Syntheses of Novel Tripodal Calix[*n*]cryptands (*n* = 4, 6) and Their Extraction Abilities toward Cations

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The tripodal calixcryptands have been one of the scarcely explored fields in calixarene chemistry due to the difficulties in their preparation. The strategy presented in this paper shows that novel tripodal calixcryptands can be conveniently prepared by directly treacing *p-tert*-butylcalix[n]arenes (*n* = 4, 6) with a multi-functional polypode reagent, e.g. 1,1,1-tris(tosyloxyethoxyethoxymethyl)propane or tetrakis(tosyloxyethoxyethoxymethyl)methane, under selected conditions. The first example of 1,2,4-tripodal calix[6]cryptands has been prepared. Novel calix[6]crown and doublecalix[4]arenes were co-prepared. The extraction abilities of these novel calixcryptands toward several alkali metal ions, ammonium and alkylammonium ions are presented.

Introduction

In calixarene chemistry,[1] calixcryptands are recent arrivals possessing cage-like structures, which, in the field of supramolecular chemistry, are expected to have better molecular recognition abilities, especially towards cations, than calixcrowns. Up to now there have been two types of calixcryptands described in the literature. The first one, cryptocalix[4]arene, in which the calix[4]arene subunit was incorporated into one arm of a cryptand by condensation of a 1,3-derived calix[4]arene with a diazacrown,[2] and the second one, tripodal calix[*n*]cryptand (*n* = 4, 6), which is composed of a calix[*n*]arene subunit and half of a cryptand subunit.[3][4] The latter has been almost unexplored due to its difficult access usually by a multi-step procedure. This paper will focus mainly on the scarcely explored tripodal calix[*n*]cryptands.

In 1997, Tuntulani et al.[3] reported the only example of a tripodal calix[4]cryptand prepared by a multi-step procedure. The total yield of this calix[4]cryptand was less than 3%, due to the rather low yield (6%) of the key intermediate, trialdehyde calix[4]arene. In 1994, Reinhoudt et al.[4] reported the synthesis of a kind of 1,3,5-tripodal calix[6]cryptand by the covalent three-point capping of a 1,3,5-trimethoxy-*p-tert*-butylcalix[6]arene with a cyclotriveratrylene (CTV). Several analogs of 1,3,5-tripodal calix[6]cryptand, i.e. capped calix[6]arenes, were also prepared.[5–7] In each case, the starting materials were 1,3,5-trimethoxy-*p-tert*-butylcalix[6]arene and a capping compound, e.g. 1,3,5-tris(bromomethyl)benzene,[5] the 1,3,5-triazine[6] or the 1,3,5-tris(mercaptomethyl)benzene derivative.[7] Recently, lower-rim 1,2,4,5-quadruply capped calix[6]arenes[8] have been prepared by treatment of a 1,4-diether of calix[6]arene with a tetrafunctional reagent, e.g. 1,2,4,5-tetrakis(bromomethyl)benzene.

Just recently, we have prepared some stabilized 1,3,5-tripodal calix[6]cryptands (**1**) with in and out isomers, by capping 1,3,5-trimethoxy-*p-tert*-butylcalix[6]arene with a key trifunctional reagent [1,1,1-tris(tosyloxyethoxyethoxymethyl)propane (**3**)] with long spacers.[9] We have also reported a novel kind of double calix[4]crown, i.e. spirobiscalix[4]crown (**2**), by treatment of *p-tert*-butylcalix[4]arene with tetrakis(tosyloxyethoxyethoxymethyl)methane (**4**).[10]

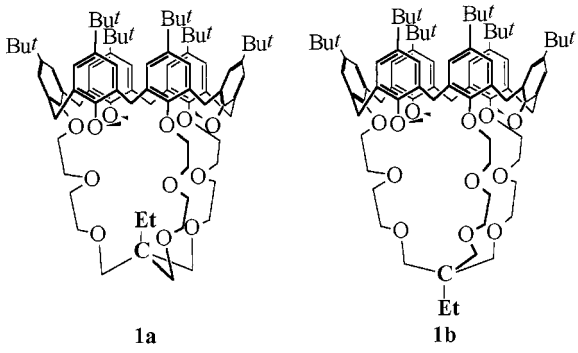

Figure 1. A couple of stabilized calix[6]cryptands (**1**): in isomer **1a** and out isomer **1b**

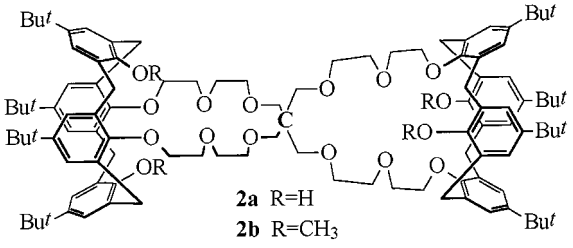

Figure 2. Spirobiscalix[4]crown **2a** and its fully methylated derivative **2b**

