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### A New Phosphonium Calix[4]arene for Selective Anion Recognition: Synthesis and Studies in Solution and in Ion Selective Electrodes

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# A New Phosphonium Calix[4]arene for Selective Anion Recognition: Synthesis and Studies in Solution and in Ion Selective Electrodes

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The synthesis and characterization of a new tetra (triphenylphosphonium) *p*-*tert*-butylcalix[4]arene **2** is presented. Its interactions with anions were studied by <sup>1</sup>H and <sup>31</sup>P NMR and UV absorption spectrophotometry, showing the biggest interaction with ClO<sub>4</sub><sup>-</sup>, I<sup>-</sup> and SCN<sup>-</sup>. Anion selectivity in ion-selective PVC-membrane electrodes (ISEs) plasticized with *o*-NPOE containing ionophore **2** was also investigated. Compound **2** shows a potentiometric response for various anions with the following selectivity pattern: ClO<sub>4</sub><sup>-</sup> > SCN<sup>-</sup> > I<sup>-</sup> > Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> > NO<sub>3</sub><sup>-</sup> > Br<sup>-</sup> > Cl<sup>-</sup>.

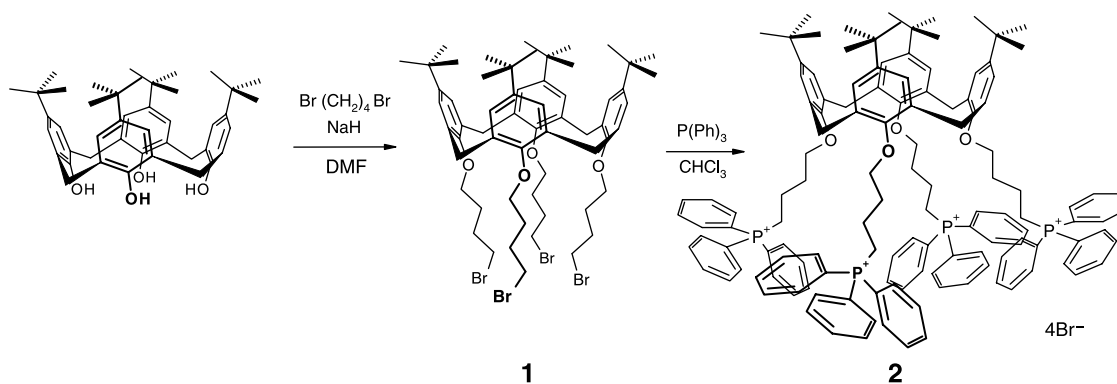
**Keywords:** Calix[4]arene; Perchlorate; Phosphonium group; Anion complexation; ISE

## INTRODUCTION

Anions play an important role in biological processes, e.g. in enzymatic reactions or in DNA coding [1]. Perturbation of the anionic equilibria in organisms may be the origin of diseases. The increase of anion concentrations in ecosystems leads to environmental problems such as eutrophication due to an excess of phosphates and nitrates or the presence of long-lived radioelements such as iodine, technetium, and selenium in their anionic forms produced by the nuclear industry [2]. Anions are relatively large and also have a wide variety of geometries which are important factors to be considered in the design of selective anion receptors. Therefore the recognition of anions is a topical challenge.

Design of sensors for monitoring the activity of chemical and biochemical species is an important issue in supramolecular chemistry [3,4]. A large number of ionophores for potentiometric sensing of cations have been developed but the number of suitable sensors for anions is still rather limited [5]. Anion binding can be achieved by neutral receptors (such as urea containing ligands) mainly through hydrogen bonding [5,6] or by positively charged ligands (for instance guanidinium or polyamine containing macrocycles) through electrostatic interaction [5,7,8]. Calixarenes were used as molecular scaffold on which to graft such functional groups [9]. For instance, the synthesis of amide [10–12], urea [13,14] or alkylammonium [15] and pyridinium [16] calixarene derivatives selective for anions were reported [17–19]. The majority of the anion-selective electrodes described so far is based on lipophilic quarternary ammonium salts behaving as anion-exchangers or on metalloporphyrins, in which the kind of metal determines the selectivity for particular anions [20–22]. Not many ligands containing phosphorus atoms were studied so far. Two such macrocycles applied in chemical sensors showed selective response for ClO<sub>4</sub><sup>-</sup> anion, with, however little discrimination of I<sup>-</sup> and SCN<sup>-</sup> [23,24]. Recently a di-(triphenylphosphonium) calix[4]arene has been synthesised which exhibited also some anion recognition properties [25,26]. By attaching four phosphonium moieties to a calix[4]-arene scaffold, it was expected to enhance the selectivity for tetrahedral or spherical anions,

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SCHEME 1

taking advantage of the preorganization of the ligand.

The synthesis and characterization of the tetra (triphenylphosphonium) *p-tert*-butylcalix[4]arene ligand **2** is reported here as well as its binding properties in solution towards a large variety of anions of different size, charge and geometry. Its behaviour in PVC-membrane electrodes is also presented. The monomeric subunit **4** was synthesised for comparison purpose. Our results are compared to those of known anion selective electrodes.

## EXPERIMENTAL

### Materials and Methods

$^1\text{H}$  and  $^{31}\text{P}$  NMR spectra were recorded in  $\text{CDCl}_3$  and  $\text{CD}_3\text{CN}$  on a Bruker SY300 MHz and a SY400 MHz, respectively. FAB mass spectra were obtained on a VG analytical ZAB HF instrument. All reagents and solvents were commercial and used without further purification, except THF which was dried and freshly distilled before used for preparation of ion selective membranes. PVC (high molecular weight poly(vinyl chloride), 2-nitrophenyl octyl ether (NPOE), bis-ethylhexylsebacate (BEHS), (2-morpholino)ethanesulfonic acid monohydrate (MES), were from Fluka selectophore. The  $\text{LiClO}_4$ ,  $\text{CsClO}_4$  and sodium salts:  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{ClO}_4^-$ ,  $\text{SCN}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$ ,  $\text{HPO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{Cr}_2\text{O}_7^{2-}$ , citrate, acetate, benzoate, and oxalate were of p.a. grade. All aqueous salt solutions were prepared with demineralized water (conductivity  $< 1.0 \mu\text{S}/\text{cm}$ ).

