Reversible Diastereoselective Photocyclization of a Diarylethene in a Single-Crystalline Phase

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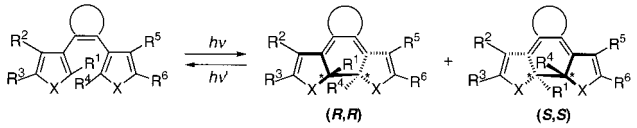
Abstract: Optically active photochromic (*S*)- and (*R*)-1-(2-methyl-5-phenyl-3-thienyl)-2-[2-(3-methyl-1-penten-1-yl)-5-phenyl-3-thienyl]-3,3,4,4,5,5-hexafluorocyclopentenes (**(*S*)-1a** and **(*R*)-1a**) were synthesized. X-ray crystallographic measurement showed that **(*S*)-1a** and **(*R*)-1a** single crystals adopted orthorhombic chiral space group $P2_12_12_1$ and the open-ring isomers were packed in the crystals in only one conformer of the possible two atropisomers. Upon irradiation with 366 nm light **(*S*)-1a** and **(*R*)-1a** underwent reversible photocyclization reactions both in solution and in the single-crystalline state, and in the crystalline phase almost only one closed-ring diastereomer was produced, while the diastereoselection was not observed in solution. The dominant diastereomer produced from **(*S*)-1a** was determined to be **(*S*,*R*,*R*)-1b** by X-ray crystallographic analysis.

Introduction

Photochromism is defined as a reversible photoisomerization between two forms having different absorption spectra.[1] So far various types of photochromic compounds, such as spirobenzopyrans, azobenzenes, fulgides, and diarylethenes, have been developed. Among the compounds, diarylethenes show characteristic reactivities. Both isomers are thermally stable and some of them undergo photochromic reactions even in the single-crystalline state.[2]

Diarylethenes undergo cyclization/cycloreversion photochromic reactions. The photochemical conrotatory cyclization produces two enantiomers (*R*,*R* and *S*,*S*) originating from two asymmetric carbon atoms. The photocyclization in solution, in general, results in the formation of two enantiomers in equal amounts. Even when a chiral substituent is introduced into the diarylethene, enrichment of one of the diastereomers hardly takes place.[3] Enrichment of one of the enantiomers or diastereomers in photochemical reactions requires chiral environments,[4] such as cavities of optically active host molecules[5] or crystals with chiral space groups.[6] Among various methods of enantio- or diastereoselection, photoreactions in chiral crystals are of general use. Here we report on diastereoselection in the photocyclization reaction of **(*S*)-1a** and **(*R*)-1a** with a chiral substituent in the crystalline phase and direct observation of the reaction process in the single crystals by X-ray crystallography.

Scheme 1. Photochromism of Diarylethene Derivatives[a]



[a] The photogenerated closed-ring isomers have two enantiomers, (*R*,*R*) and (*S*,*S*).

Results and Discussion

Photochromic Reactions in Solution. It is a necessary condition to prepare crystals with chiral space groups for the enrichment of one of the enantiomers or diastereomers in crystalline photoreactions. Although we tried to prepare such crystals by recrystallization of achiral diarylethenes with substituted thiophene and/or benzothiophene aryl groups from various solutions, we failed. Therefore, we decided to prepare chiral crystals by introducing a chiral substituent to a diarylethene. We chose 1,2-bis(2-methyl-5-phenylthiophen-3-yl)-3,3,4,4,5,5-hexafluorocyclopentene, which is known to show single-crystalline photochromism,[7] as the diarylethene and 3-methyl-1-penten-1-yl group as the chiral substituent.

