



Calix[4]arene-dithiacrown ethers: synthesis and potentiometric membrane sensing of Hg²⁺

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ABSTRACT

A series of calix[4]arene-dithiacrown-5 and -dithiacrown-6 compounds in cone and 1,3-alternate conformations has been synthesized. Responses of these ionophores to Hg²⁺ and competing metal ions were determined in solvent polymeric membrane electrodes. High potentiometric selectivity for Hg²⁺ over Na⁺ and a variety of transition and heavy metal ions was obtained.

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1. Introduction

Potentiometric methods with ion-selective electrodes (ISE)s offer several advantages, such as ease of preparation and use, relatively rapid response, reasonable selectivity, wide linear dynamic range and low cost.^{1,2} A frequently encountered type of ISE is a solvent polymeric membrane electrode. Commonly encountered ISEs of this type are polyvinyl chloride (PVC)-based membrane electrodes prepared from PVC, a plasticizer, an ionophore and other components.³

Calixarenes are metacyclophanes composed of phenolic and methylene units.^{4–6} They are versatile ionophores, which provide a platform for attachment of convergent binding groups to create host molecules primarily for attraction of simple cations, anions and small molecules. McKervey et al. first recognized that a calixarene with cation-complexing groups attached to the lower rim may possess the molecular requirements for the type of ionophore used in ISEs.^{7,8} Tetraesters of calix[4]arene were found to be excellent ionophores for Na⁺ in PVC membrane electrodes. This type of electrode is capable of measuring Na⁺ in blood.^{9,10}

In calixarene-crown ethers, also called calixcrowns, a calixarene scaffold is combined with a crown ether unit connecting two phenolic oxygens of the former with a polyether chain.^{11–16} Most common are calix[4]arene-1,3-crown compounds in which a calix[4]arene platform is connected with a polyether fragment that

bridges two distal phenolic oxygens. The first example of this ligand family, *p*-*tert*-butylcalix[4]arene-1,3-crown-6, was reported by Ungaro et al. in 1983.¹⁷

Replacement of some oxygens in the bridging polyether unit with sulfurs gives calix[4]arene-thiacrown compounds for which enhancement of the binding of soft metal ions would be anticipated. Only a few calix[4]arene-dithiacrown ethers have been reported (see compounds **1–5** in Fig. 1).^{18–23} Within this collection of ionophores, systematic structural variation is very limited.

We now describe the synthesis and evaluation of a series of calix[4]arene-dithiacrown compounds **6–11** (Fig. 2). Pairs of ionophores **6** and **10** and **7** and **11** are regioisomers in which the conformation of the calix[4]arene unit is changed from cone in the former to 1,3-alternate in the latter. Pairs of ionophores **6** and **8** and **7** and **9** are the same except for variation of the *para* substituent on the upper-rim aromatic rings from hydrogen in the former to *tert*-butyl in the latter. Finally, pairs of ionophores **6** and **7**, **8** and **9**, **10** and **11** are the same except for expansion of the dithiacrown-5 ring in the former to a dithiacrown-6 ring in the latter. Effects of these systematic structural variations on metal ion responses in PVC membrane-based electrodes are assessed. For comparison, calix[4]arene-crown-6 **12** was prepared and examined as well.

2. Results and discussion

2.1. Synthesis of new calix[4]arene-dithiacrown ionophores

Preparations of calix[4]arene-dithiacrown ethers **6**, **7**, **10** and **11** followed a common synthetic route (Scheme 1). Calix[4]arene (**13**)

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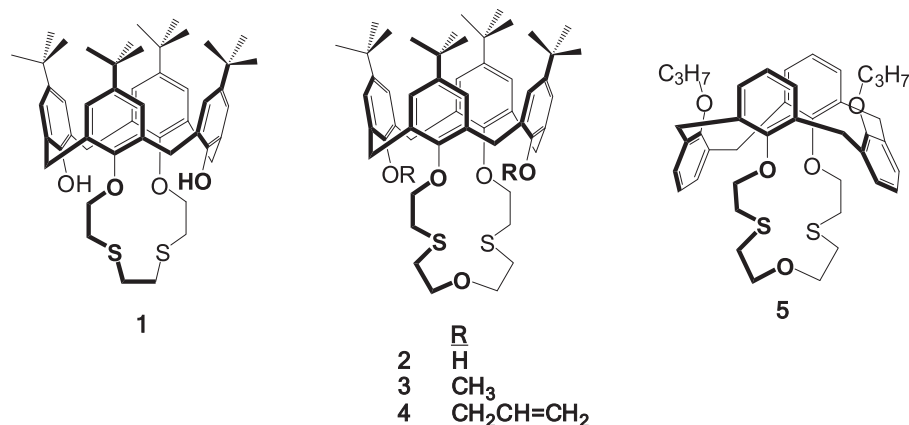


Figure 1. Structures of reported calix[4]arene-dithiacrown compounds.

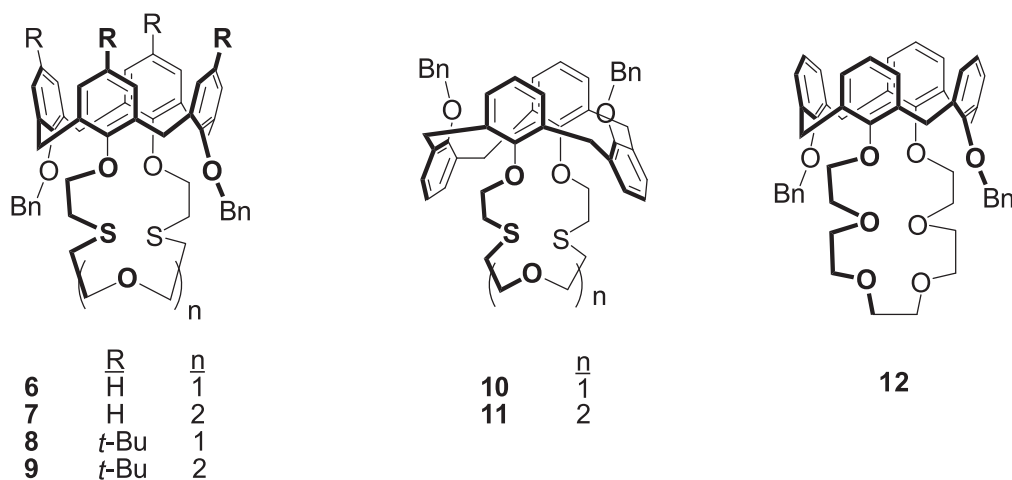


Figure 2. New dibenzyl calix[4]arene-dithiacrown compounds **6–11** and reference dibenzyl calix[4]arene-crown-6 **12**.

reacted with benzyl bromide and K₂CO₃ in MeCN at reflux gave the known cone dibenzyl calix[4]arene **14** in 90% yield. Diether **14** was treated with NaH and ethyl bromoacetate in THF at room temperature to produce a mixture of the cone dibenzyl diester **15** and the isomeric 1,3-alternate conformer **16**, which was readily separated by column chromatography on silica gel in yields of 56% and 30%, respectively. Reactions of dibenzyl diesters **15** and **16** with LAH in THF at room temperature gave dibenzyl diols **17** (90% yield) and **19** (84% yield), respectively. Attempts to convert these diols into ditosylates by reaction with TsCl in aqueous THF were unsuccessful. Therefore mesylates **18** and **20** were prepared by reaction with MsCl in CH₂Cl₂ in the presence of Et₃N with DMAP as catalyst according to a literature method.²⁴ The dibenzyl dimesylates were treated with appropriate dithiols and Cs₂CO₃ in THF at reflux to produce the dibenzyl calix[4]arene-dithiacrown ethers **6**, **7**, **10**, and **11** in moderate yields (30–65%) after purification by column chromatography on silica gel.

