



Single-Crystalline Photochromism of a Diarylethene Dimer

Seiya Kobatake,* Shunpei Kuma, and Masahiro Irie*

Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, Hakozaki 6-10-1, Higashi-ku, Fukuoka 812-8581

Received October 28, 2003; E-mail: irie@cstf.kyushu-u.ac.jp

A fluorene derivative having two diarylethene units at the 9,9'-positions was synthesized, and the photochromic behavior was examined in a single-crystalline phase as well as in solution. Upon irradiation with ultraviolet light ($\lambda = 313$ nm), a hexane solution of the diarylethene dimer (**1a**) turned blue. The blue solution was found to contain the one closed-ring form dimer (**1b**) and the two closed-ring form dimer (**1c**). Both **1b** and **1c** returned to **1a** upon irradiation with visible light ($\lambda > 500$ nm). The photocyclization quantum yields of **1a** to **1b** and **1b** to **1c** were determined to be 0.46 and 0.29, respectively. The photocycloreversion quantum yields of **1c** to **1b** and **1b** to **1a** were 5.8×10^{-3} . The single crystal of the dimer exhibited photochromism. The diarylethene chromophores were aligned almost perpendicular to each other in the crystal, and one of the units in the dimer could be selectively isomerized by irradiation with linearly polarized light.

Photochromism is a reversible photoisomerization process of a chemical species between two isomers that have different absorption spectra.^{1,2} Diarylethenes with heterocyclic aryl rings belong to a class of thermally irreversible photochromic compounds and are the most promising candidates for optoelectronic devices, such as optical memory,^{3–5} photooptical switching,^{6–8} and displays,^{9–11} because of their fatigue-resistant property.^{12,13} Recently, various types of diarylethene dimers connected with a single bond,¹⁴ phenylene,^{15,16} ethynylene,¹⁷ or diyne¹⁸ were synthesized. In most cases, only one of the diarylethene units can convert to the closed-ring form upon irradiation with ultraviolet light. When the photogenerated dimers having one open- and one closed-ring form units are irradiated with ultraviolet light, the intramolecular excited energy transfer from the open-ring form unit to the closed-ring form one prohibits the formation of the two closed-ring form dimers. The dimers connected with a phenylene group can convert to the two closed-ring form dimers.^{15,16}

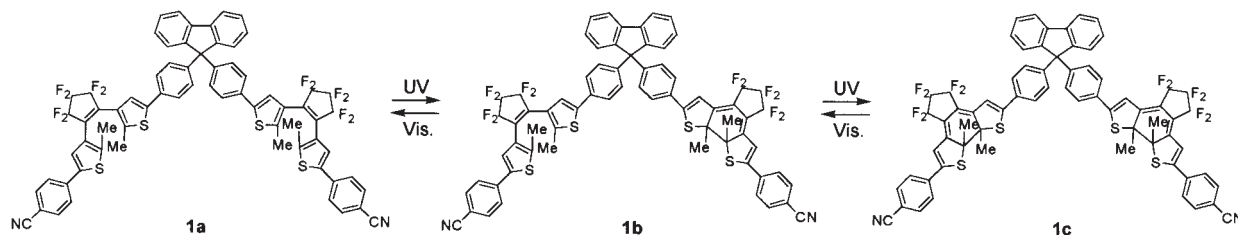
Recently, we have developed thermally irreversible and fatigue-resistant photochromic diarylethene crystals.^{4,10,11,19–30} The photoinduced coloration–decoloration cycles of the crystals can be repeated more than 10^4 times while maintaining the shape of the single crystals, and the photogenerated colored states are stable even at 100 °C. One of the characteristic properties of the single crystals is that the reaction of each molecule can be controlled with linearly polarized light. When diaryl-

ethene molecules are packed in a herringbone structure, as observed in a crystal of 1,2-bis(5-*p*-methoxyphenyl-2-methyl-3-thienyl)perfluorocyclopentene, the polarized light can induce a reaction of the molecules along the polarized direction, because the closed-ring isomers have an electronic transition moment in the direction of the long axis of the molecules. Crystal engineering to control the alignment of molecules is useful not only to endow various functions, but also to control the reaction of the crystals.

We designed a diarylethene dimer (**1a**) as shown in Scheme 1. Two diarylethene chromophores are connected to fluorene, and there is no conjugation between the two diarylethene units in the dimer. In the present work, we examined the photochromic reactivity of **1a** in solution and in the single-crystalline phase upon irradiation with linearly polarized light.

Results and Discussion

Photochromism in Hexane. Figure 1 shows the absorption spectral change of dimer **1a** in hexane. The open-ring form dimer **1a** has an absorption maximum at 309 nm. Upon irradiation with 313-nm light, the colorless hexane solution of **1a** turned blue, in which an absorption maximum was observed at 595 nm. The blue color is due to the formation of the closed-ring forms (**1b** and **1c**). The blue-colored solution was analyzed by high-performance liquid chromatography (HPLC)



Scheme 1. A diarylethene dimer linked by fluorene.

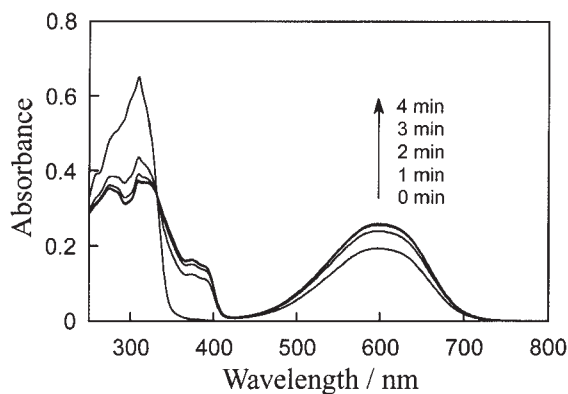


Fig. 1. Absorption spectral change of dimer **1a** (6.6×10^{-6} M) in hexane upon irradiation with 313-nm light.

