

Calixarene – Poly(dithiophene)-Based Chemically Modified Electrodes

Marco Giannetto,^[b] Giovanni Mori,^{*[b]} Anna Notti,^[c] Sebastiano Pappalardo,^{*[a]} and Melchiorre F. Parisi^[c]

Abstract: The stepwise synthesis of cone and partial cone 1,3-bridged *n*-propoxy-calix[4]crown ethers (“monomers” **2** and **3**) with an electropolymerizable 2,2'-dithiophene-3-yl-hexylene functionality at the lower rim, is described. The potential of **2** and **3** as sensing agents for alkali metal ions was investigated by ¹H NMR titration experiments with NaSCN and KSCN. The results obtained have confirmed that the presence of the heterocyclic subunit does not affect the well-known size-selectivity observed with calix[4]crowns. Monomers **2** and **3** were electropoly-

merized (Pt as a working electrode, CH₂Cl₂/CH₃CN, Bu₄NPF₆) to produce the title chemically modified electrodes (CMEs). After coating with a PVC membrane containing a lipophilic cation exchanger, CMEs based on calix[4]-crown-5 **2b** (cone) and **3b** (partial cone) were tested for the potentiometric recognition of alkali metal ions in aqueous

solution. In agreement with NMR titration studies, a satisfactory potentiometric response in terms of K⁺/Na⁺ selectivity was obtained only with CME **2b** (pK_{K/Na} 1.51). The amperometric responses of PVC-uncoated CMEs were studied by cyclic voltammetry (CV) experiments in CH₃CN solution. High Na⁺ selectivity was found with the CME based on partial cone calix[4]crown-4 **3a**, and frequency response analysis (FRA) measurements support this finding.

Keywords: calixarenes • conducting materials • chemically modified electrodes • electrochemistry • ion recognition

Introduction

Calixarene derivatives are nowadays among the most versatile and effective synthetic receptors available for the selective recognition of ions and neutral molecules.^[1] Calixarene-based receptors have thus emerged as leading sensing agents for the development of advanced sensory devices (i.e., ion selective electrodes, ISEs; chemically modified field effect transistors, CHEMFETs; ion selective field effect transistors, ISFETs).^[1a, 2] At the same time, the electropolymerization of

pyrroles or thiophenes with suitable pendant functionalities is currently being employed for the coating of electrode surfaces.^[3] Such electrodes are being extensively studied for their potential in electrocatalysis,^[4] or for their ability to sense alkali metal ions.^[5]

We recently envisaged the possibility of combining the ion-binding affinities of calix[4]arene crown ethers with the electronic/redox properties of conducting polymers (CPs),^[6] in order to create new classes of molecular sensors able to recognize and electrochemically respond to alkali metal ions. A rational design of these materials requires the presence, on the calixarene skeleton, of an appropriate moiety which would easily undergo electrooxidative polymerization directly providing CPs immobilized on the electrode surface.^[7] The ion-sensing properties of the resulting chemically modified electrodes (CMEs)^[8] could be tuned by varying the conformation of the calixarene platform, the size of the crown ether bridge, the nature of the substituents at both the upper and lower rims, and the length of the connecting spacer on the monomeric precursor.

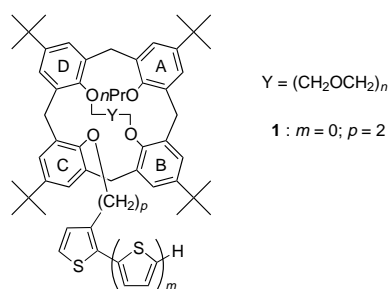
To this end, we recently designed and synthesized several conformers of 1,3-bridged calix[4]arene crown ethers **1** (*m* = 0; *p* = 2), bearing a potentially electropolymerizable 3-thienyl functionality at the lower rim.^[9] However, early attempts to electropolymerize monomers **1** under a number of different conditions, did not produce any CPs on the working electrode, but only soluble oligomeric oxidized species.^[10]

[a] Prof. S. Pappalardo
Dipartimento di Scienze Chimiche
Università di Catania, Viale A. Doria 6
95125 Catania (Italy)
Fax: (+39)095-580138
E-mail: spappalardo@dipchi.unict.it

[b] Prof. G. Mori, Dr. M. Giannetto
Dipartimento di Chimica Generale, Inorganica,
Analitica e Chimica Fisica, Università di Parma
Parco Area delle Scienze 17/A, 43100 Parma (Italy)
Fax: (+39)0521-905557
E-mail: mori@unipr.it

[c] Dr. A. Notti, Prof. M. F. Parisi
Dipartimento di Chimica Organica e Biologica
Università di Messina, Salita Sperone 31
98166 Messina (Italy)

Supporting information for this article is available on the WWW under <http://www.wiley-vch.de/home/chemistry/> or from the authors.

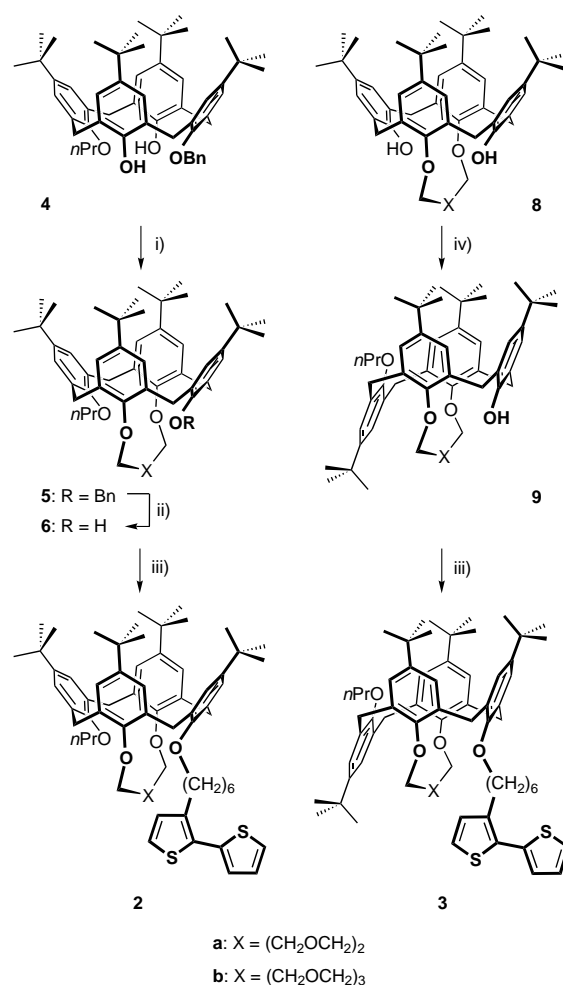


In order to promote the electropolymerization process and minimize the steric interactions between the adjacent calixarene moieties on the resulting polymer, we have now modified monomers **1** by replacing the 3-thienyl ethylene moiety with a 2,2'-dithiophene-3-yl-hexylene functionality. In this paper we describe the synthesis, structural characterization and binding studies of dithiophene-containing cone and partial cone calix[4]crown ethers **2** and **3** ($m = 1$, $p = 6$), and demonstrate that these monomers undergo electrochemical polymerization to poly(dithiophenes) with pendant calix[4]arene-crown-ether functionalities. These hybrid materials behave as useful CMEs for the electrochemical sensing of alkali metal ions.

Results and Discussion

Cone calix[4]crown ether monomers **2** and partial cone monomers **3**, endowed with a pendant 2,2'-dithiophene-3-yl-hexylene moiety at the lower rim, were synthesized using the strategy presented in Scheme 1. Cone precursors **6** were obtained by reaction of **4**^[9] with the appropriate oligoethylene glycol ditosylate and NaH in dry THF to afford cone calix[4]crown derivatives **5** (71–75% yield), followed by selective removal (Pd/C, H₂; 1 atm) of the benzyl protecting group. The Pd-catalyzed hydrogenolysis of **5** to produce **6** is highly recommended over other methods (i.e., Me₃SiCl^[9]), because the reaction is clean and proceeds smoothly in nearly quantitative yield. The partial cone precursors **9** were prepared in reasonable yield (30–38%) by direct propylation of 1,3-bridged calix[4]crowns **8**^[11] with *n*PrI and Cs₂CO₃ in refluxing CH₃CN. The final conversion of **6** and **9** into target cone and partial cone monomers **2** and **3** was accomplished in good yield (48–70%) by alkylation with the known^[12] 3-(6-bromohexyl)-2,2'-dithiophene (**7**) and NaH in dry THF (Scheme 1). The use of NaH as a base ensured that the conformation of the precursors was retained upon derivatization.

All new compounds were characterized by ¹H and ¹³C NMR spectroscopy, FAB-MS and elemental analysis. The cone structures show the expected two AX pattern ($\Delta\delta > 1.2$ ppm) for the bridging methylene protons and two resonances around $\delta = 31$ for the relevant carbons, while their partial cone counterparts display one AX ($\Delta\delta = 1.15 \pm 0.07$ ppm) and one AB system ($\Delta\delta = \leq 0.05$ ppm) for the ArCH₂Ar protons, and two resonances close to $\delta = 31$ and 39 for the corresponding carbons. The ¹H NMR spectra of **9** and **3** suggest that the *n*-propoxy group attached to the inverted phenol residue is



Scheme 1. Synthesis of monomers **2** and **3**. i) oligoethylene glycol ditosylate, NaH, THF, reflux, 24 h; ii) H₂ (1 atm), Pd/C, AcOEt, RT, 4 h; iii) 3-(6-bromohexyl)-2,2'-dithiophene (**7**), NaH, THF, reflux, 24 h; iv) *n*-PrI, Cs₂CO₃, CH₃CN, reflux, 4.5–22 h.

included inside the hydrophobic cavity generated by the three remaining aryl rings.

