



Electrochemical quartz crystal microbalance analysis of the oxidation reaction of phenols found in wines at lutetium bisphthalocyanine electrodes

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ABSTRACT

An electrochemical quartz crystal microbalance (EQCM) was used to investigate the processes associated with the mass changes accompanying the phenol oxidation catalysed by a lutetium bisphthalocyanine (LuPc₂) film-modified Pt/quartz electrode.

The study focused on the analysis of the oxidation of phenols usually found in wines, including vanillic, ferulic, caffeic and gallic acids dissolved in a hydroalcoholic solution simulating the matrix of a red wine.

It has been shown that LuPc₂ modified EQCM sensors immersed in hydroalcoholic solution exhibit significant mass changes upon electrochemical cycling produced by the ingress/egress of ions necessary to maintain the electroneutrality of the film.

Cyclic voltammograms of LuPc₂/QCM electrodes immersed in phenols also undergo mass changes associated with the ingress/egress of ions. In addition, progressive mass changes occur upon successive scans. The oxidation/reduction of monophenols produces a progressive increase in the mass, whereas ortho-diphenols show the opposite behaviour. These phenomena have been interpreted in terms of the adsorption of the phenols to the LuPc₂ layer and their capability to electropolymerise at the electrode surface.

The combination of cyclic voltammetry with electrochemical quartz microbalance (EQCM) has demonstrated its capability to elucidate the complex processes occurring at the surface of voltammetric sensors chemically modified with bisphthalocyanines.

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1. Introduction

Polyphenols are a class of antioxidants that are present in a variety of foods and beverages such as wines [1] and their dietary intake has been associated with beneficial health effects [2,3]. In addition, this family of compounds has a strong influence in the organoleptic characteristics of wines [4].

Phenolic compounds have been analysed using a variety of methods that include chromatographic, electrophoretic and optic techniques [5]. Electrochemical methods have also been extensively applied [6].

Phthalocyanines have had noticeable success in the field of electrochemical sensors because these metal complexes act as mediators for electrochemical reactions and exhibit electrocatalytic activity for a variety of reactions [7–9]. Due to these properties, phthalocyanines have been successfully used as

sensitive materials in voltammetric electrodes for the qualitative detection of polyphenolic compounds [10–12]. Moreover, voltammetric sensors based on phthalocyanines have been used as the sensing elements of electronic tongues, which consist of an array of sensors with cross-selectivity, and use mathematical procedures for signal processing based on pattern recognition and/or multivariate data analysis [13–16].

The electrochemical signals obtained from phthalocyanine-based voltammetric electrodes show a high degree of complexity due to the variety of redox processes which occur at the electrode surface. Such processes are caused by the oxidation–reduction of both the electrode material and the phenolic compounds. In addition, the interactions between the electrode modifier and the polyphenols (i.e. electrocatalytic effect) and the diffusion of ions inside the film to counterbalance the charge changes can influence the electrochemical response [12,17,18].

The importance of these voltammetric sensors makes it necessary to acquire knowledge of the processes occurring at the electrode/solution interface. In particular, it is important to investigate the movement of ions and solvent accompanying the electron transfer process. There is also a need to analyse the possible polymerisation processes occurring at the electrode surface that can

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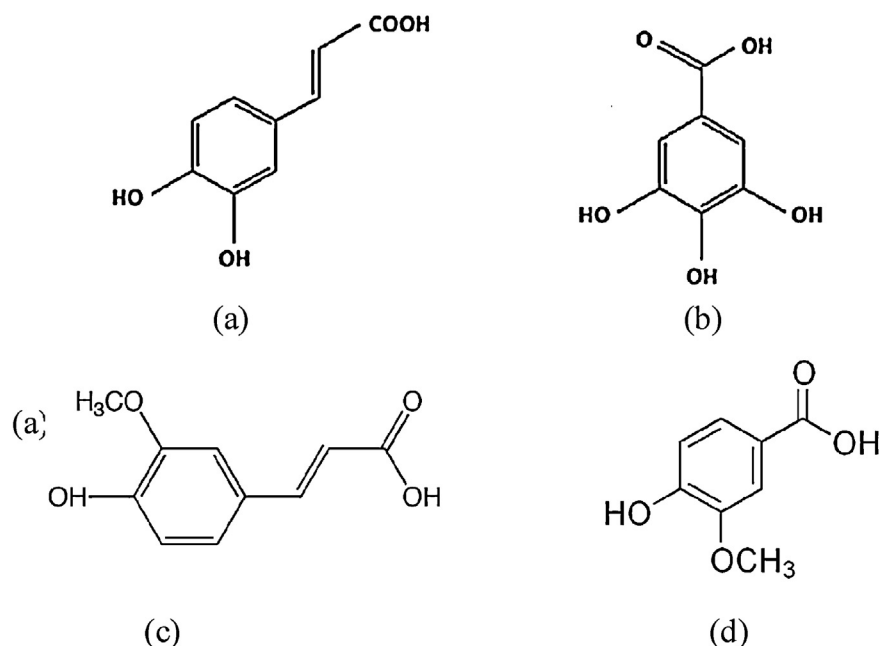


Fig. 1. Phenols included in the study: (a) caffeic acid; (b) gallic acid; (c) ferulic acid and (d) vanillic acid.

modify the activity of the sensitive layer while decreasing the lifetime of the electrodes [19].

Three decades after the introduction of the in situ application of the piezoelectric quartz crystal for researching electrochemical systems by Nomura and Iijima [20], the use of the electrochemical quartz crystal microbalance (EQCM) has become a well-established technique for the investigation of mass changes associated with electrochemical surface processes, such as electrosorption, electropolymerisation or ion insertion [21].

EQCM has been used to investigate the formation of polymeric products formed by the electro-oxidation of phenolic compounds on the surface of Au and Pt electrodes [19].

A few studies published in the field of phthalocyanines refer to QCM covered with MPcs, but these studies are limited to mass changes [22–25]. Only recently the EQCM has been applied to study the role of the movement of ions and the mass transport in the electrochemistry metallophthalocyanines (MPc) (Pc ring in oxidation state -2) [26].

