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Azo- and quinone-conjugated redox complexes—photo- and proton-coupled intramolecular reactions based on d–π interaction

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Contents

Abstract

Novel photo- and proton-coupled behavior of azo- and quinone-conjugated metal complexes based on the d–π electronic interaction is described. The quantum yield for photoisomerization of azobenzene-bridged bis(terpyridine) complexes significantly depends on the nature of the metal, counterions, and solvents. The *trans*-to-*cis* isomerization of azoferrocene proceeds not only by the photoexcitation of the π–π* transition band but also by the photoexcitation of the MLCT (d–π* transition) band. The oxidation of the ferrocene moieties occurs at 0.3 V less positive potential, and the electronic interaction between the ferrocene moieties is significantly weaker in *cis*-azoferrocene than in *trans*-azoferrocene. In a vinylene-bridged ferrocene–hydroquinone complex, the oxidation of the ferrocenyl site promotes the elimination of the hydroxyl and the vinylene protons followed by intramolecular electron transfer to form an allene and a quinonoid structure. The protonation to carbonyl groups of the anthraquinone moiety in 1-ferrocenylethynylanthraquinone causes intramolecular electron transfer leading to a novel structural change into a η^6-fulvene–cumulene Fe(II) complex. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: d–π Interaction; Azo; Photoisomerization; Quinone; Proton-coupled electron transfer; Ferrocene

1. Introduction

Intelligent molecules, the structures and properties of which are facilely and reversibly changeable by the application of external physical and chemical stimuli, have attracted much recent attention relative to the development of new molecule-based devices [1]. One category of such molecules comprises transition metal complexes with π-conjugated spacers; the combination of flexibility of d- and π-orbitals can yield unique optical, magnetic, and electronic properties. In this article, recent advances in two types of such d–π interaction systems responding to the external stimuli are described. These are redox-active metal complexes conjugated with the isomerizable azo group, and donor–

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acceptor-conjugated molecules comprising a ferrocene and a proton-responsive quinonoid compound (Fig. 1).

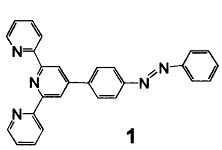
2. Isomerization of azo-conjugated complexes

The photoisomerization of organic azobenzenes is a subject of current research interest from a perspective of photon-mode high-density information storage and photo-switching devices [2–5]. The *trans*-to-*cis* change of azobenzene occurs by UV light irradiation exciting the π–π* transition, and the reverse change takes place by visible light irradiation exciting the n–π* transition or by heating, due to the fact that the thermodynamic stability of the *trans*-form is higher than that of the *cis*-form. The mechanism of photo- and thermal isomerization of organic azobenzenes has been well discussed [6–8].

Azo-conjugated transition metal complexes can provide new advanced molecular functions, based on combinations of photoisomerization of the azo group and changes in the intrinsic properties, such as the optical, redox, and magnetic properties, originating from the d-electrons. Some metal complexes including azobenzene and related compounds as a building block have been synthesized [9–14], and a number of studies on the photoisomerization of azo-conjugated metal complexes have appeared in recent years [15–21]. In this section, two types of azo-conjugated metal complexes are described. In these complexes, novel behavior due to strong d–π interaction has been found.

2.1. Azobenzene-attached bis(terpyridine) complexes—effects of metals, counterions and solvents on their photoisomerization

Azobenzene-attached terpyridine and bis(terpyridine) ligands, **1** and **2**, and their Rh(III) and Ru(II) mononuclear and dinuclear complexes with various counterions, **3**–**6**, were synthesized, and their photoisomerization behavior has been investigated [22].



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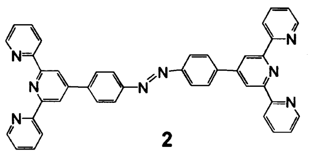

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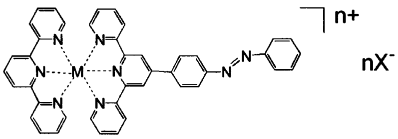
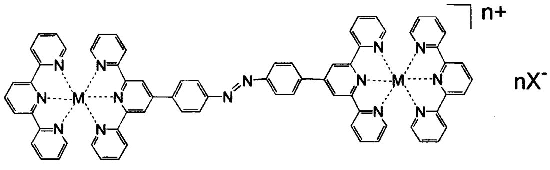
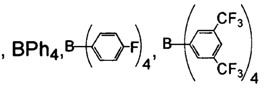


M = Rh^{III} (**3**) X = BF$_4$, PF$_6$, BPh$_4$
Ru^{II} (**4**) X = PF$_6$



M = Rh^{III} (**5**) X = Cl, Br, I, BF$_4$, PF$_6$, BPh$_4$,



$B(C_6H_4F)_4$, $B(C_6H_3(CF_3)_2)_4$

Ru^{II} (**6**) X = PF$_6$

Among the mononuclear and dinuclear Rh complexes, **3** and **5** show significant UV–vis spectral changes attributable to the *trans*-to-*cis* isomerization, including a decrease in the absorbance of the π–π* band and an increase in the longer wavelength band ascribable to the n–π* transition on 360 nm light irradiation (Fig. 2). The formation of the *cis*-form causes the ^{1}H-NMR spectral change as a higher magnetic field shift of the aromatic ring protons by weakening the electron-withdrawing effect of the azo group. In the IR spectra of the isolated *cis*-complexes, a weak peak due to the N=N stretching mode, which is IR-inactive in *trans*-complexes due to their inversion symmetry [23–25], appears at ca. 1530 cm^{-1}. Cyclic voltammetry of the *trans*-form of **5**·6BF$_4$ in Bu$_4$NBF$_4$–MeCN shows an irreversible Rh(III)/Rh(I) reduction wave at −1.01 V versus ferrocenium/ferrocene (Fc$^+$/Fc), which shifts to −1.09 V in the *cis*-form. The negative shift of the metal-centered redox potential by the *trans*-to-*cis* isomerization suggests that

