Polymorphism of 1,2-Bis(2-methyl-5-*p*-methoxyphenyl-3-thienyl)perfluorocyclopentene and Photochromic Reactivity of the Single Crystals

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Abstract: Four polymorphic crystals were obtained by recrystallization of 1,2-bis(2-methyl-5-*p*-methoxyphenyl-3-thienyl)perfluorocyclopentene (**1a**) from hexane. All crystals underwent photochromic reactions upon alternate irradiation with ultraviolet ($\lambda = 370$ nm) and visible light ($\lambda > 500$ nm). The photocyclization quantum yields were found to be close to unity irrespective of the crystal types, while the photocycloreversion quantum yields were different as much as four times depending on the conformation of the closed-ring isomers in the crystals.

Keywords: diarylethene • photochromism • polymorphism • quantum yield • single crystal

Introduction

Photochromism is referred as a light-induced reversible transformation between two isomers having different absorption spectra.[1, 2] Although a great number of photochromic compounds have been reported so far, compounds which exhibit the photochromic reactivity in the crystalline phase are very rare and in most cases photogenerated isomers are thermally unstable.[3–15] Recently we found that some diarylethene derivatives undergo single-crystalline photochromism and both initial colorless and photogenerated colored isomers are stable in the dark.[16–29] The thermally irreversible and fatigue resistant photochromic crystals can be potentially applied to various optoelectronic devices, such as holographic and three-dimensional optical recording memories.[26, 30–33]

Single-crystalline photochromism of diarylethene derivatives has following characteristics: i) The absorption spectrum of the closed-ring form isomer exhibits a distinct dichroic character and the maximum shifts to a longer wavelength in comparison with that in solution. The spectrum shift is ascribable to the difference in the conformation of the molecules between in crystal and in solution. ii) The photocyclization quantum yield in crystal is twice larger than that in solution and is close to unity. On the other hand, the photocycloreversion quantum yield in crystal varies depending on the molecules.[28] The conformation of the closed-ring isomer is considered to control the cycloreversion quantum yield, but the details have not yet been clarified. iii) The photocyclization reaction takes place without any activation energy, while the photocycloreversion reaction has to overcome a small activation energy.[22] iv) The activation energy of the thermal cycloreversion reaction in crystal is smaller than that in solution. The activation energy depends on the conformation of the open- and closed-ring isomers in crystal.[24] Photochromic performance of diarylethene derivatives in crystal strongly depends on the conformation of the molecules.

During the course of study of single-crystalline photochromism, we found that 1,2-bis(2-methyl-5-*p*-methoxyphenyl-3-thienyl)perfluorocyclopentene (**1a**) forms four polymorphic crystals when recrystallized from hexane (see Scheme 1). Each molecule has a different conformation in the four types of crystals. This enables us to study the effect of conformation on the optical property and the reactivity. In this paper, we report on the correlation between the conformation and the optical property as well as the reactivity.

Results and Discussion

Photochromism in hexane: Figure 1 shows the absorption spectral change of **1a** by irradiation with 313 nm light in hexane. Compound **1a** has the absorption maximum at 293 nm ($\varepsilon = 4.4 \times 10^4\,\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$). Upon irradiation with 313 nm light, the colorless solution of **1a** turned blue; a visible absorption band was observed at 582 nm for this solution. The blue color disappeared upon irradiation with visible light ($\lambda > 500$ nm). The spectral change could be repeated many times. The blue colored solution in the photostationary state was analyzed by HPLC. Two peaks were observed in the HPLC (silica gel column, hexane/ethyl acetate 9:1) monitored at the isosbestic point of 316 nm. The elution time of the former

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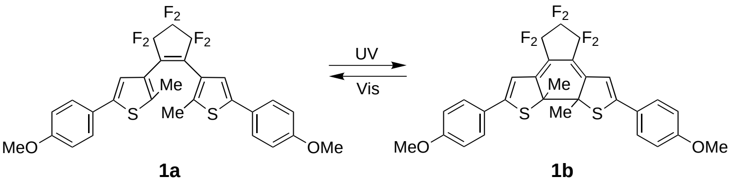

Scheme 1. Photochromism of compound **1**.

small peak was the same as that of **1a**. The latter was isolated. The structure of the compound was analyzed by ^{1}H NMR spectrum, mass spectrum, elemental analysis, and X-ray crystallography. X-ray crystallographic analysis data is shown in Table 1. All data agreed with those of **1b**. The absorption spectrum of **1b** is also shown in Figure 1. The spectrum was almost the same as that of the photostationary solution, indicating high conversion from **1a** to **1b**. The ε value for **1b** was determined to be $2.1 \times 10^4\,\text{M}^{-1}\text{cm}^{-1}$ at 582 nm. The conversion from **1a** to **1b** in the photostationary state upon irradiation with 313 nm light was 96%. Upon irradiation with visible light ($\lambda > 500$ nm), the solution turned colorless to give the same spectrum as **1a**.