### Synthesis

#### *Tetrakis*-(4-triphenylphosphonium-butoxy)-*tetrakis-p-tert*-butylcalix[4]arene tetrabromide **2**

Tetrakis-(4-bromobutoxy)-tetrakis-*p-tert*-butylcalix[4]arene **1** (1.184 g, 1.00 mmol) was dissolved

in chloroform (30 ml). After a few minutes of stirring triphenylphosphine (5.248 g, 20.00 mmol) and chloroform (20 ml) were added (Scheme 1). After 6 days of refluxing the mixture was cooled and solvent was evaporated. The residue was dissolved in dichloromethane. The excess of triphenylphosphine was precipitated from methanol and filtered. The organic layer was evaporated and the crude product was dissolved in dichloromethane. Chromatography on a silica column with 90:10 dichloromethane: methanol mixture as eluent gave tetrakis-(4-triphenylphosphonium-butoxy)-tetrakis-*p-tert*-butylcalix[4] arene tetrabromide (0.67 g, 30%).  $\text{C}_{132}\text{H}_{144}\text{O}_4\text{P}_4\text{Br}_4$   $M = 2238.10 \text{ g/mole}$   $\delta_{\text{H}}$  (300 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 7.88–7.76 (24H, m, P–Ar–H), 7.71–7.59 (36H, m, P–Ar–H), 6.63 (8H, s, Ar–H), 4.23 (4H, d,  $J = 13.0 \text{ Hz}$ , Ar– $\text{CH}_2$ –Ar), 4.01–3.78 (16H, m,  $-\text{CH}_2$ –P and Ar–O– $\text{CH}_2$ ), 2.91 (4H, d,  $J = 13.0 \text{ Hz}$ , Ar– $\text{CH}_2$ –Ar), 2.41–2.24 (8H, m,  $-\text{CH}_2-$ ), 1.72–1.56 (8H, m,  $-\text{CH}_2-$ ), 1.02 (36H, s,  $-\text{C}(\text{CH}_3)_3$ ).  $m/z$  (FAB(+)) 479.5 ( $\text{M}^{4+}$ , 100%).

#### *Tetrakis*-(4-triphenylphosphonium-butoxy)-*tetrakis-p-tert*-butylcalix[4]arene tetrahexafluorophosphate **2a**

Tetrakis-(4-triphenylphosphonium-butoxy)-tetrakis-*p-tert*-butylcalix[4]arene tetrabromide (0.100 g, 0.045 mmol) was dissolved in acetonitrile (1 ml). Then 0.062 g (0.245 mmol) of  $\text{AgPF}_6$  was dissolved in acetonitrile and added dropwise to the ligand solution. After 24 h the precipitate of NaBr was removed and the solution was evaporated. 0.090 g (0.036 mmol) of tetrakis-(4-triphenylphosphonium-butoxy)-tetrakis-*p-tert*-butylcalix[4]arene tetrahexafluorophosphate was obtained.  $\text{C}_{132}\text{H}_{144}\text{O}_4\text{P}_4(\text{PF}_6)_4$   $M = 2498.31 \text{ g/mole}$   $\delta_{\text{H}}$  (500 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 7.80–7.66 (60H, m, P–Ar–H), 7.04 (8H, s, Ar–H), 4.47 (4H, d,  $J = 13.0 \text{ Hz}$ , Ar– $\text{CH}_2$ –Ar), 4.24–4.15 (8H, m, Ar–O– $\text{CH}_2$ ), 3.47 (4H, d,  $J = 13.0 \text{ Hz}$ , Ar– $\text{CH}_2$ –Ar), 3.38–3.25 (8H, m,  $-\text{CH}_2$ –P),

2.49–2.38 (8H, m,  $-\text{CH}_2-$ ), 1.81–1.65 (8H, m,  $-\text{CH}_2-$ ), 1.12 (36H, s,  $-\text{C}(\text{CH}_3)_3$ ).

#### Tetrakis-(4-bromobutoxy)-tetrakis-*p*-tert-butylcalix[4]arene 1

The suspension of *p*-tert-butylcalix[4]arene (1.947 g, 3.00 mmol) and NaH in oil washed three times with hexane (0.700 g, 29.17 mmol) were stirred at room temperature in DMF (50 ml) for 1 h. Then 1,4-dibromobutane (12.947 g, 59.06 mmol) was added and the mixture was heated to 80°C. After 4 days of heating, the mixture was cooled and MeOH (20 ml) was added. After removing of the solvent, the residue was dissolved in dichloromethane and water and acidified with 1 M HCl. The organic layer was dried over  $\text{Na}_2\text{SO}_4$ , filtered and evaporated. After precipitation from methanol pure tetra-(4-bromobutoxy)-tetrakis-*p*-tert-butylcalix[4]arene (1.52 g, 43%) was obtained.  $\text{C}_{60}\text{H}_{84}\text{O}_4\text{Br}_4$   $M = 1188.94$  g/mole  $\delta_{\text{H}}$  (300 MHz,  $\text{CDCl}_3$ ) 6.79 (8H, s, Ar-H), 4.36 (4H, d,  $J = 13.0$  Hz, Ar- $\text{CH}_2$ -Ar), 3.91 (8H, t,  $J = 6.9$  Hz,  $-\text{CH}_2-\text{O}-$ ), 3.53 (8H, t,  $J = 6.9$  Hz,  $-\text{CH}_2-\text{Br}$ ), 3.15 (4H, d,  $J = 13.0$  Hz, Ar- $\text{CH}_2$ -Ar), 2.23–2.16 (8H, m,  $-\text{CH}_2-$ ), 2.09–1.98 (8H, m,  $-\text{CH}_2-$ ), 1.09 (36H, s,  $-\text{C}(\text{CH}_3)_3$ ).

