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A New Class of Potassium-selective Calix[4]arenes in Cone Conformation

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Benzoate modified calix[4]arenes 3–8 were synthesized from (o-bromomethyl)benzoate. EA, IR, ^{1}H and ^{13}C NMR characterizations showed that compounds 3, 4, 5, 7 and 8 were in cone conformation, while 6 was in a 1,3-alternate conformation. The solvent extraction experiments found that the cone-conformers 3 and 8 have high selectivity for K^+ as compared to Na^+. Compound 3 has an extractability of 69.8% for K^+ and 7.1% for Na^+. Compound 8 has an extractability of 80.9% for K^+ and 19.1% for Na^+. In order to elucidate the results, the complex behavior of compounds 3, 6 and 8 for K^+ were studied by ^{1}H NMR and the crystal structures of compounds 3 and 6 were determined.

Keywords: Calix[4]arene; Cone conformation; Potassium selective; Crystal structure

INTRODUCTION

Calixarenes have attracted many researchers in the fields of supramolecular and host-guest chemistry [1,2] since calixarenes offer an ideal platform for alkali metal cation selective ionophores due to their rigidity and ease of derivatization [1–3]. The majority of research on potassium-selective ionophores has focused on the development of calix[4]-crowns incorporating a crown-5 unit and on the different cation specificities of a range of calixarene conformers [4–7]. Of these, the most successful is the 1,3-alternate receptor [7], which shows higher K^+/Na^+ selectivity than the natural ionophore valinomycin. The tetraacetates of 1,3-alternate calix[4]arene [8] and dioxacalix[4]arene [9], tetra-amide of 1,3-alternate calix[4]arene [10] also proved selective for complexation of potassium, and the hexaacetate of calix[6]arene [11] has been developed as a blood sensor for potassium. However, to date, no calixarene in cone conformation shows selectivity for potassium cations over sodium cations.

In this paper we report synthesis of a new class of benzoate-type ionophores **3**–**8**. Structural studies found that they all, except **6**, are in cone conformation. Alkali metal ion binding studies showed that the cone-shaped ionophores also display a selectivity of potassium cation over sodium cation.

RESULTS AND DISCUSSION

Compounds (**3**–**8**) were characterized by elemental analysis, IR and NMR spectra (Scheme 1). The conformational characteristic of compound **3** was estimated by the splitting pattern of the $ArCH_2Ar$ methylene protons at δ 4.15 and 2.94 which showed an AB system in ^{1}H NMR spectroscopy [12]. This revealed that compound **3** was in a cone conformation. The ^{1}H NMR spectrum of compound **8** was similar to that of compound **3** and the conformation was also identified to be in a cone conformation.

By the reported procedure, compound **4** was synthesized [13]. A single peak of OH at δ6.72 was found in ^{1}H NMR, indicating that this compound is tri-substituted. The ^{1}H NMR spectrum also showed four doublets arising from the $ArCH_2Ar$ methylene protons at δ 4.24, 4.15, 3.19 and 3.04, respectively, and three singlets arising from the *p-tert*-butyl protons at δ1.34 (9H), 1.32(9H) and 0.84 (18H), respectively. All these data indicated that the compound **4** is in cone conformation.

During the synthesis of the compound **3**, compound **5** was detected when the reaction time was

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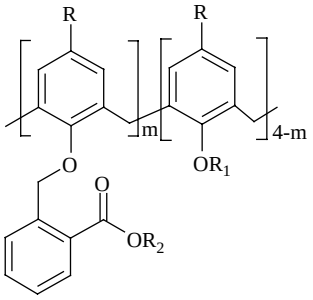

1 m=0 R=t-Bu R_1=H
2 m=0 R=H R_1=H
3 m=4 R=t-Bu R_2=CH_3
4 m=3 R=t-Bu R_1=H R_2=CH_3
5 m=2 R=t-Bu R_1=H R_2=CH_3 (25,27-distal)
6 m=4 R=H R_2=CH_3
7 m=2 R=H R_1=H R_2=CH_3 (25,27-distal)
8 m=4 R=t-Bu R_2=CH_2CH_3
9 m=0 R=t-Bu R_1=$CH_2COOCH_2CH_3$

SCHEME 1 Structure of compounds **1**–**9**.

prolonged up to 20 h. After 5 days, only compound **3** was detected, which indicated that compound **5** was completely converted to compound **3**. The ^{1}H NMR spectrum showed a typical AB pattern for the $ArCH_2Ar$ methylene protons at δ 4.41 and 3.30 ($J = 12.8$ Hz), indicating that **5** existed in a distal-cone conformation. The *tert*-butyl protons presented at δ 1.29 and 0.94 in a 1:1 ratio also confirmed the distal-cone conformation. The ^{1}H NMR spectrum of compound **7** is similar to that of compound **5**, which indicated that compound **7** is also in a distal-cone conformation.

The ^{1}H NMR spectrum of **6** showed the characteristic singlet at δ 3.63 for the $ArCH_2Ar$ methylene protons, indicating **6** is in the 1,3-alternate conformation [1]. The ^{13}C NMR showed that the absorption of $ArCH_2Ar$ is present at δ37.1, which matched δ37.0 reported by de Mendozu [14] for calix[4]arene in the 1,3-alternate conformation.

