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Electronic Supporting Information

# Constructing and finely tuning CO<sub>2</sub> traps of stable and various-pores-containing MOFs towards highly selective CO<sub>2</sub> capture

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### 1. Materials and general methods

General procedures. All chemical reagents were obtained from commercial sources and, unless otherwise noted, were used as received without further purification. Elemental analyses (C, H, N) were carried out on a Perkin-Elmer 240 analyzer. The IR spectra were obtained on a VECTOR TM 22 spectrometer with KBr pellets in the 4000~400 cm<sup>-1</sup> region. The *in situ* FTIR spectra were collected in the 4000~600 cm<sup>-1</sup> on a Bruker Tensor 27 spectrometer using KBr pellets. <sup>1</sup>H NMR spectra were recorded on a Bruker DRX-300 spectrometer with tetramethylsilane as an internal reference. Thermal gravimetric analyses (TGA) were performed under N<sub>2</sub> atmosphere (100 mL min<sup>-1</sup>) with a heating rate of 20 °C min<sup>-1</sup> using a 2960 SDT thermogravimetric analyzer. Powder X-ray diffraction (PXRD) data were collected on a Bruker D8 ADVANCE X-ray diffractometer with Cu/K $\alpha$  radiation. Morphological features were examined by SEM (Hitachi S-3400N II). Gas sorption measurements were conducted using a Micrometritics ASAP 2020 surface area and pore size analyzer up to saturated pressure at different temperatures.

#### 1.1 Synthesis of the ligands

The ligands of 1,1'-(4-carboxypyridine-2,6-diyl)bis(1H-pyrazole-4-carboxylic acid) (H<sub>3</sub>L1) and 1,1'-(4-carboxypyridine-2,6-diyl)bis(3-bromo-1H-pyrazole-4-carboxylic acid) (H<sub>3</sub>L2) were prepared following a similar strategy<sup>1</sup> and characterized by <sup>1</sup>H NMR and IR.

Preparation of H<sub>3</sub>L1: Ethyl pyrazole-4-carboxylate (6.0 g, 42.8 mmol) in anhydrous DMF (100 mL) was added dropwise to a stirring solution of NaH (1.12 g, 46.7 mmol) in anhydrous DMF (20 mL) under N<sub>2</sub>. The mixture was stirred at 100 °C for 2 h. After ethyl 2,6-dichloroisonicotinate (4.4 g, 20.0 mmol) in anhydrous DMF (80 mL) was added slowly to it, it was stirred at 130 °C under N<sub>2</sub> for 4 days and cooled to room temperature. Then, a large excess of cold water was added to it to yield a yellow solid. This yellow solid was collected, dried, purified by recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/EtOH, and hydrolyzed by refluxing in 2 mol L<sup>-1</sup> aqueous NaOH followed by

acidification with 2 mol L<sup>-1</sup> aqueous HCl to give a white solid, H<sub>3</sub>L1. Yield  $\approx$  84.5%. IR (KBr, cm<sup>-1</sup>): 3399, 3115, 2937, 2353, 1664, 1562, 1476, 1422, 1339, 1309, 1271, 1182, 1101, 1046, 1004, 963, 896, 793, 723. <sup>1</sup>H NMR (300MHz, DMSO-*d*<sub>6</sub>,  $\delta$  ppm): 13.01 (broad peak, COO<u>H</u>), 9.65 (s, 2H, Pz<u>H</u>), 8.27 (s, 2H, Pz<u>H</u>), 8.21 (s, 2H, Py<u>H</u>).



