Electronic Supplementary Material (ESI) for *CrystEngComm*

Electronic Supplementary Information

Assembly of 'discrete' $(H_2O)_{16}$ water cluster within a supramolecular compound of calixarene

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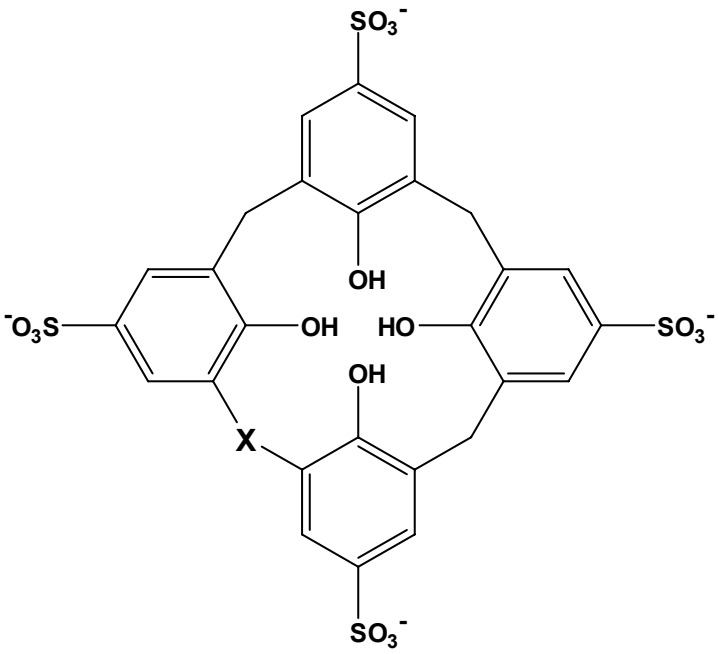
Materials and Measurements. *p*-sulfonatocalix[4]arene (H_4C4AS) was synthesized by literature method[1] and other reagents were purchased from commercial sources and used as received. TGA measurement is performed on a PYRIS DIAMOND. Powder X-ray diffraction (XRD) was determined by a Bruker D8 Advance diffractometer. FR spectra (KBr pellets) were taken on a BRUKER Vertex 70 spectrometer.

Syntheses of 1: An aqueous solution (10ml) of H_4C4AS (0.081g, 0.1 mmol) was adjusted to pH~5 by 25% $N(CH_3)_4OH$ and added $EuCl_3 \cdot 4H_2O$ (0.06 g, ca. 0.16 mmol), phenanthroline (0.04 g, ca. 0.2 mmol), this solution was transferred into a 20 ml Teflon-lined autoclave which was kept at 130 °C for 3 days and then slowly cooled to 20 °C at about 4 °C/h. The pH value of the final solution is *ca.* 3. The colorless block single crystals of **1** was carefully isolated and collected for X-ray diffraction determination. Yield: ca. 40% with respect to calixarene. Several yellow blocks by-product of C4AS-Phenanthroline (**1'**) was isolated by microscope.

Crystal data for **1'**: Monoclinic, *P2(1)/n*, a =14.1527(5) Å, b = 37.6365(14) Å, c = 15.9570(6) Å, β = 105.7450(10)°, V =8180.7(5), T = 186(2)K, R_1 = 0.1465.

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



Scheme S1. *p*-sulfonatocalix[4]arene (C4AS)

