Synthesis of Fluorescent Amorphous Diarylethenes

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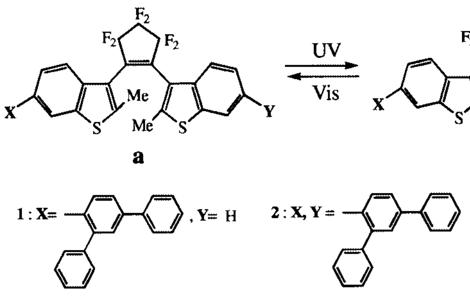
1,2-Bis(2-methyl-1-benzothiophen-3-yl)perfluorocyclopentene derivatives having 2,4-diphenylphenyl substituents at 6 and 6' positions of the benzothiophene rings were synthesized. Both mono- and di-substituted derivatives, compounds **1a** and **2a**, formed amorphous states at room temperature and their glass transition temperatures were observed at 88 °C and 127 °C, respectively. Remarkable spectral shift of the fluorescence from 650 nm to 450 nm was observed for the amorphous film of closed-ring isomer **2b** upon visible ($\lambda > 450$ nm) light irradiation.

Photochromic materials have attracted considerable attention because they are potentially useful for various photonic devices, such as optical memory, photo-optical switching and display. For the practical applications the photochromic reactions should take place in solid states, such as in polymer matries, sol–gel glasses or bulk amorphous states.[1] Among them bulk amorphous photochromic materials are the most promising for the practical use because of their optical transparency and capability to form thin films by a spin-coating method.[2–10] The aim of this paper is to synthesize diarylethenes that form the amorphous state above 100 ºC and emit fluorescence from both isomers. 1,2-Bis(2-methyl-1-benzothiophen-3-yl)perfluorocyclopentene derivatives having 2,4-diphenylphenyl substituents at 6- and 6'-positions of the benzothiophene rings, compounds **1a** and **2a**, were synthesized by Suzuki reaction of the monoiodo and diiodo derivatives of the diarylethenes with a boronic acid derivative of 2,4-diphenylbenzene. Compounds **1a** and **2a** were purified by GPC and HPLC. The structures were confirmed by ^{1}H NMR, mass spectra and elemental analysis.[11] The hexane solutions of **1a** and **2a** were irradiated with UV (280 nm > λ > 420 nm) light and the photoproducts were isolated using HPLC (silica-gel / hexane: ethyl acetate = 96:4). The photoproducts were confirmed to be **1b** and **2b** by ^{1}NMR (Scheme 1).[11]



Scheme 1.

The hexane solutions of **1b** and **2b** showed characteristic absorption bands at 529 nm and at 540 nm, respectively. Upon irradiation with visible light ($\lambda > 450$ nm), the red color disappeared to produce the open-ring isomers **1a** and **2a** that showed absorption peaks at 292 nm and 293 nm, respectively.

The bulk amorphous thin film was prepared by spin coating a toluene solution of the isolated compound **2b** on a quartz substrate. Thickness of the bulk amorphous thin film was typically 0.2 μm. Figure 1 shows the absorption spectral change of the bulk amorphous thin film. The visible absorption peak of **2b** was observed at 563 nm, which is 23 nm longer than that of **2b** in hexane. Upon irradiation with visible light ($\lambda > 450$ nm), the absorption band of **2b** decreased and a new band appeared at 299 nm, which is ascribed to **2a**. Upon irradiation with 313 nm light the visible absorption band around 560 nm again appeared. The conversion from **2a** to **2b** in the photostationary state was estimated to be 29% for the amorphous film. The photochromic reaction could be repeated more than 30 times without deterioration.

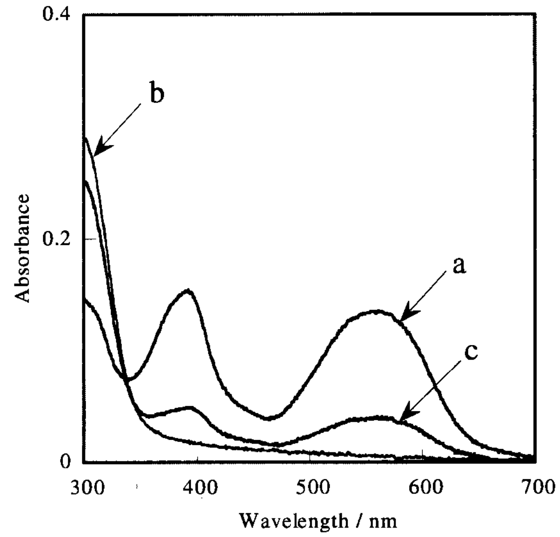


Figure 1. Absorption spectral change of bulk amorphous film **2** by photoirradiation: (a) closed-ring isomer, **2b**, (b) open-ring isomer, **2a**, generated by irradiation with visible light ($\lambda > 450$ nm) and (c) photostationary state under irradiation with 313 nm light.