Synthesis of the *p*-*tert*-butylcalixarene-dithiacrown ether analogues **8** and **9** followed essentially the same synthetic route (Scheme 2). Known dibenzyl *p*-*tert*-butylcalix[4]arene **22** was obtained in 90% yield from reaction of *p*-*tert*-butylcalix[4]arene (**21**) with benzyl bromide and K₂CO₃ in refluxing MeCN for 24 h. (Only 1 h at reflux was required in the preparation of **14**). Reaction of dibenzyl ether **22** with NaH and ethyl bromoacetate in THF at room temperature to form cone dibenzyl diester **23** in 71% yield took 5–7 days. (This was a much longer reaction period than was required for conversion of dibenzyl ether **14** into a mixture of dibenzyl diesters **15** and **16** under the same conditions.). The 1,3-

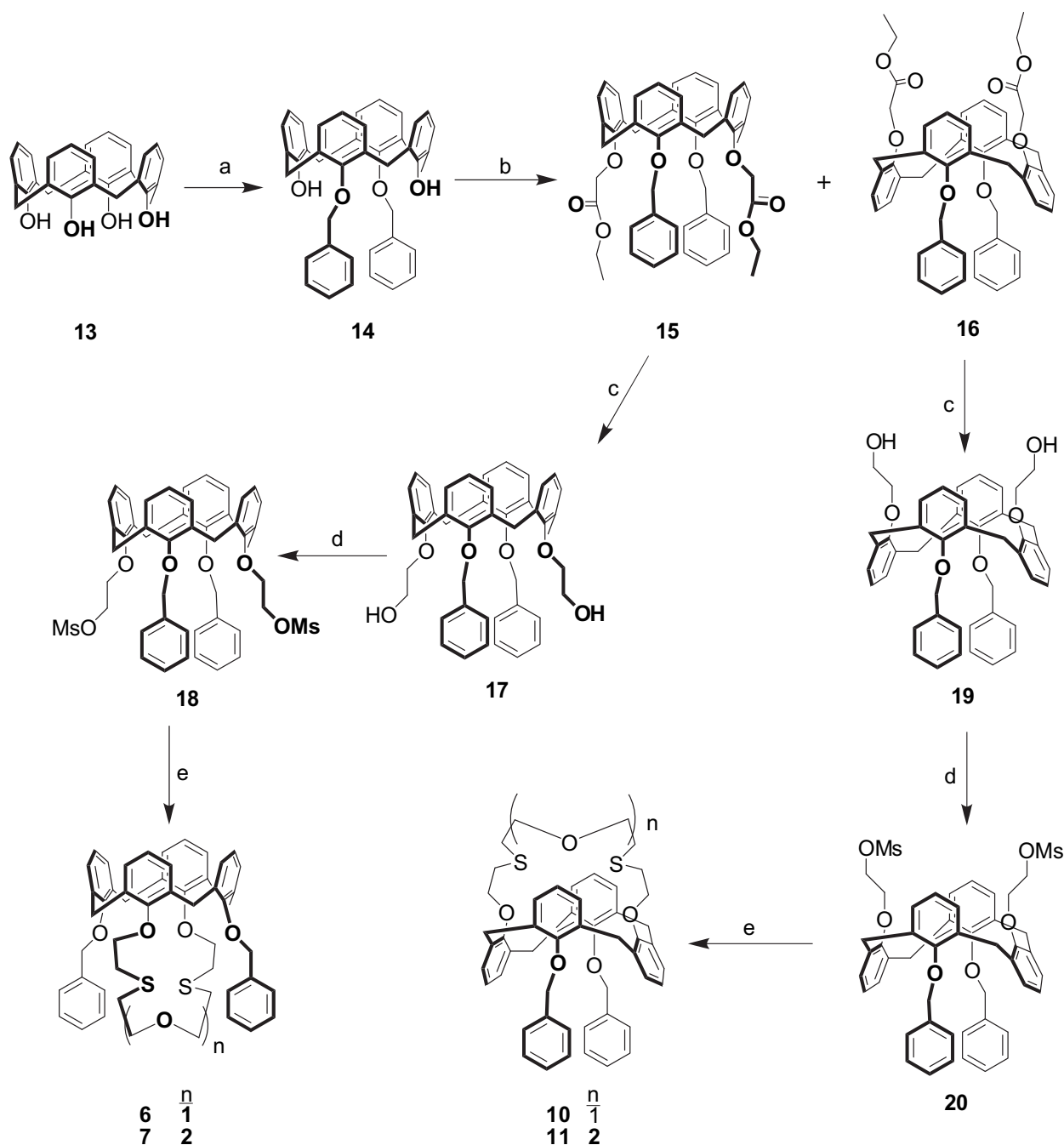
alternate dibenzyl diester isomer of cone **23** was isolated as a byproduct in 8% yield. Cone dibenzyl diester **23** was reduced with LAH in THF at room temperature to produce an 88% yield of cone dibenzyl diol **24**, which was converted into the corresponding cone dibenzyl dimesylate **25** by reaction with mesyl chloride, Et₃N and DMAP in CH₂Cl₂ at room temperature. Reaction of **25** with Cs₂CO₃ and the appropriate dithiol compounds gave cone dibenzyl *p*-*tert*-butylcalix[4]arene-dithiacrown ethers **8** and **9** in low yields of 19% and 33%, respectively.

For comparison purposes, cone dibenzyl calix[4]arene-crown-6 **12** was prepared in 62% yield by reaction of cone calix[4]arene-crown-6 with NaH and benzyl bromide in THF/DMF at room temperature.

Structures of new dibenzyl calix[4]arene-dithiacrown ethers **6–11**, as well as their previously unreported synthetic intermediates **15–17**, **19**, **23**, and **24**, were verified by ¹H and ¹³C NMR spectroscopy, IR spectroscopy (when appropriate) and combustion analysis. Dimesylate synthetic intermediates **18**, **20**, and **25** were characterized only spectroscopically. The structure of new dibenzyl calix[4]arene-crown-6 **12** was confirmed by its ¹H and ¹³C NMR spectra and combustion analysis.

2.2. Potentiometric responses of solvent polymeric membrane electrodes

The dibenzyl calix[4]arene-dithiacrown ionophores **6–11** and dibenzyl calix[4]arene-crown-6 **12** (Fig. 2) were incorporated into solvent polymeric membranes in which PVC was the polymer and

