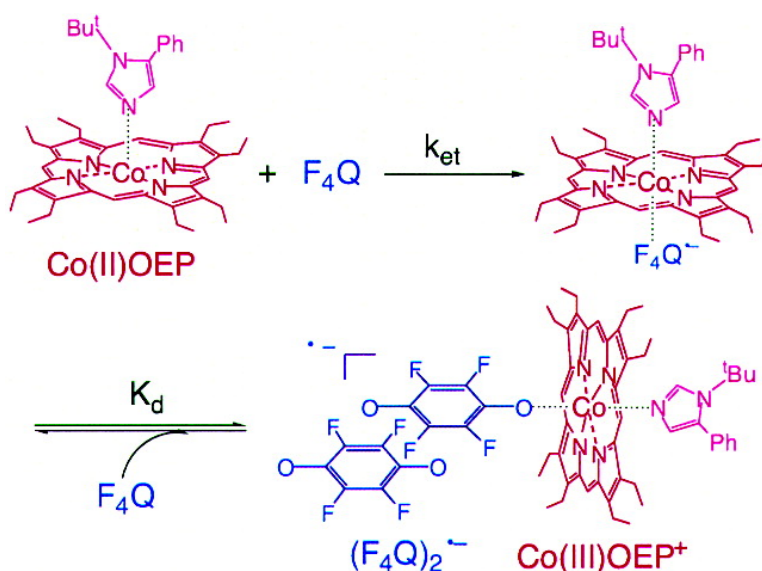Communication

Self-Promoted Electron Transfer from Cobalt(II) Porphyrin to *p*-Fluoranil To Produce a Dimer Radical Anion-Cobalt(III) Porphyrin Complex

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Self-Promoted Electron Transfer from Cobalt(II) Porphyrin to *p*-Fluoranil To Produce a Dimer Radical Anion-Cobalt(III) Porphyrin Complex

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Electron transfer is one of the most fundamental chemical reactions, playing a pivotal role not only in chemical processes but also in biological redox processes such as photosynthesis and respiration, which are essential for life.[1,2] A variety of metal enzymes are involved to control electron transfer in biological systems, where electron transfer is accompanied by transient chemical binding with metalloenzymes.[1] Introduction of a third component acting as a promoter in electron-transfer reactions provides a new perspective of electron-transfer chemistry, expanding the scope of electron-transfer systems which would otherwise be impossible to study.[3,4] Metal ions which act as Lewis acids can accelerate a number of electron-transfer processes by complexation with radical anions, produced in the electron transfer.[3,4] If the radical anion of substrate ($S^{\bullet-}$) can form a complex with unreduced neutral substrate itself (S) and the formation constant of the product ($S_2^{\bullet-}$) is large, the electron-transfer reduction of the substrate (S) would be self-promoted, because $S_2^{\bullet-}$ is thermodynamically more stabilized with increasing substrate concentration. Such self-promoted electron transfer may be regarded as a primitive case of self-organized electron transfer, which has merited considerable attention.[5] There are some examples for formation of dimer radical anion complexes ($S_2^{\bullet-}$) in solution.[6,7] However, the formation constants of dimer radical anion complexes (K_d) are normally small ($K_d = 0.6-5$ M^{-1}).[6c] As such, no self-promoted electron transfer has so far been reported.

We report herein the first example of self-promoted electron transfer from Co(II)OEP (2,3,7,8,12,13,17,18-octaethyl-21*H*,23*H*-porphine cobalt(II)) to *p*-fluoranil (F_4Q) due to the strong complex formation between the dimer radical anion [$(F_4Q)_2^{\bullet-}$] and Co(III)-OEP$^+$.

