## Supporting Information

# Wide temperature capturing of CO<sub>2</sub> from N<sub>2</sub> and CH<sub>4</sub> on a robust MOF with Brønsted acidic and Lewis basic dual functional sites

Shijian Lu,<sup>b</sup> Ya-Jie Zhang,<sup>a</sup> Ying-Jie Cheng,<sup>a</sup> Zi-Heng Qin,<sup>a</sup> Gang-Ding Wang,<sup>c</sup> Yuan Bai,<sup>e</sup> Yichao Lin,<sup>d</sup> Hetang Wang,<sup>d</sup>\* Yanwei Sui,<sup>a</sup> and Lei Hou,<sup>c</sup>\* Yong-Zhi Li,<sup>a</sup>\*

<sup>a</sup>School of Materials and Physics, China University of Mining and Technology, Xuzhou 221116, P. R. China

<sup>b</sup>Jiangsu Key Laboratory of Coal-based Greenhouse Gas Control and Utilization, Carbon Neutrality Institute, China University of Mining and Technology Xuzhou, 221116, P. R. China

<sup>c</sup>Key Laboratory of Synthetic and Natural Functional Molecule of the Ministry of Education, Shaanxi Key Laboratory of Physico-Inorganic Chemistry, College of Chemistry & Materials Science, Northwest University, Xi'an 710069, P. R. China

<sup>d</sup>School of Safety Engineering, China University of Mining and Technology, Xuzhou 221116, Jiangsu, China

eGuodian Environmental Research Institute Co., Ltd., Nanjing 210031, China

\*To whom correspondence should be addressed. E-mail: wanghetang@cumt.edu.cn (Hetang Wang), lhou2009@nwu.edu.cn (Lei Hou), Lyz2021@cumt.edu.cn (Yong-Zhi Li).

#### Materials and general methods

All solvents and organic ligand for synthesis were purchased commercially. Zinc nitrate hexahydrate (Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, purity 99.9%) was purchased from Aladdin, 4,6-bis(triazol-1-yl)isophthalic acid (H<sub>2</sub>btzip, purity 98%) was purchased from Shanghai Tensus Biotech CO.,Ltd (China), N, N-dimethylformamide (DMF, purity 99.9%), acetonitrile (CH<sub>3</sub>CN, purity 99.9%) and hydrochloride (HCl, 6 mol L<sup>-1</sup>) were purchased from Tianjin Damao chemicals reagent factory (China). Elemental analyses of C, H, and N were determined with a Perkin-Elmer 2400C elemental analyzer. Thermalgravimetric analyses (TGA) were carried out in a nitrogen stream using a Netzsch TG209F3 equipment at a heating rate of 10 °C min<sup>-1</sup>. Single crystal diffraction data were collected on a Bruker SMART APEX II CCD single crystal diffractometer. Gas adsorption measurements were performed with an automatic volumetric sorption apparatus (Micrometrics ASAP 2020M), in which the sample was activated by immersing in CH<sub>3</sub>OH for 72 hours and then heating at 423 K under vacuum for 4 hours. Breakthrough experiments were performed on a Quantachrome dynaSorb BT equipments.

### X-Ray Crystallography

A Bruker Smart Apex II CCD detector was used to collect the single crystal data at 296.15 K using Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The structure was solved by direct methods and refined by full-matrix least-squares refinement based on  $F^2$  with the SHELXTL program. The non-hydrogen atoms were refined anisotropically with the hydrogen atoms added at their geometrically ideal positions and refined isotropically. As the disordered solvent molecules in the structure cannot be located, the SQUEEZE routine of Platon program was applied in refining. The formula of complex was got by the single crystal analysis together with elemental microanalyses and TGA data. Relevant crystallographic results were listed in Table S1. Selected bond lengths and angles were provided in Table S2.

#### **Breakthrough Experiments**

The breakthrough experiment was performed on the Quantachrome dynaSorb BT equipments at 273, 298, 313 and 333 K and 1 bar with mixed gas. The activated MOF were filled into a packed column of  $\phi$  4.2×80 mm, and then the packed column was washed with Ar at a rate of 7 mL min<sup>-1</sup> at 333 K for 35 minutes to further activate the samples. Between two breakthrough experiments, the adsorbent was regenerated by Ar flow of 7 mL min<sup>-1</sup> for 35

min at 333 K to guarantee a complete removal of the adsorbed gases.

