Electronic Supplementary Information

1,2,3,4-Alternate double cone conformational extreme in the supramolecular assemblies of *p*-sulfonatocalix[8]arene

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Experimental section:

Sodium salt of *p*-sulfonatocalix[8]arene was synthesized according to the literature method[1] and other reagents were commercially available and used as received. The thermogravimetric analysis was carried out on a Perkin-Elmer TGA-7000 instrument from 40 to 800 ^{o}C, with a heating rate of 10 ^{o}C min^{-1} under a nitrogen atmosphere. FT-IR (KBr pallets) spectra were recorded using a Perkin-Elmer spectrum one FTIR Spectrophotometer.

Syntheses of compounds 1a-b, $[M(phen)_2(H_2O)]_2[M(phen)]_2[C8AS]\cdot 2H_2O$ (1a: Cu; 1b: Zn). A suspension of $CuCl_2\cdot 2H_2O$ (17.0 mg, 0.1 mmol) or $ZnCl_2$ (14.0 mg, 0.1 mmol), Na_8C8AS (83.0 mg, 0.05 mmol), and phen (40.0 mg, 0.2 mmol) in water (10 ml) was transferred into a Teflon-lined stainless-steel autoclave(20 ml). The pH value of the feed was adjusted by HCl to 1~3. The autoclave was heated to 130^{o}C in 90 minutes, kept at that temperature for 3 days, and then cooled gradually to room temperature at about 4 ^{o}C h^{-1}. The green block crystals of **1a** and colorless block crystals of **1b** suitable for X-ray diffraction analysis were isolated, yield: 23% for **1a** and 31% for **1b** with respect to C8AS. Elemental analysis for **1a** (%): found: C, 55.34; H, 3.47; N, 6.57. calcd: C, 56.13; H, 3.45; N, 6.89. The target crystals were also obtained with copper/zinc acetate as the precursor.

The crystal structure of **1a** was also determined at -87.5 ^{o}C. The formula and the asymmetric unit keep unchanged while the unit cell changes a little. Crystal Structure: **1a'**: $C_{152}H_{112}Cu_4N_{16}O_{36}S_8$, M = 3249.22 g/mol, triclinic, $P\bar{1}$, a = 15.294(3) Å, b = 15.956(3) Å, c = 16.142(3) Å, α = 71.83(3)°, β = 72.31(3)°, γ = 73.13(3)°, V = 3481 (2) Å^3, Z = 1, T = 186(2) K, R_{int} = 0.055, final R_1 = 0.0704, wR_2 = 0.1636 [$I > 2\sigma(I)$], GooF = 1.05. CCDC711618.

1 M. Makha and C. L. Raston, *Tetrahedron Lett.*, 2001, **42**, 6215-6217.

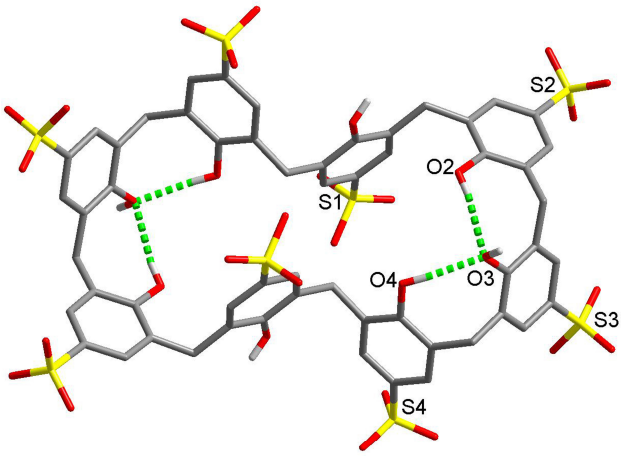

Fig. S1 Scheme of 1,2,3,4-alternater double cone conformer of C8AS with two separated L-shaped hydrogen bonds.

