

Electronic supplementary information

**A dynamic microporous magnet exhibiting room-temperature thermal hysteresis, variable  
magnetic ordering temperatures and highly selective adsorption for CO<sub>2</sub>**

Zhong-Yi Liu<sup>a</sup>, Hong Zhao<sup>a</sup>, Wei-Chao Song<sup>a</sup>, Xiu-Guang Wang<sup>a</sup>, Zheng-Yu Liu<sup>a</sup>, Xiao-Jun Zhao<sup>\*ab</sup>  
and En-Cui Yang<sup>\*a</sup>

**Materials.** 3,5-diamino-1,2,4-triazole (Hdatrz), cobalt nitrate hexahydrate and triethylamine were commercially purchased and used as received without further purification. Pyridine-2,4,6-tricarboxylic acid (H<sub>3</sub>ptc) was prepared according to the literature.<sup>1</sup> Doubly deionized water was used for the conventional synthesis.

**Physical measurement.** Fourier transform (FT) IR spectrum (KBr pellets) of the titled complexes were taken on an Avatar-370 (Nicolet) spectrometer in the range 4000–400 cm<sup>-1</sup>. Thermogravimetric analysis (TGA) experiment was performed on a Shimadzu simultaneous DTG-60A compositional analysis instrument from 295 K to 1073 K under N<sub>2</sub> atmosphere at a heating rate of 5.0 K min<sup>-1</sup>. Powder X-ray diffraction (PXRD) patterns were obtained from a Bruker D8 ADVANCE diffractometer at 40 kV and 40 mA for Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) with a scan speed of 0.1 sec/step and a step size of 0.01° in  $2\theta$ . The low-temperature *in-situ* PXRD patterns of the sample were obtained through using a wash bottle filled with liquid nitrogen, which can blow cold nitrogen and decrease the temperature of powder sample. Low temperature glue was applied to prevent the flying of sample under the nitrogen flow. The simulated PXRD pattern was calculated using single-crystal X-ray diffraction data and processed by the free Mercury v1.4 program provided by the Cambridge Crystallographic Data Center. Differential scanning calorimetry measurements were recorded using a Waters TA Q200 differential scanning calorimeter with temperature sweep rate of 3.0 K·min<sup>-1</sup>.

Magnetic susceptibilities were acquired on a Quantum Design (SQUID) magnetometer MPMS-XL-7 with crystalline sample. The crystalline sample of **1'** was sealed in a aluminum pan to avoid loss of water molecules during the magnetic measurements. The magnetic data of **1''** were collected after a *in-situ* dehydration of **1'** at 383 K for two hours in the MPMS instrument. Polythene film was used to wrapped the complex during the experiment so that the water molecules can be easily released at 383 K under vacuum conditions. The diamagnetic corrections were calculated using Pascal's constants and background corrections by experimental measurement on sample holder and aluminum pan. Gas adsorption isotherms were measured by a volumetric method using a Micromeritics ASAP 2020HD88 surface area and pore analyzer. Prior to gas adsorption measurements, sample **1'** (74.0 mg) was heated at 383 K for 10 hours under high vacuum to fully remove the water molecules.

**Synthesis of 1'.** A mixture containing Hdatrz (14.8 mg, 0.15 mmol),  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (29.1 mg, 0.10 mmol) and  $\text{H}_3\text{ptc}$  (10.6 mg, 0.05 mmol) was dissolved in mixed  $\text{H}_2\text{O}-\text{CH}_3\text{OH}$  (v:v = 6:4, 10.0 mL) and the initial pH value of the mixture was adjusted to *ca.* 7 by triethylamine. The resulting mixture was then transferred into a parr Teflon-lined stainless steel vessel (23.0 mL) and heated to 165 °C for 96 h under autogenous pressure. After the mixture was cooled to room temperature at a rate of 2.9 °C h<sup>-1</sup>, purple block-shaped crystals suitable for X-ray analysis were generated directly, washed with water, and dried in air. Yield: 53.3% based on  $\text{Co}^{\text{II}}$  salt. Anal. Calcd for  $\text{C}_{24}\text{H}_{41.5}\text{Co}_5\text{N}_{22}\text{O}_{22.75}$ : C, 22.23; H, 3.23; N, 23.76. Found: C, 22.19; H, 3.13; N, 23.80. IR (KBr,  $\text{cm}^{-1}$ ): 3355 (br), 1638 (s), 1567 (s), 1519 (m), 1443 (s), 1365 (s), 1275 (w), 1160 (s), 1075 (s), 950 (m), 860 (m), 780 (w), 731 (w), 618 (w), 543 (w).

