

Synthesis of a Tweezer-like Bis(phenylthiopropoxy)calix[4]-arene as a Cation/ π Enhanced Sensor for Ion-Selective Electrodes

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Two novel 25,27-dihydroxy-26,28-bis(3-phenylthiopropoxy)-calix[4]arene (3) and 25,27-dihydroxy-26,28-bis(3-phenylthiopropoxy)-5,11,17,23-tetra-*tert*-butylcalix[4]arene (4) were synthesized for the evaluation of their ion-selectivity in ion-selective electrodes (ISEs). ISEs based on 3 and 4 as neutral ionophores were prepared, and their selectivity coefficients for Ag^+ ($\lg K_{\text{Ag},M}^{\text{pot}}$) were investigated against other alkali metal, alkaline-earth metal, aluminum, thallium (I), lead and some transition metal ions using the separate solution method (SSM). These ISEs showed excellent Ag^+ selectivity over most of the interfering cations examined, except for Hg^{2+} and Fe^{2+} having relative smaller interference ($\lg K_{\text{Ag},M}^{\text{pot}} \leq -2.1$).

Keywords calix[4]arenes, synthesis, silver selectivity, ion-selective electrode

Introduction

In the past decade, there has been considerable interest in the use of macromolecules as elements of micro-electronic systems and sensors. Calixarenes having a rigid inherent cavity are a kind of these macromolecules, which are a category of macrocyclic platforms, and can recognize ions and organic molecules. The phenolic groups of these macrocyclic molecules can be converted into derivatives containing a wide range of functional groups.¹ Many cal-

ixarene derivatives can recognize a target metal ion by the cavity size of the cyclic molecule together with the chelating effect of their functional groups. Therefore, functionalized calixarenes are one of the most promising materials for ion-selective electrodes (ISEs). In fact, a number of calixarene derivatives, especially calix[4]arene derivatives have been exploited as the ionophores of liquid membrane electrodes which are sensitive to main group metal ions.²⁻⁹ However, transition metal ion-sensitive ionophores based on calixarene scaffolds are relatively rare.^{10,11} In the past two years, a number of calix[4]-arenes containing nitrogen, sulfur, phosphorous (III) and selenium atoms as soft binding sites for transition metal ions have been prepared in our group. Their performances as ionophores for ISEs were evaluated.¹²⁻²⁰ We found that ISEs based on these calix[4]arene derivatives exhibited excellent silver selectivity against other interfering ions. However, those ionophores containing hard donors, such as ester and hydroxy groups close to the soft donors usually show strong Hg^{2+} interference toward the selectivity of silver ion.²⁰ In addition, compared with alkyl groups, aryl groups usually give an increase of selectivity for silver ion over Hg^{2+} while they are close to the soft donors through so-called cation/ π interaction.^{15,16} These results encouraged us to devote our efforts to the design of some

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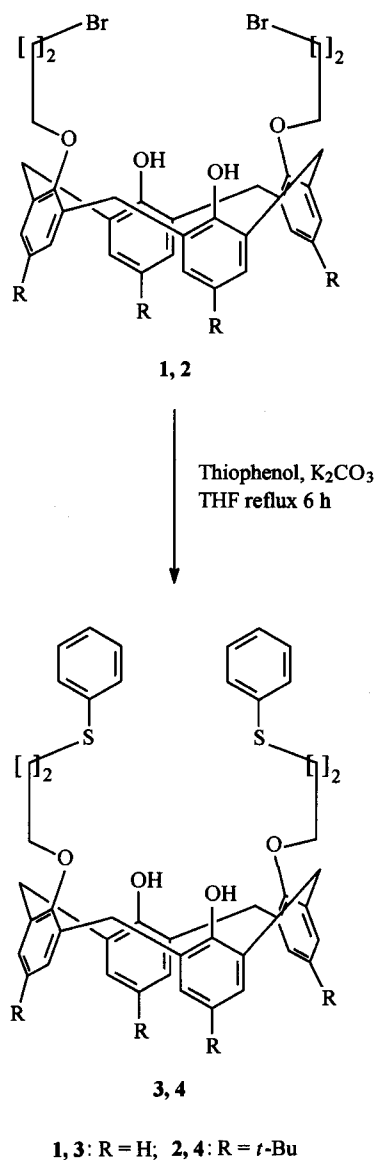
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new receptors with π systems being close to the soft donors as assistant donors to enhance the cation selectivity.