The results of the solvent extraction studies with compound **3**–**8** are summarized in Table I. The conclusions are as following:

(a) Compound **3** and **8** exhibit high extraction ability for K^+ over other alkali cations. The order of the extractibility is $K^+ > Na^+ > Cs^+ > Li^+$. In contrast, compound **9** displayed a higher selectivity for Na^+[15,16]. This difference in cation-selectivity between compounds **3**/**8** and **9** indicated that the size of ionophoric cavity is a critical factor in determining cation selectivity of calix[4]arene. The introduction of the functional binding sites, such as *o*-(methoxycarbonyl)benzyl group, would increase the cavity size of calix[4]arene, which may not greatly affect the cation selectivity due to the rigidity of the benzene ring in the pendant.

(b) The 1,3-alternate conformer **6** shows low extractibility (24.1%) for K^+ as compared to the cone conformer **3** and **8**.

(c) The nature of the alkyl group in the ester moiety of the cone tetramers also affects the extractibility toward alkali metal cations [17], because compound **8** with a more lipophilic ethyl group exhibited a higher extractibility than compound **3** with a methyl group.

TABLE I Percent extraction of alkali metal picrate into CH_2Cl_2 at 20°C*

Compound	Li^+	Na^+	K^+	Cs^+
3	6.8	19.4	69.8	7.1
4	0.0	3.8	5.6	2.7
5	2.6	4.4	4.2	3.8
6	0.0	4.7	24.1	4.0
7	0.0	2.6	7.0	0.0
8	1.4	19.1	80.9	6.4
9[15]	17.6	100	86.1	24.6

*A minimum of two runs for each ion. Standard deviation: 5%.

In order to further illustrate the selectivity described above, the ^{1}H NMR of complexed compounds **3**, **6** and **8** with KSCN were obtained (Table II). KSCN instead of KPic was used owing to the interference of the picrate protons.

The ^{1}H NMR spectra of compounds **3**, **6** and **8** were obtained at different K^+ concentrations, with salt/ligand molar ratios: 0:1, 0.4:1 and 1:1. As shown in Fig. 1, the addition of potassium cation caused significant changes in chemical shift. Most of the chemical shift difference observed between the free ligands and the complexes were localized to OCH_2Ph, $ArCH_2Ar$ and OCH_2CH_3. At a salt/ligand ratio of 0.4 (Fig. 1b), signals for both complexed and un-complexed ligands were present. This suggested that on the NMR time scale the exchange rate between the two species was slow at room temperature. At a salt/ligand ratio of 1:1 (Fig. 1c), all the signals for the free ligands disappeared. Any further significant change of new increase signals was not observed after one equivalent of KSCN, suggesting that **8** was complexed with potassium ion by 1:1 solution stoichiometry [18]. The spectrum of the 1:1 ratio complex is also indicative for the fact that this complex adopts a perfect cone conformation. This is evident from the presence of a single signal for the OCH_2Ph and a quartet signal for OCH_2CH_3 in the spectrum. The downfield shifts and the single multi-peaks of ester group protons in **8** indicated that all of the carbonyl groups participate in the coordination of K^+. A similar profile was observed with compound **3,** suggesting that **3**-K^+ is also in 1:1 solution stoichiometry and a cone conformation. As compared to compounds **3** and **8**, the ^{1}H NMR signal of $ArCH_2Ar$ in compound **6** displayed a very minor change in chemical shift

TABLE II ^{1}H NMR spectra data of the calix[4]arenes and their complexes with KSCN

Sample	Chemical Shift, δ (ppm)		
	$ArCH_2Ar$	OCH_2Ph	Protons in ester
3	4.255 (d), 2.940 (d) ($J = 12.4$ Hz)	5.292 (s)	3.687 (s, OCH_3)
3: $K^+ = 1$: 0.4 (molar ratio)	4.255 (d), 2.940 (d) 3.447 (d), 2.380 (d)	5.292 (s)	3.687 (s, OCH_3)
		5.012 (s)	4.127 (s, OCH_3)
3: $K^+ = 1$:1 (molar ratio)	3.448 (d), 2.381 (d) ($J = 10.4$ Hz)	5.012 (s)	4.128 (s, OCH_3)
6	3.635 (s)	5.274 (s)	3.870 (s, OCH_3)
6: $K^+ = 1$: 0.4 (molar ratio)	3.633 (s)	5.274 (s)	3.870 (s, OCH_3)
6: $K^+ = 1$:1 (molar ratio)	3.578 (s,br)	5.255 (s)	3.876 (s, OCH_3)
8	4.296 (d), 2.976 (d) ($J = 12.4$ Hz)	5.304 (s)	4.128 (q, OCH_2)
			1.275 (t, OCH_3)
8: $K^+ = 1$: 0.4 (molar ratio)	4.296 (d), 2.976 (d) 3.440 (d), 2.366 (d)	5.304 (s)	4.128 (q) 1.275 (t)
		4.994 (s)	4.586 (q) 1.490 (s)
8: $K^+ = 1$: 1 (molar ratio)	3.439 (d), 2.367 (d) ($J = 12.0$ Hz)	4.994 (s)	4.586 (q, OCH_2)
			1.490 (s, OCH_3)

($\Delta\delta_{max} = 0.06$ ppm) in the presence of K^+ with a salt/ligand ratio of 1.0, indicating that **6** has a very weak interaction with K^+ in solution. This is consistent with the low extractability observed with compound **6** shown in Table I.

