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Catalytic control of electron-transfer processes*

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Abstract: Catalytic control of electron-transfer processes is described for a number of photoinduced and thermal electron-transfer reactions, including back electron transfer in the charge-separated state of artificial photosynthetic compounds. The intermolecular and intramolecular electron-transfer processes are accelerated by complexation of radical anions, produced in the electron transfer, with metal ions that act as Lewis acids. Quantitative measures to determine the Lewis acidity of a variety of metal ions are given in relation with the promoting effects of metal ions in the electron-transfer reactions. The mechanistic viability of metal ion catalysis in electron-transfer reactions is demonstrated by a variety of examples of both thermal and photochemical reactions that involve metal ion-promoted electron-transfer processes as the rate-determining steps, which are made possible to proceed by complexation of radical anions with metal ions.

INTRODUCTION

Electron transfer (ET) is the most fundamental chemical reaction, playing a pivotal role in important biological redox processes such as photosynthesis and respiration. A variety of metal enzymes are involved to control electron-transfer processes in biological systems. However, catalytic control of electron-transfer reactions has yet to emerge as an identifiable field of study. The conceptual lack of catalysis in electron-transfer reactions may stem from the general belief that there may be no need of catalysis to accelerate further an electron-transfer reaction that is generally fast enough in a practical sense. This is largely true for reversible electron-transfer reactions in which electron transfer occurs only when the free-energy change of electron transfer is negative, i.e., the electron transfer is exergonic. If the electron transfer is endergonic, no net electron transfer would occur because of facile back electron transfer (BET) to regenerate the reactant pair. However, numerous chemical reactions, previously formulated by "movements of electron pairs", are now understood as processes in which an initial electron transfer from a nucleophile (reductant) to an electrophile (oxidant) produces a radical ion pair, which leads to the final products via the follow-up steps involving cleavage and formation of chemical bonds [1–6]. The follow-up steps are usually sufficiently rapid to render the initial electron transfer the rate-determining step in an overall irreversible transformation. In such a case, catalysis in the rate-determining electron-transfer step, which is usually endergonic ($\Delta G^\circ_{et} > 0$) and thereby thermodynamically unfavorable, would play an essential role to accelerate the overall redox reaction. Since electron transfer is an elementary reaction step, the acceleration of the rate of electron transfer with a "promoter" should involve change in the driving force of electron transfer by binding of the promoter with a product of electron transfer. Strictly speaking, such an acceleration effect of a "promoter" on electron transfer should not be called catalysis, since a "catalyst" should not be involved in the stoichiometry of the

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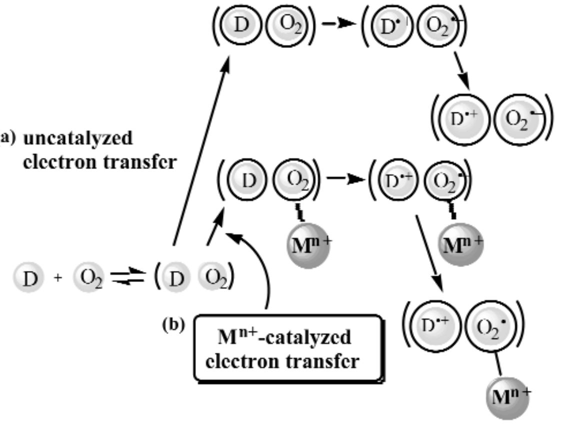
reaction. However, a "promoter" becomes equivalent to a "catalyst" when the promoted initial electron transfer is the rate-determining step in an overall irreversible transformation and the promoter is not involved in the final products.

This article is intended to focus on the catalytic control of intermolecular and intramolecular electron-transfer processes by metal ions. The catalytic reactivities of metal ions are certainly related to the Lewis acidity of metal ions employed to promote the electron-transfer reactions. Charges and ion radii are important factors to determine the Lewis acidity of metal ions. In the beginning, quantitative measures to determine the Lewis acidity of a variety of metal ions are described in relation to the catalytic reactivities. The mechanistic viability is described by showing a variety of examples of both thermal and photochemical reactions in which the rate-determining step is the metal ion-promoted electron-transfer process.

