

Photochromism of 1,2-Bis(2-methyl-6-nitro-1-benzothiophen-3-yl)-perfluorocyclopentene in a Single-Crystalline Phase: Dichroism of the Closed-Ring Form Isomer

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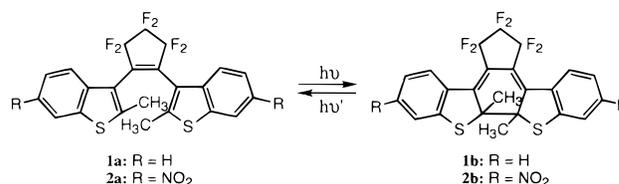
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Abstract: 1,2-Bis(2-methyl-6-nitro-1-benzothiophen-3-yl)perfluorocyclopentene was found to undergo a reversible photochromic reaction in the single-crystalline phase. Upon irradiation with 366-nm light, the single crystal turned green with keeping the crystal shape. The colored crystal showed dichroism. When the crystal was rotated under polarized light, the color changed from yellow to blue. The yellow and blue colors were attributed to two perpendicular electronic transitions at 465 and 600 nm of the closed-ring form. The two transition moments coincide with the directions of short and long axes of the closed-ring form isomers, which were regularly packed in the crystal lattice.

Introduction

Various types of photochromic compounds have been developed¹ in an attempt to apply the compounds to optoelectronic devices,^{2,3} such as optical memory, photooptical switching, and display. Although many photochromic compounds have been reported, compounds which show thermally irreversible photochromic reactivity in the crystalline phase are very rare.^{4–11} It has recently been found that some diarylperfluorocyclopentenes having thiophene rings as the aryl groups undergo photochromic reactions in the crystalline phases, and both isomers are thermally stable, even at 100 °C.^{12–15} In crystals, molecules are regularly oriented and packed in fixed conformations. In many cases, free rotation is prohibited. Therefore, photoreactivity in crystalline phases is dependent on the conformation fixed in the crystal lattice.

1,2-Bis(2-methyl-1-benzothiophen-3-yl)perfluorocyclopentene (**1a**) undergoes a thermally irreversible and fatigue-resistant photochromic reaction in solution.¹⁶ The benzothiophene aryl groups are effective to provide a fatigue-resistant property to photochromic diarylethenes. The compound is, however, photochemically inactive in the crystalline phase.¹⁷ It is desired to search for bisbenzothienylethene derivatives which show photochromic reactivity in single-crystalline phases to develop fatigue-resistant photochromic materials. Among the bisbenzothienylethene derivatives, we found that 1,2-bis(2-methyl-6-nitro-1-benzothiophen-3-yl)perfluorocyclopentene (**2a**) showed photochromic reactivity in certain crystals. The crystalline state reactivity was dependent on recrystallization solvents. In this paper, we report our studies of the correlation between the reactivity and the conformation of **2a** in crystals, and crystalline photochromism of **2**, especially dichroism of the closed-ring form isomer.



Results and Discussion

Photochromism in Solution. Figure 1 shows the absorption spectral change of **2** in hexane under irradiation with 313-nm light. The absorption coefficient (ϵ) for **2a** was determined to be $2.9 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ at 294 nm. Upon irradiation with 313-nm light, the colorless solution of **2a** in hexane turned red purple. The absorption maximum of the colored isomer was observed at 545 nm. The colored solution returned to the colorless solution

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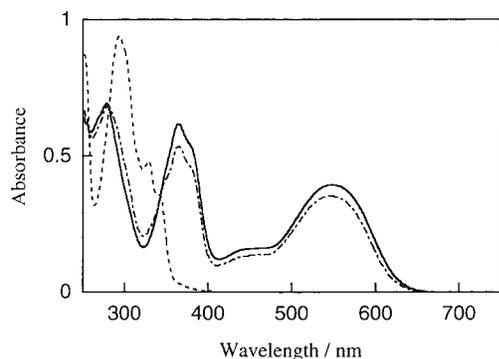


Figure 1. Absorption spectral change of **2** in hexane (3.3×10^{-5} M) after photoirradiation: **2a** (---), **2** in the photostationary state under irradiation with 313-nm light (- · -), and **2b** (—).