#### 4-Bromobutoxy-*p*-tert-butyl-phenol 3 and triphenylphosphonium-butoxy-*p*-tert-butyl-phenol bromide 4

Compounds **3** and **4** were synthesized according to the procedures which were used for the preparation of **1** and **2** (Scheme 2). Compound **3**: (60%).  $\text{C}_{14}\text{H}_{21}\text{OBr}$   $M = 285.22$  g/mole  $\delta_{\text{H}}$  (300 MHz,  $\text{CDCl}_3$ ) 7.32 (2H, d,  $J = 9.0$  Hz, Ar-H), 6.86 (2H, d,  $J = 9.0$  Hz, Ar-H), 3.99 (2H, t,  $J = 5.8$ , Ar-O- $\text{CH}_2$ ), 3.51 (2H, t,  $J = 6.6$ ,  $\text{CH}_2$ -Br), 2.14–2.03 (2H, m,  $-\text{CH}_2-$ ), 2.00–1.90 (2H, m,  $-\text{CH}_2-$ ), 1.33 (9H, s,  $-\text{C}(\text{CH}_3)_3$ ).

Compound **4**: (40%).  $\text{C}_{32}\text{H}_{36}\text{OPBr}$   $M = 547.52$  g/mole  $\delta_{\text{H}}$  (300 MHz,  $\text{CDCl}_3$ ) 7.86–7.72 (9H, m, P-Ar-H), 7.69–7.58 (6H, m, P-Ar-H), 7.23 (2H, d,

$J = 8.8$  Hz, Ar-H), 6.72 (2H, d,  $J = 8.8$  Hz, H-Ar), 4.01 (2H, t,  $J = 5.8$ , Ar-O- $\text{CH}_2$ ), 3.93–3.80 (2H, m,  $-\text{CH}_2-\text{P}$ ), 2.21–2.12 (2H, m,  $-\text{CH}_2-$ ), 1.92–1.81 (2H, m,  $-\text{CH}_2-$ ), 1.25 (9H, s,  $-\text{C}(\text{CH}_3)_3$ ).

#### NMR Studies of Anion-ligand Interaction

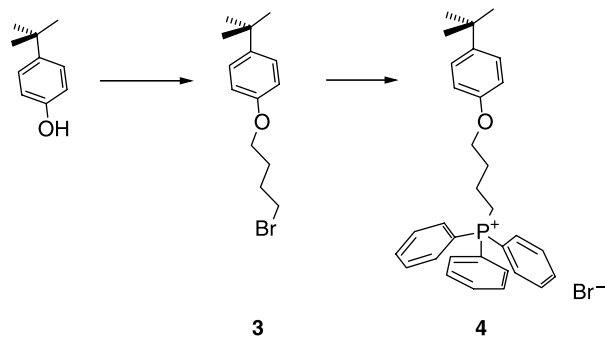
The NMR experiments were carried in  $\text{CDCl}_3$  and in  $\text{CD}_3\text{CN}$  solutions. The solution of ligand in  $\text{CDCl}_3$  was left for 24 h in contact with an excess of 6 equivalents of the solid sodium salts ( $\text{I}^-$ ,  $\text{NO}_3^-$ ,  $\text{SCN}^-$ ,  $\text{ClO}_4^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{S}_2\text{O}_3^{2-}$ ,  $\text{CrO}_4^{2-}$ ,  $\text{MoO}_4^{2-}$ ,  $\text{Cr}_2\text{O}_7^{2-}$ ) until equilibration and then the spectra were recorded. Different alkali metal ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{Cs}^+$ ) and tetraethylammonium perchlorates were dissolved in a solution of ligand in  $\text{CD}_3\text{CN}$ , the other experimental conditions remaining the same.

#### Stability Constant Determination

The procedures and experimental conditions were the same in both solvents methanol and acetonitrile, except the nature of the background electrolyte used to maintain the ionic strength constant at 0.01 M, which was NaBr in methanol and  $\text{Et}_4\text{NBr}$  in acetonitrile. Small volumes (0.05 ml) of the salt solution ( $2.5 \times 10^{-3}$  M) were added to 2 ml of the ligand solution ( $10^{-4}$  M) directly into the spectrophotometric cell thermoregulated at 25°C. For each volume added, the spectrum of the solution was recorded on a Cary 3 spectrophotometer (Varian) between 250 nm and 300 nm. 17 additions was enough to complete the titration. At least three independent experiments have been performed. The interpretation of the spectra using the program Specfit [27] led to the determination of the concentration ratio  $\beta_{x1} = [\text{A}_x\text{L}^{4-xn}]/([\text{A}^{n-}]^x[\text{L}^{4+}])$  (where  $\text{A}^{n-}$  is the anion and  $\text{L}^{4+}$  the ligand).

#### Ion Selective Membrane Electrodes (ISE)

The membranes were prepared by dissolving 4 mg of the ionophore **2** or **4**, 60 mg of PVC, 120 mg of plasticizer (*o*-NPOE), 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 incorporated into Ag/AgCl Philips electrodes bodies of IS 561 type (Moeller S.A., Zurich). Three identical electrodes were always studied [28]. The EMF measurements were carried out at 20°C using Lawson Lab 16 EMF, multi-channel voltmeter or in some cases using Metrohm 654 voltmeter. A double-junction reference Radelkis 0P0820P electrode with 1 M  $\text{CH}_3\text{COOLi}$  solution in the bridge cell was used.



