

Supplementary Information

Enhancement of adsorption selectivity for MOFs under mild activation and regeneration conditions

Zheng Niu, Sheng Fang, Jian-Gong Ma*, Xiao-Ping Zhang, and Peng Cheng*

Department of Chemistry, Key Laboratory of Advanced Energy Material Chemistry (MOE) and Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Nankai University, Tianjin 300071 (P. R. China)

Material and measurement

All chemical reagents were obtained from commercial sources and, unless otherwise noted, were used as received without further purification. Solvents were further purified following standard procedures prior to use. Elemental analysis was performed on a Perkin - Elmer 240 CHN elemental analyzer. IR spectra were recorded in the range 400 - 4000 cm^{-1} on a Bruker TENOR 27 spectrophotometer by using KBr pellets. Powder X-ray diffraction measurements (PXRD) were recorded on a D/Max-2500 X-ray diffractometer using Cu-K α radiation. The simulated powder patterns were calculated by using Mercury 2.0. Thermogravimetric analysis was performed on a Labsys NETZSCH TG 209 Setaram apparatus with a heating rate of 10°C min^{-1} under a nitrogen atmosphere. All vapor-adsorption experiments were performed on a Quantachrome IQ₂ automatic volumetric instrument. All organic adsorbents in vapor-adsorption experiments were chromatographically pure and anhydrous. The vapor-sorption measurements were performed on the instrument that was equipped with a vapor generator at 298 K. The vapor-sorption isotherms were recorded in the pressure range 10^{-3} - 0.9 P/P₀.

Synthesis of $[\text{Eu}(\text{H}_2\text{CAM})_3]\cdot 5\text{H}_2\text{O}$: The mixture of H_3CAM (H_3CAM = chelidamic acid monohydrate, 0.3 mmol, 60.30 mg), $\text{Eu}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ (0.1 mmol, 44.60 mg) and 2 mL DEF (N,N-diethylformamide) heated in 5mL glass vial at 90 °C for 7 days, and then cooled to room temperature at a rate of 2 °C h⁻¹. The block yellow crystals were obtained in 48% yield based on Eu. Elemental analysis for $[\text{Eu}(\text{H}_2\text{CAM})_3]\cdot 5\text{H}_2\text{O}$, Calc. (%): C, 31.99; H, 2.81; N, 5.33. Found (%): 32.24; 2.75; 5.39. IR (KBr, cm⁻¹): 3230 m, 2849 m, 2500 m, 2277w, 1343 s, 1153 s, 981 w, 835 w, 741 w, 689 w, 655 w, 521 m, 445 m.

Synthesis of $\{[\text{Eu}(\text{CAM})(\text{HCAM})_2\text{Mn}_2(\text{H}_2\text{O})_7]\cdot 7\text{H}_2\text{O}\}_n$ (1**):** $[\text{Eu}(\text{H}_2\text{CAM})_3]\cdot 5\text{H}_2\text{O}$ (0.1 mmol, 79.00 mg), $\text{MnCl}_2\cdot 4\text{H}_2\text{O}$ (0.3 mmol, 59.37 mg), 4mL water were heated in 20 mL Teflon cup at 120 °C for 3 days, and then cooled to room temperature at a rate of 2 °C h⁻¹. The rhomboidal colorless crystals were obtained in 76% yield based on Eu. Elemental analysis for **1**, Calc. (%): C, 23.88; H, 3.44; N, 3.98. Found (%): 23.50; 3.36; 3.84. IR (KBr, cm⁻¹): 3405s, 2316w, 1569s, 1420s, 1352m, 1259w, 1124w, 1027s, 979w, 886w, 809m, 742s, 578m, 511w.

Synthesis of $\{[\text{Eu}(\text{CAM})(\text{HCAM})_2\text{Mn}_2(\text{H}_2\text{O})_7]\cdot \text{H}_2\text{O}\cdot 0.33\text{C}_2\text{H}_5\text{OH}\}_n$ (2**):** **2** was obtained by exposing **1** in EtOH vapor atmosphere for 24 h. The transformation from single crystal **1** to single crystal **2** was confirmed by the X-ray crystallography. Elemental analysis for **2**, Calc (%): C, 27.01; H, 2.72; N, 4.36. Found (%): 26.68; 2.87; 4.52.