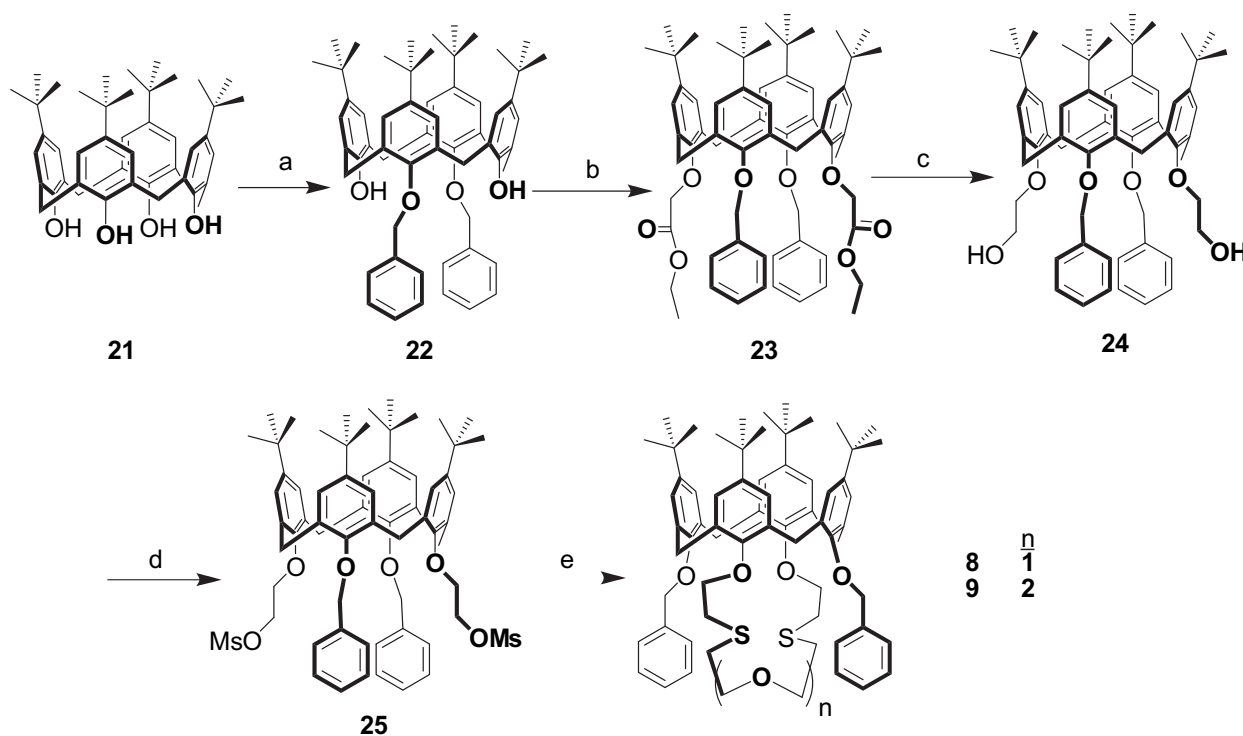


Scheme 1. Synthesis of dibenzyl calix[4]arene-dithiacrown ligands **6**, **7**, **10**, and **11**. Reagents and conditions: (a) BnBr, K_2CO_3 , MeCN, reflux; (b) NaH, $BrCH_2CO_2Et$, THF, rt; (c) LAH, THF, rt; (d) MsCl, Et_3N , DMAP, CH_2Cl_2 , rt; (e) $HSCH_2CH_2(OCH_2CH_2)_nSH$, ($n=1, 2$), Cs_2CO_3 , THF, reflux.

NPOE was the membrane solvent. For the ion-selective electrodes (ISEs) prepared from these membranes, selectivities for Hg^{2+} relative to Na^+ and the divalent transition and heavy metal ion series of Cd^{2+} , Co^{2+} , Cu^{2+} , Ni^{2+} , Pb^{2+} , and Zn^{2+} were determined by the fixed interference method.²⁵ Near-Nernstian responses (20–30 mV/decade) were obtained for all of the solvent polymeric membranes. Ionophores **7** and **9** showed Nernstian responses of 29.5 mV/decade. ISEs prepared with calix[4]arene-dithiacrown compounds **6–11** were selective for Hg^{2+} over all of the other metal ions tested. The ISE prepared with calix[4]arene-crown-6 **12** was selective for Hg^{2+} over all of the divalent metal ions, but exhibited slight selectivity for Na^+ over Hg^{2+} . Selectivity coefficients expressed as $-\log K_{Hg,M}^{Pot}$ values for Hg^{2+} over other divalent transition and heavy metal ions and Na^+ are presented in Table 1. (A larger value of $-\log K_{Hg,M}^{Pot}$ denotes a greater Hg^{2+} selectivity).

Cone dibenzyl calix[4]arene-crown-6 **12** is a reference compound with only oxygen atoms in the crown ether unit. The selectivity order for the ISE incorporating this ionophore is $Na^+ > Hg^{2+} > Pb^{2+} > Cd^{2+} > Ni^{2+} > Cu^{2+} > Co^{2+} > Zn^{2+}$. Replacement of two oxygens in the crown unit of **12** with sulfurs gives cone dibenzyl calix[4]arene-dithiacrown-6 **7**. This structural variation produces a marked change in the potentiometric selectivities of the ISEs toward Hg^{2+} giving $-\log K_{Hg,M}$ values of 2.2–3.6 for the divalent transition and heavy metal ions, as well as for Na^+ . With this substitution, the selectivity order changes to $Hg^{2+} > Pb^{2+} > Cd^{2+} > Na^+$, $Zn^{2+} > Cu^{2+} > Co^{2+} > Ni^{2+}$. Incorporation of two soft ligation sites in the crown ring of **7** markedly enhances the Hg^{2+} selectivity.

Replacement of the *para* hydrogens on the upper-rim aryl rings of cone dibenzyl calix[4]arene-dithiacrown-6 **7** with *tert*-butyl



Scheme 2. Synthesis of dibenzyl *p-tert*-butylcalix[4]arene-dithiacrown ligands **8** and **9**. Reagents and conditions: (a) BnBr, K₂CO₃, MeCN, reflux; (b) NaH, BrCH₂CO₂Et, THF, rt; (c) LAH, THF, rt; (d) MsCl, Et₃N, DMAP, CH₂Cl₂, rt; (e) HSCH₂CH₂(OCH₂CH₂)_nSH, (*n*=1, 2), Cs₂CO₃, THF, reflux.

Table 1
Potentiometric selectivities ($-\log K_{\text{Hg,M}}^{\text{Pot}}$)^{a,b} of compounds **6–12** as ionophores in solvent polymeric membrane electrodes

Ionophore	$-\log K_{\text{Hg,M}}^{\text{Pot}}$						
	Na ⁺	Cd ²⁺	Co ²⁺	Cu ²⁺	Ni ²⁺	Pb ²⁺	Zn ²⁺
6	2.27	1.88	2.94	2.26	3.09	1.76	2.75
7	3.11	2.42	3.473	39	3.56	2.21	3.11
8	2.16	1.81	2.72	1.77 ^c	1.24	1.70	2.76
9	3.04	2.26	3.28	3.39	3.55	2.13	3.13
10	1.23	1.90	1.20 ^c	0.98	0.96	1.52	1.63
11	2.04	2.98	2.96	2.92	2.98	2.28	2.74
12	0.80	1.84	2.71	2.60	2.52	1.74	2.79

^a The primary ion, Hg²⁺, corresponds to a $-\log K_{\text{Hg,M}}^{\text{Pot}}$ value of 0.

^b Standard deviation of 0.05 or less.

^c Poor electrode stability was observed.

groups produces cone dibenzyl *tert*-butylcalix[4]arene-dithiacrown-**6–9**. Comparison of the data for ISEs containing ionophores **7** and **9** in Table 1 reveals very similar potentiometric selectivities for the two ligands. Thus this structural variation is judged to have only a small effect, if any, on the Hg²⁺ selectivity.

Dibenzyl calix[4]arene-dithiacrown-**6** ionophores **7** and **11** are isomers in which the calix[4]arene scaffold is cone in the former and 1,3-alternate in the latter. Potentiometric selectivities for ISEs containing these two ionophores show high Hg²⁺ selectivities for both ionophores. When taken together, the $-\log K_{\text{Hg,M}}^{\text{Pot}}$ values for the cone isomer (2.2–3.6) appear to be slightly higher than those for the 1,3-alternate isomer (2.0–3.0). This result suggests that the primary binding of Hg²⁺ is by the crown ring, rather than cation- π interactions with the calixarene unit.

Contraction of the crown ring in ionophores **7**, **9**, and **11** from dithiacrown-**6** to dithiacrown-**5** in ionophores **6**, **8**, and **10**, respectively, uniformly decreases the potentiometric selectivity for Hg²⁺. The least selective ISE was that prepared from ionophore **10**,

which has both a smaller dithiacrown-**5** ring and a 1,3-alternate conformation of the calix[4]arene scaffold.

Of the six new dibenzyl calix[4]arene-dithiacrown compounds **6–11**, the ISE prepared with ionophore **7** provides the highest Hg²⁺ selectivity over the six divalent transition and heavy metal cations and Na⁺.

