J. Am. Chem. Soc. **2000,** *122,* 4871−4876

Photochromism of 1,2-Bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene in a Single-Crystalline Phase

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Contribution from the Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, and CREST, Japan Science and Technology Corporation, Hakozaki 6-10-1, Higashi-ku, Fukuoka 812-8581, Japan, and Institute of Advanced Material Study, Kyushu University, Kasugakoen 6-1, Fukuoka 816-8580, Japan

Received September 2, 1999. Revised Manuscript Received March 20, 2000

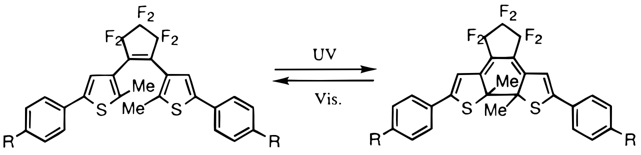
Abstract: 1,2-Bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene (**1a**) and their derivatives, 1,2-bis(2-methyl-5-*p*-tolyl-3-thienyl)perfluorocyclopentene (**2a**) and 1,2-bis(2-methyl-5-*p*-*tert*-butylphenyl-3-thienyl)-perfluorocyclopentene (**3a**), were found to undergo reversible photochromic reactions in the single-crystalline phase. Upon irradiation with 366 nm light the single crystals turned blue. The blue colored crystals returned to colorless by irradiation with visible light ($\lambda > 480$ nm). The substituents at para positions of the phenyl groups did not affect the rates of photocyclization reactions both in the single-crystalline phase and in hexane. Activation energies of the photocyclization reactions were almost zero. On the other hand, activation energies as much as 5−10 kJ mol^{-1} were observed in the photocycloreversion reactions in the single-crystalline phase. These values were smaller than those observed in solution, ca. 16 kJ mol^{-1}. Slow thermal cycloreversion reaction of the closed-ring isomer (**1b**) was observed above 150 °C. The activation energy was 139 kJ mol^{-1}.

Introduction

Photochromism is defined as a reversible transformation between two isomers having different absorption spectra by photoirradiation. Although many photochromic compounds have been so far reported,[1] compounds which show photochromic reactivity in the crystalline phase are rare.[2] Typical photochromic compounds, such as azobenzenes, spirobenzopyrans, and spirooxazines, require large geometrical structural or molecular volume changes in the photochromic reaction process. Therefore, the reactivity is lost in the rigid crystalline lattice. Reversible radical formations or hydrogen transfers are possible mechanisms for the crystalline photochromism; the former plays a role in the photochromism of triphenylimidazole dimers[3] and the latter in *N*-salicylideneanilines.[4] In these systems, photogenerated isomers are thermally unstable and return to the initial isomers in the dark. Crystalline photochromic systems which undergo thermally irreversible photochromic reactions are limited.[5,6]

Recently, we found that some dithienylperfluorocyclopentenes undergo thermally irreversible photochromic reactions even in the crystalline phase.[7−12] In the crystals the dithienylethenes are fixed in a reactive antiparallel conformation and undergo effective photocyclization reactions. The crystalline photochromic materials show a fatigue resistant character[13] and have promising potential for optoelectronic devices.

In this paper we have carried out kinetic study of photochromism of dithienylethenes **1**, **2**, and **3** in the single-crystalline phase. The reactivities in crystals were examined at various temperatures and compared with those in solution.



1a: R = H
2a: R = Me
3a: R = *t*-Bu

1b: R = H
2b: R = Me
3b: R = *t*-Bu

Results and Discussion

Photochromism in Solution. Figure 1 shows a typical absorption spectral change of **1a** in hexane upon ultraviolet light irradiation. The spectrum of the isolated colored isomer is also

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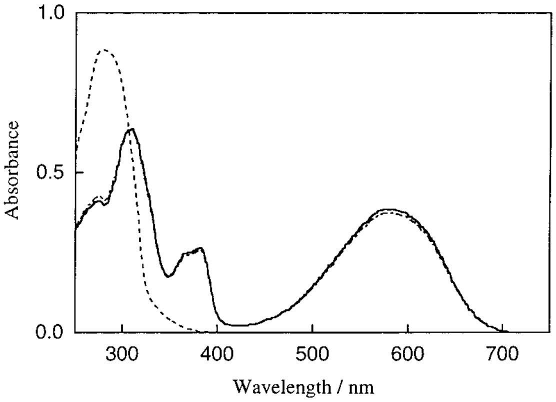
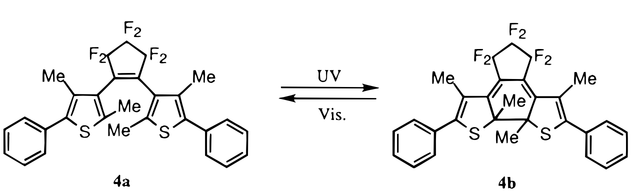


