

Large geometrical structure changes of photochromic diarylethenes upon photoirradiation

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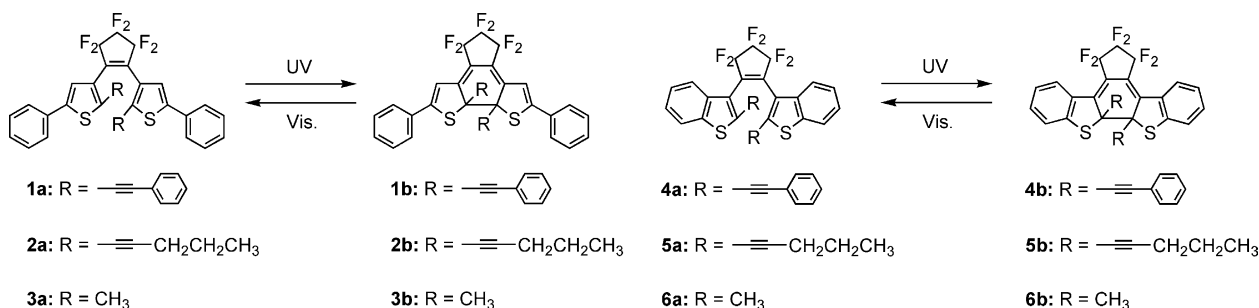
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Abstract—Photochromic diarylethene derivatives having phenylethynyl and pent-1-ynyl groups at the reactive carbons have been synthesized. These ethynyl groups enhance the cycloreversion quantum yields of diarylethenes without affecting the absorption maxima and the absorption coefficients of the closed-ring isomers. The derivatives exhibited large geometrical structural changes in the photoisomerization process.

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Various types of photochromic compounds have been developed so far to apply them to optoelectronic devices.¹ Among these compounds, diarylethenes have attracted much attention because they undergo thermally irreversible and fatigue-resistant photochromic reactions.^{2–5} Diarylethenes alter their structures between open- and closed-ring isomers along with the photoisomerization. As confirmed by X-ray crystallographic analysis, however, the motion of reactive moieties is very small and the molecular size remains similar in the photoisomerization process, which enables the photochromic reaction even in the single-crystalline state.⁴ In this letter, we report on a new feature of diarylethenes that the molecular size remarkably changes upon photoirradiation.

Four types of novel diarylethene derivatives (**1a**, **2a**, **4a**, and **5a**) shown in Scheme 1 were synthesized. 1,2-Bis(2-phenylethynyl-5-phenyl-3-thienyl)perfluorocyclopentene (**1a**)⁶ was prepared from 2,3-dibromo-5-phenylthiophene and ethynylbenzene in Sonogashira reaction condition⁷ followed by coupling with octafluorocyclopentene. 1,2-Bis(2-phenylethynyl-1-benzothien-3-yl)perfluorocyclopentene (**4a**)⁸ was prepared from 2,3-dibromobenzothiophene and ethynylbenzene according to the procedure similar to that used for **1a**. 1,2-Bis[2-(pent-1-ynyl)-5-phenyl-3-thienyl]perfluorocyclopentene (**2a**)⁹ and 1,2-bis[2-(pent-1-ynyl)-1-benzothien-3-yl]perfluorocyclopentene (**5a**)¹⁰ were synthesized using 1-pentyne instead of ethynylbenzene in the same procedure as **1a** and **4a**, respectively.



Scheme 1.

Keywords: Photochromism; Diarylethene; Substituent effect.