QUANTITATIVE MEASURE OF LEWIS ACIDITY OF METAL IONS

Because the ground-state oxygen is triplet, the direct reaction of oxygen with singlet molecules to produce singlet oxygenated product is spin-forbidden, whereas an electron transfer from a singlet electron donor to oxygen is a spin-allowed process. However, O_2 is rather difficult to reduce by electron transfer because of the largely negative one-electron reduction potential [7]. When the one-electron oxidation potential of an electron donor (D) is more positive than the one-electron reduction potential of O_2, the electron transfer is endergonic and thereby no net electron transfer takes place (Scheme 1a). In the presence of metal ions that can bind with $O_2^{\bullet-}$, however, the free-energy change of electron transfer would be negative provided that the binding energy is large enough (Scheme 1b). In fact, a variety of metal ions (M^{n+}) can form complexes with $O_2^{\bullet-}$ [8,9]. The g_{zz} value of the $O_2^{\bullet-}$-M^{n+} complex varies depending on the type of metal ions. The deviation of the g_{zz} value from the free-spin value (g_e = 2.0023) is caused by the spin-orbit interaction as given by eq. 1 under the conditions that $\Delta E >> \lambda$, where λ is the spin-orbit coupling constant (0.014 eV) and ΔE is the energy splitting of π_g levels due to the complex formation between $O_2^{\bullet-}$ and M^{n+} [9]. The ΔE value is readily determined from the g_{zz} value using eq. 1.



Scheme 1 Metal ion-promoted electron transfer from an electron donor (D) to O_2.

$$g_{zz} = g_e + 2\lambda/\Delta E \tag{1}$$

The ΔE value can be used to predict the promoting effect of M^{n+} on electron transfer from CoTPP (TPP = tetraphenylporphyrin dianion) to O_2 (eq. 2) in acetonitrile (MeCN) at 298 K. In the absence of

$$\mathrm{CoTPP} + \mathrm{O_2} \xrightarrow[k_{\mathrm{et}}]{\mathrm{M}^{n+}} \mathrm{CoTPP}^+ + \mathrm{O_2}^{\bullet -}\text{-}\mathrm{M}^{n+} \qquad (2)$$

metal ion, no electron transfer from CoTPP to O_2 occurs because the electron transfer is highly endergonic judging from the one-electron oxidation potential of CoTPP (E°_{ox} = 0.35 V vs. SCE in MeCN) and the one-electron reduction potential of O_2 (E°_{red} = –0.87 V vs. SCE) [9]. There is a striking single linear correlation between log k_{et} and ΔE of the $O_2^{\bullet -}$ complexes with not only metal ions (triflate or perchlorate salts), but also organotins, which are often used as Lewis acids to promote C–C bond formation in organic synthesis, as shown in Fig. 1 [9,10]. The remarkable correlation spans a range of almost 10^7 in the rate constant. The slope of the linear correlation between log k_{et} and ΔE is obtained as 14.0, which is close to the value of 1/2.3 kT (=16.9, where k is the Boltzmann constant and T = 298 K). This means that the variation of ΔE is well reflected in the difference in the activation free energy for the Lewis acid-promoted electron transfer from CoTPP to O_2. The stronger the binding of Lewis acid with $O_2^{\bullet -}$, the larger will be the promoting effects of metal ions and organotins. Thus, ΔE can be regarded as a good measure of the binding energies in $O_2^{\bullet -}$ complexes with metal ions and organotins. However, this method can only be applied to diamagnetic metal ions, because the paramagnetic metal ion complexes with $O_2^{\bullet -}$ give no electron spin resonance (ESR) signal. Redox-active metal ions that undergo electron-transfer reactions with $O_2^{\bullet -}$ cannot be employed, either.

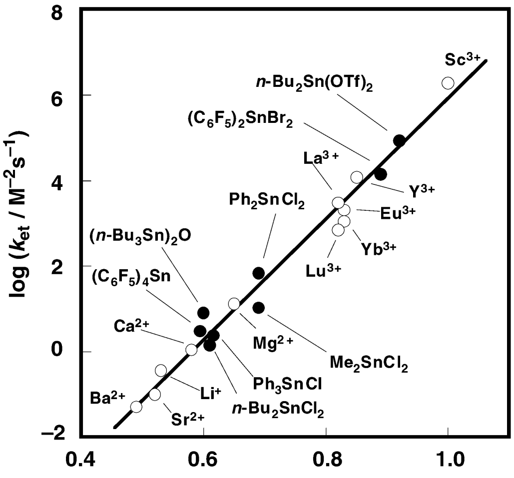
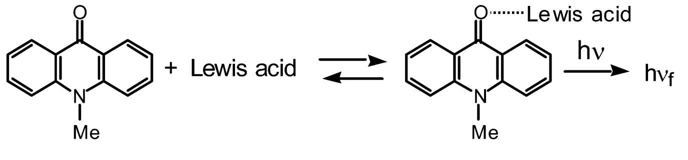


Fig. 1 Plots of log k_{et} vs. ΔE in electron transfer from (TPP)Co to O_2, promoted by metal ions (triflate or perchlorate salts) (○) and organotin compounds (●) in MeCN at 298 K.

