A Photochromic Dithienylethene That Turns Yellow by UV Irradiation

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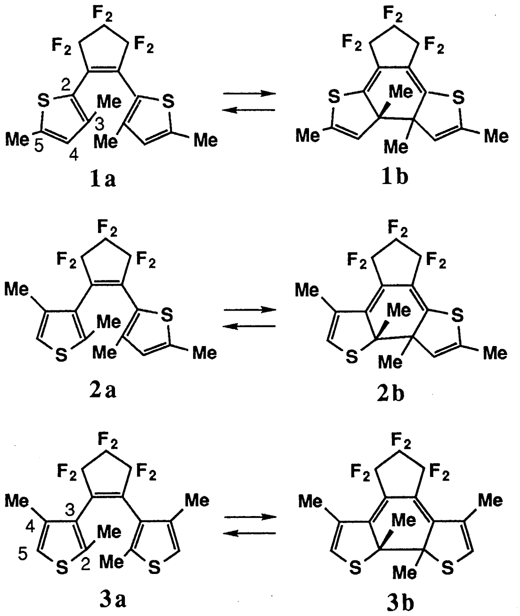
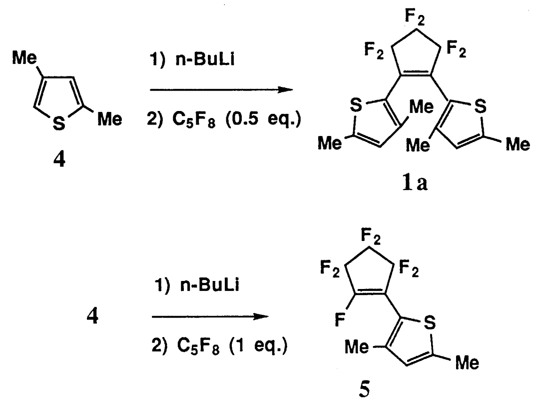
1,2-Bis(3,5-dimethyl-2-thienyl)perfluorocyclopentene which shows a reversible color change from colorless to yellow by UV irradiation was synthesized. The color of the photogenerated closed-ring forms was dependent on the substitution position of the thiophene rings to the perfluorocyclopentene moiety.

Although a great number of photochromic compounds have been reported,[1] the compounds which turn yellow upon UV photoirradiation are quite rare. Chromene[2] and spironaphthoxazine with pyrazine ring[3] are such a few examples. When we apply photochromic compounds to full color display, it is strongly desired to develop new yellow-developing compounds.

Diarylethenes containing heterocyclic rings undergo photoinduced reversible electrocyclic reactions to produce closed-ring forms that absorb light at longer wavelengths.[4-7] We have so far synthesized diarylmaleic anhydrides and diarylperfluorocyclopentenes which turn red, blue, and green. Diarylethenes which have absorption at 800 nm region have also been prepared.[6,7] In this paper, we report on a new diarylperfluorocyclopentene which turns yellow upon UV irradiation.





1,2-Bis(3,5-dimethyl-2-thienyl)perfluorocyclopentene (**1a**) was synthesized by elimination reactions of perfluorocyclopentene with 2-lithio-3,5-dimethylthiophene.[8] n-Butyl lithium (15% hexane solution, 45 ml, 72 mmol) was added to a solution of 2,4-dimethylthiophene **4** (7.7 g, 69 mmol) of diethyl ether (100 ml) at room temperature under a nitrogen atmosphere and the reaction mixture was refluxed for 1 h. After cooled down to -30 ℃, perfluorocyclopentene (4.6 ml, 34 mmol) was added. The reaction mixture was warmed up to room temperature and treated with dilute hydrochloric acid, and the product was extracted with diethyl ether. After the removal of diethyl ether, the product **1a** was purified by silica gel chromatography(hexane) and isolated in 50% yield.[9] When equimolar of perfluorocyclopentene and 2-lithio-3,5-dimethylthiophene were used, (3,5-dimethyl-2-thienyl)perfluorocyclopentene **5** was obtained in 75 % yield. 1-(2,4-Dimethyl-3-thienyl)-2-(3,5-dimethyl-2-thienyl)perfluorocyclopentene(**2a**)[10] was synthesized by the reaction of **5** (2.0 g, 6.6 mmol) with 3-lithio-2,4-dimethylthiophen. After the purification by silica gel chromatography, 1.55 g of **2a** was obtained in 60% yield.