In order to explain the results of solvent extraction, the crystal structures of compounds **3**, **6** and **8** were attempted to be determined. Unfortunately, only compound **3** showed a good result. The crystal of compound **8** couldn't be gotten for several attempts. The structural data for compound **6** was of poor quality with a final *R* value of 0.1812. Nonetheless, the data are clearly consistent with the structural conformation revealed by the NMR analysis. Crystallographic parameters of **3** and **6** were presented in Table III and selected bond lengths and bond angles were given in Tables IV and V.

Compound **3** crystallizes in space group P-1 with the molecules stacking head-to-head along the *c* axis. As shown in Fig. 2, compound **3** adopted a cone conformation in the solid state. The interplanar angles between the individual benzene rings of the calix backbone and the plane of the four methylene C atoms (C7, C14, C21 and C28) were: 126.8°, 84.7°, 50.7° and 89.9°, respectively. All the carbonyl groups in the pendants pointed towards outside of the cavity to reduce the steric hindrance. The conformation of the pendants have torsion angles of −179.2°, −146.5°, −45.0° and −178.7° for ∠C(1)–O(1)–C(45)–C(46), C(8)–O(2)–C(54)–C(55), C(15)–O(3)–C(63)–C(64) and C(22)–O(4)–C(72)–C(73), respectively. Only the pendant including C71 methyl group was clearly distorted as compared with other pendants. The distance between carbonyl oxygen O9 and O11 (in the adjacent molecule) is 2.785 Å, which is within 2-fold of a van der Waals radius of oxygen atom (2.80 Å = 2 × 1.40 Å).

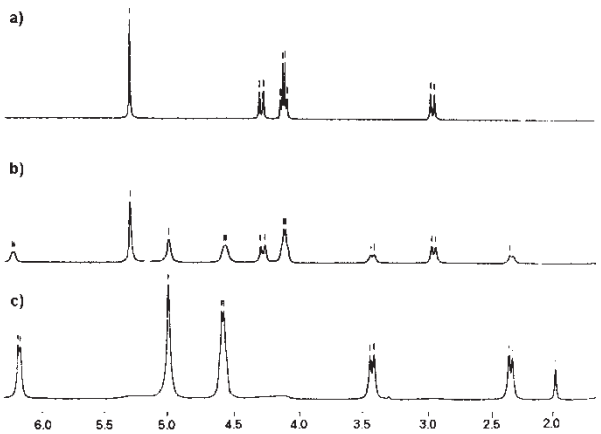

FIGURE 1 Complexation of KSCN by Compound **8**. ^{1}H NMR spectra ($CDCl_3 + CD_3OD$, 400 MHz): a) salt/ligand = 0:1 (molar ratio); b) salt/ligand = 0.4:1 (molar ratio); c) salt/ligand = 1:1 (molar ratio).

The single crystal of K^+-complexed compound **3** couldn't be obtained, which prevented to illustrate the affection of the pendant orientation by K^+ coordination. However, based on the known structure of **9**-Na^+ complex and its pendant orientation, one can predict that the pendants in the **3**-K^+ complex might assume an inward orientation as in the case of the **9**-Na^+ complex [19]. Furthermore, the pendants in compound **3** were more flexible than that of compound **9,** since they had one more carbon as compared to compound **9**. It can be assumed that the carbonyl groups of compound **3** will rotate towards the inside of the cavity of calix[4]arene to complex with potassium cation. One could also predicate that compound **8** will adopt a similar conformation and coordination manner to compound **3**.

The crystal structure of **6** was also determined. The X-ray deflection analysis of compound **6** revealed a 1,3-alternate conformation and may also shed light on the low K^+ extraction ability of compound **6** (Fig. 3). The two opposite benzene rings of calix backbone are almost parallel to each other with an interplanar angle 4.0°. The two adjacent benzene rings are completely vertical to each other. The carbonyl groups are oriented outward away from the cavity as in the case of compound **3**. Each benzene ring in the pendants is almost vertical to the connected benzene

