

Influences of Hard Donor on Cation Selectivities Closing to Soft Selenium Donor in Tweezer-like Calix[4]arene Receptors

LIU, Chang-Ying^{a,b}(刘长鹰) QIN, Da-Bin^{a,c}(秦大斌) LENG, Xue-Bing^a(冷雪冰)
 CHEN, Lang-Xing^a(陈朗星) ZENG, Xian-Shun^{*a}(曾宪顺) XU, Feng-Bo^a(徐凤波)
 LI, Qing-Shan^a(李庆山) HE, Xi-Wen^a(何锡文) ZHANG, Wen-Qin^{*a,b}(张文勤)
 ZHANG, Zheng-Zhi^{*a}(张正之)

^a State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, China

^b Department of Chemistry, Tianjin University, Tianjin 300071, China

^c China West Normal University, Nanchong, Sichuan 637002, China

Three novel 25,27-dihydroxy-26,28-bis(3-benzylselenopropoxy)-5,11,17,23-tetra-*tert*-butylcalix[4]-arene (**2**), 25,27-dihydroxy-26,28-bis[3-(2-hydroxyethylseleno)propoxy]-5,11,17,23-tetra-*tert*-butyl-calix[4]arene (**3**) and 25,27-dihydroxy-26,28-bis(3-propylselenopropoxy)-5,11,17,23-tetra-*tert*-butyl-calix[4]arene (**4**) were synthesized for the comparison of their ion-selectivity in ion-selective electrodes (ISE). X-ray structure of the CH/ π complex of **4**·CH₂Cl₂ was elucidated. ISEs based on **2**—**4** as neutral ionophores were prepared, and their selectivity coefficients for Ag⁺ (log $K_{Ag,M}^{pot}$) were investigated against some main group metal ions and transition metal ones using the fixed interference method (FIM). These ISEs showed excellent Ag⁺ selectivity over most of the interfering cations examined. It is evident that the stronger Hg²⁺ interference may not be produced while hard donors (hydroxy) are close to the soft selenium donors.

Keywords calix[4]arene, selenide, silver selectivity, ion-selective electrode

Introduction

The development of systems that are capable of sensing or recognizing and are based on host-guest concepts is an active area of current interest.¹ One of the most appealing approaches involves the development of ion-selective sensors.² Such systems have been widely used for the analysis of main group metal ions since the first use of crown ethers as the sensors of group one metal ions. As the third generation of host molecules, calixarenes have received much consideration in the past decades.³ Benefiting from their three-dimensional structures and easy modification both on the upper-rim and the lower-rim, calixarene derivatives have been widely used as host molecules, which are sensitive to metal ion, organic ammonium and some neutral guest. One of their applications is that they are widely used as neutral ionophores in the ion selective electrodes (ISE).² Like crown ethers, they are successfully used as main group metal ion selective ionophores in ISE.⁴⁻¹³ But the examples exhibiting selectivities towards transition metal ion are relatively rare.¹⁴⁻¹⁶ It is well known that ionophores containing nitrogen and sulfur as soft donors are usually used as the receptors for those of soft transition metal ions, especially silver ion. But hard donors usually gave a strong Hg²⁺ interference while closing

to the soft coordinating center.¹⁷⁻¹⁹ Recent work revealed that π -systems are also used as the soft coordinating center for silver ion via a so-called cation/ π interaction.²⁰ On the other hand, the recent results of Chen's research group²¹ and our team²² revealed that using selenium atom as soft donors both in the tweezer-like receptors and in the crown-type receptors all gave good selectivities toward soft silver ion. These results encouraged us to devote our efforts to the design of some of new receptors by simply incorporating selenium atoms as soft donors and also introduction of some hard donors or π -systems closing to the soft donors as assistant donors to comparison the influences of selective behaviors of these multifunctional receptor to the soft silver ion.

In this paper, we report the syntheses and characterization of 25,27-dihydroxy-26,28-bis(3-benzylselenopropoxy)-5,11,17,23-tetra-*tert*-butylcalix[4]arene (**2**), 25,27-dihydroxy-26,28-bis[3-(2-hydroxyethylseleno)propoxy]-5,11,17,23-tetra-*tert*-butylcalix[4]arene (**3**) and 25,27-dihydroxy-26,28-bis(3-propyl-selenopropoxy)-5,11,17,23-tetra-*tert*-butylcalix[4]arene (**4**) (Figure 1) and also their selective behaviors to silver ion monitored by electromotive force measurements of polymer membrane electrodes. The comparison of the ISE behaviors of **2**—**4** and also with those of our previous work might

* E-mail: wqzhang@tju.edu.cn

Received October 16, 2003; revised February 11, 2004; accepted April 6, 2004.

Project supported by the National Natural Science Foundation of China (No. 20102003) and the Foundation of Nankai University.

provide us further understanding of the structure-selectivity relationship of selenium functionalized ionophores in the Ag^+ -ISE and at the same time, the comparison among these results will afford us some important experiences in the receptor molecule design.

