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ORIGINAL ARTICLE

Self-assembled calix[4]arenequinhydrone on the platinum electrode by cathodic reduction of calix[4]arenediquinone

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Abstract The electrochemical reduction of di(methoxy-*p*-*tert*-butyl)calix[4]arenediquinone led to its calix[4]arenedihydroquinone. The presence of both in the solution refers to the generation of calix[4]arenequinhydrone charge-transfer complex at the electrode surface through a donor/acceptor process type. Self-assembled adlayers of calix[4]arenequinhydrone was obtained by partial electrochemical reduction. Electrochemical deposition of the last form was achieved on the platinum disk electrode at −1.16 V versus SCE (saturated calomel electrode) in aprotic solution by cathodic reduction of the starting substrate. The deposit was first characterized by cyclic voltammetry (CV) in electrolytic solution and then in electrolyte support solution and finally in a ferricyannure solution. The self-assembled product was characterized by MALDI-TOF Mass and IR spectroscopy techniques. It was observed too by SEM technique. Calix[4]arenequinhydrone is observed on the electrode surface as hexangular prisms with a length of few micrometers.

Keywords Self-assembled · Calix[4]arenequinhydrone · Cathodic reduction · Cyclic voltammetry · Electrochemical deposition

Introduction

Calix[n]arenes are an important class of macrocyclic molecules that can be easily prepared by the base-catalysed condensation of *p*-substituted phenols with formaldehyde [1]. This family of macrocyclic receptors is consisting of cyclic arrays of phenol moieties linked by methylene groups. Compounds of this type are suitable for multiple functions and therefore may be used for the preparation of complex agents for a wide variety of ionic and neutral species [2, 3]. Some studies focused on using calixarenes as building block to construct the redox-active calixarene derivatives [4]. They can be also utilized to construct chemically modified electrodes [5], which are sensitive to gas species and biologically important compounds. The sophisticated design and synthesis of calixarenes are essential to specific potential applications in diverse fields. Applications in sensors and modified electrodes continue to be popular [6, 7].

From the electrochemical point of view, the adsorption of organic molecules at electrode–electrolyte interfaces can be considered as one of the most promising approaches not only for the preparation of ordered adlayers but also for elucidating the role of adsorbed molecules properties and the nature of electrode–electrolyte interface [8, 9]. Despite a variety of reports describing the preparation and characterization of self-assembled calixarenes [10, 11].

The 5,17-di-*tert*-butyl-26,28-dimethoxycalix[4]arene-25,27-diquinone has been obtained by controlled potential electrolysis on a platinum electrode from 5,11,17,

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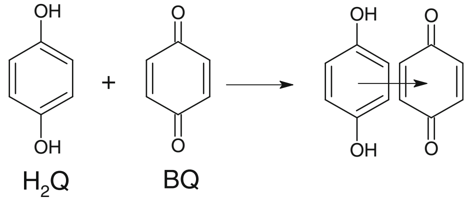
23-tetra-*tert*-butyl-26,28-dimethoxycalix[4]arene-25,27-diol [12]. The calix[4]arenediquinone derivative structure was defined [12].

In previous work, the chemical synthesis of the calix[4]arenequinhydrone has been achieved [13]. Indeed, the chemical reduction of di(methoxy-*p*-*tert*-butyl)calix[4]arenediquinone led to its calix[4]arenedihydroquinone [13]. It was also reported that the partial reduction led to the calix[4]arenequinhydrone charge transfer complex [13]. However, in recent work, the electrochemical synthesis of calix[4]arenequinhydrone charge-transfer complex derivative has been obtained as intermediary product in aprotic solution by partial oxidation of the calix[4]arenedihydroquinone [14].

In fact, calix[4]arenequinhydrone charge-transfer complex can be compared to the simple quinhydrone molecule. However, the quinhydrone molecule is a molecular complex between *p*-benzoquinone (BQ) and hydroquinone (H_2Q) (Scheme 1). Its structure reveals the formation of regular alternate donor/acceptor stacks [15, 16], while infinite molecular chains form through hydrogen bonds between the hydroxyl and the carbonyl groups. The chemical conversion of H_2Q to quinhydrone involves electron transfer coupled with proton transfer [17]. The mixture of H_2Q and BQ gives commonly the quinhydrone form. The later form may result from chemical oxidation of H_2Q with iron (III) ammonium sulphate [18]. The quinhydrone were also synthesised by electrochemical deposition from aqueous solutions of H_2Q [19].