¹H NMR titration experiments of **2** and **3** with NaSCN and KSCN (up to 2 equiv), carried out in CDCl₃/CD₃OD (1:1 v/v), showed that the introduction of a 2,2'-dithiophene functionality at the lower rim of calixcrowns was not detrimental to their binding abilities. In agreement with the known size-selectivity displayed by calixcrowns,^[13] calix[4]crown-4 monomers **2a** and **3a** formed 1:1 complexes with NaSCN and did not bind KSCN at all. Very high Na⁺/K⁺ selectivity levels, comparable to those reported by Shinkai for the structurally related (1,3)-diethoxy-calix[4]crown-4 cone and partial cone conformers,^[11] were therefore expected for **2a** and **3a**. With a NaSCN/calixcrown-4 molar ratio of 0.5, separate resonances for the complex and free monomer are simultaneously present in both cases, which indicates that **2a** and **3a** form strong complexes with Na⁺ with slow exchange kinetics on the NMR time-scale.

On the other hand, the larger calix[4]crown-5 derivatives **2b** and **3b** are best adapted for the complexation of K⁺ (slow exchange rate process on the NMR time-scale), but still allow the inclusion of the smaller Na⁺ ion. The complexation

process with Na⁺ is in fast exchange regime with cone **2b**, but unexpectedly slow with partial cone **3b**. The behavior of **3b** with Na⁺ ions apparently contrasts with the fast exchange process previously found for the Na⁺ complexation with the partial cone conformer of 1,3-bridged di-(*α*-picolyloxy)-*p*-tert-butylcalix[4]crown-5,^[13f] and may imply a different coordination geometry around the Na⁺ ion.

The solution structures of the alkali metal complexes with monomers **2** and **3** in the stated solvent mixture were inferred by a scrutiny of the complexation-induced shifts (CIS), defined as $\Delta\delta = \delta_{[\text{monomer}\cdot\text{M}^+]} - \delta_{[\text{monomer}]}$ in ppm, which are summarized in Table 1. The remarkable downfield shifts

Table 1. ¹H NMR complexation induced shifts [$\Delta\delta = \delta_{[\text{monomer}\cdot\text{M}^+]} - \delta_{[\text{monomer}]}$ in ppm] of selected protons for dithienyl calix[4]crown complexes with NaSCN and KSCN in CDCl₃/CD₃OD (1:1 v/v).

Protons	Na ⁺ ⊂ 2a	Na ⁺ ⊂ 2b	K ⁺ ⊂ 2b	Na ⁺ ⊂ 3a	Na ⁺ ⊂ 3b	K ⁺ ⊂ 3b
<i>t</i> Bu (A,C-rings)	0.28	0.35	0.42	0.03, 0.15	0.01, 0.15	0.05, 0.11
<i>t</i> Bu (B,D-rings) ^[a]	-0.11	-0.15	-0.24	-0.04	-0.05	-0.09
OCH ₂ CH ₂ CH ₃	-0.12	-0.10	-0.03	-0.13	-0.02	0.51
OCH ₂ CH ₂ CH ₃	-0.07	-0.04	-0.03	-1.25	-0.32	1.07
OCH ₂ CH ₂ CH ₃ ^[b]				0.89	1.06	1.25
ArCH ₂ Ar eq	0.32	0.28	0.28	0.27	0.21	0.13
ArCH ₂ Ar ax	-0.03	0.04	0.02	-0.12	0.04	-0.09
ArH (A,C-rings)	0.59	0.70	0.78	0.15, 0.37	0.09, 0.33	0.21, 0.38
ArH (B,D-rings)	0.10	0.04	0.06	0.00, 0.13	0.02, 0.05	0.01, -0.09

[a] Aryl rings holding the polyether chain. [b] Not measured, because the relevant protons are buried under the signals of the crown ether moiety.

observed for the aromatic (0.59–0.78 ppm) and *tert*-butyl protons (0.28–0.42 ppm) of the alkylated A,C-rings in the alkali complexes with cone monomers **2** are suggestive of a C_{2v} symmetry in the free ligands (A,C-rings in roughly parallel planes), and a pseudo-four-fold C_{4v} symmetry in the complexes (A,C-rings markedly diverging, and B,D-rings holding the polyether bridge slightly converging upon complexation). In the complex, the alkali metal ion is believed to be sitting inside the hydrophilic cavity defined by the crown ether and phenoxy oxygens, with the calix[4]arene moiety adopting an almost regular conic shape.

The *n*-propoxy group attached to the inverted phenol unit in partial cone monomers **3** proved to be a useful probe for assessing the binding sites and geometry of their complexes with alkali metal salts. Undoubtedly the *O-n*Pr substituent shows a certain propensity to fill the hydrophobic cavity of the free monomers, as shown by the upfield resonances close to $\delta = 0.0$ (Figure 1, 2, traces a), but upon Na⁺ complexation it intrudes more deeply inside the calix cup, as evidenced by the dramatic upfield CIS observed for the β -methylene group in the Na⁺ ⊂ **3a** complex ($\Delta\delta = -1.25$ ppm) (Figure 1c) and to a much lesser extent in the Na⁺ ⊂ **3b** complex ($\Delta\delta = -0.32$ ppm) (Figure 2b). The overall CIS values observed for the Na⁺ ⊂ **3a,b** complexes (Table 1) are consistent with the formation of capsular complexes, with the Na⁺ ion bound inside the hydrophilic crown ether cavity and the *n*-propoxy group acting as a stopper from the upper rim side. The remarkable upfield shift experienced by the β -methylene protons in the Na⁺ ⊂ **3a** complex is suggestive of a strong

participation by the *n*-propoxy oxygen in the stabilization of the complex, and consequently the calixarene framework is believed to approach an almost flat partial cone conformation. Obviously, the small Na⁺ ion is less tightly bound by the larger crown-5 derivative **3b**, and a ¹H NMR experiment in which one equivalent of KSCN was added to the preformed Na⁺ ⊂ **3b** complex has shown that the Na⁺ ion can easily be displaced by the better fitting K⁺ ion (Figure 2c).

A comparison between the CIS values of the *n*-propoxy group in Na⁺ ⊂ **3b** and K⁺ ⊂ **3b** complexes shows that the two ions have different binding modes. The ion–dipole interaction of the *n*-propoxy group with Na⁺ is now overcome by a

more effective cation– π interaction with the softer K⁺ ion,^[14] which pushes the *O-n*Pr group out of the calix cavity, as evidenced by the substantial downfield shift experienced by the protons of the inverted *n*-propoxy-phenyl residue (Table 1 and Figure 2b, c).

The electropolymerization of **2** and **3** on Pt disk electrodes was achieved by repetitive scan cyclic voltammetry (RSCV)^[3] under strictly controlled experimental conditions. Unsubstituted poly(dithiophene) can be obtained from acetonitrile or dichloromethane solutions.^[6, 15]

However, monomers **2** and **3** are not soluble in neat acetonitrile, whereas neat dichloromethane readily solubilizes the oligomers generated in the early stages of the process, thus preventing the attainment of the critical solubility required for the electrodeposition. Electropolymerization was therefore conducted in CH₂Cl₂/CH₃CN (1:5 v/v) containing 10⁻¹M Bu₄NPF₆ as a supporting electrolyte with a silver wire pseudoreference electrode ($E_{\text{p ferrocene}} = 0.40$ V). A typical voltammogram showing the growth of the film from monomer **2b** is depicted in Figure 3. The choice of the window potential ($E = 0.0$ –1.3 V) and particularly the anodic limit are extremely critical to obtain film deposition and to avoid over-oxidation phenomena. The oxidation peak potential of monomers **2a** and **3a** lies at 1.025 V, whereas **2b** and **3b** show the peak at 1.035 V. The resulting films were greenish-blue in color in the oxidized form, and deep red when reduced. They were soluble in CHCl₃ and THF, and insoluble in CH₃CN.

A comparison of the structural features and electrochemical behavior of monomers **1**–**3** shows that the replacement of an alkylthiophene with an alkyldithiophene calixcrown pendant and an increase in the spacer length favor the electropolymerization/deposition process. This trend closely parallels the one previously reported for mono- and dithiophene crown-ether-functionalized monomers.^[5b] In that instance, steric repulsion and/or solubility effects and more importantly the lowering of the oxidation potential due to the more extended π -system of the dithiophene moiety were invoked to account for the electrooxidative polymerization outcome.

