Thermal Cycloreversion Reaction of a Photochromic Dithienylperfluorocyclopentene with *tert*-Butoxy Substituents at the Reactive Carbons

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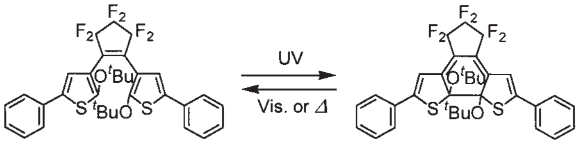
tert-Butoxy groups were introduced at 2 and 2′-positions of the thiophene rings of a dithienylperfluorocyclopentene to prepare a photochromic compound with a thermal cycloreversion reactivity and a low photocycloreversion quantum yield. The cycloreversion quantum yield was similar to the isopropyl-substituted derivative and the half-life time of the colored isomer at 100 °C was 8 s.

Photochromism is defined as a reversible isomerization between two isomers having different absorption spectra by photoirradiation.[1] Various types of photochromic compounds have been so far developed in an attempt to apply the compounds to optoelectronic devices, such as memories and switches. Among these compounds, diarylethenes are the most promising candidates for the application because of their thermally irreversibility and fatigue-resistance.[2] Recently, we have reported that dithienylethenes having bulky substituents at the reactive carbons of the thiophene rings decrease the thermal stability of the colored closed-ring isomers.[3,4] When isopropyl groups are introduced at 2 and 2′-positions of the thiophene rings of 1,2-bis(5-phenyl-3-thienyl)perfluorocyclopentene, the half-life time of the colored isomer decreased to 3.3 h at 80 °C, while the methyl-substituted derivative was stable even at 100 °C.[5] The thermal reversible photochromic reactivity is applicable for reusable imaging devices with thermal head. For the devices the image should be readily bleached at high temperature and stable under room light. To increase the thermal bleaching rate at higher temperature and keep the photostability bulky *tert*-butoxy groups were introduced to the reactive carbons, because methoxy substitution at the reactive carbons is known to decrease the cycloreversion quantum yield and provide the photostability.[6]



1a **1b**

1,2-Bis(2-*tert*-butoxy-5-phenyl-3-thienyl)perfluorocyclopentene (**1a**) was synthesized as follows. To dry THF containing 3,5-dibromo-2-*tert*-butoxythiophene[7] (6.0 g, 19 mmol) was added a 15% *n*-BuLi hexane solution (12 mL, 20 mmol) at −78 °C. Tributylborate (6.4 mL, 24 mmol) was slowly added to the reaction mixture at −78 °C, and the mixture was stirred for 1 h. Iodobenzene (3.9 g, 19 mmol), 20 wt% Na_2CO_3 (aq) (40 mL), and $Pd(PPh_3)_4$ (0.97 g, 0.82 mmol) were added to the mixture, and the mixture was refluxed for 5 h at 70 °C to form 3.9 g of 3-bromo-2-*tert*-butoxy- 5-phenylthiophene (**2**) (Yield: 65%).[8] To the mixture of **2** (2.0 g, 6.4 mmol) and 20 mL of dry THF, 4.1 mL of a *n*-BuLi hexane solution (6.7 mmol) was added at −78 °C. Then, to the solution was added 0.45 mL (3.2 mmol) of octafluorocyclopentene to yield 0.65 g (1.0 mmol) of **1a** (Yield: 32%).[9] **1a** was characterized by ^{1}H NMR spectrum, mass spectrum, and elemental analysis.

Figure 1 shows the absorption spectral change of **1** upon irradiation with 313-nm light. **1a** has the absorption maxima at 278 and 306 nm in hexane. Upon irradiation with 313-nm light, the colorless solution of **1a** turned blue, in which a visible absorption maximum was observed at 656 nm. The blue colored isomer was isolated by HPLC (silica gel; hexane/ethyl acetate = 99.5/0.5 as the eluent). From the absorption spectrum of the isolated colored isomer conversion ratio to the colored isomer in the photostationary state under irradiation with 313-nm light was determined to be 92%. The colored isomer was further examined by ^{1}H NMR spectroscopy. The methyl protons of the *tert*-butoxy substituents and protons at 4 and 4′-posotions of the thiophene rings were observed at 1.52 ppm and 7.21 ppm for the colored isomer, while those of **1a** at 1.21 ppm and 6.48 ppm, respectively. The peak shifts are similar to those observed for the methyl-substituted derivative. Based on the shifts of the absorption band and ^{1}H NMR peaks the colored isomer was assigned to the closed-ring form isomer **1b**.[2]

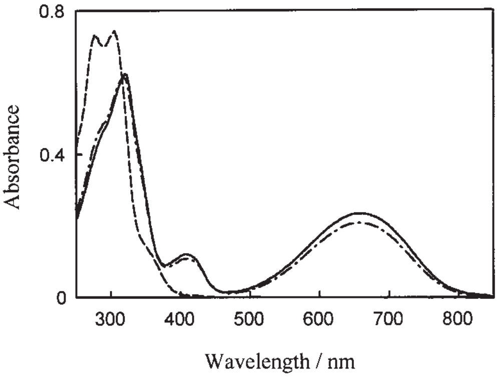


Figure 1. Absorption spectral change of **1** in hexane (2.3 × 10^{-5} mol dm^{-3}) by photoirradiation: **1a** (- - - -), **1** in the photostationary state under irradiation with 313-nm light (—-—), and **1b** (——).