The detailed various  $CO_2/N_2$  breakthrough measurements conditions are as follows: the  $CO_2/N_2/Ar$  (5:5:90, v/v/v),  $CO_2/N_2/Ar$  (3:17:80, v/v/v) mixtures were purged into a packed column with a total inlet flow rate of 8.0 mL min<sup>-1</sup> at 273, 298, 313 and 333 K and 1 bar, respectively. The detailed various  $CO_2/CH_4$  breakthrough measurements conditions are as follows: the  $CO_2/CH_4/Ar$  (5:5:90, v/v/v),  $CO_2/CH_4/Ar$  (1:9:90, v/v/v) mixtures were purged into a packed column with a total inlet flow rate of 8.0 mL min<sup>-1</sup> at 273, 298, 313 and 333 K and 333 K and 1 bar, respectively. The detailed  $CO_2/CH_4/Ar$  (1:9:90, v/v/v) mixtures were purged into a packed column with a total inlet flow rate of 8.0 mL min<sup>-1</sup> at 273, 298, 313 and 333 K and 1 bar, respectively. The detailed  $CO_2/CH_4/N_2$  breakthrough measurements conditions are as follows: the  $CO_2/CH_4/N_2/Ar$  (5:5:5:90, v/v/v) mixtures were purged into a packed column with a total inlet flow rate of 8.0 mL min<sup>-1</sup> at 273, 298, 313 and 333 K and 1 bar. For the desorption measurements: upon reaching breakthrough equilibrium, the captured gas in the column was purged by Ar gas sweeping (7 ml min<sup>-1</sup>) at 323 K.

Breakthough experiments under different relative humidities were bubbled the mixture gases through specific saturated salt solution or ultrapure water at 298 K to obtain gas streams under different RH conditions.

#### **GCMC** simulations

Grand canonical Monte Carlo (GCMC) simulations were performed for the gas adsorption in the framework by the Sorption module of Material Studio (Accelrys. Materials Studio Getting Started, release 5.0). The framework was considered to be rigid, and the optimized gas molecules were used. The partial charges for atoms of the framework were derived from QEq method and QEq neutral 1.0 parameter. One unit cell was used during the simulations. The interaction energies between the gas molecules and framework were computed through the Coulomb and Lennard-Jones 6-12 (LJ) potentials. All parameters for the atoms were modeled with the universal force field (UFF) embedded in the MS modeling package. A cutoff distance of 12.5 Å was used for LJ interactions, and the Coulombic interactions were calculated by using Ewald summation. For each run, the  $5 \times 10^6$  maximum loading steps,  $5 \times 10^6$  production steps were employed.

#### Fitting adsorption heat of pure component isotherms

$$\ln P = \ln N + 1/T \sum_{i=0}^{m} a_i N^i + \sum_{i=0}^{n} b_i N^i \qquad \qquad Q_{\rm st} = -R \sum_{i=0}^{m} a_i N^i$$

The above virial expression was used to fit the combined isotherm data for gas isomorphs at 273 and 298 K, where P is the pressure, N is the adsorbed amount, T is the temperature, ai and bi 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.

#### **Gas Selectivity Prediction via IAST**

The experimental isotherm data for pure  $CO_2 N_2$ , and  $CH_4$  were fitted using a single Langmuir-Freundlich (L-F) model:

$$q = \frac{a_1 * b_1 * P^{c1}}{1 + b_1 * P^{c1}}$$

Where q and p are adsorbed amounts and the pressure of component i, respectively.

The adsorption selectivities for binary mixtures, defined by

$$S_{i/j} = \frac{x_i^* y_j}{x_j^* y_i}$$

Were respectively calculated using the Ideal Adsorption Solution Theory (IAST). Where xi is the mole fraction of component i in the adsorbed phase and yi is the mole fraction of component i in the bulk.



Figure S1. PXRD patterns of CUMT-1.



**Figure S2.** TGA curves of as-synthesized, dichloromethane-exchanged and desolvated samples of CUMT-1.



Figure S3. N<sub>2</sub> adsorption-desorption isotherms at 77 K.



Figure S4. The pore size distribution of CUMT-1a based on the density functional theory

method.



Figure S5. a) Fitted CO<sub>2</sub> isotherms of CUMT-1a measured at 273 and 298 K, fitting results, a0 = -3711.40718, a1 = -5.97426, a2 = 0.02843, a3 = 0.00005, a4 = 5.7829E-7, b0 = 11.41528, b1 = 0.02127, b2 = -0.00002, b3 = -3.304E-7, b4 = 5.3861E-10, Chi^2 = 0.00003, R^2 = 0.99999; b) calculated CO<sub>2</sub> isosteric adsorption heat.