Figure 1. Absorption spectral change of **1** in hexane (2.4×10^{-5} M) upon irradiation with 313 nm light: **1a** (- - -), **1** in the photostationary state under irradiation with 313 nm light (— - —), and **1b** (—).

shown in Figure 1. Upon irradiation with 313 nm light the colorless hexane solution of **1a** turned blue, in which absorption maxima were observed at 306, 380, and 575 nm. The photostationary spectrum is almost the same as that of the colored isomer, indicating a high conversion from the colorless to the colored isomers by irradiation with 313 nm light. The blue colored solution returned colorless by irradiation with visible light ($\lambda > 450$ nm). The colored isomer was stable and could be isolated by HPLC (silica gel column, hexane). The molecular characteristics of the isomer were examined by ^{1}H NMR, mass spectrum, elemental analysis, and X-ray crystallography. All analysis data agreed with that of the closed-ring isomer **1b**. Similar spectral changes were observed for **2** and **3**. The absorption maxima and coefficients (ϵ) of the open- and closed-ring isomers for these three compounds are summarized in Table 1.

The quantum yields of cyclization and cycloreversion reactions were measured in hexane at room temperature, and also shown in Table 1. Any appreciable difference in the quantum yields was not observed among the three compounds. The cyclization quantum yield of **1a** ($\Phi = 0.59$) was larger than that of 1,2-bis(2,4-dimethyl-5-phenyl-3-thienyl)perfluorocyclopentene (**4a**) ($\Phi = 0.46$), which has methyl substituents at 4 and 4′ positions of the thiophene rings, while the cycloreversion quantum yields were similar ($\Phi = 0.013$ and 0.015, respectively).[14] The methyl groups at 4 and 4′ positions decreased the cyclization quantum yield.



4a **4b**

Photochromism in the Single-Crystalline Phase. Single crystals of **1a**, **2a**, and **3a** were obtained by recrystallization from hexane. The shape of the largest surface of each crystal is illustrated in Figure 2. Upon irradiation with ultraviolet light the single crystals turned blue while keeping the crystal shape. The blue colored crystals returned to colorless by irradiation with visible light ($\lambda > 480$ nm). During the coloration/decoloration cycles the crystals neither shattered nor became opaque. The crystals kept a clear transparent character.[15]

Table 1. Absorption Characteristics and Photoreactivity of Dithienylethenes in Hexane

	ϵ/M^{-1} cm^{-1} [a]		quantum yield		
compd	a	b	cyclization (λ_{max})	cycloreversion (492 nm)	convn/%[b]
1	35600 (280 nm)	15600 (575 nm)	0.59	0.013	97
2	39900 (285 nm)	18100 (580 nm)	0.53	0.0097	98
3	38000 (287 nm)	16800 (580 nm)	0.56	0.011	99

[a] Absorption coefficient at the absorption maximum. [b] Conversion from the open- to the closed-ring isomers in the photostationary state under irradiation with 313 nm light.

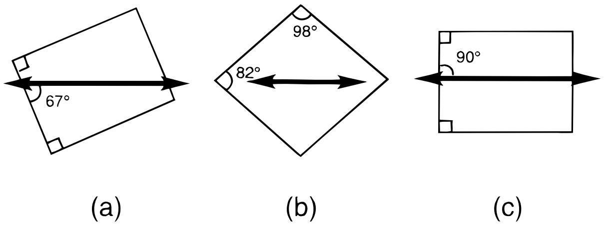


Figure 2. Crystal surface shape of **1a** (a), **2a** (b), and **3a** (c). The arrows show the maximum direction of absorption of the closed-ring isomers under polarized light.

To confirm that the color is due to the closed-ring isomers, the colored crystals were dissolved in hexane and the absorption maxima were compared with each spectrum of **1b**, **2b**, and **3b** in hexane. In all cases the spectra of the solutions containing the dissolved colored crystals were identical with those of the closed-ring isomers. The blue colors of the crystals are due to the closed-ring isomers.

