Synthesis of Novel Calix[4]arenes Having Benzothiazolylacetamidoalkoxy Pendants and Their Potential Application as Ag^+-selective Electrodes

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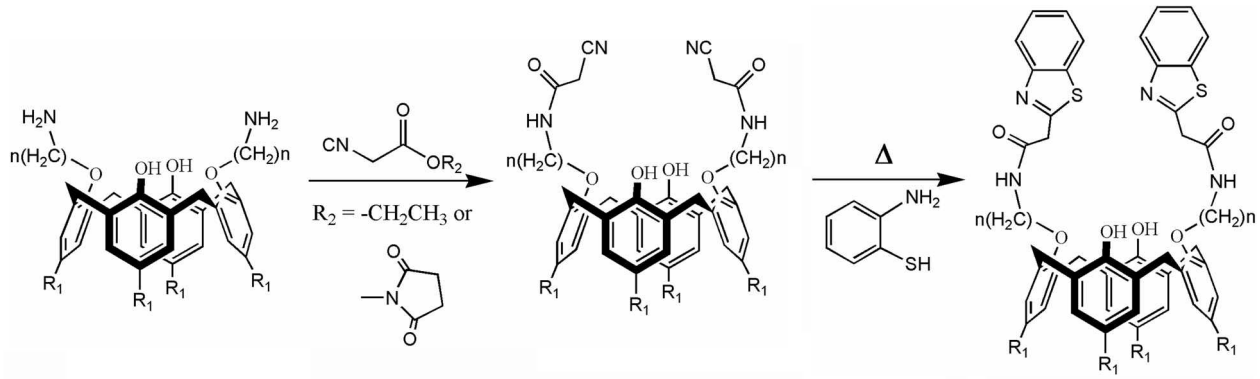
Calix[4]arenes, a class of macrocyclic compounds, are superb supramolecular building block for fabricating ion and molecular receptors.[1] Appropriately functionalized calix[4]-arenes have been used as carriers in ion selective membranes. Predominantly, calixarenes containing ester, ether, carboxylic acid and carbamate have been reported for using as ion-selective electrode (ISE) for alkali metal ions.[2,3] Only few calixarene derivatives reported by Reinhoudt and Kim have been employed as ISE for heavy metal ions such as Cu^{2+}, Hg^{2+} and Cd^{2+}.[4,5] Kimura and coworkers reported calix[4]arene derivatives incorporating substituents such as allyl, benzyl and propargyl groups being used as soft neutral carrier for silver ion sensors.[6] Mercaptobenzothiazole-appended calix[4]arene was used as Ag^+-ISE which showed the selectivity towards Ag^+ with good discrimination against Hg^{2+}.[7]

We are interested in the development of new Ag^+ receptors for use as ionophores in Ag^+-selective electrodes. Herein, we report syntheses of compounds **9** and **10** bearing two benzothiazolylacetamidobutoxy groups at the narrow rim of *p-tert*-butylcalix[4]arene and compounds **11** and **12** consisting of benzothiazolylacetamidoethoxy groups on the narrow rim of calix[4]arene. The preliminary studies using the synthesized compounds for Ag^+-selective electrodes towards metal ions were carried out to see the effect of substituent groups on sensitivity and selectivity of the ionophore.

Benzothiazolylacetamidoalkoxy calix[4]arenes, **9-12**, have been prepared in two steps as shown in Scheme 1. The first step involved the conversion of amine groups in calix[4]-arene derivatives **1-4** into corresponding cyanoacetamido groups. Using modified Salol procedure.[8] the conversion of compound **1** to compound **5** (50%) was achieved by heating **1** with ethyl cyanoacetate. However, compounds **2-4** could not react with ethyl cyanoacetate to produce compounds **6-8**. Therefore, succinimide cyanoacetate was employed instead. The cyanoacetate ester containing the succinimide group was prepared from reaction of cyanoacetic acid with *N*-hydroxysuccinimide in the presence of dicyclohexylcarbodi-imide in dry ethyl acetate. The amines **2-4** were reacted with succinimide cyanoacetate in dry CH_2Cl_2 to give cyanoacet-amido compounds **6-8** in 19%, 34% and 40% yields, respectively. The cyanoacetamido compounds **5-8** were then heated with 2-aminothiophenol to give the final products **9-12** in 59%, 64%, 64% and 20% yields, respectively.

