Pb^{2+} and Cd^{2+} selective chemically modified field effect transistors based on thioamide functionalized 1,3-alternate calix[4]arenes

PERKIN 2

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Novel calix[4]arenes fixed in the 1,3-alternate conformation and functionalized with thioamide groups have been synthesized and their selectivities for Pb^{2+} and Cd^{2+} 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 Pb^{2+} 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 Cd^{2+} reported so far.

Introduction

Only a few papers deal with the selective detection of divalent Pb^{2+} and Cd^{2+} 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 oxamides[2] and crown ethers,[3–6] but these ISEs do not respond to the free Pb^{2+}, only to the monovalent complex ions. Kamata reported several acyclic dithiocarbamate ionophores in ISEs that are selective for Pb^{2+} ions,[7] but copper interferes. The ionophore *N,N,N′,N′*-tetrabutyl-3,6-dioxaoctanedithioamide was used to introduce Cd^{2+} selectivity in plasticized PVC membranes of ISEs[8] 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 Pb^{2+} and Cd^{2+} 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 Pb^{2+} and Cd^{2+} selective receptors.

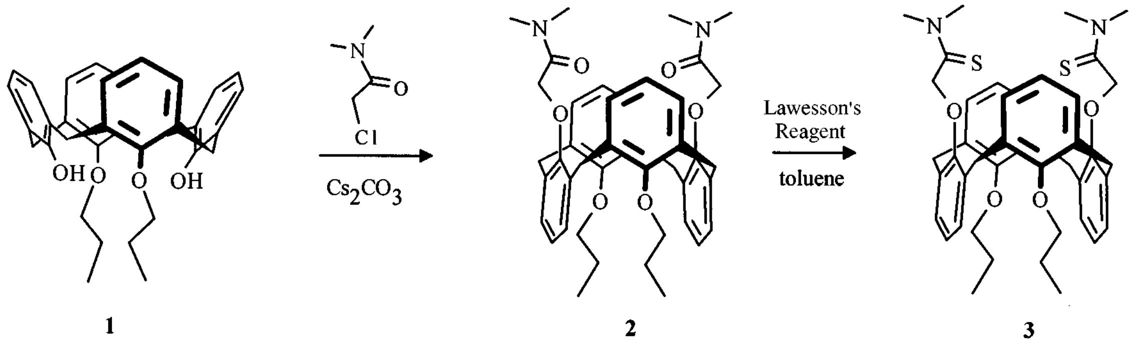
In this paper, we describe the synthesis of two novel calix[4]arenes fixed in the 1,3-alternate conformation (**3** and **8**) functionalized with different thioamide moieties and demonstrate their Pb^{2+} and Cd^{2+} selectivity in plasticized PVC and polysiloxane based CHEMFETs.

Results

Synthesis of Pb^{2+} and Cd^{2+} selective 1,3-alternate calix[4]arenes

Previously, we have reported that alkylation of calix[4]arenes in the presence of Cs_2CO_3 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 Pb^{2+} 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 ($ArCH_2Ar$) in the ^1H NMR spectrum and the triplet at *ca.* δ 37 in the ^{13}C NMR spectrum.[14] Treatment of **2** with Lawesson's reagent in toluene at 90 °C afforded the corresponding thioamide **3** in 21% overall yield.

