Structural diversities and magnetic properties of azide-containing coordination polymers based on flexible tetra-pyridinate ligands

Fan Yu,[a,*] Mi Xiang,[a] Ai-hua Li,[a] Yu-min Zhang,[a] Bao Li[b,*]

[a] Key Laboratory of Optoelectronic Chemical Materials and Devices of Ministry of Education,School of Chemical and Environmental Engineering, Jianghan University, Wuhan 430056, PR China

[b] School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan, Hubei 430074, PR China

Experimental sections

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). The ligand TPOM and TPOM2 were synthesized by a literature method.[1] 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 low temperature heat capacity had been measured by PPMS.

Synthesis of $[Mn_3(TPOM)_3(N_3)_6(H_2O)_6]_n$ (1). A mixture of NaN_3(0.2 mmol), $Mn(NO_3)_2{\cdot}4H_2O$ (0.2 mmol) and TPOM (5.5mg, 0.025 mmol) was dissolved in 8 mL of CH_3OH and H_2O with the ratio of 1:1 in a vessel . The mixture was stirred at room temperature for 30 min, and then heated at 80 ℃ for 6 hour. The final mixture was stand at room temperature for two day, and Large bulk colorless crystals were obtained from the filtrate. Yield of the reaction was ca. 25% based on TPOM. Anal. Calcd for $C_{75}H_{84}Mn_3N_{30}O_{18}$: H 4.56%, C 48.47%, N 22.61%; found H 4.12%, C 47.96%, N 22.22%. IR (KBr, cm-1): 3467, 2056, 1601, 1571, 1488, 1435, 1277, 1249, 1101, 1002, 754.

Synthesis of [Ni(TPOM)(N_3)$_2$]$_n$ (2). A mixture of NaN_3(0.2 mmol), $Ni(NO_3)_2 \cdot 6H_2O$ (0.1 mmol) and TPOM (5.5mg, 0.025 mmol) was dissolved in 8 mL of CH_3OH and H_2O with the ratio of 1:1, and was stirred at room temperature for 30 min. The final mixture was placed in a Parr Teflon-lined stainless steel vessel (25mL) under autogenous pressure and heated at 110℃ for 2 days. Block-like crystals were obtained, and crystals were filtered off, washed with mother liquid, and dried under ambient conditions. Yield of the reaction was ca. 45% based on TPOM. Anal. Calcd for **$C_{25}H_{24}Ni_2N_{16}O_4$**: H 3.31 %, C 41.14%, N 30.7% ; found H 4.01 %, C 40.76%, N 30.23%. IR (KBr, cm-1): 3436, 2059, 1608, 1506, 1419, 1303, 1203, 1025, 817.

Synthesis of $[Mn(TPOM2)_2(N_3)_2(H_2O)_3(CH_3OH)_4]_n$ **(3).** The synthesis process is very similar to **1** except for TPOM2. Yield of the reaction was ca. 30% based on TPOM2. Anal. Calcd for dyhydrated $C_{51}H_{58}MnN_{14}O_{12}$: H 5.25%, C 54.99%, N 17.60%; found H 5.85%, C 54.11%, N 17.99%. IR (KBr, cm-1): 3462, 2057, 1608, 1573, 1486, 1431, 1272, 1243, 1100, 1003, 756.

Synthesis of [Co(TPOM2)(N_3)$_2$]$_n$ (4). The synthesis process is very similar to **2** except for $Co(NO_3)_2 \cdot 6H_2O$ and TPOM2. Yield of the reaction was ca. 35% based on TPOM2. Anal. Calcd for $C_{25}H_{24}Co_2N_{16}O_4$: H 3.31%, C 41.11%, N 30.68%; found H 3.91%, C 41.02%, N 29.72%. IR (KBr, cm-1): 3440, 2064, 1602, 1573, 1481, 1434, 1302, 1155, 1101, 1012, 756.

