

## First synthesis of a '1,2-diquinone-calix[4]arene'. Interaction of its reduced form with Ag<sup>+</sup>

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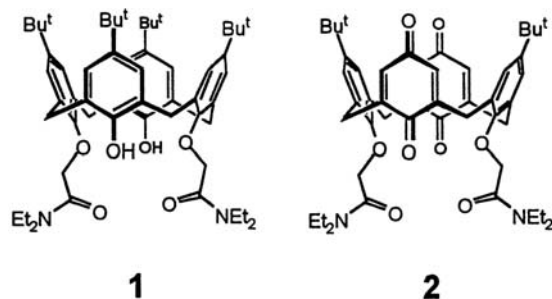
### Abstract

Electrochemical oxidation of 5,11 17,23-tetra-*tert*-butyl-25,26-bis(diphenylphosphinoylmethoxy)-27,28-dihydroxycalix[4]arene (3), a calixarene with two phosphoryl units appended on proximal positions, affords the corresponding '1,2-diquinone-calix[4]arene' (4). The formation of 4 results from nucleophilic attack of residual water on anodically generated diphenoxylum cations. Preliminary voltammetric experiments in CH<sub>3</sub>CN on a platinum electrode showed that 4 is suitable for electrochemical detection of the silver metal cation.

**Keywords:** Calixarene; Electrochemistry; Calixdiquinone; Silver(I) detection

### 1. Introduction

Calixarenes are synthetic receptors constituted by circularly arranged phenol moieties linked by methylene groups [1,2]. They can be readily substituted at the lower rim (hydroxyl groups) to produce a variety of ionophores which were shown to be suitable for complexation of Group 1 and 2 [3-5], transition metal [6-11] and lanthanide metal cations [12-17]. Among the functionalised calixarenes, the calixquinones have recently attracted considerable interest. Some of these compounds were employed for the study of interesting redox systems and charge-transfer complexes as well [18,19]. Most calixquinones have been synthesised by chemical oxidation of calixarenes that comprise unsubstituted phenol rings [20-23]. It is noteworthy that to date no calixarene with adjacent quinone units has been reported. In a recent communication we described a straightforward synthesis of the 1,3-diquinone-calix[4]arene 2 obtained in good yield by electrochemical oxidation of the corresponding dihydroxy-diamide precursor 1 [24].



Following this preliminary study on electrofunction-alised calixarenes, we now report the electrosynthesis and characterisation of the new calix[4]arenediquinone 4. For this study we used the 1,2-dihydroxy-calixarene 3 which also contains two proximal phosphoryl functions. The synthetic route is depicted in Scheme 1.

## 2. Experimental

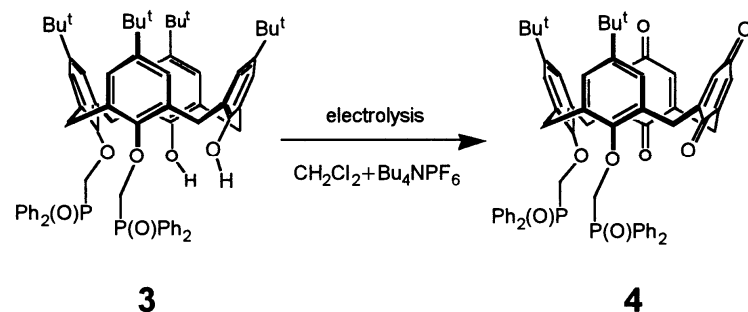
Voltammetric experiments were performed with an EG&G 263 A potentiostat modulated by EG&G PAR M270 software. All measurements were carried out at room temperature (r.t.) with a conventional three-electrode configuration consisting of platinum disk working electrode (EDI type, Radiometer), a platinum wire counter electrode, and a saturated calomel reference electrode (SCE). Spectroelectrochemical measurements were carried out in a quartz cell constructed according to the method described by Lin and Kadish [25], and fitted with a fine platinum gauze as a working electrode. The UV-vis spectra were recorded using a Hewlett-Packard 8453A diode array spectrometer. Full scan MS and MS-MS measurements were performed on a Finnigan LCQ (San Jose, CA) electrospray ion trap instrument. Solutions in  $\text{CH}_2\text{Cl}_2$  were infused at  $3 \mu\text{l min}^{-1}$ , and the spectra were acquired in the positive ion mode. The needle voltage was set at 5 kV, the heated capillary was set at  $160^\circ\text{C}$  and 10 V (the skimmer is at ground). The  $^1\text{H}$ -,  $^{31}\text{P}$ - and  $^{13}\text{C}$ -NMR spectra were recorded on a Bruker AC-250 spectrometer.

