Four-electron electrocatalytic reduction of dioxygen to water by an ion-pair cobalt porphyrin dimer adsorbed on a glassy carbon electrode

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An ion-pair porphyrin dimer, formed by reacting the tetrachloro salt of [tetrakis(*N*-methylpyridyl)porphyrinato]cobalt and the tetrasodium salt of [tetrakis(4-sulfonatophenyl)porphyrinato]cobalt, adsorbed electrochemically on a glassy carbon electrode is shown to catalytically reduce O_2 to water by four electrons.

Mimicking enzymatic catalytic reactions using metalloporphyrin dimers is an area of active research. Towards this, covalently linked porphyrin dimers are most widely used and by employing such dimers, four-electron reduction of O_2 to H_2O has been demonstrated.[1,2] That is, either Co or Fe porphyrin dimers, with closely spaced porphyrin rings (inter-ring distance *ca.* 3.5 Å), adsorbed on a glassy carbon (GC) electrode, catalyze the reduction of O_2 to H_2O at low pH. The postulated mechanism involves formation of a μ-ligated O_2 complex, followed by electrochemical reduction and protonation to produce H_2O. The inter-ring distance and the rigidity of the dimer are believed to be important factors governing the formation of the μ-ligated O_2 complex for the overall catalytic process.[1a]

Water soluble monomeric Co porphyrins, bearing either positive charges on the ring periphery, such as the tetrachloro salt of [tetrakis(*N*-methylpyridyl)porphyrinato]cobalt, [Co(TM-PyP)]Cl_4 or negative charges on the ring periphery, such as the tetrasodium salt of [tetrakis(4-sulfonatophenyl)porphyrinato]cobalt, Na_4[Co(TPPS)] (Fig. 1), are known to adsorb irreversibly on a GC electrode and catalytically reduce O_2 by two electrons to produce H_2O_2.[3] It is also known that these oppositely charged porphyrins form stable face-to-face bound porphyrin dimers with 1 : 1 molecular stoichiometry when they are mixed together in solution.[3,4] Spectroscopic investigations have shown[4] that the inter-ring distance between the porphyrin rings of these dimers is *ca.* 3.1 Å. This distance is shorter by 0.4 Å than that of a closely spaced covalently linked porphyrin dimer known to reduce O_2 directly to water.[1a] These results suggest that the ion-pair dimers should also be utilized as electrode materials for catalytic reduction of O_2. Sawaguchi *et al.*[1i] initially examined the catalytic behaviour for O_2 reduction by using electrodes coated with ion-pair Fe–Fe porphyrin dimer and reported a 12% catalytic efficiency towards four-electron reduction of O_2 to H_2O. In the present study, we have observed a catlaytic efficiency up to 98% when an ion-pair Co–Co porphyrin dimer, adsorbed electrochemically on a glassy carbon electrode, under elevated pH conditions is used.
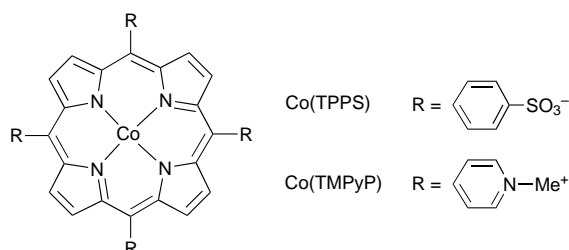
Fig. 2 shows the cyclic voltammograms‡ (CVs) for O_2 reduction on the dimer, [Co(TMPyP)][Co(TPPS)]§ adsorbed GC electrode¶ (curve 1), a monomer, Co(TMPyP)Cl_4 adsorbed GC electrode (curve 2) and a bare GC (curve 3) in O_2 saturated 0.05 M NH_4Cl.‖ Curve 4 shows the CV for the dimer adsorbed electrode in the absence of O_2. Two irreversible peaks located at $E_{pc} = -0.49$ V and $E_{pc} = -0.76$ V *vs.* Ag/AgCl, are observed for the dimer adsorbed electrode. There is a positive shift of peak potential by 360 mV for O_2 reduction for the monomer adsorbed GC electrode as compared to that observed for the bare GC electrode (Curves 2 and 3). Similar voltammetric behavior is also seen for the monomer, Co(TPPS) adsorbed electrode and a dimer, [Co(TMPyP)][(H_2TPPS)], in which only one of the porphyrins has a Co metal ion and the other is a free-base porphyrin, adsorbed electrode. These results are similar to that reported for the catalytic two-electron reduction of O_2 to peroxide.[5]

The peak potential for O_2 reduction on the dimer adsorbed electrode is located at $E_{pc} = -0.22$ V *vs.* Ag/AgCl (curve 1). This peak potential is positively shifted by 120 mV when compared to the peak potential for O_2 reduction on the monomer adsorbed electrode (curve 2). Additionally, larger, peak currents, proportional to (scan rate)$^{1/2}$, are obtained for the dimer adsorbed electrode. The positive shift of the peak potential and the larger catalytic currents for O_2 reduction on the dimer adsorbed electrode suggest the occurrence of four-electron reduction of O_2 to H_2O.[1a] In order to quantify these results, voltammetry at a rotating disk-ring electrode has been performed.

