Metal Ion-Promoted Intramolecular Electron Transfer in a Ferrocene-Naphthoquinone Linked Dyad. Continuous Change in Driving Force and Reorganization Energy with Metal Ion Concentration

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Introduction

Electron transfer plays a pivotal role not only in chemical processes but also in biological redox processes that have tremendous relevance to our life such as photosynthesis and respiration.1–4 To understand factors to control important electron-transfer processes in biological systems, electron-transfer dynamics between donor and acceptor molecules bound to proteins have been studied extensively.5,6 A number of donor–acceptor linked systems with inert rigid spacers have also been developed to study the intramolecular electron-transfer reactions between the donor (D) and acceptor (A) molecules at a fixed distance.7–15 The electron-transfer dynamics between D and A at a fixed distance are now well understood in light of donor–acceptor linked systems with inert rigid spacers have also been developed to study the intramolecular electron-transfer reactions between the donor (D) and acceptor (A) molecules at a fixed distance.7–15 The electron-transfer dynamics between D and A at a fixed distance are now well understood in light of

Abstract: Thermal intramolecular electron transfer from the ferrocene (Fc) to naphthoquinone (NQ) moiety occurs efficiently by the addition of metal triflates (M^4+; Sc(OTf)_3, Y(OTf)_3, Eu(OTf)_3) to an acetonitrile solution of a ferrocene-naphthoquinone (Fc-NQ) linked dyad with a flexible methylene and an amide spacer, although no electron transfer takes place in the absence of M^4+. The resulting semiquinone radical anion (NQ^-) is stabilized by the strong binding of M^4+ with one carbonyl oxygen of NQ^- as well as hydrogen bonding between the amide proton and the other carbonyl oxygen of NQ^- . The high stability of the Fc^-NQ^-/M^4+ complex allows us to determine the driving force of electron transfer by the conventional electrochemical method. The one-electron reduction potential of the NQ moiety of Fc-NQ is shifted to a positive direction with increasing concentration of M^4+, obeying the Nernst equation, whereas the one-electron oxidation potential of the Fc moiety remains the same. The driving force dependence of the observed rate constant (k_ET) of M^4+ -promoted intramolecular electron transfer is well evaluated in light of the Marcus theory of electron transfer. The driving force of electron transfer increases with increasing concentration of M^4+ [M^4+] , whereas the reorganization energy of electron transfer decreases with increasing [M^4+] from a large value which results from the strong binding between NQ^- and M^4+. 

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the Marcus theory of electron transfer. Once the driving force \((-\Delta G_{\text{ET}}^0)\) and reorganization energy \(\lambda_{DA}\) of electron transfer between D and A are determined, the activation free energy of electron transfer \(\Delta G^\#_{\text{ET}}\) is well predicted using the Marcus equation (eq 1).16

\[
\Delta G^\#_{\text{ET}} = (\lambda_{DA})\left(1 + \frac{\Delta G_{\text{ET}}^0}{\lambda_{DA}}\right)^2
\]

The driving force of electron transfer is obtained from the one-electron oxidation potential of electron donor \((E_{\text{ox}})\) and the one-electron reduction potential of electron acceptor \((E_{\text{red}})\) using eq 2, where \(F\) is the Faraday constant. The reorganization energy

\[
\lambda_{DA} = \frac{(\lambda_D + \lambda_A)}{2}
\]

to predict the \(\Delta G_{\text{ET}}^\#\) values using eq 1.16 In other words, the electron-transfer reactivity is automatically determined once the combination of D and A is fixed. However, it has recently been demonstrated that the slope of electron-transfer reactivity can be expanded much further by introducing a third component such as a metal ion to the D–A system provided that the metal ion can interact with one of the products of electron transfer, for example, the radical anion \((A--)\).18,19 Although photoexci-
tation of the D or A moiety or radiolysis is normally required to start the electron transfer of the D–A linked system, thermal intramolecular electron-transfer reactions of D–A linked systems, which would otherwise never occur, can be started by the addition of the appropriate metal ions.20,21 There have also been a number of examples of metal ion-promoted intramolecular electron-transfer reactions.22–26 In biological redox systems, a variety of metal ion enzymes are also involved to finely control electron-transfer processes.1

