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Thermal Intramolecular Electron Transfer in a Ferrocene – Naphthoquinone Linked Dyad Promoted by Metal Ions[**]

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Electron transfer (ET) in a fixed donor – acceptor distance plays an essential role in photosynthesis, respiration, and redox-mediated enzyme catalysis in biological redox reactions as well as many simple chemical redox reactions.[1, 2] Thus, ET reactions between donor and acceptor molecules bound to proteins have been studied extensively to understand the factors to control the ET process.[3] A number of donor – acceptor linked systems with inert rigid spacers have also been developed to study the ET reactions between the donor and acceptor molecules at a fixed distance.[4–8] In each case, however, photoexcitation of the donor or acceptor moiety or radiolysis is required to start the ET reaction. To date there has been no report on ET in donor – acceptor linked systems started thermally. This situation is taken as a matter of course since it would be impossible to connect donor and acceptor molecules if an ET occurred thermally. However, a number of examples report intermolecular ET reactions with a significant acceleration in the presence of a third component acting as a catalyst or promoter.[9, 10] Most importantly, thermal intermolecular ET reactions, which would otherwise be unlikely to occur, proceed efficiently in the presence of metal ions which can promote the ET reactions.[9, 10] In theses cases, addition of a metal ion to the donor – acceptor systems can start ET reactions. ET reactions can also be attenuated through noncovalent interactions, such as hydrogen bonding, which plays an important role in biological ET systems.[11]

We report herein the first example of an intramolecular ET reaction in a donor – acceptor linked system started thermally by addition of a metal ion. A newly designed ferrocene – naphthoquinone dyad (Fc – NQ) is employed to examine the metal-ion promoted thermal intramolecular ET reaction (Scheme 1).

Details on the synthesis and characterization of Fc – NQ are given as Supporting Information (S1 – S3). The cyclic voltammograms of Fc-NQ in acetonitrile (MeCN) exhibited two reversible one-electron redox couples of two redox-active

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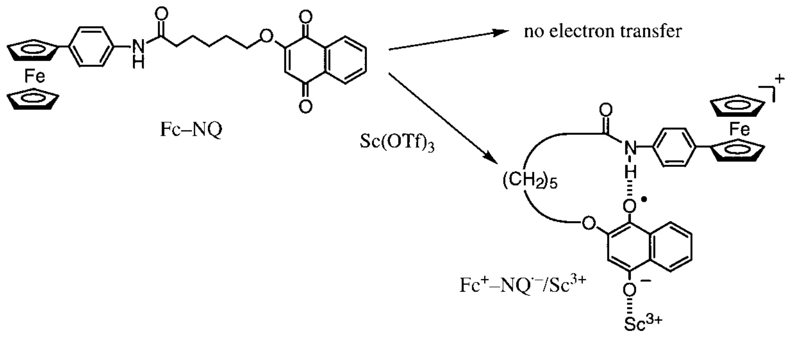
Supporting information for this article is available on the WWW under http://www.angewandte.com or from the author. Synthetic procedures of Fc – NQ (S1 – S3), the absorption spectrum of Fc – NQ in the Sc^{3+}-promoted ET (S4), ESR spectrum of Fc – NQ$^{\bullet-}$ (S5), DFT calculation of Ph – NQ$^{\bullet-}$ (S6), cyclic voltammograms of Fc – NQ in the presence of metal ions (S7) (7 pages, print/PDF).



