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A study of anion binding behaviour of 1,3-*alternate* thiacalix[4]arene–based receptors bearing urea moieties†

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Three novel thiacalix[4]arene receptors **4$_{a-c}$** each with a 1,3-*alternate* conformation and possessing two urea moieties linking various phenyl groups substituted with either *para* electron-donating or -withdrawing groups have been synthesized. The binding properties of these receptors were investigated by means of ^{1}H NMR spectroscopy and UV-vis absorption titration experiments using various anions. The structures and complexation energies were also studied by density functional theory (DFT) methods. The results suggested that receptor **4$_c$**, which possesses two *p*-(trifluoromethyl)phenyl ureido moieties, can complex most efficiently in the urea cavity and exhibits high selectivity towards F$^-$ and AcO$^-$ ions.

Introduction

Calix[*n*]arenes[1] have three-dimensional tuneable shapes and are used as molecular building blocks with potentially many applications in supramolecular chemistry. Thiacalix[4]arenes[2,3] are calix[*n*]arenes in which the phenolic groups are bridged by sulfur atoms instead of methylene groups, and have received much recent attention for potential applications in various fields across chemistry, biology and environmental science. Various anions such as F$^-$ (e.g., in dental caries prevention, in inhalation anesthetics and in the treatment of osteoporosis) also play fundamental roles in biological, medicinal, catalysis, and environmental chemistry.[4] The design and synthesis of anion-selective receptors[5] is more difficult than that of cation-selective receptors. This is due to some unique features of anions such as their much larger sizes in comparison with those

of cations, and also due to the large variety of geometries available,[6] some anions are spherical (F$^-$, Cl$^-$, Br$^-$, I$^-$) others are trigonal or Y-shaped (AcO$^-$) and others are tetrahedral (H$_2$PO$_4^-$), etc.. Anion recognition using artificially-designed receptors[6] based on calix[*n*]arenes is an important research topic in the area of supramolecular chemistry. Calix[*n*]arene urea derivatives are capable of effectively recognizing and sensing important anions via hydrogen-bonding interactions between the anions and the urea NH protons.[7,8]

Lhoták and co-workers[9] have reported anion receptors based on either upper-rim substituted calix[4]arenes or thiacalix[4]arenes which contain two *p*-nitrophenyl or *p*-tolyl urea moieties.[9a-c,h] These anion receptors exhibited effective recognition abilities towards selected anions in common organic solvents. Recently, Kumar and co-workers reported an anion receptor based on a calix[4]arene in a 1,3-*alternate* conformation and bearing containing two *p*-nitrophenyl-ureido moieties.[10] This compound exhibited strong binding and good selectivity towards Cl$^-$ ion due to strong hydrogen bonding between the Cl$^-$ ion and the N-H protons, both in THF or chloroform solutions. However, investigations concerning the influence on the acidity of the urea protons by either electron–donating or electron–withdrawing groups located on the *p*-position of phenyl groups of urea moieties in analogous thiacalix[4]arenes and the binding of various anions have received scant attension.[11j]

In this article, we report the synthesis of three novel thiacalix[4]arenes receptors **4$_{a-c}$** with a 1,3-*alternate* conformation and possessing two urea moieties linking various

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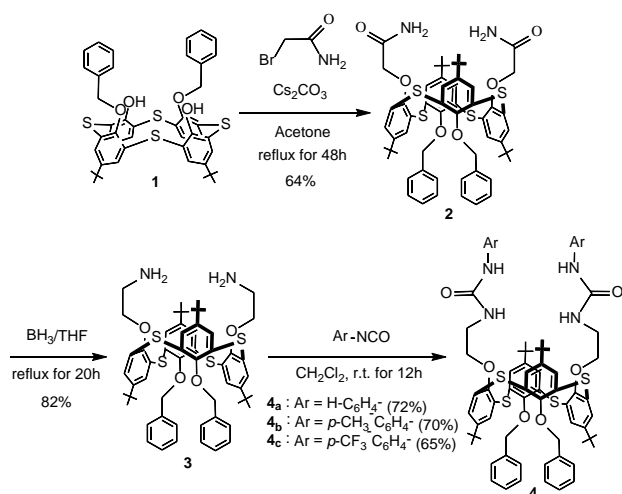*^{f}Department of Chemistry, The University of Hull, HU6 7RX, UK*