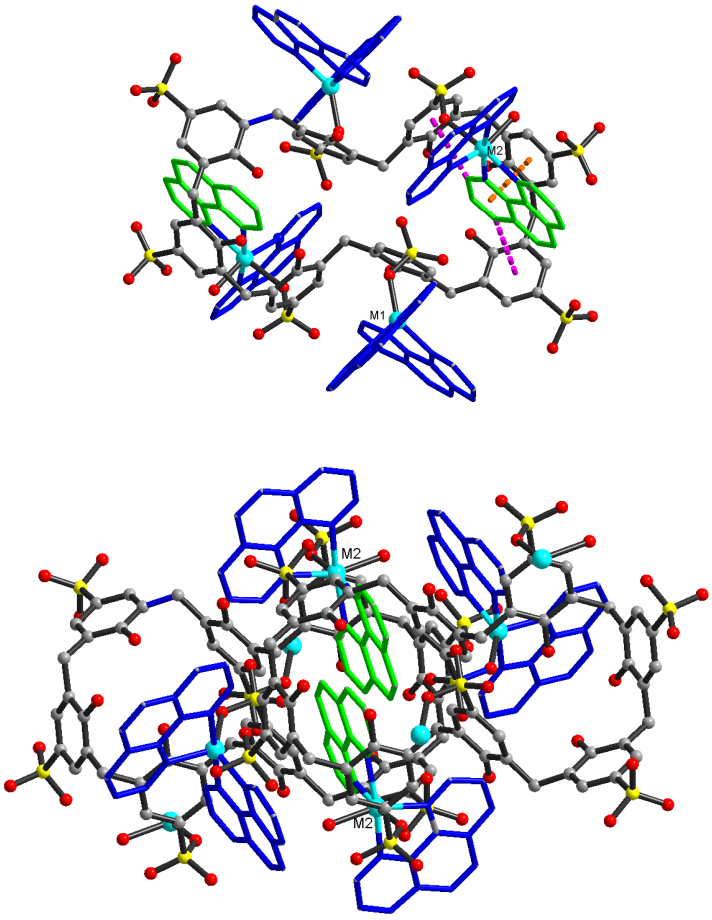

Fig. S2 A view of a tetranuclear unit showing the C-H···π and π···π interactions between the penetrated phen and calixarene (upper); and top viewof the "molecular capsule" (bottom). The encapsuled phen molecules and those outside are shown in green and blue, respectively.

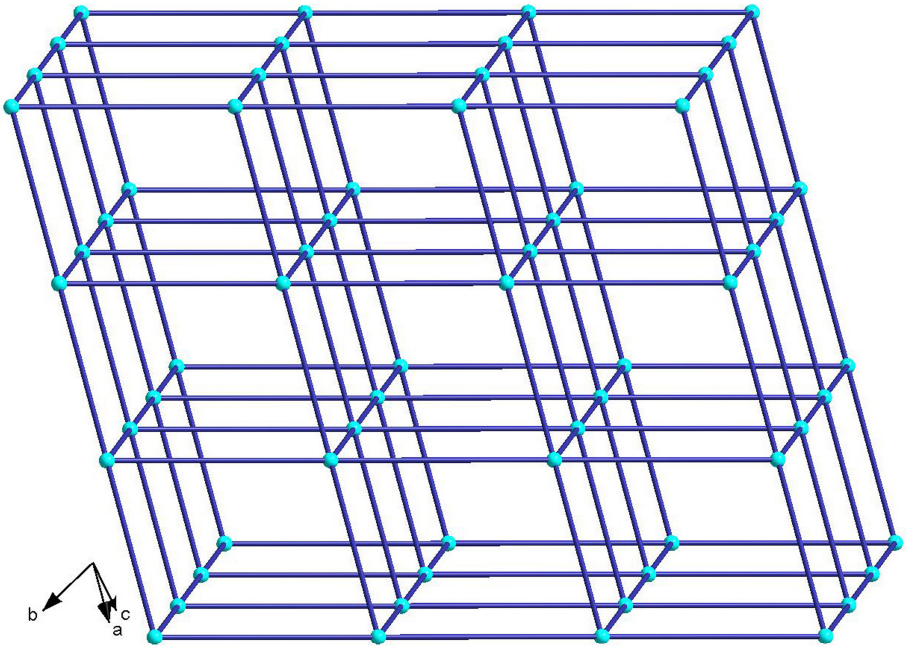

Fig. S3 3D supramolecular topology in **1** (node, tetranuclear units; blue line, supramolecular stacking interactions).

