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Proton Pump for O_2 Reduction Catalyzed by 5,10,15,20-Tetraphenylporphyrinatocobalt(II)

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Abstract: The role of 5,10,15,20-tetraphenylporphyrinatocobalt(II) ([Co(tpp)]) as a catalyst on molecular oxygen (O_2) reduction by ferrocene (Fc) and its two derivatives, 1,1′-dimethylferrocene (DFc) and decamethylferrocene (DMFc) at a polarized water|1,2-dichloroethane (DCE) interface has been studied. The water|DCE interface essentially acts as a proton pump controlled by the Galvani potential difference across the interface, driving the proton transfer from water to DCE. [Co(tpp)] catalyzed O_2 reduction by Fc, DFc and DMFc is then followed to produce hydrogen peroxide (H_2O_2). The catalytic mechanism is similar to that proposed by Fukuzumi et al. for bulk reactions. This interfacial system provides a platform for a very efficient collection of H_2O_2, by extraction immediately after its formation in DCE to the adjacent water phase, thus decreasing the possibility of degradation and further reaction with ferrocene derivatives.

Keywords: cobalt · ferrocenes · hydrogen peroxide · oxygen reduction · proton pump

Introduction

Cobalt porphyrins have been extensively studied because of their catalytic activity toward molecular oxygen (O_2) reduction reaction (ORR).[1–24] The catalytic mechanism involves coordination of O_2 to the cobalt(II) centre, which allows electron delocalization from Co^{II} to bound O_2 to form a superoxide like adduct of $Co^{III}-O_2^-$ or $Co^{III}-O_2H^\bullet$ in the presence of proton, followed by the reduction of the adduct either by an electrode or by a molecular electron donor.[13–15] In most cases, monomeric cobalt porphyrins catalyze the electroreduction of O_2 to hydrogen peroxide (H_2O_2), whereas dimeric cofacial cobalt porphyrins demonstrate the catalysis of four-electron reduction of O_2 to water.[3,7,8,10,12,15,16,24–27] Employing ferrocene derivatives as electron donors, O_2 reduction catalyzed by various cobalt porphyrins has been investigated by Fukuzumi et al. in organic media in the presence of $HClO_4$.[13–15] In the reaction scheme, the steps of electron coordination to form a superoxide adduct and its reduction by ferrocene derivatives to produce H_2O_2/H_2O and Co^{III} are fast, and that of reducing Co^{III} by ferrocene derivatives is slow and rate limiting.

Liquid|liquid interfaces offer the possibility to physically separate reactants, and to carry out interfacial reactions. Recently, O_2 reduction by decamethylferrocene (DMFc) at a polarized water|1,2-dichloroethane (DCE) interface, also called the interface between two immiscible electrolyte solutions (ITIES), has been reported.[23,28–31] In this case, one reactant, namely protons, is located in the aqueous phase, whereas the second one, namely the electron donor, is located in the organic phase. We have shown that in this biphasic system the ORR probably proceeds through a proton transfer from water to DCE followed by O_2 reduction by DMFc in DCE.[28] The H_2O_2 formed is then extracted to the adjacent water phase immediately after its formation in DCE. The oxidation of DMFc to $DMFc^+$ has also been confirmed by UV-visible spectrophotometric and electrochemical measurements. As on solid electrodes, it is possible to use electrocatalysts at polarized liquid|liquid interfaces. In the case of O_2 reduction by DMFc, different electrocatalysts,

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such as interfacially deposited platinum particles,[30] 5,10,15,20-tetraphenyl-21H,23H-porphyrin (H_2TPP)[31] and 5,10,15,20-tetraphenylporphyrinatocobalt(II) ([Co(tpp)])[23] have been studied at polarized water|DCE interfaces.