Synthesis of $\{[\text{Eu}(\text{CAM})(\text{HCAM})_2\text{Mn}_2(\text{CH}_3\text{OH})_3(\text{H}_2\text{O})_4]\cdot 2.08\text{H}_2\text{O}\cdot 0.25\text{CH}_3\text{OH}\}$ (3**):** **3** was obtained by exposing **2** in MeOH vapor atmosphere for 24 h. The transformation from single crystal **2** to single crystal **3** was confirmed by the X-ray crystallography. Elemental analysis for **3**, Calc (%): C, 28.23; H, 3.16; N, 4.16. Found (%): 27.98; 3.21; 4.39.

Crystallographic studies and refinement of the crystal structures

Crystallographic data of **1**, **2** and **3** were collected with an SuperNova, Single source at offset, Eos diffractometer with a Mo K α radiation ($\lambda = 0.71073$ Å). All the structures were solved by direct methods and refined anisotropically by full-matrix least-squares techniques based on F^2 using the SHELXS-97 and SHELXL-97 programs¹ contained on Olex 2. ² Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The hydrogen atoms of the ligand were generated geometrically; the hydrogen atoms of the water molecules were located in Fourier-difference electron density maps and refined with isotropic temperature factors. **1**, **2** and **3** crystalizes in monoclinic space group P21/n. Crystal data as well as details of data collection and refinement for the complexes are summarized in Table S1, S2 and S3. CCDC: 981839, 981840 and 981841 for **1**, **2** and **3**, respectively.

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

CCDC No	981839
Chemical formula	C ₈₄ H ₁₄₄ Eu ₄ Mn ₈ N ₁₂ O ₁₁₆
Formula weight	4225.41
Radiation	Mo K α
Wavelength (Å)	0.71073
Crystal system, space group	monoclinic, P21/n
Unit cell parameter	a= 8.9816(14) alpha=90 b= 24.4814(5) beta=99.3878(15) c= 17.3224(3) gamma=90
Volume (Å ³)	3757
Z, Calculated density (g/cm ³)	1, 1.876
F(000)	2072
Crystal size (mm)	0.5×0.3×0.2
Completeness (to theta)	0.999 (25.01)
Refinement method	Full-matrix least-squares on F ²
Goodness-of-fit on F ²	1.095

Final R indices [$I > 2\sigma(I)$]	R = 0.0420, wR2 = 0.0984
Largest diff. Peak and hole	0.912, -1.118

Table S2. Crystal data and structure refinement for **2**

CCDC No	981840
Chemical formula	$C_{86.67} H_{104} Eu_4 Mn_8 N_{12}$
Formula weight	3854.46
Radiation	Mo $K\alpha$
Wavelength (\AA)	0.71073
Crystal system, space group	monoclinic, P21/n
Unit cell parameter	a= 9.019(11) α =90 b= 24.563(5) β = 99.422(12) c= 17.339(2) γ =90
Volume (\AA^3)	3789
Z, Calculated density (g/cm^3)	1, 1.682
F(000)	1891
Crystal size (mm)	0.5×0.3×0.2
Completeness (to θ)	0.993 (25.01)
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.056
Final R indices [$I > 2\sigma(I)$]	R = 0.1031, wR2 = 0.2484

Table S3. Crystal data and structure refinement for **3**

CCDC No	981841
Chemical formula	C ₄₂ H ₄₆ Co ₄ Gd ₂ N ₆ O ₄₅
Formula weight	1905.06
Radiation	Mo K α
Wavelength (Å)	0.71073
Crystal system, space group	monoclinic, P21/n
Unit cell parameter	a= 8.9103(3) alpha=90 b= 24.1109(8) beta=98.343(3) c= 17.3062(6) gamma=90
Volume (Å ³)	3678
Z, Calculated density (g/cm ³)	1, 1.815
F(000)	1991
Crystal size (mm)	0.5×0.3×0.2
Completeness (to theta)	0.998 (25.01)
Refinement method	Full-matrix least-squares on F ²
Goodness-of-fit on F ²	1.068
Final R indices [I>2sigma(I)]	R = 0.0556, wR2 = 0.1291

1 G. M. Sheldrick, *Acta Cryst*, 2008, **A64**, 112-122

2. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339-341.

