Photochromism

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A Ferrocenylspiropyran That Functions as a Molecular Photomemory with Controllable Depth**

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Spiropyran (SP) derivatives,[1] such as 1′,3′,3′-trimethyl-6-nitrospiro[2*H*-1-benzopyran-2,2′-indoline], belong to a class of organic photochromic compounds that have been intensively investigated and have potential applications as molecular electronic devices, optical switches, and memories.[2] These dyes are converted into the colored merocyanine (MC) form upon irradiation with UV light, but revert to the colorless SP form when left in the dark or upon irradiation with visible light. The open MC form has a larger dipole moment than the closed SP form, and thus the stability of the MC form strongly depends on the electronic effects of the substituent(s) of the indolium and phenyl moieties, the solvent polarity, and the metal complexation.[3] If the donor–acceptor nature of the substituent can be controlled by a redox reaction, we can switch the balance of thermody-

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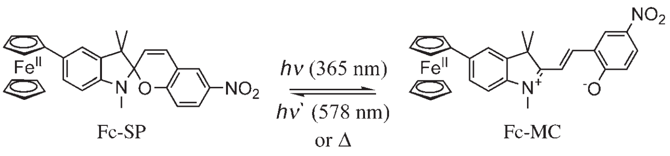
namic stability, and thus the memory depth, between the SP and MC forms. Herein, we report a new system in which the stability of the MC form can be completely and reversibly switched by a combination of SP/MC photoisomerization and a ferrocene/ferrocenium redox cycle.[4]

A 5-ferrocenylspiropyran (Fc-SP) was synthesized by condensation of 2-hydroxy-5-nitrobenzaldehyde and 5-ferrocenyl-substituted Fischer's Base in methanol (see the Supporting Information). A reversible Fe^{III}/Fe^{II} redox wave is observed at −0.03 V versus ferrocenium/ferrocene (Fc^+/Fc) in dichloromethane in the cyclic voltammogram of Fc-SP (see the Supporting Information). The UV/Vis spectrum of Fc-SP in methanol shows a π–π* transition band at $\lambda_{max} = 345$ nm ($\varepsilon = 2.9\times10^4\ \mathrm{M}^{-1}\mathrm{cm}^{-1}$; see the Supporting Information). The electron donation of the ferrocene moiety results in a lower energy of the π–π* band of Fc-SP relative to unsubstituted spiropyrans.

Irradiation of a pale-yellow solution of Fc-SP in methanol with UV light ($\lambda = 365$ nm) gave a red-purple solution with an absorption maximum wavelength of 530 nm (see the Supporting Information), which can be ascribed to the generation of the MC form (Fc-MC; Scheme 1). The molar ratio of the MC form was estimated from the photo-generated ^{1}H NMR spectral changes in [D$_4$]MeOH (see the Supporting Information) to be 75 % in the photostationary state (PSS).



Scheme 1. Photoisomerization of Fc-SP.

The λ_{max} value, yield in the PSS, and the thermodynamic stability of the MC form depend on the solvent polarity. Fc-MC exhibits negative solvatochromism, that is, its λ_{max} decreases with an increase in the Reichard empirical solvent polarity parameter, $E_T(30)$[5] (see the Supporting Information). The λ_{max} value of Fc-MC is red-shifted relative to that of the unsubstituted MC (see the Supporting Information) as a result of the ferrocene moiety acting as a donor with a resonance stabilization effect. Also, the yield of the MC form in the PSS during irradiation with UV light is lower, and thermal isomerization from the MC to the SP form is faster, in solvents with lower polarity. In dichloromethane, for example, Fc-MC ($\lambda_{max} = 578$ nm) was formed with a yield of 56 % in the PSS, which is lower than the 75 % obtained in methanol, although it isomerizes to Fc-SP within a few hours at 20 °C, much faster than in methanol.

