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The syntheses and Ag$^+$-selective electrode properties of benzothiazolylthiaalkoxy functionalized calix[4]arenes: an investigation of the structure–selectivity relationship in the ionophore-based ISEs

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Abstract—A series of benzothiazolylthiaalkoxy functionalized calix[4]arenes with different tether length between the benzothiazolyl and calix[4]aryl groups have been synthesized and characterized for comparison between the coordinate adjustment behaviors of the two benzothiazolyl groups in the generation of ion-selective electrodes (ISEs). ISEs based on these calix[4]arenes showed excellent Ag$^+$ selectivities, log $K_{\mathrm{Ag,M}}^{\mathrm{pot}} \leq -4.0$, against most of the interfering cations examined, except for Hg^{2+} having a very weak interference (log $K_{\mathrm{Ag,M}}^{\mathrm{pot}} \leq -2.5$). Their plausible recognition mechanism as well as their structure–selectivity relationships are also discussed.

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1. Introduction

Benefiting from their three-dimensional structures and easily chemically modified both at the upper- and lower-rims as well as having potential receptor properties for cations, anions and neutral molecules, calixarenes have enjoyed widespread use in various areas of science and technology. One of their successful applications is in analytical chemistry. They are useful for separations, enrichment, and analyses of ionic and neutral molecular species.[1–3] In particular, the ion-selective electrode (ISE) is an important target in analytical applications.[4,5] To improve or enhance the ion selectivities of calixarenes, a great deal of effort has been devoted to the design and synthesis of novel functionalized calixarenes in recent years.[1–3] Indeed, a large number of calixarene derivatives containing pendant ether, amide, ketonic, ester and crown ether groups have been employed in studies of ISEs sensitive to sodium ion,[6–15] potassium ion,[16] cesium ion,[17–19] thallium ion,[20] lead ion[21] and organic ammonium ions.[22] But only a few reports are concerned with calixarenes as carriers sensitive to transition metal ions in the ionophore-based ISEs.[23]

Our approach is to construct tweezer-like receptor molecules which are sensitive to transition metal ions by incorporating nitrogen, sulfur or phosphorous atoms into the lower-rim of calix[4]arenes. Reinhoudt[24] and ourselves[25] have found that this type of calix[4]arene derivative as an ionophore in ISEs exhibits a good Ag$^+$-selectivity against most interfering ions such as alkali metal, alkaline earth metal, lead and transition metal ions. The interference of Hg^{2+} towards these electrodes are also eliminated. However, when hard donors such as ester groups and hydroxy groups are close to the soft donors, the interference of Hg^{2+} is greatly increased.[26,27] The motivation for this work stems from several intrinsic problems existing in the recognition process of ionophore-based Ag$^+$-ISEs. Namely, how do the following factors influence the ISEs' behaviors: (i) type of coordinate atoms, (ii) tether length between the donors and calix[4]aryl and (iii) structure of the receptor?

In this paper,[25a] we wish to report the syntheses and characterization of 25,27-dihydroxy-26,28-bis(benzothiazolylthiaalkoxy)calix[4]arenes **9**, **11** and 25,27-dihydroxy-26,28-bis(benzothiazolylthiaalkoxy)-5,11,17,23-tetra-*tert*-butylcalix[4]arenes **10**, **12**–**14** (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 **9**–**14** with those of 25-hydroxy-26,28-dipropoxy-27-benzothiazolylthiapropoxy-5,11,17,23-tetra-*tert*-butylcalix[4]arene **18** (cone) and **19** (partial cone). The X-ray crystallographic structures of **10**,

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Keywords: calix[4]arenes; ionophores; crystal structure; silver; electrodes.

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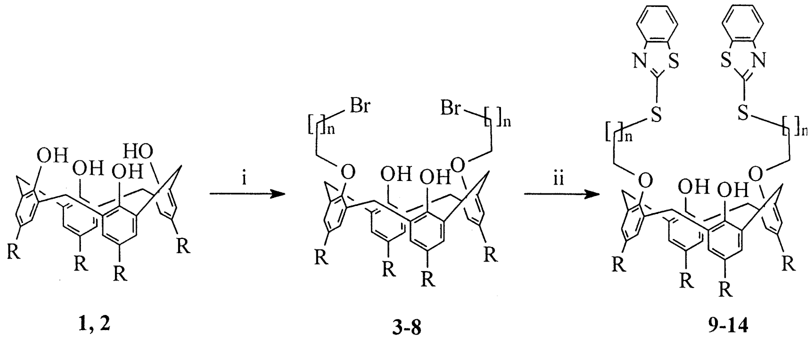


Scheme 1. **1**: R=H; **2**: R=*t*-Bu; **3**, **9**: R=H, *n*=1; **4**, **10**: R=*t*-Bu, *n*=1; **5**, **11**: R=H, *n*=2; **6**, **12**: R=*t*-Bu, *n*=2; **7**, **13**: R=*t*-Bu, *n*=3; **8**, **14**: R=*t*-Bu, *n*=5. (i) $BrCH_2(CH_2)_nBr$, K_2CO_3, CH_3CN, refluxed for 36–48 h. (ii) 2-mercaptobenzothiazole, $NaHCO_3$, THF–H_2O, refluxed for 48 h.

11, **18** and **19**, will serve our further understanding of the structure–selectivity relationship in the Ag^+-ISEs. On the other hand, comparison of the ISE behavior of **9–14**, **18**, **19** with the 25,27-dihydroxy-26,28-bis(propylthiabutoxy)-5,11,17,23-tetra-*tert*-butylcalix[4]arene **21** may provide further understanding of the competitive coordinate behavior of the sulfur atoms and the nitrogen atoms in multipoint ionophores.

2. Results and discussion

2.1. Syntheses

Calix[4]arene dibromides **4–7**[28] were prepared according to literature procedures. Compounds **3** and **8** were also synthesized following the preparation of **4–7** with good yields. ^1H NMR spectroscopy indicated that calix[4]arenes **3** and **8** are in a C_{2v} symmetrical cone conformation, which can be easily judged from the two doublets of the protons of the methylene bridge of the calix[4]arene skeleton.

Calix[4]arenes **9–14** were synthesized in yields between 75 and 95% by the reaction of calix[4]arene dibromides **3–8** with 2-mercaptobenzothiazole as shown in Scheme 1. The reaction of **3** with **2**-mercaptobenzothiazole in the presence of potassium carbonate in THF–toluene–H_2O also gave **9** in high yield. Treatment of **2** with 2-chloro-1-bromoethane in DMF in the presence of potassium carbonate gave **20** (Chart 1) in 71.5% yield. Compound **20** is confirmed by X-ray structure analysis (Fig. 1) and FAB mass spectra. The reaction of **20** with 2-mercaptobenzothiazole in THF in the presence of potassium carbonate also gave compound **10** in good yield. Two doublets for the protons of the methylene bridge of the calix[4]arene skeleton, and the separation of the *tert*-butyl resonances, as well as the separation of the aryl protons of calix[4]arene skeleton indicated that **9–14** are in a ‘pinched’ cone conformation.

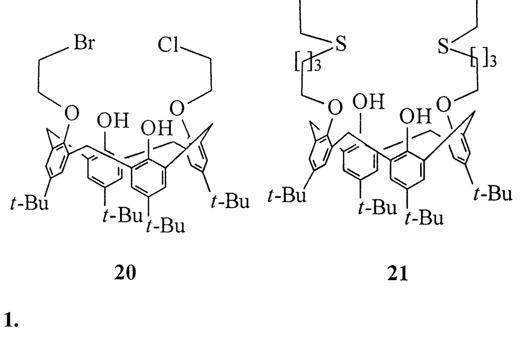


Chart 1.

Compound **10** taking a pinched cone conformation was further elucidated by X-ray crystallography as shown in Fig. 2. The aryl rings bearing the OH groups were tilted away from the cavity, which forms a dihedral angle of 105.2°, while those bearing the benzothiazolylthioethoxy groups form a dihedral angle of 47.1°. The adjacent four arenes have interplanar angles between 76.0 and 109.0°. One molecule of CH_2Cl_2 is capped in this distorted cavity as a guest via Cl/π interaction[29] and a CH/π weak interaction.[30,31] The distance of the Cl(2)–ring centroid (labeling C(3)–C(7), C(28)) is 3.40 Å, with a ring centroid–Cl(2)–C(102) angle of 156.8°. Theoretical studies[30] demonstrated a similar CH/π interaction between chloroform and benzene, energetically favored by 16.4 kJ mol^{-1} with a chloroform C–ring centroid distance of 3.36 Å, cf. 3.48 Å for C–ring centroid in **10**, which is associated with an H–ring centroid distance of 2.97 Å.