Macroelectrolysis and coulometry were carried out in the same cell, namely a three-compartment cell equipped with a platinum spiral wire ( $\phi = 1 \text{ mm}$ , 30 cm in length) as the working electrode and a platinum wire as the counter electrode. The working potential was controlled by a PJT 120-1 potentiostat (Radiometer).

All potentials are given in V versus SCE. The reference electrode was separated from the bulk solution by a fritted-glass bridge filled with the solvent and the supporting electrolyte.

5,11,17,23-Tetra-*tert*-butyl-25,26-bis(diphenylphosphino)ethoxy-27,28-dihydroxy-calix[4]arene (**3**) was prepared according to the method reported earlier [26]. Spectroscopic grade dichloromethane (Fluka) was used as received. This solvent was chosen because very often radical cations display in this solvent a higher stability than in co-ordinating solvents such as acetonitrile [27]. Moreover,  $\text{CH}_2\text{Cl}_2$  has a wide potential window, especially for oxidations. Acetonitrile was hplc grade, from Merck. Tetrabutylammonium hexafluoro-phosphate ( $\text{Bu}_4\text{NPF}_6$ , Fluka) was used as the supporting electrolyte. Solutions were deoxygenated by argon purging.

### Scheme 1.



Compound **4**, as obtained after electrolysis of **3** and purification by column chromatography (Silica gel 60,  $\text{CHCl}_3$ -MeOH, 90:10, v/v). Yield: ~52%.  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ , 250 MHz):  $\delta$  7.80-7.28 (20H, aromatic H), 6.70, 6.55, 6.52, 5.81 (4d, 4 x 2H, C=CH,  $^4J \sim 2 \text{ Hz}$ ), 4.94 and 4.58 (ABX spin system with X = P, 4H,  $\text{PCH}_2$ ,  $J(\text{AB}) = 14 \text{ Hz}$ ,  $^2J(\text{AX}) = 0$ ,  $^2J(\text{BX}) = 4 \text{ Hz}$ ), 4.82 (d, 1H, ArCH or (quinone)CH,  $^2J = 13 \text{ Hz}$ ), 4.09 (d, 2H, ArCH,  $^2J = 13 \text{ Hz}$ ), 3.46 (d, 1H, ArCH or (qui-none)CH,  $^2J = 13 \text{ Hz}$ ), 3.24 (d, 1H, ArCH or (qui-none)CH,  $^2J = 13 \text{ Hz}$ ), 3.18 (d, 1H, ArCH or (quinone)CH,  $^2J = 13 \text{ Hz}$ ), 3.00 (d, 2H, ArCH,  $^2J = 13 \text{ Hz}$ ), 1.05 (s, 18H, *t*Bu).  $^{31}\text{P}$ -NMR ( $\text{CDCl}_3$ ):  $\delta$  29.5 (s).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  187.52 and 185.66 (2s, C=O), 153.38-125.68 (aromatic C's and C=C of quinone), 70.79 (d,  $\text{PCH}_2$ ,  $J(\text{PC}) = 79 \text{ Hz}$ ), 33.92 (s,  $\text{C}(\text{CH}_3)_3$ ), 32.33 and 32.17 (2s, ArCH or (quinone)CH), 31.46 (s, 2 x , ArCH<sub>2</sub>), 31.25 (s,  $\text{C}(\text{CH}_3)_3$ ). MS (ESI POS):  $m/z$  993 [ $\text{M}^+\text{H}$ ]<sup>+</sup>. Anal. Calc. for  $\text{C}_{62}\text{H}_{58}\text{O}_8\text{P}_2 \cdot \text{H}_2\text{O}$ : C, 73.64; H, 5.98. Found: C, 73.68; H, 5.98%.

