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A series of 1,3-dialkoxycalix[4]arene dibenzocrown ethers were synthesized in the fixed 1,3-alternate conformation with good yields by the reaction of 1,3-dialkoxycalix[4]arenes with dibenzodimesylate in the presence of caesium carbonate. The three dimensional 1,3-alternate conformation was confirmed by X-ray crystal structure. Upon two phase extraction, NMR studies on the ligand–metal complex, single ion and competitive ion transport experiments through a bulk liquid membrane, 1,3-dipropylcalix[4]arene dibenzocrown-6, in which two benzo groups are symmetrically attached to the crown-6 linkage, gave one of the most efficient and selective extractabilities for caesium ion over other alkali metal ions. From supported liquid membrane experiments using **1** and **3** as organic carriers, permeation coefficients of the caesium ion were estimated to be 0.42 and 0.27 cm h⁻¹, respectively. The selectivity of caesium over sodium ion was observed to increase with permeation time.

Introduction

Since nuclear power is now extensively used as an important energy source, more radioactive waste is now generated, mostly from atomic power plants.¹ Therefore, techniques for disposing of radioactive waste safely and in as little space as possible must be found without delay. In the disposal of such waste, of particular interest have been extractants which are capable of selectively separating heat-generating nuclides and long half-life nuclides such as caesium or strontium ions.² Thus, if the caesium ions contained in radioactive waste are selectively separated, this could have a large effect on the disposal of radioactive waste in terms of stability and energy efficiency. Active and extensive research has been and continues to be directed towards the development of these extractants.

In this regard, calixcrown ethers have attracted intense interest as caesium selective extractants.^{3,4} It was reported that 1,3-distal capping of calix[4]arene at the lower rim has been achieved with polyether linkages such as a calixcrown ether,⁴ calix-doubly-crowned⁵ or double-calixcrown.⁶ Reinhoudt and co-workers reported that 1,3-dialkoxycalix[4]arene crown-6 derivatives were prepared and were found to be exceptionally selective ionophores for caesium ion due to a complexation of the caesium ion not only with the crown ether moiety but also with the two rotated aromatic nuclei (cation– π -interaction) when they are fixed in the 1,3-alternate conformation.⁴ The thorough and intensive research on the development of a calixcrown ether ligand as a caesium ion extractant, repeated by us, resulted in the finding that the introduction of benzene rings into the crown ether ring of calix[4]arene crown-6 ether can improve the selectivity for caesium ions due to the ‘flattening effect’.⁷ For instance, 1,3-alternate calix[4]arene bis(dibenzocrown) ethers in which two benzo groups are attached on both the upper and lower ether rings revealed more selective complexation with caesium ion over other alkali metal ions than those without benzo groups.

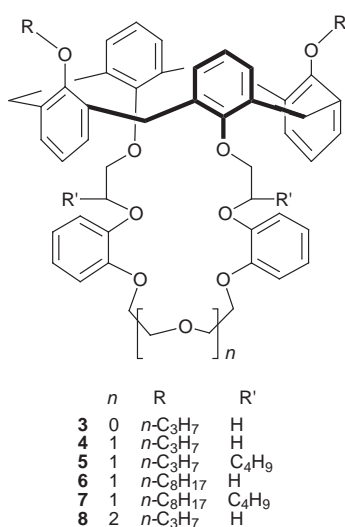
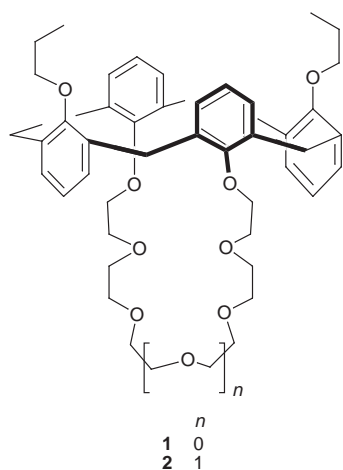
From this point of view, it is an object of the present study to improve caesium selectivity using calix[4]arene dibenzocrown ether, which functions as an organic ligand to separate caesium ions. It is another object of this study to probe the ‘flattening

effect’ on metal ion complexation in more detail. Therefore, we now report syntheses of a series of 1,3-alternate 1,3-dialkoxycalix[4]arene dibenzocrown ethers, NMR studies of the complexes, membrane transport experiments, two phase extractions, and solid state structures of the corresponding compounds. These results will enable their utilization in selective removal of caesium ion from aqueous radioactive nuclear waste which is important given current environmental concerns.

Results and discussion

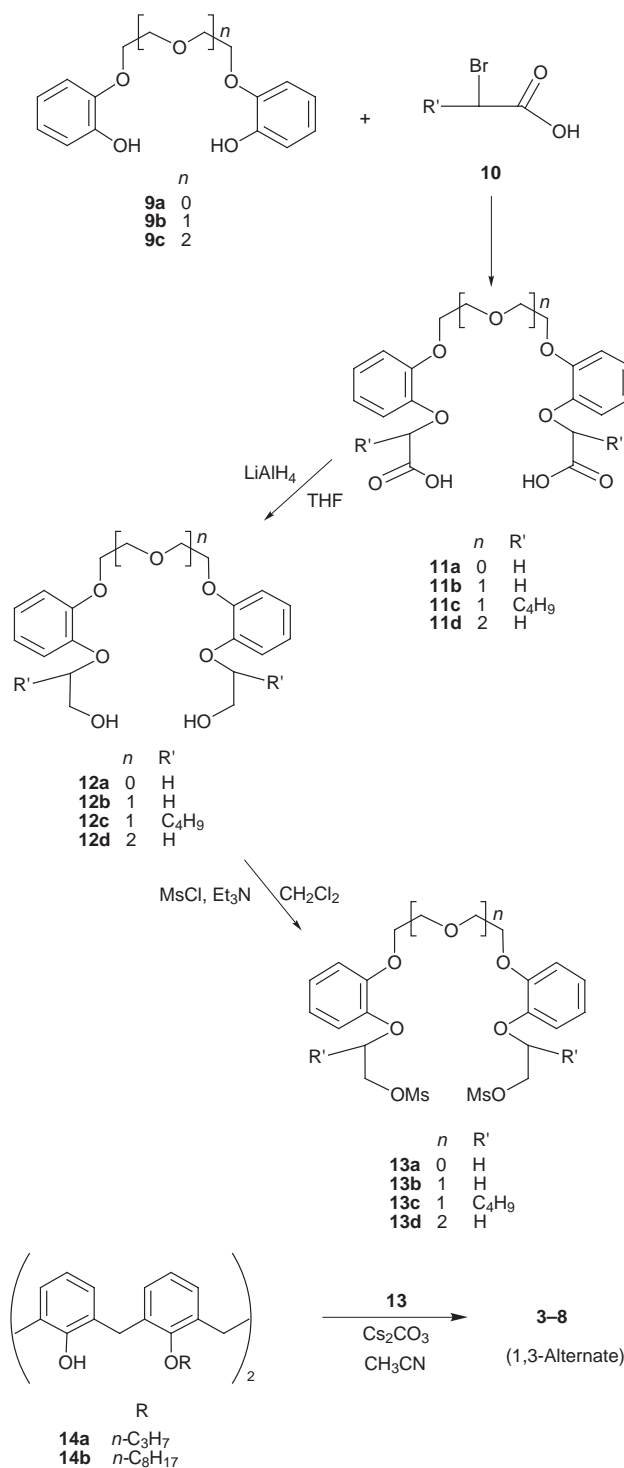
The reaction of calix[4]arene with alkylating agents in acetonitrile in the presence of K₂CO₃ is a well established synthetic method to obtain 1,3-dialkoxycalix[4]arene in the cone form.^{4,8,9} The synthetic route for the preparation of corresponding dibenzodimesylates as precursors is described in Scheme 1. For **14a** and **14b**, AB quartet splitting patterns ($J = 13$ Hz, $\Delta\nu = 378$ Hz, chemical shift difference value) in ¹H NMR spectra were observed, indicating a characteristic cone conformation.^{10,11} Also, the present study pertains to a series of dibenzodimesylate compounds, represented by the structural formulae **13a–13d** which are used as precursors for the calix[4]arene dibenzocrown ether. As seen, preparation of the precursors is accomplished in three steps: acyclic polyether dicarboxylic acids were prepared by reaction of the bisphenols and 2-bromoalkanoic acids with good yields; they were reduced to a dibenzo polyether alcohol (**12a–12d**) in the presence of LiAlH₄ in THF; and the dibenzo polyether alcohols thus obtained are reacted with methanesulfonyl chloride in the presence of triethylamine to afford the dibenzodimesylates.⁷ As a key reaction, cyclization of 1,3-dialkoxy calix[4]arene with the appropriate polyethylene glycol ditosylates in the presence of Cs₂CO₃ has been also reported in the literature.^{2,4} This cyclization reaction to give the 1,3-alternate conformers is favored by the caesium template ion.⁴ In the present study, the cyclization reaction of 1,3-dialkoxy calix[4]arene with dibenzodimesylate in the presence of Cs₂CO₃ provided the desired products with good yields.