1b in hexane was stored in the dark at room temperature. After one day the blue color solution turned to colorless. To prove that the decoloration is not due to decomposition but due to thermal cycloreversion HPLC measurement was carried out after one-day storage at room temperature. In the chart only one peak due to the initial open-ring isomer was observed. This indicates that the colored closed-ring isomer thermally returned to the open-ring isomer **1a**.

The thermal decoloration process of **1b** was examined in detail between 30 and 70 °C in decalin. Figure 2 shows the decay curves of the absorbance of the closed-ring isomer. The decay curves followed the first-order kinetics. Figure 3 shows the temperature dependence of the rate (k). The activation energy (E_a) and frequency factor (A) were $91.7\,\mathrm{kJ\,mol^{-1}}$ and $5.7 \times 10^{11}\,\mathrm{s^{-1}}$, respectively. The half-life time of the thermal cycloreversion reaction for **1b** at 70 °C was 110 s and decreased to 8 s at 100 °C. The thermal bleaching rate was remarkably increased by the introduction of the bulky *tert*-butoxy substituents in comparison to the isopropyl substituents. The bulky substituents are considered to destabilize the cyclohexadiene ring structure.

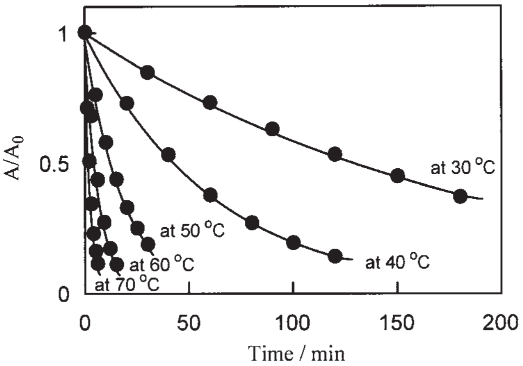


Figure 2. Thermal fading curves of **1b** in decalin.

The cyclization and cycloreversion quantum yields of **1** were measured at room temperature in hexane. The values were determined to be 0.48 (305 nm) and 0.031 (656 nm), respectively. The thermal cycloreversion reaction was negligibly small during the measurement. Both cyclization and cycloreversion quantum yields were similar to the isopropyl-substituted derivative. The *tert*-butoxy substituents strongly enhanced the thermal cycloreversion rate, while the photochemical reactivity was scarcely affected by the substitution.

The absorption maximum of **1b** was observed at longer wavelength than that of isopropyl-substituted derivative.[4,5] This suggests that electron-donating property of *tert*-butoxy groups caused spectral shift to the longer wavelength.

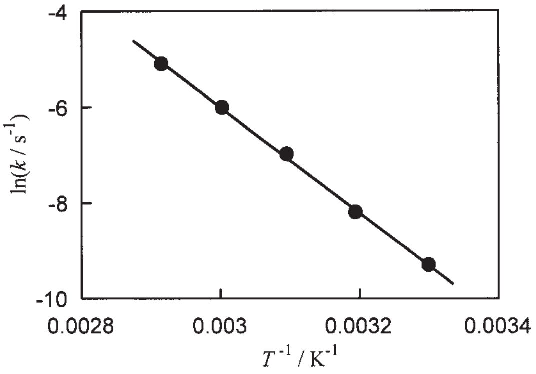


Figure 3. Temperature dependence of the thermal fading rates of **1b**.

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References and Notes

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8 **2**: pale yellowish oil: ^{1}H NMR (200 MHz, CDCl$_3$) δ 1.47 (s, 9H), 7.00 (s, 1H), 7.2–7.5 (m, 5H); MS m/z 254, 256 ($M^+ - CH_2 = C(CH_3)_2$). Anal. Calcd. for $C_{14}H_{15}BrOS$: C, 54.03; H, 4.86%. Found: C, 54.39; H, 4.83%.
9 **1a**: pale yellow colored crystals: mp 194–195 °C; ^{1}H NMR (200 MHz, CDCl$_3$) δ 1.21 (s, 18H), 7.21 (s, 2H), 7.2–7.5 (m, 10H); MS m/z 524 ($M^+ - 2CH_2 = C(CH_3)_2$). Anal. Calcd. for $C_{33}H_{30}F_6O_2S_2$: C, 62.25; H, 4.75%. Found: C, 61.90; H, 4.72%.