We report herein the driving force dependence of metal ion-promoted intramolecular electron transfer. The results are evaluated in light of the Marcus theory of electron transfer. The D–A system employed in this study is a ferrocene-naphthoquinone dyad (Fc-NQ) in which the metal ion-promoted thermal intramolecular electron-transfer reaction proceeds efficiently (Scheme 1). The metal ion complexes with NQ•‒ moiety of Fc-NQ are stable enough to determine the one-electron reduction potentials of Fe-NQ in the presence of metal ion. This enables us to determine the driving force of metal ion-promoted electron transfer and hence to examine the driving force dependence of the electron-transfer dynamics in light of the Marcus theory of electron transfer.

**Experimental Section**

**General.** 1H NMR spectra were measured on a JEOL JNM-A-300 NMR spectrometer. Fast atom bombardment mass spectra (FAB-MS) were obtained on a JEOL JMS-DX300 mass spectrometer. Melting points were recorded on a Yanagimoto micro-melting point apparatus and not corrected. IR spectra were measured on a Shimadzu FT-IR 8200 PC as KBr disks. Elemental analyses were performed on a Perkin-Elmer model 240C elemental analyzer.

**Materials.** All solvents and chemicals were of reagent grade quality, obtained commercially, and used without further purification unless otherwise noted. Tris(2,2’-bipyridyl)ruthenium(III) hexafluorophosphate \([\text{Ru(bpy)}_2(\text{PF}_6)_2]\) was prepared according to the literature.27 Scandium triflate \([\text{Sc(OTf)}_3]\) (99%, FW = 492.16) was purchased from Pacific

![Scheme 1](image)
Fc-NQ as a brown solid (55 mg, 0.10 mmol, 32%). 1H NMR (300 MHz, CDCl3): δ 8.11 (ddd, 2H, J = 2, 2.7 Hz), 7.74 (ddd, 2H, J = 2, 7.7 Hz), 7.45 (m, 4H), 7.42 (s, 1H), 6.16 (s, 1H), 4.60 (t, 2H, J = 2 Hz), 4.29 (t, 2H, J = 2 Hz), 4.06 (t, 2H, J = 7 Hz), 4.03 (s, 5H), 2.44 (t, 2H, J = 7 Hz), 1.97 (q, 2H, J = 7 Hz), 1.90 (q, 2H, J = 7 Hz), 1.64 (q, 2H, J = 7 Hz). 13C NMR (300 MHz, CDCl3): δ 184.9 (NQ, C=O), 171.1 (NQ, C=O), 159.7 (amide, C=O), 136.0 (Ph), 135.2 (NQ), 134.4 (NQ), 133.3 (NQ), 132.1 (NQ), 131.3 (NQ), 126.7 (Fc), 126.5 (Fc), 126.2 (Fc), 119.8 (Ph), 110.3 (NQ), 66.2 (−CH2−O), 37.5 (O−C−CH2), 27.6 (−CH2−), 26.0 (−CH2−), 25.2 (−CH2−). FAB-MS m/z 547. Anal. Calcd for C43H21FeN2O: C, 72.21; H, 3.68; N, 2.68. Found: C, 72.16; H, 3.76; N, 2.70.

Electrochemical Measurements. Electrochemical measurements were performed on a BAS 100 W electrochemical analyzer in deaerated MeCN containing 0.1 M Bu4NPF6 (TBAPF6) as supporting electrolyte at 298 K. A conventional three-electrode cell was used with a platinum working electrode (surface area of 0.3 mm2), a platinum wire as the counter electrode. The Pt working electrode (BAS) was routinely polished with a BAS polishing alumina suspension and rinsed with acetone before use. The measured potentials were recorded with respect to the Ag/AgNO3 (0.10 M) reference electrode. The second-harmonic alternating current voltammetry (SHACV) measurements of Fe-NQ in the presence of Y(OTf)3 were carried out with a BAS 100B electrochemical analyzer in deaerated MeCN containing 0.1 M Bu4NPF6 (TBAPF6) as supporting electrolyte. All potentials (vs Ag/Ag+) were converted to values versus SCE by adding 0.29 V. All electrochemical measurements were carried out under an atmospheric pressure of Ar.