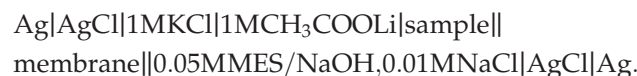
SCHEME 2

TABLE I Most important changes  $\Delta(\delta)$  in the proton<sup>a</sup> chemical shifts ( $\delta$ ) [ppm] experienced by **2** in presence of  $\text{I}^-$ ,  $\text{SCN}^-$  and  $\text{ClO}_4^-$  anions in  $\text{CDCl}_3$

	c	e	f	g	j
$\delta$ ( <b>2</b> )	6.63	2.91	4.23	3.87	3.94
$\delta$ ( <b>2</b> + NaI)	6.93	3.35	4.42	4.40	4.00
$\Delta(\delta)$	0.30	0.44	0.19	0.53	-0.06
$\delta$ ( <b>2</b> + NaSCN)	6.95	3.33	4.39	4.27	3.76
$\Delta(\delta)$	0.32	0.42	0.16	0.40	-0.18
$\delta$ ( <b>2</b> + $\text{NaClO}_4$ )	6.95	3.35	4.40	4.27	3.47
$\Delta(\delta)$	0.32	0.44	0.17	0.40	-0.47

<sup>a</sup> For the attribution of the protons see Fig. 1.

The measurements were carried out using the cells of the type:



The calibration curves were obtained by addition of standard solutions of different anions to 50 ml of 0.01 M NaCl in 0.05 M MES/NaOH buffer solution of pH = 5.5. They were also measured by successive dilution of initial  $5 \times 10^{-2}$  M salt solutions until further dilution resulted in no potential change. The NaCl was applied as the supporting electrolyte based on preliminary experiment in which studied membrane electrode showed no response for changing of  $\text{Cl}^-$  anion concentration. Potentiometric sensitivity to  $\text{ClO}_4^-$  anions was studied also by calibration of the membrane electrodes (PVC/o-NPOE/2) in pure  $\text{NaClO}_4$  water solution.

Potentiometric selectivity coefficients ( $\log K_{\text{ClO}_4, \text{I}}^{\text{pot}}$ ) were determined by the Separate Solution Method (SSM) [29] and were calculated (Eq. (1)), by using the EMF values for the measured ion activities  $a_i$  at the concentration  $10^{-2}$  M:

$$\log K_{\text{I}, \text{J}}^{\text{pot}} = \frac{(E_{\text{J}} - E_{\text{I}})z_{\text{I}}F}{2.303RT} + \left(1 - \frac{z_{\text{I}}}{z_{\text{J}}}\right) \log a_{\text{I}} \quad (1)$$

In Eq. (1),  $I$  and  $J$  correspond to the primary and the interfering anions, respectively and  $z_{\text{I}}$ ,  $z_{\text{J}}$  correspond to their charges. The values of  $\log K_{\text{ClO}_4, \text{J}}^{\text{pot}}$  were derived from measurements performed with perchorate as primary anion, i.e. the best complexed anion,  $J$  referring to the other studied anions.

Potentiometric selectivity coefficients ( $\log K_{\text{I}, \text{Cl}}^{\text{pot}}$ ) were also determined by the Fix Interference Method (FIM) [29]. The concentration of NaCl in each measured anion solution was 10 mM. Values of  $\log K_{\text{I}, \text{Cl}}^{\text{pot}}$  were determined using chloride as interfering anion and in this case,  $I$  corresponds to the other anions.

## RESULTS AND DISCUSSION

The tetra (triphenylphosphonium) *p*-*tert*-butylcalix[4]arene **2** has been obtained in 30% yield by refluxing in chloroform the tetrabromobutoxy-calix[4]arene **1** in presence of 20 equivalents of triphenylphosphine during 6 days as represented in Scheme 1. The tetrabromocalix[4]arene **1** was prepared by reacting the *p*-*tert*-butylcalix[4]arene

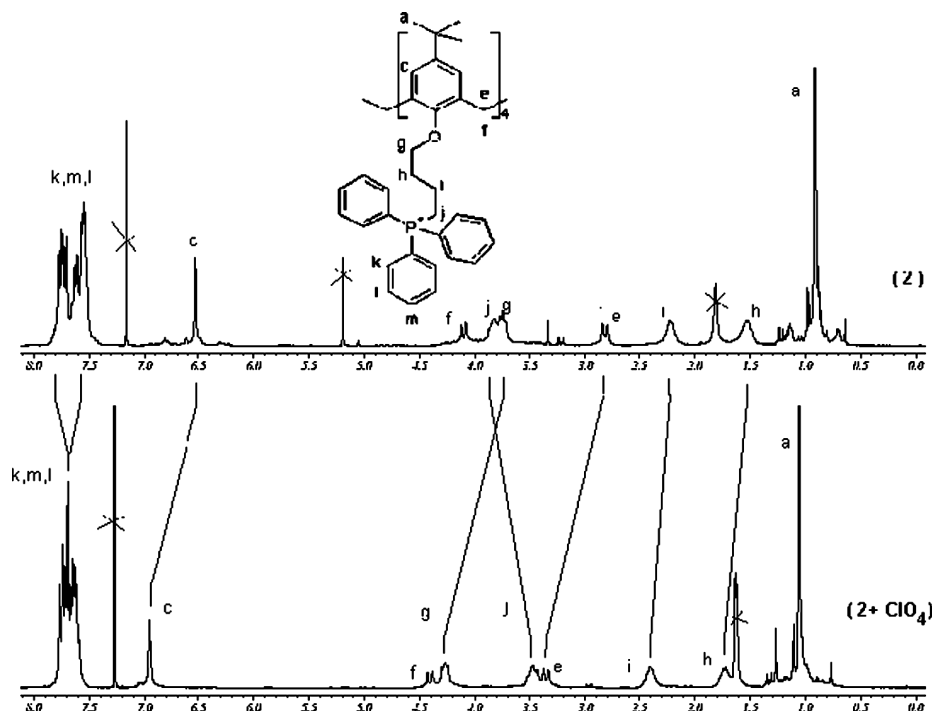


FIGURE 1 Changes in  $^1\text{H}$  NMR spectra of **2** in presence of  $\text{ClO}_4^-$  anion.

