

Pb²⁺ and Cd²⁺ selective chemically modified field effect transistors based on thioamide functionalized 1,3-alternate calix[4]arenes

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Ronny J. W. Lugtenberg, Richard J. M. Egberink, Johan F. J. Engbersen and David N. Reinhoudt*

Laboratory of Supramolecular Chemistry and Technology and MESA Research Institute, Faculty of Chemical Technology, University of Twente, PO Box 217, 7500 AE Enschede, The Netherlands

Novel calix[4]arenes fixed in the 1,3-alternate conformation and functionalized with thioamide groups have been synthesized and their selectivities for Pb²⁺ and Cd²⁺ ions in chemically modified field effect transistors (CHEMFETs) have been evaluated. The 25,27-bis(dimethylaminothiocarbonylmethoxy)-26,28-dipropoxycalix[4]arene **3** in the 1,3-alternate conformation is more selective for Pb²⁺ than the analogous cone conformer. The 1,3-alternate calix[4]arene **8** having, in the 25- and 27-positions, two pairs of vicinal thioamide moieties at the same face of the molecule, has the highest selectivities for Cd²⁺ reported so far.

Introduction

Only a few papers deal with the selective detection of divalent Pb²⁺ and Cd²⁺ ions using ion selective membrane electrodes (ISEs) or chemically modified field effect transistors (CHEMFETs).¹ For selective detection of lead with ISEs ionophores have been used which are mainly based on oxamides² and crown ethers,³⁻⁶ but these ISEs do not respond to the free Pb²⁺, only to the monovalent complex ions. Kamata reported several acyclic dithiocarbamate ionophores in ISEs that are selective for Pb²⁺ ions,⁷ but copper interferes. The ionophore *N,N,N',N'*-tetrabutyl-3,6-dioxaoctanedithioamide was used to introduce Cd²⁺ selectivity in plasticized PVC membranes of ISEs⁸ and CHEMFETs.⁹ However, this ionophore is still rather hydrophilic, which can give rise to leaching of the ionophore.

Previously, we have reported calix[4]arene derivatives with thioamide substituents that are selective receptors for Pb²⁺ and Cd²⁺ ions. These have been successfully exploited to obtain ion selectivity in chemically modified field effect transistors (CHEMFETs).¹⁰ All these calix[4]arene derivatives are *o*-substituted at the lower rim of the calix[4]arene that is fixed in the symmetrical cone conformation. Recently, it has been shown that the conformation of the calix[4]arene can have a considerable effect on the ion selectivity. The 1,3-alternate conformers of the calixarene-crown-5 and calixarene-crown-6 derivatives show a higher K⁺/Na⁺ and Cs⁺/Na⁺ selectivity, respectively, than the corresponding cone conformers.^{11,12} Due to the symmetry of the 1,3-alternate conformer the cavity is less polar. Cation- π interactions between K⁺ or Cs⁺ cations and the

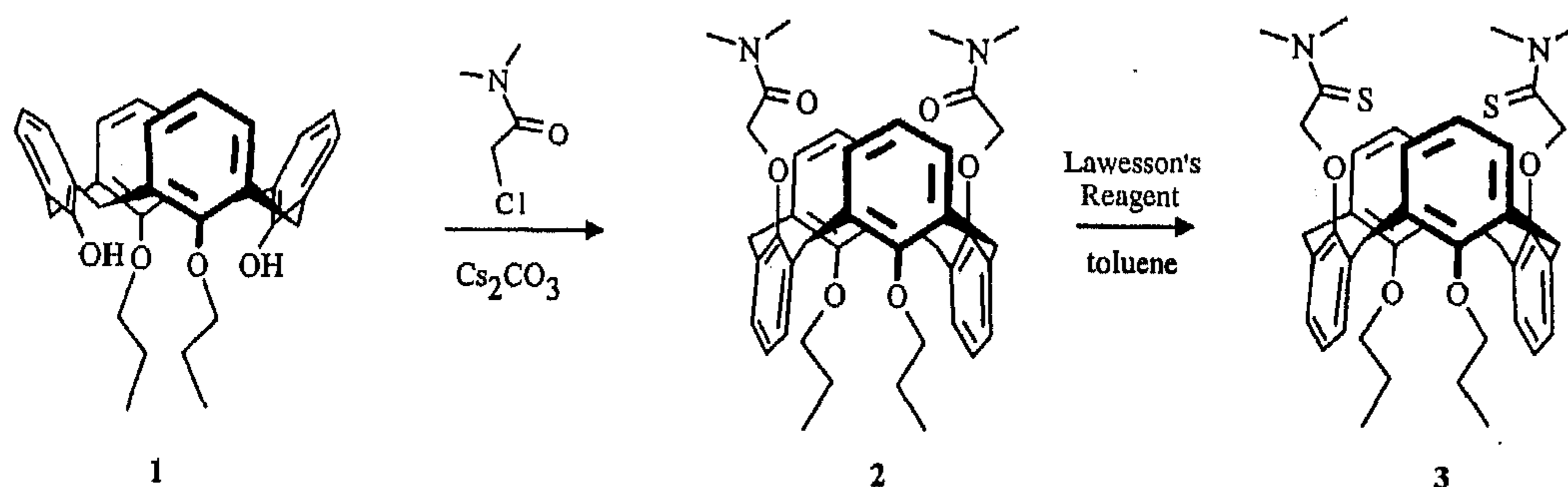
aromatic rings may favourably contribute to the selectivity. Such effects may also be of importance for the design of Pb²⁺ and Cd²⁺ selective receptors.

In this paper, we describe the synthesis of two novel calix[4]arenes fixed in the 1,3-alternate conformation (**3** and **8**) functionalized with different thioamide moieties and demonstrate their Pb²⁺ and Cd²⁺ selectivity in plasticized PVC and polysiloxane based CHEMFETs.