The reaction of 1 eq. of perfluorocyclopentene (1.21 g, 5.8 mmol) and 2 eq. of 3-lithio-2,4-dimethylthiophene afforded 2.28 g of 1,2-bis(2,4-dimethyl-3-thienyl)perfluorocyclopentene(**3a**)[11] in 56% yield.

Fig. 1 illustrates the absorption spectral change of a hexane solution of **1a** (4.8×10^{-5} mol dm^{-3}) by UV irradiation. Photoirradiation with 366 nm light in the presence of air led to decrease of the absorption at 336 nm(ε ; 1.3×10^4 dm^3 mol^{-1}cm^{-1}) and formation of a yellow solution, in which a new band appeared at 425 nm (ε ; 5.8×10^3 dm^{3}mol^{-1}cm^{-1}). This band is ascribable to the closed-ring form **1b**. ^{1}H-NMR spectra gave three new signals at 1.39, 2.02, and 5.29 ppm after UV irradiation. They are assigned to the methyl signals and the olefinic proton signal, respectively, of the closed-ring form. The ^{1}H-NMR signals and the new visible absorption band disappeared by irradiation with light of wavelength > 440 nm. At a photostationary state under irradiation with 366 nm light, the ratio of the closed-ring to the open-ring forms was 77:23. The quantum yields of the cyclization and the ring-opening reactions were determined to be 0.40 and 0.58, respectively. The quantum yields were not dependent on solvent polarity. Similar quantum yields were obtained for hexane and methanol solutions.

Photoirradiation of the hexane solution of **3a** with 288 nm light, on the other hand, led to formation of a red solution (λ max 534 nm; ε ; 5.0×10^3dm^3 mol^{-1}). The red color is

Table 1. Absorption maxima and their coefficients of the open-ring and the closed-ring forms of dithienylethenes, and the quantum yields in hexane.

	λ_{max} /nm (ε_{max})	$\Phi_{a\rightarrow b}$		λ_{max} /nm (ε_{max})	$\Phi_{b\rightarrow a}$	E_{calcd} /eV
1a	336 ($1.3 x 10^4$)	0.40 (366 nm)[a]	**1b**	425 ($5.8 x 10^3$)	0.58 (425 nm)[a]	3.65
2a	312 ($1.2 x 10^4$)	0.28 (340 nm)[a]	**2b**	469 ($4.5 x 10^3$)	0.57 (470 nm)[a]	3.46
3a	234 ($1.3 x 10^4$)	0.21 (280 nm)[a]	**3b**	534 ($5.0 x 10^3$)	0.13 (492 nm)[a]	3.26

[a] Quantum yields were measured at the wavelengths.

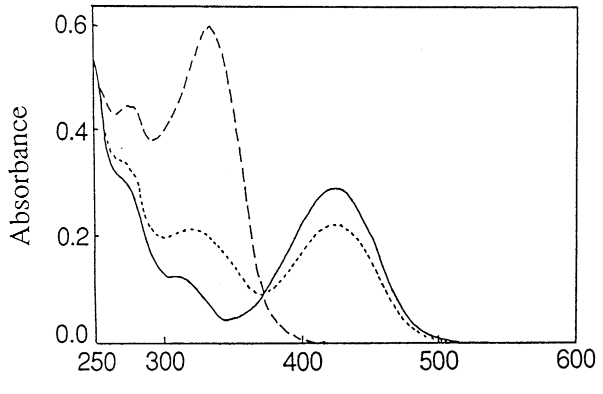


Figure 1. Absorption spectra of hexane solution of **1a**($4.8 x 10^{-5}$ mol dm^{-3})(— — —), **1b**(———), and the photostationary state (········) upon 366 nm light irradiation.

ascribable to the closed-ring form **3b**.[5] The absorption maxima of the closed-ring forms were dependent on the substitution positions of the thiophene rings.