TABLE II Most important changes  $\Delta(\delta)$  in the proton<sup>†</sup> chemical shifts ( $\delta$ )[ppm] experienced by **2** in presence of different perchlorate salts in CD<sub>3</sub>CN

	c	e	f	g	j
$\delta$ ( <b>2</b> )	6.87	2.93	4.15	3.74	3.81
$\delta$ ( <b>2</b> + LiClO <sub>4</sub> )	7.19	3.28	4.21	4.36	3.29
$\Delta(\delta)$	0.32	0.35	0.06	0.62	-0.52
$\delta$ ( <b>2</b> + NaClO <sub>4</sub> )	7.22	3.33	4.21	4.09	3.28
$\Delta(\delta)$	0.35	0.40	0.06	0.35	-0.53
$\delta$ ( <b>2</b> + CsClO <sub>4</sub> )	6.86	2.92	4.14	3.75	3.75
$\Delta(\delta)$	-0.01	-0.01	-0.01	0.01	-0.06
$\delta$ ( <b>2</b> + NEt <sub>4</sub> ClO <sub>4</sub> )	6.93	3.00	4.22	3.83	3.57
$\Delta(\delta)$	0.06	0.07	0.07	0.09	-0.24
$\delta$ ( <b>2a</b> )	6.80	2.87	4.09	3.77	3.06
$\delta$ ( <b>2a</b> + NaClO <sub>4</sub> )	7.19	3.31	4.19	4.06	3.27
$\Delta(\delta)$	0.39	0.44	0.10	0.29	0.21

<sup>†</sup> For the attribution of the protons see Fig. 1.

in DMF at 80°C during 4 days with 1,4-dibromobutane in the presence of sodium hydride. This compound adopts the cone conformation as shown by the presence in its <sup>1</sup>H NMR spectrum of an AB system at 4.36 ppm and 3.15 ppm. The monomeric unit **4** was obtained according to the same procedure in 40% yield (Scheme 2).

The affinity of ligand **2** for a series of anions of different charge, size and geometry: I<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SCN<sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, S<sub>2</sub>O<sub>3</sub><sup>2-</sup>, CrO<sub>4</sub><sup>2-</sup>, MoO<sub>4</sub><sup>2-</sup>, Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> has been studied using two approaches. A first assessment of the ligand interaction with anions was obtained using <sup>1</sup>H and <sup>31</sup>P NMR spectroscopy coupled with solid/liquid extraction. Among the anions tested only ClO<sub>4</sub><sup>-</sup>, I<sup>-</sup> and SCN<sup>-</sup> led to modifications of the signals of the ligand in CDCl<sub>3</sub> after equilibration with an excess of 6 equivalents of the solid sodium salts (Table I). These three anions are all of different geometry, and they are lipophilic [30]. They might exchange with bromide anions of the ligand because of their higher lipophilicity.

Figure 1 shows the <sup>1</sup>H NMR spectra of **2** alone and in presence of NaClO<sub>4</sub>. The important changes (expressed as  $\Delta(\delta)$ ) were observed for the CH<sub>2</sub> protons adjacent to the phenolic oxygen atoms (g atoms) and for the CH<sub>2</sub> protons adjacent to the phosphorus atoms (j atoms). They correspond to a multiplet from 4.01 ppm to 3.78 ppm which undergoes shifts and gives two multiplets from 4.32 ppm to 4.23 ppm for the g atoms and from 3.56 ppm to 3.42 ppm for the j atoms. The signals corresponding to the AB system (f,e atoms) at 4.23 ppm and 2.91 ppm in **2** are also shifted to give another AB system at 4.40 ppm and 3.35 ppm in the presence of perchlorate anion. An important shift of the signal corresponding to the aromatic protons (c atoms) is also observed (Table I). These changes clearly indicate strongest interaction of ligand with perchlorate, which is further confirmed by <sup>31</sup>P NMR. The signal of the phosphorus atoms at 25.74 ppm

in the free ligand is shifted to 24.76 ppm in the presence of perchlorate ions. In the case of iodide and thiocyanate, the signal of the phosphorus atoms is shifted to 25.55 ppm and 24.99 ppm, respectively. These changes, in agreement with the <sup>1</sup>H NMR spectra, suggest significant interactions between these anions and the ligand. It is important to note that no change was observed in the <sup>1</sup>H NMR spectra of the phosphonium monomer **4** in the presence of all these anions introduced as sodium or lithium salts.

The <sup>1</sup>H NMR experiments were repeated in deuterated acetonitrile with perchlorate salts of different alkali metals and tetraethylammonium cation. The spectra of the ligand are very similar in both solvents. The presence of NaClO<sub>4</sub> induces shifts of the same signals as in CDCl<sub>3</sub>. With LiClO<sub>4</sub>, the signal of methylene protons adjacent to the phenolic oxygen atoms (protons g) shifts from 3.74 ppm to 4.36 ppm. This shift is larger than that observed in the presence of NaClO<sub>4</sub>. With both salts the shifts corresponding to the signals of the j protons next to the P atoms (which are supposed to interact with perchlorate) are similar. With CsClO<sub>4</sub>, the only shift observed is that for the j protons, but the value is very small in comparison to the effect of the other salts (-0.06 ppm with CsClO<sub>4</sub>, -0.52 ppm with LiClO<sub>4</sub> and -0.53 ppm with NaClO<sub>4</sub>). In the case of Et<sub>4</sub>NClO<sub>4</sub> the shift of the j protons was much stronger than in case of Cs<sup>+</sup> but twice smaller than for Li<sup>+</sup> or Na<sup>+</sup> salts. The changes observed suggest that ligand/anion interaction is connected with the nature of the counter ion and its affinity to the ligand. A similar <sup>1</sup>H NMR experiment has been performed in acetonitrile with NaClO<sub>4</sub> and **2a**, equivalent to **2** in which the bromide ions have been replaced by PF<sub>6</sub><sup>-</sup> anions. The results presented in Table II show similar changes as in the case of **2** + NaClO<sub>4</sub>. With this lipophilic anion, for which no exchange is normally possible, there is still a significant shift of the j protons close to the phosphorus atoms in presence of ClO<sub>4</sub><sup>-</sup>, suggesting complexation of this anion.