We now present an electrochemical quartz crystal microbalance study of thin films of a sandwich type phthalocyanine, the lutetium bisphthalocyanine (LuPc_2) (a free radical derivative with ring in oxidation state -1.5). This derivative is of particular interest due to its rich electrochemistry and electrocatalytic properties, which are attributed to its free radical character [10,11]. In this work, LuPc_2 thin films have been used to measure tiny mass changes (order of nanograms) that occur when the sensor is immersed in hydroalcoholic solutions of antioxidants, of interest in the wine industry. Four antioxidants (caffeic acid, gallic acid, ferulic acid and vanillic acid) present in wines have been studied, and their adsorption and polymerisation processes were discussed in terms of the mass changes during the electrochemical experiment and their chemical structures.

2. Materials and methods

2.1. Reactants, QCM and electrochemistry

All reactants were purchased from Sigma–Aldrich and were used without further purification. Fig. 1 depicts the phenolic compounds used in the study.

Lutetium bisphthalocyanine (LuPc_2) was synthesised following a previously reported method [27]. The antioxidants (caffeic acid, gallic acid, vanillic acid and ferulic acid) were dissolved (0.5 mol L^{-1}) in a hydroalcoholic medium similar to that found in wines. This model solution of wine was prepared from a 12% (v/v) ethanol solution, to which 0.033 M tartaric acid was added. Then NaOH was added to give a final pH of 3.6.

QCM measurements were carried out with a quartz crystal microbalance QCM 200 model, purchased from Stanford Research Systems. The mass-sensitive oscillators were 1-in. diameter, 5-MHz AT-cut planoconvex quartz crystals coated with Pt (Pt/QCM).

LuPc_2 films were deposited onto the quartz crystal oscillators ($\text{LuPc}_2/\text{Pt/QCM}$) by means of the spin-coating technique; spin coater Mikasa 1H-D7 from a LuPc_2 chloroform solution $10^{-2} \text{ mol L}^{-1}$ by applying 700 rpm. The mass of the LuPc_2 deposited onto the electrodes was $69.09 \pm 1.37 \mu\text{g}$ ($50.43 \mu\text{g cm}^{-2}$).

The oscillators were used simultaneously as the working electrode of the electrochemical measurements. Cyclic voltammograms were carried out using a Parstat 2273 potentiostat (EG&G) using a conventional three electrode cell, where a Pt sheet was used as the counter electrode and an Ag/AgCl electrode as the reference electrode. Cyclic voltammograms and massograms were registered from 0.0 V (coinciding with the open cell voltage) to +1.3 V. The reverse bias voltage was applied from +1.3 V to -0.7 V ; the cycle was then closed by biasing the voltage from -0.7 V to 0.0 V (vs. Ag/AgCl) at a scan rate of 0.1 V s^{-1} .

2.2. Calibration of the QCM

The calibration of the quartz crystal microbalance was carried out by galvanostatic deposition of copper onto the platinum surface. A 0.5 mol L^{-1} solution of CuSO_4 in 0.1 mol L^{-1} H_2SO_4 (pH = 1.37) was subjected to a reducing potential, and copper was deposited with a fixed cathodic current of 2 mA for 70 s. Excellent linearity was observed in Δf vs. Q plots (the calibration curve was $y = 9.00 \times 10^{-5}x + 0.02$, $R^2 = 0.999$; deposition: 38 mg cm^{-2} of copper).

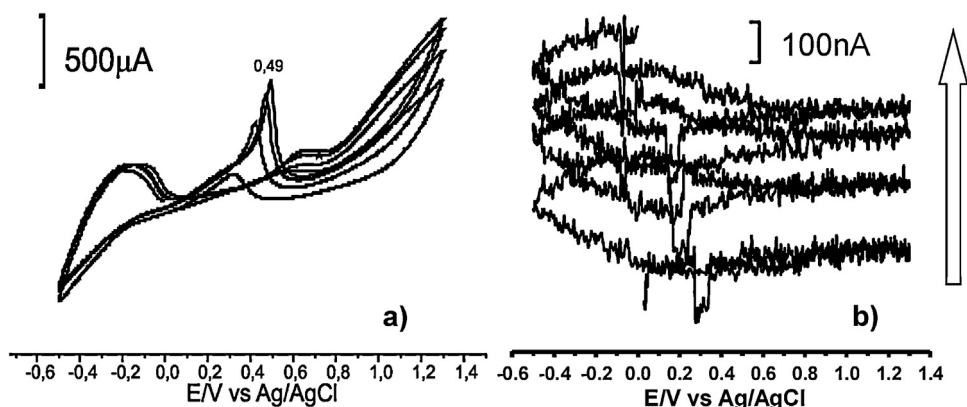
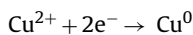


Fig. 2. Cyclic voltammogram (a) and massogram (b) of the Pt/QCM electrode immersed in the hydroalcoholic solution: 12% (v/v) ethanol, 0.033 mol L⁻¹ tartaric acid and NaOH until a final pH of 3.6 is attained. Four successive scans.

The electrochemical reaction involved in the copper electrodeposition is:



where Cu²⁺ is a hydrate ion. Using Faraday's second law:

$$\Delta q = \frac{\Delta m}{M} F \quad (1)$$

where Δq in C cm⁻² is the charge measured from the electrochemical response, Δm in g cm⁻², corresponds to the mass change of copper during the electrodeposition, and M and F are the atomic weight of copper (63.53 g mol⁻¹) and the Faraday constant, respectively.

Taking into account the Sauerbrey equation:

$$\Delta F = -2.3 \times 10^6 F_0^2 \frac{\Delta m}{A} \quad (2)$$

where ΔF is the frequency shift (in Hz), F_0 is the initial frequency (without coverage, in MHz), A is the electrode area (in cm²) and $-2.3 \times 10^6 F_0^2/A$ the sensibility factor of the quartz crystal (C_f).

By combining Eq. (1) with Eq. (2), the following expression (Eq. (3)) was obtained for use in the experimental determination of the calibration constant for the QCM:

$$C_f = \frac{M}{nF} \frac{\Delta q}{\Delta f} \quad (3)$$

where n is the number of electrons transferred in the electrochemical reaction (in the case of copper deposition $n = 2$).

In accordance with the linear plot obtained in the calibration process, the sensibility factor of the quartz crystal obtained was $C_f = 46.54 \text{ Hz } \mu\text{g}^{-1} \text{ cm}^2$, which is consistent with the theoretical value of $42.00 \text{ Hz } \mu\text{g}^{-1} \text{ cm}^2$.