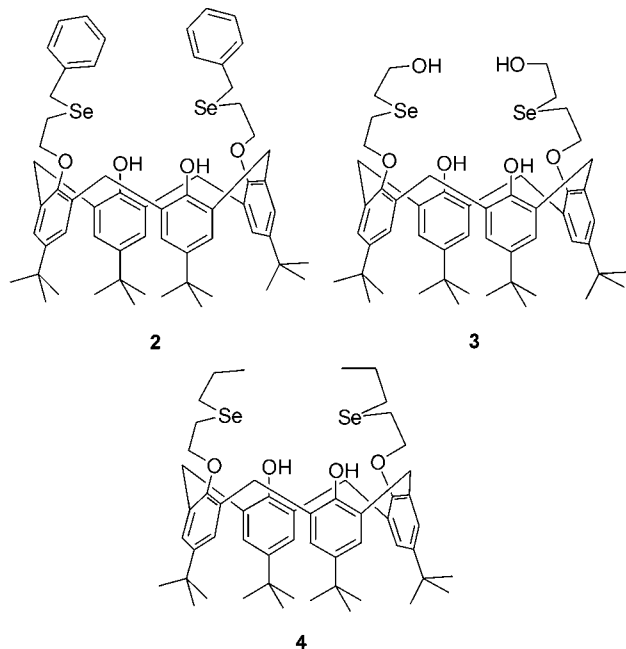


Figure 1 Structure of compounds 2—4.

Results and discussion

Syntheses

Calix[4]arene dibromide (**1**) was prepared according to literature procedures.²³ Calix[4]arenes 2—4 were synthesized in the yields between 92% and 95% by the reaction of **1** with the sodium salt of appropriate selenol which was prepared *in situ* by the reaction of dialkyl diselenide with sodium borohydride in the presence of NaOH as shown in Scheme 1. ^1H NMR spectra indicate that calix[4]arenes 2—4 keep the cone conformation. From two doublets of the protons within the methylene bridge of the calix[4]arene framework, and the separation of the aryl protons of calix[4]arene skeleton as well as the separation of the protons of the *tert*-butyls, it is

suggested that 2—4 are in a “pinched” cone conformation.

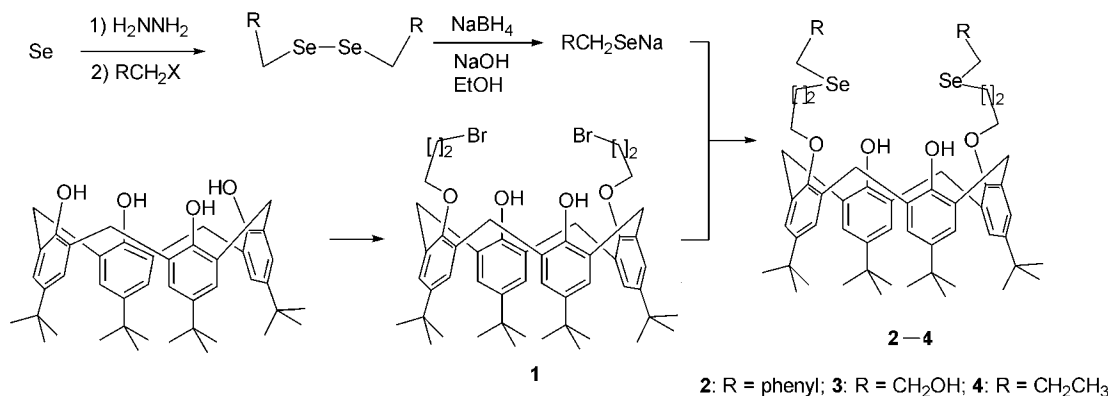
X-ray structure of 4

Crystals of **4** suitable for X-ray crystallography were grown by slow evaporation from the CH_2Cl_2 -MeOH solution of **4**, which was elucidated for determination the structure of **4** (Figure 2).²⁴ As shown in Figure 2, **4** is in a C_{2v} symmetric conformation in the solid state. The adjacent four phenyls within the calix framework form interplanar angles between 72.1° and 107.9° . The two phenyls bearing hydroxy groups were tilted away from the cavity with an interplanar angle of 88.9° . The other two phenyls that linked the side arms form an interplanar angle of 42.4° . The torsion angles of O(1)-C(23)-C(24)-C(25), C(23)-C(24)-C(25)-Se(1), C(25)-Se(1)-C(26)-C(27) and Se(1)-C(26)-C(27)-C(28) are 58.5° , 67.0° , 14.1° and 144.7° , respectively. The O...O separation of the adjacent four oxygen atoms on the lower rim of the calix[4]arene is between 0.2740 and 0.2932 nm, indicating that there are strong hydrogen bonds with O-H...O angle of 168.9° and strong O...O interactions between the four oxygen atoms. It is interesting to note that compound **4** forms a CH/ π complex with dichloromethane (Figure 2). As shown in Figure 2, one molecule of CH_2Cl_2 imbedded within the cavity of four aromatic groups as a guest via CH/ π interactions. Dichloromethane C(29) to the centroids of the four aromatic rings are 0.3574, 0.4104, 0.3574 and 0.4104 nm, respectively. The two guest hydrogen atoms are opposite to each other (Figure 2). The centroid...H separation is 0.2629 nm, with the centroid...H-C(29) angles of 168.3° .

