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Mono-ionizable calix[4]arene-benzocrown-6 ligands in 1,3-alternate conformations: synthesis, structure and silver(I) extraction

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ABSTRACT

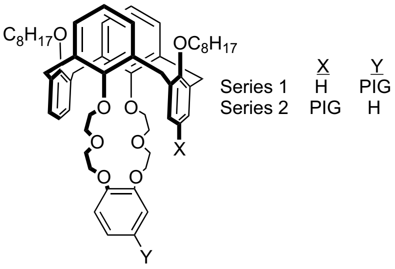
Two series of novel mono-ionizable calix[4]arene-benzocrown-6 ligands in 1,3-alternate conformations are synthesized. In one series, the proton-ionizable group (PIG) is attached to the *para* position of one aromatic ring in the calixarene framework, thereby positioning it over the polyether ring cavity. In the other series, the PIG is a substituent on the benzo group in the polyether ring. This orients the PIG away from the crown ether cavity. In addition to carboxylic acid functions, the PIGs include *N*-(X)sulfonyl carboxamide groups. With X group variation from methyl to phenyl to 4-nitrophenyl to trifluoromethyl, the acidity of the PIG is 'tuned'. Solvent extraction of Ag^+ from aqueous solutions into chloroform is used to probe the influence of structural variation within the mono-ionizable calixcrown ligand on metal ion extraction efficiency, including the identity and acidity of the PIG and its orientation with respect to the polyether ring.

1. Introduction

Calixarene-crown ether compounds, also called calixcrowns, combine a calixarene scaffold with a crown ether unit that bridges two phenolic oxygens of the former with a polyether chain.[1–6] Linking of distal phenolic oxygens in calix[4]arenes gives 1,3-bridged calix[4]crowns, while connection of the proximal oxygens produces less common, 1,2-bridged calix[4]crown compounds. It has been found that 1,3-bridged calix[4]crowns exhibit high binding affinities towards alkali and alkaline earth metal cations.[7-9]

By use of appropriate substituents, the calix[4]arene platform may be locked in different conformations (cone, partial cone, 1,3-alternate and 1,2-alternate). In calix[4]arene-crown compounds, this controls the spatial relationship between the polyether ring and constituents of the calixarene moiety, including the aromatic rings of the calixarene unit itself, as well as substituents with potential coordination sites attached via the remaining phenolic oxygens. Of particular interest in our metal ion separations research program are substituents that bear proton-ionizable groups (PIGs). When the number of acidic hydrogens in a calixcrown ligand matches the charge of the metal ion to be complexed, solvent extraction proceeds by an ion-exchange mechanism. Formation of an electroneutral, ionized ligand-metal ion complex in the organic diluent markedly enhances the efficiency of metal ion extraction by avoiding the need for concomitant transfer a hydrophilic aqueous phase anion, such as chloride, nitrate or sulfate, into the low polarity medium.

In continuation of our studies of metal ion separations by mono-ionizable calix[4]arene compounds,[10–13] we have now synthesized two series of novel mono-ionizable calix[4]arene-benzocrown-6 ligands in 1,3-alternate conformations (Fig. 1). These two series have identical crown ether units and calix[4]arene scaffolds including two lipophilic octyl groups, but differ in the spatial relationship between the PIG and the polyether unit. In Series 1, the PIG is a substituent on the benzo group in the polyether ring. This orients the PIG away from the crown ether cavity. In Series 2, the PIG is attached to an aromatic ring of the calixarene framework. This positions the PIG over the polyether ring cavity.



	X	Y
Series 1	H	PIG
Series 2	PIG	H

Figure 1. Mono-ionizable 1,3-alternate calix[4]ene-benzocrown-6 ligands with two different positions for the proton-ionizable group (PIG).

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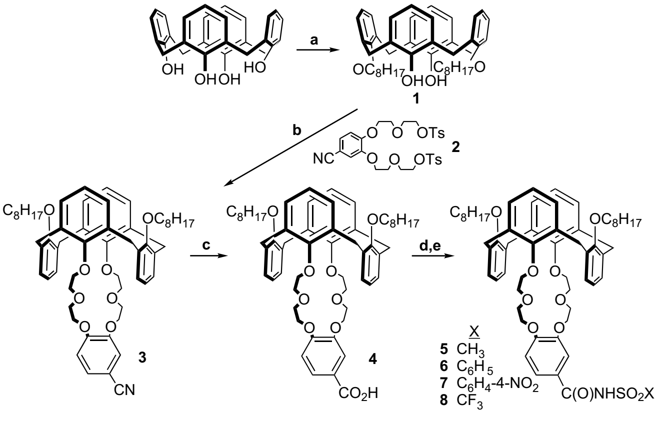
We now report synthetic routes to these two series of proton-ionizable calixcrown ligands with carboxylic acid and *N*-(X)sulfonyl carboxamide PIGs. A solid-state structure of one of the Series 2 ligands is presented. The influence of structural variation within the mono-ionizable calixcrown ligand, including the identity and acidity of the PIG and its orientation with respect to the polyether ring, on metal ion complexation efficiency, is probed by solvent extraction of Ag^+ from aqueous solutions into chloroform. Ag^+ was selected as the metal ion to study due to its reported ability to coordinate at either ethereal or π-basic sites in 1,3-alternate calix[4]crown ligands.[14]

2. Results and discussion

2.1. Synthesis of series 1 ligands

The synthetic route for the preparation of 4′-carboxy-25,27-di(octyloxy)-26,28-calix[4]arene-benzocrown-6 (**4**) and 4′-[*N*-(X)sulfonyl carbamoyl]-25,27-di(octylox)y-26,28-calix[4]arene-benzocrown-6 compounds **5**–**8** in the 1,3-alternate conformation is presented in Scheme 1.



Scheme 1. Synthesis of 1,3-alternate mono-ionizable di(octyloxy)calix[4]arene-benzocrown-6 ligands **4**–**8** of series 1. Reagents and conditions: a) K_2CO_3, $C_8H_{17}I$, MeCN, reflux; b) Cs_2CO_3, MeCN, reflux; c) KOH, aq EtOH, reflux; d) $(COCl)_2$, C_6H_6, reflux; e) XSO_2NH_2, NaH, THF, rt.

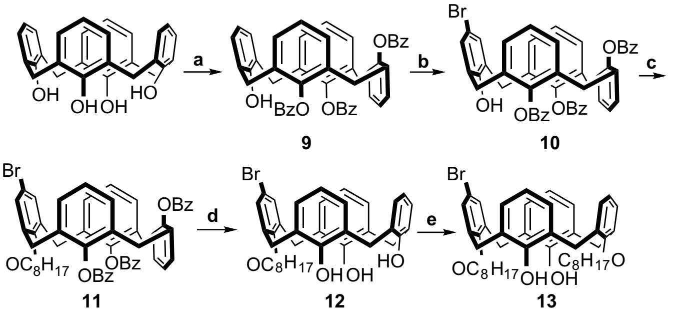
In retrosynthetic analysis, the target mono-ionizable 1,3-alternate calix[4]arene-benzocrown-6 ligands **4**–**8** can be assembled from a benzopolyether diol fragment with an appropriate substituent on the 4-position of the benzene ring and a distal dialkylated calix[4]arene unit. To obtain the 1,3-alternate conformation, the two alkyl groups are attached to the calix[4]arene scaffold first followed by coupling with an activated derivative of the diol unit.

