Supporting Information

Solvent-induced reversible single-crystal-to-single-crystal transformations observed in lanthanon complexes

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Synthesis of 1-2.

A C_2H_5OH/H_2O solution (10 mL, 5:5) of $DyCl_3$ (1 mmol), phen (1 mmol), HL (3 mmol), and Na_2CO_3 (1.5 mmol) in the ratio 1:1:3:1.5 was sealed in a Teflon reactor, and heated at 210 ˚C for 3 days, and then cooled to room temperature at 3 ˚C/h. Subsequently, colorless crystals were obtained in 82% yield based on Dy. Elemental analysis (%) for **1**: calc: C 57.32, H 4.16, N 3.61; found: C 57.40, H 4.19, N 3.67. Compound **2** could be obtained *via* two methods. The first route was by means of calcination of **1** at 160 °C under vacuum for 24 h. Elemental analysis (%): calc: C 57.79, H 3.91, N 3.74; found: C 57.83, H 3.86, N 3.77. The crystal structure was solved by single crystal X-ray diffraction and the phase purity of the bulk samples are confirmed by XRD studies. The other route was *via* hydrothermal synthesis. A water solution (10 mL) of $DyCl_3$ (1 mmol), phen (1 mmol), HL (3 mmol), and Na_2CO_3 (1.5 mmol) in the ratio 1:1:3:1.5 was sealed in a Teflon reactor, and heated at 210 ˚C for 3 days, and then cooled to room temperature at 3˚C/h. Subsequently, colorless crystals were obtained in 84% yield based on Dy. Elemental analysis (%): calc: C 57.79, H 3.91, N 3.74; found: C 57.74, H 3.95, N 3.69. The crystal structure was solved by single crystal X-ray diffraction, and the result is the same as observed in the phase obtained through calcination. Immersion of the guest-free phase **2** in C_2H_5OH/H_2O solution generated the guest-containing phase **1**. Elemental analysis (%) for it: calc: C 57.32, H 4.16, N 3.61; found: C 57.38, H 4.10, N 3.66. The transformation from **2** to **1** is confirmed by the determination of the unit cell of five single crystals selected randomly, which reveals that the unit cell of these single crystals after the above operation is the same as observed in **1**.

Crystallography. Single crystals with suitable dimensions were mounted on glass fibers using Nujol. All measurements were made on a Bruker SMART CCD area detector with a graphite monochromated Mo-Kα radiation (λ =0.71070Å). The structures were solved *via* direct methods by SHELXL-97.[18] All non-hydrogen atoms in the structure were refined anisotropically. Hydrogen atoms were introduced as fixed contributors. As our single crystal X-ray diffraction has no *in situ* function to carry out structure determination for the same single crystal of **1** and its desolvated phase of **2** (through calcination), thus, we randomly selected two single crystals from the desolvated phase to carry out single crystal X-ray diffraction. The results are described as ‘2(calcination).cif’

and '2_1(calcination).cif'. Further, to confirm phase purity of the bulk samples of the desolvated phase (through calcination), XRD studies are tested. Moreover, we also determined the crystal structure of **2** that is synthesized *via* hydrothermal reaction, and the result is described as '2.cif'.

Materials and methods: All reagents were obtained from commercial sources and used as received without further purification. Elemental analyses for C, H and N were performed by using an Elementary Vario EL analyser. Magnetic susceptibility measurements were conducted with a Quantum Design SQUID magnetometer (MPMS XL-7) in the temperature range of 2.7 to 300 K at dc = 1000 Oe. The samples used here to carry out magnetic measurement is **1**, synthesized from solvo(hydro)thermal reaction, **2**, prepared from calcination. AC measurements were performed at 2.9-10 K under various frequencies with an ac field amplitude of 3 Oe. Polycrystalline samples embedded in liquid paraffin were measured. Experimental data were corrected for the sample holder and liquid paraffin and for the diamagnetic contribution calculated from Pascal constants.

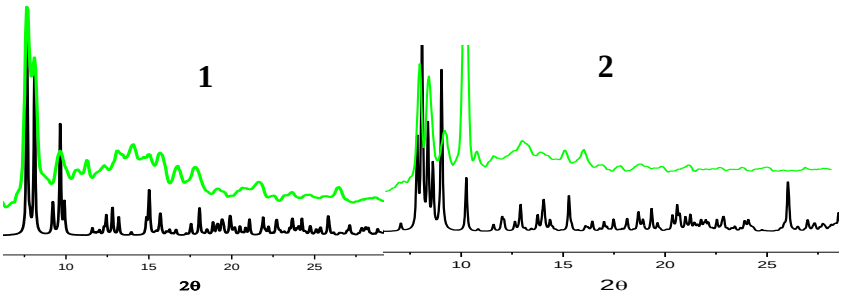

Figure S1. The experimental XRD pattern of bulk samples (green) and the calculated XRD pattern from single crystal X-ray diffraction data (black) for **1** and **2**, respectively. Note that the XRD pattern is made on the samples of **1** synthesized from solvo(hydro)thermal reaction, **2** prepared from calcination.

