Supporting Information

Pre-design and synthesis of a five-fold interpenetrated pcu-type porous coordination polymer and its CO_2/CO separation

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1. General Procedures and Materials

All the reagents and solvents were commercially available and used as received. The elemental analysis was carried out with a Perkin-Elmer 240C elemental analyzer. Thermal analyses were performed on a Universal V3.9A TA Instruments with a heating rate of 10°C/min under flowing nitrogen. The powder X-ray diffraction patterns (PXRD) measurements were carried on a Bruker axs D8 Advance 40kV, 40mA for CuK_{α} (θ = 1.5418 Å) with a scan rate of 0.2 s/deg at room temperature. Simulated powder patterns from single-crystal X-ray diffraction data were generated using Mercury 1.4.2 software. Raman was collected using a Horiba Jobin-Yvon HR800 Raman Spectrometer.

2. Synthesis of the organic building block

4,4'-[1,4-Phenylenebis(carbonylimino)]bis[benzoic acid] (H_2L^2) was synthesized according to our previous work¹. ¹H NMR (DMSO) of H_2L : δ /ppm 10.58 (s, 2H), 8.05 (s, 4H), 7.92 (m, 8H). ¹³C NMR (DMSO) of H_2L^2 : δ /ppm 170.85, 165.23, 144.08, 137.79, 130.85, 127.82, 126.65, 119.96.

3. Synthesis of NTU-26

 $Zn(NO_3)_2 \cdot 3H_2O$ (20 mg) and H_2L (10 mg) were mixed with 4 ml of DEF in a glass container and tightly capped with a Teflon vial and heated at 80 °C for two days. After cooling to room temperature, colourless and block shaped crystals were obtained. Yield: ~80% (based on ligand).

4. Single X-ray study

Single-crystal X-ray diffraction data were measured on a Bruker Smart Apex CCD diffractometer at 293 K using graphite monochromated Mo/K α radiation (λ = 0.71073 Å). Data reduction was made with the Bruker Saint program. The crystal of NJU-Bai3 was mounted in a flame sealed capillary containing a small amount of mother liquor to prevent desolvation during data collection, and data were collected at 298K. The structures were solved by direct methods and refined with full-matrix least squares technique using the SHELXTL package². Non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. Organic hydrogen atoms were placed in calculated positions with isotropic displacement parameters set to 1.2×Ueq of the attached atom. The hydrogen atoms of the ligand and water molecules could not be located, but are included in the formula. The unit cell includes a large region of disordered solvent molecules, which could not be modelled as discrete atomic sites. We employed PLATON/SQUEEZE³ to calculate the diffraction contribution of the solvent molecules and, thereby, to produce a set of solvent-free diffraction intensities; the structure was then refined again using the data generated. The crystal data are reported in Table S1.

Empirical formula $C_{66}H_{46}Zn_4O_{21}$ Formula weight1520.65Crystal systemtriclinicSpace group $P-1$ Unit cell dimensions $a = 11.2432(15)$ Å $b = 21.829(3)$ Å $c = 25.837(4)$ Å
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c = 25.837(4) Å
$\alpha = 08.020(2)^{\circ}$
$\alpha = 98.929(2)$
<i>b</i> = 92.438(2)°
γ = 94.814(2)°
Volume 6232.2(15) Å ³
Ζ 2
Density (calculated) 0.810 g/cm ³
Mu(MoKa) 0.803 mm ⁻¹
<i>F</i> ₍₀₀₀₎ 1544
Theta min-max 1.9, 25.0
Index ranges -12<=h<=13
-26<=k<=25
-17<=l<=30
Tot., Uniq. Data, R(int) 31713, 21754, 0.112
Observed data $[I > 2\sigma (I)]$ 9187
Nref, Npar 21754, 875
<i>R</i> ₁ , <i>wR</i> ₂ , S 0.0845, 0.2302, 1.03
Max Shift 0

Table S1. Crystal data and structure refinement for NTU-26 at 293 K

 $R = \Sigma ||F_o| - |F_c| |/\Sigma|F_o|, wR = \{\Sigma[w(|F_o|^2 - |F_c|^2)^2]/\Sigma[w(|F_o|^4)]\}^{1/2} \text{ and } w = 1/[\sigma^2(F_o^2) + (0.1452P)^2] \text{ where } P = (F_o^2 + 2F_c^2)/3$