TABLE III Summary of data collection, structure solution and refinement details

	3	**6**
Crystal data		
Empirical formula	$C_{80}H_{88}O_{12}$	$C_{66}H_{58}Cl_6O_{12}$
Formula weight	1241.50	1255.82
Crystal size (mm)	0.40 × 0.30 × 0.30	0.30 × 0.30 × 0.30
Color	Colorless	Colorless
Crystal system	Triclinic	Monoclinic
a (Å)	10.985(2)	27.987(6)
b (Å)	12.341(3)	17.517(4)
c (Å)	26.413(5)	13.114(3)
α (°)	88.94(3)	90
β (°)	80.02(3)	100.86(3)
γ (°)	87.74(3)	90
V (Å^3)	3523.5(12)	6314(2)
Z	2	4
Calculated density (g/cm^3)	1.170	1.321
F(000)	1328	2608
Space group	P-1	C2/c
Data collection		
Temperature (K)	293(2)	293(2)
Reflections collected/unique	9716/9716	6295/4118
R(int)	0.0000	0.0906
Data/restraints/parameters	9716/10/896	4118/3/380
θ range (°)	1.57 to 25.99	1.38 to 24.00
Absorption coefficient (mm^{-1})	0.077	0.333
Structure solution and refinement		
Refinement method	Full-matrix least-squares on F^2	
Goodness-of-fit on F^2	1.145	1.215
R [$I > 2\sigma$ (I)]	0.0859	0.1812
wR2	0.2444	0.3912
Extinction coefficient	0.0055(10)	–
Largest diff. peak and hole (e·A^{-3})	0.702 and −0.535	0.775 and −0.365

rings of calixarene with the interplanar angles of 86.4° and 86.9°, respectively. This configuration may place a restraint on carbonyl oxygens' rotation to coordinate with K^+, and consequently lower the extract ability of compound **6**. It is known that the main driving force for the extraction of potassium cations is the cation-π interaction between the backbone benzene rings and potassium cations [20].

The mean distance between the benzene ring in the calix backbone and π-conjugated benzoate sites in adjacent molecules is 3.519 Å (shortest 3.445 Å, longest 3.595 Å), indicative of an intermolecular π−π interaction [21,22]. This interaction may facilitate self-assemble of calixarene molecules in the *B*−*C* plane to form a two-dimensional sheet structure (Fig. 4). The sheet packing along *A* axis most likely through by van der Walls force forms a porous structure filled with chloroform molecules.

TABLE IV Selected bond lengths (Å) and bond angles (°) of compound **3**

O(1)–C(1)	1.398(3)	O(11)–C(79)	1.147(5)
O(2)–C(8)	1.399(3)	O(6)–C(52)	1.330(3)
O(3)–C(15)	1.393(3)	O(8)–C(61)	1.322(4)
O(4)–C(22)	1.398(3)	O(10)–C(70)	1.031(5)
O(1)–C(45)	1.435(3)	O(12)–C(79)	1.296(4)
O(2)–C(54)	1.433(3)	O(6)–C(53)	1.461(4)
O(3)–C(63)	1.422(4)	O(8)–C(62)	1.447(5)
O(4)–C(72)	1.426(3)	O(10)–C(71)	1.554(5)
O(5)–C(52)	1.205(3)	O(10)–C(71′)	1.543(7)
O(7)–C(61)	1.203(4)	O(12)–C(80)	1.449(6)
O(9)–C(70)	1.256(5)		
C(1)–O(1)–C(45)	108.58(17)	O(5)–C(52)–O(6)	122.3(3)
C(8)–O(2)–C(54)	112.13(19)	O(5)–C(52)–C(51)	125.5(2)
C(15)–O(3)–C(63)	116.5(2)	O(7)–C(61)–O(8)	120.8(3)
C(22)–O(4)–C(72)	110.65(18)	O(7)–C(61)–C(60)	126.3(3)
O(1)–C(45)–C(46)	110.7(2)	O(10)–C(70)–O(9)	144.2(5)
O(2)–C(54)–C(55)	110.7(2)	O(9)–C(70)–C(69)	112.0(4)
O(3)–C(63)–C(64)	117.8(3)	O(11)–C(79)–O(12)	119.6(4)
O(4)–C(72)–C(73)	109.9(2)	O(11)–C(79)–C(78)	125.6(3)

EXPERIMENTAL

General Remarks

Uncorrected melting points were measured on a WC-1 apparatus. Elemental analyses were determined with a Carlo Erba 1160 elemental analyzer. ^{1}H NMR and ^{13}C NMR were recorded on a Bruker DPX 400 spectrometer using $CDCl_3$ as the solvent and TMS as an internal standard. IR spectra were recorded on a Perkin–Elmer FTIR-1750 spectrophotometer as a KBr pellet. The UV spectra were recorded on a Shimadzu UV2100 UV/VIS recording spectrophotometer.

All chemicals were reagent grade and used without further purification. Compounds **1** [23] and **2** [24] were prepared according to the literature. Methyl (*o*-bromomethyl) benzoate and ethyl (*o*-bromomethyl) benzoate were synthesized according to the literature [25] without further purification; the content (85%) was confirmed by ^{1}H NMR

TABLE V Selected bond lengths (Å) and bond angles (°) of compound **6**

O(1)–C(1)	1.397(7)	O(4)–C(23)	1.341(9)
O(1)–C(16)	1.466(7)	O(4)–C(24)	1.444(12)
O(2)–C(9)	1.390(7)	O(5)–C(32)	1.233(7)
O(2)–C(25)	1.430(7)	O(6)–C(32)	1.377(8)
O(3)–C(23)	1.193(8)	O(6)–C(33)	1.469(12)
C(1)–O(1)–C(16)	113.8(4)	O(4)–C(23)–C(22)	113.7(6)
C(9)–O(2)–C(25)	108.7(4)	O(1)–C(16)–C(17)	105.6(5)
C(23)–O(4)–C(24)	120.2(7)	O(2)–C(25)–C(26)	111.2(5)
C(32)–O(6)–C(33)	116.2(6)	O(5)–C(32)–O(6)	119.5(6)
O(3)–C(23)–O(4)	118.0(6)	O(5)–C(32)–C(31)	127.1(6)
O(3)–C(23)–C(22)	128.2(7)	O(6)–C(32)–C(31)	113.2(6)

spectroscopy. All reactions were carried out in a nitrogen atmosphere.

