Extraordinarily Low Cycloreversion Quantum Yields of Photochromic Diarylethenes with Methoxy Substituents

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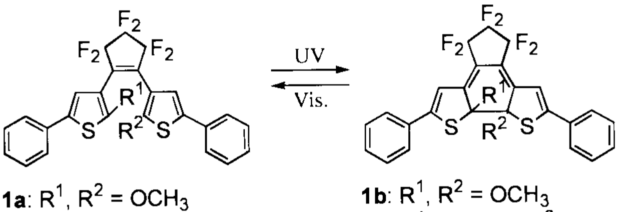
Diarylperfluorocyclopentenes having 2-methoxy-5-phenylthiophene as the aryl groups were synthesized. Introduction of two methoxy substituents instead of methyl groups at the reactive carbons of 1,2-bis(5-phenyl-3-thienyl)perfluorocyclopentene decreased the photocycloreversion quantum yield by a factor of 10^3, while the cyclization quantum yield was similar.

Photochromism is referred as a reversible photoisomerization between two isomers having different absorption spectra.[1] Among a number of photochromic compounds, diarylethenes with heterocyclic aryl groups, such as thiophene or benzothiophene aryl groups, are the most promising compounds for applications to optical memories and switches because of their thermally irreversible and fatigue resistant photochromic performance.[2] Diarylethenes having various substituents have been so far synthesized. Introduction of electron-donating substituents, such as methoxy or diethylamino groups, at para-positions of the phenyl groups of 1,2-bis(2,4-dimethyl-5-phenyl-3-thienyl)perfluorocyclopentene decreased photocycloreversion quantum yields by a factor of 2 to 6.[3] Bulky substituents at the reactive carbons of diarylethenes increased the photocyclization quantum yields and decreased the thermal stability of the closed-ring isomers.[4,5] Here, we examined the effect of methoxy substituents at the reactive carbons on the quantum yields of photocyclization and photocycloreversion. The quantum yields of methoxy-substituted derivatives (**1** and **2**) were measured and compared with those of **3**.



1a: R^1, R^2 = OCH_3
2a: R^1 = OCH_3, R^2 = CH_3
3a: R^1, R^2 = CH_3

1b: R^1, R^2 = OCH_3
2b: R^1 = OCH_3, R^2 = CH_3
3b: R^1, R^2 = CH_3

1,2-Bis(2-methoxy-5-phenyl-3-thienyl)perfluorocyclopentene (**1a**) and 1-(2-methoxy-5-phenyl-3-thienyl)-2-(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene (**2a**) were synthesized as follows. To dry ether containing 3,5-dibromo-2-methoxythiophene (24 g, 88 mmol) was added a 15% *n*-BuLi hexane solution (56 mL, 92 mmol) at –78 °C. Tributylborate (32 mL, 123 mmol) was slowly added to the reaction mixture at –78 °C, and the mixture was stirred for 2 h. Iodobenzene (18 g, 88 mmol), 20 wt% Na_2CO_3 (aq) (90 mL), and $Pd(PPh_3)_4$ (4.3 g, 0.37 mmol) were added to the mixture, and the mixture was refluxed for 5 h at 70 °C to form 15 g of 3-bromo-2-methoxy-5-phenylthiophene (**4**) (Yield: 63%). To the mixture of **4** (14 g, 52 mmol) and 140 mL of dry THF, 36 mL of a *n*-BuLi hexane solution (59 mmol) was added at –78 °C. Then, to the solution was added 3.5 mL (26 mmol) of octafluorocyclopentene to yield 2.5 g of 1-(2-methoxy-5-phenyl-3-thienyl)perfluorocyclopentene (**5**) (Yield: 25% based on octafluorocyclopentene) and 7.2 g (1.3 mmol) of **1a** (Yield: 50%).[6] A *n*-BuLi hexane solution (0.84 mL, 1.4 mmol) was added to a dry THF solution of 3-bromo-2-methyl-5-phenylthiophene[7] (0.33 g, 1.3 mmol) at –78 °C, and to the mixture was added **5** (0.50 g, 1.3 mmol) to yield 0.47 g (0.87 mmol) of **2a** (Yield: 67%).[8] 1,2-Bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene (**3a**) were synthesized by a similar method according to the literature.[7]

