



## Electrochemical preparation of conductive films of tetrapyrrolylporphyrins coordinated to four $[\text{Ru}(5\text{-NO}_2\text{-phen})_2\text{Cl}]^+$ groups

Paulina A. Dreyse<sup>a</sup>, Mauricio A. Isaacs<sup>a,\*</sup>, Patricio E. Iturriaga<sup>a</sup>, Diego A. Villagra<sup>b</sup>, María J. Aguirre<sup>c</sup>, Clifford P. Kubiak<sup>d</sup>, Starla D. Glover<sup>d</sup>, John C. Goeltz<sup>d</sup>

<sup>a</sup> Departamento de Química, Facultad de Ciencias, Universidad de Chile, Las Palmeras 3425, Casilla 653, Ñuñoa, Santiago, Chile

<sup>b</sup> Departamento de Química, Facultad de Ciencias, Universidad de Tarapacá, Avenida General Velásquez 1775, Casilla 7-D, Arica, Chile

<sup>c</sup> Departamento de Química de los Materiales, Facultad de Química y Biología, Universidad de Santiago de Chile, Avenida Libertador Bernardo O'Higgins 3363, Casilla 40, Correo 33, Santiago, Chile

<sup>d</sup> Department of Chemistry and Biochemistry, University of California San Diego, 9500 Gilman Drive MC 0358, La Jolla, CA 92093, USA

### ARTICLE INFO

#### Article history:

Received 30 October 2009

Received in revised form 3 July 2010

Accepted 9 August 2010

Available online 13 August 2010

#### Keywords:

5-NO<sub>2</sub>-1,10-phenanthroline

Tetraruthenated porphyrins

Conducting polymers

Electropolymerization

Modified electrodes

### ABSTRACT

This work describes the preparation of a new tetraruthenated porphyrin and the corresponding polymeric film. This macromolecule consists of a Ni(II) tetrapyrrolylporphyrin coordinated to four  $[\text{Ru}(5\text{-NO}_2\text{-phen})_2\text{Cl}]^+$  moieties. The 5-NO<sub>2</sub>-phen ligands are reduced at  $-0.90$  V, generating a radical anion that is able to generate polymeric coatings onto glassy carbon (GC) electrodes. These polymeric films are very stable in aqueous solutions. The polymeric films are characterized by electrochemistry, infrared spectro-electrochemistry (IR-SEC) and atomic force microscopy (AFM).

© 2010 Elsevier B.V. All rights reserved.

### 1. Introduction

Tetrapyrrolylporphyrins with four coordinated Ru(II) complexes at the periphery of the macrocycle have been studied for their unusual electrocatalytic [1,2], electroanalytical [3,4], photophysical [5] and photoelectrochemical [6–8] properties.

It is known that mixed valence complexes of Ru can undergo intramolecular electron transfer process in an extensive class of molecules [9–12]. When Ru(II) units are covalently linked to the porphyrin ring, it is possible to obtain a supramolecule that can generate simultaneous intramolecular energy transfer processes which enhance their catalytic properties [13]. These supramolecular materials have been used in modified electrodes with improved catalytic properties, generating coverages able to promote multi-electronic transfers in electrocatalytic reactions where the active site is either the metal center in the porphyrin or the Ru moieties depending on the reaction under study [13,14].

Anson et al. have reported supramolecular systems of porphyrin units coordinated to Ru(II) complexes [15,16]. The electrocatalytic reduction of oxygen was studied at GC electrodes modified by absorption of Co(II) tetrapyrrolylporphyrins with four  $[\text{Ru}(\text{NH}_3)_5]^{2+}$  groups as peripheral ligands [15,16]. Water was the product

obtained in the electroreduction of O<sub>2</sub>. The cobalt porphyrin is the site of the electrocatalysis, and the Ru complexes appended to the ring porphyrin serve as co-catalysts. The proposed mechanism has a first step where Co(II)–O<sub>2</sub> adducts were generated, and subsequently the back-bonding Ru(II) co-catalysts facilitated the reduction of coordinated O<sub>2</sub> by four electrons [16].

Research by Anson et al. has inspired other groups to explore further research using related macrocycles. Toma et al. have prepared and characterized a series of polynuclear species obtained by attaching four  $[\text{Ru}(\text{bpy})_2\text{Cl}]^+$  (bpy: 2,2'-bipyridine) groups to the pyridyl substituents of *meso*-tetra(4-pyridyl)porphyrin (TRP) and their metallated derivatives (MTRP) [17]. These compounds display rich electrochemistry and versatile catalytic activity associated with the multielectron transfers between ruthenium-bipyridine and metalloporphyrin units [17]. The supramolecular species interact very strongly with DNA leading to pronounced changes in the absorption and emission spectra of  $[\text{TRP}]\text{Cl}_4$ . Oxidative DNA base damage has been evaluated by the formation of 8-oxo-7,8-dihydro-2'-deoxyguanosine. Thus, a potential application of the tetraruthenated porphyrin in photodynamic therapy has been proposed [17]. On the other hand, when these supramolecular macrocycles were used to generate coatings in aqueous solution, the absorbed films were not stable. This is a major drawback for the use of these compounds as electrocatalysts sensors or devices [17].

\* Corresponding author. Tel.: +56 2 9787267; fax: +56 2 2713888.

E-mail address: [misaacs@uchile.cl](mailto:misaacs@uchile.cl) (M.A. Isaacs).

The electrocatalytic reduction reactions of  $\text{NO}_2^-$  and  $\text{SO}_3^{2-}$  ions have been studied using tetraruthenated porphyrins. In particular, modified electrodes have been obtained by dip-coating methods using  $[\text{CoTPyP}\{\text{Ru}(\text{bpy})_2\text{Cl}\}_4]^{4+}$  (CoTPyP: Co(III) tetra-pyridyl-porphyrin) [18]. The surfaces obtained were stable and homogeneous, and with high supporting electrolyte concentration, these surfaces have been successfully used in analytical chemistry methodologies such as flow injection analysis (FIA) [18].

Combining supramolecular porphyrins with anionic porphyrins, self-assembled films can be generated by a layer-by-layer methodology [19]. The modified electrodes were useful for the determination of both free and total  $\text{SO}_2$  in wine, specially designed for FIA. The method is useful to red, white and rosé wines. It requires only small amounts of sample and it is faster than the iodometric titration method [19].

Recently, our group has sought new and efficient electrocatalysts for applications of environment interest such as  $\text{CO}_2$  and  $\text{NO}_x^-$  reduction [20–24], as well as in electroanalytical applications such as the determination of S(IV) oxoanions [25]. A kind of used methodology to modify electrodic surfaces is by electropolymerization. Some electropolymerizable functional groups in the structure of polypyridyl and macrocyclic complexes are: 5-NH<sub>2</sub>-phen (phen: phenanthroline) [26], 5,6-NH<sub>2</sub>-phen [27] and 5,5'-NH<sub>2</sub>-bpy [28]. Also, conducting films of tetraruthenated porphyrins have been prepared containing peripheral  $\text{RuCl}_3(\text{dppb})$  moieties (dppb = 1,4-bis(diphenylphosphino)butane) [29].