3. Results and discussion

3.1. Electrochemical response of bare Pt/QCM and LuPc₂/Pt/QCM in hydroalcoholic solution

Prior to the EQCM characterisation of phenols, the electrochemical response of the bare Pt/QCM and the LuPc₂/Pt/QCM electrodes towards a hydroalcoholic solution containing tartaric acid and NaOH (free of antioxidants) was analysed. Fig. 2a shows four successive scans registered using the Pt/QCM electrode. As expected, in the presence of ethanol, the CV of the Pt/QCM electrode shows two electrochemical anodic processes at -0.18 V and 0.49 V , associated with the oxidation of ethanol (catalysed by platinum) and the formation of platinum hydroxide in different oxidation

states [28]. The formation of the platinum hydroxide was confirmed in the massograms (Fig. 2b), where a small increase in mass (100 ng in the first cycle) was observed. After 5 cycles, the electrode was passivated and the increase in mass was almost negligible.

Voltammograms of the LuPc₂/Pt/QCM electrode showed the expected redox peaks associated with the oxidation/reduction of the phthalocyanine ring in acidic media (pH = 3.6) [17,18,29]: one redox pair at ca. 0.85 V, corresponding to the one electron oxidation of the phthalocyanine ring (LuPc₂/LuPc₂⁺); a second redox pair at ca. -0.3 V , associated with the one electron reduction (LuPc₂⁻/LuPc₂); and a third pair at intermediate potentials. The origin of this third peak is the following: in acidic media, one of the Pc rings is protonated and the oxidation of the protonated ring is observed at ca. 0.4 V [17]. The intensities and potentials of the peaks changed from the first scan to the following ones. Successive scans were highly reproducible and electrodes could be cycled up to 30 times without suffering important changes in their shapes or intensities. A detailed explanation of the processes that take place is provided below.

Fig. 3a illustrates the first scan of the cyclic voltammogram and massogram registered when the LuPc₂/Pt/QCM electrode was immersed in the hydroalcoholic solution (solid line). Voltammograms started at 0.0 V, coinciding with the open cell potential of the electrode.

When applying a voltage from 0.0 V to +1.3 V, a sharp anodic peak at 0.85 V associated with the one electron oxidation of the phthalocyanine ring was observed [17,29]. In order to maintain the electroneutrality of the electrode, there must be an ingress of negative ions or an egress of positive ions. Previous works on the electrochemistry of LuPc₂ have suggested that during oxidation, cations (Na⁺ and H⁺ present in the solution) diffuse out from the phthalocyanine thin films to maintain the electroneutrality (instead of the ingress of negative ions) [30]. The diffusion of ions outside the film was confirmed by the massogram, where a mass decrease of 2120 ng was observed during the oxidation of the Pc ring (LuPc₂ → LuPc₂⁺) at 0.85 V.

It is important to notice that, in the first scan, the oxidation of the protonated form (which should be seen at ca. 0.4 V) appears as an extremely weak peak. As will be shown in the next section, this peak is clearly observed in the reverse and the subsequent scans, confirming the fact that the ingress of H⁺ causes the protonation of one of the Pc rings, giving rise to two types of molecular forms, the protonated and the non-protonated phthalocyanine.

When the voltage was reversed, an abrupt decrease of the mass (5600 ng) occurred. This large mass change could be due to the irreversible egress of ions and excess solvent out of the sensitive layer, which entered the film before the electrochemical treatment.

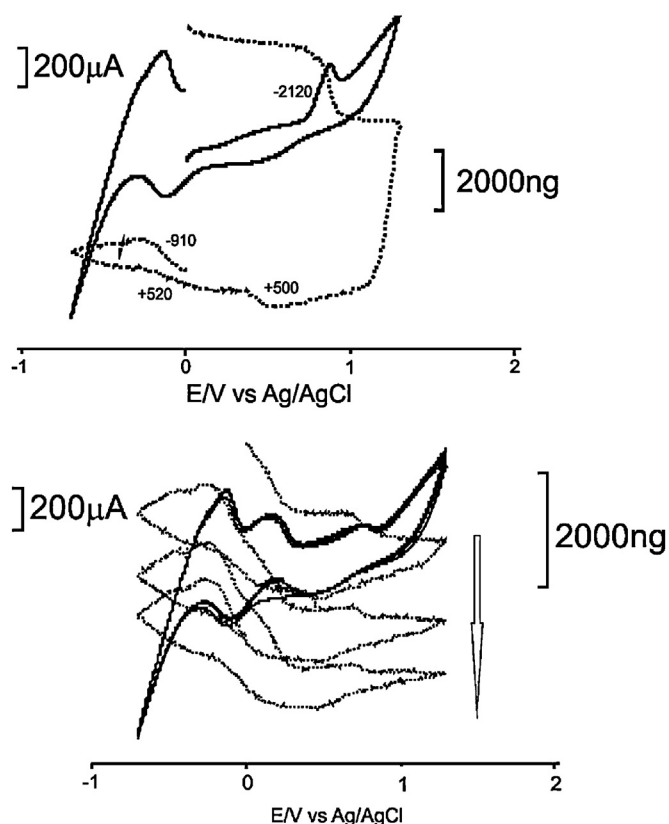


Fig. 3. Top, first CV superposed with the massogram curve; bottom, CV (2–4 cycles) and the corresponding mass changes observed for the $\text{LuPc}_2/\text{Pt}/\text{QCM}$ electrode immersed in the hydroalcoholic solution: 12% (v/v) ethanol, 0.033 mol L^{-1} tartaric acid and NaOH until a final pH of 3.6 is attained.

During the reverse scan (from +1.3 V to -0.8 V), two cathodic waves corresponding to the reversible $\text{LuPc}_2^+ \rightarrow \text{LuPc}_2$ and $(\text{LuHPc}_2)^+ \rightarrow \text{LuHPc}_2$ processes were observed at 0.6 V and -0.2 V , and were accompanied by an ingress of ions (ca. 500 ng and 520 ng, respectively) necessary to maintain the electroneutrality. The peak associated with the reduction of the phthalocyanine ring $\text{LuPc}_2 \rightarrow \text{LuPc}_2^-$ occurs at -0.4 V and was not completely observed in the voltammogram.

The cycle was then finished by applying a voltage from -0.8 V to 0.0 V . In this case, the change of polarity did not cause an important ingress/egress of ions. An intense anodic wave was observed at -0.2 V . This wave could correspond to the oxidation of the hydroalcoholic solution overlapped with the $\text{LuPc}_2^- \rightarrow \text{LuPc}_2$ and was accompanied by a decrease of mass (910 ng).

