



## Calix[4]arenes Bridged with Two Different Crown Ether Loops: Influence of Crown Size on Metal Ion Recognition

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**Abstract.** A series of calix[4]arene-*bis*-crown ethers were synthesized in a fixed 1,3-alternate conformation with good yields by the reaction of a monocyclic calixcrown ether with multi-ethyleneglycol di-*p*-toluenesulfonate in the presence of cesium carbonate. In the preparation of the monocyclic calixcrown ethers (**1** and **2**), the use of potassium carbonate as a base provided the best yield regardless of the template concept. In two phase extraction and competitive transport experiments for ligand-metal complexation, calix[4]arene biscrown (**5**) provided the best selectivity for potassium ion. When a calixbiscrown ether (**4**) bearing different sized crown ether loops coordinates to K<sup>+</sup> and Cs<sup>+</sup>, respectively, the changes of peak splitting patterns and chemical shift on <sup>1</sup>H NMR spectra are dependent on the complexed metal ion species.

**Key words:** synthesis, solvent extraction, alkali cation, crown ether, calixarene, calixarene biscrown, complexation

### 1. Introduction

Much attention has been paid lately to calixarene chemistry due to its wide application in the selective separation of specific metal or molecular inclusions [1–4]. In addition, the phenolic-4-OH of the calix[4]arene lower rim can be further functionalized to feasibly give various ionic receptors [5]. In particular, calix[4]arene crown-6 in which a pentaethylene glycol unit connects with the 1,3-dialkyloxy calix[4]arene framework within the 1,3-alternate type was known to give high cesium ion selectivity over other alkali metal ions [6–12]. This cesium ion selectivity is ascribed not only to the size agreement of the crown ether moiety based on electrostatic interaction between the electron donor atom and the metal cation, but also to two rotated aromatic nuclei (cation/ $\pi$ -interaction) [6]. A series of calix-*bis*-crowns in which two crown linkages with the same polyether length were attached

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to a calixarene framework by 1,3-alternate ways were also reported to provide a highly selective metal ion carrier [13–16]. Calix-*bis*-crown-5 and calix-*bis*-crown-6 were known to be more selective towards potassium and cesium, respectively, than other alkali metal cations. Thus, 1,3-alternate calix-*bis*-crown ethers, having the same crown ring cavity size, are easily prepared in the following reaction conditions: reflux of a solution of calixarene, polyethelene glycol ditosylate, cesium carbonate as a base, and acetonitrile as a reaction solvent. However, a calix-*bis*-crown having a different sized crown ether loop on the lower rim of the calixarene molecule is not well known, probably because the preparation and purification of the monocyclic calixcrown which is a precursor of the calix-*bis*-crown compound is not that easy.

With this in mind we are reporting the synthesis of a series of 1,3-alternate calix-*bis*-crown ethers to which the different sized crown ether loops are attached. Subsequently, the results of the complexation behavior for those compounds using competitive transporting bulk liquid membranes, two phase extraction, and  $^1\text{H}$  NMR of the complex are described.

## 2. Results and Discussion

The reaction of calix[4]arene with cyclic agents in acetonitrile in the presence of  $\text{K}_2\text{CO}_3$  is described in Scheme 1. It was reported that the use of cesium carbonate as a base gave the best yield for the synthesis of calix[4]arene *bis*-crown-6 by the cesium effect [11, 14]. However, in the preparation of calix[4]arene monocrown-5 (**1**) and the corresponding monocrown-6 (**2**) having two hydroxy groups, we found that the use of  $\text{K}_2\text{CO}_3$  as a base provides the best yield regardless of the cavity size of the crown ether loop. The reaction conditions and corresponding isolated yields are listed in Table I. To prepare monocyclic calixcrown **1** the use of cesium carbonate as a base gave a poor yield. The use of even 2 equivalents of cesium carbonate still provided a poor yield. The best reaction conditions were found to be in the case of using one equivalent of  $\text{K}_2\text{CO}_3$  as a base, acetonitrile and 24 hour reflux, providing the desired product as a 70% yield. Using 2 equivalents of  $\text{K}_2\text{CO}_3$ , several complicated conformational isomers including calix-*bis*-crown ether were revealed by TLC analysis. In the next step of cyclization (calix-*bis*-crown), the use of cesium carbonate gave optimum yield as well, regardless of the crown ether cavity size.