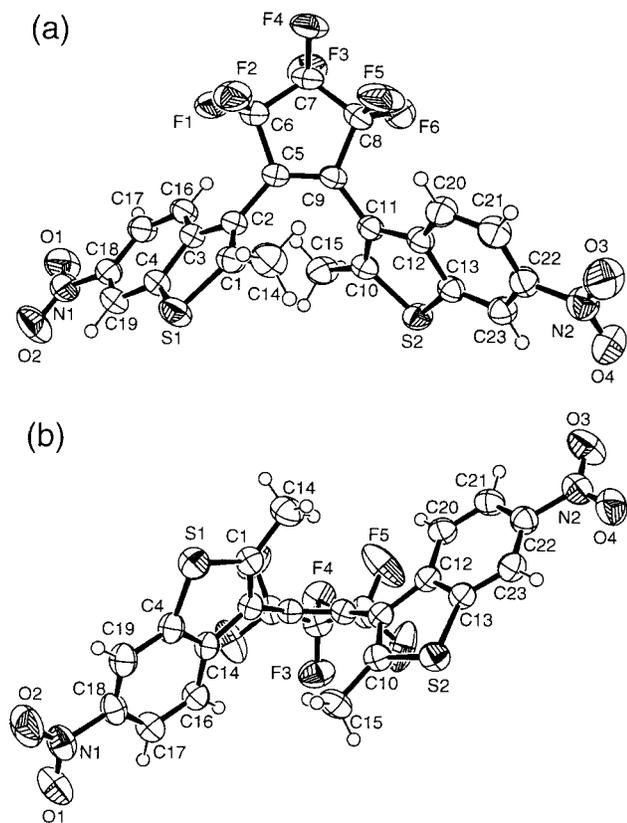


Figure 2. ORTEP drawings of top (a) and side (b) views of **2a-α**, showing 50% probability displacement ellipsoids.

of **2a** upon irradiation with visible light (>450 nm). The cyclization and cycloreversion quantum yields were determined to be 0.43 (313 nm) and 0.10 (545 nm), respectively.

The photoisomerization process of **2** in CDCl_3 was followed by ^1H NMR spectroscopy. Upon irradiation with 313-nm light, a new singlet peak appeared at 2.08 ppm, along with a decrease of the peaks at 2.32 and 2.58 ppm. The peaks at 2.32 and 2.58 ppm are assigned to the methyl protons of parallel and antiparallel conformations for **2a**, respectively.¹⁸ The ratio of parallel and antiparallel conformations was determined to be 39:61 in CDCl_3 at room temperature.^{19,20} The new peak at 2.08 ppm is assigned to the methyl protons of the closed-ring form, **2b**. Peaks at 7.6–8.7 ppm due to the benzothiophenyl protons

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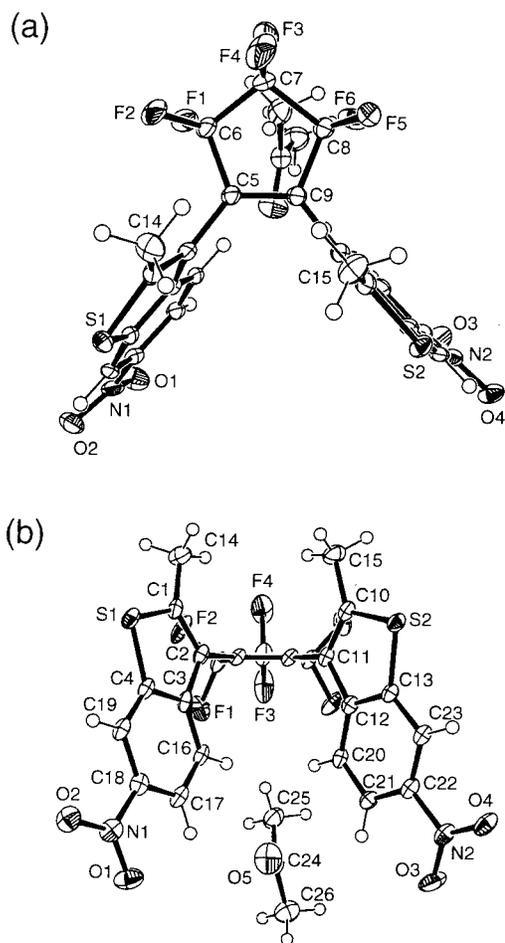


Figure 3. ORTEP drawings of top (a) and side (b) views of **2a-β**, showing 50% probability displacement ellipsoids.

of **2a** shifted to 7.9–8.2 ppm in the colored form. The shift of the benzothiophenyl protons and the singlet peak of the methyl protons in the NMR spectrum agree with the structure of the closed-ring form. The solution returned to colorless upon irradiation with visible light ($\lambda > 450$ nm), and the ^1H NMR spectrum returned to that of the open-ring form.

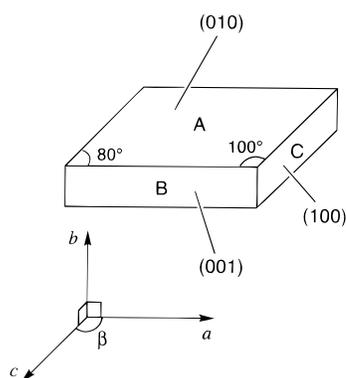
The colored isomer was isolated by HPLC. The structure of the closed-ring form, **2b**, was confirmed by ^1H NMR spectroscopy and X-ray crystallographic analysis (see Figure 13). The ϵ values for **2b** were determined to be 1.9×10^4 and 1.2×10^4 $\text{M}^{-1} \text{cm}^{-1}$ at 365 and 545 nm, respectively. The conversion to the closed-ring form in the photostationary state in hexane under irradiation with 313-nm light was determined to be 89%.

Photochromism in a Single-Crystalline Phase. (a) X-ray Crystallographic Analysis. Two types of single crystals **2a** were obtained, depending on recrystallization solvents. Single crystals **2a** obtained from hexane, benzene, toluene, and ethyl acetate were found to show photochromic reactivity in the single-crystalline phases. Upon irradiation with 366-nm light, the single crystal turned green, and the green color disappeared after irradiation with visible light (>450 nm). However, single crystals **2a** obtained from chloroform and acetone did not show any photochromic reactivity in the single-crystalline phases. These results suggest that the conformation of **2a** fixed in the crystalline phases is different among the crystals. Therefore, the structure of the two types of crystals was analyzed by an X-ray diffractometer.