3. Experimental

3.1. General

Melting points were determined with a Mel-Temp apparatus. Infrared (IR) spectra were recorded with a Nicolet IR100 FTIR spectrometer as deposits from CH₂Cl₂ solutions on NaCl plates unless otherwise mentioned. The ¹H and ¹³C NMR spectra were recorded with a Varian Unity INOVA 500 MHz FTNMR spectrometer at 500 and 126 MHz, respectively, in CDCl₃ with Me₄Si as internal standard, unless mentioned otherwise. Chemical shifts (δ) are given in ppm downfield from TMS and coupling constants values (*J*) are given in Hertz. Elemental analysis was performed by Desert Analytics Laboratory/Columbia Analytical Services (Tucson, Arizona).

Reagents were purchased from commercial suppliers and used directly unless otherwise noted. Calix[4]arene (**13**) and *p-tert*-butylcalix[4]arene (**21**) were obtained from Eburon Organics International, Inc. (Lubbock, Texas). Acetonitrile (MeCN) was dried over CaH₂ and distilled immediately before use. Tetrahydrofuran (THF) was dried over sodium with benzophenone as an indicator and distilled just before use.

For the potentiometric studies, KCl (99%) and NaCl (99%) were purchased from Sigma–Aldrich (Milwaukee, Wisconsin). Cd(NO₃)₂·6H₂O (99+%), Cu(NO₃)₂, Hg(NO₃)₂, and Ni(NO₃)₂·6H₂O were obtained from Acros Organics (Morris Plains, New Jersey). Pb(NO₃)₂ and Zn(NO₃)₂ were purchased from MCB (Norwood, Ohio) and Fisher Scientific (Fair Lawn, New Jersey), respectively. High molecular weight poly(vinyl chloride) (PVC) with an average

polymerization degree of 1100 was obtained from Wako Pure Chemical Industries (Osaka, Japan). Potassium tetrakis(*p*-chlorophenyl)borate (KTPClPB) and *ortho*-nitrophenyl octyl ether (NPOE) were purchased from Dojindo Laboratories (Kumamoto, Japan). De-ionized water was prepared by passing distilled water through three Barnsted combination ion-exchange cartridges in series and used to prepare aqueous solutions and rinse plastic bottles and glassware during the experiment.

3.2. Ligand synthesis

3.2.1. Cone 25,27-bis(benzyloxy)calix[4]arene (14). A mixture of calix[4]arene (**13**) (10.00 g, 23.60 mmol) and K_2CO_3 (3.90 g, 28.3 mmol) in MeCN (350 mL) was refluxed for 1 h under nitrogen. Benzyl bromide (8.90 g, 51.90 mmol) was added in one portion and the mixture was refluxed for 1 h. The mixture was poured into ice cold 1 N aq HCl. The precipitate was filtered and recrystallized from CH_2Cl_2 –MeOH to give **14** (13.80 g, 90%) as white crystals with mp 224–225 °C (lit. mp²⁶ 219–222 °C). ¹H NMR: δ 3.34 (d, $J=13.0$ Hz, 4H, ArCH₂Ar), 4.31 (d, $J=13.0$ Hz, 4H, ArCH₂Ar), 5.06 (s, 4H, OCH₂Ph), 6.65 (t, $J=8.0$ Hz, 2H, ArH), 6.75 (t, $J=8.0$ Hz, 2H, ArH), 6.89 (d, $J=8.0$ Hz, 4H, ArH), 7.05 (d, $J=8.0$ Hz, 4H, ArH), 7.34–7.40 (m, 6H, ArH), 7.64–7.66 (m, 4H, ArH), 7.81 (s, 2H, OH). ¹³C NMR: δ 31.4, 78.4, 118.9, 125.4, 127.4, 127.9, 128.0, 128.4, 128.7, 129.0, 133.2, 136.8, 151.9, 153.3.

3.2.2. Cone 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,27-bis(benzyloxy)calix[4]arene (22). Under the same conditions as given above for the preparation of **14**, but with refluxing of the reaction mixture for 24 h, *p*-tert-butylcalix[4]arene (**21**) (10.00 g, 15.43 mmol), K_2CO_3 (2.55 g, 18.52 mmol), and benzyl bromide (5.82 g, 33.95 mmol) in MeCN (350 mL) were combined to produce **22** (11.50 g, 90%) as a white solid with mp 220–221 °C (lit. mp²⁶ 219–220 °C). ¹H NMR: δ 0.94 (s, 18H, C(CH₃)₃), 1.28 (s, 18H, C(CH₃)₃), 3.26 (d, $J=13.0$ Hz, 4H, ArCH₂Ar), 4.28 (d, $J=13.0$ Hz, 4H, ArCH₂Ar), 5.05 (s, 4H, OCH₂Ar), 6.68 (s, 4H, ArH), 7.04 (s, 4H, ArH), 7.30 (s, 2H, OH), 7.35–7.37 (m, 6H, ArH), 7.64–7.66 (m, 4H, ArH). ¹³C NMR: δ 31.0, 31.4, 31.6, 31.7, 33.8, 33.9, 77.9, 124.9, 125.0, 125.5, 127.3, 127.5, 127.8, 127.9, 128.6, 129.6, 132.6, 133.8, 137.2, 141.3, 146.9, 149.8, 150.8.

3.2.3. Cone 25,27-bis(benzyloxy)-26,28-bis((ethoxycarbonyl)methoxy)calix[4]arene (15) and 1,3-alternate 25,27-bis(benzyloxy)-26,28-bis((ethoxycarbonyl)methoxy)calix[4]arene (16). Dibenzyl calix[4]arene **14** (4.00 g, 6.62 mmol) was stirred with NaH (1.59 g, 66.20 mmol) in THF (200 mL) for 1 h and ethyl bromoacetate (3.87 g, 23.17 mmol) was added in one portion. The mixture was stirred at room temperature overnight and then reaction was quenched by addition of small amount of water. After evaporation of the THF in vacuo, CH_2Cl_2 (150 mL) and aq 1 N HCl (150 mL) were added to the residue. The organic layer was separated, washed with water (2×250 mL), dried over $MgSO_4$ and evaporated in vacuo to give the crude product, which was chromatographed on silica gel with hexanes–EtOAc (50:1 to 4:1 gradient) as eluent to give **15** as the major product (2.90 g, 56%) and **16** as the minor product (1.50 g, 30%).

Cone dibenzyl diester **15** was a white solid with mp 125–126 °C. IR: 1759, 1734 (C=O) cm^{-1} . ¹H NMR: δ 1.20 (t, $J=7.0$ Hz, 6H, OCH₂CH₃), 3.09 (d, $J=14.0$ Hz, 4H, ArCH₂Ar), 4.07 (q, $J=7.5$ Hz, 4H, OCH₂CH₃), 4.52 (d, $J=13.0$ Hz, 4H, ArCH₂Ar), 4.55 (s, 4H, OCH₂Ar), 5.03 (s, 4H, OCH₂C(O)), 6.44–6.52 (m, 6H, ArH), 6.66–6.75 (m, 6H, ArH), 7.29–7.31 (m, 6H, ArH), 7.43–7.45 (m, 4H, ArH). ¹³C NMR: δ 14.2, 31.3, 60.4, 70.7, 76.9, 122.5, 122.6, 127.7, 128.0, 128.0, 128.7, 129.3, 134.7, 135.2, 137.8, 155.1, 156.0, 170.0. Anal. calcd for $C_{50}H_{48}O_8$: C, 77.30; H, 6.23%. Found: C, 77.03; H, 6.36%.

