Intramolecular Hydrogen Bonding Effects in Anion Binding Calixarenes

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Supplementary Information

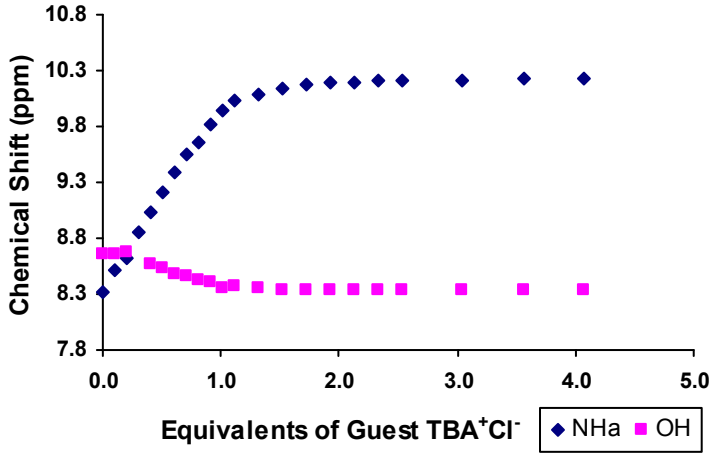


Figure S1 Titration of host 4c with TBA^+Cl^- anion in acetone solvent.

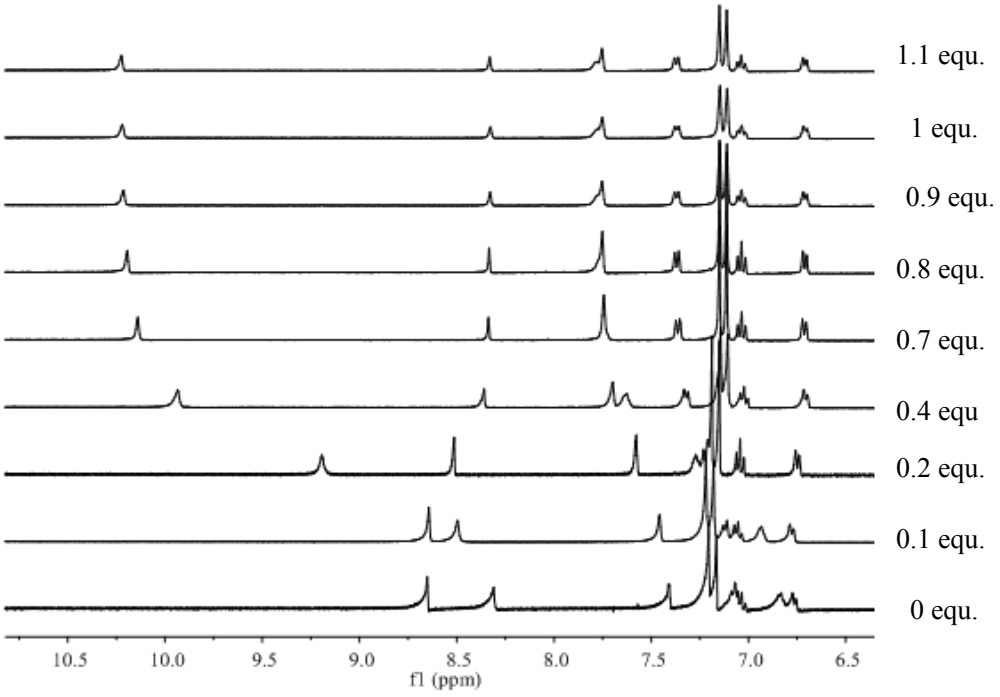


Figure S2 Titration of host 4c with TBA^+Cl^- anion in acetone solvent.

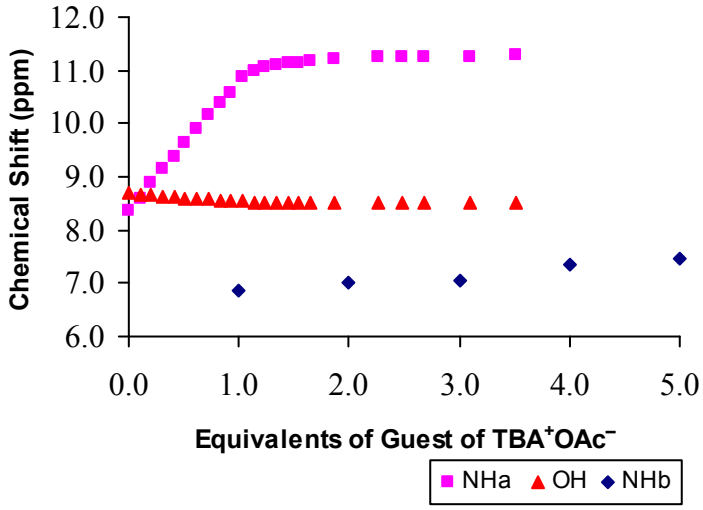


Figure S3 Titration of host 4c hosts with $TBA^{+}OAc^{-}$ anion in acetone solvent