A more convenient method to provide a quantitative measure of the Lewis acidity of metal ion salts comes from the fluorescence maxima of 10-methylacridone (AcrCO)-metal ion salt complexes (eq. 3) [11]. The fluorescence energy ($h\nu_f$) decreases with increasing the Lewis acidity of metal ion salts. There is a striking linear correlation between the $h\nu_f$ values of $^1AcrCO^*$-Lewis acid complexes and the ΔE values of the $O_2^{\bullet -}$-Lewis acid complexes derived from the g_{zz} values (vide supra) [11]. The



(3)

linear correlation between the ΔE values and the $h\nu_f$ values is given by eq. 4. The stronger the acidity of the Lewis acid, the larger is the ΔE value, the more red-shifted is the λ_{max} value, and the smaller is the $h\nu_f$ value. The good linear correlation between ΔE and $h\nu_f$ (eq. 4) demonstrates that the $h\nu_f$ values provide a quantitative measure of Lewis acidity of all kinds of metal ion salts, including paramagnetic and redox-active Lewis acids.

$$\Delta E\ (\mathrm{eV}) = -3.41\ h\nu_f\ (\mathrm{eV}) + 2.96 \tag{4}$$

CATALYTIC MECHANISM OF SUPEROXIDE DISMUTASE

Superoxide ion is toxic to cause oxidative damage of cells and thus removed by copper, zinc superoxide dismutase (Cu,Zn-SOD), which catalyzes the disproportionation (dismutation) of $O_2^{\bullet-}$ to O_2 and H_2O_2 [12]. The important role of Zn(II) ion in the bimetallic system to activate both the oxidation and reduction of $O_2^{\bullet-}$ has been revealed by a well-characterized SOD model, that is an imidazolate-bridged Cu(II)-Zn(II) heterodinuclear complex containing a dinucleating ligand, Hbdpi {Hbdpi = 4,5-bis[di(2-pyridylmethyl)aminomethyl]imidazole} [13]. The crystal structure is shown in Fig. 2 [13]. The Cu(II)-Zn(II) distance of 6.197(2) Å in the Cu(II)-Zn(II) heterodinuclear complex agrees well with that of native Cu,Zn-SOD (6.2 Å), and each metal has the pentacoordinate geometry with the imidazolate nitrogen, two pyridine nitrogens, the tertiary amine nitrogen, and a solvent (MeCN or H_2O). The Cu(II)-Zn(II) SOD model complex has a coordination site available for the binding of superoxide ion (Fig. 2). The Cu(II)-Zn(II) heterodinuclear complex exhibits the catalytic activity toward the dismutation of superoxide anions. The SOD activity of the Cu(II)-Zn(II) heterodinuclear complex was investigated by the cytochrome *c* assay using the xanthine oxidase reaction as the source of superoxide, which exhibits the highest activity among the structurally established SOD models reported so far [13].

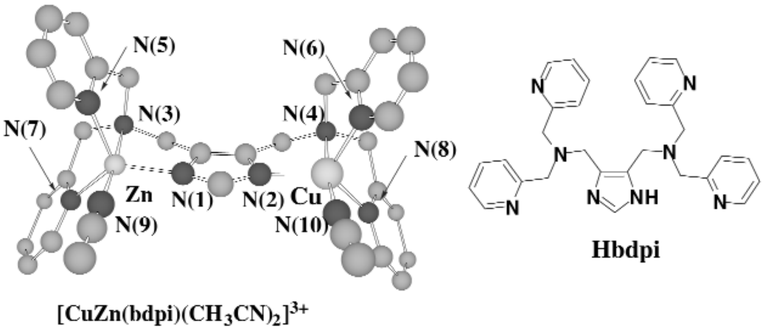
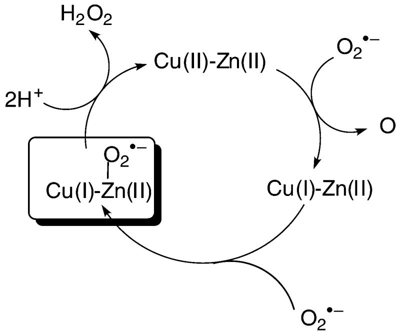


Fig. 2 Crystal structure of an SOD model complex, $[CuZn(bdpi)(CH_3CN)_2]^{3+}$.

