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Structural Conversion and Spin Separation in Bis(ferrocenylethynyl)anthraquinones Triggered by Proton-Coupled Intramolecular Electron Transfer

Masaki Murata,† Mami Yamada,† Takako Fujita,†
Kohei Kojima,† Masato Kurihara,† Kenya Kubo,†
Yoshio Kobayashi,‡ and Hiroshi Nishihara*,†

Department of Chemistry, School of Science
The University of Tokyo, Hongo
Bunkyo-Ku, Tokyo, Japan
The Institute of Physical and Chemical
Research (RIKEN), Hirosawa, Wako, Saitama, Japan

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Proton-coupled electron transfer (PCET) between donor and acceptor molecules is a fundamentally important chemical reaction closely related to various energy conversion events in biological systems.[1] We have recently reported the intramolecular PCET of 1:1-donor/acceptor compounds, 1-ferrocenylethynylanthraquinone, **1-FcAq**,[2a] and 2-(2-ferrocenylvinyl)hydroquinone, causing novel structural changes.[2b] These reactions are realized by a combination of several factors such as the PCET ability of quinones, the existence of a π-conjugated spacer between ferrocene and quinone, and a matching of donor−acceptor levels controlled by protonation. These phenomena prompted us to investigate the PCET reaction in 2:1-donor/acceptor compounds, 1,8-bis(ferrocenylethynyl)anthraquinone, **1,8-Fc$_2$Aq**, and 1,5-bis(ferrocenylethynyl)anthraquinone, **1,5-Fc$_2$Aq**, because the quinone moiety can undergo double protonation, drastically changing the acceptor level. In this communication we report that only **1,5-Fc$_2$Aq** undergoes a facile two-step proton response, leading to a doubly protonated species with unique physical properties due to the existence of three possible valence tautomers. The most favorable valence tautomer is different between the solution and solid states, and also dependent on temperature.

Two isomers, **1,8-Fc$_2$Aq** and **1,5-Fc$_2$Aq**, were synthesized by the Pd(II)−Cu(I)-catalyzed cross-coupling reaction[3a] of ethynylferrocene[3b] with 1,8-dibromoanthraquinone and 1,5-dibromoanthraquinone[3c] in 88 and 75% yields, respectively. Their structures were confirmed by X-ray crystallography (Figure S3, Supporting Information).

The spectroscopic responses of **1,8-Fc$_2$Aq** and **1,5-Fc$_2$Aq** to CF$_3$SO$_3$H in benzonitrile are significantly different. The solution of **1,8-Fc$_2$Aq** changed immediately from deep red to deep reddish-purple after the addition of the acid, corresponding to the UV−vis−near-IR absorption spectral change, as shown in Figure 1a.[4] The n-π* band of the anthraquinone moiety decreases, two MLCT bands increase in intensity at 491 and 546 nm, and a new broad band with the half-width $\Delta\nu_{1/2} = 5.4 \times 10^3$ cm^{-1} appears over the visible and near-IR regions ($\lambda_{\max} = 934$ nm). This spectral change is quite similar to that of **1-FcAq**.[2a] The protonated species of **1,8-Fc$_2$Aq** was isolated from the acidic solution, and its ESI-mass, ^{1}H NMR, ^{13}C NMR, and IR spectra revealed that **1,8-Fc$_2$Aq** undergoes a single protonation of the carbonyl oxygen adjacent to the ethynylene bond, causing a structural change to create a compound involving both ferrocenylethynyl and η^6-fulvene−cumulene moieties, [**1,8-FcFvAqH**]$^+$ (Scheme 1).[5]

