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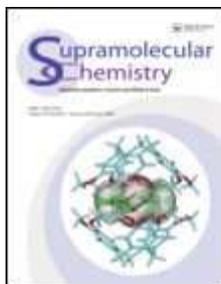
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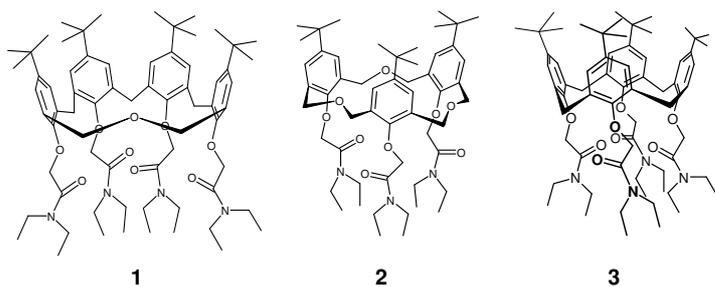
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**Ion-Selective Electrodes Based on
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For Peer Review Only

Abstract

The diethyl amides of *p-tert*-butyldihomooxacalix[4]arene (**1**), *p-tert*-butylhexahomotrioxacalix[3]arene (**2**) and *p-tert*-butylcalix[4]arene (**3**) were used as active materials in ion-selective membrane electrodes (ISE) to check the detection of different kinds of cations (Na^+ , K^+ , Cs^+ , Mg^{2+} , Ca^{2+} , Mn^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , Pb^{2+} and TMA^+). The electrode characteristics and selectivity coefficients were determined and compared. Optimisation of the PVC membrane composition was achieved using three different plasticizers (DEHA, *o*-NPOE or BBPA). Amide **3** shows selectivity for Na^+ , whereas compounds **1** and **2** exhibit the highest selectivity for Pb^{2+} among all the studied cations. The X-ray crystal structure of dihomooxacalix[4]arene tetra(diethyl)amide **1** was determined revealing it to be in the cone conformation.

Keywords: Calix[4]arene, Homooxacalixarenes, Amide derivatives, Ion-selective electrodes (ISE), Pb(II) ionophores, X-ray crystallographic structure

Introduction

Over the past three decades research in calixarene chemistry has been investigated with considerable amount of details [1, 2]. The successes in calixarene research are mainly due to their relatively easy functionalization on both upper and lower rims to give a large variety of derivatives.

In the field of host-guest chemistry, chemical sensors [3, 4] are without doubt one of the most developed applications of the calixarene molecules. In particular, the use of neutral ionophores containing carbonyl groups at the lower rim for preparing ion-selective electrodes (ISEs) has been largely investigated, since the initial work of Diamond and McKervey [5]. Among these ionophores, functionalized calixarenes with ester groups have been the most tested, but studies with ketone and amide groups have also been performed. Due to the biological importance of ions such as Na^+ , K^+ , Mg^{2+} and Ca^{2+} , those studies have been mainly focused on these kinds of cations, although ion-selective electrodes for cations other than the alkali and alkaline earth, such as transition and heavy metal cations, have also been assessed. The harmful

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3 impact that toxic metal ions such as cadmium, mercury and lead can provoke on environmental
4 quality and consequently on human health, can explain the increasing interest in finding effective
5 sensors for these metal ions. For example, the monitoring of lead in drinking water is important
6 to ensure that its concentration remains below the acceptable level. This cation forms complexes
7 with hard oxygen donor atoms as well as with nitrogen and sulphur that are considered to be
8 softer bases. Thus, a variety of compounds have been tested so far as active materials for Pb-ion-
9 selective electrodes.
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12 Following our previous studies on ion-selective electrodes based on calix[4]arene amide
13 derivatives [6, 7] we have now extended them to homooxacalixarenes [8], namely
14 dihomooxacalix[4]arene and hexahomotrioxacalix[3]arene amide derivatives [9, 10]. These are
15 calixarene analogues in which one or all of the CH₂ bridges have been replaced by CH₂OCH₂
16 groups. They are more flexible molecules than calix[4]arenes, but can still possess a *cone*
17 conformation, the most appropriate for complexation, being potential hosts for the larger cations,
18 mainly the dihomooxacalix[4]arene derivatives.
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21 In this paper the performance of *p-tert*-butyldihomooxacalix[4]arene tetra(diethyl)amide
22 (**1**) and *p-tert*-butylhexahomotrioxacalix[3]arene tri(diethyl)amide (**2**) are tested as ion-selective
23 membrane electrodes towards a large variety of cations, including alkali, alkaline earth, transition
24 and heavy metals, and using three different plasticizers (DEHA, *o*-NPOE or BBPA) in the
25 membranes. The *p-tert*-butylcalix[4]arene tetra(diethyl)amide (**3**) was also studied in this work,
26 and the results of the three derivatives (Fig. 1) are compared and discussed in terms of size and
27 conformational effects. The X-ray crystal structure of dihomooxacalix[4]arene tetraamide **1** was
28 determined.
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30 Results and discussion

