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Synthesis and Characterisation of Polyaza Crown Ether Derivatives of Calix[4]arene and Their Role as Anion Receptors

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Abstract: Novel compounds of polyaza crown ether derivatives of calix[4]arene have been synthesised. Both the ammonium and methyl ammonium derivatives, 25,27-{2,2'-[2,2'-((2,5,8-triammonium)nonyl)diphenoxyl]diethyl}-*p-tert*-butylcalix[4]arene trichloride, **1b** and 25,27-{2,2'-[2,2'-((2,5,8-dimethyl ammonium)nonyl)diphenoxy]diethyl}-*p-tert*-butylcalix[4] arene, **1d**, were studied complexation with a series of anions by ^{1}H NMR spectroscopy. The ammonium derivatives, **1b**, was found to form complexes with Cl^-, NO_3^-, AsO_2^- and CO_3^{2-} ions in which the selectivity for anions varies as $CO_3^{2-} > NO_3^- > AsO_2^- > Cl^-$. The methylammonium derivative, **1d**, however, does not show any sign of anion complexation. © 1997 Elsevier Science Ltd.

INTRODUCTION

Although anionic species play a significant role in chemistry and in biology, their complexation studies are not very well defined. However, research on coordination and supramolecular chemistry of anions has been increasingly recognized in recent years.[1] Lehn and coworkers have demonstrated interesting features of anion binding to macropolycyclic compounds.[2-5] Calix[4]arenes are another class of compounds which show many fascinating applications in the field of host-guest chemistry.[6,7] They can be modified by attaching specifically designed ion accepting moieties at the lower or upper rim. Beer et al. have demonstrated the use of calix[4]arene derivatives containing charged or neutral transition metals as anion receptor sites.[8-10] Furthermore, Reinhoudt and coworkers employed a series of UO_2-salens as neutral anion receptors and carriers.[11-12]

In this article, we report syntheses of polyaza crown ether derivatives of calix[4]arene containing secondary amines and ammonium moieties which are designed to be anionic receptor sites. We have varied the number of nitrogen atoms in the bridging cap to have 3-5 donors available for binding. Studies of anion complexation of these calix[4]arene derivatives were carried out with a series of anions such as Cl^-, Br^-, I^-, NO_3^-, AsO_2^-, CO_3^{2-}, SO_4^{2-} and PO_4^{3-} employing an NMR spectroscopic technique. The results of this study may lead to a way to utilise these calix[4]arene derivatives as anion separators in the future.

RESULTS AND DISCUSSION

Synthesis and characterisation. The Schiff base derivatives of polyaza crown ether calix[4]arene were synthesised by condensing the dialdehyde derivative, 25,27-{2,2'-[(2-formyl)phenoxyl]ethyl}-*p-tert*-butylcalix[4]arene, **1**, with an excess of the appropriate primary amines: diethylene triamine, triethylene tetramine and tetraethylene pentamine. The reaction of **1** with diethylene triamine resulted in a white solid assigned as 25,27-{2,2'-[2,2'-(1,8-((5-aza)diimino)nonylene)diphenoxyl]diethyl}-*p-tert*-butylcalix[4]arene, **1a**, in 97% yield. Triethylene tetraamine and tetraethylene pentaamine, however, reacted with **1** to give 25,27-{2,2'-[2,2'-(1,11-((5,8-diaza)diimino]dodecylene)diphenoxyl]diethyl}-*p-tert*-butylcalix[4]arene, **2a** and 25,27-{2,2'-[2,2'-(1,14-((5,8,11-triaza)diimino)pentadecylene) diphenoxyl]diethyl}-*p-tert*-butylcalix[4]arene, **3a**, as yellow solids in 24% and 28% yield, respectively. The yellow color and low solubility of **2a** and **3a** may indicate the existence of polymeric substances resulting from oligomerisation of the long aza-chain with at least two calix[4]arene units. Compounds **1a**, **2a** and **3a** were characterised by ^1H NMR spectroscopy. They exhibit typical *H*C=N signals about 8.6-8.8 ppm, similar to other relevant calix[4]arene compounds.[13] The complex pattern of ^1H NMR signals due to *tert*-$C_4\mathit{H}_9$ indicates mixtures of conformations whose possibilities are cone, partial cone, 1,2- and 1,3-alternate conformations.[14] We cannot assign the exact conformations of the compounds; however, cone and partial cone conformations are normally found for this type of calix[4]arene.[15] The elemental analyses and FAB MS also confirm the identity of these three compounds.

