

## Electronic Supplementary Information

### Microporous indium(III)-dicarboxylic frameworks with gas adsorption selectivity of CO<sub>2</sub> over N<sub>2</sub>

#### Experiment section

#### Materials and General Methods

All analytical reagents were purchased from commercial sources and used without further purification. Elemental analyses of C, H, and N were performed using an EA1110 elemental analyzer. The TG-DTA analysis was carried out by Universal Analysis 2000 thermogravimetric analyzer (TGA) in N<sub>2</sub> with a heating rate of 10 °C min<sup>-1</sup>. The IR spectrum was recorded in the range 4000-400 cm<sup>-1</sup> on a HYPERION spectrometer with a pressed KBr pellet. Crystal data were collected on a Bruker X8 APEX II-CCD single crystal X-ray diffractometer with Mo K $\alpha$  radiation ( $\lambda = 0.71073\text{\AA}$ ). The powder X-ray diffraction (PXRD) data were collected on an X'Pert-ProMPD (Holand) D/max- $\gamma$ A X-ray diffractometer with Cu K $\alpha$  radiation in a flat plate geometry. The gas sorption analysis was performed on ASAP 2020 and 2050 Xtended Pressure Sorption Analyzer. The gas adsorption selectivity (here is CO<sub>2</sub>/N<sub>2</sub>) is defined by  $S = x_A / x_B$ , where  $x_A$  and  $x_B$  are the weight percentage (%) or bulk fraction (cm<sup>3</sup>/g) of two gases adsorbed.  $x$  is measured using pure gas in the same conditions including temperature and pressure<sup>1-4</sup>.

1. Y. Tan, F. Wang, Y. Kang and J. Zhang, *Chem. Commun.*, 2011, **47**, 770.
2. K. Sumida, S. Horike, S. S. Kaye, Z. R. Herm, W. L. Queen, C. M. Brown, F. Grandjean, G. J. Long, A. Dailly and J. R. Long, *Chem. Sci.*, 2010, **1**, 184.
3. P. Cui, Y. G. Ma, H. H. Li, B. Zhao, J. R. Li, P. Cheng, P. Balbuena and H. C. Zhou, *J. Am. Chem. Soc.*, 2012, **134**, 18892.
4. L. Du, Z. Lu, K. Zhang, J. Wang, X. Zheng, Y. Pan, X. You, J. Bai, *J. Am. Chem. Soc.*, 2012, **135**, 562.

### **Synthesis of $\text{H}_5\text{In}_3\text{O}_4 (\text{C}_8\text{O}_4\text{H}_4)_3$ (1)**

A solution of  $\text{In}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  (0.1g, 0.256mmol) in 1ml DMF was added into a glass tube (about 15cm, with one tip be sealed), in which some  $\text{H}_2$ 1,3-bdc (0.04g, 0.241mmol) had been put. After adding 0.2ml ethanol to the mixture, we sealed another tip of the tube using oxy-acetylene flame. Then the tube was left in an oven at 120°C for 2 days. In general, several teflon-lined autoclave with water in them were placed around the tubes so that the reduction of temperature can be slower after shutting off the oven. And finally, cubical colorless crystals were single out from the obtained mixture (Yield 11% based on In). Anal. Calcd for  $\text{C}_{24}\text{H}_{12}\text{In}_3\text{O}_{16}$ : C 32.01, H 1.33, O 28.44 %; Found: C 32.41, H 1.45, O 29.03 %. IR (KBr pellet,  $\text{cm}^{-1}$ ): 3615, 3084, 1720, 1611, 1550, 1340, 740. CCDC number 919517.

## Synthesis of $\text{HIn}(\text{C}_8\text{O}_4\text{H}_4)_2$ (**2**)

The preparation of compound **2** was similar to **1** except that the  $\text{H}_2$ 1,4-bdc (0.04g, 0.241mmol) was used instead of  $\text{H}_2$ 1,3-bdc. Colorless crystals bunching up as clusters were collected (Yield 62% based on In). Anal. Calcd for  $\text{C}_{16}\text{H}_8\text{InO}_8$ : C 43.34, H 1.81, O 28.89 %; Found: C 43.67, H 2.05, O 29.13 %. IR (KBr pellet,  $\text{cm}^{-1}$ ): 3440, 1570, 1390, 1015, 860, 740, 540. CCDC number 919518.