Nitro functional groups also present an important area for study since they are relevant in bioelectrochemistry and pharmacology [30], with well studied reduction mechanisms in both aqueous and organic solutions. Despite the rich redox chemistry of nitro functional groups, to the best of our knowledge no publications have been reported indicating its role as an electropolymerization precursor in coordination compounds containing transition metals.

In this paper, we described the voltammetric behavior of new tetraruthenated porphyrins obtained by coordination of four  $[\text{Ru}(5\text{-NO}_2\text{-phen})_2\text{Cl}]^+$  complexes to a Ni(II) tetra(4-pyridyl)porphyrin. A protocol for the electrochemical preparation of a conducting polymer from this complex is also presented. The polymeric growth is characterized by electrochemical, IR-SEC and AFM.

## 2. Experimental

### 2.1. Materials

All the reagents and solvents were of analytical grade or better and were used without further purification. The reagents: 5,10,15,20-tetra(4-pyridyl)-21*H*,23*H*-porphyrin ( $\text{H}_2\text{TPyP}$ ), 1,10-phenanthroline monohydrate, sodium hydroxide, silver hexafluorophosphate, tetrabutylammonium hexafluorophosphate ( $\text{TBAPF}_6$ ) and nickel (II) acetate tetrahydrate (Sigma–Aldrich). Lithium chloride (Fisher). Ruthenium (III) chloride trihydrate (Pressure Chemical Co.). Zinc (II) acetate dihydrate (Merck). Sodium perchlorate monohydrate (Fluka). Tetraethylammonium perchlorate ( $\text{TEAClO}_4$ ) (G. Frederick Smith Chemical Company). The solvents: acetonitrile- $\text{d}_3$  ( $\text{CD}_3\text{CN}$ ) and 2,2,2-trifluoroethanol (Sigma–Aldrich). Absolute ethanol (Riedel-deHaën). *N,N*-dimethylformamide (DMF) (J.T. Baker). Nitric acid, sulfuric acid, chloroform, acetonitrile (ACN), methanol (MeOH), acetone, diethyl ether and glacial acetic acid (Merck).

### 2.2. Synthesis

The 5- $\text{NO}_2$ -phen ligand [31] and  $\text{Ru}(5\text{-NO}_2\text{-phen})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$  complex were prepared by literature methods [32]. Ni(II) tetra-

pyridylporphyrin (NiTPyP) was prepared by reaction with glacial acetic acid,  $\text{H}_2\text{TPyP}$  and Ni(II) acetate as it is described in published methods [33,34].

In order to achieve an effective coordination of porphyrin pyridyl groups to  $\text{Ru}(5\text{-NO}_2\text{-phen})_2\text{Cl}_2$ ,  $\text{AgPF}_6$  was first used to replace a chloride with a solvent molecule (ACN). This synthetic step is of great importance, as the solvent molecule is considerably more labile than the  $\text{Cl}^-$  ion, which improves product yield [35]. After chloride abstraction, the NiTPyP modified with four  $[\text{Ru}(5\text{-NO}_2\text{-phen})_2(\text{ACN})\text{Cl}]^+$  groups was synthesized according to the literature procedure for analogous compounds [36]. NiTPyP (54.07 mg, 0.08 mmol) was refluxed with  $[\text{Ru}(5\text{-NO}_2\text{-phen})_2(\text{ACN})\text{Cl}](\text{PF}_6) \cdot 2\text{H}_2\text{O}$  (265.22 mg, 0.33 mmol) in 30 mL of trifluoroethanol for 18 h. The solid was purified by chromatography on neutral alumina using ACN/MeOH (9:1) mixture as eluent. Yield 54.23 mg (22%). Elemental Analysis (3747.11  $\text{g mol}^{-1}$ ):  $\text{C}_{136}\text{H}_{80}\text{N}_{32}\text{NiR}_4\text{O}_{16}\text{Cl}_4(\text{PF}_6)_4 \cdot 4.5\text{H}_2\text{O}$ , exp. (calc): C, 45.2 (44.2); H, 2.8 (2.5); N, 12.2 (12.1) [18,29,36,57–63].

$^1\text{H}$  NMR ( $(\text{CD}_3)_2\text{SO}$ ) (see Fig. 1):  $\text{H}_1 = 10.46$ ;  $\text{H}_2 = 7.93$ ;  $\text{H}_3 = 9.31$ ;  $\text{H}_4 = 9.00$ ;  $\text{H}_5 = 9.20$ ;  $\text{H}_6 = 7.93$ ;  $\text{H}_7 = 9.66$ ;  $\text{H}_8 = 9.61$ ;  $\text{H}_9 = 7.93$ ;  $\text{H}_{10} = 8.56$ ;  $\text{H}_{11} = 8.98$ ;  $\text{H}_{12} = 8.43$ ;  $\text{H}_{13} = 7.93$ ;  $\text{H}_{14} = 9.54$ ;  $\text{H}_{15} = 8.80$ ;  $\text{H}_{16} = 7.75$ ;  $\text{H}_{17} = 6.97$ . IR data in KBr pellet:  $\delta$  ( $\text{C}-\text{H}$ )<sub>asym</sub> =  $1208\text{ cm}^{-1}$ ;  $\nu_s$  ( $\text{NO}_2$ ) =  $1341\text{ cm}^{-1}$ ;  $\nu_a$  ( $\text{NO}_2$ ) =  $1540\text{ cm}^{-1}$ ;  $\nu$  ( $\text{C}=\text{C}$ )<sub>aromatic</sub> =  $1420, 1451, 1513$  and  $1610\text{ cm}^{-1}$ ;  $\nu$  ( $\text{C}=\text{N}$ )<sub>aromatic</sub> =  $1635\text{ cm}^{-1}$ ;  $\nu$  ( $\text{C}-\text{H}$ )<sub>aromatic</sub> =  $3092\text{ cm}^{-1}$ . UV-vis ( $\text{CH}_3\text{OH}$ )  $\lambda_{\text{max}}$  (nm) [ $\epsilon \times 10^4\text{ M}^{-1}\text{ cm}^{-1}$ ]: 267 [26.9], 411 [28.7], 526 [5.69].

### 2.3. Measurements

The complexes were characterized by cyclic voltammetry under two different sets of equipment and conditions: (1) Cyclic voltammetry, CH Instruments potentiostat 620B. Samples were prepared with 1 mM of Ni(II) tetraruthenated porphyrin in DMF solutions containing 0.1 M  $\text{TEAClO}_4$  as supporting electrolyte. A GC working electrode  $r = 1.5\text{ mm}$  (CH Instruments), a saturated  $\text{Ag}/\text{AgCl}$  reference electrode and a Pt wire counter electrode ( $14\text{ cm}^2$ ) were used.

