

Fluorescence Property of Photochromic Diarylethenes with Indole Groups

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Diarylethenes having a fluorescent indole ring as the aryl group **1a** and **2a** were synthesized. Upon alternate irradiation with 366 nm and visible ($\lambda > 480$ nm) light, **1a** underwent reversible photocyclization reactions to produce closed-ring isomer **1b**. The fluorescence intensity also reversibly changed along with the reactions. The fluorescence quantum yields of the open-ring isomers **1a** and **2a** were 4.6 and 6.3% respectively, while the yields of the closed-ring isomers **1b** and **2b** were almost zero. The fluorescence quantum yields decreased with the increase in the photocyclization quantum yields.

Photochromic compounds attract much attention because of their potential for applications to photonics devices, such as optical memory media and photo-optical switches.^{1–5} Among various types of photochromic compounds, diarylethene derivatives are the most promising compounds for the applications because of their thermally irreversible and fatigue resistant photochromic performance (Scheme 1).^{6–8}

So far, the most convenient method to follow the photochromic reactions is to measure the absorption spectral changes. To detect the spectral changes the concentration of the photochromic compounds should be higher than 10^{-6} mol·dm⁻³ even if the optical pass length is 1 cm. In polymer thin films of 1 μ m, the concentration should be higher than 10^{-2} mol·dm⁻³. To detect the photochromic reactions at low concentrations, it is desired to develop photochromic compounds, which change fluorescent properties upon photoirradiation. The fluorescent photochromic compounds are useful for opti-

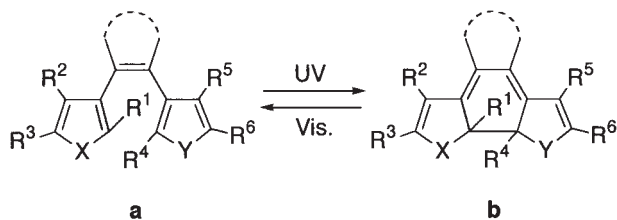
cal memory media as well as for fluorescent probes.

2-Substituted indoles are well-known to exhibit strong fluorescence.^{9–11} In the present study, we have attempted to prepare fluorescent photochromic compounds by introducing a fluorescent indole ring as the aryl groups of diarylethene derivatives (Scheme 2).

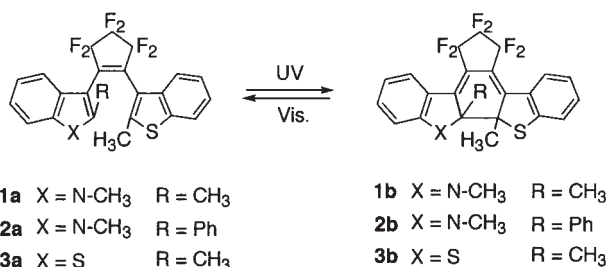
Results and Discussion

Synthesis. Diarylethene derivatives **1a** and **2a** with different 2-substituted indoles were synthesized as shown in Scheme 3. 3-Bromoindole derivatives **4** and **5** were obtained from 1,2-substituted indole by bromination with benzyltrimethylammonium tribromide.¹² The coupling reaction of monobenzothiophene-substituted perfluorocyclopentene with **4** and **5** produced diarylethenes **1a** and **2a**. **3a** was synthesized as a reference compound.⁸ **1a–3a** were purified by column chromatography and recrystallization (hexane). The structures of all compounds were confirmed by ¹H NMR, mass spectroscopy, and elemental analysis.

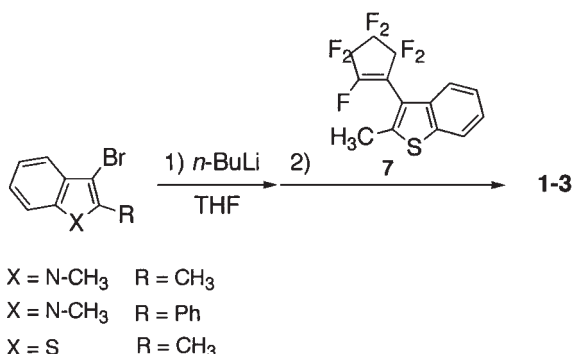
Photochromic Reactions. Figure 1 shows the absorption spectral change of **2** (3.2×10^{-5} M) in hexane by photoirradiation. Upon irradiation with 366-nm light, an absorption band around 300 nm decreased and a new band ap-



Scheme 1.