Table S1. Crystal data and structure refinements for compounds **1** and **2**.

	<b>1</b>	<b>2</b>
Empirical formula	$\text{C}_{24}\text{H}_{17}\text{In}_3\text{O}_{16}$	$\text{C}_{16}\text{H}_9\text{InO}_8$
<i>F</i> w	905.80	444.04
Crystal system	Cubic	Hexagonal
space group	Pa-3	$\text{P6}_22$
<i>a</i> (Å)	19.722(5)	14.682(6)
<i>b</i> (Å)	19.722(5)	14.682(6)
<i>c</i> (Å)	19.722(5)	12.178(7)
$\gamma$ (°)	90	120
<i>V</i> (Å <sup>3</sup> )	7671(3)	2273.4(19)
<i>Z</i>	8	3
<i>T</i> (K)	296	120
<i>D</i> <i>c</i> (g/cm <sup>3</sup> )	1.560	0.971
<i>F</i> (000)	3448	651

$R_{\text{int}}$	0.2101	0.0961
colcd reflns	49009	15247
unique reflections	3115	1906
GOF	0.961	0.901
$R_1^a [I > 2\sigma(I)]$	0.0678	0.0416
$wR_2^b$ (all data)	0.1777	0.1325

$$^a R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}; \quad ^b wR_2 = \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]}^{1/2}$$

Table S2. Selected bond distances (Å) and angles (°) for **1** and **2**.

<b>Compound 1</b>			
In(1)-O(1)	2.0414(7)	In(1)-O(6)	2.113(5)
In(1)-O(4)	2.147(4)	In(1)-O(3)	2.183(4)
In(1)-O(2)	2.189(4)	In(1)-O(5)	2.193(5)
O(1)-In(1)-O(6)	178.62(15)	O(1)-In(1)-O(4)	92.10(15)
O(6)-In(1)-O(4)	86.71(17)	O(1)-In(1)-O(3)	94.72(16)
O(6)-In(1)-O(3)	86.40(17)	O(1)-In(1)-O(2)	91.65(18)
O(1)-In(1)-O(5)	92.84(19)	O(4)-In(1)-O(5)	93.03(17)
<b>Compound 2</b>			
In(1)-O(2)	2.261(4)	In(1)-O(1)	2.271(4)
O(2)#1-In(1)-O(2)	87.17(19)	O(2)#1-In(1)-O(2)#2	95.3(2)
O(2)#2-In(1)-O(2)	162.98(19)	O(2)#1-In(1)-O(1)#2	79.35(14)
O(2)#2-In(1)-O(1)#2	57.75(14)	O(2)-In(1)-O(1)#2	139.05(15)

Symmetry code for **2**: #1 -x+1, -y+1, -z+1; #2 -x+2, -y, -z

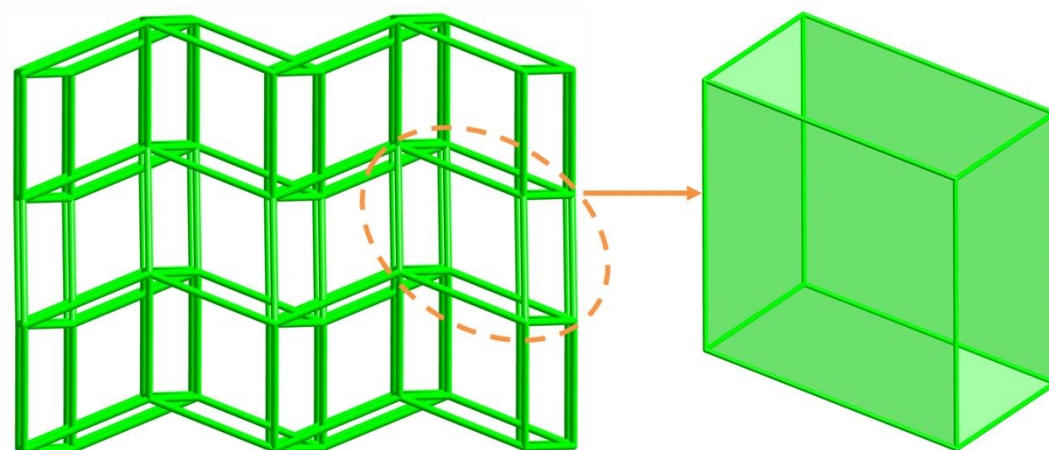


Fig S1. Topology diagram of 3D structure and the cage of compound 1.