ESR Measurements. The ESR spectra of Fe-NQ− and 2-methoxy-1,4-naphthoquinone radical anion (2-MeONQ−) were produced by the chemical reduction with the naphthalene radical anion generated by naphthalene (0.5 g) in THF with sodium (0.075 g). The concentration of the naphthalene radical anion was determined by the appearance of the absorption band at the characteristic peak of the semiquinone radical anion (e = 422 nm) = 6.0 × 103 M−1 cm−1 in MeCN produced by the titration of the naphthalene radical anion to p-benzoquinone. The solution containing the radical anion was transferred to an ESR tube under an atmospheric pressure of Ar. The ESR spectra were recorded on a JEOL X-band spectrometer (JES-REIXE) with a quartz ESR tube (1.2 mm i.d.). The ESR spectra were measured under nonsaturating microwave power conditions. The magnitude of modulation was chosen for the optimal signal-to-noise ratio.


to optimize the resolution and the signal-to-noise (S/N) ratio of the observed spectra. The g values were calibrated with an Mn$^{2+}$ marker, and the hyperfine coupling (hfc) constants were determined by computer simulation using the Calleo ESR version 1.2 program coded by Calleo Scientific on an Apple Macintosh personal computer.

Theoretical Calculations. Density functional (DFT) calculations were performed with a basis function: double-$ω$ Slater-type orbital set (frozen core: C (1s), N (1s), O (1s); ADF basis set II (large)) on a COMPAQ DS20E computer using the Amsterdam density functional (ADF) program version 1999.02 developed by Baerends et al.33 The gradient corrections of Becke88 (exchange) and Perdew86 (correlation) were included in the exchange-correlation functional. The hfc values are derived from multiplying 506.82 and the spin density values of each hydrogen.

Results and Discussion

Metal Ion-Promoted Intramolecular Electron Transfer.

No electron transfer from the ferrocene (Fc) to naphthoquinone (NQ) moiety occurs in Fc-NQ with a flexible methylene spacer including an amide linkage thermally in MeCN at 298 K, as expected from the highly positive value of free energy change of electron transfer ($\Delta G^0_{ET} = 1.19$ eV). However, addition of scandium triflate (Sc(OTf)$_3$: 1.0 \times 10^{-3}$ M) to MeCN solution of Fc-NQ (2.0 \times 10^{-3} M) results in the formation of Fc$^+$ as indicated by the appearance of the absorption band due to Fc$^+$ at 860 nm$^{34}$ with the absorption band at $\lambda_{max} = 420$ nm (Scheme 1, Figure 1). This indicates that an intramolecular electron transfer occurs in the presence of Sc$^{3+}$ to produce Fc$^+$-NQ$^-$/Sc$^{3+}$ in which Sc$^{3+}$ is bound to NQ$^-$ and that the absorption band at 420 nm is due to the NQ$^-$/Sc$^{3+}$ complex. The rates of appearance of the absorption band at 420 and 800 nm obeyed first-order kinetics, and the same first-order rate constants ($k_{ET}$) were obtained from the first-order rate constants determined at 420 nm increase linearly with increasing [Sc$^{3+}$] (Figure 2). The first-order dependence of $k_{ET}$ on [M$^n$+] is consistent with the complexation of one Sc$^{3+}$ with the NQ$^-$/moiety in Fc$^+$-NQ$^-$. The binding strength of NQ$^-$ with M$^{n+}$ is expected to vary depending on the Lewis acidity of M$^{n+}$.$^{23,35}$

The replacement of Sc$^{3+}$ by weaker acids such as Y$^{3+}$ and Eu$^{3+}$ results in a slower electron-transfer rate, and by much weaker Lewis acids such as Ba$^{2+}$, Ca$^{2+}$, and Mg$^{2+}$ results in no occurrence of electron transfer from Fc to NQ in Fc-NQ. The $k_{ET}$ values determined in the presence of various concentrations of M$^{n+}$ are summarized in Table 1.