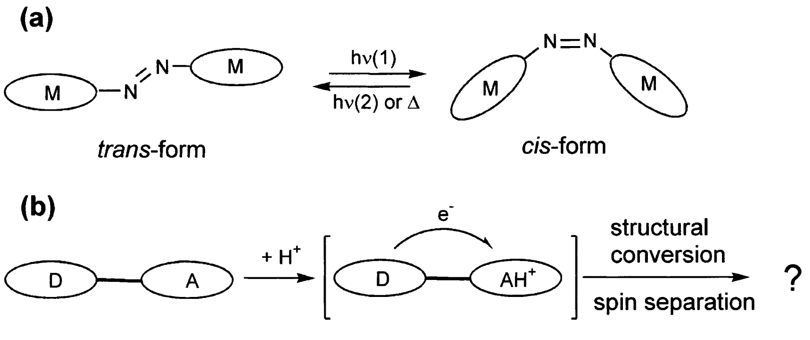


Fig. 1. Schematic illustration of d–π interaction systems responding to external stimuli: (a) the photoisomerizable azo-conjugated metal complex; and (b) the donor–acceptor-conjugated molecule causing proton-coupled intramolecular electron transfer.

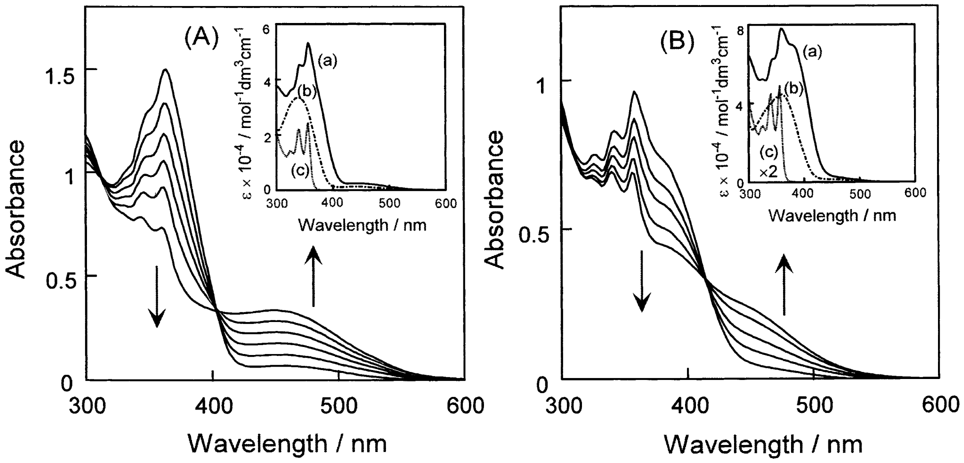


Fig. 2. (A) UV–vis absorption spectral change of $\mathbf{3}\cdot 3\mathrm{PF}_6$ (0.28 mM) in DMSO upon irradiation with a 360 nm light for 5 min. Inset: (a) the spectra of $\mathbf{3}\cdot 3\mathrm{PF}_6$; (b) **1**; and (c) Rh(terpyridine)$_2\cdot 3\mathrm{PF}_6$. (B) UV–vis absorption spectral change of $\mathbf{5}\cdot 6\mathrm{PF}_6$ (0.11 mM) in propylene carbonate upon irradiation with a 360 nm light for 40 min. Inset: (a) the spectra of $\mathbf{5}\cdot 6\mathrm{PF}_6$; (b) **2**; and (c) Rh(terpyridine)$_2\cdot 3\mathrm{PF}_6$.

Table 1
Quantum yields of **3** and **5** dependent on various solvents and counterions

Solvent [a]	Dielectric constant, ε [b]	Viscosity (η, mPa s)	$10^3\Phi_{t\to c}$					
			$\mathbf{5}\cdot 6\mathrm{BF}_4$	$\mathbf{5}\cdot 6\mathrm{PF}_6$	$\mathbf{5}\cdot 6\mathrm{BPh}_4$	$\mathbf{3}\cdot 3\mathrm{BF}_4$	$\mathbf{3}\cdot 3\mathrm{PF}_6$	$\mathbf{3}\cdot 3\mathrm{BPh}_4$
PhCN	25.9	1.27	0.34	0.062	3.9	0.29	[c]	[c]
MeCN	36.6	0.369	0.016	0.011	5.1	[c]	[c]	5.7
DMF	38.3	1.79	3.4	3.9	5.5	2.7	2.9	2.3
DMA	38.9	1.96	3.5	4.4	5.4	4.2	4.0	4.2
DMSO	47.2	1.99	0.58	1.6	3.3	1.9	1.6	2.1
PC	68.8	2.53	0.052	0.11	1.5	0.042	[c]	0.25

[a] PhCN, MeCN, DMF, DMA, DMSO, and PC are benzonitrile, acetonitrile, *N*,*N'*-dimethylformamide, *N*,*N'*-dimethylacetamide, dimethylsulfoxide, and propylene carbonate, respectively.

