



Improved silver ion-selective electrodes using novel 1,3-bis(2-benzothiazolyl)thioalkoxy-*p*-*tert*-butylcalix[4]arenes

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Abstract

1,3-Bis(2-benzothiazolyl)thioalkoxycalix[4]arenes **1** and **2** have been synthesized and found to adopt a cone conformation. Compounds **1** and **4** were characterized by X-ray analysis. Preliminary evaluation of **1** and **2** as ionophores for ion-selective electrodes is reported. © 2000 Elsevier Science Ltd. All rights reserved.

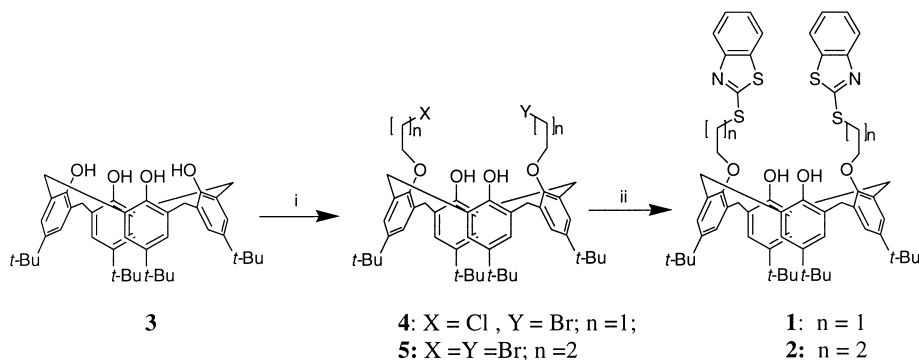
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Calixarenes are macrocyclic organic derivatives composed of a cyclic arrangement of phenol and methylene units. Functionalization of their upper and lower rims provides the calixarenes with variable inclusion capability and variable complexation characteristics.¹ Over the past decade, a number of calixarene derivatives containing pendant ether, amide, ketonic and ester groups have been incorporated as neutral carriers into ion-selective electrodes sensitive to sodium ions,² potassium ions³ and cesium ions.⁴ However, only a few papers have reported calixarene-based ion-selective electrodes sensitive to heavy metal ions such as silver⁵ and lead ions.⁶ The soft heavy metal ions, Ag⁺, Pb²⁺ and Hg²⁺ display great affinity for soft coordination centers like nitrogen and sulfur atoms. By using calixarene derivatives with functional groups containing nitrogen and sulfur atoms, the selectivity of binding to soft heavy metal ions over alkali metal ions is expected to be significantly increased.

More recently, in order to enhance their cation selectivities, enzyme mimic abilities and other physical properties, many heterocyclic groups such as pyridyl, bipyridyl, bithiazolyl have been introduced into the calixarenes both on their lower and upper rims.⁷ Here, we introduce two benzothiazolyl units into a calix[4]arene and show that the introduction of benzothiazolyl groups may enhance the selectivity of binding of calix[4]arenes to soft heavy metal ions.

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The compounds **4**⁹ and **5**⁸ were prepared by the published method. The reactions under the conditions in Scheme 1 yielded the target calix[4]arenes, **1** and **2** (Fig. 1).⁹ The compounds **1** and **2** were purified by silica gel chromatography using CH₂Cl₂ and petroleum ether (2:1) as an eluent and characterized by spectroscopy and X-ray structure analysis¹⁰ which indicated that compounds **1** and **2** exist in cone conformations.



Scheme 1. (i): X(CH₂)_nCH₂Y/K₂CO₃/CH₃CN/reflux; (ii): 2-mercaptobenzothiazole/NaHCO₃/THF–H₂O/reflux