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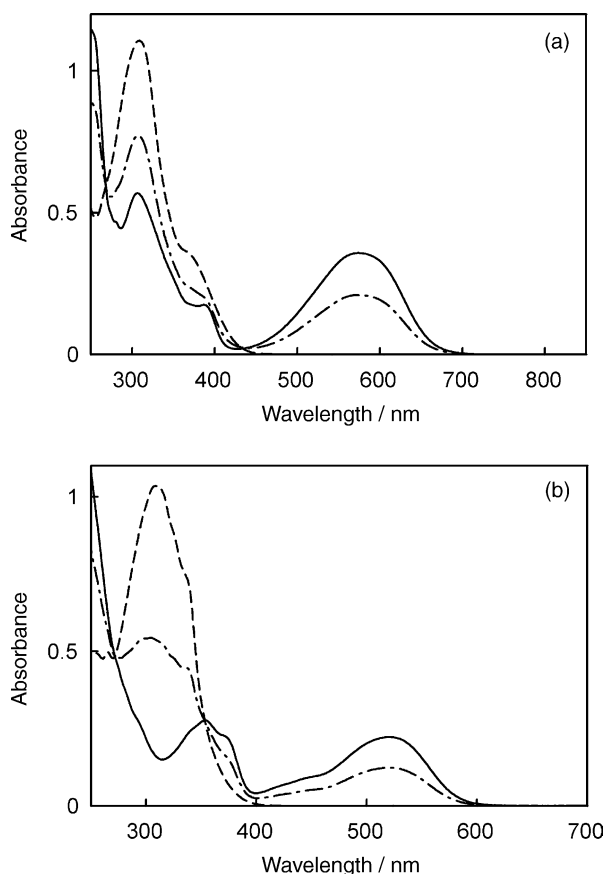


Figure 1. Absorption spectral change of **1** (2.2×10^{-5} M) (a) and **4** (2.0×10^{-5} M) (b) in hexane by photoirradiation: open-ring isomers (---), closed-ring isomers (—), and the mixture in the photostationary state under irradiation with 313-nm light (— · —).

Figure 1a shows the absorption spectra of **1a** and **1b** in hexane. **1a** has an absorption maximum at 309 nm in hexane. Upon irradiation with 313-nm light, the colorless solution of **1a** turned to blue, which is due to the formation of the closed-ring isomer **1b**.¹¹ The photo-generated **1b** was isolated by HPLC and the spectrum is shown in the figure. The blue color of **1b** in hexane disappeared upon irradiation with visible light ($\lambda > 500$ nm) and the absorption spectrum returned to

that of **1a**. The conversion from **1a** to **1b** in the photostationary state upon irradiation with 313-nm light was 56%. Thermal decoloration of **1b** was not observed even after a day at room temperature. The visible absorption maximum of **1b** was observed at 575 nm, which is the same as the methyl derivative **3b**.¹² In addition, the absorption coefficient of **1b** was also almost similar to that of **3b**.¹² These results mean that the phenylethynyl groups at the reactive carbons do not affect the main electronic structure of the closed-ring isomer compared with diarylethenes having alkoxy^{13–15} and cyano¹⁶ groups at the reactive carbons. Diarylethenes **2**,¹⁷ **4**,¹⁸ and **5**¹⁹ showed the photochromic behavior similar to **1**, and ethynyl substituents did not cause any spectral change of the closed-ring isomers even in benzothienylethenes **4** and **5**. The spectral data of each diarylethene are summarized in Table 1. The absorption spectra of the closed-ring isomers were not affected by the ethynyl groups at the reactive carbons.

To examine the substituent effect on photochromic reactivity we measured cyclization and cycloreversion quantum yields of the diarylethenes in hexane at room temperature. Table 1 summarizes the quantum yields of **1–6**. The cyclization quantum yields decreased by the introduction of the ethynyl groups. On the other hand, the substituents tend to increase the cycloreversion quantum yields. Introduction of ethynyl groups at the reactive carbons is an efficient approach to enhance the cycloreversion reactivity.

The ethynyl derivatives have long arms at the reactive carbons, which is different from most of the diarylethenes synthesized so far. X-ray crystallographic analysis of **1a** and **1b** was carried out to know the geometrical structure of the open- and closed-ring isomers. Figure 2 shows the ORTEP drawings of **1a**²¹ and **1b**.²² As can be seen from the side views, the geometrical shapes of **1a** and **1b** are quite different. The distance between the reactive carbon atoms of **1a** was determined to be 0.344 nm, which is close enough for a photocyclization reaction to take place inside the crystal.²³ However, **1** did not show any photochromism in the crystalline state. The unit cell volume per molecule expands from 803.4 \AA^3 (**1a**)²¹ to 852.8 \AA^3 (**1b**)²² in the photoisomer-