[b] From Ref. [88].

[c] No significant photoisomerization behavior was observed ($\Phi_{t\to c} < 10^{-6}$).

the azo group has a lesser electron-withdrawing effect in the *cis*-form than that of the *trans*-form.

The *cis*-to-*trans* photoisomerization upon excitation of the azo n–π* transition by 430 nm light irradiation does not occur for any of the mononuclear and dinuclear Rh complexes, whereas the thermal isomerization proceeds at a much slower rate than that of the free ligands. The temperature for the thermal isomerization increases depending on the counterion, in the following order: PF_6^- and $\mathrm{BF}_4^- >$ halide ions $\gg \mathrm{BPh}_4^-$, TFB$^-$ and TFPB$^-$, where TFB$^-$ and TFPB$^-$ denote tetrakis(4-fluorophenyl)borate and tetrakis{3,5-bis(trifluoromethyl)phenyl}borate ions, respectively [26].

Quantum yields of the *trans*-to-*cis* photoisomerization, $\Phi_{t\to c}$s, for **3** and **5** with various counterions in several solvents are listed in Table 1. The $\Phi_{t\to c}$ values are much smaller than those of organic azobenzenes [27–34], and showed a strong dependence on the counterions and solvents [26]. The photoisomerization of $\mathbf{5}\cdot 6\mathrm{BPh}_4$ proceeds more efficiently than that of $\mathbf{5}\cdot 6\mathrm{PF}_6$ or $\mathbf{5}\cdot 6\mathrm{BF}_4$. Complex $\mathbf{5}\cdot 6\mathrm{BPh}_4$ is subjected to *trans*-to-*cis* photoisomerization even in the KBr matrix, in which the free ligand does not show significant isomerization. The ion-pairing ability of the counterions contributes to the apparent rotor volume of the complexes for isomerization. The electrostatic interaction between the complex cation and the counter anion, evaluated from the ion-pairing peak distribution and intensities of ESI-MS, is weaker for large BPh_4^- than for small BF_4^- and PF_6^-, for which the order is consistent with the tendency of $\Phi_{t\to c}$. This phenomenon can be explained by the anion with the lower ion-pairing ability reducing the apparent rotor volume for the isomerization, leading to a more facile isomerization.

The solvent effects on the photoisomerization rates of **5** are also remarkable (Table 1). Two kinds of solvent effects can be considered. The first effect is the solvation of the cationic form of the Rh(III) complexes.

Stronger solvation of the complex cations occurs in more polar solvents, leading to an enlargement of the apparent rotor volume of the complex. The second effect is the weakening of the electrostatic interaction between the complex cation and the counterion by the strong solvation of both ions, resulting in a lessening of the apparent rotor volume of the complex. The complicated dependence of $\Phi_{t\rightarrow c}$ on the solvent is presumably due to the combination of these two opposite solvent effects. Although the polarity of MeCN, DMF, and DMA can be regarded as similar based on their dielectric constants, $\Phi_{t\rightarrow c}$ in these solvents varies over a wide range, especially for PF_6^- and BF_4^- salts. There have been some reports of a general tendency for the photoisomerization of organic azobenzenes to be depressed in more viscous solutions [35–38]. This tendency may appear as the lowest $\Phi_{t\rightarrow c}$ value in PhCN having the highest viscosity in the series of data for the BPh_4^- salt, in which case there is little dependency on the polarity of the solvent.

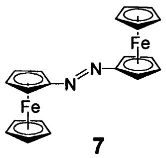
The tendencies of the solvent effects of **3** are essentially similar to those of **5**. It is notable that **3** shows a small dependence of $\Phi_{t\rightarrow c}$ on the counterion. It would be expected that the counterion of **3** would not interact with the neutral azophenyl moiety, and that the counterion would not act as an interfering factor in the motion of the azophenyl moiety.

The dinuclear Ru complex **6** showed no significant change in UV–vis absorption or ^{1}H-NMR spectra upon irradiation by 360 nm light [39], whereas a mononuclear complex, **4**, displayed slight spectral changes characteristic of *trans*-to-*cis* isomerization [26]. The *cis*-to-*trans* backward isomerization of **4** occurs slowly in the dark at room temperature (r.t.), and the isomerization is accelerated by the excitation of azo n–π* with 440 nm light irradiation.

The behavior of the femtosecond transient absorption spectra of the Rh complex $\mathbf{5}\cdot 6PF_6$ is similar to that of organic azobenzenes; at first a very broad $S_n \leftarrow S_2$ (π-π∗ state) absorption band at ca. 500 nm (within 1 ps) appears and decays rapidly [26]. Next, an intense $S_n \leftarrow S_1$ (n–π* state) absorption band at ca. 450 nm (within 2 ps) appears. The lifetime of the S_2 or S_1 state and the decay dynamics of the complexes are similar to those of organic azobenzenes [40–43], in which the *trans*-to-*cis* photoisomerization is believed to occur from the S_1 state. Our observations indicate that the photoisomerization of **5** occurs from the S_1 state. In the transient absorption spectra of the Ru complex $\mathbf{6}\cdot 4PF_6$, very fast bleaching of the Ru MLCT band at 500 nm occurs, implying that the photoisomerization behavior is depressed in response to the energy transfer from the azobenzene unit to the complex unit.

