Award Accounts

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Single-Crystalline Photochromism of Diarylethenes

Seiya Kobatake* and Masahiro Irie*

Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University,
Hakozaki 6-10-1, Higashi-ku, Fukuoka 812-8581

Received September 1, 2003; E-mail: kobatake@cstf.kyushu-u.ac.jp

Diarylethene single crystals which exhibit thermally irreversible and fatigue-resistant photochromic reactions have been developed. Upon irradiation with ultraviolet light, the colorless diarylethene crystals turn yellow, red, blue, or green, depending on the substituents of the aryl groups. Dichroism of the photogenerated absorption spectra and in situ X-ray crystallographic analysis confirmed that the diarylethene molecules underwent photochromism in the single-crystalline phase. The photocyclization quantum yields were found to depend on the distance between the reactive carbon atoms in the crystal; the yields were close to unity when the distance is less than 4.2 Å. Multi-color photochromism was demonstrated for the crystals composed of two types of diarylethenes. The diarylethene single crystals showed reversible surface morphology changes upon photoirradiation.

Photochromism is referred as a reversible transformation of a chemical species between two isomers having different absorption spectra upon photoirradiation.[1,2] The two isomers differ from one another not only in the absorption spectra but also in various physical and chemical properties, such as refractive indices, dielectric constants, oxidation–reduction potentials, and geometrical structures. The instant property changes by photoirradiation without processing lead to their use in various optoelectronic devices, such as optical memory,[3–6] photo-optical switching,[7,8] display,[9,10] and nonlinear optics.[11,12]

Typical photochromic compounds, such as azobenzene, spiropyran, spirooxazine, and naphthopyran, undergo thermally reversible photochromic reactions (Fig. 1). Photogenerated isomers are thermally unstable and return to the initial isomers in the dark. On the other hand, diarylethenes and furylfulgides exhibit thermally irreversible photochromic reactions. Photogenerated isomers are thermally stable and hardly return to the initial isomers at room temperature. In this review we describe the photochromic reactions of the thermally irreversible diarylethene derivatives in the single-crystalline phase.

Diarylethenes having heterocyclic aryl groups are the most promising photochromic candidates for the photonics applications because of their fatigue resistant and thermally irreversible properties.[13,14] Diarylethenes can be potentially used for optical memory,[15–19] photoswitching,[20–33] and display.[34]

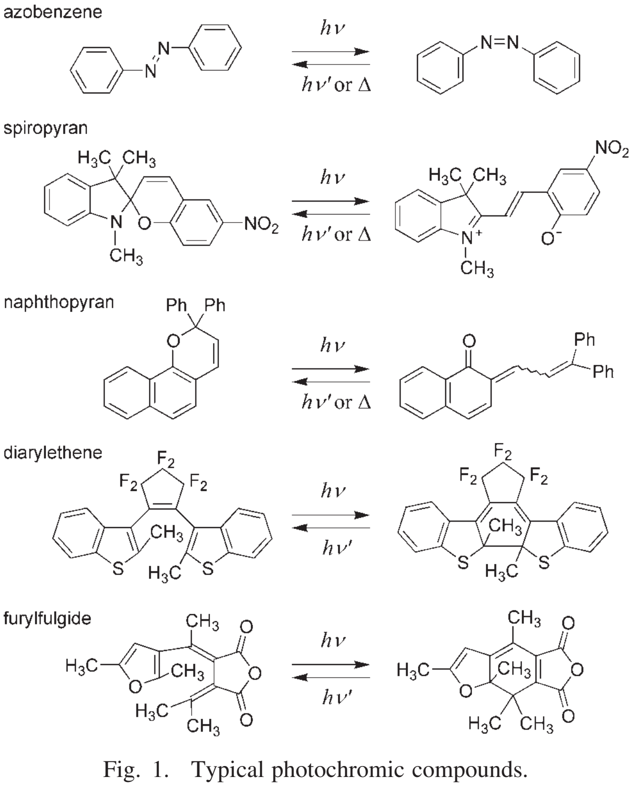

Fig. 1. Typical photochromic compounds.

Diarylethenes have two conformations: with the aryl rings in mirror symmetry (named parallel conformation) and C_2 symmetry (named antiparallel conformation) in almost equal amounts, and they interconvert with each other in solution, as shown in Fig. 2. The conrotatory cyclization can proceed only from the antiparallel conformation.[35–37] Since the lifetime of the excited state is shorter than a few nanoseconds, there is no chance for the excited photoinactive parallel conformer to convert to the photoreactive antiparallel one in the excited state.[38] The closed-ring isomer generated by irradiation with ultraviolet light from the antiparallel conformer is thermally stable. Upon irradiation with visible light, the colored closed-ring

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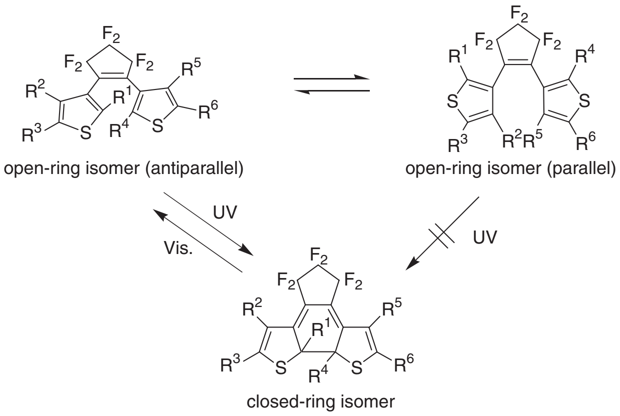

Fig. 2. Photochromic reactions of diarylethenes.

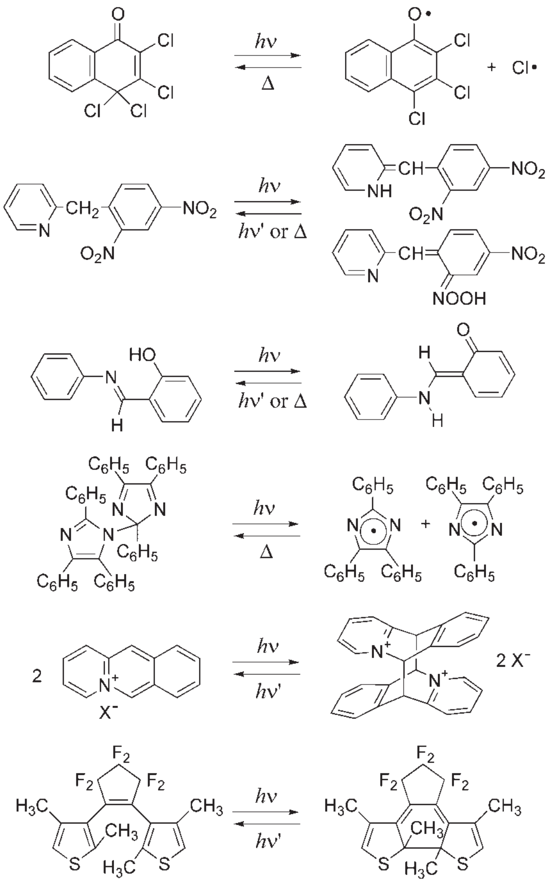

Fig. 3. Typical examples of crystalline photochromic compounds.

isomer regenerates the open-ring isomer.

Although many photochromic compounds have already been reported, compounds that show photochromic reactions in crystalline phase are rare.[39] Typical photochromic compounds such as spiropyran and azobenzene do not show any photochromism in the crystalline phase, because large geometrical structure changes are prohibited in the crystals. Typical examples of crystalline photochromic compounds are paracyclophanes,[40] triarylimidazole dimer,[41,42] diphenylmaleronitrile,[43] aziridines,[44] 2-(2,4-dinitrobenzyl)pyridine,[45–48] *N*-salicylideneanilines,[49–51] and triazenes.[52] Figure 3 shows some examples of the crystalline photochromic compounds. In many cases, the photogenerated isomers are thermally unstable and detailed crystallographic analysis of the photoproducts has not yet been carried out.

We have developed thermally irreversible and fatigue-resistant photochromic diarylethene crystals and analyzed the reactions in the crystalline phase. The colored forms are stable in the crystals even at 100 °C and seldom return to the initial colorless forms in the dark. The thermally irreversible crystalline photochromic materials are potentially applicable to optical memory, switching, and display.

1. Diarylethene Crystals and Their Color Changes by Photoirradiation

Some diarylethene derivatives were found to undergo reversible photochromic reactions in the single-crystalline phase. Figure 4 shows the derivatives which can undergo photochromism in the single-crystalline phase. Figure 5 shows the typical color changes of several diarylethene single crystals.[53] Upon irradiation with ultraviolet light, the colorless crystals change to yellow (**1**, **2**), red (**3**–**5**), blue (**6**–**11**), or green (**12**, **13**), depending on the molecular structure of the diarylethenes. The colors of the crystals are due to the formation of the closed-ring isomers. The colors remain stable so far as being stored in the dark, but the colors disappeared by irradiation with visible light. The photoinduced coloration/decoloration cycles of the crystals can be repeated more than 10^4 times while maintaining the shape of the crystals.

To confirm that the photoreactions take place inside the crystal bulk, the color changes of partially photoirradiated crystals were observed from both the top and the side of the single crystals. Figure 6 shows the photograph of diarylethene crystals **4** and **7**.[54,55] Upon irradiation with 370-nm light, the crystal surface turned red (**4**) or blue (**7**). The side view of the crystals clearly indicates that the light penetrates the crystals into the bulk and induces the photoreaction in the crystal bulk.

2. Conformation (Antiparallel and Parallel)

The open-ring form diarylethenes have two conformations, antiparallel and parallel, and the two conformations interconvert with each other in solution. The conrotatory cyclization can proceed only from the antiparallel conformation.[35–37] In crystals, on the other hand, there is no interconversion between the two conformations. In most cases, the diarylethenes are packed in the antiparallel conformation.