Scheme 2.



Scheme 3.

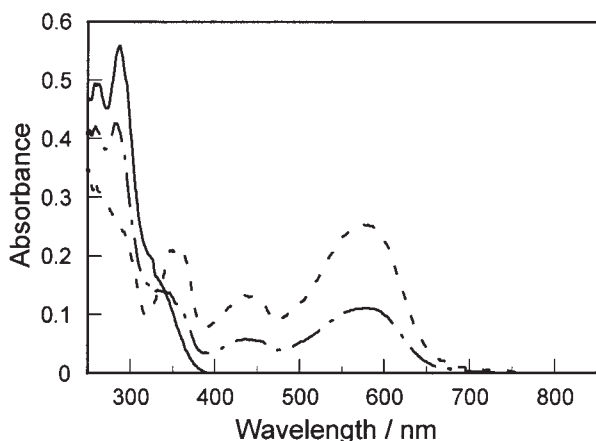


Fig. 1. Absorption spectral changes of **2** in hexane (3.2×10^{-5} M) by photoirradiation: **2a** (—), **2** in the photostationary state under irradiation with 366-nm light (-.-), and **2b** (-.-).

Table 1. Absorption Maxima of the Open- and Closed-Ring Isomers of **1–3**^{a)}

Compounds	$\lambda_{\max}/\text{nm}$	$\epsilon_{\max}/\text{M}^{-1} \text{ cm}^{-1}$
1a	260	14200
1b	556	10100
2a	296	17400
2b	586	12800
3a	258	14000
3b	517	9100

a) In hexane.

peared in the visible region. The color of the solution changed from colorless to purple, in which an absorption maximum was observed at 586 nm. When the purple solution was irradiated with visible light ($\lambda > 480$ nm), the spectrum returned back to the original one. The photogenerated colored product was stable and could be isolated by high performance liquid chromatography (HPLC, hexane/ethyl acetate). NMR and mass spectral measurement determined the structure of the colored product, the closed-ring isomer **2b**. **1** and **3** also underwent similar photochromic reactions. Table 1 summarizes the main absorption bands of the open and closed-ring form isomers **1a–3a** and **1b–3b**.

To know the details of the spectroscopic characteristics of the open- and closed-ring isomers **2a** and **2b**, we compared the absorption spectra with the indole derivatives as shown in Fig. 2. The edge of 1-methyl-2-phenylindole ($\lambda_{\max} = 295$ nm) is less than 360 nm, while the edge of **2a** ($\lambda_{\max} = 285$ nm) extends to 400 nm. The donor–acceptor interaction between the electron-donating 1-methyl-2-phenylindole unit and the electron-withdrawing perfluorocyclopentene unit is considered to shift the absorption edge. The photocyclization reaction of **2a** was also observed by irradiation with light longer than 350 nm. The result suggests that the charge-transfer excited state can enter the photocyclization channel.

Figure 3 shows the solvent effects of closed-ring isomer **2b** in several solvents. Absorption maxima changed from 586 nm to 613 nm by changing the solvent polarity from hexane to acetonitrile. Such a shift suggests the polar structure of the

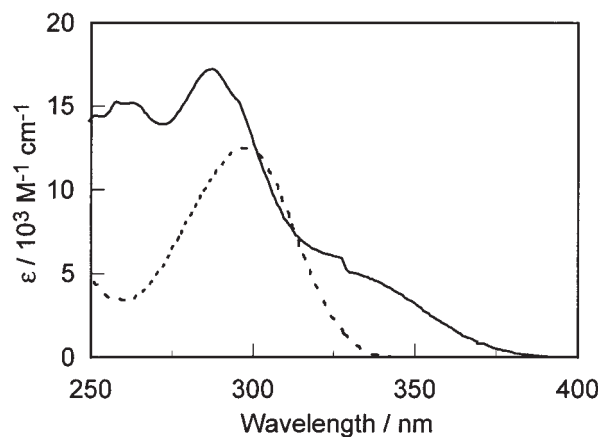


Fig. 2. Absorption spectra of **2a** (—) and 1-methyl-2-phenylindole (-.-) in hexane.

