

Structure and Luminescence of Novel 3d-4d-4f Heterometal-organic Framework Based on Double-stranded Helical Motifs

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Physical measurements. Analyses for C, H and N were carried out on a Perkin-Elmer analyzer. The thermogravimetric analyses (under oxygenated atmosphere, heating rate of 5°C/min) for **1-3** were completed on a Labsys NETZSCH TG 209 Setaram apparatus. Luminescence spectra in visible region of **1-3** were recorded by a Varian Cary Eclipse Fluorescence spectrophotometer. Variable-temperature magnetic susceptibility of **1** was measured on a Quantum Design MPMS-7 SQUID magnetometer. Diamagnetic corrections were applied with Pascal's constants for all the constituent atoms.

Preparation of 1-3. A mixture of 0.3 mmol H₃CAM (0.0603 g), 0.1 mmol Co(CH₃COO)₂·4H₂O, 0.1 mmol CdO (0.0128 g), (0.0249 g) 0.1 mmol Ln(OH)₃ and H₂O (10 mL) was placed in 25 mL Teflon reactor at 160°C for 3 days, then slowly cooled to room temperature for 3 days. The products of **1-3** were collected after washing with H₂O and diethyl ether, and the yields for **1-3** based on Ln(OH)₃ are 51%, 35% and 39%, respectively. Anal. Calc. for **1**: C 22.35, H 3.22, N 3.72; found: C 23.10, H 3.05, N 3.41; Anal. Calc. for **2**: C 22.56, H 3.24, N 3.76; found: C 23.15, H 2.99, N 3.34; Anal. Calc. for **3**: C 22.60, H 3.25, N 3.76; C 22.12, H 3.11, N 3.53.

Crystallographic studies and refinement of the crystal structures of 1-3. Diffraction intensity data for single crystals of **1-3** were collected at room temperature on a Rigaku Saturn CCD diffractometer equipped with confocal monochromated MoK α radiation ($\lambda = 0.71070 \text{ \AA}$). The structures were solved by the direct method and refined by the full-matrix least-squares method on F^2 with anisotropic thermal parameters for all non-hydrogen atoms.^{1,2} Hydrogen atoms were located geometrically and refined isotropically. The numbers of disordered water molecules in a molecular motif are 2, 8 and 8, respectively for **1-3**. There are 2, 16 and 16 water H-atoms per formula not determined in **1-3**, respectively. See the CIF file for details.

In the process of refinement, if we set two positions as Co atoms, Co atoms were isotropic; additionally, the color of crystals is red, and then we can not set two positions as Cd atoms only.

We also consider the model of one Co and one Cd atoms, unfortunately, Co and one Cd atoms were isotropic. Combining with the results of Inductively Coupled Plasma (ICP) (Ln:Cd:Co = 1:1:1), we think of the disorder Cd/Co sites. We tried different occupancies many time to determine the occupancies of Cd and Co atoms, according to the U values of Cd and Co and R1 values of refinement, the occupancies of Cd and Co are set at 0.75 and 0.25 or 0.25 and 0.75 for two positions, respectively.

- 1 Sheldrick, G. M. *SHELXS 97, Program for the Solution of Crystal Structures*; University of Göttingen: Germany, 1997.
- 2 Sheldrick, G. M. *SHELXL 97, Program for the Refinement of Crystal Structures*; University of Göttingen: Germany, 1997.

Detailed report on TGA of 1-3. Thermal gravimetric analysis (TGA) was performed on crystalline samples of **1-3** in the range of 25 to 700°C (Figure S3). The TGA results reveal that the weight loss of **1-3** between 25 and 250°C corresponds to the loss of all uncoordinated and coordinated water molecules (calcd. 22.33, 22.54 and 22.58 %).