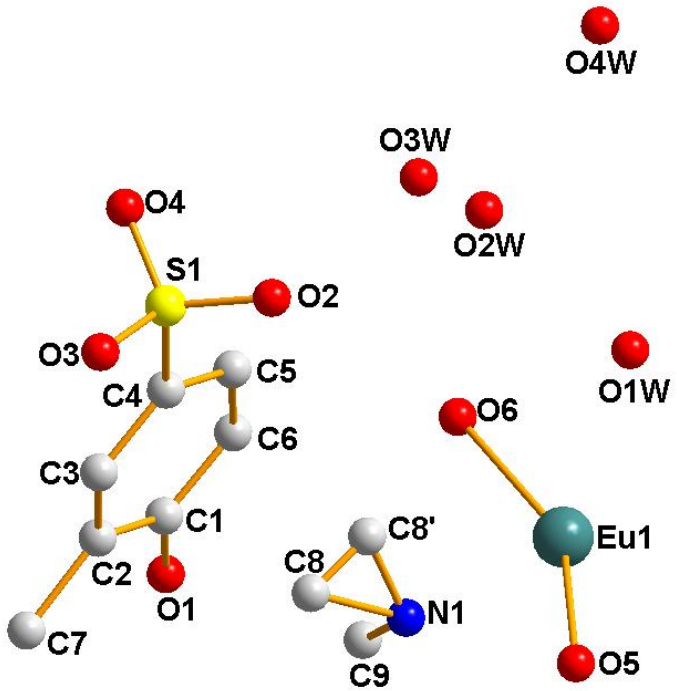


Fig. S1 Molecular structure in an asymmetric unit. Hydrogen atoms are omitted for clarity.

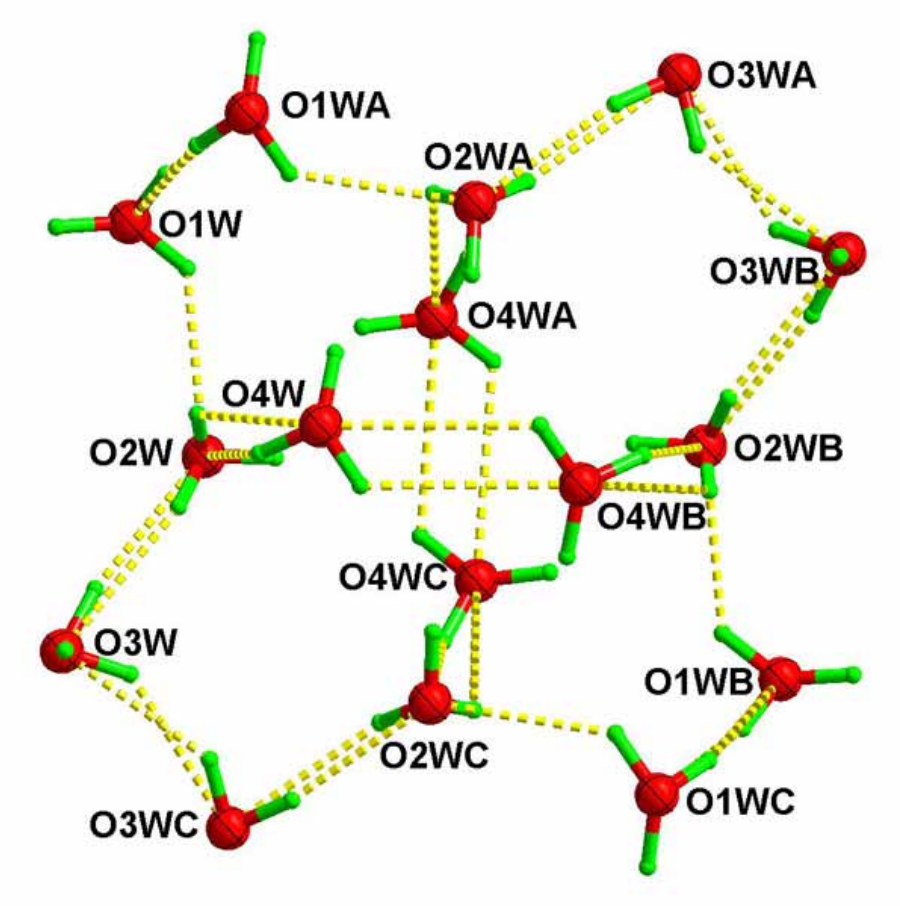


Fig. S2 A $(H_2O)_{16}$ water cluster with hydrogen atoms.

