Immobilization of Metalloporphyrins in Electropolymerized Films: Design and Applications

FETHI BEDIOUI* AND JACQUES DEVYNCK

Laboratoire d'Electrochimie et de Chimie Analytique (URA 216 du CNRS),
Ecole Nationale Supérieure de Chimie de Paris, 11 rue Pierre et Marie Curie, 75231 Paris, Cedex 05, France

CLAUDE BIED-CHARRETON

Laboratoire de Photochimie et Photophysique des Matériaux Moléculaires et Macromoléculaires
(Equipe de l'ENS-Cachan de l'URA 75 du CNRS), Département de Chimie,
Ecole Normale Supérieure de Cachan, 61 avenue du Président Wilson, 94235 Cachan, France

Received May 16, 1994

Molecular engineering and design of new controlled spatial assemblies and architectures is a field undergoing rapid growth.[1] A large variety of disciplines, especially bioinorganic chemistry, are now taking profit from the design of molecular systems. Indeed, bioinorganic structural motifs can potentially model metalloenzyme structures and functions. The aim of such modeling is to mimic natural properties in order to elucidate fundamental aspects of reactivity and mechanism.

The desire to mimic enzymatic systems has led to an active area of research involving synthetic porphyrin models of enzyme active sites, especially for monooxygenase enzymes of the cytochrome P-450.[2-4] An analysis of comparative studies dealing with the selectivity, efficiency, and stability for both synthetic porphyrin models and natural systems has shown that efficiency arises from the control of the environment of the enzyme active site.[4-7] Thus, in a first approach, the design of synthetic supramolecular architecture for porphyrin models with an elaborated steric environment (such as picnic basket porphyrins, strapped porphyrins, etc.) has been the subject of intense effort.[8] A similar approach in concept that has been advanced during the last decade involves replacing of the protein envelope of natural enzymes by a mineral or organic polymeric matrix.[9-18] This strategy is based on the fact that a polymeric matrix may provide the best arrangement for a catalytically active center as well as preventing autodestruction of the enzyme model

during catalysis. Additionally, the intrinsic diversity and selectivity of axial ligation of the porphyrinic macrocycles confer to this strategy a wide field of applications in analytical chemistry.

An especially fruitful strategy for modeling the enzymatic systems has been the use of polymeric porphyrins as molecular devices combined with electrochemistry. Therefore, the electroassisted design of modified electrode surfaces by organized porphyrinic structures has been the subject of an intense effort. In fact, one of the challenges in developing this concept is the necessity to achieve rapid electron transfer to the enzyme model active site at the electrode surface.[19-23] Conducting polymers such as polypyrrole, polythiophene, or polyaniline are attractive as possible materials for this approach.[19-22,24-27] Meanwhile, the

Fethi Bedioui (born on August 28, 1957, in Tunis, Tunisia) is Directeur de Recherche, CNRS, and works at the Ecole Nationale Supérieure de Chimie de Paris, Paris, France. He received a D.Sc. degree (under Professor B. Trémillon) in 1986 from the University of Pierre et Marie Curie in Paris. His current research interests are new molecular materials as polymer-based and zeolite and clay-encapsulated metal complexes with a particular emphasis on their application in electrochemistry and electrocatalysis.

Jacques Devynck (born on October 9, 1941, in Lille, France) is Directeur de Recherche, CNRS, and works at the Ecole Nationale Supérieure de Chimie de Paris, Paris, France. He received a D.Sc. degree (under Professor B. Trémillon) in 1971 from the University of Pierre et Marie Curie in Paris. His current research interests are molecular materials for electrochemistry and electrocatalysis and supported catalysts for methane activation in molten carbonate salts. He is now chairman of the Laboratoire d'Electrochimie et de Chimie Analytique URA 216, CNRS.

Claude Bied-Charreton (born on June 17, 1942, in Algiers, Algeria) is Directeur de Recherche, CNRS, and works at the Ecole Normale Supérieure, Cachan, France. She received a D.Sc. degree (under Professor A. Gaudemer) in 1975 from the University of Paris XI. She was a CNRS Postdoctoral Fellow at the Department of Chemistry, University of Central Florida, with Professor J. P. Idoux (1976–1977). Her research interests are porphyrin chemistry, macromolecular design, and elaboration of new materials with a particular emphasis on their application as photoactivators and chemical sensors.

(1) Bein, T., Ed. *Supramolecular Architecture*; American Chemical Society: Washington, DC, 1992.
(2) Morgan, B.; Dolphin, D. *Struct. Bonding* **1985,** *64,* 115.
(3) Momenteau, M. *Actual. Chim.* **1989,** *6,* 95.
(4) Mansuy, D., Battioni, P. In *Bioorganic Catalysis*: Reedijk, J., Ed.; Marcel Dekker: New York, 1993; p 395.
(5) Shilov, A. E. *J. Mol. Catal.* **1988,** *47,* 351.
(6) Cook, B. R.; Reinert, T. J.; Suslick, K. S. *J. Am. Chem. Soc.* **1986,** *108,* 7281.
(7) Suslick, K.; Cook; Fox, M. *J. Chem. Soc. Chem. Commun.* **1980,** 580.
(8) Collman, J. P.; Zhang, X.; Lee, V. J. Uffelman, U. S.; Brauman, J. I. *Science* **1993,** *261,* 1404, and references cited therein.
(9) Herron, N. *J. Coord. Chem.* **1988,** *19,* 25.
(10) Herron, N. *Chemtech* **1989,** 542.
(11) Mitchell, P. C. H. *Chem. Ind.* **1991,** 308.
(12) Mansuy, D. *Coord. Chem. Rev.* **1993,** *125,* 129.
(13) Karlin, K. D. *Science* **1993,** *261,* 701.
(14) Parton, R.; De Vos, D.; Jacobs, P. A. In *Zeolite Microporous Solids: Synthesis, Structure, and Reactivity*; Derouane, E. G., Ed.; Kluwer Academic Publishers: Amsterdam, 1992; p 555.
(15) Bedioui, F. *Coord. Chem. Rev.,* in press.
(16) Kojima, T.; Urata, Y.; Yonekura, H. *J. Polym. Sci., Part C, Polym. Lett.* **1990,** *28,* 129.
(17) Traylor, T. G.; Byun, Y. S.; Traylor, P. S.; Battioni, P.; Mansuy, D. *J. Am. Chem. Soc.* **1991,** *113,* 7821.
(18) Soloviera, A. B.; Lukashova, E. A.; Vorobiev, A. V.; Timashev, S. F. *React. Polym.* **1991/1992,** *16,* 9.
(19) Linford, R. G., Ed. *Electrochemical Science and Technology of Polymers*; Elsevier: London and New York, 1987.
(20) Heinze, J. *Top. Curr. Chem.* **1990,** *152,* 1.
(21) Merz, A. *Top. Curr. Chem.* **1990,** *152,* 49.
(22) Murray, R. W., Ed. *Molecular Design of Electrode Surfaces*; Wiley Interscience: New York, 1992.
(23) Gratzel, M.; Kalyanasundaram, K., Ed. *Kinetics and Catalysis in Microheterogeneous Systems*; Marcel Dekker: New York, 1991.
(24) Skotheim, T. A. Ed. *Handbook of Conducting Polymers*; Marcel Dekker: New York, 1986; Vols. 1 and 2.
(25) Deronzier, A.; Moutet, J. C. *Acc. Chem. Res.* **1989,** *22,* 249.
(26) Curran, D.; Grimshaw, J.; Perera, S. D. *Chem. Soc. Rev.* **1991,** *20,* 391.
(27) Roncali, J. *Chem. Rev.* **1992,** *92,* 711.