The 1,3-alternate dibenzyl diester **16** was a white solid with mp 120–121 °C. IR: 1756 (C=O) cm^{-1} . ¹H NMR: δ 1.27 (t, $J=7.0$ Hz, 6H,

OCH₂CH₃), 3.48 (s, 4H, OCH₂Ar), 3.60 (d, $J=14.5$ Hz, 4H, ArCH₂Ar), 3.90 (d, $J=14.5$ Hz, 4H, ArCH₂Ar), 4.16 (q, $J=7.0$ Hz, 4H, OCH₂CH₃), 4.86 (s, 4H, OCH₂C(O)), 6.40 (t, $J=7.5$ Hz, 2H, ArH), 6.70 (d, $J=8.0$ Hz, 4H, ArH), 6.79 (t, $J=7.5$ Hz, 2H, ArH), 7.13 (d, $J=6.5$ Hz, 4H, ArH), 7.17 (d, $J=7.5$ Hz, 4H, ArH), 7.35–7.41 (m, 6H, ArH). ¹³C NMR: δ 14.2, 37.1, 60.4, 68.9, 72.8, 122.4, 123.0, 127.2, 127.2, 127.9, 130.4, 131.3, 133.4, 134.8, 137.7, 155.0, 156.8, 170.0. Anal. calcd for $C_{50}H_{48}O_8$: C, 77.30; H, 6.23%. Found: C, 77.26; H, 6.31%.

3.2.4. Cone 25,27-bis(benzyloxy)-26,28-bis(2-hydroxy-ethoxy)calix[4]arene (17). Dibenzyl diester **15** (1.00 g, 1.29 mmol) was dissolved in THF (50 mL). To the solution, LAH (0.15 g, 3.87 mmol) was added and the mixture was stirred at room temperature for 48 h. Careful addition of distilled water (0.15 mL) was followed by aq 10% NaOH (0.15 mL) and then distilled water (0.45 mL). The mixture was stirred for 15 min at room temperature and the precipitate was filtered. After evaporation of the THF in vacuo, CH_2Cl_2 (50 mL) and aq 10% HCl (50 mL) were added to the residue. The organic layer was separated, washed with water (2×50 mL), dried over $MgSO_4$ and evaporated in vacuo to give cone diol **17** (0.84 g, 90%) as a white solid with mp 178–179 °C. IR: 3426 (OH) cm^{-1} . ¹H NMR: δ 2.89 (d, $J=14.0$ Hz, 4H, ArCH₂Ar), 3.77–3.80 (m, 4H, OCH₂CH₂OH), 4.07–4.08 (m, 4H, OCH₂CH₂OH), 4.21 (d, $J=13.5$ Hz, 4H, ArCH₂Ar), 4.83–4.85 (m, 6H, OH, OCH₂Ar), 6.14 (d, $J=7.5$ Hz, 4H, ArH), 6.26 (t, $J=7.5$ Hz, 2H, ArH), 6.94 (t, $J=7.5$ Hz, 2H, ArH), 7.08 (d, $J=7.5$ Hz, 4H, ArH), 7.27–7.36 (m, 10H, ArH). ¹³C NMR: δ 30.7, 61.6, 77.1, 78.2, 122.8, 122.9, 127.7, 128.3, 128.5, 129.1, 130.0, 133.2, 136.0, 136.7, 152.6, 157.1. Anal. calcd for $C_{48}H_{48}O_6 \cdot 0.2CH_2Cl_2$: C, 78.46; H, 6.61%. Found: C, 78.65; H, 6.81%.

3.2.5. 1,3-Alternate 25,27-bis(benzyloxy)-26,28-bis(2-hydroxy-ethoxy)calix[4]arene (19). The procedure for synthesizing **19** from **16** was the same as that given above for preparation of **17** from **15**. The 1,3-alternate dibenzyl diol **19** was obtained in 84% yield as a white solid with mp 152–154 °C. IR: 3399 (OH) cm^{-1} . ¹H NMR: δ 2.30 (t, $J=6.5$ Hz, 2H, OH), 3.46–3.49 (m, 4H, OCH₂CH₂OH), 3.63–3.77 (m, 12H, OCH₂CH₂OH, ArCH₂Ar), 4.74 (s, 4H, OCH₂Ar), 6.39 (t, $J=7.5$ Hz, 2H, ArH), 6.68 (d, $J=8.0$ Hz, 4H, ArH), 6.91–6.94 (m, 6H, ArH), 7.12 (d, $J=7.5$ Hz, 4H, ArH), 7.26–7.33 (m, 6H, ArH). ¹³C NMR: δ 38.0, 61.4, 71.1, 72.1, 122.9, 122.9, 127.1, 127.5, 127.7, 129.7, 130.2, 133.4, 134.4, 137.6, 155.5, 156.6. Anal. calcd for $C_{48}H_{48}O_6 \cdot 0.1CH_2Cl_2$: C, 79.21; H, 6.66%. Found: C, 78.87; H, 6.70%.

3.2.6. Cone 25,27-bis(benzyloxy)-26,28-bis(2-mesyloxyethoxy)calix[4]arene (18). A solution of diol **17** (0.72 g, 1.00 mmol), Et₃N (1.01 g, 10.00 mmol), DMAP catalyst (0.20 g) in CH_2Cl_2 (50 mL) was stirred at 0 °C for 30 min. MsCl (1.14 g, 10.00 mmol) was added in one portion and stirring was continued overnight, first at 0 °C and then eventually allowing it to warm up to room temperature. The mixture was washed with aq 1 N HCl (2×50 mL) and water (2×50 mL) and dried over $MgSO_4$. After evaporation of the CH_2Cl_2 in vacuo, the crude product was purified by chromatography on silica gel with hexanes–EtOAc (50:1 to 4:1 gradient) as eluent to give cone dibenzyl dimesylate **18** (0.61 g, 70%) as a white solid with mp 189–191 °C. ¹H NMR: δ 2.67 (s, 6H, CH₃SO₂), 3.12 (d, 4H, $J=14.0$ Hz, ArCH₂Ar), 4.24 (t, $J=6.0$ Hz, OCH₂CH₂OMs), 4.32 (d, $J=13.5$ Hz, ArCH₂Ar), 4.41 (t, $J=6.5$ Hz, OCH₂CH₂OMs), 4.74 (s, 4H, OCH₂Ar), 6.17 (d, $J=7.5$ Hz, 4H, ArH), 6.29 (t, $J=7.0$ Hz, 2H, ArH), 6.94 (t, $J=7.5$ Hz, 2H, ArH), 7.08 (d, $J=7.5$ Hz, 4H, ArH), 7.33–7.47 (m, 10H, ArH). ¹³C NMR: δ 31.0, 37.3, 68.2, 71.0, 77.9, 122.7, 123.0, 127.8, 128.3, 128.7, 129.1, 129.3, 133.0, 136.3, 137.1, 154.1, 157.0.

3.2.7. 1,3-Alternate 25,27-bis(benzyloxy)-26,28-bis(2-mesyloxyethoxy)calix[4]arene (20). The procedure given above for preparing **18** from **17** was utilized to convert **19** into **20**. The 1,3-alternate dibenzyl dimesylate **20** was obtained in 72% yield as a white solid

with mp 172–174 °C. ^1H NMR: δ 2.56 (s, 6H, CH_3SO_2), 3.68 (s, 8H, ArCH_2Ar), 3.81 (t, $J=4.5$ Hz, $\text{OCH}_2\text{CH}_2\text{OMs}$), 4.27 (t, $J=4.5$ Hz, $\text{OCH}_2\text{CH}_2\text{OMs}$), 4.81 (s, 4H, OCH_2Ar), 6.38 (t, $J=7.5$ Hz, 2H, ArH), 6.67 (d, $J=7.5$ Hz, 4H, ArH), 7.01–7.05 (m, 6H, ArH), 7.16 (d, $J=7.5$ Hz, 4H, ArH), 7.37–7.41 (m, 6H, ArH). ^{13}C NMR: δ 37.4, 37.6, 68.3, 68.7, 72.2, 123.1, 123.5, 127.1, 127.2, 127.8, 130.2, 131.5, 133.2, 134.9, 137.4, 155.0, 156.9.