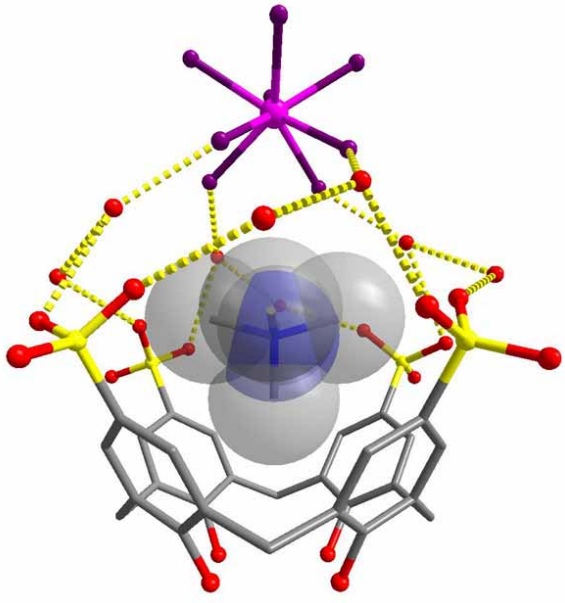


Fig. S3 A capsule structure showing $N(CH_3)_4^+$ cation deeply encapsulated in the cavity of C4AS ligand. The hydrogen atoms are omitted for clarity.

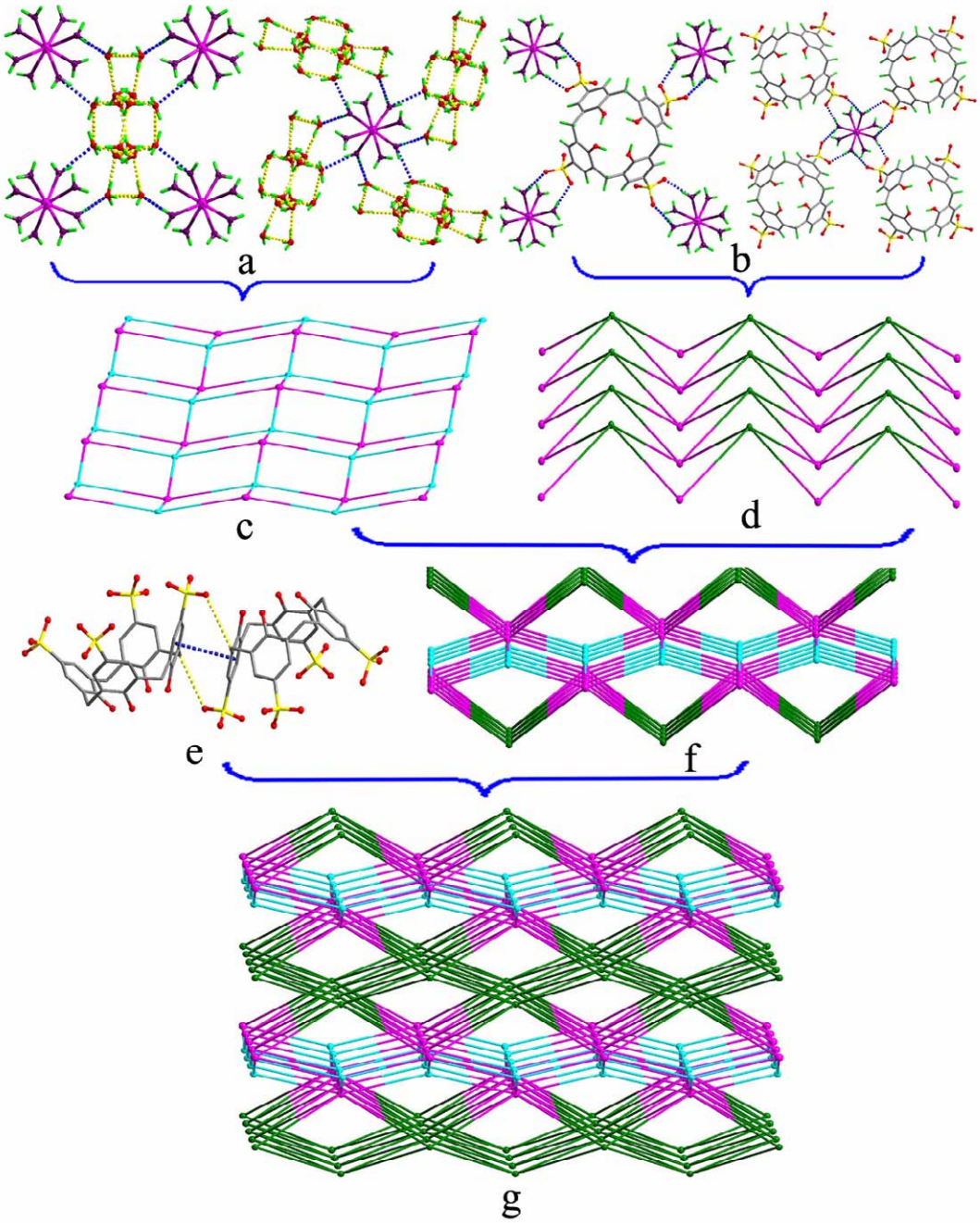


Fig. **S4** View of the formation of the 3D supramolecular structure by analyzing the supramolecular interactions step by step. The $N(CH_3)_4^+$ cations are omitted for clarity.