The absorption spectra and intensities of the crystals were measured by using a polarizing microscope to confirm that the closed-ring isomers were produced in the crystal lattice. In the measurement, polarizer and analyzer were set parallel to each other. When the plane of the polarized light coincides with the direction of the arrow shown in Figure 2, three crystals become blue. Figure 3 shows the absorption spectra of the colored crystals under the polarized light. The absorption maxima slightly shifted to longer wavelengths from 589 (**1**) to 605 nm (**3**) by introducing *tert*-butyl substituents at 4 and 4′ positions of the phenyl groups. The methyl substituted compound had the maximum at 595 nm. The absorbances at the absorption maxima were plotted by rotating the crystals under polarized light as shown in Figure 4. The absorption anisotropies were observed for all crystals of **1**, **2**, and **3**. The polar plots indicate that at a certain angle the crystals are deep blue and the color almost disappeared by rotating the crystals as much as 90°. The intensity variation by rotation depended on the substituents. The dichroism under polarized light clearly indicates that **1**, **2**, and **3** underwent the photochromic reactions in the crystal lattice.[16]

Photoreactivity in the Single-Crystalline Phase. The photocyclization reactivities of the crystals **1a**, **2a**, and **3a** were compared by measuring the absorbance changes of the colored isomers in the single crystals upon 366 nm light irradiation. The results are shown in Figure 5. The photoreactivities of **1a**

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(14) Irie, M.; Sakemura, K.; Okinaka, M.; Uchida, K. *J. Org. Chem.* **1995**, *60*, 8305.

(15) The light could penetrate as deep as ~0.5 mm and induce the reaction. The degree of conversion of microcrystals was as large as 60−70%.

(16) Powder X-ray diffraction analysis confirmed that the reactions proceeded in the crystals. The X-ray crystallographic analysis of photoirradiated single crystal **1** is currently under way. The preliminary result indicated that the photocyclization proceeded with keeping the single-crystal structure up to 8% conversion.

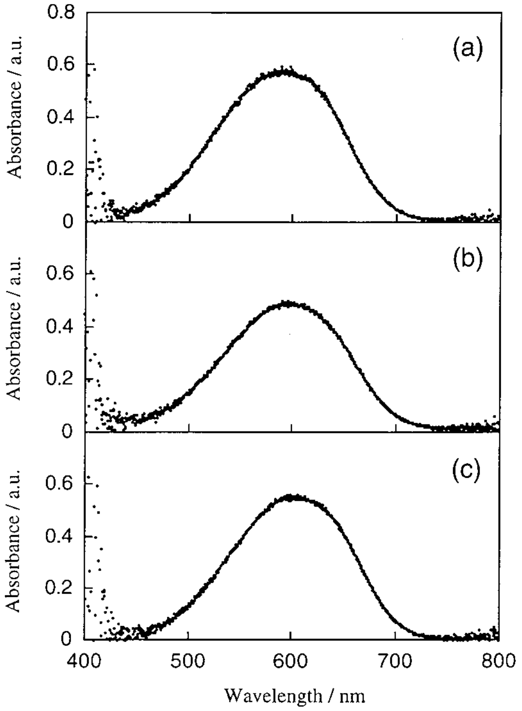

Figure 3. Absorption spectra of **1b** (a), **2b** (b), and **3b** (c) in the crystalline phases. The single crystals **1a**, **2a**, and **3a** were irradiated with 366 nm light.

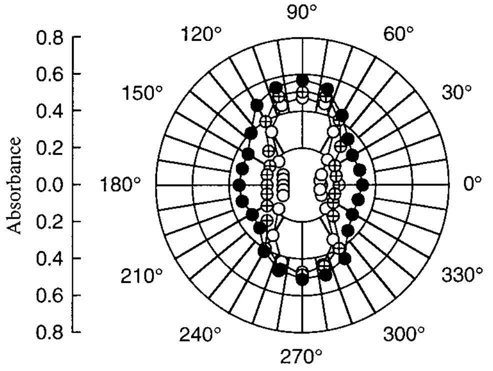

Figure 4. Polar plots of the absorbance for **1b** (●), **2b** (⊕), and **3b** (○) at the absorption maxima in the single-crystalline phases.

and **3a** were almost similar. The photoreactivity of **2a** was apparently lower than those of **1a** and **3a** by a factor of about 10. This is in contrast with the solution reactivity. In hexane solution all three compounds had similar reactivities.

