

## Hydrogen-Bonding Dynamics in Photoinduced Electron Transfer in a Ferrocene–Quinone Linked Dyad with a Rigid Amide Spacer

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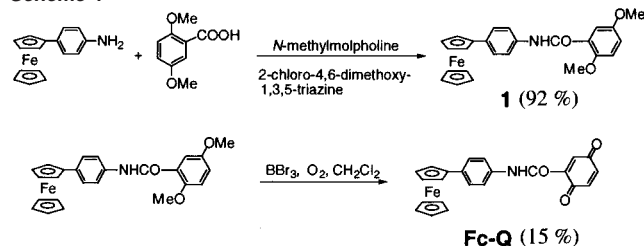
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Quinones are ubiquitous to living systems, providing important cofactors for electron transfer in photosynthesis and respiration.<sup>1</sup> In photosynthesis, two quinones termed Q<sub>a</sub> and Q<sub>b</sub> act in concert to enable efficient charge separation to take place.<sup>2,3</sup> Q<sub>a</sub> and Q<sub>b</sub> are often identical quinones: plastoquinone in higher plants and ubiquinone in bacterial systems.<sup>1</sup> Differences in the nature of the hydrogen-bonding interactions of both quinones have been suggested to result in the differing functions observed; that is, specific hydrogen bonds to nearby amino acid residues are able to tailor the quinone to perform a specific function.<sup>4,5</sup> In particular, electron-transfer reactions are known to be regulated through noncovalent interactions such as hydrogen bonding which plays an important role in biological electron-transfer systems.<sup>6–9</sup> However, there has been no report on dynamics of the hydrogen-bond formation of semiquinone radical anions upon electron-transfer reactions of quinones.

We report herein the first successful detection of hydrogen-bonding dynamics in an *intramolecular* photoinduced electron-transfer reaction of a donor–acceptor-linked system. A newly designed ferrocene–quinone dyad with an amide spacer (**Fc–Q**) is employed to examine formation of the hydrogen bonding in the one-electron reduced form (Q<sup>•−</sup>) and the dynamics in the photoinduced electron-transfer reaction from the ferrocene to the quinone moiety.

The preparation of **Fc–Q** dyad and **Fc–(Me)Q** dyad in which the N–H group is replaced by N–Me was carried out as shown in Scheme 1 (see Supporting Information, S1–S4). Single crystals of

### Scheme 1



**Fc–Q** were obtained by vapor diffusion of ether into an MeCN solution of **Fc–Q**. The crystallographic data are summarized in Supporting Information (Table, S5), and the ORTEP drawing is shown in Figure 1. The distance between ferrocene and quinone (edge-to-edge) is determined as 8.05 Å. The closest distance

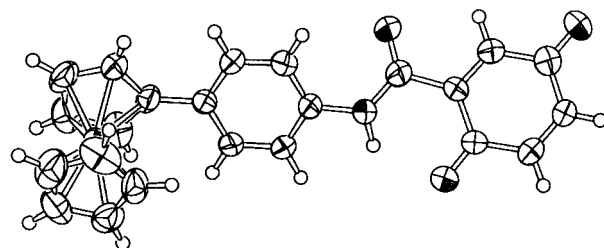


Figure 1. ORTEP drawing of **Fc–Q**.

between the quinone oxygen atom and the amide hydrogen is 2.17 Å and the C–O bond lengths of two carbonyl groups of quinone are eventually the same (1.22 Å, see S7). These results indicate that there is no hydrogen bonding between the quinone oxygen atom and the amide hydrogen in the ground state.