Calix[4]arene was reacted with 4 equiv of 1-iodooctane and 4 equiv of K_2CO_3 in MeCN at reflux to give a 90% yield of known[9] 25,27-di(octyloxy)calix[4]arene (**1**). Bis-1,2-[2′-(2″-hydroxyethoxy)-ethoxy]-4-cyanobenzene was prepared by the reported reaction[15] of 4-cyanocatechol with 2-(2-chloroethoxy)ethanol and K_2CO_3 in DMF and conversion of the resultant diol into ditosylate **2** in a 93% overall yield for the two steps. Cyclization of dialkylated calix[4]arene **1** with 1.1 equiv of ditosylate **2** and 4 equiv of Cs_2CO_3 in MeCN at reflux produced an 86% yield of 4′-cyano-25,27-di(octyloxy)-26,28-calix[4]arene-benzocrown-6 (**3**) in the 1,3-alternate conformation.[15] The conformation of **3** was confirmed by ^{1}H and ^{13}C NMR spectra, which exhibited for the methylene bridge protons ($ArCH_2Ar$) a singlet at 3.75 ppm and for the *anti* oriented aromatic rings a singlet at 37.69 ppm, respectively.

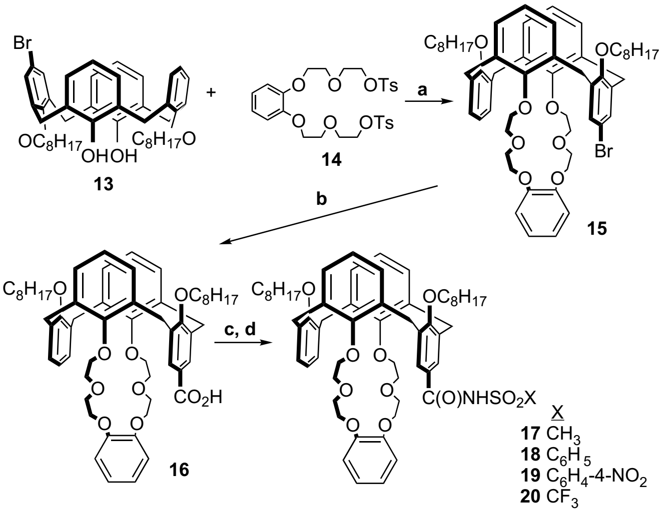
Hydrolysis of nitrile **3** by refluxing with 10% KOH in aqueous EtOH (1:1, v/v) gave a quantitative yield of 4′-(carboxy)-25,27-di(octyloxy)-26,28-calix[4]arene-benzocrown-6 (**4**). Calixcrown carboxylic acid **4** was refluxed with 4 equiv of oxalyl chloride in benzene to give the corresponding acid chloride. Conversion of **4** (C=O at 1687 cm^{-1}) to the acid chloride (C=O at 1749 cm^{-1}) was monitored by IR spectroscopy, which showed that the acid chloride was extremely moisture sensitive with conversion back to the acid **4**. The crude acid chloride was reacted with sodium salt forms of commercially available sulfonamides to give the desired 4′-[*N*-(X)sulfonyl carbamoyl]-25,27-dioctyloxy-26,28-calix[4]arene-benzo-crown-6 compounds **5**–**8** in 71–95% yields.

2.2. Synthesis of series 2 ligands

The preparative route to 5-carboxy-26,28-di(octyloxy)-25,27-calix[4]arene-benzocrown-6 (**16**) and 5-[*N*-(X)sulfonyl carbamoyl]-26,28-di(octyloxy)-25,27-calix[4]arene-benzocrown-6 compounds **17**–**20** is depicted in Schemes 2 and 3.



Scheme 2. Synthesis of precursor **13**. Reagents and conditions: a) BzCl, pyridine, rt; b) Br_2, CH_2Cl_2, rt; c) NaH, $C_8H_{17}I$, DMF, rt; d) KOH, aq EtOH, reflux; e) K_2CO_3, $C_8H_{17}I$, MeCN, reflux. (Compound **11** was in a mixture of conformations for which the partial cone was predominant.).



Scheme 3. Synthesis of 1,3-alternate mono-ionizable di(octyloxy)calix[4]arene-benzocrown-6 ligands **16**–**20** of series 2. Reagents and conditions: a) Cs_2CO_3, MeCN, reflux; b) BuLi, CO_2, THF, −75 °C; c) $(COCl)_2$, C_6H_6, reflux; d) NaH, XSO_2NH_2, THF, rt.

One requisite fragment was 5-bromo-25,27-dihydroxy-26,28-(dioctyloxy)calix[4]arene (**13**), in which the bromine atom would be converted later into a carboxylic acid function. The synthesis of calix[4]arene with a single bromine substituent on the upper rim and two octyloxy groups on the lower rim is shown in Scheme 2. Reaction of calix[4]arene with benzoyl chloride in pyridine gave tribenzoate ester **9** in a partial cone conformation.[16] Triester **9** was selectively brominated on the phenolic aromatic nucleus by reaction with Br_2 in CH_2Cl_2 at room temperature to give the partial cone conformation of monobrominated calixarene **10**[17] in quantitative yield. Alkylation of **10** with 1-iodooctane and NaH in DMF afforded a 67% yield of compound **11** for which the ^{1}H NMR spectrum indicated a mixture of conformers with the partial cone predominating. The benzoate protecting groups were removed by refluxing a suspension of **11** with KOH in aqueous EtOH to produce triphenol **12** in 79% yield. For **12**, its ^{1}H NMR spectrum established the cone conformation.

To selectively introduce a second octyl group onto the lower rim of **12**, reaction with 1-iodooctane and the weak base K_2CO_3 in MeCN was conducted at reflux for 24 h. In this reaction, the amount of base was found to be critical. The best yield (74%) was realized when 1.2 equiv of base were added. The proportion of a byproduct increased when a greater amount of base was present. The byproduct was isolated and characterized by ^{1}H NMR spectroscopy, which showed it to be a calixarene in the partial cone conformation with three octyl groups attached to the lower rim. ^{1}H NMR spectroscopy revealed that the desired product 5-bromo-25,27-dihydroxy-26,28-di(octyloxy)calix[4]arene (**13**) was in the cone conformation.

The polyether fragment was prepared by reaction of catechol, 2-(2-chloroethoxy)ethanol, and K_2CO_3 in DMF to give the corresponding diol,[6] which was converted into ditosylate **14**.

Utilization of **14** in formation of the calixcrown compound **15** is shown in Scheme 3. Condensation of the calixarene unit **13** with the polyether-containing fragment **14** was conducted with 4 equiv of Cs_2CO_3 in MeCN at reflux producing a 91% yield of the calixcrown compound **15**, for which the 1,3-alternate conformation was confirmed by ^{1}H and ^{13}C NMR spectroscopy. Treatment of **15** with BuLi in THF at $-78\,^{\circ}$C followed by bubbling CO_2 through the reaction mixture gave, after workup and purification, a 62% yield of 5-carboxy-26,28-di(octyloxy)-25,27-calix[4]arene-benzocrown-6 (**16**).

Refluxing calixcrown carboxylic acid **16** with 4 equiv of oxalyl chloride in benzene gave the corresponding acid chloride, which was reacted with the sodium salts of commercially available sulfonamides to give the mono-ionizable calix[4]arene-benzocrown-6 ligands **17**–**20** in good yields (50–82%). The conformations of **17**–**20** were verified by their ^{1}H and ^{13}C NMR spectra. In the latter, signals for the methylene bridge carbons were around 37 ppm, which is characteristic of *anti*-oriented aromatic nuclei in 1,3-alternate conformers.