Results

Synthesis of Pb²⁺ and Cd²⁺ selective 1,3-alternate calix[4]arenes
Previously, we have reported that alkylation of calix[4]arenes in the presence of Cs₂CO₃ yields tetra-*o*-alkyl calix[4]arenes in the 1,3-alternate conformation.¹³ This method has also been applied to synthesize calix[4]arene derivative **3** with two diametrically located thioamide substituents fixed in the 1,3-alternate conformation (Scheme 1). It was expected that the close proximity of the thioamide ligands introduces selectivity for Pb²⁺ ions.¹⁰

For the synthesis of **3**, 25,27-dipropoxycalix[4]arene **1**¹⁴ was first reacted with *N,N'*-dimethyl-2-chloroacetamide to yield the 1,3-alternate calix[4]arene diamide **2**.¹⁵ The 1,3-alternate conformation of **2** was confirmed by the AB quartet at *ca.* δ 3.7 for the bridging methylene groups (ArCH₂Ar) in the ¹H NMR spectrum and the triplet at *ca.* δ 37 in the ¹³C NMR spectrum.¹⁴ Treatment of **2** with Lawesson's reagent in toluene at 90 °C afforded the corresponding thioamide **3** in 21% overall yield.

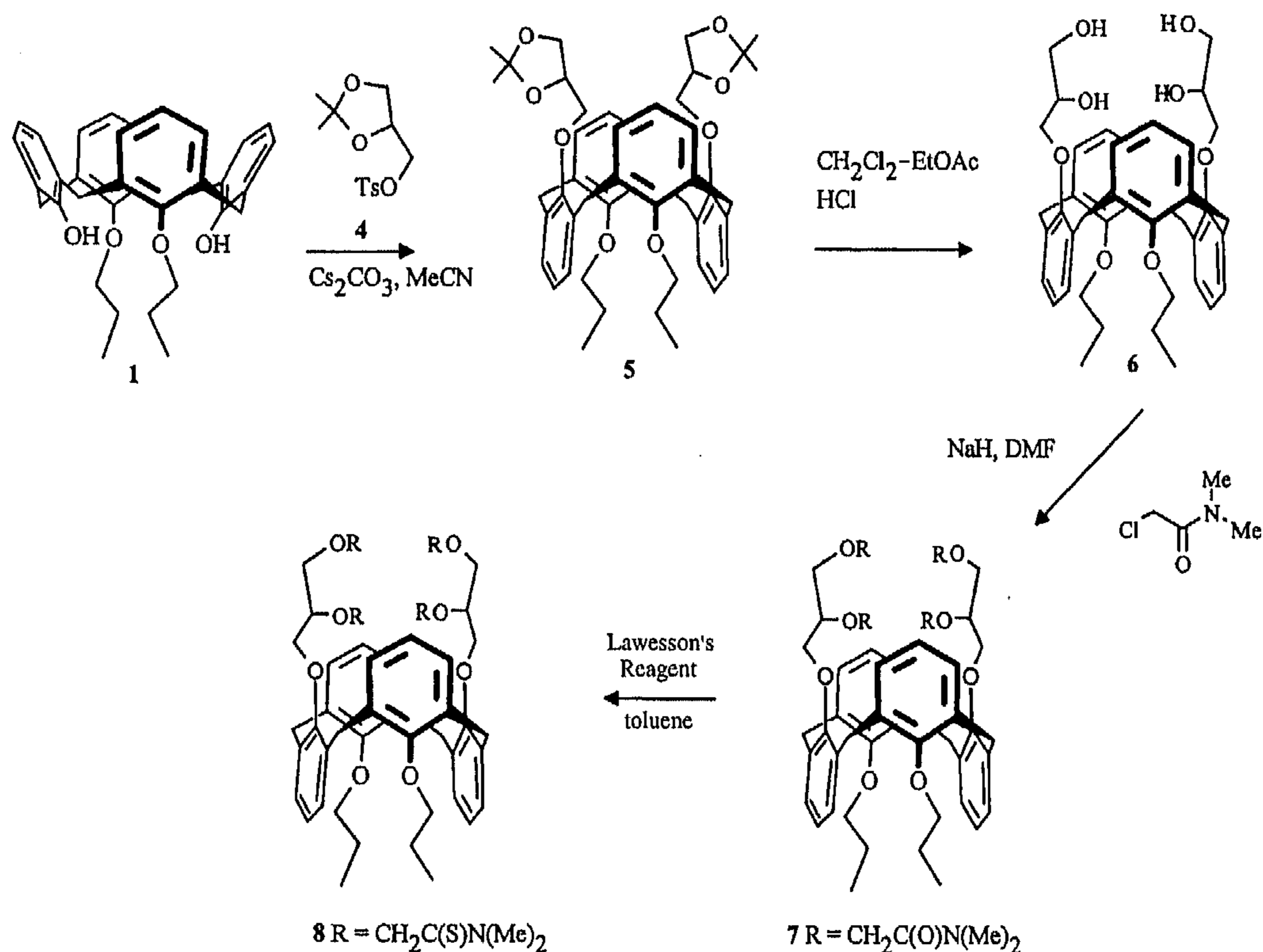


Scheme 1

Table 1 Potentiometric selectivity coefficients ($\log K_j^{pot}$)^a and sensitivities (slope/mV decade⁻¹, given in brackets)^b of CHEMFETs with Pb²⁺, **3**, **9** and Cd²⁺, **8**, selective ionophores in the presence of different interfering salts

Entry	Primary ion, i	Ionophore and membrane ^c	Interfering ion				
			0.01 M Pb ²⁺	0.01 M Cd ²⁺	0.1 M Ca ²⁺	0.1 M K ⁺	0.1 M Cu ²⁺
1	Pb ²⁺	3 , PVC/NPOE	n.a. ^d	-3.1 [30]	-4.4 [30]	-2.4 [27]	-3.0 [30]
2 ^e	Pb ²⁺	9 , PVC/NPOE	n.a.	-1.7 [22]	-4.2 [29]	-2.8 [23]	-2.7 [19]
3	Pb ²⁺	3 , PS10CN	n.a.	-3.1 [25]	-4.2 [27]	-2.6 [27]	-3.3 [25]
4	Cd ²⁺	8 , PVC/DOP	-0.7 [23]	n.a.	-3.3 [30]	-2.1 [29]	-1.5 [28]
5	Cd ²⁺	8 , PS10KT	-0.7 [21]	n.a.	-4.2 [29]	-3.0 [29]	-1.6 [25]

^a $\log K_j^{pot}$; ± 0.1 . ^b Slope: ± 2 mV decade⁻¹ [Pb²⁺] or [Cd²⁺]. ^c Membrane with 2 mass% ionophore and 75 mol% (with respect to ionophore) KTTFPB. ^d Not applicable, *i.e.* $\log K_j = 0$ by definition. ^e Data from ref. 9.