All of the compounds showed characteristic peaks of *p-tert*-butylcalix[4]arene (or calix[4]arene) building blocks and were in cone conformations which were substantiated by two doublets of the Ar-C*H*$_2$-Ar protons (J = 13-14 Hz) around 3-4 ppm in ^{1}H NMR spectra. The benzothiazolyl-acetamido groups showed two doublets and two triplets of the benzene proton of the benzothiazolyl group, one singlet for the proton in the alpha position of the carbonyl group and



1, n = 4, R_1 = t-Bu
2, n = 4, R_1 = H
3, n = 2, R_1 = t-Bu
4, n = 2, R_1 = H

5 (50%), n = 4, R_1 = t-Bu
6 (19%), n = 4, R_1 = H
7 (34%), n = 2, R_1 = t-Bu
8 (40%), n = 2, R_1 = H

9 (59%), n = 4, R_1 = t-Bu
10 (64%), n = 4, R_1 = H
11 (64%), n = 2, R_1 = t-Bu
12 (20%), n = 2, R_1 = H

Scheme 1. Synthesis pathway of benzothiazolylacetamidoalkoxycalix[4]arenes **9-12**.

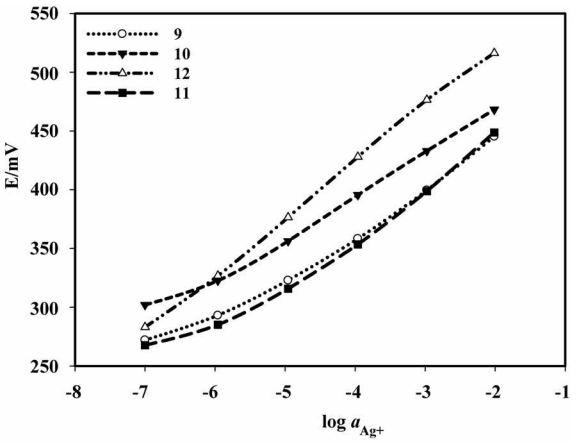


Figure 1. The response of Ag^+-ISE electrodes preparation from (○) compound **9** (▼) compound **10** (■) compound **11** and (△) compound **12**.

one broad triplet of the amide proton. Mass spectrometry and elemental analysis results also supported the proposed structures of compounds **9-12**.

PVC-based ion-selective membrane electrodes employing benzothiazolylacetamidoalkoxy calix[4]arenes **9-12** as ionophores were prepared using a membrane composition of 1.0: 65.5:33.0:0.5 (ligand:*o*-NPOE:PVC:KT*p*ClPB in weight percent) to determine the potentiometric response for Ag^+. The calibration plots of the membranes based on compounds **9-12** were obtained by converting the concentration of Ag^+ in each solution into activity using the activity coefficient from the *Debye-Huckel equation*[8] and plotted against measured emf's. The plots are shown in Figure 1 and slopes. linear range. detection limit and response time are summarized in Table 1. The **12**-ISE's showed response closer to the theoretical slope, 50.5 mV decade^{-1}. The results suggested that the length of the tethers affected Nerntian response towards Ag^+. Ionophores **11** and **12** with shorter tethers were found to give higher slope than ionophores **9** and **10**. This observation was similar to Ag^+-ISE using benzothiazolylthiaalkoxycalix[4]arene as an ionophore where the longer tethers gave the lower slope.[7]

The potentiometric selectivity coefficients of the ISE were determined by the mixed solution methods. The variation of emf at varying concentration of Ag^- in interfering ions and the calculated potentiometric selectivity coefficients are shown in Table 2. The selectivity coefficient ($\log K_{Ag,J}^{pot}$) represents the preference of ISE-**9** through ISE-**12** for Ag^+