Fig. 3(*a*) shows voltammetric curves, recorded with the use of a rotating (Pt ring)–(GC disk) electrode,** for O_2 reduction at various rotation rates. The catalyst was adsorbed on the disk.¶ Disk potential was scanned from 0.1 to −0.5 V while ring

Fig. 1 The structural formulae of the water-soluble Co porphyrins used to form ion-pair dimer
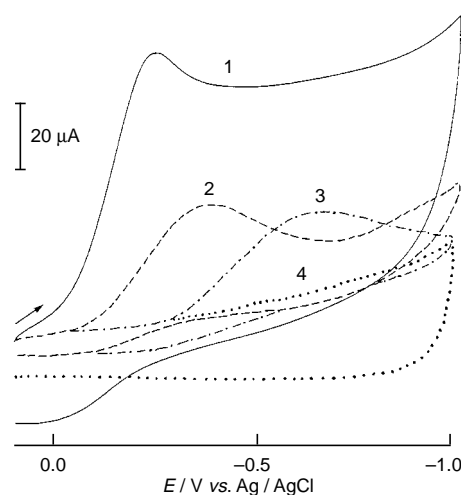

Fig. 2 Cyclic voltammograms for dioxygen reduction at [Co(TPPS)][Co(TMPyP)]/GC electrode (curve 1), Co(TMPyP)/GC electrode (curve 2) and bare glassy carbon electrode (curve 3) in O_2 saturated 0.05 M NH_4Cl. Curve 4 represents the CV of [Co(TPPS)][Co(TMPyP)] adsorbed electrode in the absence of O_2. Scan rate = 100 mV s^{-1}.

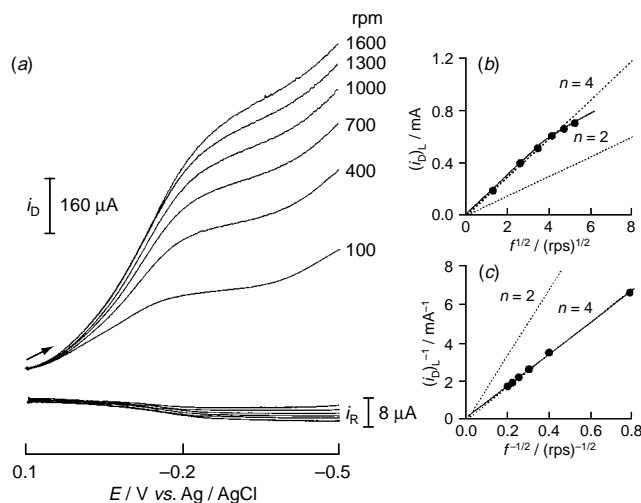**Fig. 3** (*a*) Rotating (platinum ring)–(glassy carbon disk) electrode voltammetry for the [Co(TMPyP)][Co(TPPS)] adsorbed on the disk and the O$_2$ saturated 0.05 M NH$_4$Cl aqueous solution. Ring potential, E_R = 1.0 V. Disk potential scan rate, 20 mV s^{-1}. (*b*) and (*c*) are the Levich and Koutecky–Levich plots for the plateau currents from Fig. 3(*a*). Dashed lines are calculated for the O$_2$ reduction by two and four electrons. Area of the electrode = 0.164 cm^2, concentration of O$_2$ = 0.5 mM, diffusion coefficient of O$_2$ = 2.6 × 10^{-5} cm^2 s^{-1}, kinematic viscosity = 0.01 cm s^{-1}.

potential was kept at E_R = 1.0 V in order to detect any H$_2$O$_2$ generated by a two-electron reduction process of O$_2$ at the disk.[1a] Larger disk currents have been obtained for the dimer than for the monomer adsorbed on the graphite electrodes. Levich and Koutecky–Levich plots[6] of the plateau currents from Fig. 3(*a*) are shown in Fig. 3(*b*) and (*c*). The calculated number of electrons involved in the reduction of O$_2$ from the slope of Fig. 3(*c*) is found to be 3.8 ± 0.2 electrons per O$_2$ molecule while this value for Co(TMPyP), Co(TPPS) and the Co–H$_2$ dimer adsorbed electrodes is found to be 2.0 ± 0.2 electrons. It is observed that the occurrence of four-electron reduction for the dimer adsorbed electrode is dependent on the positive switching potential, E_λ during the adsorption of the dimer onto the electrode surface. When E_λ was < 1.2 V, the number of electrons in the process was between 3 and 4.