3.2.8. General procedure for synthesis of calix[4]arene-dithiacrown ligands **6, **7**, **10**, and **11**.** Dibenzyl calix[4]arene dimesylate **18** or **20** (0.85 g, 1.00 mmol) was mixed with Cs_2CO_3 (1.63 g, 5.00 mmol) in THF (75 mL). The appropriate dithiol (1.10 mmol) was mixed with THF (10 mL) and the solution was added to the mixture during a 3 h period. The mixture was refluxed for 72 h and the THF was removed in vacuo. To the residue, CH_2Cl_2 (50 mL) and aq 1 N HCl (50 mL) were added. The organic layer was separated, washed with water (2 \times 50 mL), dried over MgSO_4 and evaporated in vacuo to give the crude product. The crude product was purified by chromatography on silica gel with hexanes–EtOAc (50:1 to 4:1 gradient) as eluent to give the dibenzyl calix[4]arene-dithiacrown compound.

3.2.8.1. Cone 25,27-bis(benzyloxy)calix[4]arene-dithiacrown-5. Compound **6** was obtained in 53% yield as a white solid with mp 266–267 °C. ^1H NMR: δ 2.23 (t, $J=7.0$ Hz, 4H, $\text{SCH}_2\text{CH}_2\text{O}$), 2.70 (t, $J=8.0$ Hz, 4H, $\text{SCH}_2\text{CH}_2\text{O}$), 3.19–3.24 (m, 8H, ArCH_2Ar , $\text{OCH}_2\text{CH}_2\text{S}$), 4.06 (t, $J=8.0$ Hz, $\text{OCH}_2\text{CH}_2\text{S}$), 4.47 (d, $J=13.0$ Hz, 4H, ArCH_2Ar), 4.67 (s, 4H, OCH_2Ar), 6.16 (d, $J=8.0$ Hz, 4H, ArH), 6.26 (t, $J=7.0$ Hz, 2H, ArH), 6.97 (t, $J=8.0$ Hz, 2H, ArH), 7.16 (d, $J=8.0$ Hz, 4H, ArH), 7.36–7.56 (m, 10H, ArH). ^{13}C NMR: δ 29.8, 30.4, 31.1, 70.7, 73.9, 77.9, 122.6, 122.6, 127.6, 128.3, 128.8, 129.1, 129.3, 132.9, 137.0, 137.5, 154.4, 156.4. Anal. calcd for $\text{C}_{50}\text{H}_{50}\text{O}_5\text{S}_2$: C, 75.53; H, 6.34; S, 8.07%. Found: C, 75.20; H, 6.64; S, 8.13%.

3.2.8.2. Cone 25,27-bis(benzyloxy)calix[4]arene-dithiacrown-6. Compound **7** was isolated in 30% yield as a white solid with mp 158–160 °C. ^1H NMR: δ 2.47 (t, $J=7.0$ Hz, 4H, $\text{SCH}_2\text{CH}_2\text{O}$), 2.86 (t, $J=8.0$ Hz, 4H, $\text{SCH}_2\text{CH}_2\text{O}$), 3.13 (d, $J=13.0$ Hz, 4H, ArCH_2Ar), 3.56 (t, $J=7.0$ Hz, 4H, $\text{OCH}_2\text{CH}_2\text{S}$), 3.58 (s, 4H, $\text{OCH}_2\text{CH}_2\text{O}$), 4.09 (t, $J=8.0$ Hz, $\text{OCH}_2\text{CH}_2\text{S}$), 4.43 (d, $J=13.0$ Hz, 4H, ArCH_2Ar), 4.72 (s, 4H, OCH_2Ar), 6.12 (d, $J=8.0$ Hz, 4H, ArH), 6.25 (t, $J=7.0$ Hz, 2H, ArH), 6.95 (t, $J=8.0$ Hz, 4H, ArH), 7.13 (d, $J=8.0$ Hz, 4H, ArH), 7.36 (t, $J=8.0$ Hz, 2H, ArH), 7.41 (t, $J=7.0$ Hz, 4H, ArH), 7.48 (t, $J=7.0$ Hz, 4H, ArH). ^{13}C NMR: δ 31.1, 31.2, 31.5, 70.6, 71.0, 73.5, 77.7, 122.4, 122.6, 127.6, 128.2, 128.6, 128.9, 129.1, 129.1, 133.0, 136.8, 137.4, 154.3, 157.2. Anal. calcd for $\text{C}_{52}\text{H}_{54}\text{O}_6\text{S}_2$: C, 74.43; H, 6.49; S, 7.64%. Found: C, 74.23; H, 7.03; S, 7.65%.

3.2.8.3. 1,3-Alternate 25,27-bis(benzyloxy)calix[4]arene-dithiacrown-5. Compound **10** was produced in 48% yield as a white solid with mp 141–142 °C. ^1H NMR: δ 2.42 (t, $J=8.0$ Hz, 4H, $\text{SCH}_2\text{CH}_2\text{O}$), 2.66 (t, $J=6.0$ Hz, 4H, $\text{SCH}_2\text{CH}_2\text{O}$), 3.51 (t, $J=7.0$ Hz, 4H, $\text{OCH}_2\text{CH}_2\text{S}$), 3.65–3.77 (m, 12H, $\text{OCH}_2\text{CH}_2\text{S}$, ArCH_2Ar), 4.70 (s, 4H, OCH_2Ar), 6.36 (t, $J=8.0$ Hz, 2H, ArH), 6.65 (d, $J=8.0$ Hz, 4H, ArH), 6.90–6.93 (m, 6H, ArH), 7.15 (d, $J=7.0$ Hz, 4H, ArH), 7.24–7.29 (m, 6H, ArH). ^{13}C NMR: δ 32.8, 33.2, 38.0, 69.6, 72.0, 73.1, 122.6, 122.6, 127.0, 127.3, 127.7, 129.5, 130.0, 133.5, 134.4, 137.9, 155.6, 156.8. Anal. calcd for $\text{C}_{50}\text{H}_{50}\text{O}_5\text{S}_2$: C, 75.53; H, 6.34; S, 8.07%. Found: C, 75.55; H, 6.48; S, 8.24%.

3.2.8.4. 1,3-Alternate 25,27-bis(benzyloxy)calix[4]arene-dithiacrown-6. Compound **11** was realized in 65% yield as a white solid with mp 124–126 °C. ^1H NMR: δ 2.52 (t, $J=8.0$ Hz, 4H, $\text{SCH}_2\text{CH}_2\text{O}$), 2.62 (t, $J=6.0$ Hz, 4H, $\text{SCH}_2\text{CH}_2\text{O}$), 3.63–3.76 (m, 20H, ArCH_2Ar , $\text{OCH}_2\text{CH}_2\text{O}$, $\text{OCH}_2\text{CH}_2\text{S}$), 4.76 (s, 4H, OCH_2Ar), 6.38 (t, $J=8.0$ Hz, 2H, ArH), 6.65 (d, $J=8.0$ Hz, 4H, ArH), 6.88 (t, $J=8.0$ Hz, 2H, ArH), 7.00–7.02 (m, 4H, ArH), 7.15 (d, $J=8.0$ Hz, 4H, ArH), 7.31–7.34 (m, 6H,

ArH). ^{13}C NMR: δ 31.6, 32.8, 37.7, 70.8, 71.0, 71.7, 72.0, 122.4, 122.5, 127.0, 127.1, 127.8, 129.9, 130.6, 133.4, 134.4, 137.9, 155.7, 156.6. Anal. calcd for $\text{C}_{52}\text{H}_{54}\text{O}_6\text{S}_2$: C, 74.43; H, 6.49. Found: C, 74.10; H, 6.73%.