Scheme 1. OTf = trifluoromethanesulfonate.

moieties at 0.38 V and −0.81 V (versus saturated calomel electrode (SCE)). The former one-electron redox potential corresponds to the Fc^+/Fc couple which agrees with the one-electron oxidation potential of ferrocene (E^0_{ox} vs SCE = 0.37 V).[12] The latter potential thereby corresponds to the $NQ/NQ^{\bullet-}$ couple. No ET from the Fc to the NQ moiety occurs thermally in Fc–NQ in MeCN at 298 K, as expected from the highly positive free energy change of electron transfer ($\Delta G^0_{et} = 1.19$ eV). Addition of 1.0 mM of magnesium perchlorate ($Mg(ClO_4)_2$) or lutetium triflate ($Lu(OTf)_3$) to an MeCN solution of Fc–NQ (2.0×10^{-4} M) resulted in no change in the visible spectrum. However, addition of scandium triflate ($Sc(OTf)_3$: 1.0 mM) to an MeCN solution of Fc–NQ (2.0×10^{-4} M) resulted in oxidation of the Fc unit as indicated by appearance of the absorption band at 860 nm arising from Fc^+ together with the absorption band at $\lambda_{max} = 420$ nm (see Supporting Information S4). This data indicates that an intramolecular ET occurs in the presence of Sc^{3+} to produce Fc^+–$NQ^{\bullet-}$ in which Sc^{3+} is bound to $NQ^{\bullet-}$ and that the absorption band at 420 nm is from the $NQ^{\bullet-}/Sc^{3+}$ complex (Scheme 1). The absorption band at 420 nm is quite different from that of Fc–$NQ^{\bullet-}$ produced by the chemical reduction of Fc–NQ with naphthalene radical anion ($\lambda_{max} = 617$ nm) and is clearly a result of complexation with the Sc^{3+} ion.

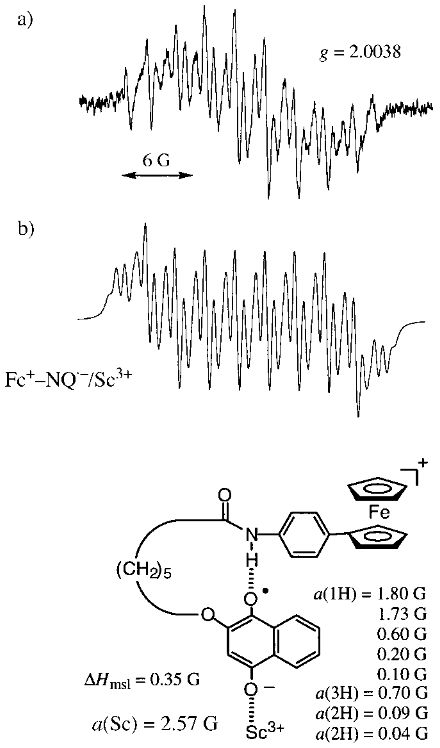


Figure 1. a) ESR spectrum of the Fc^+–$NQ^{\bullet-}/Sc^{3+}$ ion complex (9.1 mM) produced in intramolecular ET of Fc–NQ in the presence of $Sc(OTf)_3$ (20 mM) in deaerated MeCN at 298 K. b) The computer simulation spectrum.