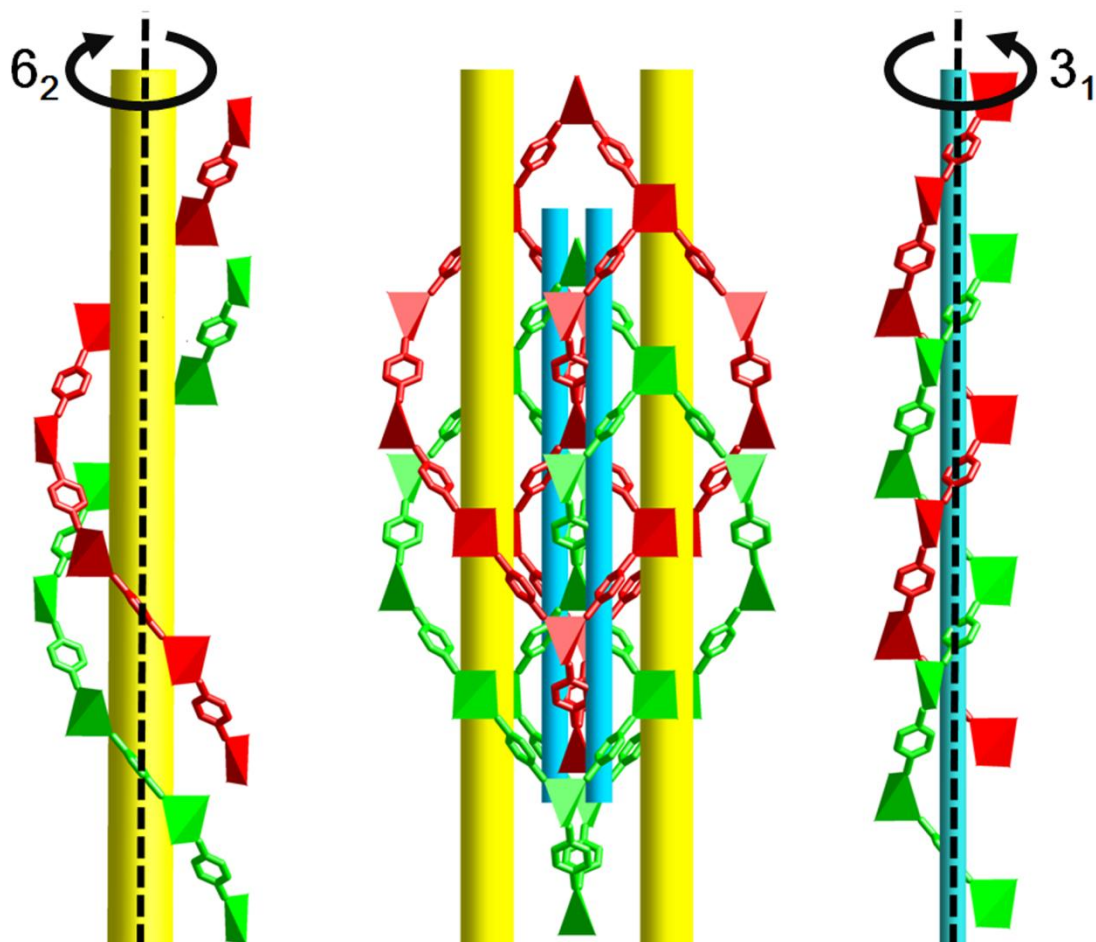


Fig S2. The interpenetrated catenane structure and the screw axis  
of compound 2.