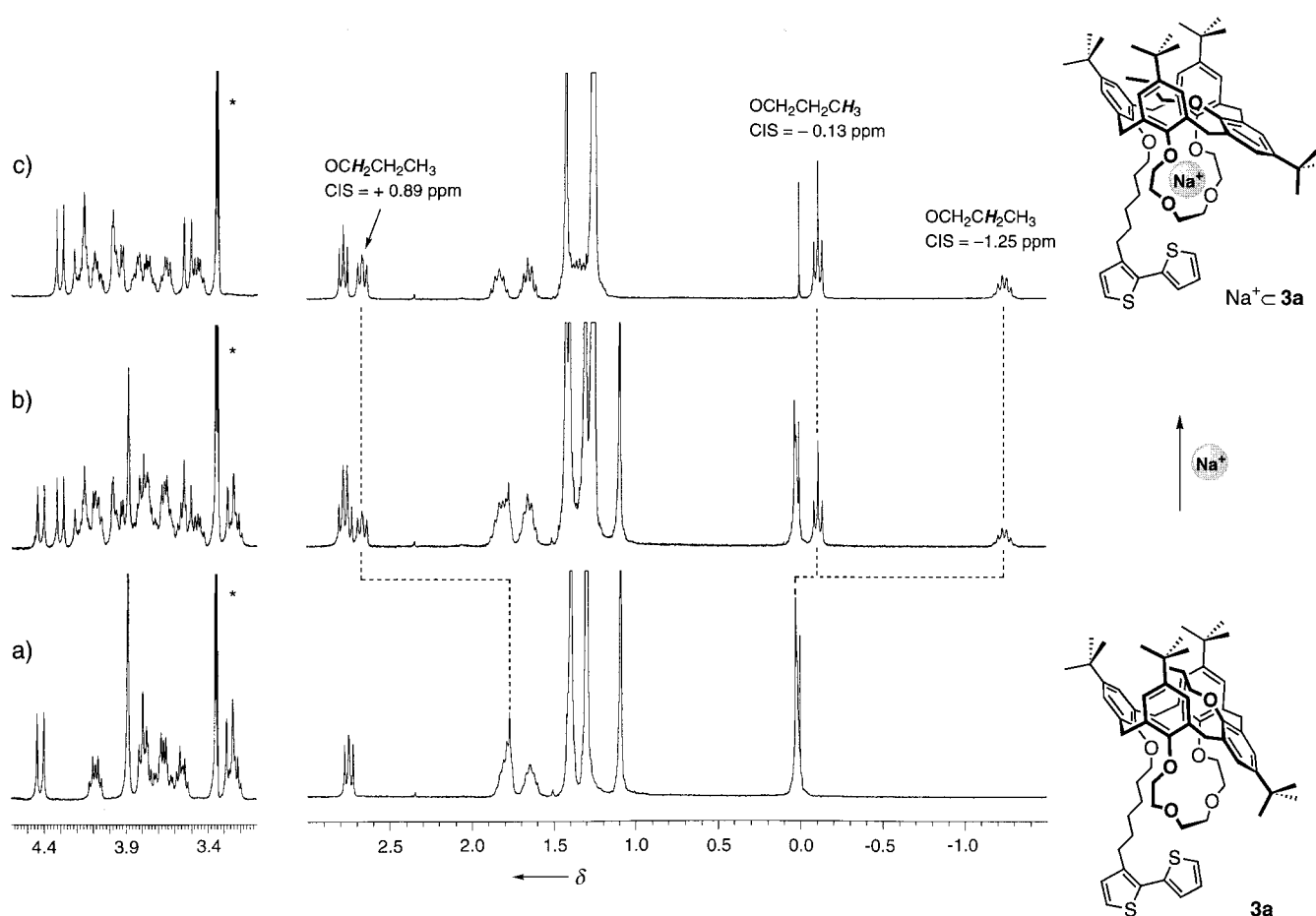


Figure 1. Selected regions of the ^1H NMR spectra (300 MHz, $\text{CDCl}_3/\text{CD}_3\text{OD}$ 1:1 v/v, 22°C) of partial cone monomer **3a** a), and spectral changes upon addition of 0.5 b) and 1.0 equiv c) of NaSCN. An asterisk indicates residual solvent peak. In the middle trace, a slow exchange rate between the free monomer and its Na^+ complex accounts for peak doubling. The upper trace ($\text{Na}^+ \cdot \mathbf{3a}$ complex) provides clear evidence that the Na^+ ion is tightly encapsulated inside the ionophoric cavity composed by the four crown ether oxygens and the ethereal oxygens of the lower rim substituents. The complexation induced shifts (CIS) for the inverted *O*-*n*Pr group indicate that this substituent intrudes very deeply inside the calix cup, acting as a stopper.

Initial studies on the CMEs **2b** and **3b** for the potentiometric recognition of K^+ ions revealed that the electrochemical behavior of the polymeric films was extremely sensitive to the oxygen dissolved in the tested aqueous solution. Thus, the films of the CMEs were set into the reduced form, using an aqueous solution of 10^{-1}M KCl containing traces of hydrazine, dried, and then coated with a dibutyl sebacate membrane supported on poly(vinylchloride) (PVC), in which only potassium tetrakis(4-chlorophenyl)borate ($\text{K}(\text{TCPB})$) was dissolved. The potentiometric response of PVC-coated CMEs **2b** and **3b** towards K^+ ions (KCl) was measured in the presence of Na^+ as interfering ions (NaCl). Their characteristic parameters, shown in Table 2, were

Table 2. Electrochemical parameters for CMEs **2b** and **3b**.^[a]

CME	Slope [mV/pK]	$\log \xi$	$\log K_{\text{K,Na}}$
2b	49.3(1.6)	-4.6(0.1)	-1.51(0.06)
3b	59.2(0.7)	-4.4(0.1)	-0.63(0.02)

[a] Standard deviations in parentheses.

determined by the fixed interference method^[16] and calculated with a non-linear regression on a modified Nicolsky–Eisenman Equation^[17] [Eq. (1)], where β is the slope (mV/pI), a_{k} is the activity of the primary ion to which the CME is reversible, $K_{\text{K,Na}}$ is the selectivity constant of the device for K^+ vs Na^+ ions, a_{Na} is the activity of the interfering ion, and ξ is an “apparent activity” present on the electrode at the beginning of the calibration in the absence of added ions. Equation (1) allows the simultaneous interpolation of several calibration curves obtained with different methods and with different interferent concentrations (see Supporting Information).

$$E = E_{\text{const}} + \beta \log(a_{\text{k}} + K_{\text{K,Na}} \cdot a_{\text{Na}} + \xi) \quad (1)$$

The potentiometric values of K^+/Na^+ selectivity shown by CMEs **2b** and **3b**, albeit moderate, are significantly higher than those determined, under identical experimental conditions, either by a PVC-coated bare Pt-electrode ($\text{p}K_{\text{K,Na}} = 0.18(0.05)$) or a PVC-coated Pt-electrode modified with unfunctionalized poly(dithiophene) ($\text{p}K_{\text{K,Na}} = 0.20(0.03)$). This experimental evidence rules out the hypothesis that the

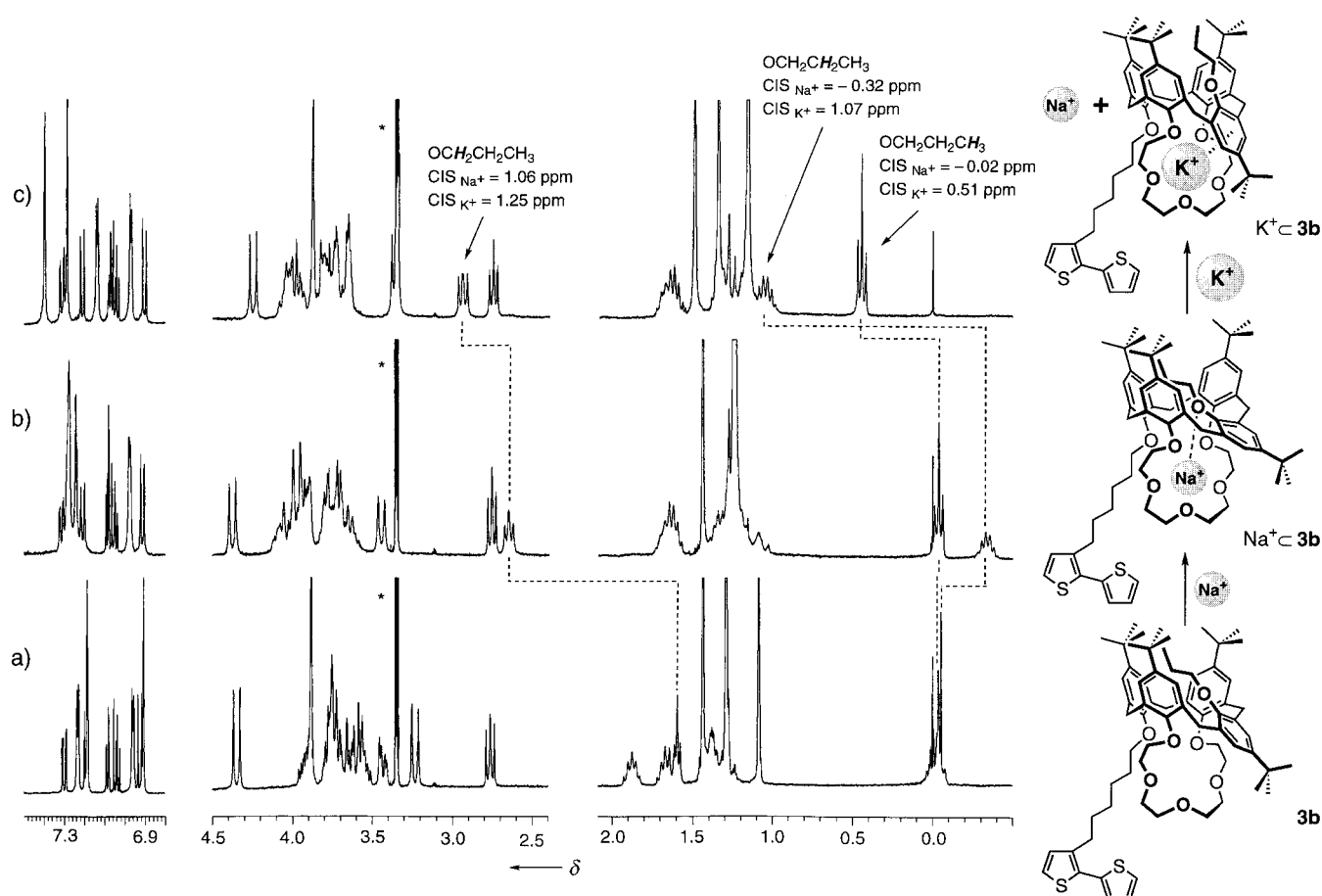


Figure 2. The three spectral regions of the ^1H NMR spectra (300 MHz, $\text{CDCl}_3/\text{CD}_3\text{OD}$ 1:1 v/v , 22°C) of **3b** a), and spectral changes upon addition of 1.0 equiv NaSCN b), and then 1.0 equiv KSCN c). An asterisk indicates residual solvent peak. A comparison of traces b) and c) emphasizes the different coordination geometry and binding sites around the encapsulated Na^+ (ion–dipole interaction with the *n*-propoxy group) or K^+ (cation– π interaction with the inverted aryl unit) ions.

