Electrocatalytic reduction of oxygen at electrodes coated with a bimetallic cobalt(II)/platinum(II) porphyrin

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Edge plane pyrolytic graphite (EPG) electrodes coated with 5-(4-pyridyl)-10,15,20-tris(3-methoxy-4-hydroxyphenyl)porphyrin and its Pt(II) and Co(II)/Pt(II) analogs undergo an electrochemical– chemical–electrochemical (ECE) reaction when anodically scanned in 1.0 M HClO₄. 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 Co(II)/Pt(II) bimetallic porphyrin show a catalytic shift of 500 mV for the reduction of O_2 when compared to the reduction of O_2 at a bare EPG electrode. An additional catalytic shift of *ca*. 100 mV is observed for O_2 reduction at an EPG electrode coated with the Co(II)/Pt(II) porphyrin which has been oxidized in 1.0 M HClO₄. In addition to the added electrocatalysis a significant percentage of O_2 reduced at the oxidized Co(II)/Pt(II) EPG electrode is converted to H₂O as determined by rotating disk electrode measurements.

Introduction

Cobalt porphyrins have been extensively studied as catalysts for the reduction of molecular oxygen.¹ The interest stems from the need to find alternatives to platinum, a costly and easily poisoned catalyst currently used in hydrogen/oxygen and alcohol/oxygen fuel cells.² Many transition-metal complexes have been investigated for their catalytic ability toward O₂ reduction but Co macrocycles have shown the most promise.³ At issue with Co macrocycles in general and specifically Co porphyrins is the fact that most are only capable of reducing molecular oxygen to hydrogen peroxide, a two-electron/two-proton process, instead of the desired four-electron/four-proton process which produces water.⁴ Reduction by two electrons lowers the efficiency of the fuel cell in addition to producing a deleterious product, H_2O_2 , unsafe for the environment and damaging to the catalyst itself.

To overcome the two electron/two proton reduction of oxygen observed for most cobalt porphyrins cofacial dicobalt bisporphyrins have been synthesized.⁵ These complexes form a μ -superoxo complex stabilizing the O₂ reduction intermediate resulting in a four-electron reduction of O₂ in acidic media. Other researchers have chosen a different route to the stabilization of the Co-peroxo reduction intermediate using multi-metallic cobalt porphyrins as the electrocatalyst.⁶ For example coordination of $Ru(NH_3)_5$ or $Os(NH_3)_5$ to the pyridyl nitrogens of cobalt(II) tetrakis(4-pyridyl)porphyrin converts this electrocatalyst from a two-electron to a four-electron O_2 reduction catalyst.⁷ The enhanced catalysis is attributed to stabilization of the Coperoxo reduction intermediate through π -backbonding from the peripheral Ru(II) or Os(II) metal centers.8 A minimum of three peripheral metal complexes are required to achieve the fourelectron reduction of oxygen.9

A practical aspect of the electrocatalyst is its stability in acidic solution the medium of choice for many fuel cells. Incorporation

of the electrocatalyst into a polymeric matrix has increased the stability and lifetime of a number of catalysts.¹⁰ Thin conductive films formed from the electropolymerization of porphyrins are used as electrocatalysts,¹¹ biosensors¹² and in electroanalysis.¹³ 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 have been used to catalyze the reactions of small molecules.¹⁴

We have been interested in combining into a single molecule the stabilizing affects associated with electropolymerization and the enhanced catalysis of multi-metallic cobalt porphyrins. We recently described the synthesis and catalytic ability of a Co(II)/Pt(II) bimetallic porphyrin which undergoes electropolymerization on graphite electrodes. These modified electrodes demonstrated enhanced electrocatalysis for O2 reduction in acidic solutions.¹⁵ It was concluded that the best catalytic behavior required polymerization of the bimetallic porphyrin, the cobalt(II) metal center and the platinum(II) peripheral metal. Removing any one of these components decreased the catalytic ability of the modified electrode. To continue this work we present here a study of Pt(II) and Co(II)/Pt(II) complexes of the previously synthesized porphyrin 5-(4-pyridyl)-10,15,20-tris(3-methoxy-4-hyroxyphenyl)porphyrin, 1 (Fig. 1).¹⁶ The synthesis, spectroscopic and electrochemical properties of the compounds in Fig. 1 are presented. Electrode adsorption studies and the electrocatalysis of molecular oxygen in acidic media using the Co(II)/Pt(II) bimetallic porphyrin is also discussed.