In this paper, we wish to report the syntheses and characterization of 25,27-dihydroxy-26,28-bis(phenylthiaproxy) calix[4]arene (**3**) and 25,27-dihydroxy-26,28-bis-(phenylthiaproxy)-5,11,17,23-tetra-*tert*-butylcalix[4]arene (**4**) (Scheme 1) and also their selective behaviors to silver ion monitored by electromotive force measurements of polymer membrane electrodes. The comparison of the ISEs behaviors of **3** and **4** with those of our previous work might provide us further understanding of the structure-selectivity relationship in the Ag^+ -ISEs.

Scheme 1



Results and discussion

Syntheses

Calix[4]arene dibromides **1** and **2** were prepared according to the reported procedures.^{15,21} Calix[4]arenes **3** and **4** were synthesized in the respective yields of 50% and 61% by the reaction of calix[4]arene dibromides **1** and **2** with thiophenol in the presence of anhydrous potassium carbonate as base as shown in Scheme 1. ^1H NMR spectra indicate that calix[4]arene **3** keeps the cone conformation. Two doublets of the protons within the methylene bridge of the calix[4]arene framework at δ 4.28 and 3.38 with $J = 12.8$ Hz, and the separation of the aryl protons of calix[4]arene skeleton (two doublets at δ 7.05 and 6.90 with the J values of 7.3 and 7.3 Hz for the *meta*-PhH, two triplets at δ 6.72 and 6.64 with the J values of 7.3 and 7.3 Hz for the *para*-PhH) suggest that **3** is in a "pinched" cone conformation. Two doublets at δ 4.20 and 3.25 with $J = 13.0$ Hz for the protons of the methylene bridge of the calix[4]arene skeleton, two singlets at δ 6.97 and 6.78 for the aryl protons within the calix scaffold and the separation of the *tert*-butyl resonance at δ 1.21 and 0.93, respectively, indicated that **4** was also in a "pinched" cone conformation.

Ag^+ selectivity

The Ag^+ selectivity of 25,27-dihydroxy-26,28-bis(phenylthiaproxy)calix[4]arene (**3**) and 25,27-dihydroxy-26,28-bis(phenylthiaproxy)-5,11,17,23-tetra-*tert*-butylcalix[4]arene (**4**) was evaluated by the potentiometric selectivity coefficients ($K_{\text{Ag},\text{M}}^{\text{pot}}$) determined for polymer membranes containing these ionophores. The polymer membrane was composed of PVC as the matrix, dibutyl phthalate (DBP) as the membrane solvent, and phenylthiaproxy functionalized calix[4]arene as the ionophore. The membranes also contained 0.5% of potassium tetrakis(*p*-chlorophenyl) borate (KTClPB) for the purpose of reducing membrane resistance and suppressing permeation of counteranions in the aqueous phase into the membrane phase. The potentiometric selectivity coefficients for Ag^+ , which were determined by the separated solution method (SSM), are illustrated in Table 1. The selectivity coefficient ($K_{\text{Ag},\text{M}}^{\text{pot}}$) represents the preference of the ISE (or PVC membrane) containing the phenylthiaproxy functionalized calix[4]arene for Ag^+

over the other cations. Therefore, the coefficient $K_{Ag,M}^{pot}$ defines the ability of an ISE (or membrane) to recognize different ions under the same conditions. The smaller the value is, the greater the electrode preference for the primary ion (I^+) over the interfering ion (M^+) is.

