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Synthesis of a tweezer-like bis(arylthiaalkoxy)calix[4]arene as a cation sensor for ion-selective electrodes: an investigation of the influence of neighboring halogen atoms on cation selectivity † ‡

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Two novel tweezer-like 25,27-dihydroxy-26,28-bis(phenylthiaethoxy)calix[4]arenes **6** and **7** were synthesized by the reaction of 25,27-dihydroxy-26,28-bis(bromoethoxy)calix[4]arenes **3** and **4** for the evaluation of their ion-selectivity in ion-selective electrodes (ISEs). X-ray structural analysis indicated that calix[4]arene **7** is in an interesting infinite linear aggregate *via* self-inclusion. For investigation of the influences of substitutes on the behavior of the ISEs, the halogen substituted aryl analogues of 25,27-dihydroxy-26,28-bis(arylthiaethoxy)calix[4]arenes **8**–**12** were also synthesized and their ISE performances were evaluated under the same conditions. ISEs based on **6**–**12** as neutral ionophores were prepared, and their selectivity coefficients for Ag^+ ($\log K^{pot}_{Ag,M}$) were investigated against other alkali metal, alkaline-earth metal, lead, 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+} having relative smaller interference ($\log K^{pot}_{Ag,Hg} \leq 2.1$). The ^{19}F NMR spectra of **9** and **9**·$AgClO_4$ were recorded for investigation the fluorine environments in the complex. The ^{19}F NMR spectra strongly suggested that the fluorine atoms on ionophore **9** participated in ligation with silver cation.

Introduction

Recently, research in the area of sensor development for metal ion detection in chemical and biological applications has received much attention. A large number of ionophores based on artificial host–guest theory and some natural hosts have been employed in ion-selective electrodes (ISEs) as neutral carriers.[1] In particular, the application of host–guest chemistry to sensor development has proved to be a very valuable detection method.[2] Up to date, receptors including crown ethers, cryptands and calixarenes have been synthesized as molecular agents for the binding of all kinds of cationic and anionic species in ISEs.[1,3] As a large family of host molecules, calixarenes have received much consideration in the past years. Since the first application of calix[4]arene tetraester as a Na^+-selective ionophore in ISEs,[4] a large number of calix[4]arene derivatives for potentiometric measurements has subsequently been reported. The success of these calix[4]arene derivatives results from the three-dimensional structure of the parent calix[4]arenes, which provide a scaffold on which various functional groups can be attached to the phenolic oxygens. In fact, many calixarenes have been successfully used as ionophores in main group metal ion-selective electrodes,[4–12] but only a few examples have shown selectivity for transition metal ions in calixarene-based ISEs.[13–16] In our previous work, calix[4]arene-based receptors which are sensitive to the Ag^+ ion by incorporating nitrogen, sulfur, selenium or phosphorus atoms on the lower-rim of the calix[4]arene scaffold have been developed.[17–20] We found that using calix[4]arene derivatives containing sulfur, nitrogen, selenium atoms as ionophores in ISEs exhibited a good Ag^+-selectivity against most of 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. However, when hard donor groups are close to these soft donors, such as hydroxy and ester groups, the lower discrimination of Hg^{2+} becomes a major problem in these ionophore-based ISEs. At the same time, some recent work has demonstrated that a π-system could provide binding sites for many cations *via* a cation–π interaction[21] and it was also employed in ionophore-based ISEs.[22] These results prompted us to design some new ionophores to investigate on the influence factors for the same type of ionophores with some different neighboring groups for understanding the implication of ion binding mechanism in ionophore-based ISEs. In this paper, ionophoric models using sulfur atoms as soft binding site and the halogens close to the soft sulfur donors as assistant donors participating in ligation with the silver ion are demonstrated.

We report herein the synthesis of two novel tweezer-like receptor molecules 25,27-dihydroxy-26,28-bis(phenylthiaethoxy)calix[4]arenes **6**–**7** and their analogues 25,27-dihydroxy-26,28-bis(arylthiaalkoxy)calix[4]arenes **8**–**12** together with 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 **6** and **7** with its halogen-substituted analogues on the chain-substituted phenyls of ionophores **8**–**12**, together with the influence of the tether length of the same type receptors towards the ISE behavior of **6**–**12** will serve to promote further understanding of the structure–selectivity relationships and the influence of halogen atoms on the Ag^+-ISEs.

Results and discussion

Syntheses

25,27-dihydroxy-26,28-bis(arylthiaalkoxy)calix[4]arenes **8**–**12** were obtained in good yields by the reaction of 25,27-

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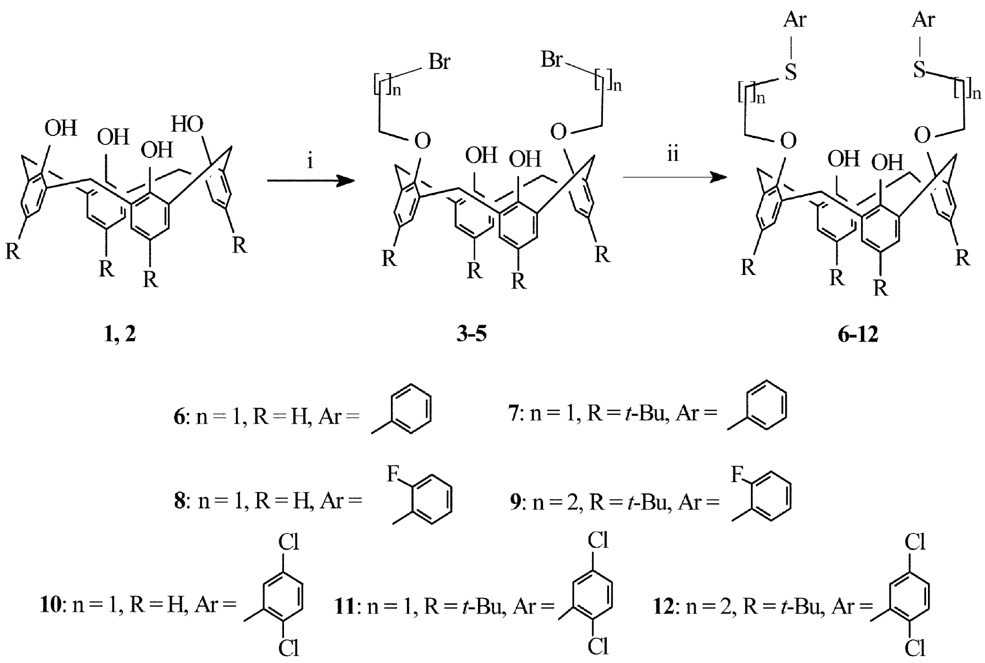
† CCDC reference number 198110. See http://www.rsc.org/suppdata/ob/b2/b211381c/ for crystallographic data in .cif format.