The present work consist in the first attempt to synthesising chemically the 5,17-di-*tert*-butyl-26,28-dimethoxycalix[4]arenediquinone ($X_4Me_2Q_2$) and studying her voltammetric behaviour. The controlled potential electrolysis demonstrates that heterogeneous reduction of the starting substrate allows to the partial electrogeneration of 5,17-di-*tert*-butyl-11,23,25,27-di-dihydroxy-26,28-dimethoxy calix[4]arene ($X_4Me_2(H_2Q)_2$). The mixture of these products led to obtain the 5,17-di-*tert*-butyl-23,25-di-dihydroxy-26,28-dimethoxy calix[4]quinhydrone ($X_4Me_2(H_2Q)Q$) (diquinone–dihydroquinone pair) as an adlayers on the platinum disc electrode in aprotic solution. The self-assembled product was analysed by MALDI-TOF Mass and IR spectroscopy techniques. It was characterized too by cyclic voltammetry (CV) and was observed by SEM technique.



Scheme 1 Schematic view of quinhydrone charge-transfer complex from dihydroquinone and *p*-BQ

Experimental

Using the synthesis procedure developed by Van Loon et al. [20], we synthesized the dimethoxycalix[4]arene ($X_4Me_2H_2$) from the calix[4]arene X_4H_4. Using the last form we synthesized the 5, 17-di-*tert*-butyl-26,28-dimethoxycalix[4]arene-27,27-diquinone ($X_4Me_2Q_2$) as described by Beer's et al. [21].

Our target molecules are 5,17-di-*tert*-butyl-26,28-dimethoxycalix[4]arene-25,27-diquinone ($X_4Me_2Q_2$), 5,17-di-*tert*-butyl-26,28-dimethoxy calix[4]arene-25,27-dihydroquinone ($X_4Me_2(H_2Q)_2$). $X_4Me_2Q_2$ was considered as the starting product for the present electrochemical study.

All chemical manipulations were carried out under argon using Schlenk tube techniques. Acetonitrile and dichloromethane were distilled from CaH_2 under argon. Diethyl ether was distilled from over sodium-benzophenone under argon. Trifluoroacetic acid and thallium (III) trifluoroacetate were purchase from Strem Chemicals and Alfa-Aesar, respectively, and used without further purification.

Spectroscopic analysis

MALDI-TOF mass analysis was performed on a PerSeptive Biosystems (Framingham, MA, USA) Voyager Elite TOF mass spectrometer equipped with a nitrogen laser ($\lambda = 337$ nm). It was operated at 20 kV in the reflectron delayed extraction mode. The spectra were recorded in the absence of matrix. ^{1}H NMR spectra were recorded on a Brucker AC-300 spectrometer. ATR diamond was used as characterization technique of spectroscopy IR and was performed with a BRUKER TENSOR 27 spectrometer. SEM technique was released by JEOL-JSM-5400 Scanning Microscopy.

Synthesis of 5,17-di-tert-butyl-26,28-dimethoxycalix[4]arene-25,27-diquinone ($X_4Me_2Q_2$)