31 *X-ray structure determination*

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33 The X-ray single crystal structural analysis revealed that dihomooxacalix[4]arene (diethyl)amide
34 **1** adopts a *pinched cone* conformation with the *tert*-butyl groups pitched away from the cavity
35 (Fig. 2). The conformation of compound **1** was analyzed by calculation of the dihedral angles
36 between the phenyl rings A, B, C, D [11]. Rings A and C are almost parallel to each other
37 (dihedral angle is only 5.15(18)°), whereas the rings B and D are almost perpendicular
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(75.75(9)°). Notably, the angle is much less than the commonly observed value of 90° for regular calix[4]arenes. The presence of the oxygen bridge (O9) is the most probable cause of this deformation. Hydrogen bonds or interactions with the solvent molecules are not observed.

Attempts to obtain crystals of the complexes metal-ligand, especially with lead, were unsuccessful.

Potentiometric Studies – ISE

The ionophoric properties of di(ethyl)amides **1**, **2** and **3** were studied by using them in ion-selective membrane electrodes (ISE). All these compounds had been synthesised according to the literature and obtained in a cone conformation [12, 13, 14]. Due to the high lipophilicity of the macrocyclic ligands possessing four (**1** and **3**) or three (**2**) *tert*-butyl groups, all the electrodes prepared were stable and long lasting. The potentiometric responses of these ISEs towards a variety of ions, including alkali (Na⁺, K⁺ and Cs⁺), alkaline earth (Mg²⁺ and Ca²⁺), transition (Mn²⁺, Cu²⁺, Zn²⁺) and heavy metals (Cd²⁺ and Pb²⁺), were measured. Among these cations with varying sizes, charges and nature, the strongest response was induced by the presence of Na⁺, K⁺ and Pb²⁺. This behaviour was expected, as the homooxa ligands are strong binders for those cations [9, 10], and it is known the high selectivity of calix[4]arene amides, like derivative **3**, for Na⁺ [15].

The electrode membrane was optimized using three different plasticizers: **bis(2-ethylhexyl) adipate** (DEHA), bis(2-butylpentyl) adipate (BBPA) and *o*-nitrophenyl octyl ether (NPOE). DEHA has a similar structure to BBPA, which in many cases is a good plasticizer for Na⁺-selective membrane electrodes (enhancing the Na⁺-response), whereas the Pb²⁺ cation usually prefers a more polar plasticizer such as NPOE. The membrane compositions and the characteristics of the electrodes are presented in Table 1 and illustrated in Figures 3 and 4.

In the case of homooxa di(ethyl)amides **1** and **2**, the data (Table 1) reveal that the use of DEHA as plasticizers gives the best results relative to both mono and divalent cations, as the slopes of the electrode responses are close to the Nernstian values (59.15 and 29.58 mV decade⁻¹, respectively). Comparison between the three calixarene based electrodes shows that homooxalixarenes **1** and **2** exhibit the best behaviour for Pb²⁺, while calix[4]arene amide **3** shows a preference for Na⁺ cations.

Potentiometric selectivities for the electrodes based on ionophores **1**, **2** and **3** in all membranes were determined by the Separate Solution Method (SSM) [16]. The selectivity coefficients expressed as $\log K_{M,X}^{\text{pot}}$ are presented in diagram form in Fig. 5. The selectivity coefficients for compound **1** are the best in PVC/NPOE membrane ($\log K_{\text{Pb,Na}}^{\text{pot}} = -2.5$). However, low upper detection limit (narrow linear range) and anionic response of this electrode (Table 1) suggest strong interaction of ligand **1** Pb(II) cation. The case of compound **2** is different. The selectivity coefficient for Pb/Na in less polar plasticizer are better ($\log K_{\text{Pb,Na}}^{\text{pot}} = -1.5$) than in PVC/NPOE membrane ($\log K_{\text{Pb,Na}}^{\text{pot}} = -0.3$). The analogous amide **3**, based on classical calix[4]arene is definitely sodium selective with selectivity coefficient $\log K_{\text{Na,Pb}}^{\text{pot}} = -3.3$.