Metalloporphyrins in Electropolymerized Films
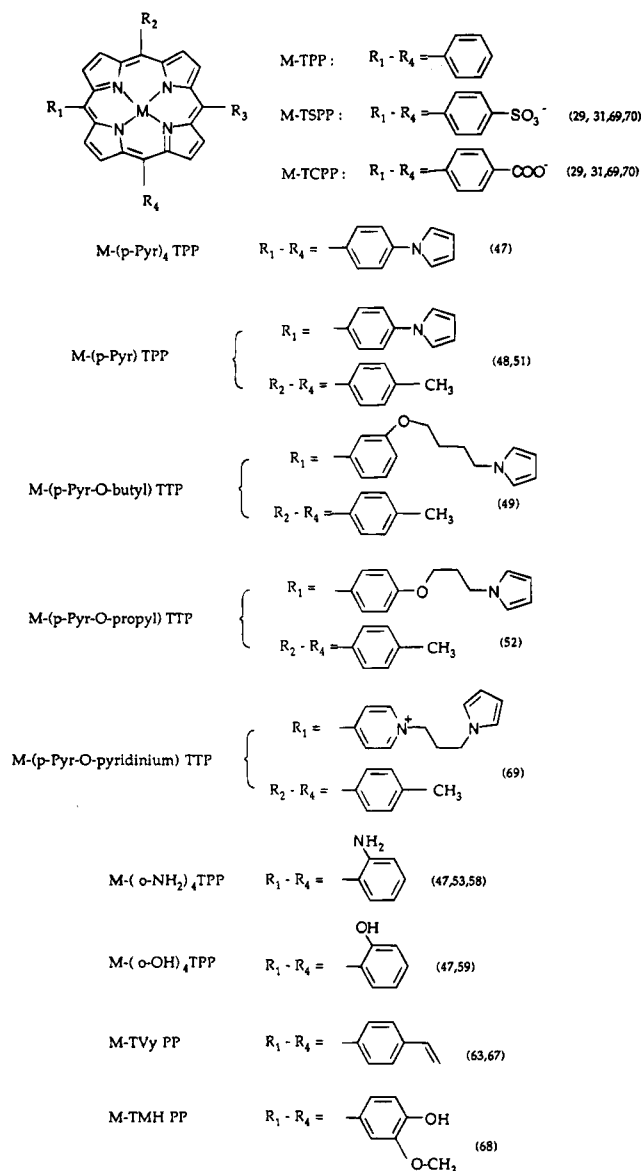
Acc. Chem. Res., Vol. 28, No. 1, 1995 **31**

Figure 1. Structures of various metalloporphyrin derivatives [M = Co(II), Zn(II), Ni(II), Mn(III), and Fe(III)].

charge transport in the porphyrinic films may act like a conducting polymer or as a hopping process between porphyrin sites. In this Account, we will address some of the recent published works that have involved the immobilization of metalloporphyrins in electropolymerized films (see some structures of the most commonly used metalloporphyrins in Figure 1). Application of these modified electrodes in the field of bioinorganic chemistry and chemical and biosensors is also described.

Electrochemical Polymerization Strategy

Electrochemical polymerization is an elegant, attractive, and easy strategy for the immobilization of metal complexes[19-21,24-26] and especially for metalloporphyrins on the surface of electrodes. The principle is based on the electrochemical oxidation (or reduction) of a suitably designed monomer to form a polymeric film incorporating the metal complex. The obtained polymeric films should be electronic conductors to ensure electron transfer within the matrix (and then the continuous growth of the polymers). Pyrrole,

thiophene, and aniline-based monomers have been the most commonly used materials.[24-27] Such chemically substituted monomers have many interesting features including a high flexibility in their molecular design. Additionally, such materials offer the possibility of using either aqueous or organic solutions to carry out the electropolymerization.

The electrochemical deposition process is controlled by the electrode potential. This can be achieved either by controlled potential, current electrolysis, or cyclic voltammetry within a well-defined potential range. Growth of the polymeric films or more precisely, control of the amount of deposited materials (or the polymer film thickness) can be easily achieved by monitoring the total charge passed during the electrooxidative (or reductive) polymerization process. In the general case, the mechanism of electropolymerization of such substituted monomers has still not been completely explained, despite the large quantity of data on this subject. However, it is now well-accepted that, in the case of pyrrole and aniline derivatives, the first step in the electropolymerization process is the electrooxidative formation of a radical cation from the chosen monomer.[24-27] This oxidation reaction is followed by a dimerization process, followed by further oxidation and coupling reactions. This leads to the formation of oligomers and polymers on the electrode surface. It also appears that the morphology and the physical properties of the polymer films depend largely upon the electrochemical polymerization conditions. Thus, one can induce a supplementary design parameter during the polymerization step by adjusting the solution composition or the electrode potential. In this way electrochemical polymerization can be carefully controlled, resulting in multilayered structures and copolymers from multicomponent solutions.

