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PAPER

Tetrakis(methylimidazole) and tetrakis(methylimidazolium) calix[4]arenes: competitive anion binding and deprotonation†

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Neutral tetrakis(methylimidazole) (**1**) and the novel cationic tetrakis(methylimidazolium) (**2**) calixarenes have been prepared and their solid-state and solution behaviour examined. The neutral imidazole forms a mono-zwitterion at elevated temperature, a feature that has been observed both in solution and in the solid-state. The cationic imidazolium exhibits a range of hydrogen bond interactions with anions, with the titration curves upon binding to basic anions suggesting sequential binding to both the upper and lower rims.

Introduction

Anions have important roles in biological systems, medicine and the environment, hence the design and synthesis of anion binding and sensing systems is highly topical.[1–6] Various intermolecular forces can be involved in the binding process. Selective binding is one of the current challenges. One way to achieve selectivity is to have a pre-organised cavity which 'fits' particular anions based upon their size and charge distribution. Tripodal imidazolium, pyridinium and cryptand based systems, in addition to calixarenes, are examples of such pre-organised cavities.[7–20] Many systems are highly dependent upon the location of the anion binding sites and can give an interesting response to anion binding. For example, an induced conformational change may bring about a photophysical, colourimetric or an electrochemical response.[21–28]

Imidazolium units are effective anion receptors due to their strong ionic hydrogen bond [$(C–H)^{+}\cdots X^{-}$] interactions.[7–10,12–15] Bis-, tris- and tetrakis-imidazolium receptors, usually built around benzene (or benzene-derived) or calixarene anchors, have been prepared and their anion binding properties reported. Calixarenes are versatile frameworks that can act as hosts for cations, anions and neutral molecules, depending upon their functionalisation. Studies on imidazolium calixarenes have shown that both cavity size and pre-organisation are important, with bis(imidazolium) calix[4]arenes showing selectivity for carboxylates, while tetrakis(imidazolium) calix[4]arenes are selective for dicarboxylates.[29] Allosteric enhancement has also been shown to play a part in binding affinity.[9] Herein we report a neutral tetrakis (methylimidazole) calix[4]arene (**1**) and a novel tetrakis(methylimidazolium) calix[4]arene (**2**) that show unusual solution and anion binding behaviour due to the presence of the acidic OH groups on the lower rim.

Results and discussion

Synthesis and structures

Tetrakis(methylimidazole) calix[4]arene **1** has previously been reported, though due to its insolubility (it is soluble only in dimethylsulfoxide) its solid-state structure has not been studied in any detail (Fig. 1).[30,31] We have developed a more simple procedure than that reported for the preparation of **1**. Reaction of 1-bromomethyl-4-hydroxy calix[4]arene (**A**) with excess imidazole in methanol yields **1** as a white solid. We have previously found that, as imidazole itself is a base, it is not necessary to use an exogenous base in these types of nucleophilic substitution reactions.[32] Compound **1** was characterised by NMR spectroscopy, mass spectrometry and elemental analysis which are consistent with the formation of a neutral tetrakis(methylimidazole) calix[4]arene. Colourless prism crystals formed by heating a saturated chloroform solution of **1** at 60 °C in a sealed vessel and allowing it to cool slowly to room temperature.

The X-ray structure of **1** (Fig. 2a) shows the expected cone-type conformation with the imidazole groups projecting upwards. Two of the imidazole groups orientate themselves with the carbon between the two nitrogen atoms (C2) pointing towards the centre of the ring, with the other two having the C2 proton pointing away, resulting in an unsymmetrical structure. Compound **1** crystallises with a molecule of chloroform contained within the cavity. The inclusion of solvent in the solid-state structures of calixarenes is often observed, with *p-tert*-butyl calix[4]arene being shown to include chloroform, toluene,