**X-ray data collection and structure determinations.** X-ray single-crystal diffraction data for the complex were collected on a Agilent SuperNova, Dual, Cu at zero, AtlasS2 diffractometer equipped with mirror-monochromated Cu-K $\alpha$  radiation ( $\lambda = 1.54184 \text{ \AA}$ ) at 273, 293 and 383 K, respectively. There was no evidence

of crystal decay during data collection. Semiempirical multiscan absorption corrections were applied *SCALE3 ABSPACK*<sup>2</sup> and the programs *CrysAlisPro*<sup>3</sup> were used for integration of the diffraction profiles. The structures were solved by direct methods and refined with the full-matrix least-squares technique using the *ShelXT* and *ShelXL* programs.<sup>4</sup> Anisotropic thermal parameters were assigned to all non-H atoms. The organic hydrogen atoms were geometrically generated. H atoms attached to the water molecule were located from difference maps and refined with isotropic temperature factors. In **1**, three lattice water molecules (O8, O12 and O13) were disordered with the site occupancy of 0.5 for O7 and O13 as well as 0.325 for O12. And two lattice water molecules (O9 and O11) of **1** are positionally disordered with occupations that refined to 0.62 and 0.38 for O9 and O9', 0.59 and 0.41 for O11 and O11'. In **1'**, one lattice water molecule (O7W) was disordered with the site occupancy of 0.5. The rest solvent molecules in **1'** and **1''** was disordered over numerous partial occupancy sites, so the SQUEEZE procedure was used.<sup>5</sup> In **1'**, the SQUEEZE calculations show the presence of 390 e/unit, meaning 48.7 e/asymmetric unit. This should be attributing to 4.87 H<sub>2</sub>O per asymmetric unit because **1'** was obtained from **1**. Summary of crystallographic data and the selected bond length and angles for the sample at different temperatures were listed in Table S1–S4. CCDC 1845672, 1845673 and 1845674 for the different crystal phases contain supplementary crystallographic data for this paper. These data can be obtained, upon request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, U.K.

**Table S1** Crystallographic data and refinement parameters for the title complex.

	<b>1</b>	<b>1'</b>	<b>1<sup>2</sup></b>
Temperature / K	273	293	383
Formula	C <sub>24</sub> H <sub>41.25</sub> Co <sub>5</sub> N <sub>22</sub> O <sub>22.65</sub>	C <sub>24</sub> H <sub>41.5</sub> Co <sub>5</sub> N <sub>22</sub> O <sub>22.75</sub>	C <sub>24</sub> H <sub>20</sub> Co <sub>5</sub> N <sub>22</sub> O <sub>12</sub>
<i>F</i> <sub>w</sub>	1296.69	1296.89	1103.26
Crystal system	monoclinic	monoclinic	monoclinic
Space group	<i>C2/c</i>	<i>C2/c</i>	<i>C2/c</i>
<i>a</i> (Å)	22.0069(18)	22.0340(5)	22.241(3)
<i>b</i> (Å)	13.8971(8)	13.5207(3)	13.4188(13)
<i>c</i> (Å)	16.1662(12)	16.9997(4)	17.268(2)
$\beta$ (°)	97.630(7)	97.990(2)	99.282(11)
<i>V</i> (Å <sup>3</sup> )	4900.4(6)	5015.3(2)	5086.0(10)
<i>Z</i>	4	4	4
<i>D</i> <sub>c</sub> (g cm <sup>-3</sup> )	1.758	1.485	1.441
<i>F</i> (000)	2625	2236	2196
Limiting indices	$-25 \leq h \leq 26$ $-16 \leq k \leq 15$ $-19 \leq l \leq 14$	$-25 \leq h \leq 27$ $-16 \leq k \leq 11$ $-21 \leq l \leq 17$	$-25 \leq h \leq 26$ $-15 \leq k \leq 15$ $-20 \leq l \leq 17$
Data / restraints / params	4291 / 18 / 359	4967 / 42 / 299	4475 / 24 / 285
<i>R</i> <sub>int</sub>	0.0561	0.0528	0.1278
<i>GOF</i> on <i>F</i> <sup>2</sup>	1.169	1.002	1.012
<i>R</i> <sub>1</sub> <sup>a</sup> , <i>wR</i> <sub>2</sub> <sup>b</sup> [ <i>I</i> > 2σ( <i>I</i> )]	0.0662, 0.1318	0.0572, 0.1446	0.0669, 0.1338

