

Supporting Information for

Reaction Vessel- and Concentration-induced Supramolecular Isomerism in Layered Lanthanide-Organic Frameworks

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General Information. Commercially available reagents were used as received without further purification. Elemental analyses (C, H, N) were performed with a PerkinElmer 240 elemental analyzer. Thermal gravimetric analysis (TGA) was performed under N₂ on a PerkinElmer TGA 7 instrument.

Synthesis of 1. H₂L¹ (12.0 mg, 0.03 mmol), 1,3-dpp (4.8 mg, 0.024 mmol) and La(NO₃)₃·6H₂O (23.4 mg, 0.054 mmol) were dissolved in 15 mL of dmf, EtOH, and H₂O (v/v, 5:2:1) in a 20 ml Teflon-lined steel bomb. Then the Teflon-lined steel bomb was left at 90 °C for 3 days. The resulting colorless crystals were collected in 50%

yield. Elemental analysis calcd (%) for **1**: C 52.50, H 5.70, N 3.22; found: C 52.30, H 5.97, N 3.90 %. Selected IR peaks (cm^{-1}): 3463 (s), 2943 (w), 1650 (s), 1599 (s), 1387 (s), 1115 (m), 1054 (m), 842 (m), 740 (m).

Synthesis of complex 2. H_2L^1 (1.2 mg, 0.003 mmol), 1,3-dpp (0.5 mg, 0.0024 mmol) and $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (2.3 mg, 0.0054 mmol) were dissolved in 1.5 mL of dmf, EtOH, and H_2O (v/v, 5:2:1) in a glass tube. The glass tube was sealed and left at 90 °C for 3 days. The resulting colorless block crystals were collected in 60% yield. Elemental analysis calcd (%) for **2**: C 52.64, H 4.76; found: C 52.87, H 4.34. Selected IR peaks (cm^{-1}): 3438 (s), 2936 (w), 1650 (s), 1591 (s), 1531 (s), 1378 (s), 1106 (m), 1054 (m), 842 (m), 731 (m).

Synthesis of complex 3. H_2L^1 (4 mg, 0.01 mmol), 1,3-dpp (1.6 mg, 0.008 mmol) and $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (7.8 mg, 0.018 mmol) were dissolved in 1.5 mL of dmf, EtOH, and H_2O (v/v, 5:2:1) in a glass tube. The glass tube was sealed and left at 90 °C for 3 days. The resulting colorless block crystals were collected in 60% yield. Elemental analysis calcd (%) for **3**: C 52.84, H 5.64, N 3.85; found: C 51.67, H 5.33, N 3.46 %. Selected IR peaks (cm^{-1}): 3336 (s), 2927 (w), 1676 (s), 1591 (s), 1548 (s), 1396 (s), 1054 (m), 859 (m).

Crystal structure determination of 1-3: Single-crystal X-ray diffraction was performed using a Bruker Apex II CCD diffractometer equipped with a fine-focus sealed-tube X-ray source (Mo $\text{K}\alpha$ radiation, graphite monochromated). Structures were solved by direct methods using SHELXTL and were refined by full-matrix least-squares on F^2 using SHELX-97. Non-hydrogen atoms were refined with

anisotropic displacement parameters during the final cycles. Hydrogen atoms were placed in calculated positions with isotropic displacement parameters set to $1.2 \times U_{\text{eq}}$ of the attached atom.

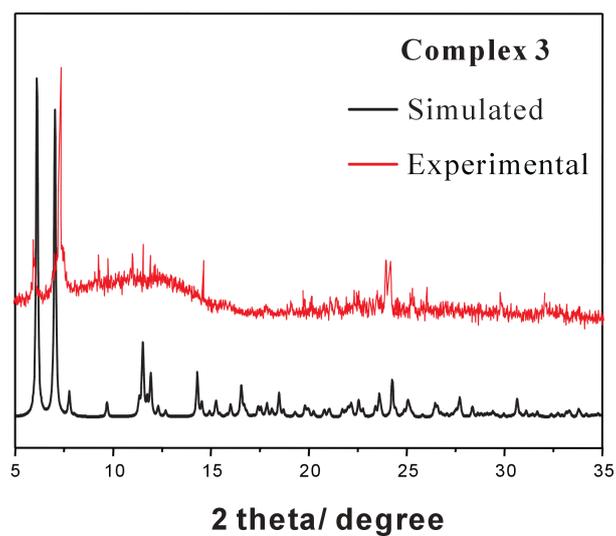
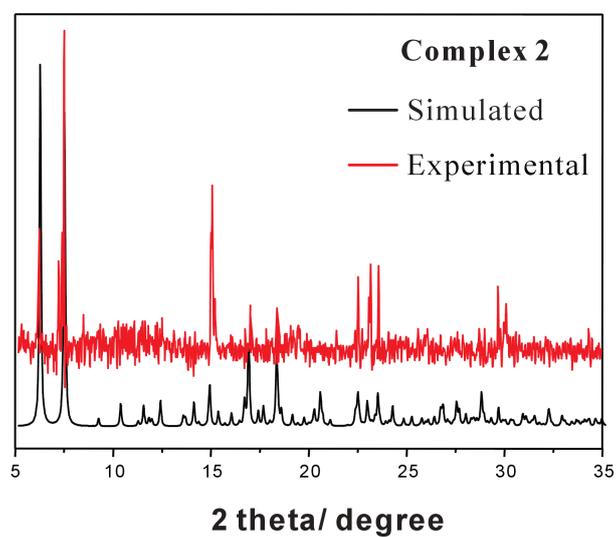
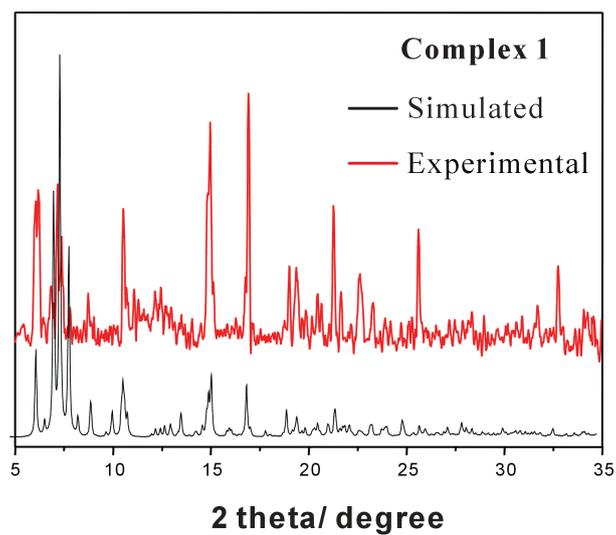