Scheme 2

Besides the Pb²⁺ selective 1,3-alternate calix[4]arene receptor **3** we have also synthesized the 1,3-alternate calix[4]arene **8** possessing the Cd²⁺ selective OCH₂CH₂OCH₂C(S)NR₂ ligands (Scheme 2).⁸ Reaction of 25,27-dipropoxycalix[4]arene **1** with (4-methylphenyl)sulfonyloxymethyldioxalane **4**¹⁶ in the presence of Cs₂CO₃ yielded the 1,3-alternate calix[4]arene derivative **5** in 75%. Deprotection of the hydroxy groups by treatment with HCl and reaction of the hydroxy groups of **6** with *N,N'*-dimethyl-2-chloroacetamide in NaH-dimethylformamide (DMF) gave calix[4]arene derivative **7**, which could be converted into the corresponding thioamide **8** with Lawesson's reagent. Throughout this reaction sequence the 1,3-alternate conformation was preserved as could be concluded from ¹H NMR spectra, which exhibit an AB quartet at *ca.* δ 3.5–3.8 for the bridging methylene groups of the calix[4]arene, and from the ¹³C NMR spectra which show a triplet at *ca.* δ 36–38 for the bridging methylene groups.¹³

Lead selective CHEMFETs

The Pb²⁺ selectivity of calix[4]arene derivative **3** was evaluated in CHEMFETs with either plasticized PVC or polysiloxane membranes. Fig. 1 shows the response of a CHEMFET with

2% (w/w) of Pb²⁺ selective calix[4]arene derivative **3** and 0.75 equiv. (with respect to the ionophore) of potassium tetrakis-[3,5-bis(trifluoromethyl)phenyl]borate (KTTFPB) in *o*-nitrophenyl octyl ether (*o*-NPOE) plasticized PVC membranes.

In the presence of a fixed concentration of 0.1 M CaCl₂ the sensor starts responding at [Pb²⁺] = 3.2 × 10⁻⁵ M and upon further increase of the Pb²⁺ activity the response is Nernstian (30 mV decade⁻¹). In Table 1 the potentiometric selectivities and sensitivities of **3** for Pb²⁺ in the presence of various alkaline (earth) and heavy metal ions are summarized. For comparison, data of CHEMFETs with the cone conformer calix[4]arene **9** are also included in Table 1.

Entry 1 shows that CHEMFETs with the 1,3-alternate dithioamide **3** in PVC/*o*-NPOE membranes exhibit Nernstian response towards Pb²⁺ ions in the presence of all different interfering ions. Comparison with the cone calix[4]arene **9** (entry 2) shows that the Pb²⁺ selectivity of **3** is higher in the presence of Cd²⁺, Ca²⁺ and Cu²⁺. In the 1,3-alternate conformation, interaction with the relatively hard oxygens of the two propoxy units is excluded and cation- π interactions favour the complexation with the more polarizable Pb²⁺ ion.¹⁷ Previously, we have found that the arrangement of four thioamide ligands at the phenolic