When the thiophene rings were attached to the ethylene moiety at 2 positions, the absorption spectrum of the closed-ring form showed hypsochromic shift in comparison with the dithienylethene that has 3-thienyl groups. The blue shift observed for **1b** suggests that the π-conjugation in the closed-ring form is localized in the cyclohexadiene structure. The sp^3 carbon atoms that were formed by the ring-closure reaction destroyed the π-conjugation in the benzo[2,1-b:5,6-b']dithiophene structure. The π-electron delocalization of **1b** is therefore completely different from **3b**, in which the π-conjugation extends through two thienyl moieties, and **1b** gives a red color.

The open-ring form **1a**, on the other hand, gave an absorption band at longer wavelengths compared with **3a**. The red shift suggests that the π-conjugation in the open-ring form extends throughout the molecule. In **3a** the π-conjugation is localized in the hexatriene structure, while in **1a** the π-conjugation has a decapentaene structure.

Open-ring form **2a** has a hybrid structure of **1a** and **3a**. **2a** has the absorption band at 312 nm (ε ; $1.2 x 10^4 dm^3 mol^{-1} cm^{-1}$). This is in between 336 nm for **1a** and 234 nm for **3a**. Upon irradiation with 334 nm light, a colorless hexane solution became orange, in which a new band appeared at 469 nm. The absorption band of **2b** is also located in between **1b** and **3b**. **2b** has a hexatriene conjugation structure, which is longer than butadiene structure of **1b** and is shorter than octatetraene structure of **3b**. The position of the absorption bands of both forms of the dithienylethenes can be interpreted by their π-conjugation lengths. The spectral characteristic was also supported by the calculation using a ZINDO program of CAChe system (Table 1, the last column).

The quantum yields of ring-closure reactions of **2a** and **3a** were obtained to be 0.28 and 0.21, respectively. The yield of **1a** (0.40) was larger than these values. The quantum yields of ring-opening reactions of the dithienylethenes that have 2-thienyl rings, **1b** and **2b**, are four times larger than that of **3b**. These results suggest that the localization of conjugation in the cyclohexadiene structure is effective to increase the ring-opening quantum yield. The quantum yields, the absorption maxima of the open-ring and the closed-ring forms, and their absorption coefficients are summerized in Table 1.

The thermal stability of the closed-ring forms **1b**-**3b** was measured in heptane in the absence of air at 80 ℃. Optical densities of these isomers remained almost constant after 500 h. The closed-ring forms of dithienylperfluorocyclopentenes **1b**-**3b** were stable irrespective of the substitution positions of the thiophene rings.[12]

References and Note

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9 **1a**: pale yellow prisms; mp 129-130 ℃. Anal. Found: C, 51.31; H, 3.66%. Calcd for $C_{17}H_{14}F_6S_2$: C, 51.51; H, 3.53%. MS(*m/z*) 396(M$^+$); ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.72 (6H, s, Me), 2.44 (6H, s, Me), 6.51 (2H, s, aromatic protons).
10 **2a**: pale yellow oil; Anal. Found: C, 51.47; H, 3.64%. Calcd for $C_{17}H_{14}F_6S_2$: C, 51.51; H, 3.53%. MS(*m/z*) 396(M$^+$); ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.99 (3H, s, Me), 2.00 (3H, s, Me), 2.25 (3H, s, Me), 2.37 (3H, s, Me), 6.50 (1H, s, aromatic proton), 6.77 (1H, s, aromatic proton).
11 **3a**: colorless prisms; mp 132-134 ℃. Anal. Found: C, 51.46; H, 3.62%. Calcd for $C_{17}H_{14}F_6S_2$: C, 51.51; H, 3.53%. MS (*m/z*) 396(M$^+$); ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.04 (6H, s, Me), 2.29 (6H, s, Me), 6.70 (2H, s, aromatic protons).
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