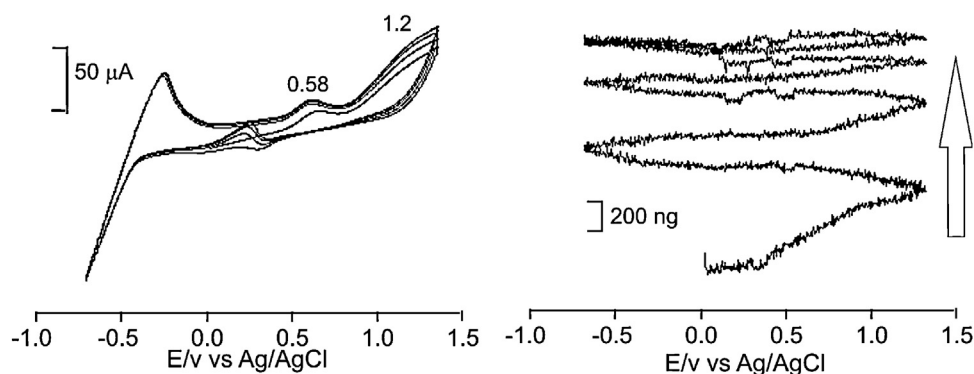


Fig. 4. Left, cyclic voltammograms; right, mass/potential curves for a Pt/QCM electrode immersed in caffeic acid in hydroalcoholic solution $5 \times 10^{-4} \text{ mol L}^{-1}$. Scan rate 0.1 V s^{-1} .

These results are in agreement with those reported in ECQM studies carried out in platinum phthalocyanine (PtPc) films, where it was demonstrated that important mass changes controlled by the ingress/egress of solvated anions occur during oxidation/reduction of the films [22]. However, when using PtPc, increases in mass during oxidation of the film (suggesting net solution and anion ingress) and mass decreases with the reduction of the film (suggesting a net egress of solution and anions during the reductive sweep) were observed. The differences with results found in our study can be attributed to the free radical nature of the LuPc_2 that is responsible for its extraordinary redox chemistry and the strong intermolecular π - π interactions that effectively influence the packing of the films.

In short, the first anodic polarisation of the LuPc_2 film in some way changes the chemical nature of the film due to the protonation of the phthalocyanine and to the irreversible egress of ions and excess solvent out of the film, having entered before the electrochemical treatment [22]. Subsequent voltammograms (up to 30 cycles) were highly reproducible, but differed from the first scan in the positions and intensities of the peaks. In addition, the oxidation of the protonated form could be clearly observed. Massograms of the second and subsequent scans are shown in Fig. 3b. It can be observed that in all cycles, anodic processes were associated with a decrease in the mass value, whereas reduction processes were associated with an increase in mass value. It is important to remark that the decrease in the mass values were much smaller than those observed during the first scan. In addition, a total mass loss of ca. 1000 ng per cycle was observed. After 30 cycles stabilisation of the massograms was not observed.

LuPc_2 is insoluble in water but soluble in apolar solvents such as chloroform. The mass reduction could be attributed to a possible (but extremely small) solubility of the LuPc_2 in EtOH, which could cause small losses of material from the film during scanning. It is also possible that excess solvent is incorporated into the film during the first scan of the virgin film and that subsequent scans produce a net loss of mass because solvent is expelled as the film relaxes after initial swelling.

3.2. Electrochemical response of bare Pt/QCM and $\text{LuPc}_2/\text{Pt}/\text{QCM}$ to polyphenols in hydroalcoholic solution

EQCM was used to study the sensing behaviour of LuPc_2 electrodes towards phenols. The compounds included in the study were four phenolic compounds containing only one hydroxyl group (vanillic and ferulic acid) or hydroxyl groups in ortho positions (caffeic and gallic acids) in their structures (Fig. 1). In order to mimic the wine environment, the antioxidants were solved in a hydroalcoholic solution.

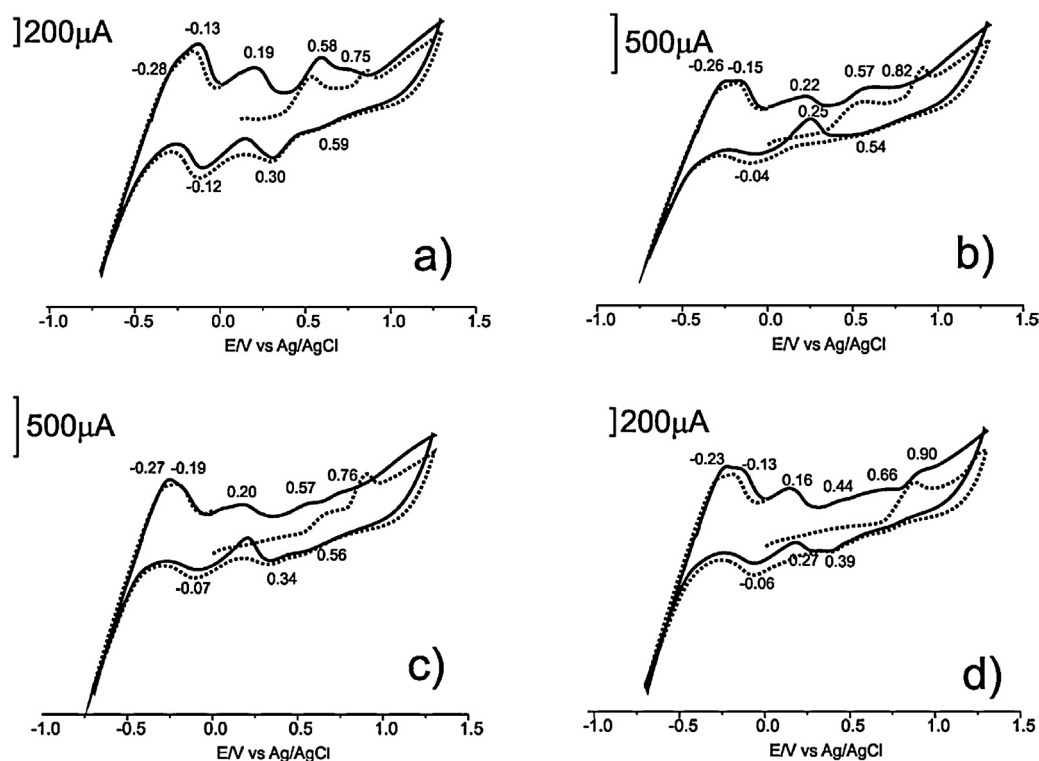


Fig. 5. Cyclic voltammograms of the LuPc₂/Pt/QCM electrode immersed in (a) caffeic acid, (b) gallic acid, (c) ferulic acid and (d) vanillic acid, $5 \times 10^{-5} \text{ mol L}^{-1}$ in hydroalcoholic solution. The dashed curve represents the first cycle. Solid line represents the fourth cycle.