As expected, negligent amounts of ring currents are observed for the Co–Co dimer adsorbed electrode when the ring potential is held at +1.0 V, *i.e.*, a potential where oxidation of H$_2$O$_2$, a two-electron reduction product of O$_2$ generated at the disk occurs. The ratio of the ring to disk current, i_R/i_D, is 0.01 for the adsorbed dimer which is much smaller than the collection efficiency of 0.36 determined with the use of the [Fe(CN)$_6$]$^{3-/2-}$ redox couple under the same solution conditions. The i_R/i_D ratio for the adsorbed dimer does not change appreciably with the rotation rate and amounts to 98% of the disk current resulting from four-electron reduction of O$_2$ to H$_2$O.[7]

For the electrode coated with the covalently linked Co porphyrin dimer, the catalytic activity towards four-electron reduction of O$_2$ depends strongly on pH.[1a] For pH > 4.5, only H$_2$O$_2$, *i.e.*, a two-electron product is formed.[1a] For the presently investigated ion-pair Co–Co dimer, the calculated 3.8 ± 0.2 number of electrons, at a relatively high pH (5.3) and low ionic strength (0.05 M), indicates its greater ability to catalyze reduction of O$_2$ by four electrons. This ability of the easy to prepare 'ion-pair' dimer to catalyze, by four-electron reduction of O$_2$ to H$_2$O at elevated solution pH is commendable. Further studies to understand the role of E_λ during the process of surface adsorption and the mechanistic details of four-electron reduction of O$_2$ using different ion-pair porphyrin dimers are in progress.

Notes and References

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‡ Cyclic voltammetry was performed on a model 263 A potentiostat/galvanostat of EG & G (Princeton, NJ) by using a typical three-electrode cell arrangement. A glassy carbon electrode (0.3 cm diameter) of BAS was used as the working electrode. A Pt wire served as the counter electrode and an Ag/AgCl electrode was used as the reference one.

§ The dimer, [Co(TMPyP)][Co(TPPS)], was synthesized by a stoichiometric reaction of [Co(TMPyP)]Cl$_4$ (100 mg) (Mid-Century Chemicals Co., Posen, IL) in 20 ml of MeOH–EtOH (1 : 1 v/v) and Na$_4$[Co(TPPS)] (117 mg) (Mid-Century Chemicals Co.) in 10 ml of MeOH–EtOH (1 : 1 v/v) at room temp. The resulting solid which precipitated was centrifuged, filtered, washed repeatedly with MeOH to yield (71%) pure dimer. UV–VIS in water, λ_{max} (log ε), 322 (4.52), 427 (5.16), 543 (0.16). Elemental analysis of the synthesized dimer revealed the presence of a large number (12 to 16) of water molecules.

¶ The GC working electrode prior to the experiments was initially cleaned with alumina powder and was further treated with 2 M H$_2$SO$_4$. The surface of the electrode was roughened by using fine quality sand paper. The porphyrin (dimer or monomer) was adsorbed on the glassy carbon electrode under multicyclic voltammetry conditions. For this, a slurry of porphyrin (*ca.* 1 mM) in 0.025 M NaCl solution was used. The potential was scanned for the range 1.2 to −0.1 V (nearly 30 cycles), until a scan-number-independent voltammogram was obtained. The electrode was then removed from the solution, rinsed thoroughly with distilled water and then immersed in the blank supporting electrolyte solution. The electrochemical measurements were performed at room temperature in 0.05 M NH$_4$Cl (pH 5.3).

‖ A 0.05 M NH$_4$Cl solution of low ionic strength (μ = 0.05) was used to avoid possible decomposition of the adsorbed ion-pair porphyrin dimer on the electrode surface.

** The rotating ring-disk electrode (RRDE) voltammetry, was performed by using a Model AFCB1 bipotentiostat, MSRX Speed Control Unit and AFMSRX Modulated Speed Rotator of Pine Instrument Co. (Grove City, PA). A model BD-95 dual channel recorder of Kipp and Zonen (Bohemia, NY) was used to record the voltammograms. Radius of the disk, gap and ring of the platinum-(glassy carbon) ring-disk electrode was 0.23, 0.25 and 0.27 cm, respectively. an Ag/AgCl and Pt wire served as the reference and auxiliary electrodes, respectively.

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