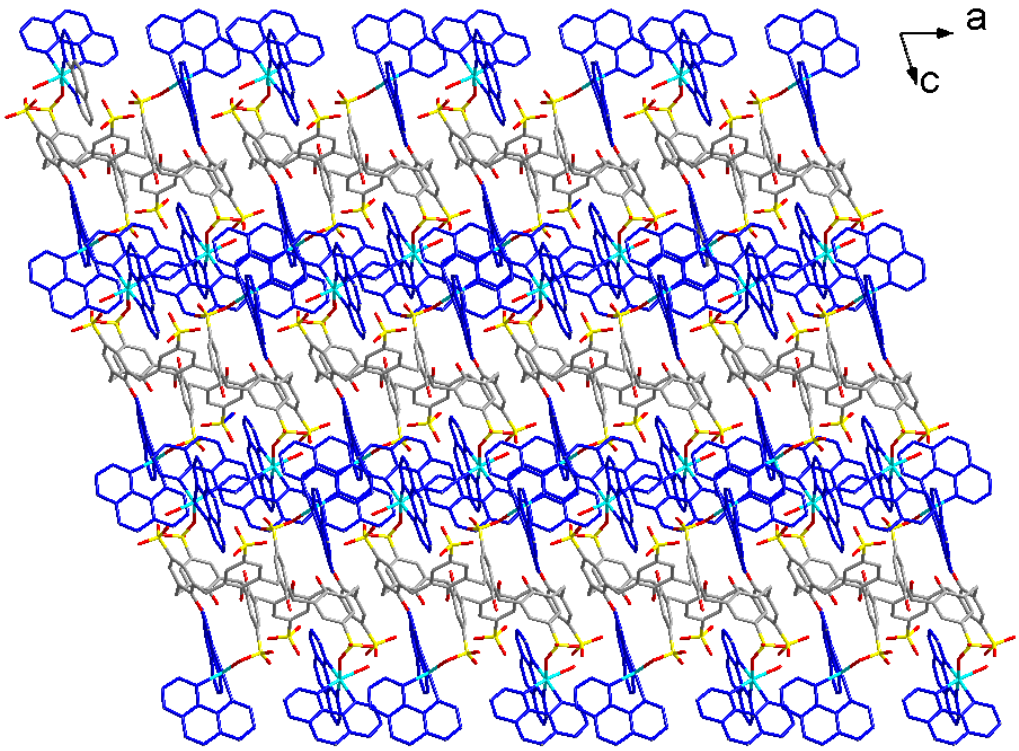

Fig. S4 Project of the extended structure of **1** showing the alternative phen layers and calixarene layers..

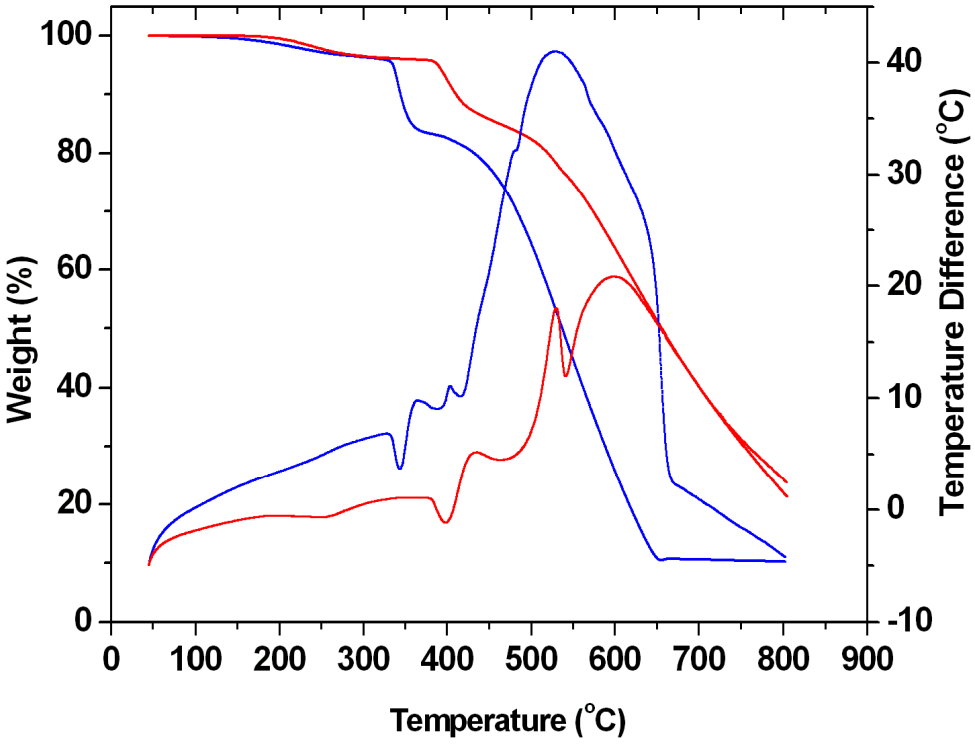

Fig. S5 TG and DTA curve of compound **1** (blue line, compound **1a**; red line, compound **1b**)..

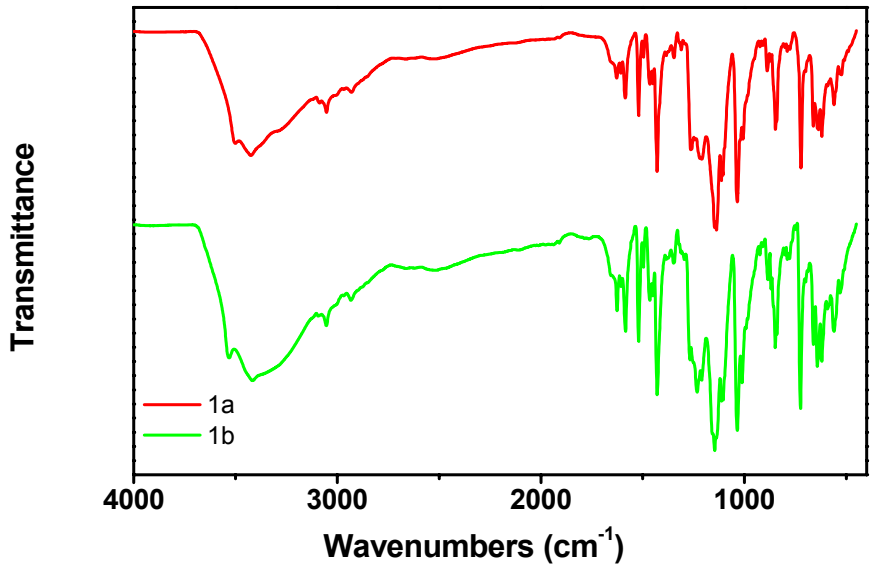

Fig. S6 IR spectrum of compound **1a** and **1b**.