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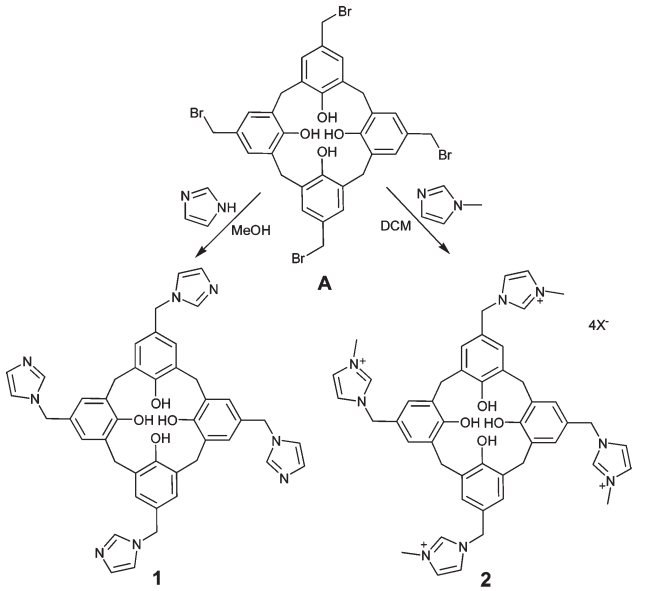

Fig. 1 Tetrakis(methylimidazole) calix[4]arene **1** and tetrakis(methylimidazolium) calix[4]arene **2** (X = Br, PF_6).

xylene and anisole.[33–35] An interesting feature of the structure is that it exists as the mono-zwitterion in the solid-state, with one of the hydroxyl groups deprotonated (O4), and one of the imidazole nitrogen atoms protonated (N4) (Fig. 2b). The proton on the imidazolium moiety of one calixarene forms a hydrogen bond with a non-protonated nitrogen (N2) on a neighbouring calixarene. The remaining two imidazole groups interact with water molecules contained within the structure, appearing to cause disorder, with the imidazole groups occupying two sites (Fig. 2c). The first deprotonation of a hydroxyl group of a calix[4]arene molecule was shown to be favourable by Grootenhuis *et al.*[36] The formation of a charged species dramatically increases the favourable electrostatic interactions of the calix[4]arene with solvent molecules. Through calculations they also showed that the hydrogen bonding of the monoanion to the neighbouring hydroxyl groups is increased, increasing the favourable intramolecular hydrogen bonding at the lower rim. The deprotonation of the second, third and fourth hydroxyl groups become progressively less favourable due to the repulsive interactions between the negatively charged oxygen atoms. As a result the observed mono-zwitterionic structure would be favourable for compound **1** to adopt.

A ^{1}H NMR spectrum of **1** in DMSO-d_6 does not indicate the presence of a zwitterion, which would likely show a high field resonance at around 9 ppm attributable to the C2 proton of the imidazolium motif. Heating the DMSO-d_6 solution, however, results in a lowering of the symmetry and the appearance of a resonance at 9.02 ppm, suggesting that the zwitterion does form at elevated temperature (Fig. 3). Upon cooling the NMR tube sample to room temperature the resonance at 9.02 ppm remains rather than reverting back to the neutral imidazole compound.† Compound **1** was heated at 60 °C in chloroform for 18 hours and the solvent removed *in vacuo*. A ^{1}H NMR spectrum of this material in DMSO-d_6 at room temperature suggests the presence of the zwitterion, indicating that it can be prepared at elevated temperature and be retained in solution.

