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Redox-Conjugated Reversible Isomerization of Ferrocenylazobenzene with a Single Green Light

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Received April 22, 2002

Change of the molecular properties including the molecular shape of photochromic molecules through photoisomerization has been intensively investigated for the application to photonic molecular devices.[1] Reversible trans−cis isomerization of azobenzenes, a representative family of photochromic molecules, is usually induced by alternating irradiation with ultraviolet (UV) and blue lights, which conduct trans-to-cis and cis-to-trans isomerization through azo $\pi-\pi^*$ excitation and azo n$-\pi^*$ excitation, respectively.[2] We have recently developed azoconjugated metal complexes as a new class of multifunctional photochromic molecules and have reported unique physical properties that are not seen in common organic azobenzenes.[3−5] The first is the trans-to-cis isomerization by a green light irradiation exciting a low-lying MLCT (metal-to-ligand charge transfer) band for azoferrocene, but the structural change of azoferrocene is photochemically irreversible.[3] The second is the reversible isomerization with a single UV light exciting the $\pi-\pi^*$ band combined with the redox state change of the metal center in the tris(bipyridine)cobalt complex-attached azobenzene but no response to visible lights for trans-to-cis isomerization.[4] The combination of these two unique properties, "reversible isomerization with a single visible light" (Scheme 1), is of great interest in the following aspects. The redox-conjugated reversible isomerization cycle using the single light can eliminate a double light source optical system emitting different wavelength lights, and the utilization of the green light instead of the UV light is advantageous in avoiding degradation of the aromatic framework of the photofunctional molecules.

A possible candidate for the isomerization using MLCT is the azo-ferrocene combined species. In this study, we therefore employed ferrocenylazobenzenes,[6] one of which, *meta*-ferrocenylazobenzene (*meta*-FcAB), achieves the reversible isomerization with a single green light by combination with the reversible redox reaction between Fe(II) and Fe(III) (Scheme 1).

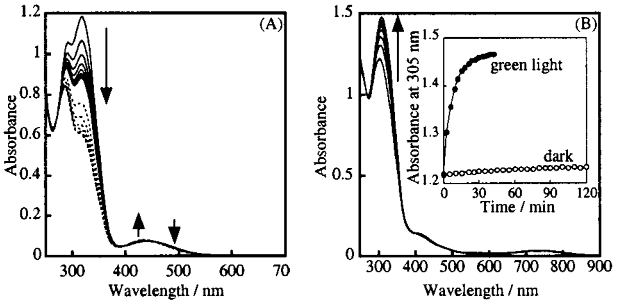
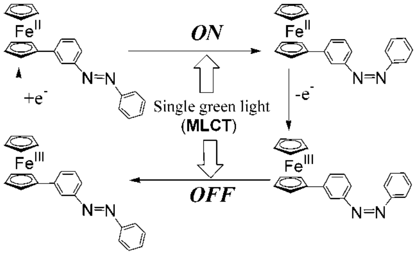


Figure 1. (A) UV−visible absorption spectral change of *trans-meta*-FcAB (5.52×10^{-5} mol dm^{-3}) in acetonitrile upon irradiation with a monochromatic light at 546 nm for 21 min (solid lines) and subsequent irradiation at 320 nm for 4 min (dotted lines). (B) UV−visible absorption spectral change of the following sample solution upon irradiation with a monochromatic light at 546 nm; (inset) time course change in absorbance at 305 nm of the sample solution upon irradiation with a monochromatic light at 546 nm (●) or in the dark (○). The sample solution was prepared by irradiation with a monochromatic light at 546 nm to *trans-meta*-FcAB in acetonitrile (5.62×10^{-5} mol dm^{-3}) to reach PSS and then oxidation with 1 equiv of [Fe(η^5-C_5H_4Cl)$_2$]PF_6.