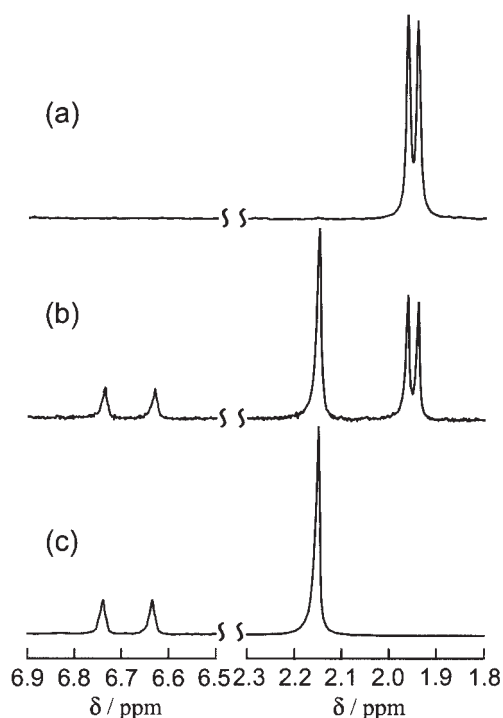


Fig. 2. ^1H NMR spectra of **1a** (a), **1b** (b), and **1c** (c) in the range of 1.8–2.3 ppm and 6.5–6.9 ppm.

with silica-gel column using hexane and ethyl acetate (9:1) as the eluent. The absorption intensity change was monitored at 330 nm, which is the isosbestic point. The open-ring form dimer **1a** was eluted at 60 min. Two colored isomers were eluted at 41 and 50 min. Each peak was isolated and analyzed by ^1H NMR spectroscopy.

Figure 2 shows the ^1H NMR spectra in the range of methyl protons and olefinic protons. The open-ring form dimer **1a** has two peaks at 1.94 and 1.96 ppm, which are due to the methyl protons at the reactive carbons. The ^1H NMR spectrum of an isomer eluted at 50 min is shown in Fig. 2b. In addition to the peaks at 1.94 and 1.96 ppm, new peaks appeared at 2.15, 6.63, and 6.74. The peak intensity ratio at 1.94, 1.96, 2.15, 6.63, and 6.74 ppm was 3:3:6:1:1. This indicates that the isomer has one open- and one closed-ring form units, and is assigned to **1b**. An isomer eluted at 41 min has no peak around 1.95 ppm. This in-

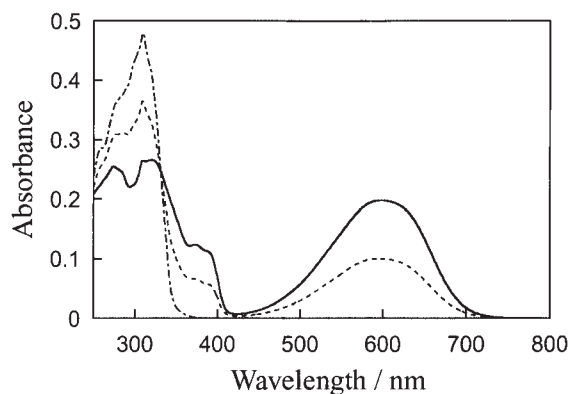


Fig. 3. Absorption spectra of **1a** (---), **1b** (---), and **1c** (—) in hexane (4.9×10^{-6} M).

Table 1. Absorption Maxima and Coefficients of **1a**, **1b**, and **1c** in Hexane

	$\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1} \text{cm}^{-1}$)
1a	309 (98500)
1b	309 (74800), 595 (20600)
1c	274 (52300), 320 (54600), 595 (40600)

dicates that the isomer has no open-ring form unit, and is assigned to **1c**. In isomer **1c**, both diarylethene units are converted to the closed-ring form.

Figure 3 shows the absorption spectra of **1a**, **1b**, and **1c** in hexane. The absorption maxima and coefficients of **1a**, **1b**, and **1c** are given in Table 1. The absorption maximum of **1b** (595 nm) is the same as that of **1c**. In addition, the absorption coefficient of **1c** ($40600 \text{ M}^{-1} \text{cm}^{-1}$) is twice as large as that of **1b** ($20600 \text{ M}^{-1} \text{cm}^{-1}$). This indicates that two diarylethene units are independent, and that there is no intramolecular interaction between them. In the photostationary state upon irradiation with 313-nm light, the ratio of **1a**, **1b**, and **1c** was 0.1:3.5:96.4. The dimer having two closed-ring form units was efficiently formed.

Quantum Yield. The photocyclization and cycloreversion quantum yields of the dimer were measured in hexane at room temperature. At first, the photocycloreversion reactions of **1c** to **1b** and **1b** to **1a** were examined. A hexane solution of **1c** (7.5×10^{-6} M) was irradiated with 595-nm light. The rates of the photoreactions were followed by measuring the ratio change of **1a**, **1b**, and **1c** by HPLC. Figure 4 shows the time dependence of the formation of **1b** and **1a**. Dimer **1b** was first produced upon irradiation with visible light. Then, **1a** was produced through **1b**. The experimental data were analyzed using the following equations:

$$dC_{1c}/dt = -I_{1c}\Phi_{1c \rightarrow 1b} \quad (1)$$

$$dC_{1b}/dt = I_{1c}\Phi_{1c \rightarrow 1b} - I_{1b}\Phi_{1b \rightarrow 1a} \quad (2)$$

$$dC_{1a}/dt = I_{1b}\Phi_{1b \rightarrow 1a} \quad (3)$$

where $I_{1c} = I_0(1 - 10^{-A_{1c}})$ and $I_{1b} = I_0(1 - 10^{-A_{1b}})$. In the above equations, I_0 is the intensity of light, and $\Phi_{1c \rightarrow 1b}$ and $\Phi_{1b \rightarrow 1a}$ are the photoreaction quantum yields of **1c** to **1b** and **1b** to **1a**, respectively. A_{1c} and A_{1b} are the absorbances of **1c** and **1b**, respectively, at the irradiation wavelength (595 nm).