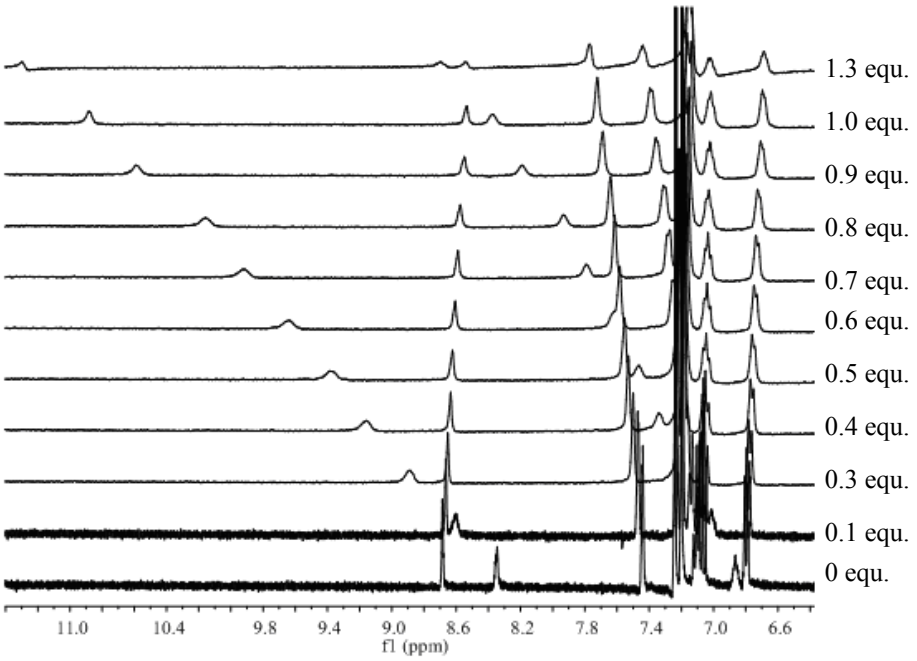


Figure S4 Stack plot obtained from titration of host 4c host with $TBA^{+}OAc^{-}$ anion in acetone solvent.

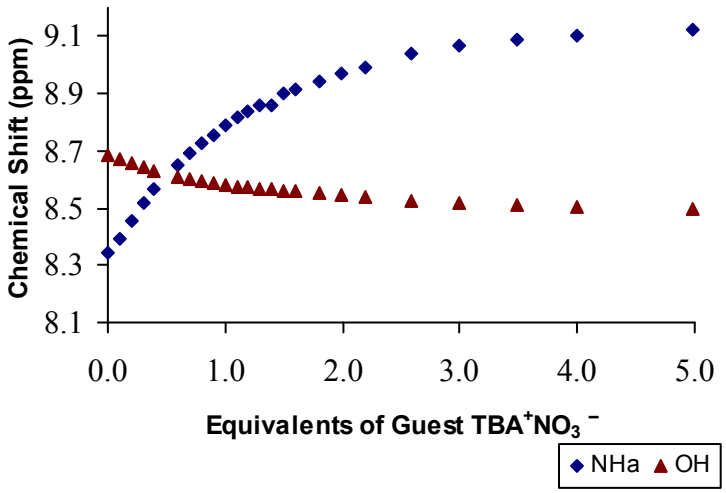


Figure S5 Titration of host 4c with $TBA^{+}NO_3^{-}$ in acetone solvent.

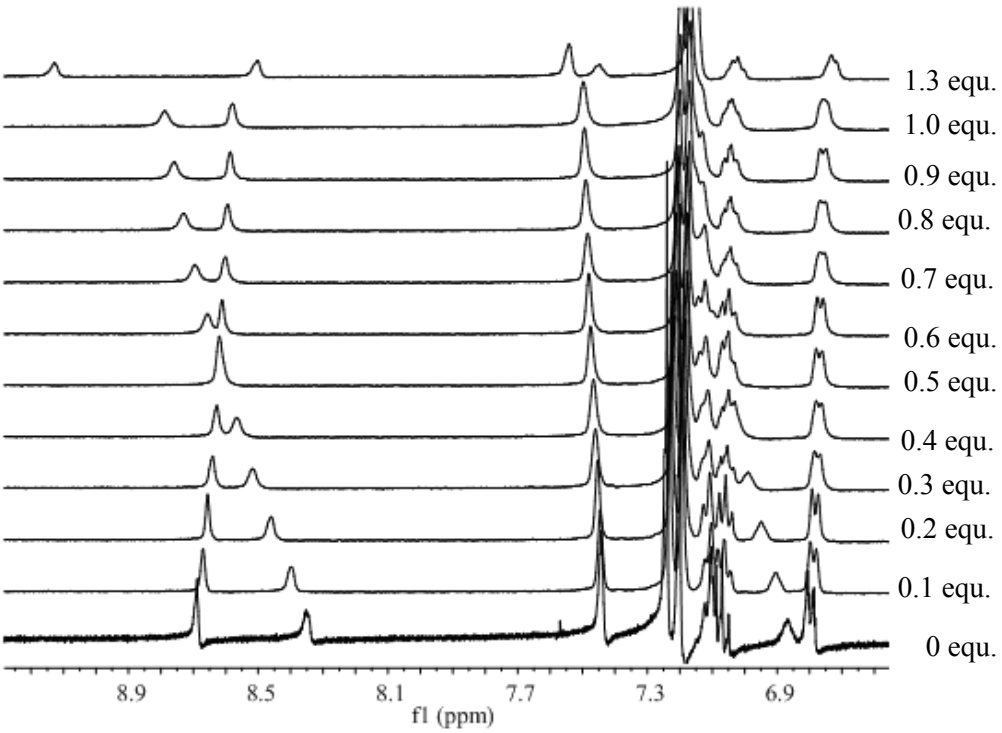


Figure S6 Stack plot obtained from titration of host 4c with $TBA^{+}NO_3^{-}$ anion in acetone.

