Supporting materials

Structural interconversion between a chain polymer and two-dimensional network accompanied by tunable magnetic properties

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1. General Information

2-hydroxy-4,6-dimethylpyrimidine (purity: 98%) was purchased from Jin Tan Hunter Chemical Co., Ltd. Other chemical reagents, which were of A.R. grade and used without further purification, were obtained from China National Medicines Corporation Ltd. The elemental analysis(C, H, N) was performed using a Vario EL III CHNOS elemental analyzer. The PXRD were measured by PANalytical X'Pert Pro diffractometer. FT-IR spectra (KBr pellets) were recorded on a Bomen MB-102 FT-IR spectrometer. Thermogravimetric analysis was performed with a Mettler Toledo TGA/SDTA 851^e analyzer. The magnetic data were measured using a Quantum Design MPMS-XL5 SQUID magnetometer.

The structure data were collected on a Rigaku Mercury CCD diffractometer for **1**, and a Rigaku 724 CCD diffractometer for **2** with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at room temperature. All absorption corrections were performed by using the multi-scan method and the structures were solved by direct methods and refined on F^2 by full-matrix least-squares methods using the SHELXL-97 program package. Non-hydrogen atoms were treated anisotropically. Hydrogen atoms bonded to the carbon atoms of the hpdc ligands in **1** and **2** were placed in their geometrically generated positions. The hydrogen atom of hydroxide ion in **1** was located from the difference Fourier map, while the hydrogen atom of hydroxide ion in **2** and all hydrogen atoms of water molecules were not found from Fourier maps and were not included in the refinement.

2. Synthesis

2-hydroxypyrimidine-4,6-dicarboxylic acid (H_3hpdc): This compound was synthesized by oxidizing 2-hydroxy-4,6-dimethylpyrimidine with $KMnO_4$ in aqueous solution according to the general experimental method (B. R. Wang, *The Reactions in Organic Synthesis*, Science Press, Beijing, 1981 (in Chinese).

[Cu_2(hpdc)(OH)(H_2O)$_4$]·H_2O: A solution 12 mL of H_3hpdc 18.4 mg (0.1 mmol) was adjusted to pH = 7 by 2 M NaOH solution, then $CuCl_2$·5H_2O (38 mg, ca. 0.2 mmol) was added to the solution and stirred for 10 min at room temperature. The final mixture was filtered and the filtrate was allowed to stand at room temperature for slow evaporation. Green block crystals were obtained in

30% yield on the basis of copper. Anal. Calcd. for $C_6H_{12}N_2O_{11}Cu_2$: C, 17.36; H, 2.91; N, 6.75. Found: C, 17.37; H, 2.76; N, 6.73%.

[Cu_2(hpdc)(OH)(H_2O)]: An aqueous solution 6 mL of H_3hpdc 18.4 mg (0.1 mmol) was adjusted to pH = 8 by 2 M NaOH solution, then $CuCl_2{\cdot}5H_2O$ (38 mg, ca. 0.2 mmol) was added and stirred for 10 min. The mixture was transferred to a Teflon-lined stainless steel vessel and kept at 160 °C for 72 h and then cooled to room temperature within 60 h. Blue flake crystals of **2** was obtained (Yield > 30%). Anal. Calcd. for $C_6H_4N_2O_7Cu_2$: C, 21.00; H, 1.17; N, 8.16. Found: C, 20.96; H, 1.09; N, 8.10%.

3. The crystallographic information

Crystal data for 1: $C_6H_{12}Cu_2N_2O_{11}$, M = 415.26, monoclinic, space group $P2_1/c$, a = 6.9264(11), b = 18.236(3), c = 10.1180(15) Å, β = 96.601(12)°, V = 1269.5(4) $Å^3$, T = 293(2) K, Z = 4, D_c = 2.173 g cm^{-3}, μ = 3.413 mm^{-1}. F_{000} = 832, GOF = 1.070, a total of 9493 reflections were collected, 2875 of which were unique (R_{int} = 0.0480). R_1 = 0.0463, wR_2 = 0.1078, for 194 parameters and 2193 reflections with $I > 2\sigma(I)$. For **2:** $C_6H_4Cu_2N_2O_7$, M = 343.19, monoclinic, $P2_1/c$, a = 4.9845(9), b = 9.456(2), c = 18.431(5) Å, β = 90.803(15)°, V = 868.6(3) $Å^3$, T = 293(2) K, Z = 4, D_c = 2.624 g cm^{-3}, μ = 4.926 mm^{-1}, F_{000} = 672, a total of 6682 reflections were collected, 1924 of which were unique (R_{int} = 0.0423). GOF = 1.109, R_1 = 0.0475, wR_2 = 0.1643 for 154 parameters and 1792 reflections with $I > 2\sigma(I)$.