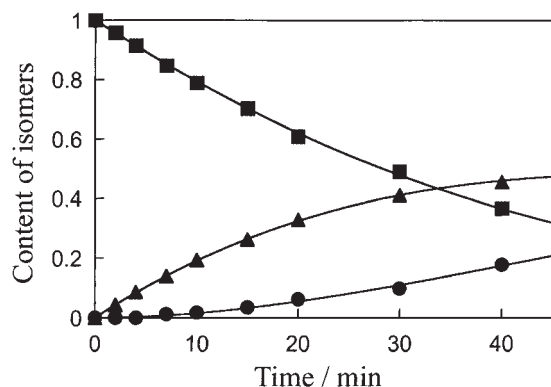


Fig. 4. Changes in the content of the isomers, **1a** (●), **1b** (▲), and **1c** (■) in the photocycloreversion reaction of **1c** upon irradiation with 595-nm light in hexane.

C_{1c} , C_{1b} , and C_{1a} are the concentrations of **1c**, **1b**, and **1a**, respectively.

A numerical simulation according to differential equations was carried out; the result is shown as solid lines in Fig. 4. The light intensity (I_0) was calibrated by the photoreaction of furylfulgide in hexane. The parameters used were as follows: $I_0 = 5.91 \times 10^{-8}$ einstein $\text{cm}^{-2} \text{s}^{-1}$, $\epsilon_{1b(595)} = 20600 \text{ M}^{-1} \text{cm}^{-1}$, $\epsilon_{1c(595)} = 40600 \text{ M}^{-1} \text{cm}^{-1}$.

The quantum yields of **1c** to **1b** and **1b** to **1a** were almost the same, which are both 5.8×10^{-3} . This indicates that there is no intramolecular interaction of the two diarylethene units.

A photocyclization quantum yield measurement was carried out as follows. Dimer **1a** was dissolved in hexane and the solution was irradiated with ultraviolet light ($\lambda = 313 \text{ nm}$). Upon irradiation with 313-nm light, **1b** was produced at first following a decrease of **1a**. During the early stage of the photoreaction, the formation of **1c** was negligible. **1c** was gradually produced. The experimental data were analyzed by the following equations:

$$dC_{1a}/dt = -I_{1a}\Phi_{1a \rightarrow 1b} + I_{1b}\Phi_{1b \rightarrow 1a} \quad (4)$$

$$dC_{1b}/dt = I_{1a}\Phi_{1a \rightarrow 1b} - I_{1b}\Phi_{1b \rightarrow 1a} - I_{1b}\Phi_{1b \rightarrow 1c} + I_{1c}\Phi_{1c \rightarrow 1b} \quad (5)$$

$$dC_{1c}/dt = I_{1b}\Phi_{1b \rightarrow 1c} - I_{1c}\Phi_{1c \rightarrow 1b} \quad (6)$$

where $I_{1a} = I_0(1 - 10^{-A_{1a}})$, $I_{1b} = I_0(1 - 10^{-A_{1b}})$, and $I_{1c} = I_0(1 - 10^{-A_{1c}})$. In the above equations, I_0 is the intensity of light and $\Phi_{1a \rightarrow 1b}$, $\Phi_{1b \rightarrow 1c}$, $\Phi_{1c \rightarrow 1b}$, and $\Phi_{1b \rightarrow 1a}$ are the reaction quantum yields of **1a** to **1b**, **1b** to **1c**, **1c** to **1b**, and **1b** to **1a**, respectively. A_{1a} , A_{1b} , and A_{1c} are the absorbances at the irradiation wavelength (313 nm). C_{1a} , C_{1b} , and C_{1c} are the concentrations of **1a**, **1b**, and **1c**, respectively.

The differential equations in Eq. (4)–(6) were numerically solved under the conditions that the photocycloreversion quantum yield of **1c** to **1b** is 5.8×10^{-3} , and the quantum yield of **1b** to **1a** at 313 nm is 2.1×10^{-3} ($= 5.8 \times 10^{-3} \times (\epsilon_{1c(313)}/(\epsilon_{1c(313)} + \epsilon_{1a(313)}))$). In the simulation, it was assumed that the photocycloreversion quantum yield does not depend on the irradiation wavelength. The intramolecular energy transfer of the open- to the closed-ring forms in **1b** was considered to be less favorable because of non- π -conjugation and non-coplanarity between the two diarylethene units. The photons absorbed in

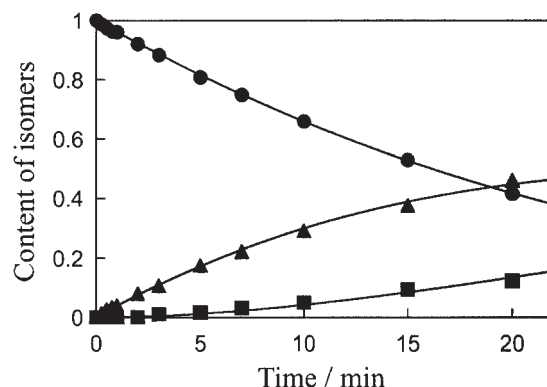


Fig. 5. Changes in the content of the isomers, **1a** (●), **1b** (▲), and **1c** (■) in the photocyclization reaction of **1a** upon irradiation with 313-nm light in hexane.

the closed-ring form unit in **1b** have a chance to isomerize **1b** to **1a**. The result is shown as solid lines in Fig. 5. The light intensity (I_0) was calibrated by the photoreaction of furylfulgide in hexane. The parameters used were as follows: $I_0 = 5.64 \times 10^{-10}$ einstein $\text{cm}^{-2} \text{s}^{-1}$, $\epsilon_{1a(313)} = 92600 \text{ M}^{-1} \text{cm}^{-1}$, $\epsilon_{1b(313)} = 71500 \text{ M}^{-1} \text{cm}^{-1}$, $\epsilon_{1c(313)} = 54200 \text{ M}^{-1} \text{cm}^{-1}$.

The photocyclization quantum yields of **1a** to **1b** and **1b** to **1c** were determined to be 0.46 and 0.29, respectively. The difference of these quantum yields is attributed to an intramolecular filter effect. The ratio of the absorption coefficients of the open- and closed-ring form units in **1b** at 313 nm is considered to be the same as the ratio of those of **1a** and **1c**. The ratio is 1:0.54. 65% of the photons absorbed in **1b** can be used for the photocyclization reaction to **1c**. Therefore, the actual photocyclization quantum yield of **1b** to **1c** for the only open-ring form unit in **1b** is determined to be 0.45 ($= 0.29/0.65$). This value is comparable with the photocyclization quantum yield of **1a** to **1b** (0.46). It can be concluded that the reactivity of the two diarylethene units is the same, even if one of the units is in the closed-ring form and that the excited energy in the open-ring form unit in **1b** is not transferred to the closed-ring form unit by an intramolecular excited energy transfer.