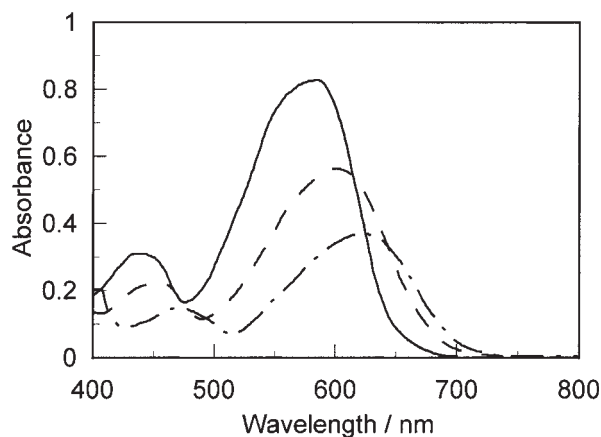


Fig. 3. Absorption spectra of **2b** in several solvents; hexane (—), ethyl acetate (-.-), and acetonitrile (-.-). The concentration of **2b** was 6.3×10^{-5} M.

closed-ring isomer **2b**.

Table 2 summarizes the photocyclization and cycloreversion quantum yields. Relatively high cyclization quantum yields were observed for **1a–3a**. **2b** was stable in the dark at room temperature. The thermal stability of the closed-ring form isomer **2b** was examined at 100–140 °C in decalin. The absorbance of the closed-ring isomers decreased slowly above 100 °C. Even at 120 °C, the half-life time was 5.5 days.

Table 2. Quantum Yields of Photochromic Reactions and Fluorescence Emission

Compounds	Φ		$\Phi_f^c)$	$\tau_0/\text{ns}^c)$
	$\Phi_{\text{cyclization}}^a)$	$\Phi_{\text{cycloreversion}}^b)$		
1	0.44	0.075	0.046	<1
2	0.26	0.21	0.063	<1
3	0.35	0.35	0.012	—

a) Irradiation at 366 nm light. Reference; furyl fluide ($\Phi_{\text{cyclization}} = 0.21$ in *n*-hexane). b) Irradiation at $\lambda_{\max}$ light ($\lambda > 480$ nm). Reference; furyl fluide ($\Phi_{\text{cycloreversion}} = 0.06$ in toluene). c) Fluorescence quantum yields of the open-ring isomers **1a–3a**. Reference; anthracene in cyclohexane ($\Phi_f = 0.31$, Ex; 366 nm).

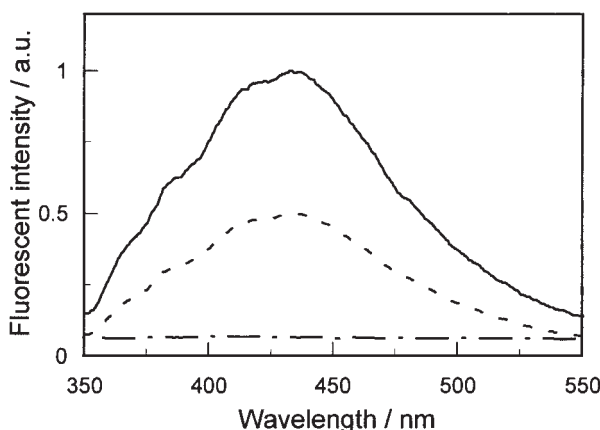


Fig. 4. Fluorescence spectral changes of **2** in hexane by photoirradiation: **2a** (—), **2** in the photostationary state under irradiation with 366-nm light (---), and **2b** (-.-).