Potentiometric selectivity coefficients reflect the ion-ligand complex formation constants directly in the membrane. The selectivity coefficients obtained for the electrodes with PVC/BBPA membranes were used to determination those constants, using the simple method proposed by Pretsch [17]. The values obtained are shown in Table 2.

The equilibrium constants are related to the estimated concentration of the species in the organic membrane phase and to the ions' activities in the aqueous phase, so they are not proper thermodynamic parameters. Values in Table 2 show that the interactions of dihomooxalix[4]arene amide **1** and of calix[4]arene amide **3** in PVC/BBPA membrane with Na^+ are of similar strength, whereas those with hexahomotrioxalix[3]arene amide **2** are weaker. This is probably due to its higher conformational flexibility. The replacement of the methylene bridges by dimethyleneoxa bridges in triamide **2** increases its flexibility. The ΔG^\ddagger barriers for conformational inversion in CDCl_3 are < 9 , 12.9 and 15.7 kcal mol^{-1} for the corresponding parent calixarenes of **2**, **1** and **3**, respectively [18]. Moreover, **2** possesses only three amide groups and consequently only six coordination sites are available to surround the cations, compared to the eight sites of the tetraamides. In the case of K^+ interactions, amide **1** exhibits the highest constant value, reflecting its larger cavity size, more suitable to accommodate a larger cation. These constants determined in the membrane for ligands **1** and **3**, although lower, follow the same selectivity trend observed in the 1:1 stability constants previously determined in methanol [9]. In the case of Pb^{2+} , triamide **2** shows the highest constant value closely followed by tetraamide **1**, whereas for **3** that value is approximately 2.5 log units lower. It seems that more important than the number of donating sites, it should be the conformational rearrangement that the pendant

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3 arms of the ligands can suffer upon complexation, to better accommodate that cation. However, it
4 is worthwhile pointing out that the coordination number of Pb^{2+} is 6 [19]. Thus, three phenolic
5 oxygen atoms and three carbonyl oxygen atoms should suffice for inclusion of that cation.
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9 The fact that plasticizers of different nature *i.e.* ether (NPOE) and ester (DEHA, BBPA)
10 induce different Pb^{2+} -selectivity in homooxalixarene amides **1** and **2** seems to suggest different
11 coordination types occur in the two membranes. The selectivity Pb^{2+}/Na^{+} of ligand **1** is better in
12 NPOE than in DEHA, which has also been observed for other calix[4]arenes. This suggests that
13 in ligand **1** the Pb^{2+} cation is complexed by the same type of oxygen atoms as in calix[4]arene **3**,
14 *i.e.* phenoxy and carbonyl oxygen atoms. By contrast, the selectivity Pb^{2+}/Na^{+} by ligand **2** in
15 NPOE is worse than in DEHA, which might suggest that Pb^{2+} cation is complexed in a different
16 part of the compound. Nevertheless, results previously obtained either by NMR or by molecular
17 mechanics / *ab initio* techniques for ligand **2** [10] and also with an analogous derivative [20],
18 indicate that the oxygen atoms of the $ArCH_2OCH_2Ar$ bridges do not participate in metal binding.
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30 Conclusions

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33 The performance of the ion-selective electrodes based on homooxalixarene amides **1** and **2** and
34 on calix[4]arene amide **3** indicated a high affinity of the homooxa ligands for the heavy metal
35 cation Pb^{2+} , whereas calix[4]arene **3** showed selectivity for Na^{+} . From the comparison between
36 the three plasticizers (DEHA, *o*-NPOE and BBPA) used in the PVC-membrane, it is clear that
37 their role is not negligible.
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42 The X-ray diffraction studies revealed a cone conformation for dihomooxalix[4]arene
43 tetra(diethyl)amide **1**, confirming that all three amides exist in the same conformer in the
44 electrode membranes.
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51 Experimental

52 *Crystallography*

Compound **1** (15 mg) was dissolved in the minimal amount of methylene chloride and treated with 1 mL of methanol. After several days transparent crystals, suitable for crystallography, were obtained.

The structure of **1** was determined by single crystal X-ray diffraction. The data were collected at 120 K on a KM4CCD diffractometer equipped with a Sapphire2 CCD detector. Enhanced X-ray Mo-K α radiation source with a graphite monochromator was used. The preliminary calculations were done using *CrysAlis* software package [11]. The structure was solved by direct methods and all non-hydrogen atoms were refined with anisotropic displacement parameters by full-matrix least squares procedure based on F^2 . All hydrogen atoms were refined using isotropic model with U_{iso} values fixed to be 1.5 times U_{eq} of C atoms for CH₃ or 1.2 times U_{eq} for CH₂ and CH groups. Refinement was carried out using *SHELXL-97* program package [21]. Ethyl group bound to N4 (labeled C63-C64) was refined as disordered over two positions with probabilities of 0.521(12) / 0.479(12).

