

## A Dramatic Elongation of the Lifetime of Charge-Separated State by Complexation with Yttrium Triflate in Ferrocene–Anthraquinone Linked Dyad

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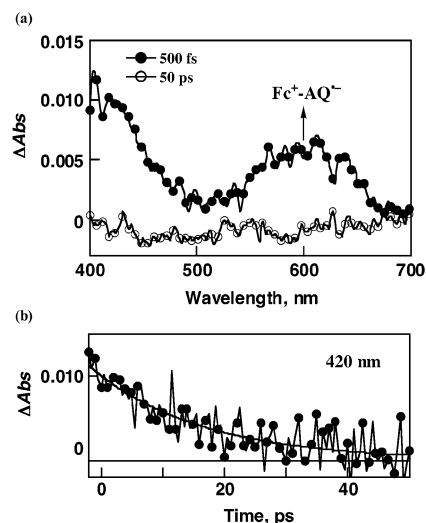
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Extensive efforts have thus far been devoted to attain long-lived charge-separated (CS) states using donor–acceptor (D–A) linked multi-array systems where multistep electron transfer is started by the initial photoinduced electron transfer, mimicking the natural photosynthetic systems.<sup>1–5</sup> Rates of electron-transfer reactions in D–A systems can be well predicted in light of the Marcus theory of electron transfer,<sup>6</sup> once the fundamental electron transfer properties of D and A moieties such as the one-electron redox potentials and the reorganization energies of electron transfer are determined in addition to their interaction. In other words, once the pair of an electron donor and acceptor with a fixed spacer is chosen, the electron-transfer reactivity is fixed automatically. Nevertheless, the electron transfer reactivity can be altered drastically by addition of a third component which can bind with the product of electron transfer.<sup>7</sup> For example, the presence of a variety of metal ions results in remarkable change in the electron-transfer reactivity of acceptors by complexation of metal ions with the radical anions of electron acceptors.<sup>7–9</sup> However, such effects of metal ions have never been applied to elongate the CS lifetime of D–A systems.

We report herein that remarkable seven million times elongation of the CS lifetime is attained by complex formation of yttrium triflate [Y(OTf)<sub>3</sub>] with the CS state in photoinduced electron transfer of a newly designed ferrocene–anthraquinone dyad (**Fc–AQ**) involving a rigid amide spacer (see Scheme 1). A **Fc–AQ** linked dyad has been employed, since AQ as well as the radical anion of AQ can bind with Y(OTf)<sub>3</sub>. Such strong binding of Y(OTf)<sub>3</sub> with AQ<sup>•–</sup> results in a substantial deceleration of the back electron transfer from AQ<sup>•–</sup> to Fc<sup>+</sup>, leading to a remarkable elongation of the CS lifetime, whereas the forward photoinduced electron transfer in both the absence and the presence of Y(OTf)<sub>3</sub> takes place within 500 fs (vide infra).<sup>9,10</sup>

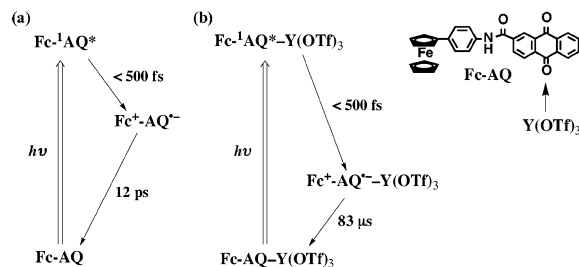
The details of preparation of **Fc–AQ** are described in Supporting Information (S1–S3). The cyclic voltammograms of **Fc–AQ** were measured in benzonitrile (PhCN), exhibiting two reversible one-electron redox couples ( $E_{ox}^0 = 0.47$  V vs SCE for Fc<sup>+</sup>/Fc couple,  $E_{red}^0 = -0.81$  V for AQ/AQ<sup>•–</sup> couple). No thermal electron transfer in **Fc–AQ** occurs in the absence or presence of Y(OTf)<sub>3</sub> due to the high endothermicity of the thermal electron transfer.

Photoexcitation of the AQ moiety in **Fc–AQ** in deaerated PhCN with femtosecond (150 fs width) laser light results in appearance of the absorption bands around 420 and 600 nm at 500 fs as shown in Figure 1a.<sup>12</sup> The absorption bands around 420 and 600 nm, which are assigned to AQ<sup>•–</sup> by comparison with the absorption spectrum of AQ<sup>•–</sup>, are produced by the chemical reduction of AQ with naphthalene radical anion (S4). The absorbance at 420 nm due to AQ<sup>•–</sup> disappears within 50 ps as shown in Figure 1a. The decay



**Figure 1.** (a) Time-resolved absorption spectra of **Fc–AQ** dyad ( $1.0 \times 10^{-4}$  M) in deaerated PhCN excited at 388 nm at 298 K. (b) The time profile at 420 nm.