---

$R_1, wR_2$ [all data]	0.0916, 0.1399	0.0807, 0.1532	0.1277, 0.1717
Residuals ( $e \cdot \text{\AA}^{-3}$ )	0.67, -1.10	0.76, -0.60	0.923, -0.910

---

**Table S2** Selected bond distances and angles for **1**.<sup>a</sup>

Co(1)–N(1)	2.123(5)	Co(1)–N(6)	2.071(5)
Co(1)–O(5)	2.245(5)	Co(2)–O(2) <sup>#2</sup>	1.962(5)
Co(2)–N(2)	1.962(5)	Co(2)–N(7)	1.993(5)
Co(2)–O(6)	1.953(5)	Co(3)–O(8)	2.167(5)
Co(3)–N(11)	2.072(5)	Co(3)–O(3)	2.181(5)
Co(3)–N(3) <sup>#3</sup>	2.076(5)	Co(3)–O(1)	2.299(4)
Co(3)–N(8) <sup>#4</sup>	2.110(5)		
N(6)–Co(1)–N(1) <sup>#1</sup>	88.9(2)	N(6)–Co(1)–N(1)	96.4(2)
N(1) <sup>#1</sup> –Co(1)–N(1)	93.6(3)	N(6)–Co(1)–O(5)	86.9(2)
N(1)–Co(1)–O(5)	90.14(18)	N(6)–Co(1)–O(5) <sup>#1</sup>	87.42(19)
N(11)–Co(3)–O(8)	85.4(2)	O(5)–Co(1)–O(5) <sup>#1</sup>	86.3(3)
O(6)–Co(2)–O(2) <sup>#2</sup>	116.4(2)	N(2)–Co(2)–N(7)	102.2(2)
O(6)–Co(2)–N(2)	118.3(2)	O(6)–Co(2)–O(7)	68.8(4)
O(2) <sup>#2</sup> –Co(2)–N(2)	104.2(2)	O(2) <sup>#2</sup> –Co(2)–O(7)	68.7(4)
O(6)–Co(2)–N(7)	108.7(3)	N(2)–Co(2)–O(7)	87.0(4)
O(2) <sup>#2</sup> –Co(2)–N(7)	105.4(2)	N(3) <sup>#3</sup> –Co(3)–O(8)	82.4(2)
N(11)–Co(3)–N(8) <sup>#4</sup>	98.0(2)	N(11)–Co(3)–O(3)	75.26(19)
N(3) <sup>#3</sup> –Co(3)–N(8) <sup>#4</sup>	94.2(2)	N(3) <sup>#3</sup> –Co(3)–O(3)	104.35(19)
N(8) <sup>#4</sup> –Co(3)–O(3)	96.45(18)	O(8)–Co(3)–O(3)	89.13(18)
N(11)–Co(3)–O(1)	74.46(18)	N(3) <sup>#3</sup> –Co(3)–O(1)	103.98(18)
N(8) <sup>#4</sup> –Co(3)–O(1)	93.44(18)	O(8)–Co(3)–O(1)	82.71(17)

---

O(3)–Co(3)–O(1)      149.15(16)

---

<sup>a</sup> Symmetry codes: #1  $1 - x, y, 3/2 - z$ ; #2  $1/2 - x, 1/2 + y, 3/2 - z$ ; #3  $x, y - 1, z$ ; #4  $x, 1 - y, 1/2 + z$ .