Further investigation presented in this paper reveals that directly treating **3** with calix[*n*]arenes (*n* = 4, 6), and **4** with calix[6]arene, may be a convenient method, with general interest, to synthesize novel tripodal calixcryptands. As

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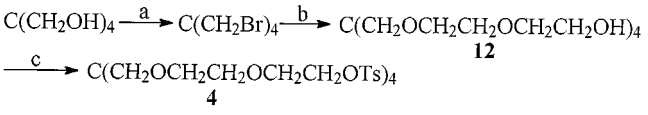
shown in Scheme 2, treating **3** with *p-tert*-butylcalix[4]arene (**5**) or *p-tert*-butylcalix[6]arene (**6**), we obtained the expected calix[4]cryptand **7** and calix[6]cryptand **10**, respectively. Interestingly, the so-obtained calix[6]cryptand **10** is a 1,2,4-triply bridged compound, which represents the first example of an asymmetric tripodal calix[6]cryptand. We have also co-prepared a novel type of double calix[4]arene **8**, in which one subunit is a calix[4]crown and another is a calix[4]arene, and a novel type of calix[6]crown **9**, in which a side chain with terminal tosyloxy group is attached to the crown moiety, which could be useful in building calix[6]arene-based macromolecules. Treating **4** with *p-tert*-butylcalix[6]arene (**6**), we obtained another special 1,2,4-tripodal calix[6]cryptand **11** which is also a novel type of double calix[6]arene.

Result and Discussion

Syntheses and Characterization

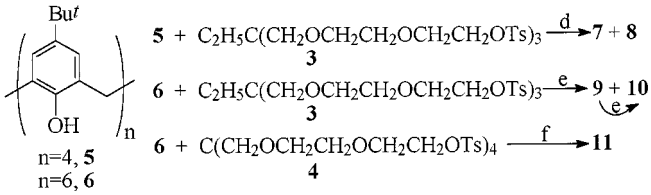
The synthesis of 1,1,1-tris(tosyloxyethoxyethoxymethyl)propane (**3**) has previously been reported.[9] The preparation of tetrakis(tosyloxyethoxyethoxymethyl)methane (**4**) is shown in Scheme 1. Bromination of tetrakis(hydroxymethyl)methane with PBr_3 afforded tetrakis(bromomethyl)methane in 53% yield.[11] The key step was accomplished by treating tetrakis(bromomethyl)methane with sodium diethylene glycolate in an excess of diethylene glycol at elevated temperature (160°C), which provided tetrakis(hydroxyethoxyethoxymethyl)methane (**12**) in a high yield of 63%. Decreasing the reaction temperature gave **12** in a yield of less than 15%. Tosylation of **12** with tosyl chloride in pyridine (in a salt/ice bath) gave the desired tetrakis(tosyloxyethoxyethoxymethyl)methane (**4**) in 45% yield after column chromatography purification. Decreasing the tosylation time of **12** from 24 to 2 hours, decreased the yield to less than 20%.



Scheme 1. Reagents and conditions: (a) PBr_3, 160°C, 18 h; (b) $Na(OCH_2CH_2)_2OH$, $H(OCH_2CH_2)_2OH$, 160°C, 20 hours; (c) TsCl, pyridine, salt/ice bath, 24 h

As can be seen in Scheme 2, the syntheses of **7** and **8** were accomplished by the improved method described for the preparation of *p-tert*-butylcalix[4]crown-5.[12] Treatment of *p-tert*-butylcalix[4]arene (**5**) with 1,1,1-tris(tosyloxyethoxyethoxymethyl)propane (**3**) in refluxing benzene in the presence of K_2CO_3 gave the desired tripodal calix[4]cryptand **7** and double calix[4]arene **8** in yields of 7% and 35%, respectively. Using polar solvents such as MeCN, THF, DMF, or Me_2CO instead of benzene and using strong bases such as NaH or *t*BuOK instead of K_2CO_3 gave rather complex crude products that were difficult to separate.

The syntheses of **9** and **10** were achieved by heating a mixture of **3** and *p-tert*-butylcalix[6]arene (**6**) (molar ratio 1:1) in THF under reflux in the presence of K_2CO_3. The products **9** and **10** were obtained in yields of 43% and 5%, respectively, after purification. In fact, we have tried several other solvents such as benzene, MeCN, or Me_2CO instead of THF, and bases such as NaH or *t*BuOK instead of K_2CO_3, but in each case the conversion of *p-tert*-butylcalix[6]arene (**6**) was low (below 50%) and the reaction products were very complex.