Here, we study the role of [Co(tpp)] as a catalyst for a two-electron reduction of O_2 by ferrocene (Fc) and its two derivatives, 1,1′-dimethylferrocene (DFc) and DMFc at the polarized water|DCE interface. In reference [23], some electrochemical characterizations were presented, but the compound was obtained from a commercial source, and was subsequently found to contain a large amount of H_2TPP, which also can effectively catalyze O_2 reduction by Fc, DFc and DMFc following a different mechanism. Here, a highly purified [Co(tpp)] product and weaker reductants than DMFc, namely DFc and Fc, were employed to study the reduction of O_2 at the water|DCE interface. The reaction was found to proceed by a catalytic mechanism similar to that proposed by Fukuzumi et al. for bulk reactions,[14,15] but in which the water|DCE interface essentially acts as a proton pump, allowing the control of the amount of protons in DCE by the Galvani potential difference across the interface. Moreover, this biphasic system also allows for the very efficient collection of H_2O_2 by extraction immediately after its formation in DCE to the adjacent water phase, thus decreasing the possibility of degradation and further reaction with ferrocene derivatives.

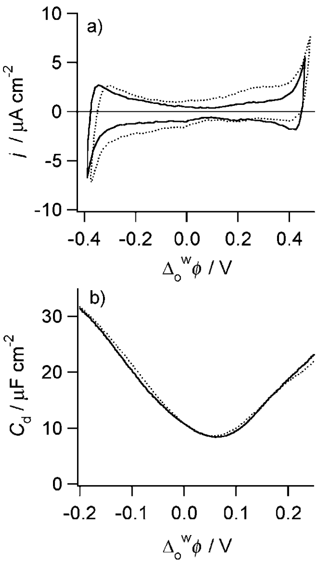
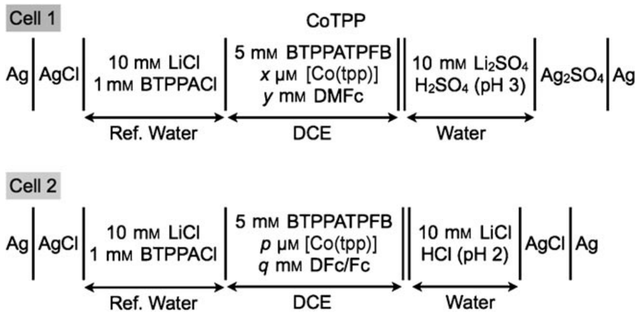


Figure 1. a) Cyclic voltammograms (50 mV s^{-1}) and b) differential capacitance curves using Cell 1: in the absence ($x = 0$, $y = 0$, ——) and presence ($x = 50$, $y = 0$, •••••) of 50 µM [Co(tpp)] in DCE.



Scheme 1. Composition of electrochemical cells used.

Results and Discussion

Electrochemistry at ITIES: The cyclic voltammograms obtained at the water|DCE interface in the absence (full line) and presence (dotted line) of [Co(tpp)] (50 µM) in DCE, using Li_2SO_4 (10 mM) and bis(triphenylphosphoranylidene)-ammonium tetrakis(pentafluorophenyl)borate (BTPPATPFB, 5 mM) as the aqueous and organic supporting electrolytes, respectively, can be seen in Figure 1a (Cell 1 in Scheme 1). The aqueous pH was adjusted to 3 by the addition of H_2SO_4. The voltammetric response in the absence of [Co(tpp)] is the classical potential window observed at the water|DCE interface, with the positive and negative limit determined by the transfer of H^+/Li^+ and SO_4^{2-} from the aqueous to the DCE phase respectively. Adding [Co(tpp)] (50 µM) does not result in any significant Faradaic charge-transfer reaction compared to that observed in the presence of the free base H_2TPP.[31] The corresponding differential capacitance measurements revealed that no adsorption of [Co(tpp)] at the interface occurs in the available potential window, as shown in Figure 1b, the differential capacitance curve in the presence of [Co(tpp)] (dotted line) matches well with that in the absence of [Co(tpp)] (full line).

The voltammetric responses of DMFc, DFc and Fc in the absence (dotted lines) and the presence of [Co(tpp)] (full lines) at the water|DCE interface are compared in Figure 2. In the presence of only DMFc in DCE, a significant current increase (dotted line) relative to the blank (full line in Figure 1a) can be observed at the positive potentials, as shown in Figure 2a. This current response arises from proton transfer followed by O_2 reduction by DMFc, as previously reported.[28] This reaction produces decamethylferrocenium ($DMFc^+$) in DCE, whose transfer across the water|DCE interface resulted in a current wave at the negative potential ($\Delta_o^w\phi_{1/2} = -0.26$ V). Further adding [Co(tpp)] in DCE led to an increase in the current at the positive potentials, as well as an increase of the ion transfer current of $DMFc^+$. These results mean that more $DMFc^+$ was generated in the presence of [Co(tpp)], highlighting the catalytic role of [Co(tpp)] on the O_2 reduction by DMFc.