Table 1. Absorption characteristics and photoreactivity^a of diarylethenes in hexane

	λ_{max} (nm) ^b	ϵ ($\text{M}^{-1} \text{cm}^{-1}$) ^c	$\Phi_{\text{a} \rightarrow \text{b}}$ ^d		λ_{max} (nm) ^e	ϵ ($\text{M}^{-1} \text{cm}^{-1}$) ^f	$\Phi_{\text{b} \rightarrow \text{a}}$ ^g	Conversion (%) ^h
1a	309	49,000	0.17	1b	575	16,000	0.32	56
2a	298	48,000	0.41	2b	575	16,000	0.27	76
3a ¹²	280	35,600	0.59	3b ¹²	575	15,600	0.013	97
4a	309	49,000	0.13	4b	520	11,000	0.55	55
5a	278	33,000	0.21	5b	520	9600	0.58	41
6a ²⁰	258	14,000	0.35	6b ²⁰	517	9100	0.35	45

^a Standard deviation of the experimental error: $\pm 10\%$.

^b Absorption maxima of the open-ring isomers in the UV region.

^c Absorption coefficients of the open-ring isomers at the absorption maxima in the UV region.

^d Photocyclization quantum yields.

^e Absorption maxima of the closed-ring isomers in the visible region.

^f Absorption coefficients of the closed-ring isomers at the absorption maxima in the visible region.

^g Photocycloreversion quantum yields.

^h Conversion from the open- to the closed-ring isomers in the photostationary state under irradiation with 313-nm light.

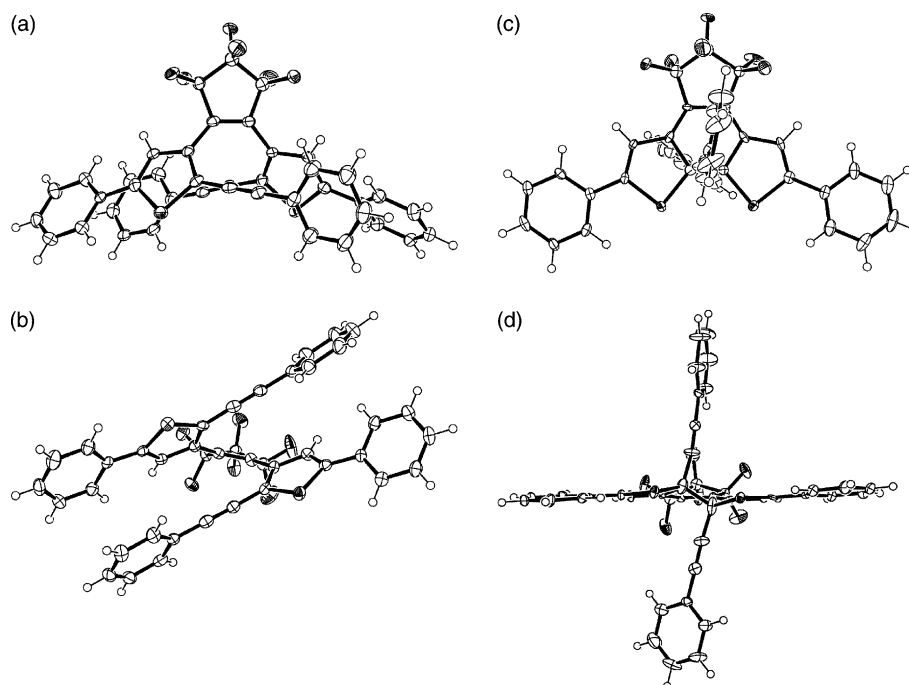


Figure 2. ORTEP drawings of top (a) and side (b) views of **1a**, and top (c) and side (d) views of **1b**, showing 50% probability displacement ellipsoids.

ization process. The atomic orbitals of the reactive carbon atoms convert from sp^2 to sp^3 , and the bond angle changes in the cyclization process. The phenylethynyl groups which stack with phenyl groups on opposite side of thiophene moieties by intramolecular aromatic interactions in **1a** (Fig. 2b) leave far from the phenyl groups and locate nearly perpendicular to the main molecular plane of **1b** (Fig. 2d).