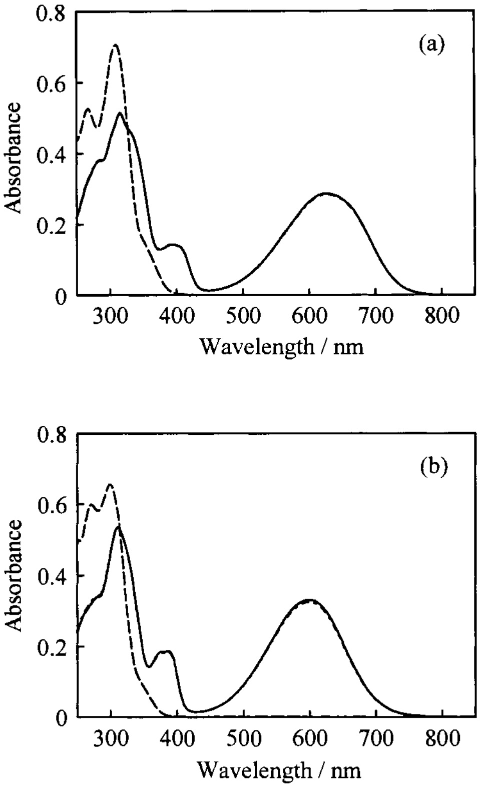


Figure 1. Absorption spectral changes of **1** (2.1×10^{-5} mol/L) (a) and **2** (2.1×10^{-5} mol/L) (b) in hexane: open-ring isomer (----), closed-ring isomer (——), the photostationary solution under irradiation with 313 nm light (–·–).

Table 1. Absorption maxima and coefficients of the open- and closed-ring isomers of diarylethenes, and the quantum yields in hexane

	λ_{max} / nm ($\varepsilon/10^4\,M^{-1}cm^{-1}$)	$\Phi_{a\rightarrow b}$		λ_{max} / nm ($\varepsilon/10^4\,M^{-1}cm^{-1}$)	$\Phi_{b\rightarrow a}$
1a	267 (2.4), 309 (3.3)	0.44 (309 nm)	**1b**	625 (1.5)	$< 2.0\times10^{-5}$ (625 nm)
2a	270 (2.8), 298 (3.1)	0.44 (298 nm)	**2b**	600 (1.6)	1.6×10^{-3} (600 nm)
3a	280 (3.6)[a]	0.59 (280 nm)[a]	**3b**	575 (1.6)[a]	1.3×10^{-2} (492 nm)[a]

[a] ref 7.

Figure 1a shows the absorption spectral change of **1** by irradiation with 313 nm light. **1a** has the absorption maxima at 267 and 309 nm in hexane. Upon irradiation with 313 nm light, the colorless solution of **1a** turned blue, in which the visible absorption maximum was observed at 625 nm. The photoirradiated sample was analyzed by HPLC (silica gel; hexane/ethyl acetate = 4/1 as the eluent). The sample gave only one peak (monitoring wavelength: 326 nm, elution time: 14 min), which was different from that of the open-ring isomer **1a** (elution time: 24 min). This indicates **1a** completely converted to the colored product. The structure of the isolated colored product was analyzed by mass spectrum, ^{1}H NMR spectrum, and elemental analysis.[9] All data agreed well with the closed-ring isomer **1b**. The absorption spectrum of **1b** is also shown in Figure 1a. The spectrum is identical with that in the photostationary state. The conversion from **1a** to **1b** in the photostationary state under irradiation with 313 nm light was 100%. The λ_{max} of **1b** in the visible light region showed a bathochromic shift as much as 50 nm in comparison with that of **3b**. The blue color was stable and never returned to the colorless form under room light. Upon irradiation with the visible light ($\lambda > 500$ nm) for 4 h, it slowly reformed the open-ring isomer, while the blue color of **3b** was bleached immediately by irradiation with the light for 1 min. The photocycloreversion reaction of **1b** was much slower than that of **3b**.

