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Full-Color Photochromism of a Fused Dithienylethene Trimer

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Light-induced reversible isomerization between two isomers having different absorption spectra is referred to as photochromism.[1] In normal photochromic systems they interconvert between only two states: "colorless" and "colored". On the other hand, in multicolor or multicomponent systems, reversible multimode switching between more than two states can be realized. In a three-color system, eight states ($2^3 = 8$) can be produced. The multicolor system is useful for multifrequency optical memories and displays. Multicolor systems can be accomplished by mixing photochromic compounds with different colors in solutions,[2a] in polymer matrixes,[2b] and in single crystals.[2c,d]

We took an approach to incorporate three photochromic units in one molecule.[3] The advantage of a one-molecule system over mixture systems is high image resolution, constant color balance in a large area, and possible application to a multifrequency single-molecule memory. In previous reports,[4,5] nonsymmetric fused dithienylethene dimers were synthesized, and two-color photochromism was demonstrated. Here we report on a fused trimer, which undergoes full-color photochromism.

Figure 1 shows the fused trimer along with anticipated photochromic reactions. Fused trimer **1** has three dithienylethene moieties: bis(2-thienyl)ethene, (2-thienyl)(3-thienyl)ethene, and bis(3-thienyl)ethene, with two thiophene rings in common. The yellow circle in Figure 1 indicates the bis(2-thienyl)ethene moiety, which is expected to develop yellow color upon cyclization, because the π-conjugation cannot extend to the rest of chromophores in the closed-ring isomer.[6] The π-conjugation of the closed-ring isomer of (2-thienyl)(3-thienyl)ethene unit (a red circle) is extended to a phenyl substituent at the 5-position of the thiophene ring to develop red color.[6] Bis(3-thienyl)ethene unit (a blue circle) would show blue color upon cyclization because the unit has π-conjugated substituents at the 5-positions of the thiophene rings.[7]

The synthesis of **1a**[8] was carried out starting from 3-bromo-2,4-dimethyl-5-trimethylsilylthiophene.[9] The synthesized compound was confirmed by NMR and mass spectroscopy. Compound **1a** was recrystallized from hexane. X-ray crystallographic analysis also confirmed the molecular structure.[10]

Upon irradiation with 313-nm light, the colorless hexane solution of **1a** turned orange via yellow. Upon further irradiation with UV light, the solution turned black. When UV (313 nm) and blue (460 nm) light was simultaneously irradiated, the solution turned sky blue. When the solution was irradiated with UV (313 nm) and red (633 nm) light, the solution turned red-orange. The solution changed to yellow when the solution was irradiated with UV (313 nm) and yellow (578 nm) light. **1** can develop blue, red, and yellow colors upon irradiation with appropriate wavelength of light, suggesting that all of the three diarylethene moieties cyclized upon irradiation.

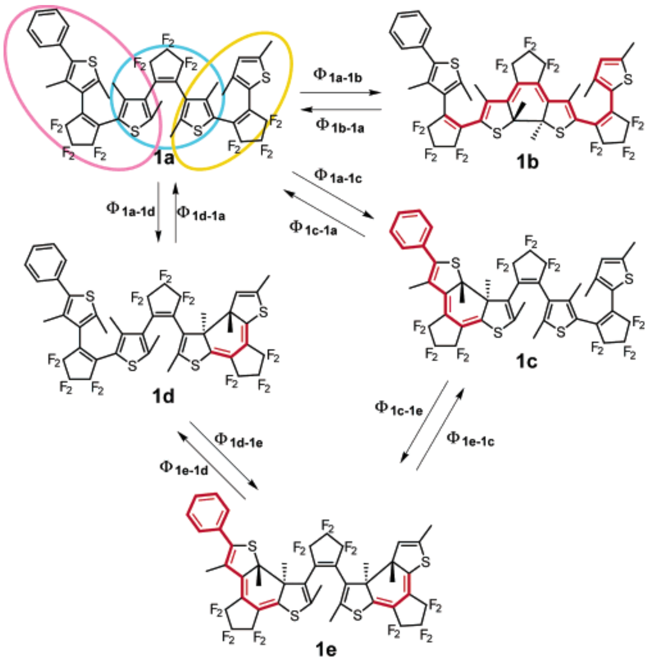

Figure 1. Photochromic reactions of dithienylethene **1**. Red line denotes the expansion of the π-conjugation.