For **1** and **2**, referring to the nuclear magnetic resonance spectrum with the use of tetramethyl silane (TMS) as a standard, AB quartet splitting patterns ( $J = 13$  Hz,  $\Delta\nu = 452$  Hz, chemical shift difference value) were observed, indicating a characteristic cone conformation. For calix[4]arene *bis*-crowns **3–7**, the singlet peak with an intensity of 8 hydrogens ( $\text{Ar}-\text{CH}_2-\text{Ar}$ ) at 3.80 ppm represented eight hydrogens of methylene connected to benzene rings and one signal at 38 ppm for bridging four methylene carbons ( $\text{Ar}-\text{CH}_2-\text{Ar}$ ) in the  $^{13}\text{C}$  NMR spectrum

Table I. Reaction conditions and yields for monocyclic calixcrown ethers **1** and **2**

| Compound | Reaction conditions                    |                    |        | Time (hr) | Yield (%)        |
|----------|--|--------------------|--------|-----------|------------------|
|          | Base & Amount                          | Solvent            | Temp.  |           |                  |
| <b>1</b> | 0.5 eq K <sub>2</sub> CO <sub>3</sub>  | CH <sub>3</sub> CN | Reflux | 24        | 52               |
|          | 1.0 eq K <sub>2</sub> CO <sub>3</sub>  | CH <sub>3</sub> CN | Reflux | 24        | 70               |
|          | 1.0 eq K <sub>2</sub> CO <sub>3</sub>  | THF                | Reflux | 24        | 10               |
|          | 2.0 eq K <sub>2</sub> CO <sub>3</sub>  | CH <sub>3</sub> CN | Reflux | 48        | 20               |
|          | 1.0 eq Cs <sub>2</sub> CO <sub>3</sub> | CH <sub>3</sub> CN | Reflux | 48        | <10 <sup>a</sup> |
|          | 2.0 eq Cs <sub>2</sub> CO <sub>3</sub> | CH <sub>3</sub> CN | Reflux | 48        | <10 <sup>a</sup> |
| <b>2</b> | 1.0 eq K <sub>2</sub> CO <sub>3</sub>  | CH <sub>3</sub> CN | Reflux | 24        | 75               |
|          | 2.0 eq K <sub>2</sub> CO <sub>3</sub>  | CH <sub>3</sub> CN | Reflux | 24        | 11 <sup>a</sup>  |
|          | 1.0 eq Cs <sub>2</sub> CO <sub>3</sub> | CH <sub>3</sub> CN | Reflux | 48        | <10 <sup>a</sup> |

<sup>a</sup>A significant amount of calix-*bis*-crown was evident with TLC analysis.

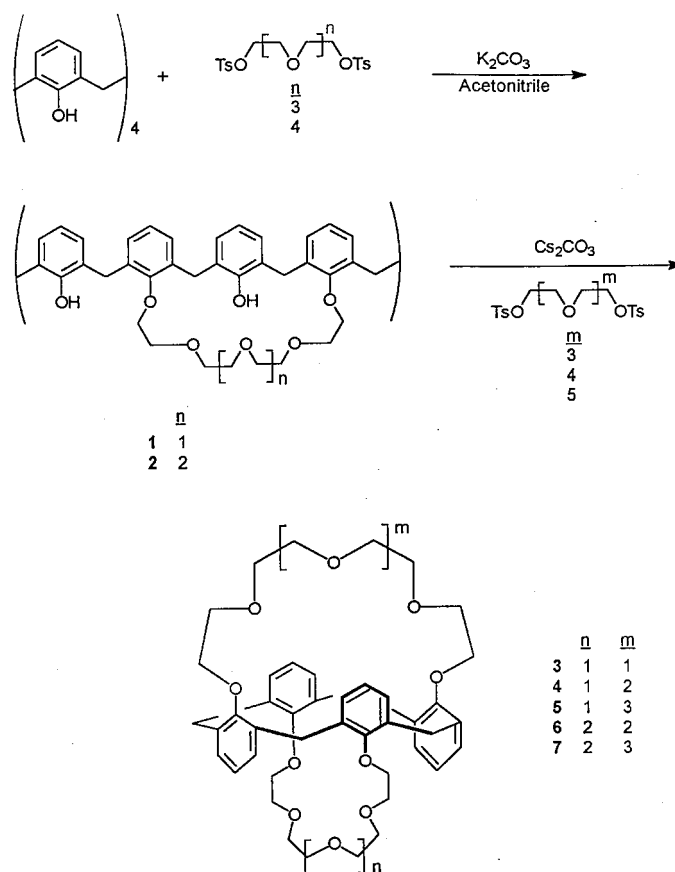
Scheme 1. Synthetic route for calix[4]arene *bis*-crown ethers.

