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Photocyclization/Cycloreversion Quantum Yields of Diarylethenes in Single Crystals

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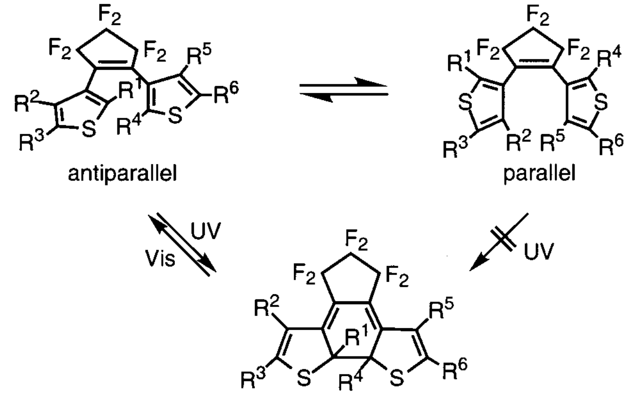
Photocyclization and photocycloreversion quantum yields of three diarylethene derivatives were determined in the single-crystalline phase. The former yields in the crystalline phase were twice as large as those in solution. This can be attributed to only photoreactive antiparallel conformers being packed in the crystals, while in solution both photoreactive antiparallel and photoinactive parallel conformers coexist in almost equal amounts. The quantum yields in the crystals were found to be extremely high and 1,2-bis(2-ethyl-5-phenyl-3-thienyl)perfluorocyclopentene (**3a**) exhibited the quantum yield of unity (100%). The latter yield of the closed-ring isomer of 1,2-bis(2,5-dimethyl-3-thienyl)perfluorocyclopentene (**1a**) was similar to that in solution, while the yields of the closed-ring isomers of 1,2-bis(2,4-dimethyl-5-phenyl-3-thienyl)perfluorocyclopentene (**2a**) and **3a** were higher than those in solution by a factor of 2 to 3. The high yields are attributable to the constrained conformation of the photogenerated closed-ring isomers in the crystal lattice.

Introduction

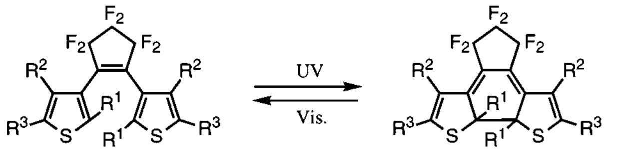
Photochromism is referred to as a photoisomerization process between two isomers having different absorption spectra.[1] Although many photochromic compounds have been so far reported, compounds which show thermally irreversible photochromic reactions in the crystalline phase are very rare.[2,3] In most cases, photogenerated isomers are thermally unstable and return to the initial isomers even in the dark.[4−8] Recently, we have developed thermally irreversible and fatigue-resistant photochromic diarylethene crystals.[9−18] The photogenerated colors of the crystals do not fade even at 100 °C.

In solution, diarylethenes have two conformations, parallel and antiparallel, in almost equal amounts, and they interconvert each other.[19,20]



The conrotatory photocyclization reaction can proceed only from the antiparallel conformation. Since the lifetime of the excited state is shorter than a few nanoseconds,[21] there is no chance for the excited photoinactive parallel conformer to convert to the photoreactive antiparallel one in the excited state.[19] Therefore, the cyclization quantum yield cannot exceed 0.5 in solution. It is indispensable to design systems with a high population of the antiparallel conformers for the increment of the yields. Although we have tried to include diarylethenes in cyclodextrin cavities to fix the conformation in antiparallel, the cyclization quantum yields of the systems have been less than 0.5.[22]

The most effective approach to increase the population is to include the molecules in the crystal lattice, in which only the antiparallel conformers can exist. Some dithienylperfluorocyclopentenes were found to be arranged to the antiparallel conformation in the crystalline phase. In this paper we have determined the cyclization/cycloreversion quantum yields of dithienylperfluorocyclopentenes **1**, **2**, and **3** in the single-crystalline phase. The single crystals were found to undergo extremely efficient photochromic reactions.