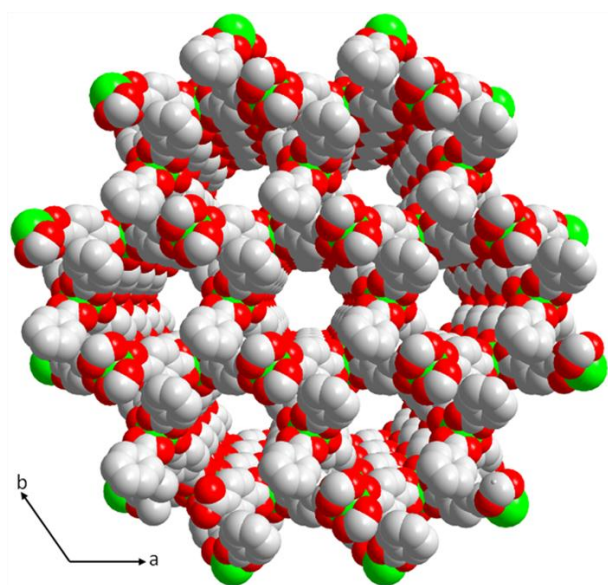


Fig S3. The left-handed channels.

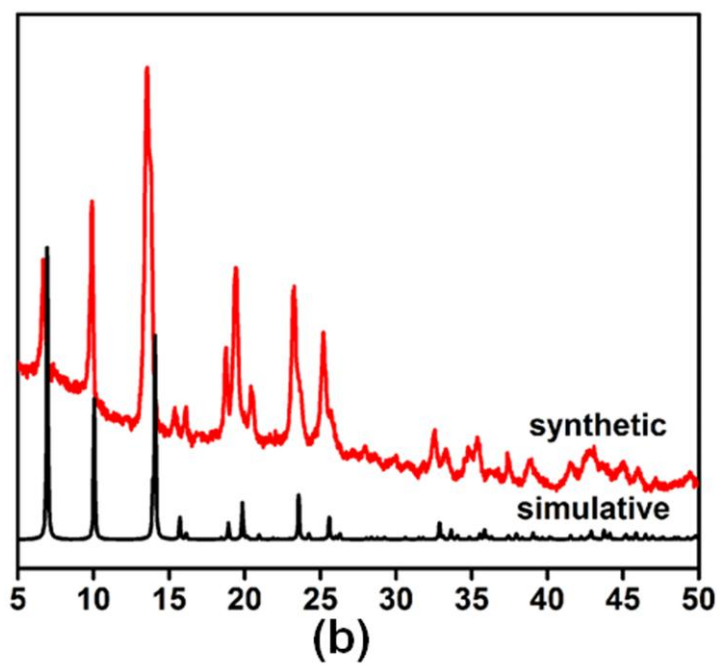
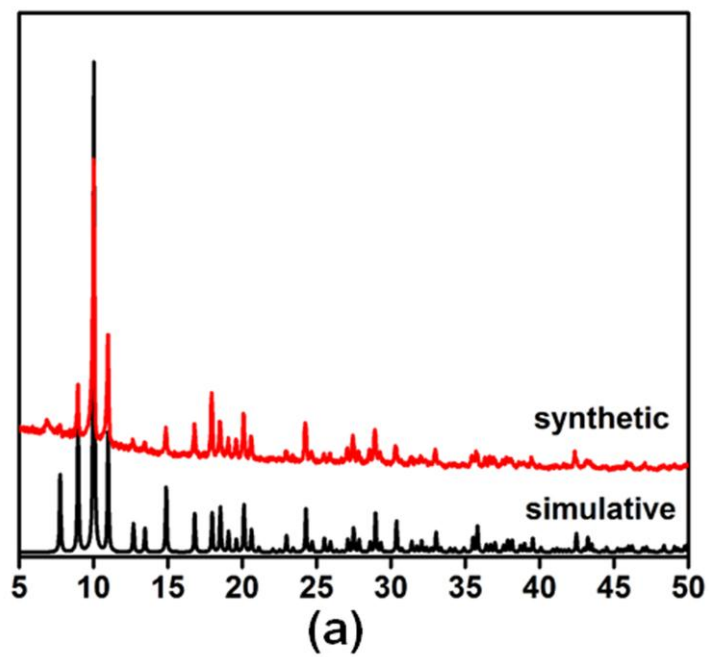


Fig S4. a) The PXR diagram of compound 1. b) The PXR diagram of compound 2.