Design and Characterization of Electropolymerized Metalloporphyrin Films

Electrochemistry of Polypyrrole Films Doped by Anionic Porphyrins. One of the first examples that involved the incorporation of metalloporphyrin complexes into polypyrrole films was based on the ion exchange properties of the oxidized polymer. Tetrasulfonated and tetracarboxy-substituted metalloporphyrins (MTSPP and MTCPP)[28-31] (and metallophthalocyanines[32-40]) have been introduced into poly-

(28) Okabayashi, K.; Ikeda, O.; Tamura, H. *J. Chem. Soc., Chem. Commun.* **1983**, 684.

(29) Bedioui, F.; Bongars, C.; Hinnen, C.; Bied-Charreton, C.; Devynck, J. *Bull. Soc. Chim. Fr.* **1985**, 679.

(30) Ikeda, O.; Okabayashi, O.; Yoshida, N.; Tamura, H. *J. Electroanal. Chem.* **1985**, *191*, 157.

(31) Bedioui, F.; Bongars, C.; Devynck, J.; Bied-Charreton, C.; Hinnen, C. *J. Electroanal. Chem.* **1986**, *207*, 87.

(32) Bull, R. A.; Fan, F. R.; Bard, A. J. *J. Electrochem. Soc.* **1984**, *131*, 687.

(33) Skotheim, T.; Velasquez Rosenthal, M.; Linkous, C. A. *J. Chem. Soc., Chem. Commun.* **1985**, 612.

(34) Mizutani, F.; Lijima, S. I.; Tanabe, Y.; Tsuda, K. *J. Chem. Soc., Chem. Commun.* **1985**, 1728.

(35) Velasquez Rosenthal, M.; Skotheim, T. A.; Linkous, C. A. *Synth. Met.* **1986**, *15*, 219.

(36) Elzing, A.; Van Der Putten, A.; Visscher, W.; Barendrecht, E. *J. Electroanal. Chem.* **1987**, *233*, 113.

(37) Jiang, R.; Dong, S. *J. Electroanal. Chem.* **1988**, *246*, 101.

(38) Choi, C. S.; Tachikawa, H. *J. Am. Chem. Soc.* **1990**, *112*, 1757.

(39) Walton, D. J.; Hadingham, D. M.; Hall, C. E.; Viney, I. V. F.; Chyla, A. *Synth. Met.* **1991**, *41-43*, 295.

(40) Saunders, B. R.; Murray, K. S.; Fleming, R. *J. Synth. Met.* **1992**, *47*, 167.

pyrrole films as counterions (or "doping" ions) during the electrochemical growth of the polymers in solutions containing pyrrole and anionic complexes as supporting electrolyte. Both the electrochemical polymerization of pyrrole and the doping of polypyrrole by anionic porphyrins were obtained in one step from aqueous solutions.[28-31] The amount of electrochemical doping of metalloporphyrins into polypyrrole was usually estimated from chemical and spectrophotometric analysis.[31] These results suggested that the number of pyrrole units interacting with one anionic group of the metalloporphyrin is three or four as mentioned by Diaz et al.[41,42] for simple anions such as ClO_4^-.

The electrochemical characterization of the polypyrrole films doped by anionic porphyrins was generally achieved by cyclic voltammetry. Unfortunately, no well-defined waves for the porphyrin redox couples were observed, which may be because they are superimposed on the large polypyrrole background. Therefore, the reported voltammograms[29,31] could either be those for the redox process of the incorporated complexes or those of the polypyrrole redox system. That is why it appears essential to couple the electrochemical characterization with spectrophotometric measurements.

The *in-situ* characterization of polypyrrole-doped porphyrin films by the visible electroreflectance technique (ER) coupled with capacitive and voltammetric measurements[29,31] was made possible because the different spectral features of the oxidized and reduced metalloporphyrin form as well as the different optical properties of the porphyrin and polypyrrole. Modulated ER measurements involve optical changes that are monitored by the applied alternative electric potential, which are related to the subsequent electrochemical process occurring in the polymer electrode. The experiments were performed by recording, at a fixed potential (E), the electroreflectance signal $(1/R)$-$(\delta R/\delta E)$ (where R is the reflectivity) as a function of the wavelength of the incident light. Additionally, the technique's sensitivity is high where relative changes in reflectivity as small as 10^{-4}–10^{-5}, corresponding to a monolayer scale, can be measured. Our electroreflectance investigations[29,31] have resulted in measuring the redox potential values for M(III)/M(II)TCPP processes in doped polypyrrole film electrodes (M = Co, Fe, and Mn). The results show that no change occurs in the porphyrin-based redox process by incorporation in the polymer matrix.

However, this method of incorporating metalloporphyrins (or other kinds of complex) into a polypyrrole matrix has a severe limitation, namely, the electrostatic binding capacity of the polymer film depends on the potential and disappears when the polypyrrole is reduced.[24,41-45] Moreover, this ion exchange capacity is restricted to one negative charge for three or four pyrrole units.

Electropolymerization of Pyrrole-Substituted Metalloporphyrins. Another approach to prepare

Figure 2. Cyclic voltammetry of vitreous carbon disk electrode ($A = 0.071$ cm^2) of Co(II)(p-pyr-O-butyl)TTP porphyrin (2 mM) in acetonitrile + 0.1 M Bu$_4$NBF$_4$ solution (scan rate = 0.15 V/s). (1), first cycle; (2), 20th cycle.

polypyrrole-based porphyrinic matrices involves the electrochemical polymerization of suitably designed pyrrole-substituted porphyrin monomers. We and others have shown that electrooxidative polymerization of pyrrole-substituted porphyrins (see Figure 1) leads to the formation of films having the electrochemical properties of the monomeric complex.[46-52]

In a typical experiment, the electrochemical polymerization of pyrrole-substituted porphyrins is achieved by cyclic voltammetry of acetonitrile or dichloromethane solutions containing the complex monomer and the supporting electrolyte, through a well-defined potential range. The evolution of the cyclic voltammograms of the cobalt porphyrin, Co(II)(p-pyr-O-butyl)TTP during repeated potential scans from −1.5 to 1.5 V/SCE (Figure 2) shows the continuous increase in the amplitude of the cyclic voltammetric peaks.[50] This indicates that a film is formed on the electrode as a consequence of electrochemical polymerization of the attached pyrrole groups.