X-Ray Structural Determination. X-ray diffraction data of **1** (0.3 × 0.2 × 0.2 mm), **2** (0.1 × 0.1 × 0.05 mm), **3** (0.3 × 0.2 × 0.2 mm) and **4** (0.3 × 0.25 × 0.20 mm) were collected on Oxford Gemini S Ultra diffractometer using Mo-$K\alpha$ (λ = 0.71073 Å) radiation at room temperature, excepted for 4 with Cu 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 leastsquares procedure based on F^2 values.[2] The hydrogen atom positions were fixed geometrically at calculated distances and allowed to ride on the parent atoms. The method of *SQUEEZE* in *PLATON* was carried out in the final crystal resolutions for **3** and **4**.[3] The cavity in 4 should be occupied y

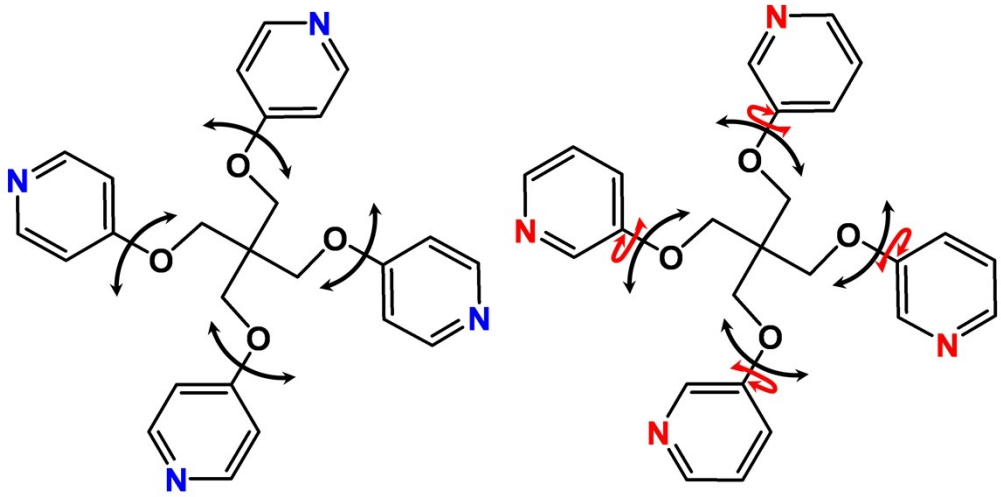
methanol and water molecules. CCDC-994432 (1), CCDC-994433 (2) , CCDC-994434 (3) and CCDC-994435 (4) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Reference:

(1) Ryan, P. E.; Lescop, C.; Laliberté, D.; Hamilton, T.; Maris,T. ; Wuest, J. D. *Inorg. Chem.* **2009**, *48*, 2793.

(2) (a) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, *32*, b115-119; b) G. M. Sheldrick, *SHELXL-97; Program for refinement of crystal structures.* University of Göttingen, Göttingen, Germany, **1997**.

(3) A. L. Spek, PLATON, Utrecht University, Utrecht, The Netherlands, 1998.



Scheme S1. the illustration of the flexibilities of TPOM and TPOM2.