Fluorescent Properties. Figure 4 shows the fluorescence spectral change of **2a** along with the photochromic reaction in hexane by UV irradiation. The fluorescence maximum was observed at 433 nm. Upon irradiation with 366-nm light, the fluorescence intensity decreased and the emission was reduced to a half in the photostationary state. The closed-ring isomer **2b** was non-fluorescent. Similar fluorescence intensity changes upon irradiation with 366-nm light were observed for **1a** and **3a**. The fluorescence quantum yields (Φ_f) of **1a–3a** by irradiation with 366-nm light were measured; values are summarized in Table 2. The highest quantum yield of 6.3% was observed for **2a**.

Indole derivatives are known to exhibit strong fluorescence. The fluorescence quantum yield of 1-methyl-2-phenylindole was reported to be 0.85 in hexane.⁹ Although diarylethenes **1a** and **2a** having an indole ring showed a higher fluorescent emission in comparison with the reference compound **3a**, the fluorescence quantum yields were much less than the value of 1-methyl-2-phenylindole. The rotation of the substituted thiophene or indole along the single bond connecting the perfluorocyclopentene unit and the contribution of the intramolecular charge transfer interaction are considered to increase radiationless transition to the ground state and reduce the yield.¹³

Comparison of Cyclization and Fluorescence Quantum Yields. The fluorescence quantum yield of **1a** was smaller than the value of **2a**, while the photocyclization quantum yield of **1a** was larger than that of **2a**, as shown in Table 2. The difference can be explained as follows. A part of the excited molecules, which can not enter a cyclization reaction channel, deactivate to the relaxed fluorescence state and emit the fluorescence.¹³ When the cyclization quantum yield is high, the number of unreacted excited molecules becomes small and the fluorescence intensity decreases.

Conclusions

Diarylethenes having an indole ring as the aryl groups **1a** and **2a** were synthesized. **1a–3a** underwent reversible photocyclization reactions by alternate irradiation with UV ($\lambda = 366$ nm) and visible ($\lambda > 480$ nm) light. The fluorescence intensity also reversibly changed with the photochromic

reactions. The fluorescence quantum yield of **2a** was as high as 6.3%.

Experimental

General. ¹H NMR spectra were recorded on a GSX-400 NMR spectrometer. Tetramethylsilane was used as an internal standard. Mass spectra were taken with a Shimadzu GCMS-QO5050A gas chromatography–mass spectrometer. Melting points were not corrected. Absorption and fluorescence spectra were measured with a Hitachi U-3410 absorption spectrophotometer and a Hitachi U-3010 fluorescence spectrophotometer, respectively. Photoirradiation was carried out using an USHIO 500W high-pressure mercury lamp or an USHIO-500W xenon lamp as the light source. Monochromatic light was obtained by passing the light through a monochromator (Ritsu MV-10N) or a band-pass filter ($\Delta\lambda_{1/2} = 15$ nm). Fluorescence lifetime was measured with a time-resolved spectrofluorometer (Hamamatsu Photonics. C4334 and C4792) excited with a 337-nm N₂ laser (ILEE. NN-100).

Materials. Solvents of spectroscopic grade were purified by distillation before use. All reactions were performed under dry argon atmosphere unless otherwise specified. The reactions were monitored by thin-layer chromatography. Column chromatography was performed on silica gel.

1-(1,2-Dimethylindol-3-yl)-2-(2-methyl-1-benzothiophen-3-yl)hexafluorocyclopentene (1a). To the solution of 3-bromo-1,2-dimethylindole (493 mg, 2.2 mmol) in anhydrous THF (40 mL) was added dropwise *n*-BuLi (1.6 M in hexane, 1.5 mL, 2.3 mmol) at -78 °C under argon atmosphere. The reaction mixture was stirred for 1 h at -78 °C. The solution was cooled down at -95 °C, and then 1-(2-methyl-1-benzothiophen-3-yl)heptafluorocyclopentene (820 mg, 2.4 mmol) in anhydrous THF (20 mL) was added. The reaction mixture was warmed up to room temperature and then saturated aqueous NH₄Cl was added. The product was extracted with ether, dried with magnesium sulfate, and concentrated. Purification was performed by column chromatography (SiO₂, hexane/ethyl acetate = 90/10) and recrystallization (hexane). 1-(1,2-Dimethylindol-3-yl)-2-(2-methyl-1-benzothiophen-3-yl)hexafluorocyclopentene was obtained as a pale-yellow solid (665 mg, 65%). The closed-ring isomer (**1b**) was isolated from UV photoirradiated hexane solution of **1a** by HPLC (hexane/ethyl acetate = 97/3).

