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Review

Metal ion-coupled and decoupled electron transfer

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Contents

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ABSTRACT

Effects of metal ions on thermal and photoinduced electron-transfer reactions from electron donors (D) to electron acceptors (A) are reviewed in terms of metal ion-coupled electron transfer (MCET) vs. metal ion-decoupled electron transfer (MDET). When electron transfer from D to A is coupled with binding of metal ions to $A^{\bullet-}$, such an electron transfer is defined as MCET in which metal ions accelerate the rates of electron transfer. A number of examples of electron-transfer reactions from D to A, which are energetically impossible to occur, are made possible by strong binding of metal ions to $A^{\bullet-}$ in MCET. The structures of metal ion complexes with $A^{\bullet-}$ are also discussed in relation with the MCET reactivity. The MCET reactivity of metal ions is shown to be enhanced with an increase in the Lewis acidity of metal ions. In contrast to MCET, strong binding of metal ions to $A^{\bullet-}$ results in deceleration of back electron transfer from metal ion complexes of $A^{\bullet-}$ to $D^{\bullet+}$ in the radical ion pair, which is produced by photoinduced electron transfer from D to A in the presence of metal ions, as compared with back electron transfer without metal ions. The deceleration of back electron transfer in the presence of metal ions results from no binding of metal ions to A. This type of electron transfer is defined as metal ion-decoupled electron transfer (MDET). The lifetimes of CS state ($D^{\bullet+}$–$A^{\bullet-}$) produced by photoinduced electron transfer from D to A in the D–A linked systems are also elongated by adding metal ions to the D–A systems because of the stabilization of the CS states by strong binding of metal ions to $A^{\bullet-}$ and the resulting slow MDET processes.

1. Introduction and background

Metal ions play pivotal roles in controlling biological electron-transfer processes of coenzymes such as flavins, quinones, etc. in photosynthesis and respiration [1–5]. Binding metal ions to electron acceptors (A) results in enhancement of an electron-acceptor ability of A, because the one-electron reduction potential of A is shifted to a positive direction by the stronger binding of metal ions to the radical anion ($A^{\bullet-}$) as compared to the binding to A [6–13]. According to the Nernst equation, the positive shift of E_{red} (ΔE_{red}) of A due to the complex formation with a metal ion (M^{n+}) is determined by the difference in the binding constants between M^{n+} complexes with A (K_{ox}) and $A^{\bullet-}$ (K_{red}) as given by Eq. (1) under the conditions that $K_{red}[M^{n+}] \gg 1$ [13].

$$\Delta E_{red} = \frac{RT}{F} \ln \left[\frac{K_{red}[M^{n+}]}{K_{ox}[M^{n+}] + 1} \right] \tag{1}$$

Thus, electron-transfer reactions from electron donors (D) to electron acceptors (A), which are not thermodynamically feasible to

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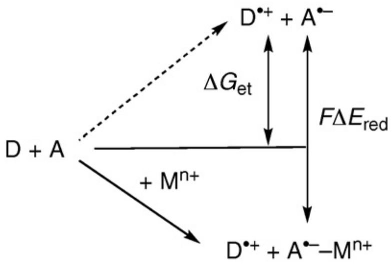
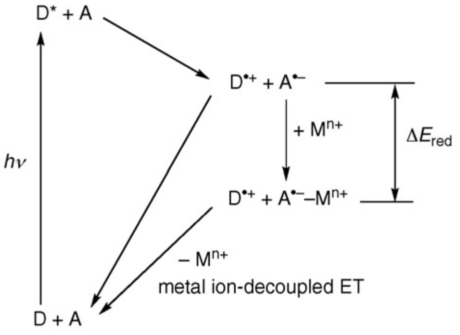


Scheme 1.



Scheme 2.

occur ($\Delta G_{et} > 0$), would occur in the presence of M^{n+} provided that the $F\Delta E_{red}$ value is larger than ΔG_{et} ($\Delta G_{et} < F\Delta E_{red}$). In such a case, the free energy change of electron transfer becomes negative ($\Delta G_{et} < 0$ in the presence of M^{n+}) as shown in Scheme 1.

Under the conditions that $K_{ox}[M^{n+}] \ll 1$, Eq. (1) is rewritten by Eq. (2). In this case, M^{n+} binds only to $A^{\bullet-}$ when virtually no

$$\Delta E_{red} = \frac{RT}{F}\ln(K_{red}[M^{n+}]) \qquad (2)$$

binding of M^{n+} occurs to A. In such a case there are two reaction pathways. One is electron transfer followed by binding of M^{n+} to $A^{\bullet-}$, when electron transfer and binding of M^{n+} to $A^{\bullet-}$ occurs is a stepwise pathway. The other is a concerted pathway when electron transfer is coupled with binding of M^{n+} to $A^{\bullet-}$. The latter pathway is normally energetically more feasible because the binding of M^{n+} is coupled with electron transfer. This is defined as metal ion-coupled electron transfer (MCET) on analogy of proton-coupled electron transfer (PCET) where protonation is coupled with electron transfer [14–17].