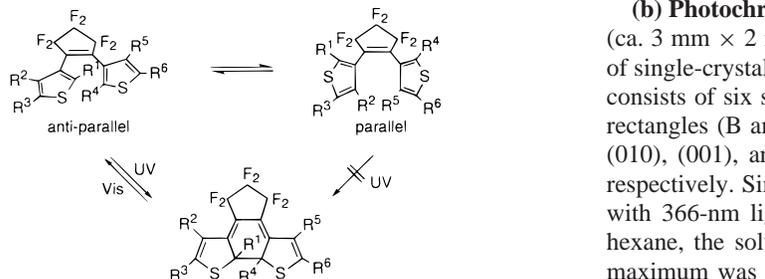
Table 1 shows the X-ray crystallographic analysis data of a single crystal (**2a-α**), obtained by recrystallization from hexane/

Table 1. Crystal Data and Structure Refinements for **2a- α** , **2a- β** , and **2b**

	2a-α	2a-β	2b
recrystallization solvent	hexane/toluene	acetone	hexane/ethyl acetate
formula	C ₂₃ H ₁₂ F ₆ N ₂ O ₄ S ₂	C ₂₆ H ₁₈ F ₆ N ₂ O ₅ S ₂	C ₂₃ H ₁₂ F ₆ N ₂ O ₄ S ₂
formula weight	558.47	616.54	558.47
temp/K	296(2)	103(2)	103(2)
crystal system	monoclinic	monoclinic	triclinic
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$
unit cell dimensions			
<i>a</i> /Å	9.941(2)	11.354(1)	11.597(1)
<i>b</i> /Å	15.748(3)	15.029(2)	13.085(1)
<i>c</i> /Å	14.492(3)	15.642(2)	14.270(1)
α /deg	90	90	83.583(1)
β /deg	100.297(4)	104.358(2)	80.643(1)
γ /deg	90	90	87.451(1)
volume/Å ³	2232.1(7)	2585.7(5)	2122.4(3)
<i>Z</i>	4	4	4
density (calcd)/(g/cm ³)	1.662	1.584	1.748
goodness-of-fit on <i>F</i> ²	1.068	1.154	1.011
final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]			
<i>R</i> 1	0.041	0.085	0.042
<i>wR</i> 2	0.125	0.240	0.100
<i>R</i> indices (all data)			
<i>R</i> 1	0.057	0.101	0.071
<i>wR</i> 2	0.132	0.250	0.115

**Figure 4.** Shape of single crystal **2a- α** and the face index.

toluene. Figure 2 shows the ORTEP drawings of **2a- α** . In solution, diarylethenes have two conformations, parallel and antiparallel, and they interconvert. The conrotatory cyclization can proceed only from the antiparallel conformation.²¹

**Figure 5.** Fatigue-resistant property of **2a** in the single crystal **2a- α** . Absorbances at 600 nm after irradiation with 405-nm light for 5 s were compared with that after the first irradiation cycle.

which an acetone molecule is included. The ORTEP drawing of **2a- β** in the crystal indicates that **2a- β** is packed in parallel conformation, which cannot undergo photocyclization reaction.²¹ The difference in reactivity between **2a- α** and **2a- β** is ascribed to the difference in the conformations of **2a**.

(b) Photochromism. A rhombus-shaped single crystal, **2a- α** (ca. 3 mm \times 2 mm \times 0.5 mm), was used for the further study of single-crystalline photochromism. The crystal shape of **2a- α** consists of six surfaces, with two parallelograms (A) and four rectangles (B and C), as illustrated in Figure 4. The planes of (010), (001), and (100) correspond to surfaces A, B, and C, respectively. Single crystal **2a- α** turned green upon irradiation with 366-nm light. When the green crystal was dissolved in hexane, the solution turned to red-purple, and the absorption maximum was observed at 545 nm, which is same as that of the closed-ring form **2b** shown in Figure 1. The green color of the crystal disappeared upon irradiation of the crystal with visible light ($\lambda > 450$ nm).

The fatigue-resistant characteristic of the crystal **2a- α** was examined by alternate irradiation with 405-nm light and visible ($\lambda > 490$ nm) light. The absorbance at 600 nm reached ca. 0.8 after irradiation of the crystal with 405-nm light (9.5 mW) for 5 s. The 600-nm band disappeared upon irradiation of the crystal with visible ($\lambda > 490$ nm) light for 5 s. The coloration/decoloration cycles were repeated many times, and the fatigue-resistant property was examined. The absorbance of the closed-ring form remained over 90% that of the first irradiation cycle,

In crystals, on the other hand, there is no exchange between the two conformers. The ORTEP drawing of **2a- α** indicates that **2a- α** is packed in photoactive antiparallel conformation in the crystal. The distance between the reacting carbon atoms was determined to be 0.384 nm, which is close enough for the reaction.^{17,22}