The electropolymerized metalloporphyrin films are usually characterized by cyclic voltammetry and UV−

(41) Kanazawa, K. K.; Diaz, A. F.; Gill, W. D.; Grant, P.; Street, G. B.; Gardini, G. P.; Kwak, J. F. *Synth. Met.* **1979/80**, *1*, 329.

(42) Diaz, A. F.; Vasquez Vallejo, J. M.; Martinez Duran, A. *IBM J. Res. Dev.* **1981**, *25*, 42.

(43) Noufi, R.; Trench, D.; Warren, L. F. *J. Electrochem. Soc.* **1981**, *128*, 2596.

(44) Zinger, B.; Miller, L. L. *J. Am. Chem. Soc.* **1985**, *106*, 6861.

(45) Miller, L. L.; Zinger, B.; Zhou, Q. N. *J. Am. Chem. Soc.* **1987**, *109*, 2267.
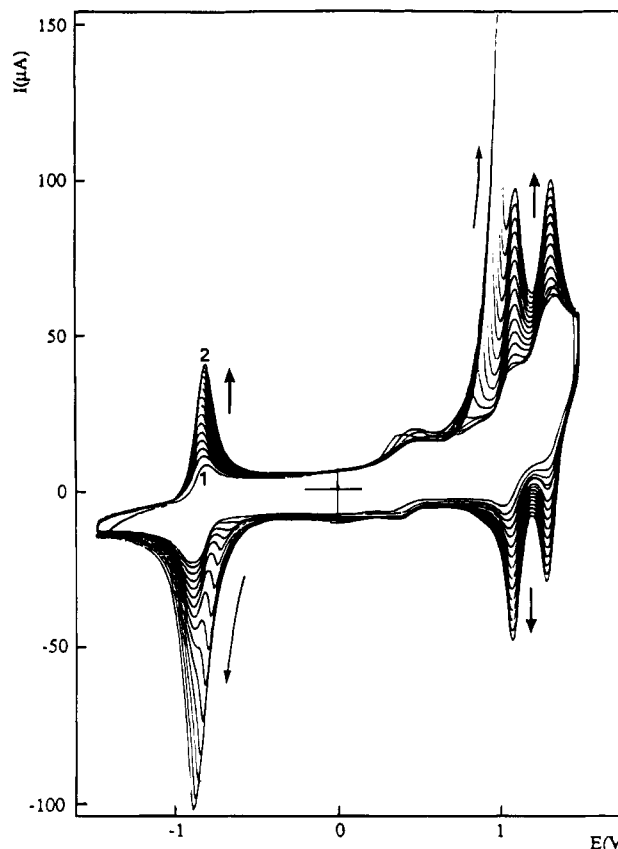
(46) Deronzier, A.; Latour, J. M. *J. Electroanal. Chem.* **1987**, *224*, 295.

(47) Bettelheim, A.; White, B. A.; Raybuck, S. A.; Murray, R. W. *Inorg. Chem.* **1987**, *26*, 1009.

(48) Bedioui, F.; Merino, A.; Devynck, J.; Mestres, C. E.; Bied-Charreton, C. *J. Electroanal. Chem.* **1988**, *239*, 433.

(49) Armengaud, C.; Moisy, P.; Bedioui, F.; Devynck, J.; Bied-Charreton, C. *J. Electroanal. Chem.* **1990**, *277*, 197.

(50) Bedioui, F.; Voisin, M.; Devynck, J.; Bied-Charreton, C. *J. Electroanal. Chem.* **1991**, *297*, 257.

(51) Ramachandraiah, G.; Bedioui, F.; Devynck, J.; Serrar, M.; Bied-Charreton, C. *J. Electroanal. Chem.* **1991**, *319*, 395.

(52) Deronzier, A.; Devaux, R.; Limozin, D.; Latour, J. M. *J. Electroanal. Chem.* **1992**, *324*, 325.

visible spectrophotometry on optically transparent electrodes.[51] These techniques reveal the formation of supported porphyrin on the electrode surface as well as provide evidence for the similarity of the electrochemical and spectrophotometric behavior of the polymer porphyrins and the starting monomers. Cyclic voltammetry can also provide useful information on the apparent surface coverage of poly(pyrroleporphyrin) film electrodes. It was shown that the configuration of the starting pyrrole or mono- or tetrasubstituted monomers (with the pyrrole group directly linked on the porphyrin macrocycle or through a flexible tether) induces a cross-linking effect due to the steric hindrance of the macrocomplex. This dramatically affects the efficiency of the electropolymerization reactions and limits the electrode surface coverages by the supported porphyrin.[47-50]

The available data show also that the conductivity of poly(pyrroleporphyrin) film decreases at low potential values ($E < -1$ V/SCE) as the film thickness increases.[49,50] In contrast, the polymer conductivity seems to be unchanged at positive potential values. This evokes a voltage-dependent conductivity similar to that described for "simple" polypyrrole films. Anyhow, the incorporation of metalloporphyrins into the polymer films imparts a typical "redox conductivity" to these materials that allows their use over a large potential range. We can even assert that at the potentials where many of the effects discussed here occur, the electron hopping process between porphyrinic sites dominates the global charge transport mechanism.

Electropolymerization of Amino-, Hydroxy-, and Vinyl-Substituted Metalloporphyrins as Well as Other Derivatives. Several types of porphyrin ligand modification have been performed to create a new family of electrochemically polymerizable complexes. The most commonly used porphyrins are the amino,[47,53-58] hydroxy,[47,59] methoxy,[60-62] vinyl-,[63-67] and other[68] substituted macrocyclic complexes. Studies of these complexes have focused on the electrochemical synthesis and characterization of conductive polymeric or copolymeric porphyrin materials.