1a: R^1 = Me, R^2 = H, R^3 = Me
2a: R^1 = R^2 = Me, R^3 = Ph
3a: R^1 = Et, R^2 = H, R^3 = Ph

1b: R^1 = Me, R^2 = H, R^3 = Me
2b: R^1 = R^2 = Me, R^3 = Ph
3b: R^1 = Et, R^2 = H, R^3 = Ph

Results and Discussion

Coloration of Crystals. Single crystals **1a**, **2a**, and **3a** were obtained by recrystallization from hexane. All crystals were colorless. Figure 1 shows the shape of the crystals. Upon irradiation with 370 nm light, a colorless single crystal **1a** turned red. When the photogenerated color of the crystal was observed under polarized light, the color intensity showed the maximum at a certain angle shown by the arrow in Figure 1a.[11] The absorption maximum of the red color was observed at 535 nm, as shown in Figure 2a. The absorbance increased with continuous photoirradiation with 370 nm light. The red color was bleached by irradiation with visible light.

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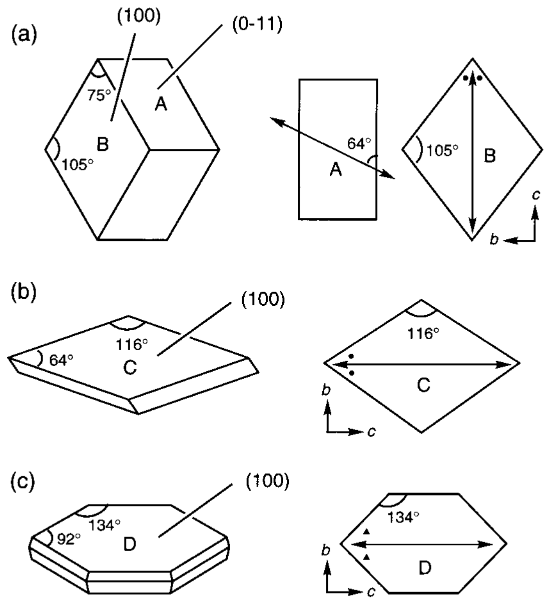

Figure 1. The shape of crystals **1a** (a), **2a** (b), and **3a** (c). The four surfaces shown in the right-hand side were irradiated with polarized light. The arrows showed the transition moment directions of visible absorption bands of the closed-ring isomers. X-ray crystallographic data are shown in refs 24−26.

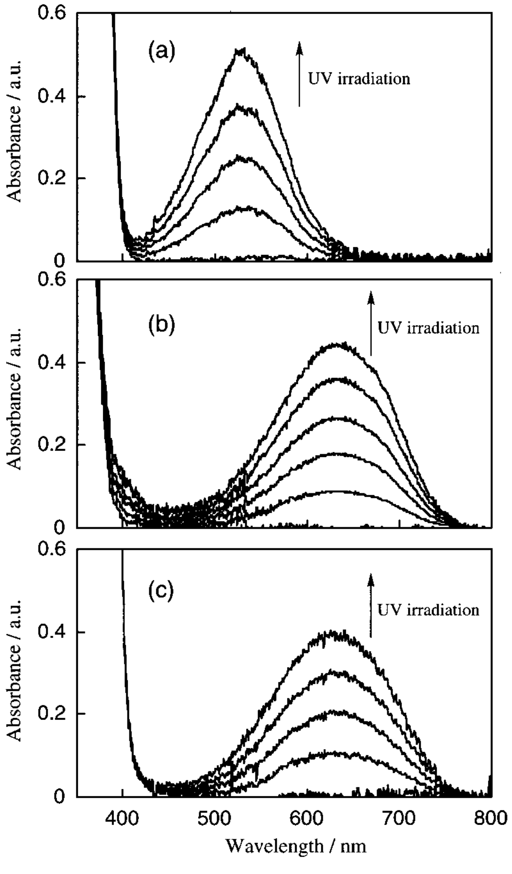

Figure 2. Polarized absorption spectral changes of the crystals **1** (a), **2** (b), and **3** (c) upon irradiation with 370 nm light.

Colorless single crystals **2a** and **3a** turned blue upon irradiation with 370 nm light.[17,18] The absorption maxima of the blue color were observed at 630 nm for both crystals, as shown in Figures 2b and 2c. The blue color disappeared by irradiation with visible light. In the dark the red and blue colors remained stable. The coloration/decoloration cycles could be repeated many times (>10^4) with keeping the crystal shape.[11] The coloration of these three crystals is due to the formation of closed-ring isomers.[9−18]

To confirm that the photoreactions take place inside the crystal bulk, the color changes of partially photoirradiated crystals were observed from both sides of the single crystals (top and side views). Figure 3a shows the photograph of crystal **1a** irradiated on surface B. Upon irradiation with 370 nm light, surface B turned red (top view). Figure 3b shows the side view of the crystal. The photograph clearly indicates that light penetrated the crystal into the bulk and induced the photoreaction. Figures 3c and 3d show another example of crystal **3a**. Upon irradiation with 370 nm light the surface C of **3a** turned blue (Figure 3c). The side view indicates that light penetrated the crystal bulk as deep as 0.5 mm to induce the reaction (Figure 3d). Crystal **2a** also showed analogous behavior. These results clearly indicate that the photoreactions took place in the crystal bulk.