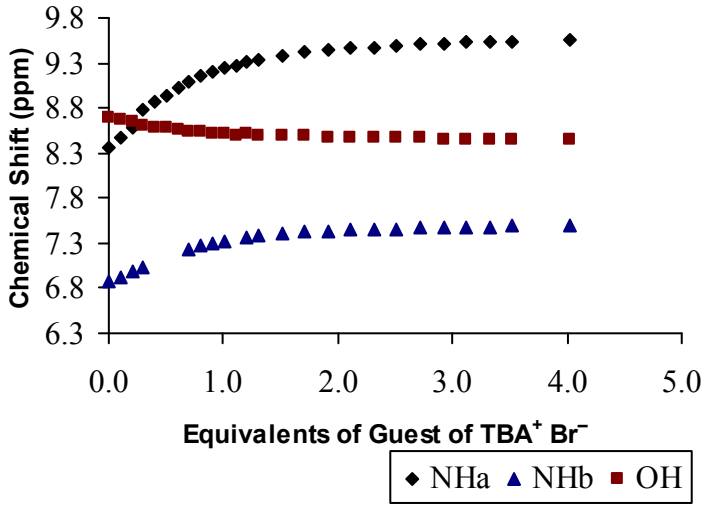


Figure S7 Titration of host 4c with $TBA^{+}Br^{-}$ in acetone.

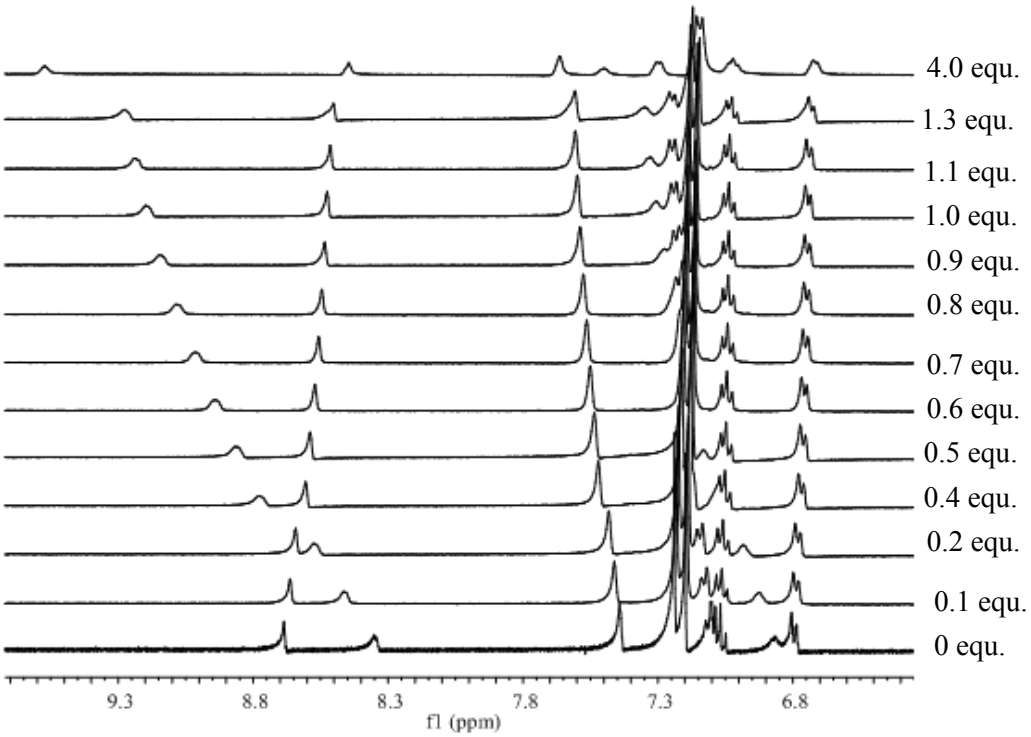


Figure S8 Stack plot obtained from titration of host 4c with TBA^{+} Br^{-} in acetone.