The ESR spectra were measured upon addition of Y(OTf)$_3$ (2.0 \times 10^{-2} M) to MeCN solution of Fc-NQ (9.1 \times 10^{-3} M) to confirm the formation of Fc$^+$-NQ$^-$/Y$^{3+}$ and Fc$^+$-NQ$^-$/Sc$^{3+}$ complexes at 298 K. The observed ESR spectra are shown in Figure 3a (Fc$^+$-NQ$^-$/Y$^{3+}$) and Figure 3b (Fc$^+$-NQ$^-$/Sc$^{3+}$). The g values are determined as 2.0337 (Fc$^+$-NQ$^-$/Y$^{3+}$) and 2.0338 (Fc$^+$-NQ$^-$/Sc$^{3+}$). The hyperfine coupling constants are different quite depending on the type of metal ion. This indicates the binding of metal ions with the NQ$^-$/moiety of Fc$^+$-NQ$^-$. The hyperfine coupling (hfc) constants are determined by the computer simulation spectra (see Supporting Information S1).

In contrast to the instability of the metal ion complexes of radical anions of p-benzoquinone derivatives,$^{26a}$ the Fc$^+$-NQ$^-$/M$^{n+}$ complex particularly in the case of the Sc$^{3+}$ complex is very stable even at 298 K.$^{36}$ Such a remarkable stability of the Fc$^+$-NQ$^-$/Sc$^{3+}$ complex may be ascribed to the hydrogen bonding of the amide proton with one carbonyl oxygen of the semi-
The semiquinone radical anion complexes with metal ions have been studied for their spin density distribution of \( \text{Fc-NQ}^- \) and \( \text{Fc-NQ}^- \), where the radical anion of \( \text{NQ}^- \) is produced by the electron-transfer reduction of \( \text{2-MeONQ}^- \) as follows.

\( \text{Fc-NQ}^- \) is produced by the electron-transfer reduction of \( \text{Fc-NQ} \) by naphthalene radical anion (Scheme 3). The ESR spectrum of \( \text{Fc-NQ}^- \) thus produced is shown in Figure 4a together with the computer simulation spectrum (Figure 4b). The g value of \( \text{Fc-NQ}^- \) in Figure 4a is determined as 2.0060, which is significantly larger than those of the metal ion complexes in Figure 3. This indicates that more spin is localized on the oxygen atom which has a large spin−orbit coupling constant in the case of \( \text{Fc-NQ}^- \) as compared to those of the metal ion complexes. The simulated hyperfine coupling constants (hfc) can be well reproduced by the ADF calculation of the oxygen atom which has a large spin−orbit coupling constant.

\( \text{Fc-NQ}^- \) in which the Fc moiety is omitted as indicated in Figure 4 (the values in parentheses). The optimized structures of \( \text{Fc-NQ}^- \) and \( \text{2-MeONQ}^- \) obtained by the Amsterdam density function (ADF) calculation with the II (large) basis set are shown in Figure 5. The O−H distance between the carbonyl oxygen of \( \text{NQ}^- \) and the amide proton in \( \text{Ph-NQ}^- \) is 1.62 Å. This value is even shorter than the hydrogen bonding distance between the semiquinone radical anion and water (1.78 Å).

The radical anion (2-MeONQ\(^-\)) without hydrogen bonding is also produced by the electron-transfer reduction of 2-MeONQ by the naphthalene radical anion as shown in Figure 4c. The simulated hfc values can also be well reproduced by the ADF calculation as indicated in Figure 4d (the values in parentheses), and they are quite different from those observed in \( \text{Fc-NQ}^- \) with hydrogen bonding.