Preparation of H<sub>3</sub>L2: Ethyl 3-bromo-1H-pyrazole-4-carboxylate (9.38 g, 42.8 mmol) in anhydrous DMF (100 mL) was added dropwise to a stirring solution of NaH (1.12 g, 46.7 mmol) in anhydrous DMF (20 mL) under N<sub>2</sub>. The mixture was stirred at 100 °C for 2 h. After ethyl 2,6-dichloroisonicotinate (4.4 g, 20.0 mmol) in anhydrous DMF (80 mL) was added slowly to it, it was stirred at 130 °C under N<sub>2</sub> for 4 days and cooled to room temperature. Then, a large excess of cold water was added to it to yield a yellow solid. This yellow solid was collected, dried, purified by recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/EtOH, and hydrolyzed by refluxing in 2 mol L<sup>-1</sup> aqueous NaOH followed by acidification with 2 mol L<sup>-1</sup> aqueous HCl to give a white solid, H<sub>3</sub>L2. Yield ≈ 86.8%. IR (KBr, cm<sup>-1</sup>): 3593, 3486, 3238, 3134, 2974, 2898, 2582, 1702, 1618, 1581, 1540, 1469, 1423, 1363, 1284, 1244, 1174, 1105, 1064, 984, 925, 893, 869, 805, 773, 746. <sup>1</sup>H NMR (300MHz, DMSO-*d*<sub>6</sub>,  $\delta$  ppm): 13.18 (broad peak, COO<u>H</u>), 9.76 (s, 2H, Pz<u>H</u>), 8.21 (s, 2H, Py<u>H</u>).



## 1.2 Synthesis of $\{Sc_3O(L1)_2(H_2O)_3(NO_3)\}_{\infty}$ (NJU-Bai50).

A mixture of Sc(NO<sub>3</sub>)<sub>3</sub>·xH<sub>2</sub>O (10 mg, 0.043 mmol), H<sub>3</sub>L1 (10 mg, 0.029 mmol), dilute HNO<sub>3</sub> (3.5 mol L<sup>-1</sup>, 0.45 mL) and 2 mL DMF was sealed in a 20 mL Pyrex tube, which was heated to 130 °C for 3 days. After cooling to the room temperature, the colorless hexagonal-plate-shaped crystals were obtained. The crystals of **NJU-Bai50** were filtered and washed with DMF. Yield  $\approx$  62.6%. Selected IR (cm<sup>-1</sup>): 3402, 3114, 2938, 2355, 1661, 1561, 1476, 1421, 1338, 1309, 1270, 1183, 1100, 1046, 1005, 963, 895, 791, 721. Anal. Calcd. (Found), C<sub>37</sub>H<sub>65</sub>Sc<sub>3</sub>N<sub>14</sub>O<sub>35</sub>: C, 31.73 (31.91); H, 4.68 (4.57); N, 14.00 (14.05)%.

# 1.3 Synthesis of $\{Sc_3O(L2)_2(H_2O)_3(NO_3)\}_{\infty}$ (NJU-Bai51).

A mixture of Sc(NO<sub>3</sub>)<sub>3</sub>·xH<sub>2</sub>O (7 mg, 0.03 mmol), H<sub>3</sub>L2 (10 mg, 0.02 mmol), concentrated HNO<sub>3</sub> (16 mol L<sup>-1</sup>, 130 µL) and 2 mL DMF was sealed in a 20 mL Pyrex tube, which was heated to 130 °C for 3 days. After cooling to the room temperature, the colorless block crystals were obtained. The crystals of **NJU-Bai51** were filtered and washed with DMF. Yield  $\approx$  65.3%. Selected IR (cm<sup>-1</sup>): 3402, 3114, 2934, 2359, 2335, 1666, 1622, 1606, 1577, 1531, 1475, 1412, 1384, 1359, 1329, 1279, 1178, 1114, 1078, 1062, 981, 897, 792, 719. Anal. Calcd. (Found), C<sub>38.5</sub>H<sub>50.5</sub>Sc<sub>3</sub>N<sub>14.5</sub>O<sub>28.5</sub>Br<sub>4</sub>: C, 28.43 (28.57); H, 3.13 (3.06); N, 12.49 (12.61)%.