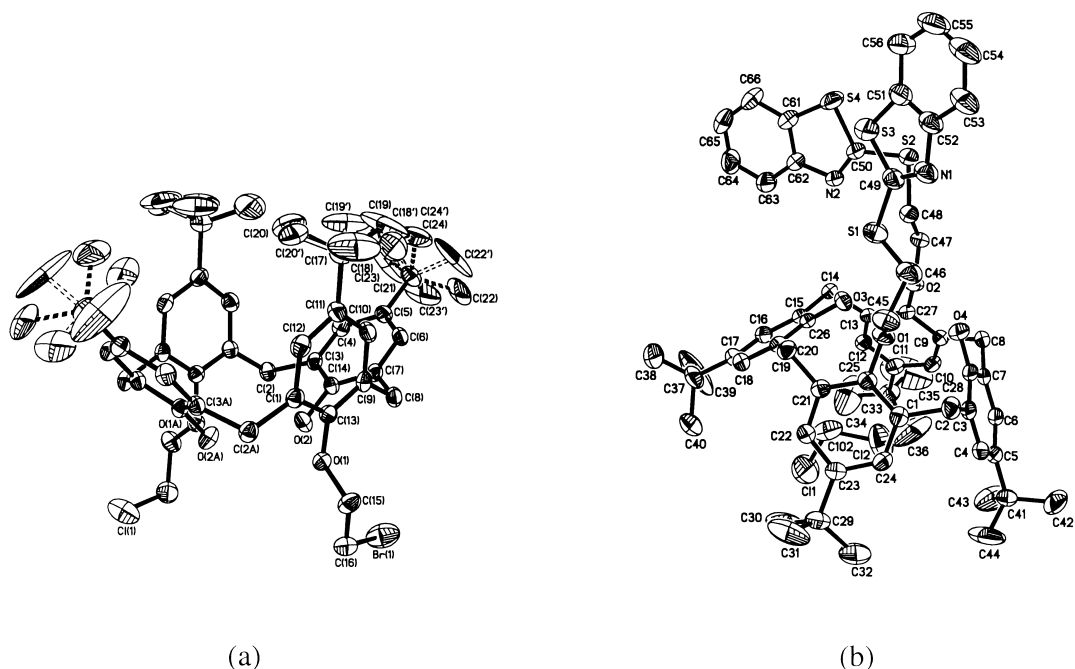


Figure 1. (a) The structure of compound **4**; (b) the structure of compound **1**

Ligands **1** and **2** were found to be good ionophores for silver ion-selective electrodes.¹¹ The EMF potential responses of Ag⁺-PVC membrane electrodes with the ionophore and without the ionophore are illustrated in Fig. 2. It was found that electrodes with ionophores **1** and **2** gave a good Nernstian response of 58 mV/decade⁻¹ to the activity of Ag⁺ ion within the concentration range 5 × 10⁻⁶–10⁻¹ M AgNO₃, within the limits of detection of between 10^{-5.5} and 10^{-5.8} M. The

membrane without the ionophore showed a linear response for Ag^+ within the concentration range 10^{-5} – 10^{-1} M and the slope was less than Nernstian (ca. 41 mV/decade $^{-1}$).

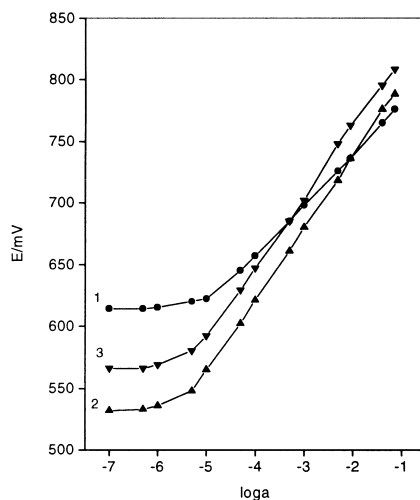


Figure 2. Potential response of Ag ion-selective electrodes based on ionophores **1**, **2** and without ionophore, respectively. (1) Without ionophore; (2) ionophore **1**; (3) ionophore **2**

Potentiometric selectivity coefficients ($\log K_{\text{Ag}/\text{M}}$) of polymeric membrane electrodes based on the carriers were evaluated. The potentiometric selectivity coefficients were measured by a mixed solution method or for strong interfering ions by the separate solution method using 0.01 M solutions of metal nitrates at a constant pH 4 (for mercury at pH 2). In this mixed-solutions method, the concentration of the silver ion is varied while that of the interference ions such as Na^+ , K^+ , NH_4^+ , Ca^{2+} , Mg^{2+} are 0.1 M, and Zn^{2+} , Cd^{2+} , Ni^{2+} , Cu^{2+} , Co^{2+} , Fe^{3+} , Pb^{2+} , Hg^{2+} are 0.01 M. The values of the selectivity coefficients are summarized in Fig. 3. As is evident from Fig. 3, the alkali metal, alkaline earth metal, lead and some common transition metal ions except Hg^{2+} give no interference in the performance of the membrane electrodes. The soft heavy metal Hg^{2+} give a relative smaller interference towards Ag^+ ion ($\log K_{\text{Ag}/\text{Hg}} < -2.6$).