Ag^+ selectivity

The Ag^+ selectivity of calix[4]arenes 2—4 were evaluated by the potentiometric selectivity coefficients ($\log K_{\text{Ag},M}^{\text{pot}}$) determined for polymer membranes containing these ionophores. The polymer membrane is composed of PVC as the matrix, dibutyl phthalate (DBP) as the membrane solvent, and a calix[4]arene as the ionophore. The membrane contains 75 mol% of potassium tetrakis(*p*-chlorophenyl)borate (KTCIPB) relative to the

Scheme 1



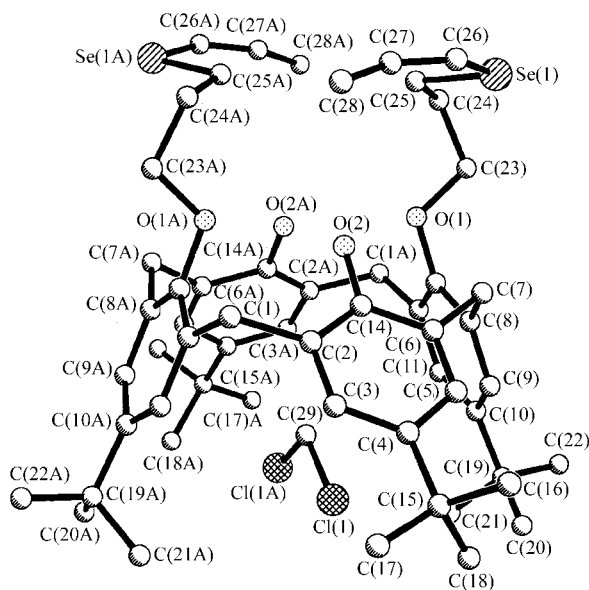


Figure 2 Crystal structure of $4 \cdot \text{CH}_2\text{Cl}_2$.

ionophore for the purpose of reducing membrane resistance and suppressing permeation of counter anions in the aqueous phase into the membrane phase. The potentiometric selectivity coefficients for Ag^+ , determined by the fixed interference method (FIM), are illustrated in Table 1. The selectivity coefficient ($\log K_{\text{Ag},\text{M}}^{\text{pot}}$) represents the preference of the ISE (or membrane) containing the calix[4]arene for Ag^+ over the other cations. Therefore, the coefficient $\log K_{\text{Ag},\text{M}}^{\text{pot}}$ defines the ability of an ISE (or membrane) to recognize different ions under the same conditions.

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

$$E = E^0 + \frac{2.303RT}{F} \log[\alpha_{\text{Ag}} + K_{\text{Ag},\text{M}}^{\text{pot}} (\alpha_{\text{M}})^{1/Z_{\text{M}}}] \quad (1)$$

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.

As can be seen from Table 1, polymer membrane containing ionophores **2–4** gave excellent $\log K_{\text{Ag},\text{M}}^{\text{pot}}$ values (≤ -3.2) against Na^+ , K^+ , NH_4^+ , Ca^{2+} , Mg^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} , which means that **2–4**-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 **2–4**-based ISEs ($\log K_{\text{Ag},\text{M}}^{\text{pot}} \leq -1.0$ for most of the present ISEs). The possible explanation is that these ions, such as Na^+ , K^+ , NH_4^+ , Ca^{2+} , Mg^{2+} , Pb^{2+} and most divalent transition metal ions with high hydration energies, can not strongly interact with selenium donors in the present ionophores, while less heavily hydrated soft Ag^+ coordinates soft selenium donors selectively. As we discussed in our previous work, the tweezer-like structure of **2–4** will largely benefit the ionophores using two points to coordinate silver ion in the most stable *trans*-conformation of two coordinated silver compounds. Although it is not exact to use the solid state of ionophores to explain the complicate ISE behavior in the liquid membrane phase, the solid conformation of the ionophore may provide us some important information for further understanding the mechanisms of the ionophore-based ISEs, at least we can predict the tendency of the ISE behavior from the solid structure of the ionophore. As can be seen from Figure 1, the two propylselenopropoxy groups like the arms of a pair of tweezer stretched along the lower-rim of calix[4]arene skeleton. The intramolecular Se··Se distance is 0.7214 nm. This conformation may favorite the ionophores using two points to coordinate with silver ion in the most stable *trans*-conformation of two coordinated silver compounds.

The fact that polymer membrane containing **3** gave larger $\log K_{\text{Ag},\text{M}}^{\text{pot}}$ values against Na^+ , K^+ and NH_4^+ ions than those of **2**- and **4**-based ISEs means that **3**-based ISEs possess lower Ag^+ selectivity than those of **2**- and **4**-based ISEs. As can be seen from Figure 1, ionophore **3** possesses two hydroxys closed to the soft selenium donors as secondary donor groups compared with **2** and **4**. With this structural feather in mind, the lower Ag^+ selectivity of ionophore **3**-based ISE than those of **2**- and **4**-based ISEs can be rationalized that the two extra oxygen atoms of the two hydroxys acting as hard donors participate in the binding with these hard ions with high hydration energies, such as Na^+ , K^+ , NH_4^+ . As can be seen from Table 1, that the selective coefficients of Pb^{2+} , Cu^{2+} and Zn^{2+} of ionophore **4**-based ISEs are about one order of magnitude lower than those of ionophore **2**-based ISEs means that **2**-based ISEs possess higher binding abilities towards Pb^{2+} , Cu^{2+} and Zn^{2+} . The structural difference between **2** and **4** is that there have two phenyls closed to the soft selenium donors in the ionophore **2**. Therefore,