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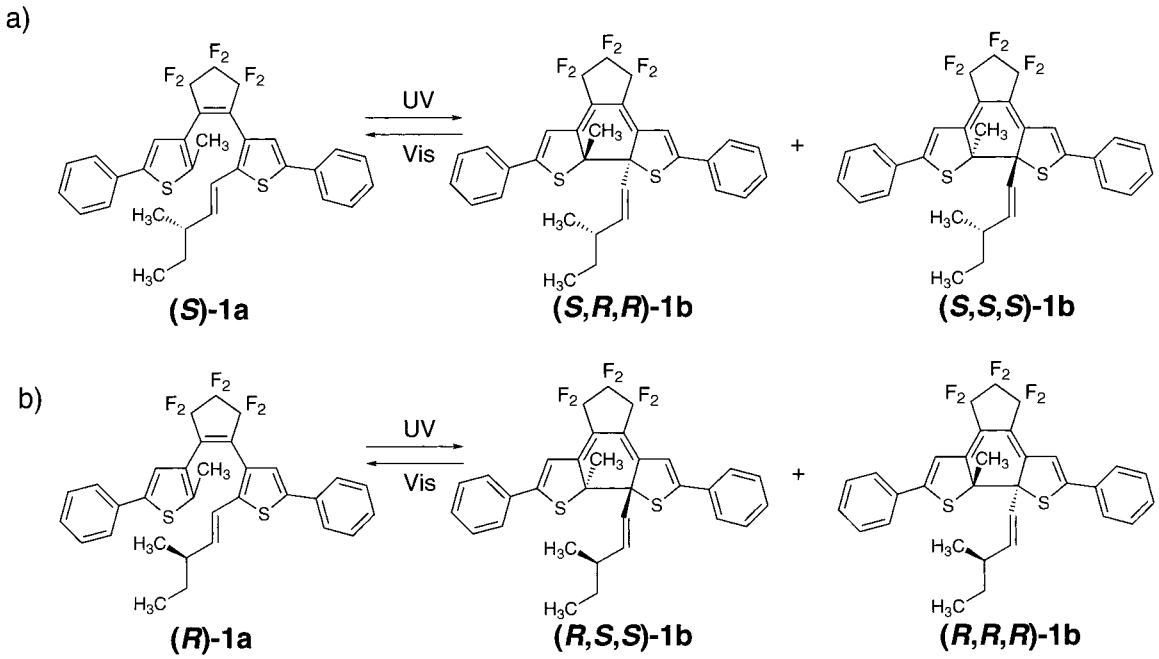
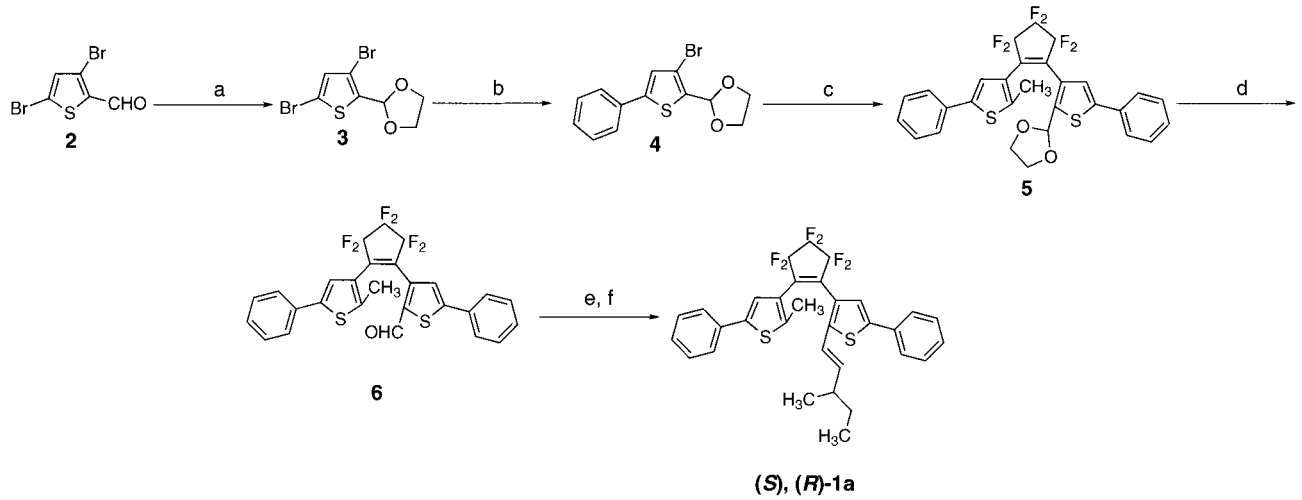
Scheme 2. Photochromism of **(*S*)-1a** and **(*R*)-1a**[a]



[a] (a) the photogenerated closed-ring isomers of **(*S*)-1a** have two diastereomers, **(*S*,*R*,*R*)-1b** and **(*S*,*S*,*S*)-1b**. (b) The photogenerated closed-ring isomers of **(*R*)-1a** have two diastereomers, **(*R*,*S*,*S*)-1b** and **(*R*,*R*,*R*)-1b**.

Scheme 3[a]



[a] Reagents and conditions: (a) ethylene glycol, *p*-toluenesulfonic acid monohydrate, benzene; (b) $Pd(PPh_3)_4$, Na_2CO_3, phenylboronic acid, THF, H_2O; (c) *n*-BuLi, 3-(2,3,3,4,4,5,5-heptafluorocyclopent-1-en-1-yl)-2-methyl-5-phenylthiophene, THF; (d) pyridinium *p*-toluenesulfonate, acetone;(e) Mg, (*R*)- or (*S*)-methylbutylbromide, THF; and (f) DMSO.

The synthesis of the chiral diarylethenes **(*S*)-1a** and **(*R*)-1a** was performed according to Scheme 3. The 3-methyl-1-penten-1-yl substituent was introduced at the 2-position of the thiophene ring by Grignard reaction of (*S*)-(+)- and (*R*)-(−)-methylbutylbromide with aldehyde **6**.

At first, we examined photoreactivity of **(*S*)-1a** in solution. Upon irradiation with 366 nm light, **(*S*)-1a** underwent a photochromic reaction in hexane solution. Figure 1a shows the absorption spectral change of compound **(*S*)-1a** (λ_{max} 288 nm, ϵ_{max} 33000 M^{-1} cm^{-1}) in hexane by photoirradiation. Upon irradiation with 366 nm light, the colorless solution of **(*S*)-1a** turned blue, in which the absorption maximum was observed at 580 nm (ϵ_{max} 14000 M^{-1} cm^{-1}). The color change is due to the formation of the closed-ring isomer of **(*S*)-1a**.[2c,g] The conversions by irradiation with 366 and 313 nm light from the open- to the closed-ring isomers were 87 and 91%, respectively. Upon irradiation with 578 nm light for 3 min, the spectrum returned back to the original. The photochromic performance of **(*R*)-1a** was identical with that for compound **(*S*)-1a** in hexane solution as shown in Figure 1b.