phenyl groups bearing either *para* electron-donating or electron-withdrawing groups, together with two benzyl groups at the opposite sides of the thiacalix[4]arene cavity.[11] In our studies, the complexation properties of **4**$_{a\sim c}$ towards F⁻, Cl⁻, Br⁻, I⁻, AcO⁻ and H$_2$PO$_4$⁻ ions were investigated by ¹H-NMR spectroscopy (with **4**$_{a\sim c}$) and UV-vis absorption (with **4**$_c$) titration experiments. Furthermore, the structures and complexation energies for all complexes of the receptors **4**$_{a\sim c}$ with various anions were also determined by theoretical studies using DFT methods.

Results and discussions

Synthesis

O-Alkylation of 1,3-*alternate*-**1** was conducted using 2 equivalents of bromoacetamide in the presence of 2 equivalents of Cs$_2$CO$_3$ according to the reported procedure, and afforded the desired 1,3-*alternate*-**2** in 60 % yield.[12] The amide reduction of 1,3-*alternate*-**2** was carried out with a large excess of BH$_3$/THF solution, and afforded the desired 1,3-*alternate*-**3** in 65 % yield. The condensation of 1,3-*alternate*-**3** with 2.2 equivalents of the appropriate isocyanate in CH$_2$Cl$_2$ furnished the receptors **4**$_{a\sim c}$ in good yields (Scheme 1). The ¹H NMR spectrum of receptors **4**$_{a\sim c}$ in CDCl$_3$ exhibits the characteristics of a 1,3-*alternate* conformation such as two singlets (18H each) for the *tert*-butyl protons, two triplets (4H each) for the -OCH$_2$CH$_2$- protons, two singlets (4H each) for the aromatic protons and two singlets (2H each) for the four urea NH protons. Moreover, concentration dependence of the ¹H NMR chemical shifts of the urea protons in receptor **4**$_c$ was not observed (Fig. S11). This (lack of) observation indicates that receptor **4**$_c$ has strong intramolecular hydrogen bonds between the two urea groups linking the *p*-(trifluoromethyl)phenyl moieties. The molecular structure of receptor **4**$_a$ was also verified by X-ray crystallographic analysis (Fig. 1, S12). Receptor **4**$_a$ was recrystallized from a mixture of
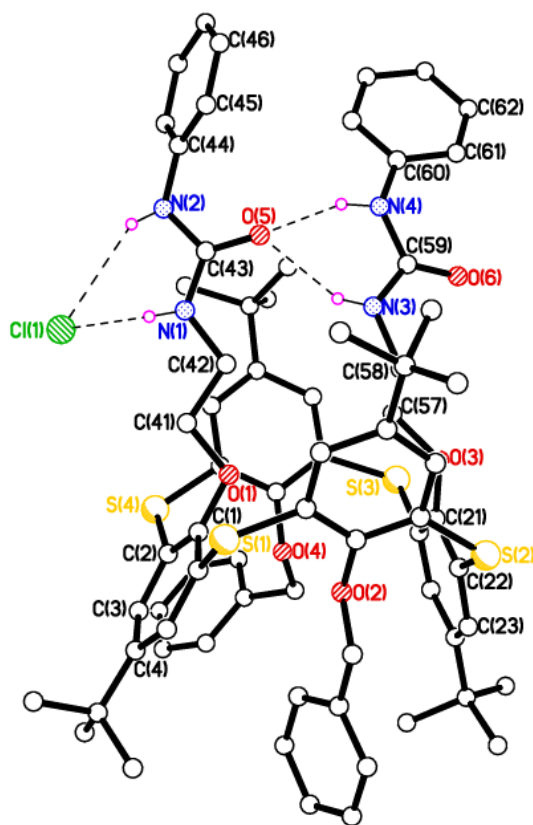

Fig. 1 X–ray crystal structure of receptor **4**$_a$·Cl⁻. H–bonds shown as dashed lines. One of four similar molecules in the asymmetric unit is shown in two orientations rotated by approx. 90°. H atoms not involved in H-bonding, minor disorder components, and solvent of crystallization are omitted for clarity. Guest used: tetrabutylammonium (TBA) salt.