Next, we attempted to combine the redox and photochemical changes of Fc-SP in dichloromethane. When a dichloromethane solution of Fc-SP was oxidized to Fc^+-SP with a stoichiometric amount of 1,1′-dichloroferrocenium hexafluorophosphate ($E^{0'} = 0.19$ V versus Fc^+/Fc),[6] new absorption peaks appeared at 515 and 1250 nm (compare Figure 1 a and b and left inset). When this oxidized solution was irradiated with 365-nm light for a length of time sufficient to reach the PSS, the 1250-nm band vanished and a new band appeared at 445 nm (Figure 1 c), that is, a marked blue shift occurs upon photoirradiation. The 445-nm band was ascribed to the isomerization from the SP to the MC form, based on the finding that subsequent reduction gave Fc-MC (see below). It should be noted that the complete disappearance of the 1250-nm band signifies that only the MC form is present in the PSS of the oxidized state, whereas the MC molar ratio in the PSS of the Fc state reaches only 56 % (Figure 2 A).

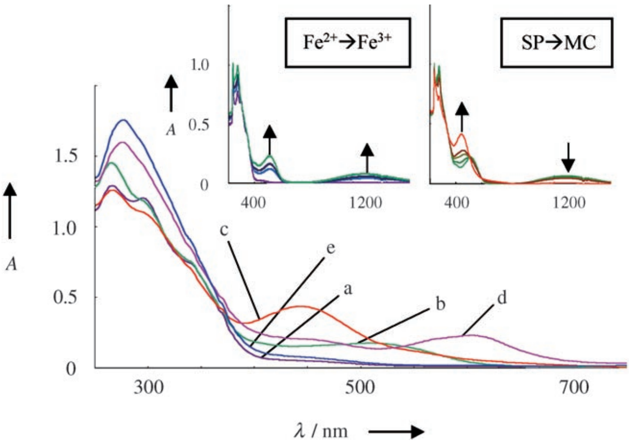


Figure 1. Sequential spectral changes of Fc-SP in dichloromethane: a) Initial state (Fc-SP), b) after oxidation with 1.0 equivalent of $[Fe(\eta^5\text{-}C_5H_4Cl)_2]PF_6$, c) after irradiation with 365-nm light, d) after reduction with 1.0 equivalent of $[Fe(\eta^5\text{-}C_5Me_5)_2]$, and e) after standing at 20 °C. Inset: UV/Vis–near-IR spectral changes from (a) to (b) (left) and from (b) to (c) (right).

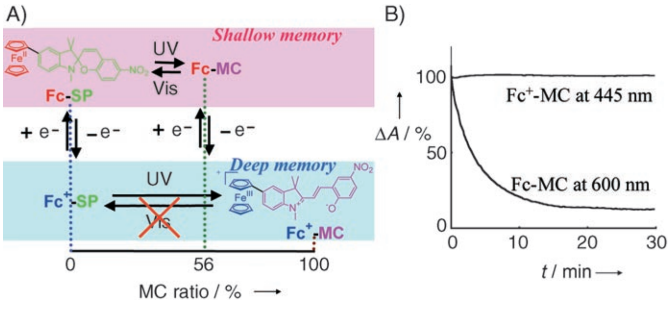


Figure 2. A) Photo- and redox reactions of Fc-SP/Fc-MC. B) The decrease in absorbance at λ_{max} of the MC forms at 20 °C in CH_2Cl_2 before and after oxidation with $[Fe(\eta^5\text{-}C_5H_4Cl)_2]PF_6$ under irradiation with 365-nm light to reach the PSS.

The ratio of the MC form remained constant after oxidation; irradiation of Fc^+-MC with UV or visible light could not cause reversion to the SP form (Figure 2 B), and thermal isomerization to the SP form hardly proceeded. In other words, Fc^+-MC is very stable towards light and heat. Previous methods to stabilize the MC state are mainly based on the Coulomb interaction of the phenolate anion with nearby cationic species.[3] The reason for the unique MC stabilization by Fc^+ in the present study has not been fully clarified, but the large blue shift of λ_{max} for Fc^+-MC relative to

Fc-MC suggests a strong electronic effect of Fc^+ as a result of π conjugation.

Chemical reduction of Fc^+-MC with a stoichiometric amount of decamethylferrocene ($E^{0\prime} = -0.59$ V versus Fc^+/Fc)[7] allowed us to reach the MC PSS, as confirmed by the appearance of the characteristic band of Fc-MC (Figure 1 d), and the MC form reverted thermally to the SP form (Figure 1 e). This reversible redox and photoisomerization cycle (Figure 2 A) indicates that the Fc state corresponds to a shallow (deletable) photomemory and the Fc^+ state to a deep (undeletable) photomemory.

