Novel bis(phenylselenoalkoxy)calix[4]arene molecular tweezer receptors as sensors for ion-selective electrodes

Xianshun Zeng,*[a] Xuebing Leng,[a] Langxing Chen,[b] Hao Sun,[a,c] Fengbo Xu,[a] Qingshan Li,[a] Xiwen He[b] and Zheng-Zhi Zhang *[a]

[a] *State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, China*
[b] *Department of Chemistry, Nankai University, Tianjin 300071, China*
[c] *Department of Chemistry, Tianjin University, Tianjin 300072, China*

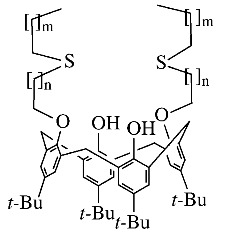
Received (in Cambridge, UK) 12th October 2001, Accepted 6th February 2002
First published as an Advance Article on the web 21st February 2002

Four tweezer-like 25,27-dihydroxy-26,28-bis(phenylselenoalkoxy)-5,11,17,23-tetra-*tert*-butylcalix[4]arenes **5**–**8** were synthesized for the evaluation of their ion-selectivity in ion-selective electrodes (ISEs). For investigation of the influences of the coordinate atoms on the ion-selectivity, 25,27-dihydroxy-26,28-bis(alkylthiaalkoxy)-5,11,17,23-tetra-*tert*-butylcalix[4]arenes **9**–**11** were also prepared and characterized. On the other hand, 1,3-bis(phenylseleno)-propane **12** was synthesized for comparison of the influences of coordinate patterns of different ionophores on the ion-selectivity of ISEs. ISEs based on **5**–**12** as neutral ionophores were prepared, and their selectivity coefficients for Ag$^+$ (log $K^{\text{pot}}_{\text{Ag,M}}$) were investigated against alkali metal, alkaline-earth metal, lead, and ammonium ions and some transition metal ions using the fixed interference method (FIM). These ISEs showed excellent Ag$^+$ selectivity over most of the interfering cations examined, except for Hg^{2+}, which had relatively smaller interference (log $K^{\text{pot}}_{\text{Ag,Hg}} \leq -1.6$).

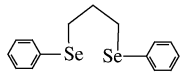
Introduction

Recently, research in the area of sensor development for metal ion detection in chemical and biological applications has received much attention. In particular, the application of host–guest chemistry to sensor development has proved to be a very valuable detection method. Numerous receptors including crown ethers, cryptands, cyclodextrins and calixarenes have been synthesized as molecular agents for the binding of all kinds of cationic and anionic species.[1,2] As for cationic sensors, much work has focused on the main group metal ions.[3–10] More recently, the molecular design of sensors containing nitrogen, sulfur or phosphorus donors with affinity for transition metal ions has received considerable attention.[11–15] In our previous work, calix[4]arene-based tweezer-like receptors which are made sensitive to Ag$^+$ ion by incorporating nitrogen, sulfur or phosphorus atoms in the lower rim of the calix[4]arene scaffold were developed.[16–20] We found that using calix[4]arene derivatives containing sulfur or nitrogen atoms as ionophores in ISEs gave a good Ag$^+$-selectivity against most interfering ions such as alkali metal ions, alkaline-earth metal ions, lead ion and transition metal ions. The interferences of Hg^{2+} towards these electrodes are almost eliminated. We also found that the nitrogen atom is a better donor than the sulfur atom or the phosphorus (III) atom both in multipoint ionophores and in tweezer-like two-point ionophores. These results prompted us to investigate some novel ionophores containing other soft donors such as selenium, and to compare their ion-selective behavior with each other for further understanding of the implications of the ion-selectivity mechanism in ionophore-based ISEs.

Here we report the synthesis of a series of novel tweezer-like receptor molecules 25,27-dihydroxy-26,28-bis(phenylselenoalkoxy)-5,11,17,23-tetra-*tert*-butylcalix[4]arenes **5**–**8** and 25,27-dihydroxy-26,28-bis(alkylthiaalkoxy)-5,11,17,23-tetra-*tert*-butylcalix[4]arenes **9**–**11** and their Ag$^+$ selectivity behavior monitored by electromotive force measurements of polymer membrane electrodes based on these novel Ag$^+$-selective ionophores. Comparison of the ISE performances of ionophores **5**–**8** with those of ionophores **9**–**11**, together with the influences of the tether length of the same type receptors on the ISE behavior of **5**–**8**, as well as the ISE behavior of 1,3-bis(phenylseleno)-propane **12** will aid further understanding of the structure–selectivity relationships and the influences of coordinate atom types on the Ag$^+$-ISEs.



9, 10, 11



12

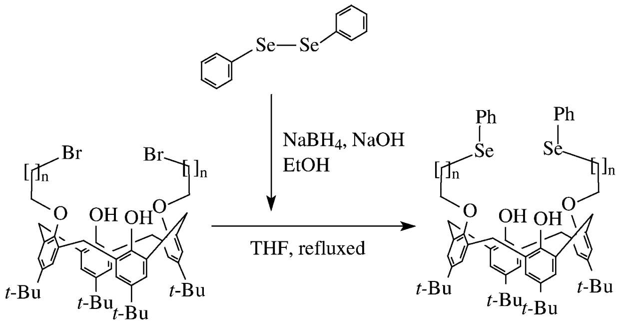
9: n = 3, m = 1; **10**: n = 5, m = 1; **11**: n = 5, m = 3.