Diarylethene **12** was recrystallized from various solvents.[56] Two types of single crystals were obtained from **12**, depending on recrystallization solvents. Single crystals obtained from hexane, benzene, toluene, or ethyl acetate showed photochromic reactions in the single-crystalline phase. Upon irradiation with 366-nm light, the crystals turned green; this green color disappeared after irradiation with visible light (>450 nm). However, single crystals obtained from chloroform or acetone did not show any photochromic reactivity in the single-crystalline phase. Figure 7a shows ORTEP drawings of a photochromic single crystal (**12-α**) obtained from hexane solution. **12** is packed in a photoactive antiparallel conformation in the crystal. The distance between the reacting carbon atoms is 3.84 Å, which is close enough for the conrotatory cyclization reaction

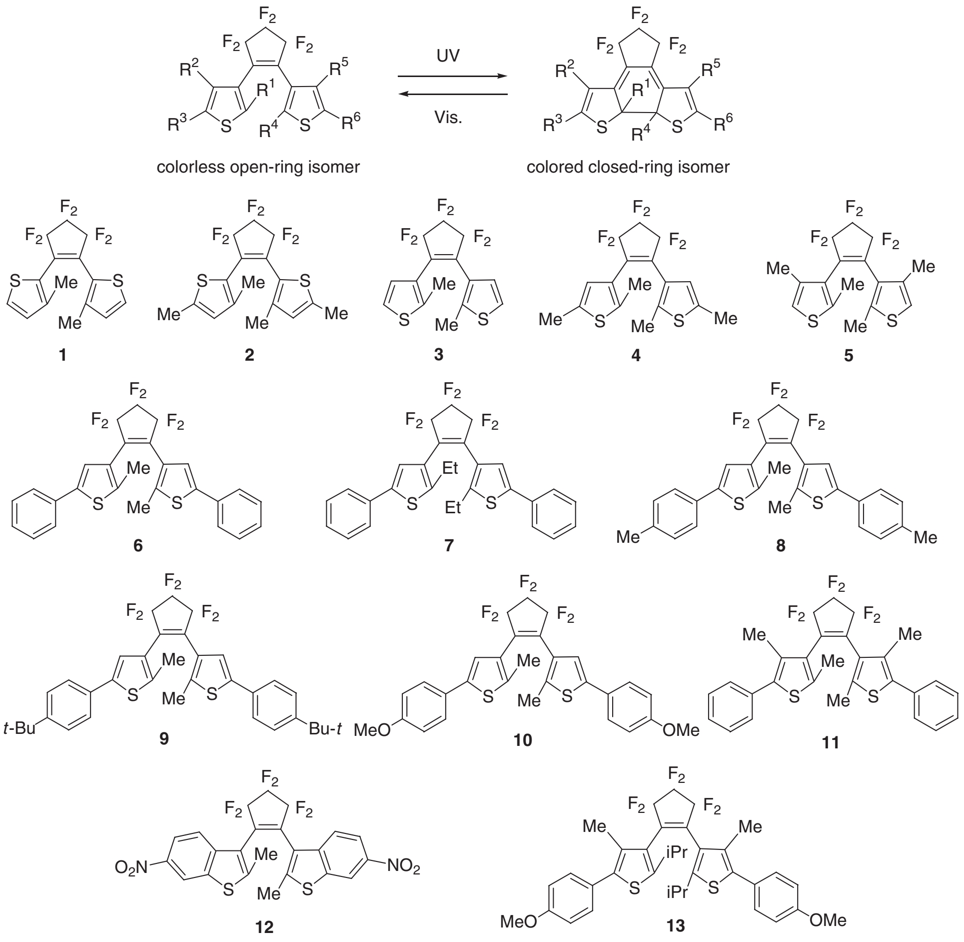

Fig. 4. Diarylethene derivatives showing single-crystalline photochromism.

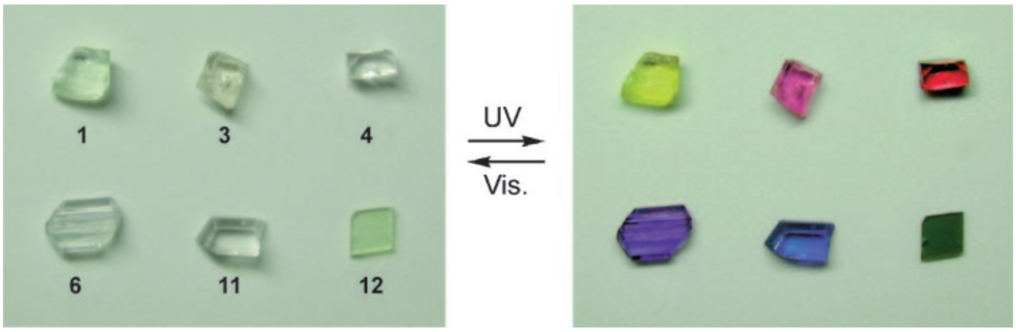

Fig. 5. Photographs of photochromic diarylethene crystals. Reprinted with permission from The Japan Academy (Ref. 53).

to take place. Figure 7b shows the ORTEP drawings of a nonphotochromic single crystal (**12-*β***) obtained from acetone solution. The acetone molecules are included in the crystal. The ORTEP drawing of **12-*β*** indicates that **12** is packed in a parallel conformation, which cannot undergo photocyclization reaction.[35] The difference in reactivity between two types of the crystals, **12-*α*** and **12-*β***, is attributed to the difference in the conformations of **12** packed in the crystals.

3. Dichroism

A rhombus-shaped single crystal **12-*α*** consists of six surfaces, with two parallelograms and four rectangles.[56] Single crystal **12-*α*** turned green upon irradiation with 366-nm light. The green color of the crystal disappeared upon irradiation with visible light ($\lambda > 450$ nm).

The color of the crystal was observed under polarized light. Figure 8 shows the setup of the polarizing microscope. The polarizer and analyzer were set in parallel each other. The colorless single crystal was put on the slideglass on the sample stage of the polarizing microscope. Figure 9 shows the color change of the crystal. Before photoirradiation, the crystal was colorless (Fig. 9a,b). Upon irradiation with 366-nm light, the crystal turned yellow at a certain angle ($\theta = 0°$). 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 that the photochromic reaction proceeds in the crystal lattice. Figure 10 shows the polarized absorption spectra of the closed ring isomer at 0° and 90° and the polar plots of absorbance at 465 and 600 nm. The maximum absorbances 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 **12-α** underwent photochromic reaction in the crystal lat-

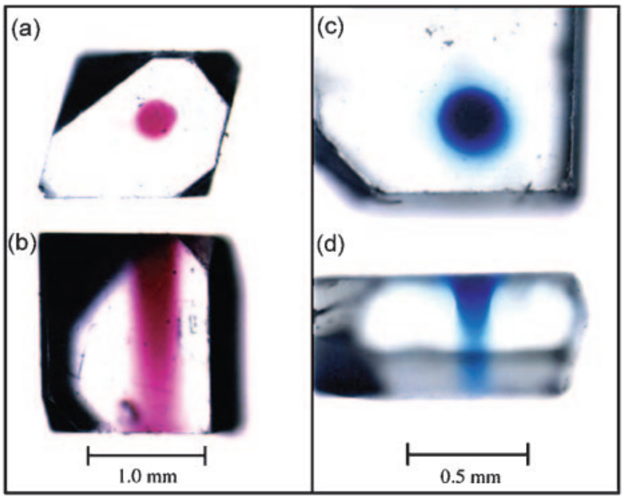

Fig. 6. Photographs of photoirradiated crystals **4** and **7**: top (a) and side views (b) of crystal **4**, top (c) and side views (d) of crystal **7**. Reprinted with permission from Refs. 54 and 55. Copyright 2000 American Chemical Society. Copyright 2002 American Chemical Society.

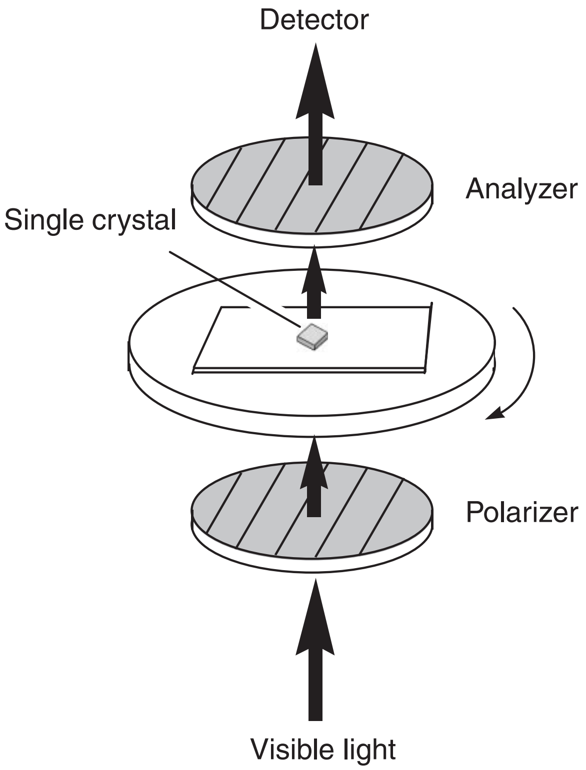

Fig. 8. Polarizing microscope to measure polarized absorption spectra.