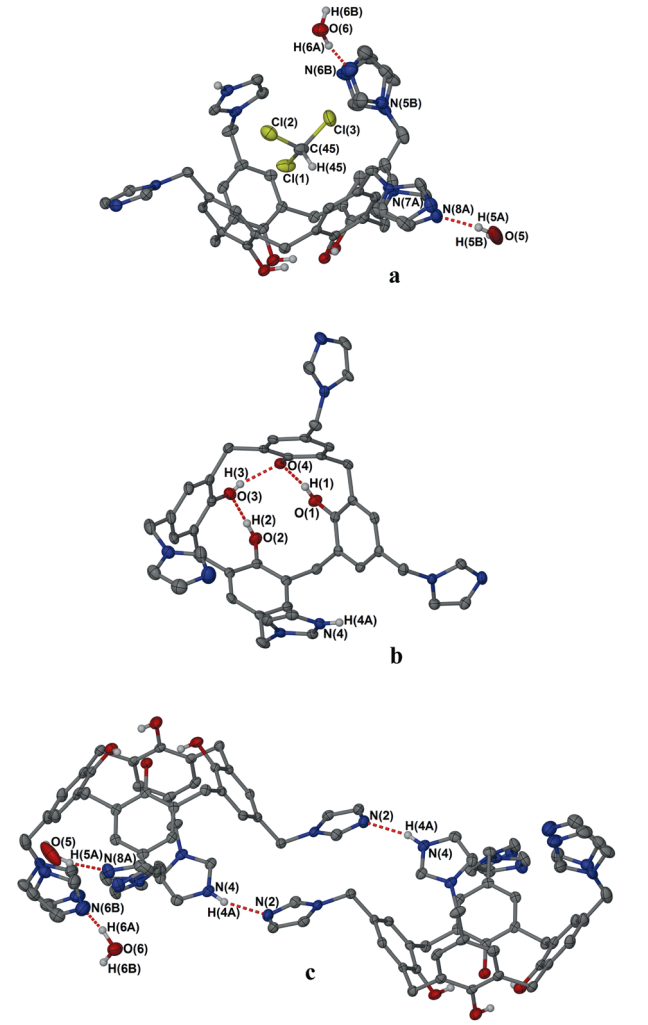

Fig. 2 X-Ray crystal structure of **1** illustrating (a) the cone conformation with a molecule of chloroform in the cavity, (b) deprotonated hydroxyl group (O4) and protonated imidazole (N4) and (c) hydrogen bonding network (some hydrogen atoms and chloroform atoms omitted for clarity, ellipsoids displayed at 50% probability).

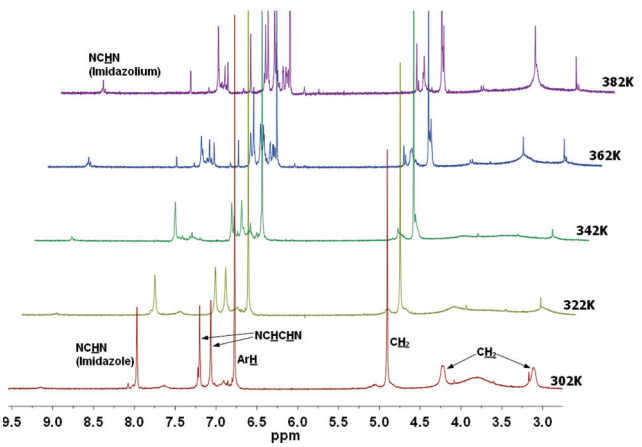

Fig. 3 VT ^{1}H NMR spectra of **1** in DMSO-d_6.

The CH_2-bridging proton signals appear as a set of broad doublets in DMSO-d_6 at 3.13 ppm and 4.21 ppm at 302 K, attributable to the interconversion of cone conformers that

occurs slowly on the NMR timescale at room temperature. At higher temperatures the interconversion is rapid, and therefore the signals coalesce to form a broad singlet at 3.7 ppm. There are, however, two sharp doublets observed at 3.21 ppm and 4.38 ppm at higher temperature, possibly due to restricted interconversion on one side of the calixarene, namely zwitterion and hydrogen bonding interactions.

Compound **1** was initially prepared as a precursor to synthesise the novel compound **2**. One approach to form imidazolium salts is through quaternization of a neutral N-substituted imidazole. We have found that **2** can be formed more cleanly and in higher yield by reacting 1-bromomethyl-4-hydroxy calix[4]arene (**A**) directly with 1-methylimidazole, rather than proceeding *via* **1**. The bromide counterions can be exchanged for hexafluorophosphate using NH_4PF_6 in water to afford the hexafluorophosphate salt of **2** as a white crystalline solid in 87% yield.