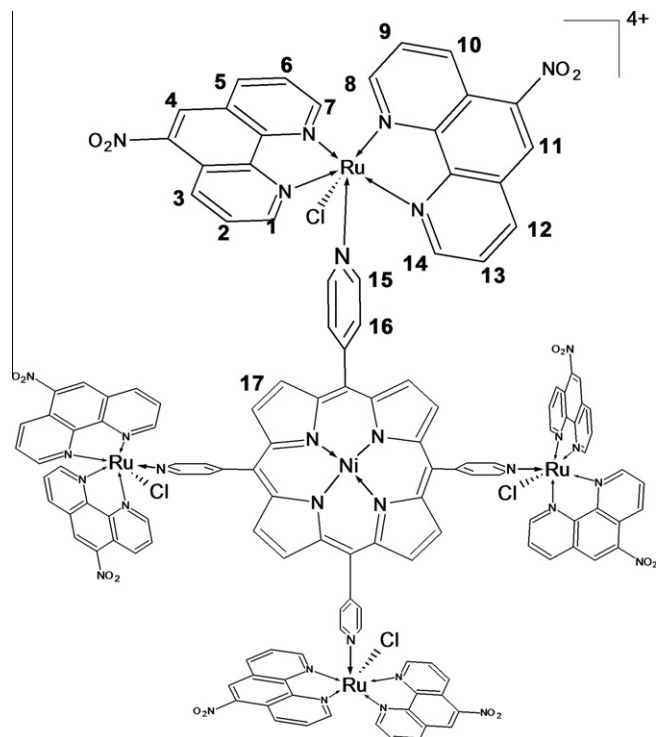


Fig. 1. Structural representation of  $[\text{NiTPyP}\{\text{Ru}(5\text{-NO}_2\text{-phen})_2\text{Cl}\}_4]^{4+}$ .

(2) BAS CV-50 W Voltammetric Analyzer. Samples were prepared with 1 mM of Ni(II) tetraruthenated porphyrin in CD<sub>3</sub>CN containing 0.1 M TBAPF<sub>6</sub> as supporting electrolyte. A Pt working electrode, a ferrocene/ferrocenium reference electrode and a Pt wire counter electrode were used. For IR-SEC, the samples using were prepared with 1 mM of Ni(II) tetraruthenated porphyrin in CD<sub>3</sub>CN solutions containing 0.1 M TBAPF<sub>6</sub> as the supporting electrolyte. All the solutions were prepared in a drybox and degassed completely before injection into spectroelectrochemical cell [37]. The electrochemical cell is surrounded by a hollow brass heat exchanger. Polished Pt foil, 4.5 mm in diameter was soldered on a brass post and served as the working electrode. A circular 0.5 mm Ag wire, placed 0.5 mm outside the perimeter of the working electrode, served as a pseudo-reference electrode. The auxiliary electrode consisted of 0.5 mm Pt wire, outside the perimeter of the reference electrode. Both wires were polished with emory cloth so that they were flushed with the surface of the Teflon base. Two Luer lock ports were pressed fitted into the aluminum/Teflon cell body. A narrow piece of Teflon tubing was inserted through each septum to allow filling/replacement of the cell, without exposing the solution to air. Custom made Teflon spacers allow for pathlengths from 50 μm to more than 3 mm. The smallest cell volume (with a 50 μm spacer) was calculated to be 3 μL. A simple two mirror reflectance accessory, modified Nicolet FT-30 part, was used to direct the light at 30° angle to the polished working electrode. Reflected IR light was then directed to a liquid nitrogen cooled MCT detector of a Mattson Research Series 1 FTIR spectrophotometer [37].

IR-SEC measurements were carried out in a Bruker Equinox 55 spectrometer along with a Pine Biopotentiostat Model AFCBP1. The IR spectra were collect in 0.05 V potential steps in a range of -1.2 to 1.5 V. All the experiments were performed under dry N<sub>2</sub> atmosphere. AFM measurements were taken on a Veeco Multi-mode AFM with a Nanoscope IIIa controller, an EX-1 extender box, and software version 4.43r8, with the AFM cover on and the sample area flushed with nitrogen run through a 0.22 μm filter.

#### 2.4. Modified working electrode

Polymeric films were grown by cyclic voltammetry on GC electrode in a 1 mM solution of [NiTPyP{Ru(5-NO<sub>2</sub>-phen)<sub>2</sub>Cl<sub>2</sub>}]<sub>4</sub><sup>4+</sup> in DMF containing 0.1 M TEAClO<sub>4</sub> as supporting electrolyte, during 50 continuous cycles between -1.2 and 1.5 V vs. Ag/AgCl at a rate of 0.5 V s<sup>-1</sup>. After polymerization, the modified electrode was rinsed with DMF, ethanol and then with doubly distilled water. CH Instruments potentiostat 620B was used.

#### 2.5. Stability test of the modified electrode

The stability of modified GC electrode was verified in 0.1 M NaClO<sub>4</sub> solution, the potential of the electrode was swept during 100 continuous cycles between -0.8 and 1.2 V. A saturated Ag/AgCl reference electrode and a Pt wire counter electrode (14 cm<sup>2</sup>) were used. CH Instruments potentiostat 620B was used.

#### 2.6. Electrocatalytic reduction of NO<sub>2</sub><sup>-</sup>

Linear sweep voltammetry was used to compare intensity currents among modified electrode and several blanks, characterizing relevant electrodic processes. Solutions were prepared with 0.01 M NaNO<sub>2</sub>/0.1 M NaClO<sub>4</sub>. A saturated Ag/AgCl reference electrode and a Pt wire counter electrode (14 cm<sup>2</sup>) were used. Also a controlled potential electrolysis was performed to determine reaction products, a potential of -0.4 V was applied during 6 h. The reaction products obtained were hydroxylamine, hydrazine and ammonia and were analyzed according to procedures described in the literature [38–40]. CH Instruments potentiostat 620B was used.

Turn-over Frequency (TOF) is defined as the mole number of product formed divided by mole of catalyst, unit of time and the area of the electrode. This parameter indicates the real catalytic activity of the modified surface. TOF were determined to each products [41].

### 3. Results and discussion

#### 3.1. Electrochemistry

The compound studied is shown in Fig. 1. Electrochemical characterization of the macrocycle was studied in DMF solution by cyclic voltammetry in the potential range -1.2 to 1.5 V (see Fig. 2). Assignment was carried out by comparison with a voltammogram of a Ni(II) tetrapyrrolylporphyrin coordinated to Ru complexes without nitro group (see inset in Fig. 2) [36].

The Ni(II) tetraruthenated porphyrin with nitro groups exhibits a reversible redox couple around  $E_{1/2} = 1.00$  V vs. Ag/AgCl attributed to the Ru(III)/Ru(II) redox pair (peak A). At negative potentials two redox processes associated with the porphyrin ring are observed, at -0.64 V, assigned to porphyrin ring → π-radical anion (peak B), and at -0.90 V, assigned to the π-radical anion → porphyrin di-anion (peak C). However, the redox process at -0.64 V is broad and irreversible, and comparing this voltammetric behavior with the analogous complex (without the nitro group) it appears that this feature is influenced by the nitro group.