2.2. Azoferrocenes—MLCT photoisomerization with drastic changes in redox properties

Azoferrocene, **7**, is one of the π-conjugated ferrocene dimers and also one of the simplest analogs of azobenzene, having two redox-active metal complex units. Its synthesis was first reported by Nesmeyanov et al. in 1961 [44,45]. Although **7** has proved to be an intriguing complex since the identification of the azo group as the representative photoisomerizable unit, only few studies on azoferrocene have appeared in the more than 30 years since its discovery. Recently, X-ray crystallography of an azoferrocene crystal obtained under ambient conditions demonstrated that the azo moiety is in the *trans*-form, and that the two cyclopentadienyl rings of the two ferrocenyl units and the azo moiety are on almost the same plane that is the best for π-conjugation [46]. The ferrocenyl moieties are on the opposite side of the plane, and the Fe–Fe distance is 6.80 Å, indicating that there are few through-space interactions between the Fe nuclei. Higher azo-bridged ferrocene oligomers such as trimers **8** and **9**, and a polymer, **10**, have also been prepared recently [46].



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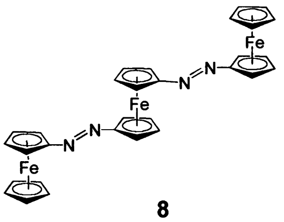

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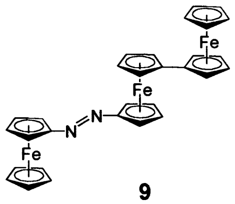

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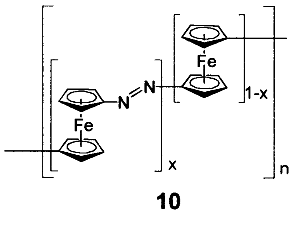

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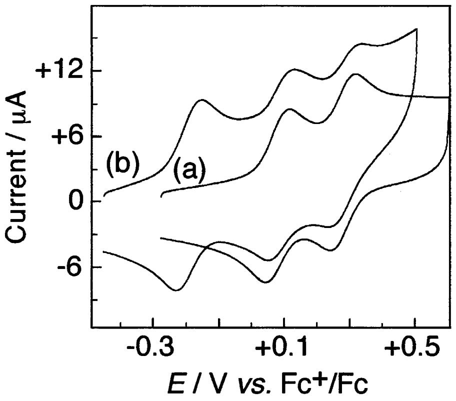


Fig. 3. Cyclic voltammograms of *trans*-**7** before (a) and after photoirradiation with a UV light (365 nm) (b) in benzonitrile containing 0.1 M Bu_4NClO_4 at 0.1 V s^{-1} scan rate under an argon atmosphere.

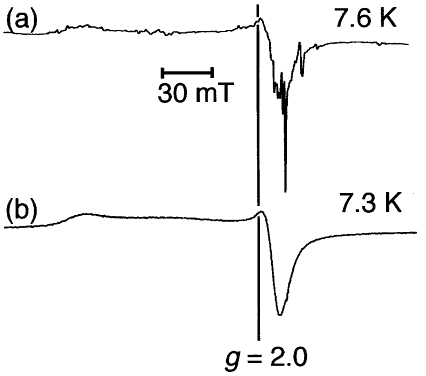


Fig. 4. EPR spectra of *trans*-**7** oxidized with 1 equiv. (a) and 2 equiv. (b) of 1,1′-dichloroferrocenium hexafluorophosphate near liquid helium temperature in benzonitrile.

The *trans*-azo bridge is similar to the vinylene bridge in that it acts as a spacer assisting in the electron exchange between the ferrocenyl moieties. The cyclic-voltammogram of **7** in Bu_4NClO_4-benzonitrile exhibits reversible 1e$^-$ oxidation waves at $E^{\circ\prime} = 0.08$ and 0.29 V versus Fc^+/Fc (Fig. 3a), indicating the formation of a thermodynamically stable mixed-valence cation. The mixed-valence cation of **7** formed in benzonitrile by 1e$^-$ chemical oxidation exhibits an EPR spectrum characterized by the superposition of narrow signals ($g = 1.9$) and a broad signal ($g_{\parallel} = 3.0$, $g_{\perp} = 1.9$) due to a ferrocenium Fe(III) cation at 7.6 K, whereas the 2e$^-$-oxidized form of **7** does not show any narrow signals (Fig. 4) [47–50]. The narrow hyperfine signals in the mixed-valence cation are possibly due to coupling with the ring protons and the nitrogen atoms caused by the delocalization of the unpaired electronic charge over the bridging ligand, Cp–N=N–Cp (Cp = η^5-cyclopentadienyl). Similar unusual hyperfine structures were observed in the EPR spectrum of a solid sample of $[Fe_2(C_5H_4)_4]I_3$ at 77 K [51]. The trimer **8** in aprotic solvents such as CH_2Cl_2 or THF exhibits a cyclic voltammogram showing reversible 2e$^-$ and 1e$^-$ oxidation waves. This behavior can be explained by the assumption that the positive charge in the monocation is localized primarily around the terminal ferrocenyl unit due to the strong electron-withdrawing effect of the azo group [46].

