

A poly(pyrrole-Cobalt(II)deuteroporphyrin) electrode for the potentiometric determination of nitrite

Serge Cosnier^{1*}, Chantal Gondran¹, Rudolf Wessel¹, Franz-Peter Montforts² and Michael Wedel²

¹Laboratoire d'Electrochimie Organique et de Photochimie Rédox, UMR CNRS 5630, Institut de Chimie Moléculaire de Grenoble, FR CNRS 2607, Université Joseph Fourier, BP 53, 38041 Grenoble Cedex 9, France. Tel. 04 76 51 49 98, Fax 04 76 51 42 67

²Institut für Organische Chemie, FB 2 Biologie, Chemie der Universität Postfach 330 440, D-28334 Bremen, Germany

* Author to whom correspondence should be addressed (Serge.Cosnier@ujf-grenoble.fr)

Received: 8 April 2003 / Accepted: 11 June 2003 / Published: 27 July 2003

Abstract: The electrochemical properties of a new Co(II) deuteroporphyrin substituted by two electropolymerizable pyrrole groups has been investigated in organic solvent. This functionalization has allowed the preparation of the first example of a cobalt deuteroporphyrin film by oxidative electropolymerization. The resulting conducting polypyrrole film exhibits the regular electroactivity of cobalt deuteroporphyrin. Compared to conventional cobalt porphyrin electrochemistry, the replacement of porphyrin macrocycle by deuteroporphyrin ring results in markedly more negative potential values for the metal-centered oxidation and reduction processes. The influence of NO_2^- as axial ligand on the reductive behavior of the electropolymerized cobalt (II) deuteroporphyrin is examined. The recognition properties of the film illustrated by the potentiometric shift of the Co(II)/(I) reduction were exploited for the determination of NO_2^- in the concentration range $2 \cdot 10^{-6}$ - $2.5 \cdot 10^{-4}$ M.

Keywords: Deuteroporphyrin, Cobalt, Polypyrrole, Modified electrode, Nitrite..

Introduction

The ingenious concept to combine intimately the recognition properties of macromolecular biological molecules to the sensitivity of transducers has led to the emergence of biosensors as valuable sensitive and selective tools in analytical chemistry. For three decades, there is a growing interest in the design of biosensors aimed at detection in the fields of food and water quality control, health, safety and environmental monitoring, biosensors based on an electrochemical transduction constituting the main category. However, most of these analytical devices suffer from poor operational and storage stabilities due to the fragility of the protein structure. In particular, the activity of immobilized enzymes may be rapidly annihilated by inhibition processes or denaturation due to protein unfolding, high temperatures or harsh chemical conditions.

A very promising approach consists of replacing biological macromolecules, in particular enzymes by catalytic or redox complexes that mimic the structure and/or the activity of the prosthetic groups of enzymes on an electrode surface. These immobilized biomimetic compounds should be more stable than enzymes in aqueous or organic media, particularly in extreme environment. Furthermore, the immobilization of such model systems on electrode is an attractive way for understanding the mechanism of enzyme-catalysed transformations. Among the conventional compounds mimicking the enzyme activities, metalloporphyrinoids complexes play a main role [1,2]. These complexes that are involved in many vital biological processes, participate via an electrochemical cycle or /and a molecular recognition process. Their immobilization on an electrode surface are often based on an electropolymerization process [3-12]. Beside immobilized iron and manganese porphyrins, cobalt complexes were also been investigated due to their promising functions as catalysts or selective complexing centers via axial ligation reactions. The latter were, for instance, successfully exploited for the study of phenol interaction [13], oxygen or NO reduction [14,15] and the detection of organohalide pollutants or nitrite [16-18].

In that context, we describe here the electrochemical characterization of a novel cobalt deuteroporphyrin substituted by two pyrrole groups and its electropolymerization (Scheme1). In addition, the potential capabilities of the resulting metalloporphyrinoid polypyrrole films for the detection of nitrite were investigated.