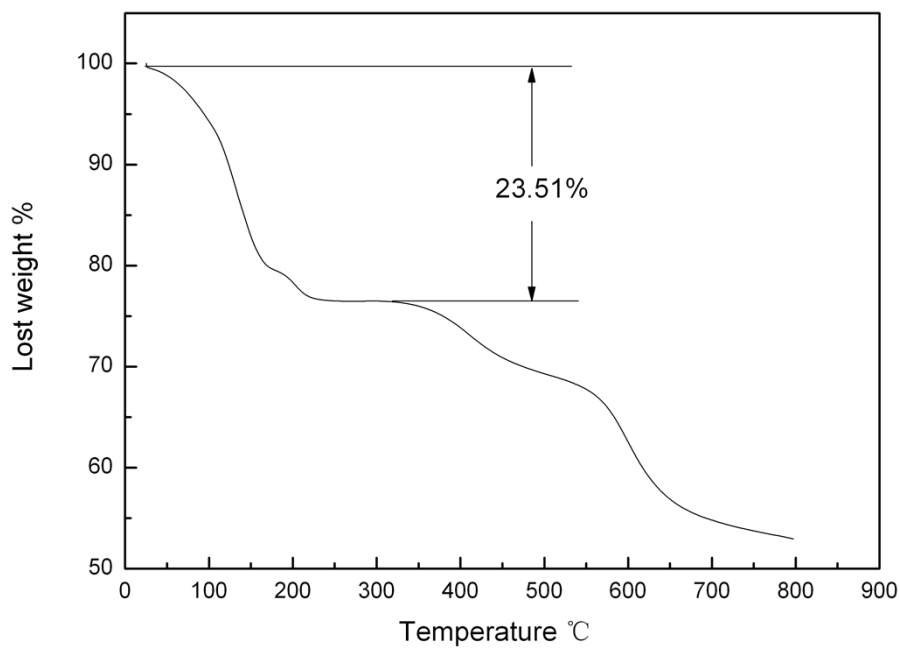


Figure S1. Thermogravimetric analysis of **1**. The 23.51% weight loss at 300 °C corresponds to the loss of fourteen water molecules per asymmetric unit (calculated 23.86%), which is also well consistent with the elemental analysis.

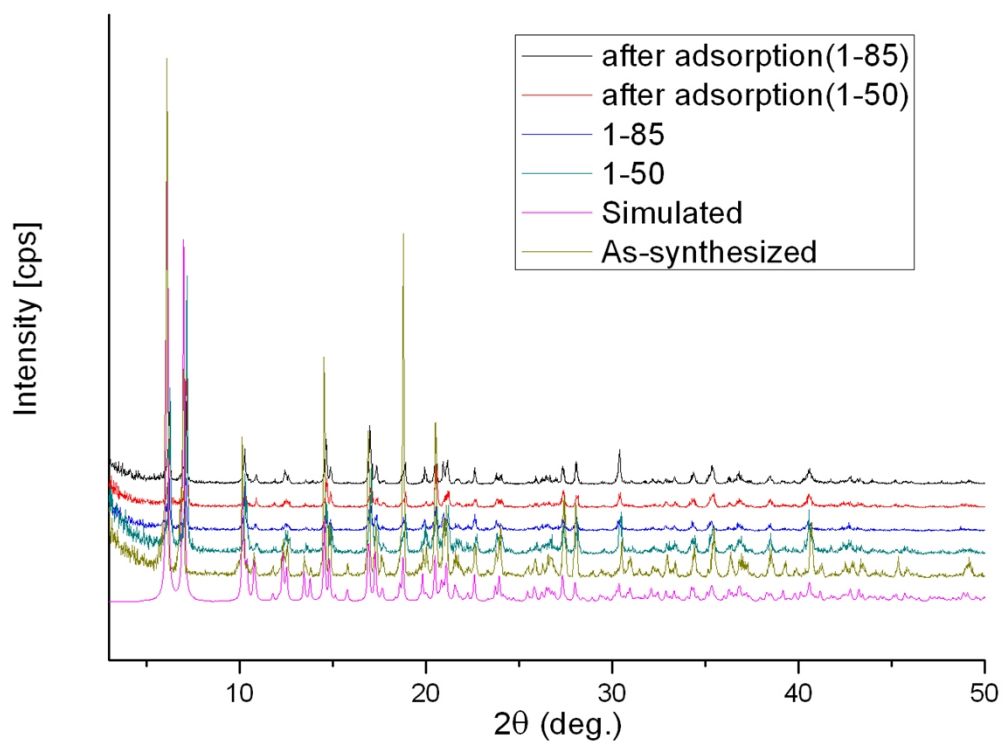


Figure S2. The powder XRD diffraction patterns of **1**, **1-50**, and **1-85**. The patterns after adsorption indicated that the framework of **1-50** and **1-85** unchanged in whole adsorption procedure.

