Multicolor Photochromism

# Photochromic Reaction of a Fused Dithienylethene: Multicolor Photochromism**

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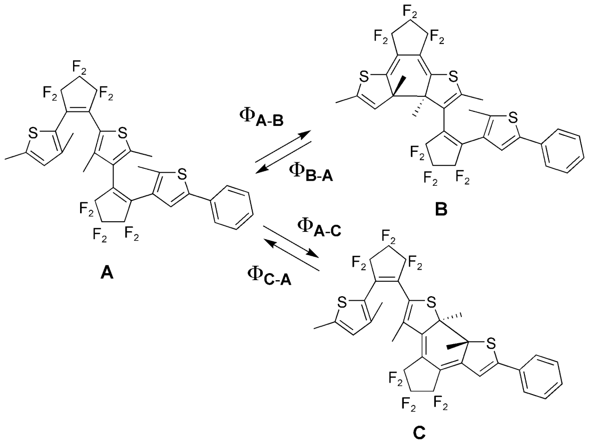
Photochromic compounds, which change their color upon irradiation with light of the appropriate wavelength, have attracted increasing attention because of the potential application to optical memory media and switching devices.[1] Diarylethenes with heterocyclic aryl groups are the most promising candidates for practical applications[2] because of their high fatigue resistance and thermal stability.[3]

Multicolor photochromism is useful for optoelectronic devices such as multifrequency optical memories and displays. Multicolor systems can be obtained by mixing photochromic compounds with different colors in solutions,[4a] in polymer matrices,[4b] and in single crystals.[4c] Herein, we took the approach to incorporate two photochromic units in one-molecule.[5,6] Some advantages of a one-molecule system over mixed systems include the high resolution available arising from local homogeneity, long-term storage stability, and applications to multi-frequency single-molecular memories.[7]

In an attempt to obtain a molecule that shows a distinct multicolor change, we have designed the nonsymmetric molecule, **A** (Scheme 1). Compound **A** has two types of dithienylethene moieties, bis(2-thienyl) and bis(3-thienyl)-ethene, with one thiophene ring in common. The closed-ring isomers of bis(2-thienyl)ethenes have their absorption maxima at shorter wavelength than those of bis(3-thienyl)-ethenes.[8] The bis(3-thienyl)ethene moiety in **A** has an extra phenyl ring, which further shifts the maximum.



*Scheme 1.* Photoreaction of the fused dithienylethene **A**, **B**, and **C**.

**A** was synthesized by the reaction of 3-(2,3,3,4,4,5,5-heptafluorocyclopent-1-en-1-yl)-2-methyl-5-phenylthiophene with lithiated 1-(3,5-dimethyl-2-thienyl)-2-(4-bromo-3,5-dimethyl-2-thienyl)perfluorocyclopentene. The structure of **A** was confirmed by mass spectroscopy, NMR spectroscopy, elemental analysis and X-ray crystallographic analysis (Figure 1).[9]

A solution of **A** in hexane turned yellow then green upon irradiation with light of 365 nm, as shown in Figure 2. Upon further irradiation with light of 313 nm, the solution turned black. When the solution was exposed simultaneously to UV (313 nm) and blue (436 nm) light, it turned blue (Figure 2, sample 5). The solution turned yellow (Figure 2, sample 2), when it was irradiated with UV (313 nm) and yellow ($\lambda >$ 500 nm) light. From this experiment it is inferred that the color change originates from two kinds of colored species.