Experimental part

Reagents

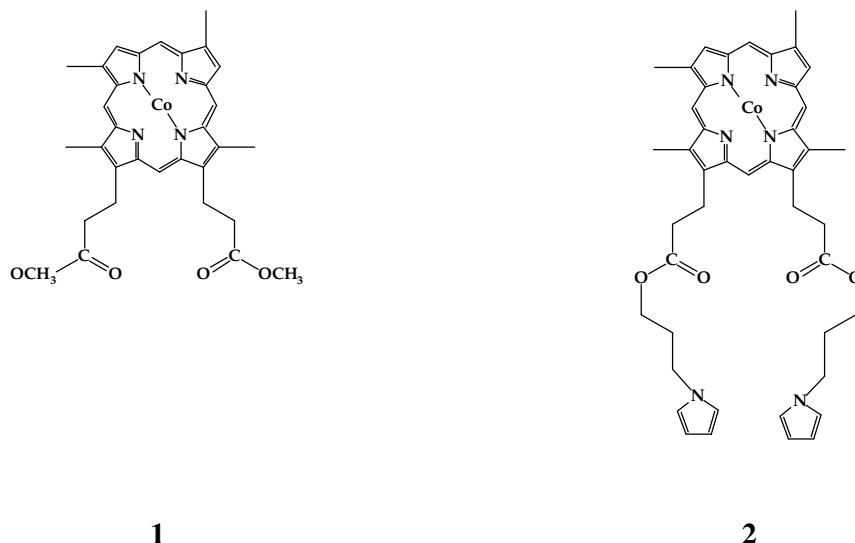
Acetonitrile (CH_3CN , Rathburn, HPLC grade) was used as received and stored under an argon atmosphere in a glove box. Tetra-*n*-butylammonium perchlorate (TBAP, Fluka) was recrystallised from ethyl acetate + cyclohexane and dried under vacuum at 80 °C for 3 days. The synthesis of **1** and **2** (scheme1) were described previously [19].

Apparatus

All electrochemical experiments were performed using a Princeton Applied Research model 173 (PAR 173) equipped with a model 179 digital coulometer and a model 175 universal programmer in conjunction with a Sefram TGM 164, X-Y/t recorder.

The electrochemical characterization of **1** and **2** in CH₃CN, the polymerization of **2** and the characterization of the resulting modified electrodes were run at room temperature under an argon atmosphere using a conventional three-electrode electrochemical cell. A Ag/10 mM Ag⁺ in CH₃CN + 0.1M TBAP electrolyte electrode was used as the reference.

The working electrodes were glassy carbon or platinum disks (diameter 3 or 5 mm). Both were systematically polished with 1 μm diamond paste (MECAPREX Press PM), cleaned with a Branson 1200 sonication apparatus and thoroughly washed successively with water, ethanol and acetone.



Scheme 1: structures of the cobalt deuteroporphyrinoids

Result and discussion

*Electroactivity of the complexes **1** and **2***

Among numerous cobalt porphyrins, most of the electrochemical studies in nonaqueous media were focused on cobalt based on the conventional complexing macrocycle tetraphenylporphyrin (CoTPP). The latter were dominated by metal-centered reactions, the most common of which involved Co(II)/Co(III) and Co(II)/Co(I) transitions that were influenced by the nature of the macrocycle.

With a view of mimicking biological processes, the remarkably similarity of deuteroporphyrin dimethylester with the active site of a variety of vitally important enzyme systems were exploited to