Scheme 1. Redox-Conjugated Photoisomerization Pathway



trans-meta-Ferrocenylazobenzene shows an azo $\pi-\pi^*$ band at λ_{max} = 318 nm and a weak visible band at 444 nm. The azo $\pi-\pi^*$ band decreased in intensity through green (546 nm) and UV light (320 nm) irradiation,[7] whose wavelengths correspond to an edge of the visible band and the maximum in the azo $\pi-\pi^*$ band, respectively (Figure 1A). ^{1}H NMR signals of the aromatic ring protons of azobenzene moiety were significantly shifted to upper-field positions after the light irradiation (Figure S2a).[8] These spectroscopic behaviors are characteristic of the trans-to-cis isomerization. The cis molar ratio reached 35% in the photostationary state (PSS) upon the green light irradiation, and the PSS was changed into a more cis-rich state (61% cis molar ratio) upon the UV light irradiation (Figure 1A and Table S1).[9] The quantum yield for the trans-to-cis isomerization, $\Phi_{t\rightarrow c}$, of *meta*-FcAB was estimated to be 0.51 for the green light (546 nm),[10] which is much higher than that (0.021) for the UV light (320 nm) and exceeds that of azobenzene ($\Phi_{t\rightarrow c}$ = 0.12 (313 nm excitation)).[11] The thermal cis-to-trans isomerization of *meta*-FcAB was very slow, and the rate constant ($k = 1.3 \times 10^{-4}$ s^{-1} at 70 °C) was consistent with that of azobenzene ($k = 1.3 \times 10^{-4}$ s^{-1} at 70 °C).

Both the chemical oxidation with 1,1′-dichloroferrocenium hexafluorophosphate, [Fe(η^5-C_5H_4Cl)$_2$]PF_6, as a one-electron oxidizing agent[12] and the electrochemical oxidation of *trans-meta*-FcAB from Fe(II) to Fe(III) caused a shift of the $\pi-\pi^*$ band to higher energy from λ_{max} = 318 to 312 nm, and a weak LMCT (ligand-to-metal charge transfer) band appeared at 730 nm.[13] The reversibility of the electrochemical redox reaction between Fe(II) and Fe(III) was high, according to the completely reversible spectral change (Figure S3). Photoisomerization of the *trans*-Fe(III) state

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10.1021/ja026625+ CCC: $22.00

was much dependent on the irradiation wavelength. Almost no decrease in the absorbance of the $\pi-\pi^*$ band in the Fe(III) state was observed under the green light irradiation, unlike the UV light irradiation. The large difference in the cis molar ratios in PSS between the Fe(II) and Fe(III) states suggests the possibility of the reversible trans−cis conversion upon the single green light irradiation by changing the oxidation state of the iron center. The following experiments proved this possibility.

An acetonitrile solution of *trans-meta*-FcAB of Fe(II) was irradiated with the green light to reach PSS (35% cis molar ratio), and the resulting mixture of trans- and cis-forms was oxidized to the Fe(III) state immediately after an addition of a stoichiometric amount of $[Fe(\eta^5\text{-}C_5H_4Cl)_2]PF_6$. After the oxidation, the recovery of absorbance of the $\pi-\pi^*$ band was not pronounced in intensity over several hours in the dark at room temperature, and the thermal isomerization to the trans-form proceeded very slowly in the Fe(III) state ($k = 8.7 \times 10^{-4}$ s^{-1} at 70 °C) (Figure 1B, inset). The green light irradiation promoted the increase in the absorbance to reach the trans-rich PSS characteristic of the Fe(III) state, suggesting that almost all of the trans-form was photorecovered (Figure 1B). These results indicate that reversible trans−cis isomerization can be achieved by a combination of “on−off switching” of the MLCT character due to the redox change between Fe(II) and Fe(III) and single green-light irradiation. The LMCT band that appeared in the Fe(III) state is not associated with the isomerization.

