

Electrooxidation of Fe, Co, Ni and Cu Metalloporphyrins on Edge-Plane Pyrolytic Graphite Electrodes and Their Electrocatalytic Ability towards the Reduction of Molecular Oxygen in Acidic Media

Gregory Richards^[a] and Shawn Swavey^{*[a]}

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Edge-plane pyrolytic graphite (EPG) electrodes coated with 5,10,15,20-tetrakis(4-hydroxy-3-methoxyphenyl)porphyrin [H₂T3M4HPP] and its Fe^{III}, Co^{II}, Ni^{II} and Cu^{II} analogs undergo an electrochemical/chemical/electrochemical (ECE) reaction when anodically scanned in 0.5 M H₂SO₄. The new redox couple formed from this anodic conditioning of the coated electrode is dependent on the pH of the solution. Roughened EPG electrodes coated with the metalloporphyrins show a catalytic shift for the reduction of O₂ when compared to the reduction of O₂ at a bare EPG electrode. An

additional catalytic shift of approximately 100 mV is observed for O₂ reduction at an EPG electrode coated with the Co^{II} porphyrin, which has been oxidized in 0.5 M H₂SO₄. In addition to the added electrocatalysis, approximately 15 % of the O₂ reduced at the oxidized Co^{II} porphyrin EPG electrode is converted to H₂O as determined by rotating-disk electrode measurements.

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Introduction

One of many alternatives to combustion engines, which use fossil fuels, under investigation is fuel cells. Fuel cells work like a galvanic cell (battery) converting chemical energy into electrical energy capable of doing work. The fuels used in this process are typically hydrogen and oxygen although methanol/oxygen fuel cells are also receiving much attention. In each case, oxygen is catalytically reduced to water at the cathode. This multi-electron process is complicated by high overpotentials, proton dependence and the formation of deleterious intermediates.^[1] Platinum is currently the catalyst of choice in fuel cells.^[2] However, alternatives to this expensive precious metal are continually being sought.

Macrocyclic complexes have been extensively studied as electrocatalysts in fuel-cell applications.^[3,4] An ideal electrocatalyst for fuel-cell applications should reduce oxygen by four electrons directly to water at a potential near the thermodynamically allowed value and should avoid formation of potentially destructive intermediates such as superoxide or hydrogen peroxide. Within the class of macrocyclic complexes, cobalt and iridium metalloporphyrins have shown the most promise for the electrocatalytic reduction of oxygen.^[5,6] Cobalt(II) porphyrins are known to reduce oxygen at the most positive potentials; however, in most cases this reduction is by two electrons to form hydrogen peroxide. Iron(II) porphyrins electrocatalytically reduce oxygen di-

rectly to water but at lower potentials than cobalt(II) porphyrins resulting in a lower energy output from the fuel cells. Studies of metal phthalocyanines for oxygen reduction in acidic media indicate the order of activity to be Fe > Co > Ni > Cu.^[7] For square-planar geometries this order has been explained by using the MO theory in which the formation of the oxygen radical involves a π - σ bond and is favored by an empty d_{z²} orbital with filled d_{xz} and d_{yz} orbitals interacting with the partially filled π^* orbitals of oxygen through π -backbonding. In the case of the Fe²⁺, Co²⁺, Ni²⁺ and Cu²⁺ metal centers in square-planar geometry all have filled d_{xz} and d_{yz} orbitals, whereas only Fe²⁺ has an empty d_{z²} orbital, and Co²⁺ has a half-filled d_{z²} orbital.^[8]

Some ingenious complexes have been synthesized in the hopes of converting cobalt(II) porphyrins into electrocatalysts capable of reducing oxygen directly to water at high positive potentials. Cofacial dicobalt porphyrins, for example, have been shown to catalyze the reduction of oxygen to water through direct interaction of both metal centers with the two oxygen atoms of O₂.^[9–11] However, few examples exist in which a monomeric cobalt porphyrin has been shown to catalyze the four-electron reduction of oxygen. In a series of studies it was shown that by coordination of 3 or 4 substitutionally inert Ru^{II}(NH₃)₅ moieties to the *meso*-pyridyl nitrogen atoms of [tetrakis(4-pyridyl)porphyrinato]-cobalt(II), adsorbed onto pyrolytic graphite electrodes, the direct four-electron reduction of oxygen to water at catalytic potentials could be achieved.^[12] It was initially thought that the peripheral Ru^{II} redox centers donated electrons to the Co^{II} metal center leading to the reduction of O₂ directly to H₂O. Subsequent studies revealed that the multi-electron

[a] Department of Chemistry, University of Dayton,
300 College Park, Dayton, OH 45469-2357, USA
E-mail: shawn.swavey@notes.udayton.edu

reduction of O_2 to H_2O with these complexes is the result of increased electron density placed on Co^{II} through π -backbonding of the pyridyl groups with the Ru^{II} groups. These complexes were found to be unstable in acidic solutions, the medium by which many fuel cells operate.

Stability of many electrocatalysts has been improved by their incorporation into polymer films and through electropolymerization of the catalysts directly onto electrode surfaces.^[13–16] Numerous studies on the electropolymerization of porphyrins onto electrode surfaces has led to the formation of thin conductive films for use in electrocatalysis,^[17] biosensors^[18] and electroanalysis.^[19] Synthetically incorporating electroactive organic pendant groups into the porphyrin framework and utilizing the ability of these groups to undergo either electro-oxidation or electro-reduction has led to the formation of polymeric arrays on the electrode surface. Electrodes modified in this manner act both as the medium and the mediator for electron transfer and have been used to catalyze the reactions of small molecules.^[20–22]

Conductive polymeric films on glassy carbon electrodes have been produced by continuous anodic cycling in basic solutions of [5,10,15,20-tetrakis(4-hydroxy-3-methoxyphenyl)porphyrinato]nickel(II).^[23a] These films have been used to detect trace amounts of nickel. Similar films have also been used to detect nitric oxide from a single cell.^[23b] Studies of [5,10,15,20-tetrakis(4-hydroxy-3-methoxyphenyl)porphyrinato]copper(II) films as p-type semiconductors have shown promise in photoelectrochemical cells converting light into chemical or electrical energy.^[23c] Reduction of oxygen to water in buffered pH 7.0 solutions has been accomplished by platinum electrodes modified with [5,10,15,20-tetrakis(4-hydroxy-3-methoxyphenyl)porphyrinato]iron(III) formed by cycling the electrode in basic solutions of the iron porphyrin.^[23d] To the best of our knowledge, electropolymerization of metal complexes of 5,10,15,20-tetrakis(4-hydroxy-3-methoxyphenyl)porphyrin in acidic solutions has not been investigated, which may lead to insights into the mechanism of the oxidative process at the electrode. In addition, these modified electrodes have not been tested for their ability to reduce oxygen in acidic solutions, the medium by which many fuel cells operate.

