Syntheses and Properties of New Pendant-armed Calix[4]arene Derivatives as Cesium Selective Ionophore

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Two new pendant-armed calix[4]arene derivatives 5 and 6 have been synthesized. The study of alkali metal picrates extraction indicates that both compounds show preference of cesium cation, compound 6 in 1,3-alternate conformation has better extractibility for Cs^+ than compound 5. The coordination behavior of compound 6 with cesium cation was studied by ^1H NMR spectroscopy. The Cs^+ selective electrode based on compound 6 exhibits a linear, near Nernstian response characteristics, the slope is 56.4 mV/decade in the concentration range of 10^{-4}—10^{-1} mol/L, the selectivity coefficient ($\log K^{pot}_{Cs,Na}$) is −3.39.

Keyword Pendant-armed, calixarene, cesium, selective

Introduction

Calixarenes, and calix[4]arenes in particular, have proved to be very useful building blocks in the synthesis of receptors of cations, anions and neutral molecules.[1,2] Recently, a family of calix[4]arene-crown-6 and calix[4]arene-bis-crown-6 derivatives were successfully prepared and highly selective ionophores for cesium ion.[3-8] Their complexation selectivities were shown to be depended on the simultaneous collaboration of the size of the crown ether ring, the polarity of the conformation and the strength of the cation/ligand-π-electron interaction.

However, it is also well known that the introductions of the functional pendant group in the lower rim have been chemically transformed into a variety of derivatives designed for the selective binding of various cations and neutral compounds.[9-13] To our knowledge, such kind of ligands as cesium ionophores was not reported.

It could be assumed that the introduction of functional binding sites such as ethoxy expanded arisyl group will increase the cavity size and the flexible pendant can coordinate alkali cation larger than potassium cation. Moreover, the cation-π interaction may exist, if the calix[4]arene is in 1,3-alternate conformer. From this point of view, two new pendant-armed calix[4]arene derivatives, 5,11,17,23-tetra-*tert*-butyl-26,28-bis[2-(*o*-methoxyphenoxy)ethoxy]-25,27-dihydroxy-calix[4]arene (**5**) and 25,26,27,28-tetra[2-(o-methoxyphenoxy)ethoxy]calix[4]arene (**6**), in 1,3-alternate conformation were synthesized. The percentage of extraction of CsPic reached 60.6% using **6** as an extractant; NaPic in organic phase could not be detected in the same condition. In order to elucidate the high selective complexation of compound **6** for Cs^+, the coordination behavior of **6** with CsI in solution was studied by ^1H NMR.

Experimental

Uncorrected melting points were measured on a WC-1 apparatus. Elemental analyses were determined with a Carlo Erba 1106 elemental analyzer. ^1H NMR and ^{13}C NMR were recorded on a Bruker DPX 400 spectrometer using $CDCl_3$ as the solvent (if not marked) and TMS as an internal standard. IR spectra were recorded on a Perkin-Elmer FTIR-1750 spectrophotometer as a

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KBr pellet. All EMF measurements were performed using an FL-G1 pH/mV meter (Hangzhou, China) allowing readings with an accuracy of ± 0.1 mV. The selectivity coefficients were analyzed by using an ISE-Computer Analyzer (New technology Co., Zhengzhou Univ., China). The presence of solvent in the analytical samples was confirmed by ^1H NMR spectroscopy. Compounds **1**[14] and **2**[15] were prepared according to the literature. Ethylene carbonate and potassium tetrakis (*p*-chlorophenyl) borate (KTpClPB) were purchased from Fluka. *o*-Nitrophenyl octyl ether was prepared according to literature.[16] THF was distilled before use. Other chemicals were of reagent grade and used without further purification.

2-*Hydroxyethyl o-methoxyphenyl ether* (**3**)

A mixture of *o*-methoxyphenol (3.7 g, 30 mmol) and ethylene carbonate (2.7 g, 33 mmol) was heated together with tetrabutylammonium iodide (10 mmol) at 155—160℃ for 3 h. The resultant mixture was dissolved in chloroform (50 mL) and then washed with water (20 mL). The organic layer was dried with anhydrous calcium chloride and subsequent distillation *in vacuo* to give the product **3** (4.4 g) in the yield of 88%, b.p. 126℃/266 Pa. ^1H NMR ($CDCl_3$) δ: 3.64 (s, 1H, OH), 3.83 (s, 3H, OCH_3), 3.92 (t, J = 6.4 Hz, 2H, CH_2OH), 4.09 (t, J = 6.4 Hz, 2H, $ArOCH_2$), 6.86—6.96 (m, 4H, ArH). IR ν: 3300, 1070 (OH), 1230 (Ar - O - C) cm^{-1}.