Experimental

Preparation of complexes

cis-Pt(DMSO)₂Cl₂ was synthesized as previously described.¹⁷

5-(4-Pyridyl)-10,15,20-tris(3-methoxy-4-hydroxyphenyl)porphyrin, 1. A modified procedure to the previous synthetic

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Fig. 1 Complexes in this study.

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procedure was used to synthesize this porphyrin. To a solution of 7.5 g (0.049 mol) of 3-methoxy-4-hydroxybenzaldehyde and 1.6 mL (0.015 mol) of 4-pyridinecarbaldehyde in 100 mL of propionic acid was added 4.4 mL (0.066 mol) of freshly distilled pyrrole. The solution was refluxed for 1 h after which it was cooled to room temperature and cautiously added to 200 mL of a 50 : 50 methanol-aqueous ammonia solution cooled in an ice-bath. The slurry was refrigerated overnight, filtered and washed (3 \times 100 mL) with methanol. The resulting black powder was extracted in a Soxhlet first with methanol for 24 h to remove polymer byproduct followed by ethyl acetate for 24 h to extract the porphyrins. The volume of the ethyl acetate extract was reduced to ca. 70 mL and chromatographed on silica gel using ethyl acetate as eluent. The second band from the column was collected giving a purple powder upon removal of the solvent 130 mg (0.17 mmol, 1.15% yield). UV-Vis (CH₂Cl₂) λ_{max}/nm (10⁻⁴ ε/M^{-1} cm⁻¹): 425 (16.6), 519 (1.13), 557 (0.78), 594 (0.46), 651 (0.43). ¹H NMR (300 MHz, CDCl₃, TMS): δ 9.03 (2H, d, 2,6-pyridyl), 8.95 (6H, m, pyrrole β), 8.79 (2H, d, pyrrole β), 8.18 (2H, d, 3,5-pyridyl), 7.79 (6H, m, 2{3-methoxy-4-hydroxyphenyl} and 6{3-methoxy-4hydroxyphenyl}), 4.01 (9H, s, m-methoxy), -2.79 (2H, s, internal pyrrole). Anal. Calc. for C₄₆H₃₅N₆O₆·1.5H₂O: C 70.76; H, 4.91; N, 8.97. Found: C, 70.97; H, 5.06; N, 8.58%.

cis-Pt(DMSO)[5-(4-pyridyl)-10,15,20-tris(3-methoxy-4-hydroxyphenyl)porphyrin|Cl₂, 2. To a solution containing 70 mg (0.093 mmol) of 1 in 20 mL of CH₂Cl₂ was added 39 mg (0.093 mmol) *cis*-Pt(DMSO)₂Cl₂ and the solution was stirred for 4 h at ambient temperature. The reaction was chromatographed on silica gel using a 50 : 50 ethyl acetate-chloroform solution as eluent. The first red band from the column was collected and the solvent removed resulting in 65 mg of a purple powder (0.056 mmol, 61% yield). UV-Vis (CH₂Cl₂) λ_{max}/nm $(10^{-4}\varepsilon/M^{-1} \text{ cm}^{-1})$: 427 (21.2), 521 (1.50), 560 (1.12), 595 (0.56), 653 (0.60). ¹H NMR (300 MHz, CDCl₃, TMS): δ 9.19 (2H, d, 2,6-pyridyl), 8.94 (4H, s, pyrrole β), 8.79 (2H, d, pyrrole β), 8.28 (2H, d, 3,5-pyridyl), 7.76 (6H, m, 3-methoxy-4-hydroxyphenyl), 4.01 (9H, s, p-methoxy), 3.62 (6H, s, DMSO), -2.79 (2H, s, internal pyrrole). Anal. Calc. for C₄₈H₄₁N₅O₇SCl₂Pt·3H₂O: C, 50.05; H, 4.11; N, 6.08. Found: C, 50.04; H, 3.83; N, 5.94%.