synthesize two new cobalt (II) deuteroporphyrin (**1**) and cobalt (II) deuteroporphyrin substituted by two pyrrole groups (**2**) following a previously reported procedure [19]. The electrochemical behavior of **1** and **2** was investigated by cyclic voltammetry at a glassy carbon electrode. Fig. 1 shows the cyclic voltammograms of **1** in $\text{CH}_3\text{CN} + 0.1 \text{ M TBAP}$. Upon reductive scanning, **1** exhibits two successive reversible peak systems at $E_{1/2} = -1.30\text{V}$ ($\Delta E_{\text{peak}} = 70\text{mV}$) and $E_{1/2} = -1.88\text{V}$ ($\Delta E_{\text{peak}} = 80\text{mV}$). As previously reported for other cobalt(II) porphyrin, the first system at -1.30V is assigned to the one-electron reduction of metal center leading to the Co(I) formation [2]. By analogy with the electrochemical behavior of tetraphenylporphyrinato cobalt(II) complexes the second redox system was attributed to the one-electron reduction of the macrocycle (deuteroporphyrin) into its radical anion ($D_p / D_p^{\bullet-}$) [20]. Rotating disk experiments indicated identical values for the current recorded at the first and second reduction process corroborating thus the monoelectronic character of the second reduction. The comparison with the electrochemical behavior of conventional cobalt(II) porphyrin indicates a slight negative shift of the Co(II)/Co(I) couple, namely -1.3 V instead of $-1.1\text{--}1.15 \text{ V}$ [2,4]. Upon oxidative scanning, **1** exhibits three successive reversible peak systems at $E_{1/2} = -0.04\text{V}$ ($\Delta E_{\text{peak}} = 80\text{mV}$), $E_{1/2} = +0.62\text{V}$ ($\Delta E_{\text{peak}} = 100\text{mV}$) and $E_{1/2} = +0.94\text{V}$ ($\Delta E_{\text{peak}} = 110\text{mV}$). The first oxidation of the cobalt deuteroporphyrin may be attributed to the oxidation of the metal center. In order to corroborate this assumption, controlled potential electrolysis was carried out at 0.3 V . The comparison of the UV-visible spectra of the cobalt complex recorded before and after the complete electrolysis shows the disappearance of the Soret band ($\lambda = 390 \text{ nm}$) while another band appears at $\lambda = 416 \text{ nm}$. As previously described for cobalt complexes, this red shift confirms that the one-electron oxidation occurs at the metal center [20-22]. It should be noted that the Co(II)/Co(III) transition occurs at a markedly less positive potential value than the half-wave potential values commonly observed for the generation of Co(III) porphyrins. Moreover, the Co(II)/Co(III) redox couple constitutes, in general, a slow process characterized by a large peak separation, namely $E_{\text{pa}}-E_{\text{pc}} = 140\text{--}200 \text{ mV}$ [21,23]. In contrast, this electron transfer kinetic appears remarkably faster for the cobalt deuteroporphyrin, the cyclic voltammogram displaying a peak separation of only 80 mV . These changes in the electrochemical behavior illustrate the influence of the deuteroporphyrin on the metal-centered reactions. Similarly to the electrochemical behavior of other cobalt porphyrins, the further two peak systems may be attributed successively to the first oxidation of deuteroporphyrin ring ($D_p / D_p^{\bullet+}$) followed by the second one-electron oxidation of deuteroporphyrin ring ($D_p^{\bullet+} / D_p^{2+}$) [2]. The cyclic voltammogram of **2** displays upon reductive scanning, two reversible systems identical to those already recorded for **1**. This indicates that the introduction of two pyrrole groups on the deuteroporphyrin ring does not affect the reductive electrochemical behavior of the cobalt complex.

Upon oxidative scanning (dashed line in Fig.1), after the reversible system assigned to the oxidation of metal center, an irreversible anodic peak appears at 0.8 V . It should be noted that the ratio of the peak intensities due to this irreversible oxidation and to the first one-electron reduction of the cobalt deuteroporphyrin, namely 7, is in good agreement with the theoretical value of 2.33 electrons per pyrrole group for their oxidation combined with 1 electron for the formation of the deuteroporphyrin cation radical. This behavior clearly indicates the catalytic oxidation of the two pyrrole groups via the electrogeneration of Co(III) $D_p^{\bullet+}$ since N-alkylpyrroles are oxidized around 1.0V [8,24].

*Electropolymerization of **2** and redox behavior of the resulting poly(pyrrole-cobalt(II) deuteroporphyrin)*

Electropolymerization properties of **2** were examined by cyclic voltammetry. Repeatedly scanning the potential over the range 0.0 V to 1.0 V, induces the continuous growth of the peak systems of the monomer. This unambiguously indicates the formation of an electrogenerated polymeric film on the electrode surface. Electropolymerization of **2** was also successfully carried out by controlled-potential oxidation at 0.8 - 1.0 V. Fig. 2 shows the cyclic voltammogram exhibited by a poly **2** electrode obtained by controlled potential electrolysis (1 mC) upon transfer into a $\text{CH}_3\text{CN} + 0.1 \text{ M}$ TBAP solution free of monomer.