Scheme 2. Reagents and conditions: (d) K_2CO_3/dry benzene, reflux, 3 d; (e) K_2CO_3/THF, reflux, 2 d; (f) *t*BuOK/dry benzene, reflux, 2 d

1,2,4-Tripodal calix[6]cryptand **11** was prepared under high dilution by refluxing a mixture of **6** and tetrakis(tosyloxyethoxyethoxymethyl)methane (**4**) in benzene using *t*BuOK as a base. The product **11** was isolated in 16% yield after column chromatography, subsequent preparative thin layer chromatography, and recrystallization.

The structures of compounds **7**–**11** were characterized by FAB-MS spectra, elemental analyses, ^{1}H-NMR spectra, and ^{13}C-NMR spectra. The ^{1}H-NMR spectrum of **7** shows three singlets (ratio 1:1:2) for the *tert*-butyl groups as well as for the aromatic protons, one singlet for the hydroxy proton, and two pairs of doublets for the protons in the calixarene methylene skeleton, which indicates that the calix[4]arene moiety adopted a cone conformation. In the ^{1}H-NMR spectrum of **8**, two singlets at δ = 10.30 (1 OH) and 9.40 (2 OH) obviously indicate that one of the two calix[4]arene subunits is mono-substituted.[13] A pair of doublets for the protons in the calix[4]arene methylene skeleton may reveal that the crowned calix[4]arene moiety adopted a cone conformation.

The ^{1}H-NMR spectrum of **9** shows one singlet at δ = 2.45, and a pair of doublets at δ = 7.37 and 7.80 for the tosyloxy group. The presence of two singlets in a 2:1 ratio for the *tert*-butyl groups seems to indicate that the calix[6]arene moiety is lower-rim 1,4-substituted. It is, however, difficult to confirm the conformation of **9** at ambient temperature due to the overlapping signals in the region of δ = 3.33–4.15. The ^{1}H-NMR spectrum of **10** shows that the structure of **10** is asymmetrical. Three singlets in a 1:2:3 ratio for the *tert*-butyl groups as well as for the aromatic protons, and two singlets in a 1:2 ratio for the hydroxy protons reveal that the calix[6]arene moiety of **10** may be 1,2,4-substituted. Three pairs of doublets (ratio 3:2:1) for the methylene protons in calixarene skeleton (one of which is disturbed by superposition with the spacers) may support the idea that **10** adopts a cone conformation at ambient temperature.[14] Since **9** is a lower-rim 1,4-bridged ca-

lix[6]crown with a side chain terminated by a tosyloxy group, one may assume that further intramolecular alkylation of the remaining phenolic groups with this terminal tosyloxy group may result in the 1,2,4-triply bridged calix[6]cryptand **10**. In fact, heating **9** in THF under reflux in the presence of K_2CO_3 gave a small amount of compound **10**. This can be considered as an indirect evidence for the 1,2,4-triply bridged structure of **10**.

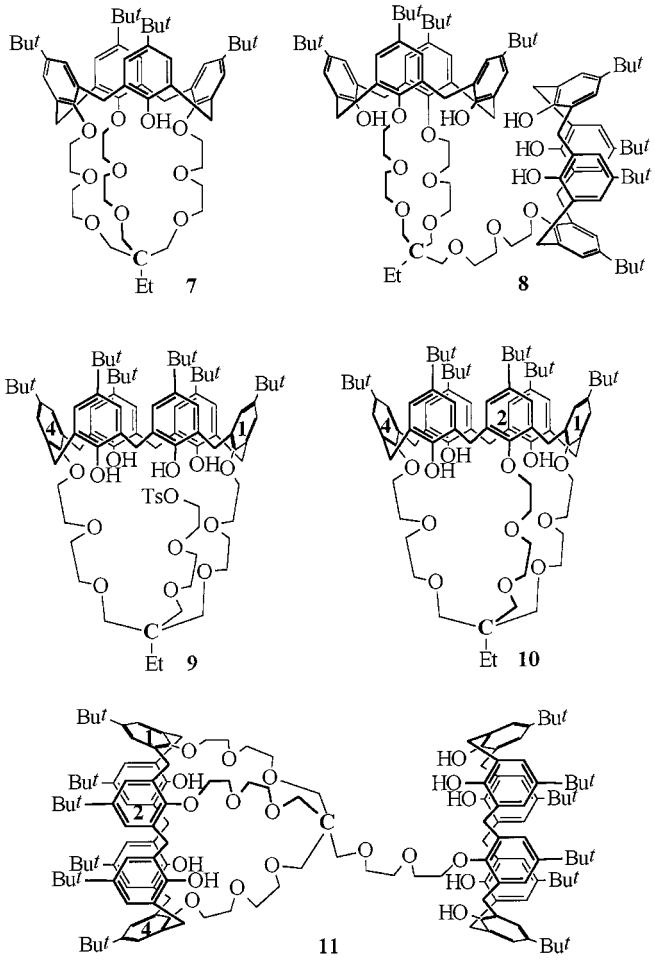


Figure 3. Novel tripodal calixcryptands **7**, **10**, and **11**, as well as the co-prepared novel doublecalix[4]arene **8** and calix[6]crown **9**