The Synthesis of dimethoxycalix[4]arene $X_4Me_2H_2$ was achieved according to the literature [20]. Several chromatographic separations were performed on silica gel 60 (SiO_2, Merk, particle size 40–63 μm). The detector used was an R410 refractometer. For the synthesis of $X_4Me_2Q_2$, the Beer protocol was followed [21]. To a solution of $Tl(OCOCF_3)_3$ (2.42 g; 4.44 mmol) in trifluoroacetic acid (5 mL), 0.5 g (0.74 mmol) of ($X_4Me_2H_2$) was added and stirred for 2 h in the dark and under argon. The trifluoroacetic acid was then removed in vacuum and the residue poured into ice-water (15 mL). The product was extracted with chloroform. The organic adlayer was then washed with water, dried over $MgSO_4$, filtered and evaporated. The residue was purified by chromatography on silica gel plates with CH_2Cl_2–$(CH_3)_2CN$ (95:5) as eluent and the ($X_4Me_2Q_2$) isolated as yellow powder (0.34 g, 79%). TLC (SiO_2, eluent CH_2Cl_2–$(CH_3)_2CO$, 90/10, v/v) $R_f = 0.85$; MALDI-TOF MS: *m/z* (relative intensity): 594 ($M + 2H^+$); 615 ($M + Na^+$); 631 ($M + K^+$). ^1H NMR (300 Hz, $CDCl_3$): δ (ppm) 1.34 [s, 18H, $C(CH_3)_3$]; 3.10 [s, 6H, OCH_3]; 3.32 [br s, 4H, $ArCH_2Ar$]; 3.78 [br s, 4H, $ArCH_2Ar$]; 6.32 [s, 4H, QuH]; 7.22 [s, 4H, ArH].

Electrochemical experiments

Tetrabutylammonium perchlorate TBAP (Fluka) was purified by recrystallization from ethanol and was used as supporting electrolyte. The acetonitrile 99% was purchased from Acros Organics and was used as received.

The electrochemical set-up consisted of a Tacussel (PGP 201) potentiostat. A three-electrode cell with compartments separated by a porous glass was used. The working electrode was a platinum disc ($\Phi = 2$ mm) (EDI type Radiometer) and the counter electrode was a platinum wire. The reference electrode (saturated calomel electrode, SCE) was separated from the bulk solution by a sintered-glass bridge filled with the solvent and the supporting electrolyte.

Prior to each measurement, the working electrode was polished with a set of fine alumina powders. All the experiments were carried out at laboratory temperature. Solutions containing TBAP 0.1 M as supporting electrolyte were protected from atmosphere with argon prior to each CV measurement and the gas flow maintained during the CV experiments.

Electrochemical deposit of 5,17-di-tert-butyl-23,25-di-dihydroxy-26,28-dimethoxy calix[4]arenequinhydrone ($X_4Me_2(H_2Q)Q$)

Macroscale electrolysis of $X_4Me_2Q_2$ (46.5 mg; 0.078 mmol; electrolysis duration 12 h) was accomplished at a potential of −1.16 V versus SCE. The $X_4Me_2(H_2Q)Q$ was deposited on the platinum electrode. MALDI-TOF MS: *m/z* 594 (M^+); 616 ($M + Na^+$); 633 ($M + K^+$). IR (KBr) 3307 (–OH), 1656 (C=O), 1605, 1489, 1302, 1207 cm^{-1}.

Results and discussion

Electroactivity of calix[4]arenediquinone ($X_4Me_2Q_2$)

The electrochemical activity of $X_4Me_2Q_2$ was investigated by CV at platinum disk electrode in CH_3CN-0.1 M TBAP. Figure 1 shows two successive cyclic voltammograms of $X_4Me_2Q_2$ at 100 mV s^{-1}. Repetitive CVs doesn't show passivation of the platinum electrode. In fact, the CV shows two cathodic peaks at potentials of $E_p(C_1) =$ −0.87 V versus SCE and $E_p(C_2) = -1.44$ V versus SCE respectively in the reduction zone. These potential values are close to those reported for other calixarenediquinones [21, 22]. The first wave (C_1) may be reasonably assigned to the one-electron reduction of quinone moiety to its anion radical Q^- [23]. On the other hand, the reduction of Q^- to Q^{2-} (dianion) corresponds to the second cathodic peak and it appears to be less reversible than that of Q/Q^- The small difference in the reduction potential of two equivalent redox couples, Q/Q^- stems from a little extra over potential due to the coulombic repulsion. The coulombic repulsion energy between two reduced quinones was determinate from voltammetry [24, 25]. The corresponding redox scheme of calix[4]arenediquinone is proposed in Scheme 2 [23].