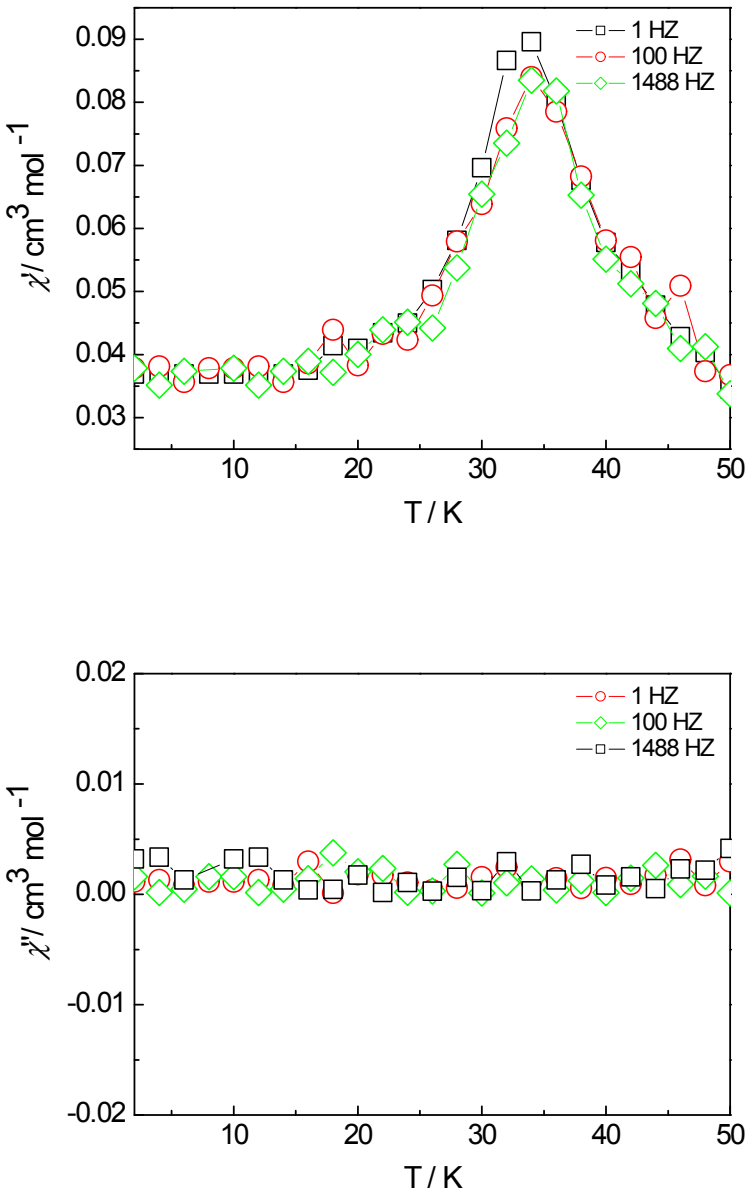


Figure S1. the in-phase and out-of-phase ac susceptibility for 2 in zero dc and 3 Oe ac applied field.

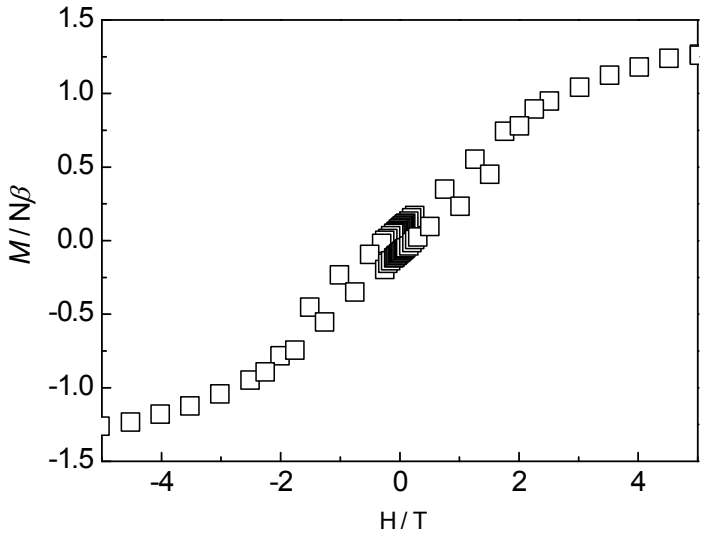


Figure S2. The hysteresis of **2** at 2.0 K.