## 3. Results and discussion

### 3.1. Redox behaviour of **3**

Fig. 1a depicts the voltammogram of **3** which was obtained at a rotating platinum-disk electrode in  $\text{CH}_2\text{Cl}_2$  containing  $0.1 \text{ mol dm}^{-3} \text{ Bu}_4\text{NPF}_6$ . In the potential range 0-2.0 V, compound **3** displays only one oxidation process at ca. 1.8 V preceded by a pre-wave near 1.3 V. This latter is possibly due to the presence of a labile

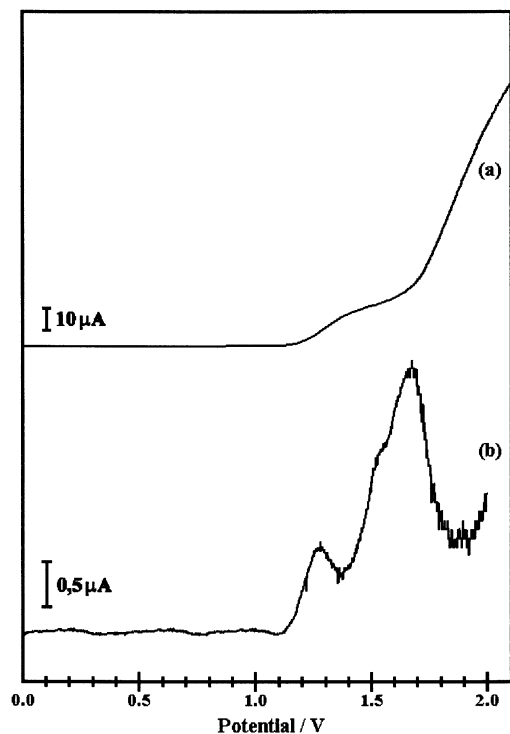
solvent-calixarene inclusion compound [28]. A partial absorption of the phenol moieties on the platinum electrode can be excluded as the pre-wave persists using a glassy carbon electrode. Detailed voltammetric studies and bulk electrolysis at constant potential followed by spectral characterisation showed no relationship between this pre-wave and the following oxidation process (vide infra). For the main oxidation process, logarithmic analysis of the current-potential curve shows the curvature expected for two closely spaced waves [29]. Square-wave voltammetry on the platinum electrode (see Fig. 1b) resolves these two closely-spaced waves whose half potentials were ca. 1.54 and 1.68 V, respectively. These results are indicative of a direct hydroxyl-hydroxyl interaction in 3.

Fig. 2 illustrates the change in the cyclic voltammogram of 3 at different scan rates between  $-0.6$  and  $+2.2$  V. At slow scan rates ( $v \leq 100$  mV s<sup>-1</sup>), the cyclic voltammogram (Fig. 2a) exhibited a poorly defined oxidation peak at ca. 1.60 V (process 1) and a well-defined oxidation peak at 1.70 V (process 2). Both oxidation processes were irreversible on this time scale, as is demonstrated by the absence of coupled reduction peaks. The peak currents for both processes were comparable. When the scan rate was increased ( $v \geq 200$  mV s<sup>-1</sup>), two broadened cathodic processes (C<sub>1</sub>, C<sub>2</sub>) centred at ca. 0.11 and -0.23 V, respectively, emerged. The cathodic peak C<sub>2</sub> is observed when the voltage scan is switched in the negative direction after the first oxidation process (peak (1)) while the cathodic peak C<sub>1</sub> appeared when the positive scan is continued beyond the second peak (2). These cathodic peaks whose intensities were enhanced as the scan rate increased, were found to correspond to the new composite oxidation peak (A) appearing at ca. 0.28 V on the second and subsequent positive scans (Fig. 3,  $v = 0.5$  Vs<sup>-1</sup>). These observations indicate the presence of a redox active species resulting from chemical reactions following the electron transfer processes. For each oxidation step of 3, (1) and (2), the peak current oxidation increases linearly with  $v^{1/2}$ . The peak potential shifted positively by ca. 90 mV per each tenfold increase in scan rate. The two oxidation peaks had a  $\Delta E = E_{pa} - E_{pa/2}$  value that varied between 80 and 130 mV for the first step and between 90 and 170 mV for the second step when  $v$  increased from 0.1 to 1.0 V s<sup>-1</sup>. These results indicate consistently that the charge transfer in each oxidation step of 3 is associated with an irreversible chemical reaction [30].