2.3. Solid-state structure of ligand 17

The solid-state structure of 5-(*N*-methanesulfonyl carbamoyl)-26,28-di(octyloxy)-25,27-calix[4]arene-benzocrown-6 (**17**) is presented in Figure 2. As expected, the calixarene ring takes a 1,3-alternate conformation enforced by the crown ether ring and the two octyl chains. These chains adopt *anti* conformations, except for a *gauche* conformation involving the ether oxygen and first three methylene carbons of one octyl group. The PIG is oriented over the crown ether cavity and forms an intramolecular NH⋯O hydrogen bond, with observed N⋯O and H⋯O distances of 2.867(4) and 2.202(4) Å, and an N–H–O angle of 132.1(2)°.

2.4. Solvent extraction of Ag^+

To probe the effects of structural variations within the 1,3-alternate mono-ionizable calix[4]arene-benzocrown-6 compounds upon metal ion complexation, solvent extraction of Ag^+ from aqueous solutions into chloroform was selected. For its complexation by 1,3-alternate calix[4]arene crown ethers, Ag^+ is of ambivalent character in that it may accommodate either ethereal or π-basic coordination sites.[14]

For solvent extraction of 1.0 mM aqueous Ag^+ solutions by 1.0 mM solutions of calixcrown ligands **4**–**8** (Series 1) in chloroform, plots of Ag^+ loading of the organic phase versus the equilibrium pH of the aqueous phase are presented in Figure 3. As expected, all five ligands are ineffective when the pH of the aqueous phase is very low. Thus in their un-ionized forms, the calixcrown compounds are ineffective in transferring Ag^+ into the organic phase.

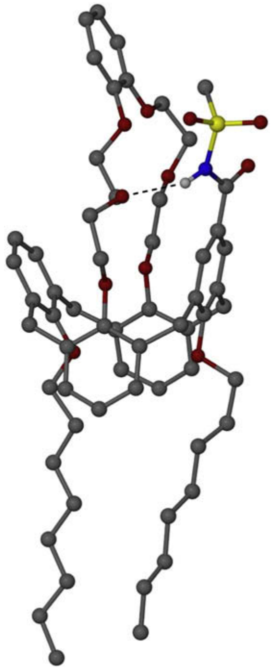


Figure 2. Solid-state structure of 5-(*N*-methanesulfonyl carbamoyl)-26,28-di-(octyloxy)-calix[4]arene-25,27-benzocrown-6 (**17**) in the 1,3-alternate conformation.

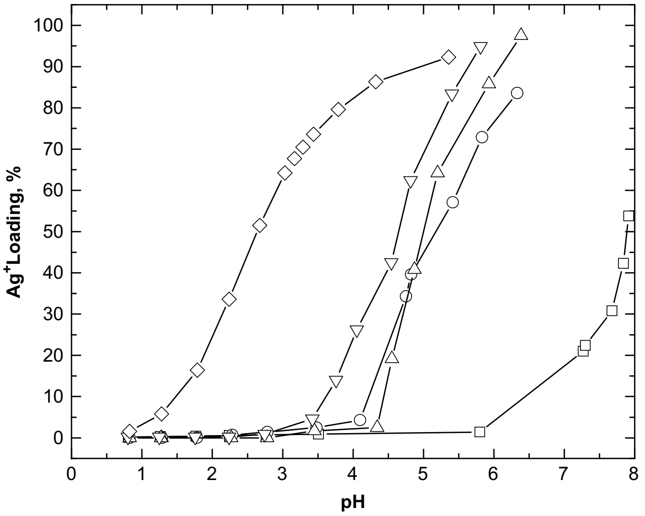


Figure 3. Percent Ag^+ loading versus the equilibrium pH of the aqueous phase for Ag^+ extraction into chloroform by ligands **4** (□), **5** (△), **6** (○), **7** (▽), **8** (◇).

For the calixcrown extractants **5**–**8** with *N*-(X)sulfonyl carboxamide PIGs, Ag^+ extraction levels reach at least 85% for 1:1 complex formation. The extractant efficiency increases with X variation in the order: $Me \sim Ph < C_6H_4\text{-}4\text{-}NO_2 \ll CF_3$. This is the order of the electron-withdrawing ability for X.[18] Comparison of these extraction profiles to that for the carboxylic acid calixcrown **5** reveals that all of the extractants with *N*-(X)sulfonyl carboxamide PIGs are more effective in transporting Ag^+ into the organic phase.

For solvent extraction of 1.0 mM aqueous Ag^+ solutions by 1.0 mM solutions of calixcrown ligands **16**–**20** (Series 2) in chloroform, plots of Ag^+ loading of the organic phase versus the equilibrium pH of the aqueous phase are shown in Figure 4. For the calixcrown ligands **17**–**20** with *N*-(X)sulfonyl carboxamide PIGs, Ag^+ extraction levels reach at least 75% for formation of 1:1 complexes. Ligand **20** with $X{=}CF_3$ is the most efficient extractant. The extraction profiles for the other three X groups are very similar.

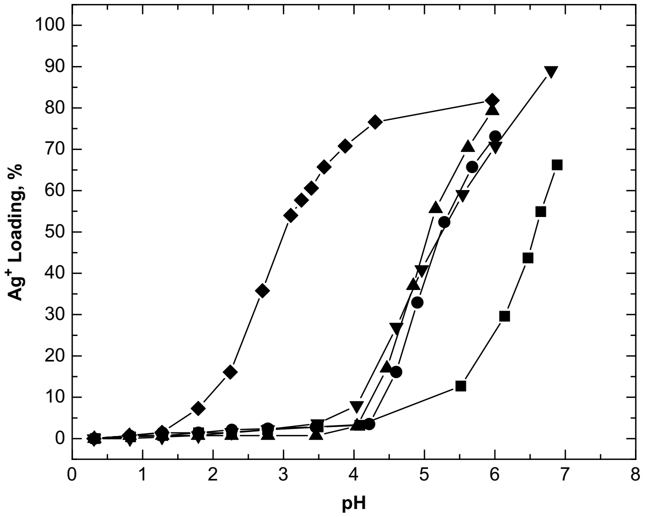


Figure 4. Percent Ag^+ loading versus the equilibrium pH of the aqueous phase for Ag^+ extraction into chloroform by ligands **16** (■), **17** (▲), **18** (•), **19** (▼), **20** (◆).

Once again the calixcrowns with *N*-(X)sulfonyl carboxamide PIGs are found to be more effective Ag^+ extractants than the corresponding carboxylic acid.

To assess the effect of PIG positioning relative to the crown ether cavity in the ligands for Ag^+ extraction, Figure 5 was constructed. In this figure, the identity of the PIG remains the same but it has two different positions. In each panel, extraction data for the PIG directed away from the polyether ring (Series 1) are shown as open circles and those for the PIG positioned over the polyether unit (Series 2) are presented as filled squares.