This report describes the synthesis and characterization by UV/Vis spectroscopy and solution electrochemistry of four metalloporphyrins synthesized by insertion of a metal ion into 5,10,15,20-tetrakis(4-hydroxy-3-methoxyphenyl)porphyrin [$H_2T3M4HPP$] (Figure 1). The adsorption of these complexes onto edge-plane pyrolytic graphite electrodes and the results of oxidation of the modified elec-

trodes in acidic media are presented. The ability of the electrooxidized modified electrodes to reduce molecular oxygen in acidic media is reported.

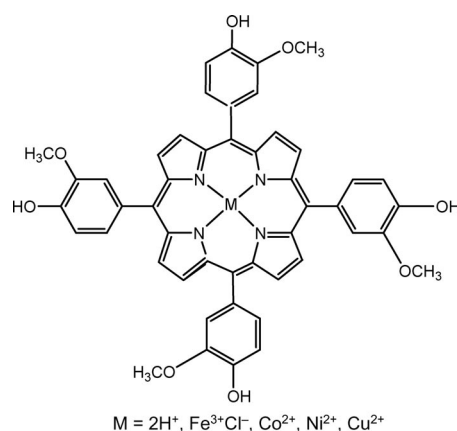


Figure 1. Structure of metalloporphyrins used in this study.

Results and Discussion

Synthesis and Characterization

Synthesis of the porphyrin, 5,10,15,20-tetrakis(4-hydroxy-3-methoxyphenyl)porphyrin [$H_2T3M4HPP$], was adapted from a previously reported procedure^[24] in which 4 equiv. of 4-hydroxy-3-methoxybenzaldehyde and 4 equiv. of freshly distilled pyrrole were refluxed in propionic acid. The crude porphyrin product precipitated from the reaction mixture upon cooling and was purified by recrystallization from thf and hot methanol. Insertion of the metal atoms into the core of the porphyrin was accomplished by reaction of the free-base porphyrin with the appropriate metal salt in dmf. The product was precipitated by addition of distilled water to the reaction mixture; yields of the metalloporphyrins were typically higher than 70%, except for the cobalt(II) porphyrin.

Electronic transitions of the free-base porphyrin and the metalloporphyrins were run in either dmf (due to solubility) or acetone in 1 cm quartz cuvettes at room temperature. The free-base porphyrin displays an intense Soret band at 427 nm and four less intense Q-bands from 500 to 650 nm. Insertion of the metal atom into the porphyrin core results in a slight shift of approximately 3–4 nm for the Soret band to higher energies with a decrease in molar absorptivity, except in the case of the copper(II) porphyrin (Table 1). The

Table 1. UV/Vis data for the free-base and metal porphyrins run in 1 cm quartz cuvettes at room temperature.

Complex	Soret band [nm] (ϵ [$10^{-4} M^{-1} cm^{-1}$])	Q-bands [nm] (ϵ [$10^{-4} M^{-1} cm^{-1}$])
$H_2T3M4HPP$	427 (28.5)	520 (14.4), 556 (10.8), 596 (4.74), 652 (6.10)
$FeT3M4HPPCl$	423 (6.80)	broad
$CoT3M4HPP$	422 (17.4)	534 (1.31)
$NiT3M4HPP$	423 (23.4)	530 (1.92)
$CuT3M4HPP$	424 (33.4)	542 (1.84), 580 (0.50)

Q-bands of the free-base porphyrin collapse into one band upon insertion of the metal atom into the porphyrin core; however, the Q-band for the iron(III) porphyrin was too broad to be reported.

Solution Electrochemistry and Spectroelectrochemistry

Solution electrochemistry was performed by using a three-electrode cell equipped with a glassy-carbon working electrode and referenced vs. the Ag/AgCl electrode. Extra-dry dmf was used as the solvent with TBAPF₆ serving as the supporting electrolyte. Solutions were purged with N₂

for 15 min prior to running cyclic voltammograms. Figure 2 compares the cyclic voltammograms of the free-base and metal porphyrins run in dry dmf solutions.

When cycled in the anodic direction the only significant oxidation process occurs for the free-base porphyrin, which undergoes a broad irreversible oxidation at $E_{pa} = 0.84$ V vs. Ag/AgCl. The metallated complexes do not show any oxidation process within the potential limits of the solvent; therefore, our focus is on the cathodic region of the cyclic voltammograms. In the cathodic direction the free-base porphyrin displays an irreversible reduction process with $E_{pc} = -1.12$ V vs. Ag/AgCl due to the one-electron irreversible reduction of the porphyrin to the anion radical (Fig-

