Molecular Design of Calixarene

Part 4

Synthesis of Novel Double-Armed *p*-(*tert*-Butyl)calix[4]arene-Derived Amides and Their Lead(II)(Pb^{2+})-Selective-Electrode Properties

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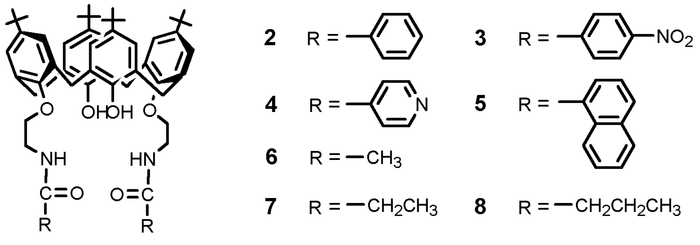
A series of novel double-armed *p*-(*tert*-butyl)calix[4]arenes, carrying benzoylamido, 4-nitrobenzoylamido, isonicotinamido, α-naphthamido, acetamido, propionamido, or butyramido groups (see **2**–**8**, resp.) were synthesized in 80–86% yield by the reaction of the lower-rim 1,3-bis(aminoethoxy)-substituted calix[4]arenediol **1** with the corresponding acylating agents. Their structures were established by elemental analysis, mass, IR, UV, and ^{1}H-NMR spectroscopy. Ion-selective electrodes (ISEs) for Pb^{2+}, carrying **2**–**8** in a PVC membrane as neutral ionophore, were prepared, and their selectivity coefficients for Pb^{2+} ($K^{pot}_{Pb,M}$) were determined against other heavy-metal ions, alkali and alkaline earth metal ions, and ammonium ions by means of the separate-solution method. The results obtained indicated that the electrodes based on the calix[4]arene-derived amides **2**–**8** as the neutral ionophores were all Pb^{2+} selective and exhibited almost theoretical *Nernstian* slopes, except for **3** and **4**. Typically, the Pb^{2+}-selective electrode based on **6**–**8** exhibited almost *Nernstian* slopes for Pb^{2+} over a relatively wide concentration range and had a fast response time as well as a long lifetime, although the silver ion interfered strongly. These ISEs based on **6**–**8** showed a relatively good Pb^{2+} selectivity against most of the interfering cations examined, except for Ag^+. The effect of the side-arm functions of calix[4]arene derivatives **2**–**8** on the *Nernstian* slopes and on the selectivity coefficients for Pb^{2+} obtained with the Pb^{2+} ISEs based on **2**–**8** is discussed.

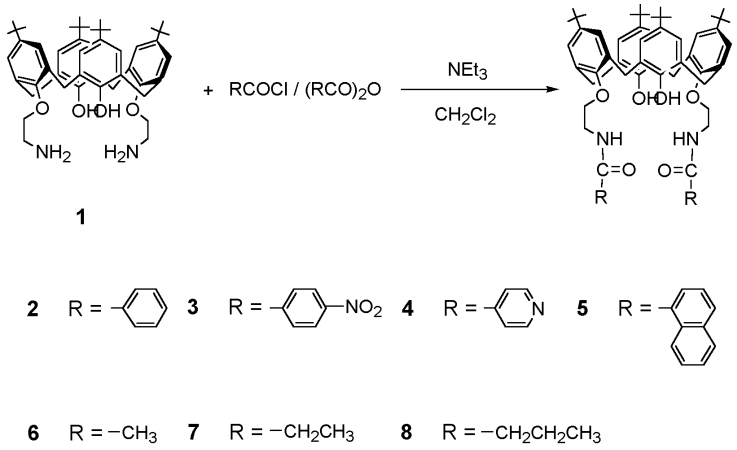
Introduction. – It is well known that calixarenes and their derivatives can be taken as receptors to recognize a wide variety of ions or inorganic and organic guest molecules, forming host-guest or supramolecular complexes, and that their efficiency and selectivity in ion/molecule binding depends not only on the ring size of the calixarenes, but also on the nature of the binding groups attached to the calixarenes [1–4]. Therefore, a great deal of effort has been devoted to the design and syntheses of calixarene derivatives in order to alter the original ion/molecule binding ability and selectivity and to expand the scope of utilization in various areas of science and technology [5–9]. One of the successful applications of calixarenes is in the field of ion-selective electrodes (ISEs) [10–16]. Indeed, some calixarene derivatives have been successfully employed in ion-selective electrodes (ISEs) that exhibit good *Nernstian* responses and selectivities for a variety of cations. Unfortunately, studies of Pb^{2+}-selective electrodes based on calixarene derivatives have scarcely been undertaken so far [17–19], although the importance of Pb^{2+}-selective electrodes for the detection of the lead level of environmental pollutants has generated increasing interest [20–26]. To the best of our knowledge, the lower-rim derivatives of calix[4]arene containing amide podands can selectively bind alkali, alkaline earth, silver, and lanthanides ions [27–29], but their complexation behavior with transition-metal ions remains unexplored. These studies prompted us to design and synthesize a series of novel calixarene-derived amides and to investigate their Pb^{2+}-selective electrode properties.