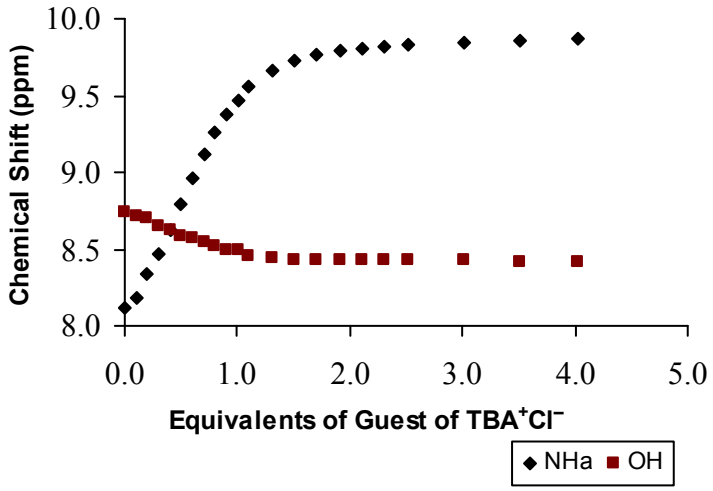


Figure S9 Titration of host 4b with TBA^+Cl^- anion in acetone.

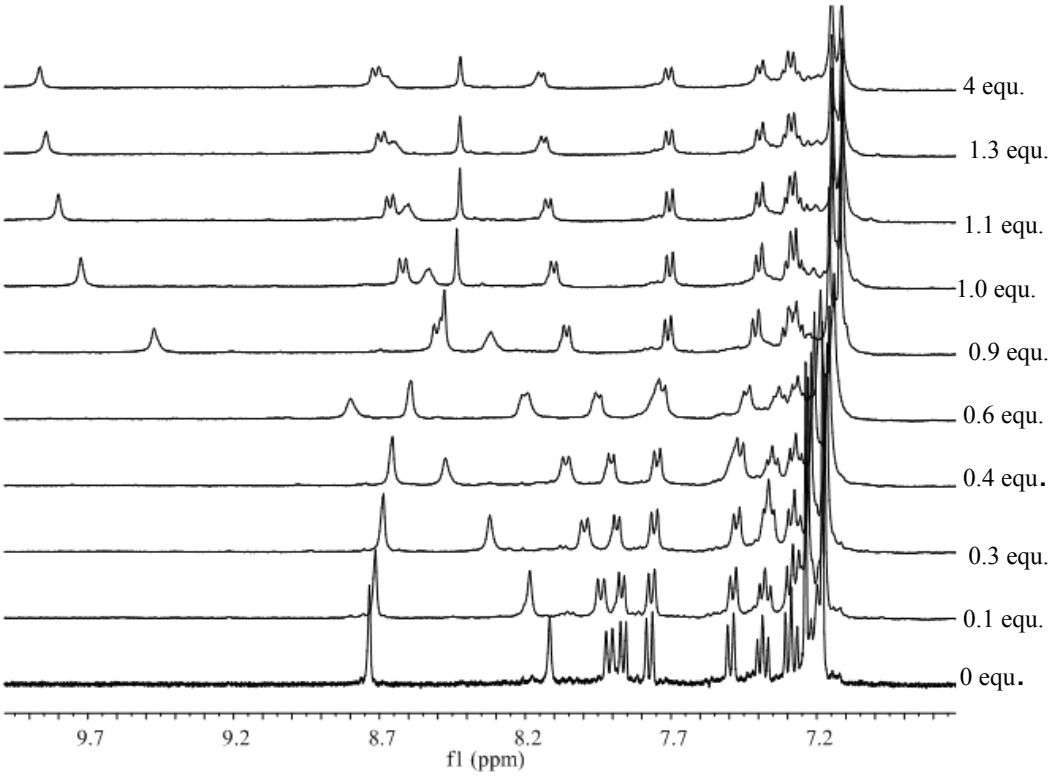


Figure S10 Stack plot obtained from titration of host 4b with TBA^+Cl^- in acetone

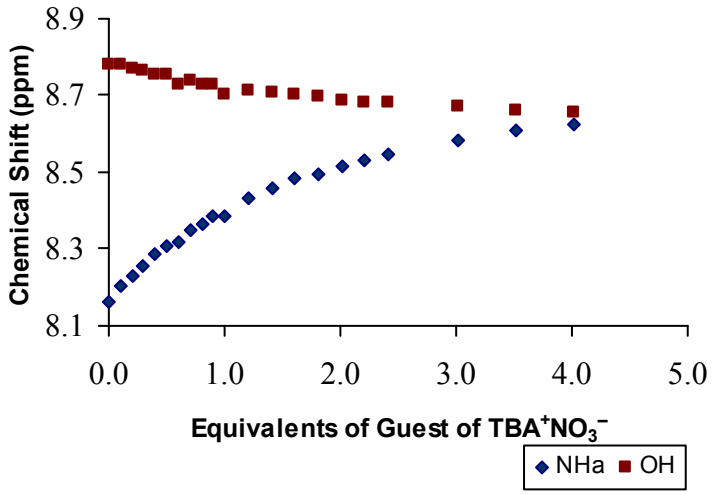


Figure S11 Titration of host 4b with $TBA^{+}NO_3^{-}$ in acetone.