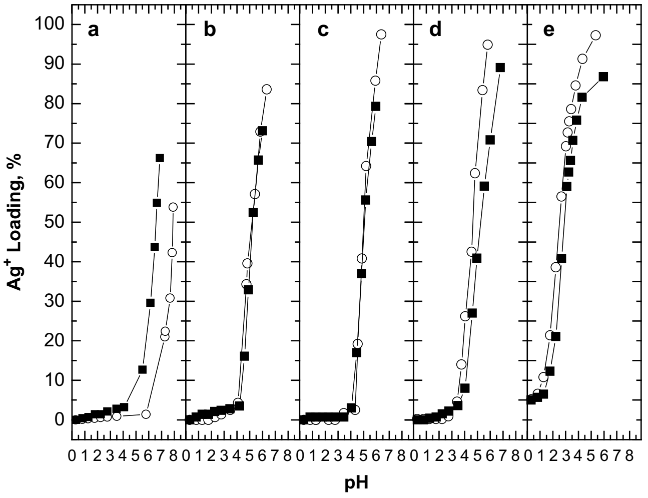


Figure 5. Comparison of Ag^+ extraction profiles for series 1 ligands (open circles) and series 2 ligands (filled squares) with the same PIG: a) carboxylic acids; b) *N*-methanesulfonyl carboxamides; c) *N*-benzenesulfonyl carboxamides; d) *N*-4-nitrobenzenesulfonyl carboxamides; and e) *N*-trifluoromethanesulfonyl carboxamides.

Does the PIG position influence the Ag^+ extraction behavior of the 1,3-alternate proton-ionizable calix[4]arene-crown-5 ligands? From the extraction data presented in Figure 5, the answers are 'yes', 'no' and 'maybe'. Focusing attention first on Figures 5b and 5c for *N*-(X)sulfonyl carboxamide PIGs with X=Me and Ph, respectively, the data points for the two ligands in each panel essentially define a common line. With no perceptible influence when the PIG's position is changed markedly, the answer is 'no'. In Figure 5d and e, the behaviors for *N*-(X)sulfonyl carboxamide PIGs with X=C_6H_4–NO_2 and CF_3, respectively, are compared. In these cases, there may be a slight favoring of ligands with the PIG pointing away from the crown ether cavity, qualifying for an answer of 'maybe'. For the ligands with a carboxylic acid PIG (Fig. 5a), the extractant with the ionized group positioned over the crown ether cavity is clearly more effective. Therefore, the answer is 'yes'.

The disparate influence of PIG positioning for the carboxylic acids and for the *N*(X)-sulfonyl carboxamides as a group, could result from the ambivalent character of Ag^+, which may accommodate either ethereal or π-basic coordinate sites in 1,3-alternate calix[4]crown ligands.[14] A carboxylate function should be a harder coordination site resulting in Ag^+ being complexed by both the ether oxygens and the carboxylate group. In this situation, it becomes important for the PIG to be appropriately positioned to interact with a polyether-complexed Ag^+. On the other hand, the ionized *N*-(X)sulfonyl carboxamide groups should be softer, perhaps allowing the Ag^+ to be positioned closer to the π-basic sites of the calixarene framework.

3. Experimental

3.1. General

Infrared spectra were taken with a Perkin–Elmer 1600 FTIR spectrophotometer as deposits from $CDCl_3$ or CH_2Cl_2 solution on sodium chloride plates. NMR spectra were obtained with a Varian Unity INOVA 500 MHz FT-NMR (^1H 500 MHz and ^{13}C 126 MHz) spectrometer in $CDCl_3$ with TMS as internal standard. Melting points were determined with a Mel-Temp melting point apparatus in capillary tubes. Elemental analysis was performed by Desert Analytics Laboratory of Tucson, Arizona.

Reagents were purchased from commercial sources and used as received, unless otherwise specified. Acetonitrile (MeCN) was dried over CaH_2 and tetrahydrofuran (THF) was dried over sodium with benzophenone as indicator. Both solvents were distilled immediately before use. *N*,*N*-Dimethylformamide (DMF) was stored over activated 4 Å molecular sieves.

Di-1,2-[2′(2″-hydroxyethoxy)ethoxy]-4-cyanobenzene was prepared by a literature method.[7] The partial cone 28-hydroxy-25,26,27-tribenzoyloxycalix[4]arene (**9**)[16] and partial cone 5-bromo-28-hydroxy-25,26,27-tribenzoyloxycalix[4]arene (**10**)[17] were synthesized by reported methods.

Syntheses of the following compounds are described in the Supplemental data: 1-iodooctane; di-1,2[2′(2″-hydroxyethoxy)-ethoxy]-4′-cyanobenzene *p*-toluenesulfonate (**2**), 1,3-alternate 4′-cyano-25,27-di(octyloxy)calix[4]arene-26,28-benzocrown-6 (**3**), bis-1,2-[2′,2″-hydroxyethoxy)ethoxy]benzene, and the ditosylate of bis-1,2-[2′(2″-hydroxyethoxy)ethoxy]benzene (**14**).

3.1.1. *1,3-Alternate 4′-carboxy-25,27-di(octyloxy)calix[4]arene-26,28-benzocrown-6 (**4**)*

A suspension of **3** (1.00 g, 1.08 mmol) in a 10% KOH solution in 1:1 aq EtOH (v/v) (80 mL) was refluxed under nitrogen for 3 h. The solution was evaporated in vacuo and 5% KOH (30 mL) was added to the residue along with CH_2Cl_2 (30 mL). The organic layer was separated and washed with 1 N HCl (30 mL) then water (30 mL) and dried over $MgSO_4$. The solvent was evaporated in vacuo yielding 1.03 g (100%) of **4** as a white solid with mp 102–104 °C. IR: 3320–2760 (O–H), 1687 (C=O) cm^{-1}. ^1H NMR: δ 7.83 and 7.81 (dd, *J*=1.8, 1.8 Hz, 0.5H), 7.72 (d, *J*=1.8 Hz, 0.5H), 7.54 (d, *J*=2.0 Hz, 0.5H), 7.43 and 7.41 (dd, *J*=2.0, 2.0 Hz, 0.5H), 7.06–6.98 (m, 9H), 6.76 (t, *J*=7.5 Hz, 2H), 6.64 (t, *J*=7.5 Hz, 2H), 6.10 (s, 1H), 4.22–4.18 (m, 4H), 3.82–3.72 (m, 12H), 3.57–3.52 (m, 8H), 3.46 (t, *J*=7 Hz, 4H), 1.36–1.24 (m, 20H), 1.19–1.17 (m, 4H), 0.92 (t, *J*=7.0 Hz, 6H). ^{13}C NMR: δ 171.0, 156.9, 156.5, 156.2, 156.2, 153.8, 148.4, 134.1, 134.1, 133.8, 133.7, 133.6, 130.0, 129.9, 129.8, 129.7, 125.2, 122.4, 122.1, 121.9, 121.5, 116.0, 112.9, 77.2, 77.0, 76.8, 72.1, 71.0, 70.7, 70.4, 70.3, 70.2, 70.0, 69.9, 69.8, 69.4, 68.5, 66.7, 37.7, 36.1, 31.9, 30.2, 29.7, 29.5, 29.4, 26.1, 25.8, 22.7, 15.1, 14.1. Anal. Calcd for $C_{59}H_{74}O_{10}$: C, 75.13; H, 7.91. Found: C, 75.31; H, 7.92%.