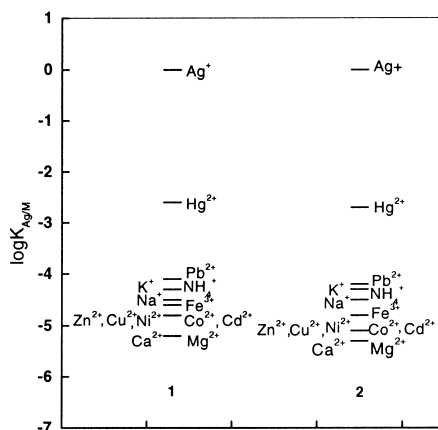


Figure 3. Selectivity coefficients ($\log K_{\text{Ag}/\text{M}}$) for PVC membrane containing ionophore **1** and **2**

Other experimental results confirmed that in sensors for monovalent cations the use of relatively nonpolar membrane material can improve the cation response and that the electrodes are not pH sensitive in the range of pH 2.5–6.5. In terms of the lifetime of the PVC membrane electrodes, response stability was observed for over a month.

Acknowledgements

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9. Selected data for **4**, **5**, **1** and **2**: compound **4**, white solid, mp 302–303°C, 200 MHz ^1H NMR (CDCl_3) δ in ppm: 7.04 (s, 6H, Ar-H, OH), 6.78 (s, 4H, Ar-H), 4.29 (d, 4H, $J=12.9$ Hz, Ar-CH-Ar), 4.24 (t, 4H, $J=6.2$ Hz, OCH_2), 3.97 (t, 2H, $J=6.2$ Hz, CH_2Cl), 3.83 (t, 2H, $J=6.2$ Hz, CH_2Br), 3.32 (d, 4H, $J=12.9$ Hz, Ar-CH-Ar), 1.27 (s, 18H, *t*-Bu-H), 0.94 (s, 18H, *t*-Bu-H). Compound **5**: white solid, mp 332–333°C, ^1H NMR (CDCl_3): 7.52 (s, 2H, OH), 7.03 (s, 4H, Ar-H), 6.84 (s, 4H, Ar-H), 4.25 (d, 4H, $J=12.9$ Hz, Ar-CH-Ar), 4.10 (t, 4H, $J=5.2$ Hz, CH_2O), 3.97 (t, 4H, $J=6.3$ Hz, CH_2Br), 3.32 (d, 4H, $J=12.9$ Hz, Ar-CH-Ar), 2.50 (m, 4H, CH_2) 1.26 (s, 18H, *t*-Bu-H), 0.98 (s, 18H, *t*-Bu-H). Compound **1**: white powder, ^1H NMR (CDCl_3): 7.87 (d, 2H, $J=7.3$ Hz, Ar-H), 7.69 (d, 2H, $J=8.3$ Hz, Ar-H), 7.38 (t, 2H, $J=6.8$ Hz, Ar-H), 7.25 (t, 2H, $J=7.3$ Hz, Ar-H), 7.07 (s, 4H, Ar-H), 6.81 (s, 4H, Ar-H), 4.39 (t, 4H, $J=4.5$ Hz, OCH_2), 4.36 (d, 4H, $J=12.9$ Hz, Ar-CH-Ar), 4.06 (t, 4H, $J=4.5$ Hz, CH_2S), 3.34 (d, 4H, $J=12.9$ Hz, Ar-CH-Ar), 1.29 (s, 18H, *t*-Bu-H), 0.96 (s, 18H, *t*-Bu-H). Compound **2**: white powder, ^1H NMR (CDCl_3): 7.86 (d, 2H, $J=7.3$ Hz, Ar-H), 7.68 (d, 2H, $J=7.3$ Hz, Ar-H), 7.35 (t, 2H, $J=7.8$ Hz, Ar-H), 7.23 (t, 2H, $J=7.3$ Hz, Ar-H), 7.05 (s, 4H, Ar-H), 6.85 (s, 4H, Ar-H), 4.26 (d, 4H, $J=13.0$ Hz, Ar-CH-Ar), 4.14 (t, 4H, $J=5.7$ Hz, OCH_2), 3.91 (t, 4H, $J=6.78$ Hz, CH_2S), 3.34 (d, 4H, $J=13.0$ Hz, Ar-CH-Ar), 2.52 (m, 4H, CH_2), 1.27 (s, 18H, *t*-Bu-H), 0.99 (s, 18H, *t*-Bu-H).
10. Single-crystal diffraction measurements of crystals **1** and **4** on a Bruker Smart 1000 diffractometer with Mo-K α ($\lambda=0.71073$ Å) at 293 K. Data for **4**: $\text{C}_{48}\text{H}_{62}\text{BrClO}_4$, $M=818.34$, Large colorless prisms were grown by slow evaporation from CH_2Cl_2 and CH_3OH . Crystal in monoclinic, space group $C2/c$, $Z=4$, $a=22.2193(18)$, $b=18.2276(15)$, $c=12.6461(10)$ Å, $\beta=114.392(2)^\circ$, $V=4664.6(7)$ Å 3 , $D_c=1.165\text{mg/mm}^3$, $\mu=0.977\text{ mm}^{-1}$, $F(000)=1736$. A total of 9642 reflections were measured, 4119 unique [$R_{\text{int}}=0.0531$]. The structure was solved by direct methods and refined on F^2 using SHELXTL software (G. M. Sheldrick, Gottingen, Germany). Final $wR_2=0.1637$, with a conventional $R_1=0.0604$ (reflections with $I>2\sigma(I)$) and a goodness-of-fit=1.032 for 300