Photochromism in Crystal. A single crystal with good crystallinity was obtained by recrystallization from a acetone/cyclohexane solution. The crystal was analyzed by X-ray crystallography. The crystallographic data are given in Table 2. The crystal has a triclinic system and a space group of $P\bar{1}$. Twelve cyclohexane molecules and four dimer molecules were included in a unit cell. Figure 6 shows an ORTEP drawing of the diarylethene dimer. The fluorene moieties are stacked by the π - π intermolecular interaction. Two diarylethenes in the dimer are aligned almost perpendicular to each other. The photochromic reactivity of diarylethene crystals depends on the distance between the reactive carbon atoms.²⁸ The dimer has distances of 3.41–3.52 Å. This indicates that the dimer can undergo photochromism in the crystalline phase.

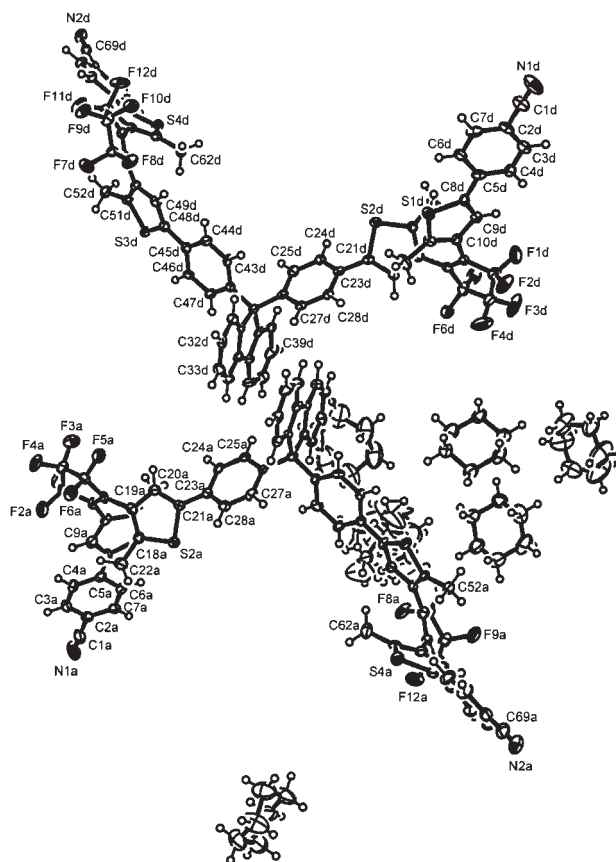
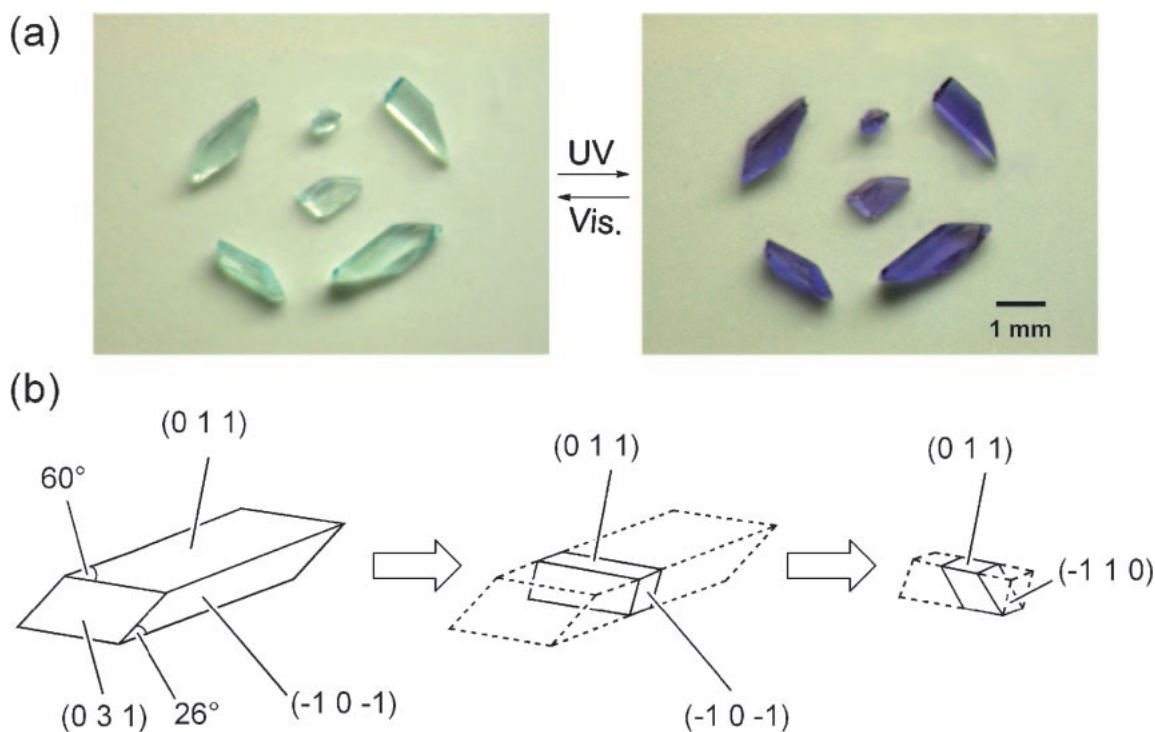
Upon irradiation with 366-nm light, the crystal turned blue, as shown in Fig. 7a. The photogenerated blue color of the crystals disappeared upon irradiation with visible light ($\lambda > 500 \text{ nm}$). The polarized absorption spectra of the crystal were measured under linearly polarized light. The crystal was irradiated on the $(-1\ 1\ 0)$ face with non-polarized 366-nm light. The