3.2. General procedure for the preparation of 1,3-alternate 3′-[*N*-(X)sulfonyl carbamoyl]-25,27-di(octyloxy)calix[4]arene-26,28-benzocrown-6 compounds 5–8

To a solution of **4** (1.30 g, 1.38 mmol) in dry benzene (25 mL), oxalyl chloride (0.70 g, 5.51 mmol) was added. The mixture was refluxed for 5 h under nitrogen and the solvent and excess oxalyl chloride were evaporated in vacuo to give the corresponding acid chloride. The appropriate sulfonamide sodium salt (2.07 mmol, 1.5 equiv) was prepared under nitrogen by adding THF (40 mL) and then NaH (0.13 g, 5.52 mmol). The mixture was stirred at room temperature for 30 min followed by dropwise addition of a solution of the acid chloride in THF (20 mL). The mixture was stirred at room temperature for 12 h. Water (20 mL) was added and the organic solvent was evaporated in vacuo. To the aq residue, CH_2Cl_2 (50 mL) was added. The organic layer was separated, washed with aqueous Na_2CO_3 (50 mL), dried over Na_2SO_4 and evaporated in vacuo. The residue was chromatographed on silica gel. The product was dissolved in CH_2Cl_2 (50 mL) and the solution was washed with 10% HCl (2×30 mL), dried over $MgSO_4$ and evaporated in vacuo.

*3.2.1. 1,3-Alternate 4′-(N-methanesulfonyl carbamoyl)-25,27-di(octyloxy)calix[4]arene-26,28-benzocrown-6 (**5**)*

Chromatography on silica gel with CH_2Cl_2/MeOH (30:1) as eluent gave a 71% yield of white solid with mp 115–120 °C. IR: 3267 (N–H), 1687 (C=O) cm^{-1}. ^1H NMR: δ 8.65 (br s, 1H), 7.52 (d, J=2.2 Hz, 1H), 7.49 and 7.47 (dd, J=2.1, 2.1 Hz, 1H), 7.06–7.00 (m, 9H), 6.76 (t, J=7.5 Hz, 2H), 6.62 (t, J=7.5 Hz, 2H), 4.21 and 4.18 (dt, J=5.0, 5.0 Hz, 4H), 3.82 (t, J=5.0 Hz, 2H), 3.76–3.74 (m, 10H), 3.59–3.53 (m, 8H), 3.49–3.46 (m, 7H), 1.37–1.25 (m, 20H), 1.21–1.18 (m, 4H), 0.92 (t, J=7.0 Hz, 6H). ^{13}C NMR: δ 165.0, 157.2, 156.5, 156.4, 156.2, 149.2, 134.4, 134.4, 134.0, 134.0, 130.3, 130.2, 130.0, 124.0, 122.4, 122.3, 122.1, 114.4, 113.3, 77.5, 77.2, 77.0, 71.2, 71.0, 70.7, 70.6, 70.4, 70.1, 70.0, 69.8, 42.1, 37.9, 32.2, 30.0, 29.8, 29.7, 26.1, 23.0, 14.4. Anal. Calcd for $C_{60}H_{77}NO_{11}S$: C, 70.63; H, 7.61; N, 1.37. Found: C, 70.57; H, 7.70; N, 1.39%.

*3.2.2. 1,3-Alternate 4′-(N-benzenesulfonyl carbamoyl)-25,27-di(octyloxy)calix[4]arene-26,28-benzocrown-6 (**6**)*

Chromatography on silica gel with CH_2Cl_2/MeOH (30:1) as eluent produced a 95% yield of white solid with mp 92–94 °C. IR: 3264 (N–H), 1694 (C=O) cm^{-1}. ^1H NMR: δ 8.20–8.18 (m, 2H), 7.70–7.60 (m, 1H), 7.59–7.56 (m, 2H), 7.47–7.45 (m, 2H), 7.02 (d, J=7.5 Hz, 8H), 6.94 (d, J=8.8 Hz, 1H), 6.76 (t, J=7.5 Hz, 2H), 6.60 (t, J=7.5 Hz, 2H), 4.16 and 4.10 (dt, J=4.9, 5.0 Hz, 4H), 3.79–3.69 (m, 12H), 3.54–3.45 (m, 12H), 1.36–1.24 (m, 20H), 1.21–1.18 (m, 4H), 0.92 (t, J=7.0 Hz, 6H). ^{13}C NMR: δ 163.6, 156.9, 156.2, 156.2, 153.6, 148.9, 138.6, 134.1, 134.1, 134.0, 133.8, 133.7, 130.0, 129.9, 129.7, 129.0, 128.6, 123.9, 122.1, 121.8, 113.8, 113.06, 77.2, 77.0, 76.8, 71.0, 70.7, 70.4, 70.2, 69.8, 69.5, 37.7, 31.9, 29.7, 29.5, 29.4, 25.8, 22.7, 14.1. Anal. Calcd for $C_{65}H_{79}NO_{11}S$: C, 72.13; H, 7.36; N, 1.29. Found: C, 71.75; H, 7.37; N, 1.24%.

*3.2.3. 1,3-Alternate 4′-(N-4-nitrophenylsulfonyl carbamoyl)-25,27-di(octyloxy)calix[4]-arene-26,28-benzocrown-6 (**7**)*

Chromatography on silica gel with CH_2Cl_2/MeOH (40:1) as eluent produced a 90% yield of yellow solid with mp 105–107 °C. IR: 3263 (N–H), 1696 (C=O) cm^{-1}. ^1H NMR: δ 9.03 (s, 1H), 8.41–8.36 (m, 4H), 7.45–7.42 (m, 2H), 7.02–6.95 (m, 9H), 6.76 (t, J=7.5 Hz, 2H), 6.58 (t, J=7.5 Hz, 2H), 4.18 (t, J=4.8 Hz, 2H), 4.11 (t, J=4.8 Hz, 2H), 3.81 (t, J=4.8 Hz, 2H), 3.76–3.69 (m, 11H), 3.56–3.45 (m, 13H), 1.36–1.24 (m, 20H), 1.21–1.16 (m, 4H), 0.92 (t, J=7.0 Hz, 6H). ^{13}C NMR: δ 163.6, 156.9, 156.2, 156.2, 154.1, 150.8, 149.0, 144.0, 134.2, 134.1, 133.7, 133.7, 130.2, 130.1, 129.8, 129.7, 124.2, 123.2, 122.2, 122.1, 121.7, 114.2, 113.0, 77.3, 77.0, 76.8, 71.0, 70.8, 70.5, 70.3, 70.1, 69.8, 69.8, 69.5, 37.6, 31.9, 29.7, 29.5, 29.4, 25.8, 22.7, 14.1. Anal. Calcd for $C_{65}H_{78}N_2O_{13}S$: C, 69.25; H, 6.97; N, 2.48. Found: C, 69.03; H, 7.07; N, 2.29%.

*3.2.4. 1,3-Alternate 4′-(N-trifluoromethanesulfonyl carbamoyl)-25,27-di(octyloxy)calix[4]-arene-26,28-benzocrown-6 (**8**)*

Chromatography on silica gel with CH_2Cl_2/MeOH (40:1) as eluent gave an 88% yield of white solid with mp 88–94 °C. IR: 3550, 3190 (N–H), 1716 (C=O) cm^{-1}. ^1H NMR: δ 7.54–7.52 (m, 2H), 7.06–7.00 (m, 9H), 6.77 (t, J=7.5 Hz, 2H), 6.63 (t, J=7.5 Hz, 2H), 4.22 (t, J=4.8 Hz, 2H), 4.15 (t, J=4.8 Hz, 2H), 3.84 (t, J=4.7 Hz, 2H), 3.75–3.71 (m, 10H), 3.60–3.59 (m, 2H), 3.56–3.53 (m, 6H), 3.47 (t, J=7.6 Hz, 4H), 1.37–1.24 (m, 20H), 1.20–1.17 (m, 4H), 0.92 (t, J=7.0 Hz, 6H). ^{13}C NMR: δ 156.96, 156.19, 148.97, 134.19, 134.14, 133.72, 133.69, 130.05, 129.81, 129.67, 122.72, 122.18, 121.77, 115.43, 114.85, 112.93, 77.25, 77.00, 76.74, 70.99, 70.80, 70.43, 70.20, 70.01, 69.87, 69.82, 69.75, 69.53, 37.69, 31.91, 29.70, 29.45, 29.41, 25.85, 22.73, 14.14. Anal. Calcd for $C_{60}H_{74}F_3NO_{11}S$: C, 67.08; H, 6.94; N, 1.30. Found: C, 67.08; H, 6.79; N, 1.27%.