**Table S3** Selected bond distances and angles for **1'**.<sup>a</sup>

Co(1)–N(6)	2.101(4)	Co(1)–N(1)	2.116(4)
Co(1)–O(5)	2.212(4)		
Co(2)–N(2)	1.983(4)	Co(2)–O(2) <sup>#3</sup>	1.998(3)
Co(2)–O(6)	1.946(4)	Co(2)–N(7)	2.008(4)
Co(3)–N(3) <sup>#3</sup>	2.000(4)	Co(3)–O(1)	2.292(3)
Co(3)–N(8) <sup>#4</sup>	2.019(4)	Co(3)–O(3)	2.160(3)
Co(3)–N(11)	2.027(4)	O(3)–Co(3)–O(1)	149.78(13)
N(6)–Co(1)–N(1)	96.04(15)	N(6)–Co(1)–N(1) <sup>#1</sup>	90.03(15)
N(1)–Co(1)–N(1) <sup>#1</sup>	92.0(2)	N(11)–Co(3)–O(1)	74.18(13)
N(6)–Co(1)–O(5) <sup>#1</sup>	86.61(16)	N(2)–Co(2)–O(7W)	82.6(2)
N(6)–Co(1)–O(5)	87.07(16)	N(1)–Co(1)–O(5)	90.54(17)
O(5) <sup>#1</sup> –Co(1)–O(5)	87.0(3)	O(6)–Co(2)–O(2) <sup>#3</sup>	116.47(17)
O(6)–Co(2)–N(2)	125.3(2)	O(6)–Co(2)–O(7W)	78.9(3)
O(2) <sup>#3</sup> –Co(2)–N(2)	107.93(15)	O(2) <sup>#4</sup> –Co(2)–O(7W)	76.0(3)
O(6)–Co(2)–N(7)	101.5(2)	N(3) <sup>#3</sup> –Co(3)–O(1)	98.42(14)
O(2) <sup>#3</sup> –Co(2)–N(7)	102.03(17)	N(8) <sup>#4</sup> –Co(3)–O(1)	96.67(14)
N(2)–Co(2)–N(7)	98.75(17)	N(3) <sup>#3</sup> –Co(3)–N(8) <sup>#4</sup>	107.73(18)
N(3) <sup>#3</sup> –Co(3)–N(11)	137.59(17)	N(8) <sup>#3</sup> –Co(3)–N(11)	114.56(17)
N(8) <sup>#4</sup> –Co(3)–O(3)	100.47(14)	N(3) <sup>#3</sup> –Co(3)–O(3)	99.79(15)
N(11)–Co(3)–O(3)	76.09(14)		

<sup>a</sup> Symmetry codes: <sup>#1</sup> 1 – x, y, 3/2 – z; <sup>#2</sup> 1/2 – x, y + 1/2, 3/2 – z; <sup>#3</sup> x, y – 1, z; <sup>#4</sup> x, 1 – y, z + 1/2.