Table 2. X-ray Crystallographic Data of **1a**

Empirical formula	C ₆₉ H ₄₀ F ₁₂ N ₂ S ₄ •3C ₆ H ₁₂
Formula weight	1505.78
Temperature	123(2) K
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
<i>a</i>	18.028(7) Å
<i>b</i>	19.901(7) Å
<i>c</i>	22.371(8) Å
α	75.943(7)°
β	78.877(7)°
γ	88.197(7)°
<i>V</i>	7639(5) Å ³
<i>Z</i>	4
Density (calculated)	1.309 g cm ⁻³
Goodness-of-fit on F^2	0.850
Final <i>R</i> indices [$I > 2\sigma(I)$]	$R1 = 0.0533$
<i>R</i> indices (all data)	$wR2 = 0.1251$

($-1\ 1\ 0$) surface was prepared by cutting the crystal, as shown in Fig. 7b. Figure 8 shows the polarized absorption spectra at angles of 0, 45, and 90°. The absorption maximum was observed at 615 nm. The absorbance at 615 nm was almost the same as that at 0 and 45°. Polar plots of the absorbance at 615 nm are also shown in Fig. 8b. Well-defined absorption anisotropy was not observed. The two diarylethene molecules in the dimer are packed in two different directions, which are almost perpendicular to each other. This is the reason why absorption anisotropy was not observed.

Partially Bleaching Reaction in Crystal. Figure 9 shows the molecular packing of the diarylethenes viewed normal to

Fig. 6. ORTEP drawing of **1a** showing the 50% probability displacement ellipsoids.Fig. 7. Photographs of crystal **1a** before and after photoirradiation with 366-nm light (a) and the crystal shape of **1a** (b).

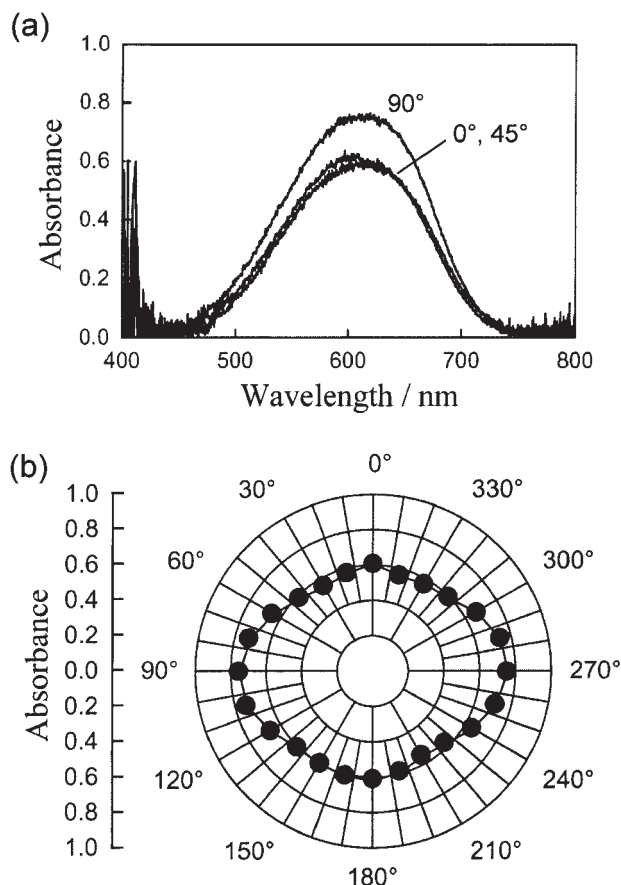


Fig. 8. Polarized absorption spectra (a) and the polar plots of the absorbance at 615 nm (b) after irradiation with non-polarized 366-nm light.

the $(-1\ 1\ 0)$ face. The long axes of the diarylethene chromophores in the dimer are aligned at an angle of 75° to each other, as shown by the blue and red arrows, when the crystal is viewed from the $(-1\ 1\ 0)$ face. This suggests that linearly polarized light can selectively isomerize the closed-ring isomers to the open-ring isomers. A colorless dimer crystal was irradiated with non-polarized 366-nm light to give a blue-colored crystal. When the crystal was irradiated with linearly polarized light ($\lambda > 570$ nm) in the direction of 45° , the colored isomers along the polarized light were preferentially bleached, and the molecules oriented perpendicularly to the irradiated polarized light remained. In other words, the diarylethene molecules shown by the red arrows in Fig. 9 were preferentially bleached under polarized light in the direction of 45° . The polarized absorption spectra and the polar plots are shown in Fig. 10. The order parameter $((A_{\parallel} - A_{\perp}) / (A_{\parallel} + 2A_{\perp}))$ was determined to be 0.51 after partial bleaching, though the value was less than 0.1 before bleaching. The increase in the order parameter up to 0.51 suggests that the partially bleaching reaction took place under the polarized light.

Conclusions

A fluorene derivative having two diarylethene units at the 9,9'-positions underwent photochromism in solution as well as in the single-crystalline phase. The two diarylethene units in the dimer are almost perpendicular to each other. Photoirra-

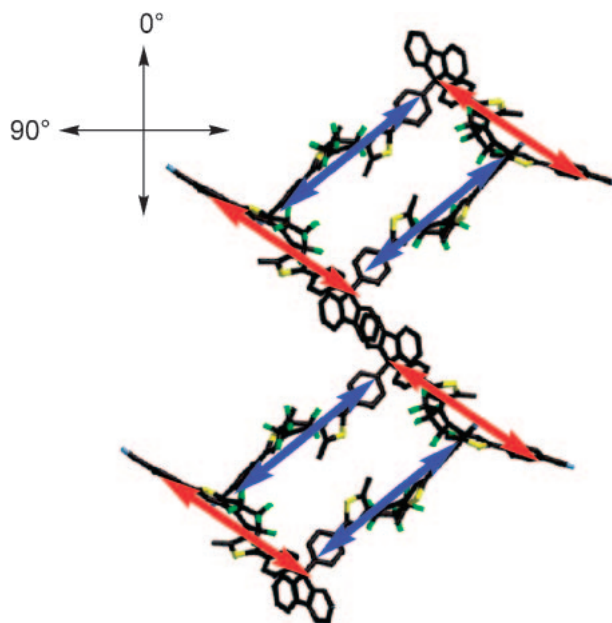


Fig. 9. Molecular packing of **1a** viewed from the $(-1\ 1\ 0)$ face. Red and blue arrows show long axes of the diarylethene chromophores.