The absorption intensity in the single-crystalline phase depends on the direction of electronic transition moments of the packed molecules. In other words, the intensity depends on the orientation of molecules in the crystal, therefore on the measuring surface. When the transition moment vector coincides with the electric field direction of the polarized light, strong absorption is observed. When the vector deviates from the polarized light direction, absorption becomes weaker. It is necessary to determine the absorption coefficients (ϵ) of the packed molecules for the comparison of real reactivities.

ϵ values of the closed-ring isomers, **1b**, **2b**, and **3b**, in the crystals were determined by comparing the absorption intensities of the closed-ring isomers under polarized light and the number of closed-ring isomer molecules, which was obtained by dissolving the colored crystals in hexane. Figure 2 showed the measuring surfaces. The ϵ values of **1b**, **2b**, and **3b** were determined to be 1.4×10^4, 1.6×10^3, and 2.0×10^4 M^{-1} cm^{-1} at the absorption maxima, respectively. Figure 5b shows the corrected photocyclization rates of **1a**, **2a**, and **3a**. The cyclization rates were similar among the three crystals.

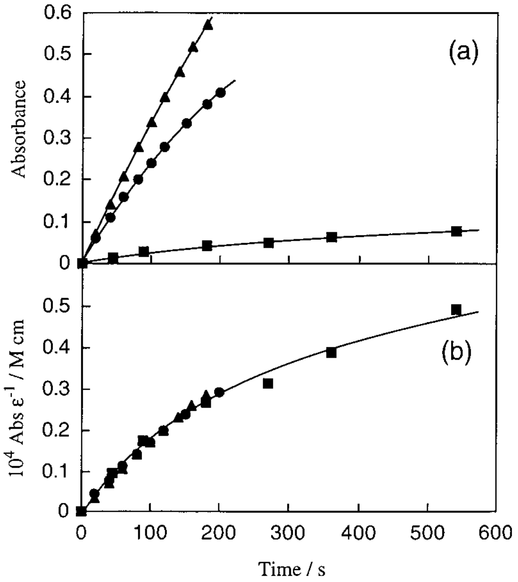

Figure 5. Coloration of single crystals of **1a** (●), **2a** (■), and **3a** (▲) by irradiation with 366 nm light: (a) apparent absorption intensity change and (b) corrected absorption intensity change by taking into account ϵ-values of the crystals. The 366 nm light was completely absorbed by the crystals.

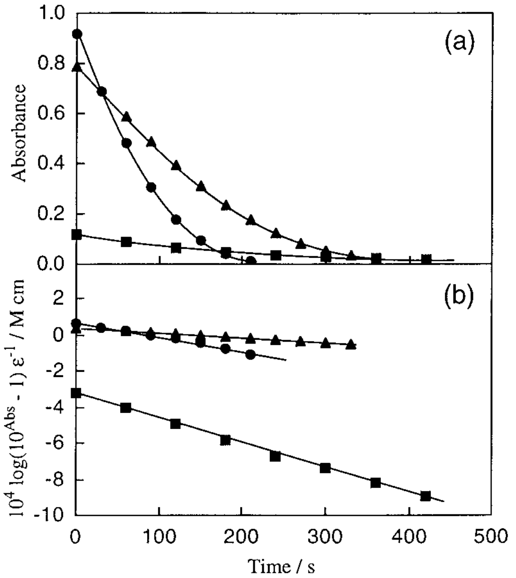

Figure 6. Bleaching of **1b** (●), **2b** (■), and **3b** (▲) in the crystalline phases by irradiation with 570 nm light: (a) apparent absorption intensity change and (b) corrected absorption intensity change by taking into account ϵ-values of the crystals.

Figure 6a shows apparent bleaching rates of the closed-ring isomers **1b**, **2b**, and **3b** in the crystalline phase upon 570 nm light irradiation. The corrected bleaching rates are shown in Figure 6b. The rates were dependent on the substituents. Among the three crystals, the fastest bleaching was observed in crystal **2a** and the slowest in crystal **3a**. The bleaching rate of **1b** in crystal **1a** was between crystals **2a** and **3a**. In solution the bleaching rates were similar to each other as shown in Table 1. This indicates that the crystal lattice controls the photocyclo-reversion reactions.