Table 1 also shows the X-ray crystallographic analysis data of another single crystal (**2a- β**), obtained by recrystallization from acetone. Figure 3 shows the ORTEP drawings of **2a- β** in

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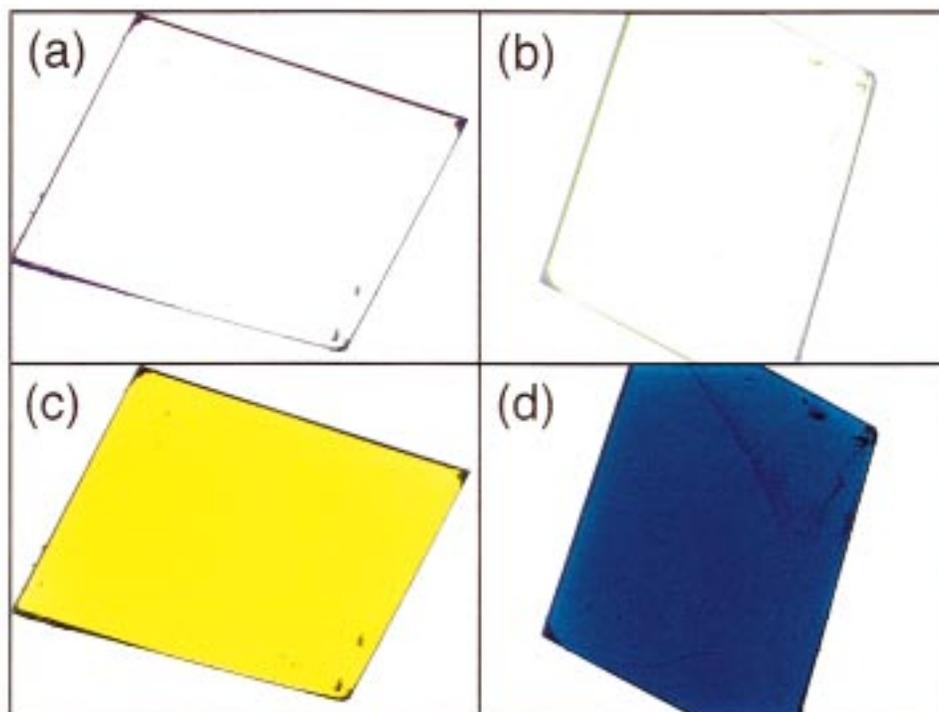


Figure 6. Photographs of single crystal **2a-α** (surface A) under polarized light before (a, $\theta = 0^\circ$; b, $\theta = 90^\circ$) and after (c, $\theta = 0^\circ$; d, $\theta = 90^\circ$) irradiation with 366-nm light. θ is the rotation angle of the crystal, as shown in Figure 7a.

even after 10 000 cycles, as shown in Figure 5. After 15 000 cycles, the crystal surface became rough, and this suppressed the coloration.

The color of the crystal was observed under polarized light. Figure 6 shows the color change of surface A. Before photoirradiation, the crystal was colorless (Figure 6a,b). Upon irradiation with 366-nm light, the crystal turned yellow at a certain angle ($\theta = 0^\circ$ shown in Figure 7a). When the crystal was rotated as much as 90° , the color turned blue. The yellow color reappeared at 180° . The clear dichroism from yellow to blue indicates that the closed-ring form isomer is regularly oriented in the crystal and the photochromic reaction proceeds in the crystal lattice.

Figure 7 shows the polarized absorption spectra of the closed-ring form isomer at 0° and 90° and the polar plots of absorbance at 465 and 600 nm. The maximum absorbance of the blue color at 600 nm appeared at 90° and 270° . The order-parameter ($(A_{\parallel} - A_{\perp}) / (A_{\parallel} + 2A_{\perp})$) was calculated to be 0.90 at 600 nm. Such a high order parameter also confirms that **2a-α** underwent photochromic reaction in the crystal lattice. The maximum absorbance of yellow color at 465 nm appeared at 0° and 180° . The polar plots indicate that the two transition moment vectors of the 465- and 600-nm bands are perpendicular to each other on surface A.

Figure 8 shows the color change of the crystal surface B. Upon irradiation with 366-nm light, surface B turned blue. No color change was observed upon rotating the crystal sample, but the color intensity changed. At a certain angle ($\theta = 0^\circ$ shown in Figure 9a), the blue color became pale. When the crystal was rotated as much as 90° , the blue color became deep. Figure 9 shows the absorption spectra and the polar plots of absorbance at 465 and 600 nm. When the sample was rotated, the spectrum intensity changed, but the absorption maximum remained at 600 nm. The polar plots of the 465- and 600-nm bands indicated that the transition moment vectors are apparently in the same direction on surface B.