Preliminary studies were carried out to evaluate the responses of the unmodified Pt/QCM electrodes towards antioxidants. Fig. 4 illustrates the response of the Pt/QCM electrode immersed in caffeic acid solved in a hydroalcoholic solution.

Voltammograms are characterised by a redox pair associated with the reversible oxidation/reduction of the caffeic acid (at $E_{1/2} = 0.44 \text{ V}$). A second intense anodic peak is observed at a higher potential (1.1 V) that, according to the literature, corresponds to the formation of polymeric products resulting from electro-oxidation. The oxidation of the alcohol appears at 0.35 V.

The deposition of the polymeric form is confirmed by the massograms that reflect an increase in mass during cycling. The largest amount of mass is deposited during the first cycle, which caused a passivation of the surface of the electrode. For this reason, the first voltammogram differs from the subsequent ones. A progressive decrease in the mass deposited upon continued scanning is observed. This result is in good agreement with the results obtained in Pt/QCM electrodes immersed in a water solution containing phenols [19]. However, in our voltammograms recorded in hydroalcoholic solution, the difference between the first cycle and the following scans is not as marked as the differences reported in water solution, indicating that passivation and fouling occur to a lesser extent.

The electrochemical behaviour of the quartz electrodes coated with LuPc₂ immersed in phenols was simultaneously studied by cyclic voltammetry and by QCM.

Fig. 5 shows the cyclic voltammograms (first and fourth cycles) registered when the LuPc₂/Pt/QCM electrode was immersed in solutions of antioxidants present in red wines.

The voltammetric signal consists of the already described peaks associated with the phthalocyanine ring and of peaks associated with the oxidation of the corresponding phenol. In addition, the phthalocyanine showed a strong electrocatalytic effect that resulted in an increase in the intensity of the response of the peaks related to the phenolic compounds. For instance, the oxidation

of caffeic acid, measured using a bare Pt/QCM electrode, which appears at 0.58 V, shows an intensity of $200 \mu\text{A}$; whereas, when the LuPc₂/Pt/QCM electrode is used, the peak intensity is $450 \mu\text{A}$. Simultaneously, the electrocatalytic activity of the LuPc₂ produces shifts in the potential values of the redox processes. For instance, the oxidation of phenol (which appears at 0.57 V when using Pt/QCM) is observed at 0.54 V for ferulic acid. The oxidation of vanillic is observed at 0.90 V (and a small peak at 0.44 V). Moreover, the interaction between the phthalocyanine and the corresponding phenol causes shifts in the position of the peak produced by the oxidation of the phthalocyanine (LuPc₂/PuPc₂⁺), which appears at 0.85 V in hydroalcoholic solution, and is observed at 0.75 V in caffeic acid, and at 0.66 V in vanillic acid.

Fig. 6 shows the first CV scan and the mass-curve registered when the LuPc₂/Pt/QCM electrode was immersed in the phenolic solutions. The changes in the mass values related to the LuPc₂ were similar to those observed in the hydroalcoholic solution. A decrease in mass occurs when the oxidation of film is reached, suggesting the expulsion of the solvated ions intercalated when the fresh film is immersed in the solution. Mass increases during the reductive sweep, suggesting a net ingress of solution and ions. Regarding the mass changes that occur during oxidation/reduction of phenols, it is important to notice that changes of mass do not coincide with the potentials where their oxidation takes place (ca. 0.57 V).

Upon successive cycling, two distinct patterns can be appreciated depending on the chemical structure of the phenols. When caffeic and gallic acids are present in the solution (both containing ortho-diphenol groups in their structure), a progressive decrease in mass is observed. Fig. 7 illustrates the mass-potential curves for the diphenols (caffeic and gallic acids) during the 2–4 cycles. The reduction in the mass value (2–4 cycles) was -2480 ng and -2280 ng for caffeic and gallic acids, respectively. This decrease suggests that the increase in mass associated with adsorption or polymerisation of diphenols is smaller than the decrease in mass produced by the expulsion of the solvated ions and solvent out of the film.