Referring to the nuclear magnetic resonance spectra (Fig. 1a),



using tetramethylsilane (TMS) as a standard, the singlet peak with an intensity of 8 hydrogens ($\text{Ar-CH}_2\text{-Ar}$) at 3.80 ppm represented eight hydrogens of methylene connected to benzene rings and one signal at 38 ppm for bridging four methylene carbons ($\text{Ar-CH}_2\text{-Ar}$) in the ^{13}C NMR spectrum indicates a characteristic 1,3-alternate conformation.^{2,4} No other isomers were indicated by this NMR measurement. This 1,3-alternate conformation was also clearly proved by the X-ray crystal structures as shown in Figs. 2 and 3 for **4** and **5**, respectively. Enhancement of the ligand-metal ion complexation ability by introduction of the dibenzo groups into the crown ether ring are fully explained by these ORTEP structures (*vide infra*). Interestingly, for **5**, the two butyl groups attached to the crown ether linkage are slightly tilted towards the inside of the crown ether cavity and therefore steric factors seem to make it more difficult for **5** to complex a specific metal ion.

Measurement of the complexation selectivity was initially conducted by the use of ^1H NMR spectroscopy as shown in Fig. 1. Ligand **3** was chosen to investigate NMR behavior because **3** showed the highest transport flux as well as the best selectivity for caesium ion among ligands **1-8**. Compound **3** is locked in the 1,3-alternate conformation as inferred from the NMR spectrum in Fig. 1a. A singlet peak at δ 3.75 in ^1H NMR for bridging four methylene hydrogens ($\text{Ar-CH}_2\text{-Ar}$) and one signal at 38 ppm for bridging four methylene carbons ($\text{Ar-CH}_2\text{-Ar}$) in the ^{13}C NMR spectrum indicates a characteristic 1,3-alternate conformation as mentioned earlier. A singlet peak at 4.44 ppm corresponds to four hydrogens of the symmetrical $-\text{OCH}_2\text{CH}_2\text{O}-$ group (H_d) of **3**. Two triplets at 3.50 (H_b) and 3.63 ppm (H_c) indicate two $-\text{OCH}_2\text{CH}_2\text{O}-$ groups connecting



Scheme 1 Synthetic route for calix[4]arene dibenzocrown ethers.

the calix[4]arene to two benzo groups. One triplet at 3.34 ppm corresponds to the dipropoxy ($-\text{OCH}_2\text{CH}_2\text{CH}_3$) group attached to the calixarene. ^1H NMR spectra of free ligand **3**, $3\cdot\text{Na}^+$, and $3\cdot\text{Cs}^+$ which are assumed to have 1:1 complexation were taken in deuterated CDCl_3 , and are given in Fig. 1 (a), (b), and (c), respectively. In spectrum (b) for $3\cdot\text{Na}^+$, no significant changes of chemical shift except peak broadening of H_b and H_c compared with spectrum (a) for free ligand **3** were observed. This is probably due to the less effective complexation with sodium ion. Interestingly, however, the $3\cdot\text{Cs}^+$ complex gave rise to remarkable changes both in chemical shift values and in splitting patterns. Two sets of triplet peaks appeared at 3.50 (H_b) and 3.63 ppm (H_c) which correspond to the peak for the crown ethereal linkage of calix[4]arene (free ligand) moved to 4.25 ppm (H_b and H_c) and appearing as a broad doublet. This

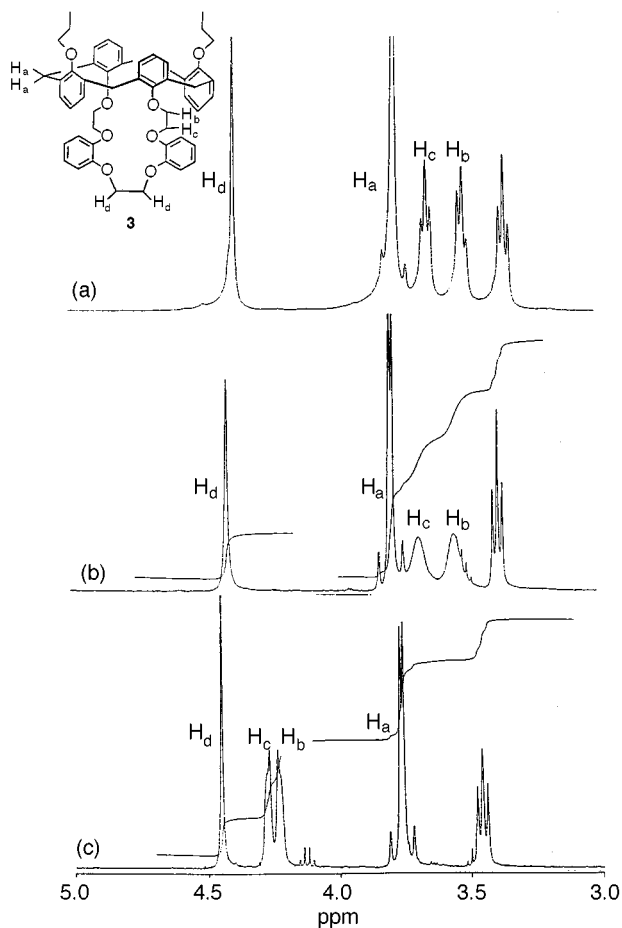


Fig. 1 Partial ^1H NMR spectra (CDCl_3) at 25 $^\circ\text{C}$, 400 MHz: (a) free ligand **3**, (b) complex of $3\cdot\text{Na}^+\text{Pic}^-$, and (c) complex of $3\cdot\text{Cs}^+\text{Pic}^-$.

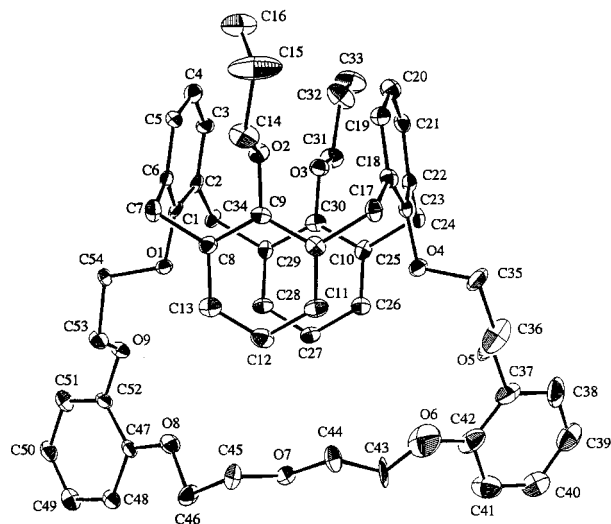


Fig. 2 Minimum overlap view of **4** showing the atom labeling scheme. The displacement ellipsoids are drawn at the 40% probability level.

is ascribed to the fact that the electron density of the crown ether linkage markedly decreases with strong ethereal oxygen–caesium complexation to give a downfield shifted peak. This caesium ion selective response over sodium ion with respect to the chemical shift changes is in excellent agreement with the results of the selective caesium ion transport and extraction experiment. Another interesting aspect found in this NMR study is that the chemical shift of $-\text{OCH}_2\text{CH}_2\text{O}-$ (H_d of **3**) changed very little, e.g., from 4.37 to 4.40 to 4.48 ppm for free ligand **3**, $3\cdot\text{Na}^+$, and $3\cdot\text{Cs}^+$, respectively. No change of the chemical shift for H_a but significant changes for H_b and H_c lead

Table 1 Single ion transport values of alkali metal ions through a bulk liquid membrane using calix[4]arene crown ethers (**1–8**)^a

Compound	Flux/ 10^{-8} mol s^{-1} m^{-2} ^b				
	Li^+	Na^+	K^+	Rb^+	Cs^+
1	0.00	1.42	1.90	20.75	78.23
2	0.00	1.22	1.45	4.55	8.35
3	0.00	0.00	2.84	44.95	130.59
4	0.00	1.92	1.28	4.35	11.87
5	0.00	1.07	2.12	2.21	5.42
6	0.00	1.51	0.77	1.03	2.90
7	0.00	0.87	0.64	1.00	1.90
8	0.00	0.87	2.17	1.69	1.03

^a Transport conditions: source phase (aqueous solution of nitrate, 0.8 mL), $\text{MNO}_3 = 0.1$ M; membrane phase (CH_2Cl_2 , 3.0 mL), (carrier) = 1.0 mM; id of glass vial = 18 mm, stirred by 13 mm Teflon-coated magnetic stirring bar driven by a Hurst Synchronous motor; receiving phase (deionized water, 5.0 mL). ^b The average value of three independent determinations. The experimental values deviate from the reported values by an average of 10%.

us to conclude that the upper four oxygens in the crown ether linkage (two $-\text{OCH}_2\text{CH}_2\text{O}-$ groups connecting calix[4]arene to two benzo groups) play a very important role in metal ion complexation, but the lower two oxygens ($-\text{OCH}_2\text{CH}_2\text{O}-$) in the ether ring provide only a small contribution to the complexation.