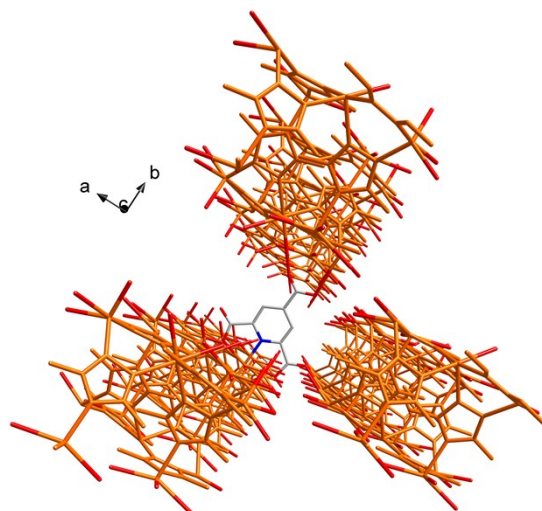




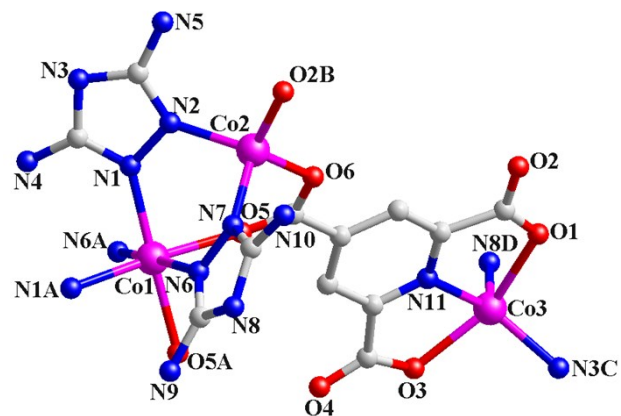
**Table S4** Selected bond distances and angles for **1<sup>2</sup>**.<sup>a</sup>

Co(1)–N(6)	2.108(5)	Co(1)–N(1)	2.117(6)
Co(1)–O(5)	2.207(5)	Co(2)–N(2)	1.964(5)
Co(2)–O(6)	1.949(5)	Co(3)–N(11)	2.027(5)
Co(2)–N(7)	1.957(6)	Co(2)–O(2) <sup>#2</sup>	1.979(4)
Co(3)–N(3) <sup>#3</sup>	2.016(5)	Co(3)–O(3)	2.078(5)
Co(3)–N(8) <sup>#4</sup>	2.016(6)	Co(3)–O(1)	2.445(5)
N(6)–Co(1)–N(1) <sup>#1</sup>	89.2(2)	N(6)–Co(1)–O(5) <sup>#1</sup>	87.8(2)
N(1) <sup>#1</sup> –Co(1)–N(1)	92.9(3)	O(5) <sup>#1</sup> –Co(1)–O(5)	84.9(3)
N(6)–Co(1)–O(5)	86.1(2)	N(1)–Co(1)–O(5)	91.3(2)
O(6)–Co(2)–N(2)	118.2(2)	O(6)–Co(2)–O(2) <sup>#2</sup>	109.6(2)
O(6)–Co(2)–N(7)	110.0(2)	N(2)–Co(2)–O(2) <sup>#2</sup>	103.2(2)
N(7)–Co(2)–N(2)	103.2(2)	N(7)–Co(2)–O(2) <sup>#2</sup>	112.5(2)
N(3) <sup>#3</sup> –Co(3)–N(8) <sup>#4</sup>	110.2(2)	N(3) <sup>#3</sup> –Co(3)–O(1)	95.60(19)
N(3) <sup>#3</sup> –Co(3)–N(11)	132.0(2)	N(8) <sup>#4</sup> –Co(3)–O(1)	95.51(19)
N(8) <sup>#4</sup> –Co(3)–N(11)	116.9(2)	N(11)–Co(3)–O(1)	71.98(18)
N(3) <sup>#3</sup> –Co(3)–O(3)	100.7(2)	O(3)–Co(3)–O(1)	149.82(18)
N(8) <sup>#4</sup> –Co(3)–O(3)	102.3(2)	N(3) <sup>#3</sup> –Co(3)–N(8) <sup>#4</sup>	110.2(2)
N(11)–Co(3)–O(3)	78.2(2)	N(6)–Co(1)–N(1)	96.5(2)