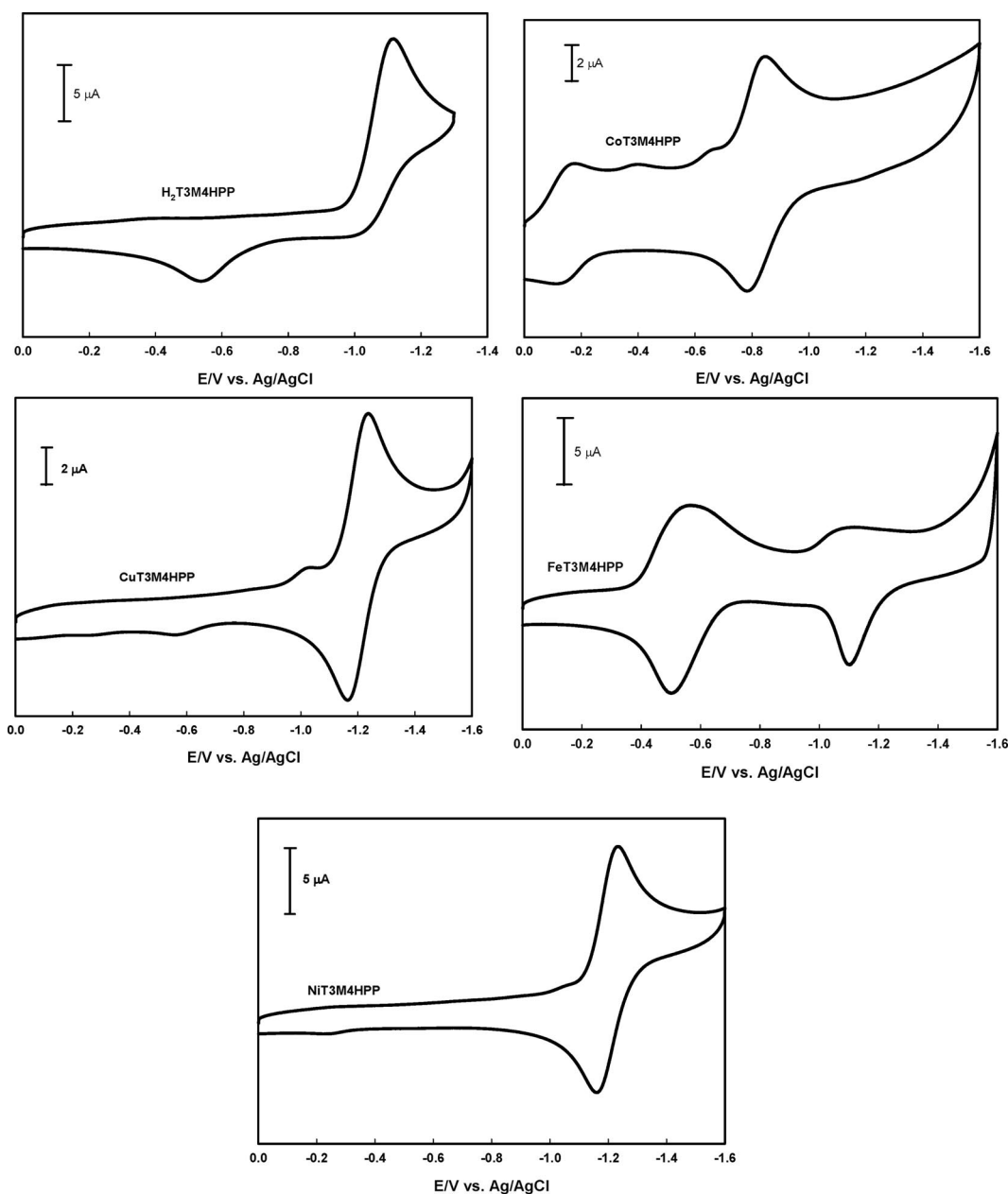


Figure 2. Cyclic voltammograms of 1.0 mM solutions of free-base porphyrin and metalloporphyrins measured under nitrogen in 0.1 M TBAPF₆ solutions of dry dmf by using a glassy-carbon working electrode. Scan rates 100 mV/s.

ure 2). A smaller oxidation wave with $E_{\text{pa}} = -0.55$ V is observed upon the return scan. Two reversible redox couples are observed upon cathodic scanning of the CoT3M4HPP solution. The first and less intense couple occurs with an $E_{1/2} = -0.15$ V ($\Delta E = 60$ mV), most likely the result of reduction of residual amounts of Co^{III} to Co^{II} . The second redox couple occurs with an $E_{1/2} = -0.82$ V ($\Delta E = 70$ mV), which is consistent with the reduction of Co^{II} to Co^{I} in dmf.^[25] Both the Cu^{II} and Ni^{II} porphyrins give reversible redox couples at $E_{1/2} = -1.20$ V ($\Delta E = 70$ mV) (Figure 2). Electrochemical studies of iron(III) porphyrins have been the focus of numerous studies.^[26] At high concentrations of dmf the Fe^{III} porphyrin is believed to be coordinated axially by two dmf molecules, whereas the reduced Fe^{II} porphyrin prefers one axial dmf coordination, which is weakly bound.^[26a] The reduction of $\text{Fe}(p\text{-CH}_3)\text{TPPCl}$ to $\text{Fe}(p\text{-CH}_3)\text{TPP}$ in neat dmf occurs with a peak potential of approximately -0.29 V vs. SCE.^[26b] FeTPPCl is reduced to FeTPP in dmf at -0.19 V vs. SCE, whereas the $(\mu\text{-oxido})\text{-bis}[(\text{tetraphenylporphyrinato})\text{iron}]$ [$(\text{Fe}^{\text{III}}\text{TPP})_2\text{O}$] is reduced at potentials near -0.9 V in dmf.^[26d] In the case of FeT3M4HPPCl a reversible redox couple is observed in the cathodic region with $E_{1/2} = -0.54$ V ($\Delta E = 70$ mV) vs. Ag/AgCl . This is more cathodic than the monomeric tetraphenylporphyrin and more anodic than the oxido-bridged tetraphenylporphyrin.^[26b] This electron is most likely going into the lowest-lying $d\pi$ orbital of the Fe metal reducing Fe^{III} to Fe^{II} . A subsequent broad reduction with $E_{\text{pc}} =$

-1.11 V is followed by the beginning of solvent breakdown. Upon reversing the scan anodically, a sharp oxidation wave at -1.10 V is observed. When the switching potential is shifted to -1.40 V, prior to solvent breakdown, the sharp oxidation wave at -1.10 V is no longer present.

To gain insight into the redox chemistry observed by cyclic voltammetry, spectroelectrochemistry experiments were performed on dilute solutions of the complexes in 0.1 M TBAPF_6 dmf solutions by using a platinum wire as auxiliary electrode and a platinum mesh working electrode. The results of these experiments are illustrated in Figure 3A–E.

The initial spectrum of the free-base porphyrin exhibits an intense Soret band at 427 nm and four less intense Q-bands. Controlled-potential electrolysis of the solution at -1.50 V vs. Ag/AgCl leads to a decrease of the Soret band and an increase of bands at 399 nm, 466 nm and 655 nm (Figure 3A). Although, based on the cyclic-voltammetry experiments, this reduction is irreversible, approximately 90% of the original spectrum was obtained upon oxidation of the more dilute spectroelectrochemical solution at 0.0 V, indicating concentration dependence. The initial spectrum of the CoT3M4HPP solution gave two overlapping Soret bands at 422 and 435 nm, consistent with the presence of both Co^{III} and Co^{II} porphyrins.^[27] Electrolysis at -0.40 V, approximately 200 mV past the first reduction peak in the cyclic voltammogram (Figure 2), shows a decrease in the band at 435 nm and an increase of the band at 422 nm (Figure 3B). This is consistent with the reduction of Co^{III} to

