

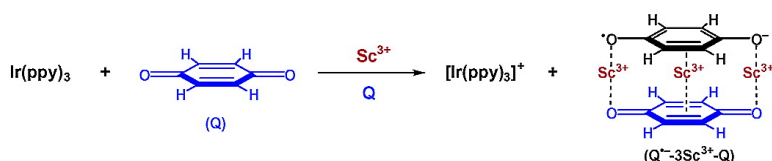
Communication

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Highly Self-Organized Electron Transfer from an Iridium Complex to *p*-Benzoquinone Due to Formation of a π -Dimer Radical Anion Complex Triply Bridged by Scandium Ions

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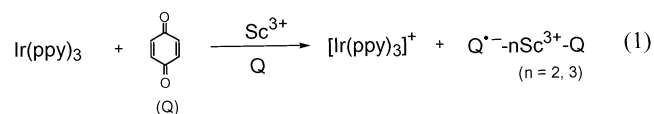
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Electron transfer is a pivotal process that controls biological redox processes such as photosynthesis and respiration, which are essential for life.^{1,2} Rates of electron transfer from electron donors to acceptors normally increase linearly with increasing concentrations of electron donors and acceptors. In contrast, self-organized electron-transfer systems involving a multiple molecular environment can lead to decreases of entropy equivalent to an increase of molecular electronic order for the activated complex, resulting in a substantial increase in the rate of electron transfer.³ In such a case, the rate of electron transfer is no longer linearly related to concentrations of reactants and promoting molecules for electron transfer. New frontiers of electron transfer to be exploited have been suggested to be in such nonlinear dynamic, self-organized electron-transfer systems as nature has developed to a high degree of perfection.³ Nonlinear high-order kinetics has been found only in chemical reactions which consist of many elementary reactions.^{4,5} In the case of well-defined electron-transfer reactions, the maximum kinetic order reported so far is second-order with respect to the concentration of metal ions which act as a promoter for electron-transfer reactions.^{6,7}

We report herein unusually high kinetic order in the scandium ion (Sc^{3+})-promoted electron-transfer reduction of *p*-benzoquinone (Q) in propionitrile (EtCN), third-order with respect to the concentration of Sc^{3+} and second-order with respect to the concentration of Q. Such high-order kinetics is shown to be ascribed to the self-organized Sc^{3+} -promoted electron-transfer reduction of Q to produce a π -dimer semiquinone radical anion complex that is triply bridged by three Sc^{3+} ions ($\text{Q}^{\cdot-}-3\text{Sc}^{3+}-\text{Q}$).

When tris(2-phenylpyridine)iridium^{8,9} $[\text{Ir}(\text{ppy})_3]$ is employed as an electron donor, no electron transfer from $[\text{Ir}(\text{ppy})_3]$ ($E^0_{\text{ox}} = 0.77$ V vs SCE)⁹ to Q ($E^0_{\text{red}} = -0.50$ V vs SCE)¹⁰ occurs, in agreement with the highly positive free energy change of electron transfer ($\Delta G_{\text{et}}^0 = 1.27$ eV). In the presence of $\text{Sc}(\text{OTf})_3$, however, an efficient electron transfer from $[\text{Ir}(\text{ppy})_3]$ to Q occurs to yield $[\text{Ir}(\text{ppy})_3]^+$ as shown in eq 1. As the reaction proceeds, the



absorption band due to $[\text{Ir}(\text{ppy})_3]$ ($\lambda_{\text{max}} = 380$ nm) decreases, accompanied by the appearance of a new absorption band ($\lambda_{\text{max}} = 580$ nm) due to the formation of $[\text{Ir}(\text{ppy})_3]^+$ with two isosbestic points at 348 and 490 nm (Figure 1).¹¹

To identify the reduced products of Q, the ESR spectra of the resulting solution were measured as shown in Figure 2. The ESR spectrum obtained at 298 K exhibits 23 hyperfine lines (Figure 2a). The computer simulation spectrum with hyperfine splitting due to eight equivalent protons ($a(8\text{H}) = 1.12$ G) and superhyperfine