Table 2. The potentiometric selectivity coefficients

Ion J	$\log K_{Ag,J}^{pot}$			
	9	**10**	**11**	**12**
Ag^-	0	0	0	0
Na^-	−3.35	no response	−3.35	no response
K^+	−3.35	no response	−3.37	no response
Ca^{2+}	−4.42	no response	−4.57	no response
Mg^{2-}	no response	no response	−4.48	no response
Cd^{2-}	no response	no response	−4.00	no response
Ni^{2+}	no response	no response	−3.95	no response
Pb^{2+}	−3.41	−3.88	−3.38	−3.98
Cu^{2-}	−3.95	−4.05	−3.99	−4.00
Hg^{2-}	−2.35	−2.70	−2.45	−2.96

over the other cations. The coefficient $K_{Ag,J}^{pot}$ defines the ability of an ISE to recognize different ions under the same conditions. The smaller the $K_{Ag,J}^{pot}$ value. the greater the electrode preference for the Ag^+ ion over the interfering ion (J).

It should be seen from Table 2 that among the calix[4]-arene-based ionophores, **10** and **12** lacking of the *tert*-butyl substituents generally gave better potentiometric selectivity coefficients than **9** and **11** containing *tert*-butyl groups. There were a number of examples reported the serious dependence of the response of some carrier based silver membrane electrodes on the amount (by mol) of a ionophore in the membrane phase.[10-12] It is obviously seen that ionophore **12** which possesses the lowest molecular weight shows the highest selectivity coefficients to Ag^+. Furthermore. all ISE's showed no response or only slight response to interfering alkali, alkali earth and transition metal ions. This can be tentatively rationalized that the four sulfur atoms or two sulfur atoms and two nitrogen atoms on the benzothiazolyl groups of **9-12** participate in the coordination with Ag^- at the same time. Oxygen atoms on the narrow rim of the calix[4]arene unit did not involve in the coordination sphere because this would lead to the interference of other ions such as Na^-, K^+. Mg^{2-} and some other divalent transition cations which had affinity towards hard donors.[7]

In summary. the ionophores **9-12** consisting of benzothiazolylacetamidoalkoxy groups were synthesized. PVC membrane electrodes incorporating such ionophores showed high selectivity and sensitivity towards silver ions. especially ISE-**12**. The studies showed that among calix[4]arene

Table 1. Response parameters of ionophores **9-12**

parameters	Ionophores			
	9	**10**	**11**	**12**
Slope (mV decade^{-1})	38.7	38.7	41.9	50.5
Linear range (log a)	−5.3 to −2.0	−6.5 to −2.0	−5.1 to −2.0	−6.9 to −2.2
Detection limit (M)	5.01×10^{-6}	3.16×10^{-7}	7.94×10^{-6}	1.26×10^{-7}
Response time (s)	< 12	< 12	< 12	< 12
Correlation coefficient (r)	0.9988	0.9999	0.9984	0.9999

derivative-ionophores. both *tert*-butyl substituents and the length of the pendant on the narrow rim affected the selectivity and sensitivity of the membranes in which the absence of *tert*-butyl group and shorter length of the pendant groups gave a better membrane electrode.

Experimental Section

Nuclear magnetic resonance (NMR) spectra were recorded on a Varian Mercury Plus 400 nuclear magnetic resonance spectrometer. In all cases. samples were dissolved in deuterated chloroform. The chemical shifts were recorded in part per million (ppm) using a residue proton as internal reference. Elemental analysis was carried out on CHNS/O analyzer (Perkin Elmers PE 2400 series II). ESI mass spectra were recorded on a Micromass Platform II. Compounds **1-4** were prepared according to literature procedure.[13,14]