Crystal data and structure refinement details for compound **1** are presented in Table 3.

Potentiometric studies

Membrane preparation and emf measurements

The membranes were prepared by dissolving about 4 mg of each ionophore, 60 mg of PVC, 120 mg of plasticizer (BBPA, DEHA or *o*-NPOE) and 0.4 mg of KTpCIPB salt with a lipophilic anion, about 184 mg in total, in 1.5 mL of dried and distilled THF. Each solution was poured into a glass ring (24 mm in diameter). After slow evaporation of the solvent overnight, several membranes of 7 mm diameter were cut from each mother membrane and were incorporated into Ag/AgCl electrode bodies of IS 561 type (Moeller S.A., Zurich). A double-junction reference electrode (Radelkis 0P0820P) and 1 M NH₄NO₃ solution in the bridge cell were used. The EMFs were measured at 20 °C using a Lawson Lab 16 EMF, multi-channel voltmeter. The electrodes were conditioned in 10⁻⁴ M HNO₃. The measurements were carried out in separate solutions of known cation concentrations starting from 10⁻⁸ to 10⁻¹ M. pH = 4 was adjusted and stabilised by addition of HNO₃. The measurements were carried using the cells of the type:

Ag|AgCl|1 M KCl|1 M NH₄NO₃| sample || membrane || 10⁻³ M MgCl₂, 10⁻⁴ M EDTA|AgCl|Ag

Determination of selectivity coefficients

The potentiometric response of the electrodes for a series of cations was studied using chlorides or nitrates. The selectivity coefficients ($\log K_{M,X}^{pot}$) were determined by the Separate Solution Method (SSM) and were calculated (equation 1) using the EMF values extrapolated from the characteristics of the electrodes studied to the cation 1 M concentration [16]:

$$\log K_{M,X}^{pot} = \frac{(E_X - E_M)z_M F}{2.303RT} + \left(1 - \frac{z_M}{z_X}\right) \log a_X$$

In eq. 1, M and X correspond to the primary and the interfering cations respectively, and z_M and z_X correspond to their charges.

Determination of complex formation constants in the electrode membrane

The values of the complex formation constants ($\log \beta$) for ionophores **1**, **2** and **3** in PVC/BBPA membranes were estimated by the method described by Pretsch *et al.* [17]. The composition of these membranes is given in Table 4. Tetramethylammonium cation (TMA^+) was used as a reference ion. The calculation is based on the assumption that the ionophores form stable 1:1 complexes with metal ions such as Na^+ , K^+ and Pb^{2+} . The values of the complex formation constants were calculated from the following equation:

$$\beta = \frac{K_{M,TMA}^{pot}(IE)}{K_{M,TMA}^{pot}(L)[L_T - R_T]} \quad (2)$$

where L_T is the total concentration of the ionophore within the membrane, R_T the total concentration of the lipophilic anionic site (KTpCIPB) in the membrane, $K_{M,TMA}^{pot}(IE)$ the selectivity coefficient for the membrane without ionophore, $K_{M,TMA}^{pot}(L)$ the selectivity coefficient for the membrane with ionophore (L) and $M = \text{Na}^+$, K^+ and Pb^{2+} .

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5 *Supplementary material available*

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7 Crystallographic data for the structure **1** reported in this paper have been deposited with the
8 Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 702250
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10 11 *Acknowledgements*

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17 Technology for X-ray crystal structure determination.
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21 22 23 24 **References**