In the present study, we wish to report the syntheses and characterization of novel double-armed calix[4]arene-derived amides **2**–**8** and their Pb^{2+}-selective electrode properties. Also selectivity coefficients for Pb^{2+} ($K^{\mathrm{pot}}_{\mathrm{Pb,M}}$) against other heavy-metal ions, alkali and alkaline earth metal ions, and ammonium ion were determined by the separate-solution method [30], which will serve our further understanding of the Pb^{2+}-selective electrodes, a little investigated area of calixarenes chemistry. Another point of interest is to examine the substituent effects of the calix[4]arene-derived amides **2**–**8** on the *Nernstian* slopes and on the selectivity coefficients for Pb^{2+} obtained with the Pb^{2+} ISEs based on **2**–**8**.



Results and Discussion. – *Synthesis of Calix[4]arene-Derived Amides.* Acid chlorides or acid anhydrides were chosen as acylating agents to introduce the desired acyl groups at the lower rim of 1,3-distally bis(2-aminoethoxy)-substituted *p*-(*tert*-butyl)calix[4]arenediol **1**; thus, in dry CH_2Cl_2 with Et_3N as catalyst, the calix[4]arene-derived amides **2**–**8** were obtained in high yields (*Scheme*). The constitutions of **2**–**8** were established by their ^{1}H-NMR and FAB-MS data and elemental analysis, and also confirmed by the amide-group absorption in the FT-IR spectra. All the amides **2**–**8** had the cone conformation, which was determined by ^{1}H-NMR (*s* for ^{t}Bu and *AB* '*q*' for bridging CH_2 of the calixarene skeleton [31]).

Scheme



Lead-Selective Electrodes. To investigate the suitability of the novel double-armed calix[4]arene-derived amides **2**–**8** as lead-ion carriers in PVC membranes, seven different membrane electrodes were prepared with the same composition of PVC as the support, 2-nitrophenyl octyl ether (*o*-NPOE) as the membrane solvent, and a calix[4]arene-derived amide as the ionophore. The membranes also contained a small amount of potassium tetrakis(4-chlorophenyl)borate (KTClPB) for the purpose of reducing membrane resistance and suppressing permeation of counter anions in the aqueous phase into the membrane phase, thus allowing to obtain reproducible and stable electrical signals. On the other hand, the internal solution of 10^{-3} M $Pb(NO_3)_2$ and $5 \cdot 10^{-2}$ M ethylenediaminetetraacetic acid disodium salt (Na_2(edta)) was applied to improve the linear *Nernstian* response range and to lower the detection limit [21–22]. The responses of the electrodes were tested initially in $Pb(NO_3)_2$ solution in the concentration range from 10^{-8} to 10^{-1} M to ensure that the electrodes were working. The detailed results from three replicate studies are illustrated in the *Table*.