The ligand-anion interaction has also been followed by UV absorption spectrophotometry in methanol and acetonitrile. No changes were observed in the spectrum of the ligand upon addition of the anions (introduced as their sodium salts) in methanol. However, in acetonitrile, significant modifications of the spectra appeared in the presence of perchlorate, thiocyanate and iodide anions, i.e. the same anions for which shifts were noticed in NMR spectroscopy. These changes were interpreted using program Specfit [27] by the formation of 1:1 (anion:ligand) complexes with sodium perchlorate ( $\log \beta_{11} = 3.81 \pm 0.02$ ) and with lithium perchlorate ( $\log \beta_{11} = 3.71 \pm 0.04$ ). Changes in presence of sodium thiocyanate were interpreted by the formation of 2:1 complex ( $\log \beta_{21} = 8.7 \pm 0.3$ ).

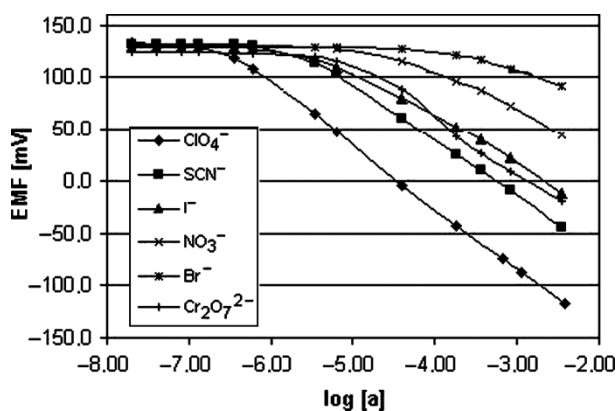


FIGURE 2 Potentiometric responses of electrode with ligand 2 to anions in MES/NaOH buffer (pH = 5.5) and ionic strength adjusted with 10 mM NaCl solution.

The different structures of the two anions (tetrahedral for perchlorate and linear for thiocyanate) may account for the difference in the stoichiometries of the complexes. The strong absorption of iodide precluded any interpretation of the spectra. In case of the other anions studied in this solvent, the very small spectral variations observed suggest only weak anion interactions with ligand 2.

Ligand 2 was applied as new sensing material in ion-selective PVC membrane electrodes (ISEs). The potentiometric response towards the same anions, including also chloride, bromide, phosphate, hydrogenophosphate, carbonate, acetate, oxalate, citrate and benzoate anions was studied using two different plasticizers: BEHS and o-NPOE in the electrode membranes. Only the membranes containing o-NPOE were stable and long lasting, so only this plasticizer was chosen for further studies. Several PVC/o-NPOE membranes were prepared but the membrane without any additives (anionic [21,31,32] or cationic [17,33] sites) was the best choice. The composition of the membrane was the following: PVC/o-NPOE (1/2) containing 2% wt of ionophore 2 or 4. Electrodes were calibrated using buffer solution (2-morpholino)ethanesulfonic acid monohydrate (MES)–NaOH (pH = 5.5) containing sodium salts

of anions. The ionic strength was adjusted with 10 mM NaCl. Sensing properties of the membrane electrode are presented in Fig. 2 and are summarized in Table III.

The electrodes showed Nernstian response and highest selectivity for  $\text{ClO}_4^-$  ions in buffered solution (pH = 5.5) and in water (pH = 6.5). They also showed close to Nernstian response to  $\text{I}^-$ ,  $\text{NO}_3^-$ ,  $\text{SCN}^-$ . There was no significant reaction for  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$ ,  $\text{HPO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ , citrate, acetate, benzoate and oxalate. Rather quick (within 15–20 s) and stable response of the electrodes was observed during the measurements and the answer was fully reversible. The lifetime of electrode with ionophore 2 is more than three weeks. Selectivity coefficients  $K_{\text{ClO}_4, j}^{\text{pot}}$  measured by the separate solution method (SSM) [29] in 10 mM buffered (pH = 5.5) or 100 mM unbuffered (pH = 6.5) solutions of the corresponding sodium salts are given in Table IV. Ligand 2 provides the following selectivity order:  $\text{ClO}_4^- > \text{SCN}^- > \text{I}^- > \text{Cr}_2\text{O}_7^{2-} > \text{NO}_3^- > \text{Br}^- > \text{Cl}^-$ , which is quite similar to the Hofmeister series observed for the typical ion exchanger, tetradodecylammonium tetrakis(4-chlorophenyl)borate (TDMACl) [3,18,34]. The selectivity pattern of electrodes containing the phosphonium monomer 4 is similar. However the slope and linear range are not as good as the corresponding values for the electrodes with compound 2.

Table V allows the comparison between the performances of ligand 2 and several perchlorate selective ionophores when incorporated in ion selective electrodes. Ligand 2 displays better potentiometric properties than protonated cyclam or its copper complex and than phosphodithiamacrocycle PS2M. For instance the detection limit is  $10^{-7} \text{ mol/dm}^3$  with ligand 2 instead of  $4.2 \times 10^{-6} \text{ mol/dm}^3$  with cyclam. Ligand 2 presents generally higher selectivities than PS2M, TDMACl, cyclam and  $[\text{Cu}(\text{cyclam})]^{2+}$ . In particular the selectivities of 2 for  $\text{ClO}_4^-$  over halides are remarkable. The best performances of ligand 2 as compared to these ligands could be exploited despite its complicated synthesis.