The elemental analysis data of **11** is in accordance with its molecular composition $C_{153}H_{204}O_{20}$. The FAB mass spectrum shows the expected molecular ion peak at *m*/*z* = 2360 as a base peak. The ^{1}H-NMR spectrum of **11** shows seven singlets (ratio 1:2:3 and 2:1:2:1) for the *tert*-butyl groups and the aromatic protons, which were assigned to the two *p*-*tert*-butylcalix[6]arene subunits, respectively. Such an integral ratio may indicate that one *p*-*tert*-butylcalix[6]-arene subunit is triply substituted while the other is singly substituted. In the region of δ = 3.40−4.73, three pairs of doublets (half of each was overlapped by superposition with OCH_2CH_2 and $ArCH_2Ar$) for $ArCH_2Ar$ can be clearly observed, which may indicate that one of the *p*-*tert*-butylcalix-[6]arene subunit adopts a cone conformation. In fact, compound **10** can be considered as an analogue of **11**. A comprehensive survey of the ^{1}H-NMR spectra of **10** and **11** reveals that **11** possesses most of the above mentioned spectral features of **10**, i.e. three singlets (ratio 1:2:3) for the *tert*-butyl groups as well as for the aromatic protons, and three doublets for the methylene protons. Thus, we can reasonably deduce that in compound **11**, the triply substituted *p*-*tert*-butylcalix[6]arene subunit is 1,2,4-intrabridged, and adopts a cone conformation.

Extraction Abilities

Examination of the CPK molecular models reveals that compounds **1a**, **1b**, **7**, and **8** are well pre-organized to extract cations. The percentage extraction by these five hosts of seven picrate salts from water into $CHCl_3$ at 25°C are summarized in Table 1. The *p*-*tert*-butylcalix[4]crown-5 (**13**)[15] (Figure 4) is used as a reference compound for extraction experiments.

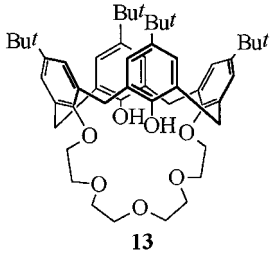


Figure 4. *p*-*tert*-Butylcalix[4]crown-5 (**13**) is used as a reference compound for extraction experiments

Table 1. Percentage extraction (% E) of picrate salts from water into $CHCl_3$ at 25 ± 1°C; arithmetic mean of several experiments, standard deviation on the mean: $\sigma_{N-1} \leq 1$

	% E						
Host	Li^+	Na^+	K^+	NH_4^+	$nPrNH_3^+$	$Me_2NH_2^+$	$Et_2NH_2^+$
1a	5.9	8.9	7.7	7.3	14.0	9.3	36.1
1b	59.8	64.5	45.0	26.6	21.1	24.4	55.0
7	49.2	46.3	44.5	32.7	30.8	16.4	36.8
8	14.5	15.7	50.4	48.6	37.2	28.5	31.1
13[a]	0.08	0.3	11.8	1.5			

[a] These data are quoted from ref.[15]

It can be seen from Table 1 that the average extraction abilities of the out-isomeric 1,3,5-tripodal calix[6]cryptand **1b**, tripodal calix[4]cryptand **7**, and the double calix[4]arene **8** are very high. The in-isomeric 1,3,5-tripodal calix[6]cryptand **1a** shows low extraction abilities.

In comparison with *p*-*tert*-butylcalix[4]crown-5 (**13**), the extraction level of calix[4] cryptand **7** is dramatically high, which reveals that, as expected, the contribution of the cryptand subunit in **7** to cation extraction is much more than that of the crown subunit in **13**.

Between **1a** and **1b**, the out isomer **1b** shows a much higher average extraction ability toward cations than the in isomer **1a**. This can be explained by considering that the spacer oxygen atoms near the ethyl group contribute with difficulty to the cation extraction in **1a** due to steric hindrance, while there is no such steric hindrance in **1b**.

For the seven cations listed in Table 1, it is interesting to note that the in-isomeric calix[6]cryptand **1a** shows greater extraction abilities toward the large alkylammonium cations, especially toward nPrNH$_3^+$ and Et$_2$NH$_2^+$, rather than the small Li$^+$, Na$^+$, K$^+$, and NH$_4^+$, which is difficult to explain.