Compounds **1a** and **2a** exhibited melting temperatures at 226 °C and 249 °C, respectively. Glass transition behavior of **1a** and **2a** were followed by a DSC method after the first melting and cooling cycle. Clear shifts of the baselines were observed at around 85 °C and 125 °C for **1a** and **2a**, respectively. The baseline shifts were attributable to the glass to liquid

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transition of the materials. Tg's of the samples **1a** and **2a** were determined from the threshold temperatures to be 88 °C and 127 °C, respectively. T_g of 127 °C is the highest value among amorphous diarylethenes so far reported.

Although fluorescence spectra of various types of diarylethenes have been examined,[8,12,13] fluorescence emission from the closed-ring isomer was scarcely observed. Only an example is 1,2-bis(2-methyl-1-benzothiophen-3-yl)perfluorocyclopentene, which gave very weak fluorescence from the closed-ring isomer at 77 K.[8]

Figure 2 shows the fluorescence spectral change of **2b** in the amorphous film at room temperature. The closed-ring isomer **2b** showed a fluorescence emission at 650 nm upon excitation with 280 nm light. The long wavelength fluorescence was also observed when excited with 530 nm light. The fluorescence excitation spectrum agreed with the absorption band of the closed-ring isomer. This result clearly indicates that the fluorescence at 650 nm is due to the closed-ring isomer. Upon irradiation with visible light (λ > 450 nm), the 650 nm fluorescence peak disappeared and a new fluorescence band appeared at 450 nm.[14] In the photostationary state under irradiation with 313 nm light both fluorescence bands at 450 nm and 650 nm were observed. The fluorescence spectral changes could be repeated upon alternate irradiations of UV and visible light. The fluorescence spectral change observed at room temperature can be potentially applicable to fluorescence readout optical memory.[15]

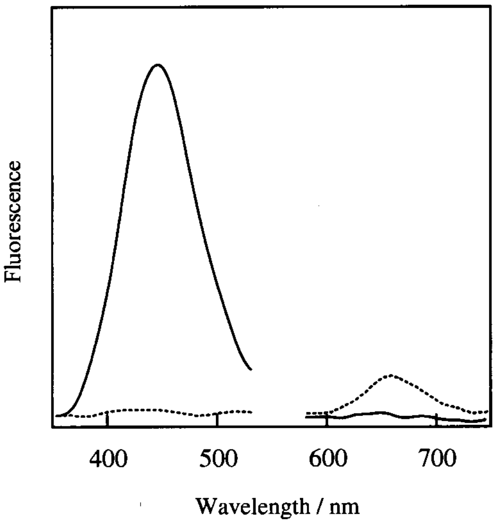

Figure 2. Fluorescence spectral change of bulk amorphous film **2** excited with 280 nm light by photoirradiation: (---) closed-ring isomer, **2b**, and (—) open-ring isomer, **2a**, generated by irradiation with visible light (λ > 450 nm).

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11 **1b**: ^{1}H NMR (200 MHz, acetone-d_6, 20 °C) δ 2.00 (s, 6H), 6.90–7.79 (m, 32H), **1a**: mp 249 °C; ^{1}H NMR (200 MHz, acetone-d_6, 20 °C) δ 2.28 (s, 4.1H), 2.58 (s, 2.9H), 6.90–7.79 (m, 32H), Anal. Calcd for $C_{59}H_{38}F_6S_2$: C, 76.60; H, 4.42%. Found: C, 76.72; H, 4.42%. **2b**: ^{1}H NMR (200 MHz, acetone-d_6, 20 °C) δ 2.01 (s, 6H), 7.08–7.93 (m, 20H), **2a**: mp 226 °C; ^{1}H NMR (200 MHz, acetone-d_6, 20 °C) δ 2.13 (s, 3.3H), 2.23(s, 2.7H), 7.08–7.93 (m, 20H), Anal. Calcd for $C_{41}H_{26}F_6S_2$: C, 70.67; H, 3.76%. Found: C, 70.89; H, 3.84%.
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