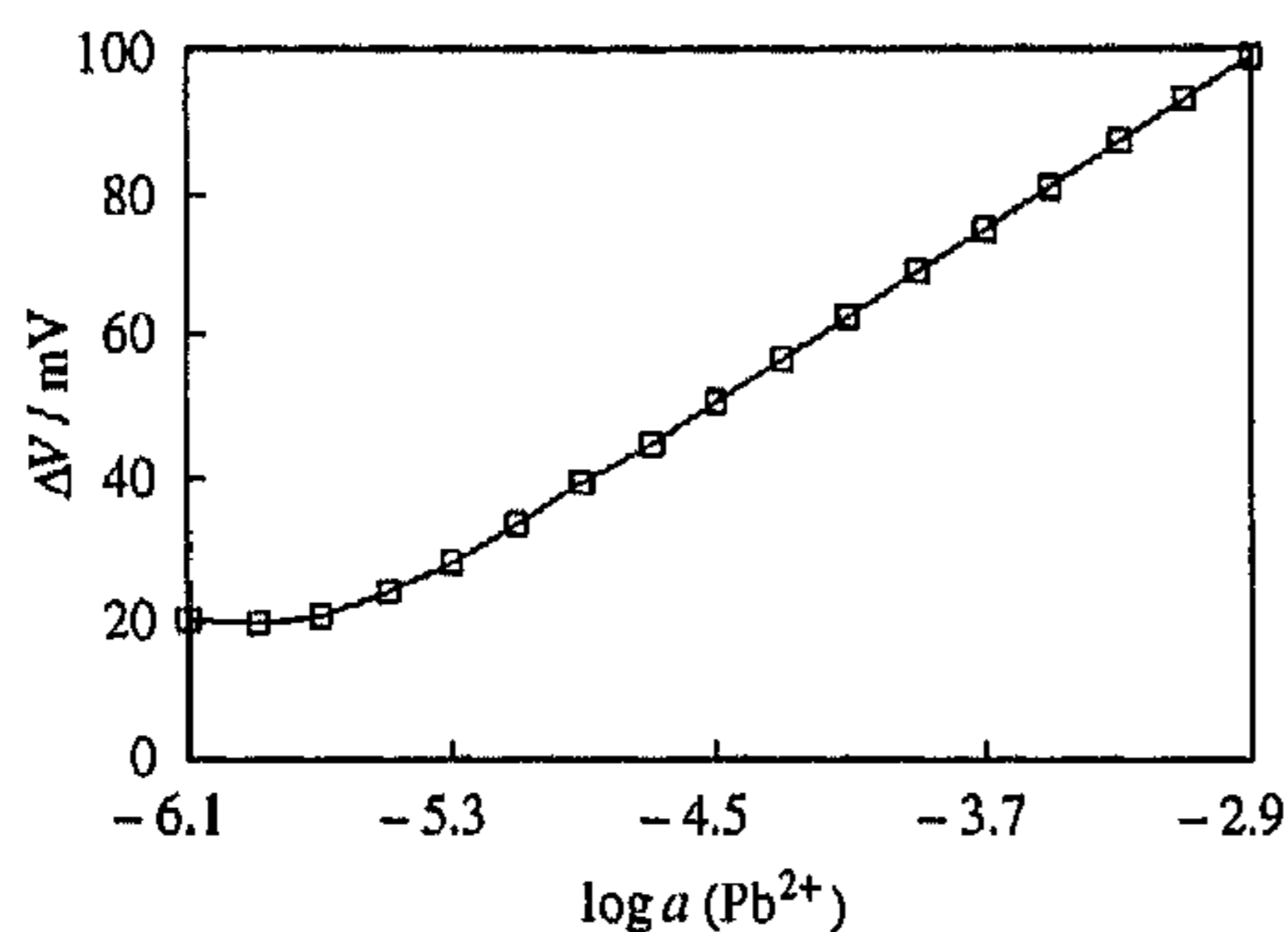
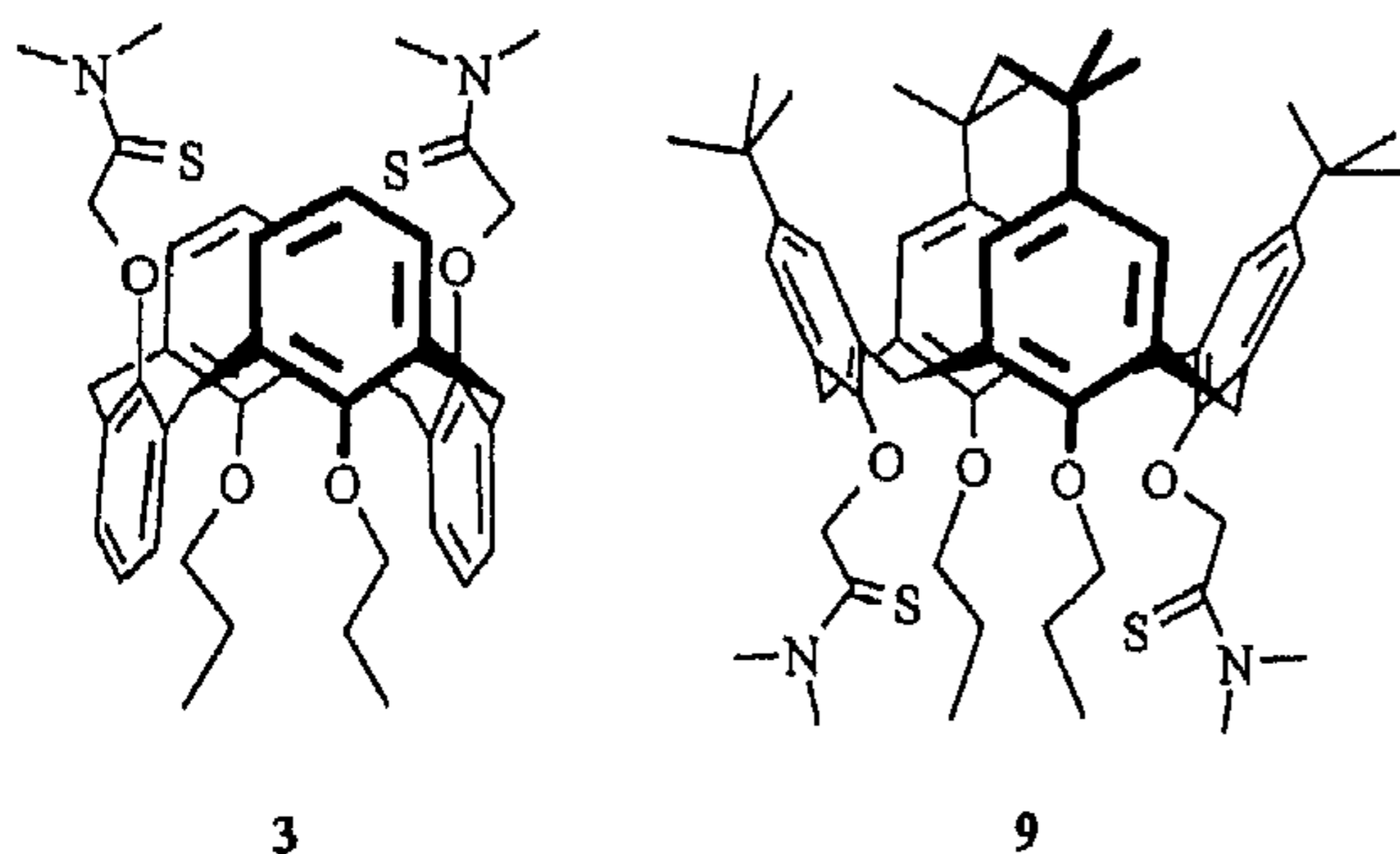


Fig. 1 Pb^{2+} response of CHEMFET with a PVC/*o*-NPOE membrane with calix[4]arene ionophore **3** in the presence of 0.1 M CaCl_2



oxygens is very favourable for the Pb^{2+} selectivity, especially in the case of potassium as the interfering ion ($\log K_{\text{Pb,K}} = -5.2$).¹⁰

Also, CHEMFETs in which calix[4]arene **3** was incorporated in 3-cyanopropyl (PS10CN) functionalized polysiloxane¹⁸