Table 1 Selectivity coefficients ($\log K_{\text{Ag},\text{M}}^{\text{pot}}$) of the electrodes based on ionophores **2–4**^a

Ions	Ag^+	Na^+	K^+	NH_4^+	Mg^{2+}	Ca^{2+}	Pb^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Cd^{2+}	Hg^{2+}
$\log K_{\text{Ag},\text{M}}^{\text{pot}}$	0	-4.3	-4.3	-4.5	-4.6	-4.5	-3.5	-3.9	-4.0	-3.7	-4.1	-1.9
	0	-3.5	-3.6	-3.2	-4.6	-4.3	-3.9	-3.8	-3.8	-3.9	-4.0	-1.0
	0	-4.3	-4.2	-4.0	-4.5	-4.5	-4.4	-4.2	-5.3	-4.6	-4.2	-2.2

^a Selectivity coefficients ($\log K_{\text{Ag},\text{M}}^{\text{pot}}$) of the electrodes based on ionophores **2–4** are mean data of two measurements using FIM.

the lower selective coefficients of Pb^{2+} , Cu^{2+} and Zn^{2+} of ionophore **4**-based ISEs than those of **2**-based ISE might be attributed to the π -systems of the branched phenyls within compound **2** participating in the coordination with these cations via cation- π interactions.²⁵ In addition, that the selective coefficient of Hg^{2+} of **3**-based ISE is one order of magnitude larger than those of **2** and **4**-based ISEs indicates that the stronger Hg^{2+} interference towards the silver cation is produced in **3**-based ISEs. It is well known that free Hg^{2+} only exists in the strong acidic medium ($\text{pH} < 2$). However, it exists usually in the form of $\text{Hg}(\text{OH})^+$ when the medium pH value is larger than 2. Therefore, the reason for the stronger Hg^{2+} interference towards the silver cation in **3**-based ISE might be enhanced by the oxygen atoms within the extra two hydroxys in the ionophore **3** via O-H...O hydrogen bonds with $\text{Hg}(\text{OH})^+$ ion.

Compared with the ISEs behaviors of **2** and **4** with their thio analogues of our previous reported results 25,27-dihydroxy-26,28-bis(propylthiaalkoxy)-5,11,17,23-tetra-*tert*-butylcalix[4]arene (**5a–5c**)^{15b,21} and 25,27-dihydroxy-26,28-bis(hydroxyethylthiaalkoxy)-5,11,17,23-tetra-*tert*-butylcalix[4]arene (**6a–6b**),¹⁸ drastic differences exist between the thio analogues and the seleno analogues. As can be seen from Figures 1 and Figure 3, the main differences between the two types of compounds are that the selenium atoms in ionophores **3** and **4** are replaced by the sulfur atoms in ionophores **5a–5c** and **6a–6b**. By the comparison of the selective coefficients of **4** with those of its thio analogues **5a–5c**, we found that there is an order of magnitude increase in the binding affinity of Na^+ , K^+ and Hg^{2+} of thio analogues **5a–5c** over those of **3** and **4**. From this results it is suggested that the more soft selenium atom is super to sulfur atom as donors in the same type of receptors as silver sensors in ionophore based ISEs. Comparing the selective behavior of **3** with those of its thio analogues **6a–6b**, we found that the strong Hg^{2+} interferences in **6a–6b** based ISEs are almost eliminated. As depicted above, sulfur donors give stronger binding abilities towards Na^+ , K^+ and Hg^{2+} for it is relatively harder than selenium atom from the widely accepted hard and soft acid and bases theory.

Besides the differences in the ion-selectivities, there are some differences in the values of properties of **2–4**-based ISEs. The response characteristics of silver ISEs such as response slope, linear range and response time are summarized in Table 2. the Nernstian slope of **2**-based ISEs is $(54.2 \pm 3.2) \text{ mV} \cdot \text{decade}^{-1}$ to the activity

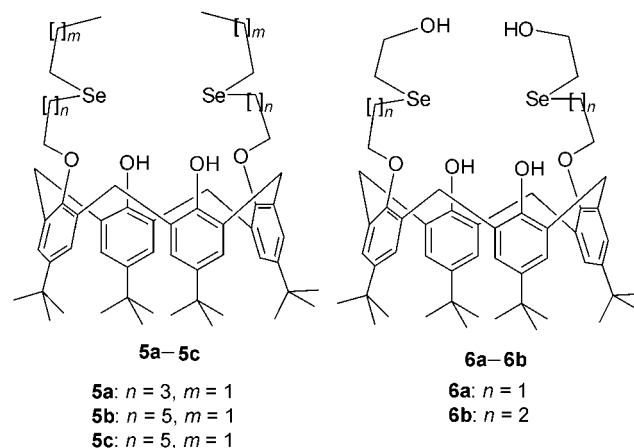


Figure 3 Structures of compounds **5a–5c** and **6a–6b**.

of Ag^+ within the activity range $10^{-6.0}—10^{-1.3} \text{ mol} \cdot \text{L}^{-1}$ AgNO_3 . The relevant values of **3** and **4**-based ISEs are (45.4 ± 1.3) and $(54.0 \pm 1.3) \text{ mV} \cdot \text{decade}^{-1}$ to the activity of Ag^+ within the activity range $10^{-5.0}—10^{-1.3}$ and $10^{-6.0}—10^{-1.3} \text{ mol} \cdot \text{L}^{-1}$ AgNO_3 , respectively. The Nernstian slopes of **2**- and **4**-based ISEs are remarkably higher than that of **3**-based ISEs. One possible explanation is that the oxygen atoms of the terminal hydroxy of ionophore **3** participated in the ligation with silver cation as the assistant donors. The extra binding with oxygen atoms causes a relatively stronger binding with the silver ion compared with that of **2**- and **4**-based ISEs. The stronger binding of silver ion might interfere in the rapid ion exchange of interfacial of membrane electrodes. From the relative narrow linear range of **3**-based ISEs, it is also suggested that ionophore **3** causes a relatively stronger binding towards silver ion than those of **2**- and **4**-based ISEs. The response time of **2–4**-based ISEs is within 12 s.

