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Novel Photoisomerization of Azoferrocene with a Low-Energy MLCT Band and Significant Change of the Redox Behavior between the *cis*- and *trans*-Isomers

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Organic azo-compounds have been intensively investigated to clarify the mechanism of isomerization[1] and to understand their applications utilizing alteration of the chemical structure[2] in terms of photoswitching and photon-mode high-density information storage devices.[3] The molecular design of photochromic materials for practical use is highly dependent on the output energy of compact semiconductor lasers, and materials responding to lower-energy light have been sought even while the durable short-wavelength compact laser capable of emitting violet light (400 nm) was being developed.[4] The isomerization of azo-bridged d-transition metal complexes would lead to a change of the intrinsic properties (e.g., optical, redox, and magnetic properties) originating from the d-electrons, which is valuable for new functional molecular systems. However, to our knowledge, few reports have cited the isomerization of azo-bridged metal complexes,[5] although numerous publications on the isomerization and its mechanism of organic compounds have appeared.[1]

Azoferrocene **1**, is one of the simplest analogues of azobenzene with two redox-active metal complex units. Synthesis of **1** was initially reported by Nesmeyanov in 1961,[6] and its related higher oligomers were reported on recently by us,[7] but no report on the isomerization reactions is currently available. Here we present the first photoinduced isomerization of **1** through $\pi-\pi^*$ transition of the azo-group with a UV light (365 nm) and metal-to-ligand charge transfer (MLCT) transition with a green light (546 nm), respectively. The low-energy isomerization is a different mode from the isomerization of general organic azobenzenes using a high-energy UV light. We also report a significant change of the redox property between the *trans*- and *cis*-isomers.

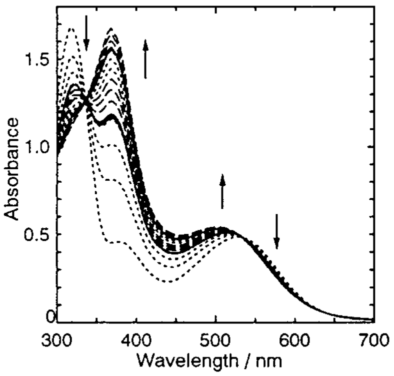
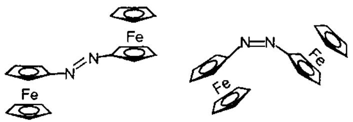


Figure 1. UV−vis absorption spectral change of *trans*-**1** (1.26×10^{-4} mol dm^{-3}) in acetonitrile under a nitrogen atmosphere upon photoirradiation with three bright lines (λ_{max} = 365, 436, and 546 nm) from a super high-pressure Hg lamp. The spectra are depicted at intervals of the photoirradiation 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.

Chart 1



trans-**1** *cis*-**1**

The UV−vis absorption spectrum of the *trans*-form of **1**, *trans*-**1**, in acetonitrile shows intense bands at 318 and 530 nm, ascribable to $\pi-\pi^*$ transition of the azo group and d$-\pi^*$ transition (MLCT) from an Fe(II) d-orbital to a π^*-orbital of the bridging ligand, Cp−N═N−Cp (Cp = η^5-cyclopentadienyl), respectively.[7,8] The $\pi-\pi^*$ band decreased and a new band at 368 nm increased in intensity, showing isosbestic points upon photoirradiation with a super high-pressure Hg lamp[9] under a nitrogen atmosphere, as shown in Figure 1. The new band is assigned to the n$-\pi^*$ transition of a photogenerated *cis*-form of **1**, *cis*-**1**. The intensity of this band is highly intense compared to that of azobenzene, suggesting that the n$-\pi^*$ transition in *cis*-**1** is allowed to a larger extent than it is in *cis*-azobenzene[1] due to more significant steric distortion around the azo group in the former (vide infra). The photoisomerization proceeded not only through the $\pi-\pi^*$ transition with a UV (365 nm) light but also through MLCT with a green (546 nm) light, though the isomerization was slow with a blue (436 nm) light. This is the first reported photoisomerization using the MLCT band at a much longer wavelength than that of the $\pi-\pi^*$ band of the azo group. The quantum yields of the photoisomerization reaction at 365 and 546 nm were estimated to be 0.002 and 0.03, respectively.[10]