The bulk liquid membrane system^{4,12} was preferentially adopted in this study to determine the transport rate of metal ions and measure the caesium ion selectivity over other alkali metal ions. The source and the receiving phase are made up of 0.8 mL of 0.1 M alkali metal nitrate and 5.0 mL of deionized water, respectively. The organic medium is composed of a solution of 3.0 mL of 1.0 mM calix[4]arene dibenzocrown ether in dichloromethane. The measured flux values from the single transport experiment are given in Table 1. In control experiments it was confirmed that no metal ion transport was observed in the absence of the carrier. For lithium ion no transport was observed in all cases due to it being the wrong size for complexation. For most of the calixarenes, stirring for 24 h at room temperature gave high transport rate values for caesium ion over other alkali metal ions. For instance, for **1** (calixcrown-6) and **2** (calixcrown-7), which are known,^{2,4} the transport rates were observed to be 78.23 and 8.35, respectively. In addition, for **3**, **4**, and **8** where the number of oxygens comprising the crown ether linkage increases from 6, to 7, and to 8, the caesium fluxes are markedly decreased by about ten-fold each from 130.59, to 11.87, and to 1.03. Those observations, originally made by Reinhoudt, show that when the calixcrown-6 ether exists in the fixed 1,3-alternate conformation, it show a selective caesium complexation due not only to an agreement in size between the crown ether cavity and caesium ion but also to the cation– π -interaction by the two rotated aromatic nuclei. Calix[4]arene crown-5 composed of five oxygens in the linkage was reported to give a potassium selectivity.^{4,13} So, we ruled out the complexation study using calix[4]arene dibenzocrown-5.

The pre-organization of binding sites prior to complexation was well known to play an important role in determining the complexation ability of the ligand.¹⁴ With this in mind, calix[4]arene dibenzocrown ether (**4**) was synthesized and was probed by X-ray crystallography, giving the structure shown in Fig. 2. Dihedral angles for $\text{O5}-\text{C7}-\text{C42}-\text{O6}$ and $\text{O8}-\text{C47}-\text{C52}-\text{O9}$ were observed to be almost 0° , which implies that crown ether cavities are well organized, able to easily incorporate the caesium ion by flattening the ethereal linkage. This flattening effect from the introduction of dibenzo groups into the calixcrown ether ring on metal ion complexation was previously reported by us. It was shown that calix[4]arene bis(dibenzocrown-6) where two dibenzo groups are attached to the upper

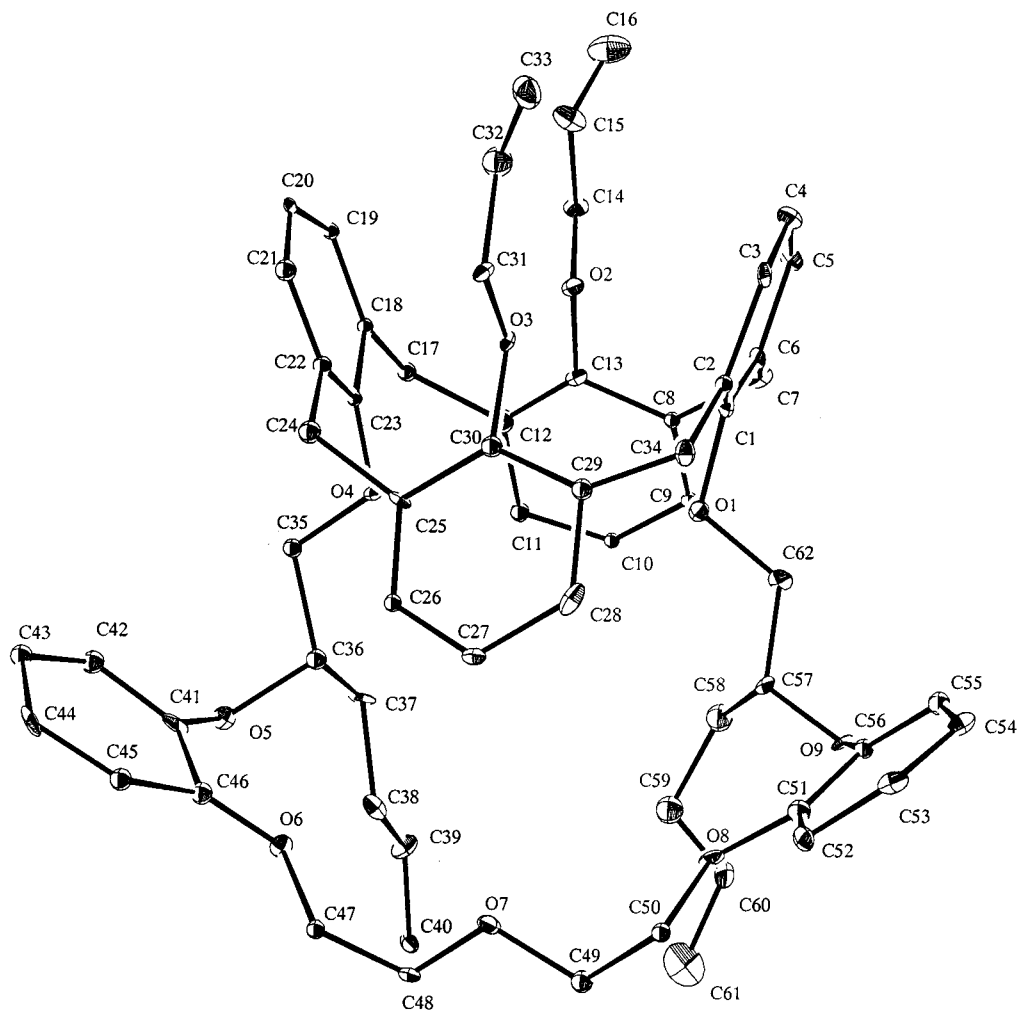


Fig. 3 Minimum overlap view of **5** showing the atom labeling scheme. The displacement ellipsoids are drawn at the 40% probability level.

and lower part of the calixarene biscrown ether ring frame provides superior selectivity and efficiency for caesium ion than does the conventional calixbiscrown ether.⁷ In accordance with the above report, attachment of two benzo groups onto the crown ether linkage in this study gives rise to an interesting result for the transport rate of a caesium ion. For example, from a set of **1** and **3** and another set of **2** and **4**, we observed flux values increasing from 78.23 to 130.59 and from 8.35 to 11.87, respectively in both cases. This observation is attributable not only to the lipophilicity of the dibenzo groups which are capable of enhancing the solubility of the complex in an organic medium but also to the rigidity and flatness of the crown ether framework enabling it to easily encapsulate the metal ion. It should be noted that replacement of sp^3 oxygens by sp^2 oxygens in the ethereal linkage provides a flattening of the glycolic chain to allow the complexation capability of the ligand to be more efficient, the so-called 'flattening effect'.^{7,15}

Of particular interest is an investigation of the influence of the alkyl side chain attached to the crown ether linkage on metal ion complexation. It was initially envisioned that the calix[4]arene dibenzo (dialkyl) crown (**5**) which has two lipophilic alkyl tails could show an enhanced capability in metal ion complexation by increased solubility of the ligand-metal ion complexes in organic media. However, we found exactly the opposite. Comparing **4** with **5** as well as **6** with **7**, respectively, the transport rates were observed to decrease in the cases of most metal ions. Considering the solid state structure of **5** depicted in Fig. 3, the two lipophilic *n*-butyl chains attached to the crown ether ring seem to be slightly tilted towards the inside of the ring cavity, sterically disfavoring encapsulation of metal ions in the crown cavity. In good agreement with this, examin-