To confirm formation of the Fc^+–$NQ^{\bullet-}/Sc^{3+}$ ion complex, the ESR spectrum was measured upon addition of $Sc(OTf)_3$ (20 mM) to an MeCN solution of Fc–NQ (9.1×10^{-3} M). The observed ESR spectrum is shown in Figure 1a together with the computer simulation spectrum (Figure 1b).[13] The hyperfine coupling constants (hfc) are determined as 1.80 (1H), 1.73 (1H), 0.60 (1H), 0.20 (1H), 0.10 (1H), 0.70 (3H), 0.09 (2H), 0.04 (2H), and 2.57 G (1Sc). The ESR spectrum of Fc–$NQ^{\bullet-}$ produced by the chemical reduction of Fc–NQ with naphthalene radical anion was also measured and the hfc values were determined by the computer simulation (see Supporting Information S5). The hfc values of Fc–$NQ^{\bullet-}$ [2.10 (1H), 1.55 (1H), 0.85 (1H), 0.80 (1H), 0.75 (1H), 0.44 (1H), 0.30 (2H), 0.10 (2H), and 0.05 G (2H)] are somewhat larger than the hfc values of protons of the Fc^+–$NQ^{\bullet-}/Sc^{3+}$ complex. The observed hfc values of Fc–$NQ^{\bullet-}$ can be reproduced by a density functional theory (DFT) calculation with a basis function: double-ζ Slater-type orbital set (frozen core: C (1s), N (1s), O (1s); ADF basis Set II) of Ph–$NQ^{\bullet-}$ in which the Fc moiety is omitted (see Supporting Information S6). The calculation predicts the hfc values of twelve protons in accordance with the experimental results: 2.38 (1H), 1.32 (1H), 1.01 (1H), 0.76 (2H), 0.41 (1H), 0.30 (2H), 0.10 (2H), and 0.05 G (2H). According to the optimized geometry the O–H distance between the quinone oxygen atom of the $NQ^{\bullet-}$ moiety and the amide hydrogen is 1.62 Å. This separation indicates hydrogen bond formation between them (S6).[14] The superhyperfine structure arising from the scandium nucleus ($I = 7/2$) observed in Figure 1a ($a(Sc) = 2.57$ G) definitely indicates the binding of Sc^{3+} ions to the quinone oxygen atom of the $NQ^{\bullet-}$ moiety in Fc^+–$NQ^{\bullet-}$.[15] The spin delocalization to the scandium nucleus results in the smaller $a(H)$ values in the Fc^+–$NQ^{\bullet-}/Sc^{3+}$ complex than those in Fc–$NQ^{\bullet-}$. The g value of the Fc^+–$NQ^{\bullet-}/Sc^{3+}$ complex (2.0038) also becomes smaller than the value of Fc–$NQ^{\bullet-}$ ($g = 2.0060$) because of the spin delocalization to scandium nucleus.

The strong binding of Sc^{3+} ions to the quinone oxygen atom of the $NQ^{\bullet-}$ moiety in Fc^+–$NQ^{\bullet-}$ resulted in a remarkable positive shift of the one-electron reduction potential of the NQ moiety (E^0_{red} versus SCE = 1.21 V), which becomes more positive than the one-electron oxidation potential of the Fc moiety (E^0_{ox} versus SCE = 0.38 V) as indicated by the cyclic voltammogram of Fc–NQ in the presence of 7.0 mM $Sc(OTf)_3$ (see Supporting Information S7). A similar but less positive shift of the one-electron reduction potential of the NQ moiety (E^0_{ox} versus SCE = 0.72 V) was observed in the presence of 7.0 mM $Eu(OTf)_3$ (S7). In these cases, intramolecular ET from the Fc to the NQ moiety becomes thermodynamically feasible.

Kinetic measurements of thermal intramolecular ET from the Fc to the NQ moiety in Fc–NQ in the presence of Sc^{3+} ion were performed on a stopped-flow spectrophotometer at 298 K. The rates of appearance of both absorption bands at 800 nm and 420 nm obeyed first-order kinetics and the same first-order rate constants (k_{obs}) were obtained from the first-order plots at both wavelengths. The k_{obs} values determined at 800 and 420 nm increase linearly with increasing Sc^{3+} ion concentration as shown in Figure 2. The first-order dependence of k_{obs} on $[Sc^{3+}]$ is consistent with the complexation of one Sc^{3+} ion with the $NQ^{\bullet -}$ moiety in $Fc^{+}-NQ^{\bullet -}$ (Scheme 1).[16] From the slope of the linear plot of k_{obs} versus $[Sc^{3+}]$ is obtained the Sc^{3+}-promoted electron transfer rate constant k_{et} as $1.6 \times 10^{3}\,\text{M}^{-1}\,\text{s}^{-1}$. The promoting effects of other metal ions were also examined and the k_{et} values were determined as 3.3 and $0.3\,\text{M}^{-1}\,\text{s}^{-1}$ in the presence of $Y(OTf)_3$ and $Eu(OTf)_3$, respectively. This order agrees with the order of Lewis acidity of the metal ions.[10a]

