Electronic Supplementary Information

Macroscopic single-crystal tubes assembled with porous supramolecular architecture of water-soluble calixarene and phenanthroline

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Experimental section:

Sodium salt of sulfonylcalix[4]arenetetrasulfonate (Na₅-L) was synthesized by literature method1 and other reagents were commercially available and used as received. TG/DTA measurement was performed in the flow of air using a SDT 2960 simultaneous DSC-TGA instrument (TA instruments). The photoluminescence emission spectra of 3 were recorded with a Hitachi F-4500 spectrophotometer equipped with a 150 W xenon lamp as the excitation source.

Syntheses of compounds 1-3. The syntheses of 1-3 were following the similar procedures. Typically, a suspension of LnCl₃·6H₂O (Ln = Gd, Sm and Tb, 0.2 mmol), 1,10-phenanthroline (0.2 mmol), and Na₅-L (0.1 mmol) in water (10 ml) was transferred into a Teflon-lined autoclave (20 ml) and heated to 130 °C in 100 minutes. The autoclave was kept at 130 °C for 3 days and then slowly cooled to 20 °C at about 4 °C/h. The light-yellow tubular single crystals of 1-3 were carefully isolated and collected for X-ray diffraction determination. Yield: ∼41% with respect to calixarene.

Structure refinement: The large second parameter in WGHT for the non-squeezed data might be attributed to more weak diffraction patterns in the high-angle region and the disordered solvent molecules.

Scheme S1 Scheme of sulfonylexil-[4]arenetetrasulfonate

Fig. S1 A view of the extended structures of 1-3 showing some calixarene bilayers separated by the phenanthroline columns (different bilayers are shown in green and red, respectively).
Fig. S2 One bilayer viewed along a direction perpendicular to the \( a \) axis showing some antiparallel calixarene assemblings separated by 1,10-phenanthroline (the outward and inward locatings of the cone calixarene are shown in green and red, respectively).

Fig. S3 A view of the extended structures showing the grid arrangement of calixarene capsules (upper) and the capsules stacked along the \( a \) axis (bottom).
Fig. S4 Optical images of the products obtained by heating the reactants at 130 °C for 12 (upper), 24 (middle) and 36 (bottom) hours.
Fig. S5 Optical image of some tubular products with a ruler under the beaker showing the length of the tubes being of several millimeters.

Fig. S6 The extended structures viewed along the $b$ axis showing parallel arranging of 1,10-phenanthroline.
Fig. S7 Supramolecular network of compounds 1-3 showing H-bondings (in yellow) and π-π interactions (in blue) among calixarenes and phenanthrolines.
Fig. S8 TG/DTA curves of 1 measured in the flow of air. The residual weight percentage of 15.04% at 800 ºC is comparable with the calculated one (15.19 % for Gd₂(SO₄)₃).

Fig. S9 Room temperature solid-state emission spectrum of 3 excited at 373 nm showing the characteristic emission bands of Tb³⁺.