Table 2 Competitive transport of Cs^+ and M^+ by a bulk liquid membrane^a using calix[4]arene crown ethers (**1–8**)

Carrier	Flux values/ $10^{-8} \text{ mol s}^{-1} \text{ m}^{-2}$					
	Li^+	Na^+	Cs^+	K^+	Rb^+	Cs^+
1	0.00	0.55	180.50	0.64	8.85	110.50
2	0.00	0.63	11.29	0.75	1.94	6.17
3	0.00	1.03	242.03	0.26	13.2	149.29
4	0.00	2.69	17.45	1.89	0.75	15.47
5	0.00	2.21	9.96	0.00	2.45	11.45
6	0.00	0.35	10.12	0.44	2.21	13.55
7	0.00	0.61	10.41	0.90	1.90	10.37
8	0.00	0.00	1.88	1.47	1.76	0.95

^a Transport conditions: source phase (aqueous solution of metal nitrate, 0.8 mL) ($CsNO_3$, 0.1 M + M^+NO_3 , 0.1 M + M^+NO_3 , 0.1 M); membrane phase (CH_2Cl_2 saturated with water, 3 mL), [carrier] = 1.0 mM; receiving phase (deionized water, 5 mL).

ations of Corey–Pauling–Koltun (CPK) space-filling models of **5** and **7** were attempted and we found that there are considerable steric hindrances to the ligands accepting the metal ions.

A competitive ion transport experiment exhibits more interesting results, as shown in Table 2. In most cases (ligands and metals), it was observed that the selectivity for competitive transport of alkali metal ions is much higher than that for single ion transport. Taking one example, in single ion experiments, the transport rate for Li^+ , Na^+ , K^+ , Rb^+ , and Cs^+ using **3** were recorded to be 0.00, 0.00, 2.84, 44.95, and 130.59 (see Table 1), respectively, thus the selectivities of Cs^+/K^+ and Cs^+/Rb^+ are about 46 and 3, respectively. However, when K^+ , Rb^+ ,

Table 3 Association constant and free energy on complexation of ligands (1–4) with alkali metal picrates at 25 °C^a

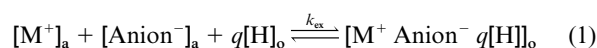
Compound	Metal ion	Log K_a/M^{-1}	$-\Delta G^\circ/kcal\ mol^{-1}$
1	Na ⁺	0.939	1.28
	K ⁺	1.222	1.53
	Rb ⁺	1.585	2.16
	Cs ⁺	3.184	4.34
2	Na ⁺	0.811	1.11
	K ⁺	0.946	1.29
	Rb ⁺	1.327	1.81
	Cs ⁺	1.687	2.31
3	Na ⁺	0.740	1.01
	K ⁺	1.085	1.48
	Rb ⁺	1.621	2.21
	Cs ⁺	3.991	5.29
4	Na ⁺	0.836	1.14
	K ⁺	0.813	1.11
	Rb ⁺	1.386	1.89
	Cs ⁺	1.702	2.32

^a The average value of three independent determinations. The experimental values deviate from the reported values by an average of 10%.

and Cs⁺ are present together in the aqueous phase (competitive ion experiment), both K⁺ and Rb⁺ were observed to show very low transport rates, resulting in high selectivities of Cs⁺/K⁺ and Cs⁺/Rb⁺, of about 574 and 11, respectively. From these results, it is noteworthy that these calix[4]arene dibenzocrown ethers can be potentially useful as selective ligating agents for radioactive caesium ions in radioactive waste, for which the competitive ion transport experiment should be applied.

To further study the selectivity and efficiency of calixarene crown ethers for caesium ion over other alkali metal ions, association constant (log K_a^M) and free energy changes (ΔG) were measured from a two phase extraction carried out by a reported method.¹³ Concentrations of picrate anion extracted from the aqueous phase into the organic phase were measured at equilibrium. For alkali metal ions compound **3** shows high caesium selectivity as shown in Table 3, which is in good agreement with the results of the NMR study along with the bulk liquid membrane experiment.

To investigate the complexation ratio between ligand and metal ion and to study the counter anion effect on extraction, solvent extraction of caesium picrate and nitrate using **3** was carried out. The extraction equilibrium and extraction constant K_{ex} are expressed in eqns. (1) and (2), where the subscripts a and



$$K_{ex} = \frac{[M^+ Anion^- q[H]]_o}{[M^+]_a [Anion^-]_a [H]_o^q} \quad (2)$$

o denote the aqueous and organic phases, respectively. Also [H] and [Anion⁻] denote the host molecule **3** and picrate or nitrate anion, respectively. The calix[4]arene and the complex [M⁺ Anion⁻ q[H]]_o are highly lipophilic and should not dissolve appreciably in the aqueous phase. Therefore, the concentration of the complex in organic phase is equal to the anion concentration extracted from the aqueous phase into the organic phase.

The distribution ratio (D_M) is expressed by eqn. (3). Expressed in logarithmic form, eqns. (2) and (3) give eqn. (4).

$$D_M = \frac{[M^+ Anion^- q[H]]_o}{[M^+]_a} \quad (3)$$

$$\log D_M/[Anion^-]_a = \log K_{ex} + q \log [H]_o \quad (4)$$

The stoichiometric coefficient (q) and extraction constant (K_{ex}) could be found from a plot of $\log D_M/[Anion^-]_a$ against

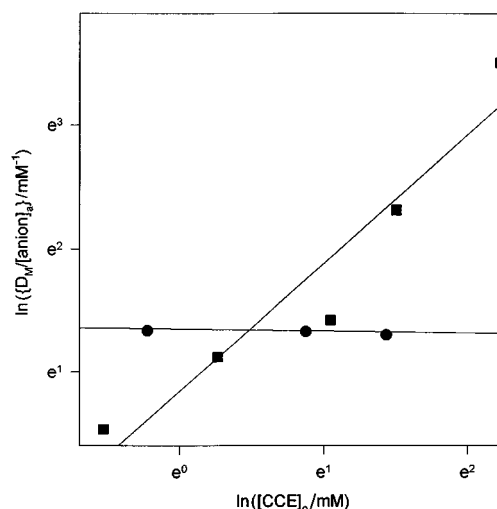


Fig. 4 Plot of $\ln \{D_M/[anion]_a\}$ vs. $\ln [CCE]_0$ for extraction of caesium picrate (■) and caesium nitrate (●) using compound **3**. Organic diluent: chloroform. CCE = calixarene crown ether.

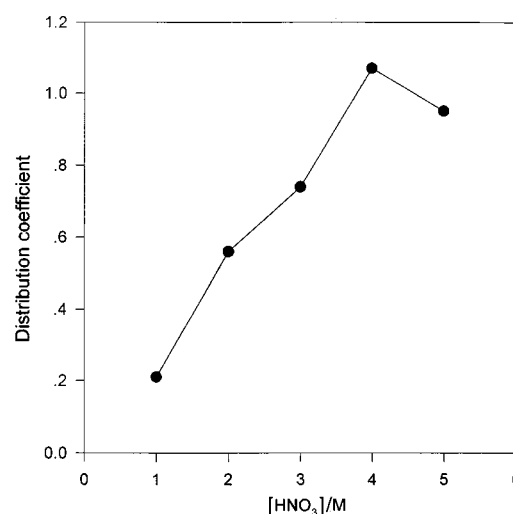


Fig. 5 Effect of nitric acid concentration on distribution coefficient of Cs⁺ using 9 mM of compound **3**. Diluent: chloroform.

log [H]_o. For calix[4]arene crown ether **3**, the plot of $\log \{D_M/[Anion^-]\}$ against $\log [H]_o$ is presented in Fig. 4. In the case of caesium picrate, the plot gives a straight line with a slope of unity. This verifies that the stoichiometric constant (q) depicted in eqn. (4) is unity, indicating that the calix[4]arene dibenzocrown ether (**3**) complexes with the metal ion in a 1:1 ratio of ligand–metal complex. The calculated extraction constant ($\ln K_{ex}^{Cs}$) was estimated similarly to be 0.845.

On the other hand, in the case of caesium nitrate, almost zero slope was obtained and the $\ln K_{ex}^{Cs}$ was estimated to be -1.746 , indicating no effect of extraction efficiency upon the concentration of the extractant. These results are attributable to an anion effect, where the low solubility of a hard anion such as NO₃⁻ in organic phase gives a decreased extractability of the metal ion.