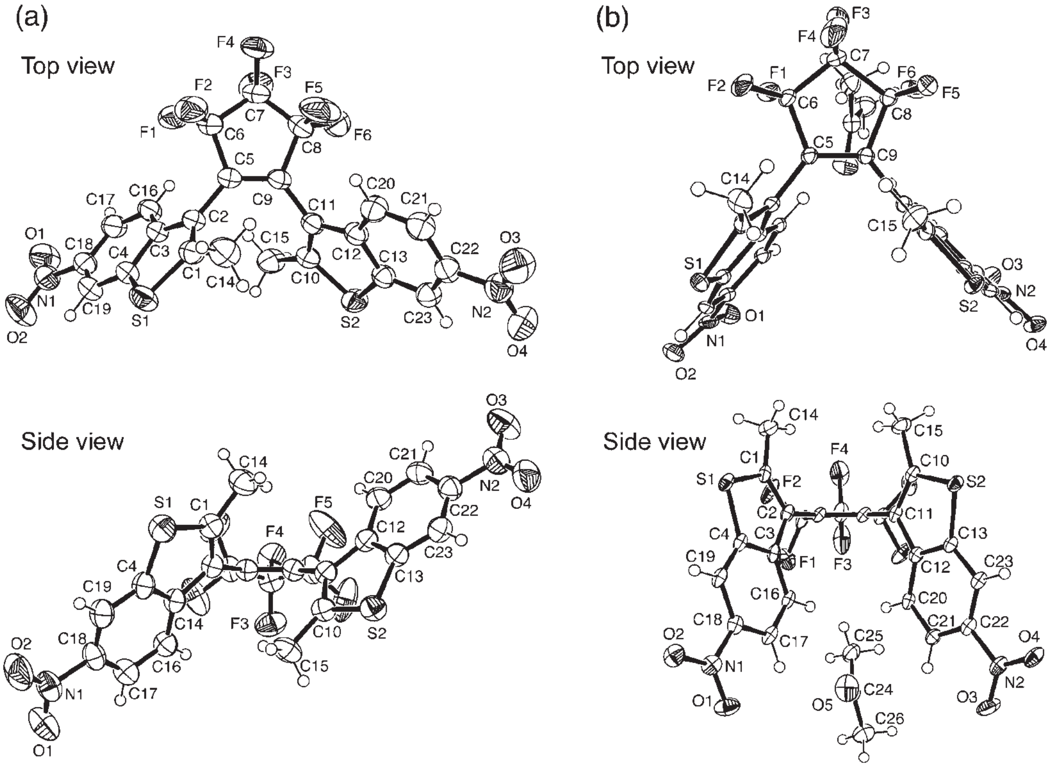

Fig. 7. ORTEP drawing of **12-α** (a) and **12-β** (b), showing the 50% probability displacement ellipsoids. Reprinted with permission from Ref. 56. Copyright 1999 American Chemical Society.

tice. The maximum absorbances 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.

According to the molecular orbital calculation of the closed-ring isomer of 1,2-bis(2-methyl-1-benzothiophen-3-yl)perfluorocyclopentene,[57] the transition moment vector of the longest absorption band ($\lambda = 528$ nm, $f = 0.162$) is in the long axis of the closed-ring isomer, and the second band ($\lambda = 430$ 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 of the benzothiophene rings.[58] Therefore, the electronic transition moment vectors of the longest absorption band ($\lambda_{\max} = 600$ nm) and the second band ($\lambda_{\max} = 465$ nm) of the closed-ring isomer of **12** are assigned to the long- and short-axes of the closed-ring isomer, respectively, as shown in Fig. 11.

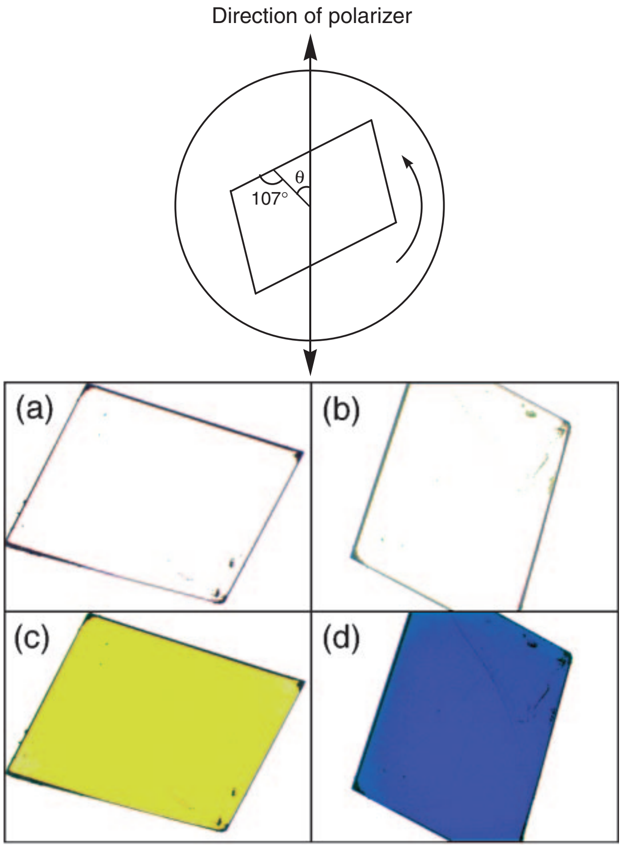

Fig. 9. Photographs of single crystal **12-α** (surface A) under polarized light before (a: $\theta = 0°$; b: $\theta = 90°$) and after (c: $\theta = 0°$; d: $\theta = 90°$) irradiation with 366-nm light. Reprinted with permission from Ref. 56. Copyright 1999 American Chemical Society.

4. X-ray Crystallographic Analysis

X-ray crystallographic analysis of **4** was carried out at 115 K and at room temperature.[59,60] At room temperature, crystal **4** belongs to the triclinic system, the space group, $P\bar{1}$. The perfluorocyclopentene ring was disordered due to puckering at room temperature (50:50). When the crystal was cooled to 115 K, the crystal system became monoclinic, $P2_1/c$. Such dis-

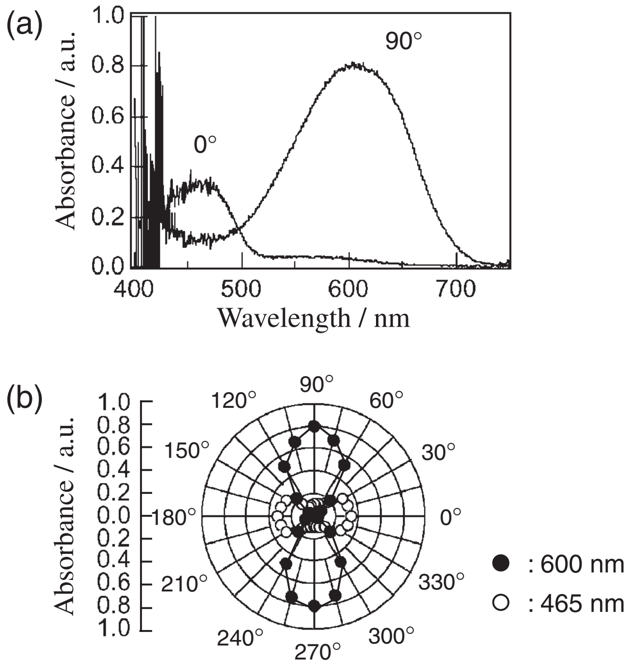

Fig. 10. Polarized absorption spectra of the photoirradiated crystal **12-α** (a) and the polar plots of the absorbance at 465 and 600 nm (b). Reprinted with permission from Ref. 56. Copyright 1999 American Chemical Society.

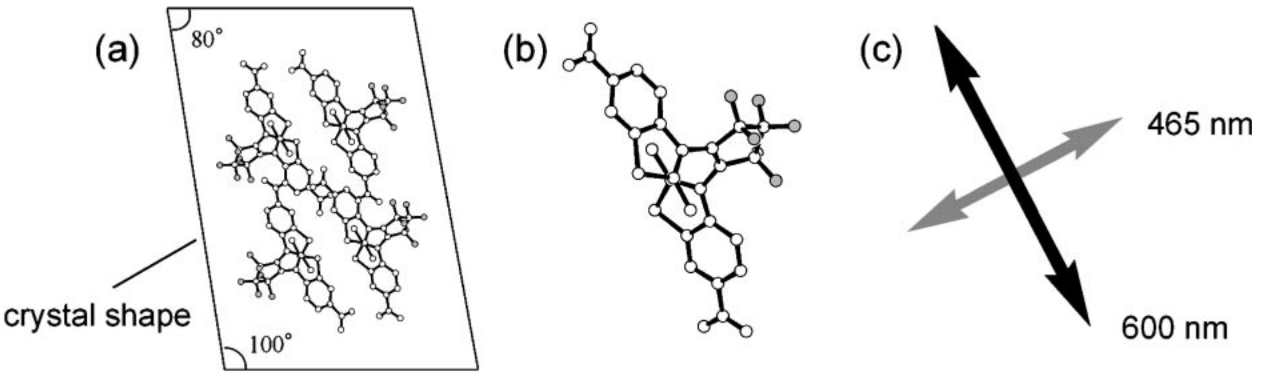

Fig. 11. Crystal shape of **12-α** (a), the molecular structure of the open-ring isomer (b), and the electronic transition moments of the closed-ring isomers (c).

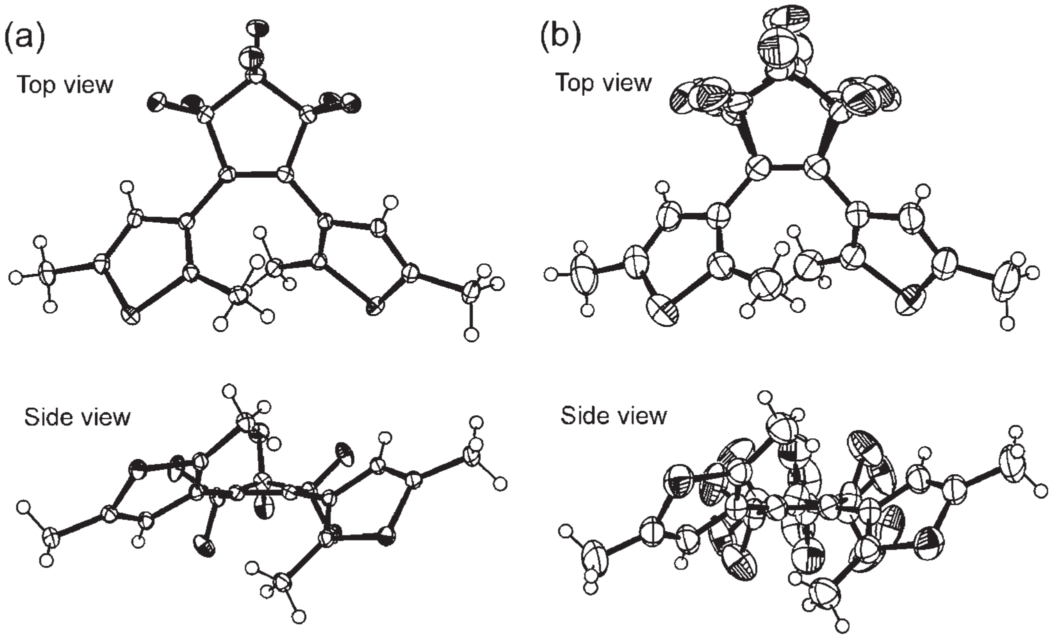

Fig. 12. ORTEP drawings of diarylethene **4** at 115 K (a) and 293 K (b) showing the 50% probability displacement ellipsoids (Refs. 59 and 60).