Figure 1b shows the absorption spectral change of **2** by irradiation with 313 nm light. **2a** has the absorption maxima at 271 and 298 nm in hexane. Upon irradiation with 313 nm light, the colorless solution of **2a** turned blue, in which the visible absorption maximum was observed at 600 nm. The colored product was isolated by HPLC (silica gel; hexane as the eluent), and the structure was analyzed by mass spectrum and ^{1}H NMR spectrum, and elemental analysis.[10] All data agreed well with the closed-ring isomer **2b**. The absorption spectrum of **2b** is also shown in Figure 1b. The conversion from **2a** to **2b** in the photostationary state under irradiation with 313 nm light was 98%. The blue color was bleached by irradiation with the visible light ($\lambda > 500$ nm) for 5 min, and the absorption spectrum returned to that of **2a**.

To compare the photocyclization and photocycloreversion reactivities of **1** and **2** with that of **3**, the quantum yields were measured. Table 1 summarizes the quantum yields, the absorption maxima of the open- and closed-ring isomers, and their absorption coefficients. The cyclization quantum yields of **1a** ($\Phi = 0.44$) and **2a** ($\Phi = 0.44$) were slightly smaller than that of **3a** ($\Phi = 0.59$). On the other hand, the cycloreversion quantum yields of **1b** and **2b** were $< 2.0 \times 10^{-5}$ and 0.0016, respectively, which were 1000 and 10 times smaller than that of **3b**. The methoxy substituents at the reactive carbons of the thienyl groups remarkably decreased the cycloreversion quantum yield. The polar factor rather than the resonance factor of the methoxy group is considered to affect the photocycloreversion reaction, because the methoxy groups in the closed-ring isomers are not conjugated with the π-conjugation of the closed-ring isomers.

The colored isomers of almost all photochromic diarylethenes are unstable under room visible light and the colors are bleached. Therefore, they can not be used for display applications, such as memory cards. The above photochemically stable photochromic compound can be potentially used to memory cards as well as write-once memory media and color dosimeters.[11]

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References and Note

1 H. Dürr and H. Bouas-Laurent, “Photochromism Molecules and Systems,” Elsevier, Amsterdam (1990).

2 M. Irie, *Chem. Rev.*, **100**, 1685 (2000).

3 M. Irie, K. Sakemura, M. Okinaka, and K. Uchida, *J. Org. Chem.*, **60**, 8305 (1995).

4 K. Uchida, E. Tsuchida, Y. Aoi, S. Nakamura, and M. Irie, *Chem. Lett.*, **1999**, 63.

5 S. Kobatake, K. Uchida, E. Tsuchida, and M. Irie, *Chem. Lett.*, **2000**, 1340.

6 **1a**: pale yellow colored crystals: mp 171.9–172.3 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.71 (s, 6H), 7.16 (s, 2H), 7.2–7.5 (m, 10H); MS *m/z* (M^+) 552. Anal. Calcd for $C_{27}H_{18}F_6O_2S_2$: C, 58.69; H, 3.28%. Found: C, 58.87; H, 3.29%.

7 M. Irie, T. Lifka, S. Kobatake, and N. Kato, *J. Am. Chem. Soc.*, **122**, 4871 (2000).

8 **2a**: pale yellow colored crystals: mp 138.1–138.6 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.04 (s, 3H), 3.64 (s, 3H), 7.07 (s, 1H), 7.2–7.5 (m, 11H); MS *m/z* (M^+) 536. Anal. Calcd for $C_{27}H_{18}F_6OS_2$: C, 60.44; H, 3.38%. Found: C, 60.48; H, 3.37%.

9 **1b**: dark blue colored crystals: mp 194–195 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.77 (s, 6H), 6.57 (s, 2H), 7.3–7.6 (m, 10H); MS *m/z* (M^+) 552. Anal. Calcd for $C_{27}H_{18}F_6O_2S_2$: C, 58.69; H, 3.28%. Found: C, 58.77; H, 3.28%.

10 **2b**: dark blue colored crystals: mp 192–193 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.30 (s, 3H), 3.56 (s, 3H), 6.45 (s, 1H), 6.71 (s, 1H), 7.3–7.6 (m, 10H); MS *m/z* (M^+) 536. Anal. Calcd for $C_{27}H_{18}F_6OS_2$: C, 60.44; H, 3.38%. Found: C, 60.68; H, 3.37%.

11 a) S. Irie, T. Yamaguchi, H. Nakazumi, S. Kobatake, and M. Irie, *Bull. Chem. Soc. Jpn.*, **72**, 1139 (1999). b) S. Irie and M. Irie, *Bull. Chem. Soc. Jpn.*, **73**, 2385 (2000).