As shown in Fig. 3, **11** adopts a cone conformation commonly found in calix[4]arenes, with the two benzothiazolyl groups stretched along the lower-rim. The inter-

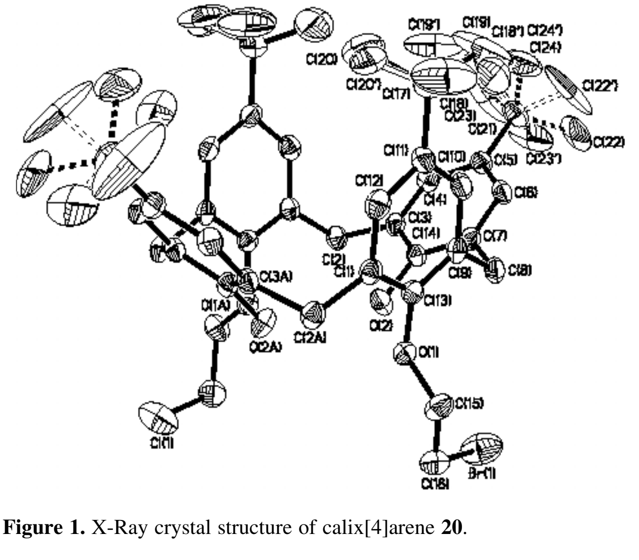


Figure 1. X-Ray crystal structure of calix[4]arene **20**.

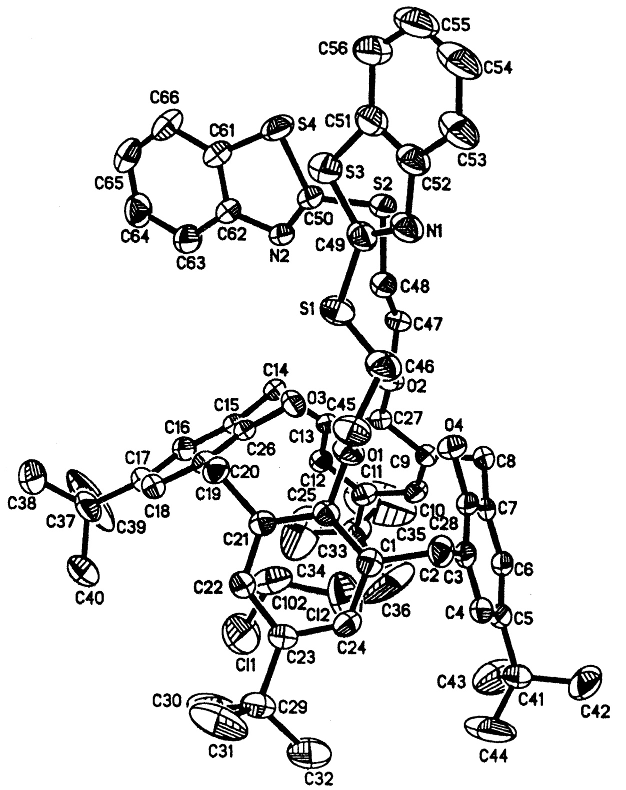


Figure 2. Structure of compound **10**·CH_2Cl_2. All H atoms are omitted for clarity.

planar angles between the planes of the four adjacent aromatic arenes are 103.9, 98.7 71.3 and 76.6°, respectively. Two opposite arenes bearing benzothiazolylthiapropoxy group have an interplanar angle of 36.5°, while the other two aromatic rings are tilted away from the calixarene cavity with an interplanar angle of 82.0°. As shown in Fig. 4, **11** forms a dimer structure via self-inclusion of the two cavities, namely one of the four phenyl groups of which formed the cavity is capped by another cavity. The attraction leading to the supramolecular structure is π–π stacking, which is formed by the partial overlapping of the two aromatic groups, and with an interplanar angle of 0°, as well as a distance of 3.44 Å between the two arenes. The centroid–centroid distance of the two aromatic rings capping each other is 4.26 Å, which is shorter than 4.6 Å defined for the extreme condition of this type of parallel-displaced π–π stacking by molecular modeling.[30,32]

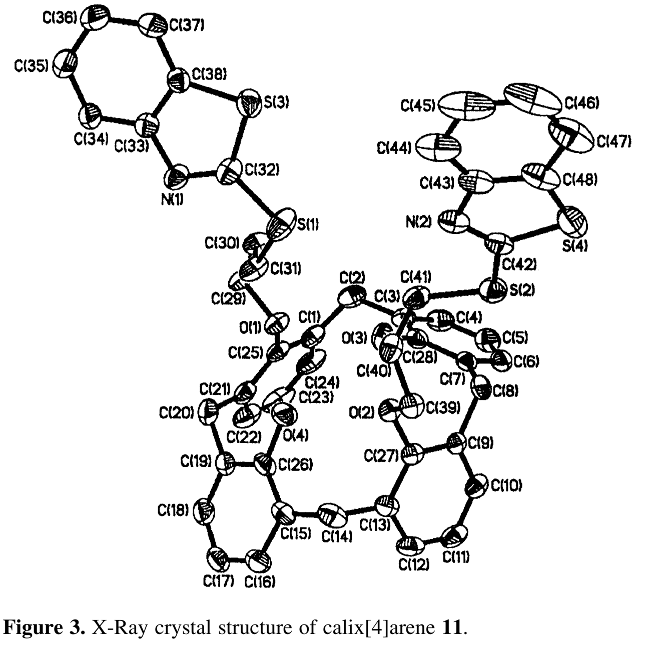


Figure 3. X-Ray crystal structure of calix[4]arene **11**.

Cone and partial cone conformers of 25-hydroxy-26,28-

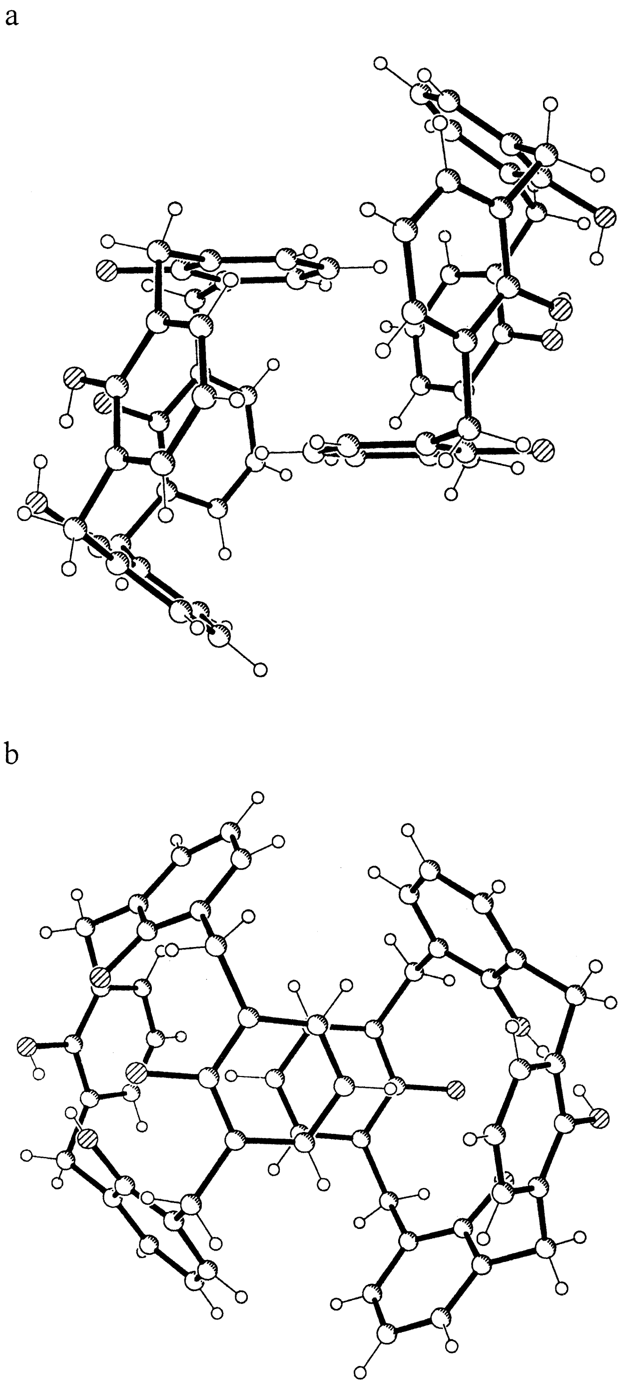


Figure 4. Dimer structure of calix[4]arene **11** via π–π stacking. (a) A side view of the parallel-displaced π–π stacking; (b) a top view of the parallel-displaced π–π stacking. C(29)–C(38), C(39)–C(48), S(1)–S(4), N(1), N(2) and C(29A)–C(38A), C(39A)–C(48A), S(1A)–S(4A), N(1A), N(2A) are omitted for clarity.

