# Supporting Information

# Efficient light hydrocarbon separation, CO<sub>2</sub> capture and conversion in a stable MOF with oxalamide-decorated polar tubes

Xiu-Yuan Li,<sup>a</sup> Yong-Zhi Li,<sup>a</sup> Yun Yang,<sup>a</sup> Lei Hou,<sup>\*a</sup> Yao-Yu Wang<sup>a</sup> and Zhonghua Zhu<sup>b</sup>

<sup>a</sup>Key Laboratory of Synthetic and Natural Functional Molecule Chemistry 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>b</sup>School of Chemical Engineering, The University of Queensland, Brisbane 4072, Australia.
\*To whom correspondence should be addressed. E-mail: lhou2009@nwu.edu.cn (L. H.).

#### Materials and general methods.

All reagents were commercially available. H<sub>4</sub>BDPO was synthesized by condensation reaction between oxalyl chloride and 5-aminoisophthalic acid.<sup>1</sup> Fourier transform infrared spectrum (FTIR) was obtained with a Nicolet FT-IR 170 SX spectrophotometer in the range 4000-400 cm<sup>-1</sup>. Elemental analyses for C, H, and N were performed with a Perkin-Elmer 2400C Elemental analyzer. Thermogravimetric analysis (TGA) was measured with a NETZSCH TG 209 thermal analyzer under a nitrogen atmosphere with a heating rate of 10 °C min<sup>-1</sup>. Powder X-ray diffraction (PXRD) pattern was recorded on a Bruker D8 ADVANCE X-ray powder diffractometer (Cu K $\alpha$ , 1.5418 Å). Gas sorption was tested with a Micrometrics ASAP 2020M apparatus. Inductively coupled plasma (ICP) spectroscopy was performed on an Agilent 725 ICP-OES spectrometer. The products of catalysis reaction were monitored by Gas chromatography (GC) with a Shimadzu GC-14CPTF. <sup>1</sup>H NMR spectra were acquired on a Bruker Ascend 400 (400 MHz) spectrometer in DMSO-*d*<sub>6</sub> with Me<sub>4</sub>Si as the internal standard.

### Synthesis of $\{[Sr(BDPO)_{0.5}(H_2O)] \cdot 2H_2O\}_n$ (1)

A mixture of H<sub>4</sub>BDPO (20.8 mg, 0.05 mmol) and SrCl<sub>2</sub>·6H<sub>2</sub>O (26.6 mg, 0.1 mmol) in DMA (3 mL) and distilled water (0.5 mL) was placed into a glass vial (10 mL) and heated at 105 °C for 72 h. Cooling the vial to room temperature at a rate of 5 °C h<sup>-1</sup> gives rise to the colorless block-shaped crystals of **1** in 68% yield. Anal. Calcd for C<sub>9</sub>H<sub>10</sub>NO<sub>8</sub>Sr: C, 31.08; H, 2.90; N, 4.03. Found: C, 31.21; H, 3.01; N, 4.15. IR data (KBr, cm<sup>-1</sup>): 3419(m), 3209(w), 3082(w), 2927(w), 1689(m), 1631(s), 1533(s), 1439(s), 1373(s), 1198(w), 1103(w), 1009(w), 906(w), 845(w), 783(m), 721(m), 594(w), 482(w).

### Catalytic Cycloaddition of CO<sub>2</sub> with Epoxides

In each individual reaction, epoxide substrate (28.6 mmol), activated 1 (0.84% mmol), and tetra-*n-tert*-butylammonium bromide (TBAB, 3.5% mmol) were added into a 15 mL Schlenk tube and continuously purged with  $CO_2$  at 1 atm. The resulting mixture

was stirred at room temperature for 48 h. The conversion of the reaction was monitored by <sup>1</sup>H NMR spectroscopy and GC.

#### Crystallography

Single crystal X-ray diffraction data was collected at 296(2) K on a Bruker SMART APEXII CCD diffractometer equipped with a graphite monochromated Mo K $\alpha$ radiation source ( $\lambda = 0.71073$  Å). The structure was solved by direct methods and refined on  $F^2$  by full-matrix least-squares methods using the SHELXTL program package.<sup>2</sup> All non-hydrogen atoms were refined anisotropically with the hydrogen atoms added to their geometrically ideal positions and refined isotropically. The solvent molecules in **1** is highly disordered, so the SQUEEZE routine of PLATON program<sup>3</sup> was adopted in structural refinement. The results of structure refinements and selected bond distances/angles are listed in Tables S1 and S2, respectively.