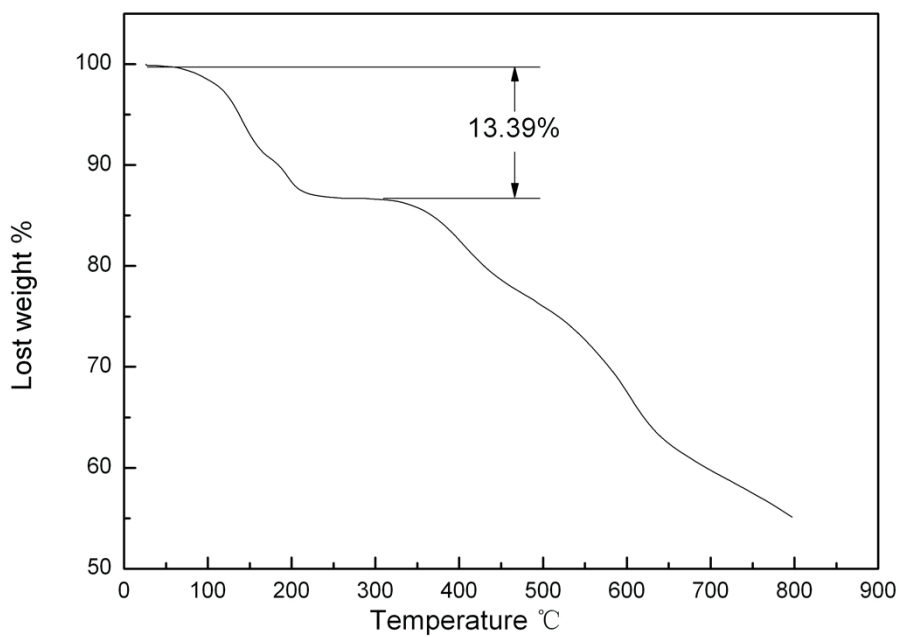


Figure S3. Thermogravimetric analysis of **1-50**. The 13.39 % weight loss at 300°C corresponds to the loss of seven water molecules per asymmetric unit of **1-50** (calculated 13.56%), which is also well consistent with the elemental analysis of **1-50** (Calc (%): C, 27.11; H, 2.38; N, 4.52. Found (%):27.23; 2.56; 5.02.).