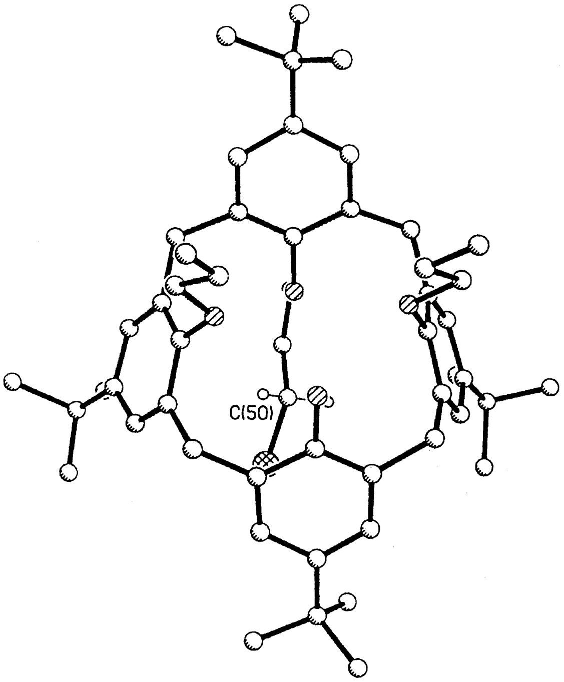
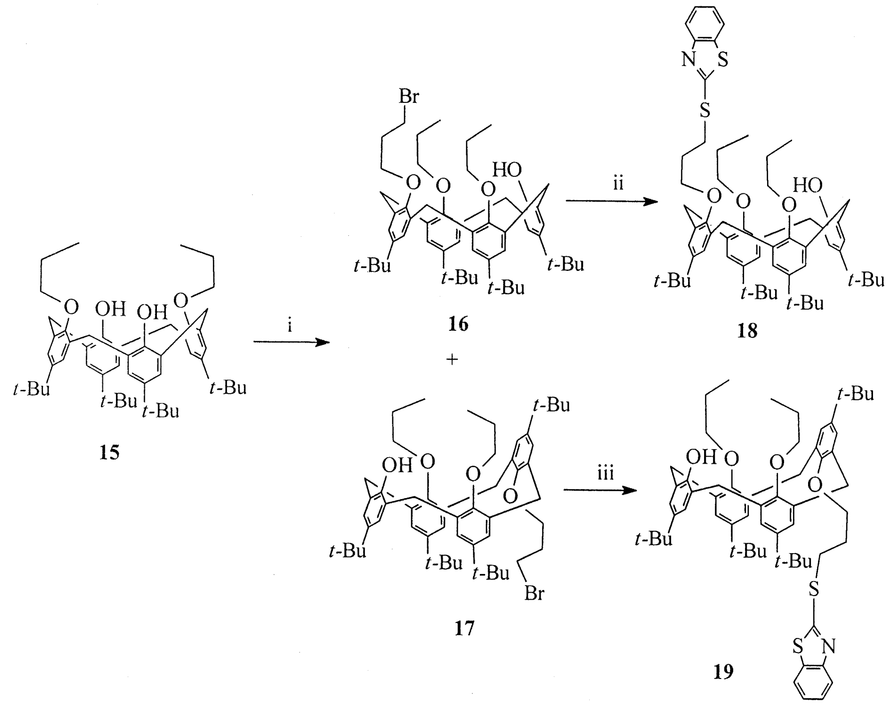


Figure 5. X-Ray crystal structure of calix[4]arene **17**.

dipropoxy-27-bisbenzo-thiazolylthiapropoxy-5,11,17,23-tetra-*tert*-butylcalix[4]arenes **18** and **19** were obtained in two steps from the known compound **15**. Treatment of **15** with 1,3-dibromopropane in THF/DMF (2:1) in the presence of NaH as base gave the cone and the partial cone isomers **16** and **17** in 53% and 38% yields after separation by column chromatography. X-Ray structure analysis proved that **17** is in a partial cone conformation (Fig. 5). The reaction of **16** and **17** with 2-mercaptobenzothiazole in the presence of NaH in THF afforded **18** and **19** in 93 and 89% yields, respectively (Scheme 2). The cone conformation of **16** and **18** are confirmed by ^{1}H NMR spectroscopy. Four doublets for the methylene bridge of calix[4]arene skeleton (nearly 4.20 and 3.10 ppm) and the separation of *tert*-butyl resonances, together with the separation of the aryl protons of the cyclic skeleton suggested that **16** and **18** exist in a distorted cone conformation in solution. The distorted cone conformation of **18** was further proven by X-ray crystallography (Fig. 6). It is interesting to note that **18** forms a dimer structure via intermolecular weak sulfur-sulfur contacts. The distances of intermolecular sulfur atoms are 3.723 Å between S(1) and S(2A), and S(1A) and S(2); 3.484 Å between S(2) and S(2A).

The two doublets at 4.17 and 3.22 ppm with a *J* value of 12.5 Hz and the singlet at 3.87 ppm for the methylene bridge of the calix[4]arene skeleton integrate with a ratio of 1:1:2, and the separation of the *tert*-butyl resonances at 1.38, 1.26 and 1.19 ppm (1:1:2) indicate that **17** is in a partial-cone conformation. This conformation was also elucidated by X-ray structural analysis (Fig. 5). The ^{1}H NMR spectra of the methylene bridge protons of the calixarene framework for the partial cone conformer **19** are similar to those of the partial cone conformer **17**. The X-ray structure of **19** unambiguously indicated that it was in a partial cone conformation as can be seen from Fig. 7. The two opposite arenes bearing hydroxy and benzothiazolylthiapropoxy groups are almost parallel, forming a dihedral angle of 7.1°, while those bearing the propoxy groups form a 57.1° dihedral angle. The torsion angles of O(4)–C(42)–C(43)–C(44), O(2)–C(39)–C(40)–C(41), O(1)–C(29)–C(30)–C(31), C(29)–C(30)–C(31)–S(2), C(32)–S(2)–C(31)–C(30) are 73.0, −172.4, 54.0, −168.2 and −68.5°, respectively.

Bisalkylthiaalkoxycalix[4]arene **21** was synthesized in a



Scheme 2. (i) NaH, $BrCH_2CH_2CH_2Br$, THF–DMF (2:1), refluxed for 6 h; (ii), (iii) NaH, 2-mercaptobenzothiazole, THF (2:1), refluxed for 10 h.

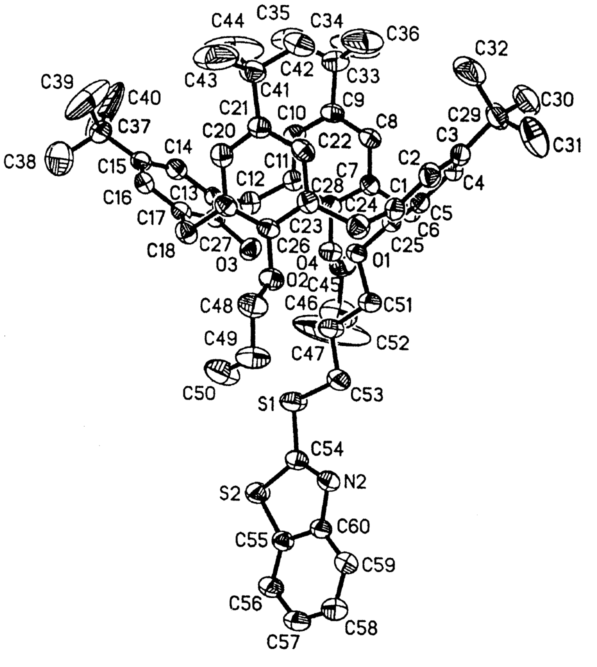


Figure 6. Diagram showing the numbering system of **18**.

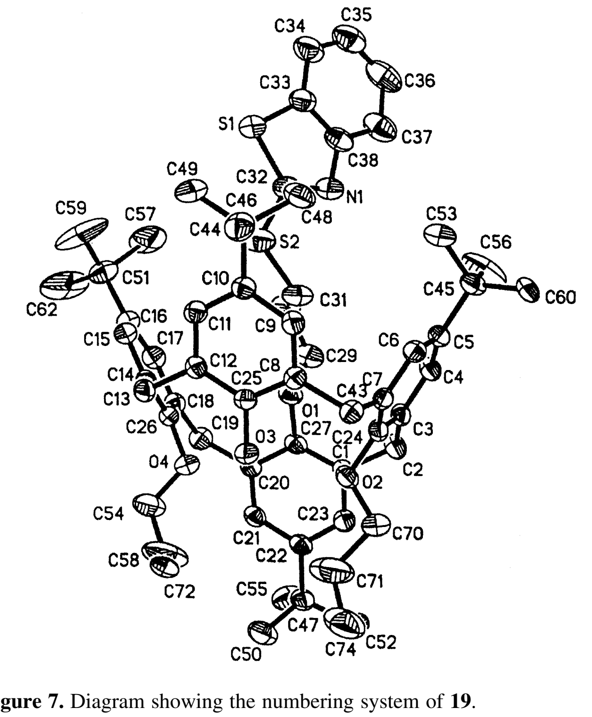


Figure 7. Diagram showing the numbering system of **19**.

good yield by the reaction of calix[4]arene dibromide **7** with propanethiol in the presence of NaH as a base at the refluxing temperature of THF under a nitrogen atmosphere.