‡ Dedicated to Prof. Zhi-Tang Huang on the occasion of his 75th birthday.



Scheme 1 Reagents and conditions: (i) BrCH$_2$(CH$_2$)$_n$Br, acetonitrile, potassium carbonate, refluxed for 24 h; (ii) thiophenol, potassium carbonate, THF, refluxed for 6 h.

dihydroxy-26,28-bis(bromoalkoxy)calix[4]arenes **3**–**5** with thiophenol in the presence of potassium carbonate as a base (Scheme 1). The products were purified by column chromatography and then recrystallized from CH$_2$Cl$_2$ and MeOH. The yields of **6**–**12** are between 59% and 74%. The ^{1}H NMR spectra of compounds **6**–**12** indicated that they kept the cone conformation in solution, which can be easily judged from the two doublets of the protons within the methylene bridge as well as the separation of the protons of the aromatic units of the calix skeleton. The protons within the chain-substituted phenyl of compounds **6** and **7** gave multiplet peaks between 7.44 ppm and 7.09 ppm. The protons within the chain-substituted phenyl groups in compounds **8**–**12** are usually separated into several groups of multiplet peaks. As can be seen from Fig. 1b, the 2′-fluorophenyls in compound **9** give four groups of multiplet peaks at 7.45 (td), 7.15 (ddd), 7.11 (dd) and 6.96 ppm (ddd), respectively. The 2′,5′-dichlorophenyls in compounds **10**–**12** usually give three groups of multiplet peaks.

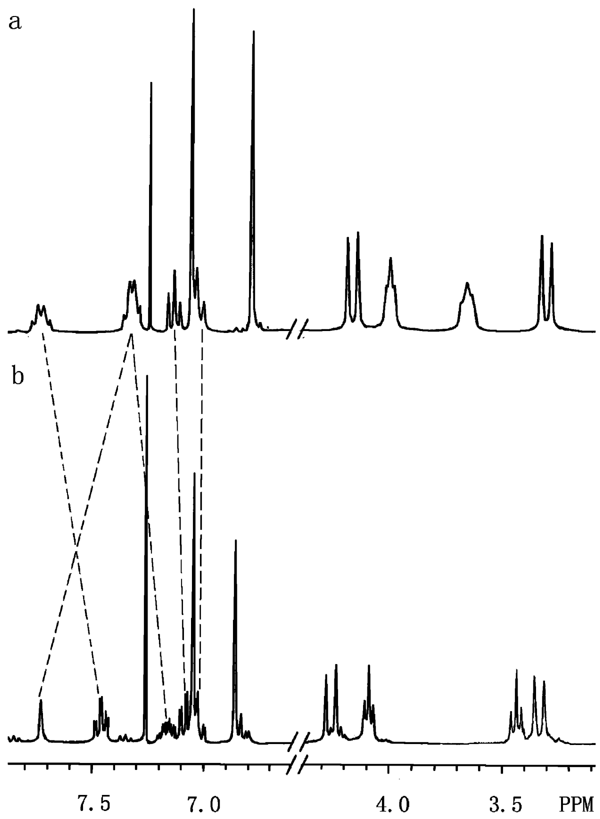


Fig. 1 ^{1}H NMR spectra of **9** (b) and **9**·AgClO$_4$ (a).

The silver complex of 25,27-dihydroxy-26,28-bis(3′-(2″-fluorophenylthia)propoxy)-5,11,17,23-tetra-*tert*-butylcalix[4]arene (**9**·AgClO$_4$) was synthesized by stirring the mixture of calix[4]arene **9** and silver perchlorate (AgClO$_4$) in methylene chloride at ambient temperature for 4 h. The resulting solution was filtered and condensed to dryness under reduced pressure. After titration with ethyl ether and filtration, **9**·AgClO$_4$ was obtained as a white powder in 95% yield. As can be seen from Fig. 1a, the protons within the 2′-fluorophenyls also give four groups of multiplet peaks. But they have downfield shift of all the eight hydrogens compared with free ligand **9**. The 5′-hydrogens give multiplets at 7.75 ppm with a downfield shift of 0.3 ppm. The 3′, 4′ and 6′ hydrogens are downfield shifted by 0.14 ppm, 0.04 ppm and 0.01 ppm, respectively. As can be seen from Fig. 1, the cone conformation of the calix skeleton also distorted with the introduction of silver cation. All of the hydrogens within the calix skeleton have shifts more or less after coordination with silver cation. To investigate the environments of the fluorine atoms in the complex, the ^{19}F NMR spectra of **9** and **9**·AgClO$_4$ were measured in CDCl$_3$ (Fig. 2). The free ionophore **9** gives strong multiplet peaks at −(34.46–34.54) ppm and weak multiplet peaks at −(34.61–34.71) ppm. These multiplets can be rationalized by the chain-substituted fluorophenyls being in conformational equilibrium with some intramolecular weak C–H ··· F hydrogen bonds in liquid medium (as illustrated in Chart 1a). The proton NMR spectra also supported this hypothesis. As can be seen from Fig. 1b, the weak multiplets at 7.85 ppm and 7.35 ppm indicated that **9** had several conformers in solution. The ^{19}F NMR spectra of **9**·AgClO$_4$ not only supported this conformational equilibrium (Fig. 2b and Chart 1b), but also suggested that the fluorine atoms participated in ligation with the silver cation. The fluorine atoms that participated in ligation with the silver cation gave a strong peak at 2.56 ppm and the free fluorine atoms gave a weak peak at 31.77 ppm. Compared with