Table II. Association constant and free energy on complexation of ligands (3–7) with alkali metal picrates at 25 °C.<sup>a</sup>

| Compound | Metal ion       | Log $K_a$ ( $M^{-1}$ ) | $-\Delta G^\circ$ (kcal/mol) |
|----------|-----------------|------------------------|------------------------------|
| <b>3</b> | Na <sup>+</sup> | 7.94                   | 10.83                        |
|          | K <sup>+</sup>  | 9.48                   | 12.93                        |
|          | Rb <sup>+</sup> | 9.25                   | 12.62                        |
|          | Cs <sup>+</sup> | 7.67                   | 10.46                        |
| <b>4</b> | Na <sup>+</sup> | 7.94                   | 10.83                        |
|          | K <sup>+</sup>  | 9.57                   | 12.78                        |
|          | Rb <sup>+</sup> | 9.18                   | 12.52                        |
|          | Cs <sup>+</sup> | 8.74                   | 11.92                        |
| <b>5</b> | Na <sup>+</sup> | 8.03                   | 10.96                        |
|          | K <sup>+</sup>  | 9.65                   | 13.17                        |
|          | Rb <sup>+</sup> | 6.43                   | 12.87                        |
|          | Cs <sup>+</sup> | 7.72                   | 10.53                        |
| <b>6</b> | Na <sup>+</sup> | 6.42                   | 8.76                         |
|          | K <sup>+</sup>  | 7.52                   | 10.26                        |
|          | Rb <sup>+</sup> | 8.48                   | 11.57                        |
|          | Cs <sup>+</sup> | 9.08                   | 12.39                        |
| <b>7</b> | Na <sup>+</sup> | 7.66                   | 10.44                        |
|          | K <sup>+</sup>  | 7.51                   | 10.24                        |
|          | Rb <sup>+</sup> | 8.23                   | 11.22                        |
|          | Cs <sup>+</sup> | 8.51                   | 11.61                        |

<sup>a</sup>The average value of three independent determinations. The experimental values deviate from the reported values by an average of 10%.

indicates the characteristic 1,3-alternate conformation [6, 11, 12, 14]. No other isomers were indicated by this NMR measurement.

Compound **3** was known to selectively complex with potassium ions by electrostatic interaction between the crown ether moiety and the metal ion based on size agreement as well as  $\pi$ -metal interaction between two 1,3-alternate phenyl rings and the metal ions [13, 14]. To measure the selectivity and efficiency of ligands **3–7** for metal ions, the concentrations of picrate anions extracted from the aqueous phase into the organic phase were measured at equilibrium.

Association constants ( $K_a$ ) and free energies ( $\Delta G$ ) were calculated as listed in Table II. The  $K_a$  and  $\Delta G$  can be expressed by the method described above as follows [17]:





$$K_a = K_{ex}/K_d \quad (4)$$

$$\Delta G = -RT \ln K_a. \quad (5)$$

Two phase extraction using ligands **3–5** and **6, 7** shows potassium and cesium selectivity, respectively. It has been reported that 1 : 1 ligand–metal ion complexation occurs when the calix[4]arene *bis*-crown ether encapsulates the alkali metal ion [13]. In the case of **4**, where crown-5 and crown-6 are simultaneously incorporated into the 1,3-alternate calixarene, we found that the association constant ( $\log K_a$ ) of potassium ion increases from 9.48 to 9.57 as does that of cesium ion from 7.67 to 8.74. In the latter case, the increment of the  $\log K_a$  value for the cesium ion is due to the fact that calixcrown-6 fits well with the cesium ion. However, an interesting point is that the binding ability of the potassium ion increases with the elongation of the upper crown loop (**3**  $\rightarrow$  **4**  $\rightarrow$  **5**). In other words, when the upper ether linkage elongates to crown-7, the highest selectivity for potassium ions was observed. More interestingly, in the case of **4**, the association constant of  $\text{K}^+$  is larger than that for  $\text{Cs}^+$ , strongly indicating that the  $\text{K}^+$  preference is more likely to occur than  $\text{Cs}^+$  when crown-5 and crown-6 are simultaneously incorporated into one calixarene molecule. The cavity size of this crown-7 framework (compound **5**) is too large to adopt the cesium ion which has one of the longest ionic radii among the known elements. Considering the CPK molecular model of complex **5** and potassium ions, it seems to us that the crown ether moiety attached to the upper part of the 1,3-alternate calix[4]arene is large so that the ether linkage could slightly push the two downward phenyl rings. Because of this phenomenon, the distance between the two downward facing phenyl rings shortens, resulting in the stronger  $\pi$ -metal complexation between the  $\pi$ -orbital of the two phenyl rings and the potassium ion.