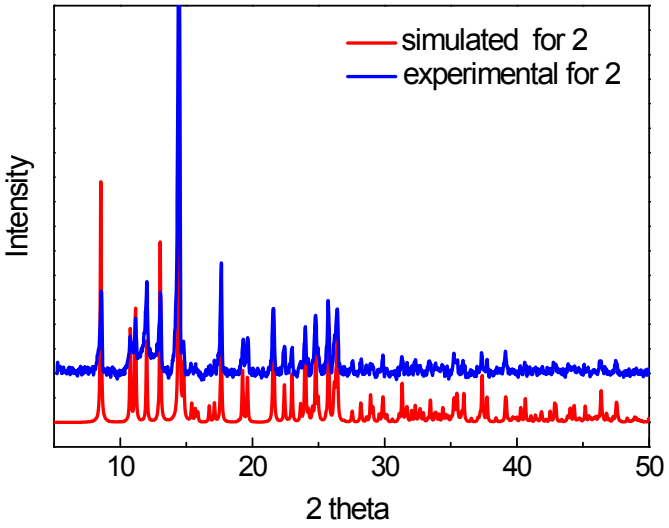


Figure S3. XRD spectra for 2

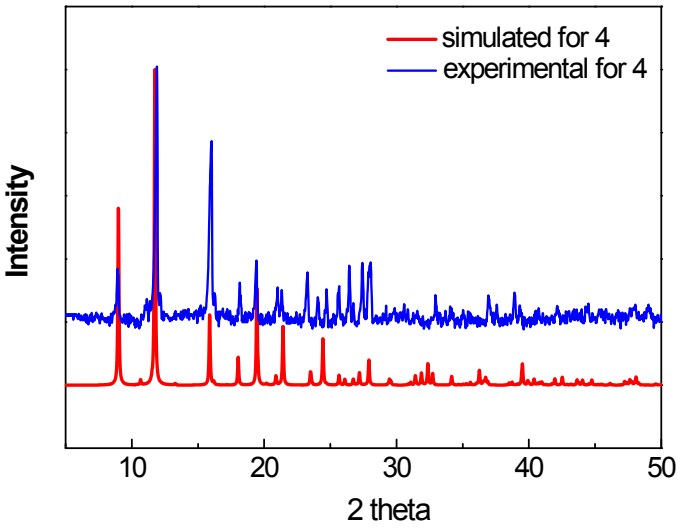


Figure S4. XRD spectra for 4

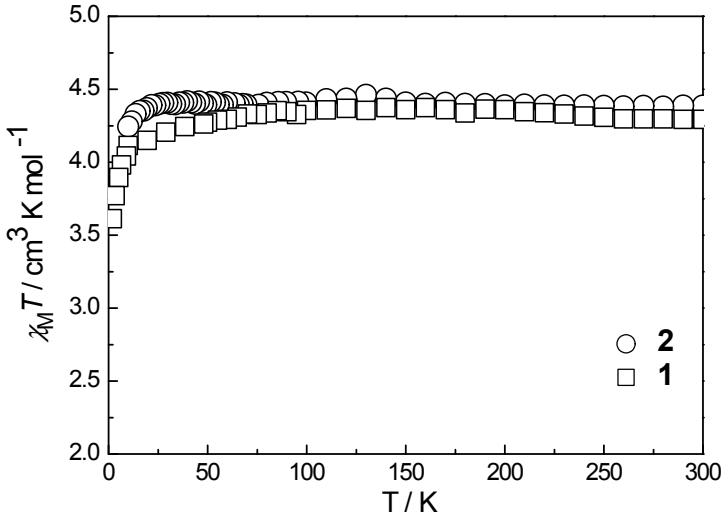


Figure S5. χ_MT and χ_M versus T plots of **2** in the temperature range of 2-300 K under 1 kOe.

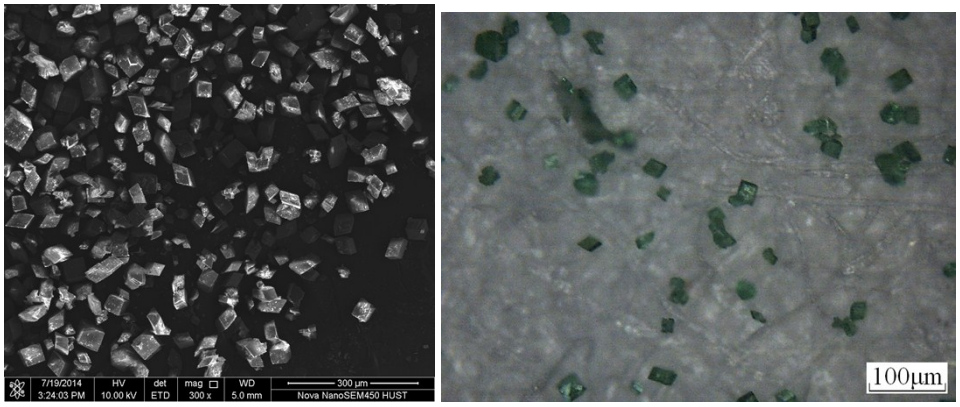


Figure S6. SEM and color-photo for 2.

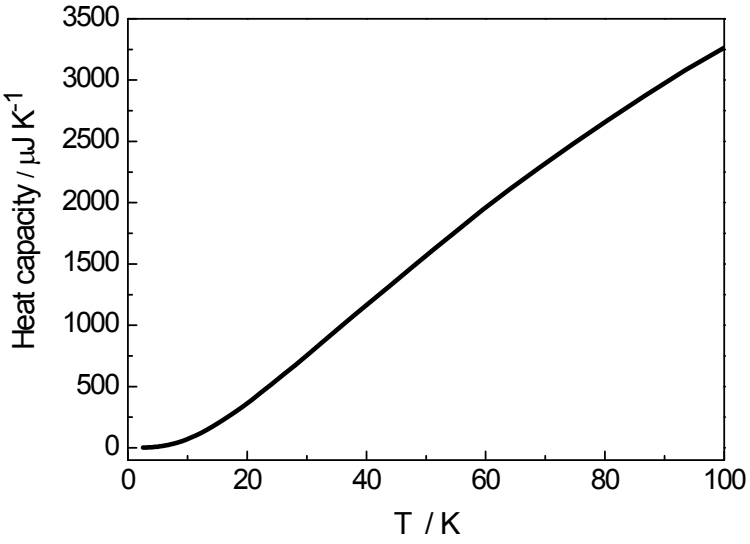


Figure S7. the low temperature heat capacity of 2 by utilizing the PPMS.