Indeed according to several reports, nitro groups undergo electrochemical reductions around -0.90 V in aprotic media a mono-electronic reversible redox process generating a radical anion [42,43]. In the case of the Ru(5-NO<sub>2</sub>-phen)<sub>2</sub>Cl<sub>2</sub> complex, the one electronic reversible redox process of nitro group occurs at -0.70 V, but when the Ru complexes are coordinated to the porphyrins, this process is irreversible and the reduction wave overlaps with the redox process of the ring porphyrin. Therefore, it

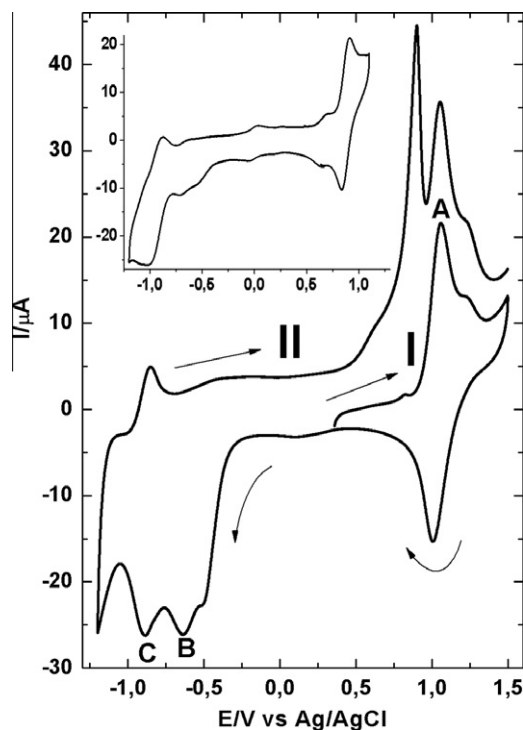


Fig. 2. Voltammetry of 1 mM [NiTPyP{Ru(5-NO<sub>2</sub>-phen)<sub>2</sub>Cl<sub>2</sub>}]<sub>4</sub><sup>4+</sup>. Inset: voltammetry of 1 mM [NiTPyP{Ru(phen)<sub>2</sub>Cl<sub>2</sub>}]<sub>4</sub><sup>4+</sup>. All experiments were performed in DMF with 0.1 M of TEAClO<sub>4</sub>, and a GC working electrode. I: first scan and II: second scan, 100 mV s<sup>-1</sup>.

may be suggested that the ring system of the porphyrin allows substantial delocalization of the electron gained in the reduction process, thereby stabilizing the formation of a different sort of porphyrin radical anion.

Finally, after the first scan, in the reverse sweep, at 0.90 V appears a narrow “pre-peak”. This pre-peak corresponds to a strongly absorbed product, derived from the tetra-ruthenated porphyrin reduction [44].

### 3.2. Preparation and characterization of the electropolymerized films

Fig. 3 shows the potentiodynamic growth performed of the polymer from  $[\text{NiTPyP}\{\text{Ru}(5\text{-NO}_2\text{-phen})_2\text{Cl}\}_4]^{4+}$ . The electropolymerizations were performed at two different scan rates: 0.1 and  $0.5 \text{ V s}^{-1}$ . Using  $0.1 \text{ V s}^{-1}$  the current did not grow at any significant value, but when the continuous cyclic voltammetry was carried out at  $0.5 \text{ V s}^{-1}$ , the current increased with the number of the cycles. This fact can be observed in the zone of the oxidation peak of the Ru(III)/Ru(II) couple. This feature needs more detailed description, the oxidation peak around 0.94 V it should correspond to the electropolymerized species adsorbed on the surface and the peak at 1.06 V it should correspond to complex not polymerized but included in the growing film process. This last species should be displayed a redox couple at values near to the value of the complex in solution (see Fig. 2) and is active while free glassy carbon surface is available. This point is discussed below in the AFM section in contrast, the current observed at potential values involving the nitro group and porphyrin redox processes ( $-0.64 \text{ V}$  and  $0.90 \text{ V}$ ) decreases its intensity, showing the expected behavior for the film growth [45]. The effective electropolymerization process at  $0.5 \text{ V s}^{-1}$  suggests that at this scan rate it is possible to trap the radical species, generating polymeric growth.

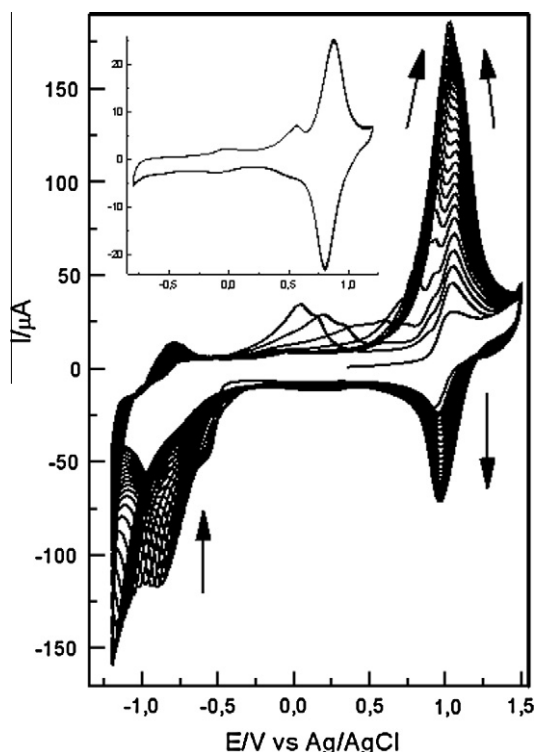


Fig. 3. Electropolymerization of  $1 \text{ mM } [\text{NiTPyP}\{\text{Ru}(5\text{-NO}_2\text{-phen})_2\text{Cl}\}_4]^{4+}$ , DMF,  $0.1 \text{ M TEAClO}_4$ , GC, from 0 to  $1.45 \text{ V}$  and then  $-1.20 \text{ V}$ , 50 cycles,  $500 \text{ mV s}^{-1}$ . Inset: Stabilization of modified GC in  $0.1 \text{ M NaClO}_4$ , 100 cycles, from  $-0.80 \text{ V}$  to  $1.20 \text{ V}$ ,  $100 \text{ mV s}^{-1}$ . Potentials are vs. Ag/AgCl.

There are three characteristics of the monomeric species that give us insight into the quality of the film that is taking shape: the relative reactivity of the radical produced in reaction, the steric effects, and the molecular location of the coupling [46]. The reactivity of the anionic radical nitro group, in the electrochemical time scale is likely the crucial step for the formation of a polymer. On the other hand, the poly-aromatic films exhibit good adherence to the electrode surfaces. They are highly insoluble, even in DMF. In consideration of these characteristics, the existence of a conductive polymer on the GC surface can be affirmed.

The electrochemistry of the reduction of nitro groups which has been described, where the nitro group is reduced to radical anion and then to radical di-anion and finally to hydroxylamine radical, thus this last species can react with other radical anions coupling to generate azo compounds [47,48]. On the other hand an electropolymerization process, according to the literature, takes place when a radical cation is formed [49]. Using the information described, it is possible to explain the behavior observed for MTRP, thus a radical cation should be formed after the oxidation (second scan, Fig. 2) of hydroxylamine radical species generated in the reduction of the nitro groups present in the macrocycle (first scan).