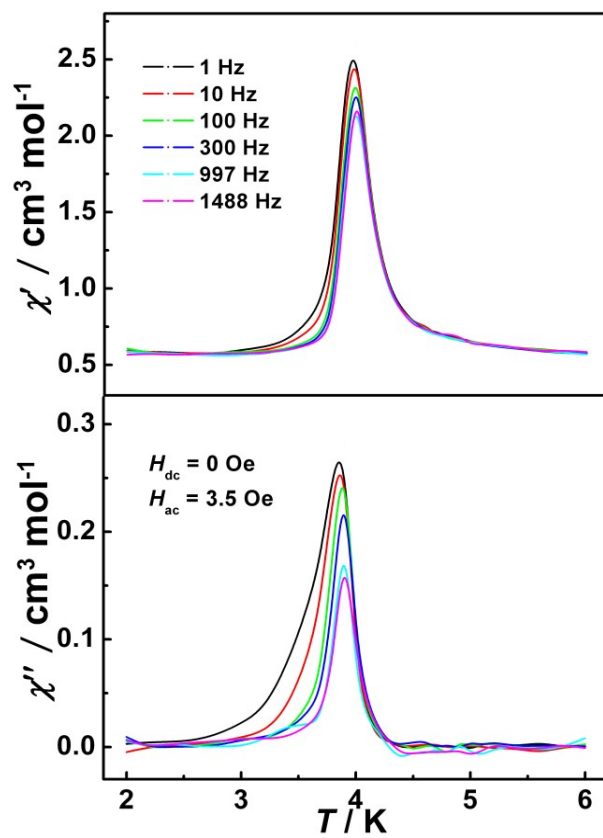
<sup>a</sup> Symmetry codes: <sup>#1</sup> 1 – x, y, 3/2 – z; <sup>#2</sup> 1/2 – x, y + 1/2, 3/2 – z; <sup>#3</sup> x, y – 1, z; <sup>#4</sup> x, 1 – y, z + 1/2.



**Fig. S1** Three-connected ptc<sup>3-</sup> linkers that aggregated three adjacent 1D broad ribbons of {Co<sub>5</sub>(datrz)<sub>4</sub>}.



**Fig. S2** Local coordination environments of Co<sup>II</sup> ions in **1'** (H atoms were omitted for clarity, symmetry codes: A = 1 - x, y, 3/2 - z; B = 1/2 - x, y + 1/2, 3/2 - z; C = x, y - 1, z; D = x, 1 - y, z + 1/2).



**Fig. S3** Temperature-dependent *ac* susceptibilities for **1** at different frequencies under  $H_{\text{dc}} = 0 \text{ Oe}$  and  $H_{\text{ac}} = 3.5 \text{ Oe}$ .

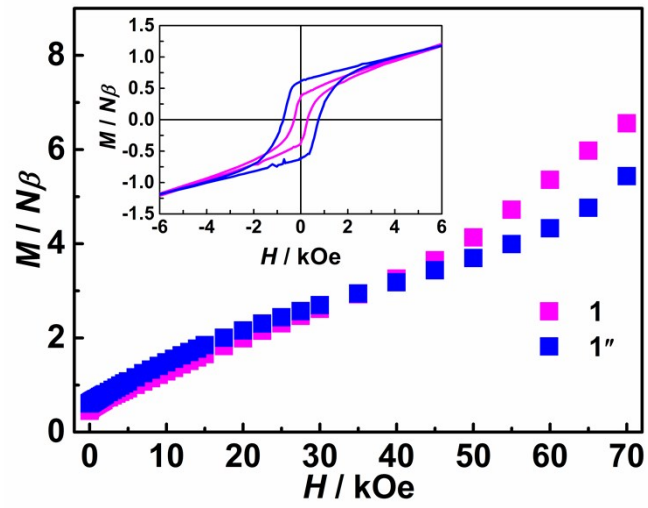


Fig. S4 Isothermal magnetization for 1 and 1<sup>2</sup> at 2.0 K (Inset: magnetic hysteresis loop of 1 and 1<sup>2</sup> at 2.0 K).