3.3. 5-Bromo-28-octyloxy-25,26,27-tri(benzoyloxy)-calix[4]arene (11)

To **10**[17] (7.00 g, 9.13 mmol) dissolved in DMF (130 mL), NaH (0.26 g, 10.95 mmol) was added and the mixture was stirred for 30 min at room temperature. Then 1-iodooctane (2.63 g, 10.95 mmol) was added and the mixture was stirred for 24 h at room temperature. A small amount of water was added carefully to destroy the excess NaH and then 10% HCl (100 mL) was added. The organic solvent was evaporated in vacuo. To the aq residue CH_2Cl_2 (200 mL) was added and the organic layer separated, washed with 10% HCl (100 mL) and then water (2×100 mL) and dried over $MgSO_4$. The solvent was evaporated in vacuo. The crude product was recrystallized from CH_2Cl_2/MeOH to yield 5.70 g (67%) of **11** with mp 258–260 °C. IR: 1729 (C=O) cm^{-1}. ^1H NMR: δ 7.87–7.85 (m, 4H), 7.79–7.76 (m, 2H), 7.65 (t, J=7.6 Hz, 5H), 7.43–7.42 (m, 2H), 7.36 (t, J=7.8 Hz, 2H), 7.19–7.17 (m, 2H), 6.81 (s, 2H), 6.70–6.68 (m, 2H), 6.64–6.52 (m, 5H), 3.78 (t, J=7.7 Hz, 4H), 3.60 (s, 4H), 3.53 (d, J=15.0 Hz, 2H), 1.87 (pen, J=7.3 Hz, 2H), 1.50–1.38 (m, 10H), 0.96 (t, J=7.0 Hz, 3H). ^{13}C NMR: δ 164.5, 163.9, 156.3, 148.2, 147.8, 136.2, 133.5, 133.5, 133.4, 133.2, 133.0, 132.0, 130.9, 130.8, 130.6, 130.3, 128.8, 128.6, 128.2, 127.6, 125.0, 124.8, 114.9, 77.2, 77.0, 76.7, 71.7, 37.1, 37.0, 31.9, 30.2, 29.8, 29.4, 25.97, 22.8, 14.2. Anal. Calcd for $C_{57}H_{51}BrO_7$: C, 73.78; H, 5.54. Found: C, 73.90; H, 5.55%.

3.4. Cone 5-bromo-28-octyloxycalix[4]arene (12)

Triester **11** (5.70 g, 6.15 mmol) was suspended in 10% KOH solution in aq EtOH (1:1, v/v) and the mixture was refluxed under nitrogen for 24 h. The mixture was evaporated in vacuo and 5% KOH (120 mL) was added to the residue along with CH_2Cl_2 (120 mL). The organic layer was separated, washed with 1 N HCl (120 mL) then water (120 mL), dried over $MgSO_4$ and evaporated in vacuo. The residue was chromatographed on silica gel with hexanes/CH_2Cl_2 (4:1) as eluent to obtain 3.00 g (79%) of **12** with mp 161–163 °C. IR: 3317 (O–H) cm^{-1}. ^1H NMR: δ 9.53 (s, 1H), 9.31 (s, 2H), 7.17 (s, 2H), 7.06–7.00 (m, 6H), 6.70 (t, J=7.5 Hz, 3H), 4.30 and 4.20 (dd, J=13.1, 13.8 Hz, 4H), 4.11 (t, J=7 Hz, 2H), 3.47 and 3.43 (dd, J=13.8, 13.1 Hz, 4H), 2.14 (pen, J=7.4 Hz, 2H), 1.67 (pen, J=7.6 Hz, 2H), 1.52–1.46 (m, 2H), 1.45–1.32 (m, 6H), 0.92 (t, J=6.9 Hz, 3H). ^{13}C NMR: δ 150.9, 150.8, 149.0, 136.3, 132.13, 129.0, 128.8, 128.7, 128.5, 128.4, 127.5, 122.1, 121.0, 118.4, 77.7, 77.3, 77.0, 76.8, 34.7, 31.8, 31.7, 31.6, 31.3, 29.9, 29.4, 29.2, 25.9, 25.3, 22.7, 22.6, 20.7, 14.1. Anal. Calcd for $C_{36}H_{39}BrO_4$: C, 70.24; H, 6.39. Found: C, 70.42; H, 6.54%.

3.5. Cone 5-bromo-26,28-di(octyloxy)calix[4]arene (13)

To **12** (3.00 g, 4.88 mmol) dissolved in MeCN (150 mL), 1-iodooctane (2.34 g, 9.76 mmol) and K_2CO_3 (0.80 g, 5.85 mmol) were added. The mixture was refluxed for 24 h and evaporated in vacuo. The residue was dissolved in CH_2Cl_2 (150 mL) and 1 N HCl (150 mL) was added. The organic layer was separated, washed with brine (2×150 mL), dried over $MgSO_4$ and evaporated in vacuo. The residue was chromatographed on silica gel with hexanes/CH_2Cl_2 (6:1) as eluent to yield 2.60 g (74%) of **13** with mp 138–140 °C. IR: 3349 (O–H) cm^{-1}. ^{1}H NMR: δ 8.18 (s, 2H), 7.07 and 7.05 (dd, J=1.3, 1.3 Hz, 2H), 7.01–6.99 (m, 4H), 6.93 (d, J=7.6 Hz, 2H), 6.76 (t, J=7.6 Hz, 1H), 6.64 (t, J=7.5 Hz, 2H), 4.30 and 4.25 (dd, J=13.0, 12.8 Hz, 4H), 3.99 and 3.95 (tt, J=6.7, 6.7 Hz, 4H), 3.38 and 3.31 (dd, J=13.1, 13.0 Hz, 4H), 2.09–2.01 (m, 4H), 1.72–1.65 (m, 4H), 1.48–1.26 (m, 16H), 0.89 (t, J=6.8 Hz, 6H). ^{13}C NMR: δ 153.3, 151.9, 151.3, 135.7, 133.4, 131.8, 129.0, 128.7, 128.5, 128.2, 127.2, 125.4, 119.1, 117.6, 77.2, 77.1, 77.0, 76.8, 76.7, 32.0, 31.9, 31.4, 31.3, 30.0, 29.9, 29.5, 29.4, 29.3, 29.2, 26.0, 25.9, 22.7, 14.1. Anal. Calcd for $C_{44}H_{55}BrO_4$: C, 72.61; H, 7.62. Found: C, 72.80; H, 7.67%.