### 2. Single-crystal X-ray structure determination

The activation and loading of single crystals in a cell was performed on a Micromeritics ASAP 2020 gas analysis system via a Swagelok® ultra-torr fittings. This system allowed precise control of activation and loading conditions in an ultra-high purity environment. Single crystals of **NJU-Bai51** were loaded inside a cell and were evacuated for 12 hours at 150 °C to obtain the guest-free **NJU-Bai51a**. Then, the sample was backfilled with CO<sub>2</sub> (760 mmHg, 298 K) and allowed to equilibrate for an hour. The CO<sub>2</sub>-loaded single crystal was removed to a dry liquid nitrogen atmosphere (153 K) for structural analysis.

Single-crystal X-ray diffraction data were measured on a Bruker D8 Venture diffractometer using graphite monochromated Mo/K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Data reduction was made with the Bruker SAINT program. The structures were solved by direct methods and refined with full-matrix least squares technique using the SHELXTL package<sup>2</sup>. 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  $1.2 \times U_{eq}$  of the attached atom. The hydrogen atoms of the ligated water molecules could not be located. The unit cell includes a large region of disordered solvent molecules, which could not be modelled as discrete atomic sites. We employed PLATON/SQUEEZE<sup>3</sup> to calculate the diffraction contribution of the solvent molecules and, thereby, to produce a set of solvent-free diffraction intensities; structures were then refined again using the data generated.

A summary of the crystallographic data are given in Table S1. CCDC 1881967-1881969 contain the supplementary crystallographic data for NJU-Bai50, NJU-Bai51, and NJU-Bai51a·( $CO_2$ )<sub>1.0</sub>. The data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK.

MOFs	NJU-Bai50	NJU-Bai51	NJU-Bai51a · (CO <sub>2</sub> ) <sub>1.0</sub>	
CCDC number	1881967	1881969	1881968	
Empirical formula	$C_{28}H_{12}N_{10}O_{16}Sc_3$	$C_{28}H_{10}Sc_{3}Br_{4}N_{11}O_{19}$	$C_{29}H_8Sc_3Br_4N_{10}O_{17}$	
Formula weight	879.36	1258.90	1222.90	
Crystal system	Hexagonal	Tetragonal	Tetragonal	
Space group	p62m	P4 <sub>2</sub> /mnm	P4 <sub>2</sub> /mnm	
T (K)	123	153	153	
<i>a</i> (Å)	18.1419(9)	17.9479(6)	17.5036(9)	

 Table S1. Crystal Data and Refinement Results for NJU-Bai50, NJU-Bai51, and NJU-Bai51a·(CO<sub>2</sub>)<sub>1.0</sub>.

<i>b</i> (Å)	18.1419(9)	17.9479(6)	17.5036(9)	
<i>c</i> (Å)	20.5197(18)	22.2481(8)	22.463(2)	
$\alpha$ (deg)	90	90	90	
$\beta$ (deg)	90	90	90	
γ (deg)	120	90	90	
$V(Å^3)$	5848.8(8)	7166.7(5)	6882.1(10)	
Ζ	3	4	4	
$\rho_{\rm calc}[{\rm g~cm^{-3}}]$	0.742	1.167	1.180	
$\mu/\mathrm{mm}^{-1}$	0.290	2.559	2.660	
F(000)	1293	5148	2364	
Crystal size [mm <sup>3</sup> ]	0.06 x 0.06 x 0.02	0.12 x 0.07 x 0.04	0.10 x 0.06 x 0.04	
Theta range [deg]	2.245 - 25.019	2.269 - 25.012	2.327 - 27.591	
Limiting indices	-21 < = h < = 21	-19 < = h < = 21	-22 < = h < = 22	
	-21 < = k < = 21	-21 < = k < = 21	-17 < = k < = 22	
	-23 < = 1 < = 24	-24 < = 1 < = 26	-28 < = 1 < = 29	
Reflns collected	3768	3409	4264	
Reflns unique	1968	2943	1758	
Completeness	100.0%	99.9%	99.6%	
Data/restraints/parameters	3768 / 120 / 119	3409 / 0 / 165	4264 / 18 / 159	
Goodness-of-fit on F <sup>2</sup>	1.014	1.054	1.297	
R1, wR2 <sup>a</sup> [I > $2\sigma(I)$ ]	0.1126, 0.2633	0.0686, 0.1896	0.1166, 0.3252	
R1, wR2 [all data]	0.1860, 0.3023	0.0778, 0.1967	0.2401, 0.4334	
$\Delta \rho_{max} / \Delta \rho_{min}$ [e. Å <sup>-3</sup> ]	1.656 / -0.932	3.089 / -1.764	2.318 / -1.800	

<sup>a</sup> R1 =  $\Sigma ||F_o| - |F_c||/|F_o|$ ; wR2 =  $[\Sigma w (\Sigma F_o^2 - F_c^2)^2 / \Sigma w (F_o^2)^2]^{1/2}$ .