cis-Pt(DMSO)[5-(4-pyridyl)-10,15,20-tris(3-methoxy-4-hydroxyphenyl)porphyrinatocobalt(II)]Cl₂, 3. To a solution of 70 mg (0.064 mmol) of 2 in 20 mL of chloroform was added 32 mg (0.13 mmol) of cobalt(II) acetate in 1.0 mL of methanol. The reaction mixture was refluxed under nitrogen for 30 min followed by reducing the volume to *ca.* 1 mL under reduced pressure. The product was precipitated by addition of 10 mL of distilled water, filtered and washed 3 × 10 mL with distilled water and dried under vacuum at 100 °C for 10 h. 35 mg of a maroon powder (0.030 mmol, 47% yield) was recovered. UV-Vis (CH₂Cl₂) $\lambda_{max}/nm (10^{-4}\varepsilon/M^{-1} cm^{-1})$: 418 (23.2), 532 (1.44). Anal. Calc. for C₄₈H₃₉N₅O₇SCl₂PtCo·5H₂O: C, 46.31; H, 3.97; N, 5.63; S, 2.58. Found: C, 46.00; H, 3.60; N, 5.73; S, 3.12%.

Materials

All reagents were analytical grade and used without further purification unless stated otherwise. 3-methoxy-4-hydroxybenzaldehyde, 4-pyridinecarbaldehyde, propionic acid, methanol, N,N'-dimethylformamide (DMF), tetrabutylammonium hexafluorophosphate (Bu₄NPF₆, used as supporting electrolyte for solution electrochemistry) and extra dry (<50 ppm H₂O) DMF for electrochemistry (ACROS), methylene chloride, perchloric acid, cobalt(II) acetate, 60-200 mesh silica gel (Fisher) were used as received. The buffer solutions and their pH values measured to ±0.01 at 25 °C using a Denver Instrument UltraBasic pH meter calibrated with standard pH 4.00 and 10.00 buffer solutions (Fisher), were as follows: 0.2 M NaH₂PO₄, 0.05 M H₃PO₄ (2.64); 0.24 M CH₃COOH, 0.05 M CH₃COONa (3.74); 0.2 M CH₃COONa, 0.05 M CH₃COOH (5.04); 0.2 M NaH₂PO₄, 0.05 M Na_2HPO_4 (6.67). Elemental analyses were performed by Atlantic Microlabs, Norcross, GA.

Procedures and instrumentation

¹H NMR spectra were recorded on a Bruker 300 MHz spectrophotometer using deuterated chloroform (CDCl₃) referenced to teteramethylsilane (TMS) as the internal standard. UV-Vis spectra were recorded at room temperature using a Schimadzu 1501 photodiode array spectrophotometer with 2 nm resolution. Samples were run in UV-grade CH_2Cl_2 in 1 cm quartz cuvettes. Solution cyclic voltammograms were recorded using a onecompartment, 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 using 0.30 μ followed by 0.05 μ alumina polish (Buehler) and then sonicated for 20 s and tapped dry with a kimwipe prior to use. Potentials were referenced to a saturated calomel electrode (SCE). The supporting electrolyte was 0.1 M Bu_4NPF_6 and the measurements were made in extra dry DMF. Adsorption of the porphyrin and metalloporphyrins 1–3 onto an edge plane pyrolytic graphite EPG electrode (AFE3T 5.0 mm diameter, Pine Instrument Co.) which had been roughened using 600 grit sandpaper was accomplished by placing 5–15 μ L aliquots of 1.0 mM acetone solutions of the porphyrin and metalloporphyrins onto the electrode surface and allowing the solvent to evaporate at 20 °C. The electrodes were then washed with distilled water and tapped dry with a kimwipe. Cyclic voltammetry and rotating disc electrode (RDE) experiments of the modified electrodes were performed using a Pine AFCBP1 bipotentiostat and an AFMSRX rotator (Pine Instrument Co.) in 1.0 M perchloric acid solutions.