Cyclization Quantum Yields. The quantum yields for these three compounds in the single-crystalline phase were measured by using a polarizing microscope connected with a photodetector. Polarizer and analyzer were set in parallel to the directions of the arrows shown in Figure 1.[23−26] The cyclization reaction was carried out upon irradiation with linearly polarized 370 nm light, and the rate of the reaction was measured by monitoring the visible absorbance of the colored closed-ring isomers.

First, the cyclization quantum yield of furyl fulgide in poly(methyl methacrylate) film (ca. 4 wt %, thickness = ca. 10 μm) was determined by comparing the photocyclization rate of furyl fulgide in hexane by using a normal procedure.[27] Then, the film was set on the sample stage of the polarizing microscope as shown in Figure 4. The polymer film was used as a reference for the measurement of cyclization rates of crystals. Both the polymer film and the crystals were irradiated with linearly polarized light. The photoirradiation area was ca. 0.8 mm^2. The crystal surface area was around 4 mm^2. The detection area was ca. 5×10^{-3} mm^2 at the center of the photoirradiated sample. In a separated experiment, it was confirmed that the quantum yield of the polymer film measured using the polarized light is identical with the yield determined using the nonpolarized light.

Figure 5 shows the absorbance changes for crystals **1**, **2**, and **3** at 535, 630, and 630 nm, respectively, by irradiation with linearly polarized 370 nm light. In all cases the absorbances of the closed-ring isomers linearly increased with irradiation time. This result indicates that the inner-filter effect due to the photogenerated colored isomers is negligible under the experimental conditions. The absorption of the polarized 370 nm light by the closed-ring isomers is considered to be low because the S_0-S_2 transition moment in the UV region is perpendicular to the S_0-S_1 transition moment in the visible region.[28] The low conversion to the colored isomers is another reason for the insignificant inner-filter effect.

The quantum yields of single crystals **1**, **2**, and **3** can be calculated by the following equation:

$$\frac{\Phi_{\text{fulgide}}\,\epsilon_{\text{fulgide}}\,(1-T_{\text{fulgide}})}{\text{Slope}_{\text{fulgide}}} = \frac{\Phi_{\text{crystal}}\,\epsilon_{\text{crystal}}\,(1-T_{\text{crystal}})}{\text{Slope}_{\text{crystal}}} \qquad (1)$$

where Φ, ϵ, Slope, and T represent the quantum yield of cyclization, the absorption coefficient at the monitoring wavelength, the slope in Figure 5, and the transmittance at 370 nm, respectively.

To know the absolute cyclization rates or the quantum yields, it is necessary to determine the absorption coefficients (ϵ values)