Table. *Properties of* Pb^{2+}*-Selective Electrodes Based on a Membrane Containing PVC* (32.9 wt.-%), o-*NPOE* (65.8 wt.-%), *Potassium Tetrakis(4-chlorophenyl)borate* (KTClPB; 50 mol-% rel. to the calix[4]arene-derived amide), *and Calix[4]arene-Derived Amide* (1 wt.-%)

Carrier	Response slope [mV/decade]	Linear range [M]	Detection limit [M]	Response time [s]	Electrode lifetime [days]
2	27.1	10^{-6}–10^{-1}	$10^{-6.5}$	< 10	60
3	24.2	10^{-5}–10^{-1}	$10^{-5.9}$	< 15	60
4	24.5	10^{-6}–10^{-2}	$10^{-6.2}$	< 15	60
5	29.8	10^{-5}–10^{-1}	$10^{-5.7}$	< 15	60
6	28.5	10^{-7}–10^{-1}	$10^{-7.2}$	< 10	60
7	28.4	10^{-6}–10^{-1}	$10^{-6.2}$	< 10	60
8	28.6	10^{-6}–10^{-1}	$10^{-6.3}$	< 10	60

As can be seen from the *Table*, the lead response functions of ISEs based on the novel double-armed calix[4]arene derived amides **2**–**8**, except for **3** and **4**, exhibited almost theoretical *Nernstian* slopes, as expected for a divalent cation. The different response characteristics of Pb^{2+} for these ligands as lead-ion carriers in the PVC membrane may be ascribed to the diverse side-arms functions attached to the lower rims of the calix[4]arene platform, resulting in different binding abilities upon complexation with Pb^{2+}. It is anticipated that the linear range and detection limit could be improved by adapting the composition of the sensor's inner filling solution, as described in the literature [21–22]. The response time was found to be less than 15 s over the range of activities and was probably limited by the rate of stirring during spiking experiments. On the whole, the Pb^{2+}-selective electrodes based on **6**–**8**, which were employed independently as carrier, exhibited almost theoretical *Nernstian* slopes for Pb^{2+} over the concentration range 10^{-6}–10^{-1} M, with a relatively fast response time of *ca.* 10 s, with a relatively good selectivity against all other ions except for Ag^+, and with a long lifetime of about two months during which no considerable divergence in potential occurred. Thus, these electrodes will have useful practical applications such as in electroplating industries, environmental monitoring, waste-water analysis, and so on.

Pb^{2+} Selectivity. The Pb^{2+} selectivities of the calix[4]arene-derived amides **2**–**8** were evaluated by the potentiometric selectivity coefficients ($K^{\mathrm{pot}}_{\mathrm{Pb,M}}$) determined for polymer

membranes containing these ionophores. The potentiometric selectivity coefficients for Pb^{2+}, which were determined by the separate-solution method in 0.01M nitrate solutions of Ag^+, Na^+, K^+, NH_4^+, Ca^{2+}, Mg^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and Cd^{2+} buffered to pH 5.0 with a magnesium acetate buffer, are illustrated in the *Figure*. The selectivity coefficient $K^{pot}_{Pb,M}$ represents the preference of the ISE (or PVC membrane) containing **2**–**8** for Pb^{2+} over the other cations. Thus, the coefficient $K^{pot}_{Pb,M}$ defines the ability of an ISE (or membrane) to distinguish different ions in the same solution. The smaller the $K^{pot}_{Pb,M}$ value, the greater the electrode preference for the primary ion (I^+) over the interfering ion (M^{n+}) [32].