2-*Tosyloxyethyl o-methoxyphenyl ether* (**4**)

p-Tosyl chloride (6 g, 31.5 mmol) was added in small portions to a mixture of **3** (5 g, 30 mmol) and dry pyridine (50 mL) at 0℃. The resultant mixture was stirred at room temperature for 48 h and poured into ice water. The precipitate was filtered and washed with water. The solid was dried *in vacuo*, recrystallized from ethanol-ethyl acetate to give white crystal of **4** (5.8 g) in the yield of 60%, m.p. 95—97℃. ^1H NMR ($CDCl_3$) δ: 2.44 (s, 3H, Tosyl-CH_3), 3.82 (s, 3H, OCH_3), 4.22 (t, J = 6.1 Hz, 2H, Tosyl-OCH_2), 4.37 (t, J = 6.1 Hz, 2H, Tosyl-OCH_2), 6.80—6.98 (m, 4H, ArH), 7.32 (d, J = 8.0 Hz, 2H, Tosyl-H), 7.82 (d, J = 8.4 Hz, 2H, Tosyl-H). IR ν: 1359 ($\nu_{SO_2}^{as}$), 1230(Ar - O - C), 1188, 1177, 1124 ($\nu_{SO_2}^{s}$) cm^{-1}. Anal. Calcd for $C_{16}H_{18}O_5S$: C 59.61; H 5.63; Found: C 60.33, H 5.68.

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

A suspension of *p-tert*-butylcalix[4]arene (**1**) (1.0 g, 1.35 mmol), anhydrous K_2CO_3 (0.38 g, 2 mmol), and 2-tosyloxylethyl o-methoxyphenyl ether (**4**) (0.96 g, 2.2 mmol) in dry CH_3CN (60 mL) was refluxed under nitrogen for 24 h. After evaporation of the solvent, the mixture was taken up in $CHCl_3$ (60 mL) and washed with HCl (1 mol/L, 2 × 30 mL) and brine (2 × 30 mL). The organic layer was dried over $MgSO_4$ and concentrated. The crude reaction mixture was separated with column chromatography (petroleum ether/$CHCl_3$2:1) to offer pure **5** (0.6 g, 46%) as a white solid, m.p. 148—150℃ (from $CHCl_3$: CH_3OH = 1 : 1). ^1H NMR δ: 0.94 (s, 18H, $C(CH_3)_3$), 1.29 (s, 18H, C-$(CH_3)_3$), 3.30 (d, J = 12.8 Hz, 4H, $ArCH_2Ar$), 3.72 (s, 6H, OCH_3), 4.36 (t, J = 5.2 Hz, 4H, anisyl-OCH_2), 4.41 (d, J = 12.8 Hz, 4H, $ArCH_2Ar$), 4.45 (t, J = 5.2 Hz, 4H, $ArOCH_2$), 6.76 (s, 4H, ArH), 7.01—6.85 (m, 8H, anisyl-H), 7.02 (s, 2H, ArOH), 7.04 (s, 4H, ArH). ^{13}C NMR ($CDCl_3$) δ: 150.70, 150.02 (**C**$_i$, Ar), 149.96, 148.27 (anisyl), 146.77, 141.23, 132.52, 127.93 (**C**$_o$, **C**$_p$, Ar), 125.51, 124.98 (ArH), 121.74, 120.92, 114.71, 112.17 (anisyl), 74.11, 67.81 (OCH_2), 55.84 (OCH_3), 33.89 (**C**$(CH_3)_3$), 33.82 (**C**-$(CH_3)_3$), 31.73 (C(**C**H_3)$_3$), 31.56 (Ar**C**H_2Ar), 31.02 (C(**C**H_3)$_3$). Anal. Calcd for $C_{62}H_{76}O_8 \cdot CH_3OH$: C 77.11, H 8.21; Found: C 77.20, H 8.00.

25, 26, 27, 28-*Tetrakis*[2-(*o-methoxyphenoxy*) *ethoxy*]-*calix*[4]*arene* (**6**)