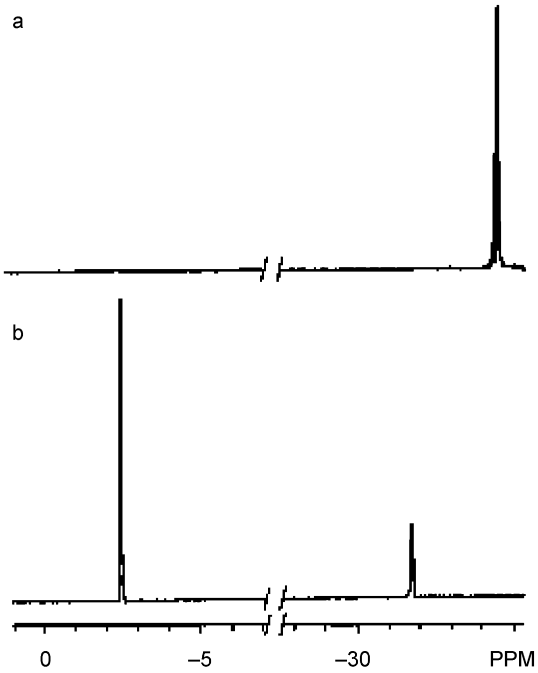


Fig. 2 ^{19}F NMR spectra of **9** (a) and **9**·$AgClO_4$ (b).

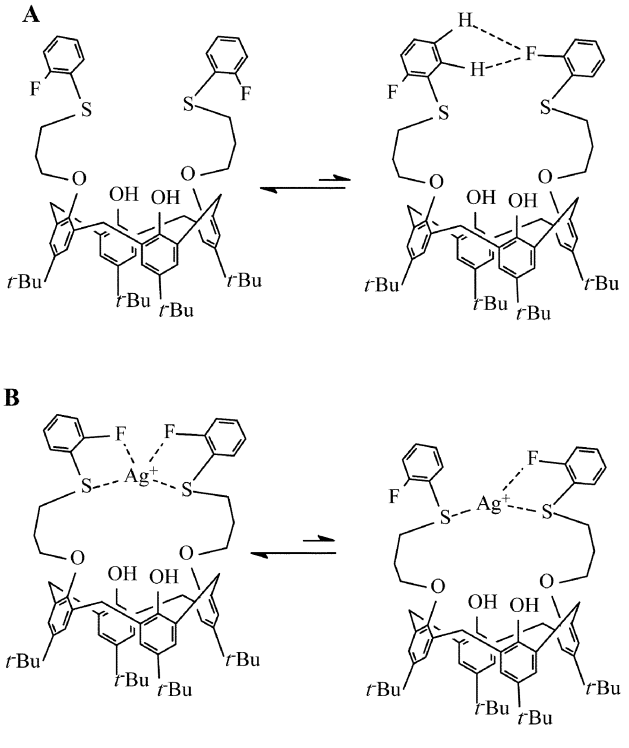


Chart 1 Conformational equilibria of **9** (A) and **9**·$AgClO_4$ (B).

the free ionophore **9**, the ligation fluorine atoms have a 32 ppm downfield shift and the free fluorine atoms have a 2.7 ppm downfield shift.

X-ray crystallography of 7

The X-ray structure of calix[4]arene **7**,[23] grown by slow evaporation from the CH_2Cl_2–MeOH solution was elucidated for determination of its structure (Fig. 3). As shown in Fig. 3, **7** is in a 'pinched' cone conformation in the solid state. The sulfur atoms (S(1) and S(2)) are disordered (only one position is shown in Fig. 3 for clarity). The adjacent four phenyls within the calix framework form interplanar angles between 71.9° and 106.3°. The two phenyls bearing hydroxy groups were tilted away from the cavity with an interplanar angle of 83.3°. The other two phenyls that linked the side arms form an interplanar angle of 45.2°. The torsion angles of the two tethers that link the phenyls and the calix skeleton are 81.4° [O(1)–C(45)–C(46)–S(1)] and 178.0° [O(3)–C(53)–C(54)–S(2)], respectively. The O ··· O separations of the adjacent four oxygen atoms on the lower rim of the calix[4]arene are between 2.74 and 2.90 Å, which indicates that there are strong hydrogen bonds and strong O ··· O interactions between the four oxygen atoms. It is interesting to note that compound **7** forms an infinite linear aggregate via self-inclusion (Fig. 4). As shown in Fig. 4, the phenyl attached to S(2) was imbedded within the hydrophobic cavity of four aromatic groups and their four *tert*-butyl substitutions as guest *via* weak interactions. Many weak interactions exist in this inclusion situation. The strongest weak interactions among all the weak contacts are the CH–π interactions. The carbons [C(8A) and C(30A)] within the *tert*-butyl groups participate in CH–π interactions from the two faces of the included phenyl. The distances of C(8A) and C(30A) to the centroid of the included phenyl are 3.99 Å and 3.85 Å, respectively. The centroid ··· H separations are 3.04 and 2.93 Å, with centroid ··· H–C(35) angles of 139.3° and 159.7°. Another type of CH–π interaction in this inclusion complex is the contacts of the aromatic C–H within the included phenyl with the π-systems of the calix unit. The hydrogen H(58a) on the C(58) forms a strong aromatic CH–π interaction with the phenyls labelled C(35A), C(36A), C(37A), C(42A), C(43A) and C(44A) of the calix framework. The C(58) ··· centroid distance is 3.67 Å, with a H(58A) ··· centroid distance of 2.80 Å and with a C(58)-H(58A) ··· centroid angle of 151.9°. However, the distance of hydrogen H(56A) to the centroid of the aromatic ring labelled C(13A), C(14A), C(15A), C(20A), C(21A) and C(22A) is relatively longer than the H(58A) ··· centroid distance (3.18 Å, and with a C(56) ··· centroid distance of 3.99 Å).