Upon oxidative scanning, two redox systems are observed at $E_{1/2} = 0.07\text{V}$ ($\Delta E_{\text{peak}} = 70\text{mV}$) and $E_{1/2} = 0.65\text{V}$ ($\Delta E_{\text{peak}} = 30\text{mV}$). The similarity of these potential values with those obtained for the positive electrochemical behavior of **1** allows to ascribe these redox couples to the successive one-electron oxidation of the metal center (Co(II) / Co(III)) and the deuteroporphyrin ring (Dp / Dp^{•+}). Upon reductive scanning, only one redox system appears at $E_{1/2} = -1.32\text{V}$ ($\Delta E_{\text{peak}} = 20\text{mV}$)

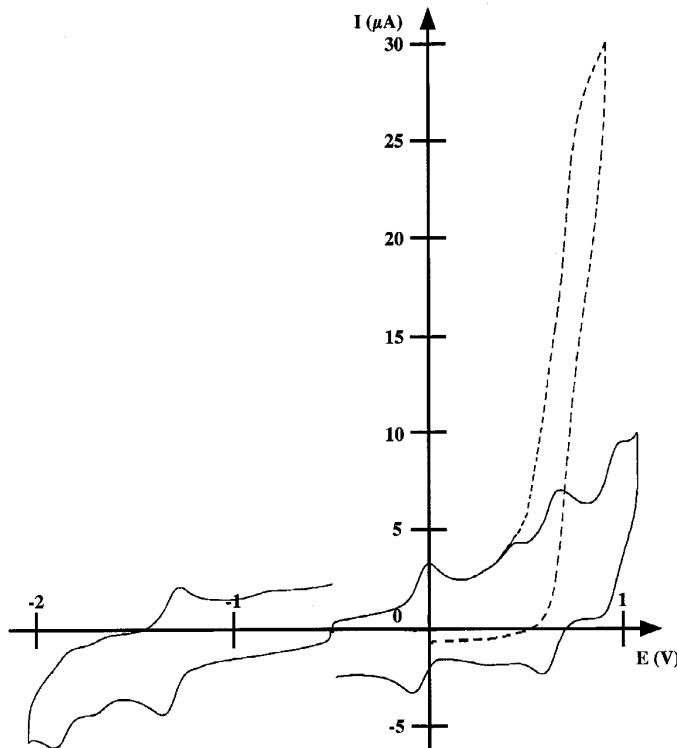


Figure 1: Cyclic voltammograms for **1** (full line) and **2** (dashed line) 0.15mM in $\text{CH}_3\text{CN} + 0.1 \text{ M}$ TBAP recorded at a carbon electrode. Scan rate: 100 mVs^{-1} .

corresponding to the reversible one-electron reduction of metal center Co(II) into Co(I). The current efficiency of the electropolymerization process was determined by dividing the charge recorded under the oxidation wave of Co (III) /Co (II) system of polymerized **2** ($19 \mu\text{C}$) by the charge passed during

the controlled potential electrolysis ($1 \mu\text{C}$) and multiplying by 6.66. Indeed, the electropolymerization process requires 2.33 electrons per pyrrole group plus 2 electrons for the oxidation of **2** into the radical cation form). The resulting electric yield, 12.6 %, is similar to those (1.5 - 6.1 %) previously reported for elaboration of polypyrrolic films functionalized by metallotetraphenylporphyrins [4, 25] or hydroporphyrin of Ni(II) [11].

