Novel Protonation-Induced Structural Conversion of an Ethynylene-Bridged Ferrocene–Anthraquinone Complex

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1-Ferrocenylethynylanthraquinone undergoes a structural arrangement into the fulvene–cumulene constitution by the protonation.

Proton-coupled electron transfer between donor and acceptor molecules has been the primary foci in the study of chemical reactions over the last several decades.[1] Quinonoid compounds are representative acceptor molecules of which redox properties can be readily controlled by external perturbation, such as protonation and solvation.[2] Recent attention has also been focused on electronic communication between redox molecular units such as ferrocene linked by a π-conjugated chain.[3] From these points of view, we considered it intriguing to investigate a system in which donor and acceptor molecules are combined by a π-conjugated linker and either the donor or acceptor undergoes proton-coupled redox reactions.

An ethynylene-bridged ferrocene–anthraquinone complex, 1-ferrocenylethynylanthraquinone (**1-FcAq**) was synthesized by the Pd(II)–Cu(I) catalyzed cross-coupling reaction[4] of ethynylferrocene[5] with 1-bromoanthraquinone[6] in a yield of 84%,[7] and its molecular structure was determined by X-ray crystallography. The ORTEP diagram of **1-FcAq** displays that the cyclopentadienyl rings of the ferrocene moiety are perpendicular to the plane of the anthraquinone moiety, as shown in Figure 1. The UV–Vis-NIR absorption spectrum of **1-FcAq** in benzonitrile shown in Figure 2(a) exhibits the specific absorption band at 511 nm, which is assignable to the MLCT transition from the Fe(II) to the ethynylanthraquinone moiety, based on the fact that a similar visible band is commonly observed in the spectra of π-conjugated ferrocene derivatives.[3,8]

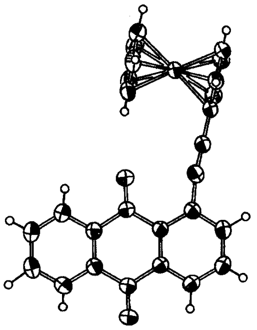


Figure 1. ORTEP drawing of **1-FcAq** with a probability level of 50%. Crystal data for **1-FcAq**. Formula, $C_{26}H_{16}O_2Fe$; formula weight 416.25; crystal system, triclinic; space group, $P\bar{1}$; a = 7.9130 (5) Å; b = 9.9530 (4) Å; c = 13.1500 (8) Å; α = 112.459 (3)°; β = 97.359 (3)°; γ = 98.343 (3)°; V = 927.7 (1) Å^3; Z = 2; reflections collected, 4061; no. of unique reflections, 3692; no. of parameters, 326; R = 0.034 ; wR = 0.096 ; $(\Delta\rho)$max = 0.51 e/Å^3.

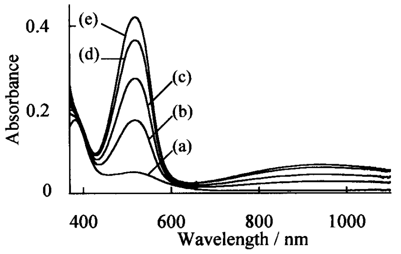
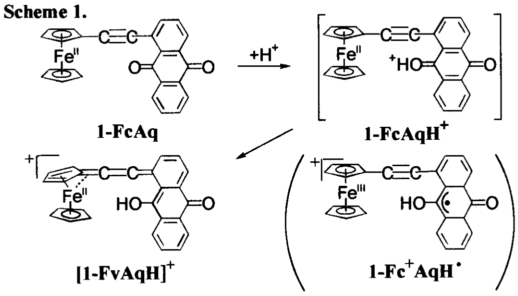


Figure 2. UV-Vis-NIR spectral change of **1-FcAq** (0.30 mmol dm^{-3}) in benzonitrile upon addition of 0 (a), 0.5 (b), 1.0 (c), 1.5 (d), and 2.0 eq. (e) of CF_3SO_3H.

The color of the **1-FcAq** solution changes immediately from red to deep-reddish-pink after the addition of CF_3SO_3H. This corresponds to the spectral change in which the MLCT band increases in intensity, and in which a new broad band with the half-width, $\Delta\nu_{1/2}$ = 5.2 × 10^3 cm^{-1} appears in visible and near-IR regions (λ_{max} = 939 nm) as shown in Figure 2. The protonated complex of **1-FcAq** was isolated,[9] and its ^{1}H-NMR, ^{13}C-NMR, IR and ESI-mass spectra as described below have confirmed that it is a unique structure involving a cumulene moiety, η^5-cyclopentadienyl-[η^6-(9-hydroxy-10-oxo-1,10-dehydro-1-anthrylidenevinylidene)-2,4-cyclopentadiene]iron(II) trifluoromethanesulfonate, [**1-FvAqH**]$^+CF_3SO_3^-$.