2.2. Ag^+ selectivity and structure–selectivity relationship

The Ag^+ selectivity of bisbenzothiazolylthiaalkoxy functionalized calix[4]arenes **9–14** were evaluated by the potentiometric selectivity coefficients ($K_{Ag,M}^{pot}$) determined for polymer membranes containing these ionophores. For comparison, the single benzothiazolylthiapropoxy functionalized calix[4]arenes **18** (cone), **19** (partial cone) and 25,27-dihydroxy-26,28-bis(propylthiabutoxy)-5,11,17,23-tetra-*tert*-butylcalix[4]arene **21** 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 mono- or bisbenzothiazolylthiaalkoxy 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^+, which were determined by the mixed-solution method, are illustrated in Table 1. The selectivity coefficient ($K_{Ag,M}^{pot}$) represents the preference of the ISE (or PVC membrane) containing the benzothiazolylthiaalkoxy functionalized calix[4]arene for Ag^+ over the other cations. Therefore, the coefficient $K_{I,M}^{pot}$ defines the ability of an ISE (or membrane) to recognize different ions under the same conditions. The smaller the $K_{I,M}^{pot}$ value, the greater the electrode preference for the primary ion (I^+) over the interfering ion (M^+).

As can be seen from Table 1, all polymer membranes containing calix[4]arene **9–14**, **18** and **19** as ionophores gave excellent log $K_{Ag,M}^{pot}$ values (≤4.1) against most of the interfering cations examined (i.e. Na^+, K^+, NH_4^+, Mg^{2+}, Ni^{2+}, Zn^{2+}, Cu^{2+}, Cd^{2+}, Co^{2+}, Fe^{3+} and Pb^{2+}), except for Hg^{2+}. It is interesting to note that, despite the different tether length incorporated between benzothiazolyl and calix[4]aryl, ISEs based on **9–14** exhibited characteristic ion selectivity tendencies which resemble each other. More interestingly, although only one benzothiazolyl group was incorporated into the cone and partial-cone conformers **18** and **19**, **18**- and **19**-based ISEs also gave the same characteristic ion selectivity tendencies as those of **9–14**-based ISEs. However, the performance of **21**-based ISE is distinctly different from the above ISEs. The performance of the present ISEs is largely superior to that displayed by traditional Ag_2S-based electrode or **21**-based ISE and is satisfactory as Ag^+-ISE. The fact that polymer membranes containing ionophores **9–14**, **18**, **19** gave excellent

Table 1. Selectivity coefficients (log $K_{Ag,M}^{pot}$) of the electrodes based on ionophores **9–14**, **18**, **19** and **21**

Ion	log $K_{Ag,M}^{pot}$								
	9	**10**	**11**	**12**	**13**	**14**	**18**	**19**	**21**
Ag^+	0	0	0	0	0	0	0	0	0
Na^+	−5.1	−4.5	−4.5	−4.7	−4.7	−3.2	−4.8	−4.7	−2.9
K^+	−4.4	−4.3	−4.5	−4.3	−4.5	−4.3	−4.5	−4.6	−2.9
NH_4^+	−5.0	−4.3	−4.5	−4.5	−4.7	−4.8	−4.5	−4.6	−4.5
Ca^{2+}	−5.6	−5.0	−5.3	−5.3	−5.3	−5.2	−5.1	−5.2	−4.3
Mg^{2+}	−5.6	−5.0	−5.3	−5.3	−5.3	−5.2	−5.1	−5.2	−4.4
Fe^{3+}	−5.1	−4.6	−4.8	−4.7	−4.9	−5.1	−4.8	−4.7	–
Co^{2+}	−5.4	−4.8	−5.0	−4.9	−5.0	−5.4	−5.0	−5.0	–
Ni^{2+}	−5.4	−4.8	−5.0	−4.9	−5.0	−5.4	−5.0	−5.0	−4.4
Cu^{2+}	−5.6	−4.8	−5.0	−5.0	−5.0	−5.4	−5.0	−5.0	−4.3
Zn^{2+}	−5.4	−4.8	−5.0	−5.0	−5.0	−5.4	−5.0	−5.0	−4.4
Cd^{2+}	−5.4	−4.8	−5.0	−5.0	−5.0	−5.4	−5.0	−5.0	−4.3
Pb^{2+}	−4.3	−4.1	−4.4	−4.3	−4.3	−4.0	−4.3	−4.4	−4.5
Hg^{2+}	−2.8	−2.7	−2.5	−2.5	−2.6	−3.2	−2.2	−2.5	−1.2

log $K_{I,M}^{pot}$ values (≤ -3.2) against Na^+, K^+, NH_4^+, Ca^{2+}, Mg^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} means that **9–14**-, **18**- and **19**-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[26,27] and traditional Ag_2S-based ISE[33] is largely eliminated in the present ISEs (log $K_{Ag,Hg}^{pot} \leq -2.5$ for most of the present ISEs). One possible explanation is that those ions with high hydration energies, such as Na^+, K^+, NH_4^+, Ca^{2+}, Mg^{2+}, Fe^{3+}, Pb^{2+} and most divalent transition metal ions, cannot strongly interact with sulfur and nitrogen donors in the ionophores, while less heavily hydrated soft Ag^+ coordinates to soft sulfur and nitrogen donors selectively. The fact that the polymer membrane containing **21** gave greater log $K_{I,M}^{pot}$ values against all the interfering ions than any one of **9–14**-, **18**- and **19**-based ISEs means that **21**-based ISE possesses lower Ag^+ selectivity than any one of **9–14**-, **18**- and **19**-based ISEs. This can be tentatively rationalized that the four sulfur atoms or two sulfur atoms and two nitrogen atoms on the benzothiazolyl groups of **9–14** all participate in the coordination with Ag^+ at the same time. This four point coordination is stronger than the two-point recognition of **21**. As can be seen from Figs. 2 and 3, the preorganized tweezer-like structure of ionophores **10** and **11** will largely benefit the ionophores using four points to coordinate silver ion. If **21** has a multipoint coordination with Ag^+ or other interfering ions, the two sulfur donors must bend toward the lower rim of the calix[4]arene scaffold to let the oxygen atoms participate in the ligation. However, this type of ligation must lead to an increase in the interference of other ions towards Ag^+, because those hard ions with high hydration energies such as Na^+, K^+, NH_4^+, Pb^{2+} and some other divalent transition cations, have affinity to hard donors, such as oxygen atoms. Therefore, the selectivity of **21**-based ISEs being lower than any one of **9–14**-based ISEs is acceptable no matter what type of ligation be adopted of the two possibilities (two-point or multipoint). Single benzothiazolylthiapropoxy group functionalized partial-cone conformer **19**-based ISE giving the same ion selectivity tendency of **9–14**-based ISEs could be rationalized that aromatic π systems of the calix[4]arene skeleton participate in the ligation. As can be seen from Fig. 7, the donor atoms (S, N) are almost capped in the cavity formed by three aromatic rings. The distances of sulfur (labeling S(1)) donor to the centroids of the three aromatic rings are between 3.98 and 5.09 Å and the nitrogen (labeling N(1)) donor to the centroids of the three aromatic rings are less than 6.50 Å, which strongly suggest that the aromatic π systems also participates in the ligation of Ag^+ via a cation–π interaction.[34] On the other hand, the flexibility of the linking arm can allow the donor atoms on the benzothiazolylthia group to coordinate Ag^+, while at the same time, allowing the π system to participate in the ligation. Why does the single benzothiazolylthiapropoxy group functionalized cone conformer **18**-based ISE give the same ion selectivity tendency of **9–14**- and **19**-based ISEs? From the view of coordinate chemistry, Ag^+ can form 2–6 coordinate complexes.[35] The lowest coordination number is two. Taking into account the tendency of two coordinate silver complexes to form a *trans*-conformation, we hypothesized that there are two patterns of ligation between ionophore **18** and Ag^+. The first one is the aromatic π system that linked the benzothiazolylthiapropoxy group participation in ligation via a cation–π interaction as described for **19**. Another possibility is that the oxygen atoms on the lower-rim participate in the ligation. Although both possibilities can explain the results, we preferred the second one for the distances of sulfur (labeling S(1)) donor to the four oxygen atoms are between 4.67 and 5.11 Å and the distances of the second sulfur (labeling S(2)) or nitrogen (labeling N(2)) donor to the four oxygen atoms are shorter than 7.92 Å. At the same time, these distances are adjustable in the solution phase due to the flexibility of the linking arm. However, the distances of S(1), S(2) and N(2) to the centroid of the benzothiazolylthiapropoxy linked aromatic ring are fairly long as shown in Fig. 6. The benzothiazolyl group bending towards the π system and allowing it to participate in the ligation might be energetically unfavorable. On the other hand, the fact that the log $K_{Ag,Hg}^{pot}$ value of **18**-based ISE is larger than that of **19**-based ISE also suggests that **18** has the second ligation pattern instead of the first one. Because free Hg^{2+} only exists in strong acidified aqueous solution (pH<2), while at pH>2, Hg^{2+} usually exists in the form of $Hg(OH)^+$, the oxygen atoms on the lower-rim of calix[4]arene may assist the ligation of coordinating atoms with $Hg(OH)^+$ through O–H···O hydrogen bonds. This might be the primary reason that the Hg^{2+} gives a larger interference of **18**-based ISE than that of **19**-based ISE, as does the ionophore **21**-based ISE.[25b]