**Figure S6**. a) Fitted CH<sub>4</sub> isotherms of CUMT-1a measured at 273 and 298 K, fitting results, a0 = -2441.69073, a1 = 34.93526, a2 = -3.01477, a3 = 0.11293, a4 = -0.00155, b0 = 9.31562, b1 = -0.12696, b2 = 0.0116, b3 = -0.00043, b4 = 5.8506E-6, Chi^2 = 0.00082, R^2 = 0.99971; b) calculated CH<sub>4</sub> isosteric adsorption heat.



Figure S7. a) Fitted N<sub>2</sub> isotherms of CUMT-1a measured at 273 and 298 K, fitting results, a0 = -2155.63901, a1 = 538.76747, a2 = -50.09678, b0 = 9.31562, b1 = -1.98, b2 = 0.18514, Chi^2 = 0.02825, R^2 = 0.98886; b) calculated N<sub>2</sub> isosteric adsorption heat.



**Figure S8.**  $CO_2$  adsorption isotherms of CUMT-1a with fitted by single L-F model at 273-333 K, 273 K: a1 = 5.82723, b1 = 0.07199, c1 = 1.1195, a2 = 1.55598, b2 = 0.00038, c2 = 1.57437, Chi^2 = 0.00005, R^2 = 0.99999; 298 K: a1 = 6.24843, b1 = 0.02032, c1 = 1.04478, a2 = 0.09963, b2 = 0.00002, c2 = 3.84062, Chi^2 = 0.00001, R^2 = 1; 313 K: a1 = 6.50697, b1 = 0.00946, c1 = 1.06783, a2 = 0.0174, b2 = 1.08141, c2 = 1.53496, Chi^2 = 1.5651E-6, R^2 = 1; 333 K: a1 = 8.61339, b1 = 0.00453, c1 = 1.02552, a2 = 0.0085, b2 = 0.27973, c2 = 0.89226, Chi^2 = 5.0714E-7, R^2 = 1.



Figure S9. CH<sub>4</sub> adsorption isotherms of CUMT-1a with fitted by single L-F model at 273-

333 K, 273 K: a1 = 5.59006, b1 = 0.00519, c1 = 1.0194, a2 = 0.01546, b2 = 0.11875, c2 = 1.47413, Chi^2 = 7.8352E-7, R^2 = 1; 298 K: a1 = 4.88285, b1 = 0.0024, c1 = 1.05813, a2 = 0.0637, b2 = 0.02305, c2 = 1.26146, Chi^2 = 3.2545E-6, R^2 = 0.99998; 313 K: a1 = 7.33901, b1 = 0.001, c1 = 1.04791, a2 = 0.01831, b2 = 0.07662, c2 = 1.36325, Chi^2 = 1.8298E-6, R^2 = 0.99998; 333 K: a1 = 5.16298, b1 = 0.00062, c1 = 1.15802, a2 = 0.04208, b2 = 0.04622, c2 = 1.31759, Chi^2 = 3.2502E-6, R^2 = 0.99993.



**Figure S10**. CH<sub>4</sub> adsorption isotherms of CUMT-1a with fitted by single L-F model at 273-333 K, 273 K: a1 = 3.0999, b1 = 0.00169, c1 = 1.07751, a2 =0.0477, b2 = 0.04481, c2 = 1.0178, Chi^2 = 7.8897E-7, R^2 = 0.99998; 298 K: a1 = 3.07278, b1 = 0.00152, c1 = 0.99126, a2 = 0.00649, b2 = 0.0001, c2 = 3.36224, Chi^2 = 3.3418E-6, R^2 = 0.99983; 313 K: a1 = 3.99779, b1 = 0.00014, c1 = 1.40515, a2 = 0.04853, b2 = 0.05662, c2 = 1.1175, Chi^2 = 2.7557E-6, R^2 = 0.99984; 333 K: a1 = 2.31742, b1 = 0.00074, c1 = 1.13036, a2 = 0.02072, b2 = 0.00433, c2 = 2.1924, Chi^2 = 2.1734E-6, R^2 = 0.99979.



**Figure S11**. Breakthrough curves for  $CO_2/CH_4$  mixture (v/v, 1/9) at 313 K, followed by desorption curves under Ar (7 mL min<sup>-1</sup>) sweeping at 323 K.



**Figure S12**. Breakthrough curves for  $CO_2/CH_4$  mixture (v/v, 5/5) at 273 K, followed by desorption curves under Ar (7 mL min<sup>-1</sup>) sweeping at 323 K.