Results and discussion

Syntheses

Diselenocalix[4]arenes **5**–**8** were synthesized in good yields by reaction of the calix[4]arene dibromides **1**–**4** with the sodium salt of selenophenol (Scheme 1). Thus, diphenyl diselenide was treated with NaBH$_4$ and NaOH in absolute ethanol. Then, the preorganized tweezer-like calix[4]arene dibromides **1**–**4** were added to the prepared ethanol solution of sodium salt of selenophenol and refluxed. The products were purified by column chromatography. The yields of **5**–**8** are between 88% and 92%. Their structures were confirmed by ^{1}H NMR spectra. Two doublets at nearly 4.23 and 3.28 ppm with the J values of about 13.0 Hz of the protons within the methylene bridges of the

DOI: 10.1039/b109238c



1-4 **5-8**

1, **5**: n = 1; **2**, **6**: n = 2; **3**, **7**: n = 3; **4**, **8**: n = 5.

Scheme 1

calix[4]aryl skeleton, the separation of the *tert*-butyl groups of nearly 1.27 and 0.97 ppm and the separation of the phenyl protons of nearly 7.02 and 6.80 ppm of the calix[4]aryl indicated that compounds **5**–**8** were in a 'pinched' cone conformation. The protons of the selenium atom-attached phenyls gave two groups of complicated peaks at nearly 7.55 and 7.20 ppm.

Bis(alkylthiaalkoxy)calix[4]arenes **9**–**11** were synthesized by the reaction of calix[4]arene dibromides **3** and **4** with propanethiol and pentanethiol in the presence of NaH as a base and purified by column chromatography. Their cone conformation can be easily judged from the two doublets of the protons within the methylene bridge of the calix[4]aryl skeleton. 1,3-Bis(phenylseleno)propane **12** was obtained in good yield by reaction of the sodium salt of selenophenol with 1,3-dibromopropane.

X-Ray crystallography of 6

The X-ray structure of calix[4]arene **6** was elucidated for determination of the structure (Fig. 1a). As shown in Fig. 1a and 1b, **6** is in a C_{2v} symmetric cone conformation in the solid state, with one molecule of CH_2Cl_2 embedded within the cavity of four aromatic groups as a guest *via* a CH–π interaction. Dichloromethane C(32) distances to the centroids of the four aromatic rings (labeled X(1A), X(1B), X(1C), X(1D), respectively) are 3.481, 3.481, 4.031 and 4.031 Å, respectively. The two guest hydrogen atoms are opposite one another (see Fig. 1b). The centroid ··· H separation is 2.547 Å, with the centroid ··· H–C(32) angle of 164.4°. The two opposite arenes which bind to guest H(32A) and H(32B) are with an interplanar angle of 38.2°. The other two aromatic rings are tilted away from the cavity with an interplanar angle of 87.7°. The torsion angles of O(2)–C(23)–C(24)–C(25) and C(23)–C(24)–C(25)–Se(1) are −55.0° and −68.3°, respectively. In addition, the selenium atoms (Se(1) and Se(2)) are disordered (only one position is shown in Fig. 1).

Ion selectivity

The Ag^+ selectivities of phenylselenoalkoxy functionalized calix[4]arenes **5**–**8** were evaluated by the potentiometric selectivity coefficients (log $K^{pot}_{Ag,M}$). For comparison, alkylthiaalkoxy functionalized calix[4]arenes **9**–**11** and 1,3-bis(phenylseleno)propane **12** were examined under the same conditions. The polymer membrane was composed of PVC as the matrix, dibutyl phthalate (DBP) as the membrane solvent, and a bis(phenylselenoalkoxy) functionalized calix[4]arene as the ionophore. The membranes also contained 75 mol% of potassium tetrakis(*p*-chlorophenyl)borate (KTClPB) relative to the ionophore 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^+, determined by the fixed interference method, are illustrated in Table 1. The selectivity coefficient (log $K^{pot}_{Ag,M}$) represents the preference of the ISE (or PVC membrane) containing the bis(phenylselenoalkoxy) functionalized calix[4]arene for Ag^+ over the other cations. Therefore, the coefficient log $K^{pot}_{I,M}$ defines the ability of an ISE (or membrane) to recognize different ions under the same conditions. The smaller the log $K^{pot}_{I,M}$ value, the greater the electrode preference for the primary ion (I^+) over the interfering ion (M^+).

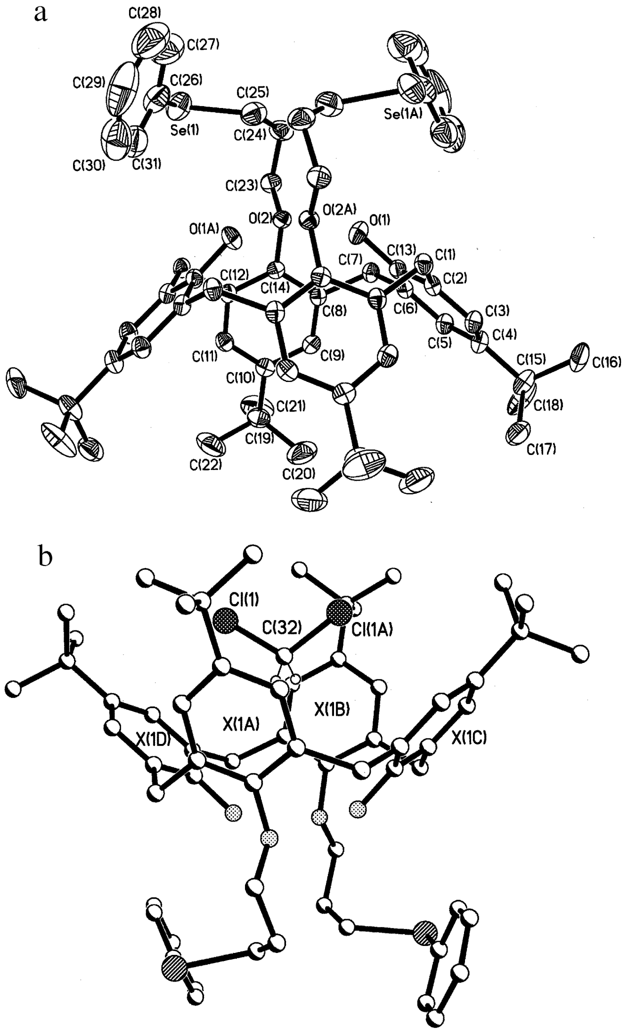


Fig. 1 The structure of **6**. a) Labeling of compound **6**; b) Structure of **6·CH$_2$Cl$_2$**.