Activation Energy. Temperature dependence of photocyclization/photocycloreversion reactions was measured in 3-me-

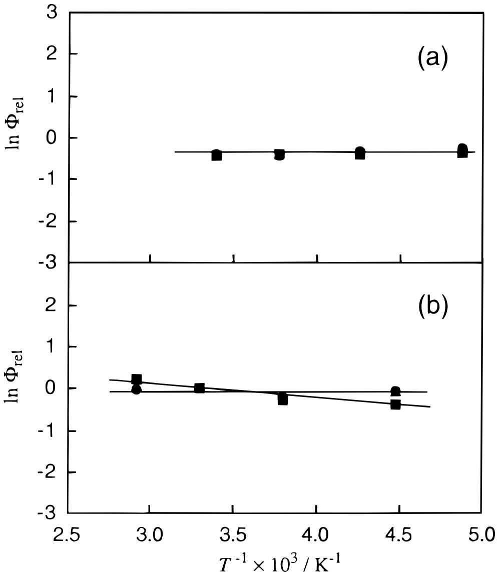

Figure 7. Temperature dependence of the rates of cyclization reactions for **1a** (●), **2a** (■), and **3a** (▲) in 3-methylpentane (a) and in the single-crystalline phases (b).

Table 2. Activation Energies of Cyclization and Cycloreversion in 3-Methylpentane and in the Crystalline Phase

	cyclization (kJ mol^{-1})		cycloreversion (kJ mol^{-1})	
compd	3-methylpentane	crystal	3-methylpentane	crystal
1	0	0	15.9	6.9
2	0	3.8	16.1	4.8
3	0	0		9.8

thylpentane solution as well as in the crystalline phase. Figure 7a,b shows the temperature dependence of the cyclization rates in 3-methylpentane and in the single-crystalline phase, respectively. In both solutions and crystals appreciable temperature dependence of the cyclization rates was not observed. The reaction rates of crystals **1a** and **3a** were the same even if the reaction temperature was changed from 70 to −50 °C. In the case of crystal **2a** there exists an activation energy, though it is very small (<4 kJ mol^{-1}).

The photocycloreversion reactions of **1b**, **2b**, and **3b** were also measured at various temperatures in 3-methylpentane and in the single-crystalline phase. The activation energies of **1b** and **2b** in 3-methylpentane were determined to be 16 kJ mol^{-1}. The activation energies in the single-crystalline phase were smaller than those in solution. They were less than 10 kJ mol^{-1} and dependent on the substituents. The lower activation energies in crystals indicate that the photogenerated colored isomers have different stability between solution and crystals. The conformation of the photogenerated closed-ring isomers in crystals contains some strain energy,[12] which possibly decreases the activation energy. The activation energies are summarized in Table 2.

Thermal stability of the colored closed-ring isomers is one of the main advantages of diarylethene photochromic performance. The blue color of the crystals remains stable even at 100 °C. To determine the stability at elevated temperatures, the decay of the absorption band at 580 nm of the crystal **1b** (or melt) was measured at 150, 170, 190, and 211 °C in the dark. The absorbance of **1b** gradually started to decrease at 150 °C. The half-life time at 150 °C was 3.3 h. The colorless product produced by heating above 200 °C was confirmed to be the open-ring isomer **1a** by ^{1}H NMR and mass spectroscopy. The temperature dependence of the thermal cycloreversion reaction rate from **1b** to **1a** showed a linear relationship between ln *k* and 1/*T*. The activation energy was determined from the slope to be 139 kJ mol^{-1}. Extrapolation of the temperature dependence indicates that the half-life time of the colored closed-ring isomer **1b** is 1900 years at 30 °C.

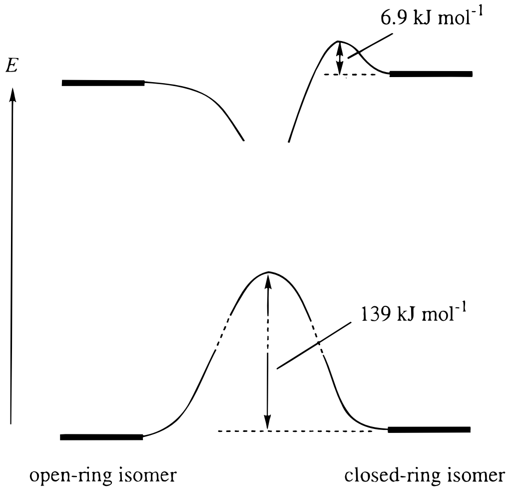

Figure 8. Energy diagram of the photochromic reaction of **1** in crystals.