It is important to note that the ligand 5-NO<sub>2</sub>-phen itself does not generate a conducting film neither the moiety  $\text{Ru}(5\text{-NO}_2\text{-phen})_2\text{Cl}_2$ . We performed experiments replicating the conditions of electropolymerization of the Fig. 3. Results show no evidences of polymeric growing, these results are displayed in Figs. S1 and S2 (Supporting information).

Thus, it is possible to deduce that the nitro group, actually influence in the electropolymerization process of the macrocycle, but considering the high complexity of the molecule including great aromatic ring, from the macrocycle and the amount of nitro groups, it is not possible to suggest an electrochemical polymerization mechanism in this stage of the research.

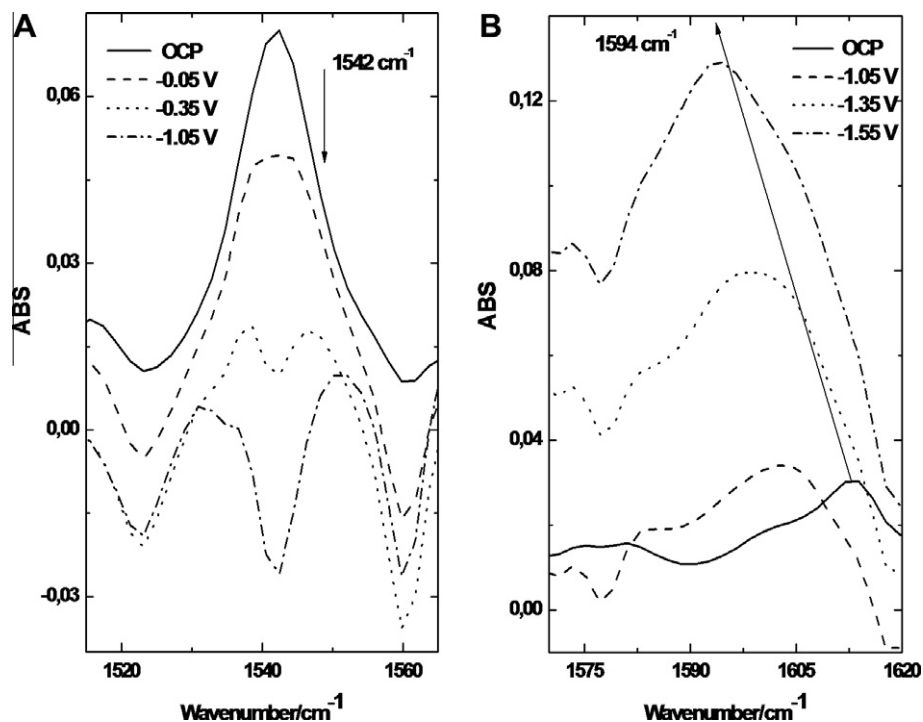
The inset in Fig. 3 shows continuous voltammetric profile of the polymeric film in aqueous solution. In this figure is possible to observe the Ru(III)/Ru(II) redox couple at  $0.90 \text{ V}$ , which does not exhibit a current decrease with the increasing number of voltammetric cycles (100 cycles), indeed the loss of charge in only a 6.3% from the original voltammogram. This is evidence of the film stability, demonstrating that the conductive film obtained under these conditions is an excellent candidate for use in electrocatalytic and electroanalytic reactions.

### 3.3. IR-SEC

The vibrational spectra of the Ni(II) tetra-ruthenated porphyrin were obtained by using reflectance IR spectroelectrochemistry. The vibrational normal modes characteristics of a nitro group in aromatic compounds are  $\nu_a(\text{NO}_2)$  and  $\nu_s(\text{NO}_2)$  in the  $1570\text{--}1500$  and  $1370\text{--}1300 \text{ cm}^{-1}$  regions respectively [50]. As explained in the previous section, the nitro group may be responsible for the film formation; therefore, we choose to observe the  $\nu_a$  band of this group to obtain more information about the electropolymerization process.

Fig. 4 presents the infrared spectroelectrochemical results of Ni(II) tetra-ruthenated porphyrin recorded at negative potentials, beginning at open circuit potential (OCP). At open circuit potential is possible to observe (see Fig. 4A) the  $\nu_a$  band of the nitro-aromatic compounds at  $1542 \text{ cm}^{-1}$ ; increasing the applied negative potential this band splits as consequence of a symmetry loss [50]. When  $-1.05 \text{ V}$  (vs. Ag wire pseudo-reference) was applied, the band was no longer present. This immediately suggests the loss of the nitro group.

In Fig. 4B can be seen the spectra recorded between OCP and  $-1.05 \text{ V}$  in the  $1560\text{--}1620 \text{ cm}^{-1}$  region. At OCP there is a band at  $1613 \text{ cm}^{-1}$ , corresponding to  $\nu(\text{C}=\text{C})_{\text{aromatic}}$ , but when  $-1.05 \text{ V}$



**Fig. 4.** Infrared spectroelectrochemistry of 1 mM NiTPyP[Ru(5-NO<sub>2</sub>-phen)<sub>2</sub>Cl]<sub>4</sub><sup>4+</sup>, CD<sub>3</sub>CN, 0.1 M TBAPF<sub>6</sub>, Pt electrode. (A) Region 1515–1565 cm<sup>-1</sup>, solid line (OCP), dash line (-0.05 V), dot line (-0.35 V) and dash dot (-1.05 V). (B) Region 1570–1630 cm<sup>-1</sup>, solid line (OCP), dash line (-1.05 V), dot line (-1.35 V) and dash dot (-1.55 V). All potentials are vs. a silver wire pseudo-reference.

are applied this band undergoes a bathochromic shift to 1603 cm<sup>-1</sup> and then this red shift increases with the application of more negative potentials. The bathochromic shift is interpreted as a consequence of an electronic delocalization in the aromatic structure of the porphyrin moiety due to the loss of an acceptor group, (nitro functional group). This fact originates a diminishing of the strength bonds in the aromatic ring C=C, showing the corresponding shift of that band to regions of lower frequency in the IR spectrum [51].

### 3.4. AFM

Contact mode AFM imaging is one of the most widely used imaging methodologies from thin films. Here, the conformations of tetra-ruthenated porphyrins deposited on an Au (1 1 1) substrate were investigated. Fig. 5 displays AFM images of surfaces modified with Ni(II) tetra-ruthenated porphyrin by drop-coating (Fig. 5A) and electropolymerization (Fig. 5B) methods respectively. In both images aggregates are visible on the gold surface. The rugosity suggests that the molecules are oriented in irregular way. Considering that the diameter of tetra-ruthenated porphyrins is approximately 2.2 nm [17], the volume of a one porphyrin unit (spheric geometry), is about 5.58 nm<sup>3</sup>. The drop coated sample shows conglomerates with 110 nm average diameter and 16.3 nm height as average (see Fig. 5A.3). Using this information it is possible to calculate the volume of one conglomerate as 41,372 nm<sup>3</sup>, then it can be estimated that the conglomerates correspond to groups of around 7414 porphyrin molecules. In the image of the surface modified by electropolymerization, well defined spheres are observed, with 300 nm average diameter and 34.3 nm average height. This corresponds to groups of 91,783 porphyrin molecules. The tip radius of curvature was not measured, and so cannot reliably be deconvolved from these observed conglomerate “widths”. Nonetheless the electropolymerized particles can reliably be described as much larger, in agreement with the polymerization observed in the electrochemistry (Fig. 2).