CHCl$_3$–CH$_3$CN (3:2, v/v) by slow evaporation. These results indicate that receptor **4**$_a$ adopts the 1,3-*alternate* conformation in the solid state. In case of receptor **4**$_a$, there are four thiacalixarenes, two Cl⁻ ions, two tetrabutylammonium ions, one chloroform and two acetonitrile molecules in the asymmetric unit. Interestingly, it was found that the two urea groups approach each other and are oriented in parallel due to the existence of dual intramolecular hydrogen bonding (in the case of receptor **4**$_a$, for the molecule shown: N(3)–H(3)···O(5) 2.13(3); N(4)–H(4)···O(5) 2.17(3) Å; for the second molecule: N(1A)–H(1A)···O(6A) 2.15(3), N(2A)–H(2A)···O(6A) 2.20(3) Å; for the third molecule: N(3B)–H(3B)···O(5B) 2.30(3), N(4B)–H(4B)···O(5B) 2.17(2) Å; for the fourth molecule: N(1C)–H(1C)···O(6C) 2.31(3), N(2C)–H(2C)···O(6C) 2.27(3) Å) (Fig. 1, S12). Moreover, in the case of receptor **4**$_a$, pairs of calixarene molecules are linked via four H-bonds between two urea NH moieties on each calixarene and Cl⁻ ion.

Scheme 1 Synthesis of receptors 1,3-*alternate*-**4**$_{a\sim c}$.

Table 1. Association constants[a] of receptors **4a-c** with anions.[b]

Host	R	Association constant K_a [M^{-1}]					
		F$^-$ Spherical	Cl$^-$ Spherical	Br$^-$ Spherical	I$^-$ Spherical	AcO$^-$ Y-shape	H$_2$PO$_4^-$ Tetrahedral
4a	H	6,745±472	2,937 ±206	1,453±102	410±29	6,305±441	2,727±191
4b	Me	3,550 ±286	1,557±109	734±51	203±14	3,033±212	1,338±94
4c	CF$_3$	13,950 ±977	6,590±461	2,920±204	883 ±62	12,878±901	5,790±405

[a] Measured in CDCl$_3$–CD$_3$CN (10:1, v/v) at 298 K by the ^{1}H NMR titration method using the chemical-shift change of the NH$_a$ proton (Fig. S13–S49); host concentration was 4.0×10^{-3} M. [b] Guests used: TBA salts.
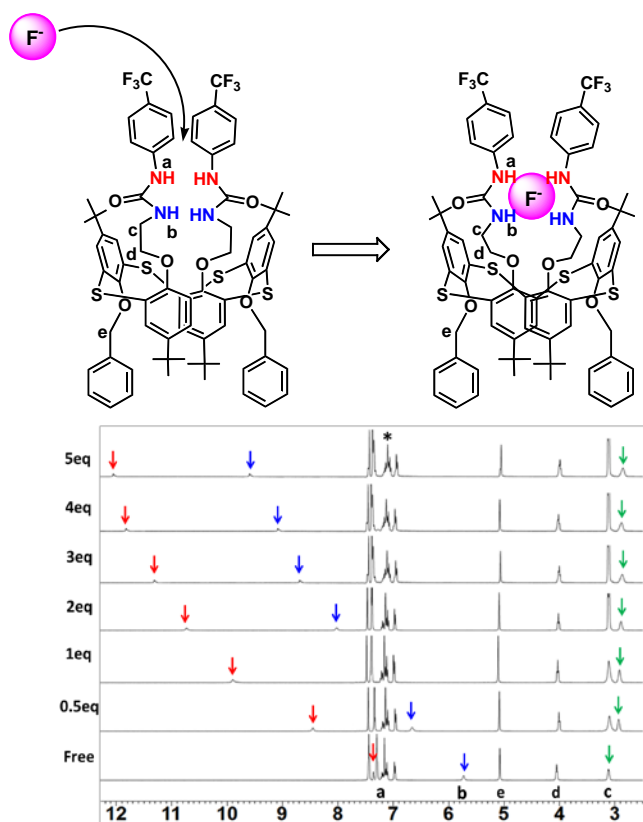

Fig. 3 Titration curves of receptor **4c** with various anions as their TBA salts in CDCl$_3$–CD$_3$CN (10:1, v/v) at 298 K.