As can be seen from Table 1, all polymer membranes containing calix[4]arenes **5**–**8** as ionophores gave excellent log $K^{pot}_{Ag,M}$) values (≤ -3.4) against most of the interfering cations examined (*i.e.*, Na^+, K^+, NH_4^+, Ca^{2+}, Mg^{2+}, Ni^{2+}, Zn^{2+}, Cu^{2+}, Cd^{2+} and Pb^{2+}), except for Hg^{2+} which gave a relatively smaller interference. It is interesting to note that, despite the different tether length incorporated between phenylseleno and calix[4]aryl, **5**–**8**-based ISEs exhibited the same characteristic ion selectivity tendencies which resemble each other. Although the bis(alkylthiaalkoxy) functionalized calix[4]arenes **9**–**11**-based ISEs also gave the same ion selectivity tendencies, the log $K^{pot}_{Ag,M}$ values are usually higher by one order of magnitude than those of the **5**–**8**-based ISEs for the same cation. The selectivity coefficients of 1,3-bis(phenylseleno)propane **12**-based ISEs are similar to those of **9**–**11**-based ISEs. Therefore, the performance of **5**–**8**-based ISEs is superior to that displayed by traditional Ag_2S-based electrode or **9**–**12**-based ISEs and is satisfactory as Ag^+-ISE. The fact that polymer membranes containing ionophores **5**–**8** gave excellent log $K^{pot}_{I,M}$ values (≤ -3.4) against Na^+, K^+, NH_4^+, Ca^{2+}, Mg^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} means that **5**–**8**-based ISEs possess high Ag^+ selectivities and only weakly respond to the above interfering ions. The

Table 1 Selectivity coefficients (log $K^{\mathrm{pot}}_{\mathrm{Ag,M}}$) of the electrodes based on ionophores **5**–**12**[a]

	log $K^{\mathrm{pot}}_{\mathrm{Ag,M}}$							
Ion	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
Ag^+	0	0	0	0	0	0	0	0
Na^+	−4.2	−4.2	−3.2	−3.5	−2.9	−3.1	−3.0	−3.5
K^+	−4.2	−4.1	−3.7	−3.4	−2.9	−3.1	−3.4	−3.2
NH_4^+	−4.4	−4.3	−4.1	−3.5	−4.5	−4.0	−3.4	−3.4
Ca^{2+}	−5.0	−5.2	−5.0	−4.6	−4.3	−4.5	−3.3	−4.1
Mg^{2+}	−5.0	−5.2	−4.9	−4.7	−4.4	−4.3	−4.0	−4.6
Ni^{2+}	−5.2	−5.3	−5.1	−4.6	−4.4	−4.3	−3.9	−4.5
Cu^{2+}	−5.2	−5.3	−4.8	−4.6	−4.3	−4.0	−3.6	−4.4
Zn^{2+}	−5.0	−5.1	−5.0	−4.5	−4.4	−4.1	−3.4	−4.3
Cd^{2+}	−5.0	−5.0	−5.2	−4.9	−4.3	−4.3	−3.9	−4.5
Pb^{2+}	−5.4	−4.9	−5.0	−4.1	−4.5	−4.4	−3.9	−4.2
Hg^{2+}	−1.7	−1.8	−1.7	−1.6	−1.2	−1.4	−1.8	−2.2

[a] Note: Selectivity coefficients (log $K^{\mathrm{pot}}_{\mathrm{Ag,M}}$) of the electrodes based on ionophores **5**–**12** are mean data of two measurements using FIM.

strong Hg^{2+} interference in some ionophore-based ISEs[12,21,22] and traditional Ag_2S-based ISEs[23] is largely eliminated in the present ISEs (log $K^{\mathrm{pot}}_{\mathrm{Ag,Hg}} \leq -1.6$ for the present ISEs). A possible explanation is that those ions with high hydration energies, such as Na^+, K^+, NH_4^+, Ca^{2+}, Mg^{2+}, Pb^{2+} and most divalent transition metal ions, cannot strongly interact with selenium donors in the ionophores, while less heavily hydrated soft Ag^+ coordinates to soft selenium donors selectively. The fact that polymer membranes containing **9**–**11** gave greater log $K^{\mathrm{pot}}_{\mathrm{I,M}}$ values against most interfering ions than any one of the **5**–**8**-based ISEs means that **9**–**11**-based ISEs possess lower Ag^+ selectivity than any one of the **5**–**8**-based ISEs. This can be tentatively rationalized as follows. The two selenium atoms in the ionophores **5**–**8** are softer than the two sulfur atoms in the ionophores **9**–**11**. Compared with sulfur donors, the hard cations with high hydration energies cannot interact strongly with the selenium donors. Thus, the softer selenium donors benefit the coordination with silver ion selectively in the membrane phase. On the other hand, the neighboring phenyl of ionophores **5**–**8** may act as a π-donor to assist the ligation of silver ion *via* so called cation–π interactions.[24] Although it is not exact to use the solid state of ionophores to explain the complicated ISE behavior in the liquid membrane phase, the solid state conformation of the ionophore may assist further understanding of the mechanisms of the ionophore-based ISEs; at least we can predict the tendencies of the ISE behavior from the solid state structure of the ionophores. As can be seen from Fig. 1, the two phenyls take an opposite orientation along the phenyl–selenium axis in the solid state. This conformation may favor the cation–π coordination patterns in the spatial orientation.