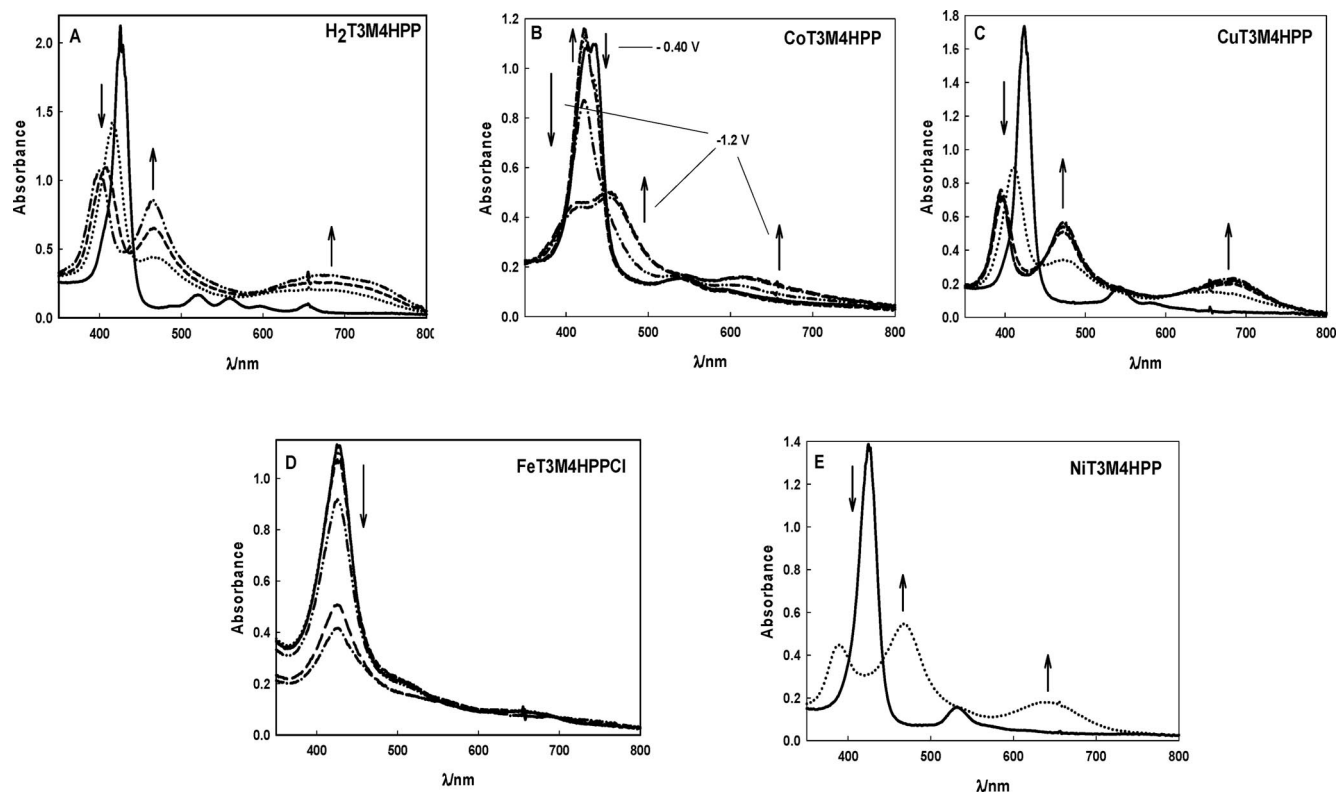


Figure 3. Spectroelectrochemical results for the controlled-potential reduction of the free-base porphyrin (A), CoT3M4HPP (B), CuT3M4HPP (C), FeT3M4HPPCl (D), and NiT3M4HPP (E) in dmf by using a platinum-mesh working electrode referenced to an Ag/AgCl electrode.

Co^{II}. Continued electrolysis at -1.2 V vs. Ag/AgCl shows the disappearance of the Soret band and new bands growing at 452 nm and 610 nm. The original spectrum, however, could not be obtained upon exhaustive oxidative electrolysis, suggesting that the reduced complex either decomposed or underwent reaction with the solvent.^[27] Controlled-potential electrolysis of the Cu^{II} and Ni^{II} porphyrins at -1.50 V vs. Ag/AgCl (Figure 3C and E, respectively) show the loss of the Soret band and new bands growing at 396, 472 and 672 nm for the Cu^{II} porphyrin and at 390, 467 and 634 nm for the Ni^{II} porphyrin. The similarity of the spectroelectrochemical results of the Cu^{II} and Ni^{II} porphyrins with each other and with the spectroelectrochemical results of the free-base porphyrin lead us to conclude that reduction of the Cu^{II} and Ni^{II} porphyrins observed by cyclic voltammetry is localized on the porphyrin ring resulting in a cation radical. Spectroelectrochemical results for the reduction of FeT3M4HPPCl in dmf (Figure 3D) at -0.80 V vs. Ag/AgCl indicate a decomposition of the complex as evidenced by a sharp decrease of the Soret band with only 50% of the original spectrum regenerated upon oxidation of the solution at 0.0 V. It is also conceivable that the complex adsorbed onto the platinum mesh electrode.

Electrode Adsorption Studies

After scoring the surface of the edge-plane pyrolytic graphite (EPG) electrode, by using 600 grit sandpaper, aliquots (10 μ L) of 0.2–0.5 mM solutions of acetone containing the desired complex were placed onto the electrode surface and the solvent allowed to evaporate under ambient conditions. Reproducible results were obtained in this manner as indicated by CV experiments. Electrochemical properties of the complexes adsorbed onto an EPG electrode were studied in 0.5 M H₂SO₄ by cyclic voltammetry.

Anodic cycling of the coated electrodes reveal an irreversible oxidation wave between 0.75 and 0.80 V vs. Ag/AgCl, for all complexes studied. On the reverse scan a new reduction wave coupled to a new oxidation wave appears with the disappearance of the initial irreversible oxidation process. The similarity between the redox chemistry of the adsorbed complexes suggests that the electrochemical process is occurring at the peripheral 4-hydroxy-3-methoxyphenyl groups. Figure 4 illustrates this behavior for an EPG electrode coated with FeT3M4HPP. A chemical step follows the initial oxidation of the 4-hydroxy-3-methoxyphenyl groups of the porphyrin (peak I in Figure 4), most likely demethylation of the methoxy substituents leading to a highly reactive “quinonoid” structure capable of reacting to form a redox-active film on the electrode surface.^[28] The newly formed quinone undergoes reduction to the hydroquinone (peak II_a in Figure 4), which is coupled to the oxidation of the hydroquinone back to the quinone form (peak II_b in Figure 4). This electrochemical/chemical/electrochemical ECE-type mechanism explains the observed electrochemical behavior of the adsorbed complexes. Electrochemical studies of eugenol [2-methoxy-4-(2-pro-

phenyl)phenol] immobilized on glassy-carbon electrodes in aqueous solutions show very similar electrochemistry to that shown in Figure 4. This behavior has been attributed to a similar ECE mechanism initiated by oxidative demethylation.^[29]

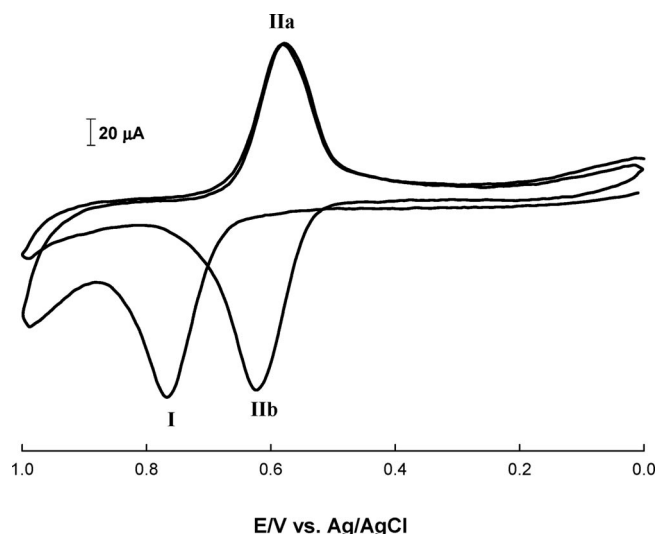


Figure 4. Cyclic voltammogram of an EPG electrode coated with FeT3M4HPPCl measured in 0.5 M H₂SO₄ at room temperature. Scan rate 50 mV/s.