Fig. 2 Binding mode of receptor 4c upon addition of F$^-$ ion at 298 K as TBA salts and partial ^{1}H NMR spectra of **4c** (4.0×10^{-3} M) in CDCl$_3$–CD$_3$CN (10:1, v/v) upon addition of F$^-$ ion at 298 K.

Binding studies

The binding properties of receptors **4a-c** in the presence of various anions as their tetrabutylammonium (TBA) salts, in CDCl$_3$–CD$_3$CN (10:1) solution, were investigated by means of ^{1}H-NMR titration spectroscopic experiments. As shown in Fig. 2, for the complexation of F$^-$ ion with receptor **4c**, the signals for the NH$_a$ protons (red)
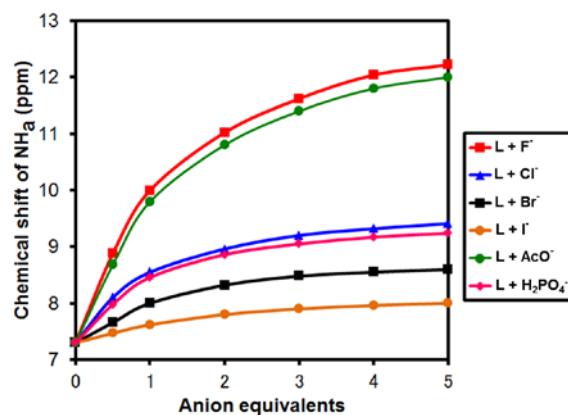
progressively shifted downfield by 4.55 ppm (δ = 7.35 to 11.9 ppm) until five equivalents of F$^-$ ion was added. On the other hand, the signals for the NH$_b$ protons (blue) progressively shifted downfield by 3.88 ppm (δ = 5.72 to 9.60 ppm) until five equivalents of F$^-$ ion were added. These results are strongly suggestive of F$^-$ ion recognition by receptor **4c** via hydrogen–bonding interactions between the F$^-$ ion and the N–H protons. The titration curves shown in Fig. 2, 3 (for **4c**) and Fig. S13–S49 show that further addition of various anions to the solution of each receptors **4a-c** in CDCl$_3$ solution, resulted in clear downfield shifts of the ^{1}H NMR signals of the NH$_a$ protons. All of the results obtained clearly suggest that anion recognition by the receptors is via hydrogen-bonding interactions between the anion and the NH protons. In particular, as shown in Fig. 2, receptor **4c** exhibited the highest selectivity amongst all of the anions tested, toward F$^-$ and AcO$^-$ ions. K_a values for receptors **4a-c** and the anions tested were determined by ^{1}H NMR spectroscopic titration experiments.[13a] (Table 1). These results suggest that the K_a values are influenced by the electron-donating or electron-withdrawing groups located at the *p*-position of the phenyl
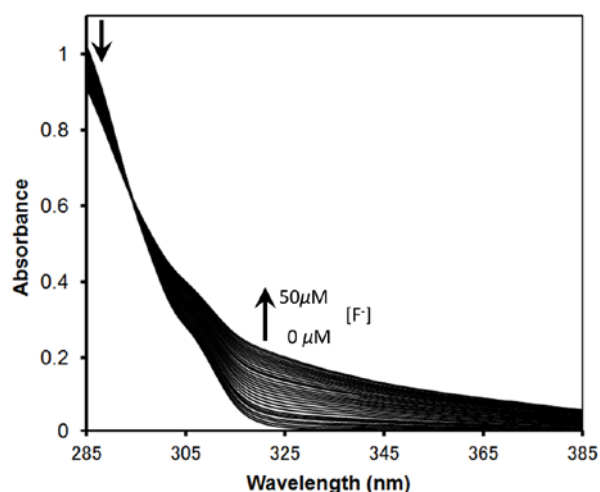
Fig. 4 UV–vis absorption spectra of receptor 4_c (2.5 µM) upon the addition of F⁻ (0–50 µM) at 298 K as a TBA salt in CH_2Cl_2.

Fig. 5 Geometry-optimized (ball-and-stick) structures of: *Left*: 4_c; *Right*: 1;1 complex of 4_c⊃F⁻. Colour code: F⁻ = magenta; nitrogen = blue; NH_a = light blue; NH_b = light green; sulphur = yellow; CF_3(fluoride) = orange; and oxygen atom = red.