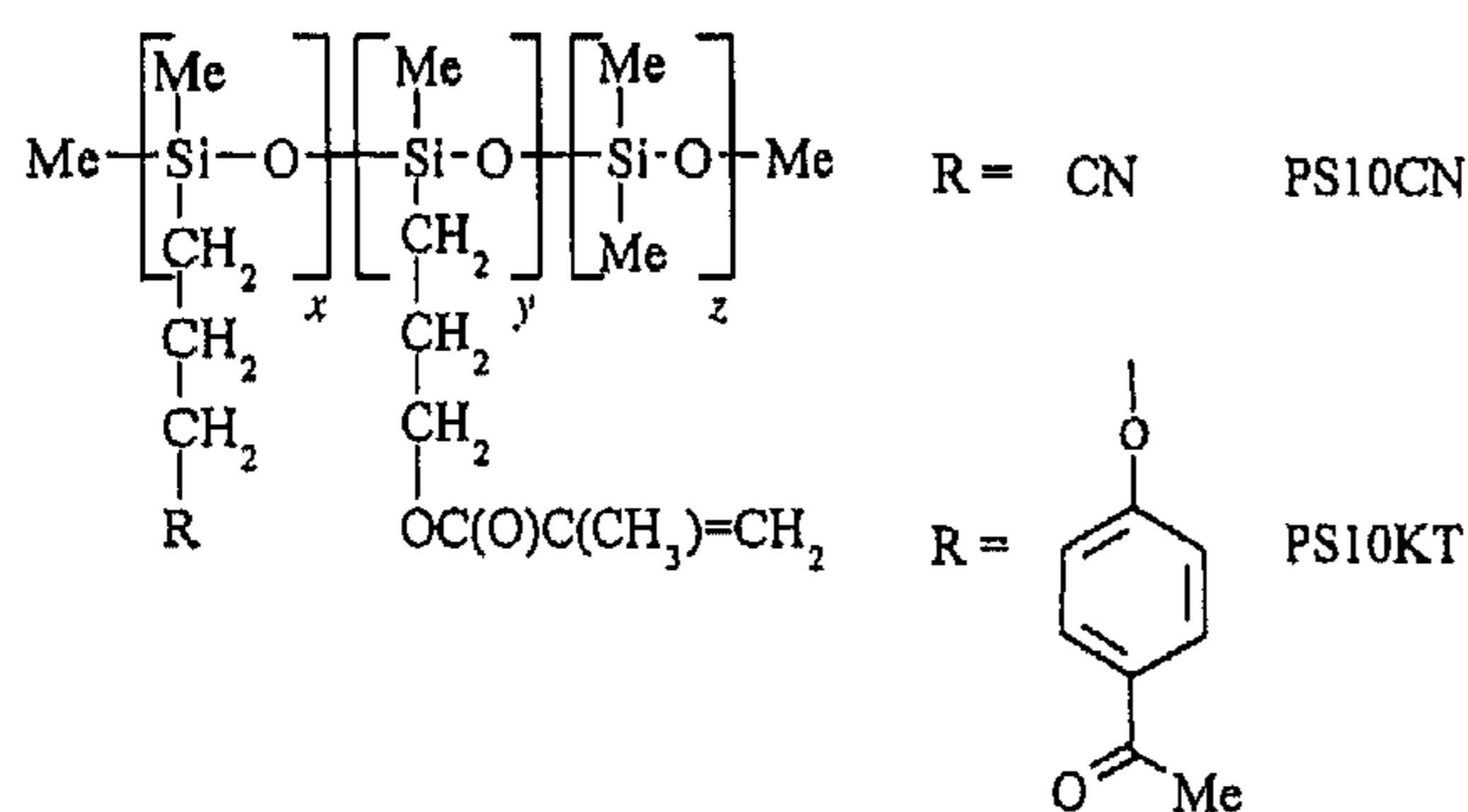


exhibit good selectivity for Pb^{2+} ions and near Nernstian slopes (entry 3). As such polysiloxane based CHEMFETs need no plasticizer, these are of interest for the development of durable sensors.^{19,20}

Cadmium selective CHEMFETs

In the Cd^{2+} selective calix[4]arene **8** the 1,3-alternate conformation was utilized to arrange two pairs of thioamide functionalities in diametrical position at the same face of the molecule. Entry 4 of Table 1 gives the potentiometric selectivity coefficients and sensitivities of CHEMFETs incorporating ionophore **8** in DOP-plasticized PVC membranes. CHEMFETs with ionophore **8** exhibited Nernstian response towards Cd^{2+} in the presence of Ca^{2+} or K^+ ions. These CHEMFETs are also selective for Cd^{2+} in the presence of Cu^{2+} ions ($\log K_{\text{Cd,Cu}} = -1.5$) which was not observed for CHEMFETs with a calix[4]arene in the cone conformation having four $\text{CH}_2\text{CH}_2\text{OCH}_2\text{C}(\text{S})\text{NMe}_2$ ligands substituted at the phenolic oxygens.¹⁰ The 1,3-alternate calix[4]arene **8** is also the first calix[4]arene which is Cd^{2+} selective in the presence of the more lipophilic Pb^{2+} ions ($\log K_{\text{Cd,Pb}} = -0.7$).