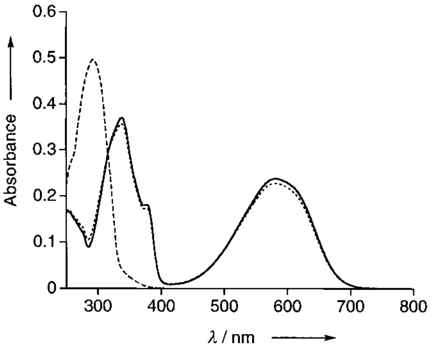

Figure 1. Absorption spectral change of **1** in hexane (1.1×10^{-5} M): **1a** (– – –), **1b** (——), and **1** in the photostationary state (- - - -).

The quantum yields of photocyclization and photocycloreversion reactions were determined in hexane to be 0.56 (by irradiation with 293 nm light) and 0.0052 (with 582 nm light), respectively. The photocyclization yield was similar to that of 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene having no methoxy substituents, while the photocycloreversion yield was reduced to a half.[22]

Polymorphism: Four kinds of crystals were obtained by slowly evaporating hexane solutions of **1a** at room temperature. Figure 2a and b show the shapes of the four crystals, which are named as **1a-*α***, ***β***, ***γ***, and ***δ***, and color changes upon irradiation with UV light. α-crystal had a well-developed surface with angles of 74 and 106°. β- and γ-crystals had surfaces with angles of 77 and 103°. δ-crystal was obtained as a needle. The melting points were 149–150°C (***α***), 136–138°C (***β***), 148–149°C (***γ***), and 135–137°C (***δ***), respectively. X-ray crystallographic analysis of the crystals was carried out to confirm the polymorphic forms, and the resulting crystallographic data are shown in Table 1. The R_1 values for the reflection with $I > 2\sigma(I)$ were less than 0.05 for all four crystals.

Table 1. Crystal data and structure refinement for **1a-*α***, **1a-*β***, **1a-*γ***, **1a-*δ***, and **1b**.

	1a-*α*	**1a-*β***	**1a-*γ***	**1a-*δ***	**1b**
formula	$C_{29}H_{22}F_6O_2S_2$	$C_{29}H_{22}F_6O_2S_2$	$C_{29}H_{22}F_6O_2S_2$	$C_{29}H_{22}F_6O_2S_2$	$C_{29}H_{22}F_6O_2S_2$
formula weight	580.59	580.59	580.59	580.59	580.59
crystal size [mm^3]	0.5 × 0.3 × 0.2	0.5 × 0.3 × 0.1	0.5 × 0.5 × 0.1	0.6 × 0.2 × 0.2	0.7 × 0.4 × 0.2
T [K]	296(2)	296(2)	296(2)	293(2)	298(2)
crystal system	monoclinic	triclinic	monoclinic	monoclinic	triclinic
space group	$C2/c$	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a [Å]	26.987(6)	11.406(2)	26.157(5)	18.727(4)	11.085(3)
b [Å]	8.806(2)	13.758(3)	9.023(2)	6.643(1)	11.239(3)
c [Å]	11.499(2)	18.229(4)	11.296(4)	21.459(4)	11.864(3)
α [°]	90	72.541(3)	90	90	83.276(4)
β [°]	91.554(4)	82.208(3)	94.500(4)	101.035(3)	65.030(3)
γ [°]	90	76.663(3)	90	90	88.198(5)
V [Å^3]	2731.7(10)	2648.4(10)	2657.9(9)	2620.1(9)	1330.5(6)
Z	4	4	4	4	2
ρ_{calcd} [g cm^{-3}]	1.412	1.456	1.451	1.472	1.449
μ [mm^{-1}]	0.261	0.270	0.269	0.273	0.268
F(000)	1192	1192	1192	1192	596
θ range [°]	1.51–27.52	1.17–27.64	0.78–27.52	1.11–27.51	1.82–27.56
reflections collected	7757	22439	15564	14677	15001
independent reflections	2934	11293	5808	5598	5772
parameters	206	833	438	354	439
goodness-of-fit on F^2	0.966	0.913	0.964	0.962	1.022
final R indices [$I > 2\sigma(I)$]					
R_1	0.0462	0.0411	0.0410	0.0389	0.0530
wR_2	0.1171	0.0831	0.1018	0.0878	0.1252
R indices (all data)					
R_1	0.0714	0.0946	0.0795	0.0810	0.0889
wR_2	0.1304	0.0982	0.1244	0.1019	0.1456
largest diff. peak/hole [e Å^{-3}]	0.229/ – 0.330	0.191/ – 0.279	0.213/ – 0.250	0.218/ – 0.188	0.242/ – 0.432