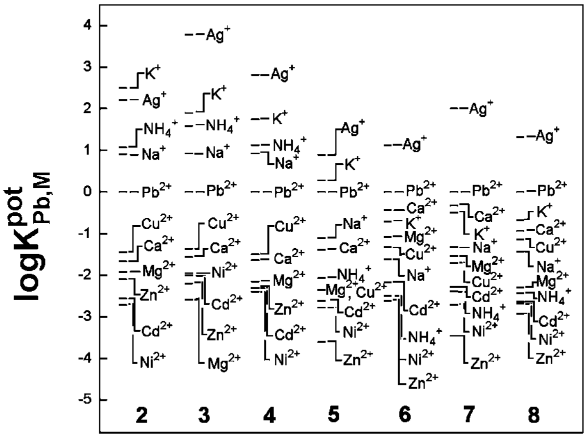


Figure. *Potentiometric selectivity coefficients* (log $K^{pot}_{Pb,M}$)*, determined by the separate-solution method for the PVC membranes containing one of the ionophore*s **2**–**8**, o-*NPOE, and KTClPB*

It is well known that the selectivity of ISEs depends not only on the membrane composition and the properties of the plasticizer employed, but also significantly on the nature of the ionophore used. Thus, the Pb^{2+} selectivity of the same membrane composition is mainly influenced by several factors, including the relative size of the cavity of the calixarene and the diameter of the cation, the surface charge density, the structural rigidity of the calixarene, the spatial arrangement of the donor atoms, the size of the three-dimensional cavity induced by the double-armed substituents attached to the lower rim of the calixarene platform, and so on. As can be seen from the *Figure*, the strongest interferent for Pb^{2+}-ISEs based on **2**–**8** is the Ag^+ ion; this is accounted for by the Ag^+ radius of 1.26 Å, which is nearest to that of Pb^{2+} (1.20 Å) and allows the Ag^+ ion to be fitted inside the pseudo-cavity formed by the carbonyl and phenolic O-atoms of **2**–**8**. Also, the selectivity coefficients $\log K^{pot}_{Pb,K} > 0$ for **2**–**5** and $\log K^{pot}_{Pb,Na^+} > 0$ and $\log K^{pot}_{Pb,NH_4^+} > 0$ for **2**–**4** obviously imply that the corresponding ionophores are more responsive to K^+, Na^+, and NH_4^+ than to Pb^{2+}, which is mainly ascribed to the slightly larger ionic radii of K^+ (1.33 Å), Na^+ (1.02 Å), and NH_4^+ (1.43 Å) compared to that of Pb^{2+} (1.20 Å) allowing a better match with the pseudo-cavity formed by the side arms of the calix[4]arene. Therefore, these electrodes can be used as a lead sensor only when the concentrations of K^+, Na^+, or NH_4^+ are less than that of Pb^{2+} in the sample. Fortunately, ionophores **6**–**8** give a relatively good selectivity for Pb^{2+} against all other ions, except for Ag^+, which may be related to the flexible aliphatic side arms at the calix[4]arene disfavoring the complexation on the interfering ions. Thus, Pb^{2+}-ISEs based on **6**–**8** will be suitable for most applications.

In line with the results obtained from the experiments and the free-energy-perturbation (FEP) simulations [28–29], we may postulate that the properties of *Nernstian* responses and the Pb^{2+} selectivity of the ISEs based on **2**–**8** result from the ability of these ionophores to discriminate various cations by the involvement of differently substituted side-arm functions at the lower rim of the calix[4]arene platform; these different side-arm functions lead to significant differences in the conformation of the chelating chains and create the hydrophilic pseudo-cavity allowing capture of metal ions, and to different binding properties of the carbonyl groups that wrap around the complexed cation.