Anion interactions

Anion binding by **2** was probed by ^{1}H NMR spectroscopic titration of various tetrabutylammonium anions. Precipitates formed during the titration experiments in CD_3CN, so the NMR spectroscopic data was obtained in DMSO-d_6. Upon addition of chloride, bromide and nitrate anions there is a downfield shift of the C2 proton of the imidazolium, clearly indicating $(C–H)^+\cdots X^-$ interactions (Fig. 4). The shift is most significant with chloride and least with nitrate which reflects decreasing basicity, though size selectivity cannot be ruled out. The anion binding stoichiometry was examined by Job's method which confirmed 1 : 1 binding for chloride and bromide (Fig. 5). Using HypNMR, fits were obtained manually for anion binding constants based upon a 1 : 1 stoichiometry (Table 1).† Automatic refinement was not possible, likely due to the broad range of CH hydrogen bonds involving not just the acidic NCHN units but also the backbone C4 and C5 protons and the lower rim hydroxyl groups. This is further evidenced by the ^{1}H NMR titration data upon addition of anions which also exhibit a change in the backbone C4 and C5 proton resonances. In **2** these appear as a singlet at 7.70 ppm and, upon addition of anion, split into two singlets, with one moving further downfield. The downfield shift is most pronounced for chloride and least for nitrate. During the NMR titration experiments chemical shift changes continued well beyond the addition of one equivalent of guest, which is inconsistent with the Job plots, suggesting weaker binding of further anions with concomitant structural changes to the calixarene.

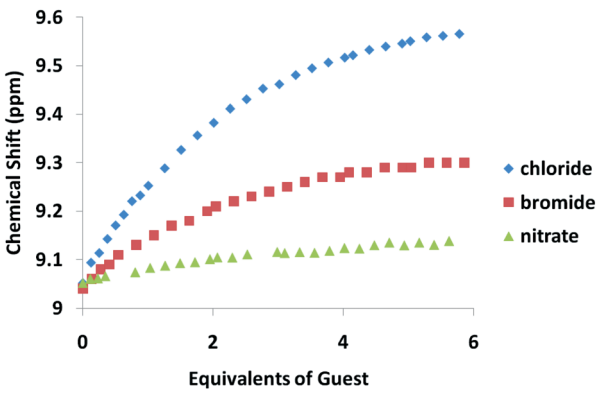

Fig. 4 ^{1}H NMR spectroscopic titration data for binding of chloride, bromide and nitrate by **2** in DMSO-d_6.

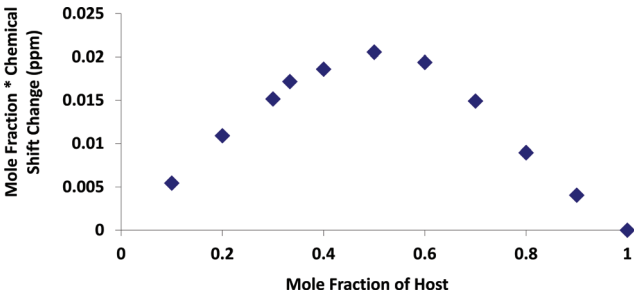

Fig. 5 Job plot in DMSO-d_6 for the interaction of **2** with Bu_4NBr.

Table 1 Binding constants for Bu_4N^+ anion salts by **2** in DMSO-d_6

Anion	log β_{11}	$\Delta\delta$ at 1 equivalent
Cl^-	1.35	0.201
Br^-	1.40	0.110
NO_3^-	1.06	0.026

An X-ray crystal structure of the bromide salt of **2** was obtained which, to the best of our knowledge, is the first structure of a cationic calix[4]arene (bearing hydroxyl groups) in the absence of a metal. The structure (Fig. 6a) shows the expected cone-type conformation with the imidazolium groups projecting upwards and, unlike **1**, is symmetrical. The oxygen atoms on the lower rim are oriented towards a bromide atom (Br3), further confirming the presence of OH···anion interactions. The molecules are arranged in 2D layers, with each layer consisting of 'back-to-back' calixarene molecules with the OH moieties pointing inwards (Fig. 6b). Each aryl ring is involved in π–π interactions with a neighbouring aromatic ring (Fig. 6c), and the layers are arranged so that the top rims bearing the imidazolium groups are pointing toward each other. Bromide atoms which are interacting with the backbone C4 protons sit between the layers, with large pores between these bridging bromide ions. The distance between closest bridging bromide ions is 10.8 Å, and between OH-coordinating bromide ions 9.8 Å, and disordered methanol molecules occupy the channels. The structure clearly shows that several hydrogen bonding interactions with guest anions exist in this calixarene due to the range of acidic protons on both the upper and the lower rims. As the channels in the structure of **2**Br are relatively large and are lined by imidazolium moieties, the material offers distinct possibilities for both catalysis and gas storage.[37,38]