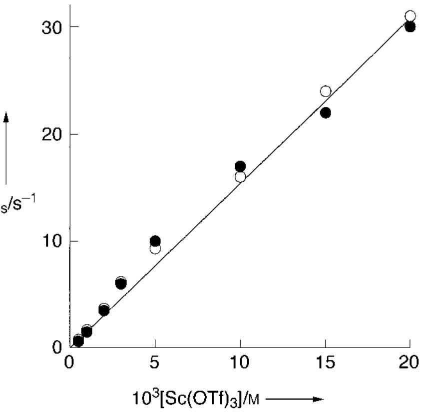


Figure 2. Plot of the rate constant (k_{obs}) determined at 800 nm (●) and 420 nm (○) versus $Sc(OTf)_3$ concentration for intramolecular ET in Fc–NQ (2.0×10^{-4} M) in the presence of $Sc(OTf)_3$ in deaerated MeCN at 298 K.

An intermolecular ET from Fc to 2-methoxy-1,4-naphthoquinone (2-MeONQ) was also examined in the presence of Sc^{3+} ions in MeCN. No ET occurred from Fc to 2-MeONQ in MeCN without Sc^{3+} ions. As is the case of the Sc^{3+}-promoted intramolecular ET in Fc–NQ, an ET from Fc to NQ occurred only in the presence of Sc^{3+} ions to yield Fc^{+} and the $NQ^{\bullet -}/Sc^{3+}$ complex. The k_{obs} value of the intermolecular ET from Fc (1.0×10^{-5} M) to 2-MeONQ (2.0×10^{-4} M) in the presence of 10 mM $Sc(OTf)_3$ was determined as $5.0 \times 10^{-2}\,\text{s}^{-1}$, which is 320 times smaller than the corresponding k_{obs} value of the Fc–NQ intramolecular ET.

In conclusion, the present study has demonstrated for the first time that intramolecular ET in a donor–acceptor linked system can be started thermally by adding an appropriate metal ion which can promote thermal ET which would otherwise be unlikely to occur. This result provides a new way to understand the factors that control thermal ET processes.

Experimental Section

Material: Scandium triflate [$Sc(OTf)_3$ (99%, F.W. = 492.16)] was obtained from Pacific Metals Co., Ltd. (Taiheiyo Kinzoku). Yttrium triflate [$Y(OTf)_3$], europium triflate [$Eu(OTf)_3$], and lutetium triflate [$Lu(OTf)_3$] were prepared by literature methods.[17] Magnesium perchlorate [$Mg(ClO_4)_2$] were obtained from Wako Pure Chemical Ind. Ltd., Japan. Chloroform-*d* was obtained from EURI SO-TOP, CEA, France. Thin-layer chromatography (TLC) and flash column chromatography were performed with Art. 5554 DC-Alufolien Kieselgel 60 F_{254} (Merck), and Fujisilicia BW300, respectively.

Synthesis and General: The synthetic routes toward Fc–NQ and the characterization and general information are described in Supporting Information.

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[13] The signal positions in Figure 1a are reproduced by the computer simulation (Figure 1b) although the agreement of the intensity ratio is rather poor probably because the difference of spin relaxation time depending on the nuclear spin quantum number.

[14] The calculation indicates that the hydrogen-bond formation with the carbonyl oxygen atom which is closer to the ether oxygen atom is more favorable by 6 kcal mol^{-1} as compared to the other case.

[15] The other oxygen atom may form a hydrogen bond with the amide proton as in the case of $Fc-NQ^{\bullet -}$.

[16] There is no saturation behavior with regard to the dependence of k_{obs} on $[Sc^{3+}]$ in Figure 2, since Sc^{3+} ions bind only with the carbonyl oxygen atom of the radical anion and do not bind with the quinone before the electron transfer. See the discussion on catalysis in electron transfer in ref. [9].

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