Template controlled synthesis of cluster-based porous coordination polymer : crystal structure, magnetism and adsorption

Xi Chen,[a] Zhao Li,[a] Rong-jia Wei,[b] Bao Li, [a,*] Tian-le Zhang,[a,*] Jun Tao[b]

[a] School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, 1037 Luoyu Road, Wuhan 430074 (China); [b] College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005 (China)

Experimental Section

Materials and General Methods. All starting materials were obtained commercially and were used without further purification. Elemental analyses for C, H, N were performed on a Perkin-Elmer 240Q elemental analyzer. The IR spectra were recorded in range of 400-4000 cm^{-1} on a Nicolet 5DX spectrometer (KBr pellets). Magnetic susceptibility measurements were carried out in the temperature range of 2–300 K with a magnetic field of 1000 Oe on Quantum Design MPMS XL-7 magnetometer. The field-dependent magnetization and hysteresis experiments were carried out at 2 K. Powder X-ray diffraction (PXRD) data were collected over the 2θ range 5 ~ 60° using a X'Pert PRO automated diffractometer at room temperature, with a step size of 0.02° in 2θ angle.

Synthesis of $[Co_3(ina)_4(N_3)_2(CH_3OH)_2]$ (1). A mixture of Hina (12.5 mg, 0.1 mmol), $Co(NO_3)_2$•$6H_2O$ (15 mg，0.05 mmol) and NaN_3 (13 mg, 0.2 mmol) was dissolved in 10 mL MeOH in 25-mL screw-capped vial. The mixture was stirred at room temperature for 5 min, and then heated at 80℃ for 2 days, and red crystals were obtained from the filtrate. Anal. Calcd for $C_{26}H_{24}Co_3N_{10}O_{10}$: H 2.97%, C 38.40%, N 17.22%; found H 3.24%, C 38.84%, N 17.93%. IR (KBr, cm^{-1}): 3369.9 2077.8 1599.2 1550.3 1387.4 1226.3 1060.9 1018.4 775.6 691.4.

Synthesis of $[Co_8(OH)(ina)_8(N_3)_8 \cdot X]$ (2). A mixture of Hina (12.5 mg, 0.1 mmol), $Co(NO_3)_2$•$6H_2O$ (15 mg，0.05 mmol), pentaerythritol（7 mg, 0.05 mmol） and NaN_3

(13 mg, 0.2 mmol) was dissolved in 12.5 mL MeOH and 1 mL H_2O in 25-mL screw-capped vial. The mixture was stirred at room temperature for 5 min, and then heated at 80℃ for 2 days, and red rod-like crystals were obtained from the filtrate. Anal. found for fresh sample : H 2.67%, C 30.78%, N 23.26%. IR (KBr, cm^{-1}): 3383.7 2077.1 1603.3 1549.9 1389.2 1230.8 1060.0 1021.9 774.7 692.5. According the results of TGA and EA results, the complete forumla of 2 might be $[Co_8(OH)(ina)_8(N_3)_8 \cdot (CH_3OH)_2(H_2O)_4]$. Calcd for $C_{50}H_{49}Co_8N_{32}O_{23}$: H 2.55%, C 30.99%, N 23.13%.

X-Ray Structural Determination. X-ray diffraction data of 1 (0.3 × 0.3 × 0.1 mm) and 2 (0.2 × 0.1 × 0.1 mm) were collected on Oxford Gemini S Ultra diffractometer using Mo-Kα (λ = 0.71073 Å) radiation at room temperature. The structures of complexes were solved by direct methods, and the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXTL using a full-matrix least squares procedure based on F^2 values.[1] The hydrogen atom positions were fixed geometrically at calculated distances and allowed to ride on the parent atoms. Structure refinement after modification of the data for the non-coordinate lattice solvent molecules with the SQUEEZE routine of PLATON of **2** led to better refinement and data convergence.[2] CCDC-1030991 (1) and CCDC-1030992 (2) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Low pressure gas sorption measurements:

Low-pressure N_2 adsorption measurements (up to 1 bar) were performed on Micromeritics ASAP 2020 M+C surface area and pore size analyzer. About 200 mg of methanol solvent-exchanged samples were activated at 90 °C for 12 hours by using the “outgas” function of the surface area analyzer. Helium was used for the estimation

of the dead volume, assuming that it is not adsorbed at any of the studied temperatures. To provide high accuracy and precision in determining P/P_0, the saturation pressure P0 was measured throughout the N_2 analyses by means of a dedicated saturation pressure transducer, which allowed us to monitor the vapor pressure for each data point. A part of the N_2 sorption isotherm in the P/P_0 range 0. 01–0.1 was fitted to the BET equation to estimate the BET surface area and the Langmuir surface area calculation was performed using all data points. The pore size distribution (PSD) was obtained from the DFT model in the Micromeritics ASAP2020 software package (assuming slit pore geometry) based on the N_2 sorption at 77 K.

References:

1. G. M. Sheldrick, *SHELXTL-PLUS, Crystal Structure Analysis Package*; Bruker Analytical X-Ray; Madison, WI, USA, **1997**.
2. PLATON program: A. L. Spek, *Acta Crystallogr. Sect. A*, **1990**, *46*, 194.

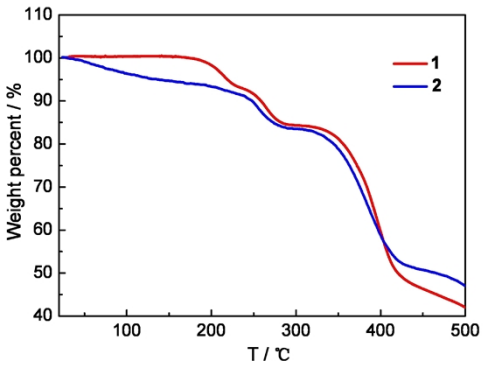

Figure S1 TGA curves of 1 and 2

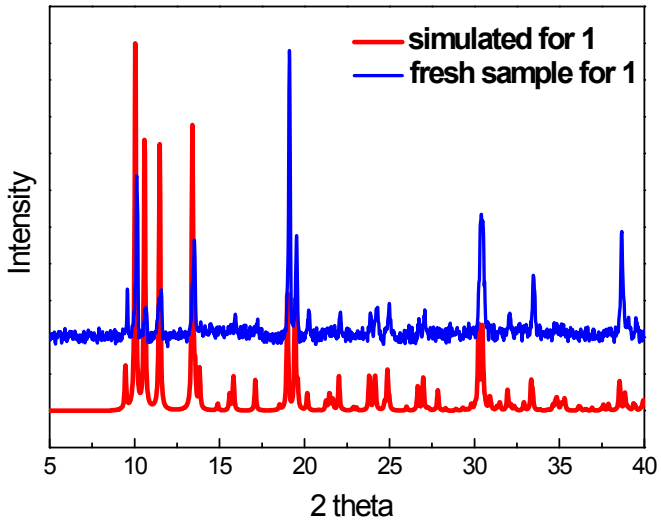

Figure S2 XRD spectra of 1

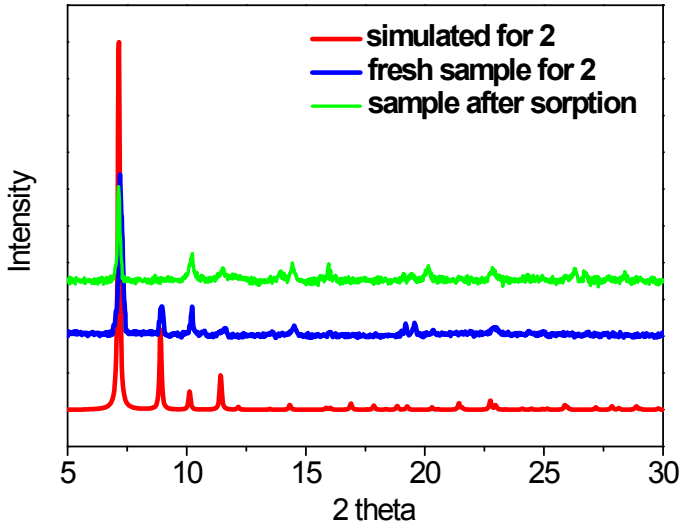

Figure S3 XRD spectra of 2

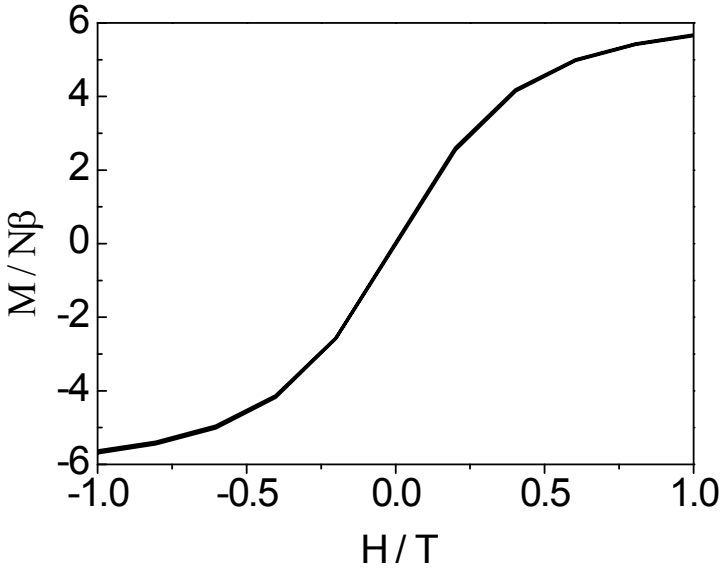

Figure S4. the hysteresis of 1

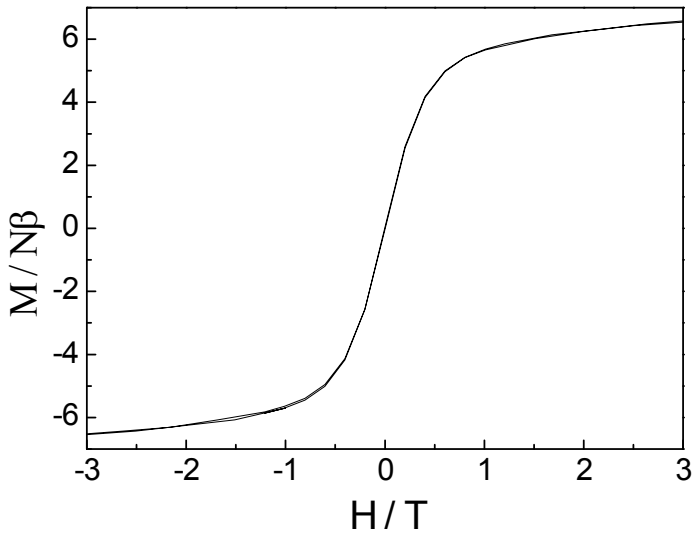

Figure S5. the hysteresis of 2

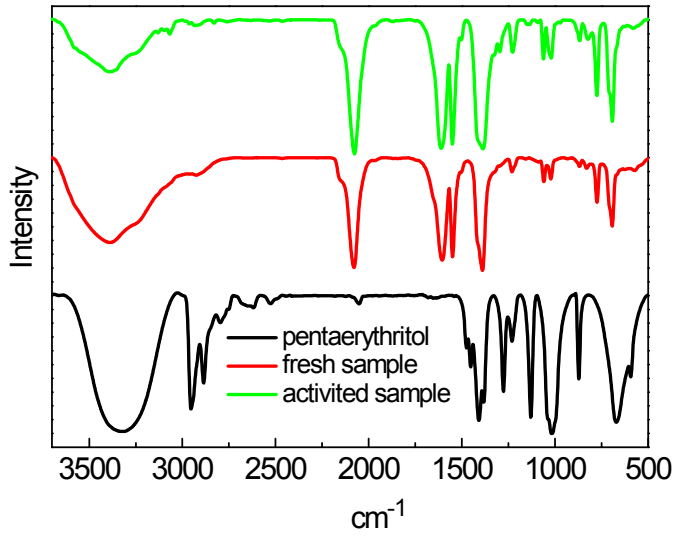

Figure S6. ir spectra of pentaerythritol, fresh sample and activated sample of 1.

The fitting of magnetism of 1:

$$\chi = \frac{N\beta^2 g^2 A}{4kTB}$$

Where A = 1+exp(2J/*k*)+10*exp(3J/*k*)

B = 1+exp(2J/*k*)+2*exp(3J/*k*)