The acidic forms of the Schiff base derivatives, 25,27-{2,2'-[2,2'-((2,5,8-triammonium)nonyl)diphenoxyl]diethyl}-*p-tert*-butylcalix[4]arene trichloride, **1b**, 25,27-{2,2'-[2,2'-((2,5,8,11-tetraammonium)dodecyl)diphenoxyl]diethyl}-*p-tert*-butylcalix[4]arene tetrachloride, **2b** and 25,27-{2,2'-[2,2'-((2,5,8,11,14-pentaammonium)pentadecyl) diphenoxyl]diethyl}-*p-tert*-butylcalix[4]arene pentachloride, **3b**, can be synthesised by reducing the corresponding Schiff base compounds **1a**, **2a**, and **3a**, respectively, with sodium borohydride and acidifying with methanolic HCl. The yields are quite high (95%, 81% and 89%, for **1b**, **2b** and **3b**, respectively) compared to the syntheses of the precursors. Due to the influence of the positive charge on the nitrogen atom, we observed $-CH_2-N\mathit{H}_2^+-CH_2-$ and $ArCH_2N\mathit{H}_2^+$ signals displaced downfield for all three compounds. For **1b**, we observed signals due to $\text{-CH}_2\text{-N}H_2^+\text{-CH}_2\text{-}$ and $\text{ArCH}_2\text{N}H_2^+$ protons at 9.99 and 9.56 ppm, respectively as shown in Fig. 1. The FAB mass spectrum displays a strong signal (100%) at m/z 1016

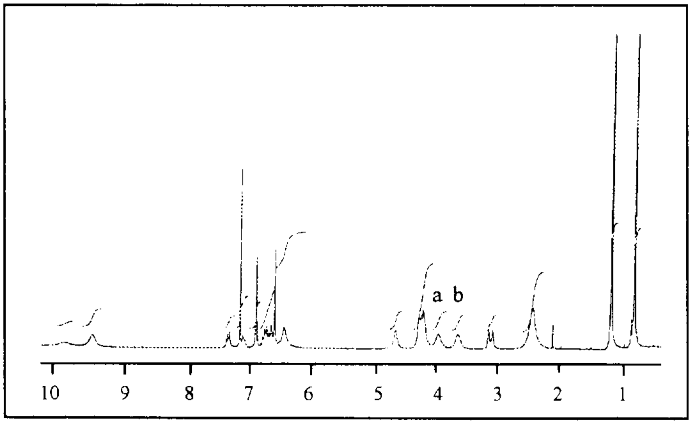
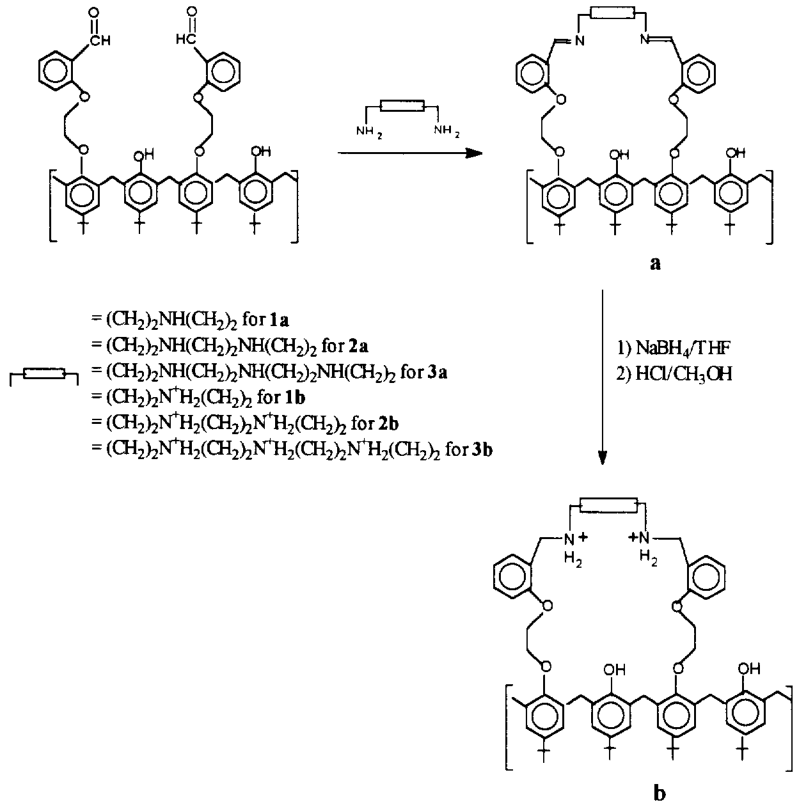