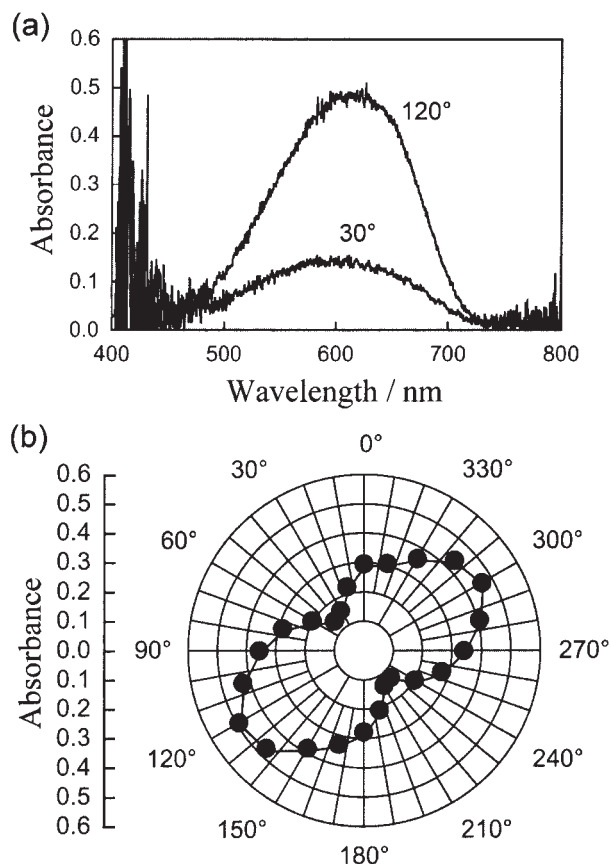


Fig. 10. Polarized absorption spectra (a) and the polar plots of the absorbance at 615 nm (b) after partially photobleaching upon irradiation with polarized 570-nm light.

diation with linearly polarized light induced partial bleaching of one of the two closed-ring forms. Such a crystal can be applied to optoelectronic devices, such as photoswitchable polarizers and multi-recording materials.

Experimental

General. The solvents used were of spectroscopic grade and purified by distillation before use. ^1H NMR spectra were recorded on a Varian Gemini 200 spectrometer (200 MHz). Tetramethylsilane was used as an internal standard. Mass spectra were taken with a Shimadzu GCMS-QP5050A gas chromatography–mass spectrometer. Absorption spectra in solution were measured with a Hitachi U-3410 absorption spectrophotometer. Photoirradiation was carried out using an Ushio 500 W super high-pressure mercury lamp or an Ushio 500 W xenon lamp as the light source. Monochromatic light was obtained by passing the light through a monochromator (Ritsu MV-10N). Absorption spectra in a single-crystal-line phase were measured using a Leica DMLP polarizing microscope connected with a Hamamatsu PMA-11 photodetector. The polarizer and analyzer were set in parallel to each other. Photoirradiation was carried out using a 75 W xenon lamp. The wavelength of the light was selected by passing the light through a band-pass filter. Diarylethene dimer **1a** was synthesized according to Scheme 2.

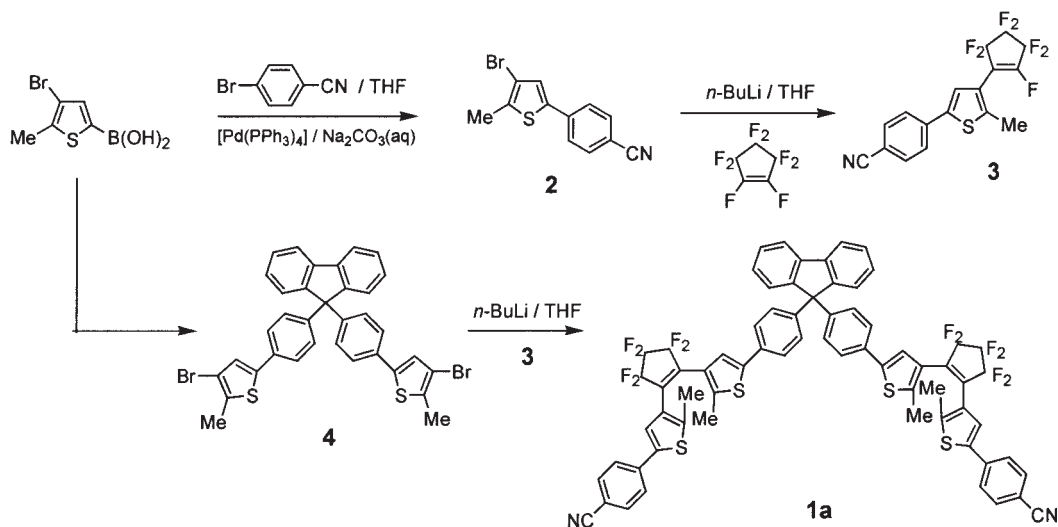
3-Bromo-5-*p*-cyanophenyl-2-methylthiophene (2). To a dry THF solution (300 mL) containing 3,5-dibromo-2-methylthiophene (30 g, 0.12 mol) was added a 15% *n*-BuLi hexane solution (77 mL, 0.12 mol) at -78°C under an argon atmosphere, and the reaction mixture was stirred for 2 h at that low temperature. Tributyl borate (47 mL, 0.18 mol) was slowly added to the reaction mixture at -78°C , and the mixture was stirred for 2 h at this temperature. A small amount of water was added to the mixture. To the reaction mixture were added 20 wt % $\text{Na}_2\text{CO}_3\text{aq}$ (280 mL), 4-bromobenzonitrile (21 g, 0.12 mol), and $[\text{Pd}(\text{PPh}_3)_4]$ (2.0 g, 1.3 mmol). The mixture was refluxed for 12 h at 80°C . The mixture was neutralized with HCl, and then extracted with diethyl ether. The organic layer was dried over MgSO_4 , filtrated, and concentrated. The residue was purified by silica-gel column chromatography using hexane/chloroform (1:1) as the eluent, and recrystallize from hexane/chloroform (10:1) to give **2** (13 g, 39%) as crystals. mp =

$124.8\text{--}125.4^\circ\text{C}$; ^1H NMR (200 MHz, CDCl_3 , 25°C , TMS) δ 2.45 (s, 3H, CH_3), 7.23 (s, 1H, thienyl proton), 7.5–7.7 (m, 4H, Ar). MS m/z 277, 279 (M^+). Anal. Calcd for $\text{C}_{12}\text{H}_8\text{BrNS}$: C, 51.81; H, 2.90%. found: C, 51.87; H, 2.86%.