In the ^{1}H NMR spectrum of *trans*-**1** in acetonitrile-d_3 after photoirradiation with the UV light or the green light, two triplets due to the Cp−N═N−Cp of *cis*-**1** appeared in upper-field positions shifted by 0.5 ppm in comparison with the triplets of *trans*-**1**.[11] The upper-field shift is caused by the shielding effect of the ring currents of the Cp rings, as they approach each other in *cis*-**1**.[12] The IR spectrum of the product after the UV light-irradiation of *trans*-**1** showed a new band at 1552 cm^{-1}, ascribable to the N═N stretch mode of *cis*-**1**.[13] The photoisomerization was

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[9] To isolate the three bright lines created by a super high-pressure Hg lamp (500 W) (Ushio Electronic Inc.), a Toshiba band-pass filter D36A was used for the UV line (365 nm), a band-pass filter L-39 and an interference filter KL-43 were used for the blue line (436 nm), and a band-pass filter Y-51 and an interference filter KL-55 were used for the green line (546 nm).

[10] The quantum yields of the photoisomerization reaction were estimated by employing potassium ferrioxalate, $K_3[Fe(C_2O_4)_3]\cdot 3H_2O$ as a chemical actinometer. See: (a) Parker, C. A. *Proc. R. Soc. London* **1953**, *A220*, 104. (b) Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London* **1956**, *A235*, 518. The value, $\Phi_{365} = 0.002$ is considerably smaller compared to $\Phi_{317} = 0.11$ of azobenzene in hexane. One possible rationale of the low Φ_{365} value is that 365 nm is at the edge of the $\pi-\pi^*$ absorption band of *trans*-azoferrocene: See ref 15.

[11] ^{1}H NMR (acetonitrile-d_3): *trans*-**1**; δ 4.84 (t, 4H, J = 2.0 Hz), 4.52 (t, 4H, 2.0), 4.25 (s, 10H). *cis*-**1**; d 4.44 (t, 4H, J = 2.0), 4.16 (s, 10H), 4.05 (t, 4H, 2.0).

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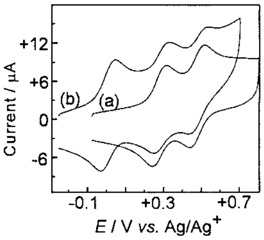

Figure 2. Cyclic voltammograms of *trans*-**1** (a), and after photoirradiation with UV light (365 nm) (b), in benzonitrile containing 0.1 mol dm^{-3} Bu_4NClO_4 at 0.1 V s^{-1} of scan rate under an argon atmosphere.

accelerated in polar solvents such as acetonitrile, benzonitrile, and DMSO, and greatly suppressed in less polar solvents such as toluene.[14] This behavior is similar to azobenzene, in which the quantum yield of *trans*-to-*cis* photoisomerization increases and that of *cis*-to-*trans* photoisomerization decreases with increasing the polarity of the solvent.[15] However, the thermal and photoisomerization of *cis*-**1** to *trans*-**1** was fairly slow in the above polar solvents even at elevated temperatures, implying that the *cis*-form is greatly stabilized in the polar media.[16] The nearly complete conversion to *cis*-**1** was achieved in the polar media by the prolonged UV light or the green light irradiation of *trans*-**1** at low concentrations ($\leq 10^{-4}$ M). On the other hand, dilution of the polar solution of *cis*-**1** with less polar solvents caused the prompt recovery of the $\pi-\pi^*$ band characteristic of *trans*-**1** in both thermal and photochemical (n$-\pi^*$ band irradiation) processes.