Table 2. Association constants[a] of receptors 4_c with anions.[b]

Anion	F⁻	Cl⁻	AcO⁻	$H_2PO_4^-$
K_a [M⁻¹]	465,405±32,578	9,060±634	418,495±29,519	8,258±578

[a] Measured in CH_2Cl_2 at 298 K by UV–vis titration method (Fig. S50–S58); host concentration was 2.5 µM. [b] Guests used: TBA salts.

ureido moieties. The K_a values for 4_c having the electron-withdrawing CF_3 groups on the phenyl ureido moieties, were greater than those for the other two receptors. The K_a values for 4_b which had the electron-donating CH_3 groups on the ureido phenyl moieties were lower than those for 4_a and 4_b. Therefore, the introduction of electron–withdrawing groups at the *p*-position of the phenyl ureido groups appears to increase the acidity of the urea protons, and hence enhance the anion-binding ability through hydrogen-bonding interactions. Furthermore, receptor 4_c had the highest K_a values of all three receptors with each of the anions tested and also had the most effective recognition ability toward F⁻ and AcO⁻ ions. Further complexation studies of 4_c with F⁻, Cl⁻, AcO⁻ and $H_2PO_4^-$ ions were carried out using UV–vis spectroscopic titration experiments. Receptor 4_c (2.5 µM) exhibits a broad absorption band at 295 nm in its UV–vis absorption spectrum. Upon addition of F⁻ ion (0–50 µM) to the solution of 4_c, Fig. 4 reveals a gradual decrease in the absorption of the band at 288 nm with a simultaneous increase in the absorption at 320 nm and a clear isosbestic point at 295 nm. From the above, it is clear that receptor 4_c bearing the CF_3 groups has the most effective recognition ability toward F⁻ ions. A Job's plot for the binding between the receptor 4_c and F⁻ ion reveals a 1:1 stoichiometry (Fig. S52), and the K_a for the complexation[13b] of receptor 4_c with F⁻ ion was determined to be 465,405 ± 32,578 M⁻¹ by the UV–vis titrations in CH_2Cl_2 solution (Fig. S51). These results strongly suggested that F⁻ ion recognition by receptor 4_c was via a hydrogen-bonding interaction between F⁻ ion and NH protons, as shown in Fig. 4. The K_a values obtained by similar UV-vis titration
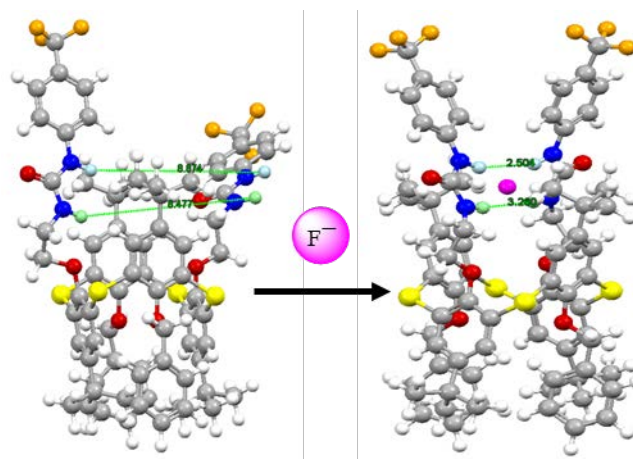
experiments of 4_c with the other anions are summarized in Table 2. To further investigate the binding properties of receptors $4_{a~c}$ with the anions tested, a computational study was carried out. The individual structures for all studies in the gas-phase were fully geometry-optimized using Gaussian 09[14] with the B3LYP level of DFT and the 3-21G basis set. Significant changes were observed for the distances between two urea NH moieties on each of the receptors $4_{a~c}$ in their anion complexes. The conformation changes for 4_c upon 1:1 complexation with F⁻ ion can be seen in Fig. 5 (more precise details for the computation studies for receptors $4_{a~c}$ with the different anions are shown in Fig. S59–S94). Fig. 5 shows the computed structure (*right*) of the 1:1 complex of 4_c with F⁻ ion. Because of the hydrogen-bonding between the F⁻ ion and two urea NH protons, distances between two urea NH moieties (NH_a···$NH_{a'}$ and NH_b···$NH_{b'}$) on two *p*-(trifluoromethyl)phenyl ureido moieties decrease from 8.783 to 2.530 (Å) and from 8.379 to 3.251 (Å), respectively. This also strongly supports the experimental evidence obtained for the formation of a 1:1 (4_c⊃F⁻) complex. The calculated complexation energies (ΔE kJ mol⁻¹) for receptors $4_{a~c}$ with the anion complexes are shown in Table 3. The trend for the complexation energies for $4_{a~c}$ are in the order: F⁻ > AcO⁻ > $H_2PO_4^-$ > Cl⁻ > Br⁻ > I⁻, which is in agreement with the trend observed for the observed complexation data obtained by means of ¹H NMR spectroscopy and UV-vis absorption titration experiments.

