Supporting Information

3d-4f Heterometal-Organic Frameworks for Efficient Capture and Conversion of CO_2

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Materials and Methods.

All the materials were commercially available and were used without further purification. Powder X-ray diffraction measurements were performed on a Ultima X-ray diffractometer equipped with Cu Kα radiation. The C, H and N microanalyses were tested at the Institute of Elemental Organic Chemistry, Nankai University. Thermogravimetric analyses (TGA) were measured by a Netzsch TG 209 TG-DTA analyzer under a nitrogen atmosphere. ^{1}HNMR spectra were recorded on a Mercury Vx-300 spectrometer in $CDCl_3$ and $CDCl_3$ (7.26 ppm) was used as internal reference. ICP measurements were measured on a IRIS Advantage spectrometer.

X-ray Crystallography

The X-ray single data of **1** and **2** was collected on a SuperNova Single Crystal Diffractometer equipped with MoKα radiation (λ = 0.71073 Å) at low temperature.

The data integration and empirical absorption corrections were carried out by SAINT programs.[1] The structures were solved by direct methods and refined anisotropically on F^2 by the full matrix least-squares techniques with SHELXS-97 and SHELXL-97 programs.[2] All the hydrogen atoms were placed geometrically and refined using a riding model.

Because there are too many disordered solvent molecules in compound **1** and **2**, their diffraction contribution were removed by using PLATON/SQUEEZE,[3] and the guest molecules were determined by the TGA and elemental analysis. Detail crystal data and structure refinement for **1 (**CCDC 1520461) and **2** (CCDC 1533607) are shown in Table S1.

Table S1. Crystal data and structure refinement for **1 and 2**.

Identification code	**1**	**2**
Empirical formula	$TbZnC_{26}H_{34.5}N_{4.5}O_{17.5}Cl$	$TbCoC_{26}H_{40.5}N_{4.5}O_{20.5}Cl$
Formula weight	949.5	996.5
Temperature/K	125.15(10)	125.9(3)
Crystal system	monoclinic	monoclinic
Space group	C2/c	C2/c
a/Å	27.9927(4)	28.0996(4)
b/Å	13.9755(2)	13.8122(3)
c/Å	22.6184(3)	22.4619(4)
α/°	90	90
β/°	99.5272(14)	99.3566(15)
γ /°	90	90
Volume/Å^3	8726.6(2)	8601.8(3)
Z	8	8
F(000)	3200.0	3176.0
Goodness-of-fit on F^2	1.046	1.028
Final *R* indexes [$I>=2\sigma(I)$]	R_1= 0.0204, wR_2= 0.0481	R_1= 0.0267, wR_2= 0.0638
Final *R* indexes [all data]	R_1= 0.0239, wR_2= 0.0495	R_1= 0.0331, wR_2= 0.0660

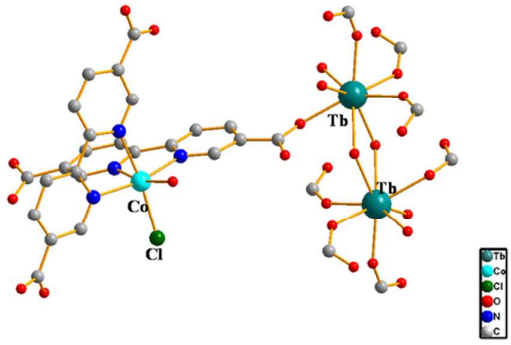

Figure S1. The coordinated environments of Tb^{3+}, Co^{2+} and $BPDC^{2-}$ ligand in compound **2**.

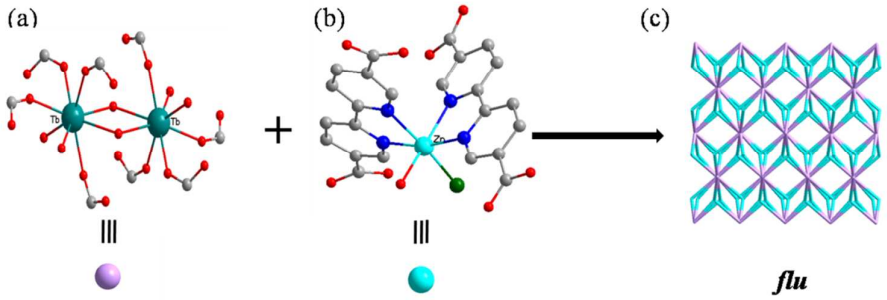

Figure S2. (a) $[Tb_2]$ unit. (b) $[Zn(BPDC)_2]$ unit. (c) ***Flu*** topology of **1**: (purple) $[Tb_2]$ unit, (blue) $[Zn(BPDC)_2]$ unit.

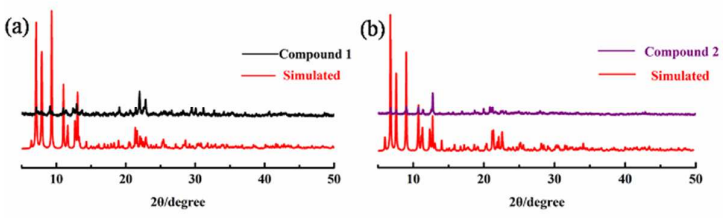

Figure S3. (a) Power XRD of simulated from single-crystal data of **1** (red) and compound **1** (dark) (b) Power XRD of simulated from single-crystal data of **2** (red) and compound **2** (purple).

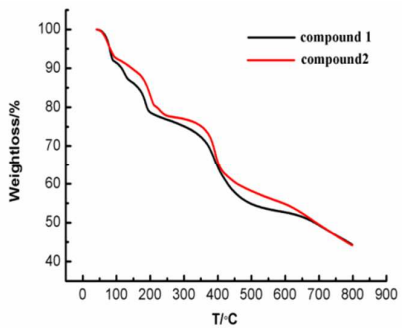

Figure S4. The TGA curves of compounds **1** (dark) and **2** (red).

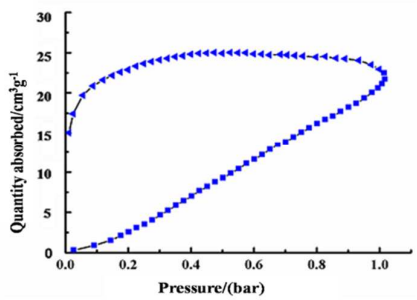

Figure S5. CO_2 isotherm of **1a** at 298 K.

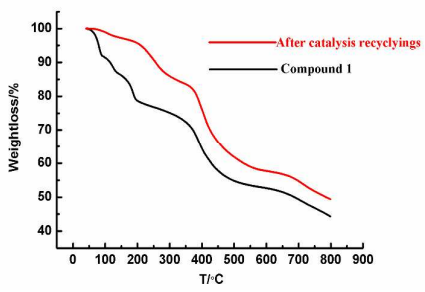

Figure S6. The TGA curves of compound **1** and after four recyclings.

References

1 SAINT^{+}, *version 6.22; Bruker AXS: Madison* **2001**.

2 Sheldrick, G. *Acta Crystallogr., Sect. A: Fundam. Crystallogr.* **2008**, *64*, 112-122.

3 Spek, A. L. *PLATON, A Multipurpose Crystallographic Tool,* Utrecht University, Utrecht, the Netherlands **2001**.