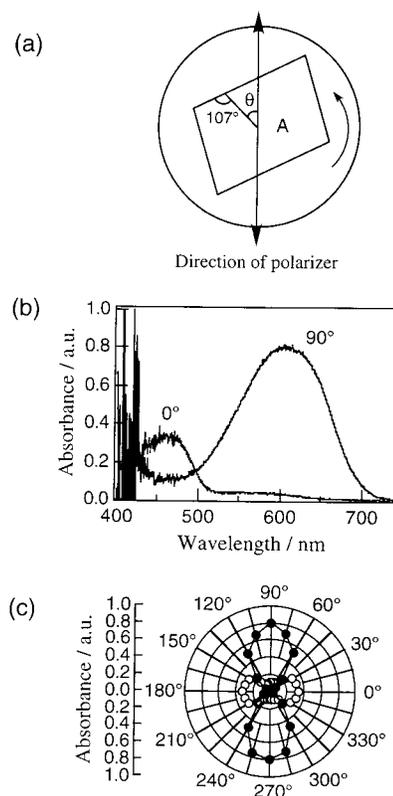


Figure 7. Polarized absorption spectra of the colored crystal of surface A: (a) direction of polarizer, (b) polarized absorption spectra, and (c) the polar plots at 465 (○) and 600 nm (●).

Figure 10 shows the color change of the crystal surface C. Upon irradiation with 366-nm light, surface C turned blue at a certain angle ($\theta = 0^\circ$ shown in Figure 11a). When the crystal was rotated as much as 90° , the color changed to green. This color change was different from those of surfaces A and B. Figure 11 shows the absorption spectra and the polar plots of

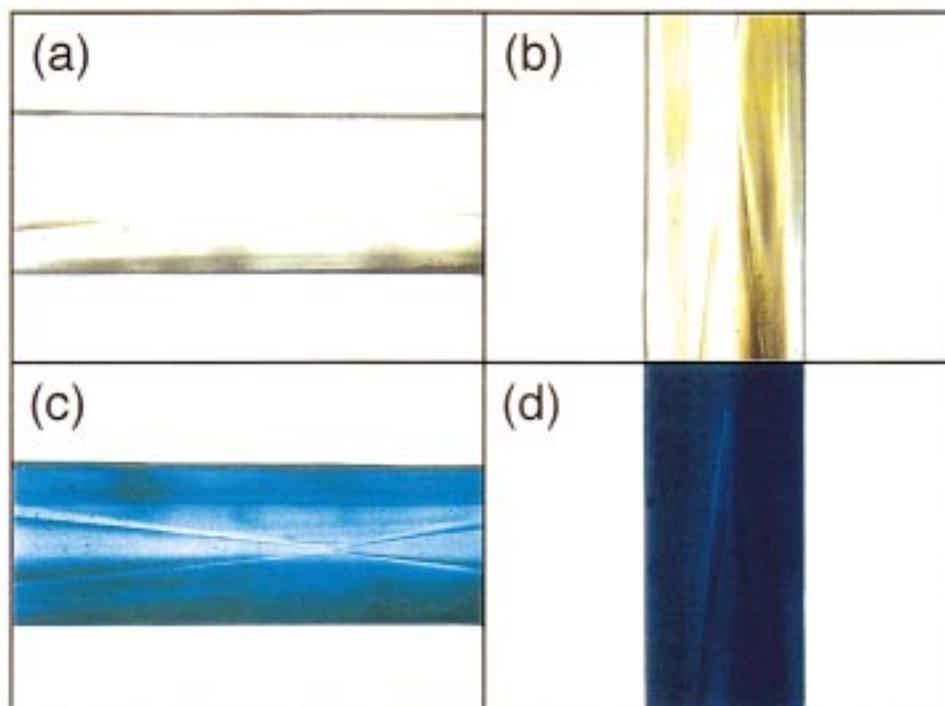


Figure 8. Photographs of single crystal **2a-α** (surface B) under polarized light before (a, $\theta = 0^\circ$; b, $\theta = 90^\circ$) and after (c, $\theta = 0^\circ$; d, $\theta = 90^\circ$) irradiation with 366-nm light. θ is the rotation angle of the crystal, as shown in Figure 9a.

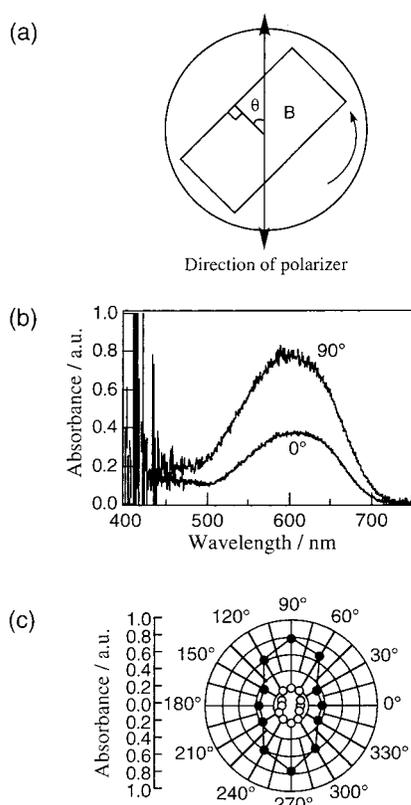


Figure 9. Polarized absorption spectra of the colored crystal of surface B: (a) direction of polarizer, (b) polarized absorption spectra, and (c) the polar plots at 465 (○) and 600 nm (●).

the 465- and 600-nm bands. When the the sample was rotated, the absorbance at 465 nm changed from 0.18 to 0.60, while the absorbance at 600 nm changed only from 0.66 to 0.44. The absorption intensities at 465 and 600 nm are similar to each other at 90° . This is why the green color was observed at 90° .