Fig. 5 shows the influence of acidity (HNO₃) in an aqueous phase on the distribution ratio using 1.0 mM of aqueous CsNO₃ as the aqueous phase and chloroform as a diluent. The result reveals that maximum Cs⁺ ion extraction took place at around 4 M HNO₃, indicating that the acidity of the aqueous feed solution is one of the most important variables upon the extraction efficiency of Cs⁺. The decrease of D_M for nitric acid concentrations greater than 4 M is ascribed to both the competitive extraction of HNO₃ by the calix[4]arene dibenzocrown ether and the decrease of the mean activity coefficient of Cs⁺ in a concentrated acidic medium. This result of the nitric acid

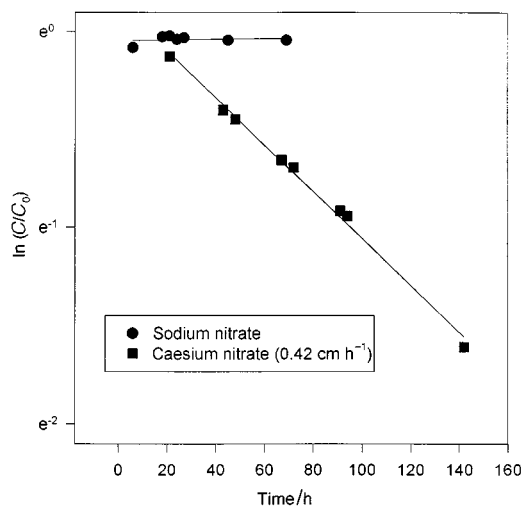


Fig. 6 Semilogarithmic plot of Cs^+ and Na^+ permeability as a function of time (h) through an SLM: $[\mathbf{1}] = 30$ mM in NPOE; feeding solution: $[\text{M}^+] = 1.0$ mM and $[\text{HNO}_3] = 4.0$ M; stripping solution: deionized water; stirring rate = 450 revolutions per minute (RPM).

based solvent extraction can be directly applied to the separation of caesium ion from radioactive waste in which 3–5 M nitric acid is usually present.

Transport of metal ions through a supported liquid membrane (SLM) occurs because a chemical gradient is established between the feed solution and the stripping solution.^{15,16} For an SLM to be industrially applicable, its stability has to be improved by the appropriate combination of a highly selective extractant, its high solubility in a hydrophobic diluent, and a high boiling point for the organic medium. For these reasons, **1** and **3** as extractants and 2-nitrophenyloctyl ether as an organic medium were selected.

The steady state permeability process of an SLM was described by eqns. (5) and (6), where J = membrane flux,

$$J = CP = - \frac{dC}{dt} \frac{V}{Q} \quad (5)$$

$$\ln(C/C_0) = -QPt/V \quad (6)$$

C = feed metal concentration at time t , C_0 = feed metal concentration at zero time, V = volume of feed concentration, Q = membrane area, P = permeability coefficient, and t = time (h). The experimental data of $\ln(C/C_0)$ vs. time are given in Fig. 6 for two different metal ions (1.0 mM of initial metal concentration for Na and Cs ions, respectively). The data points fall on a straight line of slope $-(Q/V)P$ which allows one to calculate the permeability coefficient of the SLM. This result confirms the validity of eqn. (6) to describe the concentration vs. time data. In the case of **1** and **3** as extractants, the permeation coefficient for the caesium ion was estimated to 0.42 and 0.27 cm h^{-1} , respectively. The permeation constant of sodium nitrate in the case of both **1** and **3** is too low to be calculated. Though the distribution coefficient of **3** is higher than that of **1**, the permeation coefficient of **1** was observed to be greater than that of **3** probably because of the low diffusion rate of the **3**· Cs^+ complex and the low stripping reaction rate by the stable complex formed between **3** and caesium ion. The selectivity of caesium over sodium ion increased with permeation time.

Conclusions

A series of 1,3-dialkyloxycalix[4]arene dibenzocrown ethers were synthesized in the fixed 1,3-alternate conformation with good yields. Upon bulk liquid membrane with single and competitive ion transport experiments along with two phase extrac-

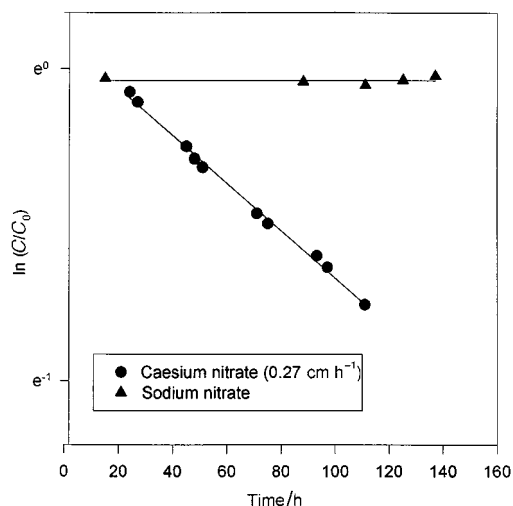


Fig. 7 Semilogarithmic plot of Cs^+ and Na^+ permeability as a function of time (h) through an SLM: $[\mathbf{3}] = 30$ mM in NPOE; feeding solution: $[\text{M}^+] = 1.0$ mM and $[\text{HNO}_3] = 4.0$ M; stripping solution: deionized water; stirring rate = 450 revolutions per minute (RPM).

tion, a calix[4]arene dibenzocrown ether in which two benzo groups were symmetrically attached to the crown-6 linkage gave one of the most efficient and selective extractabilities for caesium ion over other alkali metal ions. Significant changes of chemical shifts and splitting patterns in ^1H NMR spectra using ligand–metal ion complexes showed the caesium superiority to sodium ion. From the NMR study of the ligand–caesium ion complex, it is also proved that among the six oxygens participating in the metal ion complexation, the upper four oxygens in the crown ether linkage (two $-\text{OCH}_2\text{CH}_2\text{O}-$ groups connecting the calix[4]arene to the two benzo groups) play a very important role but the lower two oxygens ($-\text{OCH}_2\text{CH}_2\text{O}-$) provide a small contribution to the ligand–metal complexation. In SLM experiments using **1** and **3** as extractants, permeation coefficients of the caesium ion were estimated to be 0.42 and 0.27 cm h^{-1} , respectively. These synthetic developments for calixarene crown ethers could be used to selectively separate the caesium ion from the radioactive waste that causes one of our biggest environmental problems.

Experimental

Melting points were taken using a Mel-Temp of Fisher-Johns melting point apparatus without any correction. IR spectra were obtained with a Perkin-Elmer 1600 Series FT-IR with potassium bromide pellets and with deposited KBr windows for solid product and oil, respectively, and are recorded in reciprocal centimeters. ^1H and ^{13}C NMR spectra were recorded with a 400 MHz (Bruker ARX-400) and a 100 MHz spectrometer, respectively, the chemical shifts (δ) reported downfield from the internal standard, tetramethylsilane. Elemental analysis was performed by Vario EL of Elemental Analyzer in Korea Basic Science Institute in Seoul, Korea. FAB⁺ mass spectra were obtained using JEOL-JMS-HX 110A/110A High Resolution Tandem Mass Spectrometry in the Korea Basic Science Institute in Taejeon, Korea.

Unless specified otherwise, reagent grade reactants and solvents were obtained from chemical suppliers and used as received. Dry solvents were prepared as follows: tetrahydrofuran was freshly distilled from sodium metal ribbon or chunks; dichloromethane was freshly distilled from lithium aluminum hydride. Acetonitrile was pre-dried from molecular sieves (3 Å) and distilled over diphosphorous pentoxide. Compounds **9**,¹⁷ **11**,¹⁸ **12**¹⁸ and **14**⁴ were prepared as described in the literature.

Transport of alkali metal ions in a bulk liquid membrane system

Liquid membrane transport experiments were carried out as

reported earlier using a bulk liquid membrane apparatus.^{4,12} Two water phases (one containing the salt to be transported) were separated by a dichloromethane phase which constituted the membrane. The interior of the tube above the organic medium was filled with the source phase which was 0.8 mL of a solution of 0.1 M lithium, sodium, potassium, rubidium, and caesium nitrate, respectively, using a single flux method. The outer cylinder was filled with 5.0 mL of deionized water as the receiving phase. The details of the transport conditions are summarized in the footnotes of Table 1. Each experiment was repeated three times in a room thermostated to 25 ± 1 °C then 3 mL of the receiving phase was taken. The flux values (moles transported $s^{-1} m^2$) for the corresponding metal ion concentration were determined by the use of a Perkin-Elmer 2380 atomic absorption spectrophotometer. Blank experiments for which no calix[4]arene dibenzocrown ether was present were performed to determine the membrane leakage.