In contrast to this increasing association constant for potassium ions by elongation of the crown cavity size on the lower rim of the calixarene, cesium ion selectivity does not show the same propensity. Compound **6** gave the highest association constant rather than compound **7** which is not suitable as a cesium nest.

A bulk liquid membrane system was preferentially adopted in this study to determine the competitive transport rate of metal ions and to measure the specific metal ion selectivity over other alkali metal ions. The measured flux values from the competitive transport experiment are described in Table III. In the control experiments it was confirmed that no metal ion transport was observed in the absence of the carrier. Two batch experiments have been carried out. Three components composed of  $\text{Li}^+/\text{Na}^+/\text{Cs}^+$  and  $\text{K}^+/\text{Rb}^+/\text{Cs}^+$ , respectively are in the

Table III. Competitive transport of  $M^+$  by bulk liquid membrane<sup>a</sup> using calix[4]arene *bis*-crown ethers (**3–7**)

| Carrier  | Flux values ( $\times 10^{-8}$ mol s <sup>-1</sup> m <sup>-2</sup> ) |  |
|----------|--|--|
|          | Li <sup>+</sup> /Na <sup>+</sup> /Cs <sup>+</sup>                    | K <sup>+</sup> /Rb <sup>+</sup> /Cs <sup>+</sup> |
| <b>3</b> | 0.00/1.23/189.1  | 168.9/130.1/34.91                                |
| <b>4</b> | 0.00/1.03/495.3  | 106.5/81.0/163.7                                 |
| <b>5</b> | 0.00/1.76/177.1  | 190.0/24.2/45.7                                  |
| <b>6</b> | 0.00/0.62/518.5  | 103.8/50.4/392.3                                 |
| <b>7</b> | 0.00/6.05/361.1  | 68.2/55.2/356.4                                  |

<sup>a</sup>Transport condition: source phase (aqueous solution of metal nitrate, 0.1 M, 0.8 mL); membrane phase (CH<sub>2</sub>Cl<sub>2</sub> saturated with water, 3 mL), [carrier] = 1.0 mM; receiving phase (deionized water, 5 mL).

aqueous source phase, and they are competitively transported into the aqueous receiving phase through the bulk organic membrane containing calix-*bis*-crowns. In the case of **3**, high potassium ion competition was observed over rubidium and cesium ions as seen in the two phase extraction experiment due to the size agreement between calixcrown-5 and K<sup>+</sup>. Compound **4**, in which crown-5 and crown-6 are simultaneously incorporated into one calix[4]arene molecule, shows cesium ion selectivity over rubidium and potassium ions. The selectivity is opposite to the results for the two phase extraction as described earlier. So, it is currently thought that the potassium ion is strongly coordinated to the crown-5 and shows the slower decomplexation rate. An enlargement of the crown ether cavity to crown-7 (**5**) on the lower rim of the calixarene framework gave a high potassium selectivity in this transport experiment, for which the results are in good agreement with two phase extraction. Since there are no proper cavities for cesium ions in **5**, only a small number of cesium ions were able to be transported. The increment of the selectivity compared with that of **3** could be explained by the shortening distance between two downward phenyl rings as described earlier.

Measurement of the complexation selectivity was initially conducted by the use of <sup>1</sup>H NMR spectroscopy as shown in Figure 1. Ligand **4** was chosen to investigate NMR behavior because **4** has two proper cavities: crown-5 for potassium ion and crown-6 for cesium ions, respectively. Compound **4** is blocked in the 1,3-alternate conformation as inferred from the NMR spectrum (A) in Figure 1. A singlet peak at  $\delta$ 3.86 in the <sup>1</sup>H NMR for four bridging methylene hydrogens (Ar—CH<sub>2</sub>—Ar) and one signal at 38.8 ppm for the bridging methylene carbons (Ar—CH<sub>2</sub>—Ar) in the <sup>13</sup>C NMR spectrum indicates the characteristic 1,3-alternate conformation as mentioned earlier. A singlet peak at 3.70 ppm corresponds to four hydrogens of the symmetrical -OCH<sub>2</sub>CH<sub>2</sub>O- (H<sub>b</sub>) on the upper crown-6 ring of **4**. The <sup>1</sup>H NMR