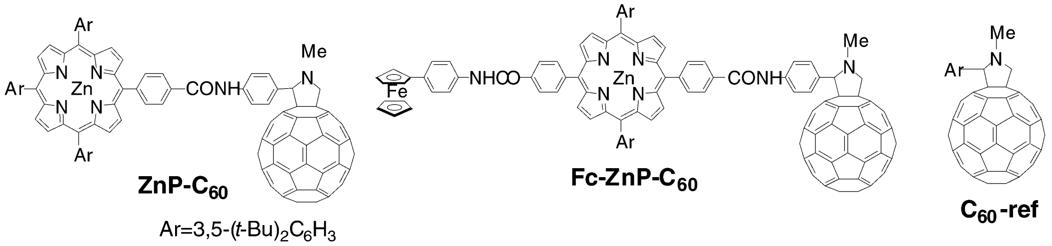
A large positive shift (about 0.2 V) in the $E_{1/2}$ value of the Cu(II)-Zn(II) complex is observed as compared to the corresponding Cu(II) mononuclear complexes [13]. This indicates that an important role of Zn(II) ion in the imidazolate-bridged Cu(II)-Zn(II) complex is to accelerate an outer-sphere electron transfer from $O_2^{\bullet-}$ to produce the Cu(I)-Zn(II) complex, when the free-energy change of electron transfer becomes thermodynamically more favorable as compared to that without Zn(II) ion [14,15]. The presence of Zn(II), which can act as a Lewis acid, is also able to accelerate an electron transfer from the Cu(I)-Zn(II) complex to $O_2^{\bullet-}$, since $O_2^{\bullet-}$ can form a complex with metal ions acting as a Lewis acid to accelerate the electron-transfer reduction of $O_2^{\bullet-}$ (vide supra). Thus, the essential role of Zn(II) ion in SODs is suggested to accelerate both the oxidation and reduction of superoxide by controlling the redox potentials of Cu(II) ion and superoxide in the catalytic cycle of SOD, as shown in Scheme 2 [14,15].



Scheme 2 Catalytic mechanism of SOD.

ARTIFICIAL PHOTOSYNTHETIC REACTION CENTER

Coordination of $O_2^{\bullet -}$ to Zn(II) ion plays an important role not only in the catalytic function of Cu,Zn-SOD (Scheme 2), but also in the novel catalytic effect of O_2 in BET from a fullerene radical anion to a zinc porphyrin moiety within photolytically generated radical ion pairs of zinc porphyrin-fullerene-linked molecules shown in Fig. 3 [16]. These zinc porphyrin-fullerene linked dyad and triads have been developed as artificial photosynthetic systems which, upon photoexcitation, give rise to long-lived charge-separated states in high quantum yields [17–19]. The charge-separated state is obtained from the photoinduced electron transfer involving the singlet and triplet excited states of ZnP and C_{60} and decays via the BET from $C_{60}^{\bullet -}$ to $ZnP^{\bullet +}$. In the presence of O_2, the decay rate of both $C_{60}^{\bullet -}$ and $ZnP^{\bullet +}$ absorption is markedly accelerated as compared to that found in the absence of O_2 [16]. The energy-transfer pathway from $ZnP^{\bullet +}$-$C_{60}^{\bullet -}$ via ZnP-$^3C_{60}^*$ has been ruled out as a major contributor to the decay of the radical ion pair, since much smaller intensity of $^1\Delta_g$ O_2 phosphorescence of the ZnP-C_{60} system is observed as compared to C_{60}-ref [16].



ZnP-C60

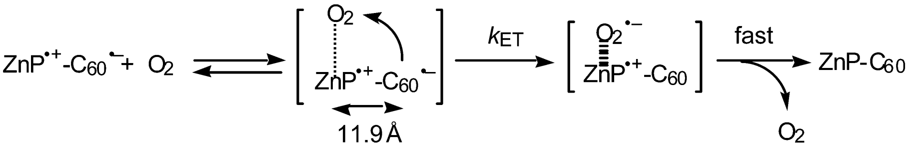
Ar=3,5-(*t*-Bu)$_2$C$_6$H$_3$

Fc-ZnP-C60

C60-ref

Fig. 3 Structures of zinc porphyrin-fullerene-linked compounds.