As shown in Table 1, the log $K^{\mathrm{pot}}_{\mathrm{Ag,M}}$ values gradually increased for the interfering Na^+, K^+, NH_4^+, Ca^{2+}, Mg^{2+} and Pb^{2+}, as well as most of the transition metal ions examined with the tether length increased between the selenium atom and calix[4]aryl for the same type of ionophores **5**–**8**. There are two possible explanations for this ion-selectivity tendency. The first one is that the coordinate adjustable abilities decrease for the two donor groups with the increase of the tether length between the selenium atom and the calix scaffold. The second one is that the ionophores gradually exhibit the signs of ditopic receptors with the increase of the tether length, namely, the four oxygen atoms on the lower rim of calix[4]arene act as a hard donor centre and the two phenylseleno groups act as a soft coordinate centre. The hard donor centre has an affinity for high hydrate ions, and the soft donor centre has an affinity for silver ion selectively.

Although the diseleno compound **12** can provide two coordination positions for guest ions, unlike the ionophores **5**–**8**, it cannot provide a *trans*-coordinating geometric configuration for silver ion. It is known that two-coordinate silver complexes are usually in a *trans*-conformation.[25] Thus, **12** might adopt some complicated coordination patterns with guest cations compared with ionophores **5**–**8** in a two-coordinate *trans*-conformation. Therefore, the selectivity for silver ion is relatively lower than that of any one of the **5**–**8**-based ISEs. The log $K^{\mathrm{pot}}_{\mathrm{Ag,M}}$ values of the interfering Na^+, K^+, NH_4^+, Ca^{2+}, Mg^{2+} and Pb^{2+}, as well as most of the transition metal ions, are larger than those of any one of the **5**–**8**-based ISEs. As can be seen from Table 1, the compound **12**-based ISE gave the weakest Hg^{2+} interference towards Ag^+ of all the **5**–**12**-based ISEs. It is known that free Hg^{2+} only exists in a strongly acidic medium (pH < 2). When the medium pH > 2, Hg^{2+} usually exists in the form of $Hg(OH)^+$. The oxygen atoms on the lower rim of the calix scaffold in the ionophores **5**–**11** will more or less assist the ligation of $Hg(OH)^+$ *via* O–H ··· O hydrogen bonds. Our previous studies have demonstrated the strongest examples of the oxygen atoms close to the soft bonding donors giving rise to a relatively strong Hg^{2+} interference towards Ag^+. Because there are no hard donors in the ionophore **12**, **12**-based ISEs give the weakest interference of Hg^{2+} towards Ag^+ of all the **5**–**12**-based ISEs.

Besides the differences in the ion-selectivities, there are some other differences in the performances of **5**–**12**-based ISEs. 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, the Nernstian slopes of **5**–**8**-based ISEs are between 54.2 ± 1.5 and 57.2 ± 1.8 mV decade^{-1} to the activity of Ag^+ in the activity range 5×10^{-6}–$1 \times 10^{-1.4}$ M $AgNO_3$. The relevant values of **9**–**11**-based ISEs are between 51.7 ± 1.8 and 52.4 ± 1.8 mV decade^{-1} to the activity of Ag^+ in the activity range 5×10^{-6}–1×10^{-2} M $AgNO_3$. The Nernstian slope of **5**–**8**-based ISEs is remarkably higher than that of **9**–**11**-based ISEs. The linear response range of **5**–**8**-based ISEs is larger by one order of magnitude than that of **9**–**11**-based ISEs. The response time of **5**–**12**-based ISEs is within 15 s. One possible explanation is that sulfur donors give relatively strong binding of silver ion compared with that of a selenium donor. The stronger binding of silver ion by a sulfur donor might interfere in the rapid ion exchange at the interface of membrane electrodes. On the other hand, the Nernstian slopes of the present tweezer-like ionophores **5**–**8**-based ISEs are better than those of diphenyl selenide, dibenzyl selenide or benzyl phenyl selenide based ISEs reported by Katsu and co-workers.[26] The ion-selectivity and the Nernstian slopes are also better than those of our previously reported phosphorus and pyridyl functionalized tweezer-like calix[4]arenes.[16]

Conclusions

Tweezer-like receptor molecules 25,27-dihydroxy-26,28-bis-(phenylselenoalkoxy)-5,11,17,23-tetra-*tert*-butylcalix[4]arenes

Table 2 The response characteristics of silver ISEs based on **5**–**12**

Ionophore	5	6	7	8	9	10	11	12
Slope[a]/mV decade^{-1}	54.9 ± 1.4	54.2 ± 1.5	57.2 ± 1.8	56.5 ± 1.6	52.0 ± 1.6	52.4 ± 1.8	51.7 ± 1.8	56.4 ± 1.5
Linear range/M	10^{-6}–$10^{-1.4}$	10^{-6}–$10^{-1.4}$	10^{-6}–$10^{-1.4}$	10^{-6}–$10^{-1.4}$	$10^{-5.3}$–10^{-2}	$10^{-5.3}$–10^{-2}	$10^{-5.3}$–10^{-2}	10^{-6}–10^{-2}
Response time/s	<10	<10	<10	<10	<15	<15	<15	<10

[a] Note: the slopes are calculated within their linear range and are mean data of four electrodes (standard deviations given at 95% confidence level) for each ionophore.

5–**8** have been synthesized as sensors for Ag^+-selective electrodes. 25,27-Dihydroxy-26,28-bis(alkylthiaalkoxy)-5,11,17,23-tetra-*tert*-butylcalix[4]arenes **9**–**11** and 1,3-bis(phenylseleno)-propane **12** were also prepared for the comparison of the ISEs' performances with **5**–**8**-based ISEs. The polymer membranes containing **5**–**8** gave good selectivity for Ag^+ ($\log K^{\mathrm{pot}}_{\mathrm{Ag,M}} \leq -3.4$) 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+}), except for Hg^{2+}. Ionophores **5**–**8**-based ISEs gave the best selectivity and sensitivity towards Ag^+ against interfering cations of the eight investigated ionophore based ISEs. The performance of the present ISEs is superior to that displayed by the traditional Ag_2S-based electrode.