Chung and co-workers [26] reported that calixarene-monoquinones show very similar redox behaviour to that of BQ. A systematic study on the effect of the number of the quinone moiety has been reported by Gómez-Kaifer et al. [27]. Also calix[4]arenediquinone shows almost the same electrochemical behaviour as calix[4]arenemonoquinone [22, 24]. These results can be explained by the mechanism suggested in our study.

An irreversible peak was observed in the anodic domain at $E_p(A_3) = 1.79$ V versus SCE. This oxidation peak is followed by a shoulder (A_4) at ca. 2.12 V versus SCE. This phenomenon corresponds to the oxidation of the *tert*-butyl anisole [28].

Chronoamperometry

Macroscale electrolysis of $X_4Me_2Q_2$ (46.5 mg; 0.078 mmol; electrolysis duration 12 h) was accomplished at a potential slightly more negative then the first cathodic wave (about −1.16 V versus SCE). Homogenization of the

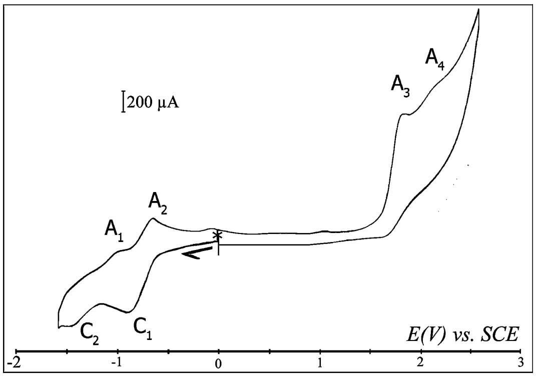
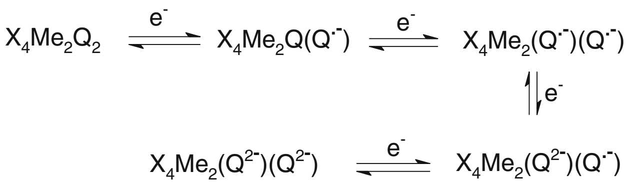


Fig. 1 Cyclic voltammogram at Pt disk electrode ($\Phi = 2$ mm) of 8 mM calix[4]arenediquinone $X_4Me_2Q_2$ in CH_3CN + 0.1 M TBAP. Sweep rate: 0.1 V s^{-1}



Scheme 2 Schematic diagram of redox mechanism in the case of calix[4]arenediquinone $X_4Me_2Q_2$

electrolytic solution was ensured by a mechanical stirring. The electrolysis was stopped when the current intensity became sufficiently low. A brown self-assembled adlayers was detected on the surface of the platinum electrode.

Electrochemical behaviour of the recovered platinum electrode

The recovered electrode was scanned in the support electrolyte solution. The resulting cyclic voltammogram is shown in Fig. 2. The CV shows two cathodic peaks C_1 and C_2 at potentials −0.79 V versus SCE and −1.21 V versus SCE respectively in the reduction compartment. By comparing with the first CV (Fig. 1) we constat that both of the potential peaks was shifted to the cathodic value. It suggests that the shifting is due to the redox reaction of the self-assembled calixarenes with the electrode surface. This result confirms the presence of the calix[4]arenediquinone and is in agreement with their developed by Gómez-Kaifer et al. [27]. In the oxidation zone, a novel anodic peak A_3 appears at potential 1.03 V versus SCE. At this stage a new electrochemically-generated molecule became apparent. This peak corresponds certainly to the tow-electron oxidation of calix[4]arenedihydroquinone to the monoprotonated calix[4]arenequinone. This result is in agreement with the oxidation of the dihydroquinone to quinhydrone form [24, 29]. In the potential range between 1.9 V versus SCE and 2 V versus SCE, two overlapped waves were noticed. These waves correspond to the oxidation of the *tert*-butyl anisole as described in the "Electroactivity of calix[4]arenediquinone ($X_4Me_2Q_2$)" section. In reverse direction, two well-defined cathodic waves (C_3 and C_4) were observed at 0.92 V versus SCE and 0.41 V versus SCE, respectively. The cathodic peak C_4 is related to the reduction of monoprotonated quinone. Similar findings were reported for the electrochemical behaviour of the quinone–H_2Q system in aprotic solvent by Eggins et al. and Parker and co-workers [17, 30]. On the other hand, the cathodic peak C_3 indicates possibly the electrolyte support solution/platinum electrode interactions. This was detected during the recording of CV of platinum electrode in the electrolyte support solution before of the addition of the calix[4]arene.