Conclusions

In this paper, we have described the synthesis and extraction abilities of several novel tripodal calixcryptands, which is an almost unexplored field at present. We think our strategy for the molecular design of calixcryptands is potentially useful for the development of novel types of calixcryptands with special ion and molecular recognition abilities. Further modification of the structure of the above calixcryptands, for example, varying the length of the spacers and/or introduction of functional groups such as esters and amides, may produce new ligands showing high extraction abilities as well as extraction selectivities toward cations.

Experimental Section

General: Melting points were recorded with a Gallenkamp melting point apparatus in open capillaries and are uncorrected. − ^{1}H-NMR spectra were recorded with Varian EM-360 L, Bruker-ARX200, Bruker-ARX300, or Bruker-ARX500 instruments. − ^{13}C-NMR spectra were recorded with Bruker-ARX200 or Bruker-ARX300 instruments. TMS was used as an internal standard. − EI and FAB mass spectra were obtained from a ZAB-HF-3F mass spectrometry instrument, with *m*-nitrobenzyl alcohol as a matrix. − Elemental analyses were performed with a Carlo−Erba 1106 Elemental Analyzer. − All solvents were purified by standard procedures before use. All other chemicals, if not stated otherwise, were analytically pure and used without further purification. All reactions were carried out under dry argon or nitrogen. K_2CO_3 was chemically pure and heated for 8 h at 600°C before use. 1,1,1-Tris-(hydroxymethyl)propane and pentaerythritol were chemically pure and used without purification. The synthesis of 1,1,1-tris(tosyloxyethoxyethoxymethyl)propane (**3**) has previously been reported.[9] Tetrakis(bromomethyl)methane was prepared according to literature procedures.[11]

Tetrakis(hydroxyethoxyethoxymethyl)methane (12): Sodium (13.0 g, 0.57 mol) was added in portions under nitrogen to diethylene glycol (190 mL, 2.00 mol) (***CAUTION!***). After stirring for 0.5 h, 11.0 g (0.03 mol) of tetrakis(bromomethyl)methane was added to the solution. The mixture was stirred at 160°C for 20 h, allowed to cool, and then quenched with acetic acid (33 mL, 0.58 mol). Most of the excess diethylene glycol was removed under reduced pressure, the residue was extracted with 30 mL of acetone, filtered, and purified by column chromatography (silica gel, diethyl ether/acetone 50:50−0:100, v/v) to give 8.7 g of **12** as a viscous liquid in 63% yield. − ^{1}H NMR ($CDCl_3$, 60 MHz): δ = 3.21 (br. s, 12 H, $-CH_2O-$ and OH), 3.60 (br. s, 32 H, $-CH_2CH_2O-$). − MS (EI, 70eV): *m*/*z* (%) = 488 (20) [M$^+$]. − $C_{21}H_{44}O_{12}$ (488.6): calcd. C 51.63, H 9.08; found C 51.57, H 9.11.

Tetrakis(tosyloxyethoxyethoxymethyl)methane (4): A solution of tosyl chloride (14.1 g, 0.073 mol) in 60 mL of pyridine was added slowly to a solution of **12** (8.2 g, 0.017 mol) at 0°C. After stirring for 24 h at 5°C, the mixture was poured into ice/water, acidified to pH = 1 with 36% HCl, and extracted three times with 70-mL portions of chloroform. The combined organic phases were washed four times with 60-mL portions of brine and dried with magnesium sulfate. Pure compound **4** was isolated by column chromatography (silica gel, dichloromethane/diethyl ether 100:0−90:10, v/v) as a pale yellow viscous liquid (9.7 g) in 53% yield. − ^{1}H NMR (90 MHz, $CDCl_3$): δ = 2.40 (s, 12 H, $ArCH_3$), 3.23 (s, 8 H, OCH_2), 3.40−3.80 (m, 24 H, OCH_2CH_2), 4.00−4.20 (m, 8 H, OCH_2CH_2), 7.32 (d, J = 7.7 Hz, 8 H, ArH), 7.68 (d, J = 7.7 Hz, 8 H, ArH). − MS (FAB): *m*/*z* (%) = 1104 (10) [M$^+$]. − $C_{49}H_{68}O_{20}S_4$ (1105.3): calcd. C 53.25, H 6.20, S 11.60; found C 53.30, H 6.18, S 11.76.