We reasoned that the nitrogen atom takes a key role in the recognition of Ag^+ in these ionophore-based membrane electrodes by the comparison of **18**-based ISE with **21**-based ISE. For the two ionophores, both the oxygen atoms on the lower-rim might participate in the ligation. If the sulfur atom on ionophore **18** is the primary donor, the tweezer-like ionophore **21** must show a better selectivity for Ag^+ against other interfering ions than that of **18**. The results are contrary to this hypothesis. The Ag^+ selectivity behavior of **18**-based ISE against other interfering ions is much better than that of **21**-based ISE, which strongly suggests that the nitrogen atom is the primary ligation donor, so do the other benzothiazolyl functionalized ionophores discussed in this context. On the other hand, as can be seen from Fig. 6, the two propyl groups located on the lower-rim of the calix[4]arene scaffold of ionophore **18** might lead to a strong hindrance against bulk $Hg(OH)^+$, So, the interfering of $Hg(OH)^+$ towards Ag^+ may be largely reduced compared with that of **21**-based ISE. Therefore, the nitrogen atoms in the benzothiazolyl groups functionalized calix[4]arenes **9–14**-, **18**- and **19**-based ISEs act as the primary donors, sulfur atoms only act as a assistant donors, namely, the high Ag^+-selectivity of **9–14**-, **18**- and **19**-based ISEs are determined by the nitrogen donors. This hypotheses was further proved by the X-ray structure analysis of the complex of **9** with silver perchlorate.[36] The N–Ag distances are 2.18 and 2.20 Å, and the distances of S–Ag are nearly 2.80 Å, respectively. Therefore, the distances of N–Ag and S–Ag in the complex of **9** with silver cations indicated that the two nitrogen atoms are the primary ligation donors in these ionophores.

Although all polymer membranes containing calix[4]arene **9–14** gave the same characteristic ion selectivity tendencies despite the differences in the tether length between the

Table 2. Properties of Ag^+-ISEs based on ionophores **9–14**, **18**, **19** and **21**

Ionophore	Slope (mV dec^{-1})	Linear range (log *a*)	Detection limit (μM)	Response time $t_{95\%}$ (s)	pH range	*R*
9	56.3	<-3.5	2.5	<10	2.5–7.0	0.9998
10	58.2	<-3.5	3.2	<10	2.5–7.0	0.9992
11	58.6	<-3.0	3.2	<10	2.5–7.0	0.9968
12	56.5	<-3.5	2.5	<12	2.0–7.0	0.9969
13	54.5	<-3.0	6.3	<12	2.5–7.0	0.9974
14	46.8	<-3.0	4.0	<12	2.5–7.0	0.9972
18	51.6	<-3.5	5.0	<12	2.5–7.0	0.9985
19	50.2	<-3.5	4.0	<10	2.5–7.0	0.9980
21	52.4	<-3.0	5.5	<10	2.5–7.0	0.9994

benzothiazolyl group and the calix[4]arene scaffold, the Nernstian slopes of these ISEs are quite different for the same type of ionophores (i.e. ionophores **10**, **12**, **13**, and **14**). The smaller the value of Nernstian slope, the longer the linking spacer between benzothiazolyl and the calix[4]-aryl as shown in Table 2. These results may be rationalized that with an increase in the tether length, the coordinate adjustment ability of the two benzothiazolyl groups are decreased. The coordinate adjustment ability may interfere the rapid interfacial ion exchange in membrane electrode. Therefore, with the increase of tether length the values of Nernstian slope decreased. The fact that the Nernstian slope of **9** (56.3 mV $decade^{-1}$) is lower than that of **11** (58.6 mV $decade^{-1}$) may be explained by the low solubility of [**9**·Ag^+] X^-.[37]

The *tert*-butyl groups on the upper-rim of the calix[4]arene skeleton also cause a interference of Nernstian slopes. As can be seen from Table 2, the values of the Nernstian slope of **10**- and **12**-based ISEs are lower than that of **11**-based ISE. Especially, **11** and **12** have the same tether length, but the Nernstian slope value of **11** (58.6 mV $decade^{-1}$) is much higher than that of **12** (56.5 mV $decade^{-1}$). These results can be rationalized that for the ionophore **12** bearing *tert*-butyl groups on the upper-rim must overcome a higher energy barrier in the coordinate adjustment of the two benzothiazolyl groups than that of **11**, namely the *tert*-butyl groups on the upper-rim is energy unfavorable. On the other hand, the intramolecular inter-*tert*-butyl groups may cause some steric hindrance during the course of the coordinate adjustment of the two benzothiazolyl groups.[38] The above two possibilities are all unfavorable for rapid interfacial ion exchange in membrane electrode.

3. Experimental

3.1. General remarks

Melting points were determined with a Boetius Block apparatus. ^1H NMR spectra were recorded on a Bruker AC-P200 spectrometer at 200 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 on a Perkin–Elmer 2400C instrument. Mass spectra were recorded on a VG ZAB-HS spectrometer. X-Ray crystallographic data were obtained on a Bruker Smart 1000 instrument. Compounds **4–7**,[28] **15**[39] were prepared according to the literature procedures.

3.2. Synthesis of calix[4]arenes

3.2.1. 25,27-Dihydroxy-26,28-bis(2-bromoethoxy)calix[4]-arene (3). A suspension of **1** (5.12 g, 12 mmol), K_2CO_3 (3.23 g, 23.5 mmol) and $BrCH_2CH_2Br$ (100 mL) in CH_3CN (500 mL) was heated at reflux with stirring for 36 h. The solvent and the excess $BrCH_2CH_2Br$ were removed under reduced pressure. The residual material was washed with 0.1 M HCl (100 mL), then with water (200 mL). After drying at 80°C for 5 h, the solid was recrystallized from CH_2Cl_2 and CH_3OH. The white powder was collected by filtration. Pure compound **3** was given in 59% yield, mp 269–271°C. ^1H NMR: 7.58 (s, 2H), 7.07 (d, 4H, J=7.4 Hz), 6.88 (d, 4H, J=7.4 Hz), 6.71 (t, 2H, J=7.4 Hz), 6.68 (t, 2H, J=7.4 Hz), 4.35 (t, 4H, J=6.0 Hz), 4.34 (d, 4H, J=12.9 Hz), 3.90 (t, 4H, J=6.0 Hz) 3.41 (d, 4H, J=12.9 Hz). ^{13}C NMR: 153.2, 151.3, 133.1, 129.1, 128.6, 127.9, 125.7, 119.2, 75.6, 31.4, 29.5. FAB/MS *m/z* 637.7 (M^+, Calcd, 638.0). Anal. calcd for $C_{32}H_{30}Br_2O_4$: C, 60.21; H, 4.74. Found: C, 59.95; H, 4.81.

3.2.2. 25,27-Dihydroxy-26,28-bis(6-bromohexoxy)-5,11,17,23-tetra-*tert*-butylcalix[4]arene (8). A mixture of **2**·PhMe (18.5 g, 25 mmol), K_2CO_3 (7.60 g, 55 mmol), 1,6-dibromohexane (100 mL) and CH_3CN (500 mL) was heated at reflux with stirring for 48 h under a nitrogen atmosphere. The solvent was removed under reduced pressure. The inorganic salts were washed with water (400 mL). The organic phase was separated and dried with anhydrous sodium sulfate. The solvent was removed under reduced pressure, and the excess 1,6-dibromohexane was removed under high vacuum. The sticky residue was recrystallised from $CHCl_3$ and CH_3OH. After filtration and drying, pure compound **8** (15 g) was obtained in 61.5% yield, mp 92–95°C. ^1H NMR: 7.03 (s, 4H), 6.82 (s, 4H), 4.28 (d, 4H, J=12.8 Hz), 3.98 (t, 4H, J=7.2 Hz), 3.48 (t, 4H, J=7.5 Hz), 3.29 (d, 4H, J=12.8 Hz), 1.95 (m, 8H), 1.70 (m, 8H), 1.27 (s, 18H), 0.98 (s, 18H). ^{13}C NMR: 150.7, 149.9, 146.7, 141.3, 132.6, 127.8, 125.4, 125.0, 76.1, 33.8, 32.8, 31.7, 31.0, 29.8, 28.0, 25.2. FAB/MS *m/z* 974.2 (M^+, Calcd, 974.4). Anal. calcd for $C_{56}H_{78}Br_2O_4$: C, 68.98; H, 8.06. Found: C, 70.09; H, 8.32.