Conclusion

In summary, three novel receptors $4_{a~c}$ bearing a thiacalix[4]arene in a 1,3-*alternate* conformation have been synthesized. These receptors possess two ureas moieties linking various aryl groups bearing electron-donating or -withdrawing groups at their *p*-positions, which act as anion-binding sites and two benzyl groups at the opposite side of thiacalix[4]arene cavity. The binding of various anions at the two urea moieties was investigated by using ¹H NMR, UV-vis absorption titration experiments. It was found that receptor 4_c has a much higher

affinity towards all of the selected anions and especially for F⁻ and AcO⁻ ions.

Experimental Section

General

All melting points were determined with a Yanagimoto MP-S1 melting point apparatus. ^{1}H-NMR spectra were determined at 300 MHz with a Nippon Denshi JEOL FT-300 NMR spectrometer with TMS as an internal reference; J-values are given in Hz. UV-vis spectra were measured with a Shimadzu 240 spectrophotometer. Mass spectra were obtained on a Nippon Denshi JMS-01SG-2 mass spectrometer at an ionization energy of 70 eV using a direct inlet system through GLC. Elemental analyses were performed by Yanaco MT-5.

Materials

Unless otherwise stated, all other reagents used were purchased from commercial sources and were used without further purification. Compounds **1**,[11d,12] **2**[12] and **3**[12] were prepared following the reported procedures.

Preparations

4$_a$: To a solution of compound **3** (150 mg, 0.166 mmol) in CH$_2$Cl$_2$ (10 mL) was added phenyl isocyanate (44 mg, 0.37 mmol) and the mixture was stirred at room temperature for 24 h under argon. The resulting precipitate was collected by filtration, washed with CH$_3$OH to give receptor **4$_a$** as a white solid. Recrystallization from CHCl$_3$–CH$_3$OH (2:1) gave receptor **4$_a$** (146 mg, 72 %) as a white solid. M.p. 200–202 °C. IR: υ_{max} (KBr)/cm^{-1}: 3220, 2958, 1683, 1542, 1439, 1214, 1206, 1137, 994, 812 and 760. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 0.85 (18H, s, tBu × 2), 1.22 (18H, s, tBu × 2), 3.05 (4H, br, CH_2NH × 2), 4.01 (4H, br, OCH_2 × 2), 5.08 (4H, s, OCH_2 × 2), 5.56 (2H, s, NH × 2), 6.90–7.22. (20H, m, Phenyl–H × 20), 7.09 (4H, s, Ar–H × 4), 7.18 (2H, s, NH × 2) and 7.41 (4H, s, Ar–H × 4) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 30.9 (CH$_3$), 31.0 (CH$_3$), 33.9 (C(CH$_3$)$_3$), 34.1 (C(CH$_3$)$_3$), 40.9 (CH$_2$), 70.8 (OCH$_2$), 72.0 (OCH$_2$), 124.6 (ArC), 125.9 (ArC), 126.2 (ArC), 126.3 (ArC), 126.5 (ArC), 126.7 (ArC), 128.0 (ArC), 128.3 (ArC), 128.5 (ArC), 128.6 (ArC), 128.8 (ArC), 129.0 (ArC), 129.1 (ArC), 129.3 (ArC), 130.0 (ArC), 132.0 (ArC), 135.2 (ArC), 142.8 (ArC), 146.1 (ArC) and 155.4 (CO) ppm. FABMS: m/z: 1224.50 (M$^+$). C$_{72}$H$_{80}$N$_4$O$_6$S$_4$ (1224.50): calcd C 70.55, H 6.58, N 4.57. Found: C 70.52, H 6.57, N 4.58.