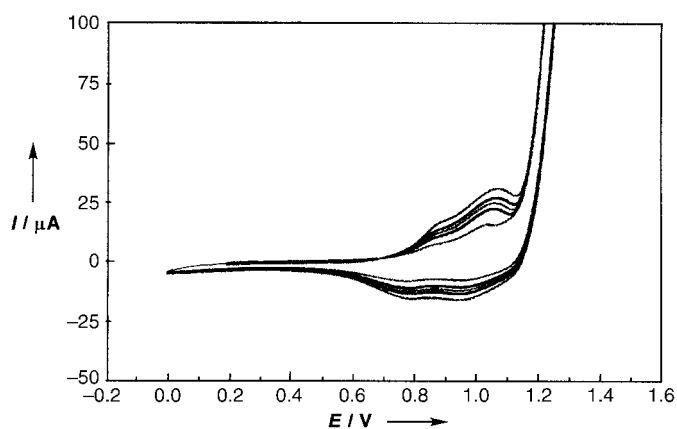


Figure 3. Cyclic voltammograms recorded during the electropolymerization of monomer **2b**. The polymer was grown on a polished Pt disk electrode of 1.35 mm radius by cycling the potential between 0.0 and 1.3 V vs Ag/AgCl at a scan rate of 100 mV s^{-1} of a solution of **2b** (10^{-2} M) and Bu_4NPF_6 (10^{-1} M) in $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ (1:5 v/v).

observed selectivity might simply be due to unspecific interactions between the ion-exchanger (K(TCPB)) and/or the solvent (dibutyl sebacate) of the PVC membrane and the

analyte ions (K^+ or Na^+) with different charge density, and confirms that an active role is played by the calixcrown moieties of the poly(dithiophene) films **2b** and **3b**. Furthermore, the lower selectivity of the partial cone CME **3b** ($\text{p}K_{\text{K,Na}} = 0.63$) with respect to the cone **2b** ($\text{p}K_{\text{K,Na}} = 1.51$), agrees with the results of NMR experiments.

Although the mechanism accounting for the potentiometric ion recognition of PVC-coated CMEs **3b** and **2b** is not yet fully understood and deserves further investigation, it is worth mentioning that, to the best of our knowledge, this is the first instance in which calixarene–poly(dithiophene)-based CMEs have successfully been employed for the recognition of alkali metal ions in aqueous solution.^[18]

The potentiometric behavior of CMEs **2a** and **3a** could not be studied, as the PVC coating was hampered by the high solubility of the film in the solvents (THF, DMF, cyclohexanone) commonly used to solubilize PVC.

The amperometric selectivity of PVC-uncoated CMEs **3a** and **2b** for alkali metal ions was studied in both aqueous and organic media. Cyclic voltammetry (CV) experiments, performed in monomer-free acetonitrile solutions, showed that the complexation of alkali metal ions strongly influences the voltammetric behavior of our electrodes. For instance, in the

case of CME **3a** the anodic peak current ($E_{pa} = 1.05$ V) of the cyclic voltammograms recorded in solutions of NaClO_4 in 10^{-1} M Bu_4NPF_6 , decreased with the increase of Na^+ concentration, ranging from 1.0×10^{-5} to 2.2×10^{-4} M (Figure 4). Con-

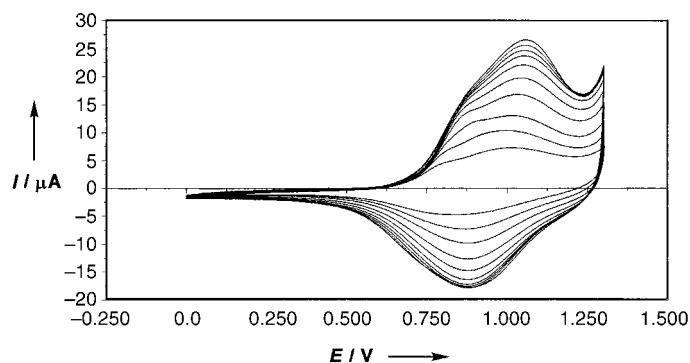


Figure 4. Cyclic voltammograms (E vs Ag/AgCl) of PVC-uncoated CME **3a** (scan rate 50 mV s^{-1}) in 10^{-1} M $\text{Bu}_4\text{NPF}_6/\text{CH}_3\text{CN}$ solution in the presence of increasing concentrations of NaClO_4 (1.0×10^{-5} – 2.2×10^{-4} M).

versely, CME **3a** was voltammetrically inactive in water, where no oxidation peak could be detected. The effect of Na^+ ions on the CV response of CME **3a** in CH_3CN can presumably be ascribed to the accumulation of positive charges (Na^+) in the calixarene moieties of the polymeric film, which electrostatically hamper the formation of positive charges on the poly(dithiophene) backbone during the oxidation process.

Figure 5 shows that the amperometric response of calixcrown-4-based CME **3a** is highly selective for Na^+ over K^+ , NH_4^+ , and Cs^+ ions, while Li^+ ion strongly interferes, as its size allows it to be included in the crown-4 moiety. Over the same

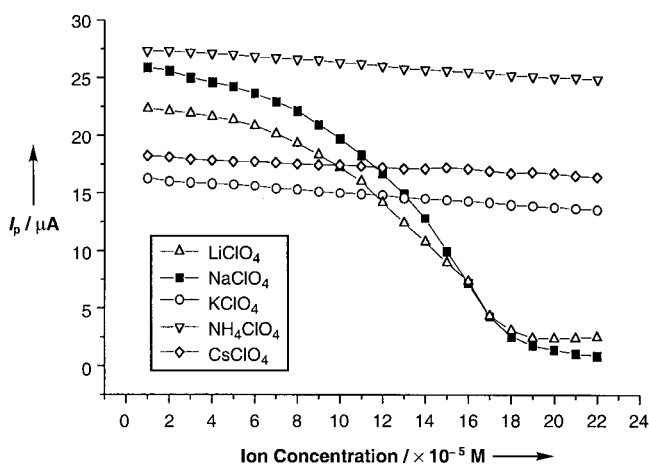


Figure 5. Correlation plots of anodic peak current vs ion concentration (Li^+ , Na^+ , K^+ , NH_4^+ , and Cs^+) obtained with CME **3a** at the potential value of 1.05 V.

concentration range of ion added (as perchlorate salts), the decrease of the peak current upon addition of Li^+ and Na^+ ions was about ten-fold that caused by K^+ , NH_4^+ , and Cs^+ ions. A control experiment carried out in an analyte-free solution did not show, after a number of successive scans, any appreciable changes in the cyclic voltammograms, thus confirming that the redox chemistry of CME **3a** is influenced

by the presence of alkali metal ions. Furthermore, since no amperometric response was obtained for the model CME based on the unsubstituted poly(dithiophene), the changes in the electronic properties of CME **3a** induced by Li^+ and Na^+ ions can be attributed to specific host–guest interactions between the calixcrown units and the target analyte. Attempts to free the Na^+ -containing film **3a** from the bound ions by rinsing with fresh CH_3CN did not restore the original electroactivity of the CME.

Calixcrown-5-based CME **2b** was amperometrically responsive to K^+ ions, but the selectivity over other alkali metal ions was poor.