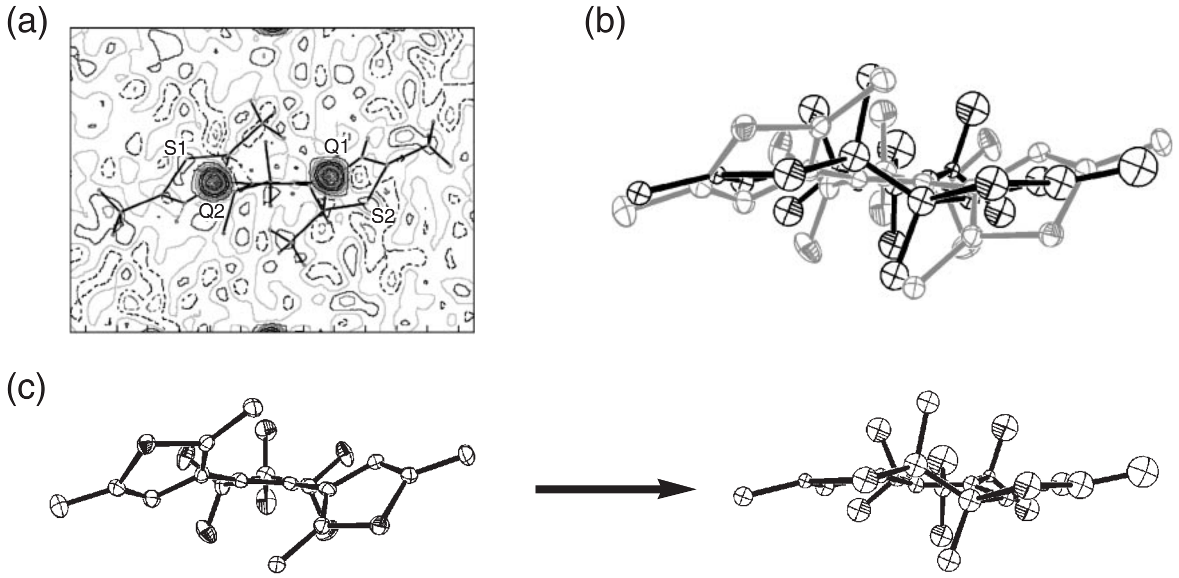

Fig. 13. $F_0 - F_c$ difference Fourier electron density maps through peaks Q1 and Q2 after the photocyclization reaction of **4** (a) and the molecular structure in the photoirradiated colored crystals (b and c) (Ref. 60).

ordered structure was not observed at 115 K. At 115 K, the molecule deviated from the C_2 symmetry. The perfluorocyclopentene ring has a dynamic motion in the crystal at room temperature. Figure 12 shows the molecular structure of **4** at 115 and 293 K. At 115 K, the distance between two reactive carbons of 1,3,5-hexatriene moiety was 3.546(2) Å, while it was 3.576(2) Å at 293 K.

Photocyclization. Diarylethene crystal **4** was irradiated with polarized 360 nm light, and the change of the unit cell dimension was determined at room temperature.[60] Although the change was small, all unit cell lengths and unit cell volumes tended to decrease during photocyclization. This corresponds to the decrease of the molecular volume by the transformation from the open-ring isomers to the closed-ring ones.

The crystal irradiated for 24 h was analyzed by X-ray crystallography.[60] The difference Fourier electron density map of the crystal is shown in Fig. 13a. The coordinates of the open-ring isomer were used for the initial model for the refinement. After the first least-square refinement, the difference Fourier map showed the existence of two quite high electron density peaks Q1 (2.24 e Å^{-3}) and Q2 (2.22 e Å^{-3}) ascribed to the sulfur atoms of the photogenerated closed-ring isomer. These peaks were apart from the nearest sulfur atoms of the open-ring isomer by 1.5 and 1.2 Å. The locations are close to positions expected for the closed-ring isomer photogenerated in a conrotatory mode. The distance between the two peaks was 3.7 Å,

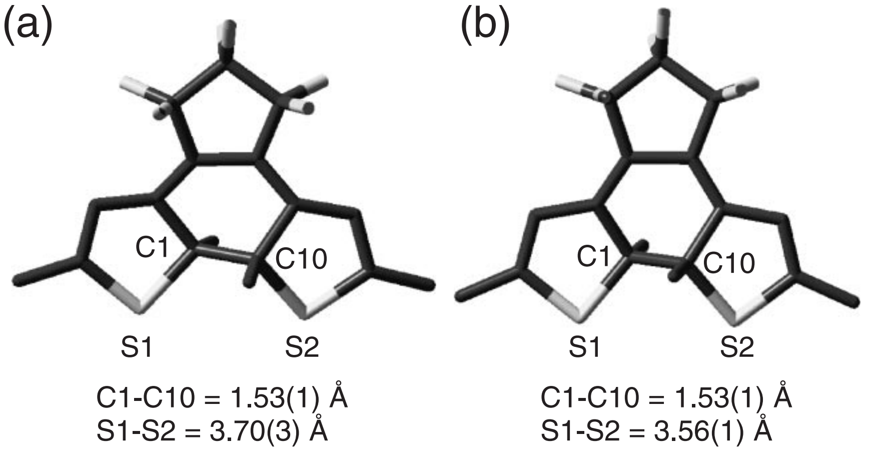

Fig. 14. The conformations of the molecular structures of the closed-ring isomers of **4** in the open-ring form crystal (a) and in the closed-ring form crystal (b) (Ref. 61).

which is slightly longer than the length of the closed-ring isomer, 3.56 Å. Electron density peaks corresponding to two carbons at the reacting points also appeared. The full-matrix least-square refinement converged well, as shown in Fig. 13b. The occupancy factor for the photogenerated closed-ring isomer was 0.084(2), which indicates that ca. 8% of the molecules in the crystal underwent the photocyclization reaction by the irradiation. In situ X-ray crystallographic analysis of the photocyclization reaction indicated that the diarylethene proceeds the photoreaction in the conrotatory mode, as shown in Fig. 13c.

The molecular structure of the photogenerated closed-ring isomer was compared with that of the isolated closed-ring isomer. Figure 14 shows the structural difference between the photogenerated closed-ring isomer in crystal **4** and the isolated closed-ring isomer in the crystal.[61] The C1–C10 bond lengths of the closed-ring isomer in both the open- and closed-ring form crystals are the same, but the distance between S1 and S2 in the open-ring form crystal is larger than that in the closed-ring form crystal. The structure of the closed-ring isomer in the open-ring form crystal is distorted.

The structure difference was reflected in the absorption maximum of the closed-ring isomer. The closed-ring isomer in the closed-ring form crystal had an absorption maximum at 485 nm and an edge at 610 nm, as shown in Fig. 15c. However, the photogenerated closed-ring isomer in the open-ring form crystal shifted to longer wavelength. The maximum was observed at 535 nm and an edge at 650 nm, as shown in Fig. 15b. The red shift of the absorption maximum of the closed-ring isomer is ascribed to the strained structure. The red shift was also confirmed from a calculation by the time-dependent density-functional theory (TD-DFT) method.[61]

Photocycloreversion. X-ray crystallographic analysis of the closed-ring isomer of **4** was examined at 123 K.[62] The molecular structure is shown in Fig. 16. The molecule has no disorder. The fused ring has a trans configuration. The photocycloreversion reaction was carried out by irradiation to the crystal with 680 nm light for 100 h. The space group was the same as the crystal before photoirradiation. The *b* axis and the unit cell volume increased as much as 0.267 and 44 Å^3, respectively. The molecular structure obtained is shown in Fig. 17. The distance between C1B and C10B atoms was 3.33(3) Å, which

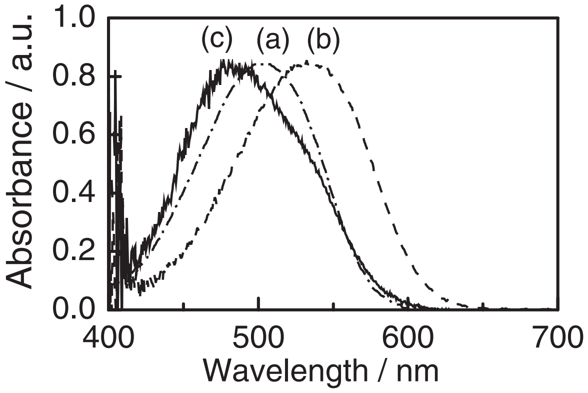

Fig. 15. Absorption spectra of the closed-ring isomer of **4** in hexane (a), in the open-ring form crystal (b), and in the closed-ring form crystal (c) (Ref. 61).

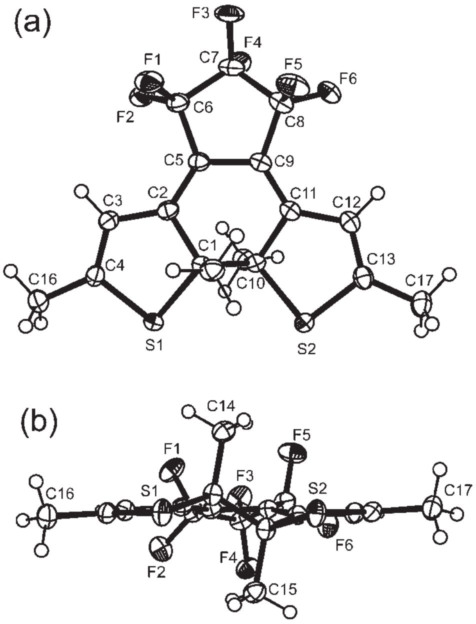

Fig. 16. ORTEP drawings of top view (a) and side view (b) of the closed-ring isomer of **4** showing the 50% probability displacement ellipsoids (Ref. 62).