Synthesis

5, 11, 17, 23-Tetra-tert-*butyl-25, 26, 27, 28-tetrakis [2-(methoxycarbonyl)benzyloxy] calix[4]arene (3)*

A suspension of 1.0 g (1.35 mmol) *p-tert*-butyl-calix[4]arene **1** (toluene), 1.9 g (13.5 mmol) anhydrous potassium carbonate, and 3.6 g (13.5 mmol) (*o*-bromomethyl) methyl benzoate in 60 mL CH_3CN was refluxed for 5 days. After being cooled, the solvent was evaporated under reduced pressure. The residue was taken up in $CHCl_3$ (60 mL) and treated with 1 N HCl (2 × 20 mL). The organic layer was separated and washed twice with water, and dried (Na_2SO_4). After the solvent was evaporated, the crude compound was recrystallized from chloroform-methanol (1:4) and afforded compound **3** (1.04 g, 62%) as a white solid, m.p. 226–228°C; ^{1}H NMR($CDCl_3$, 400 MHz) δ: 8.14 (d, $J = 7.6$ Hz, 4H), 7.34 (d, $J = 7.6$ Hz, 4H), 7.18 (t, $J = 7.6$ Hz, 4H), 6.80 (t, $J = 7.6$ Hz, 4H), 6.79 (s, 8H), 5.29 (s, 8H), 4.15 (d, $J = 12.8$ Hz, 4H), 3.69 (s, 12H), 2.94 (d, $J = 12.8$ Hz, 4H) and 1.08 (s, 36H); ^{13}C NMR($CDCl_3$, 400 MHz) δ: 167.41, 152.49, 144.57, 140.31, 133.85, 132.12, 130.33, 129.77, 128.03, 126.84, 125.21, 74.57, 51.85, 33.83, 31.46 and 30.37. IR(KBr)ν: 1723 cm^{-1} (ArC = O); Anal. calcd. for $C_{80}H_{88}O_{12}$: C 77.39, H 7.14; found: C 77.36; H 7.15.

5, 11, 17, 23-Tetra-tert-*butyl-25-hydroxy-26, 27, 28-tris[2-(methoxycarbonyl)benzyloxy] calix[4]arene (4)*

A suspension of 1.0 g (1.35 mmol) *p-tert*-butyl-calix[4]arene **1** (toluene) and 5.5 g (20.25 mmol) (*o*-bromomethyl) methyl benzoate was dissolved in 20 mL anhydrous DMF, and the solution was stirred at room temperature for 2 h in the presence of 1.3 g (4.05 mmol) $Ba(OH)_2{\cdot}8H_2O$ and 1.2 g (7.83 mmol) BaO. The reaction mixture was diluted with water (200 mL) and extracted with chloroform. The following workup is in a manner similar to that described for **3** to yield (0.98 g, 60%) compound **4** as a white solid, mp. 111–113°C; ^{1}H NMR ($CDCl_3$; 400 MHz) δ: 8.80 (d, $J = 8.0$ Hz, 1H), 7.89 (d, $J = 8.0$ Hz, 1H), 7.76 (d, $J = 7.6$ Hz, 2H), 7.47 (d, $J = 7.6$ Hz, 2H), 7.41 (t, $J = 7.6$ Hz, 1H), 7.28 ~ 7.17 (m, 5H), 7.15 (s, 2H), 7.06 (s, 2H), 6.72 (s, 1H), 6.62 (s, 1H), 6.61 (s, 1H), 6.50 (s, 1H), 6.49 (s, 1H), 5.16