TABLE III Characteristics of the electrode potentiometric response towards chosen primary anions in the presence of 10 mM NaCl. Electrodes with PVC/o-NPOE (1/2) membrane containing 2% wt. of 2 or 4

Ligand, Inner and conditioning electrolyte	Primary anion	DL† (log a)	Slope (mV)
(2), MES/NaOH/10 <sup>-2</sup> M NaCl (pH = 5.5)	$\text{ClO}_4^-$	-7.0	-58
(2), Water solution	$\text{ClO}_4^-$	-5.5	-55
(2), MES/NaOH/10 <sup>-2</sup> M NaCl (pH = 5.5)	$\text{SCN}^-$	-6.0	-55
(2), MES/NaOH/10 <sup>-2</sup> M NaCl (pH = 5.5)	$\text{I}^-$	-6.0	-52
(2), MES/NaOH/10 <sup>-2</sup> M NaCl (pH = 5.5)	$\text{NO}_3^-$	-5.0	-51
(2), MES/NaOH/10 <sup>-2</sup> M NaCl (pH = 5.5)	$\text{Br}^-$	-4.0	-44
(2), MES/NaOH/10 <sup>-2</sup> M NaCl (pH = 5.5)	$\text{Cr}_2\text{O}_7^{2-}$	-5.5	-47
(4), MES/NaOH/10 <sup>-2</sup> M NaCl (pH = 5.5)	$\text{ClO}_4^-$	-6.0	-49

† DL: detection limit.

TABLE IV Selectivity coefficients,  $\log K_{i,j}^{pot}$  of electrodes containing ligand 2 or 4, determined in buffered (pH = 5.5) and unbuffered (pH = 6.5 or 6.0) sodium salts solutions by FIM or SSM

Ligand/Method	pH	$\text{ClO}_4^-$	$\text{SCN}^-$	$\text{I}^-$	$\text{NO}_3^-$	$\text{Br}^-$	$\text{Cl}^-$	$\text{Cr}_2\text{O}_7^{2-}$
2/FIM	5.5	0	-1.2	-1.8	-2.6	-3.0	< -4.0	-
2/SSM	5.5	0	-1.3	-2.0	-2.9	-4.0	< -4.0	-1.9
2/SSM	6.5	0	-1.4	-1.9	-3.1	-3.5	< -4.0	-1.8
2/FIM	6.0	0	-1.7	-2.3	-2.4	-3.0	-4.1	-
4/SSM	5.5	0	-1.1	-1.6	-2.5	-3.5	< -4.0	-1.9

TABLE V Comparison of potentiometric properties of electrodes based on different perchlorate selective compounds

	2	TDMACI <sup>†</sup>	PS2M <sup>‡</sup>	cyclam <sup>¶</sup>	[Cu(cyclam)] <sup>2+§</sup>
S [mV]	58.0	-	-56.0	-52.5	66.0
DL [mol/dm <sup>3</sup> ]	10 <sup>-7</sup>	-	8 × 10 <sup>-7</sup>	4.2 × 10 <sup>-6</sup>	1.8 × 10 <sup>-5</sup>
X <sup>-</sup>	$\log K_{\text{ClO}_4^-}^{pot}, X$				
$\text{ClO}_4^-$	0	0	0	0	0
$\text{SCN}^-$	-1.3	-1.2	-1.0	-	-1.3
$\text{I}^-$	-2.0	-1.6	-1.8	-	-1.5
$\text{NO}_3^-$	-2.9	-3.0	-2.6	-2.6	-2.2
$\text{Br}^-$	-4.0	-3.8	-4.1	-3.1	-2.2
$\text{Cl}^-$	< -4.0	-5.0	-5.0	-3.2	-2.1
$\text{HCO}_3^-$	-	-6.4	-4.0	-2.4	-2.2
$\text{HPO}_4^{2-}$	-	-	-5.2	-3.8	-2.8
$\text{SO}_4^{2-}$	-	-7.7	-5.0	-4.4	-

<sup>†</sup> tridodecyl-methyl ammonium chloride; <sup>‡</sup> 7-phenyl-7-phospha-3,11-dithiabiocyclo[11,4,0]heptadeca-13(1),14,16-triene (PS2M); from [24]; <sup>¶</sup> 1,4,8,11-tetra (n-octyl)-1,4,8,11-tetraazacyclotetradecane (cyclam); from [35]; <sup>§</sup> from [36].

## CONCLUSION

A new tetra(triphenylphosphonium) *p-tert*-butylcalix[4]arene in the cone conformation has been synthesized. As shown by <sup>1</sup>H and <sup>31</sup>P NMR and UV spectrophotometry, the compound proved to interact selectively with some anions, namely  $\text{ClO}_4^-$ ,  $\text{SCN}^-$ , and  $\text{I}^-$ . This interaction appeared to be dependent on the nature of the alkali counter ion. This compound has also been incorporated in PVC-membrane electrodes as ionophore-sensing material for anions. The following selectivity order was found:  $\text{ClO}_4^- > \text{SCN}_6^- > \text{I}^- > \text{Cr}_2\text{O}_7^{2-} > \text{NO}_3^- > \text{Br}^- > \text{Cl}^-$  which is similar to the Hofmeister series observed for typical ion exchangers. However the performances of such electrodes are much better than the electrodes with the corresponding monomeric subunit. These results suggest that the interaction between the ligand and the anions may be a combination of electrostatic contribution and complementarity between the cavity formed by the phosphonium groups attached to the calixarene and the anion. Structural variations around this molecule, for instance those concerning the nature of the substituents on the functional groups, are currently examined in order to optimise these selectivities.