According to the molecular orbital calculation of unsubstituted compound **1**,²³ the transition moment vector of the longest absorption band (528 nm, $f = 0.162$) is in the long axis of the closed-ring form, and the second band (430 nm, $f = 0.101$) is perpendicular to that. The electronic transition property is considered to be maintained, even when nitro groups were introduced at 6 and 6' positions. Therefore, the electronic transition moment vectors of the longest absorption band ($\lambda_{\max} = 600$ nm) and the second band ($\lambda_{\max} = 465$ nm) of **2b** are assigned to the direction of x - and y -axes, respectively, as shown in Figure 12. The two benzothiophene and cyclopentene rings are almost coplanar in the closed-ring form, as determined by X-ray crystallographic analysis, shown in Table 1 and Figure 13.^{15,21,24} Therefore, the x - and y -axes correspond to the long and short axes of the closed-ring form. When **2a** was converted to **2b** in the crystal, no crystal shape change was observed. This indicates that **2b** was produced from **2a** in the crystal lattice of **2a-α**. The transition moment vectors of the 465- and 600-nm bands coincide approximately with the y - and x -axes of **2a** packed in the crystal.¹⁵

Figure 14 shows the packing diagrams of **2a**, the electronic transition moment vectors, and the polar plots on surfaces A, B, and C. The blue and yellow arrows indicate the transition moment vectors of the 600- and 465-nm bands, respectively. On surface A, the two transition moment vectors of the 465- and 600-nm bands are perpendicular to each other. Therefore, clear dichroism from yellow to blue was observed.

Two different kinds of orientation of molecules coexist on surfaces B and C. On surface B, the long axes of **2a** molecules tilt as much as $+29^\circ$ and -29° from the a -axis and are almost parallel to surface B. Therefore, the long axis of photogenerated **2b** is in the direction shown by blue arrow. The short axis of **2a** is almost perpendicular to surface B, and the absorbance of the yellow band is much smaller than that of the blue band. As

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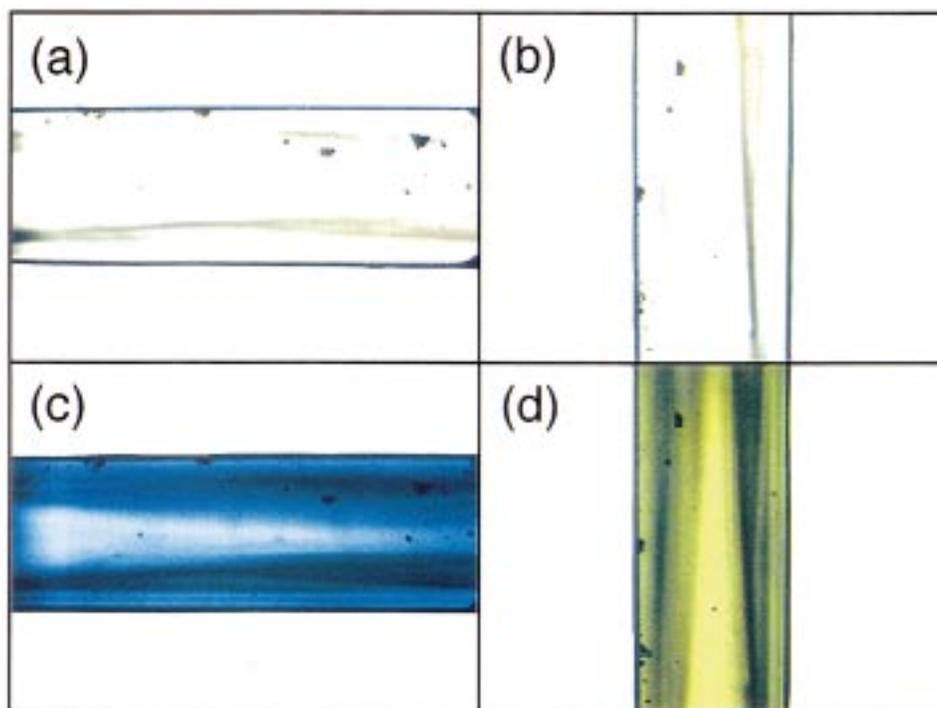


Figure 10. Photographs of single crystal **2a-α** (surface C) under polarized light before (a, $\theta = 0^\circ$; b, $\theta = 90^\circ$) and after (c, $\theta = 0^\circ$; d, $\theta = 90^\circ$) irradiation with 366-nm light. θ is the rotation angle of the crystal, as shown in Figure 11a.