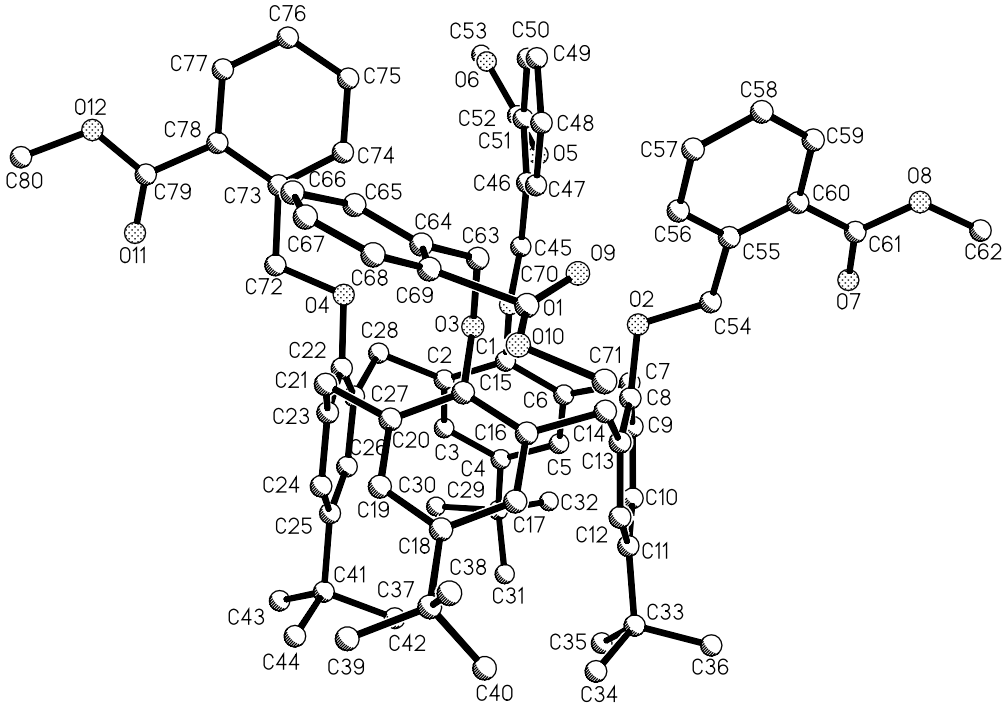

FIGURE 2 X-ray structure of compound **3**. For the clarity, the hydrogen atoms are omitted.

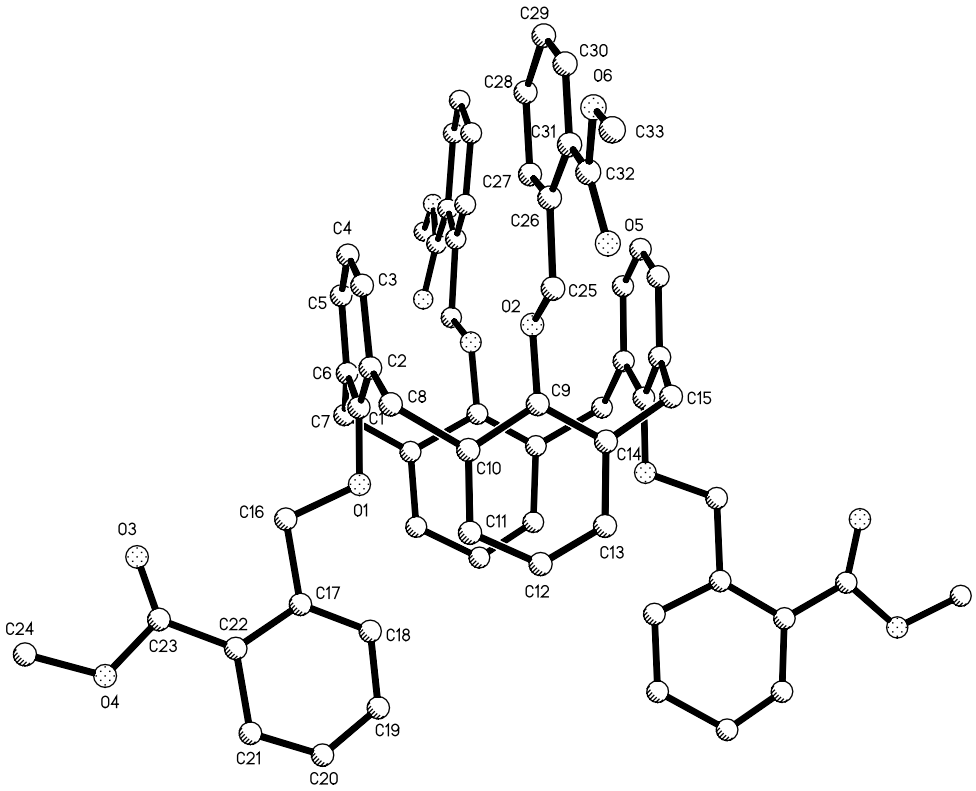

FIGURE 3 X-ray structure of compound **6**. For the clarity, the chloroform molecule and the hydrogen atoms are omitted.

(s, 2H), 5.04 (q, $J = 13.6$ Hz, 4H), 4.24 (d, $J = 13.6$ Hz, 2H), 4.15 (d, $J = 12.4$ Hz, 2H), 3.79 (s, 3H), 3.65 (s, 6H), 3.19 (d, $J = 13.2$ Hz, 2H), 3.04 (d, $J = 12.4$ Hz, 2H), 1.34 (s, 9H), 1.32(s, 9H) and 0.84 (s, 18H); ^{13}C NMR($CDCl_3$, 400 MHz) δ: 167.63, 167.35, 153.14, 150.81, 145.31, 141.05, 140.68, 138.84, 135.65, 132.88, 132.59, 132.54, 132.18, 131.85, 131.11, 130.89, 130.19, 129.82, 129.14, 128.42, 128.22, 127.42, 127.21, 126.39, 126.25, 125.94, 125.60, 125.40, 125.06, 124.91, 74.89, 74.43, 52.06, 51.94, 34.10, 33.82, 33.69, 31.73, 31.49, 31.36, 31.26, 31.03 and 30.27. IR (KBr) ν: 3423 (OH) and 1719 cm^{-1} (ArC = O); Anal. calcd. for $C_{71}H_{80}O_{10}{\cdot}CHCl_3$: C 71.31, H 6.73; found: C 71.40, H 6.72.