Results and discussion

Characterization of complexes 1-3

Synthesis of porphyrin 1 was complicated by the formation not only of polymeric material but the inevitable formation of other porphyrins expected when two different aldehydes are used. Once the majority of polymeric byproduct was removed from the reaction mixture by methanol extraction six porphyrins remained. The use of ethyl acetate to extract the porphyrins from the remaining polymeric byproduct resulted in good separation of the porphyrins by column chromatography. Attempts to extract the porphyrins into ethyl acetate prior to the methanol washing led to streaking on the column. Integration of the methoxy protons and 2,6-pyridyl protons (ratio of 9 : 2) in the NMR spectra helped identify the monopyridyl porphyrin 1. Coordination of $Pt(DMSO)Cl_2$ was straight-forward leading to complex 2 in relatively high yield. Comparison of the methoxy protons of the porphyrin, a singlet at 4.01 ppm, and the methyl protons of the Pt(II) coordinated DMSO, a singlet at 3.62 ppm, indicated coordination of the Pt(II) moiety. Repeated attempts using two different synthetic methods to insert Co(II) into the porphyrin 1 led to an insoluble product each time. For reasons that are unclear, insertion of Co(II) into the porphyrin-Pt(II) complex 2 was comparatively easy leading to a pure tractable compound, 3 (Fig. 1).

Fig. 2 illustrates the differences in the electronic spectra of the complexes 1-3 in CH₂Cl₂. A Soret band at 425 nm and four Q-bands at lower energy were observed for complex 1 (Fig. 2, dotted line). A small perturbation of the porphyrin orbitals was seen upon coordination of Pt(DMSO)Cl₂ to the peripheral pyridyl groups most noticeably resulting in a shift of the Soret band to 427 nm and increased intensity of this absorption band (Fig. 2, dashed line). Insertion of Co(II) into complex **2** increases the symmetry of the complex leading to a collapse of the four Q-bands into a single band at 532 nm. In addition the Soret band shifted to 418 nm (Fig. 2, solid line).

Fig. 3 shows the cyclic voltammograms of complexes 1-3 in extra dry DMF with a glassy carbon working electrode. All of the complexes studied display an irreversible oxidation wave at *ca*. 1.00 V *vs*. SCE suggesting, first that this process is associated with the porphyrin, most likely the 3-methoxy-4-hydroxyphenyl groups, and second there is virtually no electronic communication between the Co(II), Pt(II) metal centers and the peripheral groups of the



Fig. 2 Electronic absorption spectra in dichloromethane at room temperature for complex $1 (\dots)$, complex $2 (\dots)$ and complex $3 (\dots)$.



Fig. 3 Cyclic voltammograms of complexes 1-3 in 0.1 M Bu₄NPF₆ in DMF, scan rate = 100 mV s^{-1} , referenced to the saturated calomel electrode (SCE): (A) complex 1, (B) complex 2 and (C) complex 3.

porphyrin. A quasireversible reduction of the non-metallated porphyrin at $E_{1/2} = -1.06$ V vs. SCE (Fig. 3(A)), becomes irreversible and shifted to more negative potentials, $E_{pc} = -1.18$ V, upon coordination of Pt(DMSO)Cl₂ (Fig. 3(B)). An irreversible shoulder at $E_{pc} = -1.03$ V vs. SCE is associated with reduction of the Pt(II) center of complex **2** (Fig. 3(B)).¹⁸ The CV of complex **3** shows similar anodic behavior with a single irreversible oxidation

wave. A reversible redox couple at $E_{1/2} = -0.76$ V vs. SCE can be attributed to the Co^{II/I} redox couple while reduction of the porphyrin and Pt(II) center are shifted to more negative values (Fig. 3(C)). The Co^{III/II} couple was not observed due to slow electron transfer kinetics in DMF.¹⁹

Electrode adsorption studies

After scoring the surface of an edge plane pyrolytic graphite (EPG) electrode, using 600 grit sandpaper, 5–15 μ L of 1.0 mM solutions of acetone containing the desired complex were placed onto the electrode surface and the solvent was 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 1.0 M HClO₄ by cyclic voltammetry.

Complexes 1–3 display an irreversible oxidation, I, with $E_{\rm pa} = 0.77$, 0.81 and 0.76 V vs. SCE respectively when an EPG coated electrode was cycled in 1.0 M HClO₄ (Fig. 4(A), (B) and (C)). This oxidation wave can be associated with oxidation of the 3-methoxy-4-hydroxyphenyl peripheral groups. Upon oxidation of the adsorbed complex a chemical reaction occurs creating a new quasireversible redox couple, IIa/IIb (Fig. 4(A), (B) and (C)), with $E_{1/2} = 0.57$, 0.60 and 0.57 V for electrodes coated with complexes 1–3 respectively. Similarities between the cyclic voltammograms in



Fig. 4 Cyclic voltammograms of complexes 1–3 adsorbed on roughened EPG electrodes in 1.0 M HClO₄, scan rate = 50 mV s⁻¹, referenced to the saturated calomel electrode (SCE): (A) complex 1, (B) complex 2 and (C) complex 3.