In all cases, the films were obtained by oxidative electropolymerization of the cited substituted porphyrins from organic or aqueous solutions. The mecha-
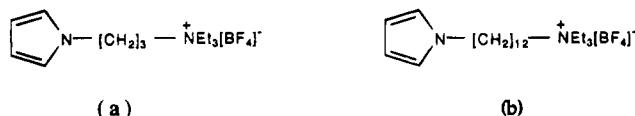

Figure 3. Structure of the (3-pyrrol-1-ylpropyl)triethylammonium tetrafluoroborate monomer (a) and the (12-pyrrol-1-yldodecyl)triethylammonium tetrafluoroborate monomer (b).

nism of metalloporphyrin film formation was suggested to be a radical-cation induced polymerization of the substituents on the periphery of the macrocycle. As it was reported for the case of polypyrrole-based porphyrin materials,[46-52] cyclic voltammetry and UV−visible spectroscopy with optically transparent electrodes were extensively used to provide information on the polymeric films (electroactivity, photometric properties, chemical stability, conductivity etc.). Based on the available data, it appears that the electrochemical polymerization of the substituted porphyrins leads to well-structured multilayer films. It also appears that the low conductivity of the formed films combined with the cross-linking effects due to the steric hindrance induced by the macrocyclic ligand confer to these material a certain number of limitations such as the limited continuous growth of the polymers due to the nonelectronic conductivity of the films. Indeed, the charge transport in many of these films acts only by electron hopping process between porphyrin sites.

Immobilization of Multicharged Metalloporphyrins into Pre-Electropolymerized Polypyrrole Films Bearing Functional Groups. Recently, attempts to incorporate water-soluble tetracarboxylated and tetrasulfonated porphyrins into polypyrrole films containing alkylammonium groups have been reported.[69,70] Poly[(pyrrolealkyl)ammonium] polymers, prepared from (3-pyrrol-1-ylpropyl)triethylammonium (noted pyr-C_3-N$^+$) and (12-pyrrol-1-yldodecyl)-triethylammonium (noted pyr-C_{12}-N$^+$) monomers (see structures in Figure 3) exhibit potential independent anion exchange behavior as well as extraction and binding of organic and inorganic anions from organic and aqueous solutions.[71-75] Furthermore, the incorporation of anionic porphyrins in the polypyrrole films was easily achieved without any limitation due to the electropolymerization reaction of the starting monomers.[69,70] It is important to note that adsorption on electrode surfaces by the amphiphilic monomer (pyr-C_{12}-N$^+$) produces, in aqueous electrolyte, an irreversibly adsorbed layer, which gives a stable polypyrrole film upon anodic electropolymerization.[70,74] This simple and monomer-saving procedure makes this approach extremely useful.

The incorporation of anionic porphyrins into poly[(pyrrolylalkyl)ammonium] films was followed by UV−visible measurements on transparent electrodes. The reported results[69,70] show clearly that the metallopor-

(53) White, B. A.; Murray, R. W. *J. Electroanal. Chem.* **1985**, *189*, 345.

(54) Macor, K. A.; Su, Y. O.; Miller, L. A.; Spiro, T. G. *Inorg. Chem.* **1987**, *26*, 2594.

(55) White, B. A.; Murray, R. W. *J. Am. Chem. Soc.* **1987**, *109*, 2576.

(56) Daunert, S.; Wallace, S.; Florido, A.; Bachas, L. G. *Anal. Chem.* **1991**, *63*, 1676.

(57) Kliza, D. M.; Meyerhoff, M. E. *Electroanalysis* **1992**, *4*, 841.

(58) Hayon, J.; Raveh, A.; Bettelheim, A. *J. Electroanal. Chem.* **1993**, *359*, 209.

(59) Blair, T. L.; Allen, J. R.; Daunert, S.; Bachas, L. G. *Anal. Chem.* **1993**, *65*, 2155.

(60) Malinski, T.; Ciszewski, A.; Bennett, J.; Fish, J. R.; Czuchajowski, L. *J. Electrochem. Soc.* **1991**, *138*, 2008.

(61) Malinski, T.; Ciszewski, A.; Fish, J.; Kubaszewski, E.; Czuchajowski, L. *Adv. Mater.* **1992**, *4*, 354.

(62) Fish, J. R.; Kubaszewski, E.; Peat, A.; Malinski, T.; Kaczor, J.; Kus, P.; Czuchajowski, L. *Chem. Mater.* **1992**, *4*, 795.

(63) Macor, K. A.; Spiro, T. G. *J. Am. Chem. Soc.* **1983**, *105*, 5601.

(64) Macor, K. A.; Spiro, T. G. *J. Electroanal. Chem.* **1984**, *163*, 223.

(65) Basu, J.; Rohatgi-Mukherjee, K. K. *Photochem. Photobiol.* **1988**, *48*, 417.

(66) Basu, J.; Rohatgi-Mukerjee, K. K. *Sol. Energy Mater.* **1991**, *21*, 317.

(67) Younathan, J.; Wood, K. S.; Meyer, T. J. *Inorg. Chem.* **1992**, *31*, 3280.

(68) Czuchajowski, L.; Bennett, J. E.; Goszczynski, S.; Wheeler, D. E.; Wisor, A. K.; Malinski, T. *J. Am. Chem. Soc.* **1989**, *111*, 607.

(69) De Gregori, I.; Carrier, M.; Deronzier, A.; Moutet, J. C.; Bedioui, F.; Devynck, J. *J. Chem. Soc. Faraday Trans.* **1992**, *88*, 1567.

(70) Bedioui, F.; Bouhier, Y.; Sorel, C.; Devynck, J.; Coche-Guerrente, L.; Deronzier, A.; Moutet, J. C. *Electrochem. Acta* **1993**, *38*, 2485.

(71) Cosnier, S.; Deronzier, A.; Moutet, J. C.; Roland, J. F. *J. Electroanal. Chem.* **1989**, *271*, 69.

(72) Pickett, C. J.; Moutet, J. C. *J. Chem. Soc. Chem. Commun.* **1989**, 188.

(73) Keita, B.; Bouaziz, D.; Nadjo, L.; Deronzier, A. *J. Electroanal. Chem.* **1990**, *279*, 187.

(74) Coche-Guerrente, L.; Deronzier, A.; Galland, B.; Labbé, P.; Moutet, J. C.; Reverdy, G. *J. Chem. Soc. Chem. Commun.* **1991**, 386.