The two colored species were isolated by HPLC. The molecular structure of the two species were determined by absorption and NMR spectroscopy[10] to be the closed-ring isomer of bis(2-thienyl)ethene moiety (**B**; Scheme 1) and bis(3-thienyl)ethene moiety (**C**; Scheme 1), which are yellow and blue, respectively. Figure 3 shows the spectra of the open-ring isomer **A** and the isolated closed-ring isomers **B** and **C**. The absorption peak of **B** is located at the absorption valley of **C**. Both **B** and **C** converted back into **A** by irradiation with visible light ($\lambda > 450$ nm). Formation of the closed-ring isomer, in which both dithienylethene units are in the

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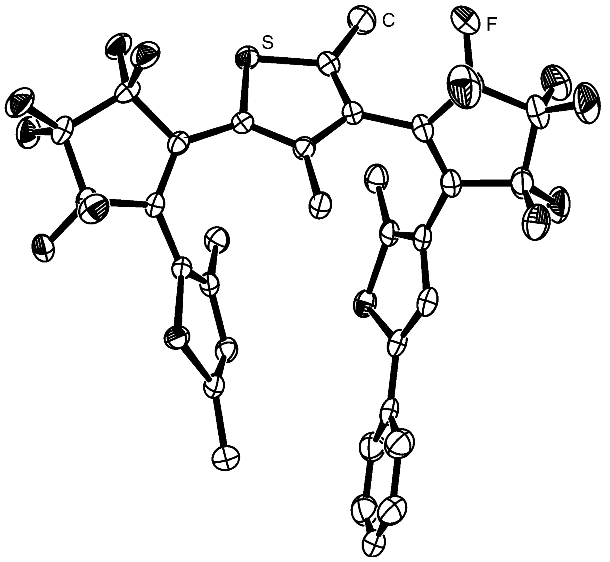

*Figure 1.* ORTEP drawing of open-ring isomer **A** (ellipsoids set at the 50% probability level). Hydrogen atoms were omitted for clarity.

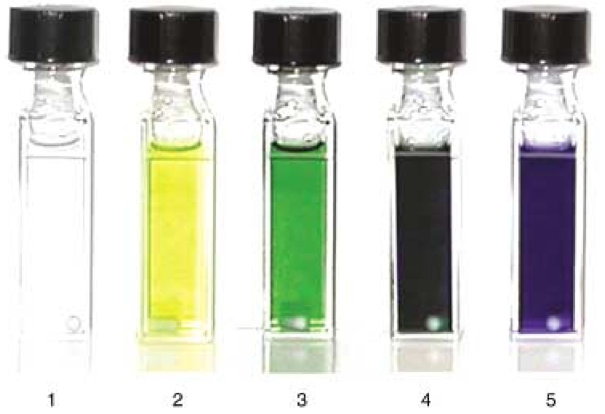

*Figure 2.* Color changes of **A** in hexane solution upon irradiation with 365 nm and 313 nm light. Sample 1: initial state; samples 2 and 3: upon irradiation with 365 nm light; sample 4: upon further irradiation with 313 nm light; sample 5: upon irradiation with 313 and 436 nm light.

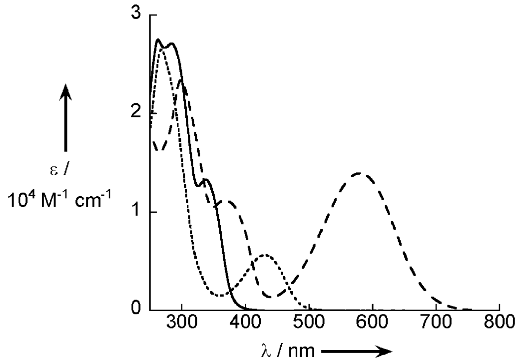

*Figure 3.* Absorption spectra of **A** (——), **B** (•••••), and **C** (-----) in hexane.

closed-ring form, was not discerned. This result is in agreement with the observation for symmetric dimers.[5a,c] Formation of both **B** and **C** upon irradiation with 313–365 nm light indicates that excited energy transfer to the bis(2-thienyl)-ethene unit with lower energy is not efficient. The energy transfer is considered to be less favorable because of non-coplanarity of the three thiophene rings, as shown in Figure 1.

A hexane solution containing **A** was irradiated with 334 nm light, and the concentration changes of **A**, **B**, and **C** were monitored by HPLC (Figure 4). At the initial stage of the photoirradiation, the formation of **B** was about four times faster than that of **C**. In the photostationary state, however, the amount of **C** was about 1.4 times larger than that of **B**. The time course of formation of **B** and **C** was analyzed based on Scheme 1, Equations (1)–(9).