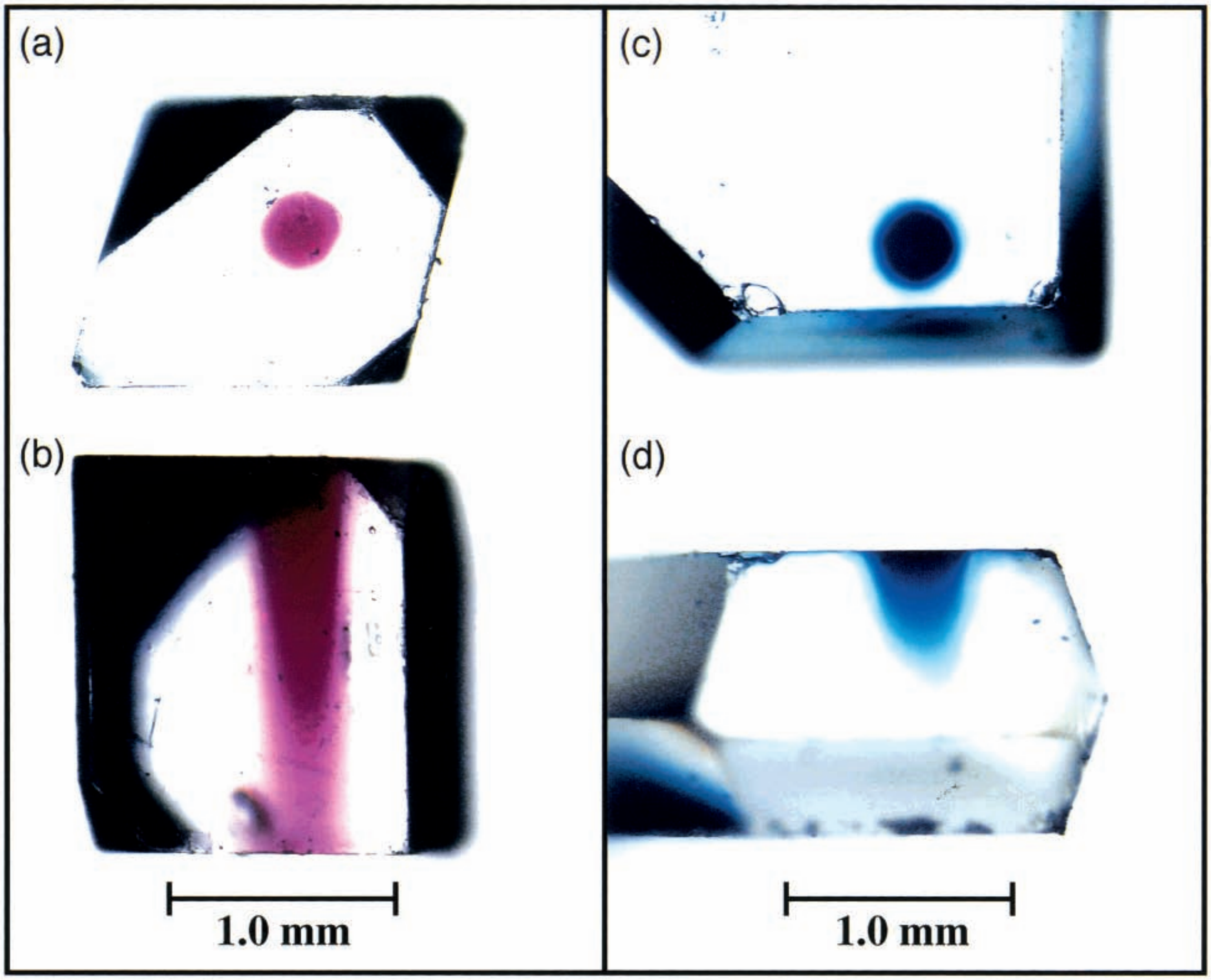

Figure 3. Photographs of photoirradiated crystals **1** and **3**: top (a) and side views (b) of crystal **1**, top (c) and side views (d) of crystal **3**.

of the colored isomers in the crystals at the monitoring wavelength. The ϵ values were determined by comparing the absorbance of the single crystals measured by the linearly polarized light and the molar numbers of the colored closed-ring isomers. The absorbance was measured at the center of the photoirradiated sample (film or crystal). Figure 6 shows the absorbance distribution of the irradiated crystal **1a**. Each point was measured by moving a small detection light (detection area: diameter: 5×10^{-3} mm^2) across the irradiated area. The absorbance at the central part was constant, while it decreased at the edge. The number of the closed-ring isomers in the photoirradiated area was estimated by measuring the absorption spectrum of a hexane solution in which the locally photoirradiated crystal was dissolved and correcting for the relative detection versus the total irradiated area, 5×10^{-3} and 0.8 mm^2, respectively.[15] The ϵ values under polarized light can be estimated by the following equation:

$$\epsilon = \text{(average absorbance at the irradiated area)}/\text{(mole number of photoirradiated closed-ring isomers in unit irradiated area)} \quad (2)$$

The ϵ values were estimated to be 1.7×10^4 (on surface A of **1b** at 535 nm), 1.1×10^3 (on surface B of **1b** at 535 nm), and 3.5×10^3 (on surface C of **2b** at 630 nm), and 3.4×10^3 M^{-1} cm^{-1} (= 10^3 mol^{-1} cm^2) (on surface D of **3b** at 630 nm). The large difference in the ϵ values is explained by the difference of the molecular arrangement in the crystals.[15] Another factor which affects the rates is the transmittance values of the samples, which were also taken into account to determine the quantum yields.