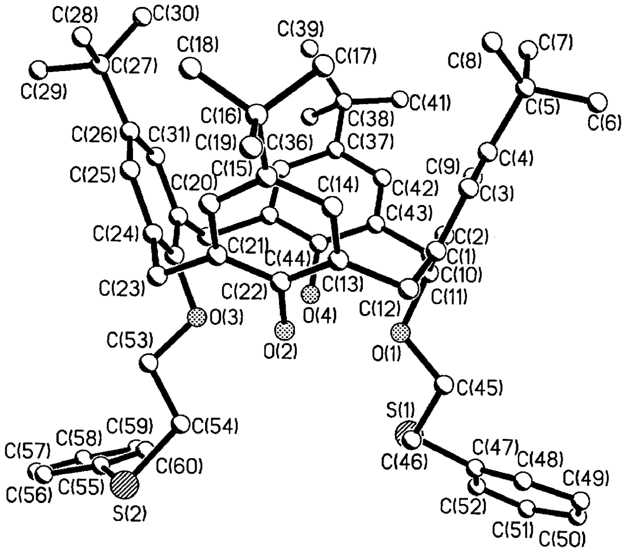


Fig. 3 X-ray structure of compound **7**. All hydrogen atoms have been omitted for clarity.

Ion selectivity

The Ag^+ selectivity of phenylthiaethoxy functionalized calix[4]-arenes **6** and **7** were evaluated by the potentiometric selectivity coefficients ($\log K^{pot}_{Ag,M}$). For comparison, arylthiaalkoxy functionalized calix[4]arene **8**–**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 arylthiaalkoxy functionalized calix[4]arene as the ionophore. The membranes also contained 75 mol% of potassium tetrakis(4-chlorophenyl)borate (KTpClPB) relative to the ionophore for the purpose of reducing membrane resist-

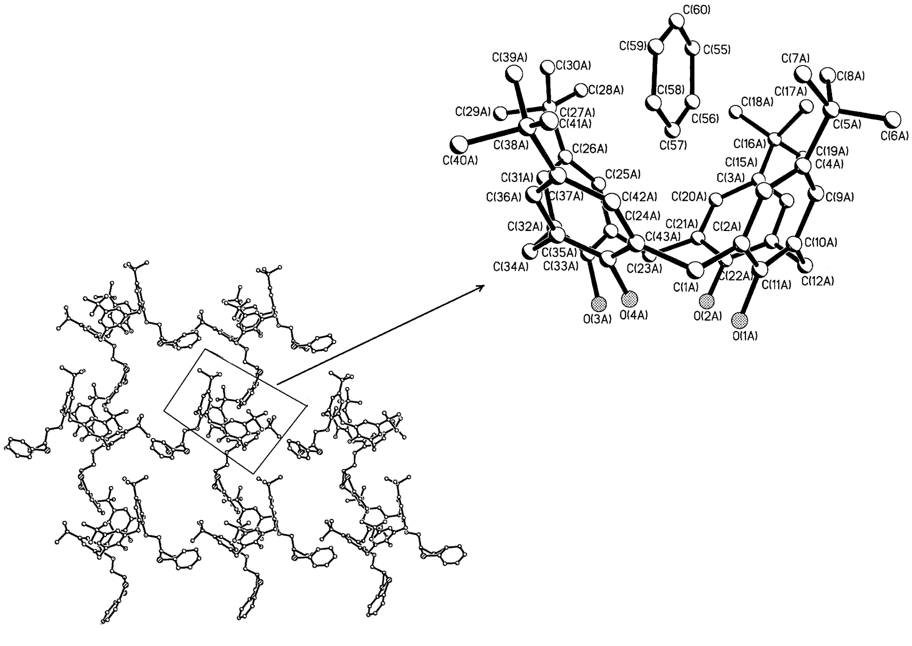


Fig. 4 Infinite linear aggregate of compound **7** *via* self-inclusion in solid state.

Table 1 Selectivity coefficient ($\log K^{pot}_{Ag,M}$) of the electrodes based on ionophores **6**–**12**

	$\log K^{pot}_{Ag,M}$						
Ion	**6**	**7**	**8**	**9**	**10**	**11**	**12**
Ag^+	0	0	0	0	0	0	0
Na^+	−4.0	−3.8	−3.9	−3.7	−4.1	−4.0	−4.0
K^+	−3.8	−3.7	−3.9	−3.8	−3.9	−3.8	−3.8
NH_4^+	−3.7	−3.8	−3.9	−3.9	−4.1	−4.0	−4.0
Ca^{2+}	−4.0	−4.3	−4.0	−3.8	−4.0	−3.9	−3.9
Mg^{2+}	−4.2	−4.3	−4.4	−4.3	−4.3	−4.3	−4.4
Ni^{2+}	−4.3	−4.2	−4.1	−4.0	−4.2	−4.2	−4.1
Cu^{2+}	−3.7	−3.6	−4.3	−4.2	−4.2	−4.2	−4.3
Zn^{2+}	−3.9	−3.8	−4.4	−4.3	−4.4	−4.4	−4.5
Cd^{2+}	−4.2	−3.8	−4.0	−3.8	−4.0	−4.0	−3.9
Pb^{2+}	−3.8	−3.7	−3.0	−3.0	−3.0	−3.0	−3.0
Hg^{2+}	−2.2	−2.3	−2.1	−2.1	−2.2	−2.1	−2.5

ance 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 arylthiaalkoxy functionalized calix[4]arene for Ag^+ over the other cations. Therefore, the coefficients $\log K^{pot}_{I,M}$ represents 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^+).

The potentiometric selectivity coefficient, $K^{pot}_{Ag,M}$ determined here is defined by the Nicolsky–Eisenman equation [eqn. (1)].