1-(5-*p*-Cyanophenyl-2-methyl-3-thienyl)heptafluorocyclopentene (3). To a dry THF solution (600 mL) containing **2** (10 g, 0.036 mol) was added a 15% *n*-BuLi hexane solution (24 mL, 0.038 mol) at -78°C under an argon atmosphere, and the reaction mixture was stirred for 1 h at that low temperature. Octafluorocyclopentene (13 mL, 0.040 mol; Nippon Zeon) was added to the reaction mixture at -78°C , and the mixture was stirred for 2.5 h at this temperature. The reaction was stopped by the addition of water. The product was extracted with diethyl ether. The organic layer was dried over MgSO_4 , filtrated, and concentrated. The residue was purified by column chromatography on silica gel using hexane/ethyl acetate (95:5) as the eluent and by recrystallization from hexane to give **1a** (3.3 g, 24%) as colorless crystals. mp = $92\text{--}93^\circ\text{C}$; ^1H NMR (200 MHz, CDCl_3 , 25°C , TMS) δ 2.51 (d, $J = 3.0$ Hz, 3H, CH_3), 7.36 (s, 1H, thienyl proton), 7.6–7.8 (m, 4H, Ar). MS m/z 391 (M^+). Anal. Calcd for $\text{C}_{17}\text{H}_8\text{F}_7\text{BrNS}$: C, 52.18; H, 2.06; N, 3.58%. Found: C, 52.37; H, 2.05; N, 3.62%.

9,9'-Bis[4-(4-bromo-5-methyl-2-thienyl)phenyl]fluorene (4). 4-Bromo-5-methylthienylboronic acid (4.9 g, 0.022 mol) was added into a flask containing THF (120 mL), 20 wt % $\text{Na}_2\text{CO}_3\text{aq}$ (50 mL), 9,9'-bis(4-bromophenyl)fluorene (3.5 g, 0.0074 mol), and $[\text{Pd}(\text{PPh}_3)_4]$ (1.3 g, 1.1 mmol). The mixture was refluxed for 12 h at 80°C , neutralized with HCl, and then extracted with diethyl ether. The organic layer was dried over MgSO_4 , filtrated, and concentrated. The residue was purified by silica-gel column chromatography using hexane/ethyl acetate (10:1) as the eluent and by HPLC on polystyrene-gel using chloroform as the eluent to give **4** (2.3 g, 48%). ^1H NMR (200 MHz, CDCl_3 , 25°C , TMS) δ 2.39 (s, 6H, CH_3), 7.03 (s, 2H, thienyl proton), 7.1–7.5 (m, 14H, Ar), 7.78 (d, $J = 7.2$ Hz, 2H, Ar). MS m/z 666, 668, 670 (1:2:1) (M^+). Anal. Calcd for $\text{C}_{35}\text{H}_{24}\text{Br}_2\text{S}_2$: C, 62.88; H, 3.62%. Found: C, 62.95; H, 3.62%.

Diarylethene Dimer (1a). To a dry THF solution (10 mL) containing **4** (0.50 g, 0.75 mmol) was added a 15% *n*-BuLi hexane solution (1.0 mL, 1.6 mmol) at -78°C under an argon atmosphere, and the reaction mixture was stirred for 30 min at the low temperature. Compound **3** (0.73 g, 1.9 mmol) in dry THF (3 mL) was add-



Scheme 2. Synthetic route of diarylethene dimer **1a**.

ed to the reaction mixture at -78°C , and the resulting mixture was stirred for 1.5 h at this temperature. The reaction was stopped by the addition of water. The product was extracted with chloroform. The organic layer was dried over MgSO_4 , filtrated, and concentrated. The residue was purified by column chromatography on silica gel using hexane/ethyl acetate (95:5) as the eluent to give **1a** (0.76 g, 81%). $^1\text{H NMR}$ (200 MHz, CDCl_3 , 25°C , TMS) δ 1.94 (s, 6H, CH_3), 1.96 (s, 6H, CH_3), 7.2–7.5 (m, 18H, Ar), 7.6–7.7 (m, 8H, Ar), 7.80 (dd, $J = 1.2, 8.0$ Hz, 2H, Ar). MS m/z 1252 (M^+). Anal. Calcd for $\text{C}_{69}\text{H}_{40}\text{F}_{12}\text{N}_2\text{S}_4$: C, 66.12; H, 3.22; N, 2.24%. Found: C, 66.10; H, 3.24; N, 2.18%.

Closed-Ring Isomers of 1a (1b and 1c). **1b** and **1c** were isolated by passing a photoirradiated solution containing **1a**, **1b**, and **1c** through a HPLC (Hitachi L-7100 pump system equipped with a Hitachi L-7400 detector, a silica-gel column (Kanto, MightySil Si 60), and hexane/ethyl acetate (9:1) as the eluent). The retention times for **1a**, **1b**, and **1c** were 60, 50, and 41 min, respectively. **1b**: $^1\text{H NMR}$ (200 MHz, CDCl_3 , 25°C , TMS) δ 1.94 (s, 3H, CH_3), 1.97 (s, 3H, CH_3), 2.15 (s, 6H, CH_3), 6.63 (s, 1H, olefinic proton), 6.74 (s, 1H, olefinic proton), 7.2–7.5 (m, 16H, Ar), 7.6–7.7 (m, 8H, Ar), 7.81 (d, $J = 7.4$ Hz, 2H, Ar). **1c**: $^1\text{H NMR}$ (200 MHz, CDCl_3 , 25°C , TMS) δ 2.16 (s, 12H, CH_3), 6.64 (s, 2H, olefinic proton), 6.74 (s, 2H, olefinic proton), 7.2–7.5 (m, 14H, Ar), 7.6–7.7 (m, 8H, Ar), 7.81 (d, $J = 7.4$ Hz, 2H, Ar).