**Figure S13**. Breakthrough curves for  $CO_2/CH_4$  mixture (v/v, 5/5) at 313 K, followed by desorption curves under Ar (7 mL min<sup>-1</sup>) sweeping at 323 K.



**Figure S14**. Breakthrough curves for  $CO_2/N_2$  mixture (v/v, 3/17) at 273 K, followed by desorption curves under Ar (7 mL min<sup>-1</sup>) sweeping at 323 K.



**Figure S15**. Breakthrough curves for  $CO_2/N_2$  mixture (v/v, 3/17) at 313 K, followed by desorption curves under Ar (7 mL min<sup>-1</sup>) sweeping at 323 K.



**Figure S16**. Breakthrough curves for  $CO_2/N_2$  mixture (v/v, 5/5) at 273 K, followed by desorption curves under Ar (7 mL min<sup>-1</sup>) sweeping at 323 K.



Figure S17. Breakthrough curves for  $CO_2/N_2$  mixture (v/v, 5/5) at 313 K, followed by desorption curves under Ar (7 mL min<sup>-1</sup>) sweeping at 323 K.

Complexes	CUMT-1		
Chemical formula	C <sub>24</sub> H <sub>14</sub> N <sub>12</sub> O <sub>8</sub> Zn		
Formula weight	663.84		
$T(\mathbf{K})$	296.15		
Crystal system	Orthorhombic		
Space group	Pbcm		
<i>a</i> (Å)	7.2862(13)		
<i>b</i> (Å)	20.206(3)		
<i>c</i> (Å)	24.765(4)		
α (°)	90		
β (°)	90		
γ (°)	90		
$V(Å^3)$	3646.0(11)		
Ζ	4		
$D_{\text{calcd.}}[\mathbf{g}\cdot\mathbf{cm}^{-3}]$	1.209		
$\mu (\mathrm{mm}^{-1})$	0.728		
F(000)	1344		
Reflns collected/unique/ $R_{int}$	15999/3280/0.1175		
Goof	0.989		
Theta range for data collection	2.016 to 24.995°		
Completeness to theta = $24.995^{\circ}$	99.5%		
Refinement method	Full-matrix least-squares on		
$R_1^{a}, wR_2^{b} [I > 2\sigma]$	0.0503, 0.1228		
$R_1^{\rm a}, wR_2^{\rm b}$ (all data)	0.0947, 0.1439		

**Table S1.** Crystal Data and Structure Refinements for CUMT-1.

CCDC number	2393759

 ${}^{a}\mathbf{R}_{1} = \Sigma(|\mathbf{F}_{o}| - |\mathbf{F}_{c}|) / \Sigma |\mathbf{F}_{o}|. \ {}^{b}\mathbf{R}_{2} = [\Sigma \mathbf{w}(\mathbf{F}_{o}^{2} - \mathbf{F}_{c}^{2})^{2} / \Sigma \mathbf{w}(\mathbf{F}_{o}^{2})^{2}]^{1/2}.$ 

Zn(1)-O(3)	2.079(2)	O(3)-Zn(1)-N(3)	94.51(12)
Zn(1)-O(3)#1	2.079(2)	O(3)#1-Zn(1)-N(3)#1	94.51(12)
Zn(1)-N(4)	2.106(3)	O(3)-Zn(1)-N(3)#1	85.49(12)
Zn(1)-N(4)#1	2.106(3)	O(3)#1-Zn(1)-N(3)	85.49(12)
Zn(1)-N(3)#1	2.081(3)	N(4)-Zn(1)-N(4)#1	180.0000
Zn(1)-N(3)	2.081(3)	N(3)#1-Zn(1)-N(4)	93.02(13)
O(3)-Zn(1)-O(3)#1	180	N(3)-Zn(1)-N(4)	86.98(13)
O(3)#1-Zn(1)-N(4)#1	87.37(11)	N(3)#1-Zn(1)-N(4)#1	86.98(13)
O(3)#1-Zn(1)-N(4)	92.62(11)	N(3)-Zn(1)-N(4)#1	93.02(13)
O(3)-Zn(1)-N(4)#1	92.63(11)	N(3)-Zn(1)-N(3)#1	180.0000
O(3)-Zn(1)-N(4)	87.38(11)		

Table S2. Selected bond lengths [Å] and angles [°] for CUMT-1.

Symmetry codes: #1 -x,-y+1,-z+1, #2 x,-y+1/2,-z+1, #3 -x+1,-y+1,-z+1, #4 x,y,-z+1/2, #5 x,-

y+3/2,-z+1.