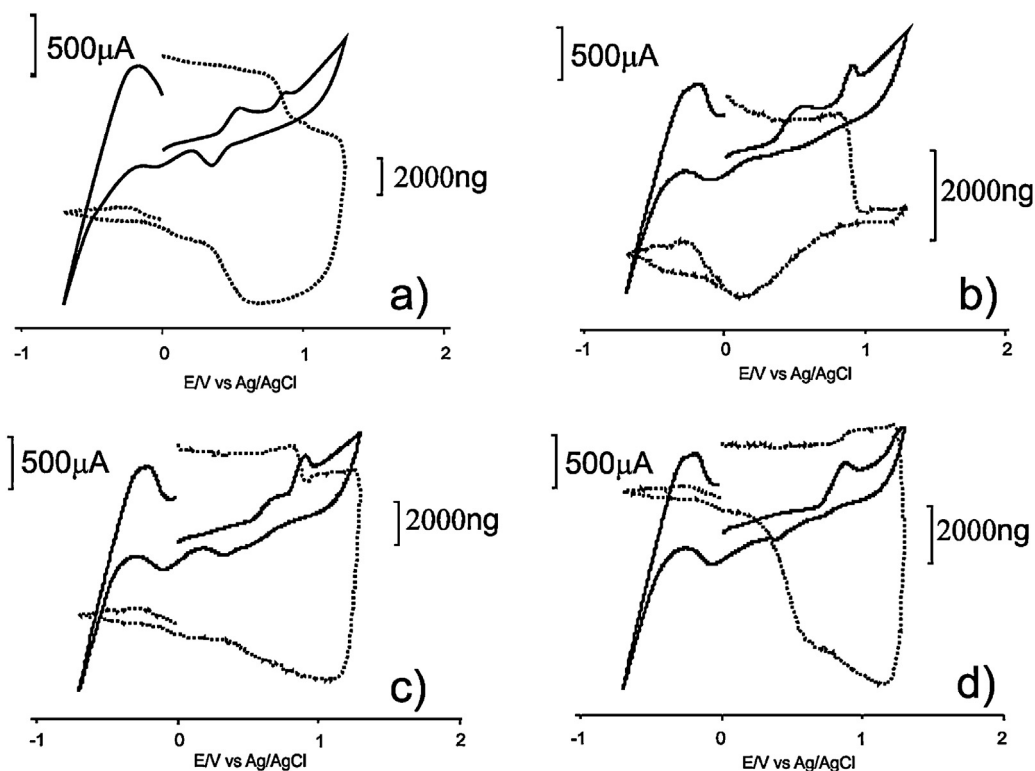


Fig. 6. The first cyclic voltammogram and their corresponding massogram curves obtained using the LuPc₂/Pt/QCM electrode immersed in (a) caffeic acid, (b) gallic acid, (c) ferulic acid and (d) vanillic acid.

On the contrary, the mass-potential curves for the monophenols (ferulic and vanillic acids) (Fig. 8) show the expected increase in mass value in cycles 2–4 (+3520 ng for ferulic acid and +1250 ng for vanillic acid). The overall variation was smaller than the change observed when the LuPc₂ was immersed in the hydroalcoholic solution (without phenols). These results indicate that monophenols have a higher tendency to adsorption or polymerisation at the electrode surface than diphenols.

In order to better understand these behaviours, further studies were carried out. When phenols are present in solution, two possible fouling mechanisms can be envisaged. One is related to the tendency of phenols to adsorb onto the surface electrode. The other one is the occurrence of an electropolymerisation process by means of the phenoxy radical of the phenol [19].

The tendency of phenols to adsorb onto the electrode surface was evaluated by exposing the crystal coated with LuPc₂ to a constant concentration of phenol ($0.5 \times 10^{-3} \text{ mol L}^{-1}$) and the mass

changes were monitored with the time. Fig. 9 illustrates the mass changes when the LuPc₂/Pt/QCM is exposed to an ortho-diphenol (gallic acid) and to a monophenol (ferulic acid).

In all cases, the mass of the crystal increased due to the adsorption of phenols onto the surface of the electrode. The mass increases observed were +180 ng, +100 ng, +310 ng and 280 ng for caffeic acid, gallic acid, ferulic acid and vanillic acid, respectively. The higher value of mass corresponds with the higher adsorption and this is observed for ferulic acid. The lower mass changes observed for the diphenols are consistent with the loss in mass corresponding to 2–4 cycles in the cyclic voltammetry experiment, because this small adsorption cannot compensate the expulsion of solvated ions and solvent molecules out of the film. However, the high adsorption tendency of ferulic and vanillic acids can compensate the loss of the mass due to the expulsion of water molecules out of the film, which coincides well with the increase in the mass value for the 2–4 cycles.

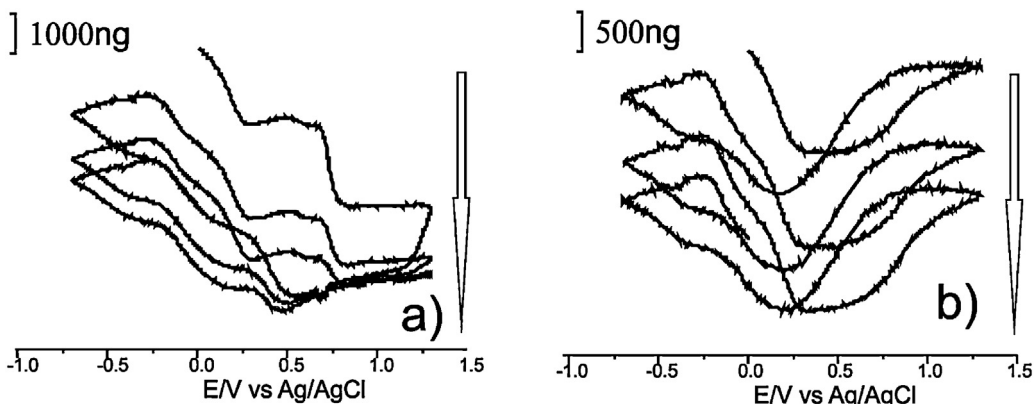


Fig. 7. Mass-potential curves obtained using the LuPc₂/Pt/QCM electrode immersed in (a) caffeic acid and (b) gallic acid.

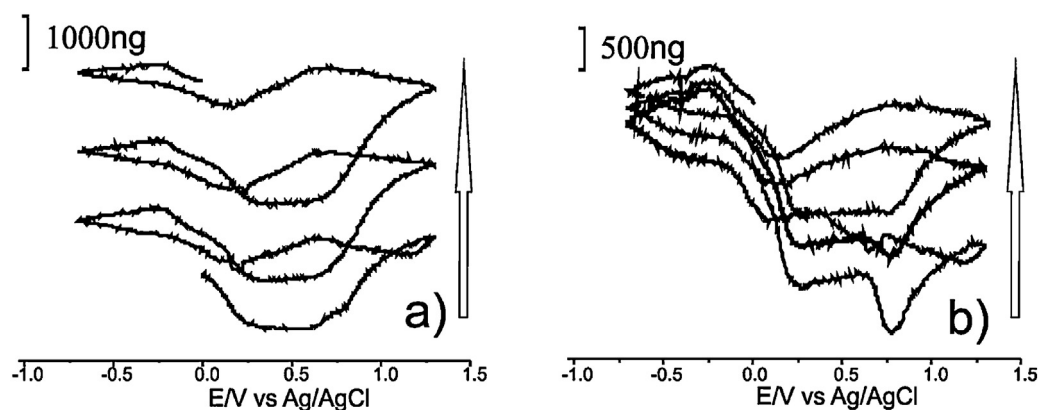


Fig. 8. Mass-potential curves obtained using the LuPc₂/Pt/QCM electrode immersed in (a) ferulic acid and (b) vanillic acid.

To check if polymerisation occurs during the electrochemical cycle, the efficiency of the electropolymerisation can be calculated taking into account the fact that the mass (m) of the polymer deposited on the electrode, following passage of a charge Q , is given by the equation:

$$m_{\text{calc}} = \frac{QM}{n_{\text{app}}F}$$

where M is the molar mass of a monomer unit within the chain, F is Faraday's constant and n_{app} the efficiency of the electropolymerisation process [31].