The Z axis magnitude of the images is perhaps of greater significance because it is less affected by factor such as tip variation. The scale (see inset Fig. 5.A.1 and 5.B.1) shows that the surface modified by conglomerates from electropolymerization are about 2.5 times bigger than those obtained by drop-coating. This suggests that through electropolymerization it is possible to obtain a more consistent film of three-dimensional growth, consistent with the morphologic studies of similar molecules [52,53].

From the charge under the voltammetric peak of Ru(III)/Ru(II) redox couple the surface excess was calculated [44]. Once normalized, the value observed was  $8.38 \times 10^{-24}$  mol/nm<sup>2</sup>. While the value extracted from AFM measurements is  $0.43 \times 10^{-24}$  mol/nm<sup>2</sup>. Both values are in the same order of magnitude, thus it can be considered in concordance. The difference observed between both methodologies can be explained in terms of porphyrins molecules incorporated in the polymeric framework that would be electrochemically active. This last result may explain the voltammogram observed in Fig. 3 where two redox processes attributed to Ru units presenting a very close oxidation potential are observed, one corresponding to the electropolymerized species and the other one corresponding to the incorporated Ru unit. Probably some of this not electropolymerized units of porphyrins are lixiviated to the aqueous solution after several voltammetric cycles, as was observed in the inset of Fig. 3.

### 3.5. Electrocatalytic reduction of NO<sub>2</sub><sup>-</sup>

The reduction of nitrite is of significant importance in remediation of environmental pollutants [54,55]. The water pollution with nitrites has dangerous consequences in human population, because this anion produces Methemoglobin (MetHgb) which is a toxic version of the hemoglobin, and provoke asphyxia symptoms and in severe cases, death [56]. For these reasons, the Ni(II) tetra-ruthenated porphyrin polymeric film was utilized in the electrochemical reduction of nitrite in aqueous medium (pH 6). The

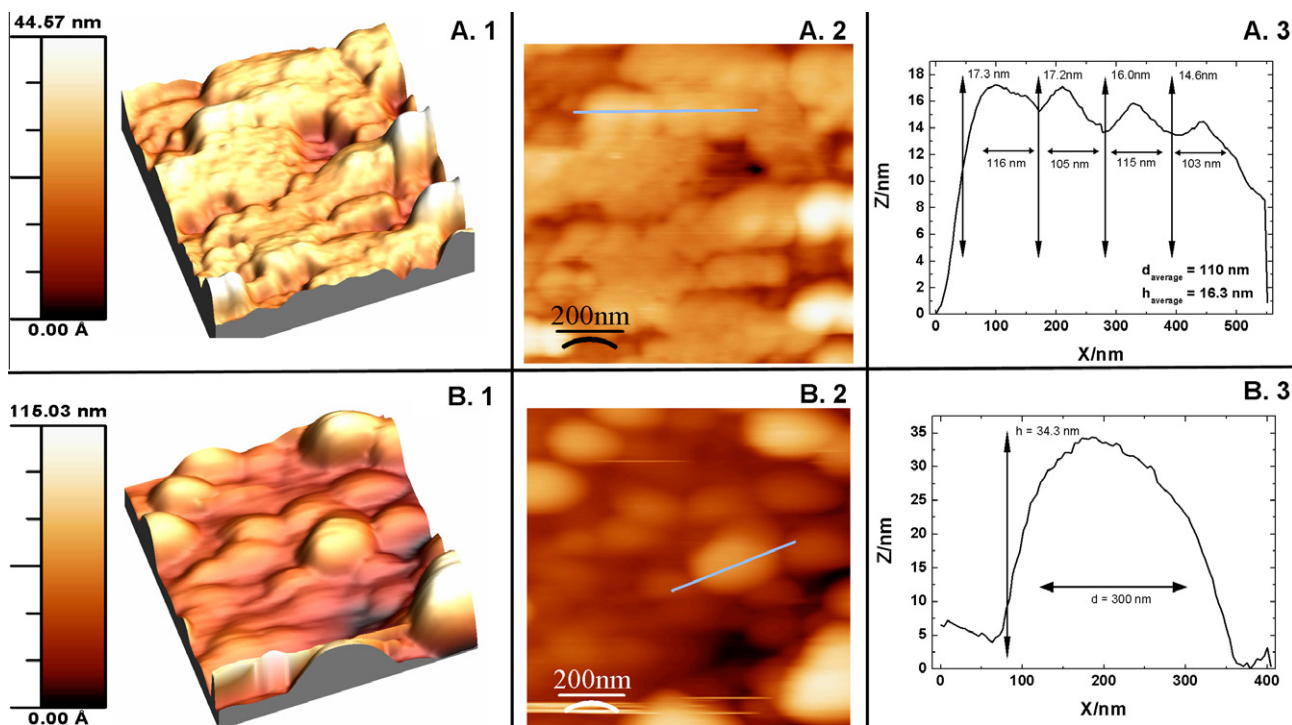


Fig. 5. AFM imagings of a flame annealed Au (111) surface modified by: (A) Drop-coating; one drop of 1 mM NiTPyP{Ru(5-NO<sub>2</sub>-phen)<sub>2</sub>Cl<sub>4</sub>}<sup>4+</sup>/DMF solution. (B) Electropolymerization; 1 mM NiTPyP{Ru(5-NO<sub>2</sub>-phen)<sub>2</sub>Cl<sub>4</sub>}<sup>4+</sup>, DMF, 0.1 M TBAPF<sub>6</sub>, from 0 to 1.45 V and then -1.20 V, 50 cycles, 500 mV s<sup>-1</sup>.

linear sweep voltammograms obtained with or without nitrite are shown in Fig. 6. The GC electrode (dot line) in presence of 0.01 M of nitrite does not have activity for the reduction of nitrite, but using the modified electrode with Ni(II) tetra-ruthenated porphyrin (solid line) a high activity for the electrocatalytic reduction of the analyte is observed in -0.3 V, where begin a current discharge, this current is effectively related with the reduction of nitrite because it is not observed when the experiment is carried out only in the support electrolyte 0.1 M NaClO<sub>4</sub> (dash line).

In order to test the catalytic activity of the polymeric film and evaluate the reaction products, controlled potential electrolysis was performed, the applied potential was -0.4 V and the time of electrolysis was 6 h. By spectrophotometric methods hydroxylamine, hydrazine and ammonium cation were detected, and the amount of product detected in the cell were: 5.38, 0.79 and

0.95 mM respectively and the turn-over frequency was NH<sub>2</sub>OH = 30.2 s<sup>-1</sup>, N<sub>2</sub>H<sub>4</sub> = 4.2 s<sup>-1</sup>, NH<sub>3</sub> = 7.1 s<sup>-1</sup>.