The reversible redox and photoisomerization cycle was also studied in a polymer matrix. Poly(ethylene oxide) and polyvinylchloride (PVC) films containing Fc-SP show a coloring to purple ($\lambda_{max} = 545$ nm) and blue ($\lambda_{max} = 578$ nm), respectively, upon irradiation with UV light (365 nm; see Figure 3 A and the Supporting Information), thus indicating the formation of the MC form; this color change can be reversed thermally or by irradiation with 546-nm light. Oxidation and re-reduction of Fc-SP in a PVC film containing Bu_4NBF_4 as an electrolyte sandwiched by two ITO electrodes occurs reversibly when the voltage between the two ITO electrodes is controlled between 0 and 2 V.

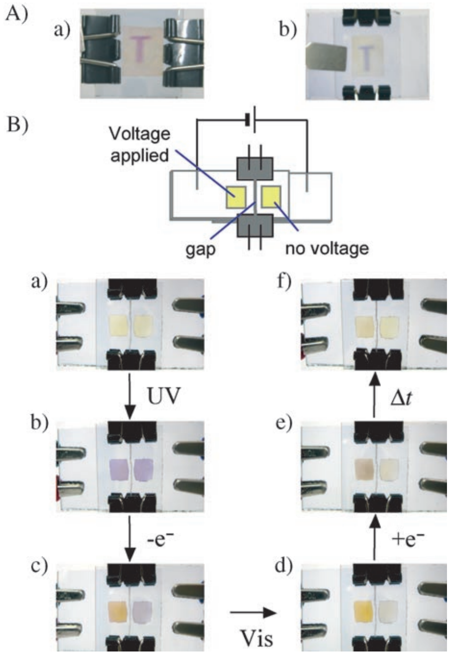


Figure 3. A) Optical changes of Fc-SP in a) poly(ethylene oxide) and b) PVC films with a photomask after irradiation at 365 nm. B) Optical changes of Fc-SP/PVC films upon irradiation at 365 nm (a–b), application of an electric field of 2 V (b–c), irradiation at 546 nm (c– d), application of an electric field of 0 V (d– e), and in the absence of further treatment (e– f). On the right-hand side an identical film sample is shown that was not subjected to the redox process (that is, to which the potential was not applied).

Figure 3 B shows the results for two identical films to only one of which (the left one) an electric field was applied. Upon irradiation at 365 nm, both of the films become purple (a to b). When charged with electricity at the ITO electrode cell, only the film on the left-hand side turns from purple to orange as a result of the oxidation of Fc-SP (c). When the films are irradiated with visible light, the color goes back to yellow (d). When the current is switched off, the re-reduction of Fc-SP takes place in the left-hand film, as seen by a change in color from yellow to brown (e). The brown color is due to a mixture of the oxidized and re-reduced MC forms in the film. When left without further treatment, the film reverts to yellow (f). These color changes demonstrate the change in readiness of the SP–MC conversion as a result of the redox change of the ferrocene site.

In conclusion, a photochromic molecule with an ability to switch between two isomeric structures by a redox change has been created. This phenomenon has been demonstrated both in solution and in solid polymer electrolytes. The system is expected to provide a new approach for the realization of molecule-based devices, and should be important in the field of semiconductor computer technology based on "random-access memory" and "read-only memory", in which the control of memory depth is becoming increasingly important.