For caffeic and gallic acids, the values calculated for n_{app} were 36.37 and 35.8, respectively (theoretical value is 2), indicating that for ortho-diphenols, the electropolymerisation process was not attained. It is possible that some of the electrogenerated dimers and oligomers diffuse away from the surface of the electrode and do not participate in the film formation. Such competition between the nucleation process and the formation of soluble oligomers results in coulometric inefficiency, that is, high n_{app} values [32]. It is possible that some ortho-diphenol molecules are adsorbed onto the surface, but that increase in mass is not enough to compensate for the loss of mass generated by the egress of solvated ions.

When monophenols were analysed, the n_{app} values calculated were lower than those calculated for the diphenols; 5.67 and 1.92 for ferulic and vanillic acids, respectively. The value obtained for the electropolymerisation efficiency of vanillic acid corresponds well with the theoretical value ($n=2$), suggesting an electropolymerisation process. During phenol oxidation to the quinone form, phenoxy radicals are initially formed as intermediates. These radicals can be further oxidised to quinines or can react irreversibly to form dimeric products. Such dimers can be oxidised once again to produce a radical, which can couple with the phenoxy radical or with a dimeric radical to produce a polymer [33]. The mass

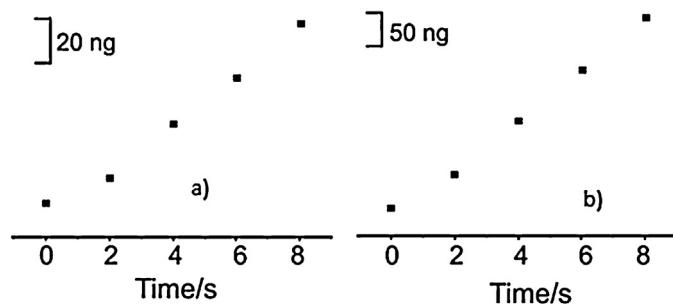


Fig. 9. Mass changes of LuPc₂/Pt/EQCM electrode in direct exposure to $0.5 \times 10^{-3} \text{ mol L}^{-1}$ of (a) gallic acid and (b) ferulic acid.

increase observed in the second to fourth cycles is then caused by the electropolymerisation of the phenols.

When ferulic acid is present in solution, the increase in the mass value (cycles 2–4) is due to the adsorption of the antioxidant onto the surface of the electrode (the electropolymerisation process was not effective, $n_{\text{app}} \neq 2$). The adsorption of ferulic acid is enough to compensate for the loss of the water molecules inside the LuPc₂ film. This result suggests that the adsorption of ferulic acid is higher as compared with that for the ortho-diphenol derivatives (which cannot compensate for the loss of water molecules).

4. Conclusions

An electrochemical quartz crystal microbalance (EQCM) has provided new insights into the electrochemical oxidation of phenolic compounds at lutetium bisphthalocyanine electrodes. It has been shown that the electrochemistry at the LuPc₂ electrode in hydroalcoholic solution is mediated by changes in the mass of the film, due to the ingress and egress of solvated ions necessary for charge compensation: solvated cations are expelled from the film during electro-oxidation and enter the film during its electro-reduction.

Mass changes accompanying the polyphenol oxidation catalysed by LuPc₂ film-modified electrodes have also been observed. In this case, mass changes are also related to the ingress and egress of solvated ions during oxidation of the LuPc₂ film. Subsequent voltammograms on the same system adopt the same typical shape, although there is, upon successive cycling, a variation in terms of the mass change that depends on the chemical nature of the phenol analysed.

The mass decreases with each scan in the presence of ortho-diphenols, whereas monodiphenols produce an increase in the mass. Comparison of the charge passed during the electrochemical cycle indicate that vanillic acid electropolymerises at the electrode surface causing an increase in mass upon successive cycling, whereas ortho-diphenols and ferulic acid do not polymerise, but are easily adsorbed at the electrode surface. For ferulic acid, adsorption compensates the expulsion of solvated ions and solvent molecules out of the film, thus explaining the increase in mass observed. In contrast, the low tendency to adsorb showed by ortho-diphenols does not compensate the expulsion of ions and solvent, and a net decrease of mass is observed.

In summary, EQCM has proven to be a helpful technique to understand the mechanisms in the electrochemical oxidation of phenols at LuPc₂ electrodes. This knowledge will be extremely useful in the development of voltammetric sensors for the analysis of antioxidants present in wines.