Fig. S1 Coordination mode of BDPO in 1.



**Fig. S2** TGA curves for **1** and desolvated sample. **1** releases all lattice water and aqua ligands below 310 °C, with a weight loss of 15.2% (calcd 15.5%). Then a thermal stable flat appears before the framework decomposed at 420 °C. TGA of desolvated **1** indicates the complete removal of solvents and coordinated water molecules.



Fig. S3 PXRD patterns of 1 obtained by different treated methods.



Fig. S4 Sorption isotherms of  $N_2$  at 77 K and PSD obtained from the  $N_2$  isotherms using NLDFT mode.



Fig. S5 Gas sorption isotherms of 1a for  $CO_2$ ,  $C_2H_6$ ,  $CH_4$  and CO at 333 K,  $CH_4$  and CO at 273 K.

#### **Calculation of Sorption Heat Using Virial 2 Model**

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

The above virial expression was used to fit the combined isotherm data for **1a** at 273.15 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. S6 (a)  $CO_2$  adsorption isotherms of 1a with fitting by Virial 2 model (b)  $CO_2$  adsorption heat calculated by the virial equation.



**Fig. S7** (a)  $CH_4$  adsorption isotherms of **1a** with fitting by Virial 2 model (b)  $CH_4$  adsorption heat calculated by the virial equation.



**Fig. S8** (a) CO adsorption isotherms of **1a** with fitting by Virial 2 model (b) CO adsorption heat calculated by the virial equation.



Fig. S9 (a)  $C_2H_6$  adsorption isotherms of 1a with fitting by Virial 2 model (b)  $C_2H_6$  adsorption heat calculated by the virial equation.

	$CO_2$	$CH_4$	СО	C <sub>2</sub> H <sub>6</sub>
a0	-3836.10063	-2406.20193	-2352.68565	-3975.70505
a1	0.4967	1.17882	3.66492	0.48732
a2	-0.02212	0.21072	1.47923	0.1703
a3	0.00035	-0.00528	-0.22359	0.00249
a4	\	\	0.0089	-0.00003
b0	12.23357	9.83126	10.36966	11.95709
b1	0.01257	\	\	\
Chi^2	0.00029	0.00078	0.00129	0.00616
R^2	0.99991	0.99968	0.99948	0.99848

Parameters obtained from the Virial 2 model fitting of the single-component adsorption isotherms at 273.15 K and 298 K.

## CO<sub>2</sub>/CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>/CH<sub>4</sub> and CO<sub>2</sub>/CO Selectivity Prediction via IAST

The experimental isotherm data for pure CO<sub>2</sub>, CH<sub>4</sub> and CO were fitted using a dual Langmuir-Freundlich (L-F) model:

$$q = \frac{a_1 * b_1 * P^{C_1}}{1 + b_1 * P^{C_1}} + \frac{a_2 * b_2 * P^{C_2}}{1 + b_2 * P^{C_2}}$$

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

The adsorption selectivities for binary mixtures of  $CO_2/CH_4$ ,  $C_2H_6/CH_4$  and  $CO_2/CO$ , 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  $x_i$  is the mole fraction of component *i* in the adsorbed phase and  $y_i$  is the mole fraction of component *i* in the bulk.