The quantum yields of the three crystals **1a**, **2a**, and **3a** are shown in Table 1 along with the values in solution. The measurement was carried out five times using different crystals for each compound and the values are averages of the five data. The quantum yields for crystals **1** (surface A), **1** (surface B), **2**, and **3** were estimated to be 0.80 ± 0.04, 0.83 ± 0.04, 0.96 ± 0.04, and 1.03 ± 0.04, respectively. The values of **1** at the surfaces A and B were the same within the error. This indicates that the values are independent of the choice of the surface. The quantum yields in the crystalline phase were twice as large as those in solution. The cyclization quantum yield of crystal **3** was unity (100%). This means that photon energy absorbed in the crystal is **quantitatively** used for the cyclization reaction. In other words, the single crystal utilizes all photon energy absorbed for the coloration chemical reaction. An extremely efficient photoreaction takes place in the crystal.

X-ray crystallographic analysis[11,16−18] of crystals **1a**, **2a**, and **3a** confirmed that diarylethene molecules in the crystals were fixed to the antiparallel conformation. The distances between the reacting carbon atoms were estimated to be 0.358, 0.396, and 0.371 nm for **1a**, **2a**, and **3a**, respectively, which are close enough for the reaction.[30] The large cyclization quantum yield in the crystalline phase is ascribed to three factors. One is the

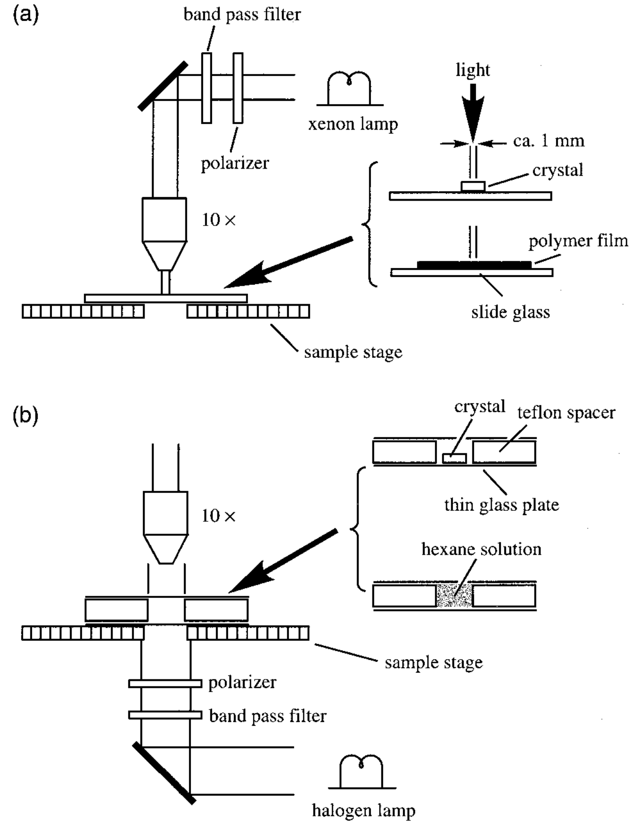

Figure 4. The sample stages and light sources used for cyclization (a) and cycloreversion reactions (b).

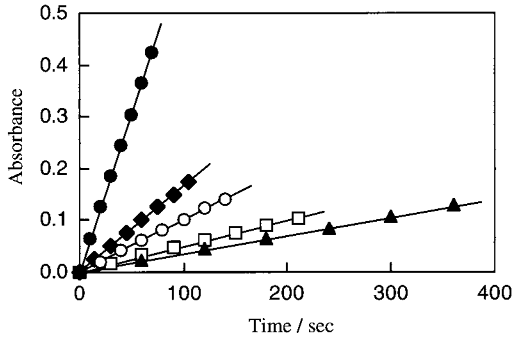

Figure 5. Coloration of crystal **1** on surface A (●) and surface B (▲), crystal **2** on surface C (○), and crystal **3** on surface D (◆) and furyl fulgide in poly(methyl methacrylate) film (□) upon irradiation with 370 nm light. The experimental points showed the absorbance (= $\log(I_0/I)$) at the absorption maxima.

high population of the photoreactive antiparallel conformation in the crystalline phase. All photoexcited molecules in the antiparallel conformation fixed in the crystal lattice readily undergo the photocyclization reactions. Other factors are the very low activation energy, almost zero, of the conrotatory cyclization reaction[15] and the rapid cyclization rate in less than 10 ps.[21] The rapid reactions prevailed over other relaxation processes, such as radiative and nonradiative transitions from the excited states to the ground state. Compounds **2a** and **3a** were nonfluorescent.