4. Structural drawing and other characterization data

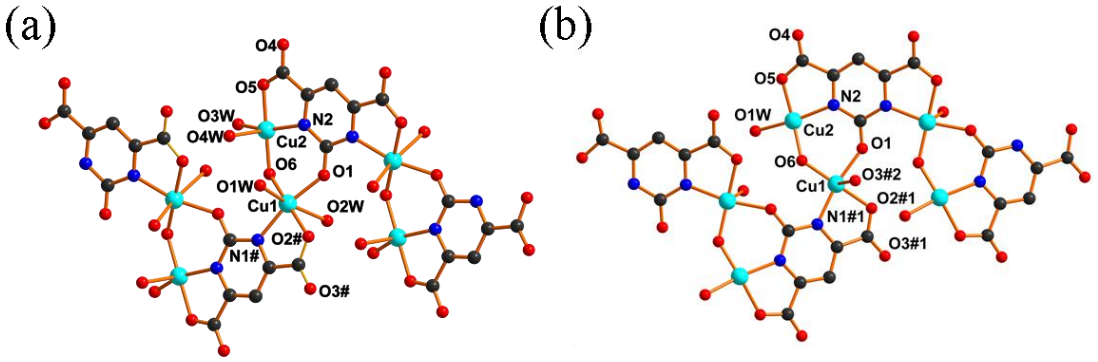

Fig. S1 (a) The coordination environments of the Cu(II) ions and the linkage modes of ligands in **1**. Atoms with “#” are symmetrically generated (#: x, 0.5-y, 0.5+z). **(b)** The coordination environment of Cu(II) ions and the linkage modes of ligands in **2**. Atom with “#1” and “#2” are symmetrically generated (#1: -x, -0.5+y, 0.5-z; #2: -1-x, -0.5+y, 0.5-z), all hydrogen atoms are omitted for clarity.

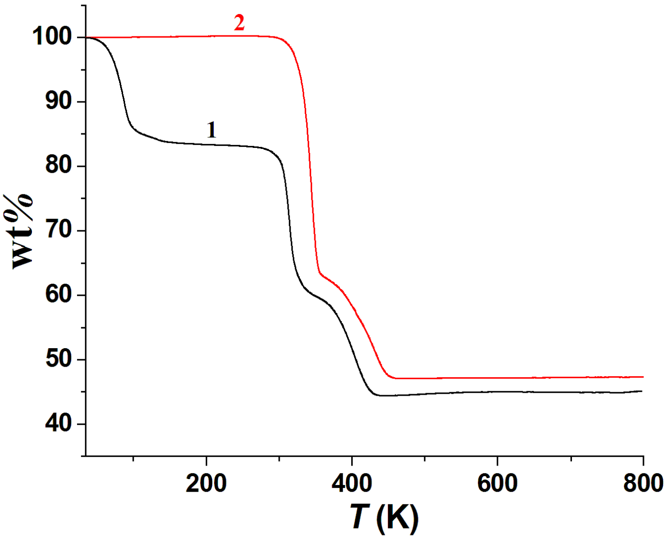

Fig. S2 Thermogravimetric analysis curves of **1** and **2**.

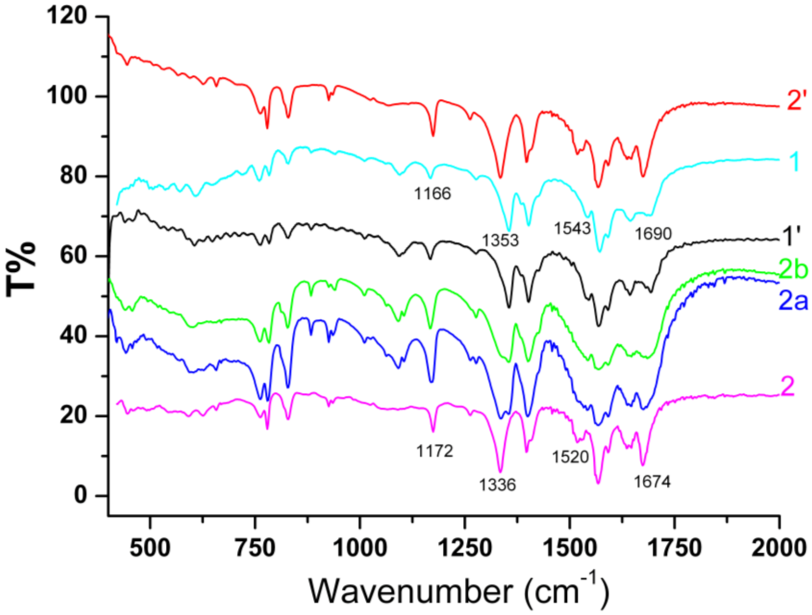

Fig. S3 The IR spectra recorded for the structural interaction between **1** and **2**. 1: single crystal **1**; 2′: Crystals of **1** were heated at 150 ºC in the moist atmosphere; 2: single crystal **2; 2a** and **2b:** powder of **2** immersed in water for 9d and 13d respectively; **1′**: powder of **2** immersed in water for three weeks.