3.6. 1,3-Alternate 5-bromo-26,28-di(octyloxy)calix[4]arene-25,27-benzocrown-6 (15)

To **13** (2.60 g, 3.58 mmol) in MeCN (500 mL) under nitrogen, Cs_2CO_3 (4.67 g, 14.32 mmol) and ditosylate **14** (2.34 g, 3.93 mmol) were added and the mixture was refluxed for 24 h. Then 10% HCl (150 mL) was added and the MeCN was evaporated in vacuo. To the aq residue CH_2Cl_2 (150 ml) was added. The organic layer was separated, washed twice with water, dried over $MgSO_4$ and evaporated in vacuo. The residue was chromatographed on silica gel with hexanes/EtOAc (10:1) as eluent, yielding 3.20 g (91%) of **15** as an oil. ^{1}H NMR: δ 7.19 (s, 2H), 7.06–6.94 (m, 10H), 6.77 (t, J=7.4 Hz, 3H), 6.67 (t, J=7.4 Hz, 1H), 4.17 (t, J=4.9 Hz, 4H), 3.84–3.74 (m, 8H), 3.70 (d, J=8.4 Hz, 3H), 3.67–3.63 (m, 3H), 3.55–3.50 (m, 6H), 3.43–3.39 (m, 4H), 1.34–1.12 (m, 24H), 0.92 and 0.91 (tt, J=7.0, 7.0 Hz, 6H). ^{13}C NMR: δ 156.7, 156.2, 156.1, 149.4, 136.5, 134.0, 133.8, 133.0, 132.2, 130.2, 129.8, 129.7, 122.4, 122.2, 121.9, 115.8, 114.4, 77.3, 77.0, 76.8, 71.0, 70.6, 70.5, 70.2, 70.1, 69.9, 37.8, 37.5, 31.9, 29.7, 29.5, 29.4, 29.4, 29.2, 25.8, 22.7, 14.1. Anal. Calcd for $C_{58}H_{73}BrO_8$: C, 71.22; H, 7.52. Found: C, 70.85; H, 7.34%.

3.7. 1,3-Alternate 5-carboxy-26,28-di(octyloxy)calix[4]arene-25,27-benzocrown-6 (16)

To a stirred solution of **14** (3.00 g, 3.07 mmol) in THF (250 mL) under nitrogen at −75 °C, 0.6 M BuLi (0.79 g, 12.28 mmol) in hexane was added, which caused the colorless solution to turn red. After 20 min at −75 °C, CO_2 was bubbled through the solution for 30 min during which time the red color disappeared. After another 15 min at −75 °C, the mixture was allowed to warm to room temperature and was quenched by careful addition of water. The solvent was evaporated in vacuo and CH_2Cl_2 was added to the residue. The organic layer was washed with 1 N HCl then water, dried over $MgSO_4$ and evaporated in vacuo. The residue was recrystallized from CH_2Cl_2/MeOH to yield 1.80 g (62%) of **16** with mp 82–86 °C. IR: 3220–2620 (O–H), 1698 (C=O) cm^{-1}. ^{1}H NMR: δ 7.74 (s, 2H), 7.03–6.91 (m, 10H), 6.78 (t, J=7.5 Hz, 2H), 6.52 (t, J=7.5 Hz, 1H), 4.19–4.09 (m, 4H), 3.87–3.84 (m, 2H), 3.77–3.66 (m, 14H), 3.55–3.49 (m, 4H), 3.41–3.35 (m, 4H), 1.42–1.13 (m, 24H), 0.93 and 0.92 (tt, J=7.0, 7.1 Hz, 6H). ^{13}C NMR: δ 170.2, 160.3, 156.6, 155.9, 148.6, 134.1, 133.9, 133.7, 133.5, 132.1, 130.2, 130.0, 122.4, 122.2, 121.7, 114.4, 96.1, 77.2, 77.0, 76.8, 71.1, 70.6, 70.5, 70.2, 69.1, 37.7, 37.7, 31.9, 31.9, 29.8, 29.7, 29.6, 29.4, 29.4, 29.2, 25.8, 25.8, 22.7, 14.2, 14.4. Anal. Calcd For $C_{59}H_{74}O_{10}\cdot 0.1CH_2Cl_2$: C, 74.59; H, 7.86. Found: C, 74.36; H, 7.73%.

3.8. General procedure for preparation of 1,3-alternate 5-[*N*-(X)sulfonyl carbamoyl]-26,28-di(octyloxy)calix[4]arene-25,27-benzocrown-6 compounds 17–20

To a solution of **16** (1.30 g, 1.38 mmol) in benzene (25 mL), oxalyl chloride (0.70 g, 5.51 mmol) was added and the mixture was refluxed for 5 h under nitrogen. The solvent and excess oxalyl chloride were evaporated in vacuo. The sodium sulfonamide salt was prepared under nitrogen by adding NaH (0.13 g, 5.52 mmol) and THF (40 mL) to the appropriate sulfonamide (2.07 mmol). The mixture was stirred at room temperature for 30 min followed by dropwise addition of a solution of the acid chloride in THF (20 mL). The mixture was stirred at room temperature for 12 h. Water (20 mL) was added carefully and the organic solvent was evaporated in vacuo. To the residue CH_2Cl_2 (50 mL) was added. The organic layer was separated, washed with aqueous Na_2CO_3 (50 ml), dried over Na_2SO_4 and evaporated in vacuo. The crude product was chromatographed on silica gel. The product was dissolved in CH_2Cl_2 (50 mL) and the solution was washed with 10% HCl (2 X 30 mL), dried over $MgSO_4$ and evaporated in vacuo.

*3.8.1. 1,3-Alternate 5-(N-methanesulfonyl carbamoyl)-26,28-di(octyloxy)calix[4]arene-25,27-benzocrown-6 (**17**)*

Chromatography on silica gel with CH_2Cl_2/MeOH (60:1) as eluent provided an 82% yield of white solid with mp 205–207 °C. IR: 3594 (N–H), 1691 (C=O) cm^{-1}. ^{1}H NMR: δ 10.37 (s, 1H), 7.61 (s, 2H), 7.06–7.03 (m, 4H), 7.00 (s, 4H), 6.96 (d, J=7.3 Hz, 2H), 6.81 (t, J=7.5 Hz, 2H), 6.52 (t, J=7.5 Hz, 1H), 4.07–4.03 (m, 2H), 3.97–3.93 (m, 2H), 3.88–3.84 (m, 2H), 3.82 (d, J=4.3 Hz, 4H), 3.74 (s, 4H), 3.72–3.65 (m, 4H), 3.57–3.46 (m, 6H), 3.41–3.37 (m, 4H), 3.20 (s, 3H), 1.47–1.43 (m, 2H), 1.35–1.12 (m, 22H), 0.93 and 0.92 (tt, J=7.0, 7.0 Hz, 6H). ^{13}C NMR: δ 168.3, 161.5, 156.8, 156.2, 149.2, 134.7, 134.3, 133.8, 132.7, 130.4, 130.3, 130.3, 129.5, 126.6, 122.5, 122.4, 122.1, 116.5, 77.3, 77.0, 76.8, 71.0, 70.8, 70.4, 70.1, 69.8, 69.6, 40.8, 37.8, 37.7, 31.9, 31.8, 29.9, 29.7, 29.6, 29.4, 29.3, 29.1, 25.8, 25.7, 22.7, 14.1. Anal. Calcd for $C_{60}H_{77}NO_{11}S$: C, 70.63; H, 7.61; N, 1.37. Found: C, 70.40; H, 7.68; N, 1.22%.