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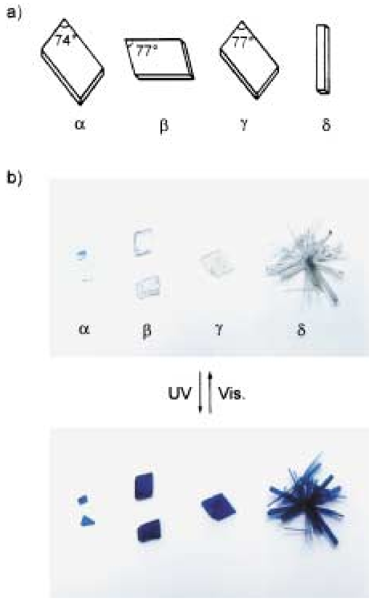

Figure 2. Crystal shapes of **1a-*α***, **1a-*β***, **1a-*γ***, and **1a-*δ*** (a), and photographs of the crystals before and after UV irradiation (b).

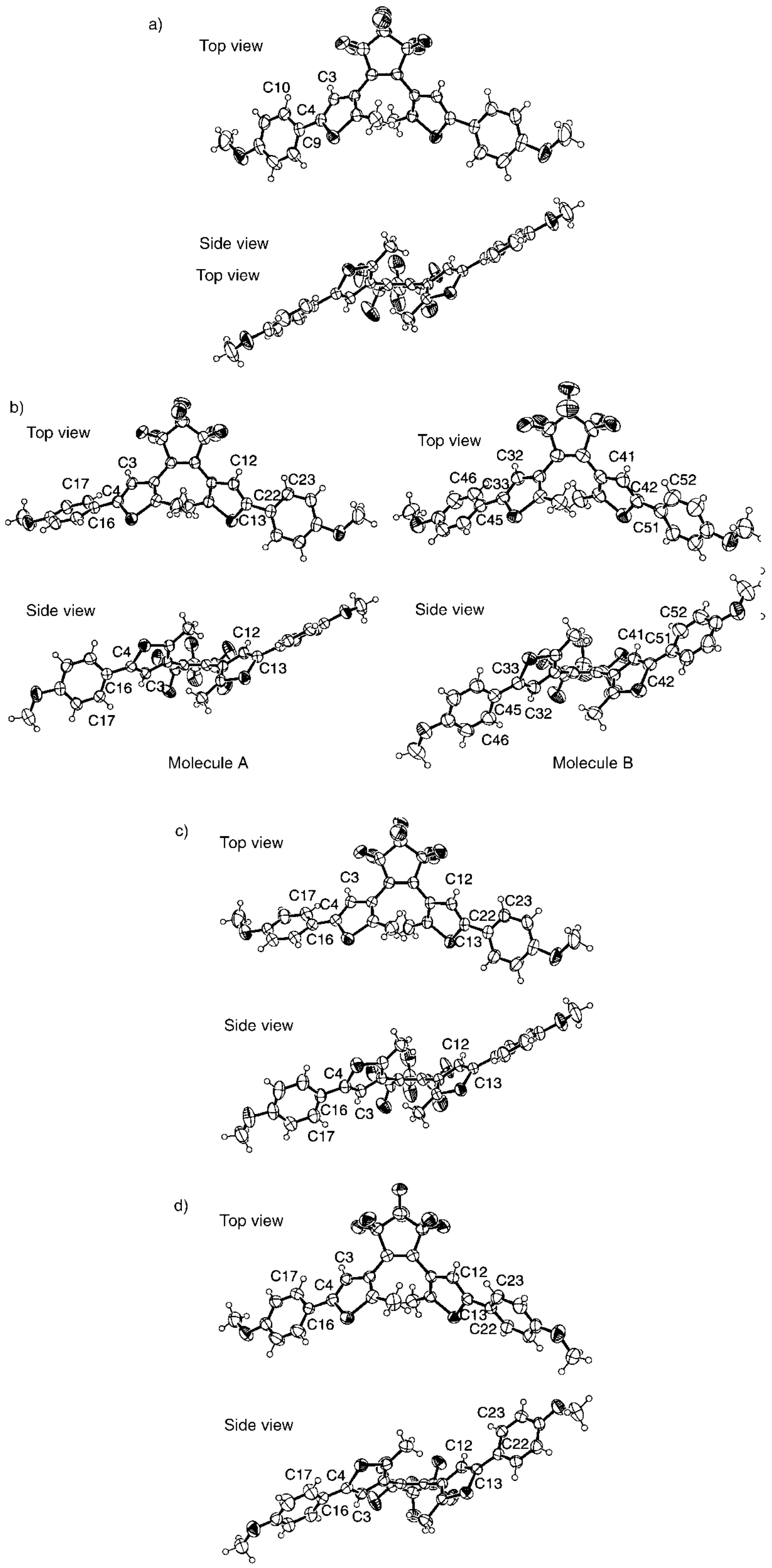

Figure 3. ORTEP drawings of **1a-*α*** (a), **1a-*β*** (b), **1a-*γ*** (c), and **1a-*δ*** (d).