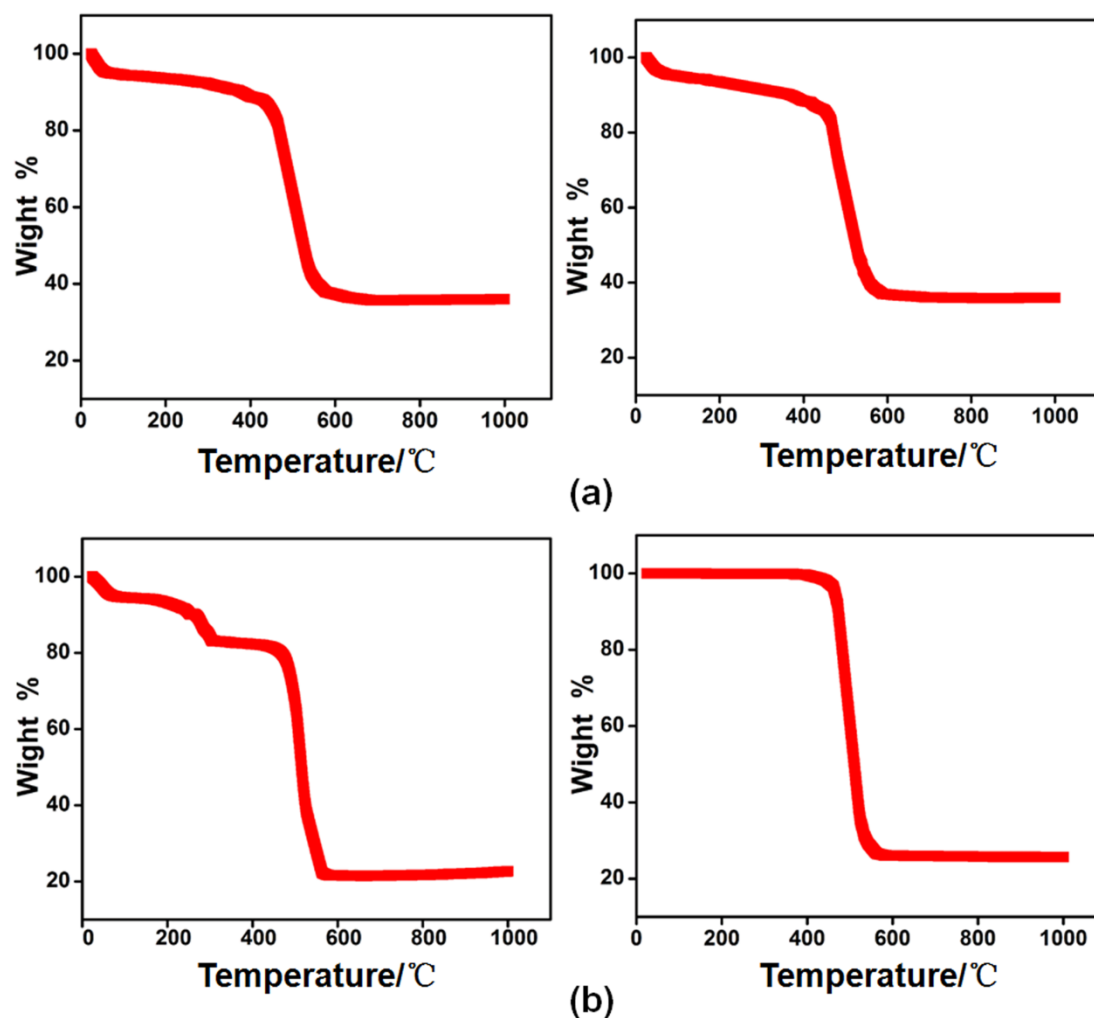


Fig S5. a) The TG curves of as-synthesized compound **1** and its desolvated products. b) The TG curves of as-synthesized compound **2** and its desolvated products.