**Figure S1.** SEM micrographs of **NJU-Bai50** samples (a, b) and **NJU-Bai51** samples (c, d). **NJU-Bai50** was comprised of small uniform particles in a range of 5.5–6 μm, whereas **NJU-Bai51** was comprised of particles ca. 10 times larger, roughly 61.5–62 μm.



Figure S2. The scandium atom is in the same plane with the four coordinated carboxylate O atoms.



Figure S3. Topological analysis of NJU-Bai50, where the  $H_3L1$  ligand is simplified as a 3-connected node, while the Sc<sub>3</sub>-trimer is reduced to a 6-connected node.



**Figure S4.** Topological analysis of **NJU-Bai51**, where the H<sub>3</sub>L2 ligand is simplified as a 3-connected node, while the Sc<sub>3</sub>-trimer is reduced to a 6-connected node.



**Figure S5.** a, b) The distance between the two opposite pyrazole H atoms in the trap of **NJU-Bai50** and **NJU-Bai51**, respectively.



**Figure S6.** One NO<sub>3</sub><sup>-</sup> anion locates in the trap of **NJU-Bai51** and shows the multiple hydrogenbonding interactions between the counter anion and the cationic framework (O1w-H1w...O6 = 2.162(2) Å, < O1w-H1w...O6 =  $136.93(0)^{\circ}$ ; C3-H3...O6 = 2.280(3) Å, < C3-H3...O6 =  $169.75(8)^{\circ}$ ; C3-H3...O7 = 2.985(5) Å, < C3-H3...O7 =  $125.61(7)^{\circ}$ ).

# 3. TG, IR, PXRD and VT-PXRD analyses



**Figure S7.** a) TGA curves of as-synthesized (dark blue) and activated (red) **NJU-Bai50**. b) TGA curves of as-synthesized (green) and activated (orange) **NJU-Bai51**.



**Figure S8.** FTIR spectra of **NJU-Bai50** and  $H_3L1$ . The N-O stretching peak around 1340 cm<sup>-1</sup> in the spectrum for **NJU-Bai50** indicates the existence of nitrate as a counter anion.<sup>4</sup>



**Figure S9.** FTIR spectra of **NJU-Bai51** and  $H_3L2$ . The N-O stretching peak around 1340 cm<sup>-1</sup> in the spectrum for **NJU-Bai51** indicates the existence of nitrate as a counter anion.<sup>4</sup>



Figure S10. (a) FTIR spectra of NJU-Bai51a at room temperature. (b) FTIR spectra of NJU-Bai51a under an equilibrium pressure of  $CO_2$  (30 Torr) at room temperature. The band at 2332 cm<sup>-1</sup> is

associated with the CO<sub>2</sub>  $v_3$  mode (asymmetric O=C=O stretching) adsorbed on NJU-Bai51a. In the high frequency range (3800 – 3500 cm<sup>-1</sup>), two complex absorptions are at about 3700 and 3600 cm<sup>-1</sup>. The nature of these two absorptions is well known and is interpreted on the basis of combination of  $v_1$  and  $v_3$  modes of CO<sub>2</sub>.<sup>5-6</sup>



Figure S11. a, b) The PXRD patterns of NJU-Bai50 and NJU-Bai51 after different treatments, respectively.



Figure S12. VT-PXRD patterns of as-synthesized sample of NJU-Bai50 under vacuum.



Figure S13. VT-PXRD patterns of as-synthesized sample of NJU-Bai51 under vacuum.