General procedures of dibenzodimesylate 13a–13d

Under nitrogen, to a solution of 13.2 mmol of **12** and 4.08 mL (2.94 g, 29.0 mmol) of triethylamine in 100 mL of dry CH_2Cl_2 was added dropwise 2.14 mL (3.33 g, 29.0 mmol) of methanesulfonyl chloride during a period of 30 min at 0 °C. Upon complete addition, the reaction mixture was stirred for 5 h at 0 °C. Reaction temperature was slowly raised up to room temperature and stirred for an additional 10 h. 50 mL of 10% aqueous sodium bicarbonate solution was added and the CH_2Cl_2 layer was separated. The organic layer was washed with water (2×20 mL) and brine (2×20 mL) followed by drying over anhydrous magnesium sulfate. Removal of CH_2Cl_2 *in vacuo* provided a colorless oil which was recrystallized from 100 mL of diethyl ether to give the desired product.

1,2-Bis[2-(2-methylsulfonyloxyethyl)phenoxy]ethane (13a). Removal of CH_2Cl_2 *in vacuo* provided a colorless oil which was recrystallized from 100 mL of diethyl ether to give 5.82 g (90%) of the desired product. Mp 158–160 °C. IR (KBr pellet, cm^{-1}) 1597, 1516, 1350 (SO_2), 1181 (SO_2). ¹H NMR ($CDCl_3$) δ 7.14–6.90 (m, 8 H, Ar-H), 4.50 (s, 4 H, $-CH_2CH_2O-$), 4.32 (s, 4 H, $-CH_2CH_2O-$), 4.25 (t, 4 H), 3.09 (s, 6 H, CH_3SO_2O-); FAB MS m/z (M^+) calcd 490.55, found 490.23. Anal. calcd for $C_{22}H_{26}O_{10}S_2$: C, 48.97; H, 5.34. Found: C, 48.90; H, 5.21%.

1,5-Bis[2-(2-methylsulfonyloxyethyl)phenoxy]-3-oxapentane (13b). 6.20 g (92%) of the desired product, a white solid, was obtained. Mp 98–99 °C: IR (KBr pellet, cm^{-1}) 1597, 1516, 1350 (SO_2), 1181 (SO_2); ¹H NMR ($DMSO-d_6$) δ 7.00–6.88 (m, 8 H, Ar-H), 4.57–4.45 (m, 4 H, $-CH_2CH_2O-$), 4.26–4.05 (m, 8 H, $-CH_2CH_2O-$), 3.85–3.75 (m, 4 H), 3.23 (s, 6 H, $CH_3SO_2OCH_2CH_2-$); FAB MS m/z (M^+) calcd 534.12, found 534.20. Anal. calcd for $C_{22}H_{30}O_{11}S_2$: C, 49.43; H, 5.61. Found: C, 49.21; H, 5.78%.

1,5-Bis[2-(1-butyl-2-methylsulfonyloxyethyl)phenoxy]-3-oxapentane (13c). 95% of the desired product as a colorless oil was obtained. IR (KBr pellet, cm^{-1}) 1597, 1516, 1350 (SO_2), 1180 (SO_2); ¹H NMR ($CDCl_3$) δ 6.99–6.88 (m, 8 H, Ar-H), 4.43–4.35 (m, 6 H), 4.16 (t, 4 H), 3.92 (t, 4 H), 3.03 (s, 6 H, CH_3SO_2O), 1.64–1.85 (m, 4 H), 1.31–1.42 (m, 8H), 0.89 (s, 6 H). Anal. calcd for $C_{30}H_{46}O_{11}S_2$: C, 55.60; H, 7.11. Found: C, 55.62; H, 7.13%.

1,8-Bis[2-(2-methylsulfonyloxyethyl)phenoxy]-3,6-dioxaoctane (13d). 88% of the desired product was obtained as a white solid. Mp 103–105 °C: IR (KBr pellet, cm^{-1}) 1597, 1516, 1348 (SO_2), 1180 (SO_2); ¹H NMR ($CDCl_3$) δ 6.92–6.90 (m, 8 H, Ar-H), 4.55–4.50 (m, 4 H, $-CH_2CH_2O-$), 4.54–4.12 (m, 8 H, $-CH_2CH_2O-$), 3.85–3.82 (m, 4 H), 3.72 (s, 4H, $-CH_2CH_2O-$),

3.17 (s, 6 H, $CH_3SO_2OCH_2CH_2-$). Anal. calcd for $C_{24}H_{34}O_{12}S_2$: C, 49.82; H, 5.92. Found: C, 49.86; H, 5.81%.

General procedures for the synthesis of calix[4]arene dibenzocrown ethers (3–8)

25,27-Dialkoxycalix[4]arene **14** (2.0 mmol) was dissolved in 50 mL of acetonitrile and added to an excess of Cs_2CO_3 (1.62 g, 5.0 mmol) and dibenzodimesylate (2.1 mmol) under nitrogen. The reaction mixture was refluxed for 24 h. Then acetonitrile was removed *in vacuo* and the residue extracted with 100 mL of methylene chloride and 50 mL of 10% aqueous HCl solution. The organic layer was separated and washed twice with water. After the organic layer was separated and dried over anhydrous magnesium sulfate followed by removing the solvent *in vacuo* to give a brownish oil. Filtration column chromatography gave **3–8**.

25,27-Bis(1-propyloxy)calix[4]arene dibenzocrown-6, 1,3-alternate (3). Filtration column chromatography with ethyl acetate–hexane = 1:6 as eluent provided pure 1,3-alternate calix[4]arene dibenzocrown ethers as a white solid in over 90% yield. Mp 229–232 °C. IR (KBr pellet, cm^{-1}); 3068 (Ar-H), 1501, 1451, 1254, 1196. ¹H NMR ($CDCl_3$) δ 7.12–6.55 (m, 20 H, Ar-H), 4.37 (s, 4 H), 3.75 (s, 8 H, Ar CH_2 Ar), 3.65–3.32 (m, 12 H), 1.25–1.16 (m, $J = 7.4$ Hz, 4 H, $OCH_2CH_2CH_3$), 0.65 (t, $J = 7.4$ Hz, 6 H, $OCH_2CH_2CH_3$). ¹³C NMR ($CDCl_3$): δ 157.5, 156.7, 152.0, 149.7, 134.8, 134.7, 130.3, 129.9, 124.7, 123.3, 123.0, 122.8, 122.3, 115.9, 72.7, 71.0, 69.0, 68.0, 38.7, 23.3, 10.7. FAB MS m/z (M^+) calcd 806.21, found 806.11. Anal. Calcd for $C_{52}H_{54}O_8$: C, 77.41; H, 6.69. Found: C, 77.30; H, 6.71%.

25,27-Bis(1-propyloxy)calix[4]arene dibenzocrown-7, 1,3-alternate (4). Recrystallized from the oil residue with 5:1 diethyl ether–hexanes: 90% yield; mp 178–181 °C; IR (KBr pellet, cm^{-1}); 3068 (Ar-H), 1501, 1451, 1254, 1196; ¹H NMR ($CDCl_3$) δ 7.02–6.87 (m, 16 H), 6.78–6.70 (m, 4 H), 4.22 (t, $J = 5.1$ Hz, 4 H), 4.08 (t, $J = 5.1$ Hz, 4 H), 3.89 (t, $J = 5.1$ Hz, 4 H), 3.76 (t, $J = 5.1$ Hz, 4 H), 3.70 (s, 8 H, Ar CH_2 Ar), 3.41 (t, $J = 7.4$ Hz, 4 H, $OCH_2CH_2CH_3$), 1.47–1.38 (m, $J = 7.4$ Hz, 4 H, $OCH_2CH_2CH_3$), 0.77 (t, $J = 7.4$ Hz, 6 H, $OCH_2CH_2CH_3$); ¹³C NMR ($CDCl_3$) δ 157.4, 156.8, 150.7, 149.8, 134.4, 134.3, 130.6, 130.5, 123.1, 122.8, 122.6, 122.3, 118.3, 116.1, 73.4, 71.1, 70.6, 69.8, 38.1, 23.7, 10.8; FAB MS m/z (M^+) calcd 850.31, found 850.30. Anal. calcd for $C_{54}H_{58}O_9$: C, 76.20; H, 6.82. Found: C, 76.18; H, 6.87%.