**Change in the One-Electron Reduction Potential of \( \text{Fc-NQ}^- \) in the Presence of Metal Ions.** The remarkable stability of \( \text{Fc}^-/\text{NQ}^-/\text{M}^{3+} \) complexes mentioned above allows us to determine the one-electron reduction potentials of \( \text{Fc-NQ}^- \) and \( \text{2-MeONQ}^- \) in the presence of various concentrations of metal ions by cyclic voltammetry measurements as shown in Figure 6. The one-electron reduction potential of the NQ moiety is observed as a well-defined reversible wave at −0.81 V (Figure 6a). In the presence of \( 7.0 \times 10^{-3} \) M \( \text{Sc}^{3+} \), the \( E_{\text{red}} \) value exhibits a remarkable positive shift from −0.81 to 1.26 V, whereas the one-electron oxidation potential of the Fc moiety remains the same irrespective of the absence or presence of \( \text{Sc}^{3+} \) (Figure 6b). The cyclic voltammograms of \( \text{Fc-NQ}^- \) in the presence of various concentrations of \( \text{Sc}^{3+} \) are shown in the Supporting Information.

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(36) The semiquinone radical anion complexes with metal ions have been only observed at low temperature by ESR. In contrast, the \( \text{Fc}^-/\text{NQ}^-/\text{Se}^{3+} \) complex has a long lifetime (>3 h) at 298 K. The \( \text{Fe}^-/\text{O}^-/\text{Se}^{3+} \) complex reported in ref 21 is also too unstable to detect the ESR spectrum at 298 K because of the fast disproportionation of the \( \text{Q}^-/\text{Se}^{3+} \) complex.

(37) The hfc values were also calculated using the B3LYP method. The ADF calculation predicts the hfc values in closer agreement with the experimental results.


(39) The one-electron oxidation potential for the Fc/Fc couple in Fc-NQ agrees with that of ferrocene (\( E_{\text{ox}}^0 \) vs SCE = 0.37 V), see: Fukuzumi, S.; Mochizuki, S.; Tanaka, T. Inorg. Chem. 1989, 28, 2459.

(40) The anodic peak current for the oxidation of the \( \text{Fc-NQ}^-/\text{Se}^{3+} \) complex is smaller than the cathodic peak current for the reduction of \( \text{Fc-NQ}^- \) in the presence of \( \text{Se}^{3+} \) because of the instability of the \( \text{Fc-NQ}^-/\text{Se}^{3+} \) complex. A similar trend is observed for cyclic voltammograms of \( \text{Fc-NQ}^- \) in the presence of other metal ions.
Information (S2). Similar positive shifts of $E_{\text{red}}$ are observed in the presence of Eu$^{3+}$ (eq 4) and Y$^{3+}$ (S3).

The positive shift of $E_{\text{red}}$ in the presence of metal ion is ascribed to the binding of metal ion with NQ$^{-}$ (eq 4) as indicated in Figure 3. In such a case, $E_{\text{red}}$ is given as a function

$$\text{Fc-NQ}^{-} + M^{n+} \rightarrow K_{\text{red}} \text{Fc-NQ}^{-}/M^{n+}$$

of the concentration of $M^{n+}$, in accordance with the Nernst equation (eq 5), where $E_{\text{red}}^0$ is the one-electron reduction potential in the absence of metal ion, $K_{\text{red}}$ is the formation constant of the Fc-NQ$^{-}$/M$^{n+}$ complex, and $K_{\text{ox}}$ is the formation constant of the Fc-NQ/M$^{n+}$ complex.\(^{41}\)

$$E_{\text{red}} = E_{\text{red}}^0 + (2.3RT/F) \times \log\{(1 + K_{\text{red}}[M^{n+}])/(1 + K_{\text{ox}}[M^{n+}])\}$$

Because $K_{\text{red}}[M^{n+}] \gg 1$, and $K_{\text{ox}}[M^{n+}] \ll 1$, eq 5 is written by eq 6, where $\Delta E_{\text{red}}$ is the potential shift in the presence of $M^{n+}$

$$\Delta E_{\text{red}} = (2.3RT/F) \log K_{\text{red}}[M^{n+}]$$

from the value in its absence.


The plots of $\Delta E_{\text{red}}$ versus log[M$^{n+}$] for the one-electron reduction of Fc-NQ$^-$ in the presence of Sc$^{3+}$ (●), Y$^{3+}$ (■), and Eu$^{3+}$ (▲) in MeCN at 198 K. The plot of each [M$^{n+}$] affords the same slope of 0.059.

