Supplementary Material (ESI) for Chemical Communications

Encapsulation and selective recognition of sulfate anion in an azamacrocycle in water

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Synthesis of L

N-methyl-2,2'-diaminodiethylamine (0.74 g, 6.3 mmol) and terephthaldehyde (0.85 g, 6.3 mmol) were dissolved separately in CH_3OH (200 mL). The solutions were allowed to drop simultaneously in CH_3OH (500 mL) at O°C over 5 h. The resulting mixture was left stirring overnight at room temperature. The solvent was evaporated and the oily product was redissolved in CH_3OH (100 mL). Then $NaBH_4$ (1.2 g, 31.72 mmol) was added in three portions over a period of 2h and the mixture was continued to stir overnight at room temperature. The solvent was evaporated to dryness. The white product was dissolved in water (100 mL) and an extraction was made with CH_2Cl_2 (3 x 50 mL). The organic combined layers were dried by anhydrous $MgSO_4$ (1.5 g). The yellowish solution was collected by filtration, and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography on a neutral-alumina column (2% CH_3OH in CH_2Cl_2) to give **1** as a white powder. Yield: 0.76 g, 55%. M.p. 88°C. ^1H NMR (500 MHz, $CDCl_3$, TMS): δ 7.19 (s, 8H, Ar*H*), 3.76 (s, 8H, ArC*H*$_2$), 2.78 (t, *J* = 5.5 Hz, 8H, NHC*H*$_2$), 2.54 (t, *J* = 5.5 Hz,8H, NC*H*$_2$), 2.17 (s, 6H, C*H*$_3$). ^{13}C NMR (125 MHz, $CDCl_3$,): δ 138.8 (Ar-*C*), 128.1 (Ar-*C*H), 56.4 (N*C*H$_2$), 53.8 (NH*C*H$_2$), 46.9 (*C*H$_3$), 42.3 (*C*H$_3$). ESI-MS: *m*/*z* (+) 439.3 $[M + H]^+$. Anal. Calcd. for $C_{26}H_{42}N_6$: C, 71.19; H, 9.65; N, 19.16. Found: C, 71.33; H, 9.67; N, 19.21.

Binding Constant (*K*): Binding constants were obtained by ^{1}H NMR (500 MHz Bruker) titrations of [H_6**L**]$(Ts)_6$·with different inorganic salt in D_2O at pH 2.1. Initial concentrations were $[\text{ligand}]_0$ = 2 mM, and $[\text{anion}]_0$ = 20 mM. Sodium salt of 3-(trimethylsilyl)propionic-2,2,3,3,-d_4 acid (TSP) in D_2O was used as an external reference in a capillary tube. The pH was adjusted with a concentrated solution of TsOH and NaOH in D_2O. Each titration was performed by 16 measurements at room temperature. The association constant *K* was calculated using Sigma Plot software, from the following equations: $\Delta\delta = ([A]_0 + [\mathbf{L}]_0 + 1/K - (([A]_0 + [\mathbf{L}]_0 + 1/K)_2 - 4[\mathbf{L}]_0[A]_0)^{1/2})\ \Delta\delta\text{max} / 2[\mathbf{L}]_0$ (where **L** = ligand and A = chloride). Error limit in *K* was less that 15%.

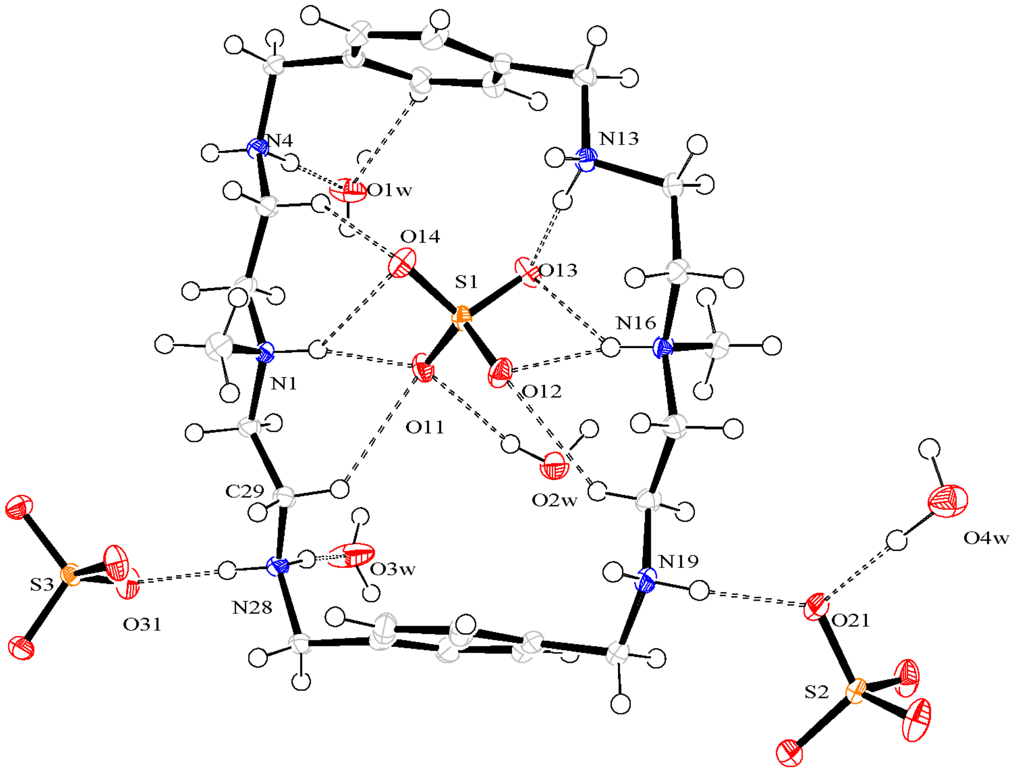

Figure S1: Crystal structure of $[[H_6\mathbf{L}(SO_4)]\cdot 2SO_4\cdot 4H_2O$ showing encapsulated and external sulfates, and external water molecules.