Conclusions

Tweezer-like receptor molecules 25,27-dihydroxy-26,28-bis(3-benzylselenopropoxy)-5,11,17,23-tetra-*tert*-butylcalix[4]arene (**2**) and its analogues **3** and **4** have been synthesized for comparing the cation/ π interactions and hard donors on the influences of Ag^+ selectivity as sensors for Ag^+ -selective electrodes. The polymer membranes containing **2–4** gave good selectivity for Ag^+ ($\log K_{\text{Ag},\text{M}}^{\text{pot}} \leq -3.2$) against most of the interfering cations examined (*i.e.*, Na^+ , K^+ , NH_4^+ , Mg^{2+} , Ca^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+}). These ionophores

Table 2 Properties of Ag^+ -ISEs based on ionophores **2–4**^a

Ionophores	Slope ^a /(mV·dec ⁻¹)	Linear range	Response time $t_{95\%}$ /s	pH range	R
2	54.2 ± 3.1	$5.0 \times 10^{-6.0}—10^{-1.3}$	<10	2–6	0.9889
3	45.4 ± 1.9	$5.0 \times 10^{-5.0}—10^{-1.3}$	<12	2–6	0.9947
4	54.0 ± 1.3	$5.0 \times 10^{-6.0}—10^{-1.3}$	<12	2–6	0.9937

^a Slopes are calculated within their linear range and are mean data of four electrodes (standard deviations given at 95% confidence level) for each ionophore.

also gave good discrimination of Hg^{2+} ($\log K_{\text{Ag,M}}^{\text{pot}} \leq -1.0$). The performance of the present ISEs is superior to that displayed by traditional Ag_2S -based electrode. The π -systems closing to the soft selenium donors within the ionophore **2** cause a relative stronger binding with Pb^{2+} , Cu^{2+} and Zn^{2+} compared with those of the ionophore **4** without π -systems closing to the soft donors. However, while the hard donor group hydroxys within the ionophore **3** closed to the soft selenium donors, a stronger binding with Na^+ , K^+ , NH_4^+ and Hg^{2+} was caused compared with those of the ionophore **4**.

Experimental

Melting points were determined with a Boetius Block apparatus. ^1H NMR spectra were recorded on a Bruker AC-P200 spectrometer at 200 MHz and on a JEOL JNM-AL 300 spectrometer at 300 MHz in CDCl_3 solution, using tetramethylsilane as an internal standard. ^{13}C NMR spectra were recorded on a Bruker AC-P200 spectrometer at 50 MHz in CDCl_3 solution. Elemental analyses were performed by Perkin-Elmer 2400C instrument. FAB/MS spectra were obtained on a VG ZAB-HS spectrometer. X-ray crystallographic data were obtained on a Bruker Smart 1000 instrument. Poly(vinyl chloride) (PVC) and potassium tetrakis(4-chlorophenylborate) (KTCIPB) were purchased from Fluka (Buchs, Switzerland). Dibutyl phthalate (DBP) was obtained from Shanghai Chemical Reagent Corporation (Shanghai, China). The silver nitrate (guaranteed reagent) and analytical reagent grade nitrates of sodium, potassium, ammonium, calcium, magnesium, cadmium, copper, nickel, zinc, lead and mercury were supplied by Tianjin Chemical Reagent Factory. All solutions were prepared with distilled deionized water. Solvents were dried and purified according to literature methods.²⁶ Compounds dipropyl diselenide, dibenzyl diselenide and bis(2-hydroxyethyl)diselenide were prepared according to the literature procedures.²⁷

25,27-Dihydroxy-26,28-bis(3-bromopropoxy)-5,11,17,23-tetra-*tert*-butylcalix[4]arene (**1**)

A modified procedure of the literature²³ preparation of **1** was carried out. A suspension of *p-tert*-butylcalix[4]arene (12.96 g, 20 mmol), K_2CO_3 (6.5 g, 47 mmol) and 1,3-dibromopropane (100 mL) in CH_3CN (700 mL) was heated at reflux with stirring for 24 h. After cooling to room temperature, the precipitate was filtered and washed with 0.1 mol·L⁻¹ HCl (100 mL), water (200 mL) and then ethyl ether (100 mL). Then the solid was dried at 100 °C for 3 h. Compound **1** (7.8 g) was obtained in 44% yield, m.p. 334–335 °C (lit. 288–290 °C),²³ and it was pure enough for next reaction without further purification.