Anion binding by **2** was also probed with tetrabutylammonium acetate and tetrabutylammonium phosphate, both of which exhibit unusual behaviour (Fig. 7). A downfield shift of the C2 proton resonance is observed up to one equivalent of guest. Following this there is a slight upfield shift of the C2 proton resonance to about 1.5 equivalents, before the resonance continues to move downfield upon further addition. It is clear from the X-ray structure of **2**Br that a range of hydrogen bonding interactions are

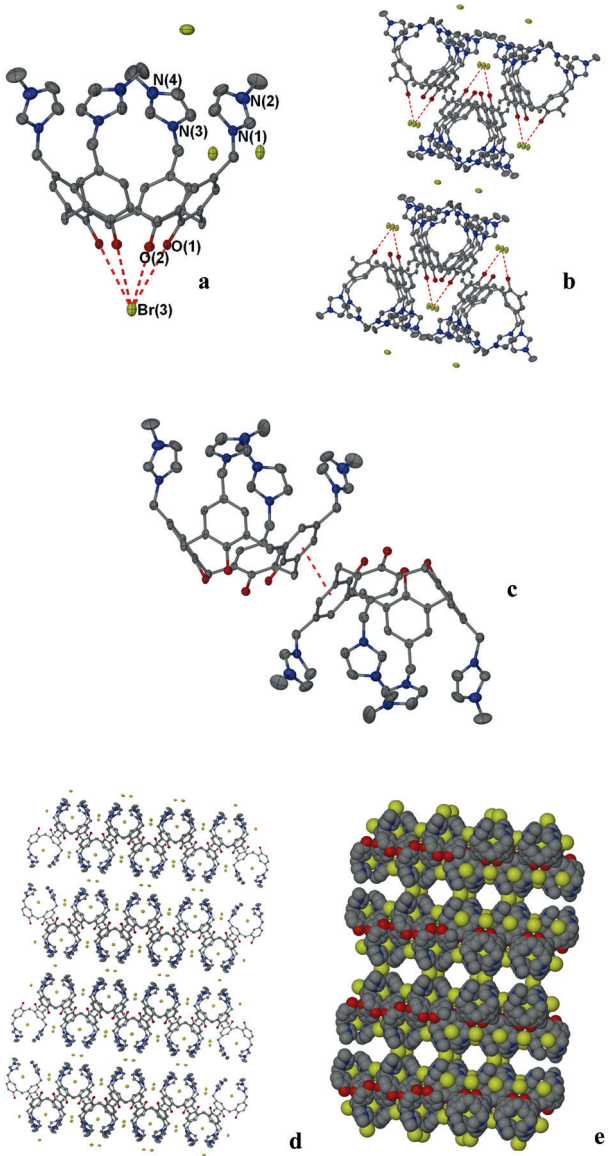

Fig. 6 X-Ray crystal structure of **2**Br (hydrogen atoms and methanol atoms omitted for clarity, ellipsoids displayed at 50% probability).

possible in **2**. As acetate and phosphate are basic anions they also have the potential to deprotonate acidic protons. The first equivalent of these guests appears to bind to the imidazolium C2 protons at the upper rim resulting in the downfield shift of the proton resonance. Following this the anions interact with a different part of the calixarene, with a change in molecular shape being the likely cause of the slight upfield chemical shift of the C2 protons. It is probable that the second equivalent of these basic anions are interacting with the acidic lower rim, causing (partial) deprotonation of one of the hydroxyl groups which will result in a slight change in shape of the calixarene. Subsequently the anions continue to interact with the C2 protons of the upper rim.