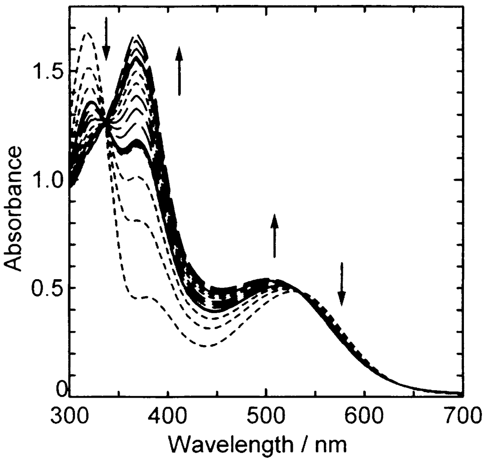


Fig. 5. UV–vis absorption spectral change of *trans*-**7** (0.126 mM) in acetonitrile under a nitrogen atmosphere under photoirradiation with three bright lines ($\lambda_{max} = 365$, 436, and 546 nm) from a super high-pressure Hg lamp. The spectra are depicted at intervals of the photoirradiation for 10 min. The irradiation with each bright line was continued for 30 min in the order of 365 (dotted lines), 436 (solid lines), and 546 (broken lines) nm, respectively.

Azo-bridged ferrocene oligomers also show a marked dependence on the redox potentials and IT-band characteristics of the solvent, as is usual for the class II mixed valence complexes [52,53]. A detailed analysis of the solvent effect on ν_{max} of the IT band of the azo-bridged ferrocene oligomers $\mathbf{7}^+$, $\mathbf{9}^+$, and $\mathbf{9}^{2+}$ indicates that the ν_{max} shift is dependent not only on the parameter in the Marcus–Hush theory ($1/D_{op} - 1/D_s$), where D_{op} and D_s are the solvent's optical and static dielectric constants, respectively, but also on the nature of the solvent as a donor or acceptor [46].

In addition to the strong π–π* transition of the azo group at 318 nm, strong d–π* transition (MLCT) bands from an Fe(II) d-orbital to a π*-orbital of Cp–N=N–Cp appear in the neutral *trans*-form of the azo-bridged ferrocene oligomers. The absorption of the MLCT band at 534 nm diminishes, and a new band appears and increases at 672 nm with the oxidation to $\mathbf{7}^+$. The new band can be identified as a ligand-to-metal charge transfer (LMCT) band associated with an electron transfer from the π orbital of the azo group to a Fe(III) d orbital. Similar LMCT bands appear in the mixed valence state of trimers **8** and **9**. A more donating solvent affords the higher IT and LMCT energies of **7**–**9** in the mixed-valence states, indicating a hole-transfer mechanism [54].

Photo-irradiation of **7** in the *trans*-form, *trans*-**7**, in acetonitrile exposed to UV (365 nm) light from a super high pressure Hg lamp [47], causes a decrease in intensity of the π–π* band and an increase in intensity of a new band at 368 nm, showing isosbestic points, as shown in Fig. 5. This spectral change indicates the occurrence of *trans*-to-*cis* isomerization, and the new band is assigned to the n–π* transition of a photogenerated *cis*-form of **7**, *cis*-**7**. The intensity of this band is highly intense compared with that of azobenzene, suggesting that the n–π* transition in *cis*-**7** is allowed largely, due to more significant steric distortion around the azo group, than it is in *cis*-azobenzene. Photoisomerization of *trans*-**7** is accelerated in polar solvents such as acetonitrile, benzonitrile, and DMSO, and greatly suppressed in less polar solvents such as toluene [47,55].

The photoisomerization of *trans*-**7** also proceeds through MLCT with a green (546 nm) light (Fig. 5). This is a rare example of isomerization using a low energy band, different from the π–π* transition band. The $\Phi_{t\to c}$ values at 365 and 546 nm light irradiation are 0.002 and 0.03, respectively [47].

The thermal and photoisomerization of *cis*-**7** to *trans*-**7** is fairly slow in the above polar solvents even at elevated temperatures, implying that the *cis*-form is greatly stabilized in the polar media [56].

In the cyclic voltammogram of *trans*-**7** in Bu_4NClO_4-benzonitrile after UV light-irradiation, an additional reversible oxidation wave originating from *cis*-**7** appears at $E^{\circ\prime} = -0.18$ V versus Fc^+/Fc, as shown in Fig. 3b. That there is no distinct separation of the two $1e^-$ (i.e. apparently one-step $2e^-$) waves indicates that the mixed-valence state is thermodynamically less stable, due to the fact that the internuclear electronic interaction between the two iron centers, Fe(II) and Fe(III), is significantly weak through the π-conjugated linker of Cp–N=N–Cp in *cis*-**7** [47]. The semiempirical PM3 calculation of *cis*-**7** shows a large deviation of Cp rings from the plane. The loss in planarity is deduced to be a dominant factor in the weakness of the internuclear electronic interaction in *cis*-**7**, and in the electrochemical independence of the two iron centers.