25,27-Dihydroxy-26,28-bis(benzylselenopropoxy)-5,11,17,23-tetra-*tert*-butylcalix[4]arene (**2**)

Dibenzyl diselenide (425 mg, 1.25 mmol), prepared

from benzyl chloride with Se_2Na_2 in 85% yield, was dissolved in anhydrous ethanol (30 mL) and benzene (30 mL) in a 100 mL-round-bottom flask. Under an atmosphere of nitrogen, solid sodium borohydride (228 mg, 6 mmol) was added in small portions to the solution until the orange color of the dibenzyl diselenide disappeared. Then, the rest sodium borohydride was added in one portion. The colorless solution was heated to reflux. Then, a solution of calix[4]arene dibromide (1 mmol) in benzene (20 mL) was added. The reaction mixture was heated at reflux for 1 h, cooled to room temperature, and poured into water (100 mL). The mixture was extracted three times with chloroform. The combined extracts were washed thoroughly with water and then dried over anhydrous sodium sulfate. The dry solution was filtered. The filtrate was evaporated to dryness under vacuum. The oily residue was purified by chromatography on silica gel with dichloromethane and petroleum ether (1 : 3, V : V). Compound **2** was synthesized as colorless oil in 95% yield. ^1H NMR (CDCl_3 , 200 MHz) δ : 7.72 (s, 2H, OH), 7.34–7.21 (m, 10H, Ph-H), 7.03 (s, 4H, Ar-H), 6.82 (s, 4H, Ar-H), 4.24 (d, $J=13.0$ Hz, 4H, ArCH_2Ar), 3.99 (t, $J=5.4$ Hz, 4H, OCH_2), 3.81 (s, 4H, CH_2Ph), 3.28 (d, $J=13.0$ Hz, 4H, ArCH_2Ar), 2.97 (t, $J=6.2$ Hz, 4H, SeCH_2), 2.24–2.12 (m, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{Se}$), 1.27 (s, 18H, *t*-Bu-H), 0.98 (s, 18H, *t*-Bu-H); FAB/MS m/z 1072.2 (M^+ , calcd 1072.4). Anal. calcd for $\text{C}_{64}\text{H}_{80}\text{O}_4\text{Se}_2$: C 71.76 H, 7.53; found C 72.01 H 7.58.

25,27-Dihydroxy-26,28-bis(3-(2-hydroxyethylseleno)propoxy)-5,11,17,23-tetra-*tert*-butylcalix[4]arene (**3**)

By similar procedures, using 2,2'-dihydroxyethyl diselenide (422 mg, 1.25 mmol) instead of dibenzyl diselenide, compound **3** was obtained as colorless oil in 95% yield. ^1H NMR (CDCl_3 , 200 MHz) δ : 7.46 (s, 2H, OH), 7.03 (s, 4H, Ar-H), 6.80 (s, 4H, Ar-H), 4.25 (d, 4H, $J=12.9$ Hz, ArCH_2Ar), 4.05 (t, $J=5.6$ Hz, 4H, $\text{ArOCH}_2\text{CH}_2$), 3.83 (t, $J=5.9$ Hz, 4H, HOCH_2CH_2), 3.30 (d, $J=12.9$ Hz, 4H, ArCH_2Ar), 3.08 (t, $J=5.9$ Hz, 4H, $\text{SeCH}_2\text{CH}_2\text{OH}$), 2.92 (t, $J=5.8$ Hz, 4H, $\text{SeCH}_2\text{CH}_2\text{CH}_2$), 2.47 (s, 2H, OH), 2.45–2.30 (m, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{Se}$), 1.26 (s, 18H, *t*-Bu-H), 0.96 (s, 18H, *t*-Bu-H); FAB/MS m/z 980.4 (M^+ , calcd 980.4). Anal. calcd for $\text{C}_{54}\text{H}_{76}\text{O}_6\text{Se}_2$: C 66.24, H 7.82; found C 65.99, H 7.85.

25,27-Dihydroxy-26,28-bis(3-propylselenopropoxy)-5,11,17,23-tetra-*tert*-butylcalix[4]arene (**4**)

By similar procedures, using 3,3'-dipropyl diselenide instead of dibenzyl diselenide, the oily residue **4** was obtained and purified by chromatography on silica gel with dichloromethane and petroleum ether as an eluant. After recrystallized from ethanol, **4** was obtained as a white powder in 92% yield, m.p. 65–66 °C. ^1H NMR (CDCl_3 , 200 MHz) δ : 7.04 (s, 2H, OH), 7.02 (s, 4H, Ar-H), 6.74 (s, 4H, Ar-H), 4.29 (d, $J=13.1$ Hz, 4H, ArCH_2Ar), 4.15 (t, 4H, $J=7.2$ Hz, OCH_2), 3.29 (d, $J=13.1$ Hz, 4H, ArCH_2Ar), 3.05 (t, $J=7.2$ Hz, 4H, $\text{SeCH}_2\text{CH}_2\text{CH}_2\text{O}$), 2.66 (t, $J=7.3$ Hz, 4H, $\text{SeCH}_2\text{CH}_2\text{CH}_2$), 2.11–1.99 (m, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{Se}$), 1.50–1.37 (m,

4H, Se-CH₂CH₂CH₃), 1.28 (s, 18H, *t*-Bu-H), 1.18 (t, *J*=6.2 Hz, 6H, CH₃), 0.92 (s, 18H, *t*-Bu-H); ¹³C NMR (CDCl₃, 50 MHz) δ : 150.50, 149.64, 146.80, 141.46, 132.34, 127.90, 125.45, 125.02, 76.34, 33.84, 32.79, 31.69, 30.97, 24.45, 22.93, 22.08, 13.58. Anal. calcd for C₅₆H₈₀O₄Se₂•CH₂Cl₂: C 64.58, H 7.80; found C 64.29, H 7.71.