Addition of F_4Q ($E_{red}^0 = -0.01$ V vs SCE) to a dry deaerated PhCN solution of Co(II)OEP ($E_{ox}^0 = 0.10$ V vs SCE) results in electron transfer from Co(II)OEP to F_4Q in the presence of a bulky base (1-*tert*-butyl-5-phenylimidazole), as confirmed by the formation of Co(III)OEP$^+$ ($\lambda_{max} = 417$ nm) together with the disappearance of Co(II)OEP ($\lambda_{max} = 395$ nm); see Supporting Information S1.[8] The appearance of a new absorption band due to the dimer radical anion at 605 nm is shown in Figure 1, where the absorbance at 605 nm increases to approach a constant value with an increase in the F_4Q concentration in the reaction with Co(II)OEP in the presence of a base. The dimer formation constant (K_d) is obtained from a plot of $1/\Delta Abs$ versus $[F_4Q]^{-1}$, whish affords the K_d value as 1800 M^{-1} (inset of Figure 1).[9,10]

The ESR spectrum observed upon addition of F_4Q (2.0×10^{-2} M) to a deaerated PhCN solution of Co(II)OEP (5.0×10^{-4} M) in the presence of a bulky base (1.0×10^{-4} M) is shown in Figure 2a, together with the computer simulation spectrum (Figure 2b). The presence of a bulky base was essential to observe the ESR signal.[11] The ESR spectrum consists of nine hyperfine lines due to eight equivalent fluorines ($I = 8 \times \frac{1}{2} = 4$) and further splitting by one cobalt nucleus ($I = \frac{7}{2}$). The hyperfine coupling constants
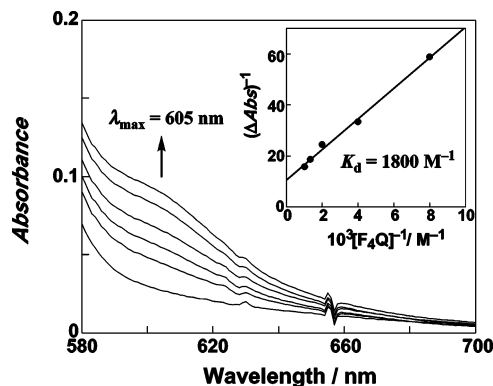

Figure 1. Spectral change at 605 nm during the addition of F_4Q (0, 1.3 × 10^{-4}, 2.5 × 10^{-4}, 5.0 × 10^{-4}, 7.5 × 10^{-4}, 1.0 × 10^{-3} M) to a PhCN solution of Co(II)OEP (2.0 × 10^{-5} M) in the presence of a bulky base (1.0 × 10^{-4} M) in deaerated PhCN at 298 K. Inset: Plots of $(\Delta Abs)^{-1}$ versus $[F_4Q]^{-1}$.
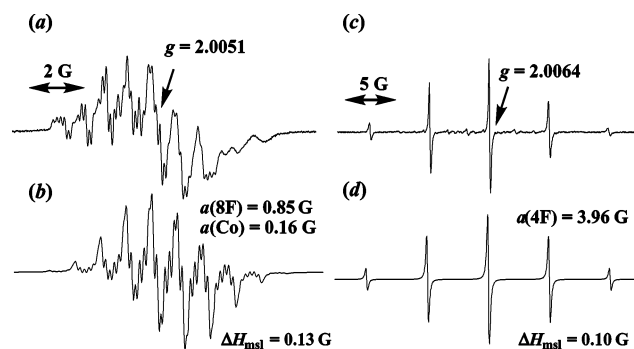

Figure 2. (a) ESR spectrum of dimer radical anion binding with Co(III)-OEP$^+$ in the presence of a bulky base in deaerated PhCN at 298 K and (b) the computer simulation spectrum. (c) ESR spectrum of $F_4Q^{\bullet-}$ in deaerated PhCN at 298 K and (d) the computer simulation spectrum.

(hfc) are determined as $a(8F) = 0.85$ G and $a(Co) = 0.16$ G.[12] This indicates formation of the dimer radical anion-cobalt(III) complex as shown in Scheme 1.