Experimental Part

General. Starting materials were commercially available unless otherwise noted. The 1,3-distally bis(2-aminoethoxy)-substituted *p*-(*tert*-butyl)calix[4]arenediol **1** was prepared according to the literature procedures [33]. High-molecular-weight poly(vinyl chloride) (PVC), potassium tetrakis(4-chlorophenylborate) (KTClPB), 2-nitrophenyl octyl ether(*o*-NPOE) were purchased in the highest purity available from *Fluka*, Buchs, Switzerland. Anal. reagent-grade tetrahydrofuran (THF) (freshly distilled before use), $CHCl_3$, ethylenediaminetetraacetic acid disodium salt and nitrates of silver, sodium, potassium, ammonium, calcium, magnesium, cadmium, copper, nickel, zinc, lead, and mercury were supplied by *Tianjin Chemical Reagent Factory.* All solns. were prepared with distilled deionized H_2O.

Potential measurements: *PXD-12* meter made in China. M.p.: *XT-4* apparatus; uncorrected. IR Spectra: *Bio-Rad FTS-135* instrument; $\tilde{\nu}$ in cm^{-1}. ^1H-NMR Spectra: *Bruker AC-P200* instrument at 200 MHz; $CDCl_3$ soln.; δ in ppm rel. to $SiMe_4$ as an internal reference, J in Hz. FAB-MS: *VG ZAB-HS* apparatus; in m/z. Elemental analyses: *Perkin-Elmer 2400C* instrument.

Calix[4]arene-Derived Amides. A sample of 1,3-distally bis(2-aminoethoxy)-substituted *p*-(*tert*-butyl)calix[4]arenediol **1** (0.27 mmol) was added to a mixture of the acid chloride or acid anhydrides (0.54 mmol) and Et_3N (0.6 ml) in dry CH_2Cl_2 (10 ml) under stirring. The mixture was continuously stirred at r.t. for 4 h, then dil. $NaHCO_3$ soln. was added to stop the reaction. The org. layer was washed to neutrality, dried (Na_2SO_4), and evaporated. The residue was recrystallized from MeOH to give the white pure calix[4]arene-derived amide in high yield.

N,N′*-{[5,11,17,23-Tetra(*tert*-butyl)-26,28-dihydroxycalix[4]arene-25,27-diyl]bis(oxyethane-2,1-diyl)}bis[benzamide]*1)) (**2**): Yield 86%: M.p. > 300°. FT-IR (KBr): 3366.3, 3060.6, 2960.0, 2870.0, 1645.5, 1538.2, 1485.8, 1362.3, 1300.1, 1199.8, 1048.5, 872.3, 711.3. ^1H-NMR: 8.30 (*s*, 2 OH); 8.23 (*t*, 2 NH); 7.94 (*d*, $J = 7.4$, 4 arom. H); 7.31–7.24 (*m*, 6 arom. H); 7.03 (*s*, 4 arom. H); 6.96 (*s*, 4 arom. H); 4.19 (*d*, $J = 12.4$, 4 H, ArCH_2Ar); 4.00 (*t*, $J = 5.0$, 4 H, CH_2O); 3.59 (br., 4 H, CH_2N); 3.41 (*d*, $J = 12.4$, 4 H, ArCH_2Ar); 1.28 (*s*, 18 H, ^{t}Bu); 1.08 (*s*, 18 H, ^{t}Bu). FAB-MS: 943.7 (M^+). Anal. calc. for $C_{62}H_{74}N_2O_6$: C 78.95, H 7.91, N 2.97; found: C 78.58, H 7.49, N 3.16.

N,N′*-{[5,11,17,23-Tetra(*tert*-butyl)-26,28-dihydroxycalix[4]arene-25,27-diyl]bis(oxyethane-2,1-diyl)}bis[4-nitrobenzamide]*1)) (**3**). Yield 90%. M.p. 277° (dec.). FT-IR (KBr): 3430.3, 3049.0, 2961.8, 2870.2, 1645.8, 1602.1, 1528.8, 1485.4, 1347.8, 1300.6, 1200.6, 1047.7, 870.5, 719.5. ^1H-NMR: 8.55 (*t*, 2 NH); 8.31 (*s*, 2 OH); 8.13 (*s*, 8 arom. H); 7.07 (*s*, 4 arom. H); 6.99 (*s*, 4 arom. H); 4.12 (*d*, $J = 12.4$, 4 H, ArCH_2Ar); 4.02 (br., 4 H, CH_2O); 3.62 (*m*, 4 H, CH_2N); 3.38 (*d*, $J = 12.4$, 4 H, ArCH_2Ar); 1.26 (*s*, 18 H, ^{t}Bu); 1.09 (*s*, 18 H, ^{t}Bu). FAB-MS: 1033.8 (M^+). Anal. calc. for $C_{62}H_{72}N_4O_{10} \cdot H_2O$: C 70.84, H 7.10, N 5.33; found: C 71.09, H 7.14, N 5.66.