3.3. General procedures for the syntheses of 9–13

To a 250 mL reactor, was added calix[4]arene dibromide

(3 mmol), 2-mercaptobenzothiazole (2.01 g, 12 mmol), $NaHCO_3$ (0.67 g, 8 mmol), H_2O (40 ml) and THF (100 mL). The mixture was refluxed for 48 h under a nitrogen atmosphere. After the solvent was condensed to about 30 mL under vacuum, the suspension residue was dissolved with CH_2Cl_2 (100 mL). The organic layer was separated and washed with water (50 mL), dried with anhydrous sodium sulfate. After filtration, the solution was condensed to dryness. The residue was purified by column chromatography (petroleum ether/CH_2Cl_2/EtOH=140:125:3). Then, the product was recrystallized from CH_2Cl_2 and CH_3OH.

3.3.1. 25,27-Dihydroxy-26,28-bis(2-benzothiazolylthiaethoxy)calix[4]arene (9). Reaction of **3** (3 mmol) with 2-mercaptobenzothiazole (8 mmol) according to the general procedure gave **9** as a white powder in 75% yield, mp 224–225.5°C. ^{1}H NMR: 7.78 (d, 2H, *J*=7.7 Hz), 7.67 (d, 2H, *J*=7.6 Hz), 7.65 (s, 2H), 7.37 (t, 2H, *J*=8.3 Hz), 7.36 (t, 2H, *J*=7.8 Hz), 7.07 (d, 4H, *J*=7.4 Hz), 7.01 (d, 4H, *J*=7.6 Hz), 6.69 (t, 2H, *J*=7.4 Hz), 6.67 (t, 2H, *J*=7.6 Hz), 4.42 (d, 4H, *J*=12.9 Hz), 4.41 (t, 4H, *J*=6.1 Hz), 4.08 (t, 4H, *J*=6.1 Hz), 3.40 (d, 4H, *J*=12.9 Hz). ^{13}C NMR ($CDCl_3$+DMSO-d_6): 164.6, 151.9, 151.8, 150.3, 133.9, 132.5, 127.9, 127.5, 126.6, 124.9, 124.6, 123.2, 120.1, 120.0, 118.2, 73.1, 52.7, 31.5, 30.1. FAB/MS *m*/*z* 810.8 (M^+, Calcd, 810.2). Anal. calcd for $C_{46}H_{38}N_2O_4S_4\cdot 1.5CH_2Cl_2$: C, 60.79; H, 4.40; N,2.98. Found: C, 60.65; H, 4.14; N, 2.99.

3.3.2. 25,27-Dihydroxy-26,28-bis(2-benzothiazolylthiaethoxy)-5,11,17,23-tetra-*tert*-butylcalix[4]arene (10). Reaction of **4** (3 mmol) with 2-mercaptobenzothiazole (8 mmol) according to the general procedure gave **10** as a white powder in 95% yield, mp 180–182°C. ^{1}H NMR: 7.87 (d, 2H, *J*=7.3 Hz), 7.69 (d, 2H, *J*=8.3 Hz), 7.38 (t, 2H, *J*=6.8 Hz), 7.25 (t, 2H, *J*=7.3 Hz), 7.07 (s, 4H), 6.81 (s, 4H), 4.39 (t, 4H, *J*=4.5 Hz), 4.36 (d, 4H, *J*=12.9 Hz), 4.06 (t, 4H, *J*=4.5 Hz), 3.34 (d, 4H, *J*=12.9 Hz), 1.29 (s, 18H), 0.96 (s, 18H). ^{13}C NMR: 165.3, 152.2, 149.9, 148.7, 146.3, 140.8, 134.5, 131.7, 127.0, 125.2, 124.9, 124.4, 123.4, 120.7, 120.2, 73.4, 33.1, 31.8, 30.9, 30.2. FAB/MS *m*/*z* 1034.5 ($[M-1]^+$, Calcd, 1035.5). Calcd for $C_{62}H_{70}N_2O_4S_4$: C, 71.92; H, 6.81; N, 2.71. Found: C, 71.70; H, 6.95; N, 2.67.

3.3.3. 25,27-Dihydroxy-26,28-bis(3-benzothiazolylthiapropoxy)calix[4]arene (11). Reaction of **5** (3 mmol) with 2-mercaptobenzothiazole (8 mmol) according to the general procedure gave **11** as a white powder in 92% yield, mp 195.5–196°C. ^{1}H NMR: 8.06 (s, 2H), 7.84 (d, 2H, *J*=6.6 Hz), 7.67 (d, 2H, *J*=6.7 Hz), 7.24 (t, 2H, *J*=7.8 Hz), 7.09 (t, 2H, *J*=7.8 Hz), 7.07 (d, 4H, *J*=7.4 Hz), 6.91 (d, 4H, *J*=7.6 Hz), 6.72 (t, 2H, *J*=7.4 Hz), 6.67 (t, 2H, *J*=7.3 Hz), 4.31 3.41(d, 4H, *J*=13.0 Hz), 4.18 (t, 4H, *J*=5.7 Hz), 3.94 (t, 4H, *J*=6.8 Hz), 3.41 (d, 4H, *J*=13.0 Hz), 2.58 (m, 4H). ^{13}C NMR: 165.7, 152.4, 150.6, 134.4, 132.4, 128.3, 127.8, 127.2, 125.2, 124.8, 123.4, 120.7, 120.1, 118.5, 73.3, 30.7, 29.5, 29.0. FAB/MS *m*/*z* 838.8 (M^+, Calcd, 838.2). Anal. calcd for $C_{48}H_{42}N_2O_4S_4\cdot 0.5CH_2Cl_2$: C, 66.08; H, 4.92; N, 3.18. Found: C, 66.31; H, 5.21; N 3.19.

3.3.4. 25,27-Dihydroxy-26,28-bis(3-benzothiazolylthiapropoxy)-5,11,17,23-tetra-*tert*-butylcalix[4]arene (12). Reaction of **6** (3 mmol) with 2-mercaptobenzothiazole (8 mmol) according to the general procedure gave **12** as a white powder in 91.5% yield, mp 181–182.5°C. ^{1}H NMR: 7.86 (d, 2H, *J*=7.3 Hz), 7.68 (d, 2H, *J*=7.3 Hz), 7.35 (t, 2H, *J*=7.8 Hz), 7.23 (t, 2H, *J*=7.3 Hz), 7.05 (s, 4H), 6.85 (s, 4H), 4.26 (d, 4H, *J*=13.0 Hz), 4.14 (t, 4H, *J*=5.7 Hz), 3.91 (t, 4H, *J*=6.78 Hz), 3.34 (d, 4H, *J*=13.0 Hz), 2.52 (m, 4H), 1.27 (s, 18H), 0.99 (s, 18H). ^{13}C NMR: 166.6, 153.3, 150.8, 149.4, 147.3, 141.7, 135.3, 132.7, 127.6, 125.8, 125.4, 124.2, 121.6, 120.9, 73.9, 34.0, 33.9, 32.1, 31.8, 31.1, 30.4, 29.9. FAB/MS *m*/*z* 1063.2 ($[M+1]^+$, Calcd, 1062.4). Calcd for $C_{64}H_{74}N_2O_4S_4\cdot CH_2Cl_2$: C, 67.98; H, 6.67; N, 2.44. Found: C, 67.98; H, 6.50; N, 2.57.

3.3.5. 25,27-Dihydroxy-26,28-bis(4-benzothiazolylthiabutoxy)-5,11,17,23-tetra-*tert*-butylcalix[4]arene (13). Reaction of **7** (3 mmol) with 2-mercaptobenzothiazole (8 mmol) according to the general procedure gave **13** as a white powder in 75% yield, mp 165–166°C. ^{1}H NMR: 8.04 (d, 2H, *J*=8.3 Hz), 7.67 (d, 1H, *J*=7.3 Hz), 7.43 (m, 4H), 7.03 (s, 4H), 6.78 (s, 4H, Ar-H), 4.22 (d, 2H, *J*=12.5 Hz), 4.18 (d, 2H, *J*=12.5 Hz), 3.91 (m, 4H), 3.60 (t, 4H, *J*=6.3 Hz), 3.28 (d, 4H, *J*=12.5 Hz), 2.19 (m, 8H), 1.26 (s, 18H), 0.94 (s, 18H). ^{13}C NMR: 167.3, 150.7, 149.7, 146.9, 141.4, 132.5, 127.7, 125.9, 125.5, 125.0, 124.1, 121.4, 120.8, 75.6, 33.8, 31.7, 30.9, 29.6, 29.1, 28.5, 26.1. FAB/MS *m*/*z* 1090.1 (M^+, Calcd, 1090.5). Anal. calcd for $C_{66}H_{78}N_2O_4S_4\cdot 0.5CH_2Cl_2$: C, 70.43; H, 7.02; N, 2.47. Found: C, 70.77; H, 6.98; N, 2.38.