5,11,17,23-Tetra-*p-tert*-butyl-25,27-bis(cyanoacetamidobutoxy)-26,28-dihydroxycalix[4]arene (5). In a 100 mL one-necked round bottom flask equipped with a magnetic bar, 5,11,17,23-tetra-*p-tert*-butyl-25,27-bis(aminobutoxy)-calix[4]arene **1** (0.34 g. 0.42 mmol). ethyl cyanoacetate (0.34 g. 2.9 mmol) were stirred under nitrogen atmosphere and heated gradually to 80 °C for 5 h. The mixture was cooled to room temperature and the residue was solubilized with 10 mL CH_2Cl_2. The solution was chromatographed on a silica column with gradient elution (CH_2Cl_2-ethyl acetate) to give **5** as a white solid after evaporation in 50% yield (0.19 g). Mp 121-122 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.52 (s, 2H, N*H*). 7.26 (s, 2H. ArO*H*), 7.11 (s. 4H. *m-H*ArOH), 6.70 (s, 4H, *m-H*ArOCH$_2$). 4.19 (d, J = 14 Hz. 4H$_A$, ArC*H*$_2$Ar). 4.01 (t. J = 6 Hz. 4H, C*H*$_2$OAr). 3.64 (q. J = 6 Hz, 4H. C*H*$_2$NH), 3.50 (s. 4H. C*H*$_2$CN), 3.39 (d, J = 13 Hz. 4H, ArC*H*$_2$Ar). 1.96 (t, J = 6 Hz. 4H. C*H*$_2$CH$_2$OAr). 1.88 (t. J = 6 Hz. 4H. C*H*$_2$CH$_2$CH$_2$OAr), 1.32 (s, 18H. *t*-C$_4$*H*$_9$), 0.87 (s. 18H. *t*-C$_4$*H*$_9$). ^{13}C-NMR (100 MHz. $CDCl_3$): δ = 162.19. 149.73. 147.64, 142.75. 131.79. 128.13, 125.66. 125.34. 115.63. 39.66. 33.94. 33.85. 31.66. 31.54. 30.87. 27.07. 26.13. MALDI-TOF MS (m/z) [M + Na]$^-$ = 948.56 (Calcd. 947.56) Anal. Calcd. for $C_{58}H_{76}N_4O_6$: C, 75.28: H, 8.28; N. 6.06. Found C. 74.19; H. 9.47; N. 5.95.

General procedures for preparation of compounds 6-8. In a 250 mL two-necked round bottom flask equipped with a magnetic bar. succinamide cyanoacetic was dissolved in CH_2Cl_2 and stirred at room temperature under nitrogen atmosphere. A solution of aminoalkoxy calix[4]arene and *N*-ethyl-di-*iso*propylamine in CH_2Cl_2 was added dropwise. The mixture was left stirring for 48 h at room temperature. The solution was extracted with 1 M HCl and washed with water. After drying over anhydrous Na_2SO_4, the organic part was evaporated to dryness under reduced pressure and the product was chromatographed on a silica column with gradient elution (CH_2Cl_2/ethyl acetate) to give benzothiazolyl-acetamido calix[4]arene as a white solid after evaporation.

25,27-Bis(cyanoacetamidobutoxy)-26,28-dihydroxycalix[4]arene (6). Yield 19%. Mp 113-115 °C. ^{1}H-NMR (400 MHz. $CDCl_3$). δ = 7.48 (s. 2H, ArO*H*), 7.32 (s. 2H. N*H*). 7.11 (d, J = 8 Hz, 4H, *m-H*ArOH). 6.85 (d, J = 8 Hz. 4H. *m-H*ArOCH$_2$), 6.76-6.70 (m, 4H, *p-H*ArOH and *p-H*ArOCH$_2$), 4.23 (d, J = 14 Hz, 4H, ArC*H*$_2$Ar). 4.02 (t, J = 6 Hz, 4H, C*H*$_2$OAr), 3.59 (q, J = 6 Hz, 4H, C*H*$_2$NH), 3.45 (s, 4H, C*H*$_2$CN), 3.43 (d, J = 14 Hz, 4H. ArC*H*$_2$Ar), 2.05 (t. J = 7 Hz. 4H, C*H*$_2$CH$_2$OAr), 1.94 (t. J = 7 Hz, 4H, C*H*$_2$CH$_2$NH). ^{13}C-NMR (100 MHz. $CDCl_3$): δ = 162.19, 152.63. 151.90, 132.71, 129.12. 128.77. 128.19, 125.49. 119.81, 115.02, 39.98. 31.34, 27.29. 26.04, 25.94. MALDI-TOF MS [M + Na]$^+$ (m/z) = 723.97 (Calcd. 723.32). Anal. Calcd. for $C_{42}H_{44}N_4O_6 \cdot 0.5H_2O$ C. 71.07: H. 6.39; N, 7.89. Found: C, 71.98: H. 6.33: N, 7.99.