(75) De Olivera, I. M.; Moutet, J. C.; Hamar-Thibault, S. *J. Mater. Chem.* **1992**, *2*, 167.

phyrins are retained by the poly[(pyrrolealkyl)ammonium] polymer due to electrostatic binding. Upon incorporation in the film, a red shift of 12−15 nm is observed for the porphyrin Soret band as well as considerable broadening.[69,70] It is noteworthy that the ability of these polymers to retain anionic porphyrins is strong. The available data also show that, beside their large size, the bulky porphyrins can be efficiently incorporated into the poly[(pyrrolealkyl)ammonium] films until total saturation of all the cationic sites is complete. Finally, the very high affinity of poly-(pyrrole-C_{12}-N^+) amphiphilic films for anionic porphyrins allows the use of such molecular materials in concentrated ionic media without a significant loss of complexes.

Finally, it appears from the major part of the reported studies that no extended analysis of the morphology and/or the structure of the porphyrinic films are available.

Catalytic and Analytical Applications of Electropolymerized Metalloporphyrin Films

Electroassisted Oxidation Reactions Using Metalloenzyme Models.
Achieving biomimetic hydrocarbon oxidations with molecular oxygen and synthetic porphyrin models of cytochrome P-450 is a field where electropolymerized metalloporphyrin films may play a significant role. Efficient high-valent metal−oxo porphyrin complexes, the reactive oxygenating intermediates, have been postulated in numerous systems.[4,76−93] Electroassisted formation of the oxo species requires the enzyme model plus molecular oxygen, an activator (such as anhydride or acid), and one or several axial ligands (such as imidazole) as shown on Figure 4 and as has been described by several groups.[83−88,90,92,94] We have shown the first examples in which a manganese porphyrin supported on a polypyrrole film[83,88,90] acts as an efficient model. We describe here some of our results obtained for the oxidation of cis-cycloctene, cycloctane, tetralin (1,2,3,4-tetrahydronaphthalene), indan, and cyclohexene by

(76) Tabushi, I.; Koga, N. *J. Am. Chem. Soc.* **1979**, *101*, 6456.

(77) Perrée-Fauvet, M.; Gaudemer, A. *J. Chem. Soc., Chem. Commun.* **1981**, 7371.

(78) Tabushi, I.; Yazaki, A. *J. Am. Chem. Soc.* **1981**, *103*, 7371.

(79) Fontecave, M.; Mansuy, D. *Tetrahedron* **1984**, *40*, 2877.

(80) Tabushi, I.; Kodera, M.; Yokoyama, M. *J. Am. Chem. Soc.* **1985**, *107*, 466.

(81) Creager, S. E.; Raybuck, A. A.; Murray, R. W. *J. Am. Chem. Soc.* **1986**, *108*, 4225.

(82) Battioni, P.; Bartoli, J. F.; Leduc, P.; Fontecave, M.; Mansuy, D. *J. Chem. Soc., Chem. Commun.* **1987**, 791.

(83) Moisy, P.; Bedioui, F.; Robin, Y.; Devynck, J. *J. Electroanal. Chem.* **1988**, *250*, 191.

(84) Leduc, P.; Battioni, P.; Bartoli, J. F.; Mansuy, D. *Tetrahedron Lett.* **1988**, *29*, 205.

(85) Nishihara, H.; Pressprich, K.; Murray, R. W.; Collman, J. P. *Inorg. Chem.* **1990**, *29*, 1000.

(86) Horwitz, C. P.; Creager, S. E.; Murray, P. W. *Inorg. Chem.* **1990**, *29*, 1006.

(87) Tsang, P. K. S.; Sawyer, D. T. *Inorg. Chem.* **1990**, *29*, 2848.

(88) Bedioui, F.; Moisy, P.; Bied-Charreton, C.; Devynck, J. *J. Chim. Phys.* **1989**, *86*, 235.

(89) Arasasinghan, R. D.; Bruice, T. C. *Inorg. Chem.* **1990**, *29*, 1422.

(90) Bedioui, F.; Guterriez Granados, S.; Bied-Charreton, C.; Devynck, J. *New J. Chem.* **1991**, *15*, 939.

(91) Lu, W. Y.; Bartoli, J. F.; Battioni, P.; Mansuy, D. *New J. Chem.* **1992**, *16*, 621.

(92) Cauquis, G.; Cosnier, S.; Deronzier, A.; Galland, B.; Limosin, D.; Moutet, J. C.; Bizot, J.; Deprez, D.; Pulicani, J. P. *J. Electroanal. Chem.* **1993**, *352*, 181.

(93) Meunier, B. *Chem. Rev.* **1992**, *92*, 1411.

(94) Gutierrez Granados, S.; Bedioui, F.; Devynck, J. *Electrochim. Acta* **1993**, *38*, 1747.
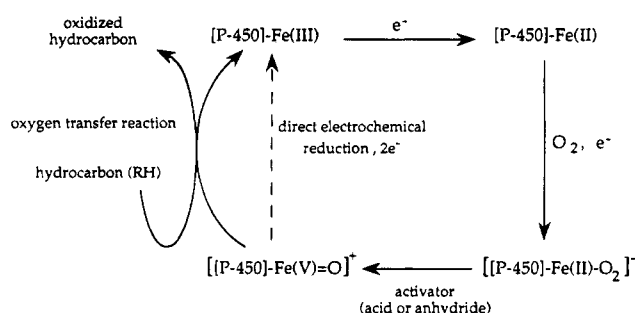
Figure 4. Simplified catalytic cycle for the oxidation of hydrocarbons (RH) by molecular oxygen and cytochrome P-450 (or its synthetic models).

molecular oxygen. O_2 was electroactivated by an electropolymerized film of a manganese porphyrin deposited on graphite tissue and carbon felt electrodes. The supported catalyst was regenerated by controlled potential electrolysis at $E = -0.5$ V/SCE.