Because the new redox couple is derived from a quinone-like structure, its redox chemistry should depend on the pH of the solution. To test this, we examined electrodes coated with the free-base porphyrin or metalloporphyrins, which had been oxidized in 0.5 M H₂SO₄, and studied the newly formed redox couple in buffered solutions of different pH. A linear relation of $E_{1/2}$ to pH with a slope of -0.060 V $\pm$ 0.010 V/pH unit indicates a $2e^-/2H^+$ process in agreement with a quinone-like surface structure.^[29] Figure 5

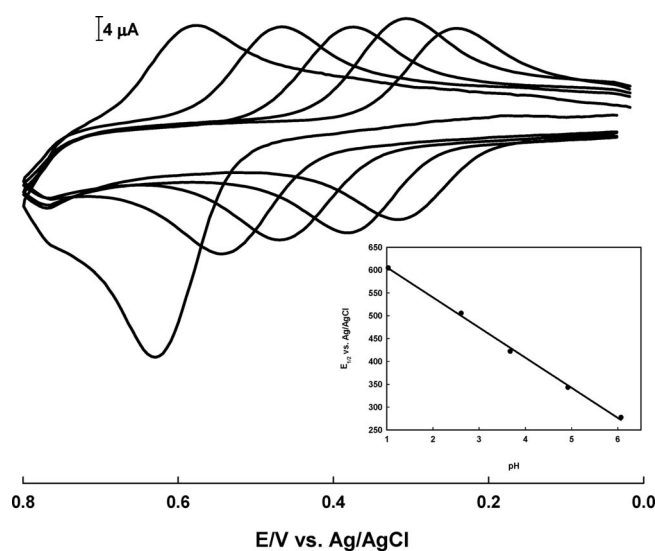


Figure 5. Cyclic voltammograms of CoT3M4HPP, adsorbed onto an EPG electrode after anodic conditioning in 0.5 M H₂SO₄, measured in buffered solutions with a pH range of 1.0–6.1. Inset: plot of $E_{1/2}$ vs. pH. Scan rate 50 mV/s.

illustrates the results of a pH study performed on an EPG electrode coated with CoT3M4HPP after it had been oxidized in 0.5 M H₂SO₄. As [H⁺] decreases the redox couple shifts to lower potentials. A plot of $E_{1/2}$ values vs. pH (inset Figure 5) gives a slope of -0.058 V/pH unit, consistent with a $2e^-/2H^+$ process.

Studies of the free-base porphyrin and the Fe, Ni and Cu porphyrins gave similar results with slopes of -0.070 V/pH unit, -0.063 V/pH unit, -0.063 V/pH unit and -0.063 V/pH unit, respectively. Further studies of the electrode surface are needed to allow us to propose an accurate structure of the surface of the electrochemically modified electrodes.

Surface concentration was determined to be 2.0×10^{-9} mol/cm² for the free-base porphyrin and 5.0×10^{-9} mol/cm² for the metal complexes. This indicates multiple layers on the surface of the electrode. Analysis of the charge under the initial oxidation wave (peak I in Figure 4) and the charge under the newly formed reduction and oxidation waves (peaks II_a and II_b, respectively) allow us to determine the number of electrons transferred per molecule during each electrochemical process using Equation (1).

$$Q = nFA\Gamma \quad (1)$$

where Q is the charge in Coulombs, n is the number of electrons transferred, F is the Faraday constant and Γ is the surface concentration in mol/cm². Assuming that all of the complexes adsorbed on the electrode are electroactive, Table 2 gives the results of this calculation.

Table 2. Values of n determined by analysis of the cyclic voltammograms of adsorbed complexes.^[a]

Complex	n (peak I)	n (peak II _a)	n (peak II _b)
H ₂ T3M4HPP	7	3	3
FeT3M4HPP	^[a]	3	3
CoT3M4HPP	7	4	4
NiT3M4HPP	6	5.5	3
CuT3M4HPP	3	2	1.5

[a] Overlapping redox waves prevented a clear determination of charge.

The data in Table 2 suggest that the assumption that all adsorbed complexes take part in the redox chemistry is most likely false. This is not entirely unexpected due to the multiple layers on the electrode. In nearly every case the coupled redox waves II_a and II_b transfer the same number of electrons for oxidation and reduction consistent with the pH studies. It is also apparent that the first oxidation involves more electrons than the subsequent redox couple formed suggesting that the newly formed quinone is accompanied by a chemical reaction (possibly polymerization), which alters the surface structure.

For adsorbed electroactive species scan-rate dependence shows peak currents increasing linearly with increasing scan rate as governed by Equation (2).^[30]

$$i_p = (n^2 F^2 / 4RT) A \Gamma \nu \quad (2)$$

where n is the number of electrons transferred per adsorbed molecule, A is the area of the electrode, Γ is the surface

concentration, ν is the scan rate in mV/s, F is the Faraday constant (96500 C/mol), R is the gas constant and T is the temperature in Kelvin. The linear dependence of the peak current on the scan rate indicates that the redox couples are due to surface-confined species and are not influenced by diffusion effects. Figure 6 illustrates the scan-rate dependence of the redox couple formed from oxidative cycling of adsorbed CuT3M4HPP on edge-plane pyrolytic graphite in acidic solution. The inset shows the linear relationship of i_{pa} vs. scan rate, with a slope equal to $(n^2 F^2 / 4RT) A \Gamma$.

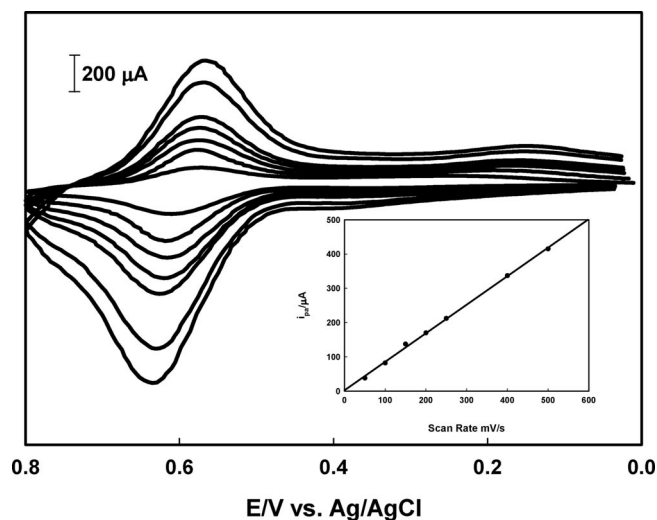


Figure 6. Scan-rate dependence for adsorbed CuT3M4HPP onto an EPG electrode after anodic cycling in 1.0 M H₂SO₄. Inset: plot of i_{pa} vs. scan rate.