spectra of the free ligand **4**, **4**·Na<sup>+</sup>, **4**·K<sup>+</sup>, and **4**·Cs<sup>+</sup>, which are assumed to have 1 : 1 complexation ratios were taken in deuterated CDCl<sub>3</sub> as indicated by (A)–(D), respectively. In spectrum (B) for **4**·Na<sup>+</sup>, no significant changes of chemical shift were observed except for peak broadening compared with spectrum (A) for free ligand **4**. This is probably due to the less effective complexation of **4** with sodium ions. Interestingly, however, the complex of **4**·K<sup>+</sup> gave rise to remarkable changes both in chemical shift values and in splitting patterns. A down-field shifted multiplet which appeared at 3.98 ppm corresponds to one of the -OCH<sub>2</sub>CH<sub>2</sub>O- which normally appeared at 3.6 ppm. This shifting is ascribed to the fact that the electron density of the crown ether linkage markedly decreases by strong ethereal oxygens-potassium complexation to give a down-field shifting. The AB splitting quartet at 3.77 ppm corresponding to the four bridging methylene hydrogens (Ar—CH<sub>2</sub>—Ar) is due to the rigid structure by ligand-metal complexation which is no longer flexible in the NMR time scale. Interestingly, the singlet peak observed at 3.70 ppm for the four hydrogens of symmetrical -OCH<sub>2</sub>CH<sub>2</sub>O- (H<sub>b</sub>) on the upper crown-6 ring did not change in either chemical shift or peak shape which led us to conclude that the potassium ion complexes into the lower rim cavity (crown-5). In the case of **4**·Cs<sup>+</sup> (spectrum D), the singlet peak for -OCH<sub>2</sub>CH<sub>2</sub>O- (H<sub>b</sub>) disappeared to give a multiplet splitting pattern due to strong complexation of ligand (crown-6)-cesium ions. In contrast to the splitting pattern change of the bridging methylene hydrogens (Ar—CH<sub>2</sub>—Ar) in **4**·K<sup>+</sup>, no significant change for **4**·Cs<sup>+</sup> was observed. This selective response in the NMR peak pattern with respect to changes of the chemical shift and peak splitting is in good agreement with the results of the selective metal ion transport and two phase extraction experiment.

### 3. Conclusions

A series of calix[4]arene-*bis*-crown ethers having different sizes of crown ether cavities were synthesized in a fixed 1,3-alternate conformation. In the preparation of the monocyclic calixcrown ether, the use of potassium carbonate as a base provided the best yield regardless of the crown ether cavity size. Calix[4]arene *bis*-crown (**6**) provided the best selectivity for potassium ions from two phase extraction and competitive transport experiments. It was also found that the extent of change of the peak splitting patterns and the chemical shift for the ligand-metal ion complex in <sup>1</sup>H NMR spectra is dependent on the metal ion species when calix-*bis*-crown ether (**4**) bearing different sized crown ether loops were adapted to complex with K<sup>+</sup> and Cs<sup>+</sup>, respectively. From these results, it is noteworthy that these calix[4]arene-*bis*-crown ethers can be potentially useful for simultaneous removal of cesium and potassium ions possibly existing in aqueous solution.