Supporting figures

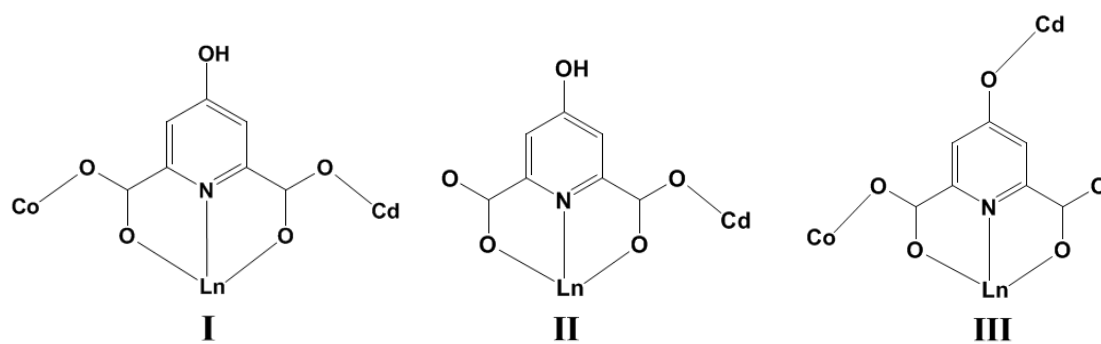


Figure S1. The coordination modes of HCAM²⁻ and CAM³⁻ ligands in 1–3.

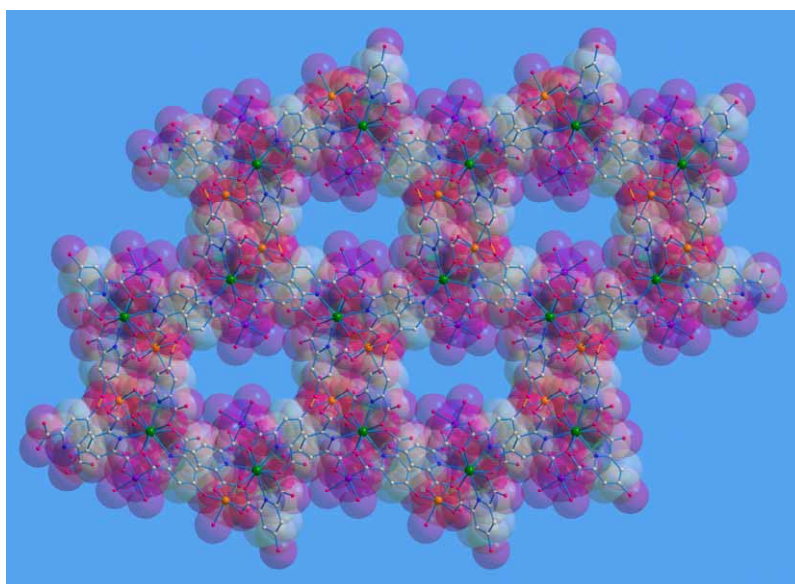


Figure S2 The 3D porous structure formed *via* intermolecular H-bonds (yellow dotted lines) of 1 in superimpose space-filling mode, H atoms are omitted for clarity. Color code: olive, Dy; purple, Co; orange, Cd; red, O; blue, N; gray, C; white, H; dotted lines, hydrogen bonds.

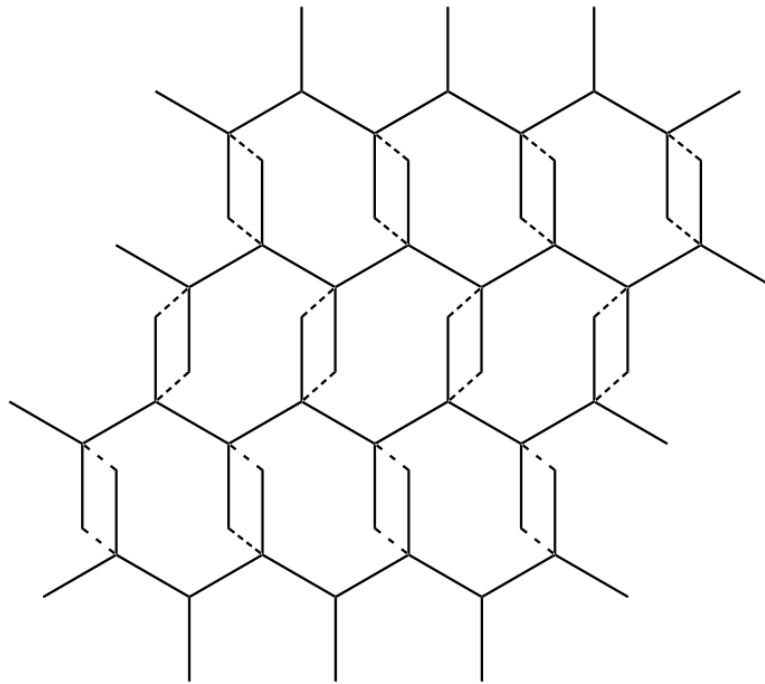


Figure S3. Architectural strategy of 3D framework constructed by 2D layers in **1-3** along *a* direction. Dotted lines represent hydrogen bonding interactions between 2D layers (solid lines).