On the other hand, the ESR spectrum of $F_4Q^{\bullet-}$ (1.0×10^{-3} M) is shown in Figure 2c together with the computer simulation spectrum (Figure 2d),[13] which consists of five hyperfine lines due to four equivalent fluorines ($I = 4 \times \frac{1}{2} = 2$). The hfc value is determined as $a(4F) = 3.96$ G. The $a(8F)$ value of the dimer radical anion [$(F_4Q)_2^{\bullet-}$][14] is determined as just one-half of the $a(4F)$ value (see Supporting Information S2). In contrast, the $a(8F)$ value (0.85 G) of the dimer radical anion-cobalt(III) complex is much smaller than one-half of the $a(4F)$ of the monomer radical anion. This indicates that the interaction between $(F_4Q)_2^{\bullet-}$ and Co(III)OEP$^+$ results in a decrease in the degree of hyperconjugation as compared to the spin polarization. The g value (2.0051) of the dimer radical anion complex that is smaller than the value of the monomer radical anion (2.0064) also results from the interaction between the dimer radical anion and Co(III)OEP$^+$. The hyperfine splitting due to eight
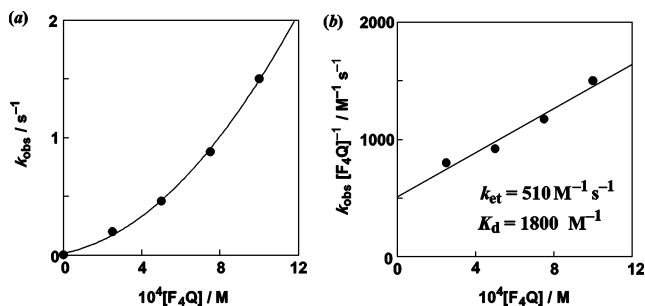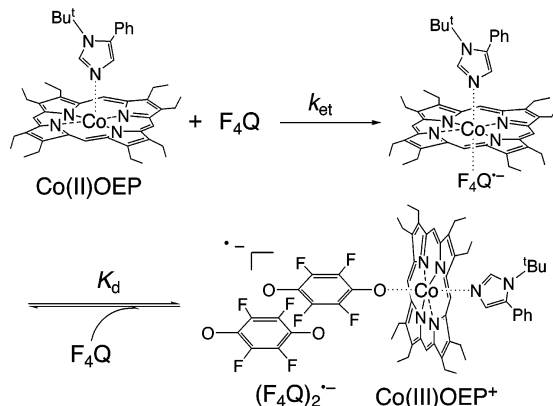
Figure 3. (a) Plots of k_{obs} versus [F_4Q] for electron transfer from Co(II)-OEP (1.0 × 10^{-5} M) to F_4Q in the presence of a bulky base (1.0 × 10^{-4} M) in deaerated PhCN at 298 K and (b) plot of $k_{obs}[F_4Q]^{-1}$ versus [F_4Q].

Scheme 1

equivalent fluorines indicates that the binding position of the dimer radical anions with Co(III)OEP$^+$ is changing rapidly at the ESR time scale.[15]

The self-promoted electron transfer due to the dimer radical anion complex in Scheme 1 is demonstrated by examining the kinetic formulation with respect to the substrate concentration. The rate of the appearance of the absorption band at 417 nm and the disappearance of the absorption band at 395 nm in electron transfer from Co(II)OEP to F_4Q in the presence of a base (1.0 × 10^{-4} M) obeyed pseudo-first-order kinetics to afford the same pseudo-first-order rate constants (k_{obs}) for electron transfer from Co(II)OEP to F_4Q, which is in large excess as compared to Co(II)OEP. The k_{obs} values increase parabolically with increasing [F_4Q] as shown in Figure 3a. Such second-order dependence of k_{obs} on [F_4Q] demonstrates self-promoted behavior in the electron transfer from Co(II)OEP to F_4Q. The second-order dependence with respect to [F_4Q] is separated from the first-order dependence as shown in Figure 3b, where the plot of $k_{obs}/[F_4Q]$ versus [F_4Q] exhibits a linear correlation as given by eq 1, where k_{et} is the rate constant of electron

$$k_{obs}/[F_4Q] = k_{et}(1 + K_d[F_4Q]) \qquad (1)$$

transfer from Co(II)OEP to F_4Q to form the monomer radical anion complex and K_d is the formation constant of the dimer radical anion complex in Scheme 1.[16] From the slope and intercept is determined the K_d value as 1800 M^{-1}, which agrees with the K_d value of the dimer radical anion complex derived independently from the spectral change in Figure 1.[17] Such agreement indicates that the self-promoted electron transfer is ascribed to formation of the dimer radical anion complex in Scheme 1. If the formation of the dimer radical anion complex occurs after the electron transfer, the electron-transfer rate would not be affected by the dimer formation. Thus, an electron transfer from Co(II)OEP to F_4Q is coupled with formation of the dimer radical anion complex.