4$_b$: To a solution of compound **3** (150 mg, 0.166 mmol) in CH$_2$Cl$_2$ (10 mL) was added p–tolyl isocyanate (48 mg, 0.37 mmol) and the mixture was stirred at room temperature for 24 h under argon. The resulting precipitate was collected by filtration, washed with CH$_3$OH to give receptor **4$_b$** as a white solid. Recrystallization from CHCl$_3$–CH$_3$OH (3:1) gave receptor **4$_b$** (146 mg, 70 %) as white solid. M.p. 203–204 °C. IR: υ_{max} (KBr)/cm^{-1}: 3301, 2946, 1605, 1583, 1426, 1211, 1196, 1123, 1016, 889 and 802. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 0.82 (18H, s, tBu × 2), 1.22 (18H, s, tBu × 2), 2.29 (6H, s, CH_3 × 2), 3.06 (4H, br, CH_2NH × 2), 4.03 (4H, br, OCH_2× 2), 5.05 (4H, s, OCH_2× 2), 5.50 (2H, br, NH × 2), 6.86 (2H, s, NH × 2), 6.96–7.18. (18H, m, Phenyl–H × 18), 7.10 (4H, s, Ar–H × 4) and 7.41 (4H, s, Ar–H × 4) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 20.0 (CH$_3$), 31.3 (CH$_3$), 34.3 (C(CH$_3$)$_3$), 39.4 (CH$_2$), 70.1 (OCH$_2$), 71.3 (OCH$_2$), 119.8 (ArC), 121.9 (ArC), 125.1 (ArC), 125.2 (ArC), 125.4 (ArC), 125.9 (ArC), 126.2 (ArC), 126.5 (ArC), 127.1 (ArC), 127.5 (ArC), 127.8 (ArC), 128.0 (ArC), 128.3 (ArC), 128.5 (ArC), 128.6 (ArC), 128.8 (ArC), 129.0 (ArC), 129.1 (ArC), 129.3 (ArC), 130.0 (ArC), 135.1 (ArC), 136.2 (ArC), 147.8 (ArC), 148.0 (ArC), 149.5 (ArC), 151.9 (ArC), 154.0 (ArC) and 158.4 (CO) ppm. FABMS: m/z: [M+H]$^+$ Calcd for C$_{74}$H$_{85}$N$_4$O$_6$S$_4$ (1253.5352) ; Found 1253.4812.

4$_c$: To a solution of compound **3** (150 mg, 0.166 mmol) in CH$_2$Cl$_2$ (10 mL) was added p–(trifluoromethyl)phenyl isocyanate (68 mg, 0.366 mmol) and the mixture was stirred at room temperature for 24 h under argon. The resulting precipitate was collected by filtration, washed with CH$_3$OH to give receptor **4$_c$** as a white solid. Recrystallization from CHCl$_3$– CH$_3$OH (3:2) gave receptor **4$_c$** (147 mg, 65%) as a white solid. M.p. 210–211 °C. IR: υ_{max} (KBr)/cm^{-1}: 3279, 2923, 1602, 1572, 1538, 1225, 1170, 1091, 1068, 905 and 794. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 0.82 (18H, s, tBu × 2), 1.19 (18H, s, tBu × 2), 3.12 (4H, br, CH_2NH × 2), 4.03 (4H, br, OCH_2 × 2), 5.08 (4H, s, OCH_2× 2), 5.75 (2H, s, NH × 2), 6.92–7.30. (18H, m, Phenyl–H × 18), 7.13 (4H, s, Ar–H × 4), 7.33 (2H, s, NH × 2) and 7.41 (4H, s, Ar–H × 4) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 32.1 (CH$_3$), 35.6 (C(CH$_3$)$_3$), 40.0 (CH$_2$), 70.1 (OCH$_2$), 70.9 (OCH$_2$), 118.1 (ArC), 118.8 (ArC), 122.2 (ArC), 122.4 (ArC), 122.7 (ArC), 122.9 (ArC), 123.0 (ArC), 123.3 (ArC), 123.6 (ArC), 124.0 (ArC), 124.4 (ArC), 124.8 (ArC), 126.1 (ArC), 126.5 (ArC), 126.8 (ArC), 127.3 (ArC), 127.8 (ArC), 128.0 (ArC), 128.7 (ArC), 129.3 (ArC), 129.5 (ArC), 138.2 (ArC), 138.9 (ArC), 149.2 (ArC), 155.2 (ArC) and 160.7 (CO) ppm. FABMS: m/z: 1361.4861 [M+H]$^+$. C$_{74}$H$_{79}$F$_6$N$_4$O$_6$S$_4$ (1361.4787): calcd C 65.27, H 5.77, N 4.11. Found: C 65.32, H 5.75, N 4.08.