For DFc and Fc (Figure 2b,c) that are weaker reductants than DMFc, a small voltammetric wave was observed at a half-wave potential of −0.05 V and 0.04 V, respectively, when only DFc or Fc is present in DCE. Each wave presents a peak-to-peak separation close to 60 mV and the peak current is linearly proportional to the square root of the scan rate. These results suggest that the two waves are a result of the monovalent ion transfer across the water|DCE interface, considering that no redox process could occur under the present experimental conditions. Therefore, they can be

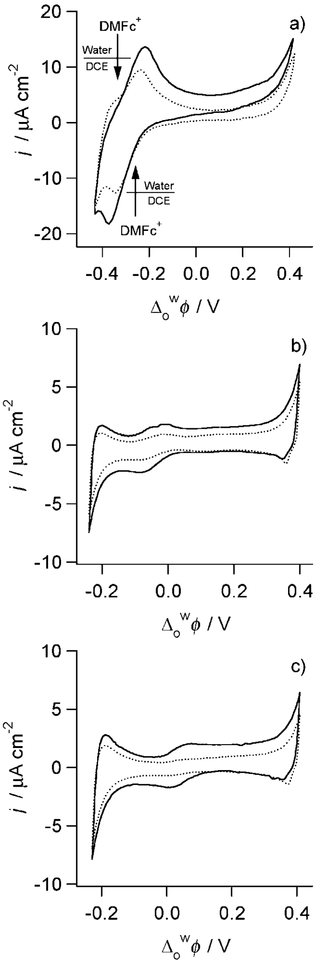


Figure 2. a) Cyclic voltammograms (50 mV s^{-1}) using Cell 1: in the presence of only 5 mM DMFc ($x=0$, $y=5$, •••••) and both 5 mM DMFc and 50 µM [Co(tpp)] ($x=50$, $y=5$, ——); b) Cyclic voltammograms (50 mV s^{-1}) using Cell 2: in the presence of only 5 mM DFc ($p=0$, $q=5$, •••••) and both 5 mM DFc and 50 µM [Co(tpp)] ($p=50$, $q=5$, ——); c) Cyclic voltammograms (50 mV s^{-1}) using Cell 2: in the presence of only 5 mM DFc ($p=0$, $q=5$, •••••) and both 5 mM DFc and 50 µM [Co(tpp)] ($p=50$, $q=5$, ——).

assigned to the ion transfer of DFc$^+$ and Fc$^+$, formed slowly in the air-saturated solution. Similar to DMFc, if [Co(tpp)] is present the ion transfer currents of DFc$^+$ and Fc$^+$ increase remarkably, suggesting that more DFc$^+$ and Fc$^+$ are produced. It convincingly verifies the catalytic role of [Co(tpp)] on the O_2 reduction, since it is known that DFc and Fc do not react with O_2 or react slowly, that is, days, in the presence of a strong acid.[14,15]

Shake flask experiments: [Co(tpp)] catalyzed O_2 reductions by Fc, DFc and DMFc at a water|DCE interface at which the polarization was chemically controlled by a common ion, so called shake flask experiments, were performed as reported previously.[28] Dissolving lithium tetrakis(pentafluorophenyl)borate (LiTPFB, 5 mM) and HCl (10 mM) in water and BTPPATPFB (5 mM) in DCE (water/DCE = 1:1 in volume), the Galvani potential difference across the interface is fixed by the common ion TPFB$^-$ at a potential greater than 0.59 V.[28,32] At this potential, proton initially present in water will partition into DCE, leading finally to a distribution of proton in two phases according to the Nernst equation. If only [Co(tpp)] is present in DCE, a Soret band ($\lambda_{max}=427$ nm) and a Q band ($\lambda_{max}=540$ nm) are observed after the shake flask experiment, which demonstrates a bathochromic shift relative to those of a fresh [Co(tpp)] solution at 410 nm and 526 nm, as shown in Figure 3.