Silver selectivity evaluated by potentiometric selectivity coefficient and membrane electrode

The typical procedure for membrane preparation is as follows: Poly(vinylchloride) (PVC) (132 mg, 32%—33%), dibutyl phthalate (DBP) (264 mg, 64%—65%), benzothiazolyl functionalized calix[4]arene (4 mg, 1%), potassium tetrakis(*p*-chlorophenyl)borate (KTPCIPB) (75 mol% relative to the ionophore) 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 THF. After injection of 0.01 mol•L⁻¹ aqueous solution of AgNO₃ as the internal solution, the electrode was conditioned by soaking in 0.01 mol•L⁻¹ aqueous solution of AgNO₃ for 24 h. The external reference electrode is a double junction type Ag/AgCl glass electrode. The composition of electrochemical cell is given as Ag|AgCl|0.001 mol•L⁻¹ AgNO₃|PVC membrane|sample solution|1 mol•L⁻¹ KNO₃|4 mol•L⁻¹ KCl|Hg₂Cl₂|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 thermostatted water bath. The EMF values were corrected by subtracting the liquid-junction potential between the external reference electrode and the sample solution in the high Ag⁺ concentration.²³

References and notes

- (a) Valeur, B.; Leray, I. *Coord. Chem. Rev.* **2000**, *205*, 3.
(b) de Silva, A. P.; Fox, D. B.; Huxley, A. J. M.; Moody, T. S. *Coord. Chem. Rev.* **2000**, *205*, 41.
(c) Gale, P. A. *Coord. Chem. Rev.* **2001**, *213*, 79.
- (a) Bakker, E.; Bühlmann, P.; Pretsch, E. *Chem. Rev.* **1997**, *97*, 3083.
(b) Bühlmann, P.; Pretsch, E.; Bakker, E. *Chem. Rev.* **1998**, *98*, 1593.
- (a) Gutsche, C. D. *Calixarenes*, The Royal Society of Chemistry: Cambridge, UK, **1998**.
(b) Ikeda, A.; Shinkai, S. *Chem. Rev.* **1997**, *97*, 1713.
(c) Böhmer, V. *Angew. Chem., Int. Ed. Engl.* **1995**, *43*, 713.
- (a) Kimura, K.; Miura, T.; Matsuo, M.; Shono, T. *Anal. Chem.* **1990**, *62*, 1510.
(b) Cunningham, K.; Svehla, G.; Harris, S. J.; McKervey, M. A. *Anal. Proc.* **1991**, *28*, 294.
- Brazozka, Z.; Lammerink, B.; Reinhoudt, D. N.; Ghidini, E.; Ungaro, R. *J. Chem. Soc., Perkin Trans. 2* **1993**, 1037.
- (a) Schaller, U.; Bakker, E.; Spichiger, U. E.; Pretsch, E. *Anal. Chem.* **1994**, *66*, 391.
(b) Metzger, E.; Aeschmann, R.; Egli, M.; Suter, G.; Dohner, R.; Ammann, D.; Dobler, M.; Simon, W. *Helv. Chim. Acta* **1986**, *69*, 1821.
(c) Xie, R. Y.; Christian, G. D. *Anal. Chem.* **1986**, *58*, 1806.
- (a) Zeng, X.; Weng, L.; Chen, L.; Ju, H.; Leng, X.; He, X.; Zhang, Z. *Z. Chin. J. Chem.* **2001**, *19*, 493.
(b) Chen, L.; Ju, H.; Zeng, X.; He, X.; Zhang, Z. *Z. Anal. Chim. Acta* **2001**, *447*, 41.
- Cadogan, A.; Diamond, D.; Smyth, M. R.; Svehla, G.; McKervey, M. A.; Seward, E. M.; Harris, S. J. *Analyst* **1990**, *115*, 1207.
- Péres-Jiméne, C.; Escriche, L.; Casabó, J. *Anal. Chim. Acta* **1998**, *371*, 155.
- (a) Attiyat, A. S.; Ibrahim, Y. A.; Christian, G. D. *Microchem. J.* **1988**, *37*, 122.
(b) Ohki, A.; Lu, J. P.; Bartsch, R. A. *Anal. Chem.* **1994**, *66*, 651.
(c) Ohki, A.; Maeda, S.; Lu, J. P.; Bartsch, R. A. *Anal. Chem.* **1994**, *66*, 1743.
- Kimura, K.; Yano, H.; Kitazawa, S.; Shono, T. *J. Chem. Soc., Perkin Trans. 2* **1986**, 1945.
- Oh, H.; Choi, E. M.; Jeong, H.; Nam, K. C.; Jeon, S. *Talanta* **2000**, *53*, 535.
- Sakaki, T.; Harada, T.; Deng, G.; Kawabata, H.; Kawahara, Y.; Shinkai, S. *J. Inclusion Phenom. Mol. Recognit. Chem.* **1992**, *14*, 285.
- (a) Malinowska, E.; Brzozka, Z.; Kasiura, K.; Egberink, R. J. M.; Reinhoudt, D. N. *Anal. Chim. Acta* **1994**, *298*, 245.
(b) Cobben, P. L. H. M.; Egberink, R. J. M.; Bomer, J. G.; Bergveld, P.; Verboom, W.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **1992**, *114*, 10573.
(c) Khalil, S. *Anal. Lett.* **2003**, *36*, 1335.
(d) Shinohara, T.; Higuchi, H.; Senba, Y.; Ohto, K.; Yoshizuka, K.; Inoue, K. *Anal. Sci.* **2001**, *17*, 889.
(e) Park, S. J.; Shon, O. J.; Rim, J. A.; Lee, J. K.; Kim, J. S.; Nam, H.; Kim, H. *Talanta* **2001**, *55*, 297.
- (a) Zeng, X.; Weng, L.; Chen, L.; Leng, X.; Zhang, Z.; He, X. *Tetrahedron Lett.* **2000**, *41*, 4917.
(b) Zeng, X.; Weng, L.; Chen, L.; Xu, F.; Li, Q.; Leng, X.; He, X.; Zhang, Z. *Z. Tetrahedron* **2002**, *58*, 2647.
- Zeng, X.; Sun, H.; Chen, L.; Leng, X.; Xu, F.; Li, Q.; He, X.; Zhang, W.; Zhang, Z. *Z. Org. Biomol. Chem.* **2003**, *1*, 1073.
- Zeng, X.; Weng, L.; Chen, L.; Leng, X.; Ju, H.; He, X.; Zhang, Z. *J. Chem. Soc., Perkin Trans. 2* **2001**, 545.
- (a) Zeng, X.; Chen, L.; Weng, L.; Leng, X.; Ju, H.; He, X.; Zhang, Z. *Z. J. Chem. Res. (S)* **2000**, 518.
(b) Ju, H.; Chen, L.; Zeng, X.; He, X.; Zhang, Z. *Z. J. Anal. Sci.* **2001**, *17*, 446.
- (a) O'Conner, K. M.; Svehla, G.; Harris, S. J.; McKervey, M. A. *Anal. Proc.* **1993**, *30*, 137.
(b) O'Conner, K. M.; Svehla, G.; Harris, S. J.; McKervey, M. A. *Talanta* **1992**, *39*, 1549.
- Kimura, K.; Yajima, S.; Tatsumi, K.; Yokoyama, M. Oue, M. *Anal. Chem.* **2000**, *72*, 5290.
- (a) Hu, X. X.; Chen, Y. Y.; Tian, Z. J.; Xue, J. D. *J. Chem.*

