A 3-dimensional coordination polymer with a fluorite structure

constructed from a semi-rigid tetrahedral ligand

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Supplementary Materials

1. Materials and Methods
Ligand tetrakis[4-(carboxyphenyl)oxamethyl]methane acid (H₄L) was prepared according to the literature (Macromolecules, 1999, 32, 4819–4825). All other reagents and solvents were commercially purchased and used without further purification. Infrared spectra were obtained on a Bruker Vector 22 spectrophotometer with KBr pellets in the 4000 – 400 cm⁻¹ region. Elemental analyses for C, H, and N were performed on a CHN-O-Rapid analyzer and an Elementar Vario MICRO analyzer. Magnetic susceptibility measurements for the crystalline samples were obtained with the use of a Quantum Design MPMS-XL7 SQUID magnetometer in the temperature range 1.8–300 K. Thermogravimetric analysis (TGA) was carried out in a nitrogen stream using Pysis 1 DTA equipment with a heating rate of 20 °C/min. Powder X-ray diffraction (PXRD) patterns were collected in the 2θ = 5–30° range with a scan speed of 0.2 sec/deg. on a Bruker D8 diffractometer with Cu Kα radiation equipped with a LynxEye detector at room temperature.

Single-crystal X-ray diffraction analysis. The suitable crystals of 1 with the dimensions ca. 0.20 × 0.18 × 0.18 mm³ were selected for single crystal X-ray diffraction and the data were collected at 291 K on a Bruker Smart CCD diffractometer with a graphite-monochromatic Kα radiation (λ = 0.71073 Å) from an enhanced optic X-ray tube. Data reductions and absorption corrections were performed using the SAINT and SADABS software packages, respectively. The structure was solved by direct methods and refined by full matrix least-squares methods on F₂ using the SHELXS-97 and SHELXL-97 programs, using atomic scattering factors for neutral atoms. Hydrogen atoms were placed in calculated positions and refined as riding atoms with a uniform value of Uiso. In the asymmetric unit, the PLATON/SQUEEZE program was used to deal with the disordered guest DMF and H₂O molecules. The final structural model was refined without the guest molecules. The identity and number of the guest molecules were determined from the IR spectra, elemental analyses, and TGA data.
Fig. S1. An ORTEP drawing of the asymmetric unit (except hydrogen) of 1 with ellipsoids at 50% probability.

Fig. S2. PXRD patterns for 1: (a) simulated (black), (b) as-synthesized (red), (c) after kept in air for weeks (green).

Figure S3. The TGA curve of compound 1.