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

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 shown in Table 1, polymer membranes incorporating calix[4]arene **6**–**12** as ionophores gave excellent $\log K^{pot}_{Ag,M}$ values (≤ -3.0) 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+} gave a relatively lower discrimination compared with other interfering cations being examined. It is interesting to note that, despite four *tert*-butyls residing on the upper-rim of ionophore **7**, ISEs based on **6** and **7** exhibited characteristic ion selectivity tendencies, which resemble each other. In other words, the *tert*-butyl on the upper-rim of **7** results in a distinct difference in ISEs. Although different halogen atoms are introduced to the chain-substituted phenyls of the calix[4]arenes **8**–**12**. **8**–**12**-based ISEs also gave the same ion selectivity tendencies as those of **6**- and **7**-based ISEs. For the same ion, the selectivity coefficients are fairly close to each other (the $\log K^{pot}_{Ag,M}$ values fluctuate by no more than 0.4 orders of magnitude for the same ion), except for the Zn^{2+}, $Cu^{2+}$and Pb^{2+}, which fluctuate by close to 0.5 orders of magnitude. As can be seen from Table 1, with the introduction of halogen atoms to the chain-substituted phenyls of **8**–**12**, the discrimination of Zn^{2+} and Cu^{2+} is larger than 0.5 orders of magnitude and the discrimination of Pb^{2+} is lower than 0.7 orders of magnitude compared with those of **6**- and **7**-based ISEs. In spite of the weak fluctuations of Zn^{2+}, Cu^{2+} and Pb^{2+}, the performance of **6**–**12**-based ISEs is superior to that displayed by a traditional Ag_2S-based electrode and is satisfactory as an Ag^+-ISE. The fact that polymer membranes containing ionophores **6**–**12** gave excellent $\log K^{pot}_{I,M}$ values (≤ -3.0) against Na^+, K^+, NH_4^+, Ca^{2+}, Mg^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} means that **6**–**12**-based ISEs possess high Ag^+ selectivity and only weakly respond to the above interfering ions. The strong Hg^{2+} interfering in some ionophore-based ISEs[24–26] and traditional Ag_2S-based ISE[27] is largely eliminated in the present ISEs ($\log K^{pot}_{Ag,Hg} \leq -2.1$ for the present ISEs). The 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, can not strongly interact with sulfur donors in the ionophores, while less heavily hydrated soft Ag^+ coordinates to soft sulfur donors selectively. The fact that polymer membrane containing **8**–**12** gave lower $\log K^{pot}_{I,M}$ values of Zn^{2+} and Cu^{2+} and larger $\log K^{pot}_{I,M}$ values of Pb^{2+} against most interfering ions than any one of **6**- and **7**-based ISEs means that **8**–**12**-based ISEs possess larger Ag^+ selectivity than any one of **6**- and **7**-based ISEs of Zn^{2+} and Cu^{2+} and lower Ag^+ selectivity than any one of **6**- and **7**-based ISEs of Pb^{2+}. This can be tentatively rationalized that the two halogen atoms closing to the soft sulfur atoms in the ionophores **8**–**12** are participation in the ligation with the cations to some extent. To prove this hypothesis, a silver perchlorate complex of **9** was prepared and characterized. Because the fluorine atom is a good ^{19}F NMR probe in the complex, the ^{19}F NMR

Table 2 The response characteristics of silver ISEs based on **6**–**12**

Ionophore	**6**	**7**	**8**	**9**	**10**	**11**	**12**
Slope/mV decade^{-1}	56.6 ± 1.2	55.5 ± 1.3	52.9 ± 0.85	50.5 ± 0.84	50.7 ± 1.3	45.9 ± 0.95	49.3 ± 1.2
Linear range/M	$10^{-5.3}$–$10^{-2.0}$	$10^{-5.3}$–$10^{-2.0}$	$10^{-5.3}$–$10^{-1.0}$	$10^{-5.3}$–$10^{-1.3}$	$10^{-5.0}$–$10^{-1.3}$	$10^{-5.0}$–$10^{-1.3}$	$10^{-5.3}$–$10^{-1.3}$
Response time/s	<10	<10	<10	<10	<10	<12	<10
R	0.9983	0.9981	0.9990	0.9980	0.9980	0.9987	0.9981

spectra were recorded for the free ligand **9** and **9**·$AgClO_4$ under the same conditions. As shown in Fig 2, the ^{19}F NMR strongly suggested that the fluorine atoms within the ionophore **9** participate in ligation with silver ion.

Comparing the potentiometric selectivity coefficients ($\log K^{pot}_{Ag,M}$) for most of main group metal ions and most of transition metal ions of compounds **6**–**12** based ISEs with our previous reported alkylthiaalkoxy functionalized calix[4]arenes,[15,16] we found that the discrimination of Na^+ and K^+ of the present described ISEs is much larger than those of alkylthiaalkoxy functionalized calix[4]arene derivatives-based ISEs.[15,16] There are two possibilities to explain these selective tendencies. The first one is that the π-systems of the phenyls of compounds **6** and **7** close to the soft sulfur donors participate in the coordinating of silver ion as assistant donors *via* cation–π interactions. In fact, many reports reveal that cation–π interactions exist widely in solid state or in solution phase.[21] The second one is that the ionophores exhibit the signs of ditopic receptors, namely, the four oxygen atoms on the lower-rim of calix[4]arene act as a hard donor center and the two arylthia groups act as a soft coordinate center. The hard donor center has an affinity for high hydrate ions, and the soft donor center has a selective affinity for the silver ion. Because the two centers are close to each other, they cooperate in the binding of cation species. Compared with the alkyl group, the bulk phenyls in ionophores **6** and **7** controlled the soft centers as the main binding site while they ligated to guest cations.