D—HA	d _{HA} (Å)	$d_{\rm D-A}$ (Å)	А _{D-H-A} (°)
N5 H5AO3	2.5600	3.271(8)	131.00
N6 H6A O8	2.4000	3.187(8)	138.00
C4 H4 O20	2.2600	2.873(15)	123.00
C20 H20 O9	2.4600	2.787(13)	100.00
C21 H21 O22	2.2500	2.809(18)	118.00
C26 H26 O17	2.3000	2.868(12)	118.00
C35 H35 O18	2.4200	2.753(16)	101.00
C39 H39 O18	2.1700	2.774(15)	122.00
C48 H48 O19	2.2400	2.828(11)	120.00
C51 H51 O4	2.4500	2.762(9)	100.00
C61 H61 O16	2.3500	2.851(11)	114.00
C62 H62 O15	2.4100	2.724(10)	100.00
С65 Н65В ОЗ	2.4500	3.359(9)	167.00
C66 H66B O16	2.4200	2.745(10)	101.00

 Table S2.
 Hydrogen bond in NTU-26.

5. Sample activation

Before the supercritical CO₂ treatment, as-synthesized samples were soaked in absolute DMF, replacing the soaking solution every 24 h for 3 days. After exchanging, the DMF-containing samples were placed inside the supercritical CO₂ dryer and the DMF was exchanged with CO₂ over a period of 4 h. During this time the liquid CO₂ was vented under positive pressure for five minutes every two hours. The rate of venting of CO₂ was always kept below the rate of filling so as to maintain a full drying chamber. Following venting, the chamber was sealed and the temperature was raised to 40 $^{\circ}$ C, at which time the chamber was slowly vented over the course of 15 h. The collected sample was transferred into the sample tube and activated under a dynamic high vacuum at room temperature for overnight to obtain the desolvated sample.

6. Adsorption experiments

In the gas sorption measurement, Ultra-high-purity grade, N₂, CO and CO₂ gases (99.995% purity) were used throughout the adsorption experiments. All of the measured sorption isotherms have been repeated several times to confirm the reproducibility within experimental error. Low-pressure N₂, CO₂ and CH₄ adsorption measurements (up to 1 bar) were performed on BEL mini analyzer. To provide high accuracy and precision in determining P/P₀, the saturation pressure P₀ was measured throughout the N₂ analyses by means of a dedicated saturation pressure transducer, which allowed us to monitor the vapor pressure for each data point. The pore size distribution was obtained from the GCMC method in the BEL mini software package based on the N₂ sorption at 77K.

7. Fitting of pure component isotherms

The isotherm data for CO, and CO₂ in NTU-26 were measured at two different temperatures 195 K, and 273 K. The data were fitted with either the single-site Langmuir or the Dual-site Langmuir model

$$q = q_{A,sat} \frac{b_A p}{1 + b_A p} + q_{B,sat} \frac{b_B p}{1 + b_B p}$$
(1)

The Langmuir parameters for each site is temperature-dependent

$$b_A = b_{A0} \exp\left(\frac{E_A}{RT}\right); \quad b_b = b_{B0} \exp\left(\frac{E_B}{RT}\right);$$

The single-site, or dual-site Langmuir parameters are provided in Table S3.

8. Isosteric heat of adsorption

The binding energies of CO, and CO_2 in NTU-26 are reflected in the isosteric heat of adsorption, Q_{st} , defined as

$$Q_{st} = RT^2 \left(\frac{\partial \ln p}{\partial T}\right)_q$$
(2)

These values were determined using the pure component isotherm fits using Clausius-Clapeyron equation.

9. IAST calculations of adsorption selectivity

In order to determine the CO_2/CO separation potential of NTU-26, IAST calculations of 80/20 mixture adsorption were performed. Figure S8 shows IAST calculations of the component loadings for adsorption of 80/20 CO/CO_2 mixtures in NTU-26 at 273 K. The adsorption selectivities are determined from

$$S_{ads} = \frac{q_1/q_2}{p_1/p_2}$$
 (3)

In equation (3), q_1 , and q_2 are the molar loadings in the adsorbed phase in equilibrium with the bulk gas phase with partial pressures p_1 , and p_2 .