Figure S1 The powder XRD patterns and the simulated one from the single-crystal diffraction data for 1-3

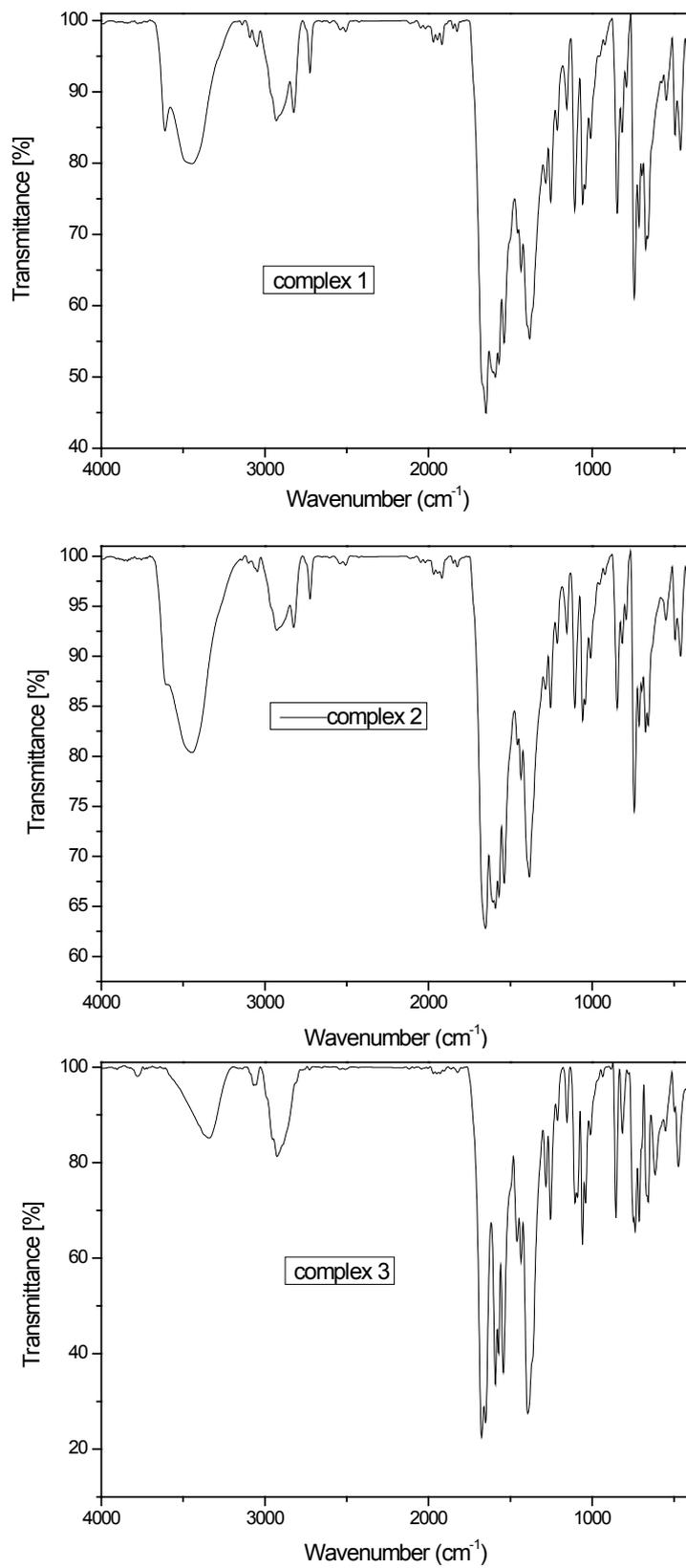


Figure S2: IR spectra of 1-3

