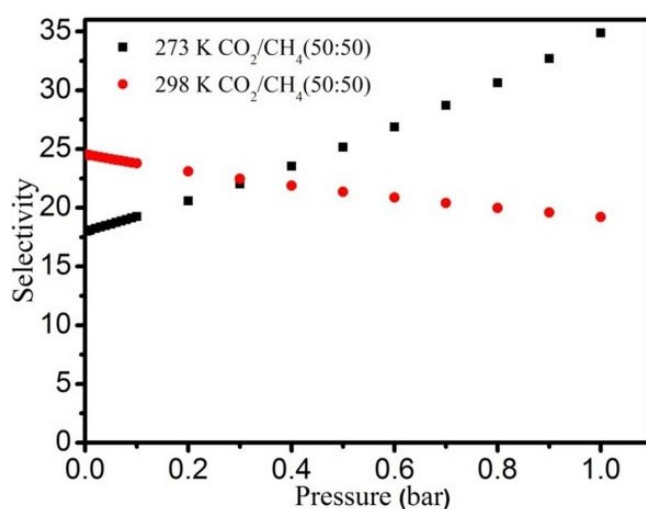


Fig.S11 IAST predicted CO₂/CH₄ selectivity at 273 K and 298 K for **1a**.

Reference:

- S1 D. Chen, X. Zhang, W. Shi, and P. Cheng, *Cryst. Growth Des.*, 2014, **14**, 6261.
- S2 Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112.
- S3 Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, 194.
- S4 PLATON; Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7.