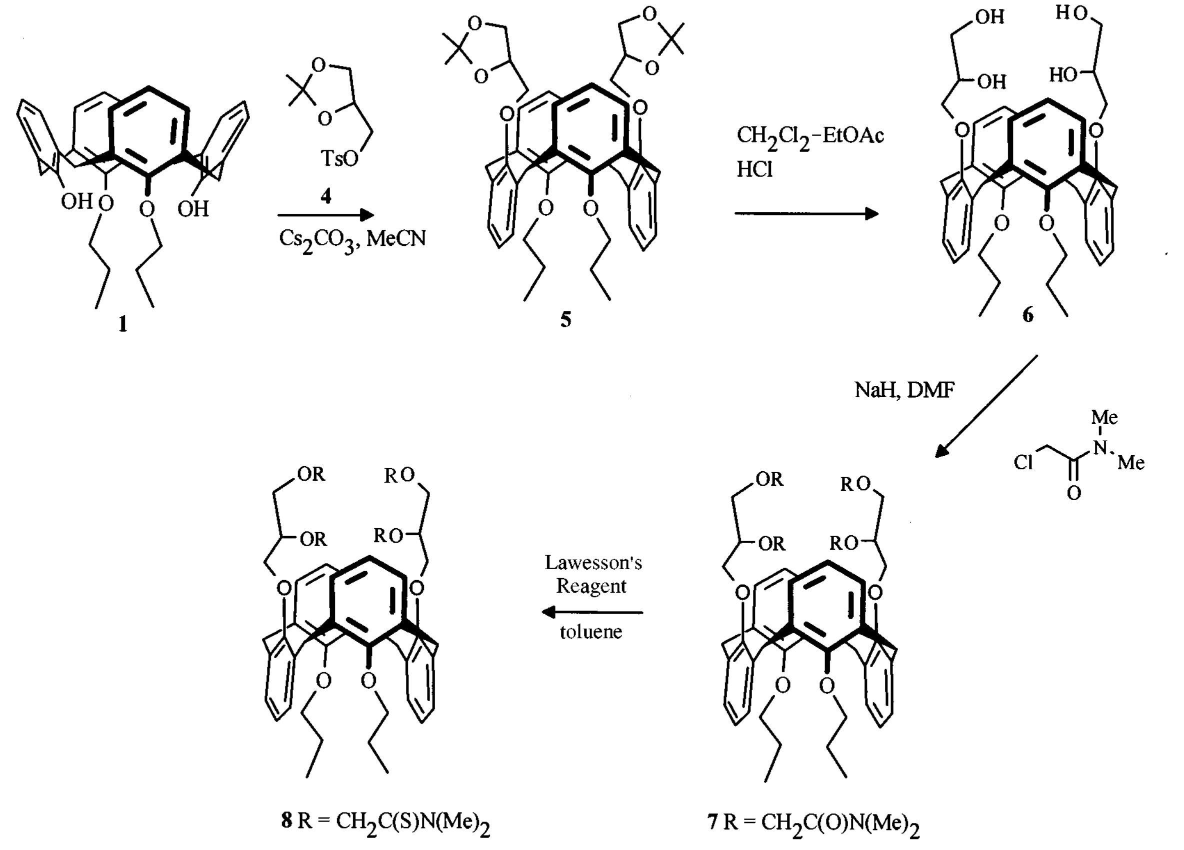


Scheme 1

Table 1 Potentiometric selectivity coefficients (log K_{ij}^{pot})[a] and sensitivities (slope/mV decade^{-1}, given in brackets)[b] of CHEMFETs with Pb^{2+}, **3**, **9** and Cd^{2+}, **8**, selective ionophores in the presence of different interfering salts

			Interfering ion				
Entry	Primary ion, i	Ionophore and membrane[c]	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_{ij}^{pot}: ±0.1. [b] Slope: ±2 mV decade^{-1} [Pb^{2+}] or [Cd^{2+}]. [c] Membrane with 2 mass% ionophore and 75 mol% (with respect to ionophore) KTTFPB. [d] Not applicable, *i.e.* log K_{ij} = 0 by definition. [e] Data from ref. 9.



Scheme 2

Besides the Pb^{2+} selective 1,3-alternate calix[4]arene receptor **3** we have also synthesized the 1,3-alternate calix[4]arene **8** possessing the Cd^{2+} selective $OCH_2CH_2OCH_2C(S)NR_2$ ligands (Scheme 2).[8] Reaction of 25,27-dipropoxycalix[4]arene **1** with (4-methylphenyl)sulfonyloxymethyldioxalane **4**[16] in the presence of Cs_2CO_3 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 ^{13}C NMR spectra which show a triplet at *ca.* δ 36–38 for the bridging methylene groups.[13]

Lead selective CHEMFETs

The Pb^{2+} 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 Pb^{2+} 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 $CaCl_2$ the sensor starts responding at [Pb^{2+}] = 3.2 × 10^{-5} M and upon further increase of the Pb^{2+} activity the response is Nernstian (30 mV decade^{-1}). In Table 1 the potentiometric selectivities and sensitivities of **3** for Pb^{2+} 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 Pb^{2+} ions in the presence of all different interfering ions. Comparison with the cone calix[4]arene **9** (entry 2) shows that the Pb^{2+} selectivity of **3** is higher in the presence of Cd^{2+}, Ca^{2+} and Cu^{2+}. 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 Pb^{2+} ion.[17] Previously, we have found that the arrangement of four thioamide ligands at the phenolic