1a: mp. 134 – 135 °C (decomp.); ¹H NMR (400 MHz, CDCl₃) δ 1.93 (s, 3H), 2.23 (s, 3H), 3.52 (s, 3H), 7.14–7.66 (s, 8H); MS m/z 467 (M⁺); Anal. Calcd for C₂₄H₁₇F₆NS: C, 61.93; H, 3.68; N, 3.01. Found: C, 61.84; H, 3.82; N, 3.05. UV-vis (hexane) $\lambda_{\max}$ (ϵ) 264 (14200), 285 (11300), 292 (10600), 300 (6700), 342 (6100). Selected data for **1b**: ¹H NMR (400 MHz, CDCl₃) δ 1.77 (s, 3H), 2.16 (s, 3H), 3.68 (s, 3H), 6.53–7.20 (s, 8H); MS m/z 467 (M⁺). UV-vis (hexane) $\lambda_{\max}$ (ϵ) 272 (15000), 347 (10600), 425 (3800), 556 (10100).

Synthesis of 1-(1-Methyl-2-phenylindol-3-yl)-2-(2-methyl-1-benzothiophen-3-yl)hexafluorocyclopentene (2a). To the solution of 3-bromo-1-methyl-2-phenylindole (630 mg, 2.2 mmol) in anhydrous THF (40 mL) was added dropwise *n*-BuLi (1.6 M in hexane, 1.5 mL, 2.3 mmol) at -78 °C under argon atmosphere. The reaction mixture was stirred for 1 h at -78 °C. The solution was cooled down at -95 °C, and then 1-(2-methyl-1-benzothiophen-3-yl)heptafluorocyclopentene (820 mg, 2.4 mmol) in anhydrous THF (20 mL) was added. The reaction mixture was warmed up to room temperature and saturated aqueous NH₄Cl was added. The product was extracted with ether, dried with magnesium sul-

fate, and concentrated. Purification was performed by column chromatography (SiO₂, hexane/ethyl acetate = 90/10) and recrystallization (hexane). 1-(1-Methyl-2-phenylindol-3-yl)-2-(2-methyl-1-benzothiophen-3-yl)hexafluorocyclopentene was obtained as pale-yellow crystals (695 mg, 60%). The closed-ring isomer (**2b**) was isolated from UV photoradiated hexane solution of **2a** by HPLC (hexane/ethyl acetate = 97/3).

2a: mp. 173–174 °C; ¹H NMR (400 MHz, CDCl₃) δ 1.78 (s, 3H), 3.38 (s, 3H), 6.77–7.87 (s, 13H); MS *m/z* 527 (M⁺). Anal. Calcd for C₂₉H₁₉F₆NS: C, 66.03; H, 3.63; N, 2.66. Found: C, 65.93; H, 3.65; N, 2.65. UV-vis (hexane) λ_{max} (ε) 264 (14400), 269 (14200), 296 (17400). Selected data for **2b**: ¹H NMR (400 MHz, CDCl₃) δ 1.52 (s, 3H), 3.78 (s, 3H), 6.53–7.20 (s, 13H); MS *m/z* 527 (M⁺). UV-vis (hexane) λ_{max} (ε) 348 (10700), 362 (10400), 437 (6200), 581 (12800).

1,2-Bis(2-methyl-1-benzothiophen-3-yl)hexafluorocyclopentene (3a). **3a** was prepared according to the method described in the literature.⁷

Photochromic Quantum Yields. The cyclization quantum yields were determined by comparing the photocyclization rate of furyl flugide in hexane by using a normal procedure.¹⁴ The cycloreversion quantum yields were also measured using furyl flugide in toluene as a reference.

Fluorescence Quantum Yields. The fluorescence quantum yields were determined using anthracene in cyclohexane (Φ_f = 0.31; excitation wavelength 366 nm) as a reference.⁹

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