The crystal system of **1a-*α*** was monoclinic *C*2/*c*, $Z = 4$. The unit cell volume was 2731.7(10) Å^3. The ORTEP drawing of **1a-*α*** is shown in Figure 3a. Half of the molecules were crystallographically independent. The perfluorocyclopentene ring was disordered equally. The distance between the reactive carbon atoms was 3.48 Å. The planes of two phenyl rings were almost parallel to the perfluorocyclopentene plane. The rotation angle between thiophene and phenyl rings (C3-C4-C9-C10) was 23.9°.

The crystal system of **1a-*β*** had a space group of triclinic $P\bar{1}$ and $Z = 4$. The unit cell volume was 2648.4(10) Å^3. Two molecules were independently packed, as indicated by molecules A and B. The distance between the reactive carbon atoms in the A molecules was 3.55 Å. The rotation angles between thiophene and phenyl rings (C3-C4-C16-C17 and C12-C13-C22-C23) were −31.9 and 33.2°, respectively. The distance between the reactive carbon atoms in the B molecules was 3.70 Å. The rotation angles between thiophene and phenyl rings (C41-C42-C51-C52 and C32-C33-C45-C46) were 2.3 and −14.4°, respectively. The perfluorocyclopentene rings were disordered in both A and B molecules.

The crystal system of **1a-*γ*** had a space group of monoclinic $P2_1/c$ and $Z = 4$. The unit cell volume was 2657.9(9) Å^3. The molecular packing was similar to that of **1a-*α***. One of the phenyl ring planes was almost parallel to the perfluorocyclopentene plane, while the other tilted. The rotation angles between thiophene and phenyl rings were −22.9 and 25.0° for C3-C4-C16-C17 and C12-C13-C22-C23, respectively. The distance between the reactive carbon atoms was 3.52 Å. The perfluorocyclopentene ring was disordered.

The crystal system of **1a-*δ*** had a space group of monoclinic $P2_1/c$ and $Z = 4$. The unit cell volume was 2620.1(9) Å^3. The planes of two phenyl rings were twist with the planes of thienyl rings. The rotation angles between thiophene and phenyl rings were 6.0 and −16.6° for C3-C4-C16-C17 and C12-C13-C22-C23, respectively. The distance between the reactive carbon atoms was 3.59 Å.

The four crystals have different space groups, unit cell volumes, conformation of the molecules, and the distance between the reactive carbon atoms. This indicates that the four crystals are polymorphic forms. The necessary conditions for the photocyclization reactions to take place in the single-crystalline phase are that the diarylethenes should have an antiparallel conformation and the distance between the reactive carbon atoms is less than 4.2 Å.[3] The thiophene rings in all four crystals have the antiparallel conformation and the distances between the reactive carbons are 3.48–3.70 Å. This indicates that all four crystals have a possibility to undergo photochromism in the crystalline phase.

Photochromism in a single-crystalline phase: All four single crystals **1a** turned blue upon irradiation with 370 nm, as shown in Figure 2b. The photogenerated blue-colored crystals were dissolved into hexane, and the absorption spectra were measured in hexane. The visible absorption maxima of all dissolved crystals were the same as that of **1b**. The photogenerated blue color of the crystals disappeared upon irradiation with visible light ($\lambda > 500$ nm).

To confirm the regular packing of the photogenerated colored isomers, the dichroism of the crystals was measured under linearly polarized light. The well-developed surfaces for α, β, γ, and δ-crystals shown in Figure 2a were (100), (001), (100), and (100) faces, respectively. Figure 4 shows the polarized absorption spectra of the four colored crystals. The absorption maxima at the highest intensity angle (||) were different among the four crystals. α-, β-, γ-, and δ-crystals gave the maxima at 630, 600, 615, and 600 nm, respectively. The absorption maxima shifted to longer wavelengths with the following order: β and $\delta < \gamma < \alpha$. This order is considered to reflect the π-conjugation length of the closed-ring isomers. As can be seen from the structures shown in Figure 3, two phenyl groups in α-crystal become to almost parallel to the perfluorocyclopentene ring by photocyclization. On the other hand, in the case of β- and δ-crystals the planes of phenyl rings tilted to the plane of perfluorocyclopentene. This means that the phenyl rings scarcely enter the π-conjugation of the central part of the closed-ring form. In the case of γ-crystal the central π-conjugation of the closed-ring form can extend to one of the phenyl rings.