3.2.9. Cone 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,27-bis(benzyloxy)-26,28-bis(((ethoxy-carbonyl)methoxy)calix[4]arene (23**) and 1,3-alternate 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,27-bis(benzyloxy)-26,28-bis(((ethoxycarbonyl)methoxy)calix[4]arene.** After a mixture of dibenzyl *p*-tert-butylcalix[4]arene **22** (4.00 g, 4.82 mmol) and NaH (1.16 g, 48.20 mmol) in THF (200 mL) was stirred at room temperature for 1 h, ethyl bromoacetate (2.82 g, 16.87 mmol) was added in one portion and the mixture was stirred at room temperature overnight. After evaporation of the THF in vacuo, CH_2Cl_2 (150 mL) and aq 1 N HCl (150 mL) were added to the residue. The organic layer was separated, washed with water (2 \times 250 mL), dried over MgSO_4 and evaporated in vacuo to give the crude product, which was chromatographed on silica gel with hexanes–EtOAc (50:1 to 4:1 gradient) as eluent to give **23** as the major product (3.43 g, 71%) and a small amount (0.35 g, 8%) of a byproduct. Cone dibenzyl diester **23** was a white solid with mp 167–169 °C. IR: 1760 ($\text{C}=\text{O}$) cm^{-1} . ^1H NMR: δ 0.96 (s, 18H, $\text{C}(\text{CH}_3)_3$), 1.18 (t, $J=7.0$ Hz, 6H, OCH_2CH_3), 1.19 (s, 18H, $\text{C}(\text{CH}_3)_3$), 3.09 (d, $J=13.0$ Hz, 4H, ArCH_2Ar), 4.01 (q, $J=7.0$ Hz, 4H, OCH_2CH_3), 4.56 (d, $J=13.0$ Hz, 4H, ArCH_2Ar), 4.58 (s, 4H, OCH_2Ar), 4.94 (s, 4H, $\text{OCH}_2\text{C}(\text{O})$), 6.60 (s, 4H, ArH), 6.90 (s, 4H, ArH), 7.31–7.34 (m, 6H, ArH), 7.46–7.48 (m, 4H, ArH). ^{13}C NMR: δ 14.1, 31.2, 31.5, 31.9, 33.7, 60.1, 70.3, 77.3, 124.8, 125.4, 127.6, 128.0, 129.2, 132.9, 134.3, 138.3, 144.6, 145.0, 152.6, 153.1, 170.6. Anal. calcd for $\text{C}_{66}\text{H}_{80}\text{O}_8 \cdot 0.1\text{CH}_2\text{Cl}_2$: C, 78.62; H, 8.00%. Found: C, 78.70; H, 8.29%.

The 1,3-alternate dibenzyl diester isomer byproduct was a white solid with mp 208–209 °C. IR: 1760 ($\text{C}=\text{O}$) cm^{-1} . ^1H NMR: δ 0.86 (s, 18H, $\text{C}(\text{CH}_3)_3$), 1.19 (t, $J=7.0$ Hz, 6H, OCH_2CH_3), 1.25 (s, 18H, $\text{C}(\text{CH}_3)_3$), 3.57 (d, $J=16.0$ Hz, 4H, ArCH_2Ar), 3.58 (s, 4H, OCH_2Ar), 3.97 (d, $J=13.0$ Hz, 4H, ArCH_2Ar), 4.08 (q, $J=7.5$ Hz, 4H, OCH_2CH_3), 4.53 (s, 4H, $\text{OCH}_2\text{C}(\text{O})$), 6.74 (s, 4H, ArH), 6.95–6.97 (m, 4H, ArH), 7.13 (s, 4H, ArH), 7.22–7.24 (m, 6H, ArH). ^{13}C NMR: δ 31.0, 31.4, 33.5, 33.9, 38.6, 60.3, 68.5, 73.0, 126.8, 127.1, 127.2, 127.7, 128.0, 133.1, 134.0, 138.2, 144.3, 144.9, 153.3, 154.3, 170.2. Anal. calcd for $\text{C}_{66}\text{H}_{80}\text{O}_8 \cdot 0.1\text{CH}_2\text{Cl}_2$: C, 78.62; H, 8.00%. Found: C, 78.33; H, 8.17%.

3.2.10. Cone 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,27-bis(benzyloxy)-26,28-bis(2-hydroxy-ethoxy)calix[4]arene (24**).** The procedure for converting compound **23** into **24** was the same as that given above for the preparation of compound **17** from **15**. The dibenzyl diol **24** was obtained in 88% yield as a white solid with mp 228–230 °C. IR: 3449 (OH) cm^{-1} . ^1H NMR: δ 0.81 (s, 18H, $\text{C}(\text{CH}_3)_3$), 1.31 (s, 18H, $\text{C}(\text{CH}_3)_3$), 2.87 (d, $J=12.5$ Hz, 4H, ArCH_2Ar), 3.83–3.86 (m, 4H, $\text{OCH}_2\text{CH}_2\text{OH}$), 3.96–3.98 (m, 4H, $\text{OCH}_2\text{CH}_2\text{OH}$), 4.16 (d, $J=12.5$ Hz, 4H, ArCH_2Ar), 4.81 (s, 4H, OCH_2Ar), 5.06 (t, $J=6.5$ Hz, 2H, OH), 6.44 (s, 4H, ArH), 7.06 (s, 4H, ArH), 7.25–7.33 (m, 10H, ArH). ^{13}C NMR: δ 30.8, 31.1, 31.7, 33.6, 34.1, 61.7, 76.8, 78.3, 124.6, 125.6, 128.1, 128.3, 130.4, 132.2, 135.4, 136.4, 145.0, 145.5, 150.1, 153.8. Anal. calcd for $\text{C}_{62}\text{H}_{76}\text{O}_6$: C, 81.18; H, 8.35%. Found: C, 80.99; H, 8.36%.

3.2.11. Cone 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,27-bis(benzyloxy)-26,28-bis(2-mesyloxy-ethoxy)calix[4]arene (25**).** The procedure for preparing compound **25** from **24** was the same as that given above for the synthesis of **18** from **17**. The dibenzyl dimesylate **25** was obtained in 84% yield as a white solid with mp 168–171 °C after chromatography on silica gel with hexanes–EtOAc (50:1 to 4:1 gradient) as eluent. ^1H NMR: δ 0.82 (s, 18H, $\text{C}(\text{CH}_3)_3$), 1.32 (s, 18H, $\text{C}(\text{CH}_3)_3$), 2.75 (s, 6H, SO_2CH_3), 3.04 (d, $J=13.0$ Hz, 4H, ArCH_2Ar), 4.18 (t, $J=6.5$ Hz, 4H, $\text{OCH}_2\text{CH}_2\text{OMs}$), 4.22 (d, $J=12.5$ Hz, 4H, ArCH_2Ar), 4.51 (t, $J=6.5$ Hz, 4H, $\text{OCH}_2\text{CH}_2\text{OMs}$), 4.76 (s, 4H, OCH_2Ar), 6.44 (s, 4H, ArH), 7.08 (s, 4H, ArH), 7.33–7.43

(m, 10H, ArH). ^{13}C NMR: δ 31.0, 31.2, 31.6, 33.6, 34.1, 37.3, 68.3, 70.5, 78.3, 124.7, 125.6, 128.2, 128.6, 129.8, 131.8, 135.2, 137.3, 144.7, 145.9, 151.5, 153.6.

3.2.12. General procedure for preparation of *p*-tert-butylcalix[4]arene-dithiacrown ligands **8 and **9**.** The procedure for preparing compounds **8** and **9** from **25** was essentially the same as that employed for the preparation of compounds **6** and **7** from **18**.