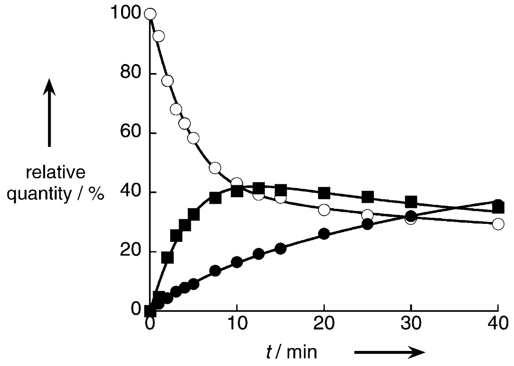

*Figure 4.* Decay of **A** (open circles) and formation of **B** (filled boxes) and **C** (filled circles) upon irradiation with 334 nm light. The solid lines were least square fitting of the concentration of **A**, **B**, and **C**.

$$\frac{dC_{\mathbf{A}}}{dt} = (-k_{\mathbf{A-B}}\,C_{\mathbf{A}} + k_{\mathbf{B-A}}\,C_{\mathbf{B}} - k_{\mathbf{A-C}}\,C_{\mathbf{A}} + k_{\mathbf{C-A}}\,C_{\mathbf{C}})\,F \tag{1}$$

$$\frac{dC_{\mathbf{B}}}{dt} = (k_{\mathbf{A-B}}\,C_{\mathbf{A}} - k_{\mathbf{B-A}}\,C_{\mathbf{B}})\,F \tag{2}$$

$$\frac{dC_{\mathbf{C}}}{dt} = (k_{\mathbf{A-C}}\,C_{\mathbf{A}} - k_{\mathbf{C-A}}\,C_{\mathbf{C}})\,F \tag{3}$$

$$F = \frac{1-10^{-A}}{A} \tag{4}$$

$$A = \varepsilon_{\mathbf{A}}\,C_{\mathbf{A}} + \varepsilon_{\mathbf{B}}\,C_{\mathbf{B}} + \varepsilon_{\mathbf{C}}\,C_{\mathbf{C}} \tag{5}$$

$$k_{\mathbf{A-B}} = \varepsilon_{\mathbf{A}}\,\Phi_{\mathbf{A-B}}\,I_0 \tag{6}$$

$$k_{\mathbf{B-A}} = \varepsilon_{\mathbf{B}}\,\Phi_{\mathbf{B-A}}\,I_0 \tag{7}$$

$$k_{\mathbf{A-C}} = \varepsilon_{\mathbf{A}}\,\Phi_{\mathbf{A-C}}\,I_0 \tag{8}$$

$$k_{\mathbf{C-A}} = \varepsilon_{\mathbf{C}}\,\Phi_{\mathbf{C-A}}\,I_0 \tag{9}$$

In these differential equations, $I_0$ is the intensity of light and $\Phi_{\mathbf{A-B}}$, $\Phi_{\mathbf{B-A}}$, $\Phi_{\mathbf{A-C}}$, and $\Phi_{\mathbf{C-A}}$ are reaction quantum yields of **A** to **B**, **B** to **A**, **A** to **C**, and **C** to **A**, respectively. $\varepsilon_{\mathbf{A}}$, $\varepsilon_{\mathbf{B}}$, and $\varepsilon_{\mathbf{C}}$ are molar absorption coefficients of **A**, **B**, and **C** at the irradiation wavelength (334 nm). $C_{\mathbf{A}}$, $C_{\mathbf{B}}$, and $C_{\mathbf{C}}$ are the concentrations of **A**, **B**, and **C**.

These differential equations were numerically solved and the results were fitted to the experimental data shown in Figure 4; the best-fit curves are shown as solid lines. The parameters used are as follows; $\varepsilon_\mathbf{A} = 1.3\times10^4\,\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$, $\varepsilon_\mathbf{B} = 3.1\times10^3\,\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$, $\varepsilon_\mathbf{C} = 1.3\times10^4\,\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$ (at 334 nm). The ratio of $\Phi_\mathbf{A-B}$:$\Phi_\mathbf{B-A}$:$\Phi_\mathbf{A-C}$:$\Phi_\mathbf{C-A}$ was calculated to be 11:44:2.5:1.0.