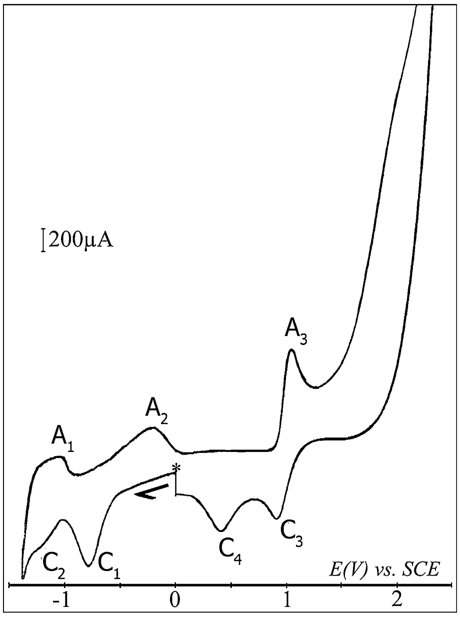


Fig. 2 Cyclic voltammogram at Pt disk electrode ($\Phi = 2$ mm) recovered with deposit of $CH_3CN + 0.1$ M TBAP solution. Sweep rate: 100 mV s^{-1}; (*) denotes the start and the final potential

Electrode surface passivation was tested by probing the electrochemistry of the ferri/ferricyanide couple on electrodes. Figure 3a shows CV scanned of the recovered platinum disk electrode in ferricyanide. By comparing with CV unregistered at clean platinum disk electrode (Fig. 3b), we shows that the electrode surface is sufficiently recovered and not completely passivated, whereas some electrochemistry residual of ferricyanide is observed. The adlayers product was characterized by MALDI-TOF and IR spectrometric analyses (structure defined in the "Experimental" section).

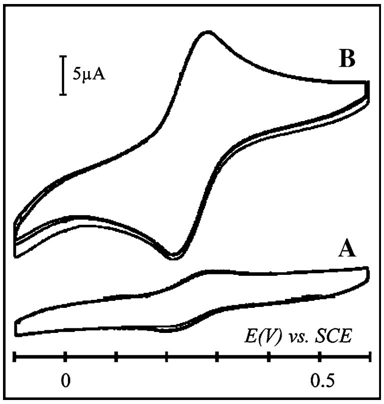


Fig. 3 CVs of ferricyanide (2 mM) in aqueous KCl (2 M) at Pt electrode (*a*) following electrodeposition through the reduction process of 1, and (*b*) at a clean Pt electrode. Sweep rate 100 mV s^{-1}