From the above kinetic studies the energy diagram for the reactions of **1** can be deduced as shown in Figure 8. The large activation energy in the ground state practically prohibits the thermal cycloreversion reaction. The absence of activation energy in the photocyclization process indicates that the molecules are in a favorable conformation for the reaction and the crystal lattice does not disturb the rotation of the thiophene rings. The very rapid photocyclization reaction of bis(2,5-dimethyl-3-thienyl)perfluorocyclopentene in less than 10 ps observed in crystal[17] is ascribed to the absence of the activation energy. The activation energy of the cycloreversion process was also very low.

X-ray Crystallographic Analysis. X-ray crystallographic analysis of the crystals of **1a**, **2a**, and **3a** was carried out to reveal the difference in the ϵ values in the three crystals. Table 3 summarizes the results. The ϵ values of the closed-ring isomers depend on the direction of the long axis of the open-ring isomers. Figure 9 shows vertical sectional views of packed molecules taken on the arrows shown in Figure 2. The angles (θ) of the long axes of the molecules to the crystal surface were measured for the three crystals and are shown in Table 4 along with ϵ values. When the molecules were packed in parallel to the surface (θ is low), the transition moment value increased. The values are considered to be proportional to $\cos^2\theta$ when the molecule has C_∞ symmetry. When the molecule has a plane where π-electrons delocalize, the transition moment value also depends on the angle between the molecular plane and the plane of the polarizing light. The relatively low ϵ value of **2b** is explained by the fact that the molecular plane is perpendicular to the vertical plane.

Conclusions

It has been demonstrated that 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene (**1a**) and its derivatives, 1,2-bis(2-methyl-5-*p*-tolyl-3-thienyl)perfluorocyclopentene (**2a**) and 1,2-bis(2-methyl-5-*p*-*tert*-butylphenyl-3-thienyl)perfluorocyclopentene (**3a**), undergo photochromic reactions in the single-crystalline phase. Upon irradiation with 366 nm light the

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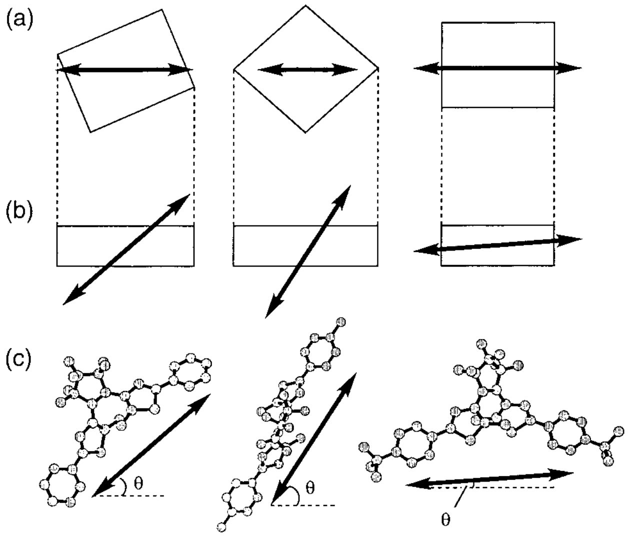
[17] Miyasaka, H.; Nobuto, T.; Itaya, A.; Tamai, N.; Irie, M. *Chem. Phys. Lett.* **1997**, *269*, 281.

Table 3. Crystal Data and Structure Refinements for **1a**, **1b**, **2a**, and **3a**

	1a	**1b**	**2a**	**3a**
formula	$C_{27}H_{18}F_6S_2$	$C_{27}H_{18}F_6S_2$	$C_{29}H_{22}F_6S_2$	$C_{35}H_{34}F_6S_2$
formula weight	520.53	520.53	548.59	632.74
temp/K	296(2)	296(2)	296(2)	296(2)
crystal system	monoclinic	triclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P\bar{1}$	$C2/c$	$P2_1/n$
unit cell dimensions				
a/Å	18.786(2)	11.770(4)	25.978(4)	14.953(1)
b/Å	11.762(1)	12.023(5)	9.251(2)	14.160(1)
c/Å	21.675(3)	9.626(3)	10.714(2)	16.028(2)
α/deg	90	94.45(3)	90	90
β/deg	96.323(2)	95.89(3)	102.708(3)	103.550(2)
γ/deg	90	60.07(3)	90	90
vol/Å^3	4759.9(10)	1173.7(7)	2511.7(7)	3299.1(6)
Z	8	2	4	4
D_{calcd}/(g/cm^3)	1.453	1.473	1.451	1.274
final R indices [$I > 2\sigma(I)$]				
$R1$	0.0485	0.0504	0.0504	0.0655
w$R2$	0.1328	0.1263	0.1365	0.1854
R indices (all data)				
$R1$	0.0806	0.0905	0.0668	0.0822
w$R2$	0.1516	0.1538	0.1492	0.2017