The slope of each plot is determined as 0.059, which agrees with the expected slope (\(=2.3RT/F\) at 298 K) by the Nernst equation (eq 6). The intercepts of linear plots in Figure 7 thus afford the binding constants $K_{\text{red}}$(Sc$^{3+}$) = $1.6 \times 10^{37}$ M$^{-1}$, $K_{\text{red}}$(Sc$^{3+}$) (Y$^{3+}$) = $1.1 \times 10^{31}$ M$^{-1}$, and $K_{\text{red}}$(Eu$^{3+}$) = $3.3 \times 10^{29}$ M$^{-1}$. The $K_{\text{red}}$ values correspond to the free energy changes of the metal ion binding: 2.20 eV (Sc$^{3+}$), 1.83 eV (Y$^{3+}$), and 1.74 eV (Eu$^{3+}$).\(^{42}\) Such a large binding energy results in a remarkable change in the driving force of electron transfer in Fc-NQ from a highly negative value to a positive value in the presence of M$^{n+}$. The driving force of electron transfer in the presence of M$^{n+}$ ($\Delta G_{\text{ET}}$) is given by eq 7

$$\Delta G_{\text{ET}} = -\Delta G_{\text{ET}}^0 + RT \ln(K_{\text{red}}[M^{n+}])$$

where $\Delta G_{\text{ET}}^0$ is the driving force in the absence of M$^{n+}$. The $\Delta G_{\text{ET}}$ values determined in the presence of various concentrations of M$^{n+}$ are summarized in Table 1.

Driving Force Dependence of Metal Ion-Promoted Electron Transfer. Figure 8 shows the driving force dependence of log $k_{\text{ET}}$ of M$^{n+}$-promoted electron transfer, where the $k_{\text{ET}}$ and $\Delta G_{\text{ET}}^0$ values are taken from Table 1. Three separate linear correlations are obtained for the case of Sc$^{3+}$, Y$^{3+}$, and Eu$^{3+}$ (Figure 8). The slope of each linear plot is determined as 16.9 (eV)$^{-1}$, which corresponds to 1/2$k_b$T at 298 K, where $k_b$ is the Boltzmann constant. This indicates that the change in driving force with concentration of M$^{n+}$ is directly reflected on the change in the activation free energy, that is, $\partial(\Delta G_{\text{ET}}^0)/\partial(\Delta G_{\text{ET}}) = 1$. This is quite different from the slope expected from the Marcus equation (eq 1): $\partial(\Delta G_{\text{ET}}^0)/\partial(\Delta G_{\text{ET}})$

\(^{42}\) Binding free energy changes are calculated as the follow equation: (binding free energy changes) $= -RT \ln(K_{\text{red}})$

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of the calculated Marcus lines with the observed lines, it is 7020 J. AM. CHEM. SOC.

Because

Scheme 4

Figure 8. Plots of log \( k_{ET} \) versus \( -\Delta G_{ET} \) in M\( ^{n+} \)-promoted intramolecular electron transfer in Fc-NQ in the addition of Sc\( ^{3+} \) ( ), Y\( ^{3+} \) ( ), and Eu\( ^{3+} \) ( ) in deaerated MeCN at 298 K. The plot of \( k_{ET} \) on each [M\( ^{n+} \)] gives a straight line with a slope of 16.9. The broken lines (a), (b), and (c) represent the fit to eq 9 with (a) \( \lambda = 4.3 \) eV, (b) \( \lambda = 4.4 \) eV, and (c) \( \lambda = 4.5 \) eV.

promoted intramolecular electron transfer in Fc-NQ is adiabatic.\(^{43}\) Hereby, \( h \) is the Planck constant. From the comparison of the calculated Marcus lines with the observed lines, it is apparent that the \( \lambda_{DA} \) value changes with the concentration of M\( ^{n+} \). Such a change of \( \lambda_{DA} \) with [M\( ^{n+} \)] can be evaluated within the context of the Marcus theory of electron transfer (vide infra).