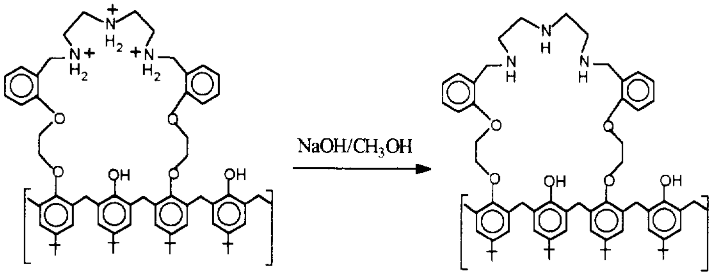
Figure 1. ^{1}H NMR spectrum of compound **1b**.



Scheme 1.

similar to the neutralised form, **1c**, *vide infra*. This may occur due to the mechanism of FAB technique. The elemental analysis, however, supports the existence of **1c**. Even though the ^{1}H NMR spectra of **2b** and **3b** are not well defined, the $-CH_2-NH_2^+-CH_2-$ signals can be observed at 9.15 and 9.25 PPM, respectively. Methyl protons on the *tert*-butyl moieties of compounds **1b-3b** give two signals around 0.90 to 1.30 PPM indicating the cone conformation of the calix[4]arene unit. The elemental analyses results are also in agreement with the proposed structure of the compounds. Scheme 1 shows the synthetic pathway of both Schiff base and acidic forms of polyaza crown ether calix[4]arene compounds.

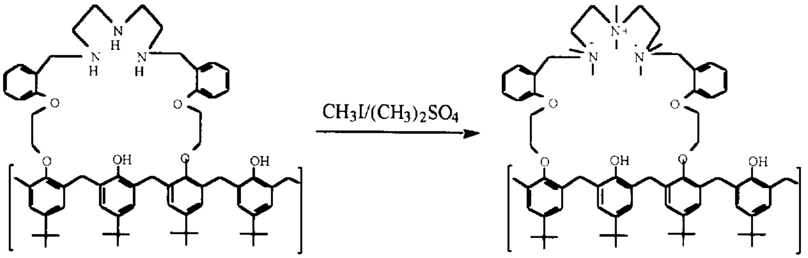
Due to the insolubility of compounds **2b** and **3b**, they are not suitable for synthesising any further derivatives. Thus, only the neutralised form of **1b**, 25,27-{2,2'-[2,2'-((2,5,8-triaza)nonyl)diphenoxyl]diethyl}-*p*-*tert*-butylcalix[4]arene, **1c**, can be obtained by neutralising its corresponding acidic form with sodium hydroxide as shown in eq. 1.



1b **1c**

(1)

The reaction of **1c** with methyl iodide and dimethylsulfate produced a methylammonium derivative, 25,27-{2,2'-[2,2'-((2,5,8-dimethylammonium)nonyl) diphenoxyl]diethyl}-*p*-*tert*-butylcalix[4]arene, **1d**, as shown in eq. 2. Characterization of **1d** was done by spectroscopy. ^{1}H NMR of **1d** shows 2 signals due to $N(CH_3)_2$ protons at 3.5 and 3.2 ppm. The FAB mass spectrum displays a strong signal (100%) at m/z 1198 corresponding to $[C_{66}H_{82}N_3O_6(CH_3)_6SO_4]^+$. However, due to the mixed counter ions (I^- and SO_4^-) elemental analysis results were not satisfactory.