Experimental

^{1}H NMR spectra were recorded on a Bruker AC-P200 spectrometer at 200 MHz in $CDCl_3$ solution. Tetramethylsilane was used as an internal standard. Elemental analyses were performed on a Perkin-Elmer 2400C instrument. FAB-MS spectra were obtained on a VG ZAB-HS spectrometer. All solvents were purified by standard procedures. Poly(vinyl chloride) (PVC) and potassium tetrakis(4-chlorophenylborate) (KTClPB) 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. Compounds **1**–**4** were prepared according to the literature procedures.[27]

General procedure A for the preparation of diselenocalix[4]arenes 5–8

Diphenyl diselenide (624 mg, 2 mmol), NaOH (240 mg, 6 mmol) and $NaBH_4$ (228 mg, 6 mmol) were added to a 250 mL flask. After the system was charged with nitrogen, anhydrous ethanol (30 mL) was added to the stirred mixture. After the mixture was refluxed for 1 h, a solution of calix[4]arene dibromide (1 mmol) in 60 mL THF was added to the yellowish transparent solution. After the addition was completed, the system was refluxed for another 6 h. Then, the solvent was removed under reduced pressure. The solid residue was dissolved in CH_2Cl_2 (50 mL) and washed with water (100 mL × 2). After the organic phase had been dried with anhydrous sodium sulfate, the filtered solution was condensed to dryness. The yellowish solid was purified by column chromatography (petroleum ether : $CHCl_3$ = 1 : 3) and then recrystallized from CH_2Cl_2 and methanol.

25,27-Dihydroxy-26,28-bis(phenylselenoethoxy)-5,11,17,23-tetra-*tert*-butylcalix[4]arene (5). Reaction of **1** (1 mmol) with diphenyl diselenide (2 mmol) according to the general procedure A gave **5** in 92% yield; mp 105–106 °C. ^{1}H NMR: 7.58(m, 4H, Se-phenyl-H), 7.23(m, 6H, Se-phenyl-H), 7.16(s, 2H, OH), 7.02(s, 4H, Ar-H), 6.75(s, 4H, Ar-H), 4.25(d, 4H, J = 13.7 Hz, $ArCH_2Ar$), 4.17(t, 4H, J = 6.8 Hz, OCH_2CH_2), 3.44(t, 4H, J = 6.8 Hz, $SeCH_2CH_2$), 3.26(d, 4H, J = 13.7 Hz, $ArCH_2Ar$), 1.26(s, 18H, *t*-Bu-H), 0.93(s, 18H, *t*Bu-H). FAB$^+$-MS *m*/*z* 1016.1 (M$^+$, Calcd, 1016.4). Calcd. for $C_{60}H_{72}O_4Se_2$: C, 70.99; H, 7.15. Found: C, 70.91; H, 7.15%.

25,27-Dihydroxy-26,28-bis(phenylselenopropoxy)-5,11,17,23-tetra-*tert*-butylcalix[4]arene (6). Reaction of **2** (1 mmol) with diphenyl diselenide (2 mmol) according to the general procedure A gave **6** in 91% yield; mp 133–134 °C. ^{1}H NMR: 7.82(s, 2H, OH), 7.62(m, 4H, Se-phenyl-H), 7.20(m, 6H, Se-phenyl-H), 7.03(s, 4H, Ar-H), 6.84(s, 4H, Ar-H), 4.23(d, 4H, J = 13.2 Hz, $ArCH_2Ar$), 4.07(t, 4H, J = 5.3 Hz, OCH_2CH_2), 3.36(t, 4H, J = 6.6 Hz, $SeCH_2CH_2$), 3.30(d, 4H, J = 13.2 Hz, $ArCH_2Ar$), 2.27(m, 4H, $SeCH_2\mathit{CH_2}CH_2$), 1.26(s, 18H, *t*-Bu-H), 0.99(s, 18H, *t*-Bu-H). FAB$^+$-MS *m*/*z* 1044.5 (M$^+$, Calcd, 1044.4). Calcd. for $C_{62}H_{76}O_4Se_2$: C, 71.38; H, 7.34. Found: C, 71.21; H, 7.48%.

25,27-Dihydroxy-26,28-bis(phenylselenobutoxy)-5,11,17,23-tetra-*tert*-butylcalix[4]arene (7). Reaction of **3** (1 mmol) with diphenyl diselenide (2 mmol) according to the general procedure A gave **7** in 86% yield; mp 98–99 °C. ^{1}H NMR: 7.72(s, 2H, OH), 7.47(m, 4H, Se-phenyl-H), 7.18(m, 6H, phenyl-H), 7.03(s, 4H, Ar-H), 6.81(s, 4H, Ar-H), 4.23(d, 4H, J = 12.7 Hz, $ArCH_2Ar$), 3.95(t, 4H, J = 4.8 Hz, OCH_2CH_2), 3.28(d, 4H, J = 12.7 Hz, $ArCH_2Ar$), 3.08(t, 4H, J = 5.3 Hz, $SeCH_2CH_2$), 2.10(m, 8H, CH_2CH_2), 1.28(s, 18H, *t*-Bu-H), 0.97(s, 18H, *t*-Bu-H). FAB$^+$-MS *m*/*z* 1072.1 (M$^+$, Calcd, 1072.4). Calcd. for $C_{64}H_{80}O_4Se_2$: C, 71.76; H, 7.53. Found: C, 71.68; H, 7.29%.