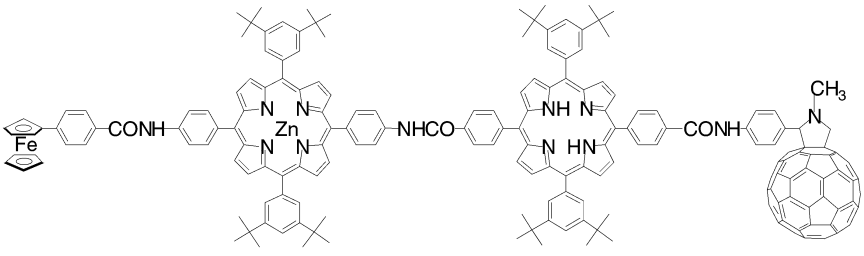
The electron transfer from $C_{60}^{\bullet -}$ to O_2 is endergonic [$\Delta G^\circ_{et} >> 0$ (0.28 eV)], judging from the one-electron reduction potentials of both species: E°_{red} of O_2 (–1.33 V vs. Fc/Fc$^+$) is significantly lower than that of C_{60}-ref (–1.05 V vs. Fc/Fc$^+$) [16]. Thus, a direct electron transfer from $C_{60}^{\bullet -}$ in $ZnP^{\bullet +}$-$C_{60}^{\bullet -}$ to O_2 is highly unlikely to occur in benzonitrile. The catalytic participation of O_2 in an intramolecular BET between $C_{60}^{\bullet -}$ and $ZnP^{\bullet +}$ in ZnP-linked C_{60} is depicted in Scheme 3 [16]. The intermolecular electron transfer from $C_{60}^{\bullet -}$ to O_2 may be initiated by the coordination of O_2 to $ZnP^{\bullet +}$, followed by electron transfer from $C_{60}^{\bullet -}$ to O_2 coordinated to $ZnP^{\bullet +}$ to yield $O_2^{\bullet -}$ bound to $ZnP^{\bullet +}$. Due to the strong binding of $O_2^{\bullet -}$ to $ZnP^{\bullet +}$, the one-electron reduction potential of O_2 is shifted toward positive values, namely, in favor of the electron transfer event. The complexation is then followed by a rapid intramolecular electron transfer from $O_2^{\bullet -}$ to $ZnP^{\bullet +}$ in the $O_2^{\bullet -}$-$ZnP^{\bullet +}$ complex to regenerate O_2 (Scheme 3). In the presence of metal ions, $O_2^{\bullet -}$ is known to coordinate to the metal ion, yielding the corresponding $O_2^{\bullet -}$-metal ion complex as described above [9]. The binding energy of $O_2^{\bullet -}$ with Zn(II) ion (ca. 0.9 eV)



Scheme 3 O_2 catalysis on BET in $ZnP^{•+}$-$C_{60}^{•-}$.

[15] is sufficient to make an electron transfer from $C_{60}^{•-}$ to O_2 energetically feasible. In contrast to the ZnP-containing donor-acceptor systems, ferrocene is a fully coordinated complex, omitting the coordination of another ligand, such as $O_2^{•-}$. This is the reason for the lack of accelerating effects by O_2 in the Fc^+-ZnP-$C_{60}^{•-}$ system [16].

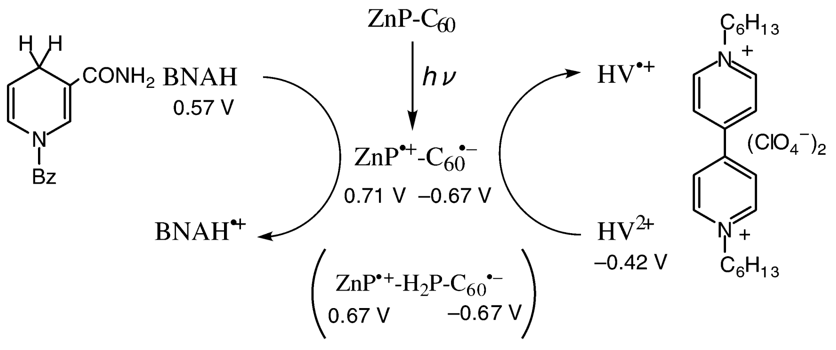
An extremely long-lived charge-separated state has been achieved successfully by extending the ferrocene-containing triad (Fc-ZnP-C_{60}) to a ferrocene (Fc)-zinc porphyrin (ZnP)-free-base porphyrin (H_2P)-C_{60} tetrad (Fc-ZnP-H_2P-C_{60}; Fig. 4) [20]. The lifetime of the resulting charge-separated state (i.e., ferricenium ion-C_{60} radical anion pair) in a frozen benzonitrile is determined as 0.38 s, which is more than one order of magnitude longer than any other *intramolecular* charge recombination processes of synthetic systems, and is comparable to that observed for the bacterial photosynthetic reaction center [20].



Fc-ZnP-H_2P-C_{60}

Fig. 4 Structure of porphyrin-fullerene-linked tetrad.