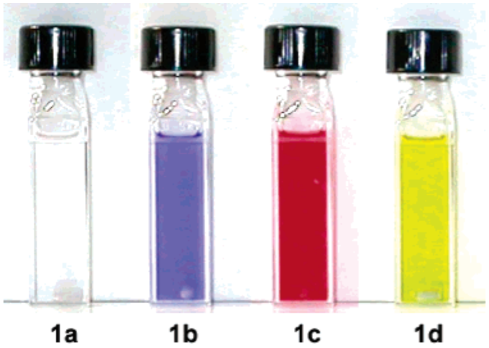

Figure 2. Colors of the open-ring isomer **1a** and the isolated closed-ring isomers **1b**−**d** in hexane solution.

HPLC analysis of the photoirradiated solution indicated the formation of four colored species. The molecular structure of the four colored species were determined by absorption spectra as the closed-ring isomer of the central bis(3-thienyl)ethene moiety (**1b**), the terminal (2-thineyl)(3-thienyl)ethene moiety (**1c**), and the terminal bis(2-thienyl)ethene moiety (**1d**) for blue, red, and yellow ones, respectively. Figure 2 shows the colors of the three species. Additionally, an orange compound was obtained and identified as the double closed-ring isomer **1e**. The color is due to the closed-ring isomer of the (2-thienyl)(3-thienyl)ethene and bis(2-thienyl)ethene units.

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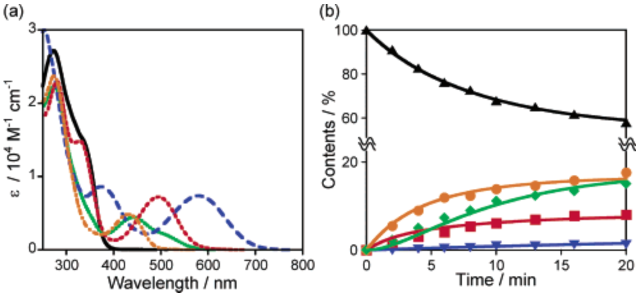

Figure 3. (a) Absorption spectra of **1a** and the isolated closed-ring isomers **1b**−**e** in hexane solution: **1a** (—, black), **1b** (− − −, blue), **1c** (- - - , red), **1d** (− · −, yellow), and **1e** (···, green). (b) Decay of the open-ring isomer **1a** (▲, black) and formation of the closed-ring isomer **1b** (▼, blue), **1c** (■, red), **1d** (●, yellow), and **1e** (◆, green) upon irradiation with 313-nm light. The solid lines were least-squares fitting of the concentrations.

Figure 3a shows the spectra of the open-ring isomer **1a** and isolated closed-ring isomers **1b**−**e**. The absorption peaks of **1b**−**d** are sufficiently separated from each other. All colored species converted back to the open-ring isomer **1a** by irradiation with visible light ($\lambda > 450$ nm). Formation of the closed-ring isomer, in which adjacent diarylethene units are in the closed-ring form, was not discerned. This result agreed with the observation of symmetric dimers and trimer[11] and asymmetric fused dimers.[5]

A hexane solution containing **1a** was irradiated with 313-nm light, and changes in concentrations of **1a**−**e** were monitored by HPLC (Figure 3b). At the initial stage of photoirradiation, **1d** was efficiently formed. In the photostationary state, however, the amounts of **1d** and **1e** became almost the same. Although the formation of **1b** was slow, the conversion gradually increased.