X-ray Crystallographic Analysis of (*S*)-1a and (*R*)-1a. Colorless rectangular-shaped single crystals of **(*S*)-1a** were obtained from a mixed solution of hexane and chloroform. The crystal structure was determined by X-ray crystallographic analysis (Figure 2 and Table 1). An **(*S*)-1a** single crystal adopted an orthorhombic chiral space group $P2_12_12_1$. The structure was determined by direct methods and successive Fourier synthesis. Full-matrix least-squares refinement of positional and thermal parameters led to the final convergence with $R_1 = 0.0464$ and $wR_2 = 0.1205$. The distance of C(1)−C(10), which are reactive carbon atoms, was 3.56 Å, which is short enough for the reaction

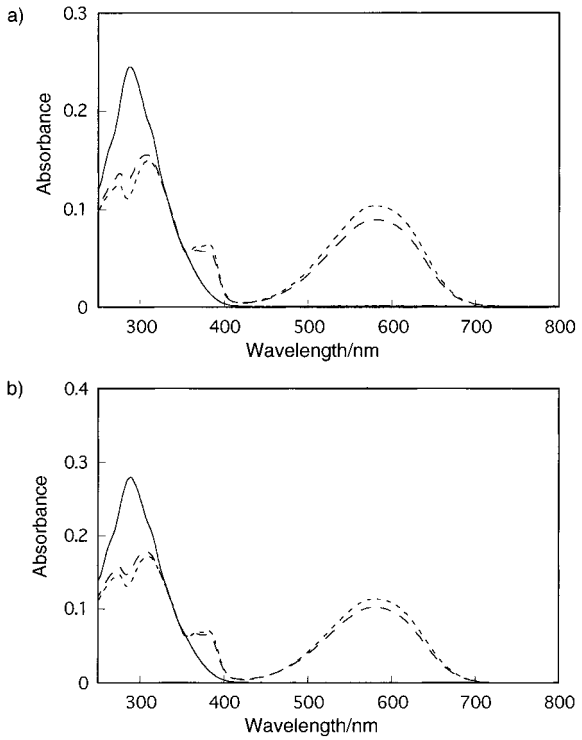


Figure 1. (a) Absorption spectra of **(*S*)-1a** in hexane ($c = 7.5 \times 10^{-6}$ M): open-ring isomer (solid line), closed-ring isomer (dotted line), and in the photostationary state under irradiation with 366 nm light (dashed line). (b) Absorption spectra of **(*R*)-1a** in hexane ($c = 8.0 \times 10^{-6}$ M): open-ring isomer (solid line), closed-ring isomer (dotted line), and in the photostationary state under irradiation with 366 nm light (dashed line).

Table 1. Crystal Data and Structure Refinement for **(*S*)-1a**, **(*S*)-1a′**, and **(*R*)-1a**

	(*S*)-1a	**(*R*)-1a**	**(*S*)-1a′**
formula		$C_{32}H_{26}F_6S_2$	
formula weight		588.65	
crystal system		orthorhombic	
space group		$P2_12_12_1$	
unit cell dimension			
a, Å	9.3904 (16)	9.3680 (10)	9.399 (2)
b, Å	11.864 (19)	11.8571(12)	11.866 (3)
c, Å	25.019 (4)	24.971 (3)	24.972 (6)
volume, Å^3	2787.3 (8)	2773.7(5)	2784.9 (12)
Z	4	4	4
density (calcd), g/cm^3	1.403	1.410	1.404
goodness-of-fit on *F*	1.048	1.041	0.891
final *R* indices [$I > 2\sigma(I)$], $R_1 =$	0.0464	0.0462	0.0660
wR_2 (all data), $wR_2 =$	0.1205	0.1149	0.1781
temperature		123 K	

to take place in the crystalline phase.[8] The open-ring isomers were packed in only one conformer of the possible two atropisomers in the crystal. The packing of molecules viewed normal to the (011) plane, which is the wide face of the crystal, is shown in Figure 3d. Crystal polymorphism was not observed.

The rectangular single crystals were also obtained from a mixed solution of hexane and chloroform of **(*R*)-1a**. The molecular configuration of **(*R*)-1a** in the crystal was the mirror image of **(*S*)-1a** as shown in Figure 2. Full-matrix least-squares refinement of positional and thermal parameters led to the final convergence with $R_1 = 0.0462$ and $wR_2 = 0.1149$. As expected, the molecular structure of **(*R*)-1a** was identical with that of **(*S*)-1a**.

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Photochromic Reactions in the Crystalline Phase. (*S*)-1a and **(*R*)-1a** underwent photochromic reactions in the single-crystalline phase. Upon irradiation with 366 nm light, the single crystals turned blue and the blue color disappeared by irradiation with visible light ($\lambda > 500$ nm). The coloration/decoloration cycles could be repeated many times while keeping the crystal shape. To know the origin of the blue color, the blue-colored crystals were dissolved into hexane, and the absorption spectrum was measured. The absorption maxima were the same as those of the closed-ring isomers shown in Figure 1. In addition a characteristic methyl signal was observed at 2.16 ppm due to the closed-ring isomer in the ^{1}H NMR spectrum of the blue colored product (see Experimental Section). These results indicate that the blue color of the crystals is due to the closed-ring isomer.