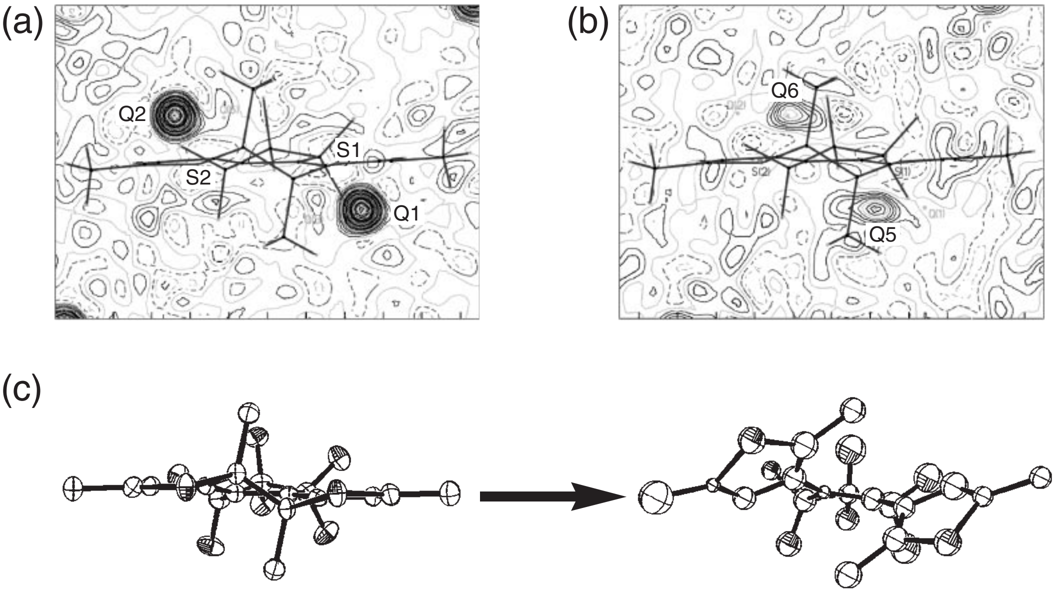

Fig. 17. $F_0 - F_c$ difference Fourier electron density maps through peaks Q1 and Q2 (a), and Q5 and Q6 (b) after the photocycloreversion reaction of **4**, and the molecular structure of the photogenerated open-ring isomer (c). Reprinted with permission from Ref. 62. Copyright 2000 American Chemical Society.

Table 1. Photocyclization/Cycloreversion Quantum Yields in Hexane and in Crystal

	In hexane		In crystal	
	$\Phi_{o\to c}$	$\Phi_{c\to o}$	$\Phi_{o\to c}$	$\Phi_{c\to o}$
4[54]	0.40	0.12	0.80, 0.83[a)]	0.10, 0.11[a)]
6[63,64]	0.59	0.013	1.0_1	0.017
7[54]	0.52	0.0081	1.0_3	0.027
8[63]	0.53	0.0097	0.98	0.029
10[65]	0.56	0.0052	0.95–1.00[b)]	0.0061–0.027[b)]
11[54,66]	0.46	0.015	0.96	0.027

a) Determined by two different surfaces. b) Diarylethene **10** has four polymorphic forms.

is also slightly shorter than the value for the open-ring isomer in the crystal, 3.576(2) Å. The distance between S1B and S2B was 5.42 Å, which is smaller than the distance between two sulfur atoms of the open-ring isomer in the crystal, 5.96 Å. The photogenerated open-ring isomer in the closed-ring form crystal has a conformation more planar than that in the most stable conformation.[59,60] The occupancy factor for the open-ring isomer converged to 0.094(2). This indicates that about 9% of the closed-ring isomers converted to the open-ring isomers by irradiation for 100 h. Since only one open-ring conformer was detected, the cycloreversion reaction proceeded topochemically in a conrotatory mode. The cyclopentene plane slightly tilted during the cyclization reaction. The center of gravity of photogenerated open-ring isomer (0.409, 0.382, 0.266) remained at the same position as that of the closed-ring isomer (0.388, 0.376, 0.269), which corresponds to a movement of less than 0.20 Å.

5. Quantum Yield

Cyclization Quantum Yields. The quantum yields of diarylethenes in the single-crystalline phase were measured by using a polarizing microscope connected with a photodetector. The setup of the measuring system and the measuring procedure are described in detail in the literature.[54]

Table 1 shows the photocyclization/cycloreversion quantum yields in crystal as well as in solution. The cyclization quantum yields in crystal were twice as large as those in solution. The low quantum yield in solution is due to the presence of molecules in non-photoactive parallel conformation, as described before. The cyclization quantum yields of crystals **6–11** were around 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.

X-ray crystallographic analysis of the crystals indicated that diarylethene molecules in the crystals were fixed to the antiparallel conformation. The distances between the reactive carbon atoms were estimated to be 3.48–3.96 Å, which are close enough for the conrotatory cyclization reactions. Figure 18 shows a correlation between the cyclization quantum yields of diarylethene crystals and the distances between the reactive carbon atoms of the diarylethenes in the crystals.[67] When the distance is larger than 4.2 Å, the photocyclization reaction in crystals is suppressed. The reaction process was analyzed based on ab initio and DFT calculation of the initial geometries, the relaxation from the Franck–Condon states, the shapes of the potential energy surface of the ground states, and the geometry

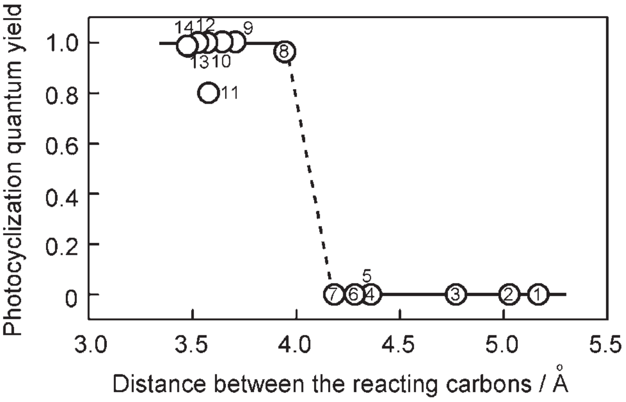

Fig. 18. Relationship between the photocyclization quantum yield and the distance between the reacting carbons. 1: 1,2-bis(2,4,5-trimethyl-3-thienyl)perfluorocyclopentene, 2: 1,2-bis(2,4-dimethyl-5-methoxyphenyl-3-thienyl)perfluorocyclopentene, 3: 1,2-bis(2-methyl-6-formylbenzothiophen-3-yl)perfluorocyclopentene, 4: 1,2-bis(2-isopropyl-4-methyl-5-phenyl-3-thienyl)perfluorocyclopentene, 5: 1,2-bis(2-methylbenzothiophen-3-yl)perfluorocyclopentene, 6: 1-(2-methylbenzothiophen-3-yl)-2-(2,6-dimethylbenzothiophen-3-yl)perfluorocyclopentene, 7: 1,2-bis(2,6-dimethylbenzothiophen-3-yl)perfluorocyclopentene, 8: compound **11**, 9: compound **7**, 10: compound **8**, 11: compound **4**, 12: compound **9**, 13: compound **8**, 14: compound **10**. Reproduced by permission of The Royal Society of Chemistry (Ref. 67).

change by the large amplitude motions.[68]

The large cyclization quantum yield in the crystalline phase can be ascribed to three factors. One is a high population of the photoreactive antiparallel conformation in the crystalline phase, in which the distance between the reacting carbon atoms is less than 4 Å. 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[35] and the rapid cyclization rate, in less than 10 ps.[38] The rapid reaction rate prevails over other relaxation processes, such as radiative and nonradiative transitions from the excited states to the ground state.

Cycloreversion Quantum Yields. The quantum yields of photocycloreversion reactions are also summarized in Table 1. The values for crystals **4** and **6** were 0.10 and 0.017, which are almost identical to those in hexane. The values for crystals **7**, **8**, and **11** were 0.027, 0.029, and 0.027, which are larger than those 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. The photogenerated isomers are in the constrained forms, which are different from the most stable closed-ring isomer conformations.

During the course of study of single-crystalline photochromism, we found that diarylethene **10** forms four polymorphic crystals: α, β, γ, and δ, when recrystallized from hexane.[65] Figure 19 shows ORTEP drawings of the four polymorphic crystals. The four crystals have different space groups, unit cell