Determination of the association constants

The association constants (K_a) were determined by using ^{1}H NMR spectroscopic titration experiments with a constant concentration of host receptor (4.0×10^{-3} M) and varying the guest concentrations (0–8.0×10^{-3} M). The ^{1}H NMR chemical shifts of the urea protons (NH) signal were used as a probe. The K_a values for the complexes of receptor **4$_{a\sim c}$** were calculated by nonlinear curve-fitting analysis of the observed chemical shifts of the NH protons according to the literature procedure.[13a]

^{1}H NMR titration experiments

A solution of Bu$_4$NX (X = F, Cl, Br, I, AcO, H$_2$PO$_4$) in CD$_3$CN (4.0×10^{-3} M) was added to a CDCl$_3$ solution of receptor **4$_{a\sim c}$** in an NMR tube. ^{1}H NMR spectra were recorded after addition of

the reactants and the temperature of the NMR probe was kept constant at 27 °C.

Crystallographic analyses of 4$_a$

Diffraction data were collected on a Bruker APEX 2 CCD diffractometer equipped with graphite-monochromated Mo-Kα radiation at 150(2)K.[15] Data were corrected for Lorentz and polarisation effects and for absorption.[15] The structures were solved by direct methods and refined by full-matrix least-squares methods, on F^2.[16] The asymmetric unit contains four calixarenes two chloride anions, two tetrabutylammonium cations, one chloroform and two acetonitrile molecules of crystallisation. Within each of the four calixarenes there are pairs of N–H···O hydrogen bonds between urea moieties to a single carbonyl O atom. Looking down on the S$_4$ square-shaped planes of the four unique calixarenes, three are approximately geometrically aligned in parallel while one, containing S(1A), is slightly twisted.

Two *t*Bu groups on calixarenes were modelled as disordered over two sets of positions for the Me groups. See tables for the occupation factors. Two *n*-butyl chains in the cations exhibit some signs of disorder, but this was not modelled. The chloroform molecule was modelled as fully disordered over two sets of positions. There are two molecules of acetonitrile of crystallisation which reside in claixarene clefts on molecules containing S(1) and S(1B).

Pairs of calixarene molecules are linked via four H-bonds between both urea N–H moieties on each calixarene and a chloride ion. *n*-butyl ammonium cations reside close to the chloride anions, due to electrostatic attraction. So, each pair of calixarenes is able to capture one chloride ion. The overall packing type is in layers.

Crystal data for **4$_a$**: $C_{144}H_{160}N_8O_{12}S_8 \cdot C_{16}H_{36}N^+ \cdot Cl^- \cdot 0.5(CHCl_3) \cdot C_2H_3N$, M = 2829.91. Triclinic, space group P^-1, a =15.1315 (5), b = 28.8618 (11), c = 35.9491 (13) Å, V = 15113.8 (9) Å^3. Z = 4, Dc = 1.244 g.cm^{-3}, $F(000)$ = 6044, T = 100 K, μ(Mo-Kα) = 0.226 cm^{-1}, λ(Mo-$K\alpha$) = 0.71073 Å, colourless crystal of size 0.16 × 0.13 × 0.04 mm^3. The total number of reflections measured, to θ_{max} = 25.3°, was 42128 of which 27707 were unique (R_{int} = 0.062); 8953 were 'observed' with $I > 2\sigma(I)$. For the 'observed' data only, R_1 = 0.068; wR_2 = 0.185 for all 42128 reflections and 3705 parameters. Residual electron density within +/– 0.86 eÅ^{-3}.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 1062186 for **4$_a$**. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: 144-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

Supporting information: ^{1}H, ^{13}C NMR & IR spectra of compounds **2**, **3** and **4**$_{a\sim c}$.

Acknowledgements

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