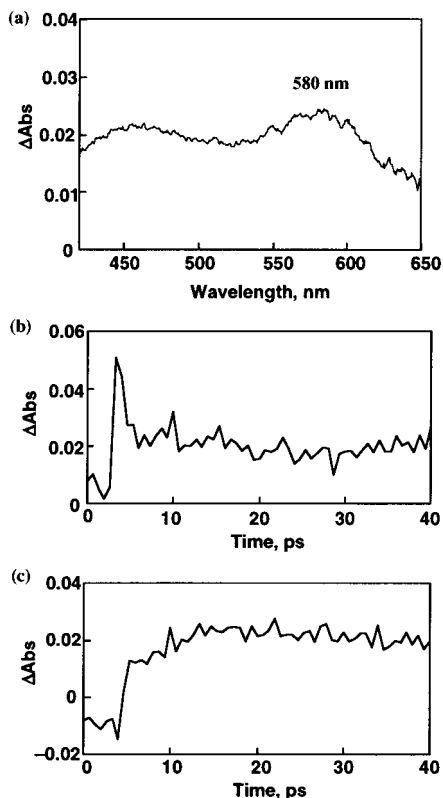
The cyclic voltammograms of **Fc–Q** exhibited two reversible one-electron redox couples of two redox active moieties at 0.39 and −0.16 V (vs SCE) in MeCN. The former one-electron redox potential corresponds to the Fc/Fc<sup>+</sup> couple that agrees with the one-electron oxidation potential of ferrocene ( $E^0_{\text{ox}}$  vs SCE = 0.37 V).<sup>10</sup> The latter potential thereby corresponds to the Q/Q<sup>•−</sup> couple.<sup>11</sup> The one-electron reduction potential of Q ( $E^0_{\text{red}}$  vs SCE = −0.16 V) of **Fc–Q** is significantly shifted to a positive direction as compared to the value of **Fc–(Me)Q** in which the amide proton is replaced by methyl group (−0.40 V). Such a large positive shift of  $E^0_{\text{red}}$  of Q thereby indicates that Q<sup>•−</sup> is stabilized by the hydrogen bonding formed with the amide proton of the spacer.

To examine the hydrogen bonding of Q<sup>•−</sup> in the dyad, the radical anion of quinone moiety of **Fc–Q** (**Fc–Q<sup>•−</sup>**) was produced by the electron-transfer reduction of **Fc–Q** by semiquinone radical anion. An electron transfer from the semiquinone radical anion to Q occurs, to produce **Fc–Q<sup>•−</sup>**. The absorption spectrum of hydrogen-bonded **Fc–Q<sup>•−</sup>** has absorption maxima at 450 and 550 nm, whereas Q<sup>•−</sup> with no hydrogen bonding of **Fc–(Me)Q<sup>•−</sup>** has the absorption maximum only at 450 nm (S8). The ESR spectrum of **Fc–Q<sup>•−</sup>** ( $g = 2.0055$ ) in MeCN at 298 K exhibits the hyperfine splitting (hfc) determined as  $a_{\text{H}} = 4.60$  (1H), 2.05 (1H), and 1.75 G (1H) (S9). The observed hfc values can be well reproduced by the density function (DFT) calculation of Ph–Q<sup>•−</sup> in which Fc is omitted at the BLYP/3-21G level which predicts the hfc values as 4.85 (1H), 2.48 (1H), and 1.12 G (1H).<sup>12</sup> The optimized geometry consistent with the experimentally determined hfc values indicates that the O–H distance between the quinone oxygen atom of Q<sup>•−</sup> and the amide hydrogen is 1.61 Å which is much shorter than the distance in the X-ray structure of neutral **Fc–Q** (Figure 1). The C–O bond length of the hydrogen-bonded carbonyl group (1.32 Å) becomes longer than the bond length of the other carbonyl group (1.30 Å)

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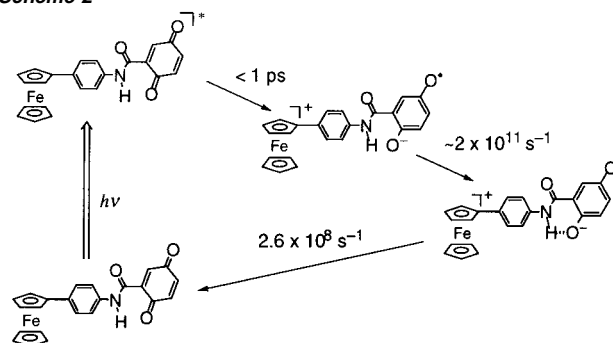
**Figure 2.** (a) Time-resolved absorption spectrum of **Fc-Q** dyad ( $5.0 \times 10^{-4}$  M) in argon-saturated PhCN excited at 388 nm (delay time: 1 ns) at 298 K. The time profile at (b) 450 nm-band and (c) at 580 nm-band.