Table 1 presents these results. They are compared to those previously obtained with the same catalyst in a homogeneous phase. The essential observations are that (1) the oxidation products are formed with a very good efficiency by the supported catalyst, up to 500 turnovers of the catalyst per hour; (2) the faradaic efficiency expressed as the ratio of moles of oxidation products analyzed to the electrochemical charge passed is relatively poor, but reached 99% in some cases; (3) the nature of the electrode material (graphite tissue or carbon felt) seems to have a small but significant influence on the chemical and faradic efficiencies of the supported catalyst for the cis-cyclooctene epoxidation reaction (Table 1, entries 5 and 6). Comparison of our results (Table 1, entries 1−6) with those reported in the homogeneous phase and using different kinds of reducing agents[82,84,85,87,91] (Table 1, entries 7−11) shows clearly that the catalytic activity of the catalyst (turnover) is largely enhanced when the complex is fixed on the electrode. This is probably due to either a preferred orientation of the supported catalyst for the approach of the hydrocarbon to the presumed active manganese site or to the high local concentration of the catalyst. However, the low faradaic yields obtained in our case are certainly due to the direct electrochemical reduction of the active oxidant, a high-valent manganese oxo complex, at the potential of electrolysis according to the electroactivity study of this oxo form of the catalyst previously reported.[86,90,94] Thus, the fixation of the catalyst onto the electrode promotes the electroreductive consumption of the active oxidant. But it is important to note that, in our case, the products are formed using a substrate/catalyst ratio higher than 6000, with similar yields compared with those obtained in homogeneous solution (with a substrate/catalyst ratio up to 400). It was also found that the recovered porphyrin polymer electrodes (stored in air, without precaution) retained 95% of their initial catalytic activity during the second run and 70% of their initial activity during the third run.[90] It also appears from these results that it is not clear to bring out any valid information on the stereospecificity of the supported catalyst. More experiments with well-adapted test reactions are needed to reflect the importance of this aspect.

Younathan et al.[67] reported a pioneering study which involved the application of electropolymerized

Table 1. Hydrocarbons Oxidation by O_2 Electrocatalyzed by Electropolymerized Manganese Porphyrin Films[a] and Various Homogeneous Catalysts

entry	catalyst	reducing agent	hydrocarbon	product(s)[b]	turnover[c] per hour	faradaic efficiency[d] (%)
1	poly(MnTTP) on carbon felt (5×10^{-8} mol)*	electrolysis at −0.5 V/SCE	tetralin (0.4 M)	tetralol* (7.2 mM)	560	98
2	poly(MnTPP) on carbon felt (3.1×10^{-8} mol)*	electrolysis at −0.5 V/SCE	indan (0.1 M)	tetralone** (7 mM) indanone (2.2 mM)	81	2
3	poly(MnTPP) on carbon felt (2.6×10^{-8} mol)*	electrolysis at −0.5 V/SCE	cyclooctane (0.1 M)	cyclooctanol (0.7 mM)	78	1.5
4	poly(MnTPP) on carbon felt (2.5×10^{-8} mol)*	electrolysis at −0.5 V/SCE	cyclohexene (0.1 M)	cyclohexene oxide (1.6 mM)	264	13
5	poly(MnTPP) on carbon felt (1.5×10^{-7} mol)*	electrolysis at −0.5 V/SCE	*cis*-cyclooctene (20 mM)	cyclooctene oxide (8.5 mM)[e]	162	8
6	poly(MnTPP) on graphite tissue ($1.5 \times \times 10^{-7}$ mol)*	electrolysis at −0.5 V/SCE	*cis*-cyclooctene (20 mM)	cyclooctene oxide (4.6 mM)	150	12
7	ClMnTPP (0.5 mM)**[f]	electrolysis at −0.4 V/SCE	*cis*-cyclooctene (0.1 M)	cyclooctene oxide (5.7 mM)	2	56
8	ClMnTPP (1 mM)*[g]	zinc powder	*cis*-cyclooctene (0.38 M) cyclooctane (0.38 M)	cyclooctene oxide (75 mM) cyclooctanol + one (22 mM)	150 28	50 15
9	ClMnTPP (1 mM)*[h]	electrolysis at −0.4 V/SCE	*cis*-cyclooctene (0.1 M) cyclooctane (0.1 M)	cyclooctene oxide cyclooctanol + one	1.7/mn 0.15/mn	45 7.5
10	ClMn-Salen (0.59 mM)*[i]	electrolysis at −0.45 V/SCE	cyclooctene (0.1 M)	cyclooctene oxide (1.4 mM)	2.4	35
11	ClMnTPP (1 mM)**[j]	zinc powder	tetralin (0.4 M) indan (0.4 M)	tetralol + tetralone (27 mM) indanol + indanone (27 mM)	9 9	36 37

[a] See text for the reaction procedure. [b] Yields obtained after 2 h of reaction, by analysis made by GC on FFAP (10%) column by comparison with authentic samples. [c] The turnovers are the number of moles of product per mole of MnTPP fixed on polypyrrole film. [d] The faradaic efficiency is expressed as the ratio of moles of product analyzed to the electrochemical charge passed (expressed in moles, assuming a two-electron reaction for the alcohols and epoxides and a four-electron reaction for the ketones). [e] Chemical yield is obtained after 3.5 h of reaction. [f] From reference 81, the reaction time is 6 h. [g] From reference 82, the reaction time is 0.5 h. [h] From reference 84, the reaction time and the chemical yields are not mentioned by authors; turnovers are given for the first 10 min. [i] From reference 86, the reaction time is not mentioned by authors. [g] From reference 91, the reaction time is 3 h. (*) Oxidation in acetonitrile solution. (**) Oxidation in dichloromethane solution.

iron protoporphyrin films to model the activity of biological systems such as the nitrite reductase enzymes. The authors have transferred the reactivity of an iron porphyrin to the electrode–solution interface by electropolymerizing the catalyst to form a thin polymeric film. Their approach was based on the fact that the polymeric structure may possess some of the properties of the biological catalyst. This is reasonable since enzyme modeling reveals that the binding site in nitrite reductase is embedded in a nonaqueous environment similar to an aprotic medium.[95] Thus, it was shown that the electropolymerized films of iron protoporphyrin(IX) dimethyl ester are effective catalysts for the electroreduction of HONO/NO_2^- or NO to N_2O, N_2, N_2OH, and NH_3.[67] The yield of N_2 was enhanced in the compact environment of the redox polymer relative to that for comparable monomeric catalyst in homogeneous solution. The authors also suggested that the sensitivity of the polymeric catalyst to millimolar quantities of HONO/NO_2^- could be used as an analytical tool for the detection of these species. In the same way, we have recently reported[70] the reactivity of a poly[(pyrrolealkyl)ammonium] film electrode containing iron(III) porphyrin toward nitric oxide in acidic aqueous solution. The formation of the iron-nitrosyl intermediate within the polypyrrole film was proven by cyclic voltammetry and spectrophotometric measurements. Malinski et al.[60] also reported a similar approach by using an electropolymerized nickel porphyrin film as a new electrode material in the electrooxidation process of water, methanol, and hydrazine to O_2, CO_2, and N_2, respectively. The authors demonstrated high catalytic activity and good effects in the electrooxidation of methanol and hydrazine with overpotentials of 110 and 360 mV, respectively.