25,27-Dihydroxy-26,28-bis(phenylselenohexoxy)-5,11,17,23-tetra-*tert*-butylcalix[4]arene (8). Reaction of **4** (1 mmol) with diphenyl diselenide (2 mmol) according to the general procedure A gave **8** in 91% yield; mp 99–100 °C. ^{1}H NMR: 7.67(s, 2H, OH), 7.48(m, 4H, Se-phenyl-H), 7.19(m, 6H, Se-phenyl-H), 7.02(s, 4H, Ar-H), 6.80(s, 4H, Ar-H), 4.24(d, 4H, J = 12.8 Hz, $ArCH_2Ar$), 3.92(t, 4H, J = 6.8 Hz, OCH_2CH_2), 3.27(d, 4H, J = 12.8 Hz, $ArCH_2Ar$), 2.98(t, 4H, J = 7.1 Hz, $SeCH_2CH_2$), 1.98, 1.82, 1.55(m, 16H, $-(CH_2)_4-$), 1.31(s, 18H, *t*-Bu-H), 0.97(s, 18H, *t*-Bu-H). FAB$^+$-MS *m*/*z* 1127.6 ($[M - 1]^+$, Calcd, 1128.5). Calcd. for $C_{68}H_{88}O_4Se_2$: C, 72.45; H, 7.87. Found: C, 72.61; H, 7.88%.

General procedure B for the preparation of dithiacalix[4]arenes 9–11

Calix[4]arene dibromide (1 mmol) was added to a 100 mL round-bottomed flask, together with anhydrous potassium carbonate (276 mg, 2 mmol), and thiol (0.5 mL) in THF (60 mL). After the system had been charged with nitrogen, the mixture was refluxed until the disappearance of calix[4]arene dibromide, monitored by TLC. Then, the solvent was removed under reduced pressure. The residue was dissolved in CH_2Cl_2 (50 mL) and washed with water (50 mL × 3). The organic phase was separated and dried with anhydrous sodium sulfate. After the filtered solution had been condensed to dryness, the yellowish residue was purified by column chromatography (petroleum ether : CH_2Cl_2, 1 : 2).

25,27-Dihydroxy-26,28-bis(propylthiabutoxy)-5,11,17,23-tetra-*tert*-butylcalix[4]arene (9). Reaction of **3** (1 mmol) with propanethiol (0.5 mL) according to the general procedure B gave **11** in 93% yield; mp 104–106 °C. ^{1}H NMR: 7.80(s, 2H, OH), 7.02(s, 4H, Ar-H), 6.81(s, 4H, Ar-H), 4.25(d, 4H, J = 12.8 Hz, ArCH$_2$Ar), 3.98(t, 4H, J = 6.4 Hz, OCH$_2$), 3.29(d, 4H, J = 12.8 Hz, ArCH$_2$Ar), 2.67(t, 4H, J = 6.4 Hz, CH$_2$), 2.52(t, 4H, J = 7.2 Hz, –CH$_2$), 2.04, 2.00(m, 8H, CH$_2$), 1.61(m, 4H, CH$_2$), 1.26(s, 18H, *t*-Bu-H), 0.97(s, 18H, *t*-Bu-H), 0.96(t, 6H, J = 7.3 Hz, SCH$_2$CH$_2$CH$_3$). FAB$^+$-MS *m*/*z* 908.2 (M$^+$, Calcd, 908.6). Calcd. for $C_{58}H_{84}O_4S_2\cdot 0.75CH_2Cl_2$: C, 72.51; H, 8.86. Found: C, 72.81; H, 9.01%.

25,27-Dihydroxy-26,28-bis(propylthiahexoxy)-5,11,17,23-tetra-*tert*-butylcalix[4]arene (10). Reaction of **4** (1 mmol) with propanethiol (0.5 mL) according to the general procedure B gave **10** in 87% yield. ^{1}H NMR: 7.82(s, 2H, OH), 7.01(s, 4H, Ar-H), 6.80(s, 4H, Ar-H), 4.26(d, 4H, J = 13.0 Hz, ArCH$_2$Ar), 3.98(t, 4H, J = 6.8 Hz, OCH$_2$), 3.29(d, 4H, J = 13.0 Hz, ArCH$_2$Ar), 2.48, 1.95(m, 24H, CH$_2$), 1.60(m, 4H, CH$_2$), 1.25(s, 18H, *t*-Bu-H), 0.97(s, 18H, *t*-Bu-H), 0.84(t, 6H, J = 7.3 Hz, –CH$_3$). FAB$^+$-MS *m*/*z* 964.9 (M$^+$, Calcd, 964.6). Calcd. for $C_{62}H_{92}O_4S_2$: C, 77.13; H, 9.60. Found: C, 77.25; H, 9.49%.

25,27-Dihydroxy-26,28-bis(pentylthiahexoxy)-5,11,17,23-tetra-*tert*-butylcalix[4]arene (11). Reaction of **4** (1 mmol) with *n*-pentanethiol (0.7 mL) according to the general procedure B gave **11** as a sticky oil in 88% yield. ^{1}H NMR: 7.84 (s, 2H, OH), 7.03 (s, 4H, Ar-H), 6.82 (s, 4H, Ar-H), 4.27 (d, 4H, J = 12.9 Hz, ArCH$_2$Ar), 3.97 (t, 4H, J = 6.8 Hz, OCH$_2$), 3.29 (d, 4H, J = 12.9 Hz, ArCH$_2$Ar), 2.58 (m, 8H, CH$_2$), 2.01, 1.65, 1.57, 1.37 (m, 28H, CH$_2$), 1.27 (s, 18H, *t*-Bu-H), 0.96 (s, 18H, *t*-Bu-H), 0.87 (t, 6H, J = 7.2 Hz, –CH$_3$). FAB$^+$-MS *m*/*z* 1020.4 (M$^+$, Calcd, 1020.7). Calcd. for $C_{66}H_{100}O_4S_2$: C, 77.59; H, 9.87. Found: C, 77.56; H, 9.59%.