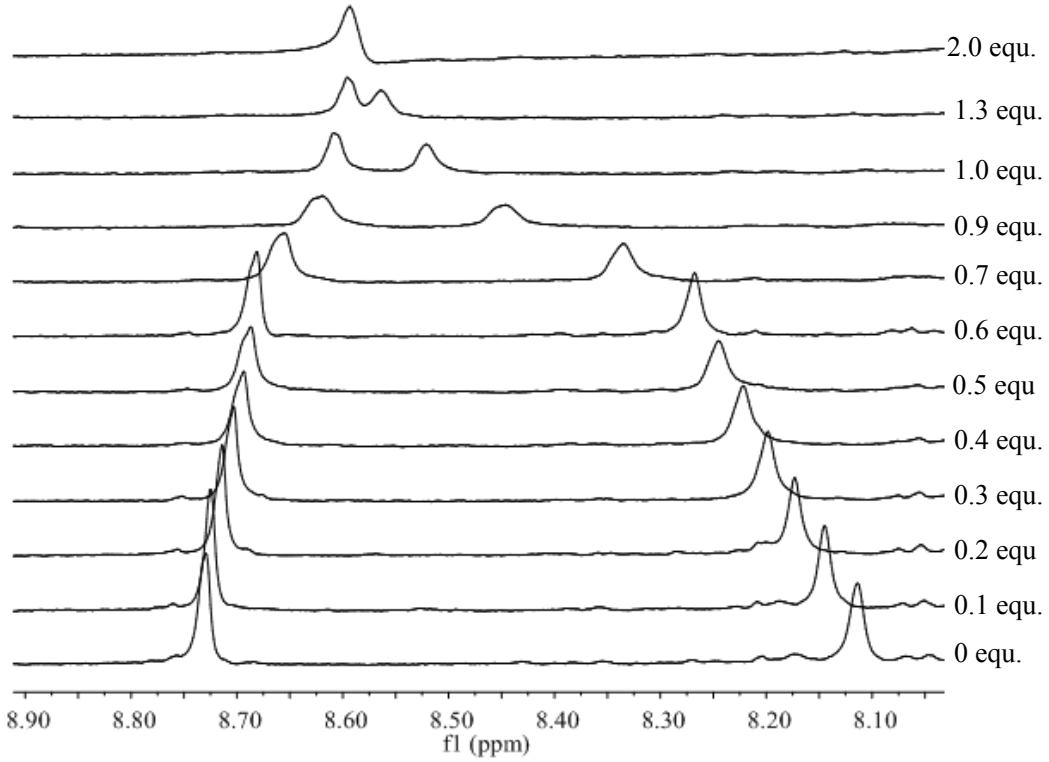


Figure S12 Stack plot obtained from titration of host 4b with $TBA^{+}NO_3^{-}$ in acetone.

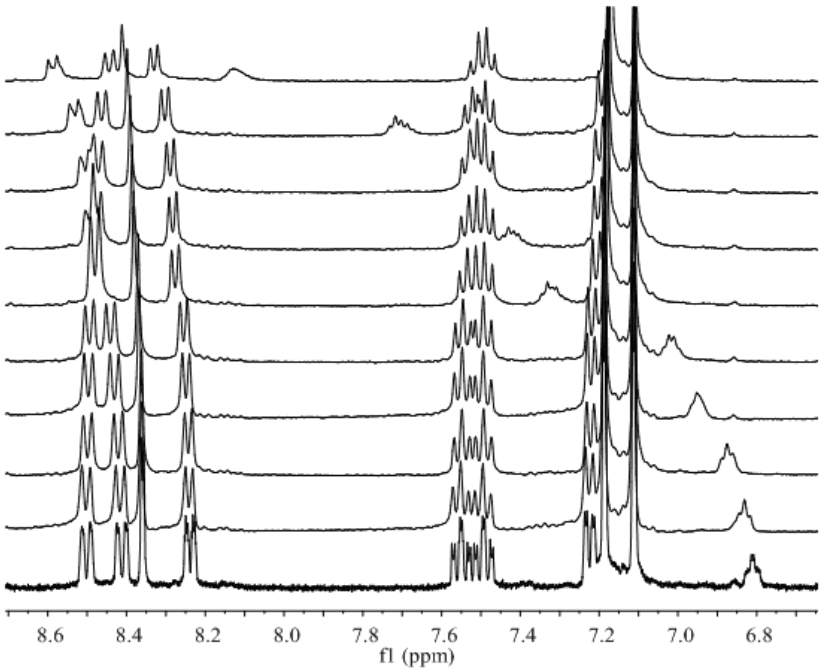


Figure S13 ^{1}H-NMR spectroscopic titration of 6 with chloride in acetone solution.