10. Transient breakthrough of mixtures in fixed bed adsorbers

The performance of industrial fixed bed adsorbers is dictated by a combination of adsorption selectivity and uptake capacity. For a proper evaluation of NTU-26, we perform transient breakthrough simulations using the simulation methodology described in the literature.⁴ For the breakthrough simulations, the following parameter values were used: length of packed bed, L = 0.3 m; voidage of packed bed, $\varepsilon = 0.4$; superficial gas velocity at inlet, u = 0.04 m/s. The transient breakthrough simulation results are presented in terms of a *dimensionless* time, τ , defined by dividing the actual time, t, by the characteristic time, $\frac{L\varepsilon}{u}$.

	Site A		Site B			
	$q_{A,sat}$	b _{A0}	E _A	q _{B,sat}	b _{B0}	E _B
	mol/kg	Pa^{-1}	kJ mol⁻¹	mol/kg	Pa^{-1}	kJ mol⁻¹
CO	0.63	3.07×10 ⁻¹¹	20.7			
CO ₂	1.2	1.5×10 ⁻¹¹	30	3.5	4.49×10 ⁻¹⁷	43

Table S3. *T*-dependent dual-site Langmuir parameters for CO, and CO₂ in NTU-26.

11. Structure of NTU-26



Fig. S1 View of the asymmetric unit of NTU-26.



Fig. S2 View of coordination geometry of four zinc atoms in the cluster of NTU-26: three tetrahedrons (blue) and a hexahedron (pink).



Fig. S3 Thermal ellipsoids of NTU-26, drawn at 50% probability.



Fig. S4 View of the five-fold interpenetrated NTU-26.



Fig. S5 Packing view of NTU-26 along b-axis: one channel with size of $4 \times 7 \text{ Å}^2$.



Fig. S6 Packing view of NTU-26 along a-axis: two kinds of channel with significant window aperture of $5 \times 8 \text{ }^2$, $6 \times 8 \text{ }^2$.

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12. Characterization of NTU-26



Fig. S7 IR of H_2L^2 and as-synthesized NTU-26: the peak shift from 1677 cm⁻¹ to 1668 cm⁻¹, indicating the coordination of carboxylate group.



Fig. S8 PXRD of **NTU-26**. For as-synthesized phase, the diffraction peak of 001 plane matches well with simulated data. However, during the measurement, the lost solvent results in decreased crystallinity of NTU-26, as its high extra-framework volume (60.0%). For activated phase, the changed diffraction peaks may be due to the partial collapse of **NTU-26** framework, supported by such long linker.



Fig. S9 TG of NTU-26. Before 150 $^{\circ}$ C, the TG curve shows that the weight loss is 45% that coincides with loss of DEF and H₂O molecules. Then, the continued weight loss corresponds to the decomposition of the ligands around 420 $^{\circ}$ C, and the final solid product at maybe ZnO.



Fig. S10 N_2 adsorption of NTU-26 at 77K.



Fig. S11 IAST calculations of the component loadings for adsorption of $80/20 \text{ CO/CO}_2$ mixtures in NTU-26 at 273 K.



Fig. S12 The isosteric heat of adsorption, Q_{st} , for CO and CO₂ in **NTU-26.** The determination of the Q_{st} is based on the Clausius-Clapeyron equation.

PCPs	Predicted CO ₂ /CO selectivity	Temperature	Refs
MCM-41	37.0	293	5
BPL carbon	7.5	273	6
I-AC	4.5	298	7
ZIF-68	19.2	273	6
ZIF-69	20.9	273	6
ZIF70	37.8	273	6
LaBTN	27.2	273	8
some	10 2-50 0	272	9
zeolites	10.2-30.0	275	
NTU-26	58.5	273	This work

Table S4. Comparison of CO_2/CO selectivity by different porous materials.

13. Notation

- *b* Langmuir constant, Pa^{-1}
- *p*_i partial pressure of species *i* in mixture, Pa
- *p*t total system pressure, Pa
- q_i component molar loading of species *i*, mol kg⁻¹
- *q*t total molar loading in mixture, mol kg⁻¹
- $q_{\rm sat}$ saturation loading, mol kg⁻¹
- L length of packed bed adsorber, m
- R gas constant, 8.314 J mol⁻¹ K⁻¹
- t time, s
- T absolute temperature, K
- *u* superficial gas velocity in packed bed, m s⁻¹

14. Greek letters

- ε voidage of packed bed, dimensionless
- au time, dimensionless

15. Subscripts

- i referring to component *i*
- t referring to total mixture

16. Refs

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