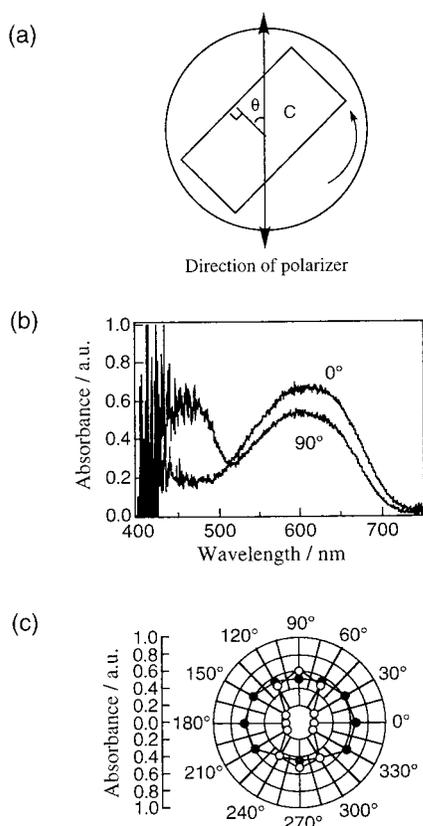


Figure 11. Polarized absorption spectra of the colored crystal of surface C: (a) direction of polarizer, (b) polarized absorption spectra, and (c) the polar plots at 465 (○) and 600 nm (●).

a result, a deep blue color was observed in the direction of the *a*-axis. On surface C, the long axes of **2a** molecules tilt as much as $+62^\circ$ and -62° from the *c*-axis, as shown by the blue arrow. This means that the blue color transition is not strong in the direction of the *c*-axis. The short axes of **2a** are almost parallel

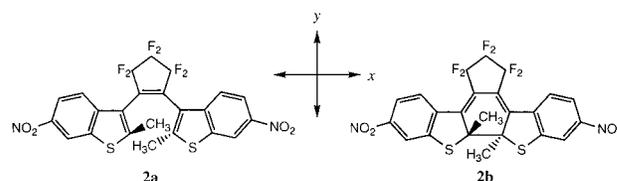


Figure 12. Molecular structures of **2a** and **2b**: *x* and *y* are the long and short axes of the molecules, respectively.

to the *c*-axis. Therefore, the blue and yellow band intensities become similar in the direction of the *c*-axis. This is why dichroism from blue to green was observed on surface C.

Conclusions

It has been demonstrated that 1,2-bis(2-methyl-6-nitro-1-benzothiophen-3-yl)perfluorocyclopentene, which was recrystallized from hexane/toluene, undergoes a photochromic reaction in the single-crystalline phase. Upon irradiation with 366-nm light, the colorless open-ring form crystal turned green, and the green color disappeared after irradiation with visible light ($\lambda > 450$ nm). The green color observed under polarized light consisted of yellow and blue, and the two colors dramatically changed when the crystal sample was rotated under polarized light. The molecular arrangement of the closed-ring form isomers was estimated from the absorption anisotropy under polarized light and compared with the molecular packing of the open-ring form isomers, which was determined by X-ray crystallographic analysis. It was concluded that the yellow and blue colors were attributed to two perpendicular electronic transitions at 465 and 600 nm, which correspond to the short and long molecular axes of the closed-ring form, respectively. The coloration/decoloration cycles of the crystal could be repeated 10 000 times, with an absorbance loss of only ca. 10%.

Experimental Section

General. Solvents used were spectroscopic grade and purified by distillation before use. ^1H NMR spectra were recorded on a Varian

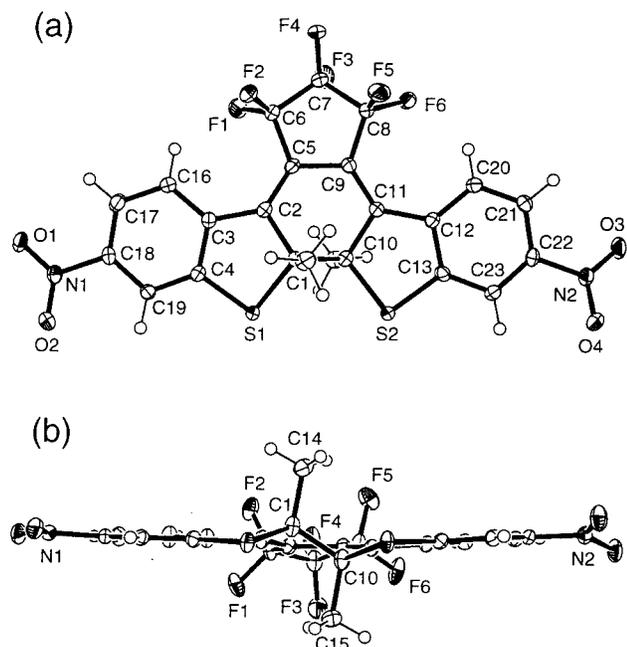


Figure 13. ORTEP drawings of top (a) and side (b) views of **2b**, showing 50% probability displacement ellipsoids. There are two independent fragments; one of them is illustrated.

Gemini 200 spectrometer (200 MHz). Tetramethylsilane was used as an internal standard. Mass spectra were taken with a Shimadzu GCMS-QP5050A gas chromatograph–mass spectrometer. Absorption spectra in a 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. The polarizer and analyzer were set parallel to each other. Photoirradiation was carried out using a USHIO 500-W high-pressure mercury lamp, a USHIO 500-W xenon lamp, or a glass fiber light source (USHIO 200-W xenon lamp). Monochromatic light was obtained by passing the light through a monochromator (Ritsu MV-10N). The crystal sample was fixed on the stage of the microscope and irradiated with the glass fiber light source. X-ray crystallographic analysis was carried out using a Bruker SMART CCD X-ray diffractometer. Fatigue resistance measurement was carried out by using an apparatus described in ref 25.