The time course of the formation of the closed-ring isomers **1b**−**e** and the decrease of the open-ring isomer **1a** was analyzed based on Figure 1 to give the ratio Φ_{1a-1b}:Φ_{1b-1a}:Φ_{1a-1c}:Φ_{1c-1a}:Φ_{1a-1d}:Φ_{1d-1a}:Φ_{1c-1e}:Φ_{1e-1c}:Φ_{1d-1e}:Φ_{1e-1d}. The ratio was calculated to be 0.0038:0.022:0.072:0.48:0.14:0.95:1:0.51:0.63:0.60.[12] The quantum yields of the cycloreversion reactions of the isolated **1b**−**d** to **1a**, Φ_{1b-1a}, Φ_{1c-1a}, and Φ_{1d-1a} were independently measured in hexane by irradiation with visible light at each absorption maximum to give $\Phi_{1b-1a} = 0.013$, $\Phi_{1c-1a} = 0.29$, and $\Phi_{1d-1a} = 0.57$. The ratio of the quantum yields agreed well with the ratio obtained from the above simulation. The quantum yields of the rest of the reactions were determined as follows: $\Phi_{1a-1b} = 0.0023$, $\Phi_{1a-1c} = 0.043$, $\Phi_{1a-1d} = 0.085$, $\Phi_{1c-1e} = 0.60$, $\Phi_{1e-1c} = 0.30$, $\Phi_{1d-1e} = 0.38$, $\Phi_{1e-1d} = 0.36$.

The cyclization quantum yields of the three photochromic units in the trimer are relatively small compared to the quantum yields of the component units. This is partly ascribed to the nonradiative decay due to the relatively large molecular size. X-ray crystallographic analysis revealed that the conformation of the central bis(3-thienyl)ethene moiety is in the twisted form. This is the reason Φ_{1a-1b} (= 0.0023) is the smallest among the three cyclization quantum yields.[13]

The cycloreversion quantum yield of the cyclohexadiene moiety at the central unit ($\Phi_{1b-1a} = 0.013$) is the smallest among the three units; $\Phi_{1c-1a} = 0.29$ and $\Phi_{1d-1a} = 0.57$. It is known that the closed-ring isomer of bis(3-thienyl)ethene with two phenyl rings at the 5-positions of the thiophene rings has a small cycloreversion quantum yield.[7] The cycloreversion quantum yield of the bis(2-thienyl)ethene moiety ($\Phi_{1d-1a} = 0.57$) is similar to the value of bis(3,5-dimethyl-2-thienyl)ethene (0.58).[6] The cycloreversion quantum yield is known not to be affected by the substitution at the 4-position of the thiophene ring.

There are three possible designs for the fused trimers that have three color components. The yellow, red, or blue components can be located in the central unit (see Figure S2 in Supporting Information). The cyclization quantum yield of the central unit was found to become very small due to the molecular distortion. To increase the conversion of the central unit, the unit should have low cycloreversion quantum yield. Among the three color components, the blue-developing unit has the lowest cycloreversion quantum yield. This is the reason blue-developing bis(3-thienyl)ethene moiety was placed in the central unit.

In conclusion, a fused dithienylethene derivative **1a** was synthesized, and its photochromic performance was examined. It was revealed that **1a** showed full-color photochromic performance by choosing appropriate wavelengths of light.

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Supporting Information Available: Experimental procedures, synthesis of **1a**, crystallographic data of **1a**, and details of the analysis of the quantum yield (PDF). X-ray structural data for **1a** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) Physical data for compound **1a**: mp 167.1−167.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.4−2.4 (24H, m), 6.44 (1H, s), 7.3−7.4 (5H, m); UV−vis λ_{max} (ϵ) 273 nm (2.7×10^4); FAB HRMS (*m/z*) $[M + H]^+$ calcd for $C_{45}H_{31}F_{18}S_4$: 1041.1021. Found: 1041.1009.
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(10) Crystallographic data for compound **1a**: $C_{45}H_{30}F_{18}S_4$, $FW = 1040.96$, triclinic $P\bar{1}$, $a = 10.420(2)$ Å, $b = 11.869(2)$ Å, $c = 18.348(4)$ Å, $\alpha = 89.164(3)°$, $\beta = 87.914(3)°$, $\gamma = 73.491(3)°$, $V = 2174.2(7)$ Å^3, $Z = 2$, $R_1 = 0.0639$ ($I > 2\sigma$), $wR_2 = 0.2417$ (all data). CCDC 261031. For the details of the crystallographical result, see Supporting Information.
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