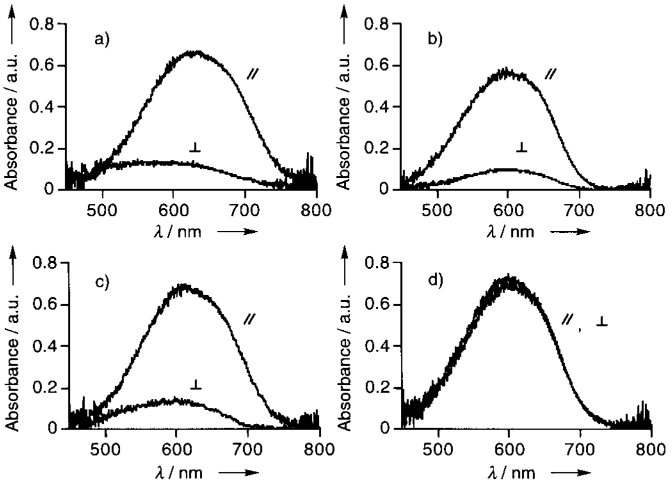

Figure 4. Absorption spectra of the photogenerated colored crystals. a) α-crystal, b) β-crystal, c) γ-crystal, d) δ-crystal.

Figure 5 shows the molecular packing and the polar plots of the absorbances. The order parameters $((A_{\parallel} - A_{\perp})/(A_{\parallel}+2A_{\perp}))$ were estimated to be 0.60 (**α**), 0.66 (**β**), and 0.59 (**γ**), respectively. The relatively large order parameters indicate that the diarylethenes undergo photochromism in the single-crystalline lattice. In the case of δ-crystal the absorption anisotropy was not observed as shown in Figures 4d and 5d. Molecules are packed in two different orientations, which are almost perpendicular to each other.

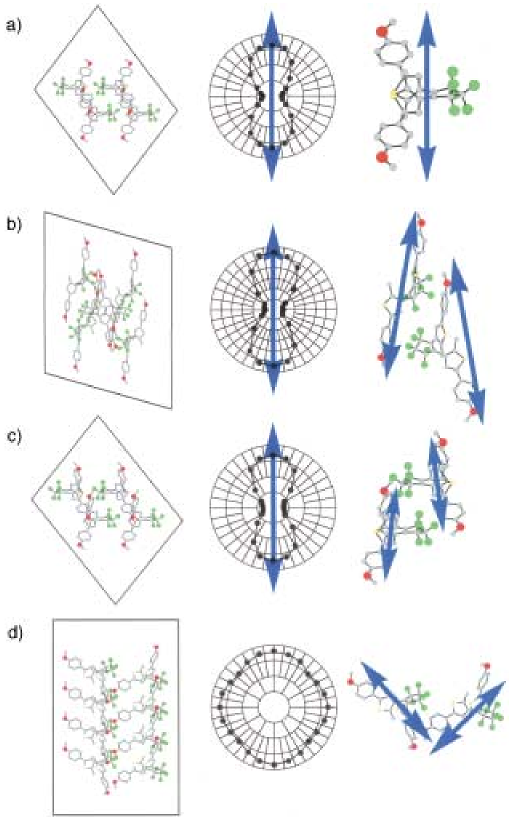

Figure 5. Packing diagrams of the open-ring isomers and polar plots of the absorbance of the photogenerated colored isomers at the absorption maximum. Right hand side shows typical molecule(s) in the crystal. a) α-crystal, b) β-crystal, c) γ-crystal, d) δ-crystal.

Partially bleaching reaction: As described above, **1a** molecules in δ-crystal are packed as shown in Figure 5d. The long axes of the molecules are oriented perpendicularly to each other. This suggests that linearly polarized light can selectively bleach the closed-ring isomers. Figure 6 shows photographs of δ-crystal under the polarized light. The colorless δ-crystal (Figure 6a) was irradiated with 370 nm non-polarized light to give the blue colored crystal as shown in Figure 6b. 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 were hardly bleached, as shown in Figure 6c. On the other hand, when the direction of the irradiated polarized light was rotated as much as 90°, the molecules in other

