

Supporting Information

3D Metal–Organic Frameworks Incorporating Water-Soluble

tetra-*p*-Sulfonatocalix[4]arene

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Experimental Section

Materials: C4AS was synthesized by literature method [1] and other reagents were purchased from commercial sources and used as received.

Synthesis of 1 and 2: LnCl₃·6H₂O (35 mg, 0.1 mmol, Ln = Nd and Eu) and 1,10-phenanthroline (20 mg, 0.1 mmol) were added to the solution of tetra-*p*-sulfonatocalix[4]arene (50 mg, 0.067 mmol in water of 5 ml) which was firstly adjusted to an acidity of pH~5 by adding tetramethylammonium hydroxide or tetraethylammonium hydroxide. And then the suspension was transferred into a Teflon-lined autoclave (20 ml) and heated to 130 °C in 90 minutes. The autoclave was kept at 130 °C for 4 days and then slowly cooled to 30 °C at about 2 °C/h. A light-yellow single crystal in the mineral quartz shape was obtained and used for the X-ray diffraction determination. Yield: ~10% with respect to C4AS. Due to easy loss of the solvent molecules (followed by the crystal cracking and breaking), no satisfactory results of elemental analyses were obtained.

The X-ray intensity data for **1- 2** were collected on a Bruker SMART APEX CCD diffractometer with graphite-monochromatized Mo-K_α radiation ($\lambda = 0.71073 \text{ \AA}$) operated at 2.0 kW (50 kV, 40 mA). The crystal structures were solved by means of Direct Methods and refined employing full-matrix least squares on F^2 (SHELXTL-97).

[1] Iki, N.; Fujimoto, T.; Miyano, S. *Chem. Lett.* **1998**, *27*, 625-626.