3.2.12.1. Cone 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,27-bis(benzyloxy)calix[4]arene-dithiacrown-5. Compound **8** was obtained in 19% yield after chromatography on silica gel with hexanes–EtOAc (50:1 to 4:1 gradient) as eluent. It was a white solid that decomposed at 272 °C before melting. ^1H NMR: δ 0.82 (s, 18H, C(CH₃)₃), 1.35 (s, 18H, C(CH₃)₃), 2.22 (t, $J=7.5$ Hz, 4H, SCH₂CH₂O), 2.81–2.84 (m, 4H, SCH₂CH₂O), 3.14 (d, $J=12.5$ Hz, 4H, ArCH₂Ar), 3.24 (t, $J=7.5$ Hz, 4H, OCH₂CH₂S), 3.99–4.03 (m, 4H, OCH₂CH₂S), 4.43 (d, $J=12.5$ Hz, 4H, ArCH₂Ar), 4.64 (s, 4H, OCH₂Ar), 6.44 (s, 4H, ArH), 7.13 (s, 4H, ArH), 7.35–7.52 (m, 10H, ArH). ^{13}C NMR: δ 30.4, 30.5, 31.1, 31.3, 31.7, 33.6, 34.1, 70.9, 73.8, 78.4, 124.6, 125.7, 128.3, 128.8, 129.9, 131.7, 135.7, 137.6, 144.6, 145.3, 152.2, 153.6. Anal. calcd for C₆₆H₈₂O₅S₂: C, 77.76; H, 8.11; S, 6.29%. Found: C, 77.38; H, 7.90; S, 5.95%.

3.2.12.2. Cone 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,27-bis(benzyloxy)calix[4]arene-dithiacrown-6. Compound **9** was isolated in 33% yield after chromatography on silica gel with hexanes–EtOAc (50:1 to 4:1 gradient) as eluent. It was a white solid with mp 240–242 °C. ^1H NMR: δ 0.81 (s, 18H, C(CH₃)₃), 1.33 (s, 18H, C(CH₃)₃), 2.56 (t, $J=6.5$ Hz, 4H, SCH₂CH₂O), 2.92–2.95 (m, 4H, SCH₂CH₂O), 3.03 (d, $J=12.5$ Hz, 4H, ArCH₂Ar), 3.67–3.69 (m, 8H, OCH₂CH₂O, SCH₂CH₂O), 3.98–4.01 (m, 4H, OCH₂CH₂S), 4.32 (d, $J=12.5$ Hz, 4H, ArCH₂Ar), 4.71 (s, 4H, OCH₂Ar), 6.42 (s, 4H, ArH), 7.10 (s, 4H, ArH), 7.35–7.43 (m, 10H, ArH). ^{13}C NMR: δ 31.1, 31.2, 31.2, 31.7, 32.0, 33.6, 34.1, 70.5, 70.6, 73.7, 78.2, 124.5, 125.5, 128.2, 128.6, 129.7, 131.9, 135.5, 137.5, 144.4, 145.2, 151.8, 153.9. Anal. calcd for C₆₈H₈₆O₆S₂: C, 76.79; H, 8.15; S, 6.03%. Found: C, 76.49; H, 7.86; S, 5.65%.

3.2.13. Cone 25,27-bis(benzyloxy)-26,28-calix[4]arene-crown-6 (12**).** To a stirred solution of calix[4]arene-crown-6²⁷ (1.00 g, 1.60 mmol) in THF (27 mL) and DMF (3 mL) under nitrogen, NaH (0.19 g, 7.92 mmol) was added and the mixture was stirred at room temperature for 15 min. Benzyl bromide (1.10 g 6.40 mmol) was added in one portion and stirring at room temperature was continued for 24 h. After careful addition of 10% aq HCl to quench the excess NaH, the mixture was evaporated in vacuo. The residue was dissolved in CH₂Cl₂ and the solution was washed with water (2×50 mL), dried over MgSO₄ and evaporated in vacuo. The residue was chromatographed on silica gel with CH₂Cl₂–MeOH (100:1) as eluent to give 0.80 g (62%) of **12** as a white solid with mp=153–155 °C. ^1H NMR: δ 3.10 (d, $J=14.0$ Hz, 4H, ArCH₂Ar), 3.34 (t, $J=5.0$ Hz, 4H, OCH₂CH₂O), 3.54 (t, $J=5.0$ Hz, 4H, OCH₂CH₂O), 3.59 (s, 4H, OCH₂CH₂O), 3.76 (t, $J=8.0$ Hz, 4H, OCH₂CH₂O), 4.16 (t, $J=8.0$ Hz, 4H, OCH₂CH₂O), 4.39 (d, $J=14.0$ Hz, 4H, ArCH₂Ar), 4.75 (s, 4H, OCH₂Ar), 6.09 (d, $J=8.0$ Hz, 4H, ArH), 6.24 (t, $J=8.0$ Hz, 2H, ArH), 6.92, (t, $J=8.0$ Hz, 2H, ArH), 7.10 (d, $J=8.0$ Hz, 4H, ArH), 7.30–7.40 (m, 6H, ArH), 7.48 (d, $J=7.0$ Hz, 4H, ArH). ^{13}C NMR: δ 30.9, 69.4, 70.5, 70.6, 70.9, 72.4, 77.5, 122.1, 122.5, 127.4, 128.0, 128.5, 129.0, 129.1, 133.2, 136.6, 137.5, 154.4, 158.1. Anal. calcd for C₅₂H₅₄O₈: C, 77.39; H, 6.74%. Found: C, 77.65; H, 6.44.

3.3. Potentiometric membrane studies

3.3.1. Preparation of PVC membranes. PVC (50 mg), NPOE (100 mg), the ionophore (5.0 mg), and KTpCIPB²⁸ (1.0 mg) were dissolved in THF (1.5 mL) to give the membrane preparation cocktail. A porous

polytetrafluorethylene (PTFE) membrane support (Analyticon Instruments Corporation, Springfield, New Jersey) was dipped first in THF and then in the membrane preparation cocktail. The membrane support was transferred to the top opening of a hollow blank cap for the 7901 L electrode (Analyticon Instruments Corporation, Springfield, New Jersey). The membrane preparation cocktail was cast on the PTFE membrane support by adding two drops every 30 min with a 1-mL glass microsyringe. Addition of the solution and evaporation of the THF was performed six times. Further evaporation of the THF at room temperature overnight yielded an elastic, translucent membrane of approximately 0.3 mm thickness. The resulting PVC cap with the coated PTFE membrane was fixed on a Denki Kagaku Keiki (DDK, Musashino, Tokyo, Japan) No. 7900 electrode body containing a AgCl wire as an internal reference electrode. An internal filling solution of 0.10 M Hg(NO₃)₂ was added to the electrode. The membrane electrode was conditioned by soaking in 0.10 M Hg(NO₃)₂ for 24 h before use. For each ionophore, two membrane electrodes were prepared.

3.3.2. Potentiometric measurements. Potentiometric measurements with a membrane electrode were carried out at room temperature with a voltage meter (Fisher Scientific, Accumet 50 pH meter), a double junction Ag–AgCl reference electrode (DDK No. 4083), and a magnetic stirrer to agitate the sample solution. The electrode cell was Ag–AgCl/4.0 M KCl/sample solution/PVC membrane/0.10 M Hg(NO₃)₂/Ag/AgCl (CHECK). Selectivity coefficients ($K_{\text{Hg}^{2+}}^{\text{Pot}}$) were determined by the fixed interference method.²⁵ The background concentrations of the interference ions were 10 mM Na⁺, Cd²⁺, Co²⁺, Cu²⁺, Ni²⁺, Pb²⁺, and Zn²⁺. Concentrations of Hg²⁺, the primary ion, were varied in the range of 3.00×10^{−7} to 3.00×10^{−2} M. For a given solvent polymeric membrane electrode, the selectivity was determined twice for each of two independently prepared membranes. The average value for the potentiometric selectivity was calculated from the values obtained for the four measurements. The standard deviation of the log K^{Pot} values from the average was 0.05 or less.

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