5,11,17,23-Tetra-*p-tert*-butyl-25,27-bis(acetamidoethoxy)-26,28-dihydroxycalix[4]arene (7). Yield 34%. Mp 271-275 °C (decomposed). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.63 (t, J = 6 Hz. 2H. N*H*), 8.28 (s. 2H, ArO*H*). 7.07 (s. 4H. *m-H*ArOH), 6.95 (s. 4H. *m-H*ArOCH$_2$). 4.21 (d, J = 13 Hz, 4H$_A$. ArC*H*$_2$Ar). 4.11 (t. J = 5 Hz, 4H, C*H*$_2$OAr). 3.99 (q. J = 4 Hz, 4H, C*H*$_2$NH). 3.41 (d, J = 13 Hz, 4H, ArC*H*$_2$Ar), 3.41 (s, 4H. C*H*$_2$CN). 1.26 (s. 18H, *t*-C$_4$*H*$_9$). 1.07 (s, 18H, *t*-C$_4$*H*$_9$). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 161.66. 149.14, 148.47, 148.24. 143.21. 132.76, 127.55, 126.13. 125.77, 114.73. 75.13, 40.03, 34.17, 33.92, 31.92, 31.56, 31.03. 26.14. MALDI-TOF MS [M + Na]$^-$ (m/z) = 892.49. (Calcd. 891.50). Anal. Calcd. $C_{54}H_{68}N_4O_6$ C, 74.61; H. 7.89: N. 6.45. Found C, 75.29; H. 7.25: N, 6.66.

25,27-Bis(cyanoacetamidoethoxy)-26,28-dihydroxycalix-arene (8). Yield 40%. Mp 281-284 °C (decomposed). ^{1}H-NMR (400 MHz. $CDCl_3$): δ = 8.39 (s. 2H, ArO*H*), 7.10 (d, J = 7 Hz, 4H, *m-H*ArOH). 6.98 (d, J = 8 Hz. 4H. *m-H*ArO-CH$_2$). 6.83 (t. J = 8 Hz. 2H, *p-H*ArOH). 6.73 (t, J = 8 Hz, 2H. *p-H*ArOCH$_2$). 4.26 (d, J = 13 Hz. 4H$_A$. ArC*H*$_2$Ar), 4.14 (t. J = 5 Hz, 4H. C*H*$_2$OAr), 4.06 (q, J = 5 Hz, 4H, C*H*$_2$NH), 3.46 (d. J = 13 Hz, 4H$_B$. ArC*H*$_2$Ar), 3.40 (s. 4H, C*H*$_2$CN). ^{13}C-NMR (100 MHz. $CDCl_3$): δ = 162.17, 151.86. 150.81, 133.01. 128.61, 128.34, 127.32. 125.32. 119.57. 116.36. 74.62. 39.24. 30.27. 25.55. MALDI-TOF MS [M + Na]$^+$ (m/z) = 667.68. (Calcd. 667.25). Anal. Calcd. $C_{38}H_{36}N_4O_6$: C. 70.79: H. 5.63; N. 8.69. Found: C. 70.13; H. 5.33; N. 8.28.

General procedures for preparation of compounds 9-12. In a 100 mL one-necked round bottom flask equipped with a magnetic bar. a cyanoacetamido calix[4]arene was mixed with 2-aminothiophenol at 1:10 mol ratio and heated at 120 °C under N_2 atmosphere for 3 h. After cooling, the product was dissolved in CH_2Cl_2 and loaded on a silica column. The column was first washed with CH_2Cl_2 to remove excess 2-aminothiophenol after then gradient eluted with a mixture of CH_2Cl_2 and ethyl acetate. The fraction containing benzothiazolylacetamido calix[4]arene was evaporated to dryness under reduced pressure to give a white solid of the desired product.