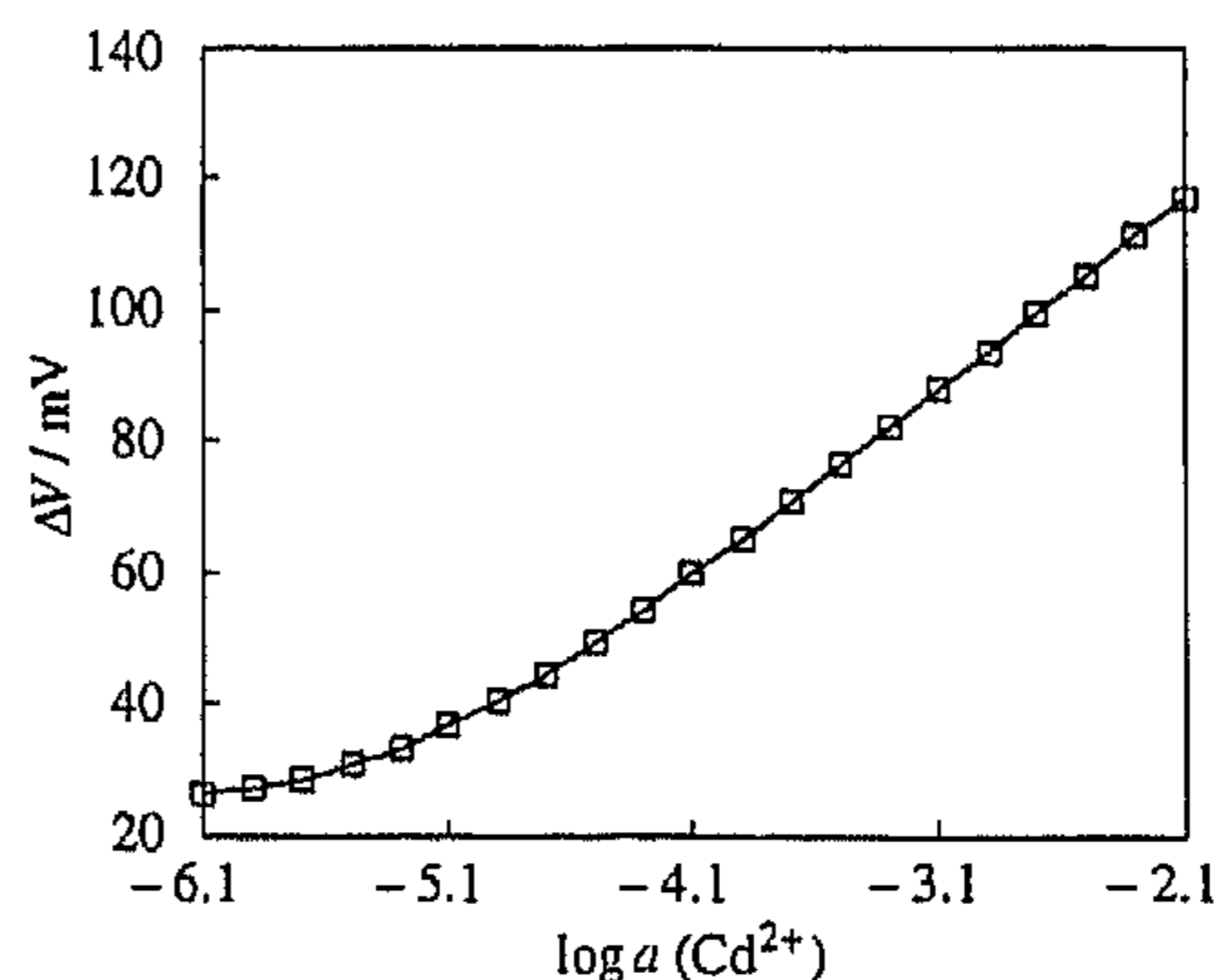


Fig. 2 Cd^{2+} response of CHEMFET with a 3-(acetylphenoxy)propyl functionalized siloxane membrane with calix[4]arene ionophore **8** in the presence of 0.1 M $\text{Ca}(\text{NO}_3)_2$

The Cd^{2+} selectivity of calix[4]arene **8** was also investigated in the different siloxane terpolymers.¹⁸ CHEMFETs with calix[4]arene **8** incorporated in 3-*p*-(acetylphenoxy)propyl (PS10KT) functionalized polysiloxane based CHEMFETs show a high selectivity for Cd^{2+} in the presence of Ca^{2+} (Fig. 2, $\log K_{\text{Cd,Ca}} = -4.2$) and K^+ ($\log K_{\text{Cd,K}} = -3.0$). These selectivities are the highest ever reported for Cd^{2+} in the presence of these ions with CHEMFETs (entry 5). Moreover, these CHEMFETs can also be used for the selective determination of Cd^{2+} ions in the presence of Cu^{2+} ions, which is not possible with the tetra-substituted cone calix[4]arene reported earlier.¹⁰

In summary, novel Pb^{2+} and Cd^{2+} selective calix[4]arenes have been synthesized in the 1,3-alternate conformation and applied in CHEMFETs in plasticized PVC and polysiloxane membranes. The 1,3-alternate calix[4]arene **3** is more selective for Pb^{2+} ions in the presence of Cd^{2+} and Cu^{2+} than the analogous calix[4]arene derivative in the cone conformation. The 1,3-alternate calix[4]arene **8** with two pairs of $\text{OCH}_2\text{CH}_2\text{OCH}_2\text{C}(\text{S})\text{NR}_2$ ligands is very selective for Cd^{2+} . CHEMFETs with this receptor in 3-(*p*-acetylphenoxy)propyl functionalized siloxane terpolymer membranes show the highest selectivity for this ion reported in the literature.

Experimental

General²¹

Melting points were determined with a Reichert melting point apparatus and are uncorrected. ^1H NMR and ^{13}C NMR spectra were recorded with Bruker AC 250 spectrometer in CDCl_3 with SiMe_4 as internal standard (J values in Hz). Positive ion FAB mass spectra were obtained with use of *m*-nitrobenzyl alcohol (NBA) as a matrix. CH_2Cl_2 was distilled from CaCl_2 , and stored over molecular sieves. Calix[4]arene derivative **1** and dioxalane derivative **4** were prepared according to literature procedures.^{14,16} Acetonitrile was dried over molecular sieves (3 Å). Analytical TLC was performed on precoated silica gel plates (SiO_2 , Merck, 60F₂₅₄). Silica gel 60 (particle size 0.040–0.063 mm, 230–400 mesh) was purchased from Merck. All commercially available chemicals were of reagent grade quality and obtained either from Acros or from Aldrich, and were used without further purification. All reactions were performed in an argon atmosphere. The presence of water in the analytical samples of compounds **2**, **3** and **6** was confirmed by ^1H NMR spectroscopy.

25,27-Bis(dimethylaminocarbonylmethoxy)-26,28-dipropoxy-calix[4]arene, 1,3-alternate **2**

A suspension of 25,27-dipropoxycalix[4]arene **1** (1.0 g, 1.97 mmol), Cs_2CO_3 (2.56 g, 7.86 mmol), and *N,N'*-dimethyl-2-chloroacetamide (0.96 g, 7.86 mmol) in CH_3CN (75 ml) was refluxed overnight. Subsequently, the solvent was removed under reduced pressure and the residue was dissolved in CH_2Cl_2

(100 ml), washed with 0.5 M HCl (100 ml), and water (200 ml). After drying with MgSO₄, the solvent was removed under reduced pressure. The crude product was purified by trituration with MeOH to give **2** as a white powder (0.66 g, 50%): mp 199–200 °C (MeOH); δ_{H} 6.95, 6.90 (d, 4H, *J* 7.5, *m*-ArH), 6.70, 6.65 (t, 2H, *J* 7.4, *p*-ArH), 4.10 [s, 4H, OCH₂C(O)], 3.75 and 3.70 (ABq, 8H, *J* 15.2, ArCH₂Ar), 3.40 (t, 4H, *J* 7.5, ArOCH₂CH₂), 2.90, 2.40 [s, 6H, N(CH₃)], 1.35 (sx, 4H, *J* 7.5, ArOCH₂CH₂), 0.75 (t, 4H, *J* 7.5, ArOCH₂CH₂CH₃); δ_{C} 168.4 [s, C(O)], 72.4 [t, ArOCH₂C(O)], 71.5 (t, ArOCH₂CH₂), 37.4 (t, ArCH₂Ar), 36.8, 35.5 [q, N(CH₃)], 22.6 (t, ArOCH₂CH₂CH₃), 10.0 (q, ArOCH₂CH₂CH₃); FAB MS (NBA), *m/z* 679.6 [(M + H)⁺, calc. 679.6]. Anal. Calcd. for C₄₂H₅₀N₂O₆·0.75H₂O: C, 72.86; H, 7.49; N, 4.04. Found: C, 72.90; H, 7.33; N, 4.06%.