*5, 11, 17, 23-Tetra-*tert*-butyl-25, 27-dihydroxy-26, 28-bis[2-(methoxycarbonyl)benzyloxy] calix[4]arene (5)*

A suspension of 1.0 g (1.35 mmol) *p-tert*-butylcalix[4]arene **1** (toluene), 0.2 g (1.35 mmol) anhydrous

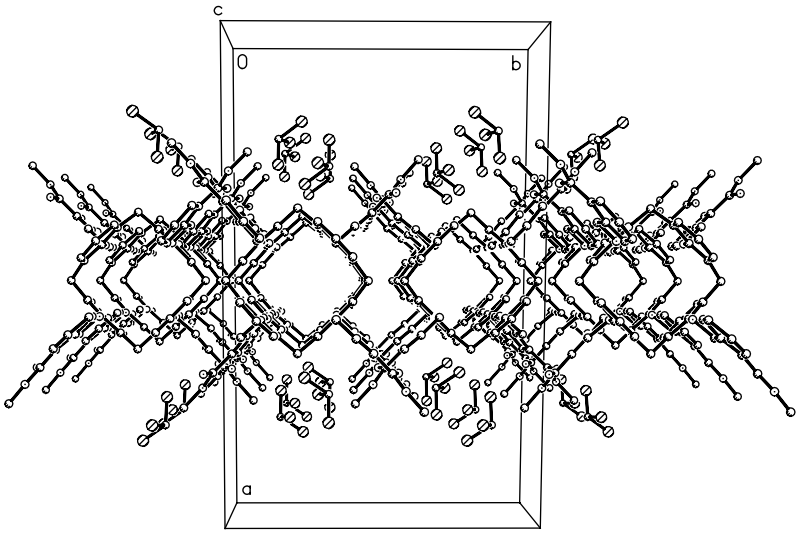

FIGURE 4 Perspective view of the crystal packing of compound **6**.

potassium carbonate, and 0.9 g (3.34 mmol) (*o*-bromomethyl) methyl benzoate in 60 mL CH_3CN was refluxed for 20 h. The following workup is in a manner similar to that described for **3** to yield compound **5** (0.84 g, 66%) as a white solid, mp. 221–222.5°C; ^{1}H NMR ($CDCl_3$; 400 MHz) δ: 8.67 (d, $J = 7.6$ Hz, 2H), 8.22 (s, 2H), 8.08 (d, $J = 7.6$ Hz, 2H), 7.51 (m, 4H), 7.24 (s, 4H), 7.19 (s, 4H), 5.54 (s, 4H), 4.38 (d, $J = 12.8$ Hz, 4H), 3.85 (s, 6H), 3.49 (d, $J = 12.8$ Hz, 4H), 1.26(s, 18H) and 1.05 (s, 18H); ^{13}C NMR($CDCl_3$, 400 MHz) δ: 167.66, 151.80, 151.29, 148.23, 142.47, 140.13, 134.20, 133.82, 131.19, 129.06, 128.50, 128.20, 127.91, 126.83, 126.43, 77.21, 52.44, 34.63, 34.37, 32.43, 31.98 and 31.31. IR (KBr) ν: 3442 (OH), 1722 (ArC═O) and 1266(C–O–C)cm^{-1}. Anal. calcd. for $C_{62}H_{72}O_8$: C 78.78, H 7.68%; found: C 78.79, H 7.71.

25, 26, 27, 28-Tetrakis[2-(methoxycarbonyl) benzyloxy] calix[4]arene (6)

A suspension of 0.5 g (1.18 mmol) calix[4]arene **2**, 6.2 g (18.8 mmol) anhydrous Cs_2CO_3, and 5.0 g (17.70 mmol) (*o*-bromomethyl) methyl benzoate in 60 mL CH_3CN was refluxed for 24 h. After being cooled, the solvent was evaporated under reduced pressure. The residue was taken up in $CHCl_3$ (60 mL) and treated with 1 N HCl (2 × 20 mL). The organic layer was separated and washed twice with water, and dried (Na_2SO_4). After the solvent was evaporated, the crude compound was recrystallized from chloroform-methanol (1:4) and afforded (0.67 g, 50%) compound **6** as a white solid, mp. 265–267°C; ^{1}H NMR($CDCl_3$, 400 MHz) δ: 8.12 (d, $J = 8.0$ Hz, 4H), 7.72 (t, $J = 7.6$ Hz, 4H), 7.52 (t, $J = 8.0$ Hz, 8H), 6.68 (d, $J = 7.6$ Hz, 8H), 6.48 (t, $J = 7.6$ Hz, 4H), 5.27 (s, 8H), 3.87 (s, 12H) and 3.63 (s, 8H); ^{13}C NMR($CDCl_3$, 400 MHz) δ: 167.24, 155.52, 140.60, 134.04, 131.86, 131.68, 130.15, 128.70, 126.63, 126.39, 121.83, 70.30, 52.02 and 37.12. IR (KBr) ν: 1718 cm^{-1} (C═O); Anal. calcd. for $C_{64}H_{56}O_{12}$·$CHCl_3$: C 68.69, H 5.05; found C 68.53, H 4.96.