1c **1d**

(2)

Anion complexation studies. Compound **1b** is a ditopic ion receptor that composes of possible 3 nitrogen and 6 oxygen donors. The molecule also has positive charges on nitrogen atoms which are neutralized by 3 Cl^- ions. Since the positive charged ligands containing ammonium moieties are well-known to form complexes with anions,[5] we utilised **1b** as an anion receptor and studied its anion complexation by ^1H NMR spectroscopy. When **1b** forms a complex with anions, the protons on the carbons adjacent to the ammonium moiety, $C\mathit{H}_2\text{-}NH_2^+\text{-}C\mathit{H}_2\text{-}$ (a) and $Ar\text{-}CH_2NH_2^+C\mathit{H}_2\text{-}$ (b), shift upfield, and the magnitude of displacement can be measured upon varying anion ratio. However, we do not observe any signal displacement of $ROAr\text{-}t\text{-}C_4\mathit{H}_9$, $ROAr\text{-}t\text{-}C_4\mathit{H}_9$, and $\mathit{H}OAr\text{-}t\text{-}C_4H_9$. The result suggests that anions have no interaction with the calix[4]arene unit and possibly bind the ligand **1b** via the three nitrogen donors in a 1:1 fashion.

Table 1 represents the relationship between mole ratio of NO_3^- ion and the complexation induced shifts of protons $C\mathit{H}_2\text{-}NH_2^+\text{-}C\mathit{H}_2\text{-}$ (a) and $Ar\text{-}CH_2NH_2^+C\mathit{H}_2\text{-}$ (b) while Fig. 2 illustrates the plot of the relationship. The magnitude of the complexation induced shifts of the proton (b) is half of that of the proton (a). We thus use the complexation induced shifts of the proton (a) to estimate the complex formation constant of NO_3^- ion with **1b**. These displacements indicate an inclusion of the highly negative moiety into the ligand **1b**, i.e. a replacement of Cl^- by NO_3^-. The complex formation constant was calculated by the method described in the experimental section to be log K = 4.4. The plot in Figure 2 also provides an evidence for 1:1 complex formation of the ligand **1b** with NO_3^- ion. ^1H NMR experiments also indicate that there is no interaction between NO_3^- ion and phenoxy protons on the calix[4]arene unit of **1b**, *vide supra*. This implies that NO_3^- ion should reside in the cavity of the ammonium bridging cap of **1b**. In a similar manner to cryptate compounds studied by Lehn and Martell,[16] the ligand **1b** should form a complex with NO_3^- by electronic or hydrogen bonding interactions with the ammonium hydrogen atoms. The possible structure of the complex **1b**•NO_3^-, **4**, can thus be deduced.

Arsenite ion, AsO_2^-, is a species which is environmetally important. Much effort has been invested in order to separate arsenic containing species from the environment. The same type of experiment done with NO_3^- ion was also performed to study the complexation of AsO_2^- ion with the ligand **1b**. We found that AsO_2^- also formed a complex with **1b** in a 1:1 manner. The complex formation constant was then estimated to be log K = 3.5.

Table 1. The relationship between mole ratio of NO_3^- ion and the complexation induced shifts of $C\mathit{H}_2$-NH_2^+-$C\mathit{H}_2$- (a) and Ar-$CH_2NH_2^+C\mathit{H}_2$- (b)

Mole Ratio NO_3^-:**1b**	CH_2-NH_2^+-CH_2- (a) (Hz)	Ar-CH_2-NH_2^+-CH_2- (b) (Hz)
0.5	40	23
1.0	43	27
1.5	53	32
2.0	51	32
2.5	67	39
3.0	53	35
3.5	53	36
4.0	53	36

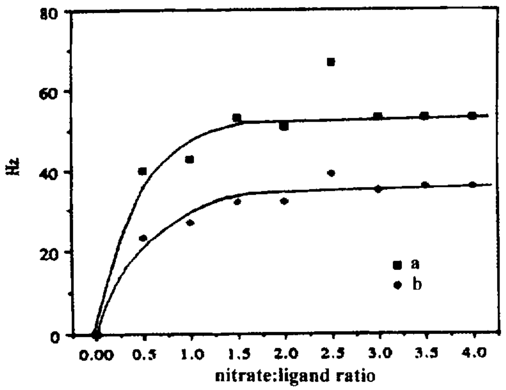
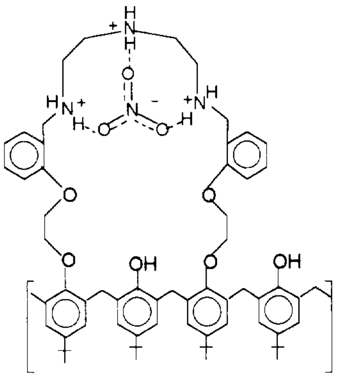


