

Redox-controlled Photoisomerization of Ferrocene-attached Spiropyran

Sayoko NAGASHIMA, Masaki MURATA, Hiroshi

NISHIHARA

Department of Chemistry, School of Science, The University of Tokyo

7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

Photochromic molecules can switch their structures reversibly between two forms by excitation with the appropriate wavelength of light. Of particular utility is the class of photochromic molecules known as spiropyrans. When they are dissolved in nonpolar solvents in the dark, or when exposed to visible light, spiropyrans are colorless. Under these conditions spiropyran exists in a nonpolar or "closed" spiro form that absorbs light predominantly in the ultraviolet region. When exposed to UV light, the spiropyran undergoes an isomerization wherein the spiro linkage is cleaved, resulting in a highly polar "open" merocyanine form that is colored. As shown in Scheme 1, the structure of this open form is a resonance hybrid between a zwitterion and a neutral quinonoid.

The coupling of changes in the electronic state accompanying photoisomerization with other physical phenomena would allow the development of multifunctional materials. The metal coordination of photochromes provides a novel and potentially powerful approach to the development of systems in which changes in the electronic state of the photochrome can induce changes in redox, magnetic, or optical properties of the metal center.

A new molecule exhibiting multi-mode structural conversion was synthesized by combining a photochromic molecule, spiropyran with ferrocene, Fc-SP, of which donor ability can be controlled by the redox reaction. UV irradiation of Fc-SP in dichloromethane results in the reversible, photochemically induced conversion from the colorless spiropyran form ($\lambda_{\max}$ 345 nm) to the intensely colored photomerocyanine form ($\lambda_{\max}$ 600 nm), Fc-MC, with first-order kinetics. Plots of the wavenumber (ν , cm^{-1}) versus the Reichardt's empirical solvent polarity parameter, $E_T(30)$, for merocyanine, MC, and ferrocene-attached merocyanine, Fc-MC (Figure 1) examined exhibit negative solvatochromism; i. e., $\lambda_{\max}$ decreases with an increase in $E_T(30)$. A red shift of the $\lambda_{\max}$ value of the Fc-MC compared with that of MC results from the ferrocene moiety as donor with a resonance stabilization effect (Scheme 1).

Dichloromethane solution of Fc-SP was irradiated with the 365-nm light to reach the photostationary state (Figure 2(a)), and the resulting mixture of SP and MC form was oxidized with a stoichiometric amount of 1,1'-dichloroferrocenium hexafluorophosphate, $[\text{Fc}^+\text{Cl}_2]\text{PF}_6$ ($E^0 = 0.19$ V versus Fc^+/Fc) (Figure 2(b)). When the oxidized solution was exposed to the 365-nm light again (Figure 2(c)), the photoisomerization promptly occurred to reach the MC rich photostationary state, in which the complex is characteristic of the Fe(III) state. The Fe(III) complex in the photostationary state upon irradiation with the 365-nm light was reduced with a stoichiometric amount of decamethylferrocene, $\text{Fc}(\text{CH}_3)_5$ ($E^0 = -0.59$ V versus Fc^+/Fc) (Figure 2(d)). Then, the Fc form complex, which is characteristic of the Fe(II) state, reverted thermally to the SP form. These phenomena reveal that a reversible isomerization can be achieved by a

combination of the reversible redox change and light irradiation (Scheme 2). We will give details of the photochromism of Fc-SP changing its redox state.

This work was supported by a grant from The 21st Century COE Program for Frontiers in Fundamental Chemistry.

Scheme 1

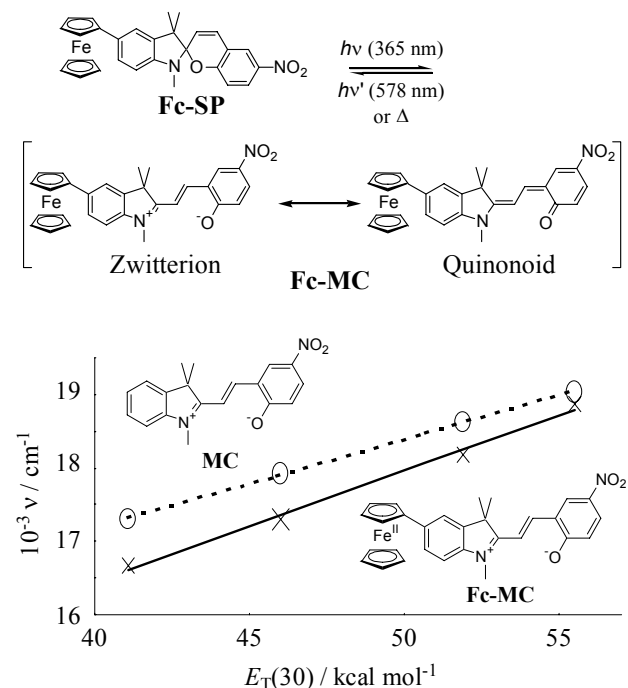


Figure 1. Plots depicting the similar solvatochromic behavior of MC (o) and Fc-MC (x).

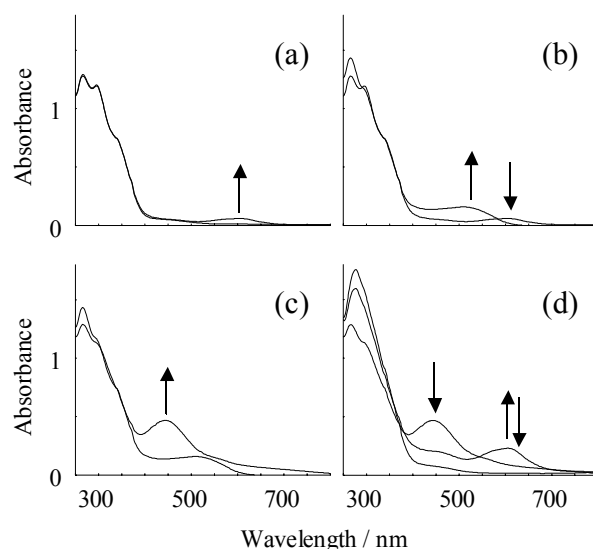


Figure 2. UV-vis spectral changes of Fc-SP in CH_2Cl_2 upon irradiation at 365 nm (a), after (a) upon addition of 1.0 eq. of $[\text{Fc}^+\text{Cl}_2]\text{PF}_6$ (b), after (b) upon irradiation at 365 nm (c), and after (c) upon addition of 1.0 eq. of $\text{Fc}(\text{CH}_3)_5$ (d).

Scheme 2