*Capabilities of the poly **2** electrode as sensor for nitrite ions*

Nitrate and nitrite are widely used as preservative and fertilization agents. A continuous exposition to these pollutants, however, can induce severe health implications. Nitrites, in particular, can react irreversibly with hemoglobin reducing thus blood ability for oxygen transport. Beside the conventional procedures of nitrite determination, an attractive approach consists to investigate the molecular

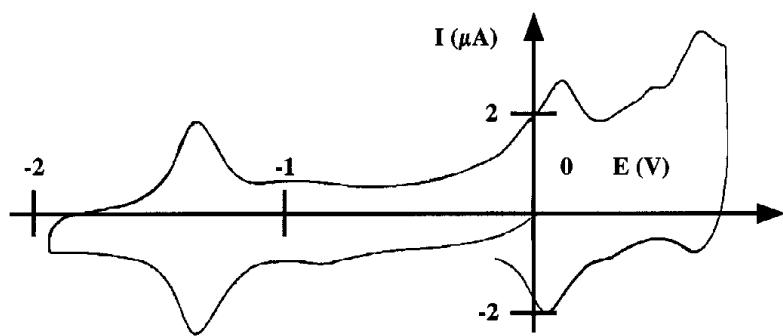
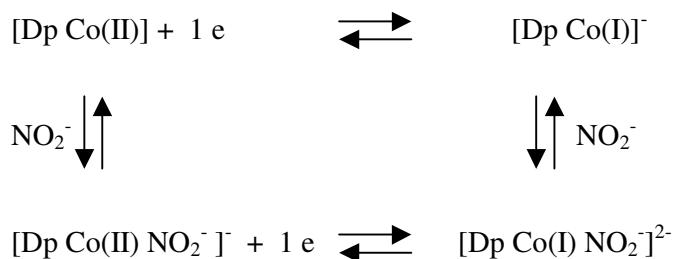


Figure 2: Cyclic voltammogram of a carbon electrode coated by a poly **2** film (1 nmolcm^{-2}) in $\text{CH}_3\text{CN} + 0.1 \text{ M TBAP}$. Scan rate: 20 mVs^{-1} .

recognition properties of cobalt complexes and to exploit their potentiometric response to nitrite or their electrocatalytic properties towards the oxidation or reduction of nitrite[18,23,26,27]. Consequently, the potential selective recognition properties of the electropolymerized cobalt deuteroporphyrin for the nitrite ions via axial ligation were examined by cyclic voltammetry in the negative region. The redox system Co(II) / (I) was indeed chosen since, generally, Co (II) porphyrins exist as five coordinate complex while Co (I) porphyrins have no axial-ligand coordination [22,28]. Fig. 3 shows the cyclic voltammograms exhibited by the poly **2** electrode upon transfer into $\text{CH}_3\text{CN} + 0.1 \text{ M TBAP}$ solution in the absence and presence of nitrite. In the absence of nitrite, the reversible one-electron reduction of metal center Co(II) into Co(I) is recorded at $E_{1/2} = -1.32\text{V}$. In the presence of nitrite ($2.9 \mu\text{M}$), the potential of this reduction is negatively shifted while no change in the initial electrochemical behavior appears on the reverse scan. It should be noted that this negative shift increases with the increase in nitrite concentration (Fig. 3). As expected, the coordination of nitrite on the Co(II) deuteroporphyrin occurs affecting thus the electrochemical response of the modified electrode. The unchanged electrochemical re-oxidation of Co(I) into Co(II) indicates that the previous step was followed by a chemical step corresponding to the release of nitrite as coordinating axial ligand.

The two possible reductive pathways for the electron-transfer at the cobalt(II) deuteroporphyrin involving four and five-coordinate species are summarized in Scheme 2.



Scheme 2: Possible one-electron transfer pathways for the reduction of the electropolymerized cobalt(II) deuteroporphyrin.