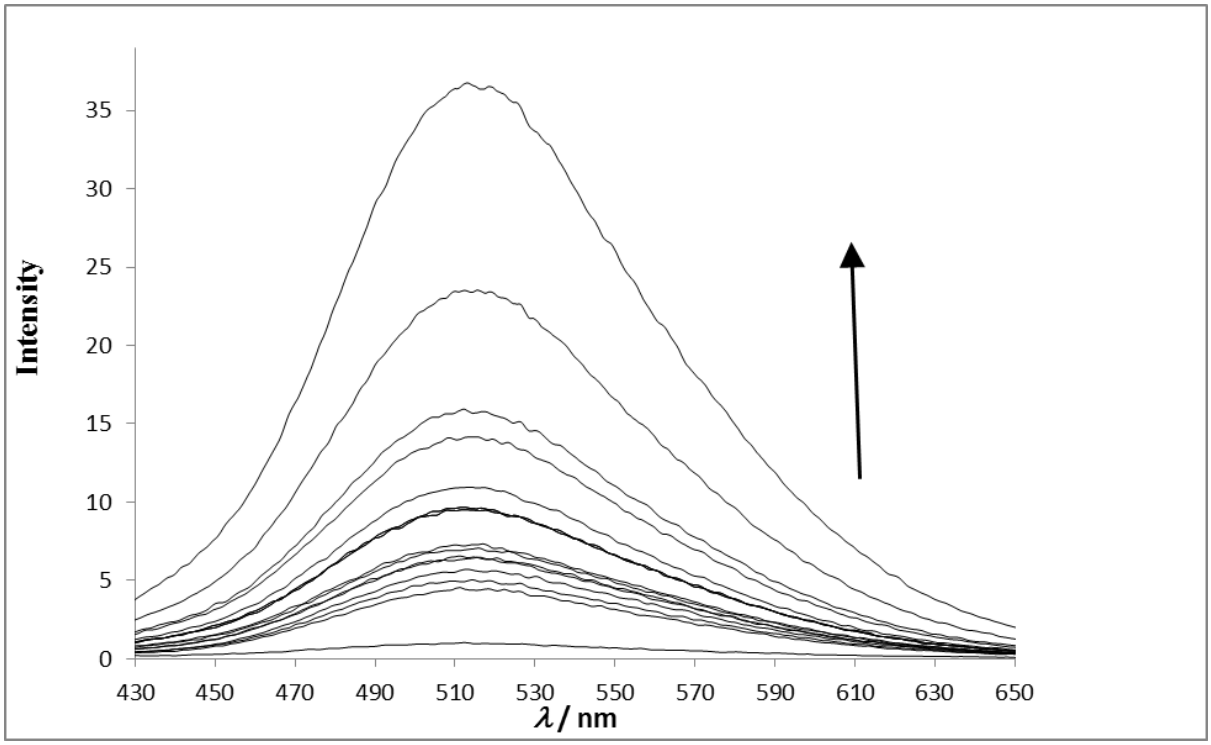


Figure S14 Titration of dansylamide receptor **5** with tetrabutylammonium chloride (λex = 340 nm, 1.63x10^{-5} M). Steps are 10, 20, 30, 40, 50, 60 100, 120, 140, 160, 180, 200, 250 and 500 molar equivalents chloride.

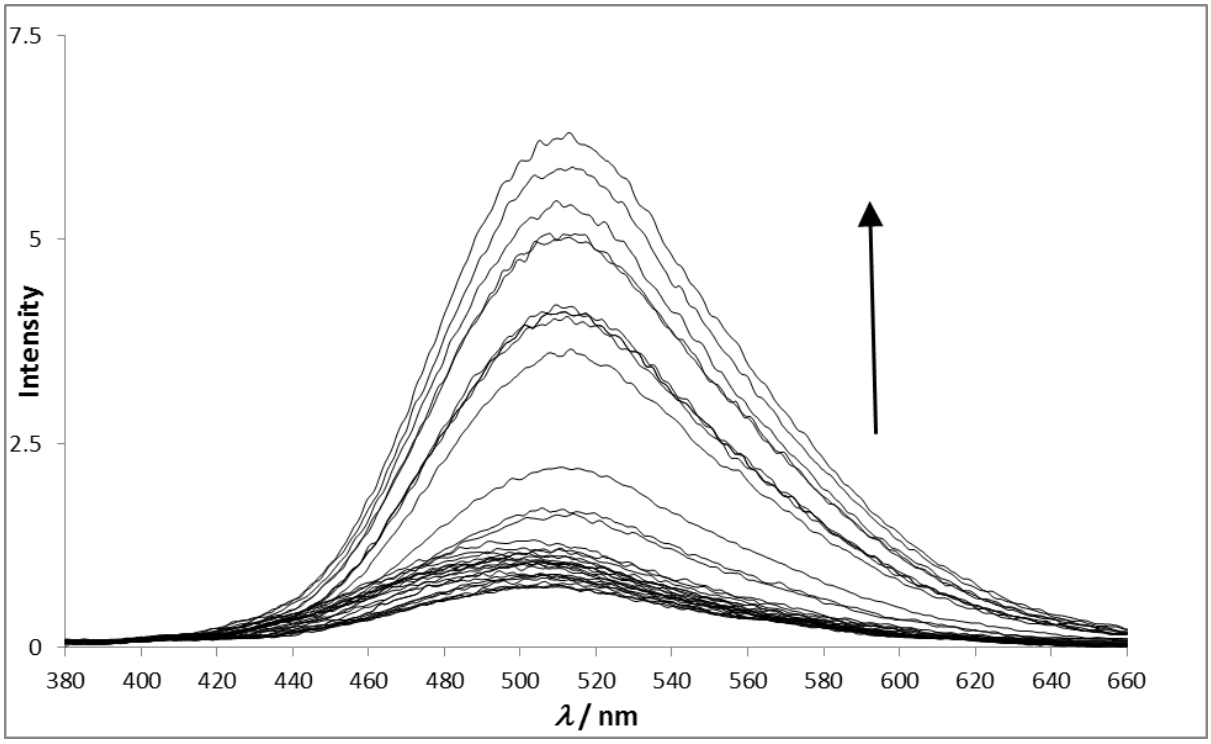
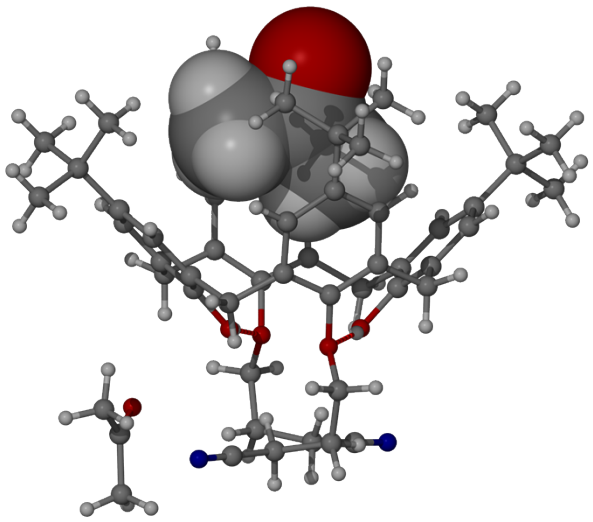