The selective recognition of Na^+ ions by CME **3a** was further investigated by means of frequency response analysis (FRA) experiments^[19] in the 10^4 – 10^{-1} Hz frequency range at the open circuit potential, using solutions analogous to those employed in the amperometric measurements. Nyquist diagrams obtained with CME **3a** show how the resistance of the polymeric film decreases with the increase of Na^+ ion concentration (Figure 6). Conversely, the resistance of a

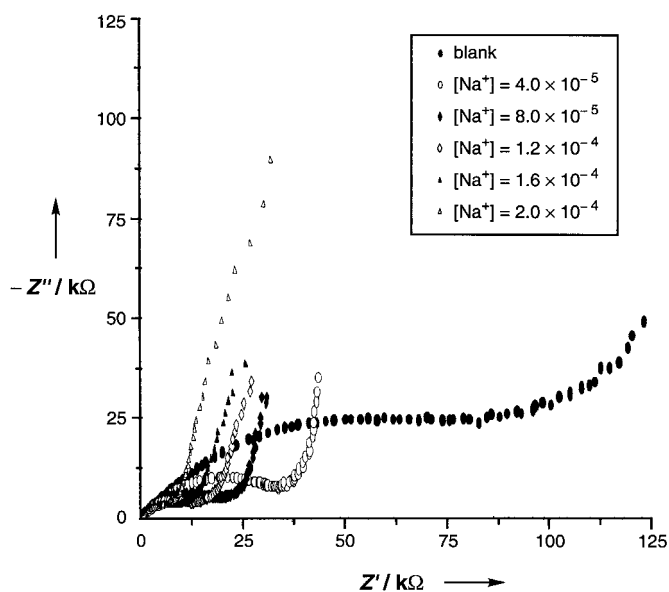


Figure 6. Nyquist diagrams (Z' indicates the real component of the impedance, and Z'' the imaginary one) recorded with CME **3a** by FRA experiments, showing a progressive decrease in polymer resistance upon exposure to increasing amounts of Na^+ ions (NaClO_4).

second film based on **3a** was substantially unchanged in the presence of increasing amounts of K^+ ions (Figure 7). The present data demonstrate that drastic changes in the film resistance are only due to the selective Na^+ ion recognition by the calixcrown unit of the CME **3a**.

In conclusion, the present study shows that dithiophene-substituted calix[4]arene-crown ethers can be conveniently electropolymerized on Pt disks, regardless of their conformation and the length of the crown ether chain, to provide ion-responsive sensory materials with interesting potentialities in both potentiometric and amperometric recognition of alkali metal ions. Fine tuning of the calixcrown monomers to generate new materials with enhanced and/or different analyte selectivities is currently in progress.

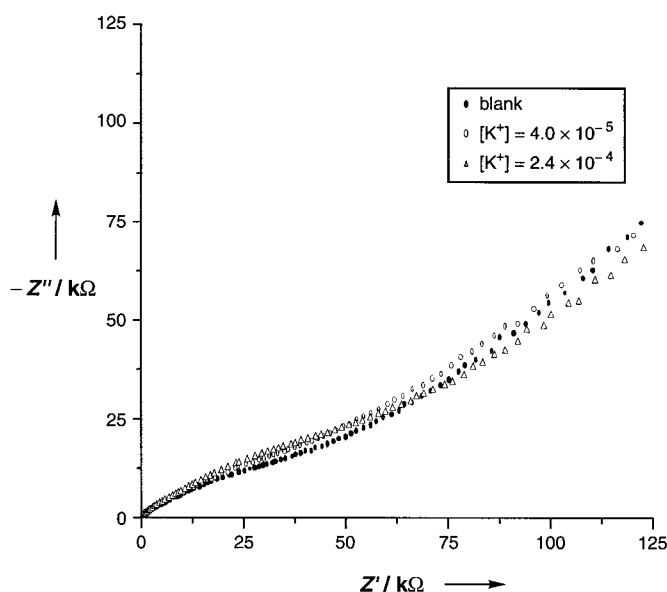


Figure 7. Nyquist diagrams (Z' indicates the real component of the impedance, and Z'' the imaginary one) recorded with CME **3a** by FRA experiments in the presence of different amounts of K^+ ions ($KClO_4$). No changes in polymer resistance is observed.

Experimental Section

General: Melting points were determined on a Kofler hot stage and are not corrected. Unless otherwise stated, 1H and ^{13}C NMR spectra were recorded in $CDCl_3$ (TMS as an internal standard) with a Varian Gemini 300 spectrometer at 300 and 75 MHz, respectively. ^{13}C NMR spectra were acquired with the APT technique. FAB(+) mass spectra were obtained with a Finnigan MAT 90 spectrometer, using 3-nitrobenzyl alcohol as a matrix. TLC was performed on silica gel coated plastic plates (Polygram SIL G/UV₂₅₄, Macherey–Nagel), and column chromatography (CC) was carried out with 230–400 mesh, Merck Kieselgel 60 silica gel. All chemicals were of the best grade commercially available and were used without purification. Dry solvents were purchased from Fluka. Compounds **4**,^[9] **7**,^[12] **8a**,^[11] **8b**,^[13] and oligoethylene glycol ditosylates^[20] were prepared according to literature procedures.

Electropolymerizations and voltammetric studies were conducted using the computerized Autolab PGSTAT 20 potentiostat (Ecochemie, Utrecht, The Netherlands) connected to a 663 VA Stand (Metrohm, Herisau, Switzerland) and controlled by Ecochemie GPES 4.4 software. Polymeric films were obtained by cycling potential for a number of 25 scans between 0 and 1.3 V in $5 \times 10^{-3} M$ monomer and 0.1 M Bu_4NPF_6 solutions. The three-electrode miniaturized cell (1 mL) was equipped with a platinum disk ($r = 1.5$ mm) working electrode and a platinum rod counter. All potential values were measured against a silver/silver chloride pseudoreference electrode with respect to which the ferrocene system showed an $E_p = 0.402$ V. FRA experiments were performed with the same equipment, controlled by Ecochemie FRA 2.3 software. Potentiometric measurements were carried out using a Radiometer PHM84 digital potentiometer (Radiometer Medical A/S, Copenhagen, Denmark). The PVC membrane is analogous to that previously used for ISEs.^[21]

5,11,17,23-Tetrakis(1,1-dimethylethyl)-25-benzyloxy-26,28-(crown-4)-27-propoxy-calix[4]arene (5a):^[22] A mixture of **4** (0.550 g, 0.704 mmol) and NaH (0.090 g, 3.75 mmol) in dry THF (40 mL) was heated under reflux for 1.5 h under stirring. Triethylene glycol ditosylate (0.353 g, 0.77 mmol) in dry THF (10 mL) was then added dropwise over 30 min, and reflux was continued for additional 20 h. The reaction was quenched by cautious addition of MeOH (2 mL), and the solvent was evaporated. The residue was partitioned between acidified water and CH_2Cl_2 . The organic layer was dried (Na_2SO_4) and concentrated to leave a solid, which upon recrystallization from CH_3CN/CH_2Cl_2 gave crown-4 **5a** (0.450 g, 71%) as colorless crystals. M.p. $> 250^\circ C$; 1H NMR: $\delta = 7.57$ –7.36 (m, 5H), 7.13 (pseudo-s,

4H), 6.49, 6.46 (s, 2H each), 4.72 (s, 2H), 4.40, 4.38 (d, $J = 12.4$ Hz, 2H each), 4.24–4.16 (m, 2H), 4.06–3.87 (m, 6H), 3.70–3.62 (m, 4H), 3.43–3.35 (m, 2H), 3.12, 3.11 (d, $J = 12.4$ Hz, 2H each), 1.94 (sextet, $J = 7.4$ Hz, 2H), 1.34, 0.83, 0.81 (s, ratio 2:1:1, 36H), 1.03 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR: $\delta = 154.7$, 152.4, 151.2 (s, C_{sp^2-O}), 144.9, 144.3, 143.7 (s, C_{sp^2-tBu}), 137.8 (s, Ph), 135.5, 135.4, 132.0, 131.8 (s, bridgehead-C), 129.9, 128.4, 128.0, 125.6, 125.5, 124.5, 124.3 (d, Ar, Ph), 78.2 (t, OCH_2Ph), 77.6 (t, $OCH_2CH_2CH_3$), 73.6, 70.6, 70.0 (t, OCH_2CH_2O), 34.1, 33.6, 33.5 (s, $C(CH_3)_3$), 31.7, 31.16, 31.10 (q, $C(CH_3)_3$), 30.6, 30.4 (t, $ArCH_2Ar$), 23.4 (t, $OCH_2CH_2CH_3$), 10.7 (q, $OCH_2CH_2CH_3$); FAB(+) MS: m/z : 895 $[MH]^+$; elemental analysis calcd (%) for $C_{60}H_{78}O_6$ (894.6): C 80.50, H 8.78; found: C 80.15, H 8.64.

5,11,17,23-Tetrakis(1,1-dimethylethyl)-25,27-(crown-4)-26-hydroxy-28-propoxy-calix[4]arene (6a):^[22] A suspension of **5a** (0.447 g, 0.5 mmol) and 10% Pd/C (50 mg) in AcOEt (25 mL) was stirred for 4 h at room temperature in the presence of H_2 (1 atm). The mixture was filtered through a bed of celite, and the filtrate was evaporated to dryness to give a solid. Recrystallization from $CHCl_3/MeOH$ gave monohydroxy-crown-4 **6a** (0.342 g, 85%). M.p. 218–220 $^\circ C$; 1H NMR: $\delta = 7.14$ (pseudo-s, 4H), 6.64 (s, 2H), 6.62 (s, 1H), 6.41 (s, 2H), 4.60–4.53 (m, 2H), 4.55, 4.40 (d, $J = 12.7$ Hz, 2H each), 3.77–3.69 (m, 2H), 3.75 (t, $J = 7.4$ Hz, 2H), 3.22, 3.15 (d, $J = 12.7$ Hz, 2H each), 1.97 (sextet, $J = 7.4$ Hz, 2H), 1.33, 0.96, 0.71 (s, ratio 2:1:1, 36H), 1.11 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR: $\delta = 154.2$ ($\times 2$), 152.2, 147.6 (s, C_{sp^2-O}), 145.8 ($\times 2$), 144.3 (s, C_{sp^2-tBu} , alkylated rings), 142.3 (s, C_{sp^2-tBu} , unalkylated ring), 135.9, 135.2, 131.7, 130.9 (s, bridgehead-C), 126.0, 125.2, 125.0, 123.8 (d, Ar), 77.7 (t, $OCH_2CH_2CH_3$), 74.6, 71.0, 70.8 (t, OCH_2CH_2O), 34.1 ($\times 2$), 33.6, 33.5 (s, $C(CH_3)_3$), 31.8 (t, $ArCH_2Ar$), 31.6 ($\times 2$), 31.2 (q, $C(CH_3)_3$), 31.1 (t, $ArCH_2Ar$), 31.0 (q, $C(CH_3)_3$), 23.7 (t, $OCH_2CH_2CH_3$), 10.7 (q, $OCH_2CH_2CH_3$); FAB(+) MS: m/z : 805 $[MH]^+$; elemental analysis calcd (%) for $C_{53}H_{72}O_6$ (804.5): C 79.05, H 9.02; found: C 78.86, H 9.15.