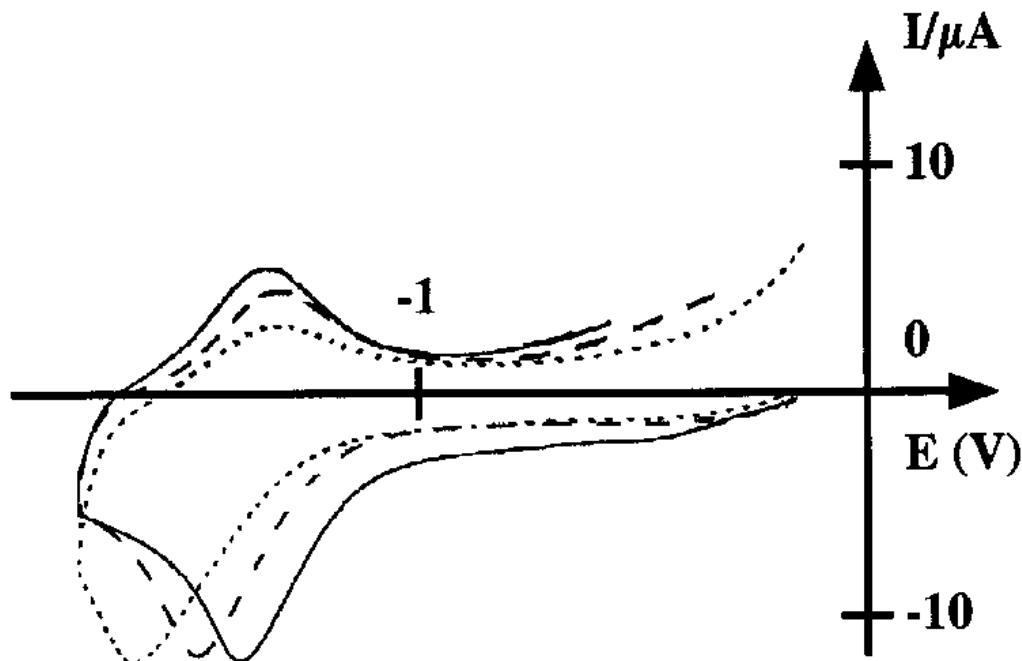


Figure 3: Cyclic voltammogram for poly **2**, $\Gamma = 4.9 \text{ nmolcm}^2$, in $\text{CH}_3\text{CN} + 0.1 \text{ M TBAP}$. Scan rate: 20 mVs^{-1} .

The potentiometric detection of nitrite was therefore examined by recording the shift of the reduction potential of $[\text{Dp Co(II)} \text{NO}_2^-]^-$ as a function of nitrite concentration. Fig.4 shows the evolution of the electrochemical response of the polymer film according to the logarithm of nitrite concentration.

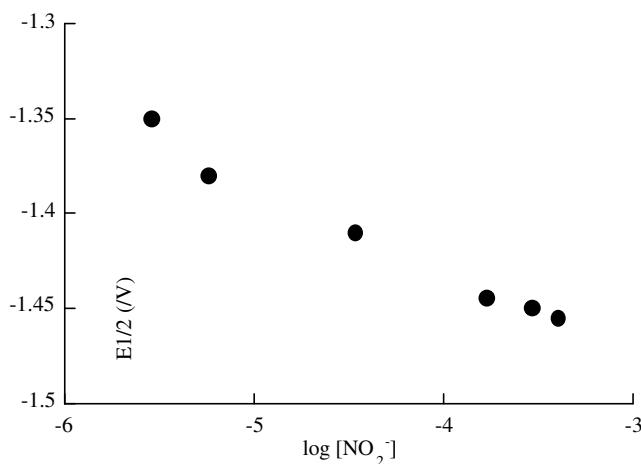


Figure 4: Effect of the nitrite concentration on the reduction potential value of the Co (II) / Co (I) transition

The resulting calibration curve exhibits a linear potential variation for nitrite concentrations ranging from 2 to 250 μM . It should be noted that the electrochemical reduction of the metallodeuteroporphyrin allows to renew the initial polymerized Co(II) form without coordinated ligand and hence to regenerate the sensing capabilities of the polymer film.

Conclusion

We have characterized and successfully electropolymerized a new cobalt(II) deuteroporphyrin derivative offering the possibility to coordinate reversibly nitrite ions. Furthermore, preliminary experiments have clearly shown that the nitrite-induced modification of the electrochemical behavior of the redox polymer may be exploited for the monitoring of this pollutant.

It is expected that this approach based on electropolymerized polymer films will be a convenient way for the elaboration of electrochemical biomimetic sensors.