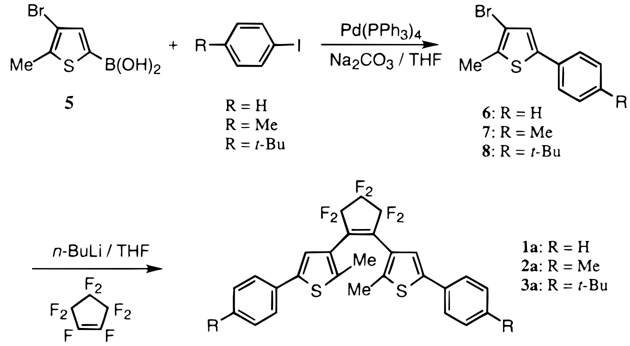
1a **2a** **3a**

Figure 9. Vertical sectional views of packed molecules in crystals **1a**, **2a**, and **3a** along with the arrows shown in Figure 2: (a) crystal surface shapes, (b) vertical sectional views, and (c) the packed molecules.

Table 4. ϵ Values of **1b**, **2b**, and **3b** in the Crystalline Phase

compd	ϵ/M^{-1} cm^{-1}	θ/deg	$\cos^2\theta$
1b	1.4×10^4	41	0.57
2b	1.6×10^3	55	0.33
3b	2.0×10^4	3	1.0

Scheme 1



colorless open-ring form crystals turned blue, and the blue color disappeared by irradiation with visible light ($\lambda > 480$ nm). The rates of photocyclization reactions were not affected by the substituents at para positions of the phenyl groups and their activation energies were almost zero in both solution and crystals. The photocycloreversion rates were dependent on the substituents and the fastest bleaching of the blue color was observed in crystal **2a**, which has methyl substituents at the para positions. The activation energies of the photocycloreversion reactions in crystals (<10 kJ mol^{-1}) were lower than those in solution (16 kJ mol^{-1}).

Experimental Section

General. Solvents used were spectroscopic grade and purified by distillation before use. ^{1}H NMR spectra (200 MHz) were recorded on a Varian Gemini 200 spectrometer using deuteriochloroform and tetramethylsilane as the solvent and the internal standard, respectively. Absorption spectra in solution were measured with a Hitachi U-3410 absorption spectrophotometer. Absorption spectra in single-crystalline phases were measured by using a Leica DMLP polarizing microscope connected with a Hamamatsu PMA-11 detector. Polarizer and analyzer were set in parallel to each other. A Mettler FP82 hot stage was used to maintain constant temperature of the crystal. Photoirradiation was carried out using a USHIO 500 W high-pressure mercury lamp or a USHIO 500 W xenon lamp as the light source. Monochromic light was obtained by passing the light through a monochromator (Ritsu MV-10N) or a band-pass filter ($\Delta\lambda_{1/2} = 15$ nm). X-ray crystallographic analysis was carried out with a Bruker SMART CCD diffractometer or a Enraf-Nonius FR250 diffractometer.

Determination of ϵ Values in Crystal. Absorbance (A) is defined as the following equation:

$$A = \log(I_0/I) = \epsilon n/S$$

where I_0 and I are the light intensity before and after passing through the sample, respectively. n and S represent the molar number of closed-ring isomer molecules presented in the light path and the irradiated area, respectively. A (=$\log(I_0/I)$) in the crystal was determined using polarized light. n was determined by dissolving the colored crystal in hexane and measuring the absorption spectrum (ϵ values in hexane solution are known, see Table 1). The ϵ values were calculated from the values of A, n, and S.

3-Bromo-2-methyl-5-phenylthiophene (6). 6 was prepared by reacting 3-bromo-2-methyl-5-thienylboronic acid (**5**)[18] (1.33 g; 6.0 mmol) with iodobenzene (1.22 g; 6.0 mmol) in the presence of Pd-(PPh$_3$)$_4$ (208 mg; 0.18 mmol) and Na$_2$CO$_3$ (1.59 g; 15 mmol) in tetrahydrofuran (THF) (50 mL containing 10% water) for 6 h at 70

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[18] Gilat, S. L.; Kawai, S. H.; Lehn, J.-M. *Chem. Eur. J.* **1995**, *1*, 275.