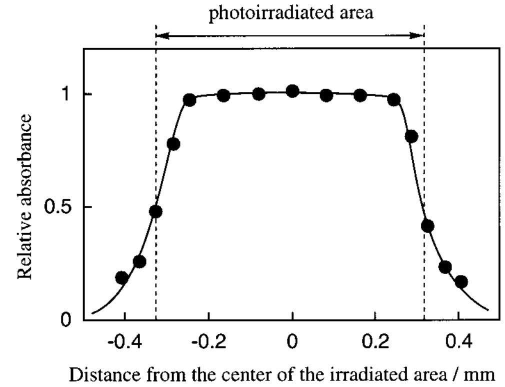

Figure 6. Absorbance changes at 535 nm at each part of the irradiation area on surface A of crystal **1**.

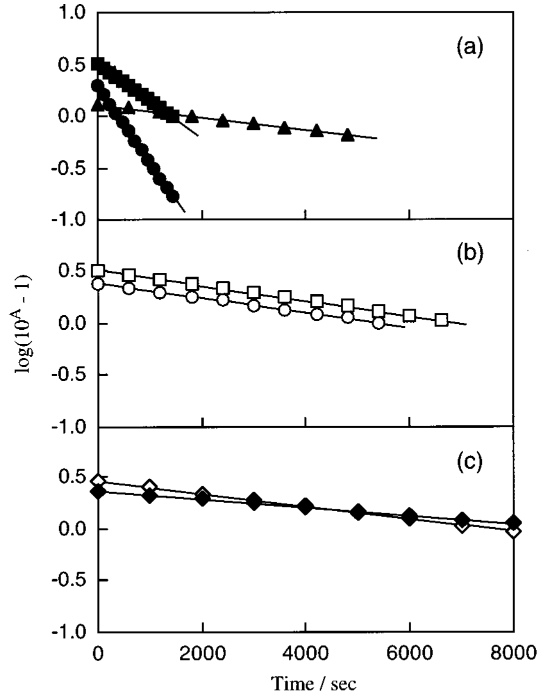

Figure 7. Bleaching of crystal **1** (a) on surface A (●) and surface B (▲), crystal **2** (b) on surface C (○), and crystal **3** (c) on surface D (◆) and **1** (■), **2** (□), and **3** (◇) in hexane upon irradiation with linearly polarized 533 (**1**) and 618 nm lights (**2** and **3**). Absorbance (= $\log(I_0/I)$) was measured at 533, 618, and 618 nm for **1**, **2**, and **3**, respectively.

Cycloreversion Quantum Yields. Figure 7 shows absorption intensity changes in the photocycloreversion reactions for crystals **1**, **2**, and **3** upon irradiation with linearly polarized 533, 618, and 618 nm light, respectively. The experimental setup is shown in Figure 4b. In the cycloreversion quantum yield

TABLE 1: Quantum Yields of Cyclization and Cycloreversion Reactions

	1			**2**		**3**	
		crystal			crystal		crystal
	hexane	surface A	surface B	hexane[a]	surface C	hexane	surface D
cyclization	0.40 ± 0.02[b]	0.80 ± 0.04[c]	0.83 ± 0.04[c]	0.46 ± 0.02[b]	0.96 ± 0.04[c]	0.52 ± 0.03[d]	1.03 ± 0.04[c]
cycloreversion	0.12 ± 0.01[e]	0.10 ± 0.01[e]	0.11 ± 0.01[e]	0.015 ± 0.002[f]	0.027 ± 0.002[f]	0.0081 ± 0.0004[f]	0.027 ± 0.002[f]

[a] Ref 29. [b] Upon irradiation with 313 nm light. [c] Upon irradiation with 370 nm light. [d] Upon irradiation with 286 nm light. [e] Upon irradiation with 533 nm light. [f] Upon irradiation with 618 nm light.