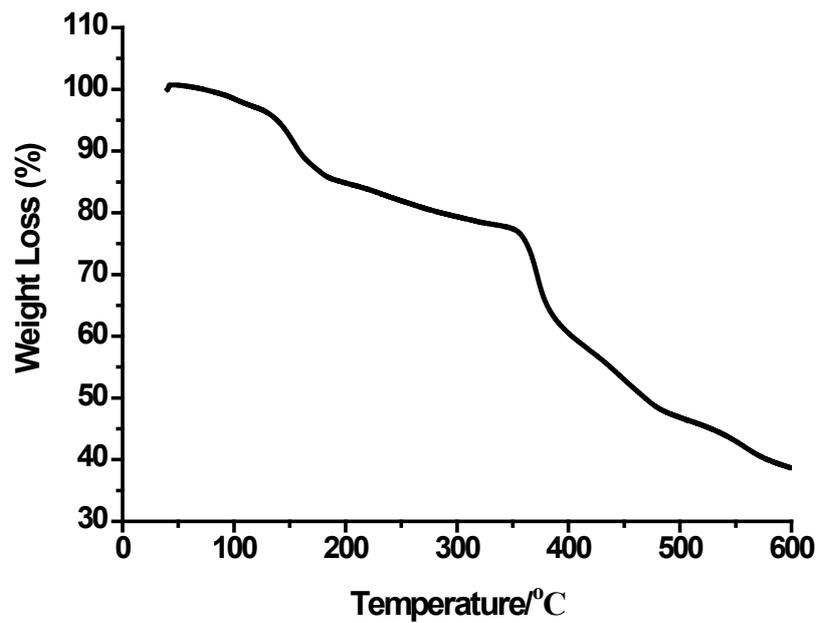


Figure S3. TGA for 1.

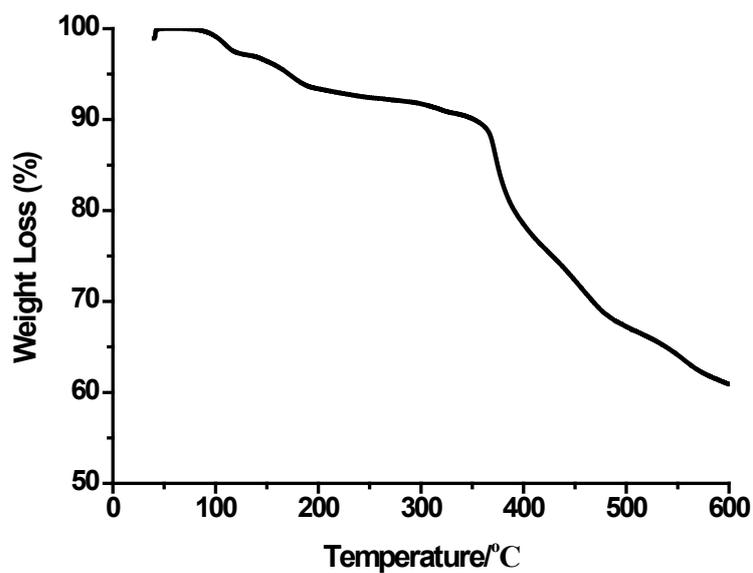


Figure S4 TGA for 2.

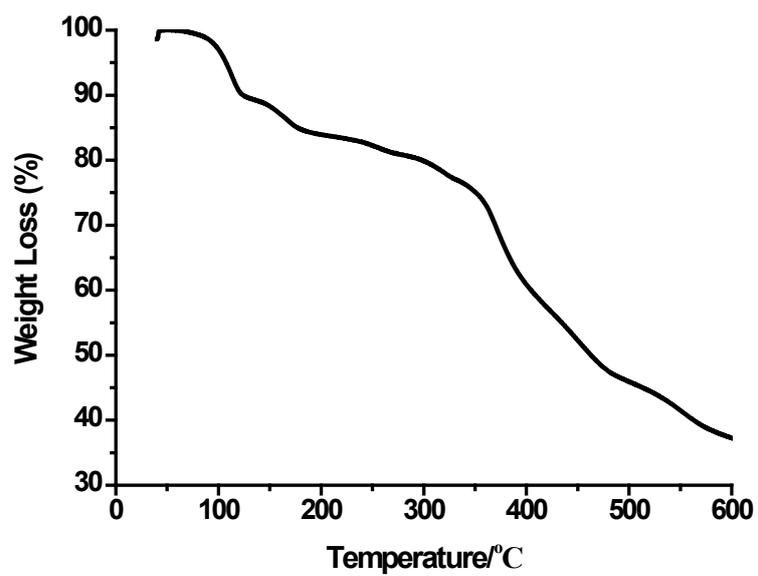


Figure S5. TGA for 3.