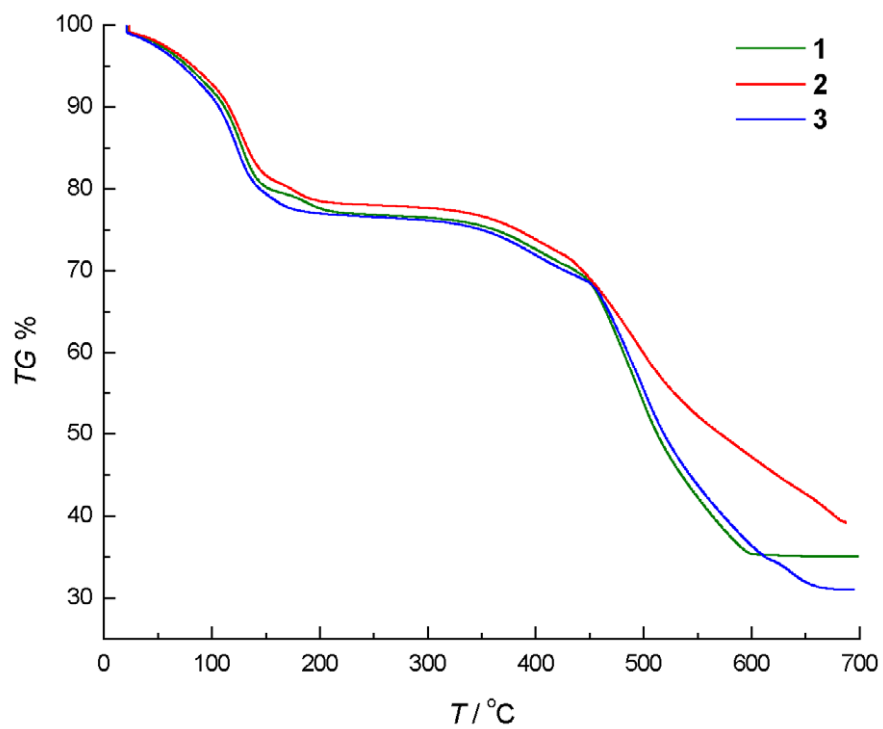


Figure S4. TG diagram of **1-3**.

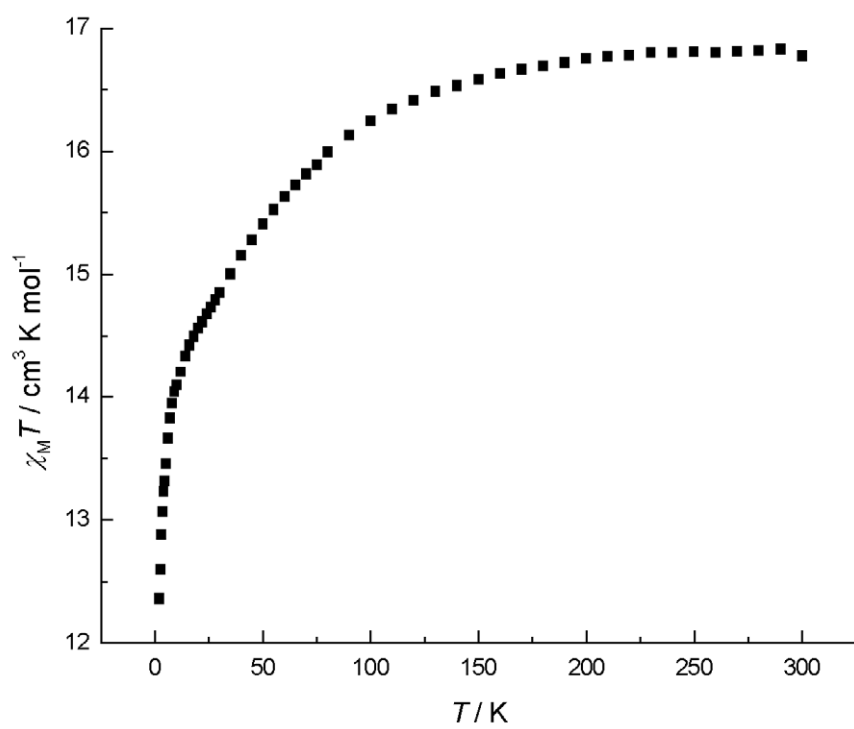


Figure S5. The plot of $\chi_M T$ versus T for **1**.