The notable features in the ^{1}H-NMR spectrum of [**1-FvAqH**]$^+CF_3SO_3^-$ in CD_3CN are that a new singlet due to the hydroxy group appears at δ 8.23 ppm and that two double-doublets at 4.67 and 4.33 ppm due to the cyclopentadienyl ring connecting to the ethynyl group of **1-FcAq** shift to the lower field by 1 ppm compared with **1-FcAq** according to the conversion into the fulvene structure. In the ^{13}C-NMR spectrum of [**1-FvAqH**]$^+$, one of the two signals of carbonyl carbons in the anthraquinone moiety of **1-FcAq** at δ 183.1 and 182.1 ppm disappears, accompanied by appearance of a new signal of a quaternary carbon in the region of aromatic ring carbons of the anthraquinone moiety at 120–140 ppm. Instead of the two signals of the ethynyl carbons at 96.2 and 86.1 ppm, two signals ascribable to cumulene carbons appear in significantly lower field (171.1 and 167.8 ppm). The two signals derived from the ferrocenyl carbons (72.2 and 70.0 ppm) and the signal derived from the quaternary carbon (66.1 ppm) connecting to the ethynylene group of **1-FcAq** are shifted to the lower field (76.2 and 70.1 ppm) and to the higher field (55.3 ppm), respectively, corresponding to fulvene carbons in [**1-FvAqH**]$^+$. These chemical shift values of [**1-FvAqH**]$^+$ are quite similar to those of $[Fe(C_5H_5)(fulvene)]^+$,[10a–d] of which molecular structure with marked bent of exocyclic C=C bond indicates that the fulvene unit of $[Fe(C_5H_5)(fulvene)]^+$ has a nature of both the η^4- and η^6-coordination.[10e] This implies that there is a significant contribution of the 18e$^-$ form. The IR spectrum of [**1-FvAqH**]$^+CF_3SO_3^-$ shows the disappearance of the ν(C≡C) band of **1-FcAq**, and the molecular ion peak of [**1-FvAqH**]$^+$ (*m/z* 417) detected in the ESI-mass spectrum indicates the addition of one hydrogen atom to **1-FcAq** (*m/z* 416) in composition.

Scheme 1.



The reaction mechanism to form [**1-FvAqH**]$^+$ can be proposed as given in Scheme 1, in which the protonation to one of the carbonyl oxygen atoms of the anthraquinone moiety occurs to produce transient species of **1-FcAqH**$^+$, followed by the intramolecular electron transfer from the cyclopentadienyl ion to the protonated anthraquinone, resulting in a structural change of the π-conjugated chain into the specific fulvene–cumulene without oxidation of the iron center of Fe(II).[11] The increase in intensity of the MLCT band (λ_{max} = 511 nm) shown in Figure 2 is due to the significant change of the π-conjugated system. The band at λ_{max} = 939 nm of [**1-FvAqH**]$^+$ might be ascribed to the valence tautomerization into **1-FcAqH**$^+$ or a spin-separated form, **1-Fc**$^+$**AqH**$^\bullet$(see Scheme 1), since such a broad low-energy band has been recognized in other valence tautomerization complexes.[12] This consideration is supported by the fact that the solvent effect on λ_{max} is large; λ_{max} = 1051 nm in dichloromethane which is less polar than benzonitrile.

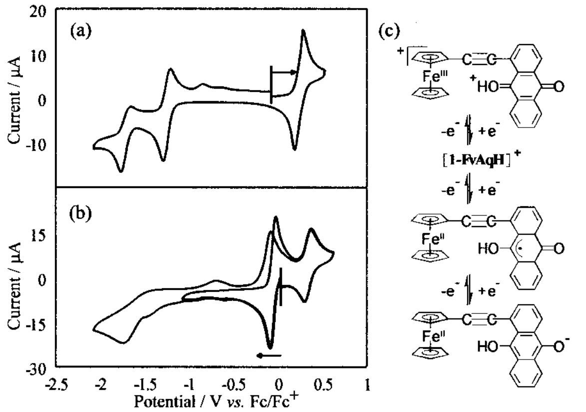


Figure 3. Cyclic voltammograms of **1-FcAq** (1.0 mmol dm^{-3}) in 0.1 mol dm^{-3} Bu_4NClO_4-CH_2Cl_2 (a) and [**1-FvAqH**]$^+CF_3SO_3^-$ (1.0 mmol dm^{-3}) in 0.1 mol dm^{-3} Bu_4NClO_4-CH_3CN (b) at a 3 mm-o.d. glassy carbon disk electrode at 50 mV s^{-1}. (c) A proposed redox process of [**1-FvAqH**]$^+$.