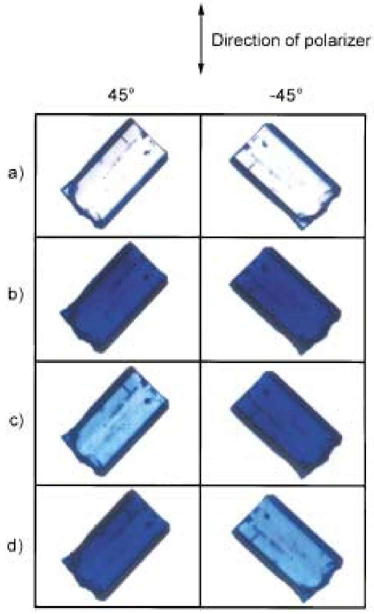

Figure 6. Photographs of δ-crystal observed under polarized light: a) δ-crystal, b) after non-polarized UV light irradiation, c and d) after partial bleaching by linearly polarized light in the direction of 45° and −45°.

direction were preferentially bleached as shown in Figure 6d. The order parameter of 0.75 was obtained after the partial bleaching.

Quantum yields in crystal: In crystal, the conformation of individual molecule is fixed in the crystal lattice. In general, the photoreactivity depends on the conformation. Therefore, the reactivity in crystal is influenced by the packing of molecules in crystal. The cyclization and cycloreversion quantum yields in the four polymorphic crystals were measured according to the method described in the literature.[27, 28] The photocyclization reaction was carried out by irradiation with 370 nm polarized light. The quantum yields are summarized in Table 2. The cyclization quantum yields of **1a**-α, β, γ, and δ were very similar and close to unity. This indicates that the cyclization reaction took place in almost 100% efficiency, that is, all photon energy absorbed by the crystal is used for the chemical reaction. This extremely high efficiency is ascribed to that the distance between the reacting carbon atoms of the open-ring isomers in the four polymorphic crystals are short enough for the photocyclization reaction.[3, 22, 28]

The cycloreversion quantum yields were determined for the photogenerated blue colored crystals by irradiation with 618 nm light. The quantum yields are also shown in Table 2. The yields of α- and γ-crystals were almost similar and slightly larger than the yield in hexane. On the other hand, the yields of β- and δ-crystals were much larger than the yield in solution by a factor of 5. The difference of the cycloreversion quantum yield between α- and γ-crystals and β- and δ-crystals correlates well with the absorption maxima of the closed-ring isomers. The closed-ring isomers with the absorption maxima of 600 nm (β- and δ-crystals) were efficiently bleached, while the isomers with the absorption maxima at longer wavelengths (α- and γ-crystals) kept the photostability as in solution.

Table 2. Photocyclization/cycloreversion quantum yields.

	in hexane	in crystal			
		α	β	γ	δ
λ_{max}[a] [nm]	582	630	600	615	600
ε[a,b] [$\mathrm{M^{-1}cm^{-1}}$]	21000	4700	24000	4600	6400
cyclization	0.56	0.98	1.00	0.97	0.95
cycloreversion	0.0052	0.0064	0.026	0.0061	0.027

[a] λ_{max} and ε value at the longest wavelength of the photogenerated closed-ring isomer. [b] The ε values were estimated at the strongest absorption direction under polarized light.

The correlation suggests that the π-conjugation length, or the conformation of the phenyl and thiophene rings, of the closed-ring isomer controls the quantum yields. When the π-conjugation extension is limited to the thiophene rings, the absorption maximum is expected to appear at a shorter wavelength region and cycloreversion quantum yield increases. On the other hand, when the π-conjugation extends to the *p*-methoxyphenyl rings, the absorption maximum shifts to a longer wavelength region and the quantum yield decreases. The correlation between the conformation of the closed-ring isomer and the absorption maximum was further examined using semi-empirical molecular orbital calculations.

Simulation of the structure of the closed-ring isomer: The molecular structures of the closed-ring isomers in α- and δ-crystals were simulated based on the X-ray crystallographic data for 1,2-bis(2,5-dimethyl-3-thienyl)perfluorocyclopentene; the structure of the photogenerated closed-ring isomer in the open-ring isomer crystal was precisely determined.[23] The closed-ring isomer was constructed by replacing the methyl groups of 1,2-bis(2,5-dimethyl-3-thienyl)perfluorocyclopentene with *p*-methoxyphenyl groups. The angle between the thiophene and the phenyl rings was determined by assuming that only the thiophene rings rotate as much as 22.2° and the phenyl rings do not follow the rotation during the photocyclization.[34] The rotation angles between the thiophene and the phenyl rings became 1.7° for α-crystal, and −16.2° and −38.8° for δ-crystal. The structures are shown in Figure 7. As can be seen from the structures in α-crystal, the two phenyl rings are in the same plane as the thiophene rings and the molecule has high planarity. On the other hand, they are twisted in the δ-crystal. Employing these structures, the absorption spectra of the photogenerated closed-ring isomers in α- and δ-crystals were calculated using the program MOS-F with CNDO/S method (Fujitsu). The lowest energy absorption peaks were calculated at 477.21 and 454.45 nm for α- and δ-crystals, respectively. The closed-ring isomer in α-crystal, which has higher planarity, gave the absorption peak at longer wavelength than that in δ-crystal.[35] This simulation supports the conclusion that the differences in the absorption maxima and the photocycloreversion quantum yields among the four crystals are due to the difference in the conformation of the molecules in crystal.