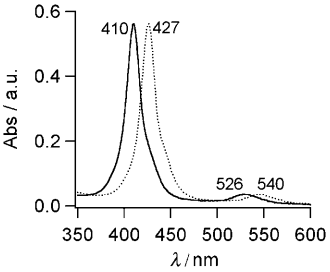


Figure 3. Absorption spectra of 1 µM [Co(tpp)] in DCE freshly prepared (——) and after a shake flask experiment (•••••).

This shift corresponds to proton facilitated oxygenation of [Co(tpp)] to form an adduct $[\{Co^{III}(tpp)\}^+{-}O_2^-]$.[14,15,33]

As a control experiment, O_2 reduction by DMFc, DFc and Fc in the absence of [Co(tpp)] was also performed. O_2 reduction by Fc and DFc occurs as evidenced by the detection of Fc$^+$ at 620 nm and DFc$^+$ at 652 nm, respectively, as shown in Figure 4b,c. However, the reaction proceeds rather slowly and it takes several hours to observe the evolution of Fc$^+$ and DFc$^+$ absorption bands. In contrast, O_2 reduction by DMFc is much faster, as demonstrated in Figure 4a, and in tens of minutes all of the DMFc is consumed. The difference in O_2 reduction ability for Fc, DFc and DMFc is in agreement with that previously reported.[14,15]

Upon an addition of [Co(tpp)], the rise of the absorption bands at 779, 652 and 620 nm, corresponding to DMFc$^+$, DFc$^+$ and Fc$^+$, respectively, could be immediately observed, as displayed in Figure 5a. A time profile of the formation of Fc$^+$ in the absence and presence of [Co(tpp)] (compared in Figure 5b) shows that the oxidation of Fc is much faster in the presence of [Co(tpp)]. These results suggest that [Co(tpp)] has a catalytic role in the O_2 reduction by ferrocene compounds. As for the top aqueous phase, excess NaI (equivalent to 0.1 M) was added and UV-visible spectroscopic measurements revealed the absorption characteristics of I_3^- ($\lambda_{max}=287$, 352 nm), as shown in Figure 5b. The detection of I_3^- confirms the production of H_2O_2 in the shake flask experiment, since H_2O_2 is a strong oxidant that can oxidize I^- to I_3^-.[15,28] One more point should be mentioned is that in the shake flask experiments, the Q band of [Co(tpp)] ($\lambda_{max}=526$ nm) was observed for all three ferrocene compounds, whereas that of $[Co^{III}(tpp)]^+$ ($\lambda_{max}=540$ nm) was not, as shown in Figure 5a. This result suggests the reduction of $[Co^{III}(tpp)]^+$ by Fc and its two derivatives.

Mechanisms: Based on above experimental results, it can be concluded that two-electron reduction of O_2 to H_2O_2 by

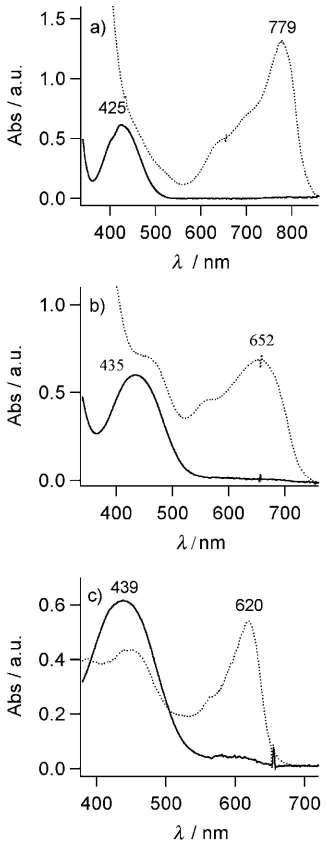


Figure 4. Absorption spectra of a) 5 mм DMFc, b) DFc and c) Fc in DCE freshly prepared (——) and after shake flask experiments (•••••) for DMFc (30 minutes) and DFc and Fc (24 hours).

