Supplementary Information

1D Infinite Silver(I) Chains Reside in the Big Cavities Built by the Novel p-Sulfonatocalix[4]arene-Trisilver Blocks†

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Materials and Measurements

*p*-sulfonatocalix[4]arene was prepared according to literature methods,\textsuperscript{S1} while other chemicals were of reagent-grade quality obtained from commercial sources and used without further purification. Elemental analysis was performed with a German Elementary Varil EL III instrument. IR spectra was recorded in the range 4000–400 cm\(^{-1}\) with a Magna 750 FT-IR spectrometer using KBr pellets. TGA analysis was carried out with a Netzsch STA449C unit, at a heating rate of 10 °C min\(^{-1}\) under nitrogen from 30 to 1000 °C. Fluorescent spectra were measured at 293K and 10K with an Edinburgh FL-FS90 TCSPC system. The power X-ray diffraction (XRD) was recorded by a RIGAKU-DMAX2500 X-ray diffractometer using Cu K\(\alpha\) radiation (\(\lambda = 0.154\) nm) at a scanning rate of 5°/min for 2\(\theta\) ranging from 5° to 65°.

Synthesis of the Complex 1

*p*-sulfonatocalix[4]arene (0.1 mmol, 83mg) and AgNO\(_3\) (0.2 mmol, 34mg) were mixed in a distilled water (12 mL) solution. Ligand 2, 2\(^{-}\)-bipyridine (0.2 mmol, 32mg) was added to the above solution. The mixture was stirred for 3 hours and then heated to be boiled with stirring. Slow concentration of the filtrate at room temperature for several days and then colorless block crystals of complex 1 (40mg) were obtained in 53% yield based on 2, 2\(^{-}\)-bpy.

Anal. Calcd. for complex 1: calcd. C, 46.12; H, 3.84; N, 7.34; O, 18.17. found C, 46.09; H, 3.76; N, 7.29; O, 18.35. IR (KBr disk, \(\nu\) cm\(^{-1}\)): 3393 (m), 3162 (s), 3077 (s), 1588 (s), 1451 (m), 1436 (s), 1387 (w), 1228 (s), 1144 (s), 1034 (s), 1007 (s), 774 (s), 737 (w), 656 (s), 629 (s), 553 (s), 519 (w).

X-ray Data Collection and Structure Determination

Data collection for 1 was performed on a Rigaku-CCD diffractometer equipped with a graphite monochromated Mo-K\(\alpha\) radiation (\(\lambda = 0.71073\) Å) by using the \(\omega\)-scan mode at 150 K. All absorption corrections were applied using the CrystalClear program.\textsuperscript{S2} The structures were solved by direct
methods, the metal atoms were located from the E-maps, and other non-hydrogen atoms were derived from the successive difference Fourier peaks. The organic hydrogen atoms were positioned geometrically, and allowed to ride on their parent C atoms. The hydrogen atoms on the partial water molecules were located in difference density maps and were refined as riding using the instruction AFIX 3, and no attempt was made to locate the hydrogen atoms of disorder water molecules. The structure was refined on $F^2$ by full-matrix least-squares using the SHELXTL-97 program package.\(^{S3}\) The partial occupancy of the lattice water molecules (i.e. O25A & O25B and O26A & O26B) is supported by the TGA and Elemental analyses data.

The crystallography data ($R_{int} = 0.0335$, $GooF = 1.079$, $R_1 = 0.0614$, $wR_2 = 0.1932$) of complex 1 is good and reasonable especially for the complicated regimes including the C4AS-based complexes. And complex 1 is well characterized structurally and supported by the XRD, TGA and elemental analyses. For complex 1, its $R_1$ value is almost two times higher than $R_{int}$, which is common for C4AS regimes.\(^{5b,S4}\) And it may be due to the complicated regime of complex 1 and the disorder of the lattice water molecules in 1.

(S2) CrystalClear Version 1.3.6, RIGAKU/MSC(2004), Rigaku/MSC, 9009 New Trails Drive, The Woodlands, TX77381-5209, USA.
(S3) (a) Sheldrick, G. M. SHELXS 97, Program for crystal Structure Solution, 1997, University of Göttingen. (b) Sheldrick, G. M. SHELXL 97, Program for crystal Structure Refinement, 1997, University of Göttingen.
**Fig. S1** A portion of the hydrogen bonds in the hydrophobic layer (only unrepeatable hydrogen bonds are labeled). The hydrogen-bonding interactions are in dashed red lines (symmetry codes: A 1+x, y, z; B x, 1+y, z.).

**Fig. S2** The X-ray asymmetric unit of complex 1 with the displacement ellipsoids at the 30% probability level (symmetry codes: A 1-x, -y, 1-z; B -x, -y, 2-z; C -x-1, -y, 2-z.). Dissociative water molecules and hydrogen atoms have been omitted for clarity.
**Fig. S3** Normalized emission spectra of complex 1 in the solid state at 293 K ($\lambda_{ex} = 375$ nm) and 10 K ($\lambda_{ex} = 346$ nm).

**Fig. S4** The TG curve of complex 1 has two weight loss in the temperature ranges of 30-103 °C (3.00%) and 160-217 °C (4.80%), corresponding to the loss of eight and twelve lattice water molecules, respectively. It reaches another plateau until 303 °C before the framework decomposes.
**Fig. S5** XRD of complex 1.