refined parameters. Crystal data for **1**: $\text{C}_{62}\text{H}_{70}\text{N}_2\text{O}_4\text{S}_4 \cdot 2\text{CH}_2\text{Cl}_2$, $M = 1205.29$, large colorless prisms were grown by slow evaporation from CH_2Cl_2 and CH_3OH . Crystals were triclinic, $P\bar{1}$, $Z = 2$, $a = 12.259(4)$, $b = 15.370(5)$, $c = 18.155(6)$ Å, $\beta = 102.246(6)^\circ$, $V = 3237.4(18)$ Å³, $D_c = 1.236 \text{ mg/mm}^3$, $\mu = 0.358 \text{ mm}^{-1}$, $F(000) = 1272$. A total of 13541 reflections were measured, 11327 unique [$R_{\text{int}} = 0.0151$] on a Bruker Smart 1000 diffractometer using graphite monochomatized Mo-K α radiation ($\lambda = 0.71073$ Å) at 293(2) K. The structure was refined on F^2 using full-matrix least-squares to an $wR_2 = 0.2551$, with a conventional $R_1 = 0.0836$ (on 8334 reflections with $I > 2\sigma(I)$) and a goodness-of-fit = 1.032 for 712 refined parameters. Most hydrogen atom position were calculated and allowed to ride on the carbon to which they were bonded assuring a C–H bond length of 0.95 Å. Crystallographic data (excluding structure factors) for the structures reported here have been deposited with the Cambridge Crystallographic data Centre as supplementary publication CCDC 141226 and 141227. CCDC-copies of the data can be obtained on application to CCDC, 12 Union Rd., Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

11. The general procedure for the preparation of the polymeric membrane was as follows. The ligand (**1**, 4 mg), plasticizer (263 mg), PVC (132 mg) and KTCIPB (1 mg) were mixed and dissolved in tetrahydrofuran (THF). The resulting PVC–THF syrup was poured into a glass mould and THF was allowed to evaporate off at room temperature over 24 h. A flexible, transparent membrane of thickness 0.2–0.4 mm was obtained. The discs of 6 mm diameter were cut using a cork borer, then pasted onto the PVC tip clipped to the end of the electrode body which consisted of an Ag–AgCl wire immersed in an internal solution of 0.01 M silver nitrate. The PVC membrane electrodes were pre-conditioned by immersion in a 0.01 M silver nitrate at least 12 h prior to use. For each membrane composition two electrodes were prepared. The representative electrochemical cell for the EMF measurement was as follows: Ag, AgCl|int. soln. (0.01 M AgNO_3)|PVC membrane|sample|salt bridge (1 M KNO_3)|3MKCl| Hg_2Cl_2 , Hg.