5,11,17,23-Tetrakis(1,1-dimethylethyl)-25,27-(crown-5)-26-hydroxy-28-propoxy-calix[4]arene (6b):^[22] Pd/C-catalyzed hydrogenolysis of **5b** under conditions analogous to those described for **5a**, afforded monohydroxy-crown-5 **6b** (93%). The physical and spectral data are coincident with those reported in the literature.^[9]

Propylation of 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,27-(crown-4)-26,28-dihydroxycalix[4]arene (8a): A mixture of crown-4 diol **8a** (0.686 g, 0.9 mmol) and Cs_2CO_3 (0.293 g, 0.9 mmol) in dry CH_3CN (25 mL) was refluxed under stirring for 1 h. Then $nPrI$ (0.595 g, 3.5 mmol) was added and the mixture was heated at reflux. After 6 h, a second portion of $nPrI$ (0.595 g, 3.5 mmol) was added, and reflux was continued for a total of 22 h. After cooling, the solvent was evaporated and the residue was washed with a dilute aqueous $Na_2S_2O_3$, then with water and dried (Na_2SO_4). The crude product obtained by evaporation of the solvent was purified by CC (silica gel, eluent: hexanes/AcOEt 6:1 \rightarrow 2:1 v/v) to afford **9a** (0.277 g, 38%). M.p. 200–202 $^\circ C$ (CH_3CN/CH_2Cl_2); 1H NMR: $\delta = 7.32$ (s, 1H), 7.14, 7.02 (s, 2H each), 7.17/6.95 (ABq, $J = 2.6$ Hz, 4H), 4.38/3.30 (AX, $J = 12.5$ Hz, 4H), 3.97–3.49 (m, 16H), 1.92 (t, $J = 7.8$ Hz, 2H), 1.42, 1.22, 1.21 (s, ratio 1:2:1, 36H), 0.05 (sextet, $J = 7.8$ Hz, 2H), -0.59 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR: $\delta = 154.3$, 153.0 ($\times 2$), 149.4 (s, C_{sp^2-O}), 146.0 ($\times 2$), 144.1 (s, C_{sp^2-tBu} , alkylated rings), 141.8 (s, C_{sp^2-tBu} , unalkylated ring), 134.6, 133.7, 133.2, 129.1 (s, bridgehead-C), 126.5, 125.9, 125.5, 124.2 (d, Ar), 71.3 (t, $OCH_2CH_2CH_3$), 72.7, 70.2, 69.3 (t, OCH_2CH_2O), 39.6 (t, $ArCH_2Ar$), 34.1, 34.0 ($\times 2$), 33.8 (s, $C(CH_3)_3$), 31.9 (t, $ArCH_2Ar$), 31.8, 31.6, 31.4 ($\times 2$) (q, $C(CH_3)_3$), 21.2 (t, $OCH_2CH_2CH_3$), 8.6 (q, $OCH_2CH_2CH_3$); FAB(+) MS: m/z : 805 $[MH]^+$; elemental analysis calcd (%) for $C_{53}H_{72}O_6$ (804.5): C 79.05, H 9.02; found: C 79.27, H 8.88.

Propylation of 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,27-crown-5-26,28-dihydroxycalix[4]arene (8b): A mixture of crown-5 diol **8b** (1.536 g, 1.9 mmol) and Cs_2CO_3 (0.620 g, 1.9 mmol) in dry CH_3CN (30 mL) was refluxed under stirring for 1 h. Then $nPrI$ (0.258 g, 1.5 mmol) in CH_3CN (20 mL) was added dropwise and the mixture was heated at reflux for 4.5 h. After cooling, the solvent was evaporated and the residue was partitioned between 1N HCl and CH_2Cl_2 . The organic layer was washed with a dilute aqueous $Na_2S_2O_3$, then with water and dried (Na_2SO_4). The crude product obtained after evaporation of the solvent was purified by CC (silica gel, hexanes/AcOEt 8:1 v/v) to give colorless crystals of **9b** (0.400 g, 30%). M.p. 238–240 $^\circ C$ ($MeOH/CH_2Cl_2$); 1H NMR: $\delta = 7.22$, 7.04 (s, 2H each), 7.02 (s, 1H), 6.98/6.96 (ABq, $J = 2.4$ Hz, 4H), 4.41/3.20 (AX, $J = 12.9$ Hz, 4H), 4.12 (dt, $J = 10.1$, 3.0 Hz, 2H), 4.00–3.93

(m, 2H), 3.86/3.81 (ABq, $J = 16.5$ Hz, 4H), 3.78–3.59 (m, 12H), 2.09 (t, $J = 8.2$ Hz, 2H), 1.45, 1.28, 1.14 (s, ratio 1:1:2, 36H), 0.95 (sextet, $J = 7.5$ Hz, 2H), -0.13 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR: $\delta = 154.3, 152.4$ ($\times 2$), 150.3 (s, $\text{C}_{\text{sp}^2}\text{-O}$), 145.7 ($\times 2$), 143.7 (s, $\text{C}_{\text{sp}^2}\text{-tBu}$, alkylated rings), 141.0 (s, $\text{C}_{\text{sp}^2}\text{-tBu}$, unalkylated ring), 133.9, 133.7, 133.4, 127.9 (s, bridgehead-C), 127.1, 126.1, 125.9, 124.7 (d, Ar), 73.8, 72.7, 71.3, 70.7, 70.3 (t, $\text{OCH}_2\text{CH}_2\text{O}$, $\text{OCH}_2\text{CH}_2\text{CH}_3$), 38.9 (t, ArCH_2Ar), 34.1, 33.9 ($\times 2$), 33.8 (s, $\text{C}(\text{CH}_3)_3$), 31.9, 31.7, 31.2 ($\times 2$) (q, $\text{C}(\text{CH}_3)_3$), 30.9 (t, ArCH_2Ar), 22.6 (t, $\text{OCH}_2\text{CH}_2\text{CH}_3$), 9.1 (q, $\text{OCH}_2\text{CH}_2\text{CH}_3$); FAB(+) MS: m/z : 849 [MH] $^+$; elemental analysis calcd (%) for $\text{C}_{55}\text{H}_{76}\text{O}_7$ (848.5): C 77.79, H 9.02; found: C 77.47, H 8.95.

Alkylation of monopropylated calix[4]crowns with 3'-(6-bromohexyl)-2,2'-dithiophene (7)

General procedure: A stirred suspension of the appropriate *n*-propoxy-calix[4]crown (0.2 mmol) and NaH (14.4 mg, 0.6 mmol) in dry THF (10 mL) was refluxed for 1 h under inert atmosphere. Then a solution of **7** (72 mg, 0.22 mmol) in THF (10 mL) was added through cannula, and reflux was continued for 24 h. After cooling, the reaction mixture was quenched with MeOH (2 mL), and concentrated to dryness. The crude product was taken up in aqueous ethanol and heated under reflux for 12–48 h. After extraction with CHCl_3 , the organic layer was dried over anhydrous Na_2SO_4 and concentrated. The residue was purified either by silica gel CC and/or recrystallization from EtOH.