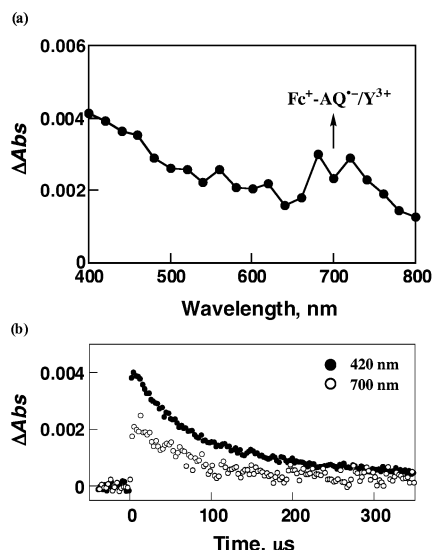
### Scheme 1



process obeys first-order kinetics with the lifetime of 12 ps (Figure 1b). This indicates that electron transfer from Fc to the singlet excited state of AQ occurs efficiently to produce the CS state (**Fc<sup>+</sup>–AQ<sup>•–</sup>**) within 500 fs and decays via back electron transfer to the ground state with a lifetime of 12 ps (Scheme 1a).<sup>13</sup>

In the presence of Y(OTf)<sub>3</sub> ( $1.0 \times 10^{-2}$  M) as well, photoexcitation of the **Fc–AQ** system using a femtosecond laser results in efficient electron transfer from Fc to AQ within 500 fs (S5). However, the transient absorption band, observed at 700 nm in the presence of Y(OTf)<sub>3</sub> (S5), is significantly red-shifted as compared with that observed at 600 nm in the absence of Y(OTf)<sub>3</sub> (Figure 1a). Such a red shift has been reported for the complex formation of semiquinone radical anions with metal ions.<sup>7,8</sup> In addition, virtually the same absorption band at 700 nm is observed in intermolecular photoinduced electron transfer from Fc to AQ-ref (anthraquinone-2-carboxylic acid) in the presence of Y(OTf)<sub>3</sub> (S6). Thus, the absorption band at 700 nm in the presence of Y(OTf)<sub>3</sub> is

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**Figure 2.** (a) Time-resolved absorption spectrum of  $\text{Fc-AQ}$  ( $1.0 \times 10^{-4}$  M) and  $\text{Y(OTf)}_3$  ( $1.0 \times 10^{-2}$  M) in deaerated PhCN at 250 ns after laser pulse excitation (355 nm) at 298 K. (b) The time profile at 420 nm (●) and 700 nm (○).

assigned due to the  $\text{Fc}^+-\text{AQ}^--\text{Y(OTf)}_3$  complex. The same transient absorption spectrum of  $\text{Fc-AQ}$  is observed in the presence of  $\text{Y(OTf)}_3$  ( $1.0 \times 10^{-2}$  M) at a longer time scale (250 ns) after the photoexcitation using a nanosecond laser as shown in Figure 2a. The decay of absorbance at 420 and 700 nm due to the  $\text{Fc}^+-\text{AQ}^--\text{Y(OTf)}_3$  complex obeys first-order kinetics to afford the identical CS lifetime that is determined as 83  $\mu\text{s}$  (Figure 2b). The CS lifetime is seven million times longer than the lifetime in the absence of  $\text{Y(OTf)}_3$  (12 ps). Such remarkable elongation of the CS lifetime may be ascribed to the strong binding of  $\text{Y(OTf)}_3$  with  $\text{AQ}^-$ , which causes a drastic change in the reorganization energy as well as the driving force of electron transfer. The binding of  $\text{Y(OTf)}_3$  with AQ is examined by the absorption spectral change of AQ due to complexation with  $\text{Y(OTf)}_3$ . The binding constant is determined as  $1100 \text{ M}^{-1}$  in PhCN at 298 K (S7). The initial absorbance at 700 nm due to the  $\text{Fc}^+-\text{AQ}^--\text{Y(OTf)}_3$  complex increases with increasing concentration of  $\text{Y(OTf)}_3$  to reach a constant value where most AQ molecules in  $\text{Fc-AQ}$  form the complex with  $\text{Y(OTf)}_3$  at  $[\text{Y(OTf)}_3] > 1.0 \times 10^{-2}$  M. On the other hand, the CS lifetime remains the same irrespective of concentration of  $\text{Y(OTf)}_3$ .