Fig. 4 suggest Co(II) and Pt(II) coordination has little effect on the redox chemistry of the adsorbed complexes, further evidence to support the proposition that the irreversible oxidation is localized on the peripheral groups of the porphyrin. The chemical step which follows oxidation of the 3-methoxy-4-hydroxyphenyl groups of the porphyrin is 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.²⁰

Since 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 complexes 1-3 which had been oxidized in 1.0 M HClO₄ 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 -0.059 ± 0.005 V/pH unit indicates a $1e^{-}/1H^{+}$ process in agreement with a quinone like surface structure.²¹ Fig. 5 illustrates the results of a pH study performed on an EPG electrode coated with complex 1 after it had been oxidized in 1.0 M HClO₄. As the [H⁺] decreases the redox couple shifts to lower potentials. A plot of $E_{1/2}$ values vs. pH (Fig. 5, inset) is linear with a slope of -0.064V/pH unit consistent with a 1e⁻/1H⁺ process. Similar studies of complexes 2 and 3 give linear $E_{1/2}$ vs. pH relationships with slopes of -0.059 and -0.054 V per 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.



Fig. 5 Cyclic voltammograms of complex 1 adsorbed onto an EPG electrode after anodic conditioning in 1.0 M HClO₄: (---) pH 0.30, (---) pH 2.64, (\cdots) pH 3.74, (---) pH 5.04, (--) pH 6.67.

O₂ Electrocatalysis

The electrocatalytic reduction of O₂ in 1.0 M HClO₄ was studied at an EPG electrode coated with the Co(II)/Pt(II) porphyrin **3** using cyclic voltammetry and rotating disk electrode (RDE) voltammetry. Reduction of O₂ at a bare EPG electrode in air saturated 1.0 M HClO₄ occurs with an $E_{1/2} = -0.35$ V vs. SCE. An EPG electrode coated with the Co(II)/Pt(II) porphyrin **3** in air saturated 1.0 M HClO₄ reduces O₂ with an $E_{1/2} = 0.14$ V vs. SCE (Fig. 6, dotted line) a catalytic shift of 500 mV compared to the bare EPG electrode. A catalytic shift of nearly 600 mV when



Fig. 6 O_2 reduction at an EPG electrode coated with complex 3 in air saturated 1.0 M HClO₄ prior to oxidation of the surface adsorbed complex (---) and after anodic conditioning (—), scan rate = 100 mV s⁻¹, referenced to the saturated calomel electrode (SCE).

compared to the bare EPG electrode is observed for O_2 reduction at an EPG electrode coated with **3** after oxidation of the surface confined complex (Fig. 6, solid line).

Fig. 7(A) illustrates the results of the RDE experiment performed on an EPG electrode coated with **3** in air-saturated 1.0 M HClO₄ prior to oxidation of the adsorbed complex. A plot of the diffusion-limited current density *vs*. the square root of the rotation rate, the Levich plot, indicates a deviation from linearity at higher rotation rates attributed to a potential independent rate limiting step²² (Fig. 7(B)). The Koutecky–Levich plot (Fig. 7(C)), relates the plateau current density to the rotation rate using eqn (1):²³

$$1/I_{\rm L} = 1/I_{\rm k} + 1/B\omega^{1/2} \tag{1}$$

$$B = 0.2nFCv^{-1/6}D^{2/3}$$

where $I_{\rm L}$ is the current density (A cm⁻²), *n* is the number of electrons for the reaction, *F* is the Faraday constant (96 500 C mol⁻¹), *D* is the diffusion coefficient of O₂ in the solution $(2.0 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1})$, *v* is the kinematic viscosity of the solution $(0.01 \text{ cm}^2 \text{ s}^{-1})$, *C* is the concentration of O₂ in the air-saturated solution (0.25 mM), and ω is the rotation rate (rpm). I_k is the kinetic current density for O₂ reduction and can be calculated from the intercept of the Koutecky–Levich plot. The slope for the Koutecky–Levich plot for the experimental data is very near the slope for the theoretical n = 2 line giving a value for n = 2.3 (Fig. 7(C)). Enhanced catalytic activity toward O₂ reduction by *para*-hydroxyphenyl substituted Co(II) porphyrins has been attributed to the electron-donating ability of these substituents.²⁴ The majority of O₂ is electrocatalytically reduced to H₂O₂, 2e⁻ process, at the EPG electrode coated with **3** prior to oxidation of the adsorbed complex.