The cyclic voltammogram of *trans*-**1** in Bu_4NClO_4−benzonitrile exhibits reversible 1e$^-$ oxidation waves at $E^{0'} = 0.29$ and 0.50 V versus Ag/Ag$^+$ (Figure 2a),[7] indicating the formation of a thermodynamically stable mixed-valence cation.[7,17] An additional reversible oxidation wave appeared at $E^{0'} = 0.03$ V in the benzonitrile solution of *trans*-**1** after the UV light-irradiation (Figure 2b). This new reversible wave is originated from *cis*-**1**. 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*-**1**. This consideration is supported by the result that no IT band was detected when *cis*-**1** was oxidized with 1 equiv of 1,1′-dichloroferrocenium hexafluorophosphate ($[FcCl_2]PF_6$) with $E^{0'} = 0.50$ V versus Ag/Ag$^+$ in Bu_4NClO_4-benzonitrile, *trans*-**1** showed an intervalence transfer band (IT band) in the near-IR region in the same oxidation conditions.[7]

The mixed-valence cation of *trans*-**1** formed in benzonitrile by 1e$^-$ oxidation with 1 equiv of $[FcCl_2]PF_6$ exhibits an ESR 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 (Figure 3a).[18] A similar unusual ESR spectrum was reported on a solid sample of $[Fe_2(C_5H_4)_4]I_3$ at 77 K by Hendrickson et al., indicating exchange narrowing and some weak hyperfine structures due to coupling with the ring protons.[19] The narrow hyperfine signals in the mixed-valence cation of *trans*-**1** are possibly due to coupling with the ring protons and nitrogen atoms of the bridging Cp−N═N−Cp ligand. The *g*-value largely deviating from $g_e = 2.0023$ of a free electron indicates the presence of spin−orbit couplings with a large contribution of d-orbitals of the iron center and the delocalization of unpaired electronic charge over the bridging Cp−N═N−Cp ligand.[20] An ESR hyperfine-structure in relation to the similar narrow hyperfine signals was not detected in benzonitrile solution of *cis*-**1** oxidized by 1 equiv of $[FcCl_2]PF_6$, and the observed signal was ascribed to ferrocenium cations ($g_{\parallel} = 2.99$, $g_{\perp} = 1.92$), as shown in Figure 3b. This suggests that the chemical oxidation of *cis*-**1** leads to the formation of the dioxidized form, *cis*-$\mathbf{1}^{2+}$, possessing negligible exchange interaction between two iron centers.[19]

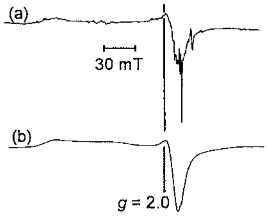

Figure 3. ESR spectra of *trans*-**1** oxidized with 1 equiv of 1,1′-dichloroferrocenium hexafluorophosphate at 7.6 K (a), and *cis*-**1** oxidized with 1 equiv of the oxidizing agent at 6.3 K (b), in benzonitrile under a nitrogen atmosphere.

The molecular structure of *trans*-**1** determined by X-ray crystallography shows that the Cp rings and the azo group locate nearly on a plane,[7] apposite to the effective internuclear electronic interaction that occurs through the π-conjugation. The same structure as the X-ray structure of *trans*-**1** was obtained by semiempirical PM3 minimization. The PM3 calculation of *cis*-**1** showed a large deviation of Cp rings from the plane. The loss of the planarity is deduced to be a dominant factor in the weakness of the internuclear electronic interaction in *cis*-**1** and in the electrochemical independence of the two iron centers. The 28 nm higher energy shift of the MLCT band of *cis*-**1** verifies that the low planarity raises the π^* orbital energy level, which is higher than that of *trans*-**1**.

In summary, we demonstrated novel photoisomerization of *trans*-**1** leading to stable formation of the *cis*-**1** in polar media through not only the $\pi-\pi^*$ transition but also through d$-\pi^*$ transition (MLCT) with green-light irradiation. We observed that the oxidation wave of *cis*-**1** was shifted to have 0.3 V more negative potential than the waves of *trans*-**1** and that the mixed-valence state of *cis*-**1** was thermodynamically less stable. It is concluded that the significant difference in redox properties between the *trans* and *cis* isomers of **1** is caused by the change of structure (π-planarity) of the Cp−N═N−Cp ligand. The low-energy photoisomerization mode using MLCT and the change of redox properties linked with the isomerization provide a new strategy for molecular design of optically and electronically functional materials.

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Supporting Information Available: Molecular structures of *trans*-**1** and *cis*-**1** calculated by the semiempirical PM3 minimization (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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