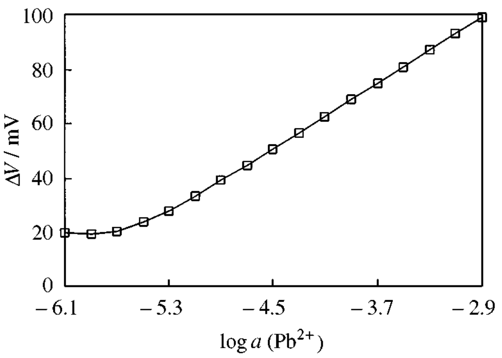
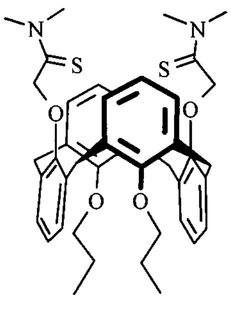
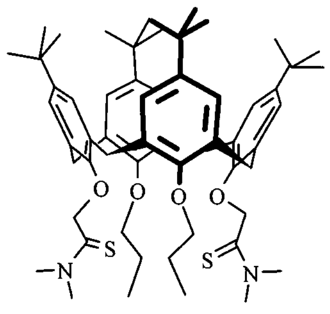


Fig. 1 Pb^{2+} response of CHEMFET with a PVC/*o*-NPOE membrane with calix[4]arene ionophore **3** in the presence of 0.1 M $CaCl_2$



3



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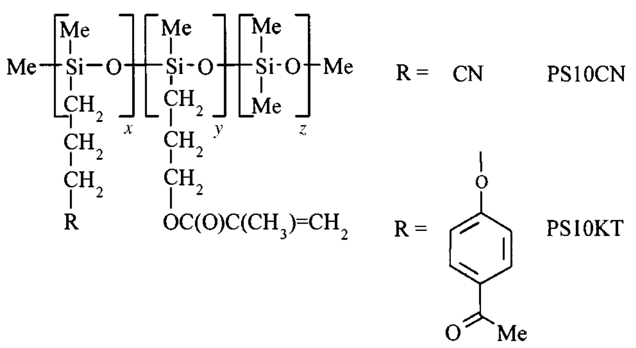
oxygens is very favourable for the Pb^{2+} selectivity, especially in the case of potassium as the interfering ion ($\log K_{Pb,K} = -5.2$).[10]

Also, CHEMFETs in which calix[4]arene **3** was incorporated in 3-cyanopropyl (PS10CN) functionalized polysiloxane[18] 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 ($\log K_{Cd,Cu} = -1.5$) which was not observed for CHEMFETs with a calix[4]arene in the cone conformation having four $CH_2CH_2OCH_2C(S)NMe_2$ 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 ($\log K_{Cd,Pb} = -0.7$).

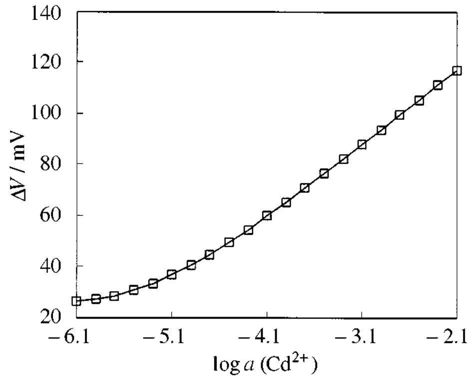


Fig. 2 Cd^{2+} response of CHEMFET with a 3-(acetylphenoxy)propyl functionalized siloxane membrane with calix[4]arene ionophore **8** in the presence of 0.1 M $Ca(NO_3)_2$

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, $\log K_{Cd,Ca} = -4.2$) and K^+ ($\log K_{Cd,K} = -3.0$). 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 tetrasubstituted 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 $OCH_2CH_2OCH_2C(S)NR_2$ 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

General[21]