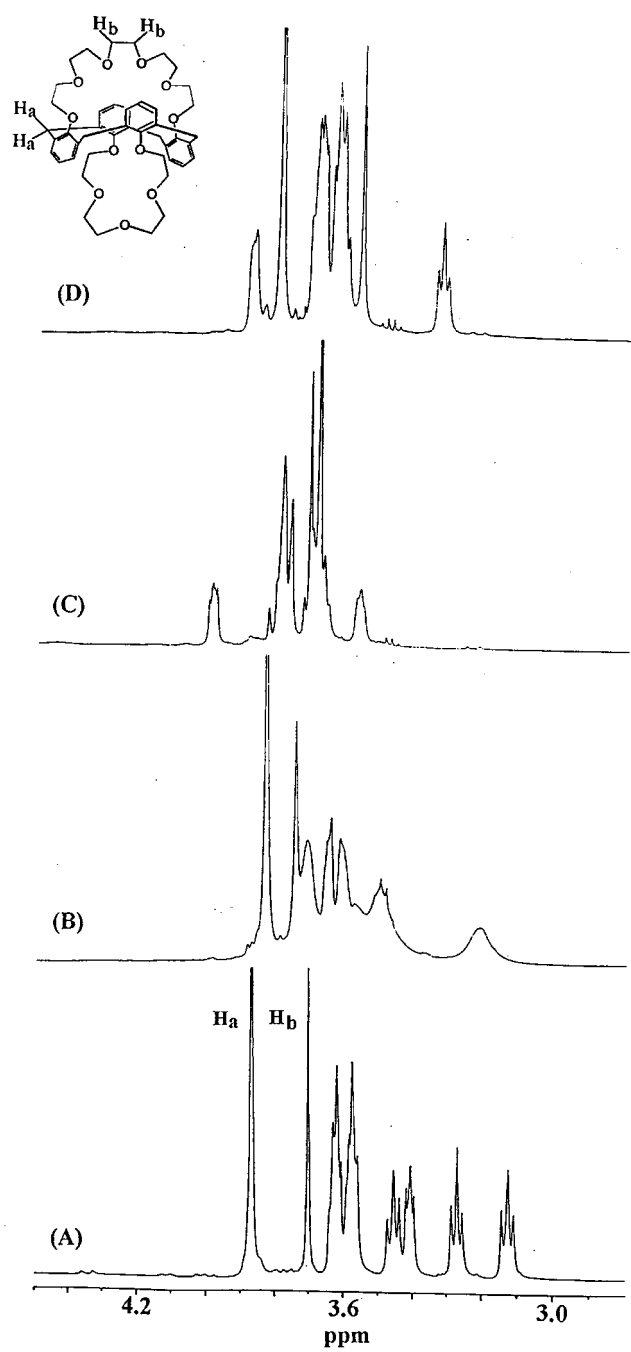


Figure 1. Partial  $^1\text{H}$  NMR spectra ( $\text{CDCl}_3$ ) at  $25^\circ\text{C}$ , 400 MHz: (A) free ligand **4**, (B) complex of  $4\cdot\text{Na}^+\text{Pic}^-$ , (C) complex of  $4\cdot\text{K}^+\text{Pic}^-$ , and (D) complex of  $4\cdot\text{Cs}^+\text{Pic}^-$ .



## 4. Experimental

### 4.1. INSTRUMENTS AND CHEMICALS

Melting points were taken by the use of a Mel-Temp of Fisher-Johns melting point apparatus without any correction. IR spectra were obtained with a Perkin-Elmer 1600 Series FT-IR on potassium bromide pellets and on deposited KBr windows in the case of solid products and oils, respectively, and were recorded in reciprocal centimeters.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded with a 400 MHz (Bruker ARX-400) and 100 MHz spectrometer, respectively, the chemical shifts ( $\delta$ ) reported downfield from the internal standard, tetramethylsilane. Elemental analysis was performed by Vario EL of Elemental Analyzer in the Korea Basic Science Institute in Seoul, Korea. FAB<sup>+</sup> mass spectra were obtained from the 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: dichloromethane was freshly distilled from lithium aluminum hydride. Acetonitrile was pre-dried from molecular sieves (3 Å) and distilled over diphosphorous pentoxide. Compounds **3** [12, 14], and **6** [13, 14] were prepared as described in the literature.

### 4.2. SYNTHESIS

#### 4.2.1. Calix[4]arene monocrown-5 (**1**).

Under nitrogen, a solution of calix[4]arene (3.0 g, 7.1 mmol), tetraethyleneglycol di-*p*-toluenesulfonate (3.55 g, 7.1 mmol), and  $\text{K}_2\text{CO}_3$  (0.98g, 7.1 mmol) in 100 mL of acetonitrile was heated to reflux temperature. After reflux for 24 hrs, acetonitrile was removed *in vacuo*. To the brownish solid, 100 mL of 5% HCl aqueous solution and 50 mL of  $\text{CH}_2\text{Cl}_2$  were added and the organic layer was separated and washed with 50 mL of HCl aqueous solution. The organic layer was dried over anhydrous  $\text{MgSO}_4$  and the solvent was evaporated *in vacuo* to give a brownish oil. Column chromatography was conducted with EtOAc-Hexane (1 : 3) as eluent to give the desired product (2.9 g) as a white solid in 70% yield. M.p.: 275–276 °C. IR (KBr pellet,  $\text{cm}^{-1}$ ) 3398, 2939, 1590, 1464, 1336, 1251, 1127, 1050, 919, 810, 760, 610.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.76 (s, 2 H, ArO-*H*), 7.10–6.67 (m, 12 H, Ar-*H*), 4.46 (d, 4 H, ArCH<sub>2</sub>Ar), 4.29 (s, 4 H, -CH<sub>2</sub>CH<sub>2</sub>O-), 4.28–3.86 (m, 12 H), 3.34 (d, 4 H, ArCH<sub>2</sub>Ar). FAB MS  $m/z$  ( $\text{M}^+$ ) Calcd: 582.5; found: 583.