It should be noted that the photoisomerization and thermal isomerization behavior of ferrocenylazobenzenes is strongly influenced by the substitution position of the ferrocenyl moiety on the benzene ring. *trans-para*-Ferrocenylazobenzene (*trans-para*-FcAB) exhibits an intense visible MLCT band (494 nm) and a largely red-shifted azo $\pi-\pi^*$ band ($\lambda_{max} = 352$ nm) as compared to azobenzene (317 nm) or *trans-meta*-FcAB (318 nm). The trans-to-cis isomerization proceeded with $\Phi_{t\rightarrow c} = 0.0033$ by irradiation with a UV light (350 nm) to reach a 41% cis molar ratio in PSS (Figures S2b and S4). However, the MLCT in *para*-FcAB is not effective for the trans-to-cis conversion (Table S1), whereas the cis-to-trans back reaction can be promoted even by an orange light at 600 nm, which corresponds to the edge of the MLCT band, instead of a blue light (∼450 nm). The thermodynamic stability of the cis-form was remarkably reduced by the oxidation, because the fast recovery of the $\pi-\pi^*$ band in intensity due to the transformation of the cis-form into the trans-form was observed immediately after the oxidation of the photogenerated trans−cis mixture at room temperature. The cis-to-trans thermal isomerization rate could be estimated to be 3.8×10^{-3} s^{-1} only at a low temperature (5 °C).

It is of great interest that the green light caused a much higher cis molar ratio in *meta*-FcAB than in *para*-FcAB and azobenzene. We therefore carried out time-dependent density functional theory (TD-DFT) calculations for *meta*- and *para*-FcABs in the trans-form, to investigate a singlet excited state in which the isomerization occurs.[14] The calculated excitation energies in the trans-forms were in reasonable agreement with the experimental values, and the observed trends in the experimental absorption spectra were correctly reproduced (Table S2). Noticeable features in the nature of the excited states of the *trans-meta*-FcAB are that the azo n−π^* strongly mixes with the MLCT configuration and that the initial orbital for the 3.02 eV MLCT state is delocalized over Fe and the Cp ring rather than localized on the iron (Figure S5a). The presence of the MLCT character is the reason that the molar extinction coefficient of the visible band ($\lambda_{max} = 444$ nm, $\epsilon = 1.86 \times 10^3$ mol^{-1} dm^3 cm^{-1}) is much larger than that of the n−π^* band of *trans*-azobenzene ($\lambda_{max} = 444$ nm, $\epsilon = 5.15 \times 10^2$ mol^{-1} dm^3 cm^{-1}). The origin of the visible band in *meta*-FcAB is different from that of *para*-FcAB, because the initial orbital for the 2.51 eV MLCT state of the latter is localized on the iron (Figure S5b). The green-light-induced trans-to-cis isomerization of *meta*-FcAB possibly occurs on the potential energy surface for the MLCT excited state. In fact, the almost complete absence of a response to the green light for the cis-formation in the Fe(III) state is caused by the disappearance of the MLCT character in the Fe(II) state by the oxidation to Fe(III).

Acknowledgment. This work was supported by Grants-in-Aid for scientific research (Nos. 10149102, 11167217, and 11309003) from the Ministry of Education, Science, Sports, and Culture, Japan, the Ogasawara Foundation for the Promotion of Science and Engineering, the Mitsubishi Chemical Corp. Fund, and the Tokyo Ohka Foundation.

Supporting Information Available: ^{1}H NMR spectra of *meta*- and *para*-FcAB after photoirradiation to reach PSS (Figure S2), UV−visible absorption spectral change of *meta*-FcAB under electrochemical oxidation (Figure S3), UV−vis absorption spectral change of *para*-FcAB upon photoirradiation (Figure S4), the molecular orbitals contributing to the MLCT of *trans-meta*-FcAB and *trans-para*-FcAB (Figure S5), the cis molar ratios in PSS (Table S1), and experimental and theoretical excitation energies by the TD-DFT calculation (Table S2) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Horie, K.; Ushiki, H. *Molecular Photonics*; Wiley-VCH (Kodansha): Tokyo, 2000. (b) Liu, Z. F.; Hashimoto, K.; Fujishima, A. *Nature* **1990**, *347*, 658−660. (c) Ikeda, T.; Tsutsumi, O. *Science* **1995**, *268*, 1873−1875. (d) Irie, M. *Chem. Rev.* **2000**, *100*, 1685−1716. (e) Ichimura, K.; Oh, S.-K.; Nakagawa, M. *Science* **2000**, *288*, 1624−1626.