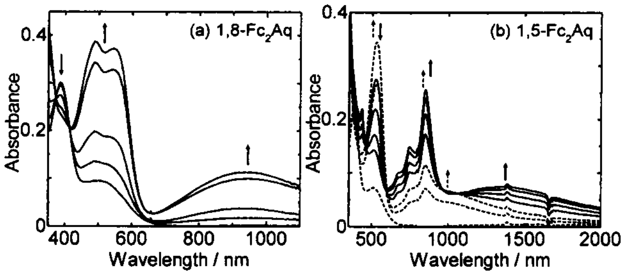
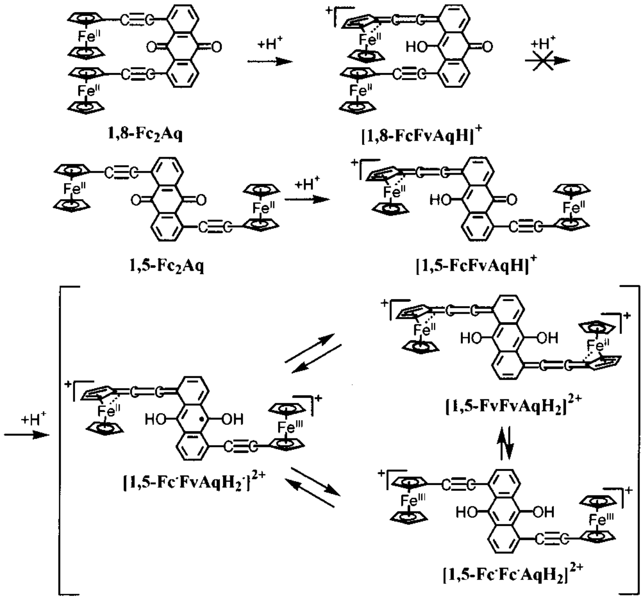


Figure 1. (a) UV−vis−near-IR spectral change of **1,8-Fc$_2$Aq** (5×10^{-5} M) in benzonitrile upon the addition of 0−2 equiv of CF$_3$SO$_3$H. (b) UV−vis−near-IR spectral change of **1,5-Fc$_2$Aq** (5×10^{-5} M) in benzonitrile upon the addition of 0−2 equiv (dotted lines and arrows) and 2−4 equiv (solid lines and arrows) of CF$_3$SO$_3$H.

Scheme 1



In contrast, the addition of several equivalents of CF$_3$SO$_3$H into a benzonitrile solution of **1,5-Fc$_2$Aq** resulted in a two-step color change, initially to deep reddish-purple, and then to deep-green.[4] ESI-mass spectra have indicated that deep reddish-purple and deep-green solutions are derived from singly and doubly protonated species, respectively.[6] The first spectral change in the UV−vis−near-IR absorption spectra, as depicted by the dotted lines in Figure lb, is quite similar to those of **1-FcAq**[2a] and **1,8-Fc$_2$Aq**, suggesting a conversion to a similar fulvene−Fe(II) complex−cumulene structure, [**1,5-FcFvAqH**]$^+$. In the second step, the MLCT band at $\lambda_{\max} = 522$ nm decreases in intensity, two intense bands appear at 748 and 850 nm, and the broad band with the half-width ($\Delta\nu_{1/2} = 7.2 \times 10^3$ cm^{-1}, $\lambda_{\max} = 909$ nm) is shifted to longer wavelength ($\Delta\nu_{1/2} = 5.2 \times 10^3$ cm^{-1}, $\lambda_{\max} = 1309$ nm) (Figure 1b, solid line). The two bands in the visible region are quite similar to those of the semiquinone form of anthraquinone derivatives.[7] The EPR spectrum of the frozen acidic

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† The University of Tokyo.

‡ The Institute of Physical and Chemical Research (RIKEN).

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(4) Similar spectral change by protonation was also observed in a dilute solution in acetonitrile, dichloromethane, or chloroform.

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(6) The molecular ion peak of mono- (*m*/*z* 625) and doubly protonated **1,5-Fc$_2$Aq** (*m*/*z* 626) indicated an increase of one and two hydrogen atoms from **1,5-Fc$_2$Aq** (*m*/*z* 624) on the basis of the ESI and FAB mass spectra, respectively.

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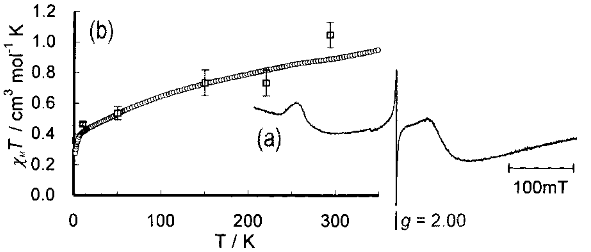

Figure 2. (a) The EPR spectrum of doubly protonated **1,5-Fc$_2$Aq** in the solid state at 6.6 K. (b) The $\chi_M T-T$ plot of doubly protonated **1,5-Fc$_2$Aq** (○) and $\chi_M T$ values estimated from the EPR *g* values and ^{57}Fe Mössbauer ϕ values (□).

acetonitrile solution of **1,5-Fc$_2$Aq** at 5.0 K showed a strong, sharp signal at $g = 2.02$ assignable to a semiquinone radical of the anthraquinone moiety as well as weak broad signals at $g_{\parallel} = 4.12$ and $g_{\perp} = 1.5$ originating from a ferrocenium cation including an Fe(III) nucleus (Figure S4, Supporting Information).[8] These spectroscopic results suggest the generation of a spin-separated form, [**1,5-Fc$^\bullet$FvAqH$_2^\bullet$**]$^{2+}$ (Scheme 1).