°C. **6** was purified by column chromatography on SiO_2 using hexane as the eluent and 1.1 g obtained as colorless crystals in 50% yield: mp 72−73 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.41 (s, 3H), 7.10 (s, 1H), 7.33−7.51 (m, 5H); MS *m*/*z* (M^+) 252, 254. Anal. Calcd for $C_{11}H_9BrS$: C, 52.19; H, 3.58. Found: C, 52.04; H, 3.70.

3-Bromo-2-methyl-5-*p*-tolylthiophene (7). **7** was prepared by a method similar to that used for **6** and obtained as colorless crystals: mp 96 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.36 (s, 3H), 2.41 (s, 3H), 7.06 (s, 1H), 7.17−7.40 (m, 4H); MS *m*/*z* (M^+) 266, 268. Anal. Calcd for $C_{12}H_{11}BrS$: C, 53.94; H, 4.15. Found: C, 53.61; H, 4.32.

3-Bromo-2-methyl-5-(*p*-*tert*-butylphenyl)thiophene (8). **8** was prepared by a method similar to that used for **6** and obtained as colorless crystals: mp 65 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.32 (s, 9H), 2.39 (s, 3H), 7.05 (s, 1H), 7.25−7.55 (m, 4H); MS *m*/*z* (M^+) 308, 310. Anal. Calcd for $C_{15}H_{17}BrS$: C, 58.25; H, 5.54. Found: C, 58.38; H, 5.86.

1,2-Bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene (1a). To a stirred solution of **6** (1.01 g; 4.0 mmol) in THF was added dropwise a 15% *n*-BuLi/hexane solution (2.6 mL; 4.3 mmol) at −78 °C under nitrogen atmosphere. Stirring was continued for 20 min at the low temperature. Perfluorocyclopentene (0.42 g; 2.0 mmol, Nippon Zeon) was slowly added to the reaction mixture at −78 °C, and the mixture was stirred for 3 h at that temperature. The reaction was stopped by the addition of methanol. The product was extracted with ether. The organic layer was washed with 1 N HCl aqueous solution and water. The organic layer was dried over $MgSO_4$, filtrated, and evaporated. The crude product was purified by column chromatography on SiO_2 using toluene/hexane (1:3) as the eluent and by recrystallization from hexane to give 0.85 g of **1a** in 81% yield as colorless cubes: mp 139−140 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.97, (s, 6H), 7.28 (s, 2H), 7.2−7.6 (m, 10 H); MS *m*/*z* (M^+) 520. Anal. Calcd for $C_{27}H_{18}F_6S_2$: C, 62.30, H, 3.49. Found: C, 62.66; H, 3.72.

Closed-Ring Isomer of 1a (1b). **1b** was isolated by passing a photostationary solution containing **1a** and **1b** through a HPLC (Hitachi L-6250 HPLC system, silica gel column, hexane as the eluent): mp 193 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.18 (s, 6H), 6.68 (s, 2H), 7.3−7.7 (m, 10 H); MS *m*/*z* (M^+) 520. Anal. Calcd for $C_{27}H_{18}F_6S_2$: C, 62.30, H, 3.49. Found: C, 62.39; H, 3.50.

1,2-Bis(2-methyl-5-*p*-tolyl-3-thienyl)perfluorocyclopentene (2a). **2a** was prepared by a method similar to that used for **1a** and obtained as colorless prisms: mp 160 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.96 (s, 6H), 2.35 (s, 6H), 7.24 (s, 2H), 7.23−7.47 (m, 8H); MS *m*/*z* (M^+) 548. Anal. Calcd for $C_{29}H_{22}F_6S_2$: C, 63.49; H, 4.04. Found: C, 63.77; H, 4.31.

1,2-Bis(2-methyl-5-*p*-*tert*-butylphenyl-3-thienyl)perfluorocyclopentene (3a). **3a** was prepared by a method similar to that used for **1a** and obtained as colorless prisms: mp 195 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.32 (s, 18H), 1.98 (s, 6H), 7.23 (s, 2H), 7.39−7.47 (m, 8H); MS *m*/*z* (M^+) 632. Anal. Calcd for $C_{35}H_{34}F_6S_2$: C, 66.44; H, 5.42. Found: C, 66.18; H, 5.69.

Acknowledgment. This work was supported by CREST (Core Research for Evolutional Science and Technology) of Japan Science and Technology Corp. (JST). We also thank NIPPON ZEON CO., Ltd. for their supply of chemicals.

Supporting Information Available: X-ray structural information on **1a**, **1b**, **2a**, and **3a** (PDF) and an X-ray crystallographic file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA993181H