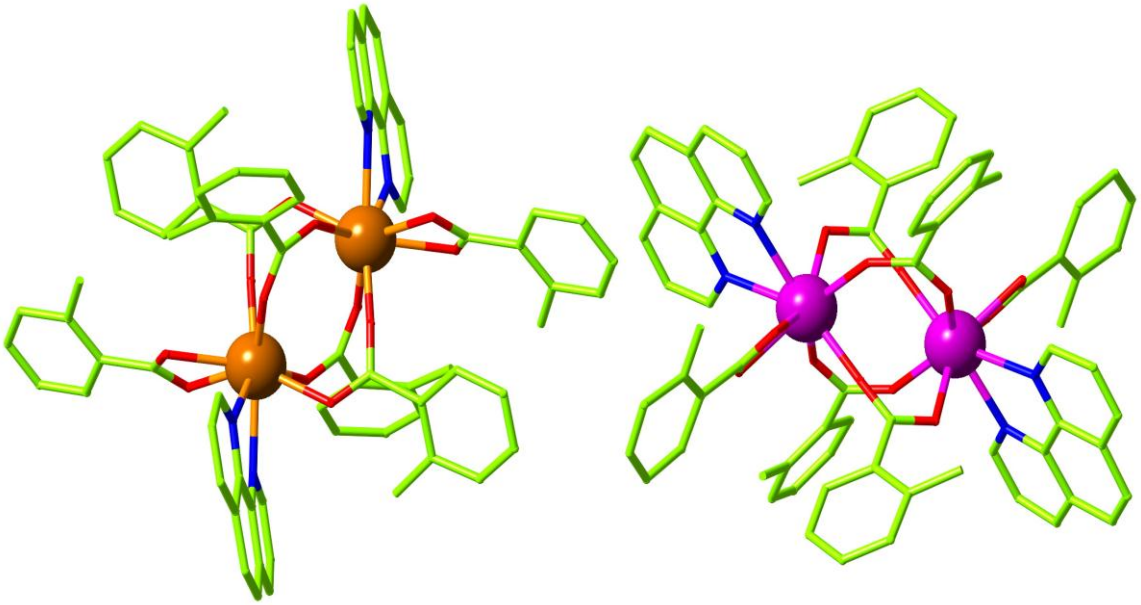

Figure S2. The two crystallographically distinct clusters in **1**; Dy1 atoms are shown in pink, while Dy2 atoms are shown in orange.

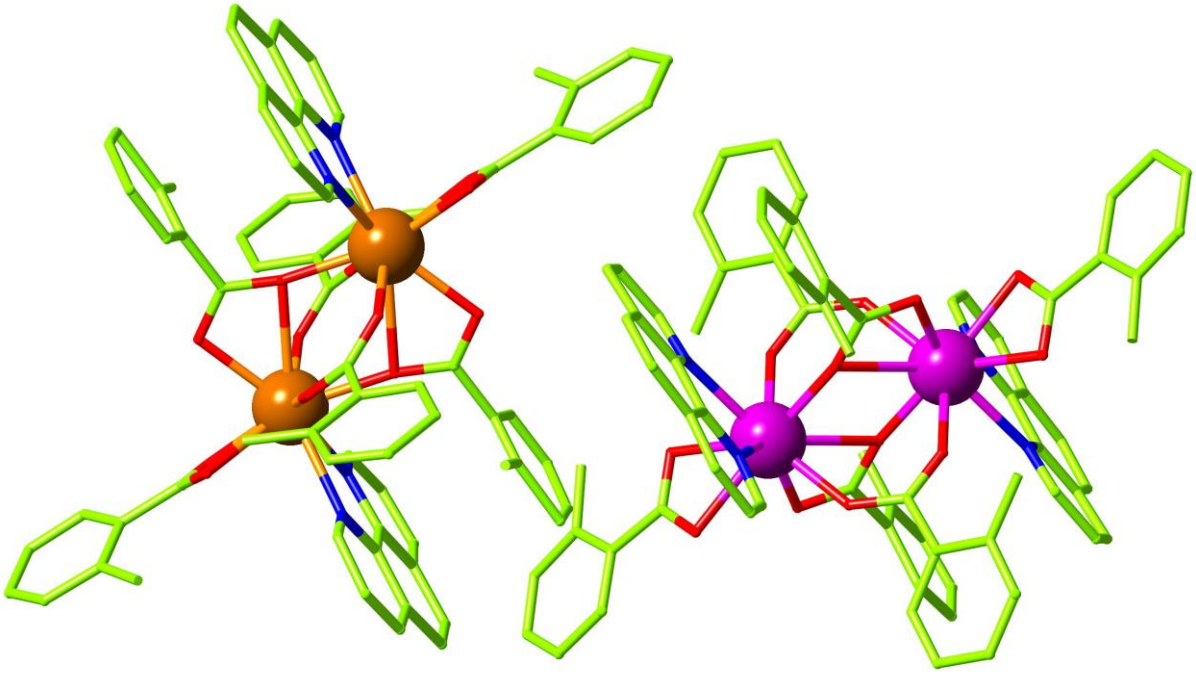

Figure S3. The two crystallographically distinct clusters in **2**; Dy1 atoms are shown in pink, while Dy2 atoms are shown in orange.