The \( \lambda_{DA} \) value consists of \( \lambda_D \) for the electron self-exchange between D and D\( ^{n+} \) and \( \lambda_A \) for that between A and A\( ^{n+} \) (eq 3). Because the metal ion is involved only in the acceptor part, the dependence of \( \lambda_A \) on [M\( ^{n+} \)] should be considered. The electron self-exchange between Fc-NQ and the Fc-NQ\(^{-}/M^{n+} \) complex occurs via formation of the Fc-NQ/M\( ^{n+} \) complex as shown in Scheme 4. According to Scheme 4, the electron self-exchange rate constant \( k_{ex} \) is given by eq 9, where \( Z \) is the frequency factor for an intermolecular reaction, and \( \lambda_{A0} \) is the reorganization energy for the electron self-exchange between Fc-NQ/M\( ^{n+} \) and Fc-NQ\(^{-}/M^{n+} \). The reorganization energy between Fc-NQ and Fc-NQ\(^{-}/M^{n+} \) \( (\lambda_A) \) is then given by eq 10, by comparing eq 9 with \( k_{ex} = Z \exp(\lambda_A/4k_BT) \). From eq 3, the reorganization

\( k_{ET} = (k_BT/h) \exp(-\Delta G_{ET}^+/k_BT) \) (8)

\( \lambda_{DA} = \lambda_A - 4RT \ln(K_{m[M^{n+}]})) \) (10)

\( \lambda_{DA} = \lambda_{DA0} - 2RT \ln(K_{m[M^{n+}]})) \) (11)

Because \( \lambda_{DA} \gg -\Delta G_{ET} \) in Figure 8, eq 1 is simplified to eq 12 under the present experimental conditions. The driving force dependence of \( k_{ET} \) is derived from eqs 8, 11, and 12 as eq 13

\( \Delta G_{ET} = (\lambda_{DA0}/4) + (\Delta G_{ET}/2) \) (12)

\( -RT \ln(k_{ET}/[M^{n+}])^{1/2} = C + (\Delta G_{ET}/2) \) (13)

where \( C \) is a constant which is independent of the concentration of M\( ^{n+} \), given by eq 14.

\( C = (\lambda_{DA0}/4) - RT \ln(k_BT(K_{m[M^{n+}]}^{1/2}/h) \) (14)
Using this relation, we determined the $\Delta H_A^q$ value as 0.86 eV from the $\Delta H_{\text{obs}}^q$ value (0.54 eV) and the reported value of $\Delta H_D^q$ (0.22 eV). Thus, the $\lambda_A^0$ value is estimated as 3.44 eV, because $\Delta H_A^q - \Delta H_D^q < 0$. The reorganization energy $\lambda_A^0$ consists of twice the stabilization energy of the NQ$^{-}$/Sc$^{3+}$ complex with the optimized structure as compared to the NQ$^{2-}$/Sc$^{3+}$ complex with the same nuclear configuration as the neutral NQ/Sc$^{3+}$ complex. Because the stabilization free energy is obtained as 2.20 eV, which is derived from the $K_{\text{red}}$ value for the NQ$^{2-}$/Sc$^{3+}$ complex (vide supra), the $\lambda_A^0$ value is estimated as 4.40 eV. This value is consistent with the estimation from the $\Delta H_A^q$ value: $\lambda_A^0 > 3.44$ eV.

In conclusion, metal ion-promoted intramolecular electron transfer in Fe-NQ proceeds via strong binding of the NQ$^{-}$ moiety with metal ion, which results in a drastic change of the free energy change of electron transfer from a highly positive value to a highly negative value. Such a drastic change of driving force of electron transfer is accompanied by a large reorganization energy required for the metal ion-promoted electron transfer. The driving force dependence of $k_{\text{ET}}$ of the metal ion-promoted intramolecular electron transfer can be well evaluated within the context of the Marcus theory of electron transfer in which the driving force increases with increasing concentrations of metal ions, whereas the reorganization energy of electron transfer decreases with concentrations of metal ions.

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Supporting Information Available: ESR simulation of Fe$^{2+}$/NQ$^{2-}$/M$^{n+}$ (S1), CVs of Fe-NQ in the presence of Sc$^{3+}$ (S2), and CV and SHACV of Fe-NQ in the presence of Y$^{3+}$ (S3) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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