# 4. Low-pressure gas sorption measurements

**Sample activation.** The as-synthesized samples of **NJU-Bai50** and **NJU-Bai51** were soaked in acetonitrile and methanol for 3 days, respectively, with acetonitrile and methanol refreshing every 8 hours. Then, the solvent-exchanged samples (**NJU-Bai50** and **NJU-Bai51**) were activated at 150 °C under vacuum for 12 hours.

Low-pressure gas (N<sub>2</sub>, CO<sub>2</sub>, CH<sub>4</sub>) sorption isotherms (up to 1 bar) were performed on Micromeritics ASAP 2020 M+C surface area and pore size analyzer. Before gas sorption measurements, about 400 mg samples were activated by using the "outgas" function of the surface area analyzer. For all isotherms, warm and cold free space correction measurements were performed using ultra-high purity He gas (UHP grade 5.0, 99.999% purity). The specific surface areas were determined using the Brunauer-Emmett-Teller (BET) and the Langmuir equation from the N<sub>2</sub> sorption data at 77 K. When applying the BET theory, we made sure that our analysis satisfied the two consistency criteria as detailed by Walton and co-workers<sup>7-8</sup>. For the Langmuir surface area, data from the whole adsorption data were used. The pore size distribution (PSD) was obtained from the DFT model in the Micromeritics ASAP2020 software package based on the N<sub>2</sub> sorption isotherm.



**Figure S14.** a) N<sub>2</sub> adsorption (closed) / desorption (open) isotherms of **NJU-Bai50** at 77 K. b) V[1-(P/P<sub>0</sub>)] vs P/P<sub>0</sub> for **NJU-Bai50**, only the range below P/P<sub>0</sub> = 0.03 satisfies the first consistency criterion for applying the BET theory. Inset: Plot of the linear region for the BET equation.



**Figure S15.** a) N<sub>2</sub> adsorption (closed) / desorption (open) isotherms of NJU-Bai51 at 77 K. b) V[1-(P/P<sub>0</sub>)] vs P/P<sub>0</sub> for NJU-Bai51, only the range below P/P<sub>0</sub> = 0.035 satisfies the first consistency criterion for applying the BET theory. Inset: Plot of the linear region for the BET equation.



Figure S16. a, b) The pore size distribution curves of NJU-Bai50 and NJU-Bai51, respectively.



**Figure S17.** a) CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub> adsorption (closed) /desorption (open) isotherms for NJU-Bai50 and NJU-Bai51 at 273 K. b) CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub> adsorption (closed) /desorption (open) isotherms for NJU-Bai50 and NJU-Bai51 at 298 K



Figure S18. The twice CO<sub>2</sub> adsorption isotherms for NJU-Bai50 at 298 K and extremely low pressure.



Figure S19. a) N<sub>2</sub> adsorption (closed) / desorption (open) isotherms of water-treated NJU-Bai50.
b) N<sub>2</sub> adsorption (closed) / desorption (open) isotherms of water-treated NJU-Bai51.

# 5. Calculations of isosteric heat of adsorption $(Q_{st})$

A virial-type<sup>9</sup> expression comprising the temperature-independent parameters  $a_i$  and  $b_j$  was employed to calculate the enthalpies of adsorption for CO<sub>2</sub> (at 273 and 298 K) on NJU-Bai50 and NJU-Bai51. In each case, the data were fitted using the equation:

$$\ln P = \ln N + 1 / T \sum_{i=0}^{m} a_i N^i + \sum_{j=0}^{n} b_j N^j$$

Here, *P* is the pressure expressed in Torr, *N* is the amount adsorbed in mmol g<sup>-1</sup>, *T* is the temperature in K,  $a_i$  and  $b_j$  are virial coefficients, and *m*, *n* represent the number of coefficients required to adequately describe the isotherms (*m* and *n* were gradually increased until the contribution of extra added *a* and *b* coefficients was deemed to be statistically insignificant towards the overall fit, and the average value of the squared deviations from the experimental values was minimized). The values of the virial coefficients  $a_0$  through  $a_m$  were then used to calculate the isosteric heat of adsorption using the following expression.

$$Q_{st} = -R \sum_{i=0}^{m} a_i N^i$$

 $Q_{st}$  is the coverage-dependent isosteric heat of adsorption and *R* is the universal gas constant. The heat of CO<sub>2</sub> sorption for **NJU-Bai50** and **NJU-Bai51** in the manuscript is determined by using the low pressure gas sorption data measured in the pressure range from 0-1 bar (273 and 298 K), which is fitted by the virial-equation very well (R<sup>2</sup> > 0.9999).