Calix[4]cryptand 7 and Double Calix[4]arene 8: A mixture of *p*-*tert*-butylcalix[4]arene (**5**) (3.70 g, 5.00 mmol) and 1,1,1-tris(tosyloxyethoxyethoxymethyl)propane (**3**) (2.15 g, 2.50 mmol) in 350 mL of dry benzene was heated under reflux in the presence of K_2CO_3 (1.73 g, 12.50 mmol) for 3 d. The reaction mixture was allowed to cool and washed with brine. The organic layer was separated and dried with $MgSO_4$. The solvent was evaporated and the residue subjected to column chromatography (silica gel, chloroform/diethyl ether 10:1, v/v) to give two crude products, **7** and **8**. Recrystallization of crude **7** from MeCN gave pure **7** (0.18 g, 7% yield) as a white powder, m.p. 224−226°C. An analytical sample of **7** was further recrystallized from chloroform/methanol to give colorless crystal, m.p. 230−231°C. Pure **8** was obtained by repeated column chromatography (silica gel, dichloromethane/diethyl ether 9:1−7:3, v/v) as a colorless, amorphous solid (1.43 g, 35% yield).

Compound 7: ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.81 (t, J = 7.2 Hz, 3 H, CH_3, disturbed by superposition with *tert*-butyl), 0.83 [s, 18 H, $C(CH_3)_3$], 1.26 (q, J = 7.2 Hz, 2 H, $-CH_2-$, disturbed by superpositon with *tert*-butyl), 1.315 [s, 9 H, $C(CH_3)_3$], 1.321 [s, 9 H, $C(CH_3)_3$], 3.21 (d, J = 13.3 Hz, 2 H, $ArCH_2Ar$), 3.22 (d, J = 12.6 Hz, 2 H, $ArCH_2Ar$), 3.31 (s, 2 H, Et−C−CH_2-), 3.45 [s, 4 H, Et−C$(CH_2)_2$], 3.60−3.66 (m, 6 H, OCH_2CH_2), 3.76−3.84 (m, 12 H, OCH_2CH_2), 3.99−4.19 (m, 4 H, OCH_2CH_2), 4.27 (d, J = 12.6 Hz, 2 H, $ArCH_2Ar$), 4.38−4.43 (m, 2 H, OCH_2), 4.54 (d, J = 13.3 Hz, 2 H, $ArCH_2Ar$), 6.11 (s, 1 H, OH), 6.53 (s, 4 H, ArH), 7.02 (s, 2 H, ArH), 7.11 (s, 2 H, ArH). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 7.4, 22.4, 30.8, 30.9, 36.1 (2 × C), 31.5, 31.7, 33.6 (2 × C), 34.0, 43.2, 70.1, 70.4, 70.6, 71.0, 71.5, 71.6, 72.4, 72.6, 75.2, 124.7, 124.9, 125.0, 125.6, 125.7, 131.9, 132.5, 135.5, 140.6, 145.3, 145.7, 151.2 (2 × C), 153.4. − MS (FAB): *m*/*z* (%) = 992 (30) [M$^+$], 1015 (100) [M$^+$ + Na]. − $C_{62}H_{88}O_{10}$ (993.4): calcd. C 74.97, H 8.93; found C 74.81, H 8.97.

Compound 8: ^{1}H NMR (500 Hz, $CDCl_3$): δ = 0.81 (t, J = 7.1 Hz, 3 H, CH_3), 0.97 [s, 9 H, $(CH_3)_3$], 1.17 (q, J = 7.1 Hz, 2 H, $-CH_2-$, disturbed by superposition with *tert*-butyl), 1.19 [s, 18 H, $C(CH_3)_3$], 1.22 [s, 18 H, $C(CH_3)_3$], 1.26 [s, 9 H, $C(CH_3)_3$], 1.28 [s, 18 H, $C(CH_3)_3$], 3.28 (d, J = 12.7 Hz, 4 H, $ArCH_2Ar$), 3.31 (s, 2 H, Et−C−CH_2), 3.40 [s, 4 H, Et−C$(CH_2)_2$], 3.46 (br. s, 2 H, OCH_2CH_2), 3.61 (br. s, 4 H, OCH_2CH_2), 3.70 (s, 4 H, $ArCH_2Ar$), 3.79 (br. s, 2 H, OCH_2CH_2), 3.88 (br. s, 4 H, OCH_2CH_2), 4.05 (br. s, 2 H, OCH_2CH_2), 4.12 (br. s, 4 H, OCH_2CH_2), 4.26 (br. s, 2 H, OCH_2CH_2), 4.28 (s, 4 H, $ArCH_2Ar$), 4.35 (br. s, 4 H, OCH_2CH_2),