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1) The systematic name of calix[4]arene is *pentacyclo[19.3.1.1*^{3,7}*.1*^{9,13}*.1*^{15,19}*]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene.*

N,N′-*{[5,11,17,23-Tetra(*tert*-butyl)-26,28-dihydroxycalix[4]arene-25,27-diyl]bis(oxyethane-2,1-diyl)}bis-[pyridine-4-carboxamide]*[1]) (**4**): Yield 84%. M.p. 268 – 270°. FT-IR (KBr): 3457.2, 3362.4, 3046.0, 2958.7, 2906.2, 2869.4, 1667.0, 1644.4, 1592.6, 1547.3, 1484.2, 1418.9, 1361.5, 1301.1, 1198.9, 1121.9, 1048.7, 920.7, 871.6. ^{1}H-NMR: 9.57 (*s*, 2 OH); 9.06 (*t*, 2 NH); 8.67 (*d*, $J = 5.6$, 4 H, Py); 7.49 (*d*, $J = 5.6$, 4 H, Py); 6.99 (*s*, 4 arom. H); 6.78 (*s*, 4 arom. H); 4.23 (*d*, $J = 12.8$, 4 H, ArCH_2Ar); 4.08 (br., 4 H, CH_2O); 3.92 (*m*, 4 H, CH_2N); 3.33 (*d*, $J = 12.8$, 4 H, ArCH_2Ar); 1.23 (*s*, 18 H, ^{t}Bu); 0.93 (*s*, 18 H, ^{t}Bu). FAB-MS: 945.8 (M^+). Anal. calc. for $C_{60}H_{72}N_4O_6$: C 76.24, H 7.68, N 5.93; found: C 76.15, H 7.46, N 5.85.

N,N′-*{[5,11,17,23-Tetra(*tert*-butyl)-26,28-dihydroxycalix[4]arene-25,27-diyl]bis(oxyethane-2,1-diyl)}bis-[naphthalene-1-carboxamide]*[1]) (**5**): Yield 82%. M.p. 155 – 157°. FT-IR (KBr): 3412.0, 3049.7, 2959.7, 2906.2, 2869.3, 1656.4, 1593.2, 1484.9, 1362.7, 1299.1, 1199.7, 1050.9, 871.5, 781.6. ^{1}H-NMR: (*s*, 2 OH); 8.05 (*t*, 2 NH); 7.78 – 7.40 (*m*, 14 arom. H); 6.92 (*s*, 4 arom. H); 6.83 (*s*, 4 arom. H); 3.91 (*d*, $J = 12.4$, 4 H, ArCH_2Ar); 3.80 (br., 4 H, CH_2O); 3.39 (*m*, 4 H, CH_2N); 3.26 (*d*, $J = 12.4$, 4 H, ArCH_2Ar); 1.22 (*s*, 18 H, ^{t}Bu); 1.02 (*s*, 18 H, ^{t}Bu). FAB-MS: 1065.4 ($[M + \mathrm{Na}]^+$). Anal. calc. for $C_{70}H_{78}N_2O_6$: C 80.62, H 7.49, N 2.69; found: C 80.92, H 7.32, N 2.60.