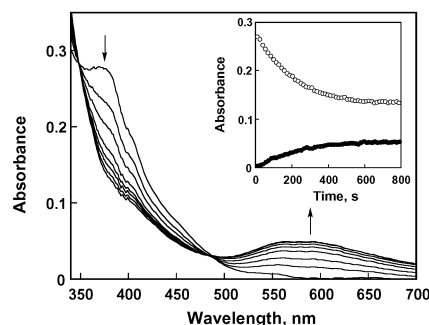


Figure 1. Spectral changes observed in the electron transfer from $[\text{Ir}(\text{ppy})_3]$ (1.5×10^{-5} M) to Q (4.8×10^{-4} M) in the presence of $\text{Sc}(\text{OTf})_3$ (9.7×10^{-2} M) in EtCN at 233 K. Inset: Time course of the absorption change at $\lambda = 380$ nm (○) and 580 nm (●).

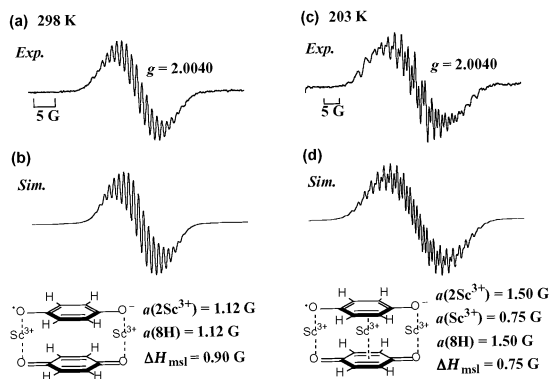


Figure 2. ESR spectra of an EtCN solution of $[\text{Ir}(\text{ppy})_3]$ (2.3×10^{-4} M) and Q (3.4×10^{-1} M) in the presence of $\text{Sc}(\text{OTf})_3$ (4.8×10^{-1} M) at (a) 298 K and (c) 203 K. The computer simulation spectra are shown in (b) and (d).

splitting due to two equivalent Sc^{3+} ions ($a(2\text{Sc}^{3+}) = 1.12$ G) is shown in Figure 2b. The complete agreement of the observed ESR spectrum (Figure 2a) with the computer simulation spectrum (Figure 2b) indicates that $\text{Q}^{\cdot-}$ forms a π -dimer with Q, which is bridged by two equivalent Sc^{3+} ions ($\text{Q}^{\cdot-}-2\text{Sc}^{3+}-\text{Q}$); see the structure below Figure 2b. It should be noted that there is no monomer radical anion detected by ESR. When the temperature is lowered to 203 K, the ESR spectrum is changed to exhibit further superhyperfine splitting due to additional Sc^{3+} ion (Figure 2c). The computer simulation spectrum affords hyperfine $a(8\text{H}) = 1.50$ G, $a(2\text{Sc}^{3+}) = 1.50$ G, and $a(\text{Sc}^{3+}) = 0.75$ G (Figure 2d). This indicates that the dimer radical anion ($\text{Q})_2^{\cdot-}$ is bridged by two equivalent Sc^{3+} ions and an additional Sc^{3+} ion which may be placed between the π planes of ($\text{Q})_2^{\cdot-}$ to produce the $\text{Q}^{\cdot-}-3\text{Sc}^{3+}-\text{Q}$ complex as shown in the structure below Figure 2d. Formation of the $\text{Q}^{\cdot-}-3\text{Sc}^{3+}-\text{Q}$ complex was also confirmed by the absorption spectra. A new

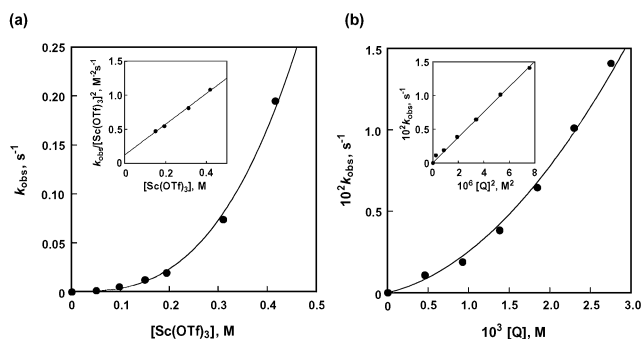


Figure 3. (a) Dependence of k_{obs} on $[\text{Sc}(\text{OTf})_3]$ for the electron transfer from $\text{Ir}(\text{ppy})_3$ (1.5×10^{-5} M) to Q (4.8×10^{-4} M) in the presence of $\text{Sc}(\text{OTf})_3$ in EtCN at 233 K. Inset: Plot of $k_{\text{obs}}/[\text{Sc}(\text{OTf})_3]^2$ versus $[\text{Sc}(\text{OTf})_3]$. (b) Dependence of k_{obs} on $[\text{Q}]$ for the electron transfer from $\text{Ir}(\text{ppy})_3$ (1.5×10^{-5} M) to Q in the presence of $\text{Sc}(\text{OTf})_3$ (5.1×10^{-2} M) in EtCN at 233 K. Inset: Plot of k_{obs} versus $[\text{Q}]^2$.