4.51 (d, *J* = 12.7 Hz, 4 H, $ArCH_2Ar$), 6.82 (s, 4 H, ArH), 6.97 (s, 2 H, ArH), 7.03 (s, 2 H, ArH), 7.04 (s, 4 H, ArH), 7.08 (s, 4 H, ArH), 7.41 (s, 2 H, OH), 9.40 (s, 2 H, OH), 10.30 (s, 1 H, OH). − ^{13}C NMR (125 MHz, $CDCl_3$): δ = 7.5, 22.7, 31.0, 31.3, 31.5 (2 × C), 31.7 (2 × C), 32.0, 33.8, 33.9 (2 × C), 34.0, 34.2, 43.4, 70.0 (2 × C), 70.7, 71.0, 71.1, 71.4, 125.0, 125.5, 125.6 (2 × C), 125.7, 126.3, 127.7, 127.8, 128.2, 128.3, 132.7, 133.8, 143.0, 143.5, 146.9, 148.0, 148.3, 149.4, 149.8, 150.7. − MS (FAB): *m*/*z* (%) = 1641 (70) [MH^+]. − $C_{106}H_{144}O_{14}$ (1642.3): calcd. C 77.52, H 8.84; found C 77.60, H 8.73.

Calix[6]crown 9 and 1,2,4-Tripodal Calix[6]cryptand 10: A mixture of *p*-*tert*-butylcalix[6]arene (**6**) (3 g, 3.09 mmol) and 1,1,1-tris(tosyloxyethoxyethoxymethyl)propane (**3**) (2.66 g, 3.09 mmol) in dry THF (450 mL) was heated under reflux in the presence of K_2CO_3 (4.27 g, 30.94 mmol) under nitrogen for 2 d. The solvent was evaporated. 200 mL of chloroform was added and the solution was washed with brine, and dried with Mg_2SO_4. The solvent was again evaporated. The residue was separated by column chromatography (silica gel, chloroform/diethyl ether 7:1, v/v) into two crude products, **9** and **10**. Pure **9** was obtained by repeated column chromatography, as a pale yellow, amorphous solid (1.97 g, 43%). Recrystallization of crude **10** from acetonitrile gave pure **10** (0.20 g, 5%) as a white powder, m.p.199−200°C. An analytical sample of **10** was further recrystallized from $CHCl_3$/MeOH to give colorless crystals, m.p. 204−205°C.

Compound 9: ^1H NMR (300 Hz, $CDCl_3$): δ = 0.85 (t, *J* = 7.5 Hz, 3 H, CH_3), 1.15 [s, 18 H, $C(CH_3)_3$], 1.30 [s, 36 H, $C(CH_3)_3$], 1.41 (q, *J* = 7.5 Hz, 2 H, $-CH_2-$), 2.45 (s, 3 H, $ArCH_3$), 3.33−4.15 (m, 40 H, OCH_2CH_2 and $ArCH_2Ar$), 4.52 (d, *J* = 14.7 Hz, 2 H, $ArCH_2Ar$), 6.90−7.17 (m, 12 H, ArH), 7.37 (d, *J* = 8.3 Hz, 2 H, ArH), 7.80 (d, *J* = 8.3 Hz, 2 H, ArH), 8.13 (br. s, 4 H, OH). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 7.5, 21.5, 30.5, 31.3, 31.4, 32.3, 33.7, 34.1, 43.0, 68.5, 68.6, 69.2, 70.3, 70.4, 70.8, 70.9, 71.3, 71.4, 73.4, 124.8, 125.5, 126.1, 126.5, 126.6, 127.1, 127.2, 127.8, 129.6, 132.8, 133.4, 142.4, 143.5, 143.5, 146.8, 148.1, 151.0. − MS (FAB): *m*/*z* (%) = 1488 (40) [M^+], 1511 (25) [M^+ + Na]. − $C_{91}H_{124}SO_{15}$ (1490.0): calcd. C 73.35, H 8.39, S 2.15; found C 73.40, H 8.31, S 2.20.

Compound 10: ^1H NMR (500 Hz, $CDCl_3$): δ = 0.77 (t, *J* = 7.3 Hz, 3 H, CH_3), 0.87 [s, 9 H, $C(CH_3)_3$], 1.21 [s, 18 H, $C(CH_3)_3$], 1.26 [s, 27 H, $C(CH_3)_3$], 1.29 (q, *J* = 7.3 Hz, 2 H, $-CH_2$, disturbed by superposition with *tert*-butyl), 3.36 (d, *J* = 13.5 Hz, 2 H, $ArCH_2Ar$), 3.54 (d, *J* = 14.0 Hz, 3 H, $ArCH_2Ar$), 3.64 (d, *J* = 16.3 Hz, 1 H, $ArCH_2Ar$), 3.71−4.28 (m, 32 H, OCH_2CH_2 and $ArCH_2Ar$), 4.32 (d, *J* = 16.3 Hz, 1 H, $ArCH_2Ar$), 4.64 (d, *J* = 14.0 Hz, 3 H, $ArCH_2Ar$), 6.53 (s, 2 H, ArH), 6.94 (s, 4 H, ArH), 7.12 (s, 6 H, ArH), 7.91 (br. s, 2 H, OH), 8.27 (s, 1 H, OH). − ^{13}C NMR (50 MHz, $CDCl_3$): 7.6, 29.5, 31.0, 31.1, 31.3, 31.4, 32.2, 33.7, 33.8, 34.0, 43.2, 70.5, 71.1, 71.2, 71.6, 72.3, 125.2, 125.4, 125.6, 125.9, 126.2, 126.5, 127.2, 132.3, 133.5, 133.8, 142.7, 145.9, 147.9, 149.0, 152.1, 169.7. − MS (FAB): *m*/*z* (%) = 1316 (10) [M^+], 1340 (100) [MH^+ + Na]. − $C_{84}H_{116}O_{12}$ (1317.8): calcd. C 76.56, H 8.87; found C 76.80, H 9.01.