A suspension of calix[4]arene (**2**) (1.0 g, 2.36 mmol), anhydrous K_2CO_3 (0.65 g, 4.72 mmol), and 2-tosyloxyethyl *o*-methoxyphenyl ether (**4**) (1.60 g, 5 mmol) in dry CH_3CN (50 mL) was refluxed under nitrogen for 7 days. The workup was similar to that described for **5**. The residue was purified with column chromatography (petroleum ether/EtOAc 8:1) to give pure white solid **6** (1.23 g, 51%). m.p. 167—169℃ (from $CHCl_3$:CH_3OH = 1:1). ^{1}H NMR δ: 3.70 (s, 8H, $ArCH_2Ar$), 3.86 (s, 12H, OCH_3), 4.03 (t, J = 5.2 Hz, 8H, anisyl-OCH_2), 4.13 (t, J = 5.2 Hz, 8H, $ArOCH_2$), 6.57 (t, J = 7.6 Hz, 4H, ArH), 6.90—6.95 (m, 16H, anisyl-H), 7.10 (d, J = 7.6 Hz, 8H, ArH). ^{13}C NMR ($CDCl_3$) δ: 155.77 (C_i, Ar), 149.77, 148.42 (anisyl), 133.67, 130.23, 122.27 (C_p, C_o, C_m, Ar), 121.47, 120.95, 114.13, 111.84 (anisyl), 70.02, 68.12 (OCH_2), 55.85 (OCH_3), 36.05 ($ArCH_2Ar$). Anal. Calcd for $C_{64}H_{64}O_{12}$: C 74.98, H 6.29; Found: C 75.08, H, 6.32.

Solvent extraction

Two-phase solvent extraction was carried out between water (5.0 mL, [MPic] = 2.50 × 10^{-4} mol/L, [MOH] = 0.10 mol/L, [MCl] = 0.50 mol/L, M^+ = Na^+, K^+, Cs^+) and dichloromethane (5.0 mL, [Compound **5** or **6**] = 2.50 × 10^{-4} mol/L). The two-phase mixture was shaken for 30 min at 25℃. The preliminary experiment showed that 30 min was enough to attain the distribution equilibrium. The extractibility was determined spectrophotometrically from the picrate ion in the aqueous phase at 355 nm. Control experiments showed that no picrate extraction occurred in the absence of compound **5** or **6**.

^{1}H NMR *complexation experiments*

From stock solution (1.0 mol/L) of CsI in CD_3COCD_3 (CD_3COCD_3 was used instead of $CDCl_3$ owing to the low solubility of CsI in $CDCl_3$, and CsI was used instead of CsPic owing to the interference of the picrate protons), aliquots were withdrawn with a 10 μL syringe and added to a CD_3COCD_3 solution ($\approx 10^{-2}$ mol/L) of compound **6** directly in the NMR tube. The spectra were registered after each addition and the temperature of the NMR probe was kept at 25℃.

Electrode fabrication and EMF *measurement*

Poly(vinyl chloride) membrane for ion-selective electrodes was prepared in a conventional way.[17] The typical composition (W/W) of a membrane was as follows: 1% of the respective ionophore, 33% of poly-(vinyl chloride), 65.7% of *o*-nitrophenyl octyl ether and 0.3% potassium tetrakis(4-chlorophenyl) borate. All the components were dissolved in freshly distilled THF. The solution was poured into a glass ring (28 mm, i.d.) located on a glass plate. THF was evaporated slowly to obtain a tough flexible membrane with 0.1—0.2 mm thickness. The EMF measurements were carried out at 25 ± 0.1℃ by using a pH/mV meter equipped with a double-junction type reference electrode. The representative electrochemical cell for EMF measurements was of the following type: Ag-AgCl | internal solution (0.10 mol/L CsCl) | PVC membrane | measured solution | 0.10 mol/L NH_4NO_3 | reference electrode. The electrode was conditioned over night in a 0.10 mol/L CsCl solution before measurements. The slope of the electrodes was determined according to IUPAC recommendations.[18] The selective coefficients, $K^{pot}_{Cs,M}$, were determined by using a fixed interference method (FIM) with background concentration of 0.10 mol/L for the interference ions. All sample solutions contained $MgCl_2$ (0.1 mol/L) as an ionic strength buffer.

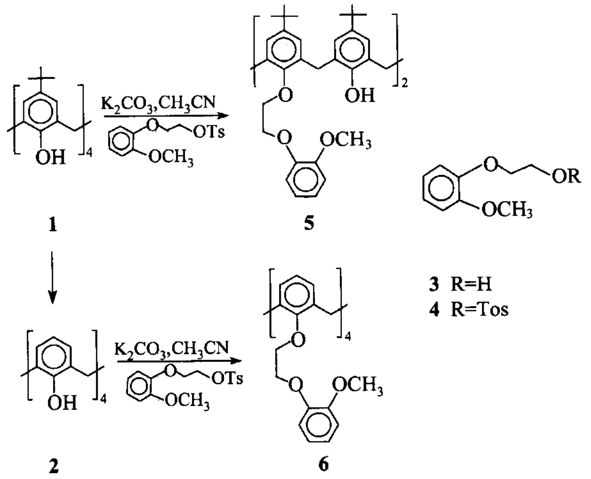
Results and discussion

Syntheses and structural analyses

Compounds **5** and **6** were synthesized according to Scheme 1. The structure of compound **5** was analyzed by ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum shows a typical AB pattern for the methylene bridge protons at δ 4.41 and 3.30 (J = 12.8 Hz), indicating that compound **5** exists in the distal-cone conformation. The tert-butyl protons are also present at δ 1.29 and 0.94 in a 1:1 ratio corresponding to a distal-cone conformation.