O₂ Electrocatalysis

The electrocatalytic reduction of O₂ in air-saturated 0.5 M H₂SO₄ was studied at an EPG electrode coated with the free-base porphyrin or the metalloporphyrins by using rotating-disk-electrode (RDE) voltammetry. Reduction of O₂ at a bare EPG electrode in air-saturated 0.5 M H₂SO₄ occurs with an $E_{1/2} = -0.35$ V vs. Ag/AgCl. When coated with the free-base porphyrin, no appreciable electrocatalysis over the bare electrode was observed. An EPG electrode coated with CuT3M4HPP reduces molecular oxygen with an $E_{1/2} = 0.10$ V vs. Ag/AgCl, a catalytic shift of 450 mV compared to the bare electrode. Oxidation of the CuT3M4HPP-modified electrode to create the quinone-like surface does not affect the catalytic ability of the electrode. In the case of an EPG electrode coated with NiT3M4HPP, oxygen reduction occurs with an $E_{1/2} = 0.20$ V vs. Ag/AgCl, a catalytic shift of 550 mV compared to the bare electrode. However, no change in the catalytic ability of this modified electrode was observed upon oxidation. RDE studies of the CuT3M4HPP and NiT3M4HPP electrodes did not give reproducible results, and therefore it was not possible to analyze the mechanism of oxygen reduction at these electrodes.

When coated with FeT3M4HPPCl, the EPG electrode reduces oxygen with an $E_{1/2} = 0.05$ V vs. Ag/AgCl, a catalytic shift of 400 mV compared to the bare EPG electrode.

RDE studies of the iron porphyrin modified electrode did not give consistent plateau currents and therefore could not be further analyzed. However, when the iron porphyrin electrode was first oxidized to create the quinone-like structure on the electrode prior to oxygen reduction studies, more consistent plateau currents were obtained (Figure 7). It should be mentioned, however, that oxidation of the coated electrode did not make the surface more catalytic relative to reduction of oxygen at the un-oxidized coated electrode.

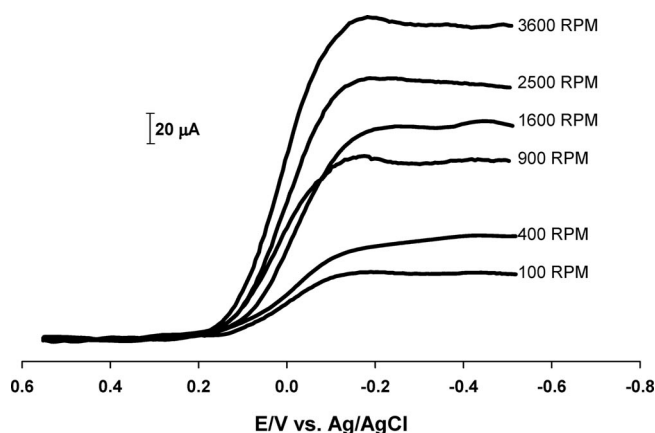


Figure 7. Reduction of O_2 at a rotating-disk electrode coated with FeT3M4HPPCl after oxidation. Current-potential curves in air-saturated 0.5 M H_2SO_4 . Scan rate 10 mV/s.

The Koutecký–Levich plot (Figure 8) relates the plateau-current density to the rotation rate by using Equation (3).^[31]

$$\frac{1}{I_L} = \frac{1}{I_k} + \frac{1}{B\omega^{1/2}}$$

$$B = 0.2nFCv^{-1/6}D^{2/3} \quad (3)$$

where I_L is the diffusion-limited current, I_k is the current density ($A\,cm^{-2}$), n is the number of electrons for the reaction, F is the Faraday constant ($96500\,C\,mol^{-1}$), D is the

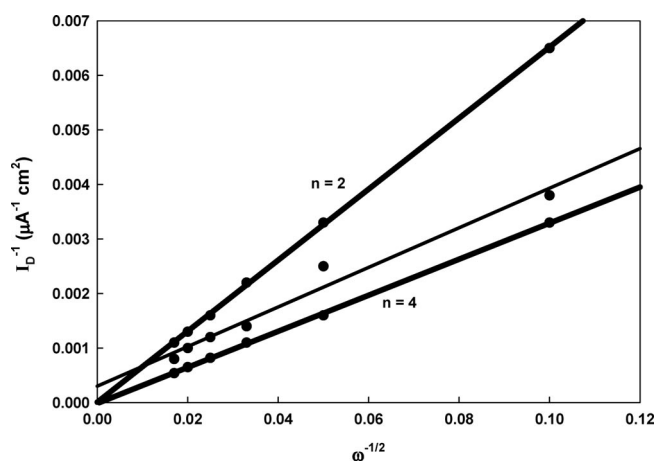


Figure 8. Koutecký–Levich plot of the inverse of the plateau current vs. the inverse of the square root of the rotation rate for the curves in Figure 7. The theoretical two-electron and four-electron lines are marked $n = 2$ and $n = 4$, respectively.

diffusion coefficient of O_2 in the solution ($2.0 \times 10^{-5}\,cm^2\,s^{-1}$), ν is the kinematic viscosity of the solution ($0.01\,cm^2\,s^{-1}$), C is the concentration of O_2 in the air-saturated solution (0.2 mM), and ω is the rotation rate (rpm). I_k is the kinetic current density for O_2 reduction and can be calculated from the intercept of the Koutecký–Levich plot. The slope for the Koutecký–Levich plot for the experimental data is the same as the slope for the theoretical $n = 4$ line giving a value of $n = 4$ (Figure 8). This indicates that the FeT3M4HPP reduces oxygen directly to water by a four-electron process.

Figure 9 illustrates the results of oxygen reduction at an EPG electrode coated with CoT3M4HPP in an air-saturated 0.5 M H_2SO_4 solution. The $E_{1/2}$ for reduction of oxygen at this electrode is 0.15 V vs. Ag/AgCl, a catalytic shift of 500 mV compared to the bare EPG electrode. From this data it can be observed that the reaction kinetics for the reduction of oxygen at this electrode is relatively slow suggested by the constant rise in the plateau currents.

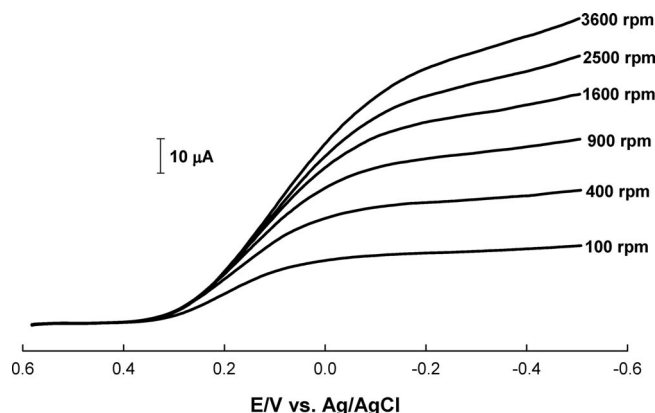


Figure 9. Reduction of O_2 at a rotating-disk electrode coated with CoT3M4HPP prior to oxidation. Current-potential curves in air-saturated 0.5 M H_2SO_4 . Scan rate 10 mV/s.