Conclusion

1,2-Bis(2-methyl-5-*p*-methoxyphenyl-3-thienyl)perfluorocyclopentene (**1a**) formed four polymorphic crystals. All of the

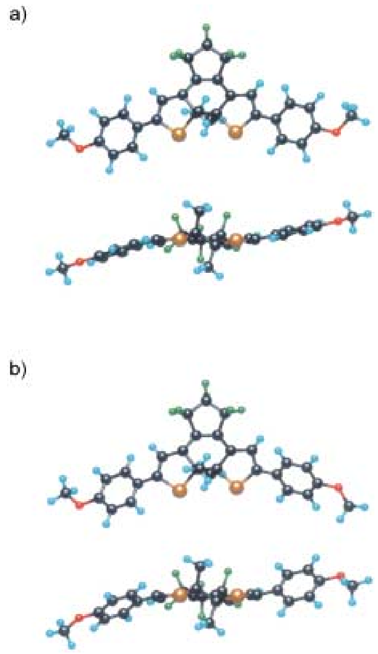

Figure 7. Simulated structures of the photogenerated closed-ring isomers in α-crystal (a) and δ-crystal (b).

four crystals underwent photochromism in the single-crystalline phase. The photocyclization quantum yields were found to be close to unity for all crystals. On the other hand, the photocycloreversion quantum yields depended on the conformation of the closed-ring isomers in the crystals and well correlated with the absorption maxima of the closed-ring isomers.

Experimental Section

General: Solvents used were spectroscopic grade and purified by distillation before use. ^{1}H 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 coupled 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 sources. Monochromic light was obtained by passing the light through a monochrometer (Ritsu MV-10N). Absorption spectra in a single-crystalline phase were measured by using a Leica DMLP polarizing microscope connected with a Hamamatsu PMA-11 photodetector. Polarizer and analyzer were set in parallel to each other. The quantum yields were measured according to a method described in the literature.[27, 28] Photoirradiation was carried out using a 75 W xenon lamp or a 100 W halogen lamp as the light sources attached with the microscope. The wavelength of the light used for the photocyclization and photocycloreversion reactions in a single-crystalline phase was selected by passing the light through a band pass filter. The selected wavelengths were 370 nm ($\Delta\lambda_{1/2} = 20$ nm) for cyclization reactions and 618 nm ($\Delta\lambda_{1/2} = 14$ nm) for cycloreversion reactions.

3-Bromo-2-methyl-5-(*p*-methoxyphenyl)thiophene (2): A 15% *n*BuLi hexane solution (44 mL, 0.072 mol) was added at −78 °C under nitrogen atmosphere to a dry THF solution (170 mL) containing 3,5-dibromo-2-methylthiophene (17 g, 0.066 mol), and the solution was stirred for 3 h at the low temperature. Tri-*n*-butylborate (27 mL, 0.10 mol) was slowly added to the reaction mixture at −78 °C, and the mixture was stirred for 2 h at the temperature. A small amount of water was added to the mixture. To the reaction mixture were added 20 wt% Na_2CO_3 aq (135 mL), 4-iodoanisole (15 g, 0.066 mol), and $Pd(PPh_3)_4$ (2.2 g, 0.0019 mol). The mixture was heated under reflux for 11 h at 70 °C. The mixture was neutralized with HCl, and then was 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 as the eluent and recrystallization from methanol to give **2** (11 g, 61%) as crystals. M.p. 108–109 °C; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 2.40$ (s, 3H; CH_3), 3.83 (s, 3H; OCH_3), 6.90 (d, $J = 8.7$ Hz, 2H; phenyl protons), 6.98 (s, 1H; thienyl proton), 7.43 (d, $J = 8.7$ Hz, 2H; phenyl protons); MS: m/z: 282, 284 [M^+]; elemental analysis calcd (%) for $C_{12}H_{11}BrOS$ (283.19): C 50.90, H 3.92; found: C 50.91, H 3.83.