**Figure S20.** a, b) The details of virial equation (solid lines) fitting to the experimental CO<sub>2</sub> adsorption data (symbols) for NJU-Bai50 and NJU-Bai51, respectively.



**Figure S21.** a, b) The details of virial equation (solid lines) fitting to the experimental CH<sub>4</sub> adsorption data (symbols) for NJU-Bai50 and NJU-Bai51, respectively.



**Figure S22.** a, b) The isosteric CO<sub>2</sub> and CH<sub>4</sub> adsorption enthalpies of **NJU-Bai50** and **NJU-Bai51**, respectively.

# 6. IAST calculation

IAST (ideal adsorption solution theory)<sup>10-12</sup> was used to predict binary mixture adsorption from the experimental pure-gas isotherms. In order to perform the integrations required by IAST, the singlecomponent isotherms should be fitted by a proper model. In practice, several methods to do this are available. We found for this set of data that the dual-site Langmuir-Freundlich equation was successful in fitting the data. As can be seen in Figure S20-21 and Table S2-5, the model fits the isotherms very well ( $R^2 > 0.9999$ ).

$$q = \frac{q_{m,1}b_1p^{1/n_1}}{1+b_1p^{1/n_1}} + \frac{q_{m,2}b_2p^{1/n_2}}{1+b_2p^{1/n_2}}$$

Here, P is the pressure of the bulk gas at equilibrium with the adsorbed phase (kPa), q is the adsorbed amount per mass of adsorbent (mmol  $g^{-1}$ ),  $q_{m,1}$  and  $q_{m,2}$  are the saturation capacities of sites 1 and 2 (mmol  $g^{-1}$ ),  $b_1$  and  $b_2$  are the affinity coefficients of sites 1 and 2 (1/kPa), and  $n_1$  and  $n_2$  represent the deviations from an ideal homogeneous surface. The fitted parameters were then used to predict multi-component adsorption with IAST.

The selectivity  $S_{A/B}$  in a binary mixture of components A and B is defined as  $(x_A/y_A)/(x_B/y_B)$ , where  $x_i$  and  $y_i$  are the mole fractions of component i (i = A, B) in the adsorbed and bulk phases, respectively.



Figure S23. a, b) IAST predicted selectivity for  $CO_2/N_2$  (15/85) and  $CO_2/CH_4$  (50/50) mixture of NJU-Bai50 and NJU-Bai51 at 273 K and 298K, respectively.



**Figure S24.** a, b) Low pressure gas adsorption isotherms and the dual-site Langmuir-Freundlich (DSLF) fit lines of CO<sub>2</sub>, N<sub>2</sub> and CH<sub>4</sub> in **NJU-Bai50** at 273 K and 298 K, respectively.



**Figure S25.** a, b) Low pressure gas adsorption isotherms and the dual-site Langmuir-Freundlich (DSLF) fit lines of CO<sub>2</sub>, N<sub>2</sub> and CH<sub>4</sub> in **NJU-Bai51** at 273 K and 298 K, respectively.