The color of the crystal was observed under polarized light. Figure 3 shows the absorption anisotropy and the polar plot. At a certain angle, the crystal had a deep blue color (Figure 3a). When the crystal was rotated as much as 90°, the color almost disappeared (Figure 3b). The absorption maximum shifted from 645 to 620 nm by rotating the sample. The shift is ascribed to the contribution of the short axis electronic transition, as shown in Figure 3d. The changes of the blue-color intensity and the absorption maximum by rotating the crystal sample indicate that the closed-ring isomers are regularly oriented in the crystal (Figure 3c,d). In other words, the photochromic reaction took place in the crystal lattice.[2]

Asymmetric Induction. Diastereoselectivity in the cyclization process was examined in solution as well as in the crystalline phase. The photoirradiated sample was analyzed with a reversed-phase HPLC column (Mightysil RP-18 GP, CH_3CN/H_2O = 75:25 volume ratio). The monitoring wavelength used was 580 nm, because only the closed-ring isomer of **(*S*)-1a** has absorption at the visible wavelength. It was possible to separate the two diastereomers with the conventional reversed-phase HPLC column. The closed-ring isomers produced in hexane, CH_3CN, and THF solutions by irradiation with 366 nm light were a mixture of equal amounts of two diastereomers, **(*S*,*R*,*R*)-1b** and **(*S*,*S*,*S*)-1b**. There was not diastereomeric excess in all solvents studied here as shown in Figure 4a.

The ratio of the two diastereomers dramatically changed in the crystalline phase reaction, as shown in Figure 4b,c. A 500 W super high-pressure mercury lamp was employed as the light source for the photocyclization of **(*S*)-1a** or **(*R*)-1a** in the crystalline phase. The irradiation wavelengths of light were 366, 405, and 435 nm. The longer wavelength of light increased the conversion. Table 2 shows the relation between conversion and d.e. (diastereomeric excess) value.

The reaction was completely diastereoselective when the conversion was less than 6%. The d.e. slightly decreased when the conversion increased over 10%. The slight decrease of selectivity is attributable to distortion of the crystal lattice as the reaction proceeds.

X-ray Crystallographic Analysis of the Photocyclization Reaction in the Single-Crystalline Phase. To know the details of the diastereoselection in the crystalline phase, direct observation of the reaction process by X-ray crystallography was carried out.[2f] To detect the reaction process by X-ray crystallography, it is required to increase the conversion higher than 5%. Linearly polarized 440 nm light was used as the light source to penetrate the light into the crystal bulk. At 440 nm **(*S*)-1a** has the absorption tail and the absorption of the closed-ring isomer is minimum as shown in Figure 3. The direction of polarization of irradiation light was selected parallel to the *a*-axis and normal

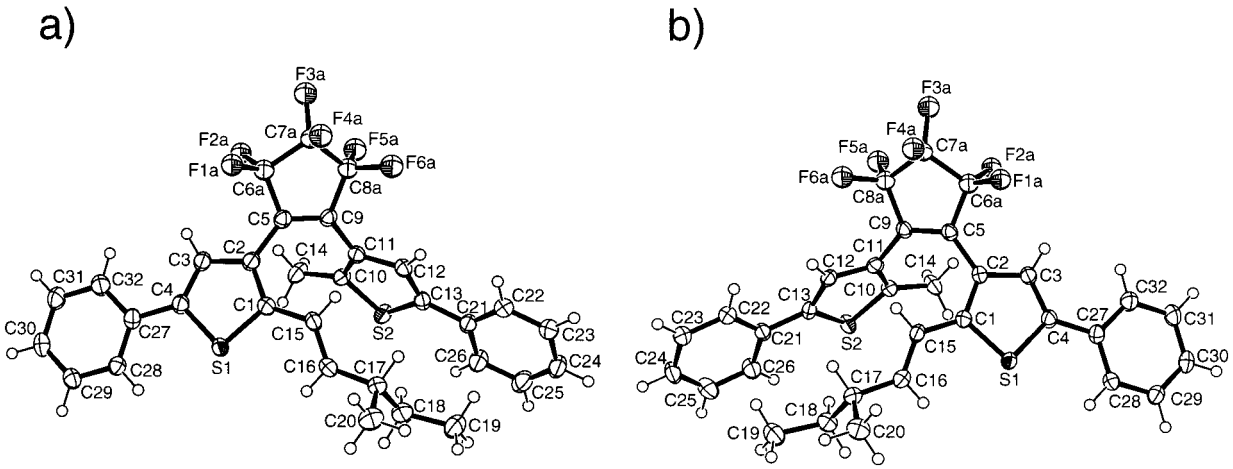

Figure 2. ORTEP drawing of the absolute configuration of (a) **(*S*)-1a** and (b) **(*R*)-1a**.