3.3.6. 25,27-Dihydroxy-26,28-bis(6-benzothiazolylthiahexoxy)-5,11,17,23-tetra-*tert*-butylcalix[4]arene (14). To a 100 mL round-bottom flask, was added **8** (975 mg, 1 mmol), 2-mercaptobenzothiazole (418 mg, 2.5 mmol), K_2CO_3 (345 mg, 2.5 mmol) and THF (50 mL). The suspension was refluxed for 20 h under nitrogen. The solvent was removed under reduced pressure. The residual was dissolved in CH_2Cl_2 (50 mL) and washed with water (50 mL×3). The organic layer was separated, and dried with anhydrous sodium sulfate. The solvent was removed, and the residual was purified by column chromatography (petroleum ether/CH_2Cl_2=1:2). Compound **14** (1.08 g) was given as white foam in 94% yield, mp 112–114°C. ^{1}H NMR: 8.02 (d, 2H, *J*=7.3 Hz), 7.67 (d, 2H, *J*=7.3 Hz), 7.64 (s, 2H), 7.50 (t, 2H, *J*=7.3 Hz), 7.42 (t, 2H, *J*=7.3 Hz), 7.02 (s, 4H), 6.79 (s, 4H), 4.23 (d, 4H, *J*=12.6 Hz), 3.95 (t, 4H, *J*=5.8 Hz), 3.50 (t, 4H, *J*=6.7 Hz), 3.27 (d, 4H, *J*=12.6 Hz), 1.96 (m, 8H), 1.71 (m, 8H), 1.26 (s, 18H), 0.96 (s, 18H). ^{13}C NMR: 167.4, 153.3, 150.8, 149.9, 146.7, 141.4, 135.1, 132.7, 127.8, 126.0, 125.5, 125.1, 124.1, 121.4, 120.9, 76.2, 33.9, 33.8, 31.8, 31.1, 29.9, 29.3, 28.6, 25.5. FAB/MS *m*/*z* 1147.1 (M^+, Calcd, 1146.5). Anal. calcd for $C_{70}H_{86}N_2O_4S_4$: C, 73.25; H, 7.55; N, 2.44. Found: C, 73.37; H, 7.48; N, 2.30.

3.3.7. Synthesis of 10 by the reaction of 20 with 2-mercaptobenzothiazole. To a 100 mL reactor, was added **20** (818 mg, 1 mmol), 2-mercaptobenzothiazole (503 mg, 3 mmol), potassium carbonate (414 mg, 3 mmol) and THF (60 mL). After the atmosphere was displaced with nitrogen, the suspension was refluxed for 10 h. The solvent was removed under reduced pressure. The solid residue was triturated with water, and then with methanol. The solid materials were collected by filtration and then recrystallized from CH_2Cl_2 and methanol. **10** was obtained as white powder in 85% yield.

3.3.8. 25-Hydroxy-26,28-dipropoxy-27-(3-bromopropoxy)-5,11,17,23-tetra-*tert*-butylcalix[4]-arene (16) (cone) and (17) (partial cone). To a 250 mL reactor, was charged **15** (7.31 g, 10 mmol), THF (100 mL), DMF (50 mL), NaH (0.72 g, 30 mmol). The mixture was stirred for 0.5 h at room temperature, then 1,3-dibromopropane (30 mL, ca. 0.29 mol) was added in one portion. The mixture was refluxed for 6 h under a nitrogen atmosphere. The solvent was removed under reduced pressure. The residue was dissolved in CH_2Cl_2 (100 mL), washed with water (100 mL). The organic layer was separated and dried. The solvent was condensed to dryness, and the residue was purified by column chromatography (petroleum ether/CH_2Cl_2=2:1). **16**, **17** were obtained in 53% (4.51 g), and 38% (3.25 g) yields, respectively. **16**: white powder, mp 102–103°C. ^{1}H NMR: 7.14, 7.04, 6.48 (s, 8H), 4.22, 4.19, 3.16, 3.09 (d, 8H, *J*=12.8 Hz), 3.97 (t, 2H, *J*=6.2 Hz), 3.84 (m, 6H); 2.96 (m, 2H), 2.05, 1.93 (m, 4H), 1.32, 1.30, 0.79 (s, 36H), 1.05 (t, 6H, *J*=6.9 Hz). FAB/MS *m*/*z* 854.1 (M^+, Calcd, 854.5). Calcd for $C_{53}H_{73}BrO_4{\cdot}0.5CH_2Cl_2$: C, 71.68; H, 8.34. Found: C, 71.59; H, 8.03. **17**: white powder, mp 194–195°C. ^{1}H NMR: 7.28 (s, 1H), 7.18 (s, 2H), 7.05 (s, 2H), 7.01 (s, 2H), 6.94 (s, 2H), 4.17 (d, 2H, *J*=12.5 Hz), 3.87 (s, 4H), 3.78 (m, 4H); 3.58 (m, 4H), 3.22 (d, 2H, *J*=12.5 Hz), 1.95 (m, 2H), 1.60 (m, 4H), 1.38 (s, 9H), 1.26 (s, 9H), 1.19 (s, 18H), 0.94 (t, 6H, *J*=6.9 Hz). ^{13}C NMR: 153.7, 152.9, 149.6, 146.1, 144.4, 142.3, 134.1, 133.7, 128.9, 127.2, 125.8, 124.6, 75.4, 68.5, 39.2, 34.1, 33.9, 33.0, 31.7, 31.5, 28.2, 22.9, 10.4. FAB/MS *m*/*z* 853.8 (M^+, Calcd, 854.5). Calcd. for $C_{53}H_{73}BrO_4$: C, 74.54; H, 8.61. Found: C, 74.59; H 8.43.

3.3.9. 25-Hydroxy-26,28-dipropoxy-27-(3-benzothiazolylthiapropoxy)-5,11,17,23-tetra-*tert*-butyl-calix[4]arene (18) (cone). To a THF (25 mL) solution of 2-mercaptobenzothiazole (0.26 g, 1.5 mmol) was added NaH (36 mg, 1.5 mmol). The suspension was stirred for 0.5 h under nitrogen atmosphere. Then, **16** (0.42 g, 0.47 mmol) was added. The solution was refluxed for 10 h. The solvent was removed under reduced pressure. The residue was taken up in CH_2Cl_2 (50 mL), and washed with water (100 mL) and brine (100 mL). After drying with anhydrous magnesium sulfate, the solvent was removed. The residue was purified by column chromatography (petroleum ether/CH_2Cl_2=1:2). 0.41 g of product was obtained as a white powder in 93% yield, mp 184–186°C. ^{1}H NMR: 7.97 (d, 1H, *J*=7.3 Hz), 7.82 (d, 1H, *J*=7.3 Hz), 7.38 (t, 1H, *J*=7.2 Hz), 7.29 (t, 1H, *J*=7.4 Hz), 7.14, 7.04, 6.49, 6.47 (s, 8H), 4.18, 4.16, 3.20 3.17 (d, 4H, *J*=12.9 Hz), 4.05 (t, 2H, *J*=7.2 Hz), 3.72 (m, 6H), 2.94 (m, 2H), 1.85 (m, 4H), 1.33, 1.31, 0.79 (s, 36H), 0.97 (t, 6H, *J*=9.1 Hz). ^{13}C NMR: 167.9, 153.9, 153.4, 151.6, 145.9, 145.1, 141.4, 135.9, 135.2, 132.0, 131.8, 129.2, 125.9, 125.7, 125.0, 124.8, 124.6, 124.1, 121.4, 120.9, 78.0, 73.1, 34.2, 33.7, 31.8, 31.4, 31.1, 29.2, 23.4, 10.7. FAB/MS *m*/*z* 940.1 (M^+, Calcd, 939.5). Calcd. for $C_{60}H_{77}NO_4S_2$: C, 76.63; H, 8.25; N, 1.49. Found: C, 76.35; H, 8.27; N 1.56.