measurement the hexane solutions of diarylethenes were used as references, because the cycloreversion quantum yield of the polymer film containing furyl fulgide is strongly dependent on the irradiating wavelengths.[27] The colored crystals were obtained by irradiation of crystals **1a**, **2a**, and **3a** with ultraviolet light from underneath the sample stage. The photocycloreversion quantum yields (Φ') were determined using those in hexane solution as references and calculated by the following equation:

$$\frac{\Phi'_{\text{solution}}\,\epsilon_{\text{solution}}}{\text{Slope}'_{\text{solution}}} = \frac{\Phi'_{\text{crystal}}\,\epsilon_{\text{crystal}}}{\text{Slope}'_{\text{crystal}}} \qquad (3)$$

where Slope′ indicates the slopes shown in Figure 7. The quantum yields of photocycloreversion reactions are summarized in Table 1. The value for crystal **1** was 0.10−0.11, which is almost similar to that in hexane. The Φ' values for crystals **2** and **3** were 0.027, which are larger than the values in hexane by a factor of 2 to 3. The large quantum yields are ascribed to the special conformation of the photogenerated closed-ring isomers in the crystal lattice.[15] The photogenerated isomers are in the constrained forms, which are different from the most stable closed-ring isomer conformation, and this is the reason for the low activation energy of the photocycloreversion reactions in crystals[15] and higher cycloreversion quantum yields.

Conclusions

In this paper we determined photochromic reaction quantum yields in the single-crystalline phase for the first time. The single crystals of dithienylperfluorocyclopentene derivatives constitute extremely efficient photochromic systems. In addition to the very efficient photocoloration reactivity, the colored states were thermally stable even at 100 °C and the coloration/decoloration cycles in the crystalline state could be repeated many times ($>10^4$) without denaturation. This class of crystalline photochromic compounds can be potentially applied to photonics devices, such as optical memories or photooptical switches.

Experimental Section

Materials. 1,2-Bis(2,5-dimethyl-3-thienyl)perfluorocyclopentene (**1a**), 1,2-bis(2,4-dimethyl-5-phenyl-3-thienyl)perfluorocyclopentene (**2a**), and 1,2-bis(2-ethyl-5-phenyl-3-thienyl)perfluorocyclopentene (**3a**) were synthesized according to the methods described in the literature.[11,17,29] Single crystals were obtained by recrystallization from hexane. Crystal size is as follows: crystal **1a** (~ 1.5 × 1.5 × 1.5 mm), crystal **2a** (~ 2.5 × 2.5 × 0.5 mm), and crystal **3a** (~ 2.5 × 2.5 × 1.0 mm). Solvents used were spectroscopic grade and were purified by distillation before use.

Polarized Absorption Spectra in a Single-Crystalline Phase. Polarized absorption spectra were measured by using a Leica DMLP or a JASCO MICRO-20 polarizing microscope connected with a Hamamatsu PMA-11 photodetector.

Photoirradiation. A xenon lamp (75 W) and a halogen lamp (100 W) were used as the light sources for ultraviolet and visible light irradiation, respectively. The wavelength of the light used for the photocyclization and photocycloreversion reactions 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 of **1**, **2**, and **3**, and 533 nm ($\Delta\lambda_{1/2} = 12$ nm), 618 nm ($\Delta\lambda_{1/2} = 14$ nm), and 618 nm ($\Delta\lambda_{1/2} = 14$ nm) for cycloreversion reactions of **1**, **2**, and **3**, respectively.

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

$$A = \log(I_0/I) = \epsilon n/S \qquad (4)$$

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 the 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, the direction of which were fixed to those shown by arrows in Figure 1. n was determined by dissolving the colored crystal into hexane and measuring the absorption spectrum (ϵ values in hexane solution are known). The ϵ values in crystal were calculated from the values of A, n, and S.

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(23) Along the directions the plane of polarized light is not distorted. This was confirmed under a cross polarized condition.

(24) X-ray crystallographic data of **1a**: monoclinic, space group $P2_1/c$, $Z = 4$, $a = 17.144(1)$ Å, $b = 8.772(1)$ Å, $c = 11.227(1)$ Å, $\beta = 92.949(1)°$; also see ref 16.

(25) X-ray crystallographic data of **2a**: monoclinic, space group $C2/c$, $Z = 4$, $a = 24.023(4)$ Å, $b = 8.466(2)$ Å, $c = 13.350(2)$ Å, $\beta = 109.235(3)°$; also see ref 18.

(26) X-ray crystallographic data of **3a**: orthorhombic, space group *Pbcn*, $Z = 4$, $a = 22.277(3)$ Å, $b = 10.951(2)$ Å, $c = 10.569(2)$ Å; also see ref 17.

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