5,11,17,23-Tetrakis(1,1-dimethylethyl)-25,27-(crown-5) $^\alpha$ -26-[[6-(2,2'-dithiophene-3-yl)hexyl]oxy] $^\alpha$ -28-propoxy $^\alpha$ -calix[4]arene (2a)^[22] Purified by CC (AcOEt/MeOH 95:5 *v/v*); 48% yield; foamy; ^1H NMR: $\delta = 7.25$ (dd, $J = 5.0, 1.3$ Hz, 1H), 7.16 (d, $J = 5.1$ Hz, 1H), 7.13 (s, 4H), 7.09 (dd, $J = 3.6, 1.3$ Hz, 1H), 7.01 (dd, $J = 5.0, 3.6$ Hz, 1H), 6.93 (d, $J = 5.1$ Hz, 1H), 6.47 (s, 4H), 4.38, 4.37 (d, $J = 12.4$ Hz, 2H each), 4.34, 4.03 (t, $J = 6.0$ Hz, 4H each), 3.83 (s, 4H), 3.70 (t, $J = 7.1$ Hz, 2H), 3.68 (t, $J = 7.2$ Hz, 2H), 3.14, 3.13 (d, $J = 12.4$ Hz, 2H each), 2.77 (t, $J = 7.7$ Hz, 2H), 2.03–1.90 (m, 4H), 1.76–1.40 (m, 4H), 1.34, 0.82 (s, ratio 1:1, 36H), 1.30 (m, 2H), 1.06 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR: $\delta = 154.6$ ($\times 2$), 152.3 ($\times 2$) (s, $\text{C}_{\text{sp}^2}\text{-O}$), 144.9 ($\times 2$), 143.8 ($\times 2$) (s, $\text{C}_{\text{sp}^2}\text{-tBu}$), 139.5 (s, ThTh), 135.5 ($\times 2$), 131.8 ($\times 2$) (s, bridgehead-C), 130.5 (s, ThTh), 129.9, 127.3, 126.0, 125.6 ($\times 2$), 125.3, 124.3 ($\times 2$), 123.7 (d, Ar, ThTh), 77.7 (t, $\text{OCH}_2\text{CH}_2\text{CH}_3$), 75.9 (t, $\text{OCH}_2(\text{CH}_2)_5\text{ThTh}$), 73.6, 70.9, 70.2 (t, $\text{OCH}_2\text{CH}_2\text{O}$), 34.1 ($\times 2$), 33.6 ($\times 2$) (s, $\text{C}(\text{CH}_3)_3$), 31.7 ($\times 2$), 31.1 ($\times 2$) (q, $\text{C}(\text{CH}_3)_3$), 30.8, 30.5, 30.3, 29.7, 29.5, 29.1, 26.1 (t, $\text{OCH}_2(\text{CH}_2)_5\text{ThTh}$, ArCH_2Ar), 23.5 (t, $\text{OCH}_2\text{CH}_2\text{CH}_3$), 10.8 (q, $\text{OCH}_2\text{CH}_2\text{CH}_3$); FAB(+) MS: m/z : 1053 [MH] $^+$; elemental analysis calcd (%) for $\text{C}_{67}\text{H}_{88}\text{O}_6\text{S}_2$ (1052.6): C 76.38, H 8.43, S 6.07; found: C 76.27, H 8.33, S 5.85.

5,11,17,23-Tetrakis(1,1-dimethylethyl)-25,27-(crown-5) $^\alpha$ -26-[[6-(2,2'-dithiophene-3-yl)hexyl]oxy] $^\alpha$ -28-propoxy $^\alpha$ -calix[4]arene (2b)^[22] Purified by direct recrystallization of the crude reaction mixture; 58% yield. M.p. 173–176 °C (EtOH); ^1H NMR: $\delta = 7.26$ (dd, $J = 5.2, 1.3$ Hz, 1H), 7.16 (d, $J = 5.3$ Hz, 1H), 7.11 (s, 4H), 7.09 (dd, $J = 3.6, 1.3$ Hz, 1H), 7.03 (dd, $J = 5.2, 3.6$ Hz, 1H), 6.93 (d, $J = 5.3$ Hz, 1H), 6.42 (s, 4H), 4.35, 4.34 (d, $J = 12.5$ Hz, 2H each), 4.30–4.18 (m, 8H), 3.78–3.66 (m, 12H), 3.13, 3.12 (d, $J = 12.5$ Hz, 2H each), 2.77 (t, $J = 7.7$ Hz, 2H), 2.01–1.89 (m, 4H), 1.73–1.62 (m, 2H), 1.53–1.42 (m, 4H), 1.34, 0.80 (s, ratio 1:1, 36H), 1.04 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR: $\delta = 155.0, 152.3$ (s, $\text{C}_{\text{sp}^2}\text{-O}$), 144.9 ($\times 2$), 143.93, 143.90 (s, $\text{C}_{\text{sp}^2}\text{-tBu}$), 139.41 (s, ThTh), 135.39, 135.35, 131.7 ($\times 2$) (s, bridgehead-C), 130.5 (s, ThTh), 129.8, 127.3, 126.0, 125.5 ($\times 2$), 125.3, 124.4 ($\times 2$), 123.7 (d, Ar, ThTh), 77.7 (t, $\text{OCH}_2\text{CH}_2\text{CH}_3$), 75.9 (t, $\text{OCH}_2(\text{CH}_2)_5\text{ThTh}$), 72.5, 71.9, 71.2, 70.1 (t, $\text{OCH}_2\text{CH}_2\text{O}$), 34.1 ($\times 2$), 33.5 ($\times 2$) (s, $\text{C}(\text{CH}_3)_3$), 31.7 ($\times 2$), 31.1 ($\times 2$) (q, $\text{C}(\text{CH}_3)_3$), 31.0 ($\times 3$), 30.7, 30.3, 29.0, 26.1 (t, $\text{OCH}_2(\text{CH}_2)_5\text{ThTh}$, ArCH_2Ar), 23.5 (t, $\text{OCH}_2\text{CH}_2\text{CH}_3$), 10.7 (q, $\text{OCH}_2\text{CH}_2\text{CH}_3$); FAB(+) MS: m/z : 1097 [MH] $^+$; elemental analysis calcd (%) for $\text{C}_{69}\text{H}_{92}\text{O}_7\text{S}_2$ (1096.6): C 75.50, H 8.45, S 5.83; found: C 75.32, H 8.30, S 5.95.

5,11,17,23-Tetrakis(1,1-dimethylethyl)-25,27-(crown-4) $^\alpha$ -26-[[6-(2,2'-dithiophene-3-yl)hexyl]oxy] $^\alpha$ -28-propoxy $^\beta$ -calix[4]arene (3a)^[22] Purified by two subsequent CC (eluent: first column, cyclohexane/AcOEt 9:1 *v/v*; second column, hexanes/AcOEt 4:1 *v/v*); 64% yield. M.p. 115–117 °C (EtOH); ^1H NMR: $\delta = 7.26$ (dd, $J = 4.9, 1.1$ Hz, 1H), 7.21/6.94 (ABq, $J = 2.5$ Hz, 4H), 7.15 (d, $J = 5.2$ Hz, 1H), 7.09 (s, 2H), 7.08 (dd, $J = 3.6, 1.1$ Hz, 1H), 7.03 (dd, $J = 4.9, 3.6$ Hz, 1H), 6.90 (d, $J = 5.2$ Hz, 1H), 6.88 (s, 2H), 4.41/3.23 (AX, $J = 12.1$ Hz, 4H), 4.03 (dt, $J = 10.2, 6.0$ Hz, 2H), 3.87 (pseudo-s, 4H), 3.80–3.51 (m, 8H), 3.78 (t, $J = 7.5$ Hz, 2H), 3.19 (dt, $J = 10.2, 6.0$ Hz, 2H), 2.73 (t,

$J = 7.8$ Hz, 2H), 1.90 (t, $J = 5.5$ Hz, 2H), 1.81 (quin, $J = 7.4$ Hz, 2H), 1.63 (quin, $J = 7.4$ Hz, 2H), 1.44–1.30 (m, 4H), 1.38, 1.28, 1.08 (s, ratio 1:2:1, 36H), 0.01– -0.10 (m, 5H); ^{13}C NMR: $\delta = 154.8, 154.1$ ($\times 2$), 152.8 (s, $\text{C}_{\text{sp}^2}\text{-O}$), 145.3 ($\times 2$), 144.2, 143.9 (s, $\text{C}_{\text{sp}^2}\text{-tBu}$), 139.5 (s, ThTh), 136.1, 133.4, 133.1, 132.6 (s, bridgehead-C), 130.5 (s, ThTh), 129.8, 127.3, 126.1, 126.0, 125.8, 125.5, 125.3, 124.5, 123.7 (d, Ar, ThTh), 76.0 (t, $\text{OCH}_2(\text{CH}_2)_5\text{ThTh}$), 72.5, 69.9, 69.3 (t, $\text{OCH}_2\text{CH}_2\text{O}$), 70.5 (t, $\text{OCH}_2\text{CH}_2\text{CH}_3$), 38.7 (t, ArCH_2Ar), 34.02 ($\times 2$), 34.00, 33.9 (s, $\text{C}(\text{CH}_3)_3$), 31.7, 31.6 ($\times 2$), 31.3 (q, $\text{C}(\text{CH}_3)_3$), 30.7, 30.4, 29.8, 29.4, 29.0, 25.9 (t, $\text{OCH}_2(\text{CH}_2)_5\text{ThTh}$, ArCH_2Ar), 22.2 (t, $\text{OCH}_2\text{CH}_2\text{CH}_3$), 10.1 (q, $\text{OCH}_2\text{CH}_2\text{CH}_3$); FAB(+) MS: m/z : 1053 [MH] $^+$; elemental analysis calcd (%) for $\text{C}_{67}\text{H}_{88}\text{O}_6\text{S}_2$ (1052.6): C 76.38, H 8.43, S 6.07; found: C 76.11, H 8.36, S 5.94.