#### 4.2.2. Calix[4]arene monocrown-6 (**2**).

The preparation method is the same as that of compound **1** except that pentaethyleneglycol di-*p*-toluenesulfonate was used. 75% yield. M.p.: 302–304 °C. IR (KBr pellet,  $\text{cm}^{-1}$ ): 3150, 2926, 2865, 1594, 1459, 1413, 1204, 1084, 839, 753.  $^1\text{H}$

NMR(CDCl<sub>3</sub>):  $\delta$  7.79 (s, 2 H, ArO-H), 7.11 (d, 4 H), 6.85 (d, 4 H), 6.70 (q, 4 H), 4.4 (d, 4 H, Ar-CH<sub>2</sub>-Ar), 4.44–3.83 (m, 16 H, -CH<sub>2</sub>CH<sub>2</sub>O-), 3.36 (s, 4 H), 3.37 (d, 4 H, Ar-CH<sub>2</sub>-Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>): 153.97, 152.80, 133.82, 129.59, 129.16, 128.85, 125.88, 119.56, 72.27, 71.69, 71.65, 70.52, 31.75. FAB MS  $m/z$  (M<sup>+</sup>) Calcd: 626.2; found: 623.

#### 4.2.3. Calix[4]arene biscrown ether (4)

Under nitrogen, pentaethyleneglycol di-*p*-toluenesulfonate (1.88 g, 3.4 mmol) was added to a solution of monocyclic calixarene **1** (2.0 g, 3.4 mmol) and cesium carbonate (5.5 g, 17.0 mmol) in 100 mL of acetonitrile and refluxed for 48 hrs. After removal of acetonitrile in vacuo, 100 mL of 5% HCl aqueous solution and 50 mL of CH<sub>2</sub>Cl<sub>2</sub> were added and the organic layer was separated and washed with 50 mL of HCl aqueous solution. The organic layer was dried over anhydrous MgSO<sub>4</sub> and the solvent was evaporated *in vacuo* to give a brownish oil. Column chromatography was conducted with EtOAc-hexane (1 : 2) as eluent to give the desired product (2.1 g) as a white solid in 80% yield. M.p.: 118–120 °C. IR (KBr pellet, cm<sup>-1</sup>) 3011, 2926, 2871, 1729, 1575, 1461, 1252, 1214, 1145, 1034, 834, 765, 733. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.12–6.74 (m, 12 H, Ar-H), 3.86 (s, 8 H, Ar-CH<sub>2</sub>-Ar), 3.70 (s, 4 H, -CH<sub>2</sub>CH<sub>2</sub>O-), 3.63–3.11 (m, 32 H, -CH<sub>2</sub>CH<sub>2</sub>O-). FAB MS  $m/z$  (M<sup>+</sup>) Calcd: 736.3; found: 764. Anal. Calcd for C<sub>42</sub>H<sub>56</sub>O<sub>11</sub>: C, 68.47; H, 7.60. Found: C, 68.50; H, 7.58.

#### 4.2.4. Calix[4]arene biscrown ether (5)

The preparation method is the same as that of **4** except that hexaethyleneglycol di-*p*-toluenesulfonate was used. Column chromatography using EtOAc-hexane (1 : 2) gave an oil with 80% yield. IR (KBr neat cm<sup>-1</sup>): 2928, 2859, 1737, 1461, 1366, 1212, 1201, 1150, 1099, 954, 833, 772, 730. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.26–7.08 (m, 8 H), 6.91–6.86 (m, 4 H), 3.85 (s, 8 H), 3.70 (s, 8 H, Ar-CH<sub>2</sub>-Ar), 3.64–3.56 (m, 16H), 3.44–3.39 (m, 8 H), 3.10 (q, 8 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm): 157.08, 156.85, 134.76, 134.69, 130.14, 130.07, 123.40, 73.42, 71.63, 71.45, 71.38, 71.34, 71.23, 70.52, 70.12, 69.67, 68.91, 38.87, 38.73, 38.61. FAB MS  $m/z$  (M<sup>+</sup>) Calcd: 780.2; found: 780.7.

#### 4.2.5. Calix[4]arene biscrown ether (7)

The preparation method is the same as that of **5** except that **2** and hexaethyleneglycol di-*p*-toluenesulfonate were used. Column chromatography using EtOAc-hexane (1 : 2) gave an oil with 80% yield. IR (KBr neat, cm<sup>-1</sup>): 3016, 2922, 2242, 1457, 1350, 1296, 1247, 1207, 1095, 1092, 843, 763, 731, 646, 633. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  6.98 (t, 6 H), 6.77 (t, 6 H), 3.69 (s, 8 H, Ar-CH<sub>2</sub>-Ar), 3.65–3.5 (m, 22 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm): 157.1, 156.9, 134.5, 134.3, 130.7, 130.5, 123.1, 123.0, 71.7, 71.6, 71.43, 71.36, 71.26, 70.6, 70.5, 70.3, 70.1, 40.7, 38.3. FAB MS  $m/z$  (M<sup>+</sup>) Calcd: 824.2; found: 824.8.