Figure S15 Titration of dansylamide receptor **6** with tetrabutylammonium chloride (λex = 340 nm, 3.12×10^{-6} M) up to 500 molar equivalents chloride.

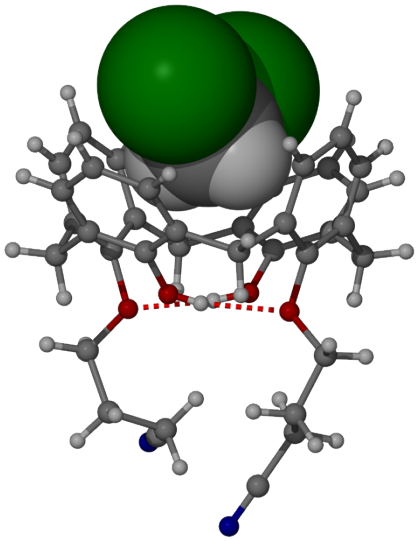
Additional X-ray Crystal structures

S1. Nitrile precursor 5,11,17,23–tetra-t-butyl-25,27-bis[(cyanopropyl)oxy]-26,28-dihydroxycalix[4]arene acetone solvate.



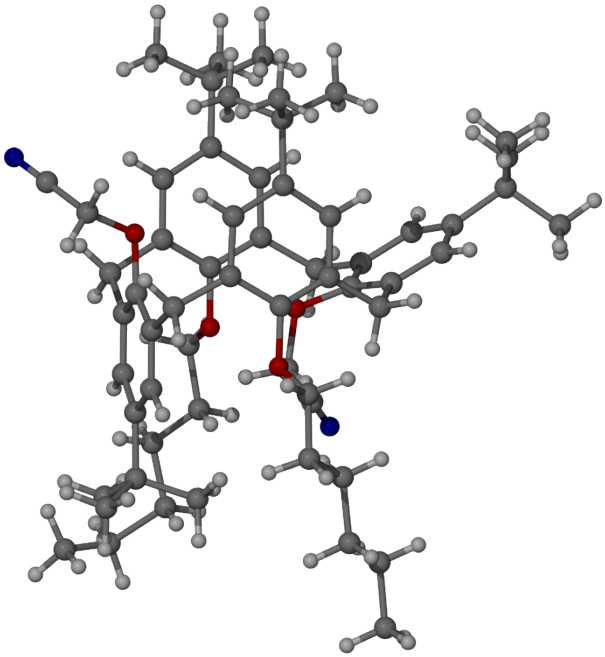
Empirical formula	$C_{52}\ H_{56}\ N_2\ O_4\ .\ 4\ C_3H_6O$	
Formula weight	957.30	
Temperature	120(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 21.951(4) Å	α= 90°.
	b = 12.163(3) Å	β= 91.17(1)°.
	c = 21.185(3) Å	γ = 90°.
Volume	5654.8(18) $Å^3$	
Z	4	
Density (calculated)	1.124 Mg/m^3	
Absorption coefficient	0.072 mm^{-1}	
F(000)	2080	
Crystal size	0.47 x 0.29 x 0.20 mm^3	
Theta range for data collection	3.25 to 27.50°.	
Index ranges	-28<=h<=28, -15<=k<=15, -27<=l<=27	
Reflections collected	41276	
Independent reflections	6490 [R(int) = 0.0496]	
Completeness to theta = 27.50°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0000 and 0.6259	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6490 / 24 / 321	
Goodness-of-fit on F^2	1.029	
Final R indices [I>2sigma(I)]	R_1 = 0.0649, wR_2 = 0.1746	
R indices (all data)	R_1 = 0.0784, wR_2 = 0.1923	
Largest diff. peak and hole	0.577 and -0.574 e.$Å^{-3}$	

S2. Nitrile precursor 25,27-bis[(cyanopropyl)oxy]-26,28-dihydroxycalix[4]arene dichloromethane solvate.