Besides the differences in the ion-selectivities, there are some differences in the values of the properties of **6**–**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 **6**- and **7**-based ISEs are 56.6 ± 1.2 and 55.5 ± 1.3 mV decade^{-1} to the activity of Ag^+ within the activity range $10^{-5.3}$–$10^{-2.0}$ M $AgNO_3$. The relevant values of **8**–**12**-based ISEs are between 52.9 ± 0.85 and 45.9 ± 0.95 mV decade^{-1} to the activity of Ag^+ within the activity range $10^{-5.3}$–$10^{-1.0}$ M $AgNO_3$. The Nernstian slope of **6**- and **7**-based ISEs is remarkably higher than that of **8**–**12**-based ISEs. One possible explanation is that the halogen atoms participated in the ligation with silver cation when it is close to the sulfur donors. The extra binding with halogens causes a relatively strong binding of the silver ion compared with that of **6**- and **7**-based ISEs. The stronger binding of the silver ion might interfere in the rapid ion exchange at the membrane electrodes' interface. The response time of **6**–**12**-based ISEs is within 12 s.

Conclusions

Tweezer-like receptor molecules 25,27-dihydroxy-26,28-bis-(phenylthiaethoxy) calix[4]arenes **6** and **7** have been synthesized as sensors for Ag^+-selective electrodes. 25,27-dihydroxy-26,28-bis(arylthiaalkoxy) calix[4]arenes **8**–**12** were also prepared for the comparison of the performance of **6**- and **7**-based ISEs. The polymer membranes containing **6**–**12** gave good selectivity for Ag^+ ($\log K^{pot}_{Ag,M} \leq -3.0$) 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 also gave good discrimination of Hg^{2+}($\log K^{pot}_{Ag,M} \leq -2.1$). The performance of the present ISEs is superior to that displayed by a traditional Ag_2S-based electrode. The halogen atoms participated in the ligation with silver cation being proved by ^{19}F NMR spectra.

Experimental section

General remarks

Melting points were determined with a Boetius Block apparatus. ^1H NMR spectra were recorded on a JEOL JNM-AL 300 spectrometer at 300 MHz in $CDCl_3$ solution, using tetramethylsilane as an internal standard. 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), 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. Solvents were dried and purified according to literature methods.[28] Compounds **3**–**5** were prepared according to the literature procedures.[25,29]

General procedures for the preparation of 25,27-dihydroxy-26,28-bis(arylthiaalkoxy)calix[4]arenes 6–12

In a 100 mL round-bottomed flask, was added anhydrous potassium carbonate (170 mg, 1.23 mmol), thiophenol or substituted thiophenol (4 mmol), THF (50 ml) and calix[4]arene dibromide (0.5 mmol). The system was degassed, and then the suspension was refluxed under nitrogen for 6 h. The solvent was removed under reduced pressure. The residue was dissolved with water (200 mL) and dichloromethane (30 mL). The organic layer was separated and washed with water (20 mL × 2). The final separated organic layer was dried with anhydrous magnesium sulfate. After filtration, the filtrate was condensed to dryness. The solid residue was purified by column chromatography (petroleum ether/CH_2Cl_2, 3 : 1). The obtained product was further purified by recrystallization from ethanol.

25,27-Dihydroxy-26,28-bis(2′-phenylthiaethoxy)calix[4]arene (6).

Calix[4]arene **6** was obtained as a white powder in 72% yield (250 mg) by the reaction of **3** (319 mg, 0.5 mmol) with thiophenol according to the general procedure, mp169–170 °C. ^1H NMR(200 MHz, $CDCl_3$): 7.85(s, 2H, OH), 7.44–7.22(m, 10H, Ph–H), 7.04(d, *J* = 7.4 Hz, 4H, *m*-Ar–H), 6.90(d, *J* = 7.3 Hz, 4H, *m*-Ar–H), 6.69(t, *J* = 7.3 Hz, 2H, *p*-Ar–H), 6.65(t, *J* = 7.3 Hz, 2H, *p*-Ar–H), 4.30(d, *J* = 13.1 Hz, 4H, $ArCH_2Ar$), 4.16(t, *J* = 7.1 Hz, 4H, OCH_2), 3.47(t, *J* = 7.1 Hz, 4H, SCH_2), 3.34(d, *J* = 13.1 Hz, 4H, $ArCH_2Ar$). FAB/MS *m*/*z* 696.2 ([M + 1]$^+$, Calc. 696.4). Calc. for $C_{44}H_{40}O_4S_2$: C, 75.83; H, 5.79. Found: C, 76.03; H, 6.00.

25,27-Dihydroxy-26,28-bis(2′-phenylthiaethoxy)-5,11,17,23-tetra-*tert*-butylcalix[4]arene (7)

The above procedure was repeated starting with 25,27-dihydroxy-26,28-bis(2′-bromoethoxy)-5,11,17,23-tetra-*tert*-butylcalix[4]arene (**4**) (431 mg, 0.5 mmol) to get a white powder of **7** in 61% yield (282 mg), mp 159–160 °C. ^1H NMR: 7.65(s, 2H, OH), 7.36–7.09(m, 10H, Ph–H), 6.97(s, 4H, Ar–H), 6.71(s, 4H, Ar–H), 4.21(d, J = 12.9 Hz, 4H, ArCH$_2$Ar), 4.05(t, J = 5.3 Hz, 4H, OCH$_2$), 3.45(t, J = 5.3 Hz, 4H, SCH$_2$), 3.21(d, J = 12.9 Hz, 4H, ArCH$_2$Ar), 1.21(s, 18H, *t*-Bu–H), 0.88(s, 18H, *t*-Bu–H). FAB/MS *m/z* 921.4 ([M + 1]$^+$, Calc., 920.5). Calc. for $C_{60}H_{72}O_4S_2$: C, 78.22; H, 7.88. Found: C, 78.51; H, 7.90.

25,27-Dihydroxy-26,28-bis(2′-(2″-florophenylthia)ethoxy)-calix[4]arene (8).