Acknowledgements

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- 1a**: Yellow crystals: mp 176.0–177.0 °C; ^1H NMR (200 MHz, CDCl_3) δ 7.1–7.3 (m, 22H); MS m/z (M^+) 692. Anal. Calcd for $\text{C}_{41}\text{H}_{22}\text{F}_6\text{S}_2$: C, 71.09; H, 3.20. Found: C, 71.07; H, 3.16.
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- 4a**: Two polymorphic crystals, colorless and yellow crystals, were obtained from **4a**. Both were identified by **4a** by X-ray crystallography: mp 213.5–214.5 °C (colorless crystals); ^1H NMR (200 MHz, CDCl_3) δ 6.9–7.8 (m, 18H); MS m/z (M^+) 640. Anal. Calcd for $\text{C}_{37}\text{H}_{18}\text{F}_6\text{S}_2$: C, 69.37; H, 2.83. Found: C, 69.03; H, 2.74.
- 2a**: Yellow crystals: mp 98.0–99.0 °C; ^1H NMR (200 MHz, CDCl_3) δ 0.8 (t, $J = 7$ Hz, 6H), 1.4 (sex, $J = 7$ Hz, 4H), 2.1 (t, $J = 7$ Hz, 4H), 7.3–7.6 (m, 12H); MS m/z (M^+) 624. Anal. Calcd for $\text{C}_{35}\text{H}_{26}\text{F}_6\text{S}_2$: C, 67.29; H, 4.20. Found: C, 67.36; H, 4.24.
- 5a**: Colorless crystals: mp 149.0–150.0 °C; ^1H NMR (200 MHz, CDCl_3) δ 1.1 (t, $J = 7$ Hz, 6H), 1.6 (sex, $J = 7$ Hz, 4H), 2.4 (t, $J = 7$ Hz, 4H), 7.2–7.8 (m, 8H); MS m/z (M^+) 572. Anal. Calcd for $\text{C}_{31}\text{H}_{22}\text{F}_6\text{S}_2$: C, 65.02; H, 3.87. Found: C, 65.03; H, 3.85.
- 1b** was isolated by HPLC (silica gel; hexane/ethyl acetate = 90/10 as the eluent). **1a** and **1b** were eluted at 20 and 32 min, respectively.
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- 2b** was isolated by HPLC (silica gel; hexane/ethyl acetate = 99/1 as the eluent). **2a** and **2b** were eluted at 29 and 41 min, respectively.

18. **4b** was isolated by HPLC (silica gel; hexane/ethyl acetate = 90/10 as the eluent). **4a** and **4b** were eluted at 26 and 35 min, respectively.
19. **5b** was isolated by HPLC (silica gel; hexane/ethyl acetate = 99/1 as the eluent). **5a** and **5b** were eluted at 27 and 30 min, respectively.
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21. Crystal data for **1a**: $C_{41}H_{22}F_6S_2$, MW = 692.73, monoclinic, space group $P2_1/c$, $Z = 4$, $T = 123(2)$ K, $a = 16.522(4)$ Å, $b = 10.594(2)$ Å, $c = 18.586(4)$ Å, $\beta = 98.949(4)^\circ$, $V = 3213.6(12)$ Å³, goodness of fit = 0.964, $R1[I > 2\sigma(I)] = 0.0527$, $wR2(\text{all data}) = 0.1339$. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 219008.
22. Crystal data for **1b**: $C_{41}H_{22}F_6S_2$, MW = 692.73, monoclinic, space group $P2_1/n$, $Z = 4$, $T = 123(2)$ K, $a = 11.015(4)$ Å, $b = 26.499(10)$ Å, $c = 11.902(4)$ Å, $\beta = 100.955(6)^\circ$, $V = 3411(2)$ Å³, goodness of fit = 1.020, $R1[I > 2\sigma(I)] = 0.0623$, $wR2(\text{all data}) = 0.1690$. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 219009.
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