25,27-Bis(dimethylaminothiocarbonylmethoxy)-26,28-dipropoxycalix[4]arene, 1,3-alternate 3

A mixture of **2** (0.40 g, 0.59 mmol) and Lawesson's reagent (0.25 g, 0.62 mmol) in toluene (50 ml) was heated overnight at 90 °C. Subsequently, the solvent was removed under reduced pressure. The residue was purified by column chromatography (SiO₂-CH₂Cl₂) to remove traces of Lawesson's material; subsequently the eluent was changed to CH₂Cl₂-EtOAc 99:1, to yield **3** as a light-yellow powder (0.32 g, 42%): mp 286–288 °C (MeOH); δ_{H} 7.00, 6.95 (d, 4H, *J* 7.4, *m*-ArH), 6.80, 6.70 (t, 2H, *J* 7.3, *p*-ArH), 4.70 [s, 4H, OCH₂C(O)], 3.80 and 3.75 (ABq, 8H, *J* 15.7, ArCH₂Ar), 3.45 (t, 4H, *J* 7.8, ArOCH₂CH₂), 3.45, 2.65 [s, 6H, N(CH₃)], 1.35 (sx, 4H, *J* 7.7, ArOCH₂CH₂), 0.75 (t, 4H, *J* 7.4, ArOCH₂CH₂CH₃); δ_{C} 196.4 [s, C(S)], 79.4 [t, ArOCH₂C(S)], 71.9 (t, ArOCH₂CH₂), 44.5, 42.6 [q, N(CH₃)], 37.9 (t, ArCH₂Ar), 22.4 (t, ArOCH₂CH₂CH₃), 9.9 (q, ArOCH₂CH₂CH₃); FAB MS (NBA), *m/z* 733.9 [(M + Na)⁺, calc. 733.8]. Anal. Calcd. for C₄₂H₅₀N₂O₄S₂·0.5H₂O: C, 70.06; H, 7.14; N, 3.89. Found: C, 69.95; H, 7.02; N, 3.88%.

25,27-Bis(2,2-dimethyl-1,3-dioxalan-4-ylmethoxy)-26,28-dipropoxycalix[4]arene, 1,3-alternate 5

A suspension of 25,27-dipropoxycalix[4]arene **1** (5.0 g, 9.8 mmol), Cs₂CO₃ (12.81 g, 39.3 mmol) and **4** (8.71 g, 30.4 mmol) in CH₃CN (300 ml) was refluxed for 2 d. Subsequently, the solvent was removed under reduced pressure and the residue was dissolved in CH₂Cl₂ (200 ml), washed with 0.5 M HCl (200 ml), a saturated solution of NH₄Cl (200 ml) and water (200 ml). After drying with MgSO₄, the solvent was removed under reduced pressure. The crude product was purified by trituration with MeOH to give **5** as a white powder (5.4 g, 75%): mp 173–174 °C (MeOH); δ_{H} 7.10–7.00 (m, 8H, *m*-ArH), 6.85–6.70 (m, 4H, *p*-ArH), 4.25–4.20 [m, 2H, CH(CH₂)], 3.85–3.75 (m, 4H, OCH₂), 3.75 and 3.70 (ABq, 8H, *J* 15.0, ArCH₂Ar), 3.65–3.45 (m, 4H, ArOCH₂CHCH₂, and m, 4H, ArOCH₂CHCH₂), 1.55–1.40 [m, 12H, C(CH₃)₂ and m, 4H, OCH₂CH₂CH₃], 0.90–0.80 (m, 6H, OCH₂CH₂CH₃); δ_{C} 109.1 [s, C(CH₃)₂], 74.2 (d, ArOCH₂CHCH₂), 73.2 (t, ArOCH₂CHCH₂), 72.4 (t, ArOCH₂CH₂CH₃), 67.1 (t, ArOCH₂CHCH₂), 36.7 (t, ArCH₂-Ar), 27.0, 25.5 [q, C(CH₃)₂], 23.0 (t, ArOCH₂CH₂CH₃), 10.2 (q, ArOCH₂CH₂CH₃); FAB MS (NBA), *m/z* 759.3 [(M + Na)⁺, calc. 759.3]. Anal. Calcd. for C₄₆H₅₆O₈: C, 74.97; H, 7.65. Found: C, 75.05; H, 7.73%.

25,27-Bis(2,3-dihydroxypropoxy)-26,28-dipropoxycalix[4]arene, 1,3-alternate 6

To a solution of **5** (4.0 g, 5.4 mmol) in EtOH-CH₂Cl₂ (4:1; 150 ml) 1 M HCl (25 ml) was added and the mixture was stirred at room temp. for 1 h. Subsequently, the solvents were evaporated under reduced pressure. The residue was taken up in CH₂Cl₂ (100 ml) and washed with water (2 × 100 ml). The organic layer was dried with MgSO₄ and the solvent was removed under reduced pressure. The crude product was purified by column chromatography [SiO₂; tetrahydrofuran (THF)-EtOAc, 95:5] to give **6** as a white powder (1.5 g, 42%): mp 270–272 °C

(MeOH); δ_{H} 7.05–6.95 (m, 8H, *m*-ArH), 6.90–6.75 (m, 4H, *p*-ArH), 3.80 and 3.75 (ABq, 8H, *J* 14.6, ArCH₂Ar), 3.75–3.65 [m, 2H, CH(CH₂)], 3.45–3.20 (m, 4H, ArOCH₂CHCH₂, m, 4H, ArOCH₂CHCH₂, and m, 4H, OCH₂CH₂CH₃), 0.95–0.80 (sx, 4H, OCH₂CH₂), 0.60–0.50 (m, 6H, CH₂CH₂CH₃); δ_{C} 77.2 (d, ArOCH₂CHCH₂), 71.9 (t, ArOCH₂CH₂CH₃), 69.6 (t, ArOCH₂CHCH₂), 63.5 (t, ArOCH₂CHCH₂), 38.1 (t, ArCH₂-Ar), 22.0, 21.8 (t, ArOCH₂CH₂CH₃), 9.89, 9.80 (q, ArOCH₂-CH₂CH₃); FAB MS (NBA), *m/z* 679.2 [(M + Na)⁺, calc. 679.2]. Anal. Calcd. for C₄₀H₄₈O₈·0.25H₂O: C, 72.64; H, 7.34. Found: C, 72.69; H, 7.31%.

