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Inorganic Chemistry Communications



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Enhanced O₂ electrocatalysis by a highly conjugated cobalt(II) porphyrin

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ARTICLE INFO

Article history: Received 15 October 2012 Accepted 26 November 2012 Available online 16 December 2012

Keywords: Electrocatalysis Oxygen reduction Fused-pyrrole Cobalt porphyrin

ABSTRACT

Cobalt(II) tetraphenyltetranaphthoporphyrin, with extended conjugation at the pyrrole units, has been synthesized and its spectroscopic and electrocatalytic behavior toward the reduction of oxygen has been investigated. The new complex shows a red shift for the Soret band of 75 nm compared to its cobalt(II) tetraphenylporphyrin analog. In addition, the new complex shows enhanced electrocatalytic ability for the reduction of oxygen in acidic media converting over 50% of the oxygen directly to water, a four electron process at relatively high potentials.

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Introduction: There has been a growing interest in the spectroscopic effects of extending the conjugation of porphyrins through fusing of aromatic groups to the pyrrole units [1]. Red shifted porphyrin complexes have found use in photodynamic therapy [2], non-linear optics [3], and solar energy conversion [4]. Many of these highly conjugated complexes have exhibited 100 to 150 nm red shifts in the Soret (B band) band of the porphyrins when compared to their pyrrole analog complexes [5]. We have recently become interested in looking at the effects of these extended π -systems, containing cobalt(II) metal centers, on the electrocatalysis of molecular oxygen in acidic media. A great deal of work on metallo-porphyrins, specifically cobalt porphyrins, as electrocatalysts for oxygen reduction has seen numerous examples of dicobalt cofacial and multinuclear cobalt porphyrins capable of catalyzing the reduction of oxygen by four electrons to water [6]. But for a few exceptions [7] mononuclear cobalt(II) porphyrins are known to reduce oxygen at catalytic potentials by two electrons, to form hydrogen peroxide, rather than the desired four electron process to form water. This, of course, has limited the use of cobalt porphyrins as replacements for the currently used platinum catalysts found in most fuel cells. In our first attempt at investigating the effects of extended conjugation we chose one of the simplest known two electron cobalt porphyrin oxygen reduction catalysts, namely, cobalt(II) tetraphenylporphyrin (CoTPP). To extend the conjugation we fused naphthylene groups to the pyrrole subunits and inserted cobalt(II) to give the cobalt(II) tetraphenyltetranaphthoporphyrin (CoTPTNP).



Results and discussion: Using an adaptation of Barton–Zard chemistry [8], 1-nitronaphthalene was reacted with ethyl isocyanoacetate in the presence of a strong non-nucleophilic phosphazine base to give naphtho[1,2-c]pyrrole in excellent yields [9]. Removal of the ester group was accomplished by refluxing the pyrrole in ethylene glycol containing potassium hydroxide under nitrogen for 30 min. The resulting fused pyrrole was reacted, by a slightly altered procedure of the Lindsey method [5b], with benzaldehyde (under nitrogen) in the presence of catalytic amounts of BF₃·Et₂O in dry methylene chloride at -50 °C for 2 h followed by 48 h at room temperature.

Addition of excess tetrachloro 1,4-benzoquinone (*p*-chloranil) followed by chromatography gave the tetraphenyltetranaphthoporphyrin in ca. 9% yield. The first band from the column was the partially oxidized porphodimethene, H₄TPTNP (MALDI TOF: found, *m*/*z* = 1017.3, M⁺, calc. for [C₇₆H₄₈N₄] 1017.2), followed by the target tetraphenyltetranaphthoporphyrin, H₂TPTNP. Insertion of cobalt(II) was accomplished by reacting a slight excess of cobalt(II) acetate with the porphodimethene or porphyrin in refluxing DMF under nitrogen for 30 min to give the cobalt(II) porphodimethene, CoH₂TPTNP (MALDI TOF: found, *m*/*z* = 1074.2, M⁺, calc. for [C₇₆H₄₆N₄Co] 1074.1) and the cobalt(II) tetraphenyltetranaphthoporphyrin, CoTPTNP [10] in ca. 70% yield for both. The reaction is illustrated in Scheme 1.