due to the weakening of the C–O bond by the hydrogen bonding with the amide proton. To confirm the hydrogen bond formation upon the electron-transfer reduction of **Fc-Q**, photoinduced electron transfer from the Fc to the Q moiety is examined using a laser flash photolysis technique (vide infra).

Photoexcitation of the Q moiety in **Fc-Q** in deaerated PhCN with 388 nm femtosecond (150 fs width) laser light results in the appearance of a new absorption band at 580 nm as shown in Figure 2.<sup>13</sup> In contrast, no such absorption band was observed at 580 nm in the case of **Fc-(Me)Q**. Thus, the absorption band at 580 nm corresponds to the band due to the hydrogen-bonded  $\text{Q}^{\cdot-}$  which is significantly red-shifted as compared to the diagnostic absorption band of semiquinone radical anion at 450 nm.<sup>14,15</sup> The time course of the rise and decay of the transient absorption at 450 and 580 nm is shown in Figure 2 (part b and c, respectively). The absorption at 450 nm appears immediately upon the laser excitation within 1 ps and decays with a first-order rate constant of  $\sim 2 \times 10^{11} \text{ s}^{-1}$  ( $\tau = \sim 5$  ps) accompanied by the rise in absorption at 580 nm due to the hydrogen-bonded  $\text{Q}^{\cdot-}$  which decays at a longer time scale, obeying first-order kinetics with a rate constant of  $2.6 \times 10^8 \text{ s}^{-1}$ .<sup>16</sup> This indicates that electron transfer from Fc to the singlet excited state of Q occurs rapidly to produce  $\text{Fc}^+-\text{Q}^{\cdot-}$  without changing the conformation ( $< 1$  ps), that  $\text{Q}^{\cdot-}$  then forms hydrogen bonding with the amide proton of the spacer ( $\tau = \sim 5$  ps), and that the resulting radical ion pair decays via a back electron transfer to the ground state as shown in Scheme 2.

In conclusion, the present study has demonstrated for the first time the dynamics of hydrogen-bonding formation in intramolecular photoinduced electron transfer from an electron donor moiety to a quinone with a rigid amide spacer.

**Scheme 2**



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**Supporting Information Available:** Synthetic procedures of **Fc-Q** and **Fc-(Me)Q**, the crystallographic data of **Fc-Q**, the selected bond distances, spectral data of **Fc-Q** $^{\cdot-}$  and **Fc-(Me)Q** $^{\cdot-}$  (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (14) The  $\lambda_{\text{max}}$  value of the hydrogen-bonded  $\text{Q}^{\cdot-}$  varies slightly depending on the system: 580 nm for  $\text{Fc}^+-\text{Q}^{\cdot-}$  (Figure 2a) and 550 nm for  $\text{Fc-Q}^{\cdot-}$  (S8). For the  $\lambda_{\text{max}}$  value of  $\text{Fc-(Me)Q}^{\cdot-}$  without hydrogen bonding (450 nm), see: Fukuzumi, S.; Nakanishi, I.; Maruta, J.; Yorise, T.; Suenobu, T.; Itoh, S.; Arakawa, R.; Kadish, K. M. *J. Am. Chem. Soc.* **1998**, *120*, 6673.
- (15) The transient absorption due to the  $\text{Fc}^+$  part was not detected probably because of the low extinction coefficient of  $\text{Fc}^+$ .<sup>10</sup>
- (16) The absorption at 450 nm due to  $\text{Q}^{\cdot-}$  with no hydrogen bonding decays to the residual absorbance due to the hydrogen-bonded  $\text{Q}^{\cdot-}$  (S8). This coincides with the rise in absorbance at 580 nm.

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