- 25
26
27 (1) Gutsche, C. D. In *Calixarenes Revisited*; Stoddart, J. F., Ed.; The Royal Society of Chemistry:
28 Cambridge, 1998.
29
30 (2) *Calixarenes 2001*; Asfari, Z.; Böhmer, V.; Harrofield, J.; Vicens, J., Eds.; Kluwer Academic:
31 Dordrecht, 2001.
32
33 (3) Diamond, D.; McKervey, M. A. *Chem. Soc. Rev.* **1996**, 15–24.
34
35 (4) Cadogan, F.; Nolan, K.; Diamond, D. In *Calixarenes 2001*; Asfari, Z.; Böhmer, V.;
36 Harrofield, J.; Vicens, J., Eds.; Kluwer Academic: Dordrecht, 2001; pp 627–641.
37
38 (5) Diamond, D.; Svehla, G.; Seward, E. M.; McKervey, M. A. *Anal. Chim. Acta* **1988**, *204*, 223–
39 231.
40
41 (6) Bochenska, M.; Banach, R.; Zielinska, A.; Kravtsov, V. *J. Incl. Phenom. Macrocyclic Chem.*
42 **2001**, *39*, 219–228.
43
44 (7) Bochenska, M.; Lesinska, U. *Chem. Anal.* **2006**, *51*, 879–887.
45
46 (8) Masci, B. In *Calixarenes 2001*; Asfari, Z.; Böhmer, V.; Harrofield, J.; Vicens, J., Eds.;
47 Kluwer Academic: Dordrecht, 2001; pp 235–249.
48
49 (9) Marcos, P. M.; Félix, S.; Ascenso, J. R.; Segurado, M. A. P.; Pereira, J. L. C.; Khazaeli-Parsa,
50 P.; Hubscher-Bruder, V.; Arnaud-Neu, F. *New J. Chem.* **2004**, *28*, 748–755.
51
52 (10) Marcos, P. M.; Ascenso, J. R.; Cragg, P. J. *Supramol. Chem.* **2007**, *19*, 199–206.
53
54
55
56
57
58
59
60

- 1
2
3 (11) Oxford Diffraction, *CrysAlis CCD* and *CrysAlis RED*, Version 1.171 Oxford Diffraction
4 Ltd. Abington, Oxfordshire, England, **2005**.
5
6 (12) Félix, S.; Ascenso, J. R.; Lamartine, R.; Pereira, J. L. C. *Tetrahedron* **1999**, *55*, 8539–8546.
7
8 (13) (a) Matsumoto, T.; Nishio, S.; Takeshita, M.; Shinkai, S. *Tetrahedron* **1995**, *51*, 4647–4654.
9
10 (b) Cragg, P. J.; Drew, M. G. B.; Steed, J. W. *Supramol. Chem.* **1999**, *11*, 5–15.
11
12 (14) (a) A. Arduini, E. Ghidini, A. Pochini, R. Ungaro, G. Andreetti, G. Calestani and F.
13 Ugozzoli, *J. Incl. Phenom.* **1988**, *6*, 119–134. (b) Lesinska, U.; Bochenska, M. *Synthesis* **2006**,
14 *16*, 2671–2676.
15
16 (15) Arnaud-Neu, F.; Barrett, G.; Fanni, S.; Marrs, D.; McGregor, W.; McKervey, M. A.;
17 Schwing-Weill, M. J.; Vetrogon, V.; Wechsler, S. *J. Chem. Soc., Perkin Trans.2* **1995**, 453–461.
18
19 (16) (a) Bakker, E.; Pretsch, E.; Buhlmann, P. *Anal. Chem.* **2000**, *72*, 1127–1133. (b) Umezawa,
20 Y.; Buhlmann, P.; Umezawa, K.; Tohda, K.; Amemiya, S. *Pure Appl. Chem.* **2000**, *72*, 1851–
21 2082.
22
23 (17) Ceresa, A.; Pretsch, E. *Anal. Chim. Acta* **1999**, *395*, 41–52.
24
25 (18) Gutsche, C. D.; Bauer, L. J. *J. Am. Chem. Soc.* **1985**, *107*, 6052–6059.
26
27 (19) Lee, J. D. In *Concise Inorganic Chemistry*; Wiley-Blackwell: Oxford, 1999.
28
29 (20) Marcos, P. M.; Ascenso, J. R.; Segurado, M. A. P.; Bernardino, R. J.; Cragg, P. J.
30 *Tetrahedron* **2009**, *65*, 496–503.
31
32 (21) Sheldrick, G. M. *Acta Cryst.* **2008**, *A64*, 112–122.
33
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Table 1 Characteristics of the electrodes

Ionophore	Plasticizer	Detected Ion	Slope/mV decade ⁻¹	Linear range (-log C)
1	DEHA	Na ⁺	50.3	5 – 1
		K ⁺	49.7	4.5 – 1
		Pb ²⁺	28.8	5.5 – 2
2	DEHA	Na ⁺	52.3	4.5 – 1
		K ⁺	46.5	4 – 1
		Pb ²⁺	30.5	6 – 2
1	NPOE	Na ⁺	34	5.5 – 2
		K ⁺	39.4	5 – 2
		Pb ²⁺	37.4	6 – 4
2	NPOE	Na ⁺	46.2	4.5 – 1
		K ⁺	26.7	4 – 1
		Pb ²⁺	31.4	5.5 – 2
1	BBPA	Na ⁺	50.3	5 – 2
		K ⁺	43.4	5 – 2
		Pb ²⁺	39.6	5 – 3
2	BBPA	Na ⁺	51.2	4 – 1
		K ⁺	47.2	3 – 1
		Pb ²⁺	51.3	6 – 1
3	BBPA	Na ⁺	62.5	5 – 2
		K ⁺	39.2	3 – 1
		Pb ²⁺	35.4	4 – 1