DMFc, DFc and Fc, could be effectively catalyzed by [Co(tpp)]. This is in agreement with a conclusion that made previously that monomeric cobalt porphyrins only catalyze two-electron reduction of O_2.[14,15] One of advantages of the present system is that the liquid|liquid interface acts as a proton pump, controlled by the interfacial Galvani potential difference, driving the proton transfer from water to DCE. The transfer of proton could be favoured by $[\{Co^{III}(tpp)\}^{+}{-}O_2^{-}]$ to form $[\{Co^{III}(tpp)\}^{+}{-}O_2H^{\bullet}]$, followed by its reduction by ferrocene derivatives to generate H_2O_2 and regeneration of [Co(tpp)] from $[Co^{III}(tpp)]^{+}$ by ferrocene derivatives, see Equations (1)–(4):

$$H^{+}_{(w)} \rightarrow H^{+}_{(DCE)} \tag{1}$$

$$[Co(tpp)]_{(DCE)} + O_{2(DCE)} + H^{+}_{(DCE)} \rightarrow [\{Co(tpp)\}^{+}{-}O_2H^{\bullet}]_{(DCE)} \tag{2}$$

$$[\{Co(tpp)\}^{+}{-}O_2H^{\bullet}]_{(DCE)} + Fc_{(DCE)} + H^{+}_{(DCE)} \rightarrow [Co(tpp)]^{+}_{(DCE)} + H_2O_{2(DCE)} + Fc^{+}_{(DCE)} \tag{3}$$

$$[Co(tpp)]^{+}_{(DCE)} + Fc_{(DCE)} \rightarrow [Co(tpp)]_{(DCE)} + Fc^{+}_{(DCE)} \tag{4}$$

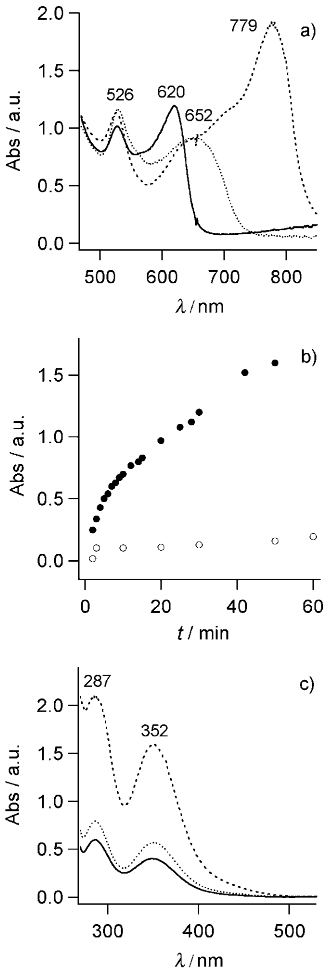
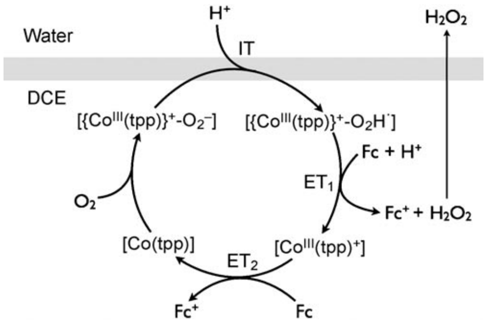


Figure 5. a) Absorption spectra of the DCE phase after 30 minutes of shake flask experiments in presence of 50 μм [Co(tpp)] with 5 mм DMFc (-----), DFc (•••••) and Fc (——); b) Time profile of the formation of Fc^{+} in the absence (○) and presence (●) of 50 μм [Co(tpp)] in DCE during the shake flask experiments; c) Absorption spectra of the aqueous phase after treated with excess NaI after 30 minutes of shake flask experiments in presence of 50 μм [Co(tpp)] with 5 mм DMFc (-----), DFc (•••••) and Fc (——).