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Scheme 1. Synthesis of CoTPTNP.

Electronic spectroscopy of the free-base tetraphenylporphyrin (H_2 TPP) and its cobalt(II) analog (CoTPP) in dichloromethane gave Soret bands at 418 nm and 411 nm, respectively.

Fig. 1 shows the electronic spectra of H₄TPTNP, CoH₂TPTNP, H₂TPTNP and CoTPTNP in dichloromethane. The peak absorbance for the free-base naphtho-fused porphodimethene (blue line, Fig. 1A) appears at 517 nm, nearly a 100 nm redshift compared to the free-base tetraphenylporphyrin. Insertion of cobalt(II) shifts the Soret band even farther to the red with a peak absorbance at 544 nm (green line, Fig. 1A), approximately a 150 nm shift compared to the cobalt(II) tetraphenylporphyrin. The nearly 30 nm red shift after insertion of a metal into the porphodimethene has been linked to structural changes of the macrocycle after metalation [11]. A broad Soret band (530 nm) with very weak Q-bands is observed for H₂TPTNP (Fig. 1B, blue line) in dichloromethane. Upon addition of TFA, protonation of the porphyrin leads to formation of the cationic porphyrin and a much sharper Soret band (549 nm, Fig. 1B red line) and well defined Q-bands (657 nm and 686 nm) which has been linked to increased distortions caused by the meso-substituents [5c]. Insertion of cobalt(II) into H₂TPTNP results in a shift of the Soret band and Q-bands to higher energy (486 nm, 626 nm, 671 nm) as expected for a d⁷ metal. Molar absorptivities of the complexes are in the tens of thousands; however, considerably less than the parent tetraphenylporphyrin and its cobalt(II) analog due to saddling of the ligand [5b].

The electrocatalytic reduction of molecular oxygen in 1.0 M H₂SO₄ was studied at a roughened edge plane pyrolytic graphite (EPG) electrode coated with the Co(II) porphyrin complexes using rotating disk electrode (RDE) voltammetry. Small aliquots, ca. 10 μ L, of mM solutions of the complexes in acetone were added to the surface of the roughened EPG electrode and the solvent was allowed to evaporate. Fig. 2 illustrates a comparison of the bare EPG electrode (red line), an EPG electrode coated with CoTPP (green line), an EPG electrode coated with CoH₂TPTNP (black line), and an EPG electrode coated

with CoTPTNP (blue line) at 1000 rpm in air saturated 1.0 M H₂SO₄. The bare electrode shows the reduction of molecular oxygen with an $E_{1/2} = -0.35$ V vs. SCE. Reduction of molecular oxygen at the EPG electrode coated with CoTPP shows enhanced catalysis with an $E_{1/2} = 0.16$ V vs. SCE, a catalytic shift of ca. 500 mV compared to the bare electrode. When the EPG electrode is coated with the cobalt porphodimethene (CoH₂TPTNP), the $E_{1/2}$ value for the reduction of oxygen shifts to an even greater catalytic potential of 0.22 V vs. SCE; 60 mV more positive than the CoTPP complex. In addition the current is higher than the current observed for the CoTPP coated electrode suggesting that some of the molecular oxygen is being reduced to water.

The EPG electrode coated with the fully oxidized CoTPTNP complex displays an $E_{1/2}$ value of 0.30 V vs. SCE, an additional shift of 80 mV compared to the partially oxidized CoH₂TPTNP complex and a 140 mV catalytic shift compared to CoTPP, with considerably higher current values for the reduction of oxygen.

To determine the number of electrons transferred to oxygen by the CoH_2TPTNP and CoTPTNP coated electrodes, RDE experiments were performed at various rotation rates (Fig. 3A and B, respectively) and the diffusion limited current plotted according the Koutecky– Levich equation (Eq. (1)) [12].

$$\begin{aligned} &1/l_{\rm L} = 1/l_{\rm k} + 1/B\omega^{1/2} \\ &B = 0.2 nFC \nu^{-1/6} D^{2/3} \end{aligned}$$

Where I_L is the current density (μ A cm⁻²), n is the number of electrons for the reaction, F is the Faraday constant (96,500 Cmol⁻¹), D is the diffusion coefficient for oxygen in solution (2.0×10^{-5} cm² s⁻¹), v is the kinematic viscosity of the solution (0.01 cm² s⁻¹), C is the concentration of oxygen in the air-saturated solution (0.25 mM), and ω is the rotation rate (rpm).