### 4.3. COMPETITIVE TRANSPORT OF ALKALI METAL IONS THROUGH A BULK LIQUID MEMBRANE

Liquid membrane transport experiments were carried out as reported earlier using a bulk liquid membrane apparatus. Two separated 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 media was filled with the source phase composed of 0.8 mL of 0.1 M solution of lithium, sodium and cesium nitrate. A second batch containing 0.8 mL of 0.1 M solution of potassium, rubidium, and cesium nitrate was made. The outer cylinder was filled with 5.0 mL of deionized water as a receiving phase. The details of the transport conditions are summarized in the footnotes of Table II. Each experiment was repeated three times in a room thermostated to  $25 \pm 1$  °C then 3 mL of the receiving phase was taken. The flux values (moles transported/sec  $m^2$ ) for 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 *bis*-crown ether was present were performed.

### 4.4. NMR OF COMPLEXES

#### 4.4.1. Preparation of the NMR sample

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded with a 400 MHz (Bruker ARX-400) and a 100 MHz spectrometer, respectively, the chemical shifts ( $\delta$ ) were reported downfield from the internal standard, tetramethylsilane. NMR samples for metal picrate complexes were prepared as follows. A mixture of organic ligand **4** (20 mg) dissolved in  $\text{CDCl}_3$  (10 mL) and excess metal picrate (over at least 5 equivalents) was stirred for 1 h. After filtration of the precipitated excess metal picrate, the filtrate was dried *in vacuo* to give a yellow solid complex  $\mathbf{4}\cdot\text{M}^+\text{Pic}^-$ .

#### 4.4.2. $\mathbf{4}\cdot\text{Na}^+\text{Pic}^-$ (400 MHz; $\text{CDCl}_3$ )

$\delta$  8.89 (s, 0.1 H, Ar-*H* of picrate), 7.35–6.74 (m, 12 H, Ar-*H*), 3.83 (s, 8 H, Ar $\text{CH}_2\text{Ar}$ ), 3.74 (s, 4 H,  $-\text{OCH}_2\text{CH}_2\text{O}-$ , upper middle part of ether ring), 3.70–3.12 (m, 32 H).  $^{13}\text{C}$  NMR (100 MHz;  $\text{CDCl}_3$ ) 142.5, 134.7, 130.5, 127.3, 127.2, 123.7, 71.7, 71.4, 71.1, 70.5, 38.7.

#### 4.4.3. $\mathbf{4}\cdot\text{K}^+\text{Pic}^-$ (400 MHz; $\text{CDCl}_3$ )

$\delta$  8.79 (s, 2 H, Ar-*H* of picrate), 7.38–6.78 (m, 12 H, Ar-*H*), 4.00–3.98 (m, 4 H,  $-\text{OCH}_2\text{CH}_2\text{O}-$ ), 3.80–3.45 (m, 32 H).  $^{13}\text{C}$  NMR (100 MHz;  $\text{CDCl}_3$ ) 157.9, 155.4, 142.7, 136.8, 134.0, 132.1, 131.5, 127.2, 124.8, 123.1, 72.1, 71.9, 71.7, 71.4, 70.8, 70.6, 37.8.

4.4.4.  $4\text{-Cs}^+\text{Pic}^-$  (400 MHz;  $\text{CDCl}_3$ )

$\delta$  8.85 (s, 2 H, Ar-*H* of picrate), 7.33–6.92 (m, 12 H, Ar-*H*), 4.00–3.88 (m, 4 H,  $-\text{OCH}_2\text{CH}_2\text{O}-$ ), 3.80 (s, 8 H,  $\text{ArCH}_2\text{Ar}$ ), 3.68–3.57 (m, 28 H), 3.33 (t, 4 H,  $-\text{OCH}_2\text{CH}_2\text{O}-$ ).  $^{13}\text{C}$  NMR (100 MHz;  $\text{CDCl}_3$ ) 157.16, 157.11, 142.7, 136.4, 133.8, 131.4, 131.1, 127.3, 126.2, 124.2, 73.8, 73.3, 71.5, 71.3, 71.2, 71.0, 70.4, 68.8, 38.3.

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