1,2-Bis(2-methyl-5-*p*-methoxyphenyl-3-thienyl)perfluorocyclopentene (1a): A 15% *n*BuLi hexane solution (17 mL, 0.028 mol) was added at −78 °C under nitrogen atmosphere to a dry THF solution (370 mL) containing **2** (7.3 g, 0.026 mol), and the solution was stirred for 3 h at the low temperature. Octafluorocyclopentene (1.7 mL, 0.013 mol; Nippon Zeon) was slowly added to the reaction mixture at −78 °C, and the mixture was stirred for 4.5 h at the temperature. The reaction was stopped by the addition of methanol. 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 (4:1) as the eluent and by recrystallization from ethanol to give **1a** (5.5 g, 72%) as colorless crystals. ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.94$ (s, 3H; CH_3), 3.84 (s, 3H; OCH_3), 6.91 (d, $J = 8.6$ Hz, 2H; phenyl protons), 7.16 (s, 1H; thienyl proton), 7.47 (d, $J = 8.6$ Hz, 2H; phenyl protons); MS: m/z: 580 [M^+]; elemental analysis calcd (%) for $C_{29}H_{22}F_6O_2S_2$ (580.61): C 59.99, H 3.82; found: C 60.08, H 3.87.

Closed-ring isomer of 1a (1b): Compound **1b** was isolated by passing a photostationary solution containing **1a** and **1b** through a HPLC (Hitachi L-6250 pump system equipped with Hitachi L-7400 detector, and silica gel column (Kanto, MightySil Si 60), using hexane/ethyl acetate 9:1 as the eluent. Retention time was 37 (**1a**) and 48 min (**1b**). M.p. 181–182 °C; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 2.14$ (s, 3H; CH_3), 3.87 (s, 3H; OCH_3), 6.58 (s, 1H; olefinic proton), 6.93 (d, $J = 8.8$ Hz, 2H; phenyl protons), 7.53 (d, $J = 8.8$ Hz, 2H; phenyl protons); MS: m/z: 580 [M^+]; elemental analysis calcd (%) for $C_{29}H_{22}F_6O_2S_2$ (580.61): C 59.99, H 3.82; found: C 60.09, H 3.80.

X-ray diffraction: X-ray crystallographic analysis was carried out with a Bruker SMART1000 CCD-based diffractometer (50 kV, 40 mA) with $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). The data were collected as a series of ω-scan frames, each with a width of 0.3° per 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 the global refinement. The structure was solved by direct methods using SHELXS-86[36] and refined by full least-squares on F^2 using SHELXL-97.[37] The positions of all hydrogen atoms were calculated geometrically and refined by the riding model. CCDC-185942 (**1a-α**), CCDC-185943 (**1a-β**), CCDC-185944 (**1a-γ**), CCDC-185945 (**1a-δ**), CCDC-185946 (**1b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk).

Simulation of the structure of the closed-ring isomer: For the central part consisting of the thiophene and the perfluorocyclopentene rings, the structure of the photogenerated closed-ring isomer in crystal of 1,2-bis(2,5-dimethyl-3-thienyl)perfluorocyclopentene was employed.[23] From the X-ray crystallographic data, the thiophene rings rotate by 22.2° during the photocyclization reaction. In the software winMOPAC (Fujitsu), two methyl groups were replaced with *p*-methoxy phenyl groups, and its conformation was set under the assumption that the thiophene rings rotate and the *p*-methoxy phenyl rings keep its conformation during the photocyclization reaction.

Calculation of absorption spectra: MOS-F (Fujitsu) with CNDO/S method was used for these calculations. Twenty molecular orbitals were taken into account for calculation (default value). Coordinates of the closed-ring isomers in α- and δ-crystals, which obtained by the above simulations, were used for the model structure.

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[34] The structure of the photogenerated closed-ring isomer in the crystal of 1,2-bis(2,5-dimethyl-3-thienyl)perfluorocyclopentene was employed for the central part consisting of the thiophene and the perfluorocyclopentene rings. From the X-ray crystallographic data, the thiophene rings rotate by 22.2° during the photocyclization reaction.

[35] In fact, the exact structure of the photogenerated closed-ring isomer in the open-ring isomer crystal is not known. However, it is safe to say that the structure of the closed-ring isomer is in between the two limiting structures. One is a structure obtained under the assumption that phenyl rings do not rotate during the photocyclization reaction (demonstrated in the text), and the other is a structure obtained under the assumption that the phenyl rings rotate together with the thiophene rings keeping the rotation angles in the open-ring isomer. In the latter case, the angles between the thiophene and the phenyl rings of the simulated closed-ring isomers were calculated to be 23.9° for α-crystal, and 6.0 and $-16.6°$ for δ-crystal. Then, the lowest energy absorption peaks located at 473.73 and 473.32 nm for α- and δ-crystals, respectively.

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