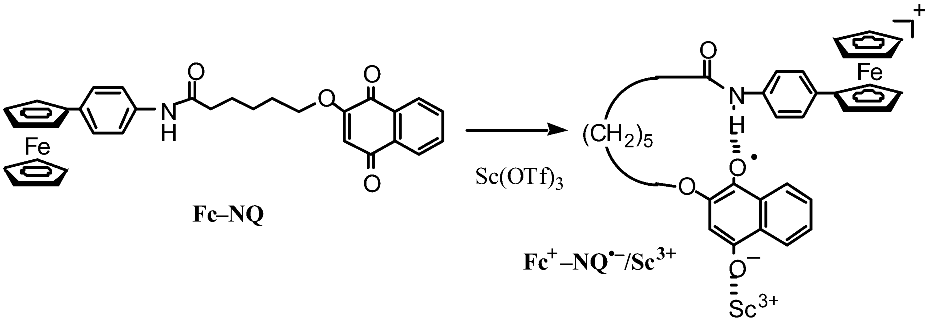
Both ZnP-C_{60} and ZnP-H_2P-C_{60} donor-acceptor ensembles in Fig. 4 act as efficient photocatalysts for the uphill oxidation of NADH analogs by HV^{2+} (Scheme 4) [21]. In the case of ZnP-C_{60}, the quantum yield of the photocatalytic reaction increases with increasing concentration of HV^{2+} or an NADH analog (BNAH: 1-benzyl-1,4-dihydronicotinamide) to reach a limiting value of 0.99, which agrees with the quantum yields of radical ion pair formation, $ZnP^{•+}$-$C_{60}^{•-}$ [21]. In the presence of oxygen, the lifetimes of the radical ion pairs are, however, markedly reduced due to an oxygen-catalyzed BET process between $C_{60}^{•-}$ and $ZnP^{•+}$ (Scheme 3).



Scheme 4 Photocatalytic reduction of HV^{2+} by BNAH.

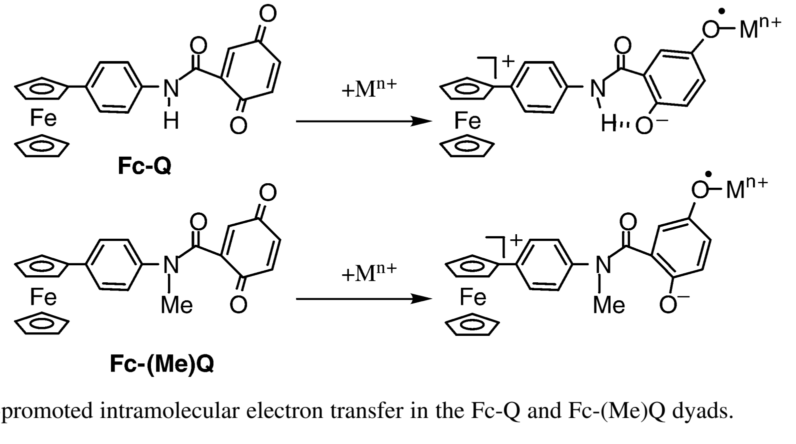
CATALYTIC CONTROL OF INTRAMOLECULAR ELECTRON TRANSFER

As described above, photoexcitation of the donor or acceptor moiety is required to start the electron-transfer reaction of donor-acceptor-linked systems. However, an intramolecular electron-transfer reaction of a donor-acceptor-linked system can also be started thermally by addition of a metal ion [22]. Addition of scandium triflate [$Sc(OTf)_3$] to an MeCN solution of ferrocene-naphthoquinone dyad (Fc-NQ) resulted in formation of the Fc^+-$NQ^{\bullet -}/Sc^{3+}$ complex as indicated by appearance of the absorption band due to the Fc^+ moiety at 860 nm together with the absorption band at λ_{max} = 420 nm owing to the $NQ^{\bullet -}/Sc^{3+}$ moiety (Scheme 5).



Scheme 5 Sc^{3+}-promoted intramolecular electron transfer from Fc to NQ in the Fc-NQ dyad.

A thermal intramolecular electron-transfer reaction from Fc to Q in ferrocene-benzoquinone dyad (Fc-Q) also occurs efficiently in the presence of metal ions (M^{n+}) [23]. The Fc-(Me)Q dyad, in which the N-H group acting as a hydrogen-bond acceptor, is replaced by N-Me, is also employed to examine the effect of the hydrogen bond on the metal ion-promoted intramolecular electron transfer (Scheme 6) [23]. The promoting effects of metal ions vary significantly depending on the Lewis acidity of metal ions. The k_{et} values of M^{n+}-promoted electron transfer in Fc-Q are linearly correlated with the ΔE values and each value is ca. 10^4 times larger than the k_{et} values of Fc-(Me)Q as shown in Fig. 5 [23]. The 10^4 times difference in the k_{et} values corresponds to the difference in the one-electron reduction potential between Fc-Q ($E°_{red}$ vs. SCE = –0.16 V) and Fc-(Me)Q ($E°_{red}$ vs. SCE = –0.40 V). The stabilization of the $Q^{\bullet -}$ moiety by hydrogen bonding with the amide proton in Fc-$Q^{\bullet -}$ results in the positive shift in $E°_{red}$ of Fc-Q as compared to Fc-(Me)Q in which the amide proton is replaced by the methyl group. Thus, the remarkable difference in the k_{et} values between Fc-Q and Fc-(Me)Q is ascribed to the effect of hydrogen bond formed between the $Q^{\bullet -}$ moiety and the amide proton in Fc^+-$Q^{\bullet -}$.