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## References

- [1] Beer, P. D.; Hayes, E. *Coord. Chem. Rev.* **2003**, *240*, 167.
- [2] Sessler, J. L.; Sansom, P. I.; Andrievsky, A.; Kral, V. In *Supramolecular Chemistry of Anions*; Bianchi, A., Bowman-James, K., Garcia-Espana, E., Eds.; John Wiley-VCH: New York, 1997; ch. 10, p 355.
- [3] Bakker, E.; Buhlmann, P.; Pretsch, E. *Chem. Rev.* **1997**, *97*, 3124.
- [4] Buhlmann, P.; Pretsch, E.; Bakker, E. *Chem. Rev.* **1998**, *98*, 1593.
- [5] Beer, P. D.; Gale, P. A. *Angew. Chem. Int. Ed.* **2001**, *40*, 486.
- [6] Amemiya, S.; Buhlmann, P.; Umezawa, Y.; Jagessar, R. C.; Burns, D. H. *Anal. Chem.* **1999**, *71*, 1049.
- [7] Schmidchen, F. P.; Berger, M. *Chem. Rev.* **1997**, *97*, 1609.
- [8] Beer, P. D.; Cadman, J. *Coord. Chem. Rev.* **2000**, *205*, 31 (see also Gale, P.A. *Coord. Chem. Rev.* **2001**, *213*, 79; Gale, P.A. *Coord. Chem. Rev.* **2003**, *240*, 191).
- [9] Matthews, S. E.; Beer, P. D. In *Calixarenes 2001*; Asfari, Z., Böhmer, V., Harrowfield, J., Vicens, J., Eds.; Kluwer Academic: Dordrecht, 2001; ch. 23, p 421.
- [10] Falana, O. M.; Koch, H. F.; Roundhill, D. M.; Lumetta, G. J.; Hay, B. P. *Chem. Commun.* **1998**, 503.
- [11] Cameron, B. R.; Loeb, S. *Chem. Commun.* **1997**, 573.
- [12] Nam, K. C.; Chun, J. C.; Kang, S. O.; Ko, S. W. *Bull. Korean Chem. Soc.* **1999**, *20*, 1108.
- [13] Scheerder, J.; Fochi, M.; Engbersen, J. F. J.; Reinhoudt, D. N. *J. Org. Chem.* **1994**, *59*, 7815.
- [14] Scheerder, J.; Engbersen, J. F. J.; Casnati, A.; Ungaro, R.; Reinhoudt, D. N. *J. Org. Chem.* **1995**, *60*, 6448.
- [15] Georgiev, E. M.; Wolf, N.; Roundhill, D. M. *Polyhedron* **1997**, *16*, 1581.
- [16] Beer, P. D.; Drew, M. G. B.; Gradwell, K. J. *Chem. Soc. Perkin Trans. 2* **2000**, 511.
- [17] Wróblewski, W.; Brzózka, Z.; Rudkevich, D. M.; Reinhoudt, D. N. *Sens. Actuators B* **1996**, *37*, 151.
- [18] Rudkevich, D. M.; Verboom, W.; Reinhoudt, D. N. *Tetrahedron Lett.* **1994**, *35*, 7131.



- [19] Rudkevich, D. M.; Verboom, W.; Reinhoudt, D. N. *J. Org. Chem.* **1994**, *59*, 3683.
- [20] Malinowska, E.; Niedziolka, J.; Meyerhoff, M. E. *Anal. Chim. Acta* **2001**, *432*, 67.
- [21] Malinowska, E.; Gorski, L.; Meyerhoff, M. E. *Anal. Chim. Acta* **2002**, *468*, 133.
- [22] Maeda, H.; Osuka, A.; Furuta, H. *J. Incl. Phenom.* **2004**, *49*, 33.
- [23] Savage, P. B.; Holmgren, S. K.; Gellman, S. H. *J. Am. Chem. Soc.* **1994**, *116*, 4069.
- [24] Casabo, J.; Eschriche, L.; Perez-Jimenez, C.; Errachid, A. *Anal. Chim. Acta* **1996**, *320*, 63.
- [25] Pomecko, R.; Asfari, Z.; Hubscher-Bruder, V.; Arnaud-Neu, F.; Vicens, J.; Bochenska, M.; XXVIIIth International Symposium on Macrocyclic Chemistry, Gdansk University of Technology, Gdansk, Poland, 13–18 July 2003.
- [26] Hamdi, A.; Nam, K. C.; Ryu, B. J.; Kim, J. S.; Vicens, J. *Tetrahedron Lett.* **2004**, *45*, 4689.
- [27] Gampp, H.; Maeder, M.; Meyer, C. J.; Zuberbühler, A. D. *Talanta* **1986**, *33*, 943.
- [28] Bochenska, M.; Zielinska, A.; Pomecko, R.; Hubscher-Bruder, V.; Arnaud-Neu, F. *J. Incl. Phenom.* **2005**, *52*, 129.
- [29] Umezawa, Y.; Buhlmann, P.; Umezawa, K.; Tohda, K.; Amemiya, S. *Pure Appl. Chem.* **2000**, *72*, 1851 (see also Umezawa, Y.; Buhlmann, P.; Umezawa, K.; Hamada, N.; Aoki, H. *Pure Appl. Chem.* **2002**, *74*, 923).
- [30] Moyer, B. A.; Bonnesen, P. V. In *Supramolecular Chemistry of Anions*; Bianchi, A., Bowman-James, K., Garcia-Espana, E., Eds.; John Wiley-VCH: New York, 1997; ch. 1, p 1.
- [31] Schaller, U.; Bakker, E.; Spichiger, U. E.; Pretsch, E. *Anal. Chem.* **1994**, *66*, 391.
- [32] Bakker, E.; Malinowska, E.; Schiller, R. D.; Meyerhoff, M. E. *Talanta* **1994**, *41*, 881.
- [33] Amemiya, S.; Buhlmann, P.; Pretsch, E.; Rusterholz, B.; Umezawa, Y. *Anal. Chem.* **2000**, *72*, 1618.
- [34] Egorov, V. V.; Rakhmanko, E. M.; Okaev, E.; Nazarov, V.; Pomelyenok, E.; Pavlova, T. *Electroanalysis* **2004**, *16*, 1459.
- [35] Lizondo-Sabater, J.; Segui, M.-J.; Martinez-Manez, R. *Sens. Actuators B*, **2004**, *101*, 20.
- [36] Segui, M.-J.; Sancenon, F.; Martinez-Manez, R. *Analyst* **2002**, *127*, 387.