3. Intramolecular electron transfer in ferrocene–quinone-conjugated compounds

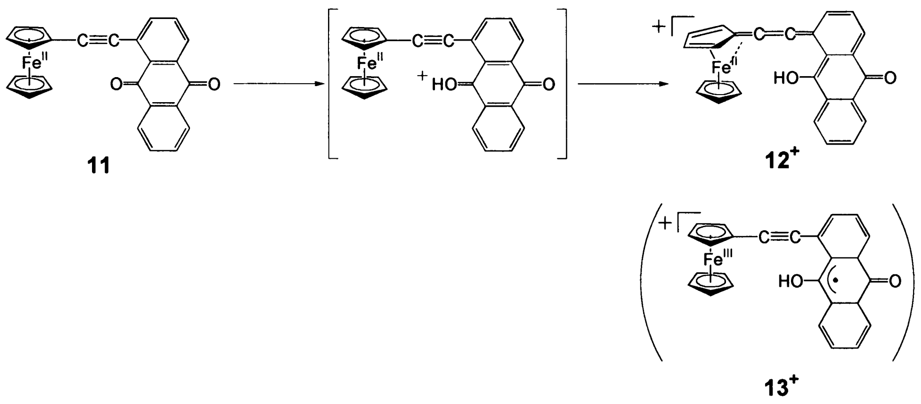
One category of conjugated ferrocene systems is constructed by combining ferrocene with the electron-accepting molecular units. Because the ferrocenyl moiety works as a good donor, these donor–acceptor-conjugated compounds have attracted much attention for their fluctuating electronic structures, which are sensitive to outer fields, and exhibit a novel behavior resulting from their second-order non-linear optical (NLO) properties [57,58] and facile intramolecular electron transfer, which brings about drastic changes in their structure and physical properties. Quinonoid compounds are one of the most versatile electron-accepting and proton-responsive organic molecules [59]. They are employed in covalently and non-covalently linked donor–acceptor systems of particular interest in the study of proton-coupled electron transfer [60–62] and photo-induced electron transfer [63–66]. Thus, the quinonoid compound linked to ferrocene by a π-conjugated spacer provides insight into the proton-coupled intramolecular electron transfer, because the redox potentials of the two molecules are similar and the redox potential of the quinonoid molecule can be readily controlled by an external perturbation such as protonation and solvation [67,68]. In this section, two types of ferrocene–quinone-conjugated systems are described. The complexes exhibit novel structural changes induced by the proton-coupled intramolecular reactions.

3.1. Ethynylene-bridged anthraquinone–ferrocene complexes—protonation-induced structural change and intramolecular electron transfer

A ferrocene–quinone-conjugated compound, **11**, undergoes a drastic structural rearrangement into the fulvene–cumulene structure by the proton-coupled intramolecular electron transfer from the ferrocene to the anthraquinone moiety [69]. The X-ray crystallography of **11** shows that the cyclopentadienyl rings of the ferrocenyl moiety are perpendicular to the plane of the anthraquinone moiety, and the UV–vis absorption spectrum in benzonitrile exhibits a specific absorption band at 510 nm, which is attributable to the MLCT transition from the Fe(II) to the ethynyl-anthraquinone moiety.

The color of the solution of **11** changes immediately from red to deep reddish-pink after the addition of a stoichiometric amount of CF_3SO_3H. This corresponds to the spectral change in which the MLCT band increases in intensity, and a new broad band, with the half-width $\Delta\nu_{1/2} = 5.2 \times 10^3$ cm^{-1}, appears in the near-IR regions ($\lambda_{max} = 939$ nm). The protonated complex of **11** is a diamagnetic complex with a unique structure involving a cumulene moiety, **12**·CF_3SO_3.

Notable features in the ^{1}H-NMR spectrum of **12**·CF_3SO_3 in CD_3CN include a new singlet due to the hydroxyl group appearing at δ 8.23 ppm, and the two double-doublets, one at 4.67 and the other at 4.33 ppm, due to the cyclopentadienyl (Cp) ring connecting the ethynyl group of **11**, shift to the lower field by 1 ppm in comparison with **11**, which shifts in accordance with the conversion into the fulvene structure. 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 positions (171.1 and 167.8 ppm). These chemical shift values of **12**·CF_3SO_3



Scheme 1.

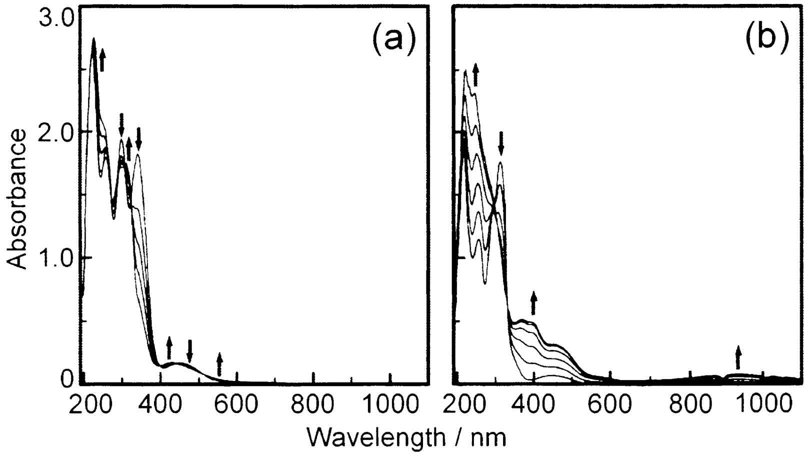
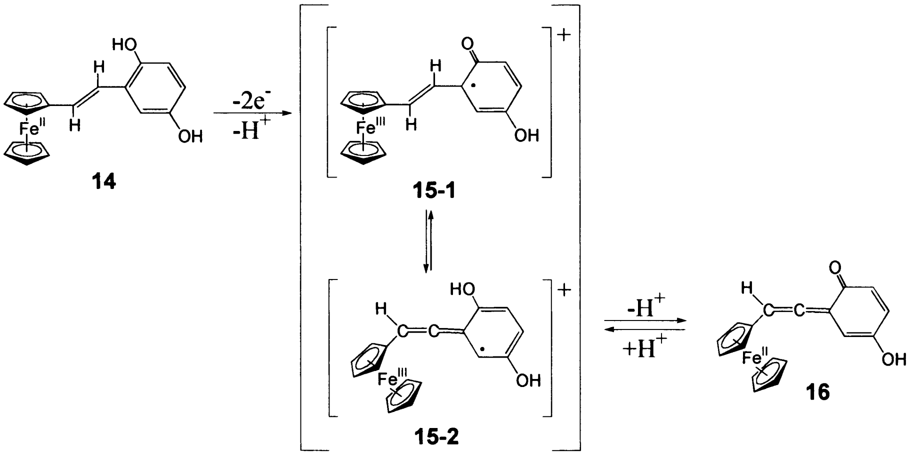