The potentiometric selectivity coefficient, $K_{Ag,M}^{pot}$, determined here is defined by the Nicolsky-Eisenman equation [Eq. (1)].

$$E = E^0 + \frac{2.303RT}{F} \lg [a_{Ag} + K_{Ag,M}^{pot} (a_M)^{1/Z_M}] \quad (1)$$

where E represents the experimentally observed potential, R the gas constant, T the thermodynamic temperature in K, F the Faraday constant, a_{Ag} the Ag^+ activity, a_M the activity of the interfering cation, and Z_M the charge of the interfering cation. The selectivity coefficients were determined by a mixed-solution method.²² In order to evaluate the selectivity of the Ag^+ over other cations, the separated solution method (SSM) was employed. According to this method, the potentiometric selectivity coefficients, $K_{Ag,M}^{pot}$, can be evaluated from the potential measurements on solutions containing a fixed concentration of the interfering ions (M^{n+}) and varying the concentration of Ag^+ ion using Eq. (2).

$$K_{Ag,M}^{pot} = a_{Ag} / (a_M)^{1/Z_M} \quad (2)$$

The resulting $\lg K_{Ag,M}^{pot}$ values are summarized in Table 1.

As can be seen from Table 1, polymer membranes containing bis(phenylthiaproxy)calix[4]arene **3** and **4** as sensors gave excellent $\lg K_{Ag,M}^{pot}$ values (≤ -3.3) against most of the interfering cations examined (*i. e.*, Li^+ , Na^+ , K^+ , Cs^+ , NH_4^+ , Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} , Al^{3+} , Tl^+ , Ni^{2+} , Zn^{2+} , Cu^{2+} , Cd^{2+} , Co^{2+} , Fe^{3+} , Pb^{2+} , *etc.*), except for Hg^{2+} and Fe^{2+} . It is interesting to note that, despite four *tert*-butyls residing on the upper-rim of ionophore **4**, ISEs based on **3** and **4** exhibited characteristic ion selectivity tendencies, which resembled each other. The performance of the present ISEs is largely superior to that displayed by traditional Ag_2S -based electrode and is satisfactory as Ag^+ -ISE. In fact, polymer membranes containing ionophores **3** and **4** gave excellent $\lg K_{Ag,M}^{pot}$ values (≤ -3.3) against Li^+ , Na^+ , K^+ , Cs^+ , NH_4^+ , Ca^{2+} , Mg^{2+} , Sr^{2+} , Ba^{2+} , Al^{3+} ,

Tl^+ , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} , indicating that **3** and **4**-based ISEs possess high Ag^+ selectivities and only weakly respond to the above interfering ions. The strong Hg^{2+} interference of some ionophore-based ISEs and traditional Ag_2S -based ISE is largely eliminated in **3** and **4**-based ISEs ($\lg K_{Ag,M}^{pot} \leq -2.1$ for most of the present ISEs). The possible explanation is that those ions with high hydration energies, such as Li^+ , Na^+ , K^+ , Cs^+ , NH_4^+ , Ca^{2+} , Mg^{2+} , Sr^{2+} , Ba^{2+} , Al^{3+} , Tl^+ , Pb^{2+} and most divalent transition metal ions, cannot strongly interact with sulfur donors in the ionophores, while less heavily hydrated soft Ag^+ coordinates soft sulfur donors selectively. As we discussed previously, the tweezer-like structures of **3** and **4** will largely benefit the ionophores using two points to coordinate silver ion in the most stable *trans*-conformation of two coordinated silver compounds.

Table 1 Selectivity coefficients ($\lg K_{Ag,M}^{pot}$) of the electrodes based on ionophores **3** and **4**

Ion	$\lg K_{Ag,M}^{pot}$	
	3	4
Ag^+	0	0
Li^+	-4.6	-4.3
Na^+	-4.2	-3.6
K^+	-4.2	-4.4
Cs^+	-4.8	-4.0
NH_4^+	-4.0	-4.1
Mg^{2+}	-5.1	-5.8
Ca^{2+}	-5.3	-5.4
Sr^{2+}	-5.1	-6.4
Ba^{2+}	-5.1	-6.4
Al^{3+}	-4.9	-5.7
Tl^+	-4.8	-3.7
Pb^{2+}	-3.8	-4.2
Fe^{2+}	-2.1	-3.5
Fe^{3+}	-3.9	-3.7
Co^{2+}	-5.1	-4.4
Ni^{2+}	-5.0	-5.6
Cu^{2+}	-4.3	-5.3
Zn^{2+}	-3.3	-4.4
Cd^{2+}	-4.5	-4.5
Hg^{2+}	-2.2	-2.6