Figure 2. The plot of the displacement of the complexation induced shifts of $C\mathit{H}_2$-NH_2^+-$C\mathit{H}_2$- (a) and Ar-$CH_2NH_2^+C\mathit{H}_2$- (b) versus mole ratio of NO_3^-.



4

The complexation study of **1b** with halide ions has also been carried out. There is no signal displacement of the protons (a) and (b) found for the complexation study of **1b** with Br^- ion suggesting no complexation occurred. For I^-, only slight displacement of the NMR signals has been observed after the ratio of **1b**:I^- reached 1:1; therefore, the reaction progresses so slowly that the complex formation constant cannot be calculated. The result may be attributable to the hydrogen bonding effect, which cannot be applied to I^- and Br^-, or to the size exclusion of these anions by the ligand **1b**.

For basic anions such as PO_4^{3-}, CO_3^{2-} and SO_4^{2-}, we observed interesting inclusion phenomena when complexation studies with the ligand **1b** were performed. The first two anions react with **1b** to form complexes; however, upon increasing the mole ratio of anions, deprotonation of **1b** takes place. The deprotonation processes can be distinguished from complexation by large upfield shifts of signals due to $-CH_2NH_2^+CH_2-$ and $ArCH_2NH_2^+CH_2$ protons from 3.99 and 3.69 to 2.49 and 2.38 ppm (> 200 Hz), respectively corresponding to those found in the isolated compound **1c** while the complexation processes give the chemical induced shift of those protons no larger than 0.4 ppm (< 80 Hz) as observed in cases of NO_3^- and AsO_2^- ions. The deprotonation of **1b** by PO_4^{3-} and CO_3^{2-} ions occurs completely at the mole ratio of anion to ligand of 4:1. We, therefore, cannot calculate the complex formation constant for these anions. Nevertheless, a competitive study between NO_3^- and CO_3^{2-} can be carried out employing ^1H NMR spectrocopy. When CO_3^{2-} was added to the solution of complex **1b**•NO_3^- in a 1:1 proportion, we found that the signals of protons $CH_2-NH_2^+-CH_2-$ and $Ar-CH_2NH_2^+CH_2-$ shifted from 3.78 and 3.56 to 2.91 and 2.89 ppm, respectively corresponding to those signals observed in the direct complexation of CO_3^{2-} with the ligand **1b** (1:1 ratio). In an opposite manner to both PO_4^{3-} and CO_3^{2-} ions, SO_4^{2-} ion does not yield any displacement of signals due to $-CH_2NH_2^+CH_2-$ and $ArCH_2NH_2^+CH_2$ protons at all.

We tried to avoid the deprotonation of **1b** by synthesising the ammonium derivative, **1d**, which contains methyl group on nitrogen atoms instead of protons. Unfortunately, we do not observe any signal changes upon anion titration experiments as found in the precursor **1b**. The result indicates that either hydrogen bonding between host-guest plays an important role in this study or the steric hindrance from the methyl group may prohibit the inclusion of anions in **1d**.

It can be concluded that anion size, hydrogen bonding properties and Lewis basic character of anions have a great deal of influence on complexation ability with the ligand **1b**. This study also implies that only anions that have suitable size (1.71 - 1.75 Å) can fit in the cavity of the nitrogen donors of **1b**.[17] The anion selectivity of the ligand **1b** varies as follows: $CO_3^{2-} > NO_3^- > AsO_2^- > Cl^-$. This compound may be applied as an anion separator. Especially, the possible application of the ligand **1b** in the separation of toxic anions such as arsenic-containing species from the environment will be further investigated in our laboratory.

EXPERIMENTAL SECTION

All reagents and solvents were of reagent grade quality, obtained from commercial suppliers, and used without further purification. ^{1}H NMR spectra were recorded in $CDCl_3$ on Bruker AFC-200. Mass spectra were determined using VG-Analytical ZAB HF mass spectrometer. Elemental analyses were carried out at the Scientific and Technological Research Equipment Center of Chulalongkorn University.