5,11,17,23-Tetrakis(1,1-dimethylethyl)-25,27-(crown-5) $^\alpha$ -26-[[6-(2,2'-bithiophene-3-yl)hexyl]oxy] $^\alpha$ -28-propoxy $^\beta$ -calix[4]arene (3b)^[22] Purified by two subsequent CC (eluent: first column, cyclohexane/AcOEt 9:1 *v/v*; second column, hexanes/AcOEt 4:1 *v/v*); 70% yield. M.p. 125–127 °C (EtOH); ^1H NMR: $\delta = 7.27$ (dd, $J = 5.1, 1.2$ Hz, 1H), 7.19/6.93 (ABq, $J = 2.4$ Hz, 4H), 7.152 (d, $J = 5.2$ Hz, 1H), 7.150 (s, 2H), 7.08 (dd, $J = 3.6, 1.2$ Hz, 1H), 7.03 (dd, $J = 5.1, 3.6$ Hz, 1H), 6.90 (d, $J = 5.2$ Hz, 1H), 6.88 (s, 2H), 4.33/3.20 (AX, $J = 12.0$ Hz, 4H), 3.91–3.39 (m, 18H), 3.86 (pseudo-s, 4H), 2.74 (t, $J = 7.6$ Hz, 2H), 1.87 (quint, $J = 7.5$ Hz, 2H), 1.76 (t, $J = 5.8$ Hz, 2H), 1.65 (quint, $J = 7.5$ Hz, 2H), 1.43, 1.27, 1.07 (s, ratio 1:2:1, 36H), 1.42–1.30 (m, 4H), -0.02 – -0.14 (m, 5H); ^{13}C NMR: $\delta = 154.4, 154.1$ ($\times 2$), 152.4 (s, $\text{C}_{\text{sp}^2}\text{-O}$), 145.2, 144.0 (s, $\text{C}_{\text{sp}^2}\text{-tBu}$), 139.3, 133.3 (s, ThTh), 135.9, 133.4, 133.2, 132.6 (s, bridgehead-C), 129.7, 128.8, 127.3, 126.0, 125.9, 125.7, 125.3, 124.8, 123.7 (d, Ar, ThTh), 76.1 (t, $\text{OCH}_2(\text{CH}_2)_5\text{ThTh}$), 73.7, 71.2, 71.0, 70.5 (t, $\text{OCH}_2\text{CH}_2\text{O}$), 70.8 (t, $\text{OCH}_2\text{CH}_2\text{CH}_3$), 38.9 (t, ArCH_2Ar), 34.0 ($\times 3$), 33.8 (s, $\text{C}(\text{CH}_3)_3$), 31.7, 31.6 ($\times 2$), 31.3 (q, $\text{C}(\text{CH}_3)_3$), 30.6, 30.3, 30.1, 29.7, 29.0, 25.9 (t, $\text{OCH}_2(\text{CH}_2)_5\text{ThTh}$, ArCH_2Ar), 22.3 (t, $\text{OCH}_2\text{CH}_2\text{CH}_3$), 10.2 (q, $\text{OCH}_2\text{CH}_2\text{CH}_3$); FAB(+) MS: m/z : 1097 [MH] $^+$; elemental analysis calcd (%) for $\text{C}_{69}\text{H}_{92}\text{O}_7\text{S}_2$ (1096.6): C 75.50, H 8.45, S 5.83; found: C 75.33, H 8.36, S 5.71.

Acknowledgements

We thank Dr. P. Fallini (Università di Parma) for help with the experimental work, and MURST for financial support.

- [1] a) C. D. Gutsche, Calixarenes Revisited in *Monographs in Supramolecular Chemistry, Vol. 6* (Ed.: J. F. Stoddart), The Royal Society of Chemistry, Cambridge, **1998**; b) V. Böhmer, *Angew. Chem.* **1995**, *107*, 785–818; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 713–745; c) Calixarenes, a Versatile Class of Macrocyclic Compounds (Eds.: J. Vicens, V. Böhmer), Kluwer Academic, Dordrecht, **1991**.
- [2] D. Diamond, M. A. McKervey, *Chem. Soc. Rev.* **1996**, *25*, 15–24; D. N. Reinhoudt, *Recl. Trav. Chim. Pays-Bas* **1996**, *115*, 109–118; K. M. O'Connor, D. W. M. Arrigan, G. Svehla, *Electroanalysis* **1995**, *7*, 205–215.
- [3] S. J. Higgins, *Chem. Soc. Rev.* **1997**, *26*, 247–257, and references therein.
- [4] F. Bedioui, J. Devynck, C. Bied-Charreton, *Acc. Chem. Res.* **1995**, *28*, 30–36; A. Deronzier, J. C. Moutet, *Coord. Chem. Rev.* **1996**, *147*, 339–371.
- [5] See for example: a) H. K. Youssoufi, M. Hmyene, F. Garnier, D. Delabouglise, *J. Chem. Soc. Chem. Commun.* **1993**, 1550–1552; b) P. Bäuerle, S. Scheib, *Adv. Mater.* **1993**, *5*, 848–853.
- [6] J. Roncali, *Chem. Rev.* **1992**, *92*, 711–738.
- [7] The chemical copolymerization and electrochemical properties of a calixarene-functionalized dithiophene have recently been described: M. J. Marsella, R. J. Newland, P. J. Carrol, T. M. Swager, *J. Am. Chem. Soc.* **1995**, *117*, 9842–9848.
- [8] R. D. McCullough, *Adv. Mater.* **1998**, *10*, 93–116.
- [9] G. Ferguson, J. F. Gallagher, A. J. Lough, A. Notti, S. Pappalardo, M. F. Parisi, *J. Org. Chem.* **1999**, *64*, 5876–5885; corrigendum: G. Ferguson, J. F. Gallagher, A. J. Lough, A. Notti, S. Pappalardo, M. F. Parisi, *J. Org. Chem.* **2000**, *65*, 930.
- [10] No electrodeposition was observed by varying the solvent (CH_2Cl_2 , $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ mixtures), the monomer concentration (10^{-3} – 10^{-1}M), the supporting electrolyte (Bu_4NPF_6 , Bu_4NBF_4 , Et_4NBr), the working

electrode (Pt, Au, glassy carbon), and the conditions of potential application (potentiodynamic, potentiostatic). The anodic current peaks (E_{pa}) occurred above 1.7 V vs Ag/AgCl, and progressively decreased in intensity during scanning, indicating that the oxidation only concerns the monomer diffusing to the electrode.

- [11] H. Yamamoto, S. Shinkai, *Chem. Lett.* **1994**, 1115–1118.
- [12] L. Huchet, S. Akoudad, J. Roncali, *Adv. Mater.* **1998**, *10*, 541–545.
- [13] a) E. Ghidini, F. Ugozzoli, R. Ungaro, S. Harkema, A. Abu El-Fadl, D. N. Reinhoudt, *J. Am. Chem. Soc.* **1990**, *112*, 6979–6985; b) Z. Brzozka, B. Lammerink, D. N. Reinhoudt, E. Ghidini, R. Ungaro, *J. Chem. Soc. Perkin Trans. 2* **1993**, 1037–1040; c) A. Casnati, A. Pochini, R. Ungaro, C. Bocchi, F. Ugozzoli, R. J. M. Egberink, H. Struijk, R. Lugtenberg, F. de Jong, D. N. Reinhoudt, *Chem. Eur. J.* **1996**, *2*, 436–445; d) R. Ungaro, A. Casnati, F. Ugozzoli, A. Pochini, J.-F. Dozol, C. Hill, H. Rouquette, *Angew. Chem.* **1994**, *106*, 1551–1553; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1506–1509; e) A. Casnati, A. Pochini, R. Ungaro, F. Ugozzoli, F. Arnaud, S. Fanni, M.-J. Schwing, R. J. M. Egberink, F. de Jong, D. N. Reinhoudt, *J. Am. Chem. Soc.* **1995**, *117*, 2767–2777; f) F. Arnaud-Neu, G. Ferguson, S. Fuangswasdi, A. Notti, S. Pappalardo, M. F. Parisi, A. Petringa, *J. Org. Chem.* **1998**, *63*, 7770–7779.
- [14] F. Ugozzoli, O. Ori, A. Casnati, A. Pochini, R. Ungaro, D. N. Reinhoudt, *Supramol. Chem.* **1995**, *5*, 179–184.
- [15] R. J. Waltman, J. Bargon, *Can. J. Chem.* **1986**, *64*, 76–95; R. J. Waltman, J. Bargon, A. F. Diaz, *J. Phys. Chem.* **1983**, *87*, 1459–1463.
- [16] C. Maccà, *Anal. Chim. Acta* **1996**, *321*, 1–10, and references therein.
- [17] G. Mori, M. Giannetto, *Ann. Chim. (Rome)* **1999**, *89*, 601–611; D. Diamond, F. J. Sàez de Viteri, *Analyst* **1994**, *119*, 749–758.
- [18] Unsuccessful attempts have been made to use electropolymerized pyrrole-containing calix[4]arene films for the detection of alkali metal ions: A. Buffenoir, G. Bidan, *Synth. Met.* **1999**, *102*, 1300–1301; Z. Chen, P. A. Gale, P. D. Beer, *J. Electroanal. Chem.* **1995**, *393*, 113–117.
- [19] A. J. Bard, L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, Wiley, New York, **1980**, Chapter 9; Z. B. Stoyanov, B. M. Grafov, B. S. Savova-Stoyanov, V. V. Elkin, *Electrochemical Impedance*, Nauka, Moscow, **1991**.
- [20] M. Ouchi, Y. Inoue, T. Kanzaki, T. Hakushi, *J. Org. Chem.* **1984**, *49*, 1408–1412.
- [21] M. Giannetto, G. Mori, A. Notti, S. Pappalardo, M. F. Parisi, *Anal. Chem.* **1998**, *70*, 4631–4635; C. Bocchi, M. Careri, A. Casnati, G. Mori, *Anal. Chem.* **1995**, *67*, 4234–4638.
- [22] Notations α and β were introduced by Shinkai to define the stereochemistry of calix[4]arene atropisomers having mixed substituents at the lower rim: K. Iwamoto, K. Araki, S. Shinkai, *Tetrahedron* **1991**, *47*, 4325–4342.

Received: August 8, 2000

Revised version: December 23, 2000 [F2659]