This last result is very significant because affirms that the catalyst of poly-Ni(II) tetra-ruthenated porphyrin is active towards multi-electronic transfers. These values can be considered relevant because were obtained in an electrolysis at -0.4 V, a potential very positive indicating the fine electrocatalytic character of the modified electrode, also we can deduce a selective character of the modified electrode since is clear the tendency to obtain a four electron reduction product such as hydroxylamine.

These facts provide us an interesting challenge to work at a selective catalysts design for reduction of nitrite to various compounds to provide industrially useful intermediates for the production of many chemicals.

#### 4. Conclusions

The redox processes of this new macromolecule are similar to those previously reported for the analogous meso-tetra(4-pyridyl)porphyrins coordinated to [Ru(phen)<sub>2</sub>Cl]<sup>+</sup> complexes [36], with the notable exception of the reduction associated with nitro group. Critically, this allow for facile reductive electropolymerization.

Continuous cyclic voltammetry showed increasing charge under the voltammetric signals with the number of scans. This pattern is compatible with an electropolymerization process, generating stable coverages in aqueous solution, and making the compound very interesting as a potential electrocatalyst in reductions of environmental contaminants or for sensor applications.

IR spectroelectrochemistry experiments following the intensity of the nitro group band, revealed the depletion of this band at negative potentials. Thus, it is possible to affirm that the electropolymerization process takes place when nitro substituents are reduced. The radical species are able to react at a scan rate 0.5 V s<sup>-1</sup>, promoting chain growth of the film at the electrode surface. Morphologic information acquired by AFM also showed a topography consistent with a polymeric film.

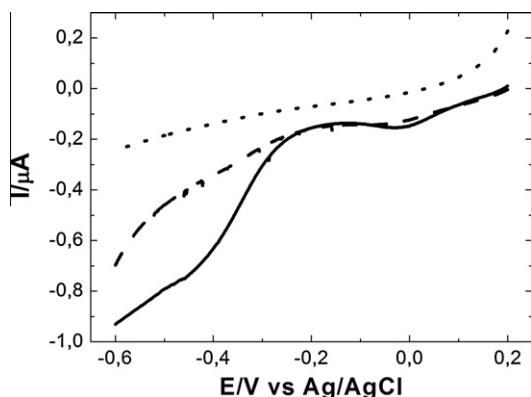


Fig. 6. Linear sweep voltammograms of bare glassy carbon electrode (dot line) in 0.01 M NaNO<sub>2</sub>/0.1 M NaClO<sub>4</sub>, modified electrode with poly-Ni(II) tetra-ruthenated porphyrin in 0.1 M NaClO<sub>4</sub> (dash line) and in 0.01 M NaNO<sub>2</sub>/0.1 M NaClO<sub>4</sub> (solid line). All experiment are vs. Ag/AgCl reference at 5 mV s<sup>-1</sup>.

Finally, the polymeric film is effective in the reduction of nitrite, providing an encouraging result for new catalysts design.

### Acknowledgments

The authors acknowledge: the financial support of Programa Bicentenario en Ciencia y Tecnología, CONICYT-Banco Mundial, Anillo ACT-24 Project, Fundación Andes C14060-40 Project and UTA-4741-10 Project. P.D. acknowledges CONICYT Doctoral and AT-24080067 Fellowships. P.D. acknowledges the financial support of MECESUP UCH 0601 international exchange program.

### Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jelechem.2010.08.007](https://doi.org/10.1016/j.jelechem.2010.08.007).