1,2-Bis(2-methyl-6-nitro-1-benzothiophen-3-yl)perfluorocyclopentene (2a). To a solution of acetic acid (60 mL) and acetic anhydrous (5 mL) was added 1,2-bis(2-methyl-1-benzothiophen-3-yl)perfluorocyclopentene (**1a**)¹⁶ (3.0 g) at 10 °C. Fuming nitrate (3 mL) was slowly added to the solution while the temperature was kept below 10 °C. The mixture was stirred overnight at room temperature. Cold water was added to the mixture. The solution was neutralized and extracted with ethyl acetate. The organic layer was dried over MgSO₄, filtrated, and concentrated. The residue was purified by column chromatography on silica gel using hexane/ethyl acetate (4:1) as the eluent and by recrystallization from hexane to give 2.1 g of **2a** in 58% yield as a pale yellow crystal: mp = 200–201 °C; ¹H NMR (200 MHz, CDCl₃) δ 2.32 and 2.58 (s, 6H, CH₃), 7.6–8.7 (m, 6H, Ar); MS *m/z* (M⁺) 558. Anal. Calcd for C₂₃H₁₂F₆N₂O₄S₂: C, 49.47; H, 2.17; N, 5.02. Found: C, 49.59; H, 2.15; N, 4.97.

Closed-Ring Form for 2a (2b). **2b** was isolated by passing a photostationary solution containing **2a** and **2b** through a HPLC (Hitachi L-6250 HPLC system, silica gel column, hexane/ethyl acetate (4:1) as

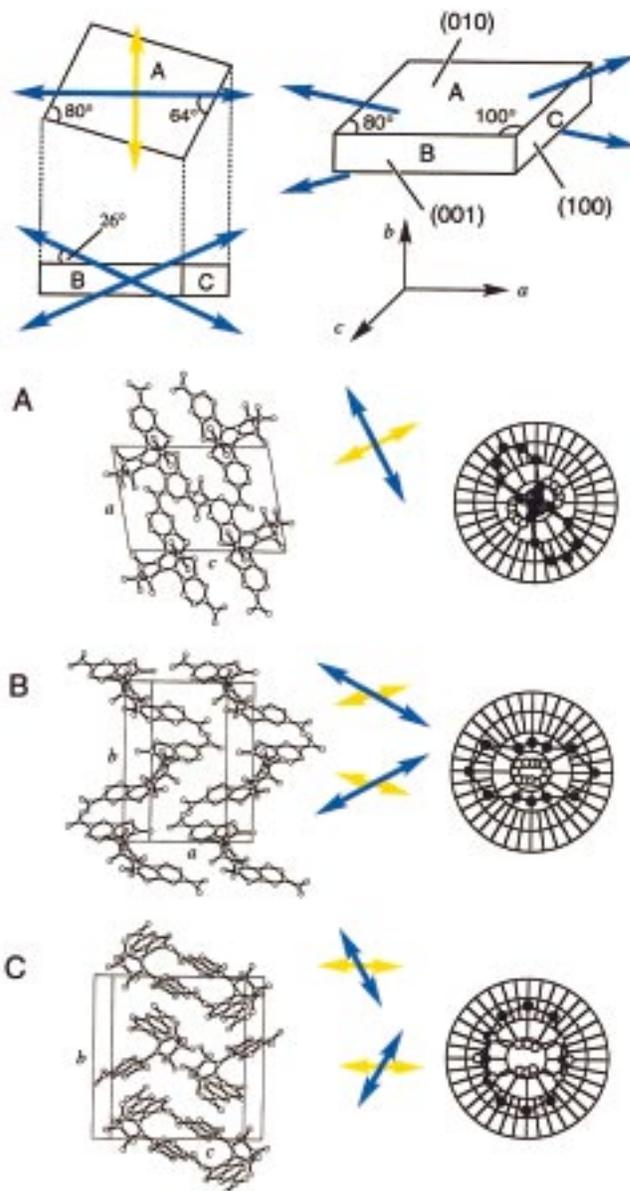


Figure 14. Packing diagrams of **2a** and polar plots of absorbance of **2b** at 465 (○) and 600 nm (●) of surfaces A (010), B (001), and C (100). The arrows indicate the transition moment vectors of 465- (yellow arrow) and 600-nm (blue arrow) absorptions for **2b**.

the eluent): no melting point below 250 °C; ¹H NMR (200 MHz, CDCl₃) δ 2.08 (s, 6H, CH₃), 7.9–8.2 (m, 6H, Ar); MS *m/z* (M⁺) 558. Anal. Calcd for C₂₃H₁₂F₆N₂O₄S₂: C, 49.47; H, 2.17; N, 5.02. Found: C, 49.82; H, 2.24; N, 4.99.

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Supporting Information Available: X-ray structural information on **2a-α**, **2a-β**, and **2b** (PDF). An X-ray crystallographic file, in CIF format, is also available. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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