Fig. 6. (a) UV–vis–near-IR absorption spectral change of **14** (1.2 mM) in methanol upon stepwise addition of 0–2.0 equiv. of 1,1′-dichloroferrocenium hexafluorophosphate under a nitrogen atmosphere. Light path length is 1 mm. (b) UV–vis–near-IR absorption spectral change of **16** (1.2 mM) in acetonitrile upon stepwise addition of 0-100 equivalents of CF_3SO_3H under a nitrogen atmosphere. Light path length is 1 mm.

are quite similar to those of $[Fe(C_5H_5)(fulvene)]^+$[70–73], the molecular structure of which, with a marked bent of exocyclic C=C bond, indicates that the fulvene unit of $[Fe(C_5H_5)(fulvene)]^+$ is characterized by both η^4- and η^6-coordination [74]. This implies a significantcontribution of the $18e^-$ form rather than the $16e^-$ form. The IR spectrum of **12** · CF_3SO_3 shows the disap-pearance of the ν(C≡C) band of **11**, and the molecular ion peak of **12**$^+$ (m/z 417) detected in the ESI-MS indicates the addition of one hydrogen atom to the composition of **11** (m/z 416).

The reaction mechanism to form **12**$^+$ can be proposed as given in Scheme 1, in which protonation to one of the carbonyl oxygen atoms of the anthraquinone moiety occurs to produce a transient species of **12**$^+$, 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 the oxidation of the iron center of Fe(II) [57,75–77]. The increase in intensity of the MLCT band ($\lambda_{max} = 511$ nm) is due to the significant change of the π-conjugated system. The band at $\lambda_{max} = 939$ nm of **12**$^+$ might be ascribed to the valence tautomerization into **12**$^+$, or into a spin-separated form, **13**$^+$ (see Scheme 1), given that such a broad low-energy band has been recognized in other valence tautomerization complexes [78,79]. This consideration is supported by the fact that the solvent effect on λ_{max} is large; $\lambda_{max} = 1051$ nm in dichloromethane, which is less polar than benzonitrile.

The deprotonated form, **11**, shows reversible two-step $1e^-$ reduction at $E^{\circ\prime} = -1.26$ and -1.71 V versus Fc^+/Fc derived from the anthraquinone moiety, and reversible $1e^-$ oxidation at $E^{\circ\prime} = 0.22$ V due to the ferrocenyl moiety in Bu_4NClO_4–CH_2Cl_2. The first reduction potential shifts dramatically in the positive direction to $E^{\circ\prime} = -0.06$ V, and the oxidation potential shifts moderately in the positive direction to $E^{\circ\prime} = 0.33$ V in the protonation product, **12**$^+$, whereas the second reduction potential has not changed much. These results correspond to the structural changes in both the ferrocenyl and anthraquinone moieties by protonation.



Scheme 2.

3.2. *A vinylene-bridged ferrocene–hydroquinone complex—proton-coupled redox behavior with intramolecular electron transfer*

Proton-coupled intramolecular electron transfer has also been investigated for another quinonoid compound, **14**, linked to the ferrocene moiety by a π-conjugated spacer [80]. The compound **14** was synthesized by the Wittig coupling with ferrocenylmethyltriphenylphosphonium bromide and 2,5-ditosylbenzaldehyde [81], followed by the deprotection of the tosyl group. Chemical oxidation of **14** by $[Fe(\eta^5\text{-}C_5H_4Cl)_2]PF_6$ in methanol shows a drastic decrease of the UV–vis absorption band at 342 nm, and an increase of the band at 312 nm, as shown in Fig. 6a, affording the $2e^-$-oxidized form, **16**, which consists of an unusual allene and a quinonoid structure, with the loss of two hydrogen atoms from **14**.

In the ^{1}H-NMR spectrum of **16** in acetone-d_6, two doublets at δ 6.88 and 7.02 ppm derived from the vinylene protons of **14** disappear and a new singlet appears at 6.67 ppm. One of the two singlets at 7.60 and 7.81 ppm, due to non-equivalent hydroxyl protons of **14**, is not detected in **16**, and the remaining singlet at 8.00 ppm immediately disappears by H/D exchange on addition of D_2O. Owing to one of the two vinylene carbons of **14**, a new ^{13}C-NMR signal as a quaternary carbon appears in a lower field position at 131.6 ppm with the disappearance of the signal. The ^{13}C-NMR spectrum of **16** also indicates that the ferrocenyl structure is maintained without the oxidation-induced significant change into a fulvene-like structure [69,82]. The IR spectrum of **16** exhibits weak bands around 1900 cm^{-1} that are ascribable to the C–C stretching of the allene structure. The compound **16** is considered a structural isomer of both 2-(2-ferrocenylvinyl)-*p*-benzoquinone and 2-(ferrocenylethynyl)hydroquinone. It is of substantial interest that the oxidation of **14** favors the release of two hydrogen atoms—one from the vinylene and the other from the hydroxyl group—to disintegrate the ordinarily stable aromatic structure of **14**.