By using *p*-H-calix[4]arene **2** instead of *p*-*tert*-butylcalix[4]arene, the tetraalkylated calix[4]arene **6** in 1,3-alternate conformation was obtained under the same condition. The ^{1}H NMR spectrum of compound **6** shows that the characteristic peak for the $ArCH_2Ar$ methylene protons gives a singlet at δ 3.70, indicating that compound **6** is in the 1,3-alternate conformation. The similar result was also reported by Reinhoudt *et al*.[19] The ^{13}C NMR spectrum shows the absorption of $ArCH_2Ar$ is present at δ 36.05, which slightly deviates from that of δ 37.0 mentioned by de Mendozu *et al*.[20] for calix[4]arene in the 1,3-alternative conformation.

Scheme 1 Syntheses of compounds **5** and **6**



Two-phase solvent extraction

The percentage extraction for alkali picrates by using **5** and **6** are summarized in Table 1. The results show that **6** exhibits highly selectivity and complexation for cesium cation, while sodium cation could not be detected in the organic phase. The extractibility of compound **5** is poorer than that of **6**, although it had a preference for Cs^+. It can be seen that in compounds **5** and **6**, the pendant not only is longer, but also contains flexible ethylene group and certain coordination sites. Therefore, compounds **5** and **6** can provide ionophoric cavities for alkali metal cations. However, the ionophoric cavity can only attain a certain size which is suitable for Cs^+ owing to the steric effect of the rigid anisyl groups. As a result, both compounds have a preference of Cs^+ to Na^+ and K^+. Moreover, compound **6** contains four attached pendants and is a 1,3-alternate conformer which is sterically less crowed. It means that compound **6** has two equivalent coordination cavities at the two opposite sides of the calix backbone, whereas compound **5** has only one coordination cavity. So cooperated with the cation-π interaction which is confirmed by following ^1H NMR study, compound **6** shows better extractibility for Cs^+ than that of compound **5**.

Table 1 Percent extraction of alkali metal picrates in CH_2Cl_2 at 25℃[a]

Compound	Extractibility (%)		
	Na^+	K^+	Cs^+
5	0	6.4	25.2
6	0	36.0	60.6

[a] Aqueous phase (5.0 mL) contains M^+Pic^- (2.50×10^{-4} mol/L), MOH (0.10 mol/L), and MCl (0.50 mol/L) [$M^+ = Na^+$, K^+, Cs^+]. Organic phase (CH_2Cl_2, 5.0 mL) contains compound **5** or **6** (2.50×10^{-4} mol/L).

^1H NMR *study of coordination behavior of compound* 6

In order to further elucidate the interaction of ionophore **6** and Cs^+, the coordination behavior of compound **6** with CsI was studied by using NMR. The ^1H NMR spectra of free compound and complex are shown in Table 2, respectively.

Table 2 ^1H NMR spectra data of compound **6** and its complexes with CsI

	6	**6** + Cs^+ (1:1)	**6** + Cs^+ (1:10)
$ArCH_2Ar$	3.721 (s)	3.903 (s)	3.958 (s)
OCH_2CH_2O	4.165 (t, J = 5.2 Hz) 4.037 (t, J = 5.2 Hz)	4.187 (t, J = 2.4 Hz) 4.161 (t, J = 2.4 Hz)	4.207 (s)
OCH_3	3.814 (s)	3.812 (s)	3.833 (s)
Ar-H (p)	6.525 (t, J = 7.6 Hz)	6.719 (t, J = 7.6 Hz)	6.779 (t, J = 7.6 Hz)
Ar-H (m)	7.202 (d, J = 7.6 Hz)	7.272(d, J = 7.6 Hz)	7.202 (d, J = 7.6 Hz)
Anisyl-H	6.997 (d, J = 7.6 Hz, 1H) 6.993 (d, J = 7.6 Hz, 1H) 6.902 (m, 2H)	7.072—6.921 (m)	7.104—6.948 (m)