When F_4Q is replaced by p-chloranil (Cl_4Q: $E_{red}^0 = 0$ V vs SCE), no self-promoted electron transfer was observed (S5).[18] In the case of $(F_4Q)_2{}^{\bullet-}$, polar stacking may be strong because $(F_4Q)_2{}^{\bullet-}$ is highly polarized, as indicated by ADF calculations: fluorines (-0.38 to -0.39) and oxygens (-0.52 to -0.53) are negatively charged, whereas carbons ($0.32-0.38$) are positively charged.[19]

In conclusion, we have demonstrated the first example of self-promoted electron transfer from a cobalt(II) porphyrin to p-fluoranil due to the formation of a strong complex between the dimer radical anion and the resulting cobalt(III) porphyrin.

Supporting Information Available: UV–vis spectra observed in electron transfer from Co(II)OEP to F_4Q (S1), ESR spectrum of $(F_4Q)_2{}^{\bullet-}$ (S2), NIR spectra of $(F_4Q)_2{}^{\bullet-}$ (S3), plots for determination of K_d of $(F_4Q)_2{}^{\bullet-}$ (S4), and plots of k_{obs} versus [Cl_4Q] (S5) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) For dimer radical cations, see: (a) Fukin, G. K.; Lindeman, S. V.; Kochi, J. K. *J. Am. Chem. Soc.* **2002**, *124*, 8329. (b) Lindeman, S. V.; Rosokha, S. V.; Sun, D.; Kochi, J. K. *J. Am. Chem. Soc.* **2002**, *124*, 843.
(8) The one-electron oxidation potential ($E_{ox}^0 = 0.10$ V vs SCE) of Co(II)-OEP in the presence of a bulky base is shifted to a positive direction as compared to the E_{ox}^0 value (0.31 V vs SCE) in the absence of a base in deaerated PhCN.
(9) The K_d value is determined using the relation, $1/\Delta Abs = 1/(\epsilon K_d[CoOEP]-[F_4Q]) + 1/\epsilon[CoOEP]$.
(10) In the absence of base, the K_d value was also determined from the plot of $(\Delta Abs)^{-1}$ ($\lambda_{max} = 610$ nm) versus [F_4Q]$^{-1}$ as 1200 M^{-1}.
(11) When a much less bulky base (triethylamine) is employed, no ESR signal was detected. This indicates that the bulky base stabilizes the dimer radical anion-Co(III) porphyrin complex.
(12) The other hfc values may be smaller than the line width (0.13 G).
(13) $F_4Q^{\bullet-}$ was produced by the one-electron reduction of F_4Q with semiquinone radical anion ($Q^{\bullet-}$) generated by the proportionation reaction of Q and QH$_2$ in the presence of a base. See: Fukuzumi, S.; Nakanishi, I.; Suenobu, T.; Kadish, K. M. *J. Am. Chem. Soc.* **1999**, *121*, 3468.
(14) $(F_4Q)_2{}^{\bullet-}$ was produced in the presence of large excess F_4Q.
(15) However, the reason all F are equivalent and the structure of the dimer radical anion complex have yet to be fully clarified.
(16) The kinetic formulation is virtually the same as the case of metal ion-promoted electron transfer where the radical anion is stabilized by complexation with the metal ion; see ref 4a.
(17) In the absence of base, the k_{et} and K_d values were also determined from the plots of $k_{obs}[F_4Q]^{-1}$ versus [F_4Q] as 490 M^{-1} s^{-1} and 1100 M^{-1}, respectively. The K_d value is larger than the value (210 M^{-1}) of $(F_4Q)_2{}^{\bullet-}$ without Co(III)OEP due to the binding of Co(III)OEP. See Supporting Information S3 and S4.
(18) No observation of self-promoted electron transfer from Co(II)OEP to Cl_4Q may be ascribed to the low K_d value (4 M^{-1} in MeCN) for the formation of $(Cl_4Q)_2{}^{\bullet-}$ as reported by Kochi et al.[6c]
(19) DFT calculations were performed with a basis function: double-ζ Slater-type orbital set {frozen core: C (1s), N (1s), O (1s); ADF basis set V (a small core)} on a COMPAQ DS20E computer using the Amsterdam Density Functional (ADF) program version 1999.02 developed by Baerends et al. See: te Valde, B.; Baerends, E. J. *J. Comput. Phys.* **1992**, *99*, 84.

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