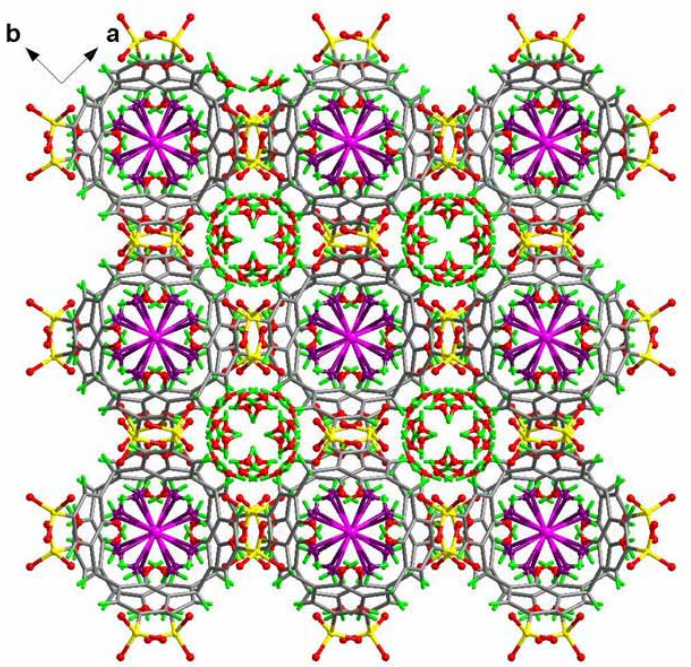


Fig. S5 The 3D supramolecular structure showing water filled channels in the *ab* plane. The $(CH_3)_4N^+$ cations are omitted for clarity.