The preparation of the dialdehyde derivative of calix[4]arene, 25,27-{2,2'-[(2-formyl)phenoxyl]ethyl}-*p-tert*-butylcalix[4]arene, **1**, was previously reported.[13]

Preparation of 25,27-{2,2'-[2,2'-(1,8-((5-aza)diimino)nonylene) diphenoxyl]diethyl}-*p-tert*-butylcalix[4]arene, 1a, 25,27-{2,2'-[2,2'-(1,11-((5,8-diaza)diimino)dodecylene)diphenoxyl]diethyl}-*p-tert*-butylcalix[4]arene, 2a and 25,27-{2,2'-[2,2'-(1,14-((5,8,11-triaza)diimino)pentadecylene)diphenoxyl]diethyl}-*p-tert*-butylcalix[4]arene, 3a: general procedure. Into a 500 mL 2-necked round bottom flask containing 25,27-bis[2-[1-formyl-2-phenyl)oxy]ethyl]-*p-tert*-butylcalix[4]arene (3.00 g, 3.10 mmol) and acetonitrile (250 mL) was added dropwise appropriate amines (approximately 3.90 mmol) in methanol (50 mL). The reaction mixture was refluxed under nitrogen for 9 h to give a white precipitate which was then filtered and washed with methanol. (3.01 g, 97%).

Characterization for 1a. ^{1}H NMR (δ in $CDCl_3$): 8.77, 8.67 (s, 2H, CHN); 7.85-6.18 (m, aromatic protons); 4.80-3.30 (m, 16H, $ArCH_2NH$, OCH_2CH_2O and NCH_2CH_2N); 4.31, 3.33 (d, 8H, $ArCH_AH_BAr$, J_{AB} = 13 Hz); 1.50-0.70 (m, 36H, HOAr-t-C_4H_9 and ROAr-t-C_4H_9). FAB MS (m/z): 1012.3. Anal. calcd. for $C_{66}H_{81}O_6N_3$; C, 77.76; H, 8.70; N, 4.12. found: C, 77.69; H, 8.09; N, 4.19.

Characterization for 2a. ^{1}H NMR (δ in $CDCl_3$): 8.73 (s, 2H, CHN); 7.82-6.58 (m, 18H, aromatic); 4.70-3.01 (m, 28H, $ArCH_ACH_BAr$, OCH_2CH_2O, NCH_2CH_2N and NH); 1.30-0.82 (m, 36H, HOAr-t-C_4H_9 and ROAr-t-C_4H_9). Anal. calcd. for $C_{68}H_{86}O_6N_4 \cdot CH_3OH$; C, 76.21; H, 8.34; N, 5.15. found: C, 76.14; H, 8.26; N, 4.68.

Characterization for 3a. ^{1}H NMR (δ in $CDCl_3$): 8.72 (s, broad, 2H, CHN); 7.94-6.57 (m, 18H, aromatic); 4.76 (m, 35H, $ArCH_ACH_BAr$, OCH_2CH_2O, NCH_2CH_2N and NH); 1.30-0.82 (m, 36H, HOAr-t-C_4H_9 and ROAr-t-C_4H_9). Anal. calcd. for $C_{70}H_{95}O_6N_5 \cdot CH_3OH$; C, 75.16; H, 8.79; N, 6.17. found: C, 75.68; H, 8.68; N, 5.89.

Preparation of 25,27-{2,2'-[2,2'-((2,5,8-triammonium)nonyl)diphenoxyl]diethyl}-*p-tert*-butylcalix[4]arene trichloride, 1b, 25,27-{2,2'-[2,2'-((2,5,8,11-tetraammonium)dodecyl)diphenoxyl]diethyl}-*p-tert*-butylcalix[4]arene tetrachloride, 2b

and 25,27-{2,2'-[2,2'-((2,5,8,11,14-pentaammonium)pentadecyl)diphenoxyl]diethyl}-*p*-*tert*-butylcalix[4]arene pentachloride, 3b: general procedure: general procedure. **1a** or **2a** or **3a** (approximately 6.14 mmol) was stirred with sodium borohydride (3.49 g, 92.10 mmol) in dry tetrahydrofuran under nitrogen for two hours. The unreacted sodium borohydride was then quenched with a copious amount of water. The solution was evaporated to dryness, and the solid residue was extracted with dichloromethane. The organic layer was dried over sodium sulfate and evaporated to dryness. The solid was then acidified with hydrochloric acid in methanol (0.74% v/v) until the pH of the solution reached 1. Upon removal of methanol, the product precipitated as a white solid. (6.20 g, 89%).