General Procedure of X-ray Crystallographic Analysis. An X-ray crystallographic analysis was performed using a Bruker SMART1000 CCD-based diffractometer (50 kV, 40 mA) with Mo $\text{K}\alpha$ radiation. The crystals were cooled at 123 K by a cryostat (Rigaku GN2). The data were collected as a series of ω -scan frames, each with a width of 0.3° /frame. The crystal-to-detector distance was 5.124 cm. Crystal decay was monitored by repeating the 50 initial frames at the end of data collection and analyzing the duplicate reflections. Data reduction was performed using SAINT software, which corrects for Lorentz and polarization effects, as well as decay. The cell constants were determined by a global refinement. The structures were solved by direct methods using SHELXS-86,³¹ and refined by full least-squares on F^2 using SHELXL-97.³² The positions of all hydrogen atoms were calculated geometrically and refined by the riding model. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number CCDC-230686.

This work was partly supported by the Grants-in-Aid for Scientific Research (S) (No. 15105006), Scientific Research on Priority Areas (Nos. 15033252 and 12131211), and the 21st century COE program from the Ministry of Education, Culture, Sports, Science and Technology. We thank Nippon Zeon Co., Ltd. for their supply of octafluorocyclopentene.

References

- 1 G. H. Brown, "Photochromism," Wiley-Interscience, New York (1971).
- 2 H. Dürr and H. Bouas-Laurent, "Photochromism: Molecules and Systems," Elsevier, Amsterdam (1990).
- 3 S. Kawata and Y. Kawata, *Chem. Rev.*, **100**, 1777 (2000).

- 4 T. Fukaminato, S. Kobatake, T. Kawai, and M. Irie, *Proc. Japan Acad., Ser. B*, **77**, 30 (2001).
- 5 M. Irie, T. Fukaminato, T. Sasaki, N. Tamai, and T. Kawai, *Nature*, **420**, 759 (2002).
- 6 K. Nakatani and J. A. Delaire, *Chem. Mater.*, **9**, 2682 (1997).
- 7 K. Matsuda and M. Irie, *J. Am. Chem. Soc.*, **122**, 8309 (2000).
- 8 K. Matsuda and M. Irie, *Chem.—Eur. J.*, **7**, 3466 (2001).
- 9 K. Morimitsu, K. Shibata, S. Kobatake, and M. Irie, *J. Org. Chem.*, **67**, 4574 (2002).
- 10 M. Morimoto, S. Kobatake, and M. Irie, *Adv. Mater.*, **14**, 1027 (2002).
- 11 M. Morimoto, S. Kobatake, and M. Irie, *J. Am. Chem. Soc.*, **125**, 11080 (2003).
- 12 M. Irie and K. Uchida, *Bull. Chem. Soc. Jpn.*, **71**, 985 (1998).
- 13 M. Irie, *Chem. Rev.*, **100**, 1685 (2000).
- 14 A. Peters and N. R. Branda, *Adv. Mater. Opt. Electron.*, **10**, 245 (2000).
- 15 K. Matsuda and M. Irie, *J. Am. Chem. Soc.*, **123**, 9896 (2001).
- 16 S. Kobatake and M. Irie, *Tetrahedron*, **59**, 8359 (2003).
- 17 T. Kaieda, S. Kobatake, H. Miyasaka, M. Murakami, N. Iwai, Y. Nagata, A. Itaya, and M. Irie, *J. Am. Chem. Soc.*, **124**, 2015 (2002).
- 18 K. Yagi and M. Irie, *Chem. Lett.*, **32**, 848 (2003).
- 19 M. Irie, K. Uchida, T. Eriguchi, and H. Tsuzuki, *Chem. Lett.*, **1995**, 899.
- 20 K. Uchida and M. Irie, *Chem. Lett.*, **1995**, 969.
- 21 a) S. Kobatake, T. Yamada, K. Uchida, N. Kato, and M. Irie, *J. Am. Chem. Soc.*, **121**, 2380 (1999). b) T. Yamada, S. Kobatake, K. Muto, and M. Irie, *J. Am. Chem. Soc.*, **122**, 1589 (2000). c) T. Yamada, S. Kobatake, and M. Irie, *Bull. Chem. Soc. Jpn.*, **73**, 2179 (2000).
- 22 S. Kobatake, M. Yamada, T. Yamada, and M. Irie, *J. Am. Chem. Soc.*, **121**, 8450 (1999).
- 23 a) M. Irie, T. Lifka, S. Kobatake, and N. Kato, *J. Am. Chem. Soc.*, **122**, 4871 (2000). b) T. Yamada, K. Muto, S. Kobatake, and M. Irie, *J. Org. Chem.*, **66**, 6164 (2000).
- 24 T. Kodani, K. Matsuda, T. Yamada, S. Kobatake, and M. Irie, *J. Am. Chem. Soc.*, **122**, 9631 (2000).
- 25 S. Yamamoto, K. Matsuda, and M. Irie, *Angew. Chem., Int. Ed.*, **42**, 1936 (2003).
- 26 K. Matsuda, K. Takayama, and M. Irie, *Chem. Commun.*, **2001**, 363.
- 27 M. Irie, S. Kobatake, and M. Horichi, *Science*, **291**, 1769 (2001).
- 28 a) K. Shibata, K. Muto, S. Kobatake, and M. Irie, *J. Phys. Chem. A*, **106**, 209 (2002). b) S. Kobatake, K. Uchida, E. Tsuchida, and M. Irie, *Chem. Commun.*, **2002**, 2804.
- 29 T. Yamada, S. Kobatake, and M. Irie, *Bull. Chem. Soc. Jpn.*, **75**, 167 (2002).
- 30 M. Morimoto, S. Kobatake, and M. Irie, *Chem.—Eur. J.*, **9**, 621 (2003).
- 31 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, **46**, 467 (1990).
- 32 G. M. Sheldrick, "SHELXL-97, Program for Crystal Structure Refinement," Universität Göttingen, Göttingen (1997).