Table 2. Complex formation constants ($\log \beta$)^a

Ionophore	Na ⁺	K ⁺	Pb ²⁺
1	5.51±0.08	5.08±0.03	7.93±0.05
2	4.83±0.08	3.80±0.05	8.22±0.05
3	5.52±0.04	2.85±0.04	5.58±0.02

^a Standard deviation shown are from at least three replicate measurements

Table 3. Crystal data and structure refinement details for **1**

Identification code	1	
Empirical formula	C ₆₉ H ₁₀₂ N ₄ O ₉	
Molecular weight	1131.55	
Temperature	120(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 10.9809(10) Å	α = 97.039(9)°.
	b = 13.7265(19) Å	β = 94.628(7)°.
	c = 22.678(2) Å	γ = 100.731(10)°.
Volume	3314.3(6) Å ³	
Z	2	
Density (calculated)	1.134 Mg/m ³	
Absorption coefficient	0.074 mm ⁻¹	
F(000)	1232	
Crystal size	0.41 x 0.13 x 0.12 mm ³	
Theta range for data collection	2.36 to 25.50°.	
Index ranges	-13<=h<=13, -16<=k<=12, -26<=l<=27	
Reflections collected	24116	
Independent reflections	12324 [R(int) = 0.0540]	
Completeness to theta = 25.50°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1 and 0.97425	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	12324 / 0 / 770	
Goodness-of-fit on F ²	1.018	
Final R indices [I>2σ(I)]	R1 = 0.0743, wR2 = 0.2015	
R indices (all data)	R1 = 0.1187, wR2 = 0.2283	
Largest diff. peak and hole	0.759 and -0.313 e.Å ⁻³	

Table 4 Composition of the PVC/BBPA membranes

	L_T (mmol/kg)	R_T KTCIPB (mmol/kg)	BBPA (mg)	PVC (mg)
Blank	0	5.52	121.0	61.0
1	24.21	5.40	120.5	61.5
2	23.85	5.43	120.0	60.0
3	23.13	5.33	120.0	62.5

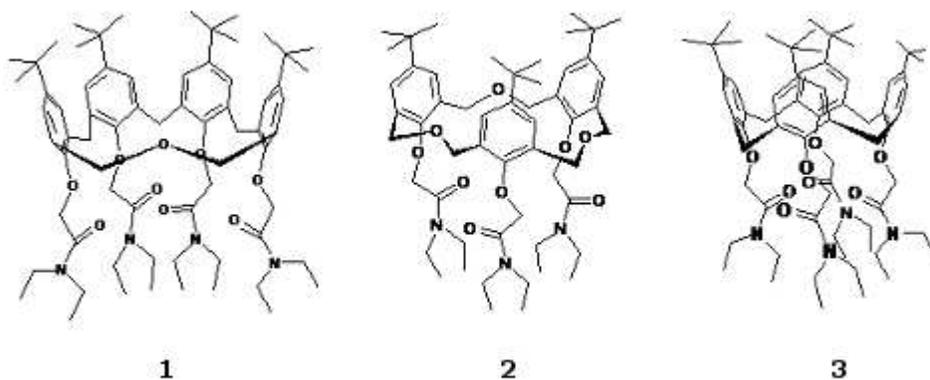
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3 Figure 1. Structural formula of the calixarenes studied.

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5 Figure 2. Crystal structure of dihomooxacalix[4]arene tetra(diethyl)amide **1**.

6
7 Figure 3. Electrode characteristics containing ligand **1** in a PVC/BBPA membrane.

8
9 Figure 4. Electrode characteristics containing ligand **2** in a PVC/BBPA membrane.