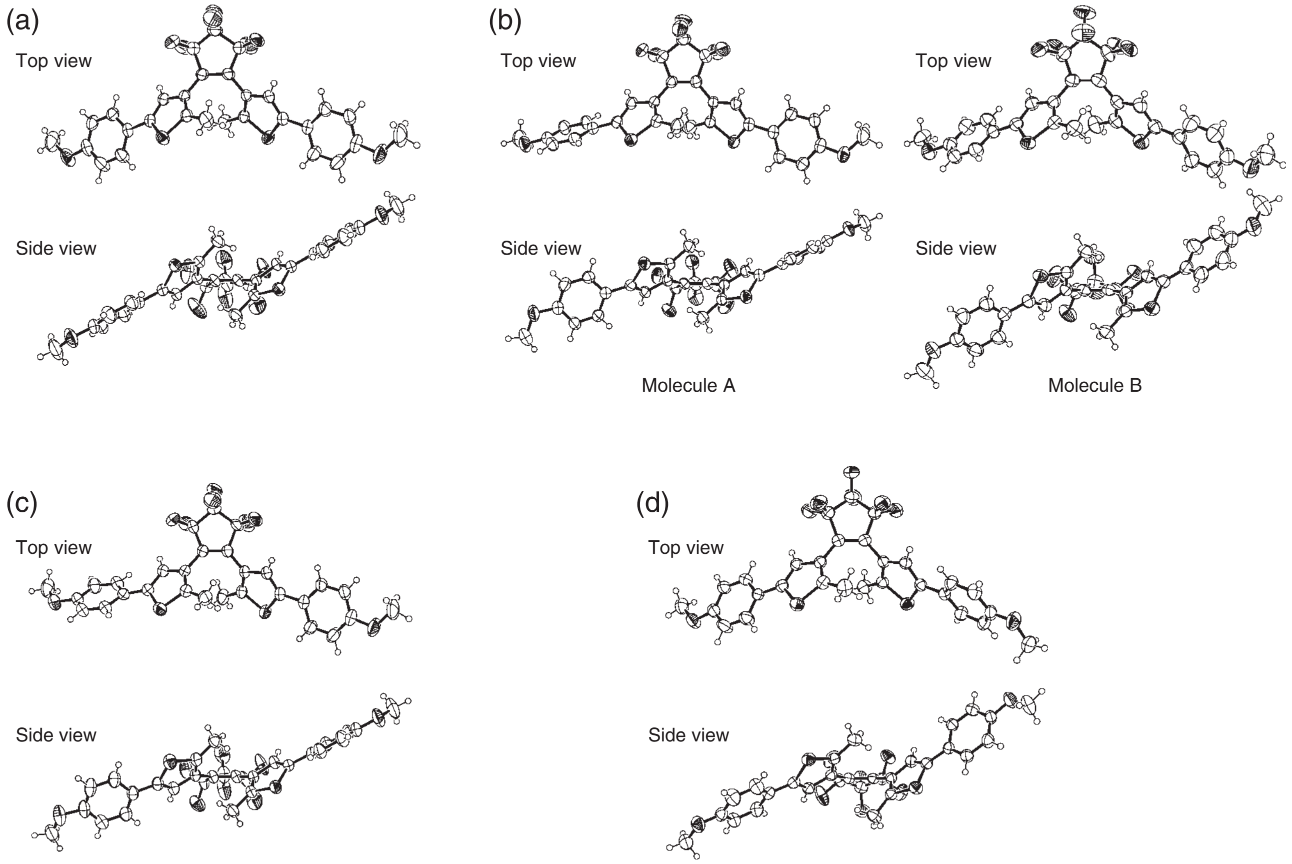

Fig. 19. ORTEP drawings of **10-α** (a), **10-β** (b), **10-γ** (c), and **10-δ** (d), showing the 50% probability displacement ellipsoids. Reproduced by permission of Wiley-VCH (Ref. 65).

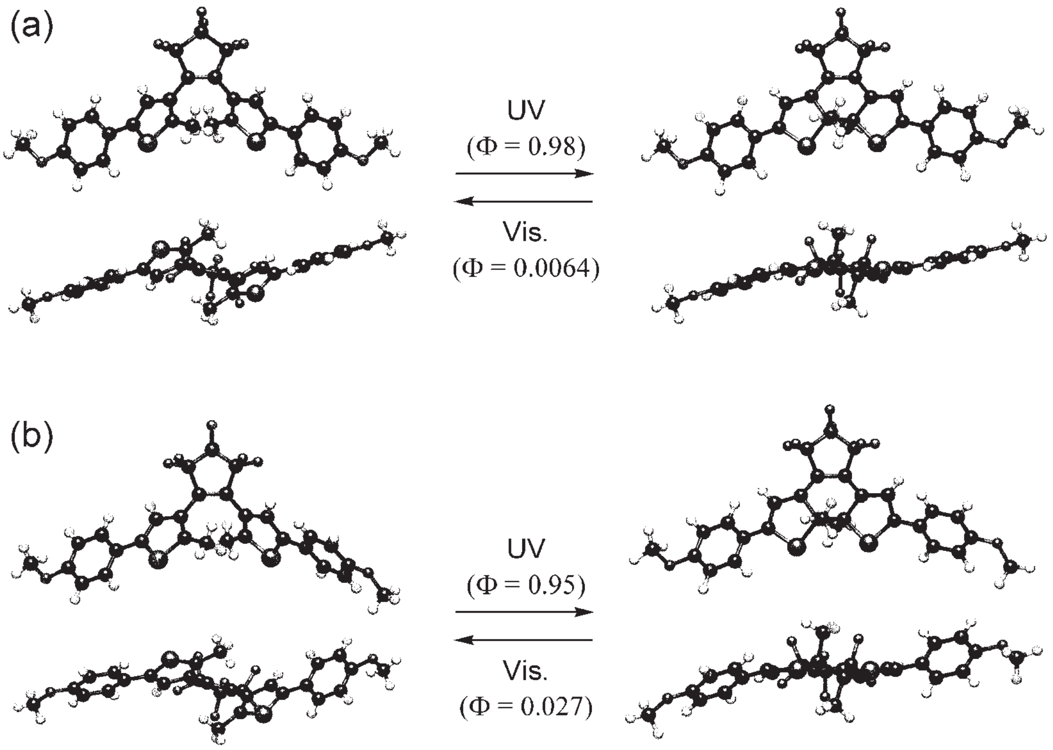

Fig. 20. Geometrical structure changes and photocyclization/cycloreversion quantum yields of crystal **10-α** (a) and crystal **10-δ**. Reproduced by permission of Wiley-VCH (Ref. 65).

volumes, conformation of the molecules, and the distance between the reactive carbon atoms. 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.

The correlations between the conformation and the optical properties as well as the reactivity were examined.[65] The cyclization quantum yields were independent of the conformations. Four polymorphic crystals gave almost same cyclization quantum yields, around 0.95–1.0. The cycloreversion quantum yields of α- and γ-crystals (0.0064 and 0.0061, respectively) were almost identical to that in hexane (0.0052). On the other hand, the yields of β- and δ-crystals (0.026 and 0.027, respectively) 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 same photostability as in solution.

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 (Fig. 20b). 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 (Fig. 20a).

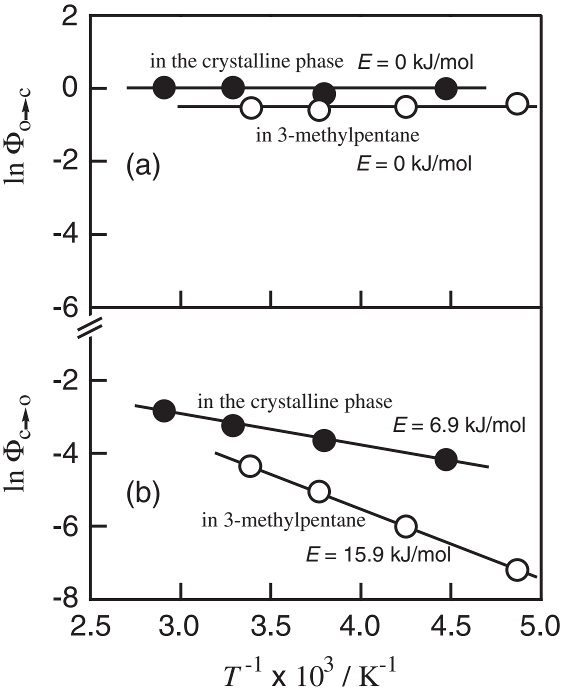

Fig. 21. Temperature dependence of the cyclization (a) and cycloreversion (b) quantum yields of diarylethene **16**.

Temperature Dependence of Quantum Yields. Temperature dependence of photocyclization/photocycloreversion reactions was measured in 3-methylpentane solution as well as in the crystalline phase.[63] Figure 21 shows the temperature dependence of the cyclization quantum yields of diarylethene **6** in

3-methylpentane and in the single-crystalline phase. In both solutions and crystals, no appreciable temperature dependence of the cyclization quantum yields was observed. The activation energy in the photocyclization process was almost zero.

The photocycloreversion reaction of **6** was also measured at various temperatures in 3-methylpentane and in the single-crystalline phase. There is an energy barrier in the excited state of the closed-ring isomer; whereas it is very low.[69] The activation energy in 3-methylpentane was determined to be 16 $\mathrm{kJ\,mol^{-1}}$. The activation energy in the single-crystalline phase was smaller than that in solution. The lower activation energy in crystals indicates that the photogenerated colored isomers have different stability between in solution and in crystals. The conformation of the photogenerated closed-ring isomers in crystals contains some strain energy,[61] which may decrease the activation energy.

The absence of activation energy in the photocyclization process indicates that the molecules are in a favorable conformation for the reaction and the crystal lattice does not disturb the rotation of the thiophene rings. The very rapid photocyclization reaction of diarylethene **4** in less than 10 ps observed in the crystal[38] is ascribed to the absence of the activation energy.

6. Conrotatory Thermal Cycloreversion

Thermal stability of the colored closed-ring isomers is one of the main advantages of diarylethene photochromic performance. The photogenerated blue color of the diarylethene crystal **6** remains stable even at 100 °C.[63] The colorless product produced by heating above 200 °C was confirmed to be the open-ring isomer by ^{1}H NMR and mass spectroscopy. The temperature dependence of the thermal cycloreversion reaction rate from the closed-ring isomer to the open-ring isomer at 150–211 °C showed a linear relationship between $\ln k$ and $1/T$. The activation energy was determined from the slope to be 139 $\mathrm{kJ\,mol^{-1}}$. Extrapolation of the temperature dependence indicates that the half-life time of the colored closed-ring isomer is 1900 years at 30 °C. The large activation energy in the ground state practically prohibits the thermal cycloreversion reaction.

Introduction of bulky substituents at the 2- and 2′-positions of the thiophene or benzothiophene aryl groups changes the thermal stability of the closed-ring isomer.[70–73] The thermal stability of diarylethene **7** having ethyl substituents at the 2- and 2′-positions of thiophene groups was examined in toluene and in the crystal.[55] The closed-ring isomer of **7** was heated in toluene for 50 h at 120 °C to follow the bleaching reaction. The absorption spectrum of the bleached solution was the same as that of the open-ring isomer **7**. This indicates that the thermal cycloreversion reaction took place at 120 °C.

The reaction mode in the thermal cycloreversion reaction of the closed-ring isomer of **7** was examined by in situ X-ray crystallographic analysis.[55] The photocyclization/photocycloreversion reactions of diarylethenes in crystals proceed in the conrotatory mode.[60,62] On the other hand, diarylethene crystal **7** was not shattered even after the photocyclization/thermal cycloreversion reactions were repeated many times. This means that the photogenerated closed-ring isomer returns to the open-ring isomer in a conrotatory mode by the thermal cycloreversion reaction.