N,N′-*{[5,11,17,23-Tetra(*tert*-butyl)-26,28-dihydroxycalix[4]arene-25,27-diyl]bis(oxyethane-2,1-diyl)}bis-[acetamide]*[1]) (**6**): Yield 86%. M.p. 249 – 251°. FT-IR (KBr): 3317.4, 3047.9, 2959.1, 2906.2, 2869.3, 1659.7, 1548.9, 1484.4, 1464.4, 1362.6, 1297.7, 1201.1, 872.1, 780.5. ^{1}H-NMR: 8.66 (*s*, 2 OH); 8.14 (*t*, 2 NH); 7.05 (*s*, 4 arom. H), 7.01 (*s*, 4 arom. H); 4.25 (*d*, $J = 12.8$, 4 H, ArCH_2Ar); 4.08 (*t*, $J = 5.4$, 4 H, CH_2O); 3.89 (*m*, 4 H, CH_2N); 3.43 (*d*, $J = 12.8$, 4 H, ArCH_2Ar); 2.09 (*s*, 2 MeCO); 1.22 (*s*, 18 H, ^{t}Bu); 1.11 (*s*, 18 H, ^{t}Bu). FAB-MS: 819.2 ($[M + 1]^+$). Anal. calc. for $C_{52}H_{70}N_2O_6$: C 76.25, H 8.61; N 3.42; found: C 76.05, H 8.40, N 3.36.

N,N′-*{[5,11,17,23-Tetra(*tert*-butyl)-26,28-dihydroxycalix[4]arene-25,27-diyl]bis(oxyethane-2,1-diyl)}bis[propanamide]*[1]) (**7**): Yield 82%. M.p. 216 – 218°. FT-IR (KBr): 3320.9, 3047.6, 2959.6, 2906.2, 2870.1, 1660.3, 1547.7, 1484.3, 1464.1, 1361.9, 1299.5, 1200.9, 1124.2, 1051.9, 923.6, 872.0. ^{1}H-NMR: 8.76 (*s*, 2 OH); 8.10 (*t*, 2 NH); 7.04 (*s*, 4 arom. H); 7.02 (*s*, 4 arom. H); 4.22 (*d*, $J = 12.6$, 4 H, ArCH_2Ar); 4.05 (*t*, $J = 5.2$, 4 H, CH_2O); 3.82 (*m*, 4 H, CH_2N); 3.42 (*d*, $J = 12.6$, 4 H, ArCH_2Ar); 2.28 (*q*, 2 MeCH_2CO); 1.22 (*s*, 18 H, ^{t}Bu); 1.17 (*t*, 2 *Me*CH_2CO); 1.12 (*s*, 18 H, ^{t}Bu). FAB-MS: 847.1 ($[M + 1]^+$). Anal. calc. for $C_{54}H_{74}N_2O_6$: C 76.56, H 8.80, N 3.31; found: C 76.41, H 8.50, N 3.13.

N,N′-*{[5,11,17,23-Tetra(*tert*-butyl)-26,28-dihydroxycalix[4]arene-25,27diyl]bis(oxyethane-2,1-diyl)}bis[butanamide]*[1]) (**8**): Yield 80%. M.p. 235 – 237°. FT-IR (KBr): 3310.6, 3049.2, 2959.1, 2906.2, 2870.5, 1652.2, 1548.2, 1484.7, 1464.5, 1361.4, 1299.0, 1198.2, 1124.6, 1054.5, 872.7. ^{1}H-NMR: 8.69 (*s*, 2 OH); 8.14 (*t*, 2 NH); 7.04 (*s*, 4 arom. H); 7.01 (*s*, 4 arom. H); 4.25 (*d*, $J = 12.8$, 4 H, ArCH_2Ar); 4.08 (*t*, $J = 5.4$, 4 H, OCH_2); 3.89 (*m*, 4 H, CH_2N); 3.43 (*d*, $J = 12.8$, 4 H, ArCH_2Ar); 2.27 (*t*, $J = 7.8$, 4 H, CH_2); 1.71 (*m*, 4 H, CH_2); 1.22 (*s*, 18 H, ^{t}Bu); 1.11 (*s*, 18 H, ^{t}Bu); 0.91 (*t*, $J = 7.8$, 2 Me). FAB-MS: 875.1 (M^+). Anal. calc. for $C_{56}H_{78}N_2O_6$: C 76.85, H 8.98, N 3.20; found: C 76.80, H 9.05, N 2.94.