This reaction chain leads to a reaction cycle displayed in Scheme 2, which is very similar to that proposed by Fukuzu-



Scheme 2. Reaction scheme of the proton pump controlled by the Galvani potential difference for [Co(tpp)] catalyzed O_2 reduction by ferrocene compounds. IT = ion transfer, ET = electron transfer.

mi et al. for the homogenously [Co(tpp)] catalyzed O_2 reduction by ferrocene derivatives.[14,15]

As proven by the quantity of H_2O_2 generated by DMFc, DFc and Fc, which follows an order of DMFc > DFc > Fc with a molar ratio of 4:1.3:1 (Figure 5c); the reduction of $[Co(tpp)]^+$ by DMFc, DFc or Fc is the rate limiting step. However, it should be mentioned that the reaction rate is in part controlled by the mass transport of proton across the water|DCE interface [Eq. (1)]. Shake flask experiments indicated that the rate of formation of ferrocenium was dependent on the Galvani potential difference tuned by using various common ions.

Conclusion

The catalytic role of [Co(tpp)] on the O_2 reduction by Fc and its two derivatives, DFc and DMFc has been studied at a polarized water|DCE interface. The interface essentially acts as a proton pump controlled by the Galvani potential difference across the interface, driving the proton transfer from water to DCE, which is followed by [Co(tpp)] catalyzed O_2 reduction by Fc, DFc and DMFc to produce H_2O_2. The catalytic mechanism is similar to that proposed by Fukuzumi et al. for bulk reactions.[14,15] This interfacial system favours the collection of H_2O_2, by extraction immediately after its formation in DCE to the adjacent water phase, thus preventing degradation and further reaction with ferrocene derivatives, which for bulk systems usually leads to an overall reaction stoichiometry higher than 2.[14,31]

Experimental Section

Chemicals: All chemicals are analytical grade and used as received without further purification. Decamethylferrocene (DMFc, 99%) was purchased from Alfa Aesar. Sulfuric acid (H_2SO_4, 5 M), ferrocene (Fc, 98%) and 1,1′-dimethylferrocene (DFc, 97%) were ordered from Sigma–Aldrich. Hydrochloric acid (HCl, 32%) was obtained from Merck. Lithium chloride (LiCl, > 99%), sodium iodide (NaI, > 99%) bis(triphenylphosphoranylidene)ammonium chloride (BTPPACl, > 98%), tetramethylammonium chloride (TMACl, > 98.0%), and 1,2-dichloroethane (DCE, ≥ 99.8%) were bought from Fluka. Lithium tetrakis(pentafluorophenyl)borate (LiTPFB) was provided by Boulder Scientific Company. Bis(triphenylphosphoranylidene)-ammonium tetrakis(pentafluorophenyl)borate (BTPPATPFB) was prepared by metathesis of BTPPACl and LiTPFB in a methanol/water (V/V = 2) mixture, followed by recrystallization in acetone. The aqueous solutions were prepared with ultrapure water from a Milli-Q system (Millipore Milli-Q185). [Co(tpp)] was synthesized following the typical procedure.[34]

Electrochemical measurements: The electrochemical experiments were performed on an Ivium Compact Stat in a four-electrode configuration by using a conventional glass cell with a cross section of 1.53 cm^2. The electrolyte compositions of the cells are illustrated in Figure 1. The potential reported is the Galvani potential difference obtained by correcting the applied potential with respect to the formal ion transfer potential of tetramethylammonium (TMA^+), $\Delta_o^w\phi^o_{TMA^+} = 0.16$ V.[32]

Shake flask experiment: The two-phase reaction controlled by common ions was run in a quartz cuvette (10 mm × 10 mm). A solution containing DMFc/DFc/Fc (5 mM) and/or [Co(tpp)] (50 μM) in DCE (1.5 mL) was added first, followed by the addition of an aqueous solution (1.5 mL) containing HCl (10 mM) on the top. The aqueous and organic salts of common ion, LiTPFB and BTPPATPFB, were added in the same concentration of 5 mM. The UV-visible spectrum of the DCE phase was measured directly. The aqueous phase was separated and titrated with excess NaI (equivalent to 0.1 M) prior to the UV-visible spectroscopic measurement. The UV-visible spectra were measured by using an Ocean Optical CHEM2000 spectrophotometer.

Acknowledgements

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