Fig. S10 Adsorption isotherms of 1a at 298 K (a) and 333 K (b) with fitting by dual L-F model.

adsorption isotherms.						
298 K	CO <sub>2</sub>	$C_2H_6$	CH <sub>4</sub>	СО		
a1	4.52117	1.97673	2.27817	3.25962		
b1	0.01839	0.11197	0.00137	9.21389E-4		
<b>c</b> 1	0.9451	1.03644	1.18363	0.95321		
a2	0.43054	0.93048	0.11312	1.38046		
b2	0.00179	0.0028	0.04384	9.22173E-4		
c2	1.78367	1.26111	0.99093	0.9532		
Chi^2	4.39327E-6	3.08224E-7	6.43748E-8	1.99547E-7		
R^2	1	1	1	0.99998		
333 K	$CO_2$	$C_2H_6$	$CH_4$	CO		
<b>a</b> 1	2.86611	1.52454	1.45107	0.70883		
b1	0.00791	0.01214	0.00231	2.45015E-4		
<b>c</b> 1	0.97072	0.79348	0.99722	1.4614		
a2	0.63995	1.07961	0.03917	0.04234		
b2	7.52594E-5	0.03235	9.30733E-9	0.03239		
c2	1.94345	1.10672	3.96079	1.09589		

5.97923E-8

1

3.16031E-8

1

5.54432E-8

0.99998

Chi^2

 $R^2$ 

7.77208E-8

1

Parameters obtained from the dual Langmuir-Freundlich fitting of the single-component



Fig. S11 Recycle experiments for the cycloaddition of CO<sub>2</sub> and PO.



Fig. S12 PXRD patterns of 1a after 5 cycles of the CO<sub>2</sub> cycloaddition with PO.



**Fig. S13** Hot filtration tests for the cycloaddition of  $CO_2$  with PO. The hot filtration tests were done by filtering the catalyst from reaction solution at 12 h, and the filtrate was reacted continuously for another 36 h. After 12 h, it shows the very slow increase of conversion of PO, resulting from the solo catalysis of TBAB. (Table 1, entry 2, conversion is 18.7%).



Fig. S14 Tentative mechanism for the cycloaddition of  $CO_2$  with epoxides to produce cyclic carbonates.



Fig. S15 Interactions between the framework and PO molecules.

#### **GCMC Simulation Methodology**

Grand canonical Monte Carlo (GCMC) simulations were performed for the adsorption of  $CO_2$  in **1a** by the Sorption module of Material Studio.<sup>4</sup> The framework and  $CO_2$  molecule were considered to be rigid. The partial charges for carbon and oxygen atoms of  $CO_2$  molecules were 0.576*e* and -0.288*e*, respectively.<sup>5</sup> The partial charges for atoms of **1a** were derived from QEq method and QEq\_neutral1.0 parameter (Table S4). One unit cell was used during the simulations. The interaction energies between  $CO_2$  and framework were computed through the Coulomb and Lennard-Jones 6-12 (LJ) potentials. All parameters for  $CO_2$ 

molecule and atoms of **1a** were modeled with the universal forcefield (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.



Fig. S16 <sup>1</sup>H NMR spectrum of cyclic carbonate (Table 1, entry 3).



Fig. S17 <sup>1</sup>H NMR spectrum of cyclic carbonate (Table 1, entry 4).



Fig. S18 <sup>1</sup>H NMR spectrum of cyclic carbonate (Table 1, entry 5).

Complex	1
Molecular formula	C <sub>9</sub> H <sub>6</sub> NO <sub>6</sub> Sr
Formula weight	311.77
Temperature	296(2)
Crystal system	Hexagonal
Space group	<i>P</i> 6 <sub>2</sub> 22
<i>a</i> (Å)	13.4335(15)
<i>b</i> (Å)	13.4335(15)
<i>c</i> (Å)	23.428(2)
α (°)	90
eta (°)	90
γ (°)	120
$V(Å^3)$	3661.4(7)
Ζ	12
$\rho$ (g/cm <sup>3</sup> )	1.697
F(000)	1836
Reflections collected	18110
Goodness-of-fit on $F^2$	1.062
$R_1^{a}[I \geq 2\sigma(I)]$	0.0957
$wR_2^{b}[I \ge 2\sigma(I)]$	0.2360

 Table S1. Crystal data and structure refinement for 1.

<sup>a</sup>  $R_1 = \sum (|F_o| - |F_c|) / \sum |F_o|$ . <sup>b</sup>  $wR_2 = [\sum w (F_o^2 - F_c^2)^2 / \sum w (F_o^2)^2]^{1/2}$ .

Table S2. Selected bond distances (Å) and angles (°) for 1.