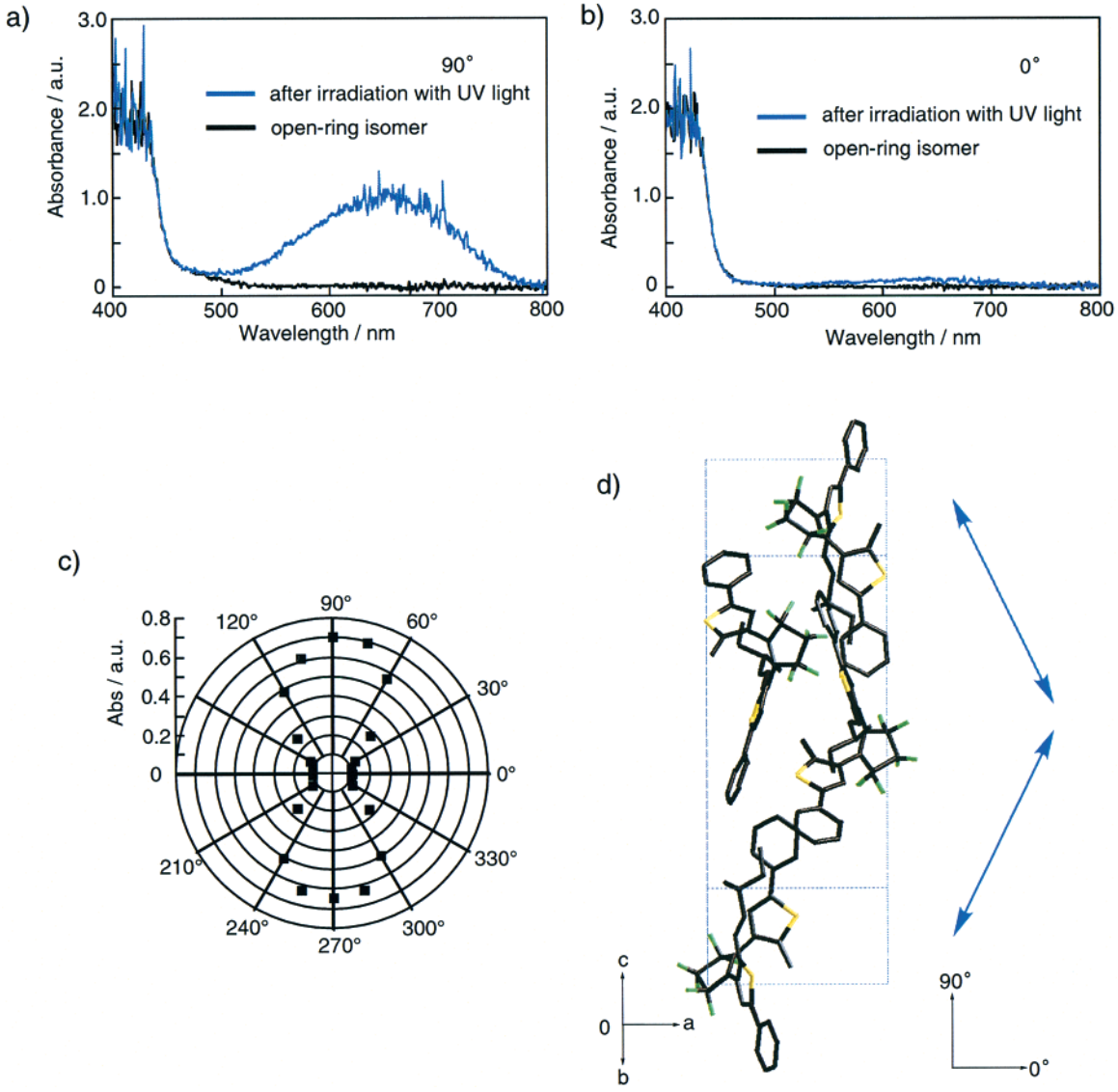

Figure 3. (a, b) Polarized absorption spectra of the colored crystal on the (011) face (see text); (c) polar plot at 645 nm; and (d) packing of the molecules viewed normal to the (011) face. Arrows denote the direction of transition moment of absorption at 645 nm.

to the (011) face so that the photogenerated blue color intensity becomes minimum as shown in Figure 3b. Irradiation was continued for 73 h. The colorless crystal turned deep blue. This deep blue crystal was denoted by **(*S*)-1a′**.

X-ray crystallographic analysis data of **(*S*)-1a′** are shown in Table 1. The unit cell parameters were almost identical even after irradiation. The coordinates of the open-ring isomer **(*S*)-1a** were used for the initial model for the refinement. After the

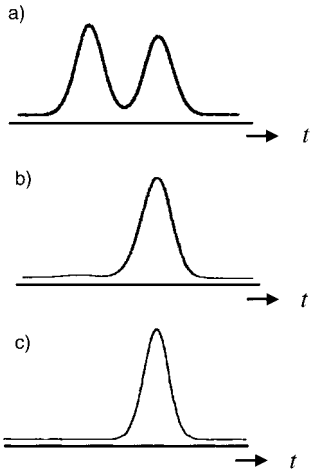

Figure 4. Diastereoselectivity of photoirradiated sample of **(*S*)-1a** and **(*R*)-1a** by HPLC analysis at 580 nm (Mightysil RP-18 GP, CH_3CN/H_2O = 75:25 volume ratio): (a) photocyclization reaction in hexane solution; (b) photocyclization reaction in the single-crystalline phase of **(*S*)-1a** (conversion = 13.2%); and (c) photocyclization reaction in the single-crystalline phase of **(*R*)-1a** (conversion = 6.0%).

Table 2. Asymmetric Induction in the Crystalline Phase Photochromism of **(*S*)-1a** and **(*R*)-1**a

conversion, %[a]	d.e., %[b]
1.7[c,e]	>99
2.9[c,f]	>99
6.0[d,g]	>99
9.3[c,g]	97.2
11.9[c,g]	96.7
13.2[c,g]	95.0

[a] Determined by HPLC using Superspher Si60 (MERCK). [b] Determined by HPLC using Mightysil RP-18 GP (KANTO CHEMICALS). [c] **(*S*)-1a**. [d] **(*R*)-1a**. [e] Irradiation with 366 nm light. [f] Irradiation with 405 nm light. [g] Irradiation with 435 nm light.