5,11,17,23-Tetra-*p-tert*-butyl-25,27-bis(benzothiazolyl-acetamidobutoxy)-26,28-dihydroxycalix[4]arene (9). Yield 59%. Mp 109-111 °C. ^{1}H-NMR (400 MHz. $CDCl_3$): δ = 7.93 (d. 2H. J = 8 Hz. BTAr*H*). 7.84 (br. 2H, N*H*), 7.77 (d, J = 8 Hz. 2H. BTAr*H*). 7.40 (t. J = 7 Hz. 2H. BTAr*H*). 7.39 (t. J = 8 Hz. 2H. BTAr*H*). 7.38 (s. 2H. ArO*H*). 7.04 (s. 4H. *m*-

*H*ArOH), 6.76 (s, 4H, *m*-*H*ArOCH$_2$), 4.19 (d, J = 13 Hz, 4H$_A$, ArC*H*$_2$Ar), 4.14 (s, 4H, C*H*$_2$BT), 3.94 (t, 4H, J = 6.0 Hz, C*H*$_2$OAr), 3.50 (q, J = 6 Hz, 4H, C*H*$_2$NH), 3.28 (d, J = 13 Hz, 4H$_B$, ArC*H*$_2$Ar), 1.97 (q, J = 7 Hz, 4H, C*H*$_2$CH$_2$OAr), 1.88 (q, J = 7 Hz, 4H, CH$_2$C*H*$_2$NH), 1.29 (s, 18 H, *t*-C$_4$*H*$_9$), 0.93 (s, 18 H, *t*-C$_4$*H*$_9$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 165.0, 152.7, 150.3, 149.7, 147.0, 141.8, 135.4, 132.4, 127.8, 126.0, 125.5, 125.13, 125.08, 122.7, 121.6, 76.5, 41.3, 39.6, 33.91, 33.85, 31.7, 31.6, 31.0, 27.1, 26.1; *ESI-MS* 1175.3. ESI-MS 1175.3 [M + Cl]$^-$ (calcd 1177.1). Anal. calcd. for $C_{70}H_{84}N_4O_6S_2$: C, 73.65; H, 7.42; N, 4.91. Found: C, 73.68; H, 7.45; N, 4.94.

25,27-Bis(benzothiazolylacetamidobutoxy)-26,28-dihydroxycalix[4]arene (10). Yield 64%. Mp 107-109 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.05 (br, 2H, N*H*), 8.00 (s, 2H, ArO*H*), 7.99 (d, J = 8 Hz, 2H, BTAr*H*), 7.82 (d, J = 7 Hz, 2H, BTAr*H*), 7.46 (t, J = 7 Hz, 2H, BTAr*H*), 7.42 (t, J = 8, 2H, BTAr*H*), 7.07 (d, J = 8 Hz, 4H, *m*-*H*ArOH), 6.91 (d, J = 8 Hz, 4H, *m*-*H*ArOCH$_2$), 6.75 (t, J = 7 Hz, 2H, *p*-*H*ArOH), 6.69 (t, J = 7 Hz, 2H, *p*-*H*ArOCH$_2$), 4.26 (s, 4H, C*H*$_2$BT), 4.25 (d, J = 14 Hz, 4H$_A$, ArC*H*$_2$Ar), 4.02 (t, J = 6 Hz, 4H, C*H*$_2$OAr), 3.54 (q, J = 6 Hz, 4H, C*H*$_2$NH), 3.38 (d, J = 13 Hz, 4H, ArC*H*$_2$Ar), 2.08-2.05 (m, 4H, C*H*$_2$CH$_2$OAr), 1.99 (q, J = 7 Hz, 4H, CH$_2$C*H*$_2$NH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 165.4, 153.0, 151.8, 135.1, 133.1, 129.0, 128.5, 128.1, 126.3, 125.4, 125.3, 122.4, 121.7, 119.3, 76.4, 41.0, 39.6, 31.3, 27.3, 25.9. ESI-MS 951.1 [M + Cl]$^-$ (calcd 952.7). Anal. calcd. for $C_{54}H_{52}N_4O_6S_2$: C, 70.72; H, 5.71; N, 6.11. Found: C, 70.73; H, 5.69; N, 6.11.