According to the Woodward–Hoffmann rules[74] the thermal cycloreversion reaction of cyclohexadiene derivatives should proceed in disrotatory mode. It is of interest to reveal the mechanism of the cycloreversion reaction to understand the thermal stability of the closed-ring isomers. The thermal cycloreversion reaction in the crystal was followed by X-ray crystallography. After heating the closed-ring form crystal of **7** at 100 °C for 256 h, four new peaks appeared around the sulfur atoms and the reactive carbon atoms, as shown in Fig. 22a. The new peaks were assigned to those of the open-ring isomer. The occupancy factor for the open-ring isomer converged to 0.078, which means that around 8% of the closed-ring isomers thermally converted to the open-ring isomers. The generated open-ring

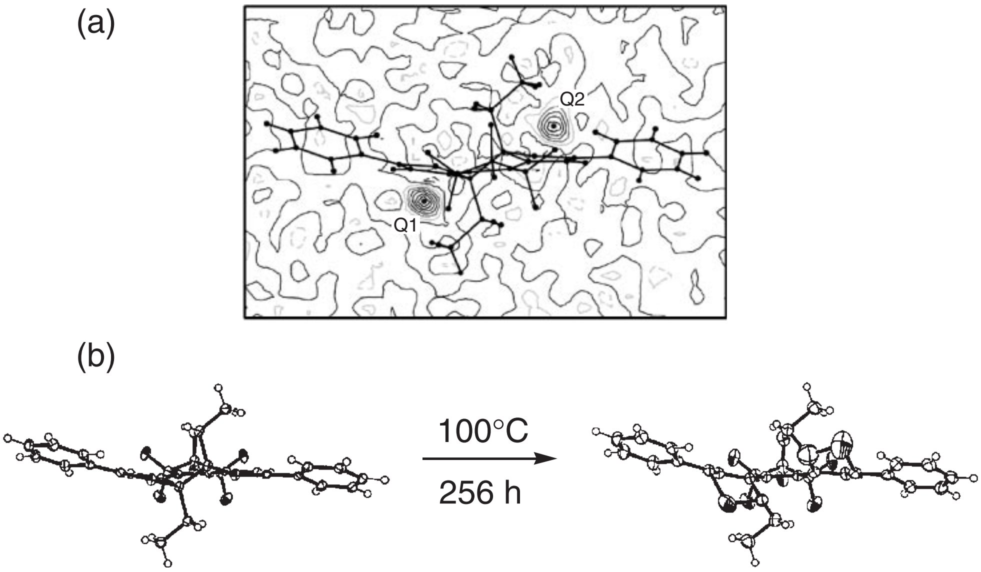

Fig. 22. $F_0 - F_c$ difference Fourier electron density maps through peaks Q1 and Q2 after the thermal cycloreversion reaction of **7** (a) and the molecular structures before and after the reaction (b). Reprinted with permission from Ref. 55. Copyright 2000 American Chemical Society.

isomer indicated that the thermal cycloreversion reaction proceeded in a conrotatory mode, as shown in Fig. 22b. The conrotatory thermal cycloreversion reaction can explain the thermal stability of the closed-ring isomers when the aryl groups have low aromatic stabilization energies.[35]

The thermal cycloreversion reaction rates were followed in toluene, in the open-ring form crystal, and in closed-ring form crystal at various temperatures. Figure 23 shows the temperature dependence of the bleaching reaction. From the plots, the activation energy (E_a) and frequency factor (A) were determined. The A values (2.7–5.3×10^{12} s^{-1}) are almost the same in the three cases. The E_a value increased in the following order: 120 kJ mol^{-1} (in the open-ring form crystal) $<$ 128 kJ mol^{-1} (in toluene) $<$ 137 kJ mol^{-1} (in the closed-ring form crystal). From the kinetic studies the energy diagrams for the thermal cycloreversion reactions of **7** in the ground state were obtained as shown in Fig. 24. The energy level of the open-ring isomer in the open-ring form crystal is similar to that in toluene and that of the closed-ring isomer in the closed-ring form crystal is also similar to that in toluene. On the other hand, the closed-ring isomer photogenerated in the open-ring form crystal is considered to be less stable than the closed-ring isomer in toluene and in the closed-ring form crystal. Also, the open-ring isomer produced by the thermal cycloreversion reaction in the crystal is less stable than the open-ring isomer in toluene and in the open-ring form crystal. It was confirmed that the open-ring isomer photogenerated in the closed-ring form crystal has a constrained conformation.[62] The thermally generated open-ring isomer is also considered to be in the constrained conformation.

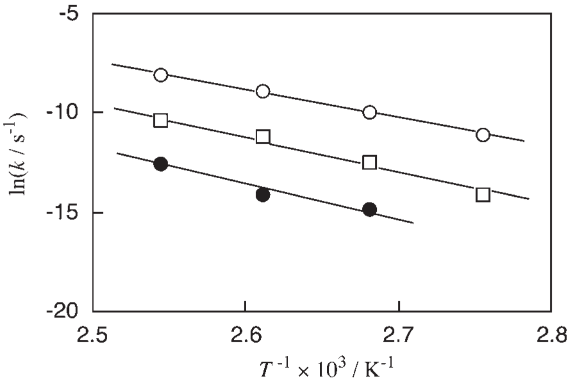

Fig. 23. Temperature dependence of thermal cycloreversion reaction rates of **7** in toluene (□), in the open-ring form crystal (○), and in the closed-ring form crystal (●). Reprinted with permission from Ref. 55. Copyright 2000 American Chemical Society.

7. Multi-Colored Crystal

In one-component photochromic crystals, they interconvert only between "colorless" and "colored" states. On the other hand, in multi-component systems composed of different kinds of photochromic compounds, reversible multi-mode switching between more than two states can be realized by the combination of two states of each component. The multi-component or multi-colored systems of diarylethenes have been reported by Lehn et al.[34] They demonstrated that absorption properties of the multi-component diarylethene mixture in solution, as well as on silica-gel plates, can be modulated by controlling wavelengths, duration, and slit-width of the irradiation applied. A fused diarylethene dimer which consists of two different photochromic units has also been demonstrated.[75] Although these systems exhibit multi-colors, photocoloration/decoloration cycles, photocoloration efficiency, resolution of the colored images, and stability of the colored state are limited. Ideal systems are multi-colored single crystals because of their high durability, high efficiency of photocoloration, and molecular scale high resolution. Two-component diarylethene crystals have been developed.[76,77]

A colorless crystal was obtained by recrystallization of a mixture of **4** and **10** (90:10) from ethanol.[77] When the ratio of **10** in the solution was increased, the quality of crystals became worse. The crystal shape was a rhombus and similar to that of the single crystal of **4**.[59] The molar ratio of **4** and **10** in the crystal was 99:1. The colorless crystal **4**/**10** turned purple upon irradiation with 370-nm light. The absorption band has a maximum at 535 nm and a shoulder around 650 nm. The absorption maximum of 535 nm is ascribed to the closed-ring isomer of **4**. The purple crystal turned red by partially bleaching

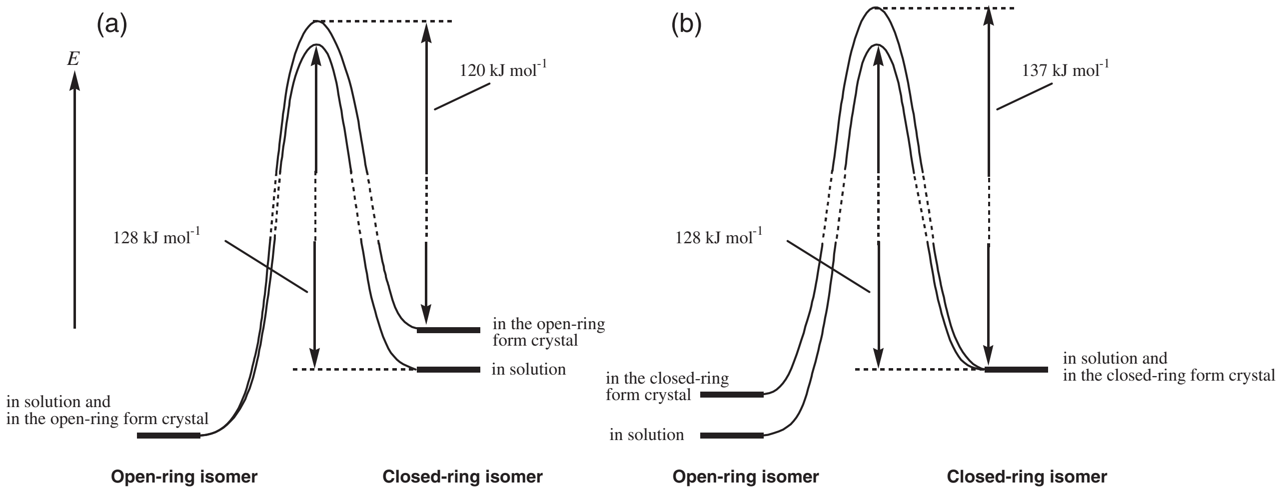

Fig. 24. Energy diagram of the open- and closed-ring isomers of **7** (Ref. 55).