Characterization for 1b. ^{1}H NMR (δ in $CDCl_3$): 9.99 (s, broad, 2H, $CH_2N\mathit{H}_2^+CH_2$); 9.56 (s, broad, $ArCH_2N\mathit{H}_2^+$); 7.43 (d, 2H, aromatic); 7.39 (m, 2H, aromatic); 6.97 (s, 4H, HOAr*H*); 6.84-6.58 (m, 6H, aromatic and ArO*H*); 6.67 (s, 4H, $ArC\mathit{H}_2NH$); 4.26, 3.19(d, 8H, $ArC\mathit{H}_A\mathit{H}_BAr$, J_{AB} = 13 Hz); 4.25 (s, 8H, $OC\mathit{H}_2C\mathit{H}_2O$); 3.99 (s, 4H, $C\mathit{H}_2NH_2^+C\mathit{H}_2$); 3.69 (s, 4H, $ArCH_2NH^+C\mathit{H}_2$); 1.22 , 0.85 (s, 18H, HOAr-*t*-$C_4\mathit{H}_9$ and ROAr-*t*-$C_4\mathit{H}_9$). FAB MS. (m/z): 1016.4. Anal. calcd. for $C_{68}H_{88}O_6N_3Cl_3{\cdot}3H_2O$; C, 67.26; H, 8.04; N, 3.57. found: C, 67.03; H, 7.54; N, 3.57.

Characterization for 2b. ^{1}H NMR (δ in $CDCl_3$): 9.15 (s, broad, 8H, N*H*); 7.30-6.71 (m, 18H, aromatic); 4.70-2.84 (m, 32H, $ArC\mathit{H}_AC\mathit{H}_BAr$, $OC\mathit{H}_2C\mathit{H}_2O$ and $NC\mathit{H}_2C\mathit{H}_2N$); 1.23 (s, 18H, HOAr-*t*-$C_4\mathit{H}_9$); 0.87 (s, 18H, ROAr-*t*-$C_4\mathit{H}_9$).

Characterization for 3b. ^{1}H NMR (δ in $CDCl_3$): 9.25 (s, broad, 8H, N*H*); 7.42-6.40 (m, 18H, aromatic); 4.72-2.74 (m, 36H, $ArC\mathit{H}_AC\mathit{H}_BAr$, $OC\mathit{H}_2C\mathit{H}_2O$ and $NC\mathit{H}_2C\mathit{H}_2N$); 1.19 (s, 18H, HOAr-*t*-$C_4\mathit{H}_9$); 0.89 (s, 18H, ROAr-*t*-$C_4\mathit{H}_9$). Anal. calcd. for $C_{70}H_{104}O_6N_5Cl_5{\cdot}3CH_3OH$; C, 61.79; H, 8.53; N, 4.94. found: C, 61.91; H, 8.52; N, 4.60.

Preparation of 25,27-{2,2'-[2,2'-((2,5,8-triaza)nonyl)diphenoxyl]diethyl}-*p*-*tert*-butylcalix[4]arene, 1c. **1b** (3.00 g, 2.66 mmol) was neutralized with sodium hydroxide (0.32 g, 8.00 mmol) in methanol (120 mL). The solvent was evaporated to dryness under reduced pressure, and the residue was extracted with dichloromethane to obtain an organic layer. Upon removal of the solvent, a white solid precipitated. (2.4 g, 89%)