Cyclic voltammetry of **1-FcAq** in 0.1 mol dm^{-3} Bu_4NClO_4–CH_2Cl_2 shows reversible two-step 1e$^-$ reduction at $E^{0'}$ = –1.26 and –1.71 V vs ferrocene/ferrocenium derived from the anthraquinone moiety and reversible 1e$^-$ oxidation at $E^{0'}$ = 0.22 V due to the ferrocene moiety (Figure 3(a)). The protonation product, [**1-FvAqH**]$^+$ exhibits quasi-reversible 1e$^-$ wave at $E^{0'}$ = –0.06 V and considerably irreversible 1e$^-$ wave at E_{pc} = –1.80 V in the reduction process, and quasi-reversible 1e$^-$ oxidation wave at $E^{0'}$ = 0.33 V in the cyclic voltammogram in 0.1 mol dm^{-3} Bu_4NClO_4–CH_3CN (Figure 3(b)). The significant shift of the first reduction potential in the positive direction and the positive shift of the oxidation potential by 0.11 V in comparison with **1-FcAq** corresponds to the structural changes in both ferrocene and anthraquinone moieties by protonation. We at present postulate the redox process of [**1-FvAqH**]$^+$ as shown in Figure 3(c) based on the redox behavior of quinones.[2b]

In summary, we observed the novel protonation-induced structural conversion in a donor–acceptor conjugated molecule, which caused a drastic change in physical properties. This discovery should lead to a new strategy for designing novel functional molecular systems.[13]

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7 Selected data for **1-FcAq**. ^{1}H-NMR ($CDCl_3$): δ 8.39 (m, 1H), 8.30 (m, 2H), 7.93 (dd, 1H, J = 7.8, 1.5 Hz), 7.77 (m, 3H), 4.67 (dd, 2H, J = 1.8, 1.8 Hz), 4.35 (s, 5H), 4.33 (dd, 2H, J = 1.8, 1.8 Hz). ^{13}C-NMR (CD_2Cl_2): δ 183.1 (CO), 182.1 (CO), 140.5 (Ph), 134.9 (Ph), 134.7 (Ph), 134.0 (Ph), 133.4 (Ph), 133.2 (Ph), 133.1 (Ph), 127.6 (Ph), 127.0 (Ph), 126.9 (Ph), 124.7 (Ph), 96.2 (C≡C), 86.1 (C≡C), 72.2 (Cp), 70.7 (Cp), 70.0 (Cp), 66.1 (Cp). Anal. Calcd for $C_{26}H_{16}O_2Fe$: C, 75.02; H, 3.87%. Found: C, 74.73; H, 3.94%.

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9 Selected data for **[1-FvAqH]**$^+CF_3SO_3^-$. ^{1}H-NMR (CD_3CN): δ 8.68 (dd, 1H, J = 4.3, 2.6 Hz), 8.57 (dd, 1H, J = 7.1, 1.0 Hz), 8.44 (dd, 1H, J = 4.3, 2.6 Hz), 8.35 (dd, 1H, J = 8.6, 7.1 Hz), 8.23 (s, 1H), 8.20 (dd, 1H, J = 8.6, 1.0 Hz), 8.09 (m, 2H), 5.41 (dd, 2H, J = 1.7, 1.7 Hz), 5.06 (dd, 2H, J = 1.7, 1.7 Hz), 4.35 (s, 5H). ^{13}C-NMR (CD_3CN): δ 180.8 (CO), 171.1 (cumulene), 167.8 (cumulene), 142.2 (anthrasemiquinone (AqH)), 141.7 (AqH), 138.0 (AqH), 136.7 (AqH), 135.1 (AqH), 134.4 (AqH), 134.0 (AqH), 130.6 (AqH), 130.2 (AqH), 129.2 (AqH), 128.1 (AqH), 121.1 (AqH), 116.6 ($CF_3SO_3^-$), 76.2 (fulvene (Fv)), 72.8 (Cp), 70.1 (Fv), 55.3 (Fv). Anal. Calcd for $C_{27}H_{17}F_3FeO_5S \cdot 0.1CH_2Cl_2$: C, 56.63; H, 3.02%. Found: C, 56.62; H, 3.34%.

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