25,27-Bis(1-propyloxy)calix[4]arene dibenzo(dibutyl)crown-7, 1,3-alternate (5). Recrystallization from the oil residue with 5:1 diethyl ether–hexanes gave a white solid with 64% yield. Mp 179–181 °C; IR (KBr pellet, cm^{-1}); 3068 (Ar-H), 1501, 1451, 1254, 1196; ¹H NMR ($CDCl_3$) δ 7.04–6.83 (m, 16 H), 6.78–6.70 (m, 4 H), 4.29 (t, $J = 5.1$ Hz, 2 H, $-OCH(C_4H_9)CH_2O-$), 4.33–4.19 (m, $J = 5.1$ Hz, 4 H), 4.07–4.00 (m, 4 H), 3.86–3.82 (m, 2 H), 3.64–3.40 (m, 6 H), 3.56 (s, 8 H, Ar CH_2 Ar), 1.66–1.27 (m, 16 H), 0.92–0.85 (m, 12 H). FAB MS m/z (M^+) calcd 962.52, found 962.50. Anal. calcd for $C_{62}H_{74}O_9$: C, 77.29; H, 7.68. Found: C, 77.30; H, 7.60%.

25,27-Bis(1-octyloxy)calix[4]arene dibenzocrown-8, 1,3-alternate (6). Recrystallization from the oil residue with hexanes gave the white solid with 92% yield. Mp 124–127 °C; IR (KBr pellet, cm^{-1}) 1593, 1501, 1455, 1254, 1208; ¹H NMR ($CDCl_3$) δ 7.08–6.91 (m, 16 H), 6.78–6.70 (m, 4 H), 4.23 (t, $J = 5.1$ Hz, 4 H, $-OCH_2CH_2O-$), 4.08 (t, $J = 5.0$ Hz, 4 H, $-OCH_2CH_2O-$), 3.88 (t, $J = 5.1$ Hz, 4 H, $-OCH_2CH_2O-$), 3.73 (t, $J = 5.1$ Hz, 4 H, $-OCH_2CH_2O-$), 3.71 (s, 8 H, Ar CH_2 Ar), 3.44 (t, $J = 7.4$ Hz, 4 H, $OCH_2(CH_2)_6CH_3$), 1.80–1.40 (m, $J = 7.4$ Hz, 4 H, $OCH_2(CH_2)_6CH_3$), 0.91 (t, $J = 7.4$ Hz, 6 H, $OCH_2(CH_2)_6CH_3$); ¹³C NMR ($CDCl_3$) δ 157.5, 156.8, 150.7, 149.8, 134.5, 134.0, 130.6,

130.5, 123.1, 122.9, 122.7, 122.3, 118.3, 116.1, 71.9, 71.1, 70.6, 69.97, 69.90, 38.2 (ArCH₂Ar), 32.6, 30.43, 30.41, 30.13, 26.6, 23.4 (OCH₂(CH₂)₆CH₃), 14.8 (OCH₂(CH₂)₆CH₃); FAB MS *m/z* (M⁺) calcd 990.20, found 990.10. Anal. calcd for C₆₄H₇₈O₉: C, 77.57; H, 7.87. Found: C, 77.60; H, 7.77%.

25,27-Bis(1-octyloxy)calix[4]arene dibenzo(dibutyl) crown-7, 1,3-alternate (7). Obtained as an oil: 58% yield; IR (KBr window, cm⁻¹); 3068 (Ar-H), 1504, 1455, 1258, 1208; ¹H NMR (CDCl₃) δ 7.04 (m, 20 H), 4.20 (t, *J* = 5.1 Hz, 4 H), 4.38 (t, *J* = 5.1 Hz, 2 H, -OCH(C₄H₉)CH₂O-), 4.37–4.18 (m, *J* = 5.1 Hz, 4 H), 4.07–4.01 (m, 4 H), 3.86–3.82 (m, 2 H), 3.63–3.49 (m, 6 H), 3.55 (s, 8 H, ArCH₂Ar), 1.60–1.47 (m, 8 H), 1.31 (br s, 28 H), 0.73–0.91 (m, 12 H). FAB MS *m/z* (M⁺) calcd 1102.51, found 1102.43. Anal. calcd for C₇₂H₉₄O₉: C, 78.40; H, 8.53. Found: C, 78.29; H, 8.58%.

25,27-Bis(1-propyloxy)calix[4]arene dibenzocrown-8, 1,3-alternate (8). Obtained as a white solid: 58% yield; mp 184–188 °C; IR (KBr window, cm⁻¹); 3065 (Ar-H), 2933, 2885, 1590, 1505, 1451, 1251, 1197, 1127, 1042, 926, 756; ¹H NMR (CDCl₃) δ 7.35–6.63 (m, 20 H), 4.15 (s, 8 H, ArCH₂Ar), 4.01 (s, 4 H), 3.81 (t, 3 H, -OCH₂CH₂CH₃), 3.64–3.50 (m, 160 H), 1.60–1.47 (m, 4 H, -OCH₂CH₂CH₃), 0.91 (t, 6 H, -OCH₂CH₂CH₃). FAB MS *m/z* (M⁺) calcd 1102.51, found 1102.43. Anal. calcd for C₅₆H₆₂O₁₀: C, 75.15; H, 6.98. Found: C, 75.21; H, 6.99%.

NMR of complex

¹H and ¹³C NMR spectra were recorded with a 400 MHz (Bruker ARX-400) and a 100 MHz spectrometer, respectively, the chemical shifts (δ) reported downfield from the internal standard, tetramethylsilane. NMR samples for metal picrate complexes were prepared as follows. A mixture of organic ligand **3** (30 mg) dissolved in CDCl₃ (10 mL) and excess metal picrate complexes were prepared as follows. A mixture of organic ligand **3** (30 mg) dissolved in CDCl₃ (10 mL) and excess metal picrate (over 5 equivalents) was stirred for 1 h. After filtration of precipitated excess metal picrate, the filtrate was dried *in vacuo* to give a yellow solid complex 3·M⁺Pic⁻.

3·Na⁺Pic⁻. (400 MHz; CDCl₃) δ 8.84 (s, 2 H, Ar-H of picrate), 7.12–6.57 (m, 20 H, Ar-H), 4.40 (s, 4 H, Ar-OCH₂-CH₂O-Ar, lower part of ether ring), 3.78 (AB q, 8 H, ArCH₂-Ar), 3.67–3.49 (br d, 8 H, Ar-OCH₂CH₂O-, upper part of ether ring), 3.37 (t, 4 H, -OCH₂CH₂CH₃), 1.22–1.40 (m, *J* = 7.4 Hz, 4 H, -OCH₂CH₂CH₃), 0.82 (t, *J* = 7.4 Hz, 6 H, -OCH₂CH₂CH₃). ¹³C NMR (100 MHz; CDCl₃) δ 157.4, 156.6, 149.5, 134.7, 134.6, 130.4, 130.0, 124.7, 123.2, 123.1, 122.3, 115.8, 72.7, 70.9, 69.0, 68.0, 38.8, 23.2, 10.7.

3·Cs⁺Pic⁻. (400 MHz; CDCl₃) δ 8.68 (s, 2 H, Ar-H of picrate), 7.27–6.52 (m, 20 H, Ar-H), 4.44 (s, 4 H, Ar-OCH₂-CH₂O-Ar, lower part of ether ring), 4.25 (d, 8 H, Ar-OCH₂-CH₂O-, upper part of ether ring), 3.75 (AB q, 8 H, ArCH₂Ar), 3.45 (t, 4 H, -OCH₂CH₂CH₃), 1.25–1.40 (m, *J* = 7.4 Hz, 4 H, -OCH₂CH₂CH₃), 0.80 (t, *J* = 7.4 Hz, 6 H, -OCH₂CH₂CH₃). ¹³C NMR (100 MHz; CDCl₃) δ 158.4, 157.0, 147.8, 147.5, 142.0, 136.6, 133.4, 131.8, 131.0, 127.1, 123.9, 122.6, 112.8, 112.1, 72.4, 67.8, 38.7, 22.8, 10.4.