absorption band was observed at $\lambda_{\text{max}} = 604$ nm due to the $\text{Q}^{\cdot-} - 3\text{Sc}^{3+} - \text{Q}$ complex in the electron transfer from $\text{Ir}(\text{ppy})_3$ to Q in the presence of Sc^{3+} at a high concentration (0.58 M) in EtCN at 203 K (see Supporting Information S2).^{12,13}

The rate of electron transfer was determined by monitoring a decrease in absorbance at 380 nm due to $\text{Ir}(\text{ppy})_3$ and an increase in absorbance at 580 nm due to $[\text{Ir}(\text{ppy})_3]^+$. Under the pseudo-first-order kinetic conditions in the presence of a large excess of Q and Sc^{3+} as compared to $\text{Ir}(\text{ppy})_3$, the rate obeys pseudo-first-order kinetics (see the first-order plot in Supporting Information S3). The dependence of the observed pseudo-first-order rate constant (k_{obs}) on $[\text{Sc}^{3+}]$ is shown in Figure 3a, where the k_{obs} value increases, exhibiting a second-order dependence on $[\text{Sc}^{3+}]$ at low concentrations, changing to a third-order dependence at high concentrations. The dependence of k_{obs} on $[\text{Q}]$ was also examined for the electron transfer from $\text{Ir}(\text{ppy})_3$ to Q at various concentrations of Q at a constant concentration of Sc^{3+} . The k_{obs} value increases with $[\text{Q}]$ to show a second-order dependence on $[\text{Q}]$ as shown in Figure 3b. Such a second-order dependence of k_{obs} on $[\text{Q}]$ demonstrates self-promoted behavior in the Sc^{3+} -promoted electron transfer from $\text{Ir}(\text{ppy})_3$ to Q to produce the dimer radical anion complexes with Sc^{3+} ions.¹³

There is no interaction between Q and Sc^{3+} as indicated by the lack of spectral change of Q in the presence of Sc^{3+} . Thus, the high-order kinetic dependence with respect to $[\text{Sc}^{3+}]$ and $[\text{Q}]$ in Figure 3 is ascribed to formation of the $\text{Q}^{\cdot-} - 2\text{Sc}^{3+} - \text{Q}$ and $\text{Q}^{\cdot-} - 3\text{Sc}^{3+} - \text{Q}$ complexes observed in Figure 2. Such complex formation of $\text{Q}^{\cdot-}$ with Q and Sc^{3+} should result in a positive shift of the formal standard potential of the $\text{Q}^{\cdot-}/\text{Q}$ couple (E),¹⁴ and the Nernst equation is given by eq 2, where E^0 is the formal standard potential of the

$$E = E^0 + (2.3RT/F) \log\{K_1[\text{Q}][\text{Sc}^{3+}]^2(1 + K_2[\text{Sc}^{3+}])\} \quad (2)$$

$\text{Q}^{\cdot-}/\text{Q}$ couple in the absence of Sc^{3+} , K_1 is the formation constant for $\text{Q}^{\cdot-} - 2\text{Sc}^{3+} - \text{Q}$, and K_2 is the formation constant for $\text{Q}^{\cdot-} - 3\text{Sc}^{3+} - \text{Q}$ formed between $\text{Q}^{\cdot-} - 2\text{Sc}^{3+} - \text{Q}$ and Sc^{3+} .