10 Figure 5. Potentiometric selectivity coefficients of ligands **1**, **2** versus Pb^{2+} in PVC/DEHA and
11 PVC/NPOE membrane ($\log K^{\text{pot}}_{\text{Pb,M}}$) and of ligand **3** versus Na^+ in PVC/DEHA ($\log K^{\text{pot}}_{\text{Na,M}}$) for
12 comparison.
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172x77mm (72 x 72 DPI)

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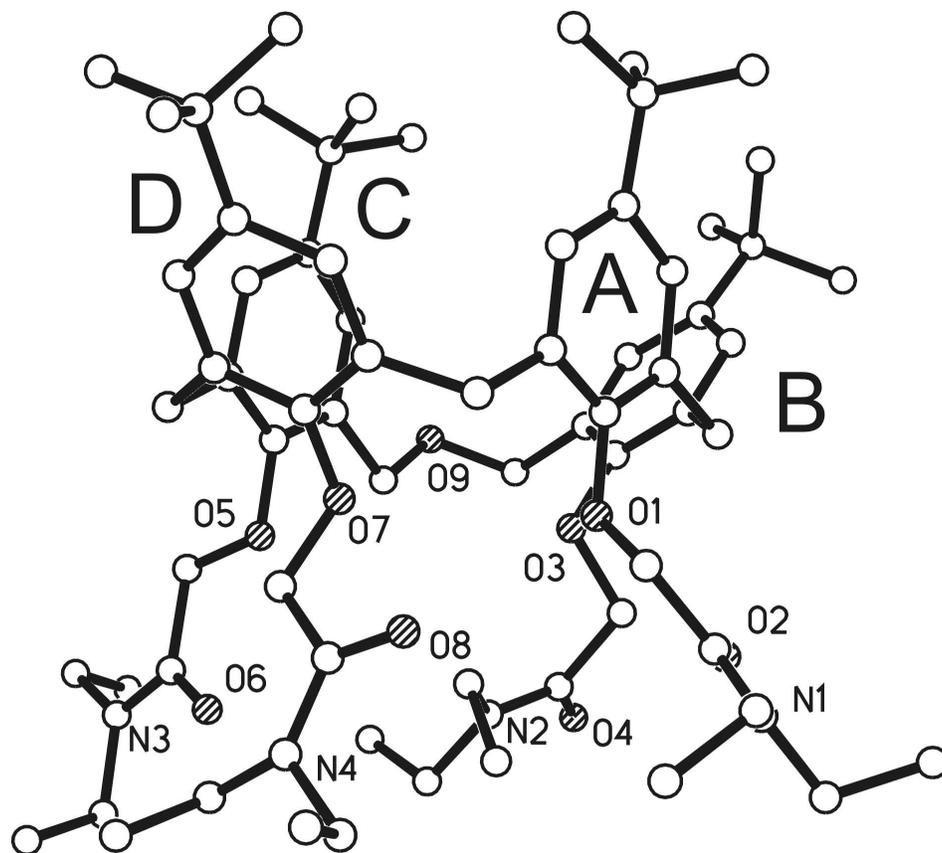
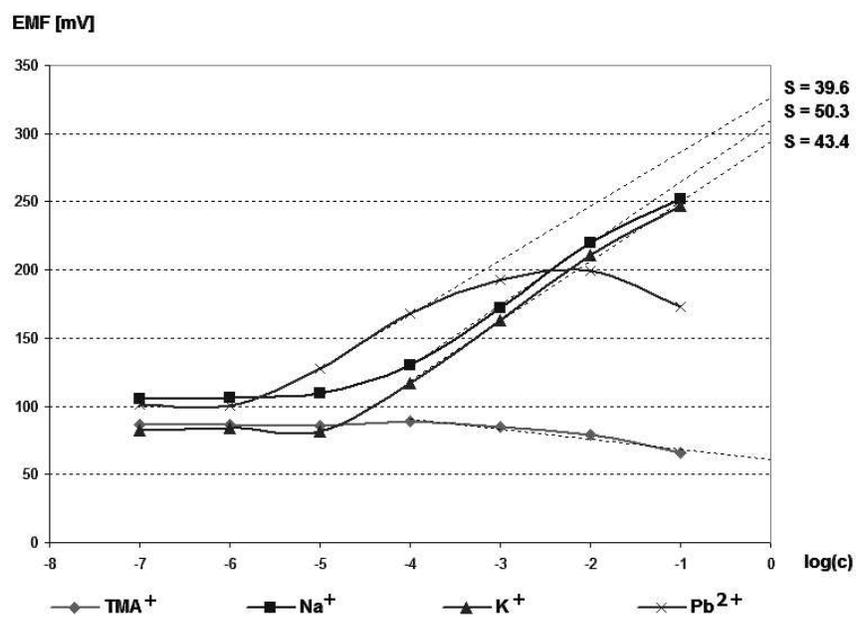