Electrochemistry of the protonated compounds supported the reactions given in Scheme 1. The series of monoprotonated complexes exhibits a reversible two-step one-electron reduction of the protonated anthraquinone moiety (AqH) in the cyclic voltammograms in Bu$_4$NClO$_4$/dichloromethane, whose potentials are largely shifted to more positive than those of nonprotonated forms (Table S1, Supporting Information). The reversible oxidation waves of non- and monoprotonated complexes are derived from the metal-centered oxidation of the ferrocenyl (Fc) and fulvene complex (Fv) moieties. In [**1,5-Fc$^\bullet$FvAqH$_2^\bullet$**]$^{2+}$, the redox reaction occurs in a different pattern from that of non- and monoprotonated complexes, with the rest potential being positioned between the reduction wave of the ferrocenium moiety (Fc$^+$) and the oxidation wave of Fv. Therefore, based on the above results, the spin-separated form, [**1,5-Fc$^\bullet$FvAqH$_2^\bullet$**]$^{2+}$, among the three possible canonical structures, [**1,5-Fc$^\bullet$FvAqH$_2^\bullet$**]$^{2+}$, [**1,5-FvFvAqH$_2$**]$^{2+}$, and [**1,5-Fc$^\bullet$Fc$^\bullet$AqH$_2$**]$^{2+}$, is considered to be the most thermodynamically favorable in solution as the doubly protonated species of **1,5-Fc$_2$Aq**.

The difference in second-protonation capability between 1,8- and 1,5- isomers can be attributed to the discrepancy in the conjugation of ferrocene moieties with the carbonyl moieties. Two ferrocenyl groups in **1,5-Fc$_2$Aq** conjugate with different carbonyl moieties, whereas those in **1,8-Fc$_2$Aq** conjugate with the same carbonyl moiety. Thus a second-protonation can occur only in [**1,5-FcFvAqH**]$^+$.

Protonation of **1,5-Fc$_2$Aq** (10−30 mM) with CF$_3$SO$_3$H in dichloromethane afforded a deep-green precipitate (species A), of which the ESI-mass spectrum indicated the formation of doubly protonated structure. Its UV−vis−near-IR absorption spectrum in Nujol mull, showing the $^2E_{2g} \rightarrow {}^2E_{1u}$ transition characteristic of a ferrocenium ion ($\lambda_{max} = 766$ nm)[8b] and significantly broad absorption (1456 nm) (Figure S5a, Supporting Information), is different from that of [**1,5-Fc$^\bullet$FvAqH$_2^\bullet$**]$^{2+}$. The spectrum was gradually changed into that of [**1,5-Fc$^\bullet$FvAqH$_2^\bullet$**]$^{2+}$, with isosbestic points appearing after dissolution in acetonitrile (Figure S5b, Supporting Information). These results suggest that species A is a valence tautomer of [**1,5-Fc$^\bullet$FvAqH$_2^\bullet$**]$^{2+}$.

The ^{57}Fe Mössbauer spectra of species A designate strong temperature-dependence. The spectrum at 10 K (Figure S6a, Supporting Information) shows the superposition of two components of Fe(II) (QS = 2.10 mms^{-1}, IS = 0.40 mms^{-1}) and Fe(III) nuclei (QS = 0.30 mms^{-1}, IS = 0.40 mms^{-1}), for which the areal intensity ratio (ϕ = Fe(III)/[Fe(II) + Fe(III)]) is 0.44 (±0.01). The QS value of the Fe(II) component is smaller than the value of the Fe(II) nucleus of the nonprotonated **1,5-Fc$_2$Aq** (QS = 2.39 mms^{-1}, IS = 0.55 mms^{-1}, at 9.2 K), and this smaller QS value indicates a conversion to the fulvene−Fe(II) complex structure through protonation.[5c] The absorption of the ferrocenium−Fe(III) nucleus increases compared to that of Fe(II), when the temperature is raised, as shown in the spectrum at 293 K (Figure S6b, Supporting Information). The ϕ values at 50, 150, 220, and 293 K were estimated to be 0.51 (±0.04), 0.70 (±0.08), 0.70 (±0.08), and 1.00 (±0.09), respectively.