Because Sc^{3+} has no effect on the oxidation potential of $\text{Ir}(\text{ppy})_3$, the free energy change of electron transfer from $\text{Ir}(\text{ppy})_3$ to Q in the presence of Sc^{3+} decreases according to eq 2. If such a change in the energetics is directly reflected in the transition state of self-organized electron transfer,¹⁵ the dependence of the observed pseudo-first-order rate constant of electron transfer (k_{obs}) on $[\text{Sc}^{3+}]$ is derived from eq 2, as given by eq 3

$$k_{\text{obs}} = k_0 K_1 [\text{Q}]^2 [\text{Sc}^{3+}]^2 (1 + K_2 [\text{Sc}^{3+}]) \quad (3)$$

where k_0 is the rate constant in the absence of Sc^{3+} . This equation agrees with the second-order dependence of k_{obs} on $[\text{Q}]$ (Figure 3b). The dependence of k_{obs} on $[\text{Sc}^{3+}]$ (Figure 3a) also agrees with eq 3 as indicated by the linear plot of $k_{\text{obs}}/[\text{Sc}^{3+}]^2$ versus $[\text{Sc}^{3+}]$ (inset in Figure 3a). From the slope and intercept are obtained K_2 and $k_0 K_1$ values of 18 M^{-1} and $5.4 \times 10^5 \text{ M}^{-4} \text{ s}^{-1}$, respectively. The K_2 value is consistent with the absorbance change at 604 nm due to the $\text{Q}^{\cdot-} - 3\text{Sc}^{3+} - \text{Q}$ complex in the electron transfer from $\text{Ir}(\text{ppy})_3$ to Q in the presence of a large excess of Sc^{3+} in EtCN at 233 K.¹⁶

In conclusion, rates of self-organized electron transfer from $\text{Ir}(\text{ppy})_3$ to Q promoted by Sc^{3+} exhibit unusually high-order kinetics due to the formation of the triply bridged π -dimer semiquinone radical anion complex with three Sc^{3+} ions ($\text{Q}^{\cdot-} - 3\text{Sc}^{3+} - \text{Q}$). This is the first example of highly self-organized electron transfer.

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Supporting Information Available: The absorption spectra of $[\text{Ir}(\text{ppy})_3]^+$ (S1), the absorption spectra of $\text{Q}^{\cdot-} - 3\text{Sc}^{3+} - \text{Q}$ (S2), the first-order plots (S3), and SHACV of Q in the presence of Sc^{3+} (S4) (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (13) The λ_{max} value of $[\text{Ir}(\text{ppy})_3]^+$ is determined from titration of $\text{Ir}(\text{ppy})_3$ by tris(4-bromophenyl)aminium hexachloroantimonate; see Supporting Information S1.
- (14) The absorption band due to the $\text{Q}^{\cdot-} - 3\text{Sc}^{3+} - \text{Q}$ complex ($\lambda_{\text{max}} = 604$ nm) was also observed in proportionation between hydroquinone (QH_2) and Q in the presence of Sc^{3+} (5.8×10^{-1} M) (S2). This absorption band overlaps with that due to $[\text{Ir}(\text{ppy})_3]^+$ ($\lambda_{\text{max}} = 580$ nm), whereas that due to the $\text{Q}^{\cdot-} - 2\text{Sc}^{3+} - \text{Q}$ complex has no absorption in this region.
- (15) For the π -dimer radical anion, see: Ganesan, V.; Rosokha, S. V.; Kochi, J. K. *J. Am. Chem. Soc.* **2003**, *125*, 2559.
- (16) The E value of Q (9.9×10^{-3} M) in the presence of Sc^{3+} (0.37 M) was determined by second harmonic ac voltammetry (SHACV) in EtCN at 233 K as 0.82 V (vs SCE), which is shifted by +1.32 V as compared to the E^0 value in the absence of Sc^{3+} (see Supporting Information S4).
- (17) For the detailed analysis on the driving force dependence of the electron-transfer rate constant in the presence of metal ions in which electron transfer is coupled with the complex formation with metal ions, see: Okamoto, K.; Imahori, H.; Fukuzumi, S. *J. Am. Chem. Soc.* **2003**, *125*, 7014.
- (18) The absorbance due to the $\text{Q}^{\cdot-} - 3\text{Sc}^{3+} - \text{Q}$ complex increases with increasing concentration of Sc^{3+} to reach a constant value at $[\text{Sc}^{3+}] > 0.5$ M. This indicates that the formation constant for the $\text{Q}^{\cdot-} - 3\text{Sc}^{3+} - \text{Q}$ complex is ca. 20 M^{-1} .

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