Acknowledgment

This work was in part financially supported by the COST D15 program of the European Community.

References

1. Biegsga, M.; Pyrzynska, K.; Trojanowicz, M. Porphyrins in analytical chemistry. A review. *Talanta* **2000**, 51, 209-224.
2. Kadish, K. M.; Van Caemelbecke, E.; Royal, G. In *The porphyrin Handbook*; Kadish, K. M.; Smith, K. M.; Guilard, R. Eds; Academic Press; San Diego, 2000; Vol. 8, Chapter 55, p 1.

3. Younathan, J. N.; Wood, K. S.; Meyer, T. J. Electrocatalytic Reduction of Nitrite and Nitrosyl by Iron(III) Protoporphyrin XI Dimethyl Ester Immobilized in Electropolymerized Film. *Inorg. Chem.* **1992**, 31, 3280-3285.
4. Deronzier, A.; Devaux, R.; Limosin, D.; Latour, M. Poly(pyrrole-metallotetraphenylporphyrin)-modified electrodes. *J. Electroanal. Chem.*, **1992**, 324, 325-337.
5. Bediouï, F.; Devynck, J.; Bied-Charreton, C. Immobilization of Metalloporphyrins in Electropolymerized Films: Design and Applications. *Acc. Chem. Res.* **1995**, 28, 30-36.
6. Carvalho de Medeiros, A. M.; Cosnier, S.; Deronzier, A.; Moutet, J.-C. Synthesis and Characterization of a New Series of Nickel(II) *meso*-Tetrakis(polyfluorophenyl)porphyrins Functionalized by Pyrrole Groups and Their Electropolymerized Films. *Inorg. Chem.* **1996**, 35, 2659-2664.
7. Cosnier, S.; Walter, A.; Montforts, F.-P. A Poly(pyrrole-copper(II) deuteroporphyrin) Modified Electrode. *J. Porphyrins and Phthalocyanines* **1998**, 2, 39-43.
8. Cosnier, S.; Gondran, C.; Wessel, R.; Montforts, F.-P.; Wedel, M. Poly(pyrrole-metallodeuteroporphyrin)electrodes: towards electrochemical biomimetic devices. *J. Electroanal. Chem.* **2000**, 488, 83-91.
9. Diab, N.; Schuhmann, W. Electropolymerized manganese porphyrin/polypyrrole films as catalytic surfaces for oxidation of nitric oxide. *Electrochim. Acta* **2001**, 47, 265-273.
10. Griveau, S.; Bediouï, F. Electrocatalytic Oxidation of 2-Mercaptoethanol by Electropolymerized Cobalt Porphyrin Film on Vitreous Carbon Electrodes. *Electroanalysis* **2001**, 13, 253-256.
11. Cosnier, S.; Gondran, C.; Gorgy, K.; Wessel, R.; Montforts, F.-P.; Wedel, M. Electrogeneration and characterization of poly(pyrrole-nickel(II)chlorine)electrode. *Electrochim. Com.* **2002**, 4, 426-430.
12. Chen, G. N.; Zhao, Z. F.; Wang, X. L.; Duan, J. P.; Chen, H.Q. Electrochemical behavior of tryptophan and its derivatives at a glassy carbon electrode modified with hemin. *Anal. Chim. Acta* **2002**, 452, 245-254.
13. Campo Dall'Orto, V.; Danilowicz, C.; Hurst, J.; Lo Balbo, A.; Rezzano, I. Studies of the Interaction Between Metalloporphyrin Films and Phenols in a Preconcentration Type Sensor. *Electroanalysis* **1998**, 10, 127-131.
14. Okada, T.; Gokita, M.; Yuasa, M.; Sekine, I. Oxygen Reduction Characteristics of Heat Treated Catalysts Based on Cobalt Porphyrin Ion Complexes. *J. Electrochem. Soc.* **1998**, 45, 815-822.
15. Cheng, S.-H.; Su, Y. O. Electrocatalysis of Nitric Oxide Reduction by Water-Soluble Cobalt Porphyrin. Spectral and Electrochemical Studies. *Inorg. Chem.* **1994**, 33, 5847-5854.
16. Dobson, D. J.; Saini, S. Porphyrin-Modified Electrodes as Biomimetic Sensors of the Determination of Organohalide Pollutants in Aqueous Samples. *Anal. Chem.* **1997**, 69, 3532-3538.
17. Vilchez-Aguado, F.; Gutierrez-Granados, S.; Sucar-Succar, S.; Bied-Charreton, C.; Bediouï, F. Electrocatalysis of the reduction of trichloroacetic acid by polypyrrole-cobalt porphyrin modified electrodes. *New J. Chem.* **1997**, 21, 1009-1013.