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References

- [1] F. Saura-Calixto, M.E. Díaz-Rubio, Polyphenols associated with dietary fibre in wine – a wine polyphenols gap? *Food Research International* 40 (2007) 613–619.
- [2] A. Crozier, I.B. Jaganath, M.N. Clifford, Dietary phenolics: chemistry, bioavailability and effects on health, *Natural Product Reports* 26 (2009) 1001–1043.
- [3] L.D. Mello, D. Del Rio, L.G. Costa, M.E.J. Lean, A. Crozier, Polyphenols health. What compounds are involved?, *Nutrition, Metabolism, and Cardiovascular Diseases* 20 (2010) 1–6.
- [4] M. del Alamo, I. Nevares, L.M. Carcel, Redox potential evolution during red wine aging in alternative systems, *Analytica Chimica Acta* 563 (2006) 255–263.
- [5] L.A. Kartsova, A.V. Alekseeva, Chromatographic electrophoretic methods for determining polyphenol compounds, *Journal of Analytical Chemistry* 63 (2008) 1024–1033.
- [6] P.A. Kilmartin, H. Zou, A.L. Waterhouse, A cyclic voltammetry method suitable for characterizing antioxidant properties of wine and wine phenolics, *Journal of Agricultural and Food Chemistry* 49 (2001) 1957–1965.
- [7] J.H. Zagal, S. Griveau, J.F. Silva, T. Nyokong, F. Bedioui, Metallophthalocyanine-based molecular materials as catalysts for electrochemical reactions, *Coordination Chemistry Reviews* 254 (2010) 2755–3279.
- [8] L. Valli, Phthalocyanine-based Langmuir–Blodgett films as chemical sensors, *Advances in Colloid and Interface Science* 116 (2005) 13–44.
- [9] A.B. Sorokin, E.V. Kudrik, Phthalocyanine metal complexes: versatile catalysts for selective oxidation and bleaching, *Catalysis Today* 159 (2011) 37–46.
- [10] M.L. Rodríguez-Méndez, M. Gay, J.A. de Saja, New insights into sensors based on radical bisphthalocyanines, *Journal of Porphyrins and Phthalocyanines* 13 (2009) 1159–1167.
- [11] C. Apetrei, I. Apetrei, J.A. de Saja, M.L. Rodríguez-Méndez, Carbon paste electrodes made from different carbonaceous materials: application in the study of antioxidants, *Sensors* 11 (2011) 1328–1344.
- [12] S. Casilli, M. De Luca, C. Apetrei, V. Parra, A.A. Arrieta, L. Valli, J. Jiang, M.L. Rodríguez-Méndez, J.A. de Saja, Langmuir–Blodgett Langmuir–Shaeffer films of homoleptic and heteroleptic phthalocyanine complexes as voltammetric sensors: applications to the study of antioxidants, *Applied Surface Science* 246 (2005) 304.
- [13] Y.G. Vlasov, Y.E. Ermolenko, A.V. Legin, A.M. Rudnitskaya, V. Kolodnikov, Chemical sensors and their systems, *Journal of Analytical Chemistry* 65 (2010) 880–890.
- [14] M. Del Valle, Electronic tongues employing electrochemical sensors, *Electroanalysis* 22 (2010) 1539–1555.
- [15] M.L. Rodríguez-Méndez, V. Parra, C. Apetrei, S. Villanueva, M. Gay, N. Prieto, J. Martínez, J.A. de Saja, Electronic tongue based on voltammetric electrodes modified with materials showing complementary electroactive properties. Applications, *Microchimica Acta* 163 (2008) 23–31.
- [16] C. Apetrei, I. Apetrei, I. Nevares, M. del Alamo, V. Parra, M.L. Rodríguez-Méndez, J.A. de Saja, Using an e-tongue based on voltammetric electrodes to discriminate among red wines aged in oak barrels or aged using alternative methods – correlation between electrochemical signals and analytical parameters, *Electrochimica Acta* 52 (2007) 2588–2594.
- [17] M. Gay, M.L. Rodríguez-Méndez, J.A. de Saja, Films of lutetium bisphthalocyanine nanowires as electrochemical sensors, *Langmuir* 26 (2010) 19217–19224.
- [18] M. Gay-Martín, R. Muñoz, J.A. de Saja, M.L. Rodríguez-Méndez, Multisensor system based on bisphthalocyanine nanowires for the detection of antioxidants, *Electrochimica Acta* 68 (2012) 88–94.
- [19] M. Ferreira, H. Varela, R.M. Torresi, G. Tremiliosi-Filho, Electrode passivation caused by polymerization of different phenolic compounds, *Electrochimica Acta* 52 (2006) 434–442.
- [20] T. Nomura, M. Iiyama, Electrolytic determination of nanomolar concentrations of silver in solution with a piezoelectric quartz crystal, *Analytica Chimica Acta* 131 (1981) 97–102.
- [21] M.R. Deakin, D.A. Buttry, Electrochemical applications of the quartz crystal microbalance, *Analytical Chemistry* 61 (1989) 1147A.
- [22] M. Harbeck, D. Dilek, D. Erbahar, I. Gürol, E. Musluoğlu, V. Ahsen, Z. Öztürk, Phthalocyanines as sensitive coatings for QCM sensors operating in liquids for the detection of organic compounds, *Sensors and Actuators B* 150 (2010) 346–354.
- [23] C. Çoban, E. Demirbaş, Detection of volatile organic compounds in aqueous solutions by phthalocyanine coated quartz crystal microbalance, *Sensor Letters* 4 (2006) 446–451.
- [24] Y. Açıkbaz, M. Evyapan, T. Ceyhan, R. Çapan, Ö. Bekaroğlu, Characterization and organic vapor sensing properties of Langmuir–Blodgett film using a new three oxygen-linked phthalocyanine incorporating lutetium, *Sensors and Actuators B* 135 (2009) 426–429.
- [25] L. Giotta, G. Giancane, D. Mastrogiacomo, T. Basova, P. Metrangolo, L. Valli, Phenol chemisorption onto phthalocyanine thin layers probed by ATR-FTIR difference spectroscopy. Affiliation information, *Physical Chemistry Chemical Physics* 11 (2009) 2161–2165.
- [26] R.J.C. Brown, D.J.L. Brett, A.R.J. Kucernak, An electrochemical quartz crystal microbalance study of platinum phthalocyanine thin films, *Journal of Electroanalytical Chemistry* 633 (2009) 339–346.
- [27] M. Linaje, M.C. Quintanilla, A. González, J.L. del Valle, G. Alcaide, M.L. Rodríguez-Méndez, Improvement of the synthesis of lutetium bisphthalocyanine using the Taguchi method, *Analyst* 125 (2000) 341.
- [28] S. Andreescu, D. Andreescu, O.A. Sadiq, A new electrocatalytic mechanism for the oxidation of phenols at platinum electrodes, *Electrochemistry Communications* 5 (2003) 681–688.
- [29] K.M. Kadish, T. Nakanishi, A.G. Gurek, V. Ahsen, I. Yilmaz, Electrochemistry of a double-decker lutetium(III) phthalocyanine in aqueous media. The first evidence for five reductions, *Journal of Physical Chemistry B* 105 (2001) 9817–9821.
- [30] A. Arrieta, M.L. Rodríguez-Méndez, J.A. de Saja, Langmuir–Blodgett film and carbon paste electrodes based on phthalocyanines as sensing units for taste, *Sensors and Actuators B* 95 (2003) 357–365.
- [31] J. Wang, M. Jiang, F. Lu, Electrochemical quartz crystal microbalance investigation of surface fouling due to phenol oxidation, *Journal of Electroanalytical Chemistry* 444 (1998) 127–132.
- [32] Z. Ež Erskis, G. Stalnis, Z. Jusys, Electropolymerization of chlorinated phenols on a Pt electrode in alkaline solution. Part II: an electrochemical quartz crystal microbalance study, *Journal of Applied Electrochemistry* 32 (2002) 49–55.
- [33] V.D. Pokhodenko, V.A. Khizhnyi, V.A. Bidzilya, Stable phenoxy-radicals, *Russian Chemistry Review* 37 (1968).

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