(2) (a) Rau, H. In *Photochromism: Molecular and Systems*; Dürr, H.; B.-Laurent, H., Eds.; Elsevier: Amsterdam, 1990; pp 165−192. (b) Tamai, N.; Miyasaka, H. *Chem. Rev.* **2000**, *100*, 1875−1890.

(3) Kurihara, M.; Matsuda, T.; Hirooka, A.; Yutaka, T.; Nishihara, H. *J. Am. Chem. Soc.* **2000**, *122*, 12373−12374.

(4) Kume, S.; Kurihara, M.; Nishihara, H. *Chem. Commun.* **2001**, 1656−1657.

(5) (a) Yutaka, T.; Mori, I.; Kurihara, M.; Mizutani, J.; Kubo, K.; Furusho, S.; Matsumura, K.; Tamai, N.; Nishihara, H. *Inorg. Chem.* **2001**, *40*, 4986−4995. (b) Nihei, M.; Kurihara, M.; Mizutani, J.; Nishihara, H. *Chem. Lett.* **2001**, 852−853

(6) (a) Coe, B. J.; Jones, C. J.; McCleverty, J. A.; Wieghardt, K.; Stötzel, S. *J. Chem. Soc., Dalton Trans.* **1992**, 719−721. (b) Herr, B. R.; Mirkin, C. A. *J. Am. Chem. Soc.* **1994**, *116*, 1157−1158. (c) Kersten, H.; Boldt, P. *J. Prakt. Chem.* **1996**, *338*, 129−139. (d) Campo, J. A.; Cano, M.; Heras, J. V.; L.-Garabito, C.; Pinilla, E.; Torres, R.; Rojo, G.; A.-López, F. *J. Mater. Chem.* **1999**, *9*, 899−907.

(7) The photoirradiation was performed with a 500 W super-high-pressure Hg lamp (Ushio Electronic Inc.), and the light wavelength was selected with a monochromator (Jasco CT-10T).

(8) R.-Bohner, S.; Kruger, M.; Oesterhelt, D.; Moroder, L.; Nagele, T.; Wachtveitl, J. *J. Photochem. Photobiol., A* **1997**, *105*, 235−248.

(9) The cis molar ratio in PSS was estimated from an integral ratio of the ^{1}H NMR signals of cyclopentadienyl ring protons.

(10) Gade, R.; Porada, T. *J. Photochem. Photobiol., A* **1997**, *107*, 27−34.

(11) Rau, H. *J. Photochem.* **1984**, *26*, 221−225.

(12) Kurosawa, M.; Nankawa, T.; Matsuda, T.; Kubo, K.; Kurihara, M.; Nishihara, H. *Inorg. Chem.* **1999**, *38*, 5113−5123.

(13) The oxidation of *meta*- and *para*-FcAB in the trans-form from Fe(II) to Fe(III) occurs at the same potential ($E^{0'} = 0.04$ V versus ferrocenium/ferrocene). The oxidation potential of the ferrocenyl moiety was not changed by photoirradiation leading to trans-to-cis isomerization of the azo group.

(14) In the DFT calculations, the three-parametrized Becke−Lee−Yang−Parr (B3LYP) hybrid exchange-correlation functional was employed. For comparisons with the UV−visible absorption spectra observed in acetonitrile, the solvent effect was taken into account by means of the polarized continuum model (PCM). The core electrons of Fe and the first-row elements were replaced with effective core potentials (ECPs), and their valence orbitals were described with the double-ζ basis set prepared for the ECPs. For hydrogen, the 4-31G basis set was used. The geometries of these compounds were optimized with the DFT(B3LYP) method without the solvent effect. The present calculations were implemented with the Gaussian 98 (revision A.7) program.

JA026625+