Scheme 6 M^{n+}-promoted intramolecular electron transfer in the Fc-Q and Fc-(Me)Q dyads.

In the case of photoinduced electron in the Fc-Q dyad, electron transfer from Fc to the singlet excited state of Q occurs rapidly to produce Fc-$Q^{\bullet -}$ without changing the conformation (<1 ps), and then $Q^{\bullet -}$ forms the hydrogen bonding with the amide proton of the spacer (τ = ~5 ps) [24].

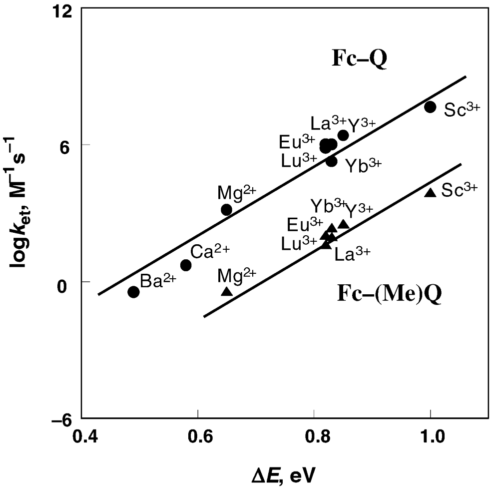
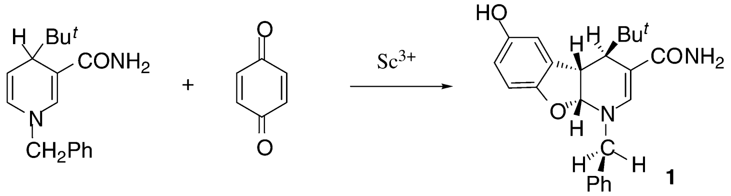


Fig. 5 Plots of log k_{et} vs. ΔE in M^{n+}-promoted electron transfer in Fc-Q and Fc-(Me)Q in MeCN 298 K.