(95) Spence, J. T. In *Metal Ions in Biological Systems*, Siegel, H., Ed.; Marcel Dekker: New York, 1976; Vol. 5, Chapter 6.

Electropolymerized Metalloporphyrin Films as Chemical and Biosensors. Several authors have recently reported the potential use of electropolymerized metalloporphyrin films as new electrode materials for anion detection and pH measurements. For example, Daunert et al.[56] reported that anion-selective membrane electrodes can be prepared by electropolymerizing aniline-substituted cobalt tetraphenylporphyrin complexes onto a glassy carbon surface. It was shown that the resulting electrodes are highly selective toward the detection of thiocyanate and nitrite anions. The mechanism by which these metalloporphyrin electrode sensors operate is probably related to the well-known axial complexation capability of the central metal cation of the porphyrin toward different kinds of anions and bases. The same authors also reported a detection limit of 5×10^{-7} M for these ion-selective electrodes, which have lifetimes of more than 2 months.[56]

Meyerhoff et al.[57] have reported the use of a non-metalated porphyrin film as an ion-selective electrode. They have shown that the electropolymerized films offer significant selectivity for the detection of iodide over a wide range of anions. The lifetime of these electrodes was estimated by analyzing some of their characteristics such as sensitivity and detection limits. The effect of pH on the detection of iodide by the film-supported electrodes was also established. For pH values from 3 to 8, there is relatively little effect of the pH on the electrochemical response of the electrodes. At pH values higher than 8, the electrode response is affected by the interference by hydroxide ions.

More recently, hydroxy-substituted cobalt tetraphenylporphyrins electropolymerized onto an optically transparent electrode and adapted onto the tip of an optic fiber were used as sensing materials for the development of optic fibers as pH sensors.[59] The pH

36 *Acc. Chem. Res., Vol. 28, No. 1, 1995*

Bedioui et al.

values by these chemically modified optic fibers were monitored by spectrophotometric measurement of the Soret band wavelength for the supported porphyrin.

As far as biological applications of electropolymerized metalloporphyrin films are concerned, only a few, but significant, examples are reported in the literature. Malinski et al.[96] reported in 1992 a very interesting application of an electropolymerized nickel porphyrin film electrode for *in-situ* measurements of nitric oxide in biological systems. The reported microsensor (diameter 0.5−0.8 μm) consisted of several layers of p-type electropolymerized porphyrin film and cation exchange membrane (nafion) deposited on a sharp carbon microfiber. The sensor has been applied to amperometric measurements of nitric oxide release from a single endothelial cell in a pulmonary artery[97] as well as for the determination of NO in blood[96] and in other biological medium.[98−100] The authors reported that these biosensors exhibit a response time shorter than 10 ms and claimed a detection limit of 10 nM. However, no convincing experimental data clearly support these claims. Nevertheless, these studies offered a very exciting and interesting application for the electropolymerized metalloporphyrins films in the field of biological research. Such an approach was previously attempted by Bailey et al.[101] by applying the modification of conventional scale electrodes with conductive nickel porphyrin films to ultra-microelectrodes for the detection of nickel in a single biological cell.

Electropolymerized Metalloporphyrin Films for Solar Energy Conversion. Producing photocurrents from electropolymerized porphyrin films was first attempted by Basu and Rohatgi-Mukerjee.[66] The polymer material was prepared from a vinyl-substi-tuted zinc porphyrin by either controlled potential oxidation or continuous scan cyclic voltammetry. The production of photocurrents was achieved by irradiation of the polymer film by visible light with intensities of approximately 0.4 μA/cm for an open-circuit potential of 125 mV. Later, Malinski et al.[61] reported that electropolymerized methoxy, hydroxy-substituted copper tetraphenylporphyrin films with p-type semiconductor properties are efficient for solar energy conversion. In a typical experiment, the porphyrinic polymer was directly illuminated by visible light, and the resulting photocurrent was measured with a plateau at 0.2 μA/cm, a quantum yield of 21.6%, and a conversion efficiency of 0.16. The calculated conversion efficiency is 10 orders of magnitude higher than those reported for the monomeric porphyrin in homogeneous solution.[102] No long-term stability was reported, and the authors stated that no decline in efficiency was observed during a 5-h run.

Conclusion

It appears from the studies on the electrochemical design of metalloporphyrin films described above that the idea of building new molecular devices having catalytic and analytical properties is realistic. The use of electropolymerization techniques provides an elegant way to buildup multilayered structures and architectures. In the case of biomimetic catalysis, the polymer matrix, which can be compared to a protein, prevents supported metalloporphyrin degradation and controls the access of substrate molecules to the reactive centers. In most cases, the reactivity of the supported catalysts is largely enhanced. The electropolymerized metalloporphyrin films also appear to be powerful new analytical tools, especially for biosensoring. The significant developments in biosensor science and technology, such as the design of ultra-microelectrodes, should stimulate intense exploration of this field of research.

(96) Taha, Z.; Malinski, T. *Nature* **1992**, *358*, 676.

(97) Malinski, T.; Taha, Z.; Grunfield, S.; Burewicz, A.; Tomboulian, P.; Kiechle, F. *Anal. Chim. Acta* **1993**, *279*, 135.

(98) Malinski, T.; Bailey, F.; Zhang, Z. G.; Chopp, M. *J. Cereb. Blood Flow Metab.* **1993**, *13*, 355.

(99) Malinski, T.; Taha, Z.; Grunfeld, S.; Patton, S.; Kapturczak, M.; Tomboulian, P. *Biochem. Biophys. Res. Commun.* **1993**, *193*, 1076.

(100) Malinski, T.; Radomski, M. W.; Taha, Z.; Moncada, S. *Biochem. Biophys. Res. Commun.* **1993**, *194*, 960.

(101) Bailey, F.; Malinski, T.; Kiechle, F. *Anal. Chem.* **1991**, *63*, 395.

(102) Perrier, G.; Gauthier, R.; Dao, L. H. *J. Electrochem. Soc.* **1988**, *135*, 598.