TG experiments of compounds **1** and **2**, and their desolvated products were performed under N<sub>2</sub> atmosphere with a heating rate of 10 °C/min in the temperature range of 0-1000 °C. In Figure S1a, the TG curves indicated three dissociative water molecular eliminated from the network (calcd 5.61%; found 5.52%). The loss of bonded water molecular and the bdc species corresponded to the range of 110 to 550°C (calcd 58.60%; found 58.26%). After 550°C, a plateau with a value of 36.22% was



observed. Little change happened after the solvent exchange of compound **1**. It may be because the dissociative water molecular was sealed in the framework and simple methods cannot force it out of the framework. In Figure S1b, we can clearly observe the weight loss of two dissociated water molecular (calcd 6.69%; found 6.35%) and two dissociated dimethylamine molecular (calcd 10.78%; found 10.69 %). Then, the bdc species removed in the range of 450 to 570°C (calcd 60.99%; found 60.43%). After 570°C, a plateau with a value of 22.62% was observed. The TG curves indicated that the guest molecular can be effectively from the structure of compound **2**.

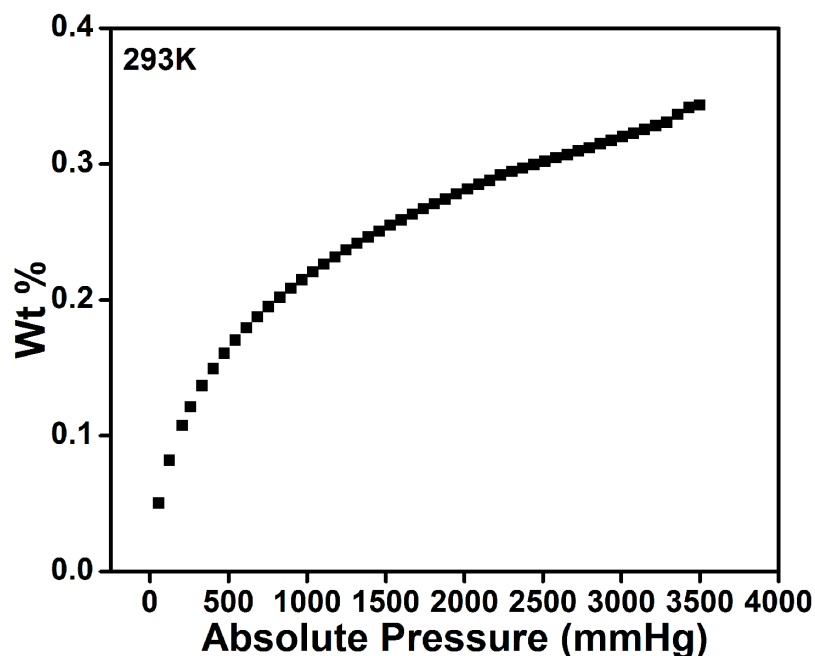


Fig S6. CO<sub>2</sub> adsorption isotherms for compound **1** at 293K.