^{1}H NMR (δ in $CDCl_3$): 7.24-7.14 (m, 4H, aromatic); 7.03 (s, 4H, HOAr*H*); 6.91-6.78 (m, 4H, aromatic); 6.70 (s, 4H, aromatic); 4.44, 3.24 (d, 4H, $ArC\mathit{H}_AC\mathit{H}_BAr$, J_{AB} = 13 Hz); 4.36, 4.29(s, 8H, $OC\mathit{H}_2C\mathit{H}_2O$); 3.82 (s, 4H, $ArC\mathit{H}_2NH$); 2.49 (s, 4H, $C\mathit{H}_2NH_2C\mathit{H}_2$); 2.38 (s, 2H, $ArCH_2NH_2C\mathit{H}_2$); 1.28 , 0.89 (s, 18H, HOAr-*t*-$C_4\mathit{H}_9$ and ROAr-*t*-$C_4\mathit{H}_9$). FAB MS (m/z): 1016.4. Anal. calcd. for $C_{66}H_{85}O_6N_3$; C, 77.98; H, 8.43; N, 4.14. found: C, 77.78; H, 8.08; N, 4.56.

Preparation of 25,27-{2,2'-[2,2'-((2,5,8-dimethylammonium)nonyl) diphenoxyl]diethyl}-*p-tert*-butylcalix[4]arene, 1d. **1c** (0.35 g, 3.45 mmol), methyl iodide (3.0 mL, 34.5 mmol), potassium carbonate (5.50 g, 40.00 mmol) and acetonitrile (250 mL) were mixed in a 500 mL 2-necked round bottom flask. The mixture was refluxed under nitrogen for 21 hours. The supernatant solution was then separated by filtration and evaporated to dryness. The residue was redissolved in acetonitrile (250 mL). To the solution was added dimethylsulfate (0.70 mL, 7.30 mmol), and it was refluxed under nitrogen for 5 hours. A white solid precipitated and was separated by filtration. (2.46 g, 54%)

^{1}H NMR (δ in $CDCl_3$): 7.58-6.65 (complex m, 16H, aromatic); 4.88 (s, broad, 4H, $ArCH_2NH$); 4.71 (t, 8H, NCH_2CH_2N); 4.33 (s, 8H, OCH_2CH_2O); 4.23, 3.29 (d, 4H, $ArCH_ACH_BAr$, J_{AB} = 13 Hz); 3.59, 3.29 (s, 18H, $N(CH_3)_2$); 2.50 (s, broad, 8H, NCH_2CH_2); 1.25 , 0.84 (s, 18H, HOAr-*t*-C_4H_9 and ROAr-*t*-C_4H_9). FAB MS (m/z) for $C_{66}H_{82}N_3O_6(CH_3)_6SO_4$: 1198.7 (100%).

Inclusion studies of compounds 1b and anion salts (KI, KBr, Na_3PO_4, Na_2SO_4, Na_2CO_3, $NaNO_3$ and $NaAsO_2$) by ^{1}H NMR spectrometry. Typically, anion salts were added into a CH_2Cl_2 solution (10 mL) of the ligand **1b** (0.025 mmol). The mixture was stirred for 48 h and then filtered. The solvent was removed from the filtrant by a rotary evaporator to yield white solids. The reaction was repeated by varying the amount of anions added from 0:1 to 4:1 anion to the ligand ratio. The solids obtained were then analysed by ^{1}H NMR spectroscopy.

^{1}H NMR data analyses. Analyses of the data at equilibrium in order to estimate the stability constant can be performed using the following equations:

$$A + L \overset{K}{\rightleftharpoons} AL \qquad A = \text{anion, } L = \mathbf{1b}$$

Stability constant, $K = [AL]/[A][L]$

$$\delta_{obsd} = \delta_L X_L + \delta_{AL} X_{AL} \tag{1}$$

X_L is mole fraction of L, $X_L = [L]/C_L^0$ (2)

X_{AL} is mole fraction of AL, $X_{AL} = K[A][L]/C_L^0$ (3)

Mass balance equation:

$$C_L^0 = [L] + [AL]$$

$$C_A^0 = [A] + [AL]$$

Then,

$$[L] = C_L^0/1 + K[A] \qquad (4)$$

$$[A] = C_A^0/1 + K[L] \qquad (5)$$

The set of equations was solved by iteration.[18] Starting with an initial estimate of the free anion concentration [A], the first value of [L] could be obtained from equation 4 and used to calculate a more accurate estimate of [A] from equation 5. This procedure was repeated until convergence occurred. The converged values of [A] and [L] were used in the calculation of the mole fraction from equations 1-3. The values for K were obtained by fitting the calculated δ_{obsd} to the experimental values.

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