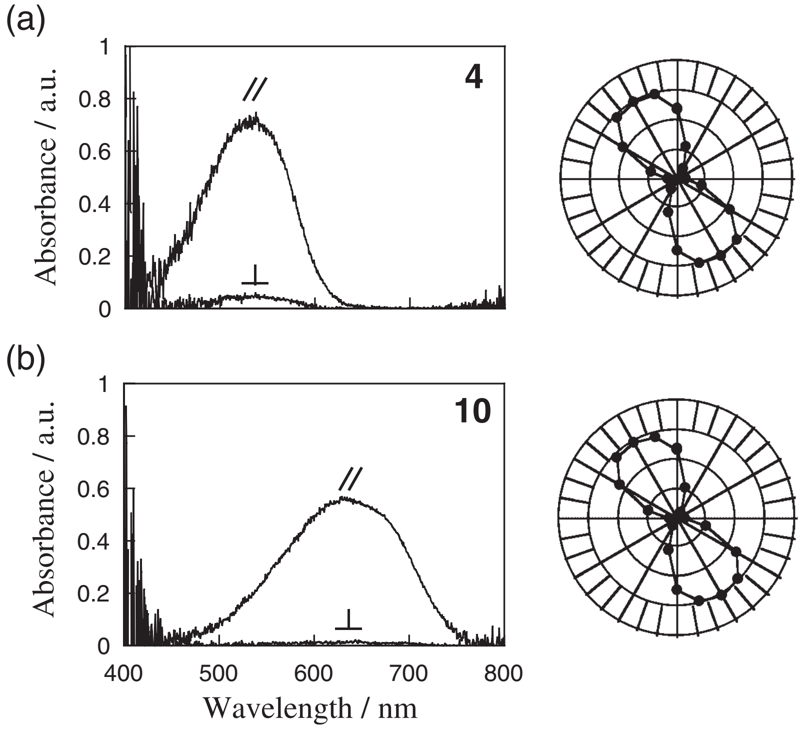

Fig. 25. Polarized absorption spectra of the closed-ring isomers of **4** (a) and **10** (b) and its polar plots. Reproduced by permission of Wiley-VCH (Ref. 77).

with 692-nm light. Upon irradiation with 405-nm light, the colorless crystal turned blue. The relatively large absorption around 650 nm indicates that the closed-ring isomer of **10** is predominantly produced by 405-nm light irradiation. The purple, red, and blue colors were completely bleached upon irradiation with visible light ($\lambda > 450$ nm), and the crystal **4**/**10** returned to colorless.

Figure 25 shows the polarized absorption spectra of **4** and **10** in the crystal **4**/**10** and the polar plots of the absorbance at 535 nm and 630 nm for **4** and **10**, respectively. The absorption bands ($\lambda_{\text{max}} = 535$ nm for **4** and $\lambda_{\text{max}} = 630$ nm for **10**) correspond to the long-axis electronic transitions of the closed-ring isomers. The absorption anisotropy of **10** in the crystal **4**/**10** was similar to that of **4**. This indicates that **10** in the crystal **4**/**10** is substitutionally incorporated in the **4** host crystal, and both components undergo photochromic reactions in the crystal lattice. The long-axis electronic transition moments of the photogenerated closed-ring isomers **4** and **10** are parallel to each other.

To demonstrate the color change to red or blue, crystals with different composition ratios of **4** and **10** were prepared. By recrystallization of a mixture of **4** and **10** (95:5) from ethanol, a crystal with a molar ratio of 99.6:0.4 was obtained. Figure 26 shows a photograph of the partially colored crystal of **4**/**10**. The colorless crystal turned red upon irradiation with 370-nm light, and turned blue by 405-nm light. Upon irradiation with both 370- and 405-nm light, it turned purple. When each colored spot is regarded as a bit in optical recording media, four kinds of information: such as colorless, red, blue, and purple, could be written into the crystal by changing the wavelength of irradiating light. The recording density of the two-wavelength recording using the two-component photochromic crystal is twice as large as that of usual one-component crystal systems.

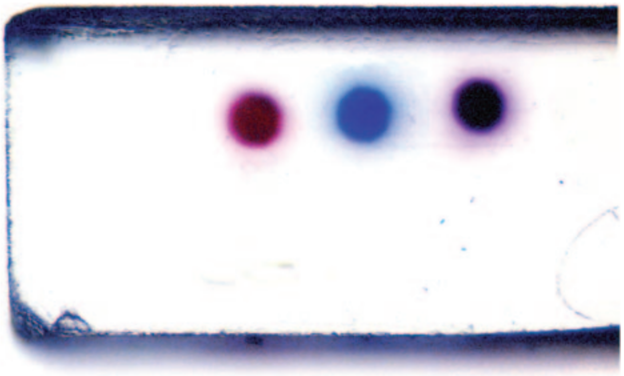

Fig. 26. Photograph of partially colored crystal **4**/**10**. (left): irradiated with 370-nm light. (middle): irradiated with 405-nm light. (right): irradiated with both 370- and 405-nm light. Reproduced by permission of Wiley-VCH (Ref. 77).

8. Crystal Surface Changes

Morphological changes of photoreactive single-crystal surfaces were reported initially by Kaupp,[78] who found that photodimerizations of *trans*-cinnamic acids[79] and anthracenes[80,81] in the crystalline phase induced the surface morphological changes. The morphological changes were attributed to phase-rebuilding of the surface molecules upon photoisomerization. The changes were irreversible, however, and a critical claim that local heating may contribute to some extent to the morphological changes still remained.[82]

The colorless single crystal of diarylethene **11** turned blue

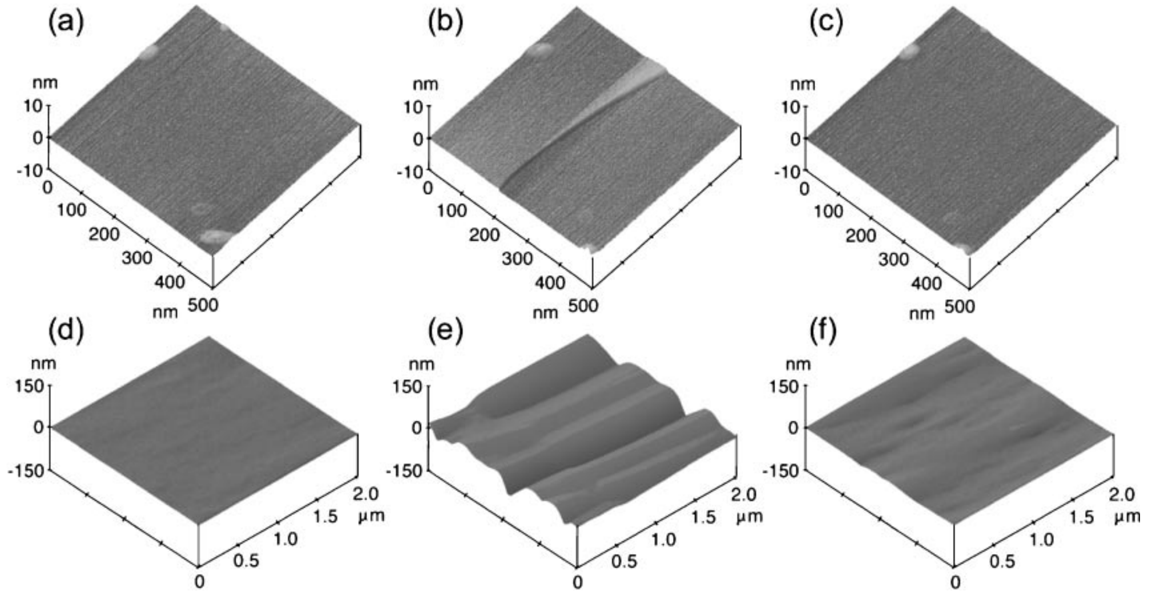

Fig. 27. AFM images of the (100) crystal surface (a–c) and the (010) surface (d–f) of crystal **11**: before photoirradiation (a and d), after irradiation with 366-nm light for 10 s (b) and 15 s (e), and after irradiation with visible light ($\lambda > 500$ nm) (c and f). Reproduced by permission of the American Association for the Advancement of Science (Ref. 83).

upon irradiation with 366-nm light. The color change resulted from the formation of the closed-ring isomer. The morphological changes of the crystal surfaces that accompany the change in coloration were observed with an atomic force microscope.[83] The two crystal surfaces, (100) and (010), were used for observation of the surface morphological changes. The crystal surface of crystal **11** before photoirradiation was flat (Fig. 27a). Upon irradiation for more than 10 s with 366-nm light (intensity 12 mW/cm^2), steps appeared on the (100) surface (Fig. 27b). No step formation was discerned during the initial 10-s irradiation but appeared after the induction period. The step height was 1.0 ± 0.1 nm. The step disappeared by bleaching upon irradiation with visible light ($\lambda > 500$ nm) (Fig. 27c). When the irradiation time was prolonged, the number of the steps increased and steps with heights of 2.0 ± 0.2 nm and 3.0 ± 0.3 nm appeared. The height was always a multiple of the minimum step height (1.0 ± 0.1 nm), and we did not observe any steps with a height lower than the unit height (1.0 ± 0.1 nm). The morphological change was reversible and correlated with the color change of the crystal. The AFM images of the (010) surface before and after UV irradiation are shown in Fig. 27d–f. Upon irradiation for 15 s with 366-nm light (intensity 12 mW/cm^2), the crystal turned blue and valleys appeared on the crystal surface. The depth of the valley was estimated to be 10 to 50 nm. The valley almost disappeared by bleaching upon irradiation with visible light ($\lambda > 500$ nm) (Fig. 27f). The morphological change was again reversible and correlated with the color change.

Conclusion

Thermally irreversible and fatigue-resistant photochromic diarylethene crystals have been developed. Such diarylethene crystals have the following characteristics: (i) both isomers are thermally stable, (ii) coloration/decoloration cycles can be repeated more than 10^4, (iii) the response time is as fast as 10 ps, (iv) the crystals show various colors depending on the substituents, (v) the closed-ring isomers exhibit a distinct dichroism in the absorption spectrum, (vi) a multi-component single crystal show multi-color photochromism, (vii) the cyclization quantum yields are as large as unity, (viii) the crystal surfaces show reversible morphological changes upon photoirradiation.

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Seiya Kobatake was born in Kawanishi, Hyogo in 1969. He received his B. S. (1991), M. S. (1993), and Ph. D. (1996) from Osaka City University. In 1996–1997, he spent as a postdoctoral researcher at the Institute of Polymer Science, The University of Akron, U.S.A. In 1998, he joined the group of Professor Masahiro Irie, as a researcher of CREST, JST. Since 2000 he has been a research associate at the Graduate School of Engineering, Kyushu University. His current research has been focused on the photochromism of diarylethene crystals and their application. He received the Chemical Society of Japan Award for Young Chemists for 2002.