25,27-Bis[2,3-bis(dimethylaminocarbonylmethoxy)propoxy]-26,28-dipropoxycalix[4]arene, 1,3-alternate 7

A suspension of **6** (2.00 g, 3.00 mmol) and sodium hydride (60%) (1.21 g, 30.0 mmol), freed from mineral oil by washing with hexane (2 × 5 ml) in DMF (50 ml), was stirred at room temp. for 1 h. Subsequently, *N,N*-dimethyl-2-chloroacetamide (3.70 g, 30.0 mmol) was added and the mixture was stirred overnight at 60 °C. The solvent was removed under reduced pressure, the residue was taken up in CH₂Cl₂ (100 ml) and washed with 1 M HCl (100 ml), followed by washing with NH₄Cl (100 ml) and water (2 × 100 ml). The solvent of the organic layer was removed under reduced pressure to give **7** as an oil (1.94 g, 65%). An analytical amount was purified with preparative TLC (SiO₂; THF-MeOH, 95:5); δ_{H} 7.05–6.95 (m, 8H, *m*-ArH), 6.60, 6.55 (t, 2H, *J* 7.4, *p*-ArH), 4.40, 4.35, [s, 2H, OCH₂C(O)], 4.25 [s, 4H, OCH₂C(O)], 4.45–4.35 (m, 4H, OCH₂CH₂), 3.80–3.75 (m, 4H, ArOCH₂CH₂CH₂, and m, 4H, ArOCH₂CHCH₂), 3.65 (t, ArOCH₂CH₂), 3.55 and 3.50 (ABq, *J* 14.8, ArCH₂Ar), 3.00, 2.95 [s, 12H, N(CH₃)], 1.80 (sx, ArOCH₂CH₂), 1.00 (t, OCH₂CH₂CH₃); δ_{C} 169.4, 169.0 (s, C=O), 78.6 (d, ArOCH₂CHCH₂), 74.3 (t, ArOCH₂CHCH₂), 73.0, 71.5 [t, OCH₂C(O)], 70.3 (t, ArOCH₂CH₂CH₃), 69.7 (t, ArOCH₂CHCH₂), 37.5 (t, ArCH₂Ar), 36.4, 35.5 [q, N(CH₃)], 23.8 (t, ArOCH₂CH₂CH₃), 10.6 (q, ArOCH₂CH₂CH₃); FAB MS (NBA), *m/z* 1019.5 [(M + Na)⁺, calc. for C₅₆H₇₆N₄O₁₂: 1019.6].

25,27-Bis[2,3-bis(dimethylaminothiocarbonylmethoxy)propoxy]-26,28-dipropoxycalix[4]arene, 1,3-alternate 8

A mixture of **7** (0.72 g, 0.72 mmol) and Lawesson's reagent (0.61 g, 1.51 mmol) in toluene (100 ml) was heated overnight at 90 °C. Subsequently, the solvent was removed under reduced pressure. The residue was purified by column chromatography (SiO₂-CH₂Cl₂ to remove traces of Lawesson's material; later the eluent was changed to CH₂Cl₂-EtOAc, 9:1) to yield **8** as a light-yellow powder (0.39 g, 51%): mp 240–242 °C (MeOH); δ_{H} 7.10–6.95 (m, 8H, *m*-ArH), 6.75–6.65 (m, 4H, *p*-ArH), 4.75–4.55 [m, 8H, C(S)CH₂], 4.20 (m, 2H, CHCH₂), 3.90–3.75 (m, 4H, ArOCH₂CHCH₂, and m, 4H, ArOCH₂CHCH₂), 3.65 (t, 4H, *J* 7.2, OCH₂CH₂), 3.80 and 3.75 (ABq, 8H, *J* 14.5, ArCH₂Ar), 3.45–3.40 (m, 24H, NCH₃), 1.80 (st, 4H, *J* 7.3, ArOCH₂CH₂), 1.05 (t, 6H, *J* 7.4, CH₂CH₃); δ_{C} 197.5, 197.0 (s, C=S), 78.5, 77.8 [t, OCH₂C(S)], 77.0 (t, ArOCH₂CHCH₂), 74.3 (t, ArOCH₂CHCH₂), 72.2 (t, ArOCH₂CH₂CH₃), 70.3 (ArOCH₂CHCH₂), 44.5, 42.2 (q, NCH₃), 35.5 (t, ArCH₂Ar), 23.8 (t, OCH₂CH₂), 10.6 (q, CH₂CH₃); FAB MS spectrum (NBA), *m/z* 1061.5 [M⁺, calc. 1061.5]. Anal. Calcd. for C₅₆H₇₆N₄O₈S₄: C, 63.36; H, 7.21; N, 5.27. Found: C, 63.02, H, 7.09, N, 5.13%.

CHEMFETs

Reagents. High molecular weight (HMW) PVC was obtained from Acros. THF was freshly distilled from sodium benzophenone ketyl. The siloxane terpolymers used were prepared according to literature procedures.¹⁸ Bis(2-ethylhexyl) adipate and potassium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate were purchased from Fluka. 2,2'-Dimethoxy-2-phenylacetophenone used as a photoinitiator was obtained from Acros.

Lead(II) chloride was purchased from Johnson Matthey (ultrapure). All other chloride or nitrate salts used were of analytical reagent grade (Merck Schuchardt). All solutions were made with deionized, doubly distilled water.

Fabrication of CHEMFETs. CHEMFETs were prepared from ISFETs with dimensions of 1.2×3 mm. Details of fabrication of the ISFETs modified with poly(hydroxyethylmethacrylate) hydrogel (polyHEMA) have been described previously.^{22,23} The modified ISFETs were mounted on a printed circuit board, wire bonded and encapsulated with epoxy resin (Hysol H-W 796/C8 W795) or with silicone rubber (Dow Corning 3140 RTV). The poly HEMA-layer of the ISFETs was conditioned by immersion in a 0.01 M solution of the primary ion at pH = 4 (for Cd^{2+} with HNO_3 , and for Pb^{2+} with HCl). The casting procedures of plasticized PVC membranes and the polysiloxane membranes have been carried out as described earlier.^{10,18}

CHEMFET measurements. The CHEMFET measurements were carried out as described before and the same experimental setup was used.¹⁸ The potentiometric selectivity coefficients, K_{ij}^{pot} , were determined by the fixed interference method (FIM).²⁴ Before starting the measurements, the membranes were conditioned in a 0.01 M primary ion solution at pH 4 overnight.

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