1,2,4-Tripodal Calix[6]cryptand (11): A mixture of *p*-*tert*-butylcalix[6]arene (**6**) (1.94 g, 2.0 mmol) and *t*BuOK (0.45 g, 4.0 mmol) in dry benzene (350 mL) was heated under reflux under nitrogen for 2 h. Tetrakis(tosyloxyethoxyethoxymethyl)methane (**4**) (1.11 g, 1 mmol) in 100 mL of benzene was then added dropwise over 24 h. The mixture was heated under reflux for another 24 h. The solvent was evaporated, 50 mL of chloroform was added, and the solution was washed with brine, and dried with Mg_2SO_4. The solvent was again evaporated and the residue subjected to column chromatography (silica gel, chloroform/diethyl ether 90:10−50:50, v/v) to give a crude product. Further purification of the crude product by preparative thin layer chromatography (silica gel, dichloromethane/diethyl ether 12:1, v/v) and subsequent recrystallization from CH_2Cl_2/MeOH gave **11** (0.38 g) as a white solid in a yield of 16%, m.p.148−149°C. − ^1H NMR (200 Hz, $CDCl_3$): δ = 0.95 [s, 9 H, $C(CH_3)_3$], 1.11 [s, 18 H, $C(CH_3)_3$], 1.12 [s, 27 H, $C(CH_3)_3$], 1.15 [s, 9 H, $C(CH_3)_3$], 1.17 [s, 18 H, $C(CH_3)_3$], 1.21 [s, 9 H, $C(CH_3)_3$], 1.26 [s, 18 H, $C(CH_3)_3$], 3.40 (d, *J* = 13.0 Hz, 2 H, $ArCH_2Ar$), 3.54−4.00 (m, 58 H, OCH_2CH_2 and $ArCH_2Ar$), 4.51 (d, *J* = 16.5 Hz, 2 H, $ArCH_2Ar$), 4.73 (d, *J* = 13.8 Hz, 2 H, $ArCH_2Ar$), 6.86 (s, 2 H, ArH), 6.96 (s, 4 H, ArH), 6.99 (s, 6 H, ArH), 7.05 (s, 2 H, ArH), 7.11 (s, 4 H, ArH), 7.12 (s, 4 H, ArH), 7.23 (s, 2 H, ArH), 8.25 (br. s, 2 H, OH), 8.79 (br. s, 6 H, OH). − MS (FAB): *m*/*z* (%) = 2360 (100) [M^+], 2383 (80) [M^+ + Na], 2399 (50) [M^+ + K]. − $C_{153}H_{204}O_{20}$ (2363.3): calcd. C 77.76, H 8.70; found C 77.50, H 8.73.

Percentage Extraction (% E) Measurements:[16] The UV/Vis measurements were recorded with a Shimadzu-240 UV/Vis spectrophotometer, equipped with two thermostatically controlled cell compartments. The picrate extraction experiment was carried out at 25 ± 1°C. Doubly distilled water was used for all aqueous solutions. Solutions (5 × 10^{-3} M) of the host calixarenes were prepared in $CHCl_3$. Solutions (5 × 10^{-3} M) of the picrate salts were prepared in doubly distilled water. Equal volumes (1.00 mL) of the two solutions were shaken vigorously for 5 min in a 5-mL tube. This was repeated 3 times, and the solutions were left standing until phase separation was complete. A sample (0.10 mL) of the organic phase was removed using a 250-μL syringe, and diluted to 5.00 mL with MeCN. The absorbance (A) of the dilute solution was then recorded at 380 nm. The concentration (*c*) of picrate ion in the dilute solution was determined according to the Lambert−Beer Law, and the percentage extraction (% E) was then calculated. Control experiments showed that no picrate extraction occurred in the absence of a calixarene host.

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