The response characteristics of silver ISEs such as response slope, linear range and response time are summarized in Table 2. As can be seen from Table 2, although ionophores **3** and **4**-based ISEs gave the same characteristic ion selectivity tendencies, whether the *tert*-butyl groups exist on the upper-rim of the calix scaffold or not, the Nernstian slopes of the two ISEs are pretty different. It is known that the higher the Nernstian slope, the higher the ISE response. The Nernstian slope of ISE based on **4** ($59.2 \text{ mV} \cdot \text{decade}^{-1}$) was higher than that of ISE based on ionophore **3** ($54.2 \text{ mV} \cdot \text{decade}^{-1}$). These results mean that ISE based on ionophore **4** gave a higher Nernstian response than that based on ionophore **3**. The possible explanation is that the solubility of the complex $[\mathbf{3} \cdot \text{Ag}^+] \cdot \text{X}^-$ is quite low, which is sparsely soluble in organic solvent or water. The lower solubility of $[\mathbf{3} \cdot \text{Ag}^+] \cdot \text{X}^-$ may be unfavorable for rapid interfacial ion exchange in membrane electrode. In addition, the Nernstian slopes of **3** and **4**-based ISEs are remarkably higher than those of ISEs based on our previously reported alkylthiaalkoxy groups functionalized calix[4]arene derivatives.¹⁶ We suggest that the phenyl groups close to the soft sulfur donors might assist the soft sulfur donors in chelating the silver ion via cation/ π interactions as depicted for phenylselenoalkoxy group functionalized calix[4]arenes as ionophores in ISEs.¹⁶

Comparing the selective values for most of main group metal ions and most of transition metal ions of compounds **3** and **4** with that of alkylthiaalkoxy functionalized calix[4]arenes,^{15,16} we found that the selectivity of silver ion of compounds **3** and **4** is much higher than those of alkylthiaalkoxy functionalized calix[4]arene derivatives-based ISEs.^{15,16} These selective values also suggest that the π systems of the phenyl groups close to the soft sulfur donors participate in the coordination of silver ion as assistant donors. In fact, many reports reveal that cation/ π interactions widely exist in solid state or in solution phase.²³

Experimental

Melting points were taken on a Thomas-Hoover melting point apparatus and are uncorrected. ¹H NMR spectra were recorded on a Bruker AC-P200 spectrometer at 200 MHz in CDCl₃ solution. Tetramethylsilane was used as an internal standard. Elemental analyses were performed on a Perkin-Elmer 2400C instrument. Mass spectra were recorded on a VG ZAB-HS spectrometer. All solvents were purified by standard procedures.

Preparation of 25, 27-dihydroxy-26, 28-bis(3-phenylthiaproxy) calix[4]arene (3)

In a 100 mL round-bottomed flask, was added anhydrous potassium carbonate (170 mg, 1.23 mmol), thiophenol (0.4 mL, *ca.* 3.9 mmol), THF (50 mL) and calix[4]arene dibromide (**1**) (333 mg, 0.5 mmol). The system was degassed, then the suspension was refluxed under nitrogen for 6 h. The solvent was removed under reduced pressure. The residue was dissolved with water (200 mL) and dichloromethane (30 mL). The organic layer was separated and washed with water (20 mL \times 2). The finally separated organic layer was dried with anhydrous magnesium sulfate. After filtration, the filtrate was condensed to dryness. The solid residue was purified by column chromatography (petroleum ether/CH₂Cl₂, *V/V* = 3/1). The obtained product was further purified by recrystallization from ethanol. This was obtained as a white powder in 50% yield, m.p. 128–130 °C; ¹H NMR δ : 8.02 (s, 2H, OH), 7.39–7.10 (m, 10H, PhH), 7.05 (d, *J* = 7.4 Hz, 4H, *m*-ArH), 6.90 (d, *J* = 7.3 Hz, 4H, *m*-ArH), 6.72 (t, *J* = 7.3 Hz, 2H, *p*-ArH), 6.64 (t, *J* = 7.4 Hz; 2H, *p*-ArH), 4.28 (d, *J* = 12.8 Hz, 4H, ArCH₂Ar), 4.10 (t, *J* = 5.8 Hz, 4H, OCH₂), 3.47 (t, *J* = 6.2 Hz, 4H, SCH₂), 3.38 (d, *J* = 12.8 Hz, 4H, ArCH₂Ar), 2.15–2.10 (m, 4H, CH₂); FAB/MS *m/z*: 724.6 (M⁺, calcd 724.9).