The ^1H NMR spectra show that the addition of Cs^+ gives rise to remarkable changes both in chemical shift value and in splitting pattern of compound **6**. Two sets of triplet peaks for OCH_2CH_2O groups of free compound at δ 4.04 and 4.17 move to 4.16 and 4.19, respectively, and appear as two broad triplets when the mole ratio of compound **6** to Cs^+ reaches 1∶1. This may be ascribed to the fact that the electron density of the OCH_2CH_2O groups is remarkably decreased by the strong ethereal oxygen-cesium complexation which leads to a downfield shifted peak. The arene protons (ArH) in the calix backbone shift to downfield due to the presence of the cation-π interaction. The downfield shift of protons in $ArCH_2Ar$ also reflects this interaction.[21] The peak of OCH_3 group has minute change, indicating that the oxygen atom in this group does not participate in the coordination with cesium cation. So, the cesium cation is trapped in the cavity composed of two phenolic oxygens, two ethereal oxygens and two π-basic benzene rings, by both metal-oxygen electrostatic interactions and cation-π interactions.

It is interesting to note that the ^1H NMR spectrum of **6**·Cs^+ (mole ratio 1∶1) gives symmetrical peaks for the OCH_2CH_2O group. Since there are two coordination cavities in the opposite sides of compound **6**, it is suggested that cesium cation could fill alternatively in these cavities.[21]

When the mole ratio of **6**∶Cs^+ reaches 1∶2, the ^1H NMR is the same as that of 1∶1. This could be explained by the electrostatic repulsion between two Cs^+ ions because the two coordination cavities in the 1,3-alternate conformers are very close to each other.[22] The ^1H NMR spectrum of compound **6** in the presence for extreme cesium cation (10-fold) was also studied. The result shows that the two sets of triplet peaks for the OCH_2CH_2O group of free compound move to 4.20 and appear as a single peak. It indicates that the two coordination cavities are all filled with cesium cations, *i.e.*, the complex mole ratio of compound **6** to Cs^+ changes to 1∶2 in the presence of extreme cesium cation. Although there is electrostatic repulsion between two coordination cavities, the high concentration of cesium cation drives the equilibrium towards the formation of 1∶2 complex. Therefore, it also can explain why compound **6** extracts more Cs^+ into organic phase than compound **5** under the same condition.

Response characteristics of ion selective electrode

The slopes for potentiometric response based on compounds **5** and **6** towards the alkali metal ions are shown in Table 3. The electrode based on compound **6** exhibits a linear, near Nernstian response characteristics for Cs^+. The slope is 56.4 mV/decade in the concentration range of 10^{-4}—10^{-1} mol/L. Potentiometric selectivities of ISE for Cs^+ over other alkali metal cations, alkaline earth metal cations, and H^+, NH_4^+ have been assessed (Fig. 1). The electrode shows a high Cs^+ selectivity relative to Na^+ ($\log K^{pot}_{Cs,Na} = -3.39$). The reproducibility and lifetime of the electrode were also investigated. Potential readings of the electrode dipped alternately three times into stirred tested solution of Cs^+ (10^{-3} and 10^{-2} mol/L) show standard deviations within 0.4 mV. The electrode has demonstrated an effective lifetime of at least two months by a consecutive use of the electrode for the sample solutions studied. All these results show that compound **6** could be used as an ionophore for Cs^+-PVC membrane selective electrode.

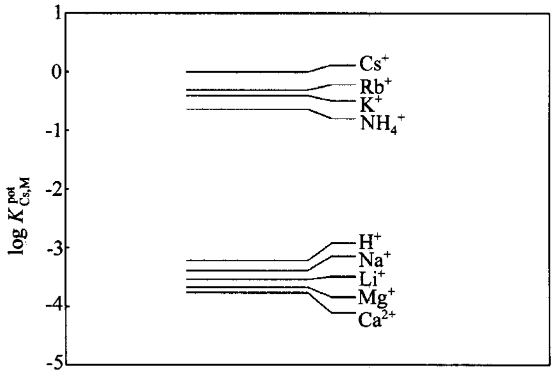


Fig. 1 Selectivity coefficients of various interfering ions.

Table 3 Potentiometric response characteristics of the electrode doped compounds **5** or **6**

Compound	Tested ions	Slope (mV/decade)	Linear range (mol/L)	Correction coefficients
5	Na^+	−2.3	10^{-4}—10^{-2}	−0.8927
	K^+	14.4	10^{-3}—10^{-1}	0.9910
	Cs^+	14.6	10^{-4}—10^{-1}	0.9755
6	Na^+	−10.4	10^{-5}—10^{-1}	−0.5574
	K^+	39.8	10^{-4}—10^{-1}	0.9998
	Cs^+	56.4	10^{-4}—10^{-1}	0.9998

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