1,3-Bis(phenylseleno)propane (12). Diphenyl diselenide (512 mg, 1.6 mmol), NaOH (192 mg, 4.8 mmol) and NaBH$_4$ (182 mg, 4.8 mmol) were added to a 250 mL flask. After the system had been charged with nitrogen, anhydrous ethanol (30 mL) was added to the stirred mixture. After the mixture had been refluxed for 1 h, a solution of 1,3-dibromopropane (212 µL, *ca.* 1.52 mmol) in 60 mL THF was added dropwise to the yellowish transparent solution. After the addition was completed, the system was refluxed for another 6 h. Then, the solvent was removed under reduced pressure. The oily residue was dissolved in CH$_2$Cl$_2$ (50 mL) and washed with water (50 mL × 2). After the organic phase had been dried with anhydrous sodium sulfate, the filtered solution was condensed to dryness. The yellowish oil was purified by column chromatography (petroleum ether : CHCl$_3$ = 3 : 1). **15** was obtained as a yellowish oil (0.323 g) in 60% yield. ^{1}H NMR: 7.45–7.41 (m, 4H), 7.23–7.20 (m, 6H), 2.97 (t, 4H, J = 7.2 Hz), 2.02 (m, 2H, J = 7.2 Hz). FAB$^+$-MS *m*/*z* 355.7 (M$^+$, Calcd, 355.9). Calcd. for $C_{15}H_{16}Se_2$: C, 58.86; H, 4.55. Found: C, 59.41; H, 4.21%.

Membrane electrode preparation

A typical procedure for membrane preparation is as follows. Poly(vinyl chloride) (PVC) (132 mg, 33%), dibutyl phthalate (DBP) (264 mg, 65–66%), benzothiazolyl functionalized calix[4]arene (4 mg, 1%) and potassium tetrakis(*p*-chlorophenyl)-borate (KTClPB) (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 32 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. After injection of 0.01 M aqueous solution of AgNO$_3$ as the internal solution, the electrode was conditioned by soaking in 0.01 M aqueous solution of AgNO$_3$ for 24 h before measurements. The reference electrode is a double junction type of saturated Hg/Hg$_2$Cl$_2$ electrode with 3 M KNO$_3$ as bridge electrolyte.

Table 3 Crystal data and refinement parameters

Data	6
Formula	$C_{62}H_{76}O_4Se_2\cdot CH_2Cl_2$
Formula wt/g mol^{-1}	1128.07
T/K	293(2)
Wavelength/Å	0.71073
Crystal system	Monoclinic
Space group	$C2/c$
a/Å	21.4021(18)
b/Å	12.7375(11)
c/Å	21.3752(18)
α/deg	90
β/deg	90.207(2)
γ/deg	90
V/Å^3	5827.0(9)
Z	4
D_c/Mg m^{-3}	1.286
F(000)	2360
Crystal size/mm	0.3 × 0.2 × 0.15
μ (Mo Kα)/mm^{-1}	1.406
θ range/deg	1.86 to 25.03
Reflns collected	11775
Independent reflns	5140
R_{int}	0.0210
Restraints	0
Parameters	330
$GOOF$	1.050
R_1	0.0543
wR_2	0.1597

EMF Measurements

All EMF (electromotive force) measurements were made at 25 ± 0.1 °C, using a pH/mV meter. Sample solutions were 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 in the high Ag$^+$ concentration. The composition of the electrochemical cell is given as Ag·AgCl|0.01 M AgNO$_3$|PVC membrane |sample solution |3 M KNO$_3$ |saturated KCl|Hg$_2$Cl$_2$·Hg.

Selectivity coefficients

The potentiometric selectivity coefficients $K^{\mathrm{pot}}_{\mathrm{Ag,M}}$ determined here are defined in the Nicolsky–Eisenman equation (eqn. (1)).

$$E = E^0 + \frac{2.303RT}{F}\log\,[a_{\mathrm{Ag}} + K^{\mathrm{pot}}_{\mathrm{Ag,M}}(a_{\mathrm{M}})^{1/Z_{\mathrm{M}}}] \tag{1}$$

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 foreign cation, and Z_{M} the charge of the foreign cation. The selectivity coefficients were determined by the fixed interference method (FIM).[28] According to this method, the potentiometric selectivity coefficients, $K^{\mathrm{pot}}_{\mathrm{Ag,M}}$, can be evaluated from the potential measurements on solutions containing a fixed concentration of the interfering ions (M^{n+}) and varying amounts of Ag$^+$ ion concentration by using eqn. (2)

$$K^{\mathrm{pot}}_{\mathrm{Ag,M}} = a_{\mathrm{Ag}}/(a_{\mathrm{M}})^{1/Z_{\mathrm{M}}} \tag{2}$$

The resulting log $K^{\mathrm{pot}}_{\mathrm{Ag,M}}$ values are summarized in Table 1.

Crystallographic structural determination

Crystals of **6** suitable for X-ray crystallography were grown by slow evaporation from the CH$_2$Cl$_2$–MeOH solution of **6**. X-ray crystallographic data were obtained on a Bruker SMART 1000 instrument. Structures were solved with the SHELXS-97 software. Crystal, data collection, and refinement parameters are given in Table 3.[29]

Acknowledgements

The National Natural Science Foundation of China and the Foundation of Nankai University supported this work.

References

1 P. A. Gale, *Coord. Chem. Rev.*, 2001, **213**, 79.

2 (*a*) E. Bakker, P. Bühlmann and E. Pretsch, *Chem. Rev.*, 1997, **97**, 3083; (*b*) P. Bühlmann, E. Pretsch and E. Bakker, *Chem. Rev.*, 1998, **98**, 1593.

3 (*a*) K. Kimura, T. Miura, M. Matsuo and T. Shono, *Anal. Chem.*, 1990, **62**, 1510; (*b*) K. Cunningham, G. Svehla, S. J. Harris and M. A. McKervey, *Anal. Proc.*, 1991, **28**, 294.