Table 2 Properties of Ag⁺-ISEs based on ionophores **3** and **4**

Ionophores	Slope (mV/dec.)	Linear range	Detection limit ($\mu\text{mol/L}$)	Response time <i>t</i> _{95%} (s)	pH range	R
3	54.2	5.0×10^{-6} – 1×10^{-1}	1.9×10^{-6}	< 10	2–6	0.9994
4	59.2	5.0×10^{-6} – 1×10^{-2}	2.7×10^{-6}	< 10	2–6	0.9996

Anal. calcd for $C_{46}H_{44}O_4S_2$: C 76.21, H 6.12; found C 76.33, H 6.03.

Preparation of 25,27-dihydroxy-26,28-bis(3-phenylthiaproxy)-5,11,17,23-tetra-tert-butylcalix[4]arene (4)

The above procedure was repeated starting with calix[4]arene dibromide (**2**) (445 mg, 0.5 mmol) to get a white powder in 61% yield, m. p. 156–158 °C; 1H NMR δ : 7.51 (s, 2H, OH), 7.33–7.13 (m, 10H, PhH), 6.97 (s, 4H, ArH), 6.78 (s, 4H, ArH), 4.20 (d, $J = 13.0$ Hz, 4H, $ArCH_2Ar$), 4.01 (t, $J = 5.8$ Hz, 4H, OCH_2), 3.36 (t, $J = 6.2$ Hz, 4H, SCH_2), 3.25 (d, $J = 13.0$ Hz, 4H, $ArCH_2Ar$), 2.06–2.00 (m, 4H, CH_2), 1.21 (s, 18H, *t*-BuH), 0.93 (s, 18H, *t*BuH); FAB/MS m/z : 949.1 (M^+ , calcd 949.4). Anal. calcd for $C_{62}H_{76}O_4S_2$: C 78.44, H 8.07; found C 78.51, H 7.98.

Silver selectivity evaluated by potentiometric selectivity coefficient and membrane electrode

The typical procedure for membrane preparation is as follows: poly(vinylchloride) (PVC) (60 mg, 32.5%), dibutyl phthalate (DBP) (120 mg, 64.9%), phenylthiaproxy functionalized calix[4]arene (4 mg, 2.1%), potassium tetrakis(*p*-chlorophenyl) borate (KTCIPB) (1 mg, 0.5%) were dissolved in 5 mL of THF. This solution was then poured into a flat-bottomed petri dish of 16 mm inner diameter and 50 mm height. Gradual evaporation of the solvent at room temperature gave a transparent, flexible membrane of about 0.3 mm in thickness. A disk of 7 mm in diameter was cut from the PVC membrane and incorporated into a PVC tube tip with 5% THF solution in water. After injection of 0.01 mol/L aqueous solution of $AgNO_3$ as the internal solution, the electrode was conditioned by soaking in 0.01 mol/L aqueous solution of $AgNO_3$ for 24 h. The external reference electrode is a double junction type Ag/AgCl glass electrode. The composition of the electrochemical cell is given as $Ag | AgCl | 0.01$ mol/L $AgNO_3$ | PVC membrane | sample solution | 1 mol/L KNO_3 | 4 mol/L KCl | Hg_2Cl_2 | Hg.

EMF Measurements

All EMF (electromotive force) measurements were made at (25 ± 1) °C, using a pH/mV meter. The sample

solution was magnetically stirred and kept in a thermostated water bath. The EMF values were corrected by subtracting the liquid-junction potential between the external reference electrode and the sample solution with high Ag^+ concentration.²⁴

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