Conclusions

In conclusion we have shown that the neutral tetrakis(methylimidazole) calix[4]arene **1** can exist as the mono-zwitterion both in solution and in the solid-state. The zwitterion has the potential to be a host for salts, with a cation in the cavity engaging in cation–π interactions and the anion hydrogen bonding to the imidazolium. We are currently investigating the synthesis of soluble imidazole calixarenes with the potential to act as hosts for salts. The cationic tetrakis(methylimidazolium) calix[4]arene **2** has a plethora of acidic CH groups which take part in beneficial hydrogen bond interactions with anions, which has been observed in solution and in the solid-state. The location of the interaction site with basic anions appears to be selective depending upon the concentration of anions compared to calixarene. This offers the possibility of sensing, or communication between the different binding regions, which is dependent upon anion concentration. We are currently investigating the effect of different solvents within the calixarene cavity to examine potential neutral guest modulated anion binding and deprotonation behaviour.

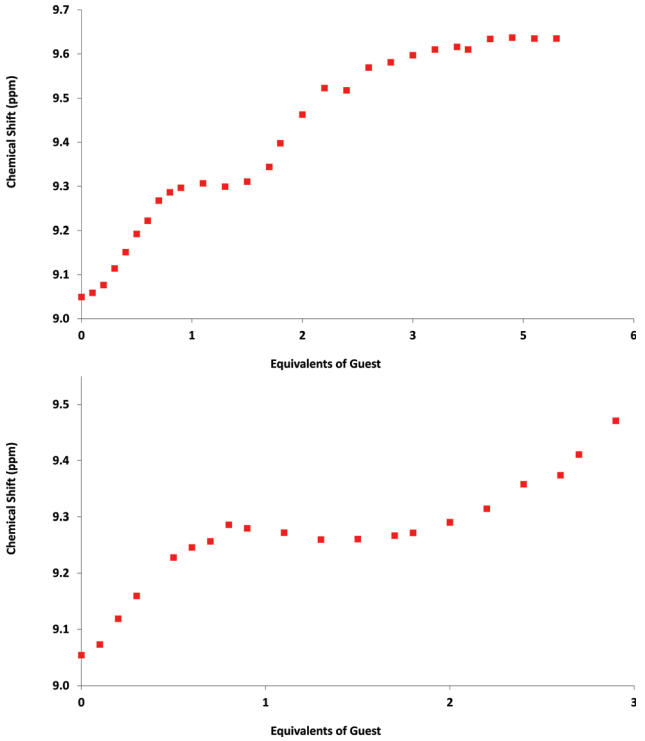

Fig. 7 ^{1}H NMR spectroscopic titration data for binding of acetate (top) and dihydrogen phosphate (bottom) by **2** in DMSO-d_6.

Experimental

All reagents were used as supplied or prepared as outlined without need for further purification. 1-^{t}Butyl-4-hydroxy calix[4]arene[39] and 4-hydroxy calix[4]arene[40] were prepared according to literature procedure. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX300 spectrometer (operating frequency 300.1 MHz for ^{1}H and 75.48 MHz for ^{13}C) or on a Bruker DRX500 spectrometer (operating frequency 500.13 MHz for ^{1}H and 125.03 MHz for ^{13}C). Chemical shift values are quoted in parts per million (ppm, δ) and coupling constants J are quoted in Hertz (Hz). Microanalyses were performed by Mr Martin Huscroft and Mr Ian Blakeley in the University of Leeds, School

of Chemistry. Mass spectra were collected by Ms Tanya Marinko-Covell either on a Bruker Daltonics (micro T.O.F.) instrument operating in the electrospray mode or a GCT Premier (T.O.F.) instrument operating in electron impact mode using methanol or acetonitrile as solvent. X-ray diffraction data were collected on a Bruker Nonius X8 diffractometer fitted with an Apex II detector with Mo-K_α radiation (λ = 0.71073 Å).

1-Bromomethyl-4-hydroxy calix[4]arene (A)

Zn powder (0.115 g, 1.77 mmol) was added to glacial acetic acid (62 mL) followed by HBr (33% wt in acetic acid, 7.5 mL) and stirred for 30 minutes. 4-Hydroxy calix[4]arene (1.50 g, 3.54 mmol), paraformaldehyde (5.60 g, 187 mmol) and HBr solution (37 mL) were added and the mixture heated at 90 °C for 72 hours. The solution was cooled to room temperature and the precipitate collected under reduced pressure, washed with water (2 × 20 mL) and dried by washing with diethyl ether (2 × 30 mL). The product was collected as a white solid (2.06 g, 73%). ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 10.02 (s, 4H, OH), 7.03 (s, 8H, Ar–H), 4.25 (s, 8H, CH_2), 4.14 (br, 4H, CH_2), 3.16 (br, 4H, CH_2). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 300 K): δ = 147.91 (C), 130.68 (C), 128.93 (CH), 127.26 (C), 32.25 (CH_2), 30.56 (CH_2).