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, $60F_{254}$). 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-dipropoxycalix[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 $MgSO_4$, 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, $OCH_2C(O)$], 3.75 and 3.70 (ABq, 8H, *J* 15.2, $ArCH_2Ar$), 3.40 (t, 4H, *J* 7.5, $ArOCH_2CH_2$), 2.90, 2.40 [s, 6H, $N(CH_3)$], 1.35 (sx, 4H, *J* 7.5, $ArOCH_2CH_2$), 0.75 (t, 4H, *J* 7.5, $ArOCH_2CH_2CH_3$); δ_C 168.4 [s, C(O)], 72.4 [t, $ArOCH_2C(O)$], 71.5 (t, $ArOCH_2CH_2$), 37.4 (t, $ArCH_2Ar$), 36.8, 35.5 [q, $N(CH_3)$], 22.6 (t, $ArOCH_2CH_2CH_3$), 10.0 (q, $ArOCH_2CH_2CH_3$); FAB MS (NBA), *m/z* 679.6 [$(M + H)^+$, calc. 679.6]. Anal. Calcd. for $C_{42}H_{50}N_2O_6\cdot0.75H_2O$: 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 (SiO_2–CH_2Cl_2) to remove traces of Lawesson's material; subsequently the eluent was changed to CH_2Cl_2–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, $OCH_2C(O)$], 3.80 and 3.75 (ABq, 8H, *J* 15.7, $ArCH_2Ar$), 3.45 (t, 4H, *J* 7.8, $ArOCH_2CH_2$), 3.45, 2.65 [s, 6H, $N(CH_3)$], 1.35 (sx, 4H, *J* 7.7, $ArOCH_2CH_2$), 0.75 (t, 4H, *J* 7.4, $ArOCH_2CH_2CH_3$); δ_C 196.4 [s, C(S)], 79.4 [t, $ArOCH_2C(S)$], 71.9 (t, $ArOCH_2CH_2$), 44.5, 42.6 [q, $N(CH_3)$], 37.9 (t, $ArCH_2Ar$), 22.4 (t, $ArOCH_2CH_2CH_3$), 9.9 (q, $ArOCH_2CH_2CH_3$); FAB MS (NBA), *m/z* 733.9 [$(M + Na)^+$, calc. 733.8]. Anal. Calcd. for $C_{42}H_{50}N_2O_4S_2\cdot0.5H_2O$: 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), Cs_2CO_3 (12.81 g, 39.3 mmol) and **4** (8.71 g, 30.4 mmol) in CH_3CN (300 ml) was refluxed for 2 d. Subsequently, the solvent was removed under reduced pressure and the residue was dissolved in CH_2Cl_2 (200 ml), washed with 0.5 M HCl (200 ml), a saturated solution of NH_4Cl (200 ml) and water (200 ml). After drying with $MgSO_4$, 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, $CH(CH_2)$], 3.85–3.75 (m, 4H, OCH_2), 3.75 and 3.70 (ABq, 8H, *J* 15.0, $ArCH_2Ar$), 3.65–3.45 (m, 4H, $ArOCH_2CHCH_2$, and m, 4H, $ArOCH_2CHCH_2$), 1.55–1.40 [m, 12H, $C(CH_3)_2$ and m, 4H, $OCH_2CH_2CH_3$], 0.90–0.80 (m, 6H, $OCH_2CH_2CH_3$); δ_C 109.1 [s, $C(CH_3)_2$], 74.2 (d, $ArOCH_2CHCH_2$), 73.2 (t, $ArOCH_2CHCH_2$), 72.4 (t, $ArOCH_2CH_2CH_3$), 67.1 (t, $ArOCH_2CHCH_2$), 36.7 (t, $ArCH_2Ar$), 27.0, 25.5 [q, $C(CH_3)_2$], 23.0 (t, $ArOCH_2CH_2CH_3$), 10.2 (q, $ArOCH_2CH_2CH_3$); FAB MS (NBA), *m/z* 759.3 [$(M + Na)^+$, calc. 759.3]. Anal. Calcd. for $C_{46}H_{56}O_8$: 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–CH_2Cl_2 (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 CH_2Cl_2 (100 ml) and washed with water (2 × 100 ml). The organic layer was dried with $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by column chromatography [SiO_2: 