Sr1-O4#1	2.512(11)	O4#1-Sr1-O4#2	87.9(9)	O1W-Sr2-O1#1	69.2(5)
Sr1-O4#2	2.512(11)	O4#1-Sr1-O2	84.4(4)	O1W-Sr2-O3#4	108.2(5)
Sr1-O2	2.523(13)	O4#2-Sr1-O2	110.7(4)	O1#1-Sr2-O3#4	177.0(3)

Sr1-O2#3	2.523(13)	O4#2-Sr1-O2#3	84.4(4)	O1-Sr2-O3#4	103.9(4)
Sr1-O5#4	2.651(12)	O2-Sr1-O2#3	159.5(6)	O4#6-Sr2-O3#4	111.7(3)
Sr1-O5#5	2.651(12)	O4#1-Sr1-O5#4	154.4(4)	O4#2-Sr2-O3#4	75.5(4)
Sr1-O1	2.884(14)	O4#2-Sr1-O5#4	106.0(5)	O3#6-Sr2-O3#4	65.5(5)
Sr1-O1#3	2.884(14)	O2-Sr1-O5#4	70.6(4)	O3#7-Sr2-O3#4	75.5(6)
Sr2-O1W#1	2.515(18)	O2#3-Sr1-O5#4	92.3(4)	O4#1-Sr1-O2#3	110.7(4)
Sr2-O1W	2.515(18)	O4#1-Sr1-O5#5	106.0(5)	O1#1-Sr2-O3#7	103.9(4)
Sr2-O1#1	2.534(10)	O4#2-Sr1-O5#5	154.4(4)	O1-Sr2-O3#7	177.0(3)
Sr2-O1	2.534(10)	O2-Sr1-O5#5	92.3(4)	O4#6-Sr2-O3#7	75.5(4)
Sr2-O4#6	2.611(14)	O2#3-Sr1-O5#5	70.6(4)	O4#2-Sr2-O3#7	111.7(3)
Sr2-O4#2	2.611(14)	O5#4-Sr1-O5#5	70.4(7)	O3#2-Sr2-O3#7	65.5(5)
Sr2-O3#6	2.645(15)	O4#1-Sr1-O1	96.0(4)	O1W#1-Sr2-O1	69.2(5)
Sr2-O3#2	2.645(15)	O4#2-Sr1-O1	66.7(3)	01W-Sr2-O1	123.5(6)
O1W-Sr2-O3#6	103.5(5)	O2#3-Sr1-O1	139.9(4)	O1#1-Sr2-O1	76.8(6)
O1#1-Sr2-O3#6	116.2(4)	O5#4-Sr1-O1	71.1(4)	O1W#1-Sr2-O4#6	73.9(5)
O1-Sr2-O3#6	132.1(3)	O5#5-Sr1-O1	130.9(4)	O1W-Sr2-O4#6	107.2(6)
O4#6-Sr2-O3#6	50.4(3)	O4#1-Sr1-O1#3	66.7(3)	O1#1-Sr2-O4#6	70.8(4)
O4#2-Sr2-O3#6	138.1(4)	O4#2-Sr1-O1#3	96.0(4)	O1-Sr2-O4#6	102.1(5)
O1W#1-Sr2-O3#2	103.5(5)	O2-Sr1-O1#3	139.9(4)	O1W#1-Sr2-O4#2	107.2(6)
O1W-Sr2-O3#2	65.7(5)	O5#4-Sr1-O1#3	130.9(4)	O1W-Sr2-O4#2	73.9(5)
O1#1-Sr2-O3#2	132.1(3)	O5#5-Sr1-O1#3	71.1(4)	O1#1-Sr2-O4#2	102.1(5)

Symmetry transformations used to generate equivalent atoms: #1 -x+1, -y+1, z; #2 x-y+1, y+1, -z; #3 -x+y+1, y, -z; #4 y, -x+y, z-1/3; #5 -x+1, -x+y, -z+1/3; #6 -x+y, y, -z; #7 -y+1, xy+1, z-1/3.

**Table S3.** Comparison of  $CO_2/CH_4$  selectivity calculated by the IAST method for the equimolar mixture at 1 atm and 298 K of **1a** with the selected MOFs.