Upon oxidation of the CoT3M4HPP-coated EPG electrode in 0.5 M H_2SO_4 the rise in current is much sharper indicating faster electrode kinetics (Figure 10). The $E_{1/2}$ for the reduction of oxygen at this oxidized electrode is 0.25 V vs. Ag/AgCl, a catalytic shift of 600 mV compared to the bare electrode and a catalytic shift of 100 mV compared to the CoT3M4HPP-coated EPG electrode prior to oxidation (Figure 10).

Comparison of the Koutecký–Levich plots for the CoT3M4HPP-coated electrodes prior to and after oxidation is illustrated in Figure 11. Prior to oxidation, the Koutecký–Levich line is identical in slope to the theoretical $n = 2$ line indicating that prior to oxidation CoT3M4HPP reduces oxygen by two electrons to form hydrogen peroxide. The slope of the Koutecký–Levich line for the data after oxidation of the CoT3M4HPP-coated electrode lies between the theoretical $n = 2$ and $n = 4$ lines but is closer to the slope of the $n = 2$ line. The value for n from this line is 2.3 suggesting that 15% of the oxygen that is reduced at

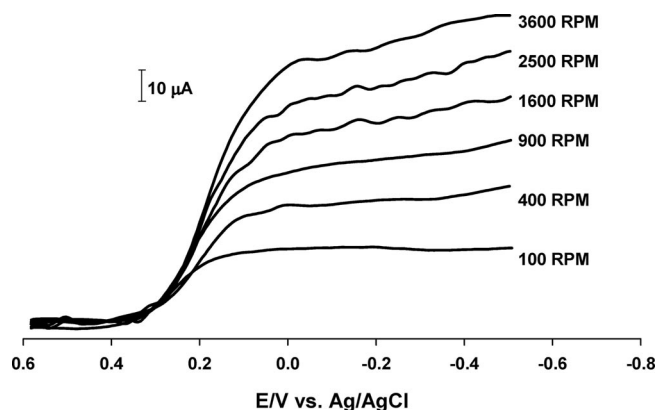


Figure 10. Reduction of O_2 at a rotating-disk electrode coated with CoT3M4HPP after oxidation. Current-potential curves in air-saturated 0.5 M H_2SO_4 . Scan rate 10 mV/s.

this electrode is reduced directly to water by four electrons, whereas 85% of the oxygen is reduced by two electrons to hydrogen peroxide.

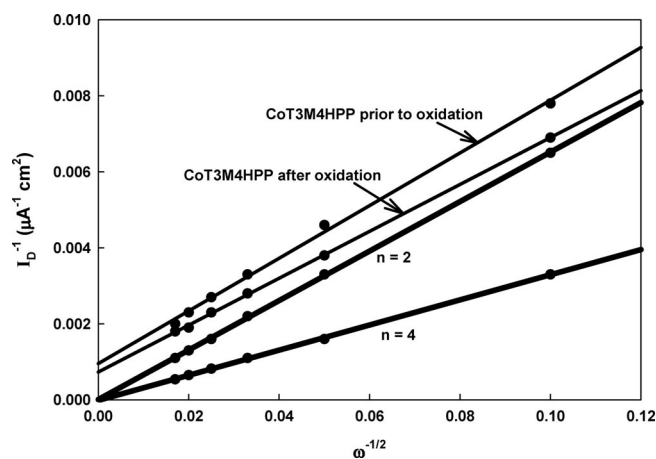


Figure 11. Koutecký–Levich plots of the inverse of the plateau current vs. the inverse of the square root of the rotation rate for the curves in Figures 9 and 10. The theoretical two-electron and four-electron lines are marked $n = 2$ and $n = 4$, respectively.

In a previous study we showed that a similar complex, *cis*-Pt(dmsO){[5-(4-pyridyl)-10,15,20-tris(4-hydroxy-3-methoxyphenyl)porphyrinato]cobalt(II)}Cl₂, in which one of the 4-hydroxy-3-methoxyphenyl substituents is replaced with a pyridyl group coordinated to a Pt^{II} complex could effectively reduce more than 65% of the oxygen directly to water at potentials similar to those observed for the Co^{II} porphyrin in the current study.^[33] This is considerably higher than the 15% observed for the [tetrakis(4-hydroxy-3-methoxyphenyl)porphyrinato]cobalt(II) of this study. It is speculated that the Pt^{II} moiety places more electron density on the Co^{II} center facilitating the Co^{II}–O₂ interaction, which leads to a transfer of four electrons. It is clear that enhancing the electrocatalytic ability of the Co^{II} complex of this study requires more than formation of the new surface com-

plex generated by anodic cycling. Further studies with different peripheral metal complexes are underway to investigate this phenomenon.

Conclusions

This paper reports on the synthesis and characterization, by UV/Vis spectroscopy and cyclic voltammetry, of a series of metalloporphyrins (Figure 1). Adsorption of these complexes onto EPG electrodes followed by oxidation in 0.5 M H_2SO_4 results in a new redox-active, pH-dependent modified electrode. All of the metalloporphyrins catalyze the reduction of oxygen relative to the bare EPG electrode prior to formation of the new redox couple by oxidation. RDE studies of the Fe^{III} porphyrin, after oxidation, indicate that this modified electrode reduces oxygen by four electrons directly to water. When the Co^{II} porphyrin is placed on the EPG electrode and oxidized in 0.5 M H_2SO_4 , its ability to reduce oxygen is improved relative to the coated electrode prior to oxidation. It was not possible to analyze the Ni^{II} and Cu^{II} porphyrin coated electrodes by RDE, because of the instability of the complex in acidic solution, even after oxidation of the electrode.

Experimental Section

Materials: All reagents were analytical grade and used without further purification, unless stated otherwise. Acetone, methanol, dimethylformamide (dmf), tetrabutylammonium hexafluorophosphate (TBAPF₆, used as a supporting electrolyte for solution electrochemistry) and extra-dry (<50 ppm H_2O) dmf for electrochemistry (ACROS), sulfuric acid, cobalt(II) acetate, iron(II) chloride, copper(II) chloride, and nickel(II) chloride were used as received. The pH of the buffer solutions were measured to ± 0.01 at 25 °C by using a Denver Instrument UltraBasic pH meter calibrated with standard pH 4.00 and 10.00 buffer solutions (Fisher): 2.61 (0.2 M NaH_2PO_4 , 0.05 M H_3PO_4), 3.67 (0.24 M CH_3COOH , 0.05 M CH_3COONa), 4.92 (0.2 M CH_3COONa , 0.05 M CH_3COOH), 6.07 (0.2 M NaH_2PO_4 , 0.05 M Na_2HPO_4). Elemental analyses were performed by Atlantic Microlabs, Norcross, GA.