Membrane and Electrode Preparation. The typical procedure for membrane preparation is as follows: Poly(vinyl chloride) (PVC) (32.9 wt.-%), 2-nitrophenyl octyl ether (*o*-NPOE) (65.8 wt.-%), potassium tetrakis(4-chlorophenyl)borate (KTClPB) (50 mol-% rel. to the calix[4]arene-derived amide), and calix[4]-arene-derived amide (1 wt.-%) were dissolved in 5 ml of THF. This soln. was poured into a flat-bottomed *Petri* dish of 32 mm inner diameter and 50 mm height. Gradual evaporation of the solvent at r.t. gave a transparent, flexible membrane of *ca.* 0.3 mm thickness. A disk of 7 mm in diameter was cut from the PVC membrane and incorporated into PVC tube tip with 5% THF/H_2O. After injection of 0.001M aq. $Pb(NO_3)_2$ soln. and $5 \cdot 10^{-2}$ M ethylenediaminetetraacetic acid disodium salt (Na_2(edta)) as the internal soln., the electrode was conditioned by soaking in 0.001M aq. $Pb(NO_3)_2$ soln. for 48 h. The composition of the electrochemical cell is given as $Hg_2Cl_2 \cdot Hg$ | 3M KCl | 1M KNO_3 | sample || PVC membrane || internal soln. || Ag · AgCl.

EMF Measurements. The performance of the electrodes was investigated by measuring their potential in $Pb(NO_3)_2$ solns. prepared in the concentration range 10^{-8} – 10^{-1} M by serial dilution at a constant pH of 5.0. All solns. were freshly prepared by dilution from the stock standard 10^{-1} M $Pb(NO_3)_2$ soln. with doubly distilled H_2O buffered to pH 5.0 with a magnesium acetate buffer. All EMF (electromotive force) measurements were performed at the electrode equilibration intervals of 2 min and at constant temp. (25 ± 0.1°) with a *PXD-12* potentiometer. Sample solns. were magnetically stirred and kept in a thermostatic water bath.

Selectivity Coefficients. The selectivity of these electrodes for Pb^{2+} ion against a series of monovalent and divalent cations was estimated by the separate-solution method in 0.01M nitrate soln. of Ag^+, Na^+, K^+, NH_4^+, Ca^{2+}, Mg^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and Cd^{2+} buffered to pH 5.0 with a magnesium acetate buffer. The potentiometric selectivity coefficient $K^{\mathrm{pot}}_{\mathrm{Pb,M}}$ determined here are defined by *Eqn. 1* where E°_{Pb} and E°_{M} = potential by extrapolating the response function for Pb^{2+} and M^{n+} resp., to 1M activity, E_{Pb} and E_{M} = experimentally observed potentials, R = gas constant, T = thermodynamic temperature in K, F = *Faraday* constant, a_{Pb} = Pb^{2+} activity,

a_M = activity of the interfering cation, and n = charge of the interfering cation. Ion activities were estimated by the *Debye-Hückel* equation [34].

$$K^{\mathrm{pot}}_{\mathrm{Pb,M}} = \frac{a_{\mathrm{Pb}}}{a_{\mathrm{M}}^{2/n}} \exp\left[\frac{2F(E_{\mathrm{M}} - E_{\mathrm{Pb}})}{RT}\right] = \exp\left[\frac{2F(E^{\circ}_{\mathrm{M}} - E^{\circ}_{\mathrm{Pb}})}{RT}\right] \quad (1)$$

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