Reaction of **3** (319 mg, 0.5 mmol) with 2-fluorothiophenol according to the general procedure gave **8** as a white powder in 59% yield (216 mg), mp 176–178 °C. ^{1}H NMR(300 MHz, CDCl$_3$): 7.68(s, 2H, OH), 7.42(td, 2H, J = 7.5 Hz, J = 1.5 Hz, Ph–H), 7.13(ddd, 2H, J = 7.8 Hz, J = 1.5 Hz, J = 1.8 Hz, Ph–H), 7.00(d, 2H, J = 7.8 Hz, Ph–H), 6.98(d, 4H, J = 7.5 Hz, *m*-Ar–H), 6.96(m, 2H, Ph–H), 6.78(d, 4H, J = 7.8 Hz, *m*-Ar–H), 6.62(t, 2H, J = 7.8 Hz, *p*-Ar–H), 6.59(t, 2H, J = 7.5 Hz, *p*-Ar–H), 4.22(d, 4H, J = 12.9 Hz, ArCH$_2$Ar), 4.08(t, 4H, J = 7.0 Hz, OCH$_2$), 3.48(t, 4H, J = 7.0 Hz, SCH$_2$), 3.28(d, 4H, J = 12.9 Hz, ArCH$_2$Ar). FAB/MS *m/z* 732.1 (M$^+$, Calc., 732.2). Calc. for $C_{44}H_{38}F_2O_4S_2\cdot 1/3CH_2Cl_2$: C, 69.95; H, 5.12. Found: C, 69.76; H, 5.41.

25,27-Dihydroxy-26,28-bis(3′-(2″-florophenylthia)propoxy)-5,11,17,23-tetra-*tert*-butylcalix [4]arene (9).

The above procedure was repeated starting with 25,27-dihydroxy-26,28-bis(3′-bromo-propoxy)-5,11,17,23-tetra-*tert*-butylcalix[4]arene **5** (445 mg, 0.5 mmol) to get a white powder of **9** in 74% yield (362 mg), mp 81–82 °C. ^{1}H NMR(300 MHz, CDCl$_3$): 7.73(s, 2H, OH), 7.45(td, 2H, J = 7.7 Hz, J = 1.8 Hz, Ph–H), 7.15(ddd, 2H, J = 6.3 Hz, J = 1.8 Hz, J = 2.7 Hz, Ph–H), 7.11(dd, 2H, J = 7.5 Hz, J = 1.5 Hz, Ph–H), 7.04(s, 4H, Ar–H), 7.03(ddd, 2H, J = 7.8 Hz, J = 1.8 Hz, J = 1.5 Hz, Ph–H), 6.86(s, 4H, Ar–H), 4.26(d, 4H, J = 12.9 Hz, ArCH$_2$Ar), 4.09(t, 4H, J = 5.7 Hz, OCH$_2$), 3.43(t, 4H, J = 6.9 Hz, SCH$_2$), 3.33(d, 4H, J = 12.9 Hz, ArCH$_2$Ar), 2.21(m, 4H, OCH$_2$*CH$_2$*), 1.27(s, 18H, *t*-Bu–H), 1.00(s, 18H, *t*-Bu–H); ^{19}F NMR(282 MHz, CDCl$_3$): −34.46~ − 34.54(m), − 34.61~ − 34.71(m); FAB/MS *m/z* 984.2 (M$^+$, Calc., 984.5). Calc. for $C_{62}H_{74}F_2O_4S_2\cdot CH_2Cl_2$: C, 70.83; H, 7.17. Found: C, 71.13; H, 7.22.

25,27-Dihydroxy-26,28-bis(2′-(2″,5″-dichlorophenylthia)ethoxy)-calix[4]arene (10).

Reaction of **3** (319 mg, 0.5 mmol) with 2,5-dichlorothiophenol according to the general procedure gave **10** as a white powder in 62% yield (257 mg), mp 203–204 °C. ^{1}H NMR (300 MHz, CDCl$_3$): 7.61(s, 2H, OH), 7.27(d, 2H, J = 2.4 Hz, Ph–H), 7.17(d, 2H, J = 8.4 Hz, Ph–H), 7.02(d, 4H, J = 6.9 Hz, *m*-Ar–H), 6.99(dd, 2H, J = 8.4 Hz, J = 2.4 Hz, Ph–H), 6.82(d, 4H, J = 7.5 Hz, *m*-Ar–H), 6.66(t, J = 6.9 Hz, 2H, *p*-Ar–H), 6.61(t, J = 7.5 Hz, 2H, *p*-Ar–H), 4.25(d, 4H, J = 13.2 Hz, ArCH$_2$Ar), 4.15(t, 4H, J = 6.9 Hz, OCH$_2$), 3.53(t, 4H, J = 6.9 Hz, SCH$_2$), 3.34(d, 4H, J = 13.2 Hz, ArCH$_2$Ar). FAB/MS *m/z* 834.3 (M$^+$, Calc., 834.1). Calc. for $C_{44}H_{36}Cl_4O_4S_2$: C, 63.31; H, 4.35. Found: C, 63.12; H, 4.38.

25,27-Dihydroxy-26,28-bis(2′-(2″,5″-dichlorophenylthia)ethoxy)-5,11,17,23-tetra-*tert*-butyl-calix[4]arene (11).

The above procedure was repeated starting with **4** (431 mg, 0.5 mmol) to get a white powder of **11** in 65% yield (342 mg), mp 135−136 °C. ^{1}H NMR(300 MHz, CDCl$_3$): 7.23(d, 2H, J = 2.4 Hz, Ph–H), 7.19(d, 2H, J = 8.4 Hz, Ph–H), 7.08(s, 2H, OH), 7.01(dd, 2H, J = 8.4 Hz, J = 2.4 Hz, Ph–H), 6.99(s, 4H, Ar–H), 6.75(s, 4H, Ar–H), 4.23(d, 4H, J = 13.2 Hz, ArCH$_2$Ar), 4.13(t, 4H, J = 6.6 Hz, OCH$_2$), 3.48(t, 4H, J = 6.6 Hz, SCH$_2$), 3.28(d, 4H, J = 13.2 Hz, ArCH$_2$Ar), 1.23(s, 18H, *t*-Bu–H), 0.90(s, 18H, *t*-Bu–H). FAB/MS *m/z* 1059.2 ([M + 1]$^+$, Calc., 1058.3). Calc. for $C_{60}H_{68}Cl_4O_4S_2\cdot 0.5CH_2Cl_2$: C, 65.96; H, 6.31. Found: C, 65.85; H, 6.33.