The EPR spectrum of the solid state of the doubly protonated **1,5-Fc$_2$Aq** at 6.6 K showed a superposition of two components of Fe(III) nuclei from a ferrocenium cation ($g_{\parallel} = 3.93$, $g_{\perp} = 1.59$)[8] and a semiquinone radical of the anthraquinone moiety ($g = 2.00$) (Figure 2a). The ratio in signal intensity of the semiquinone radical to the ferrocenium cation is considerably smaller in the solid state than in the frozen solution state (vide supra). The $\chi_M T-T$ plot of this doubly protonated **1,5-Fc$_2$Aq** is shown in Figure 2b. The $\chi_M T$ value decreases with decreases in temperature.

The temperature-dependent change of the ^{57}Fe Mössbauer spectra can be ascribed to the thermal equilibrium between the three valence tautomers, [**1,5-FvFvAqH$_2$**]$^{2+}$, [**1,5-Fc$^\bullet$FvAqH$_2^\bullet$**]$^{2+}$, and [**1,5-Fc$^\bullet$Fc$^\bullet$AqH$_2$**]$^{2+}$ in the solid state (Scheme 1). At higher temperatures, the paramagnetic [**1,5-Fc$^\bullet$ Fc$^\bullet$AqH$_2$**]$^{2+}$, with its two ferrocenium Fe(III) nuclei, is dominantly formed. The $\chi_M T$ value at 348 K is 0.95 cm^{3}mol^{-1}K, which is close to the calculated $\chi_M T$ value of 1.05 for [**1,5-Fc$^\bullet$Fc$^\bullet$AqH$_2$**]$^{2+}$, as estimated from the EPR *g* values. With decreases in temperature, [**1,5-Fc$^\bullet$Fc$^\bullet$AqH$_2$**]$^{2+}$ might primarily be transformed into the diamagnetic [**1,5-FvFvAqH$_2$**]$^{2+}$, which has two fulvene−Fe(II) and doubly protonated anthrahydroquinone moieties, as the calculated $\chi_M T$ values in typical temperatures estimated from the EPR *g* values and ^{57}Fe Mössbauer ϕ values[9] correspond well with the experimental $\chi_M T$ values (Figure 2b). A small distribution of [**1,5-Fc$^\bullet$FvAqH$_2^\bullet$**]$^{2+}$, which is dominant in the solution, cannot be ruled out at low temperature in the solid state because of the existence of a weak EPR signal for the radical (Figure 2a).

In summary, we have described novel intramolecular PCET causing a drastic change in structure and physical properties in the donor−acceptor conjugated complexes, **1,8-Fc$_2$Aq** and **1,5-Fc$_2$Aq**. In particular, the doubly protonated form of **1,5-Fc$_2$Aq** reaches an equilibrium involving three valence tautomers, depending on the matrix and temperature. These findings should be useful in designing novel functional molecular systems.[10]

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Supporting Information Available: Characterization data for **1,5-Fc$_2$Aq**, **1,8-Fc$_2$Aq**, and these protonated species, their redox potentials (Table S1), ORTEP viewers of **1,5-Fc$_2$Aq** and **1,8-Fc$_2$Aq** (Figure S3), the EPR spectrum of the frozen acidic acetonitrile solution of **1,5-Fc$_2$Aq** (Figure S4), the absorption spectrum of the doubly protonated **1,5-Fc$_2$Aq** solid in Nujol mull and after its dissolution in acetonitrile (Figure S5), and ^{57}Fe Mössbauer spectra of doubly protonated **1,5-Fc$_2$Aq** solid at 10 K and 293 K (Figure S6) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) Assuming a thermal equilibrium between paramagnetic [**1,5-Fc$^\bullet$Fc$^\bullet$AqH$_2$**]$^{2+}$ ($\chi_M T$ = 1.05 cm^{3}mol^{-1}K, estimated from the EPR *g* values) and diamagnetic [**1,5-FvFvAqH$_2$**]$^{2+}$, the $\chi_M T$ values were calculated from the mol ratio of species obtained from ^{57}Fe Mössbauer ϕ values.

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