Fig. 8(A) illustrates the results of O_2 reduction at an EPG electrode coated with **3**, after surface oxidation, in an air saturated 1.0 M HClO₄ solution. The Levich plot reveals similar deviation from linearity related to the kinetics of Co(II)–O₂ bond formation (Fig. 8(B)). The Koutecky–Levich plot of this data (Fig. 8(C)), gives an *n* value of 3.3 suggesting that a significant amount of O_2 is reduced directly to H₂O at this electrochemically modified surface.

Analysis of the Koutecky-Levich intercept before and after oxidation of the adsorbed complex using eqn (2) reveals information about the current-limiting formation of the $Co-O_2$ bond:

$$I_{\rm k} = nFk\Gamma C_{\rm O_2} \tag{2}$$

where Γ is the surface concentration of catalyst on the electrode (mol cm⁻²) and *k* is the second-order rate constant associated with the current-limiting reaction between Co(II) and O₂ (M⁻¹ s⁻¹). Without a detailed understanding of the structure of the adsorbed complexes after oxidation it is difficult to determine with any certainty the surface concentration, therefore a quantitative look at the rate constant *k* in eqn (2) is not possible. We can however determine qualitatively the effect of oxidation of complex **3** on the rate of interaction between Co(II) and O₂. The ratio of I_k^{b}/n , where n = 2.3, before oxidation to I_k^{a}/n , where n = 3.3, after oxidation gives a relationship between the rate constants k^{b} before and k^{a} after oxidation. The value for this ratio is near unity ($k^{\text{b}} = k^{\text{a}}$).



Fig. 7 Reduction of O_2 at a rotating disk electrode coated with complex 3 prior to oxidation. (A) current–potential curves in air-saturated 1.0 M HClO₄, scan rate = 10 mV s⁻¹. (B) Levich plot of plateau current *vs.* square root of the rotation rate for the curves in (A). (C) Koutecky–Levich plot of the inverse of the plateau current *vs.* the inverse of the square root of the rotation rate for the curves in (A). The theoretical two- and four-electron lines are marked n = 2 and 4, respectively.



Fig. 8 Reduction of O₂ at a rotating disk electrode coated with complex **3** after anodic conditioning. (A) current-potential curves in air-saturated 1.0 M HClO₄, scan rate = 10 mV s⁻¹. (B) Levich plot of plateau current *vs.* square root of the rotation rate for the curves in (A). (C) Koutecky–Levich plot of the inverse of the plateau current *vs.* the inverse of the square root of the rotation rate for the curves in (A). The theoretical two- and four-electron lines are marked n = 2 and 4, respectively.

This seemingly unremarkable finding indicates that the rate of formation of the $Co-O_2$ bond is unaffected by electrooxidation of the surface confined complex, **3**. Therefore the macrocycle core seems to be intact after oxidation. The enhanced catalytic ability resulting from oxidation of the adsorbed complex may result from formation of a more stable cobalt–peroxo interaction. The role of the oxidation as well as the resulting structure of the oxidized complex and the role of Pt(II) in the stabilization of this interaction is currently being studied.

Conclusions

To summarize we have synthesized and characterized by ¹H NMR, UV-Vis spectroscopy and cyclic voltammetry two new metalloporphyrins, complexes **2** and **3** (Fig. 1). Adsorption of these complexes onto EPG electrodes followed by oxidation in 1.0 M HClO₄ results in a new redox active modified electrode which electrocatalytically reduces O_2 to H_2O_2 and H_2O . Studies are currently underway to probe the effect of the number of Pt(II) groups coordinated to the porphyrin periphery on the electrocatalytic reduction of O_2 in acidic media.

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