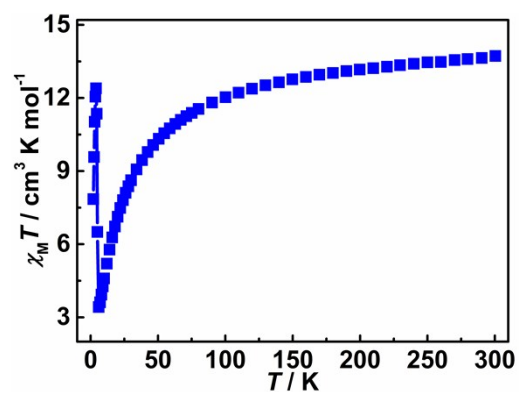
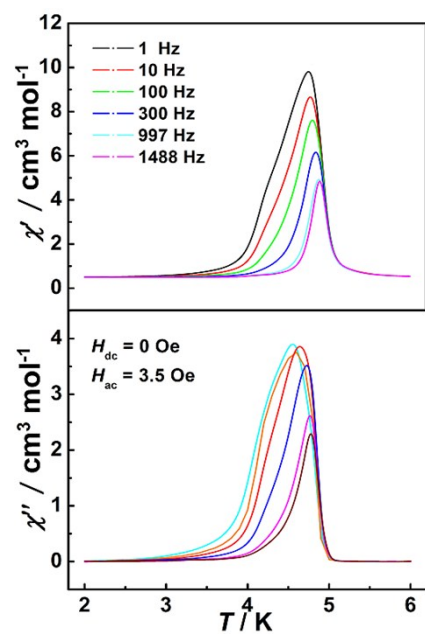
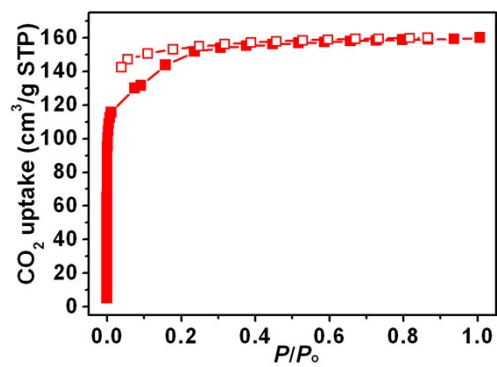


Fig. S5 Plot of  $\chi_M T$  vs  $T$  for  $1^2$ .

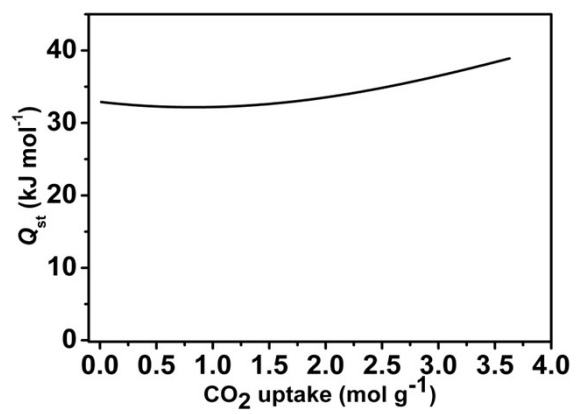


**Fig. S6** Temperature-dependent *ac* susceptibilities for **1<sup>2</sup>** at different frequencies under  $H_{dc} = 0 \text{ Oe}$  and  $H_{ac} = 3.5 \text{ Oe}$ .

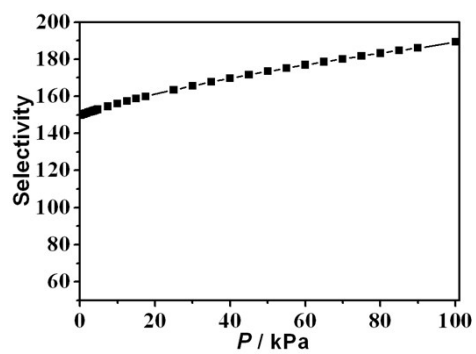




**Fig. S7** The CO<sub>2</sub> absorption isotherm for **1<sup>2</sup>** measured at 195 K (STP: standard temperature and pressure).



**Fig. S8** Absorption enthalpy of CO<sub>2</sub> as a function of loading for **1<sup>2</sup>**.



**Fig. S9** Adsorption selectivity for **1<sup>2</sup>** predicted by IAST for a mixture of CO<sub>2</sub> (15%) and N<sub>2</sub> (85%).

## Reference

1. L. Syper, K. Kloc and J. Mzochowski, *Tetrahedron* 1980, **36**, 123.
2. *SCALE3 ABSPACK*: Empirical absorption correction, CrysAlis–Software package, Oxford Diffraction Ltd., Oxford, 2006.
3. *CrysAlisPro*, Agilent Technologies: Yarnton, Oxfordshire, England, 2010.
4. (a) Sheldrick, G. M. *ShelXT*, Göttingen University: Göttingen, Germany, 2015. (b) Sheldrick, G. M. *ShelXL*, GöttingenUniversity: Göttingen, Germany, 2008.
5. A. L. Spek, *Acta Cryst.*, 2009, **D65**, 148.