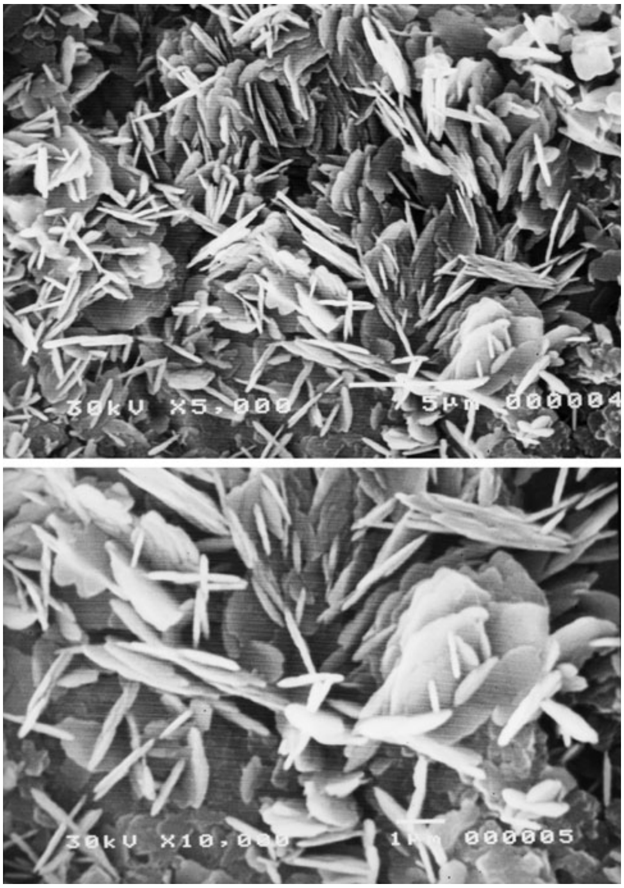


Fig. 4 **a** and **b**: SEM images of self-assembled calix[4]arenequinhydrone on platinum electrode

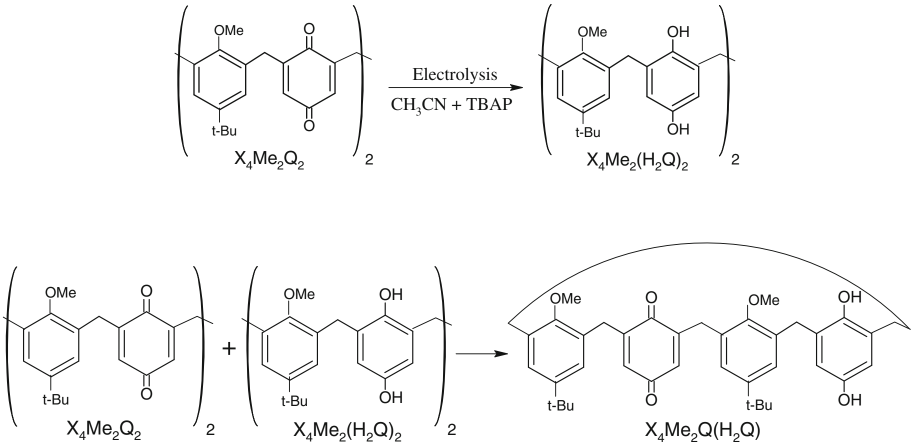
SEM characterizations

The morphology of electrodeposited film was analysed by SEM technique. Figure 4 shows the SEM images of a crystal produced from acetonitrile solution. The film is not homogeneous. The photograph shows hexangular prisms with a length of few micrometers. These characteristics which are in agreement with a quinhydrone single crystals [19, 31].

Taking into account the voltammetric patterns, the spectrometric analyses and the SEM result, we shows that the calix[4]arenequinhydrone may be formed by following the classical mechanism of quinhydrone formation by the mixture of dihydroquinone and *p*-BQ [18]. When the electrolysis was performed at a potential more negative then the first reduction peak (C_1), we electrogenerated the calix[4]arenedihydroquinone. The later reacts with calix[4]arenediquinone to give calix[4]arenequinhydrone form in solution and was deposit, afterward, on the platinum disk following the mechanism showed in the Scheme 3.

Conclusion

It has been shown that, by applying a cathodic potential at −1.16 V versus ECS in aprotic solution of the calix[4]arenediquinone, a self-assembled adlayer were observed on the platinum electrode. The electrodeposit was characterized by CV in electrolytic, in electrolyte support and in ferricyannure solutions. The electrochemically characterisation of the modified platinum electrode shows the electrogeneration of a new product which is calix[4]arenedihydroquinone. The formed product $X_4Me_2(H_2Q)$ appears in the solution and react with ($X_4Me_2Q_2$) to give a complex molecular. The new molecular specie was almost certainly the calix[4]arenequinhydrone $X_4Me_2(H_2Q)Q$. This result was confirmed by MALDI-TOF MS and IR spectroscopic analyses. The SEM characterisation shows that the expected product crystallised to give hexangular prisms.



Scheme 3 Schematic of electrogeneration mechanism of dimethoxycalix[4]arenequinhydrone ($X_4Me_2Q(H_2Q)$) from dimethoxycalix[4]arenediquinone ($X_4Me_2Q_2$) and dimethoxycalix[4]arenedihydroquinone ($X_4Me_2(H_2Q)_2$)

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