Tetrakis(methylimidazole) calix[4]arene 1

1-Bromomethyl-4-hydroxy calix[4]arene **A** (2.00 g, 2.53 mmol) and imidazole (6.88 g, 101 mmol) were added to a Schlenk flask and the reagents degassed. Anhydrous methanol (70 mL) was added and the solution heated at 75 °C for 72 hours. The reaction mixture was allowed to cool before water (100 mL) was added resulting in the formation of a white precipitate. The precipitate was collected by reduced pressure filtration, washed with water (2 × 50 mL) then dried by washing with diethyl ether (2 × 50 mL). The product was collected as an off white solid. Yield: 0.400 g (21%). Mp: 240–242 °C. ^{1}H NMR (300 MHz, DMSO-d_6, 300 K): δ = 7.95 (s, 4H, NHCN), 7.72 (s, 4H, NCH), 7.06 (s, 4H, NCH), 6.80 (s, 8H, Ar–H), 4.91 (s, 8H, CH_2), 4.21 (br, 4H, CH_2), 3.13 (br, 4H, CH_2), OH resonance not observed. ^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6, 300 K): δ = 154.94 (C), 137.01 (CH), 130.76 (C), 127.47 (CH), 126.94 (CH), 126.30 (C), 120.38 (CH), 50.28 (CH_2), 32.61 (CH_2). MS (ESI$^+$): *m*/*z* 745.3 [M + H]$^+$, 767.3 [M + Na]$^+$. HRMS (EI$^+$): Calcd for $C_{44}H_{41}N_8O_4$ [M + H]$^+$: 745.3245. Found: 745.3228. Calcd for $C_{44}H_{40}N_8NaO_4$ [M + Na]$^+$: 767.3065. Found: 767.3039. Anal. calcd for $C_{44}H_{40}N_8O_4{\cdot}3H_2O$: C, 66.15%; H, 5.80%; N, 14.03%. Found: C, 66.50%; H, 5.50%; N, 14.65%. Recrystallisation from chloroform resulted in colourless prism crystals that were suitable for single crystal X-ray diffraction. M = 891.23, monoclinic, a = 10.0579(8)Å, b = 40.788(3)Å, c = 10.7646(9)Å, α = 90.00°, β = 101.688(4)°, γ = 90.00°, U = 4324.5(6)Å^3, T = 150(2) K, space group $P2_1/c$, Z = 4, μ(Mo-K_α) = 0.270 mm^{-1}, 61 030 reflections measured, 9587 unique reflections (R_{int} = 0.0443). The final R_1 values were 0.0492 ($I > 2\sigma(I)$). The final w$R(F^2)$ values were 0.1009 ($I > 2\sigma(I)$). The final R_1 values were 0.0799 (all data). The final w$R(F^2)$ values were 0.1133 (all data). The goodness of fit on F^2 was 1.031.