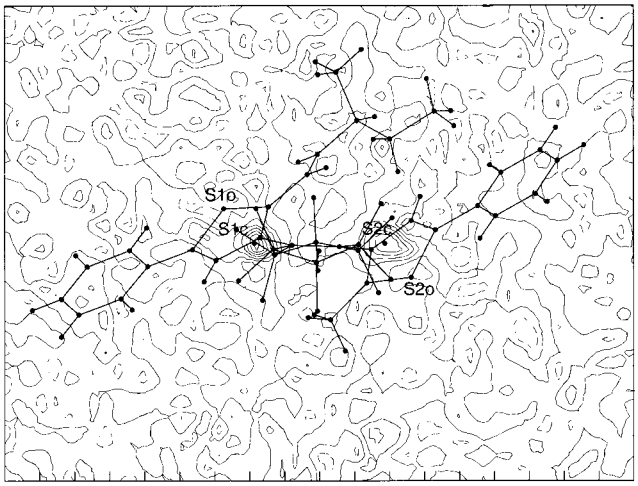

Figure 5. Difference Fourier electron density map of **(*S*)-1a** photoirradiated with 440 nm light for 73 h. **(*S*,*R*,*R*)-1b** was generated topochemically (conversion = 8%).

first least-squares refinement, the difference Fourier electron density map (Figure 5) showed the existence of two quite high electron density peaks (0.99 and 0.94 e·Å^{-3}) comes from the sulfur atoms of the photogenerated closed-ring isomer. The distance between the two sulfur atoms was 3.68 Å, which is close to the distance of the closed-ring isomer of 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene, 3.65 Å.[7] The positions are close to those expected for the closed-ring isomer

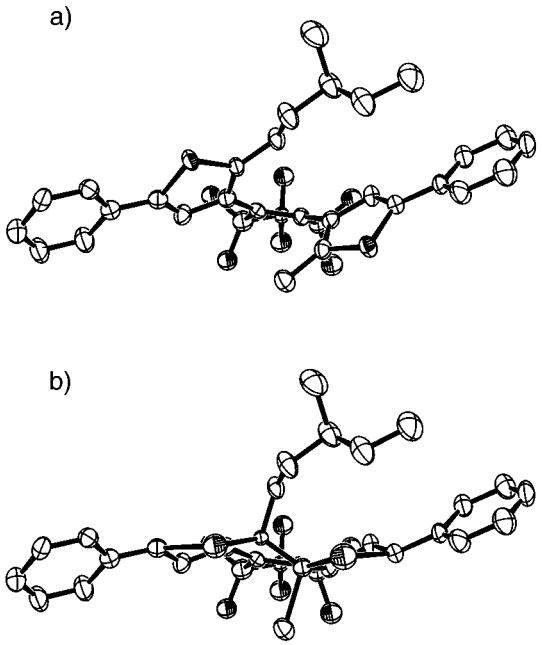

Figure 6. ORTEP drawing of (a) **(*S*)-1a** and (b) photogenerated closed-ring isomer **(*S*,*R*,*R*)-1b**. Hydrogen atoms are omitted for clarity. Irradiation wavelength: 440 nm. Irradiation time: 73 h.

photogenerated in a conrotatory mode. Electron density peaks corresponding to two carbons at reaction points also appeared (0.35 and 0.30 e·Å^{-3}). These peaks were assigned as the closed-ring isomer **(*S*,*R*,*R*)-1b**. The displacement factors of the photogenerated closed-ring isomer were refined isotropically. Using the model, the full-matrix least-squares refinement was well converged (R_1 = 0.0660 for the data with $I > 2\sigma(I)$, wR_2 = 0.1781 for all data). Judging from the structure of the closed-ring isomer, it can be concluded that only one diastereomer was formed in the crystal. According to the atom occupancy factor, the conversion from **(*S*)-1a** to **(*S*,*R*,*R*)-1b** was about 8%. The final molecular structure of the closed-ring isomer **(*S*,*R*,*R*)-1b** and the structure of the open-ring isomer **(*S*)-1a** are shown in Figure 6. The structure change indicates that the topochemically controlled cyclization reaction took place in the crystalline phase. The closed-ring isomer (b) of Figure 6 was produced from the open-ring isomer (a) by the minimal conrotatory rotation of the two thiophene rings. Upon irradiation with visible light (λ > 500 nm), the peaks of **(*S*,*R*,*R*)-1b** disappeared.

Conclusions

Optically active (*S*)- and (*R*)-1-(2-methyl-5-phenyl-3-thienyl)-2-[2-(3-methyl-1-penten-1-yl)-5-phenyl-3-thienyl]-3,3,4,4,5,5-hexafluorocyclopentenes (**(*S*)-1a** and **(*R*)-1a**) underwent photochromic reactions both in hexane solution and in the single-crystalline state. Although equal amounts of two diastereomers of the closed-ring isomers were produced in solution by irradiation with 366 nm light, the diastereoselective photocyclization reaction took place in the single crystal. The X-ray crystallography proved that the reaction was topochemically regulated by the crystal lattice.

Experimental Section

A. Materials. ^{1}H NMR spectra were recorded on a Varian Gemini 200 spectrometer (200 MHz). Tetramethylsilane was used as internal standard. UV−vis spectra were recorded on a Hitachi U-3500 spec-

trophotometer. Mass spectra were obtained by JEOL JMS-HX110A instruments. Melting points are not corrected.

All reactions were performed under an atmosphere of dry argon unless otherwise specified. All reactions were monitored by thin-layer chromatography carried out on 0.2-mm E. Merck silica gel plates (60F-254). Column chromatography was performed on silica gel (E. Merck, 70−230 mesh).

3,5-Dibromo-2-(2,5-dioxolanyl)thiophene (3). A solution of 3,5-dibromothiophene-2-carbaldehyde (**2**) (13.0 g, 47 mmol), ethylene glycol (2.8 mL, 5.2 mmol), and *p*-toluenesulfonic acid monohydrate (0.1 g, 0.49 mmol) in benzene (100 mL) was refluxed for 13 h with a Dean−Stark condenser. The reaction mixture was poured into aqueous sodium bicarbonate, extracted with ether, washed with aqueous sodium bicarbonate and water, dried ($MgSO_4$), and concentrated. Dioxolane **3** (14.3 g, 96%) was obtained as an oily product: ^{1}H NMR ($CDCl_3$) δ 3.97−4.17 (m, 4 H), 6.06 (s, 1 H), 6.94 (s, 1 H); HRMS (FAB) *m*/*z* 312.852 ([M + H]$^+$), calcd for $C_7H_7Br_2O_2S$ 312.853.