5,10,15,20-Tetrakis(4-hydroxy-3-methoxyphenyl)porphyrin [H₂T3-M4HPP]: A solution of propionic acid (70 mL), 4-hydroxy-3-methoxybenzaldehyde (2.85 g, 18.7 mmol) and freshly distilled pyrrole (1.30 mL, 18.7 mmol) were refluxed for 30 min. The purple precipitate was filtered and washed with cold methanol. The crude product was dissolved in thf and crystallized by the addition of hot methanol. Yield 0.26 g (7.0%). UV/Vis (dmf): λ_{max} [nm] (ϵ [$10^{-4} \text{ M}^{-1} \text{ cm}^{-1}$]) = 427 (28.5), 520 (14.4), 556 (10.8), 596 (4.74), 652 (6.10).

[5,10,15,20-Tetrakis(4-hydroxy-3-methoxyphenyl)porphyrinato]cobalt(II): Cobalt(II) acetate (0.0560 g, 0.225 mmol) was added to a solution of H₂T3M4HPP (0.149 g, 0.188 mmol) in dmf (10.0 mL). The reaction mixture was refluxed under nitrogen for 30 min. The product was precipitated by the addition of distilled water (20 mL), filtered, washed with distilled water ($3 \times 10 \text{ mL}$) and air-dried. Yield 0.0803 g (48.9%) of a purple powder. UV/Vis (acetone): λ_{max} [nm] (ϵ [$10^{-4} \text{ M}^{-1} \text{ cm}^{-1}$]) = 422 (17.4), 534 (1.31). C₄₈H₃₆CoN₄O₈ · H₂O (873.78): calcd. C 65.98, H 4.38, N 6.41; found C 65.44, H 4.70, N 6.22.

[5,10,15,20-Tetrakis(4-hydroxy-3-methoxyphenyl)porphyrinato]iron(III): Iron(II) chloride (0.0151 g, 0.0751 mmol) was added to a solution of H₂T3M4HPP (0.0532 g, 0.0626 mmol) in dmf (10.0 mL). The reaction mixture was refluxed under nitrogen for 30 min. The product was precipitated by the addition of distilled water (20 mL), filtered, washed with distilled water (3 × 10 mL) and air-dried. Yield 0.0395 g (74.0%) of a purple powder. UV/Vis (acetone): λ_{max} [nm] (ϵ [10⁻⁴ M⁻¹ cm⁻¹]) = 423 (6.80). C₄₈H₃₆ClFeN₄O₈ (888.13): calcd. C 64.91, H 4.46, N 6.51; found C 64.80, H 4.46, N 7.15.

[5,10,15,20-Tetrakis(4-hydroxy-3-methoxyphenyl)porphyrinato]copper(II): Copper(II) chloride (0.0110 g, 0.0751 mmol) was added to a solution of H₂T3M4HPP (0.0517 g, 0.0626 mmol) in dmf (10.0 mL). The reaction mixture was refluxed under nitrogen for 30 min. The product was precipitated by the addition of distilled water (20 mL), filtered, washed with distilled water (3 × 10 mL) and air-dried. Yield 0.0504 g (93.6%) of a maroon powder. UV/Vis (acetone): λ_{max} [nm] (ϵ [10⁻⁴ M⁻¹ cm⁻¹]) = 424 (33.4), 542 (1.84), 580 (0.50). C₄₈H₃₆CuN₄O₈ (860.38): calcd. C 67.01, H 4.22, N 6.51; found C 67.11, H 4.35, N 6.24.

[5,10,15,20-Tetrakis(4-hydroxy-3-methoxyphenyl)porphyrinato]nickel(II): Nickel(II) chloride (0.0189 g, 0.0751 mmol) was added to a solution of H₂T3M4HPP (0.0516 g, 0.0626 mmol) in dmf (10.0 mL). The reaction mixture was refluxed under nitrogen for 30 min. The product was precipitated by the addition of distilled water (20 mL), filtered, washed with distilled water (3 × 10 mL) and air-dried. Yield 0.0484 g (90.4%) of a purple powder. UV/Vis (acetone): λ_{max} [nm] (ϵ [10⁻⁴ M⁻¹ cm⁻¹]) = 423 (23.4), 530 (1.92). C₄₈H₃₆N₄NiO₈·H₂O (873.54): calcd. C 66.00, H 4.38, N 6.72; found C 65.45, H 4.39, N 6.77.

Procedures and Instrumentation: UV/Vis spectra were recorded at room temperature by using a Shimadzu 1501 photodiode-array spectrophotometer with 2 nm resolution. Samples were measured in reagent-grade acetone in 1 cm quartz cuvettes. Solution cyclic voltammograms were recorded by using a one-compartment, three-electrode cell (model 630A electrochemical analyzer from CH-Instruments) equipped with a platinum-wire auxiliary electrode. The working electrode was a 2.0 mm diameter glassy-carbon electrode from CH-Instruments. The working electrode was polished first by using 0.30 μ followed by 0.05 μ alumina polish (Buehler) and tapped dry with a Kimwipe prior to use. Potentials were referenced to an Ag/AgCl electrode. The supporting electrolyte was 0.1 M Bu₄NPF₆, and the measurements were carried out in extra-dry dmf. Spectroelectrochemical measurements were conducted according to a previously described method by using a locally constructed H-cell, which uses a quartz cuvette as the working compartment.^[32] The working and auxiliary compartments were separated by a fine porous-glass frit. The working electrode was a high-surface-area platinum mesh, and the auxiliary electrode was a platinum wire. The reference electrode was Ag/AgCl (0.50 V vs. SHE). The measurements were made in 0.1 M TBAPF₆ dmf solutions that were approximately 1 × 10⁻⁶ M in metal complex. The electrolysis potential was controlled by a CH-Instruments 630A electrochemical analyzer. Adsorption of the porphyrin and metalloporphyrins onto edge-plane pyrolytic-graphite EPG electrode (AFE3T 5.0 mm diameter, Pine Instrument Co.), which had been roughened by using 600 grit sandpaper, was accomplished by placing 10 μ L aliquots of 0.2 mM (porphyrin) or 0.5 mM (metalloporphyrins) acetone solutions onto the electrode surface and allowing the solvent to evaporate at room temperature. Cyclic voltammetry and rotating disc electrode (RDE) experiments of the modified electrodes were performed by using a Pine AFCBP1 bipotentiostat and an AFMSRX rotator (Pine Instrument Co.) in 0.5 M sulfuric acid solutions.

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