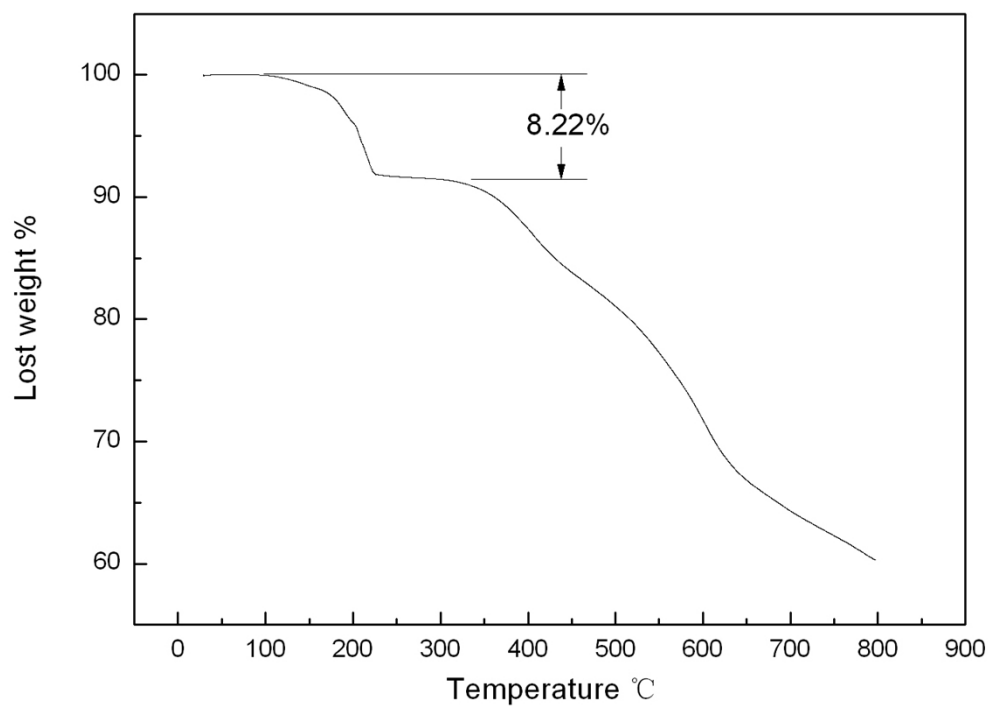


Figure S4. Thermogravimetric analysis of **1-85**. The 8.22 % weight loss at 300°C corresponds to the loss of three water molecules per asymmetric unit of **1-50** (calculated 8.21%), which is also well consistent with the elemental analysis of **1-85** (Calc. (%): C, 28.78; H, 1.84; N, 4.80. Found (%): 29.05; 1.90; 4.92.).

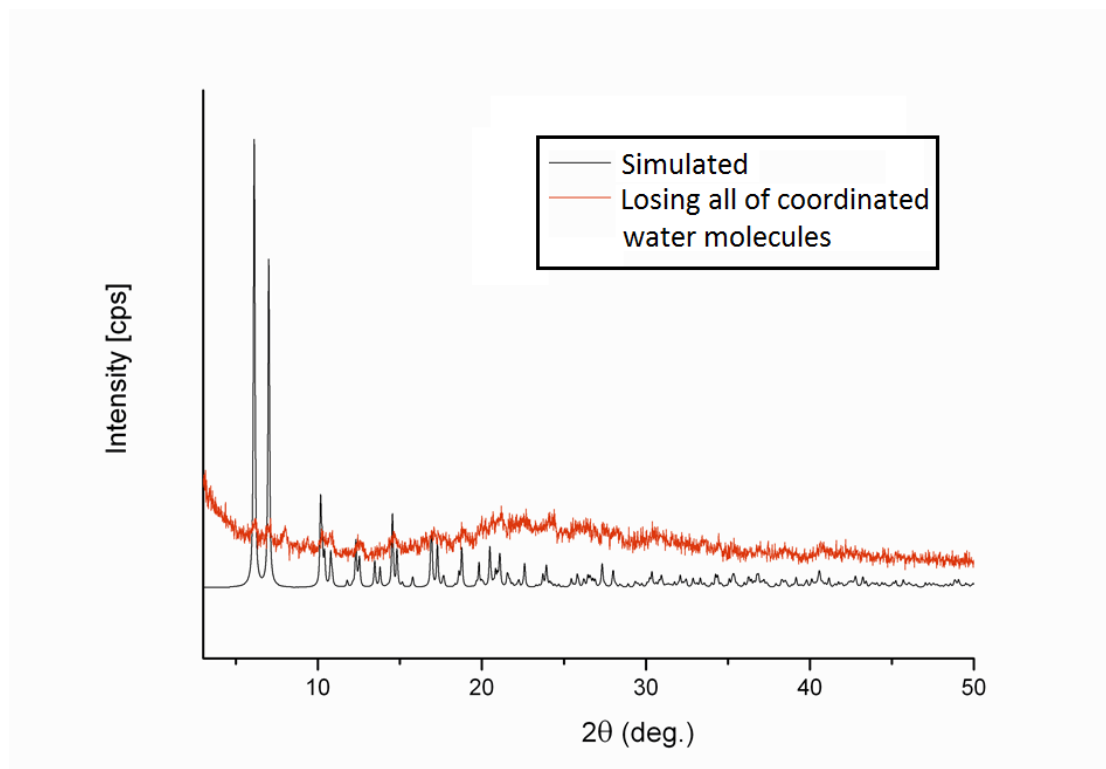


Figure S5. The powder XRD diffraction patterns of **1** with lost all of coordinated water molecules and the simulated patterns of **1**. The patterns indicated that the remove of all coordinated water molecules will cause the collapse of the framework of **1**.