25, 27-Dihydroxy-26, 28-bis[2-(methoxycarbonyl) benzyloxy] calix[4]arene (7)

0.50 g (1.18 mmol) Calix[4]arene **2** was treated with 0.85 g (2.95 mmol) (*o*-bromomethyl) methyl benzoate in the presence of 0.16 g (1.18 mmol) anhydrous K_2CO_3 in anhydrous CH_3CN (40 mL) in a manner similar to that described for **3** to yield (0.60 g, 70%) compound **7** as a white solid, mp. 234–236°C; ^{1}H NMR($CDCl_3$, 400 MHz) δ: 8.69 (d, $J = 7.6$ Hz, 2H), 8.08 (d, $J = 7.6$ Hz, 2H), 7.68 (s, 2H), 7.49 (t, $J = 7.6$ Hz, 2H), 7.41 (t, $J = 7.6$ Hz, 2H), 7.08 (d, $J = 7.6$ Hz, 4H), 6.87 (d, $J = 7.6$ Hz, 4H), 6.75 (t, $J = 7.6$ Hz, 2H), 6.68 (t, $J = 7.6$ Hz, 2H), 5.51 (s, 4H), 4.32 (d, $J = 13.2$ Hz, 4H), 3.88 (s, 6H) and 3.39 (d, $J = 13.2$ Hz, 4H); ^{13}C NMR($CDCl_3$, 400 MHz) δ: 167.21, 153.35, 152.12, 140.00, 133.77, 132.89, 130.57, 129.01, 128.54, 127.86, 127.17, 126.98, 126.72, 125.42, 118.95, 76.26, 52.13 and 31.32. IR (KBr) ν: 3439 (OH) and 1722(C═O) cm^{-1}; Anal. calcd. for $C_{46}H_{40}O_8$: C 76.65, H 5.59; found: C 76.24, H 5.57.

*5, 11, 17, 23-Tetra-***tert***-butyl-25, 26, 27, 28-tetrakis [2-(ethoxycarbonyl)benzyloxy] calix[4]arene (8)*

1.0 g (1.35 mmol) *p-tert*-Butylcalix[4]arene **1** was treated with 3.9 g (13.5 mmol) (*o*-bromomethyl) ethyl benzoate in the presence of 1.9 g (13.5 mmol) anhydrous K_2CO_3 in anhydrous CH_3CN in a manner similar to that described for **3** to yield compound **8** (1.26 g, 70%) as a white solid, mp.178–180°C; ^{1}H NMR($CDCl_3$, 400 MHz) δ: 8.19 (d, $J = 7.6$ Hz, 4H), 7.86 (d, $J = 7.6$ Hz, 4H), 7.17 (t, $J = 7.2$ Hz, 4H), 6.81 (s, 8H), 6.75 (t, $J = 7.2$ Hz, 4H), 5.30 (s, 8H), 4.29 (d, $J = 12.8$ Hz, 4H), 4.13 (m, 8H), 2.98 (d, $J = 12.8$ Hz, 4H), 1.2 (t, $J = 7.2$ Hz, 12H) and 1.08 (s, 36H); ^{13}C NMR($CDCl_3$, 400 MHz) δ: 166.94, 152.78, 144.51, 133.75, 132.10, 130.04, 129.77, 128.06, 126.69, 125.23, 74.81, 60.67, 33.83, 31.46, 30.43 and 14.21. IR (KBr) ν: 1718 (C═O) cm^{-1}; Anal. calcd. for $C_{84}H_{96}O_{12}$·CH_3OH: C 76.77, H 7.58; found: C 76.53, H 7.29.

Solvent Extraction

Two-phase solvent-extraction was carried out between water (5.0 mL, [alkali picrate] $= 2.50 \times 10^{-4}$ M, [MOH] $= 0.10$ M, [MCl] $= 0.50$ M, $M^+ = Li^+$, Na^+, K^+, Cs^+) and dichloromethane (5.0 mL, [Ionophore] $= 2.50 \times 10^{-3}$M) [15]. The two-phase mixture was shaken for 30 min at 25°C. The preliminary experiment showed that this period is enough to attain the distribution equilibrium. The extraction efficiency was determined spectrophotometrically from the decrease in the absorbency of the picrate ion in the aqueous phase at 355 nm. Control experiments showed that no picrate extraction occurred in the absence of a calix[4]arene derivative.

^{1}H NMR Complexation Experiments

From stock solution (1.0 mol/L) of KSCN in CD_3OD, aliquots were withdrawn with a 10μL syringe and added to a $CDCl_3$ solution ($\approx 10^{-2}$ mol/L) of the ligand directly in the NMR tube. The spectra were registered after each addition and the temperature of the NMR probe kept constant at 25°C.

X-ray Crystal Structure Determination of Compounds 3 and 6

A colorless prismatic crystal was mounted on a glass fiber. All measurements were conducted on a Rigaku Raxiv-IV imaging plate with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The data were

collected for Lorentz and polarization effects. The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were performed using the teXsan crystallographic software package.

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