- Res. (S)* **1999**, 332.
- (b) Chen, Y. Y.; Chen, Y. K.; Lu, L. R.; Gong, S. L. *Chem. J. Chin. Univ.* **1999**, 20, 1570.
- 22 (a) Zeng, X.; Leng, X.; Chen, L.; Sun, H.; Xu, F.; Li, Q.; He, X.; Zhang, Z. *J. Chem. Soc., Perkin Trans. 2* **2002**, 796.
(b) Zeng, X.; Han, X.; Chen, L.; Li, Q.; Xu, F.; He, X.; Zhang, Z. *Tetrahedron Lett.* **2002**, 43, 131.
- 23 Li, Z. T.; Ji, G. Z.; Zhao, C. K.; Yuan, S. D.; Ding, H.; Huang, C.; Du, A. L.; Wei, M. *J. Org. Chem.* **1999**, 64, 3572.
- 24 Data for **4**: C₅₇H₈₂Cl₂O₄Se₂, *M*=1060.04, m.p. 65—66 °C, *D*_c=1.194 mg/mm³, *Z*=8, *F*(000)=2232. Single-crystal diffraction measurement of crystal on a Bruker Smart 1000 diffractometer with Mo K α (λ =0.071073 nm) at 293(2) K. μ =1.384 mm⁻¹. A total of 11953 reflections were measured, 5205 [*R*(int)=0.0423] unique. The structure was solved by direct method and refined on *F*² using SHELXTL software (Sheldrick, G. M., Gottingen, Germany). Final *wR*₂=0.2494, with a conventional *R*₁=0.0793 [reflections with *I*>2 σ (*I*)] and a *GOOF*=1.043 for 289 refined parameters.
- 25 (a) Ma, J. C.; Dougherty, D. A. *Chem. Rev.* **1997**, 97, 1303.
(b) Xu, F.; Weng, L.; Sun, L.; Zhang, Z. Z.; Zhou, Z. *Organometallics* **2000**, 19, 2658.
(c) Xu, F.; Li, Q.; Wu, L.; Zeng, X.; Leng, X.; Chow, Y.; Zhang, Z. *Organometallics* **2003**, 22, 633.
(d) Ikeda, A.; Shinkai, S. *J. Am. Chem. Soc.* **1994**, 116, 3102.
(e) Inokuchi, F.; Miyahara, Y.; Inazu, T.; Shinkai, S. *Angew. Chem., Int. Ed. Engl.* **1995**, 34, 1364.
- 26 Perrin, D. D.; Amarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd edn., Pergamon Press, Oxford, **1989**.
- 27 Hu, X.; Tian, Z.; Lu, X.; Chen, Y. *Synth. Commun.* **1997**, 27, 553.

(E0310168 SONG, J. P.)