These results indicate that photoexcitation of the  $\text{Fc-AQ-Y(OTf)}_3$  complex affords the CS state complex:  $\text{Fc}^+-\text{AQ}^--\text{Y(OTf)}_3$  within 500 fs (Scheme 1b). We have previously reported that naphthoquinone radical anion forms a strong complex with  $\text{Y(OTf)}_3$ , the binding constant of which was determined as  $1.1 \times 10^{31} \text{ M}^{-1}$ .<sup>8b</sup> The large reorganization energy of the CR process in the presence of  $\text{Y(OTf)}_3$  results from the strong binding of  $\text{AQ}^-$  with  $\text{Y(OTf)}_3$ , since the CR process requires the significant weakening of the binding to generate AQ which has a weaker binding with  $\text{Y(OTf)}_3$ .<sup>14,15</sup>

In such a case, the back electron transfer is in the Marcus normal region,<sup>6</sup> where the driving force of the back electron transfer is smaller than the reorganization energy value, and the back electron-transfer rate decreases to elongate the CS lifetime with increasing the  $\lambda$  value. Thus, the remarkable seven million times elongation of the CS lifetime in the presence of  $\text{Y(OTf)}_3$  (Scheme 1b) results from the strong binding of  $\text{Y(OTf)}_3$  with the  $\text{AQ}^-$  moiety of  $\text{Fc}^+-\text{AQ}^-$ , which causes a substantial increase in the  $\lambda$  value of electron transfer and a decrease in the driving force of electron transfer.

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**Supporting Information Available:** Synthetic procedures of  $\text{Fc-AQ}$  and experimental details (S1–S3), a UV–vis spectrum of  $\text{Fc-AQ}^-$  (S4), a transient absorption spectrum of  $\text{Fc}^+-\text{AQ}^--\text{Y(OTf)}_3$  at 500 fs in the presence of  $\text{Y(OTf)}_3$  (S5), a transient absorption spectrum of  $(\text{AQ-ref})^-/\text{Y}^{3+}$  (S6), plot of  $(\Delta\text{Abs})^{-1}$  vs  $[\text{Y}^{3+}]^{-1}$  for complex formation between  $\text{Fc-AQ}$  with  $\text{Y(OTf)}_3$  (S7), differential pulse voltammogram of  $\text{Fc-AQ}$  with  $1.0 \times 10^{-2}$  M  $\text{Y(OTf)}_3$  (S8), and Eyring plot of CS lifetime in the presence of  $1.0 \times 10^{-2}$  M  $\text{Y(OTf)}_3$  (S9) (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (9) Electron transfer is also controlled by proton as well as metal ions. For the proton-coupled electron transfer, see: (a) Cukier, R. I.; Nocera, D. G. *Annu. Rev. Phys. Chem.* **1998**, *49*, 337. (b) Kohen, A.; Klinman, J. P. *Acc. Chem. Res.* **1998**, *31*, 397. (c) Hammes-Schiffer, S. *Acc. Chem. Res.* **2001**, *34*, 273.
- (10)  $\text{Y(OTf)}_3$  is chosen as a Lewis acid which has a suitable Lewis acidity for this study.  $\text{Sc(OTf)}_3$  which is a stronger Lewis acid than  $\text{Y(OTf)}_3$  can promote thermal electron transfer from the Fc to AQ moiety, whereas the weaker Lewis acids than  $\text{Y(OTf)}_3$  cannot bind with the AQ moiety. For the Lewis acidity of metal triflates, see ref 11.
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- (12) Since the CS state is observed within 500 fs, the electron transfer may occur from Fc to the singlet excited state of AQ rather than to the triplet excited state which may be formed at the time scale of longer than picoseconds.
- (13) For photoinduced electron transfer from Fc to Q in  $\text{Fc-Q}$ , see: Fukuzumi, S.; Yoshida, Y.; Okamoto, K.; Imahori, H.; Araki, Y.; Ito, O. *J. Am. Chem. Soc.* **2002**, *124*, 6794.
- (14) The strong binding of  $\text{AQ}^-$  with  $\text{Y(OTf)}_3$  results in a positive shift of the one-electron reduction potential of the AQ moiety in  $\text{Fc-AQ}$  in the presence of  $1.0 \times 10^{-2}$  M  $\text{Y(OTf)}_3$  (0.05 V vs SCE, see Supporting Information S8) in PhCN as compared with the value in its absence (−0.89 V). The driving force in the presence of  $1.0 \times 10^{-2}$  M  $\text{Y(OTf)}_3$  (0.42 eV) becomes much smaller than that in its absence (1.28 eV).
- (15) Eyring plot of CS lifetime in  $\text{Fc-AQ}$  in the presence of  $1.0 \times 10^{-2}$  M  $\text{Y(OTf)}_3$  has been obtained as large reorganization energy as 2.9 eV, see S9.

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