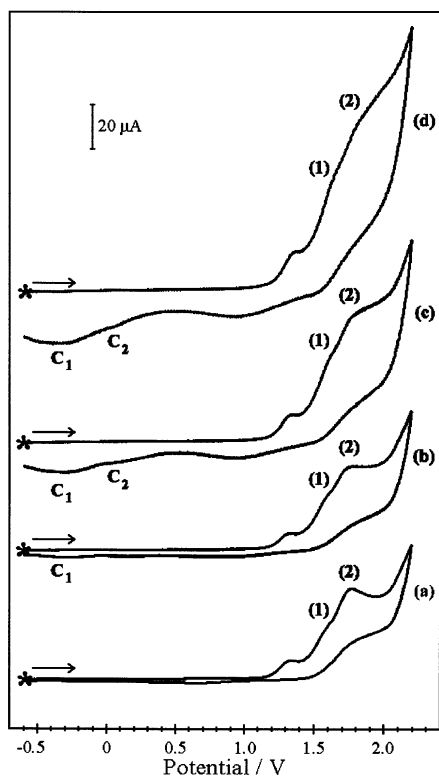
Controlled-potential coulometry carried out on solutions of 3 (ca. 0.015 mmol, electrolysis duration ca. 1.5 h) at potentials corresponding to the second anodic peak (2) gave  $n_e$  value of 4.3. When controlled-potential oxidation was carried out in the potential range of 1.4-1.6 V,  $n$  values in the range of 1.8-2.3 were obtained. Therefore, the number of electrons involved in each oxidation step of 3 is two.

The electrooxidation of 3 was also investigated by thin-layer spectroelectrochemistry. A typical experiment had a duration of 200-300 s. The spectra recorded as the potential was stepped incrementally from 0.6 to 2.1 V are depicted in Fig. 4. When applying a potential limited to the pre-wave, no spectral change was observed. This result is in keeping with our observation that there is no relationship between the pre-wave and the two main oxidation processes, (1) and (2). Fig. 4a shows the spectral changes observed when the potential was stepped from 0.6 to 1.6 V (first oxidation step). As the oxidation of 3 proceeds, there is a decrease of peak intensity at 288 nm (original absorption band). At the same time a new absorption band at ca. 270 nm and a broad peak in the range 300-350 nm appeared. In addition, two isosbestic points at ca. 282 and 300 nm (ill-defined) were observed within a few seconds after the generation of the oxidised species. The stepping back of the potential from 1.6 to 0.6 V did not regenerate the original spectrum of the starting material. This indicates that the first charge transfer did not produce 3<sup>+•</sup>. As is seen in Fig. 4b, similar changes in the spectra were observed when the potential was stepped from 0.6 to 2.0 V (full oxidation potential range of 3). The peak at 288 nm continued to decrease while the peak at ca. 270 nm and the broad absorption in the range 300-350 nm increased considerably. The two isosbestic points present near 282 and 300 nm are better defined, thus indicating the formation of a new species during the oxidation of 3. Again the original spectrum of 3 could not be regenerated during the return potential sweep. These findings corroborate the CV data and hence establish that the electrochemical oxidation of 3 is chemically irreversible. On the other hand, the observed spectral changes are particularly characteristic in that the peaks are in a wavelength region that is usual for carbonyl group in phenoxylum ions generated anodically from the phenolic compounds [31].