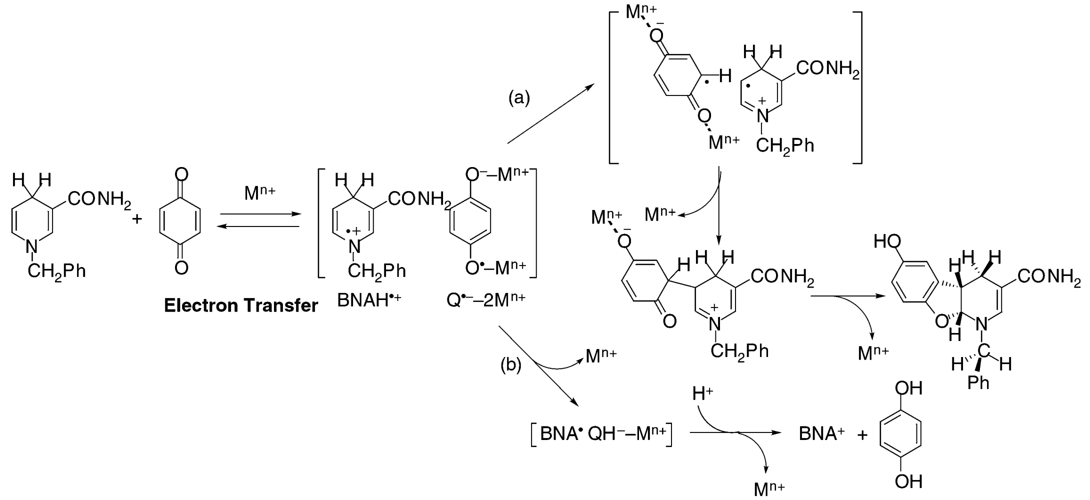
CATALYTIC CONTROL OF ELECTRON TRANSFER AND THE SUBSEQUENT STEP

The Mg^{2+}-catalyzed hydride transfer from BNAH to Q is known to proceed via a Mg^{2+}-promoted electron transfer from BNAH to Q, followed by a proton transfer from the resulting $BNAH^{\bullet +}$ to the $Q^{\bullet -}$-$2Mg^{2+}$ complex and the subsequent fast electron transfer from $BNA^{\bullet}$ to QH^{-}-Mg^{2+} [25]. When BNAH is replaced by 1-benzyl-4-*t*-butyl-1,4-dihydronicotinamide (*t*-BuBNAH), no reaction occurs between *t*-BuBNAH and Q in a deaerated MeCN. In the presence of $Sc(OTf)_3$, the Lewis acidity of which is much stronger than Mg^{2+}, however, cycloaddition reaction of *t*-BuBNAH with Q rather than hydride transfer occurs efficiently at 298 K (eq. 5) [26]. Kinetic comparison between the Sc^{3+}-catalyzed cycloaddition not only the electron and the Sc^{3+}-promoted electron-transfer reduction of Q together with the absence of the deuterium kinetic isotope effects indicates that the addition reaction proceeds via the Sc^{3+}-promoted electron transfer from *t*-BuBNAH and BNAH to Q. The change in the type of reaction depending on the Lewis acidity of the metal ion is well accommodated in the electron-transfer mechanism in Scheme 7 [26]. The initial rate-determining electron transfer from BNAH to Q results in the formation of radical ion pair ($BNAH^{\bullet +}$ and $Q^{\bullet -}$) where $Q^{\bullet -}$ forms 1:1 and 1:2 complexes with Sc^{3+}. The proton transfer from $BNAH^{\bullet +}$ to the $Q^{\bullet -}$-$2Sc^{3+}$ complex may be retarded because of the strong Lewis acidity of Sc^{3+}. In such a case, the initial electron transfer is followed by the radical coupling between $Q^{\bullet -}$ and $BNAH^{\bullet +}$ to give the zwitterionic intermediate, which is eventually



(5)

converted to the cycloadduct **1** (Scheme 7a). The proton transfer from $BNAH^{\bullet +}$ to the $Q^{\bullet -}$-$2M^{n+}$ complex is accelerated with decreasing of the Lewis acidity to the metal ion (M^{n+}) due to the stronger basicity of the $Q^{\bullet -}$-$2M^{n+}$ complex (Scheme 7b). This is the reason why the hydride-transfer pathway from BNAH to Q becomes dominant in the presence of a much weaker Lewis acid (e.g., Mg^{2+}) as compared to the selective cycloaddition reaction in the presence of Sc^{3+}. Thus, the Lewis acidity of metal ion can control the transfer step, but also the subsequent chemical step.



Scheme 7 Mechanism of M^{n+}-catalyzed reaction of BNAH with Q.

Rates of Diels–Alder cycloaddition of anthracenes with *p*-benzoquinone and its derivatives, as well as rates of hydride-transfer reactions from 10-methyl-9,10-dihydroacridine ($AcrH_2$) to the same series of *p*-benzoquinones, are accelerated significantly in the presence of metal ions in acetonitrile [26,27]. Extensive comparison of the catalytic effects of metal ions in electron transfer from one-electron reductants (cobalt tetraphenylporphyrin and decamethylferrocene) to *p*-benzoquinones with those in the Diels–Alder reactions of the quinones as well as the hydride transfer reactions has revealed that the catalysis of metal ions in each case is ascribed to the 1:1 and 1:2 complexes formed between the corresponding semiquinone radical anions and metal ions [27]. The catalytic reactivities of a variety of metal ions in each reaction are well correlated with the ΔE values in Figs. 1 and 5 [28]. Hydride transfer from $AcrH_2$ to 3,6-diphenyl-1,2,4,5-tetrazine (Ph_2Tz), which contains N=N double bond, occurs efficiently in the presence of $Sc(OTf)_3$ via Sc^{3+}-promoted electron transfer in MeCN at 298 K, whereas no reaction occurs in the absence of Sc^{3+} [29].

CONCLUSION AND OUTLOOK

In this article, it has been demonstrated that binding of metal ion with the substrate radical anion plays an important role in controlling the electron-transfer reactivity of the substrate. The catalytic reactivities of metal ions are related to the Lewis acidity of metal ions, which can be evaluated quantitatively based on the g_{zz} values of ESR spectra of metal ion $O_2^{\bullet -}$ complexes and the fluorescence maxima of 10-methylacridone (AcrCO)-metal ion salt complexes. The Lewis acidity of metal ion has been shown to control not only the electron-transfer step, but also the subsequent chemical step in the overall redox reactions. There are more examples for the catalytic control of electron-transfer reactions of metal ions, other than those described in this article [30–33]. There still remains a wealth of important fundamental questions with regard to catalytic control of electron-transfer reactions, which have been only partially explored so far, and which certainly deserve much more detailed attention in the future.

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