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, $ArCH_2Ar$), 3.75–3.65 [m, 2H, $CH(CH_2)$], 3.45–3.20 (m, 4H, $ArOCH_2CHCH_2$, m, 4H, $ArOCH_2CHCH_2$, and m, 4H, $OCH_2CH_2CH_3$), 0.95–0.80 (sx, 4H, OCH_2CH_2), 0.60–0.50 (m, 6H, $CH_2CH_2CH_3$); δ_C 77.2 (d, $ArOCH_2CHCH_2$), 71.9 (t, $ArOCH_2CH_2CH_3$), 69.6 (t, $ArOCH_2CHCH_2$), 63.5 (t, $ArOCH_2CHCH_2$), 38.1 (t, $ArCH_2Ar$), 22.0, 21.8 (t, $ArOCH_2CH_2CH_3$), 9.89, 9.80 (q, $ArOCH_2CH_2CH_3$); FAB MS (NBA), *m/z* 679.2 [$(M + Na)^+$, calc. 679.2]. Anal. Calcd. for $C_{40}H_{48}O_8\cdot0.25H_2O$: 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 CH_2Cl_2 (100 ml) and washed with 1 M HCl (100 ml), followed by washing with NH_4Cl (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 (SiO_2: 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, $OCH_2C(O)$], 4.25 [s, 4H, $OCH_2C(O)$], 4.45–4.35 (m, 4H, $OCHCH_2$), 3.80–3.75 (m, 4H, $ArOCH_2CH$, and m, 4H, $ArOCH_2CHCH_2$), 3.65 (t, $ArOCH_2CH_2$), 3.55 and 3.50 (ABq, *J* 14.8, $ArCH_2Ar$), 3.00, 2.95 [s, 12H, $N(CH_3)$], 1.80 (sx, $ArOCH_2CH_2$), 1.00 (t, $OCH_2CH_2CH_3$); δ_C 169.4, 169.0 (s, C=O), 78.6 (d, $ArOCH_2CHCH_2$), 74.3 (t, $ArOCH_2CHCH_2$), 73.0, 71.5 [t, $OCH_2C(O)$], 70.3 (t, $ArOCH_2CH_2CH_3$), 69.7 (t, $ArOCH_2CHCH_2$), 37.5 (t, $ArCH_2Ar$), 36.4, 35.5 [q, $N(CH_3)$], 23.8 (t, $ArOCH_2CH_2CH_3$), 10.6 (q, $ArOCH_2CH_2CH_3$); FAB MS (NBA), *m/z* 1019.5 [$(M + Na)^+$, calcd. for $C_{56}H_{76}N_4O_{12}$: 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 (SiO_2–CH_2Cl_2 to remove traces of Lawesson's material; later the eluent was changed to CH_2Cl_2–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, $C(S)CH_2$], 4.20 (m, 2H, $CHCH_2$), 3.90–3.75 (m, 4H, $ArOCH_2CHCH_2$, and m, 4H, $ArOCH_2CHCH_2$), 3.65 (t, 4H, *J* 7.2, OCH_2CH_2), 3.80 and 3.75 (ABq, 8H, *J* 14.5, $ArCH_2Ar$), 3.45–3.40 (m, 24H, NCH_3), 1.80 (st, 4H, *J* 7.3, $ArOCH_2CH_2$), 1.05 (t, 6H, *J* 7.4, CH_2CH_3); δ_C 197.5, 197.0 (s, C=S), 78.5, 77.8 [t, $OCH_2C(S)$], 77.0 (t, $ArOCH_2CHCH_2$), 74.3 (t, $ArOCH_2CHCH_2$), 72.2 (t, $ArOCH_2CH_2CH_3$), 70.3 ($ArOCH_2CHCH_2$), 44.5, 42.2 (q, NCH_3), 35.5 (t, $ArCH_2Ar$), 23.8 (t, OCH_2CH_2), 10.6 (q, CH_2CH_3); FAB MS spectrum (NBA), *m/z* 1061.5 [M^+, calc. 1061.5]. Anal. Calcd. for $C_{56}H_{76}N_4O_8S_4$: 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, $K_{i,j}^{pot}$, 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.

Acknowledgements

We thank B. Myrzinska (Warsaw) for having carried out some of the CHEMFET measurements. The Technology Foundation (STW), Technical Science Branch of the Netherlands Organization for Scientific Research (NWO) is gratefully acknowledged for financial support.

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Paper 6/08063D
Received 28*th November* 1996
Accepted 6*th March* 1997