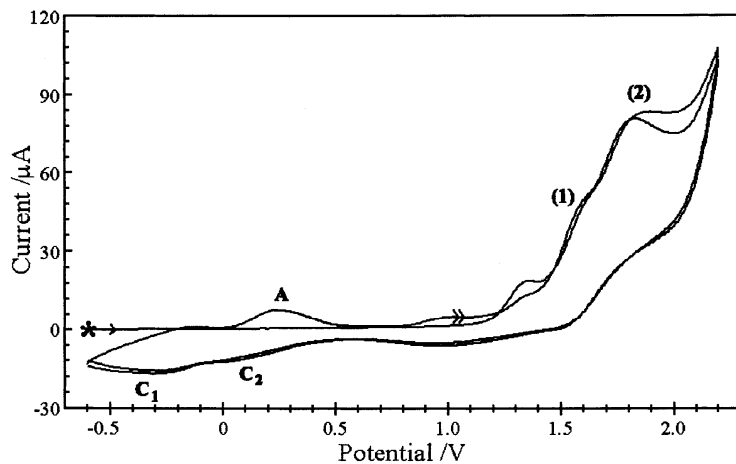
**Fig. 1.** Voltammetry of 1.5 mM **3** in  $\text{CH}_2\text{Cl}_2 + 0.1 \text{ mol dm}^{-3} \text{Bu}_4\text{NPF}_6$ : (a) rotating disk voltammogram (rotation rate  $1000 \text{ rev min}^{-1}$ , scan rate  $10 \text{ mV s}^{-1}$ ); (b) square-wave voltammogram, step potential 2 mV, amplitude 25 mV and frequency 10 Hz.



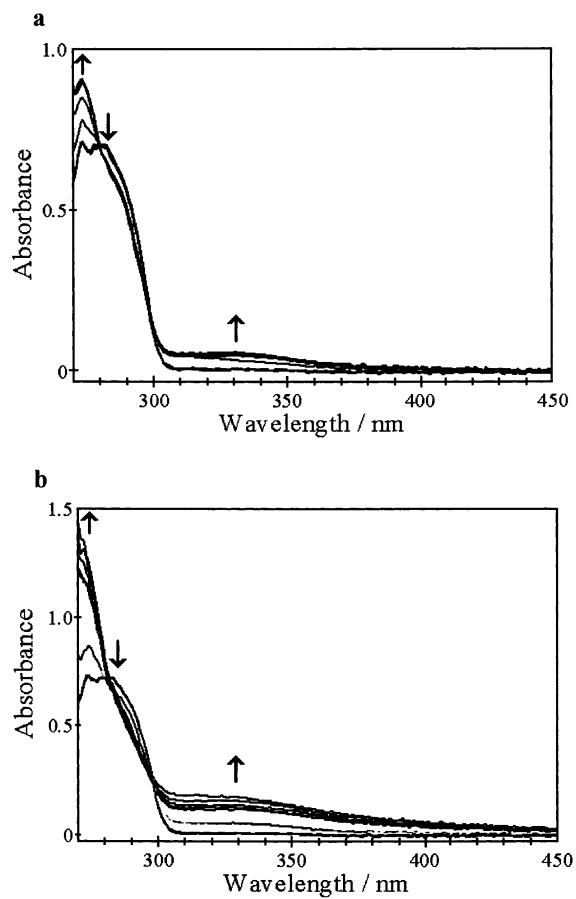
**Fig. 2.** Cyclic voltammograms of 1.5 mM **3** in  $\text{CH}_2\text{Cl}_2 + 0.1 \text{ mol dm}^{-3} \text{Bu}_4\text{NPF}_6$  at various scan rates. Scan rates from (a) to (d) were: 100, 200, 500 and  $1000 \text{ mV s}^{-1}$ . (\*) denotes the initial and final potential.



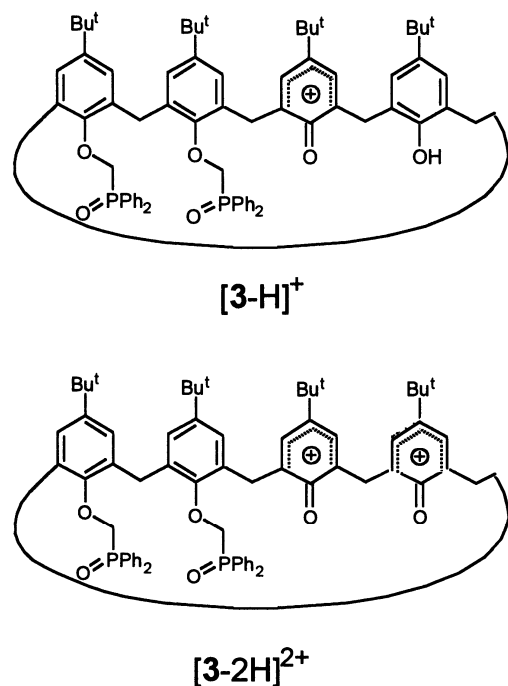
**Fig. 3.** Repetitive CVs (three) of 1.5 mM **3** in  $\text{CH}_2\text{Cl}_2$  ( $0.1 \text{ mol dm}^{-3} \text{ Bu}_4\text{NPF}_6$ ). Scan rate  $0.5 \text{ V s}^{-1}$ . (\*) denotes the initial and final potential.