**Table S2.** Dual-site Langmuir-Freundlich parameters for pure  $CO_2$ ,  $N_2$  and  $CH_4$  isotherms in NJU-Bai50 at 273 K

	NJU-Bai50							
	CO <sub>2</sub>	N <sub>2</sub>	$CH_4$					
<b>R</b> <sup>2</sup>	0.999999871483931	0.999999167995114	0.999999832828569					
<i>q</i> <sub>m,1</sub>	3.82585094053461	0.590095253144252	14.3128244311371					
q <sub>m,2</sub>	12.400673758296	0.326520532422161	0.0218347691445725					
<b>b</b> <sub>1</sub>	0.0256769861933253	0.00572807477831289	0.000818316413619882					
b <sub>2</sub>	0.000160089147429921	2.39399660131193E-5	0.0622790985181444					

$n_1$	0.920487745058654	1.04071818760613	1.02692489443172
n <sub>2</sub>	1.65328793028643	2.04787396040505	0.92032549662624

**Table S3.** Dual-site Langmuir-Freundlich parameters for pure  $CO_2$ ,  $N_2$  and  $CH_4$  isotherms in NJU-Bai50 at 298 K

	NJU-Bai50							
	CO <sub>2</sub>	N <sub>2</sub>	CH <sub>4</sub>					
R <sup>2</sup>	0.999999864281916	0.999999442384565	0.999999860272389					
q <sub>m,1</sub>	0.224455895124508	0.128908009460014	19.7097935899318					
q <sub>m,2</sub>	123.18697643415	0.197022541629212	0.00034728215484724					
<b>b</b> <sub>1</sub>	0.0170732998368104	0.000295867695226612	0.000380170474990052					
b <sub>2</sub>	0.000284315519546474	0.0116842597610943	8.95738825722687E-11					
<b>n</b> <sub>1</sub>	0.923142230757542	1.74168427352479	0.997094165061918					
n <sub>2</sub>	0.936116595340525	0.997366142728549	7.51661790324082					

**Table S4.** Dual-site Langmuir-Freundlich parameters for pure  $CO_2$ ,  $N_2$  and  $CH_4$  isotherms in NJU-Bai51 at 273 K

	NJU-Bai51							
	$CO_2$	N <sub>2</sub>	$CH_4$					
R <sup>2</sup>	0.99999899927153	0.999999913400303	0.999999983241442					
<i>q</i> <sub>m,1</sub>	1.24725120420804	0.00119069664149278	7.05141378622562					
q <sub>m,2</sub>	8.78490671713795	2.1084358453578	0.147903483757645					
<b>b</b> <sub>1</sub>	0.43836723478028	0.219166118630917	0.00159998489843601					
b <sub>2</sub>	0.00581261568753979	0.00206385291438443	0.0358817399449932					
<b>n</b> <sub>1</sub>	0.328911011186346	1.55217941340895	1.06304180993711					
n <sub>2</sub>	1.13960977136511	1.01612642481584	0.890079277610212					

**Table S5.** Dual-site Langmuir-Freundlich parameters for pure  $CO_2$ ,  $N_2$  and  $CH_4$  isotherms in NJU-Bai51 at 298 K

		NJU-Bai51			
	$CO_2$	$N_2$	CH <sub>4</sub>		
R <sup>2</sup>	0.999996642260737	0.999999643172511	0.999999946742324		
<i>q</i> <sub>m,1</sub>	0.51289921926358	0.326551737600869	8.08639569349106		
q <sub>m,2</sub>	10.2118041399432	0.160377524732898	0.000546240182927996		
<b>b</b> <sub>1</sub>	0.912370930175507	0.00781723404670321	0.00107799177042948		

b <sub>2</sub>	0.00304029735137153	0.00015348850241561	5.68984343766668E-6
		1	
n <sub>1</sub>	0.501264279666385	1.00511709649713	0.992976859190937
n <sub>2</sub>	1.03768353823549	1.78032449243671	4.07873262997583

**Table S6.** BET Surface Areas, Pore volumes, CO<sub>2</sub> Uptakes, Enthalpies, Selectivities of **NJU-Bai50**, **NJU-Bai51** and some MOFs at room temperature.