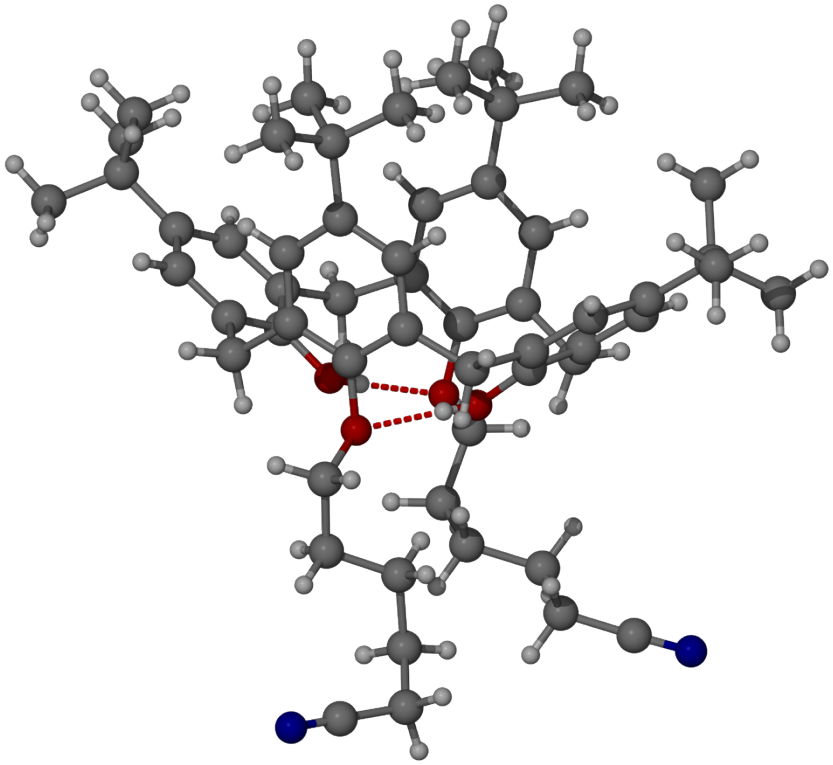
Crystal data for S2: $C_{37}H_{36}Cl_2N_2O_4$, M = 643.58, colourless block, 0.20 × 0.20 × 0.10 mm^3, orthorhombic, space group $P2_12_12_1$ (No. 19), a = 10.0646(11), b = 15.6235(17), c = 20.246(2) Å, V = 3183.5(6) Å^3, Z = 4, D_c = 1.343 g/cm^3, F_{000} = 1352, SMART 1k, MoKα radiation, λ = 0.71073 Å, T = 120(2)K, $2\theta_{max}$ = 46.6º, 21304 reflections collected, 4585 unique (R_{int} = 0.0937). Final *GooF* = 0.982, *R1* = 0.0470, *wR2* = 0.0789, *R* indices based on 3616 reflections with I >2σ(I) (refinement on F^2), 414 parameters, 0 restraints. Lp and absorption corrections applied, μ = 0.248 mm^{-1}. Absolute structure parameter = 0.09(7) (Flack, H. D. *Acta Cryst*. **1983**, *A39*, 876-881).

S3. Nitrile precursor partial cone 5,11,17,23–tetra-t-butyl-25,27-bis[(cyanomethyl)oxy]-26,28-dihexyloxycalix[4]arene.



Crystal data for S3: $C_{60}H_{82}N_2O_4$, M = 895.28, 0.40 × 0.10 × 0.05 mm^3, monoclinic, space group $C2/c$ (No. 15), a = 27.48(2), b = 20.311(15), c = 19.585(14) Å, β = 92.34(6)°, V = 10923(14) Å^3, Z = 8, D_c = 1.089 g/cm^3, F_{000} = 3904, MoKα radiation, λ = 0.71073 Å, T = 120(2)K, $2\theta_{max}$ = 46.5º, 8720 reflections collected, 5304 unique (R_{int} = 0.1034). Final *GooF* = 0.792, *R1* = 0.0648, *wR2* = 0.1364, *R* indices based on 2080 reflections with I >2σ(I) (refinement on F^2), 609 parameters, 0 restraints. Lp and absorption corrections applied, μ = 0.067 mm^{-1}.

S4. Nitrile precursor 5,11,17,23–tetra-t-butyl-25,27-bis[(cyanopentyl)oxy]-26,28-dihydroxycalix[4]arene.



Crystal data for S4: $C_{56}H_{74}N_2O_4$, M = 839.17, block colourless, 0.30 × 0.20 × 0.20 mm^3, triclinic, space group P-1 (No. 2), a = 13.4692(15), b = 15.0701(16), c = 15.3241(16) Å, α = 91.994(2), β = 115.710(2), γ = 109.003(2)°, V = 2592.6(5) Å^3, Z = 2, D_c = 1.075 g/cm^3, F_{000} = 912, SMART 1k, MoKα radiation, λ = 0.71073 Å, T = 120(2)K, $2\theta_{max}$ = 58.3º, 26960 reflections collected, 13617 unique (R_{int} = 0.0422). Final *GooF* = 1.016, *R1* = 0.0713, *wR2* = 0.1566, *R* indices based on 7827 reflections with I >2σ(I) (refinement on F^2), 595 parameters, 0 restraints. Lp and absorption corrections applied, μ = 0.066 mm^{-1}.