18. Malinowska, E.; Meyerhoff, M. E. Role of axial ligation on potentiometric response of Co(III) tetraphenylporphyrin-doped polymeric membranes to nitrite ions. *Anal. Chim. Acta* **1995**, *300*, 33-43.
19. Wedel, M.; Walter, A.; Montforts, F.-P. Synthesis of Metalloporphyrins and Metallochlorins for Immobilization on Electrode Surfaces. *Eur. J. Org. Chem.* **2001**, 1681-1687.
20. D'Souza, F.; Villard, A.; Van Caemelbecke, E.; Franzen, M.; Boschi, T.; Tagliatesta, P.; Kadish, K. M. Electrochemical and Spectrochemical Behaviour of Cobalt(III), Cobalt(II), and Cobalt(I) Complexes of *meso*-Tetraphenylporphyrinate Bearing Bromides on the •-Pyrrole Positions. *Inorg. Chem.* **1993**, *32*, 4042-4048.
21. Zheng, G. D.; Yan, Y.; Gao, S.; Tong, S. L.; Gao, D.; Zhen, K. J. The reactive Mechanism of alkyl halides with carbon dioxide catalyzed by 5,10,15,20,-Tetraphenyl porphyrin cobalt (CoTPP). *Electrochim. Acta* **1996**, *41*, 177-182.
22. Araullo-McAdams, C.; Kadish, K. M. Electrochemistry, Spectroscopy, and Reactivity of (meso-Tetrakis(1-methylpyridinium-4-yl)porphyrinato)cobalt(III,II,I) in Nonaqueous Media. *Inorg. Chem.* **1990**, *29*, 2749-2757.
23. Araki, K.; Angnes, L.; Azevedo, C. M. N.; Toma, H. E. Electrochemistry of tetraruthenated cobalt porphyrin and its use in modified electrodes as sensors of reducing analytes. *J. Electroanal. Chem.* **1995**, *397*, 205-210.
24. Deronzier, A.; Moutet, J.-C. Polypyrrole films containing metal complexes: syntheses and applications. *Coord. Chem. Rev.* **1996**, *147*, 339-371.
25. Cauquis, G.; Cosnier, S.; Deronzier, A.; Galland, B.; Limosin, D.; Moutet, J.-C.; Bizot, J.; Deprez D.; Pulicani, J.-P. Poly(pyrrole-manganese porphyrin): a catalytic electrode material as a model system for olefin epoxidation and drug metabolism with molecular oxygen. *J. Electroanal. Chem.*, **1993**, *352*, 181-195.
26. Thamae M.; Nyokong T. Cobalt(II) porphyrzin catalysed reduction of nitrite. *J. Electroanal. Chem.* **1999**, *470*, 126-135.
27. Malinowska, E.; Niedziolka, J.; Meyerhoff, M. E. Potentiometric and spectroscopic characterization of anion selective electrodes based on metal(III) porphyrin ionophores in polyurethane membranes. *Anal. Chim. Acta* **2001**, *432*, 67-78.
28. Ann Walker F.; Beroiz, D.; Kadish K. M. Electronic Effects in Transition Metal Porphyrins. 2. The Sensitivity of Redox and Ligand Addition Reactions in Para-Substituted Tetraphenylporphyrin Complexes of Cobalt(II). *J. of Am. Chem. Soc.* **1976**, *98*, 3484-3489.

Sample Availability: Available from the authors.