4 Z. Brazozka, B. Lammerink, D. N. Reinhoudt, E. Ghidini and R. Ungaro, *J. Chem. Soc., Perkin Trans. 2*, 1993, 1037.

5 (*a*) U. Schaller, E. Bakker, U. E. Spichiger and E. Pretsch, *Anal. Chem.*, 1994, **66**, 391; (*b*) E. Metzger, R. Aeschimann, M. Egli, G. Suter, R. Dohner, D. Ammann, M. Dobler and W. Simon, *Helv. Chim. Acta*, 1986, **69**, 1821; (*c*) R. Y. Xie and G. D. Christian, *Anal. Chem.*, 1986, **58**, 1806.

6 (*a*) X. Zeng, L. Weng, L. Chen, H. Ju, X. Leng, X. He and Z. Z. Zhang, *Chin. J. Chem.*, 2001, **19**, 493; (*b*) L. Chen, H. Ju, X. Zeng, X. He and Z. Z. Zhang, *Anal. Chim. Acta*, 2001, **447**, 41.

7 A. Cadogan, D. Diamond, M. R. Smyth, G. Svehla, M. A. McKervey, E. M. Seward and S. J. Harris, *Analyst*, 1990, **115**, 1207.

8 C. Péres-Jiméne, L. Escriche and J. Casabó, *Anal. Chim. Acta*, 1998, **371**, 155.

9 (*a*) A. S. Attiyat, Y. A. Ibrahim and G. D. Christian, *Microchem. J.*, 1988, **37**, 122; (*b*) A. Ohki, J. P. Lu and R. A. Bartsch, *Anal. Chem.*, 1994, **66**, 651; (*c*) A. Ohki, S. Maeda, J. P. Lu and R. A. Bartsch, *Anal. Chem.*, 1994, **66**, 1743.

10 K. Kimura, H. Yano, S. Kitazawa and T. Shono, *J. Chem. Soc., Perkin Trans. 2*, 1986, 1945.

11 S. Chung, W. Kim, S. B. Park, I. Yoon, S. S. Lee and D. D. Sung, *Chem. Commun.*, 1997, 965.

12 K. M. O'Conner, G. Svehla, S. J. Harris and M. A. McKervey, *Anal. Proc.*, 1993, **30**, 137.

13 (*a*) E. Malinowska, Z. Brzozka, K. Kasiura, R. J. M. Egberink and D. N. Reinhoudt, *Anal. Chim. Acta*, 1994, **298**, 245; (*b*) P. L. H. M. Cobben, R. J. M. Egberink, J. G. Bomer, P. Bergveld, W. Verboom and D. N. Reinhoudt, *J. Am. Chem. Soc.*, 1992, **114**, 10573.

14 (*a*) M. T. Lai and J. S. Shih, *Analyst*, 1986, **111**, 891; (*b*) S. K. Srivastava, V. K. Gupta and S. Jain, *Anal. Chem.*, 1996, **68**, 1272.

15 J. S. Kim, A. Ohk, R. Ueki, T. Ishizuka, T. Shimotashiro and S. Maeda, *Talanta*, 1999, **48**, 705.

16 X. Zeng, L. Weng, L. Chen, X. Leng, H. Ju, X. He and Z. Z. Zhang, *J. Chem. Soc., Perkin Trans. 2*, 2001, 545.

17 X. Zeng, L. Weng, L. Chen, X. Leng, Z. Z. Zhang and X. He, *Tetrahedron Lett.*, 2000, **41**, 4917.

18 X. Zeng, L. Weng and Z. Z. Zhang, *Chem. Lett.*, 2001, 550.

19 L. Chen, X. Zeng, X. He and Z. Z. Zhang, *Fresenius J. Anal. Chem.*, 2000, **367**, 535.

20 L. Chen, H. Ju, X. Zeng, X. He and Z. Z. Zhang, *Anal. Chim. Acta*, 2001, **437**, 191.

21 K. M. O'Conner, G. Svehla, S. J. Harris and M. A. McKervey, *Talanta*, 1992, **39**, 1549.

22 (*a*) X. Zeng, L. Chen, L. Weng, X. Leng, H. Ju, X. He and Z. Z. Zhang, *J. Chem. Res. (S)*, 2000, 518; (*b*) H. Ju, L. Chen, X. Zeng, X. He and Z. Z. Zhang, *Fenxi Kexue Xuebao*, 2001, in the press.

23 Y. Umezawa (Ed.), *Handbook of Ion-Selective Electrodes: Selectivity Coefficients*, CRC Press, Boca Raton, FL, 1990.

24 (*a*) J. C. Ma and D. A. Dougherty, *Chem. Rev.*, 1997, **97**, 1303; (*b*) See also our work about Ag^+–π interaction in the solid state: F. Xu, L. Weng, L. Sun, Z. Z. Zhang and Z. Zhou, *Organometallics*, 2000, **19**, 2658; (*c*) A. Ikeda and S. Shinkai, *J. Am. Chem. Soc.*, 1994, **116**, 3102; (*d*) F. Inokuchi, Y. Miyahara, T. Inazu and S. Shinkai, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1364.

25 M. Munakata, L. P. Wu and T. Kuroda-Sowa, *Adv. Inorg. Chem.*, 1999, **46**, 173.

26 T. Katsu and D. Xu, *Anal. Lett.*, 1998, **31**, 1979.

27 Z. T. Li, G. Z. Ji, C. K. Zhao, S. D. Yuan, H. Ding, C. Huang, A. L. Du and M. Wei, *J. Org. Chem.*, 1999, **64**, 3572.

28 G. G. Guilbault, R. A. Durst, M. S. Frant, H. Freiser, E. H. Hansen, T. S. Light, E. Pungor, G. Rechnitz, N. M. Rice, T. J. Rohm, W. Simon and J. D. R. Thomas, *Pure Appl. Chem.*, 1976, **48**, 127.

29 CCDC reference number 172823. See http://www.rsc.org/suppdata/p2/b1/b109238c/ for crystallographic files in .cif or other electronic format.