Extraction equilibrium

To obtain various properties of the extraction equilibrium such as the distribution ratio of the caesium ion (*D_M*), the extraction equilibrium constant (*K_{ex}*) and the stoichiometric coefficient between extractant and caesium, an aqueous solution (20 mL) containing 1.0 mM caesium nitrate, 0.2 mM caesium picrate, respectively and an organic solution of the same volume according to extraction concentration (0.8–10.0 mM) were mixed and equilibrated by shaking at 32 °C. Caesium concentration of nitrate and picrate type in the aqueous solution was analyzed with AA (Varian Co.) and UV (Shimadzu Co.) respect-

Table 4 Experimental data for the X-ray diffraction studies on compound **4**

Formula	C ₅₄ H ₅₈ O ₉
FW	851.04
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> /Å	20.979(5)
<i>b</i> /Å	12.7224(11)
<i>c</i> /Å	17.618(6)
<i>α</i> /°	90.0
<i>β</i> /°	98.88(3)
<i>γ</i> /°	90.0
<i>V</i> /Å ³	4645.9(18)
<i>Z</i>	4
<i>F</i> (000)	1816
Calculated density/g cm ⁻³	1.217
Radiation/Å (Mo-Kα)	0.71069
No. of reflns for measd	25
2θ range/°	22.58–28.42
<i>μ</i> /mm ⁻¹	0.08
Temperature/K	283
Crystal size/mm	0.4 × 0.36 × 0.46
Color	colorless
Diffractometer	Enraf-Nonius CAD-4
Data collection method	<i>ω</i> /2θ
Scan width	0.8 + 0.34 tan θ
Absorption correction	none
No. of unique reflns	8140
No. of observed reflns (<i>I</i> _o ≥ 2σ <i>I</i> _o)	3599
θ _{max}	25.0°
<i>hkl</i> range	0 24; 0 15; -20 20
Interval/min	240
Standard reflns	7 1 -9, 10 0 -8, 11 0 -6
Orientation check reflcn	7 1 -9
Intensity variation (%)	less than 1.312
<i>R</i> _{int}	0.0590
No. of parameters	568
<i>R</i> , <i>R</i> _w	0.0893, 0.1397
GOF	1.320
(Δσ) _{max}	0.000
(Δρ) _{max} (e Å ⁻³)	0.750
(Δρ) _{min} (e Å ⁻³)	-0.775
Extinction correction	none

ively. The amount of caesium complex in the organic solution was calculated from the mass balance of caesium and stoichiometric coefficient between extractant and the caesium ion. Co-transport ion concentration in the aqueous solution was varied between 1–5 M with HNO₃ to determine the distribution coefficient. To determine the association constants and free energy changes for ligand–metal complexation, metal picrates were prepared by the reaction of picric acid and the corresponding metal carbonate. The concentration of the picrate stock solution was made to 1.0 mM in deionized water and diluted to 0.2 mM for the complexation experiment. The host was prepared as 1.0 mM solution in chloroform. From each solution, 1.0 mL was taken and mixed in a centrifuge tube with a Teflon-coated magnetic stirring bar and vigorously shaken for at least 1 h with a Vortex shaker. The mixture was centrifuged for 1 h to completely separate the two layers. Chloroform solution (1.0 mL) was taken and diluted with 1 mL of acetonitrile. Concentrations of picrate anion extracted from the aqueous phase into the organic layer were determined by a UV spectrophotometer (λ_{max} = 368 nm).

Measurements of selectivity and permeation using SLM

Organic diluents such as chloroform, toluene, dodecane as well as 2-nitrophenyloctyl ether (NPOE) were used. Caesium and sodium of picrate and nitrate types, respectively were used as the solute for permeating ions for a supported liquid membrane. The support was a porous polymer membrane of polypropylene, Celgard 2400 (Hoechst Celanese Co.). According to the manufacturer's specification, the average pore size was 0.04 μm–0.12 μm. Porosity was 41%. The average thickness of the

Table 5 Experimental data for the X-ray diffraction studies on compound **5**

Formula	C ₆₂ H ₇₄ O ₉
FW	963.21
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁
<i>a</i> /Å	13.110(4)
<i>b</i> /Å	18.355(3)
<i>c</i> /Å	11.861(10)
<i>a</i> °	90.0
<i>β</i> °	97.92(4)
<i>γ</i> °	90.0
<i>V</i> /Å ³	2827(3)
<i>Z</i>	2
<i>F</i> (000)	1036
Calculated density/g cm ⁻³	1.132
Radiation/Å (Mo-Kα)	0.71069
No. of reflns for measd	22
<i>θ</i> range/°	8.32–12.72
<i>μ</i> /mm ⁻¹	0.074
Temperature/K	288
Crystal size/mm	0.4 × 0.187 × 0.33
Color	colorless
Diffractometer	Enraf-Nonius CAD-4
Data collection method	<i>w</i> / <i>2θ</i>
Scan width	0.8 + 0.34 tan <i>θ</i>
Absorption correction	none
No. of unique reflns	4568
No. of observed reflns (<i>I</i> _o ≥ 2σ <i>I</i> _o)	993
<i>θ</i> _{max}	24°
<i>hkl</i> range	–14 14; 0 20; 0 13
Interval/min	240
Standard reflns	4 1 4; –5 –6 –2; 3 –10 1
Orientation check refln	4 1 4
Intensity variation (%)	less than 1.032
<i>R</i> _{int}	0.000
No. of parameters	485
<i>R</i> , <i>R</i> _w	0.0619, 0.0847
GOF	0.859
(Δ/σ) _{max}	0.000
(Δ/ρ) _{max} (e Å ⁻³)	0.209
(Δ/ρ) _{min} (e Å ⁻³)	–0.174
Extinction correction	none

membrane was 25.4 μm. All other chemicals used were of AR or GR grade unless specified otherwise. The single stage SLM measurements were carried out with a simple two compartment permeation cell which consisted of a feed solution (250 mL) separated from the stripping solution (250 mL) by a liquid membrane having an effective membrane area of 7.065 cm². The pores of the porous polymer support were filled with NPOE containing extractant (**1** or **3**) under vacuum as described by Lee *et al.*¹⁹ The feed and stripping solutions were mechanically stirred at about 450 rpm at 32 °C to avoid concentration polarization conditions at the membrane interfaces and in the bulk of the solutions.

X-Ray crystal determinations

Colorless single crystals of approximate size 0.4 × 0.36 × 0.46 mm for **4** and 0.4 × 0.18 × 0.33 mm for **5**, respectively were mounted and aligned on a CAD-4 diffractometer with graphite monochromated Mo-Kα radiation, and accurate cell parameters and an orientation matrix were determined from the least-squares fit of 25 accurately centered reflections with a *θ* range of 11.29 to 14.21° for **4** and 22 reflections with a *θ* range of 8.32 to 12.72° for **5**. Intensity data were collected in the *ω*/*2θ* scan mode to a maximum *2θ* of 25° for **4** and of 24° for **5**. Three standard reflections (7, 1, –0; 10, 0, –0; 11, 0, –6) for **4** and (4, 1, 4; –5, –6, –2; 3, –10, 1) for **5** were measured every 300 min, and the intensities of the standards remained constant within 1.312% for **4** and 1.032% for **5** throughout data collection (Enraf-Nonius, 1994). Data were corrected for Lorentz and polarization effects. No absorption correction was applied.

The program used to solve the structures was SHELX86

(Sheldrick, 1990).²⁰ The program used to refine the structures and to prepare materials for publication was SHELXL97 (Sheldrick, 1997)²¹ in WinGX (Farrugia, 1998).²² For **4**, all non-H atoms were refined with anisotropic displacement parameters. But for **5**, only 27 atoms out of 71 non-H atoms were refined anisotropically because the rest gave non-positive temperature factors if refined anisotropically and additionally six bond distances were restrained to be 1.4 Å during the refinement. All hydrogen atoms were placed in calculated positions and were allowed to ride upon the appropriate carbon or nitrogen atoms.

Final reliability factors for 3599 unique observed reflections [*I*_o > 2σ(*I*_o)] for **4** were *R* = 0.0893 and *ωR* = 0.1397 with (Δ/σ)_{max} = 0.000, Δρ_{max}/Δρ_{min} = 0.750/–0.775 e Å⁻³ in Δρ map and *S* = 1.320, and those for 993 unique observed reflections [*I*_o > 2σ(*I*_o)] for **5** were *R* = 0.0619 and *ωR* = 0.0873 with (Δ/σ)_{max} = 0.000, Δρ_{max}/Δρ_{min} = 0.209/–0.174 e Å⁻³ in Δρ map and *S* = 0.874.

The rather negative results for compound **5** might be attributed to the small number of unique observed reflections. ORTEPII (Johnson, 1976)²³ was used for the molecular graphics.

Full crystallographic details, excluding structure factor tables, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 2*, available via the RSC web page (<http://www.rsc.org/authors>). Any request to the CCDC for this material should quote the full literature citation and the reference number 188/156. See <http://www.rsc.org/suppdata/p2/1999/837/> for crystallographic files in .cif format.

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