3-Bromo-2-(2,5-dioxolanyl)-5-phenylthiophene (4). A mixture of $Pd(PPh_3)_4$ (2.1 g, 1.8 mmol), dibromo compounds **3** (5.8 g, 18 mmol), and THF (120 mL) was stirred for 0.5 h; phenylboronic acid (2.4 g, 20 mmol) and a suspension of Na_2CO_3 (9.6 g, 91.0 mmol) in 60 mL of water were subsequently added. The mixture was stirred and refluxed for 7 h and allowed to cool to room temperature. Ether was added, and the organic layer was collected and the water layer was extracted with ether. The organic layers were dried over $MgSO_4$, and the solvents were evaporated. Purification of the crude product by column chromatography (silica gel, $CHCl_3$/hexane = 1:1) afforded phenylthiophene derivative **4** (3.1 g, 55%) as an oily product:^{1}H NMR ($CDCl_3$) δ 4.01−4.23 (m, 4 H), 6.14 (s, 1 H), 7.15 (s, 1 H), 7.31−7.71 (m, 5 H); HRMS (FAB) *m*/*z* 310.973 ([M + H]$^+$), calcd for $C_7H_7Br_2O_2S$ 310.974.

1-(2-Methyl-5-phenyl-3-thienyl)-2-[2-(2,5-dioxolanyl)-5-phenyl-3-thienyl]-3,3,4,4,5,5-hexafluorocyclopentene (5). To a well-stirred solution of monobromo compound **4** (1.5 g, 4.8 mmol) in anhydrous THF (50 mL) under Ar at −78 °C was added dropwise a solution of *n*-BuLi (3.2 mL, 5.3 mmol) and stirring was continued for 1.5 h at −78 °C. Then, a solution of 3-(2,3,3,4,4,5,5-heptafluorocyclopent-1-en-1-yl)-2-methyl-5-phenylthiophene (1.9 g, 5.3 mmol) was added dropwise. The mixture was stirred for 5 h and allowed to warm to room temperature and water was added. The resultant mixture was then extracted with ether and the organic extract was washed with brine and dried ($MgSO_4$). The solvent was removed. Column chromatography (silica gel, $CHCl_3$/hexane = 1:1) afforded dithienylethene **5** (1.2 g, 43%) as an oily product: ^{1}H NMR ($CDCl_3$) δ 1.99 (s, 3H), 3.78−3.99 (m, 4 H), 5.37 (s, 1 H), 7.26−7.63 (m, 12 H); HRMS (FAB) *m*/*z* 579.090 ([M + H]$^+$), calcd for $C_{29}H_{21}F_6O_2S_2$ 579.088.

1-(2-Methyl-5-phenyl-3-thienyl)-2-(2-formyl-5-phenyl-3-thienyl)-3,3,4,4,5,5-hexafluorocyclopentene (6). A solution of dithienylethene **5** (2.7 g, 4.7 mmol) in wet acetone (40 mL) containing pyridinium tosylate (2.3 g, 9.2 mmol) was refluxed for 12 h. The mixture was cooled to room temperature and water was added. The resultant mixture was then extracted with ether and the organic extract was washed with brine and dried ($MgSO_4$). The solvent was removed in vacuo. Finally, purification of the crude product by recrystallization afforded slightly yellow crystals of dithienylethene **6** (2.2 g, 95%): mp 132−133 °C; ^{1}H NMR ($CDCl_3$) δ 2.00 (s, 3 H), 7.21−7.69 (m, 12 H), 9.56 (s, 1 H); HRMS (FAB) *m*/*z* 535.063 ([M + H]$^+$), calcd for $C_{27}H_{17}F_6OS_2$ 535.062.

(*S*)-1-(2-Methyl-5-phenyl-3-thienyl)-2-[2-(3-methyl-1-penten-1-yl)-5-phenyl-3-thienyl]-3,3,4,4,5,5-hexafluorocyclopentene ((*S*)-1a). To a stirred solution of (*S*)-(+)-methylbutylbromide (0.24 mL, 1.9 mmol) in 15 mL of anhydrous THF was added a powder of Mg (45 mg, 1.9 mmol) under Ar at room temperature. After 1 h, dithienylethene **6** (300 mg, 0.6 mmol) was added and stirring was continued for 1 h at room temperature. The resultant mixture was then extracted with ether and the organic extract was washed with brine and dried ($MgSO_4$). The solvent was removed. Finally, purification of the crude product by preparative thin-layer chromatography (silica gel, $CHCl_3$/hexane = 1:1) afforded 1-(2-methyl-5-phenyl-3-thienyl)-2-[2-(3-methyl-1-hydroxy-1-pentyl)-5-phenyl-3-thienyl]-3,3,4,4,5,5-hexafluorocyclopentene (170 mg, 50%) as an oily product. A stirred solution of 1-(2-methyl-5-phenyl-3-thienyl)-2-[2-(3-methyl-1-hydroxy-1-pentyl)-5-phenyl-3-thienyl]-3,3,4,4,5,5-hexafluorocyclopentene (210 mg, 0.35 mmol) in 10 mL of DMF was heated at 170 °C for 13 h.[9] The mixture was cooled to room temperature and then water was added. The resultant mixture was extracted with ether and the organic extract was washed with brine and dried ($MgSO_4$). Finally, purification of the crude product by preparative thin-layer chromatography (hexane) and recrystallization afforded dithienyletene **(*S*)-1a** (80 mg, 39%) as slightly yellow crystals: mp 116.7−117.2 °C; ^{1}H NMR ($CDCl_3$) δ 0.62 (t, J = 6.2 Hz, 3 H), 0.78 (d, J = 10 Hz, 3 H), 1.10−1.23 (m, 2 H), 1.78−1.92 (m, 1 H), 1.94 (s, 3 H), 5.85−5.99 (m, 2 H), 7.21−7.65 (m, 12 H); UV−vis (hexane) λ_{max} (ϵ) 288 (33000); HRMS (FAB) *m*/*z* 588.1378 ([M]$^+$), calcd for $C_{32}H_{26}F_6S_2$ 588.1380.