3.3.10. 25-Hydroxy-26,28-dipropoxy-27-(3-benzothiazolylthiapropoxy)-5,11,17,23-tetra-*tert*-butylcalix[4]-arene (19) (partial cone). Compound **19** was synthesized as a white powder in 89% yield by the method of preparation of **18**, mp 149–150°C. ^{1}H NMR: 7.99 (d, 1H, *J*=7.3 Hz), 7.70 (d, 1H, *J*=7.3 Hz), 7.43 (t, 1H, *J*=7.8 Hz), 7.32 (t, 1H, *J*=6.8 Hz), 7.18 (s, 2H), 7.02 (s, 2H), 6.98 (s, 2H), 6.90 (s, 2H), 4.18 (d, 2H, *J*=12.5 Hz), 3.86 (s, 8H), 3.82 (m, 4H), 3.55 (m, 2H), 3.21(d, 4H, *J*=12.5 Hz), 3.05 (t, 2H, *J*=6.3 Hz), 1.66 (m, 4H), 1.52 (m, 2H), 1.36 (s, 9H), 1.27 (s, 9H), 1.09 (s, 18H), 0.92 (t, 6H, *J*=7.4 Hz). ^{13}C NMR: 166.9, 154.3, 153.4, 152.8, 149.8, 145.6, 144.3, 141.9, 135.2, 133.9, 133.1, 132.6, 129.3, 127.1, 126.1, 125.9, 125.7, 124.5, 124.0, 121.5, 120.9, 75.5, 69.1, 39.0, 33.9, 31.8, 31.5, 29.6, 23.1, 10.5. FAB/MS *m*/*z* 939.4 (M^+, Calcd, 939.5). Calcd. for $C_{60}H_{77}NO_4S_2$: C, 76.63; H, 8.25; N, 1.49. Found: C, 76.18; H, 8.30; N 1.68.

3.3.11. 25,27-Dihydroxy-26-(2-Bromoethoxy)-28-(2-chloroethoxy)-5,11,17,23-tetra-*tert*-butylcalix[4]arene (20). Compound **2**·PhMe (5.7 g, 7.7 mmol) and 1-bromo-2-chloroethane (5 mL, ca. 60 mmol) were dissolved in DMF (100 mL), and the solution was heated in the presence of K_2CO_3 (2.13 g, 15.4 mmol) at 60–65°C for 24 h. The reaction mixture was diluted with water (750 mL) and extracted with $CHCl_3$ (200 mL). The separated chloroform layer was dried over $MgSO_4$. After filtration, the filtrate was concentrated to dryness. The residue was recrystallized from CH_2Cl_2–CH_3OH. The white powder of **20** (4.5 g) was given in 71.5% yield, mp 302–303; ^{1}H NMR: 7.04 (s, 6H), 6.78 (s, 4H), 4.29 (d, 4H, *J*=12.9 Hz), 4.24 (t, 4H, *J*=6.2 Hz), 3.97 (t, 2H, *J*=6.2 Hz), 3.83 (t, 2H, *J*=6.2 Hz), 3.32 (d, 4H, *J*=12.9 Hz), 1.27 (s, 18H), 0.94 (s, 18H). FAB/MS *m*/*z* 818.3 (M^+, Calcd, 818.1). Calcd. for $C_{48}H_{62}BrClO_4$: C, 70.44; H, 7.64. Found: C, 70.38; H, 7.30.

3.3.12. 25,27-Dihydroxy-26,28-bispropylthiabutoxy-5,11,17,23-tetra-*tert*-butylcalix[4]arene (21). Calix[4]arene dibromide (918 mg, 1 mmol) was added to a 100 mL round-bottomed flask, together with sodium hydride (56 mg, 2.5 mmol), and propanethiol (0.5 mL) in THF (50 mL). After the system was charged with nitrogen, the mixture was refluxed until the disappearance of calix[4]-arens dibromide as 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×2). The organic phase was separated and dried with anhydrous sodium sulfate. After the solvent was removed, the yellowish residue was purified by column chromatography (petroleum ether/CH_2Cl_2, 1:2). **21** (846 mg) was obtained as a white foam in 93% yield, mp 104–106°C; ^{1}H NMR: 7.80 (s, 2H), 7.02 (s, 4H), 6.81 (s, 4H), 4.25 (d, 4H, *J*=12.8 Hz), 3.98 (t, 4H, *J*=6.4 Hz), 3.29 (d, 4H, *J*=12.8 Hz), 2.67 (t, 4H, *J*=6.4 Hz), 2.52 (t, 4H, *J*=7.2 Hz), 2.04, 2.00 (m, 8H), 1.61 (m, 4H), 1.26 (s, 18H), 0.97 (s, 18H), 0.96 (t, 6H, *J*=7.3 Hz). FAB/MS *m*/*z* 908.2 (M^+, Calcd, 908.6). Calcd for $C_{58}H_{84}O_4S_2{\cdot}0.5CH_2Cl_2$: C, 73.73; H, 8.99. Found: C, 73.81; H, 9.01.

Table 3. Crystal data and data collection parameters

Data	**10**	**11**	**17**	**18**	**19**	**20**
Formula	$C_{62}H_{70}N_2O_4S_4\cdot 2CH_2Cl_2$	$C_{48}H_{42}N_2O_4S_4$	$C_{53}H_{73}BrO_4$	$C_{60}H_{77}NO_4S_4$	$C_{60}H_{77}NO_4S_4$	$C_{48}H_{62}BrClO_4$
Formula wt (g mol^{-1})	1205.29	839.08	854.02	940.35	940.35	818.34
T (K)	293(2)	293(2)	293(2)	298(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Orthorhombic	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$Pna2(1)$	$P\bar{1}$	$P2(1)/n$	$C2/c$
a (Å)	12.259(4)	10.1846(10)	26.9126(11)	17.7072(14)	10.1884(5)	22.2193(18)
b (Å)	15.370(5)	13.1086(12)	22.4394(9)	19.2162(15)	40.0749(18)	18.2276(15)
c (Å)	18.155(6)	16.5714(16)	8.7117(3)	20.2661(15)	13.4198(6)	12.6461(10)
α (°)	95.357(6)	71.661(2)	90	93.302(2)	90	90
β (°)	102.246(6)	104.369(2)	90	108.899(2)	95.3650	114.392
γ (°)	101.896(6)	76.920(2)	90	115.974(2)	90	90
V ($Å^3$)	3237.4(18)	2088.6(3)	5261.0(4)	5701.6(8)	5455.3(4)	4664.6(7)
Z	2	2	4	4	4	4
D_c (Mg m^{-3})	1.236	1.334	1.078	1.095	1.145	1.165
F (000)	1272	880	1832	2032	2032	1736
Cryst size (mm)	0.2×0.35×0.4	0.45×0.4×0.3	0.3×0.4×0.45	0.1×0.25×0.3	0.3×0.35×0.4	0.4×0.2×0.02
μ (Mo Kα) (mm^{-1})	0.358	0.289	0.820	0.137	0.143	0.977
θ range (°)	1.37–25.03	1.52–25.03	1.76–25.03	1.09–25.03	1.61–25.03	1.50–25.02
Reflns collected	13541	8784	21280	23826	22721	9642
Independent reflns	8334	7354	9162	19961	9609	4119
R_{int}	0.0151	0.0166	0.0333	0.0385	0.0399	0.0531
Restraints	3	0	1	0	0	12
Parameters	712	524	534	1207	637	300
GOOF	1.032	0.895	0.961	0.950	1.017	1.033
R_1/wR_2	0.0836/0.2551	0.0494/0.1010	0.075/0.1967	0.0791/0.1992	0.0653/0.1798	0.0604/0.1637

Note: Crystal data were deposited with CCDC. CCDC numbers are 141227 for **10**, 143888 for **11**, 176622 for **17**, 176623 for **18**, 176624 for **19**, 141226 for **20**.

3.4. Silver selectivity evaluated by potentiometric selectivity coefficient. Membrane electrode

The typical procedure for membrane preparation is as follows: Poly(vinylchloride) (PVC) (132 mg, 33%), dibutyl phthalate (DBP) (264 mg, 66%), benzothiazolyl functionallized calix[4]arene (4 mg, 1%), 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 in water. 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 2 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 M $AgNO_3$|PVC membrane| sample solution |1 M KNO_3|4 M KCl|Hg_2Cl_2|Hg.

3.5. EMF measurements

All EMF (electromotive force) measurements were made at 25°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 in the high Ag^+ concentration.

3.6. Selectivity coefficients

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

$$E = E^0 + \frac{2.303RT}{F}\log\left[\alpha_{Ag} + K^{pot}_{Ag,M}(\alpha_M)^{1/Z_M}\right] \tag{1}$$

where E represents the experimentally observed potential, R the gas constant, T the thermodynamic temperature in K, F the Faraday constant, α_{Ag} the Ag^+ activity, α_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. In order to evaluate the selectivity of the Ag^+ over other cations, the mixed-solution method was employed.[40] 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)

$$K^{pot}_{Ag,M} = \alpha_{Ag}/(\alpha_M)^{1/Z_M} \tag{2}$$

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

3.7. Crystallographic structural determination

Crystals of **10**, **11**, **17**, **18**, **19**, **20** suitable for X-ray crystallography were grown by slow evaporation from the CH_2Cl_2–MeOH solution of **10**, **11**, **17**, **18**, **19** and **20**, respectively. X-Ray crystallographic data were obtained on a Bruker Smart 1000 instrument. Crystals, data collection, and refinement parameters are given in Table 3.

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