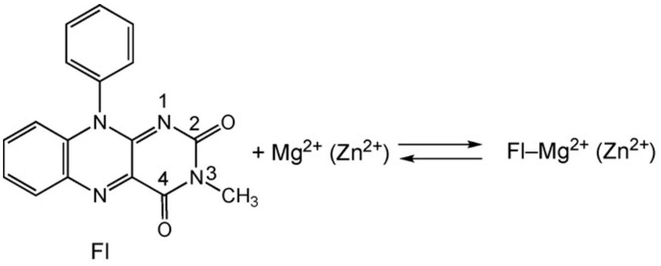
In contrast to the case of metal ion-coupled electron transfer (MCET), the binding of M^{n+} to $A^{\bullet-}$ results in a decrease in the ET driving force of back electron transfer from $A^{\bullet-}$–M^{n+} to $D^{\bullet+}$ by ΔE_{red}, following photoinduced electron transfer from the excited state of D (D*: * denotes the excited state) to A, as shown in Scheme 2. Photoinduced electron transfer from D to A* also affords $D^{\bullet+}$ and $A^{\bullet-}$, and the driving force of back electron transfer from $A^{\bullet-}$ to $D^{\bullet+}$ becomes smaller by the binding of M^{n+} to $A^{\bullet-}$ (ΔE_{red}). Such a decrease in the ET driving force results in deceleration of the rate of back electron transfer, which is accompanied by release of M^{n+}. The electron transfer from $A^{\bullet-}$–M^{n+} to $D^{\bullet+}$ in Scheme 2 is regarded as metal ion-decoupled electron transfer (MDET) in contrast to metal ion-coupled electron transfer (MCET) in Scheme 1.

We would like to focus on contrasting effects of metal ions on MCET and MDET reactions in this review article. First a number of examples of MCET reactions are presented for both intermolecular and intramolecular ET reactions when ET rates are accelerated by binding of M^{n+} to electron acceptors and the radical anions. Then, intramolecular MDET reactions are discussed in relation with elongation of lifetimes of the charge-separated states by metal ions.

2. Intermolecular MCET

2.1. Flavins

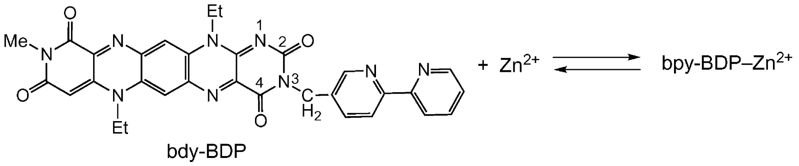
Positive shifts of the one-electron reduction potentials of electron acceptors by binding of metal ions were first reported for flavin analogs [18]. Flavins are a ubiquitous and structurally and functionally diverse class of redox-active coenzymes that use the redox-active heteroaromatics to mediate a variety of thermal and photoinduced electron-transfer processes over a wide range of redox potentials [19–23]. Flavins are known to bind various metal ions [24–27]. For example, a flavin analog (Fl: 3-methyl-10-phenylisoalloxazine) forms complexes with metal ions such as Mg^{2+} and Zn^{2+}, Eq. (3) [18]. The formation constants K of Fl with



(3)

Mg^{2+} and Zn^{2+} were determined from the change in the absorption spectra by the complex formation to be 1.7×10^2 and $4.8 \times 10\,M^{-1}$, respectively [18]. Metal ions bind to the C2-carbonyl oxygen because only the C=O stretching band due to the C2-carbonyl group of Fl was significantly red-shifted by the binding of metal ions [18b]. The positive shift in the one-electron reduction potential of the singlet excited state of Fl ($^1Fl^*$) by binding of Mg^{2+} was 0.32 V [18b]. This potential shift is large enough to make photoinduced electron transfer from toluene to $^1Fl^*$ possible to occur [18b]. In the absence of Mg^{2+} no photoinduced electron transfer from toluene to $^1Fl^*$ occurs, whereas the fluorescence of $^1Fl^*$–Mg^{2+} is quenched efficiently via photoinduced electron transfer from toluene to $^1Fl^*$–Mg^{2+} (Scheme 3) [18b].

Much stronger binding of Zn^{2+} to a flavin analog than Fl in Eq. (3) has been achieved using benzodipteridine bearing a bipyridin-6-ylmethyl moiety (bpy-BDP) that acts as a metal ion binding site (Eq. (4)) [28]. The metal ion bound at the bipyridine moiety of



(4)

bpy-BDP is able to interact with BDP skeleton because the interaction of the metal ion bound at the bipyridine moiety with C(2)=O or C(4)=O carbonyl oxygen atoms is geometrically possible [28]. The