Closed-Ring Isomer (1:1 Mixture of (*S*,*R*,*R*)-1b and (*S*,*S*,*S*)-1b). The closed-ring isomer (1:1 mixture of **(*S*,*R*,*R*)-1b** and **(*S*,*S*,*S*)-1b**) was separated by HPLC using silica gel columns (Superspher Si60 MERCK) in normal phase (hexane/AcOEt = 97:3). The retention time of open-ring isomer was 7.0 min and that of the closed-ring isomer was 8.6 min (flow rate = 0.7 mL/min): ^{1}H NMR ($CDCl_3$) δ 0.69−0.74 (m, 3 H), 0.86−0.89 (m, 3 H), 1.24−1.27 (m, 3 H), 2.16 (s, 3 H), 5.49−5.63 (m, 1 H), 6.43−6.49 (m, 1 H), 6.64 (s, 1 H), 6.76 (s, 1 H), 7.40−7.59 (m, 10 H); UV−vis (hexane) λ_{max} (ϵ) 274 (17000), 310 (20000), 580 (14000).

(*R*)-1-(2-Methyl-5-phenyl-3-thienyl)-2-[2-(3-methyl-1-penten-1-yl)-5-phenyl-3-thienyl]-3,3,4,4,5,5-hexafluorocyclopentene ((*R*)-1a). The synthetic procedure was same for **(*S*)-1a** except (*R*)-(−)-methylbutylbromide[10] was used instead of (*S*)-(+)-methylbutylbromide: mp 117−118 °C; ^{1}H NMR ($CDCl_3$) δ 0.62 (t, J = 6.2 Hz, 3 H), 0.78 (d, J = 10 Hz, 3 H), 1.10−1.23 (m, 2 H), 1.78−1.92 (m, 1 H), 1.94 (s, 3 H), 5.85−5.99 (m, 2 H), 7.21−7.65 (m, 12 H); HRMS (FAB) *m*/*z* 588.1382 ([M]$^+$), calcd for $C_{32}H_{26}F_6S_2$ 588.1380.

B. Photochemical Measurements. Solvents used for physical measurement were spectroscopic grade and purified by distillation before use. Absorption spectra were measured on a spectrophotometer (Hitachi U-3500). Absorption spectra in the single-crystalline phase were measured using a Leica DMLP polarizing microscope connected with a Hamamatsu PMA-11 detector. The polarizer and analyzer were set parallel to each other.

Photoirradiation was carried out using a USHIO 500 W super high-pressure mercury lamp and a USHIO 500-W xenon lamp. Mercury lines of 366, 405, 435, and 578 nm were isolated by passing the light through a combination of a Toshiba band-pass filter or a cutoff filter and a monochromator (Ritsu MC-20L).

HPLC was performed on a Hitachi L-7100 pump coupled with a Hitachi L-7400 UV detector. Silica gel columns (Superspher Si60 MERCK) in normal phase (hexane/AcOEt = 97:3) were used to separate the closed-ring isomers. Silica gel columns (Mightysil RP-18 GP KANTO chemicals) in reversed phase (CH_3CN/H_2O = 75:25) were used to analyze the diastereomers.

C. Crystallography. The data collection was performed on a Bruker SMART1000 CCD-based diffractometer (50 kV, 40 mA) with Mo Kα radiation. 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 5.118 cm. Crystal decay was monitored by repeating the 50 initial frames at the end data collection and analyzing the duplicate reflections. Data reduction was performed using SAINT software, which corrects for Lorentz and polarization effects, and decay. The cell constants were calculated by global refinement. The structure was solved by direct methods using SHELXS-86[11] and refined by full least-squares on F^2 using SHELXL-97.[12] The positions of all hydrogen atoms were calculated geometrically and refined by the riding model. The disordered part was refined isotropically.

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Photoirradiation for the X-ray crystallographic analysis was carried out with a USHIO 500-W Xe lamp. Linearly polarized monochromatic 440 nm light was obtained by passing light through a cutoff filter, a monochromator (Ritsu MC-20L) and a Gram-Tompson polarizer. For the photocyclization reaction, the (011) face was irradiated with the linearly polarized 440 nm light. The direction of polarization of irradiation light was selected parallel to the *a*-axis and normal to the (011) face. Irradiation was continued for 73 h. For the cycloreversion reaction, the crystal was exposed to nonpolarized 578 nm light for 1 h.

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Supporting Information Available: Tables of X-ray structural data for **(*S*)-1a**, **(*R*)-1a**, and photoirradiated **(*S*)-1a** (PDF). An X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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