5,11,17,23-Tetra-*p*-*tert*-butyl-25,27-bis(benzothiazolylacetamidoethoxy)-26,28-dihydroxycalix[4] arene (11). Yield 64% (0.16 g). Mp 249-251 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.85 (br, 2H, N*H*), 8.37 (s, 2H, ArO*H*), 7.94 (d, J = 8 Hz, 2H, BTAr*H*), 7.80 (d, J = 8 Hz, 2H, BTAr*H*), 7.45 (t, J = 8 Hz, 2H, BTAr*H*), 7.37 (t, J = 8 Hz, 2H, BTAr*H*), 7.00 (s, 4H, *m*-*H*ArOH), 6.97 (s, 4H, *m*-*H*ArOCH$_2$), 4.24 (s, 4H, C*H*$_2$BT), 4.18 (d, J = 13 Hz, 4H$_A$, ArC*H*$_2$Ar), 4.08 (t, J = 5 Hz, 4H, C*H*$_2$OAr), 3.82 (q, J = 5 Hz, 4H, C*H*$_2$NH), 3.33 (d, J = 13 Hz, 4H, ArC*H*$_2$Ar), 1.28 (s, 18H, *t*-C$_4$*H*$_9$), 1.19 (s, 18H, *t*-C$_4$*H*$_9$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 164.5, 152.4, 149.2, 148.6, 148.0, 142.7, 135.7, 133.0, 127.6, 126.02, 125.98, 125.6, 125.1, 122.5, 121.6, 75.5, 41.7, 39.6, 34.1, 33.8, 32.1, 31.6, 31.0. ESI-MS 1120.5 [M + Cl]$^-$ (calcd 1120.94). Anal. calcd. for $C_{66}H_{76}N_4O_6S_2$: C, 73.03; H, 7.06; N, 5.16. Found: C, 73.03; H, 7.08; N, 5.12.

25,27-Bis(benzothiazolylacetamidobutoxy)-26,28-dihydroxycalix[4]arene (12). Yield 20% (0.054 g). Mp 232-235 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): 8.70 (br, 2H, N*H*), 8.13 (s, 2H, ArO*H*), 7.95 (d, J = 8 Hz, 2H, BTAr*H*), 7.78 (d, J = 8 Hz, 2H, BTAr*H*), 7.47 (t, J = 7 Hz, 2H, BTAr*H*), 7.38 (t, J = 8 Hz, 2H, BTAr*H*), 6.95 (d, J = 7 Hz, 4H, *m*-*H*ArOH), 6.91 (d, J = 8 Hz, 4H, *m*-*H*ArOCH$_2$), 6.78 (t, J = 8 Hz, 2H, *p*-*H*ArOH), 6.61 (t, J = 8 Hz, 2H, *p*-*H*ArOCH$_2$), 4.27 (s, 4H, COC*H*$_2$), 4.17 (d, J = 14 Hz, 4H$_A$, ArC*H*$_2$Ar), 4.14 (t, J = 8 Hz, 4H, C*H*$_2$OAr), 3.89 (q, J = 4 Hz, 4H, C*H*$_2$NH), 3.32 (d, J = 13 Hz, 4H, ArC*H*$_2$Ar). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 164.4, 152.6, 151.9, 150.5, 135.6, 133.3, 129.2, 128.7, 128.0, 126.2, 126.0, 125.1, 122.5, 121.6, 120.2, 75.5, 60.4, 41.7, 39.7, 31.3. ESI-MS 895.4 [M + Cl]$^-$ (calcd 896.5). Anal. calcd. for $C_{54}H_{44}N_4O_6S_2 \cdot H_2O$: C, 68.32; H, 5.27; N, 6.37. Found: C, 67.70; H, 5.16; N, 6.06.

Ion-selective electrode preparation and measurements. The ion-selective membrane was prepared using the procedure described by Craggs and colleague.[15] The weighed amount of ligands, plasticizer (*o*-nitrophenyloctylether, *o*-NPOE), cation exchanger (potassium tetrakis(*p*-chlorophenyl)borate, KT*p*ClPB) and PVC were mixed in a vial with 6 mL THF. The weight percent composition of the membrane was 1.0:65.5:33.0:0.5 (ligand: *o*-NPOE:PVC:KT*p*ClPB). Four to five PVC-tubes (5 mm i.d., 3 mm-wall thickness, 30 mm long) were glued at one end with PVC-THF solution and put on the membrane. After the solvent was evaporated, the membrane around each tube was cut to obtain a PVC-tube with membrane sealed at one end. The open-end of the PVC-tube was then fitted into a glass tube after which made into a ISE by filling with 0.10 M $AgNO_3$ and putting in a Ag/AgCl electrode. The ISE was pre-conditioned by immersing in a 0.010 M $AgNO_3$ solution for 12 h before used.

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