A formation mechanism of **16** proposed is shown in Scheme 2. The oxidation of **1** initially occurs at the ferrocenyl site to form a ferrocenium state of Fe(III), based on the fact that the reversible redox wave due to the ferrocenyl site is observed at the potential $E^{\circ\prime} = -0.11$ V versus Fc^+/Fc more positive than the potentials of irreversible oxidation waves due to the hydroquinone site ($E_{pa} = 0.39$ and 0.79 V) in acetonitrile, and the redox potential of the oxidizing agent $[Fe(C_5H_4Cl)_2]PF_6$ (0.23 V vs. Fc^+/Fc) is located between the potentials of the ferrocenyl and the hydroquinone sites [83]. The strong electron-withdrawing effect of the ferrocenium moiety causes the immediate elimination of a proton. The proton elimination from the hydroquinone moiety and the vinylene moiety followed by further 1-electron oxidation resulted in formation of the semiquinone radical intermediates **15-1** and **15-2**, respectively. The structural change between **15-1** and **15-2** occurs likely through the proton exchange between the carbonyl oxygen and the allene carbon, which are located nearby. A further proton-elimination reaction from the vinylene carbon of **15-1** or from the hydroxyl group of **15-2** affords the stable compound **16**, in which the iron center is reduced. It is considered that the deprotonation of **15-1** is less likely than that of **15-2**, and that the structural change between **15-1** and **15-2** plays an important role in the formation mechanism of **16** including the allene and quinonoid structure.

The UV–vis–near-IR absorption spectral change of **16** in acetonitrile, upon stepwise addition of CF_3SO_3H (0–100 equiv.), indicates an interesting proton response, as shown in Fig. 6b. The new intense bands appearing at 400 and 456 nm, the molar extinction coefficients, εs, of which are estimated at 4.0×10^3 and 2.5×10^3 M^{-1} cm^{-1}, respectively, are similar to those of the free semiquinone radical [59,84,85], and the weak shoulder band at 600 nm with $\varepsilon = 350$ M^{-1} cm^{-1} can be attributed to the $^2E_{2g} \rightarrow {}^2E_{1u}$ transition of the ferrocenium ion [86]. The EPR spectrum of the frozen solution of the product at 6.4 K exhibits a well-resolved signal ($g_{\parallel} = 3.97$, $g_{\perp} = 1.64$) attributable to a ferrocenium cation including the paramagnetic Fe(III) nuclei [47–50]. The appearance of the ferrocenium state of Fe(III) from diamagnetic **16** results in the generation of an odd number of electrons; i.e. generation of a semiquinone radical through an intramolecular electron transfer. The semiquinone radical is not detected in the EPR spectrum, probably due to the fluctuation of the electron spin states, which is supported by the significant broadening of the axial signal of the ferrocenium moiety. These facts indicate that the diamagnetic **16** can be converted to the paramagnetic semiquinone–ferrocenium compound **15-1** through the protonation of **16**. A broad absorption band is observed at 1000 nm in the near-IR spectrum of **15-1**. This band may be due to LMCT at the Fe(III) center—i.e. photo-induced valence tautomerization [78,79] between the Fe(III) center and the semiquinone—given that radical complexes exhibit long-wavelength bands due to low-lying transitions originating from the singly occupied molecular orbitals (SOMO) [87].

The two protonation sites exist in **16** to form **15-1**. The protonation of the allene carbon leads to the direct formation of **15-1** via an intramolecular electron transfer from the ferrocenyl to the quinonoid site. The protonation of the carbonyl oxygen of the quinonoid site forms **15-2**, and requires the structural change into **15-1**; i.e. from the allene to the vinylene bonding. When 100 equiv. of CF_3SO_3H was added all at once, a transient UV–vis absorption spectrum was observed, which spectrum gradually changed to that of **15-1**. This implies a two-step transformation, and supports the idea that the transient species is produced by the protonation of the carbonyl oxygen. Interestingly, when **14** is oxidized by 2 equiv. of $[Fe(C_5H_4Cl)_2]PF_6$ in acetonitrile, the observed UV–vis–near-IR absorption spectrum at r.t. and the EPR spectrum at 6.9 K are quite similar to those of the protonated form of **16**. The addition of methanol into the acetonitrile solution of **15-1** causes the UV–vis–near-IR absorption spectrum to change into that of **16**. This means that methanol assists in the proton elimination from **15-1**, and supports the consideration that the intermediate **15-1** should be included in the formation process of **16** from **14** in methanol.

In summary, an unusual structural change of a vinylene-bridged ferrocene–hydroquinone compound, **14**, was observed to occur by the two-electron oxidation and the two-proton elimination in methanol. The oxidation product, **16**, which includes an allene and a quinonoid structure, exhibited a unique proton response, leading to an exchange of the magnetic properties.

4. Concluding remarks

In this article, recent studies on the fundamental properties of π-conjugated transition metal complex systems with photo- and proton-responding abilities have been overviewed. Intramolecular events caused by external stimuli in such complexes depend significantly on the combination of metal complex units and π-conjugated systems. It is important to understand the mechanism and dynamics of these systems in elucidating fundamental concepts regarding the development of molecular-based devices.

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