The quantum yields of cycloreversion reactions of **B** and **C** to **A**, $\Phi_\mathbf{B-A}$ and $\Phi_\mathbf{C-A}$ were measured in hexane by irradiating the sample with visible light at each absorption maximum. $\Phi_\mathbf{B-A}$ and $\Phi_\mathbf{C-A}$ were found to be 0.57 and 0.013, respectively, and this ratio (44:1) agrees well with the ratio obtained from the above simulation (44:1). The quantum yields of the cyclization reactions of **A** to **B** and **A** to **C**, $\Phi_\mathbf{A-B}$ and $\Phi_\mathbf{A-C}$ were found to be 0.14 and 0.032, respectively. The quantum yields are summarized in Table 1. The difference in the cyclization quantum yields ($\Phi_\mathbf{A-B} > \Phi_\mathbf{A-C}$) favors the formation of **B** and the difference in the cycloreversion quantum yields ($\Phi_\mathbf{B-A} \gg \Phi_\mathbf{C-A}$) leads to a higher yield of **C** at the photostationary state.

***Table 1:*** Photoreaction quantum yields of the fused dithienylethene.

| $\Phi_\mathrm{A-B}$ | $\Phi_\mathrm{B-A}$ | $\Phi_\mathrm{A-C}$ | $\Phi_\mathrm{C-A}$ |
|---|---|---|---|
| 0.14 | 0.57 | 0.032 | 0.013 |

Irradiation of the black solution with visible light of $\lambda > 580$ nm led to the disappearance of **C** only, and the solution turned yellow because only **C** absorbs in that region of the visible spectrum. On the other hand, upon irradiation of the black solution with visible light of $\lambda > 420$ nm, the solution turned blue because the cycloreversion quantum yield of **B** is much larger than that of **C**. Upon irradiation with light of 436 nm, the blue color scarcely bleached (Figure 2). The colors completely disappeared when the sample was exposed continuously to visible light of $\lambda > 420$ nm.

In conclusion, we have developed a new fused dithienylethene derivative **A** and studied its novel photochromic performance. Different colors can be obtained by irradiating **A** with different wavelengths and for different periods of time. This phenomenon is characteristic of fused diarylethenes.

## *Experimental Section*

Hexane of spectroscopic grade was distilled before use. Absorption spectra in a solution were measured with a Hitachi U-3500 absorption spectrophotometer. Photoirradiation was carried out by using a USHIO USH-500D 500 W high-pressure mercury lamp as the light source. Monochromatic light was obtained by passing the light through a Ritsu MC-20L monochromator.

Quantum yields for cycloreversion reactions were determined with monochromatic light of a Xe lamp at each absorption maximum of the samples and references. Colored hexane solutions of 1,2-bis(3,5-dimethyl-2-thienyl)perfluorocyclopentene[8] and 1,2-bis(2-methylbenzothiophene-3-yl)perfluorocyclopentene[11] were used as the reference.

Synthesis and characterization of the compounds: $^1$H NMR spectrum was recorded on a JEOL GSX400 spectrometer (400 MHz). Tetramethylsilane (TMS) was used as an internal standard. Mass spectrum was taken with a Shimadzu GCMS-QP5050A (EI) and a JOEL JMS-GC mate II (FAB). The melting point was measured using a Laboratory Devices MEL-TEMP II.