Tetrakis(methylimidazolium)bromide calix[4]arene 2Br

1-Bromomethyl-4-hydroxy calix[4]arene **A** (1.00 g, 1.26 mmol) was added to a Schlenk flask and degassed. Anhydrous dichloromethane (50 mL) was added, followed by *N*-methyl imidazole (0.460 mL, 5.60 mmol). The solution was stirred at room temperature, under a nitrogen atmosphere, for 12 hours. The product precipitated from solution as a white solid that was collected by filtration, washed with dichloromethane (3 × 20 mL), and dried *in vacuo*. Yield: 1.20 g (84%). ^{1}H NMR (500 MHz, DMSO-d_6, 300 K): δ = 9.31 (s, 4H, NCHN), 7.80 (s, 4H, CH), 7.70 (s, 4H, CH), 7.17 (s, 8H, CH), 5.12 (s, 8H, CH_2), 3.86 (s, 12H, CH_3), bridging CH_2 resonances not observed due to ring inversion at room temperature rendering them broad, OH resonance not observed. ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6, 300 K): δ = 152.97 (C), 136.21 (CH), 129.65 (C), 128.78 (CH), 123.53 (CH), 121.91 (CH), 51.73 (CH_2), 35.64 (CH_3). MS (ESI$^+$): *m*/*z* 1147.1 [M + Na]$^+$, 963.2 [M − 2Br − H]$^+$, 881.3 [M − 3Br − 2H]$^+$. Colourless crystals that were suitable for single crystal X-ray diffraction were grown by slow evaporation of diethyl ether into a methanol solution of **2**Br. M = 629.92, monoclinic, a = 17.580(2) Å, b = 39.483(5) Å, c = 11.719(2) Å, α = 90.00°, β = 130.147(4)°, γ = 90.00°, U = 6217.9(14) Å^3, T = 150(2) K, space group $C2/m$, Z = 8, μ(Mo-K_α) = 0.264 mm^{-1}, 36 400 reflections measured, 6240 unique reflections (R_{int} = 0.0669). The final R_1 values were 0.0628 ($I > 2\sigma(I)$). The final w$R(F^2)$ values were 0.1780 ($I > 2\sigma(I)$). The final R_1 values were 0.1115 (all data). The final w$R(F^2)$ values were 0.2041 (all data). The goodness of fit on F^2 was 1.061.

Tetrakis(methylimidazolium)hexafluorophosphate calix[4]arene 2PF$_6$

Tetrakis(methylimidazolium)bromide calix[4]arene **2**Br (0.580 g, 5.15 mmol) was dissolved in H_2O (10 mL) and a H_2O solution (10 mL) of NH_4PF_6 (0.240 g, 1.47 mmol) was added dropwise with stirring. The mixture was stirred for 30 minutes, filtered, and the solid washed with water (3 × 5 mL) followed by diethyl ether (3 × 5 mL), and dried in air. The product was collected as a white solid. Yield: 0.550 g (87%). Mp: 214–216 °C. ^{1}H NMR (500 MHz, DMSO-d_6, 300 K): δ = 9.03 (s, 4H, NCHN), 7.70 (s, 4H, CH), 7.67 (s, 4H, CH), 7.11 (s, 8H, CH), 5.09 (s, 8H, CH_2), 3.86 (s, 12H, CH_3), bridging CH_2 resonances not observed due to ring inversion at room temperature rendering them broad, OH resonance not observed. ^{1}H NMR (500 MHz, CD_3CN, 248 K): δ = 9.47 (s, 4H, OH), 8.47 (s, 4H, NCHN), 7.32 (s, 4H, CH), 7.26 (s, 4H, CH), 7.15 (s, 8H, CH), 5.03 (s, 8H, CH_2), 4.17 (br, 4H, CH_2), 3.78 (s, 12H, CH_3), 3.50 (br, 4H, CH_2). ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6, 300 K): δ = 152.14 (C), 136.14 (CH), 129.36 (C), 128.83 (CH), 123.84 (CH), 122.11 (CH), 51.77 (CH_2), 38.96 (CH_3). MS (ESI$^+$): *m*/*z* 1239.3 [M − PF]$^+$. HRMS (EI$^+$): Calcd for $C_{48}H_{52}F_{18}N_8O_4P_3$ [M − PF_6]$^+$: 1239.3031. Found: 1239.3047. Anal. calcd for $C_{48}H_{52}F_{24}N_8O_4P_4{\cdot}2H_2O$: C, 40.57%; H, 3.88%; N, 7.99%. Found: C, 40.95%; H, 3.85%; N, 7.80%.

^{1}H NMR spectroscopic titration experiments

^{1}H NMR spectroscopic titration experiments were carried out using a Bruker DPX300 spectrometer running at 300.1 MHz, at

room temperature. All chemical shifts are reported in ppm. A specific concentration of host, typically 15–23 mM, was made up in a single NMR tube in DMSO-d_6 (0.8 mL). The anions, as their tetrabutylammonium salts, were made up to 1 mL, 10 times the concentration of the host, with DMSO-d_6. 20 μL aliquots of the guest were added to the NMR tube and the spectra recorded after each addition.

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