Figure 2. Crystal structure of dihomooxalix[4]arene tetra(diethyl)amide 1.
84x84mm (600 x 600 DPI)



312x213mm (72 x 72 DPI)

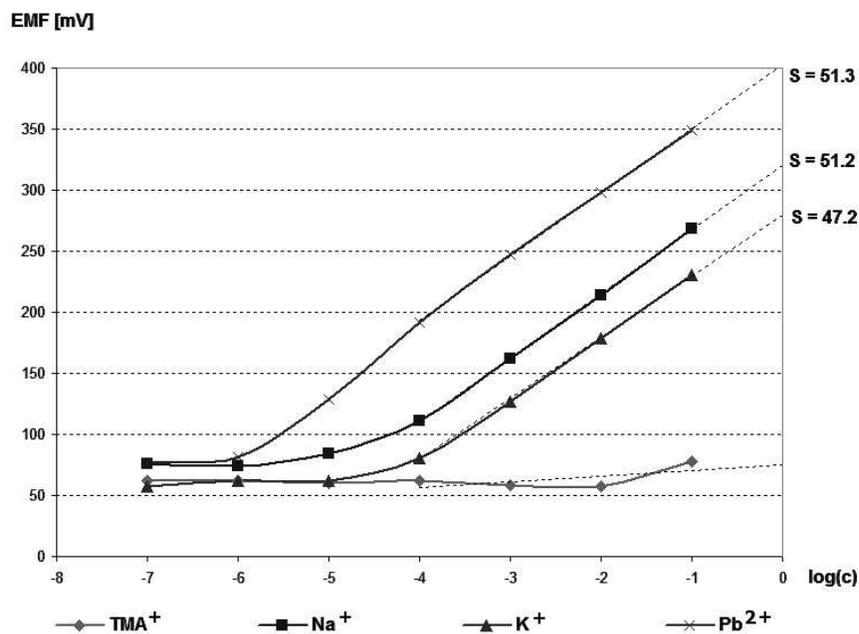


Figure 4. Electrode characteristics containing ligand 2 in a PVC/BBPA membrane.
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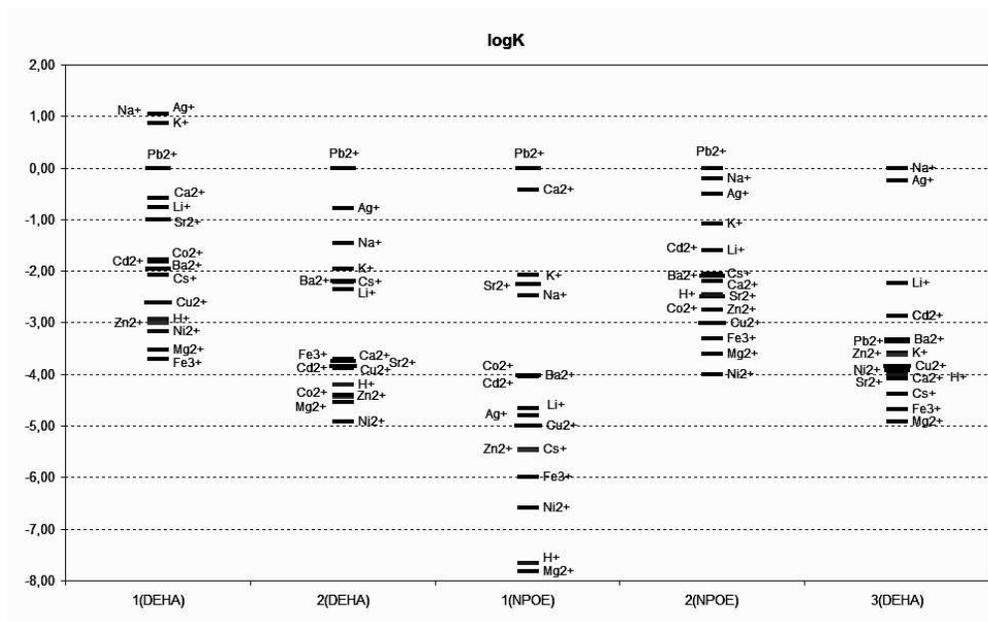


Figure 5. Potentiometric selectivity coefficients of ligands 1, 2 versus Pb²⁺ in PVC/DEHA and PVC/NPOE membrane ($\log K_{potPb,M}$) and of ligand 3 versus Na⁺ in PVC/DEHA ($\log K_{potNa,M}$) for comparison.

342x213mm (72 x 72 DPI)