**Fig. 4.** Thin-layer spectral changes associated with oxidation of **3** in  $\text{CH}_2\text{Cl}_2$  containing  $0.1 \text{ mol dm}^{-3} \text{ Bu}_4\text{NPF}_6$ . Spectra were monitored as the potential was (a) scanned from 0.6 to 1.6 V (first oxidation step), and (b) stepped from 0.6 to 2.0 (overall oxidation potential range). Scan rate =  $10 \text{ mV s}^{-1}$ .



The results of the voltammetric, spectroscopic and coulometric studies clearly show that each oxidation step of 3 is a two-electron process (four electrons overall) on the coulometry time-scale. Consistent with a number of studies on polyphenols compounds, it is plausible that each oxidation step of 3 proceeds according to an ECE mechanism rather than a EEC one [32,33]. We therefore suggest that on the time scale of the voltammetric measurements the products formed after the first and the second oxidation of 3 are the mono- and di-phenoxylium ions  $[3-H]^+$  and  $[3-2H]^{2+}$ , respectively.



### 3.2. Electro synthesis of diquinone 4

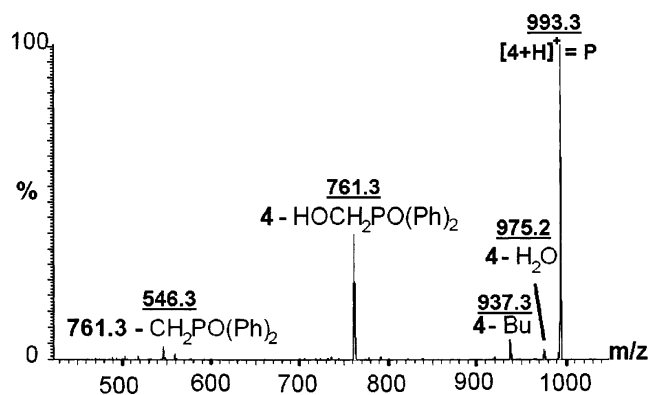
It is well known that under conditions of macroelectrolysis requiring long duration experiments, phenolic compounds are readily converted into the corresponding quinones. Hence, the feasibility of the direct preparation of 4 was explored.

To do this, macroscale electrolysis at 1.9 V corresponding to the second oxidation of 3 was carried out on 50 mg (0.046 mmol, electrolysis duration 4-5 h) of 3 in  $CH_2Cl_2 + 0.2 \text{ mol dm}^{-3} Bu_4NPF_6$ . When the level of intensity became sufficiently low, the electrolysis was stopped. About 1-2 h after the electrolysis, the solvent was removed in vacuo. The residue was dissolved in diethylether. The ether solution was filtered and the solvent was evaporated in vacuo. The reaction products were separated by Flash column chromatography on silica gel (60, Merck), using a mixture of chloroform and methanol (90:10, v/v) as eluent. The main product, 4, elutes first. The ESI mass spectrum (positive ion) showed an intense peak at  $m/z = 993.3$ , corresponding to  $[4 + H]^+$  (P). The MS-MS spectrum of 4 showed fragmentation peaks at  $m/z = 975.2$  (P -  $H_2O$ ),  $m/z = 937.3$  (P -  $^tBu$ ),  $m/z = 761.3$  (P -  $Ph_2P(O)CH_2OH$ ) and  $m/z = 5463$  (P +  $H^+$  -  $2 \times Ph_2P(O)CH_2O$ ) (Fig. 5). The  $^1H$ ,  $^{31}P$ - and  $^{13}C$ -NMR spectra are consistent with the proposed structure (see Section 2). In particular the  $^{13}C$ -NMR spectrum displays the two expected carbonyl signals (187.52 and 185.66 ppm), while the  $^{31}P$ -NMR spectrum shows a single peak at 29.5 ppm (cf. 26.6 ppm for 3). A cyclic voltammogram obtained from 4 showed two reduction processes in  $CH_2Cl_2 + 0.1 \text{ mol dm}^{-3} Bu_4NPF_6$ . The same observations were made using MeCN, but in this case a third reduction process also occurred due to the more negative solvent window (Fig. 6). The cathodic peak potentials at -0.59 V (peak 1), -1.07 V (peak 2) and -1.70 V (peak 3) fall in the range observed for other calix-diquinones [24,34-40]. Based on literature reports, the first and second waves may reasonably be assigned to the consecutive one-electron reductions of each quinone moiety, while the third wave corresponds to two simultaneous one-electron reductions of the dianion intermediate [39]. Finally, we note that the electrochemical behaviour of 4 is similar to that of calix-diquinones having the quinone units in distal positions [38].