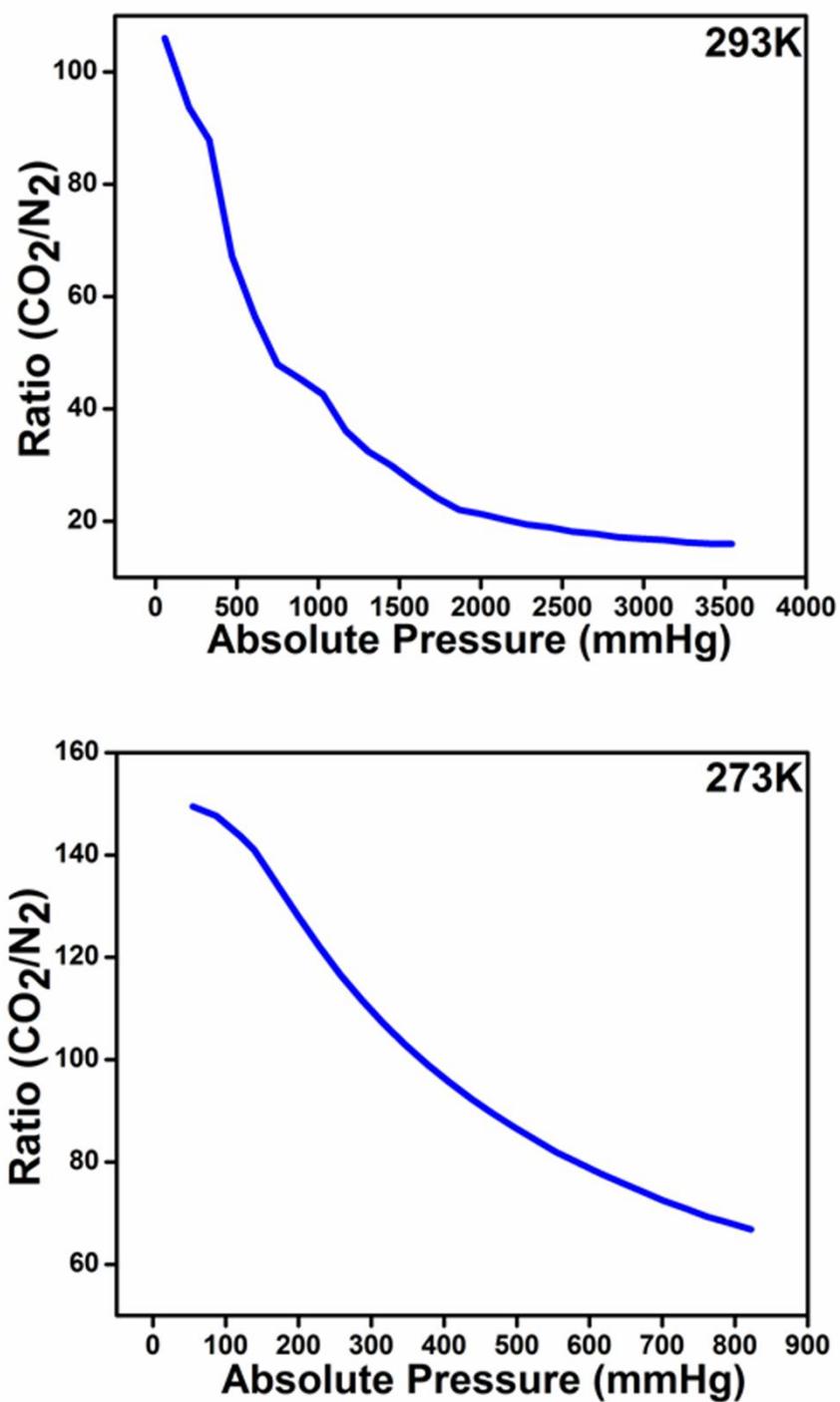


Fig S7. The ratio of CO<sub>2</sub>/N<sub>2</sub> under different pressure at 293K and 273K, respectively.

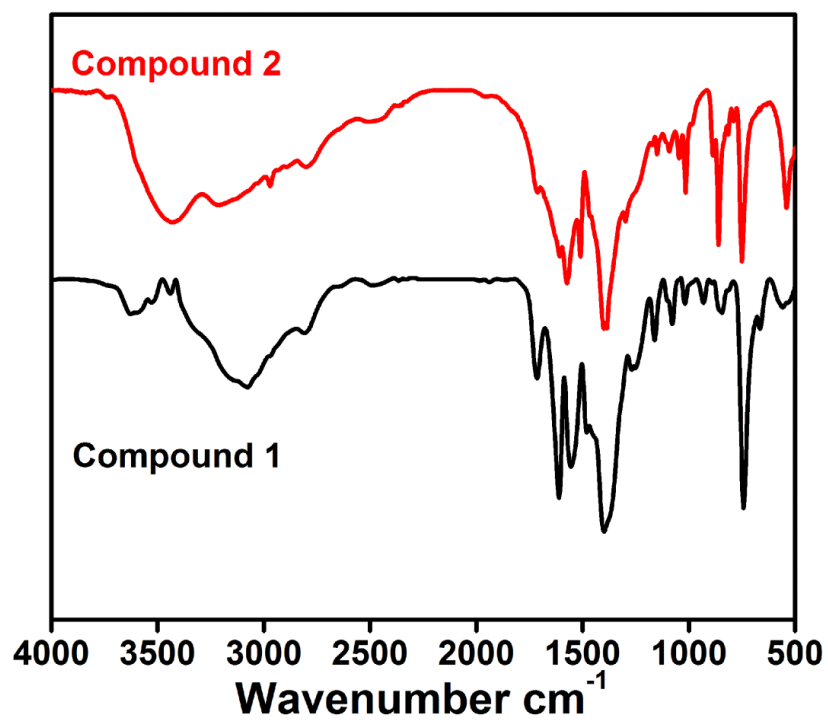


Fig S8. The IR spectrum of compounds **1** and **2**.