25,27-Dihydroxy-26,28-bis(3′-(2″,5″-dichlorophenylthia)-propoxy)-5,11,17,23-tetra-*tert*-butylcalix[4]arene (12).

The above procedure was repeated starting with **5** (445 mg, 0.5 mmol) to get a white powder of **12** in 73% yield (395 mg), mp 84–85 °C. ^{1}H NMR(300 MHz, CDCl$_3$): 7.63 (s, 2H, OH), 7.34(d, 2H, J = 1.8 Hz, Ph–H), 7.21(d, 2H, J = 7.9 Hz, Ph–H), 7.02(s, 4H, Ar–H), 6.99(dd, 2H, J = 7.9 Hz, J = 1.8 Hz, Ph–H), 6.84(s, 4H, Ar–H), 4.25(d, 4H, J = 12.9 Hz, ArCH$_2$Ar), 4.10(t, 4H, J = 5.6 Hz, OCH$_2$), 3.50(t, 4H, J = 6.7 Hz, SCH$_2$), 3.32(d, 4H, J = 12.9 Hz, ArCH$_2$Ar), 2.23(m, 4H, *CH$_2$*CH$_2$S), 1.26(s, 18H, *t*-Bu–H), 0.98(s, 18H, *t*-Bu–H). FAB/MS *m/z* 1086.4 ([M + 1]$^+$, Calc., 1086.2). Calc. for $C_{62}H_{72}Cl_4O_4S_2\cdot 0.5CH_2Cl_2$: C, 66.45; H, 6.51. Found: C, 66.26; H, 6.58.

Silver complex of 25,27-dihydroxy-26,28-bis(3′-(2″-florophenylthia)propoxy)-5,11,17,23- tetra-*tert*-butylcalix[4]arene (9·AgClO$_4$)

To a 50 mL reactor, was added calix[4]arene **9** (50 mg, 0.05 mmol), silver perchlorate (AgClO$_4$) (10.3 mg, 0.05 mmol) and methylene chloride (30 mL). The mixture was stirred for 4 h at ambient temperature. The resulting solution was filtered. The filtrate was condensed to dryness under reduced pressure. Ethyl ether (10 mL) was added to the colorless residue and stirred for 1 h. The white precipitates were filtered off and washed with ether (5 mL). **9**·AgClO$_4$ was obtained in 95% yield (57.5 mg). ^{1}H NMR(300 MHz, CDCl$_3$): 7.75(dd, 2H, J = 7.5 Hz, J = 1.5 Hz, Ph–H), 7.29(m, 4H, Ph–H, OH), 7.15(t, 2H, J = 7.5 Hz, Ph–H), 7.06(s, 4H, Ar–H), 7.04(t, 2H, J = 7.8 Hz, Ph–H), 6.79(s, 4H, Ar–H), 4.18(d, 4H, J = 12.9 Hz, ArCH$_2$Ar), 4.02(t, 4H, J = 4.8 Hz, OCH$_2$), 3.68(t, 4H, J = 3.6 Hz, SCH$_2$), 3.32(d, 4H, J = 12.9 Hz, ArCH$_2$Ar), 2.21(m, 4H, OCH$_2$*CH$_2$*), 1.29(s, 18H, *t*-Bu–H), 0.95(s, 18H, *t*-Bu–H); ^{19}F NMR(282 MHz, CDCl$_3$): −2.56(s); FAB/MS *m/z* 1091.3 ([M-ClO$_4$]$^+$, Calc., 1091.5). Calc. for $C_{62}H_{74}F_2O_4S_2\cdot AgClO_4$: C, 62.44; H, 6.25. Found: C, 62.25; H, 6.19%.

Silver selectivity evaluated by potentiometric selectivity coefficient and membrane electrode

The typical procedure for membrane preparation is as follows: Poly(vinylchloride) (PVC) (120 mg, 32–33%), dibutyl phthalate (DBP) (240 mg, 64–65%), phenylthiapropoxy functionalized calix[4]arene (4 mg, 1%), potassium tetrakis(*p*-chlorophenyl)-borate (KTClPB) (0.75%) 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 0.001 M aqueous solution of AgNO$_3$ as the internal solution, the electrode was conditioned by soaking in 0.001 M aqueous solution of AgNO$_3$ for 24 h. The external reference electrode is a double junction type Ag/AgCl glass electrode. The composition of the electrochemical cell is given as Ag|AgCl|0.001 M AgNO$_3$¦ PVC membrane¦sample solution|1 M KNO$_3$|4 M KCl|Hg$_2$Cl$_2$|Hg.

EMF measurements

All EMF (electromotive force) measurements were made at 25 ± 1 °C, using a pH/mV meter. The sample solution was magnetically stirred and kept in a thermostated water bath. The performance of the electrodes was investigated by measuring their potential in 10^{-7}~10^{-1} M solution of AgNO$_3$. 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.

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23 Single-crystal diffraction measurement of crystal on a Bruker Smart 1000 diffractometer with Mo–Kα (λ = 0.71073 Å) at 293(2) K. Data for **7**: $C_{60}H_{72}O_4S_2$, M = 921.30, crystal in monoclinic, space group $P2(1)/c$, Z = 4, a = 17.511(5), b = 14.597(3), c = 22.804(5) Å,β = 111.552(3)°, V = 5422(2) Å^3, D_c = 1.129 mg mm^{-3}, μ = 0.142 mm^{-1}, F(000) = 1984. A total of 22149 reflections were measured, 9584 [R(int) = 0.0701] unique. The structure was solved by direct method, and refined on F^2 using SHELXTL software (G. M. Sheldrick, Göttingen, Germany). The occupancies of the disordered atoms were decided from their thermal parameters. Final wR_2 = 0.2423, with a conventional R_1 = 0.0842 (reflections with $I > 2\sigma(I)$), and a GOOF = 1.013 for 675 refined parameters. Crystallographic data are available as electronic supplementary information (ESI). †.

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