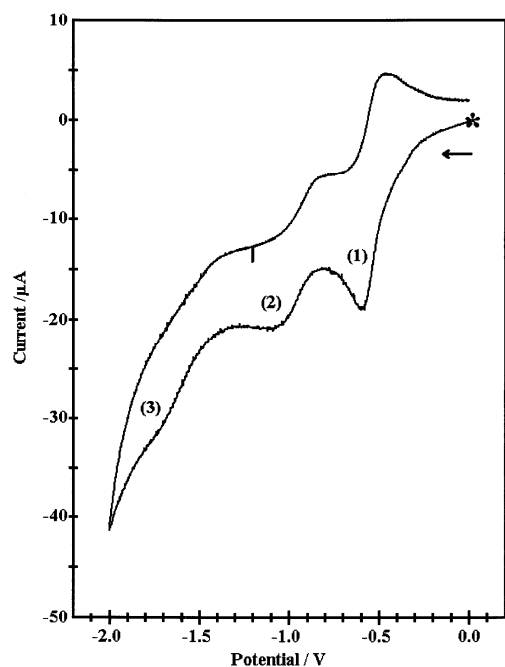
We have not made any investigation concerning the reaction mechanism leading to 4. However, we can assume that the predominant reaction pathway involves nucleophilic attack of residual water on the diphenoxylum

cation  $[3\text{-}2\text{H}]^{2+}$  with subsequent elimination of two  $\text{'Bu}$  groups. The latter step involves an exchange of a further  $2 \times 2$  electrons which obviously could not be measured exactly because the oxidative cleavage of the  $\text{'Bu}$  groups is slow. Such a pathway has been proposed for other quinones [41].

**Fig. 5.** MS-MS spectrum of 4 in dichloromethane. P represents  $[4 + \text{H}]^+$ .



**Fig. 6.** Cyclic voltammogram of 2.2 mM 1,2-calix[4]arenequinone, 4 in  $\text{CH}_3\text{CN} + 0.1 \text{ mol dm}^{-3} \text{ Bu}_4\text{NPF}_6$ . Scan rate  $100 \text{ mVs}^{-1}$ . (\*) denotes the initial and final potential.