	DET	Pore	CO <sub>2</sub> uptake (wt%)		0	Selectivity <sup>a</sup>		Tomn		
MOFs	$\frac{DEI}{(m^2 g^{-1})}$	volume	at 0.4	at 0.15	at 1	$Q_{st, CO2}$	CO <sub>2</sub> /	CO <sub>2</sub> /	(K)	Ref.
	(mg)	(cm <sup>3</sup> g <sup>-1</sup> )	mbar	bar	bar	(K5 11101 )	$N_2$	$\mathrm{CH}_4$	(13)	
NJU-Bai50	2015	0.80	0.0079	2.11	10.6	26.6	30.5	4.4	298	This work
NJU-Bai51	1280	0.50	0.57	3.81	12.3	33.3	545.7	10.7	298	This work
SMT-1	$153^{b}$	0.097		0.71	2.7	35.0			296	13
PCN-88'	3042			2.30	12.1	25.0	12.3	5.8	296	13
MIL-100(Al)	1145	0.61		1.56	6.6	22.5	15.0	10.4	298	14
PCN-88	3308			3.28	15.5	27.0	15.2	7.0	296	13
ZIF-78	620	0.27		3.32	9.1		41.4		298	15
SIFSIX-2-Cu-i	735	0.26	0.30	9.19	19.2	31.9	140	33	298	16
Mg-MOF-74	1495		0.39	21.16	26.0	47	182.1		296	17-19
mmen-Mg <sub>2</sub> (dobpdc)	70		8.09	12.10	14.5	71	$200^{c}$		298	20
UTSA-16	628	0.31		9.44	15.9	34.6	314.7		296	19
mmen-CuBTTri	870		0.22	9.48	15.4	96	327.0		298	21
Zn <sub>2</sub> (bpdc) <sub>2</sub> (bpee)				2.23	4.7	32.5-33	493.8 <sup>c</sup>		298	22
Zn <sub>4</sub> O(L3) <sub>1.5</sub>				4.81	14.3		580.8 <sup>c</sup>		298	23
PEI-MIL-101-100	608.4	0.29		15.60	18.0		600 <sup>c</sup>		298	24
PEI-MIL-101-125	182.9	0.095		14.48	16.1		$770^{c}$		298	24
SIFSIX-3-Zn	250 <sup>d</sup>		0.57	9.66	10.1	45	1818	231	298	16
SIFSIX-3-Cu	300 <sup>d</sup>		5.17	9.33		54	>25000		298	25
	T A GTT			1.0 10			~		~	A

<sup>*a*</sup> Selectivity obtained from IAST calculations. <sup>*b*</sup> Calculated from 195 K CO<sub>2</sub> isotherm. <sup>*c*</sup> S = $(q_1/q_2)/(p_1/p_2)$ . <sup>*d*</sup> Calculated from 298 K CO<sub>2</sub> isotherm.

# 7. Breakthrough experiments

Breakthrough system used in this study is hand-made according to the literatures<sup>26-</sup>

<sup>30</sup>. The flow rates of all gases are regulated by mass flow controllers, and the effluent

gas stream from the column is monitored by a gas chromatography (GC). All measurements were performed following a protocol established by the literatures<sup>26-28</sup>. Activated sample **NJU-Bai51** (382 mg) was packed into a stainless-steel column (12 cm length  $\times$  0.30 cm internal diameter) and the remaining volume in the column was filled by glass wool. The packed column was initially purged with helium gas for 30 mins until no other gases were detected in the effluent. Then, a CO<sub>2</sub> flow and N<sub>2</sub> flow (total is 10 mL min<sup>-1</sup>: 15/85), a CO<sub>2</sub> flow and CH<sub>4</sub> flow (total is 10 mL min<sup>-1</sup>: 50/50) were dosed into the column. In the study of water effect on CO<sub>2</sub>/N<sub>2</sub> adsorption, the wet effluent was premixed with N<sub>2</sub> and CO<sub>2</sub> through passing a gas bubbler containing water. The water concentration was determined to be about 5% using a mass spectrometer. A breakthrough of CO<sub>2</sub> was determined when the concentration of effluent CO<sub>2</sub> reached 1% of the feed concentration. Breakthrough times were calculated by subtracting the time to breakthrough using a sample bed packed only with stainless steel beads and cotton plugs from the observed breakthrough time.

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