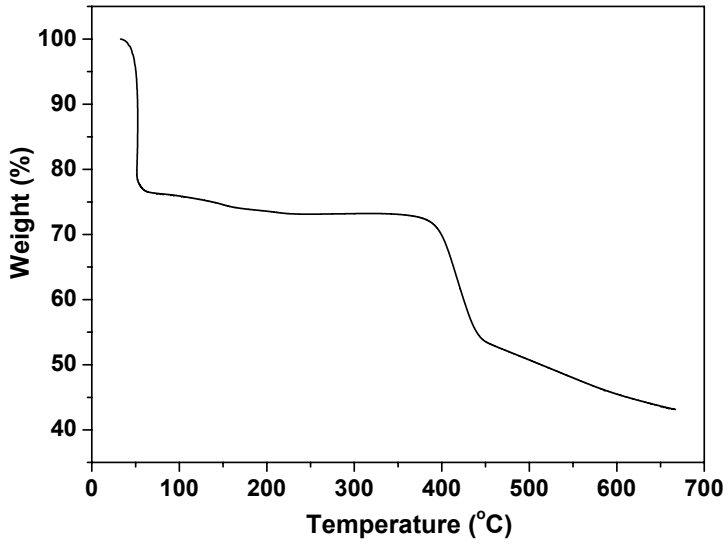


Fig. **S6** TGA curve for compound **1.**

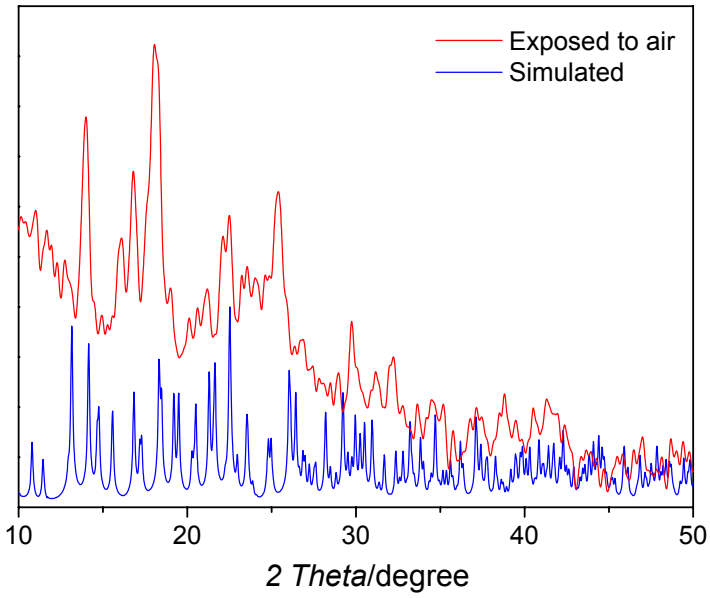


Fig. S7. Simulated spectra of **1** (blue) and spectra of **1** exposed to in air (red)

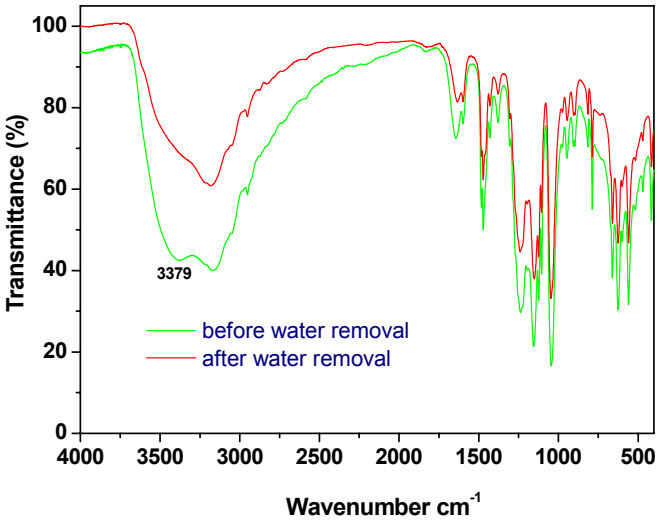


Fig. S8. The infrared spectra of **1** before (green) and after water removal (red).

Table S1 Hydrogen–Bonding Geometry (Å, °) complex **1**

D–H···A	D–H	H···A	D···A	<D–H···A	Symmetry code
O(1W)–H(1WA)···O(2)	0.85	2.22	3.049(5)	164	y,1/2-x,z
O(1W)–H(1WA)···O(3)	0.85	2.37	2.999(4)	132	y,1/2-x,z
O(1W)–H(1WC)···O(1W)	0.85	1.96	2.778(5)	161	-1/2+y,1/2+x,1/2-z
O(1W)–H(1WB)···O(2W)	0.85	2.11	2.771(6)	134	x, y, z
O(2W)–H(2WB)···O(4W)	0.85	2.27	2.843(6)	125	x, y, z
O(2W)–H(2WC)···O(3W)	0.85	2.08	2.798(6)	142	x, y, z
O(3W)–H(3WA)···O(4)	0.85	2.00	2.849(4)	174	-1/2-x,1/2-y,z
O(3W)–H(3WB)···O(2W)	0.85	1.97	2.798(6)	166	x, y, z
O(4W)–H(4WB)···O(4W)	0.85	2.46	2.967(6)	119	-y,-x,1/2-z
O(4W)–H(4WC)···O(2W)	0.85	2.20	2.843(6)	133	
O(4W)–H(4WB)···O(2)	0.85	2.51	3.135(5)	131	-1/2-x,1/2-y,z
O(5)–H(5B)···O(4)	0.85	1.89	2.732(4)	170	1/2+y,1/2+x,1/2-z
O(5)–H(5C)···O(3)	0.85	1.84	2.688(4)	171	1/2+x,-y,1/2-z
O(6)–H(6A)···O(4W)	0.85	1.95	2.787(5)	166	-1/2+y,1/2+x,1/2-z
O(6)–H(6B)···O(1W)	0.85	1.86	2.705(5)	178	1/2-y,x,z
C(3)–H(3A)···O(3W)	0.95	2.54	3.482(5)	171	1/2-y,x,z
C(5)–H(5A)···O(3W)	0.95	2.54	3.477(5)	170	x, y, z
C(7)–H(7B)···O(4)	0.99	2.45	3.396(4)	161	-x,-y,-z
C(8)–H(8C)···O(2)	0.96	2.51	3.322 (1)	143	1/2-y,x,z