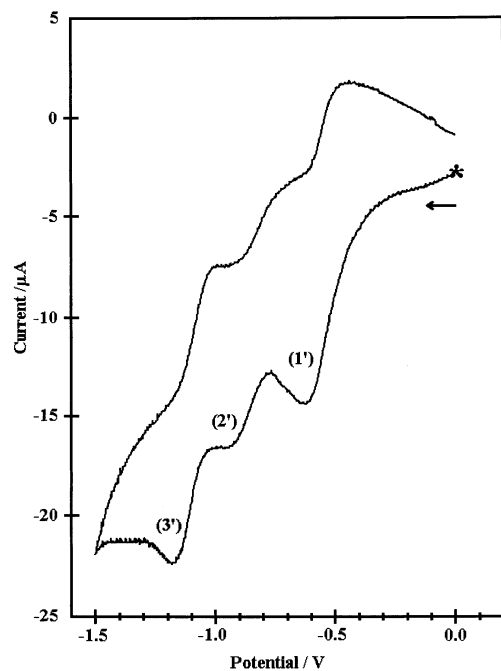


### 3.3. Electrochemistry of 4 in the presence of $\text{Ag}^+$

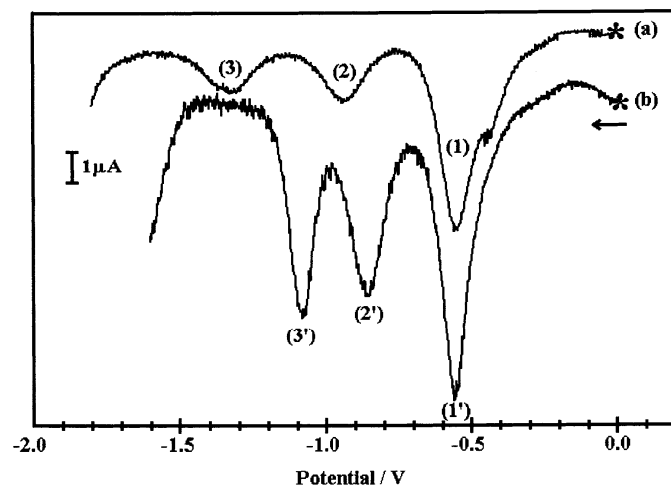
In order to evaluate the ability of 4 to interact with metal cations, we briefly investigated the redox behaviour of this diquinone in the presence of  $\text{Ag}^+$ . The cyclic and square wave voltammetry studies were performed in the presence of  $\text{AgCF}_3\text{SO}_3$  in  $\text{CH}_3\text{CN} + 0.1 \text{ mol dm}^{-3} \text{ Bu}_4\text{NPF}_6$  (Figs. 7 and 8). With respect to the electrochemical behaviour of free 4 (see Fig. 6), no significant change was observed for the first reduction process. However, the shapes and the reduction potentials of the second and the third waves undergo a drastic change. Pronounced reversibility for wave 3 and substantial positive shifts (see Figs. 7 and 8) for the second and third steps, respectively, were observed. These findings strongly suggest the formation of a silver complex at the lower rim of the calixarene involving both the mono radical anion formed after the first reduction and the keto group of the adjacent unreduced quinone. Indeed molecular models show that two proximal upper-rim oxygen atoms may act as a chelator towards an  $\text{Ag}^+$  cation. The formation of such a complex would also explain why protonation of

the reduced quinone in acetonitrile becomes more difficult. Further experiments are needed to elucidate the precise structure of the complex formed (e. g. whether the phosphoryl units are involved in metal cation binding) and also to explain why  $\text{Ag}^+$  does not interact with unreduced 3. The electrochemical behaviour of 4 alone and in the presence of other metal cations is currently being investigated.

**Fig. 7.** Cyclic voltammogram of 2.2 mM 4 in  $\text{CH}_3\text{CN}$  ( $0.1 \text{ mol dm}^{-3} \text{Bu}_4\text{NPF}_6$ ) in the presence of 1-2 molar equivalents of  $\text{Ag}^+$ . Scan rate  $100 \text{ mV s}^{-1}$ . (\*) denotes the initial and final potential.



**Fig. 8.** Square-wave voltammograms of 2.2 mM 4 in the absence (a) and presence (b) of 1-2 molar equivalents of  $\text{Ag}^+$  in  $\text{CH}_3\text{CN}$  ( $0.1 \text{ mol dm}^{-3} \text{Bu}_4\text{NPF}_6$ ) recorded at 10 Hz.



#### 4. Conclusion

The present study describes the electrochemical behaviour of the difunctionalised calix[4]arene 3. Macroelectrolysis of 3 results in the first synthesis of a 1,2-calix[4]arene diquinone (4). The monoanion derived from this novel calixarene interacts with  $\text{Ag}^+$ , forming a complex, which facilitates full reduction of the diquinone. This work opens the way to the detection of transition metal cations with 1,2-diquinone calixarenes.



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