Experimental Section

Synthesis of **1** (prepared according to a report on the synthesis of 3-ferrocenylnitrobenzene): Ferrocene (6.69 g, 0.0361 mol) was added to sulfuric acid (specific gravity = 1.84, 40 mL). The resulting deep-blue ferrocenium solution was stirred at room temperature for 3 h. A solution of sodium nitrite (0.80 g, 0.0116 mol) in water (5 mL) at less than 0 °C was added dropwise to a solution of 5-amino-1,3,3-trimethyl-2-methyleneindoline (1.83 g, 0.0972 mol) in 1:1 water/hydrochloric acid (specific gravity 1.18, 10 mL) with stirring. The mixture was stirred at less than 0 °C for 3 h to ensure complete diazotization. Copper powder (2.0 g) was added to the ferrocenium solution as a catalyst, and the diazonium solution was then added dropwise with vigorous stirring. The nitrogen effervescence ceased after stirring for 4 h, and ascorbic acid (5.0 g) was added to reduce the starting ferrocenium to ferrocene. The product was extracted with dichloromethane. The combined organic extracts were dried with sodium sulfate, filtered through Celite, and the solvent was eliminated. The dark solid thus obtained was purified by column chromatography on alumina with an increasing proportion of ethyl acetate in *n*-hexane as the eluent. The first yellow-orange band was eluted with pure hexane and yielded unchanged ferrocene. The third yellow band, which eluted with ethyl acetate/hexane (50:50), was collected. The yellow component was evaporated to yield 97.9 mg (0.274 mmol, 2.81 %) of **1** as a brown solid. ^1H NMR (400 MHz, CD_2Cl_2, room temperature): $\delta = 1.37$ (s, 6 H), 3.03 (s, 3 H), 3.84 (s, 2 H), 4.03 (s, 5 H), 4.23 (t, $J = 2.0$ Hz, 2 H), 4.53 (t, $J = 2.0$ Hz, 2 H), 6.45 (d, $J = 8.0$ Hz, 1 H), 7.18 (d, $J = 1.6$ Hz, 1 H), 7.25 ppm (dd, $J = 8.0, 1.6$ Hz, 1 H); MALDI-TOF-MS: m/z 357 [M^+].

Synthesis of Fc-SP: Compound **1** (38.8 mg, 1.09 mmol) and 2-hydroxy-5-nitrobenzaldehyde (18.7 mg, 1.11 mmol) were stirred at room temperature in anhydrous methanol for 1.5 h. The resulting mixture was separated by column chromatography on alumina using ethyl acetate/hexane (1:5, v/v) as the eluent. The yellow band was collected and the solvent evaporated to yield 20.3 mg (0.400 mmol, 36.9 %) of Fc-SP as a greenish-yellow powder. Elemental analysis (%) calcd for $C_{29}H_{26}FeN_2O_3$: C 68.79, H 5.18, N 5.53; found C 68.54, H 5.31, N 5.31; ^1H NMR (400 MHz, CD_2Cl_2, room temperature): $\delta =$ 1.21 (s, 3 H), 1.32 (s, 3 H), 2.74 (s, 3 H), 4.05 (s, 5 H), 4.26 (t, $J = 1.9$ Hz, 2 H), 4.53 (t, $J = 1.9$ Hz, 2 H), 5.89 (d, $J = 10.4$ Hz, 1 H), 6.49 (d, $J = 8.0$ Hz, 1 H), 6.82 (d, $J = 10.0$ Hz, 1 H), 6.97 (d, $J = 10.4$ Hz, 1 H), 7.21 (d, $J = 1.7$ Hz, 1 H), 7.33 (dd, $J = 10.0, 1.7$ Hz, 1 H), 8.00 (dd, $J = 8.0$, 2.9 Hz, 1H), 8.02 ppm (d, $J = 2.9$ Hz, 1H); MALDI-TOF-MS: m/z 506 [M^+].

Polymer-electrolyte experiment: Photoirradiation was carried out with a USHIO high-pressure mercury lamp as the light source. The bright lines were selected with a monochromator (Jasco, CT-10) or with a glass filter (Toshiba). Two kinds of polymer were investigated. One polyelectrolyte (FB-011, DAISO Research Laboratories; thickness: 40 μm) consisted of the ternary copolymer of ethylene oxide (EO), 2-(2-methoxyethoxy)ethyl glycidyl ether (EM-2), and allyl glycidyl ether (AGE), with an EO/EM-2/AGE molar ratio of 82:12:1.8. Lithium bis(trifluoromethansulfonyl)imide (LiTFSI) was added as a supporting salt ([Li]/[O] = 0.06:1). The other polymer (Toughnyl, Japan Wavelock Co.; thickness: 100 μm) contained PVC. A solution of $n\mathrm{Bu_4NBF_4}$ was introduced into the PVC film as an electrolyte and the solvents evaporated. The Fc-SP solution was swollen in these polymer films and the solvent was removed. The dried polymer films were pitched with two ITO-coated glass electrodes. The voltage was controlled with a Hokuto Denko HSV-100 automatic polarization system.

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