MOF	Selectivity	Ref.
[Zn(mtz) <sub>2</sub> ], UTSA-49	33.7	6
Cu-TDPDA	13.8	7
MAF-X7	12.6	8
This work	12.5	
$[H_2N(Me)_2]_2[Zn_4(L)_2(H_2O)_{1.5}] \cdot 5DMF \cdot H_2O$	12	9
$[Cu(bpy)_2(SiF_6)]$	10.5	10
[Mn <sub>2</sub> (Hcbptz) <sub>2</sub> (Cl)(H <sub>2</sub> O)]Cl·DMF·0.5CH <sub>3</sub> CN	10.3	11
ZIF-96	10.2	12
UiO-66-AD6	10.0	13
UiO-66-AD10	9.3	13
ZIF-97	9.1	12
ZIF-93	8.2	12
UiO-66-AD4	8.0	13
UiO-66-AD8	7.3	13

UiO-66	6.9	13
[Cu(INIA)]	4.3	14
ZIF-25	2.53	12
UMCM-1	1.82	15

Table S4. The atomic partial charges (e) in 1a.

Sr1	1.20876	04	-0.459195	C3	-0.204035	C8	0.569293
Sr2	1.21018	05	-0.484046	C4	-0.115295	C9	0.413322
01	-0.474667	N1	-0.548801	C5	-0.137364	H1	0.275459
02	-0.547190	C1	0.609848	C6	0.0610148	H3	0.161611
03	-0.455936	C2	-0.0706152	C7	-0.150365	H5	0.188592
						H7	0.158904

#### REFERENCES

- N. H. Alsmail, M. Suyetin, Y. Yan, R. Cabot, C. P. Krap, J. Lü, L. Easun, T. E. Bichoutskaia, W. Lewis, A. J. Blake and M. Schröder, *Chem-Eur. J.*, 2014, 20, 7317-7324.
- 2 G. M. Sheldrick, *SHELXL-97: Program for Crystal Structure Refinement*, University of Göttingen: Germany, 1997.
- 3 A. L. Spek, J. Appl. Crystallogr. 2003, 36, 7-13.
- 4 Accelrys, Materials Studio Getting Started, release 5.0; Accelrys Software, Inc.: San Diego, CA, 2009.
- 5 A. Hirotani, K. Mizukami, R. Miura, H. Takaba, T. Miya, A. Fahmi, A. Stirling, M. Kuboand and A. Miyamoto, *Appl. Surf. Sci.*, 1997, **120**, 81-84.
- 6 S. Xiong, Y. Gong, H. Wang, H. Wang, Q. Liu, M. Gu, X. Wang, B. Chen and Z. Wang, *Chem. Commun.*, 2014, **50**, 12101-12104.
- 7 Z. Zhang, Z. Li and J. Li, *Langmuir*, 2012, 28, 12122-12133.
- 8 J. Lin, W. Xue, J. Zhang and X. Chen, Chem. Commun., 2011, 47, 926-928.
- 9 B. Liu, Y. Jiang, Z. Li, L. Hou and Y. Wang, Inorg. Chem. Front., 2015, 2, 550-557.
- S. D. Burd, S. Ma, J. A. Perman, B. J. Sikora, R. Q. Snurr, P. K. Thallapally, J. Tian, L. Wojtas and M. J. Zaworotko, *J. Am. Chem. Soc.*, 2012, **134**, 3663-3666.
- 11 H. Wang, W. Shi, L. Hou, G. Li, Z. Zhu and Y. Wang, Chem-Eur. J., 2015, 21, 16525-

16531.

- Y. Houndonougbo, C. Signer, N. He, W. Morris, H. Furukawa, K. G. Ray, D. L. Olmsted, M. Asta, B. B. Laird and O. M. Yaghi, *J. Phys. Chem. C*, 2013, 117, 10326-10335.
- 13 D. H. Hong and M. P. Suh, Chem-Eur. J. 2014, 20, 426-434.
- 14 Y. Xiong, Y. Fan, R. Yang, S. Chen, M. Pan, J. Jiang and C. Su, *Chem. Commun.*, 2014, 50, 14631-14634.
- 15 X. Peng, X. Cheng and D. Cao, J. Mater. Chem., 2011, 21, 11259-11270.