1-(3,5-dimethyl-2-thienyl)-2-(4-bromo-3,5-dimethyl-2-thienyl)-perfluorocyclopentene was synthesized as follows: $Br_2$ (0.73 g, 0.23 mL, 4.3 mmol) was added to a solution of bis(3,5-dimethyl-2-thienyl)perfluorocyclopentene[8] (1.59 g, 4.0 mmol) and $FeCl_3$ (13 mg, 0.08 mmol, 2 mol %) in $CHCl_3$ (6.4 mL) at less than 5 °C under an Ar atmosphere. After the mixture was stirred for 1 h at 0 °C, aqueous $Na_2S_2O_3$ was added to the reaction mixture and extracted with $CHCl_3$, washed with brine, dried over $MgSO_4$, and concentrated. Column chromatography (silica, hexane) gave 1-(3,5-dimethyl-2-thienyl)-2-(4-bromo-3,5-dimethyl-2-thienyl)perfluorocyclopentene (1.0 g, 53 %): mp 81.1–82.0 °C; $^1$H NMR (200 MHz, $CDCl_3$): $\delta = 1.73$ (3 H, s); 1.75 (3 H, s); 2.43 (3 H, s); 2.45 (3 H, s); 6.53 ppm (1 H, s); MS $m/z$ $[M^+]$ 474. Elemental analysis calcd (%) for $C_{17}H_{13}BrF_6S_2$: C 42.96, H 2.76; found: C 43.08, H 2.73.

Fused dithienylethene **A** was synthesized as follows: A solution of *t*BuLi in hexane (1.51 M, 0.49 mL) was added dropwise to a solution of 1-(3,5-dimethyl-2-thienyl)-2-(4-bromo-3,5-dimethyl-2-thienyl)perfluorocyclopentene (0.16 g, 0.33 mmol) in dry ether (3 mL) at less than −95 °C under an Ar atmosphere. After the mixture was stirred for 5 min at this temperature, 3-(2,3,3,4,4,5,5-heptafluorocyclopent-1-en-1-yl)-2-methy-5-phenylthiophene[12] (0.12 g, 0.33 mmol) in THF (2 mL) was added dropwise. The reaction mixture was allowed to warm up to room temperature. Aqueous $NH_4Cl$ was added to the reaction mixture, which was extracted by ether, washed with water, dried over $MgSO_4$ and concentrated. Column chromatography (silica, hexane) gave **A** (0.031 g, 12 %). mp 132.0–132.7 °C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta = 1.37$ (3 H, s), 1.43 (3 H, s), 2.10 (3 H, s), 2.14 (3 H, s), 2.42 (3 H, s), 6.25 (1 H, s), 7.02 (1 H, s), 7.3–7.6 ppm (5 H, m); FAB HRMS ($m/z$) $[M]^+$ calcd for $C_{33}H_{22}F_{12}S_3$: 742.0692; found: 742.0686. Elemental analysis calcd (%) for $C_{33}H_{22}F_{12}S_3$: C 53.37, H 2.99; found: C 53.67, H 3.02.

Closed-ring isomers of the fused dithienylethene, **B** and **C**, were isolated by passing a photoirradiated solution containing **A**, **B**, and **C** through HPLC. $^1$H NMR (400 MHz, $CDCl_3$) data for **B**: $\delta = 0.86$ (2.1 H, s), 1.02 (0.9 H, s), 1.55 (0.9 H, s), 1.60 (2.1 H, s), 2.00 (2.1 H, s), 2.00 (0.9 H, s), 2.07 (0.9 H, s), 2.08 (2.1 H, s), 2.42 (0.9 H, s), 2.51 (2.1 H, s), 5.25 (0.7 H, s), 5.34 (0.3 H, s), 6.84 (0.3 H, s), 6.97 (0.7 H, s), 7.3–7.5 ppm (5 H, m); $\lambda_\mathrm{max} = 431$ nm ($\varepsilon = 5.6\times10^3\,\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$);[13a] for **C**: $^1$H NMR (400 MHz, $CDCl_3$): $\delta = 1.59$ (3 H, s), 2.15 (3 H, s), 2.17 (3 H, s), 2.17 (3 H, s), 2.48 (3 H, s), 6.66 (1 H, s), 6.69 (1 H, s), 7.4–7.6 ppm (5 H, m); $\lambda_\mathrm{max} = 580$ nm ($\varepsilon = 1.4\times10^4\,\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$).[13b]

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