Fig. 3 illustrates the results of the RDE experiments and the Koutecky–Levich plot of the limiting current. Results of RDE experiments



Fig. 1. Electronic spectra: A) of H4TPTNP (blue) and CoH₂TPTNP (green) in dichloromethane. B) H2TPTNP (blue) and in the presence of less than 1% TFA (red). C) H2TPTNP (blue) and CoTPTNP (green) in dichloromethane.

run on an EPG electrode coated with CoTPP gave (from the slope of the Koutecky–Levich plot) an n value of 2. As expected the CoTPP complex reduces oxygen by two electrons to hydrogen peroxide (data not shown). From the data in Fig. 3 the slope of the Koutecky–Levich plot for the EPG electrode coated with CoH₂TPTNP (red line Fig. 3C) gives an n value of 2.6 electrons for each molecule of oxygen; while the value for the CoTPTNP coated electrode gave an n value of 3.2 electrons for each molecule of oxygen



Fig. 2. Comparison of the reduction of oxygen in 1.0 M H_2SO_4 at an EPG electrode, bare (red line), coated with CoTPP (green line), coated with CoH₂TPTNP (black line), coated with CoTPTNP (blue line), and coated with CoTPTNP in nitrogen saturated 1.0 M H_2SO_4 at 1000 rpm, scan rate = 10 mV/s.

reduction are occurring, with one of those pathways being the direct four electron reduction of oxygen to water.

The intercept of the Koutecky–Levich plot gives the kinetic current density, I_k , for the reduction of oxygen. This has been related to the rate of formation of the Co–O₂ bond, k [13] (Eq. (2)).

$$I_{k} = nFk\Gamma C_{02}$$
⁽²⁾

Where n is the number of electrons transferred and Γ is the surface complex concentration. It is; however, difficult to determine the true surface concentration by the method used in this study to adsorb the complex onto the roughened EPG electrode. Assuming that the surface concentration is the same for each of the complexes studied (which is reasonable since the same amount of each complex was added to the EPG electrode) and that all of the cobalt porphyrin molecules added to the EPG surface are electroactive toward the reduction of oxygen, a more difficult assumption, then the following preliminary analysis of the kinetic current is conjectured. Ik for CoTPP from the Koutecky-Levich plot is ca. 900 μ A/cm², it is 1500 μ A/cm² for CoH₂TPTNP, and 2300 μ A/cm² for CoTPTNP. Dividing by their respective n values reveals that $k(COH_2TPTNP) = 1.23 k(COTPP)$, suggesting that formation of the $Co-O_2$ bond is 1.23 times faster for CoH₂TPTNP compared to its analog complex. The ratio of k(CoTPTNP)/ k(CoTPP) is 1.70 indicating that the formation of the $Co-O_2$ bond for CoTPTNP is nearly twice as fast than for CoTPP and 1.36 times faster than $Co-O_2$ bond formation for the partially oxidized CoH_2 TPTNP cobalt(II) porphodimethene.

Conclusions: In summary, a new conjugated cobalt(II) porphyrin (CoTPTNP) has been synthesized and characterized. A significant red shift in the Soret band is observed for this new complex compared to its analog cobalt(II) tetraphenylporphyrin complex. In addition, enhanced reduction of oxygen in acidic media is observed for the conjugated system with a shift to more catalytic potentials and greater current density upon reduction of oxygen, as determined by analysis of the Koutecky–Levich plot. This opens a new avenue for investigating other conjugated porphyrin complexes as potential electrocatalysts for oxygen reduction. We are currently looking at computational methods to determine the effect of the extended π -system on the d-orbitals of the cobalt(II) metal center.



Fig. 3. Reduction of oxygen at a rotating disk electrode coated with CoH_2TPTNP (A) and CoTPTNP (B); current–potential curves in air-saturated 1.0 M H_2SO_4 , scan rate = 10 mV/s. (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, red line and B, blue line). The theoretical two and four electron lines are marked n=2 and n=4, respectively.

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