### References

- [1] C. Shi, F.C. Anson, *Inorg. Chem.* 31 (1992) 5078.
- [2] I. Mayer, H.E. Toma, K. Araki, *J. Electroanal. Chem.* 590 (2006) 111.
- [3] M.S.M. Quintino, K. Araki, H.E. Toma, L. Angnes, *Talanta* 68 (2006) 1281.
- [4] M.S.M. Quintino, H. Winnischofer, K. Araki, H.E. Toma, L. Angnes, *Analyst* 130 (2005) 221.
- [5] A. Prodi, M.T. Indelli, C.J. Kleverlaan, E. Alessio, F. Scandola, *Coord. Chem. Rev.* 229 (2002) 51.
- [6] M.R. Wasielewski, *Chem. Rev.* 92 (1992) 435.
- [7] K. Araki, C.A. Silva, H.E. Toma, L.H. Catalani, M.H.G. Medeiros, P. Di Mascio, *J. Inorg. Biochem.* 78 (2000) 269.
- [8] H. Winnischofer, A.L. Barboza Formiga, M. Nakamura, H.E. Toma, K. Araki, A.F. Nogueira, *Photochem. Photobiol. Sci.* 4 (2005) 359.
- [9] B.J. Lear, S.D. Glover, J.C. Salsman, C.H. Londergan, C.P. Kubiak, *J. Am. Chem. Soc.* 129 (2007) 12772.
- [10] C.H. Londergan, J.C. Salsman, S.R. Ronco, C.P. Kubiak, *Inorg. Chem.* 42 (2003) 926.
- [11] J.C. Salsman, C.P. Kubiak, *J. Am. Chem. Soc.* 127 (2005) 2382.
- [12] R.W. Callahan, F.R. Keene, T.J. Meyer, D.J. Salmon, *J. Am. Chem. Soc.* 99 (1977) 1064.
- [13] B. Steiger, C. Shi, F.C. Anson, *Inorg. Chem.* 32 (1993) 2107.
- [14] N. Rea, B. Looch, D. Lexa, *Inorg. Chim. Acta* 312 (2001) 53.
- [15] H.Z. Yu, J.S. Baskin, B. Steiger, F.C. Anson, A.H. Zewail, *J. Am. Chem. Soc.* 121 (1999) 484.
- [16] F.C. Anson, C. Shi, B. Steiger, *Acc. Chem. Res.* 30 (1997) 437.
- [17] H.E. Toma, K. Araki, *Coord. Chem. Rev.* 196 (2000) 307.
- [18] K. Araki, L. Angnes, C.M.N. Azevedo, H.E. Toma, *J. Electroanal. Chem.* 397 (1995) 205.
- [19] C.M.N. Azevedo, K. Araki, H.E. Toma, L. Angnes, *Anal. Chim. Acta* 387 (1999) 175.
- [20] P. Dreyse, G. Ramirez, A. Riquelme, M. Isaacs, *J. Chil. Chem. Soc.* 51 (2006) 923.
- [21] C. San Martín, P. Dreyse, C. García, K. Calfuman, D. Villagra, M. Isaacs, *J. Chil. Chem. Soc.* 52 (2007) 1305.
- [22] F. Armijo, M. Isaacs, G. Ramírez, E. Trollund, J. Canales, M.J. Aguirre, *J. Electroanal. Chem.* 566 (2004) 315.
- [23] M. Isaacs, J. Canales, M.J. Aguirre, G. Estiú, F. Caruso, G. Ferraudi, J. Costamagna, *Inorg. Chim. Acta* 339 (2002) 224.
- [24] M. Isaacs, F. Armijo, G. Ramírez, E. Trollund, S.R. Biaggio, J. Costamagna, M.J. Aguirre, *J. Mol. Catal. A: Chem.* 229 (2005) 249.
- [25] F. Fuenzalida, P. Dreyse, D. Villagra, B. Matsuhuro, L. Mendoza, M.J. Aguirre, M. Isaacs, *J. Coord. Chem.* 62 (2009) 130.
- [26] M.E. Vol'pin, G.N. Novodarova, E.M. Kolosova, N.V. Guzhova, A.A. Kononenko, Yu N. Lejkin, *Inorg. Chim. Acta* 50 (1981) 21.
- [27] S. Bodige, F.M. MacDonnell, *Tetrahedron Lett.* 38 (1997) 8159.
- [28] C. Janiak, S. Deblon, H.-P. Wu, M. Kolm, P. Klüfers, H. Piotrowski, P. Mayer, *Eur. J. Inorg. Chem.* (1999) 1507.
- [29] L.R. Dinelli, G. Von Poelhsitz, E.E. Castellano, J. Ellena, S.E. Galembeck, A.A. Batista, *Inorg. Chem.* 48 (2009) 4692.
- [30] L.J. Núñez-Vergara, P. Santander, P.A. Navarrete-Encina, J.A. Squella, *J. Electroanal. Chem.* 580 (2005) 135.
- [31] E. Amouyal, J.C. Chambron, A. Homsí, J.P. Sauvage, *J. Chem. Soc. Dalton Trans.* 6 (1990) 1841.
- [32] B.P. Sullivan, D.J. Salmon, T.J. Meyer, *Inorg. Chem.* 17 (1978) 3334.
- [33] P. Rothmund, A.R. Menotti, *J. Am. Chem. Soc.* 70 (1948) 1808.
- [34] E.B. Fleischer, *Inorg. Chem.* 1 (1962) 493.
- [35] A.H. Hoveyda, D.G. Gillingham, J.J. Van Veldhuizen, O. Kataoka, S.B. Garber, J.S. Kinsbury, J.P.A. Harrity, *Org. Biomol. Chem.* 2 (2004) 8.
- [36] K. Araki, A.L. Araújo, M. Toyama, M. Franco, C.M.N. Azevedo, L. Angnes, H.E. Toma, *J. Porphyrins Phthalocyanines* 2 (1998) 467.
- [37] I.S. Zavarine, C.P. Kubiak, *J. Electroanal. Chem.* 495 (2001) 106.
- [38] A. Afkhami, T. Madrakian, A. Maleki, *Anal. Sci.* 22 (2006) 329.
- [39] D.O. Caldiz, L. Lanfranconi, L.V. Fernández, M. Nasetta, *Revista latinoamericana de la Papa* 11 (1999) 164.
- [40] A.D. Eaton, L.S. Chesceri, E.W. Rice, A.E. Greenberg, *Standard Methods for the Examination of Water and Waste Water*, 20th ed., APHA, AWWA, WEF, Washington, 2002.
- [41] I. Taniguchi, N. Nakashima, K. Matsushita, K. Yasukouchi, *J. Electroanal. Chem.* 224 (1987) 199.
- [42] G. Kokkinidis, A. Kelaidopoulou, *J. Electroanal. Chem.* 414 (1996) 197.
- [43] S. Bollo, E. Soto-Bustamante, J.L. Nuñez-Vergara, J.A. Squella, *J. Electroanal. Chem.* 492 (2000) 54.
- [44] A.J. Bard, L.R. Faulkner, *Electrochemical Methods: Fundamentals and application*, second ed., John Wiley & Sons, Inc., New York, USA, 2001.
- [45] F.W.N. Nyasulu, H.A. Mottola, *J. Electroanal. Chem.* 239 (1988) 175.
- [46] J.M. Pingarrón, P. Sánchez, P. Química, *Electroanalítica: Fundamentos y Aplicaciones*, first ed., Editorial Síntesis, S.A. Madrid, España, 2003.
- [47] M. Vijay, B. Sahay, M. Gupta, I.K. Sharma, P.S. Verma, *Asian J. Exp. Sci.* 21 (2007) 377.
- [48] M. Vijay, G. Wadhvani, H. Agarwal, I.K. Sharma, P.S. Verma, *Asian J. Exp. Sci.* 21 (2007) 389.
- [49] *Electrochemistry of Conducting Polymers—Persistent Models and New Concepts* Jurgen Heinze, Bernardo A. Frontana-Urbe and Sabine Ludwigs. *Chem. Rev.* doi:10.1021/cr900226k.
- [50] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds, Part B: Applications in Coordination, Organometallic, and Bioinorganic Chemistry*, fifth ed., John Wiley & Sons, Inc., New York, USA, 1997.
- [51] C. Kvarnström, H. Neugebauer, A. Ivaska, *Infrared spectroelectrochemistry on conducting polymers and fullerenes*, in: H.S. Nalwa (Ed.), *Advanced Functional Molecules and Polymers*, vol. 2, Godon and Breach Sci. Publ., Tokyo, 2001, pp. 139–170 (Chapter 6).
- [52] D.M. Sarno, L.J. Matienzo, W.E. Jones, *Mater. Res. Soc. Proc.* 648 (2001) 1.
- [53] J. Hofkens, L. Latterini, P. Vanoppen, H. Faes, K. Jeuris, S. De Feyter, J. Kerimo, P.F. Barbara, F.C. De Schryver, A.E. Rowan, R.J.M. Nolte, *J. Phys. Chem. B* 101 (1997) 10588.
- [54] J.D. Genders, D. Hartsough, D.T. Hobbs, *J. Appl. Electrochem.* 26 (1996) 1.
- [55] D.H. Coleman, R.E. White, D.T. Hobbs, *J. Electrochem. Soc.* 142 (1995) 1152.
- [56] K. Imaizumi, I. Tyuma, K. Imai, H. Kosaka, Y. Ueda, *Int. Arch. Occup. Environ. Health* 45 (1980) 97.
- [57] K. Araki, H. Toma, *J. Coord. Chem.* 30 (1993) 9.
- [58] H. Winnischofer, S. de Souza Lima, K. Araki, H. Toma, *Anal. Chim. Acta* 480 (2003) 97.
- [59] I. Mayer, M. Nakamura, H.E. Toma, K. Araki, *Electrochim. Acta* 52 (2006) 263.
- [60] D. Marek, M. Narra, A. Schneider, S. Swavey, *Inorg. Chim. Acta* 359 (2006) 789.
- [61] X. Liu, J. Liu, K. Jin, X. Yang, Q. Peng, L. Sun, *Tetrahedron* 61 (2005) 5655.
- [62] H. Kon, K. Tsuge, T. Imamura, Y. Sasaki, N. Kitamura, *Inorg. Chem.* 45 (2006) 6875.
- [63] K. Araki, S. Dovidauskas, H. Winnischofer, A.D.P. Alexiou, H. Eisi Toma, *J. Electroanal. Chem.* 498 (2001) 152.