*3.8.2. 1,3-Alternate 5-(N-benzenesulfonyl carbamoyl)-26,28-di(octyloxy)calix[4]arene-25,27-benzocrown-6 (**18**)*

Chromatography on silica gel with CH_2Cl_2/MeOH (80:1) as eluent gave a 75% yield of white solid with mp 162–164 °C. IR: 3598 (N–H), 1698 (C=O) cm^{-1}. ^{1}H NMR: δ 11.39 (s, 1H), 8.12 and 8.10 (dd, J=1.1, 1.2 Hz, 2H), 7.47–7.44 (m, 3H), 7.25–7.22 (m, 2H), 7.04–6.95 (m, 9H), 6.76 (t, J=7.5 Hz, 2H), 6.39 (t, J=7.5 Hz, 1H), 4.07–4.03 (m, 2H), 3.99–3.95 (m, 2H), 3.83–3.80 (m, 2H), 3.74–3.65 (m, 13H), 3.60 (t, J=7.5 Hz, 2H), 3.50–3.45 (m, 4H), 3.38–3.34 (m, 2H), 1.61–1.56 (m, 2H), 1.44–1.43 (m, 2H), 1.37–1.21 (m, 20H), 0.94–0.90 (m, 6H). ^{13}C NMR: δ 167.9, 161.3, 156.6, 156.0, 148.5, 139.6, 134.5, 133.8, 133.7, 132.9, 132.6, 130.9, 130.7, 130.4, 129.9, 128.6, 128.3, 127.4, 122.3, 122.1, 121.7, 113.8, 77.3, 77.0, 76.8, 71.8, 71.6, 71.1, 69.9, 69.5, 68.4, 37.3, 31.9, 30.1, 29.7, 29.7, 29.4, 29.4, 25.9, 25.8, 22.7, 14.1. Anal. Calcd for $C_{65}H_{79}NO_{11}S$: C, 72.13; H, 7.36; N, 1.29. Found: C, 71.99; H, 7.17; N, 1.24%.

*3.8.3. 1,3-Alternate 5-(N-4-nitrobenzenesulfonyl carbamoyl)-26,28-di(octyloxy)calix[4]-arene-25,27-benzocrown-6 (**19**)*

Chromatography on silica gel with CH_2Cl_2/MeOH (100:1) as eluent produced a 50% yield of yellow solid with mp 84–86 °C. IR: 3598 (N–H), 1699 (C=O) cm^{-1}. ^{1}H NMR: δ 11.61 (s, 1H), 8.30–8.28 (m, 2H), 7.97–7.94 (m, 2H), 7.49 (s, 2H), 7.06–7.03 (m, 6H), 7.00–6.97 (m, 2H), 6.94 (d, J=7.6 Hz, 2H), 6.77 (t, J=7.5 Hz, 2H), 6.39 (t, J=7.5 Hz, 1H), 3.95–3.92 (m, 4H), 3.80–3.77 (m, 2H), 3.75–3.60 (m, 14H), 3.56–3.51 (m, 4H), 3.47 (t, J=7.6 Hz, 2H), 3.33 and 3.31 (tt, J=4.8, 5.0 Hz, 2H), 1.62–1.56 (m, 2H), 1.43–1.20 (m, 22H), 0.94–0.90 (m, 6H). ^{13} NMR: δ 168.0, 161.6, 156.7, 156.0, 150.0, 148.3, 145.1, 134.7, 134.0, 133.6, 132.4, 130.9, 130.7, 130.7, 130.0, 129.7, 126.8, 123.4, 122.2, 122.1, 122.0, 114.2, 77.2, 77.0, 76.7, 71.8, 71.6, 71.0, 69.7, 69.5, 68.4, 37.3, 37.3, 31.9, 31.8, 30.1, 29.7, 29.5, 29.4, 29.3, 25.8, 25.8, 22.7, 14.1. Anal. Calcd for $C_{65}H_{78}N_2O_{13}S\cdot 1.3CH_2Cl_2$: C, 64.33; H, 6.59; N, 2.26. Found: C, 64.36; H, 6.26; N, 2.09%.

*3.8.4. 1,3-Alternate 5-(N-trifluoromethanesulfonyl carbamoyl)-26,28-di(octyloxy)calix[4]-arene-25,27-benzocrown-6 (**20**)*

Chromatography on silica gel with CH_2Cl_2/MeOH (70:1) as eluent gave a 71% yield of white solid with mp 217–220 °C. IR: 3583 (N–H), 1725 (C=O) cm^{-1}. ^{1}H NMR: δ 7.56 (s, 2H), 7.06 (d, J=7.6 Hz, 4H), 7.00–6.99 (m, 6H), 6.81 (t, J=7.5 Hz, 2H), 6.47 (t, J=7.5 Hz, 1H), 4.10–4.09 (m, 4H), 3.79–3.73 (m, 14H), 3.65–3.57 (m, 6H), 3.47–3.43 (m, 4H), 1.53–1.49 (m, 2H), 1.38–1.17 (m, 22H), 0.94 and 0.93 (tt, J=7.0, 7.0 Hz, 6H). ^{13}C NMR: δ 166.8, 162.1, 156.6, 156.0, 148.6, 135.0, 133.9, 133.8, 132.4, 131.0, 130.7, 130.0, 126.4, 122.4, 122.2, 121.7, 114.0, 84.3, 77.3, 77.0, 76.8, 71.7, 71.6, 71.1, 70.1, 69.7, 68.7, 37.4, 31.9, 30.1, 29.7, 29.6, 29.4, 29.4, 25.9, 25.8, 22.7, 14.1. Anal. Calcd for $C_{60}H_{74}F_3NO_{11}S$: C, 67.08; H, 6.94; N, 1.30. Found: C, 66.94; H, 6.94; N, 1.38%.

3.9. Solid-state structure determination for ligand 17

Single crystals were obtained by slow evaporation of a $CHCl_3$/EtOH solution of **17**. Single-crystal X-ray data were collected on a Bruker SMART APEX CCD diffractometer with fine-focus MoKα radiation (λ=0.71073 Å), operated at 50 kV and 30 mA. The structure was solved by direct methods and refined on F^2 using the SHELXTL software package.[19] Absorption corrections were applied using SADABS, part of the SHELXTL package. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in idealized positions and refined with a riding model.

Crystal data for **17**: $C_{60}H_{77}NO_{11}S$, M=1020.29, 0.41×0.29×0.22 mm^3, triclinic, space group P-1 (No. 2), a=13.6541(15), b=14.2125(15), c=15.6432(17) Å, α=96.567(2), β=104.916(2), γ=106.054(2)°, V=2762.2(5) Å^3, Z=2, D_c=1.227 g/cm^3, F_{000}=1096, MoKα radiation, λ=0.71073 Å, T=173(2) K, $2\theta_{max}$=56.7°, 34,638 reflections collected, 13,683 unique (R_{int}=0.0233). Final GOF=1.192, $R1$=0.0723, $wR2$=0.1640, R indices based on 12,273 reflections with $I>2\sigma(I)$ (refinement on F^2), 661 parameters, 0 restraints. Lp and absorption corrections applied, μ=0.119 mm^{-1}.

Crystal data for **17** have been deposited with the Cambridge Crystallographic Data Centre under reference CCDC 727689.

3.10. Solvent extraction of Ag$^+$

A 1.0 mM aqueous $AgNO_3$ solution (2.0 mL, pH adjusted with HNO_3 or tetramethylammonium hydroxide) and a 1.0 mM solution of the calixcrown in $CHCl_3$ (2.0 mL) were vortexed for 15 min. After centrifuging for 10 min to insure phase separation, a 0.50-mL sample of the aqueous phase was removed and diluted to 10.0 mL with deionized water. The pH of the extracted aqueous phase was measured and the residual concentration of Ag$^+$ in the diluted aqueous phase was determined by atomic absorption spectrophotometry.

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Supplementary data

Supplementary data associated with this article can be found in online version, at doi:10.1016/j.tet.2009.07.006.

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