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Photochromism of Mixed Crystals Containing Bisthienyl-, Bisthiazolyl-, and Bisoxazolylethene Derivatives

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Abstract: Single crystals composed of two or three different kinds of diarylethenes, having similar geometrical structures but different colors in the closed-ring isomers, 1,2-bis(2-methyl-5-phenyl-3-thienyl)-perfluorocyclopentene (**1a**), 1,2-bis(5-methyl-2-phenyl- 4-thiazolyl)perfluorocyclopentene (**2a**), and 1,2-bis-(5-methyl-2-phenyl-4-oxazolyl)perfluorocyclopentene (**3a**) have been prepared in an attempt to form single crystals which exhibit different colors, depending on illumination wavelengths. When **1a** and **2a** are mixed in ethanol and the content of **2a** in the feed is higher than that of **1a**, only a needle-shaped crystal is obtained. The crystal shape is similar to that of **2a**. On the other hand, high content of **1a** in the feed leads to formation of a block-shaped crystal, of which the shape is similar to that of **1a**. At a feed ratio of 1:1 for **1a** and **2a**, two types of crystals such as needle- and block-shapes are obtained from the same batch. Mixed crystals composed of three kinds of derivatives **1a**/**2a**/**3a** have also been prepared. A crystal composed of the three derivatives in the molar ratio of 32 (**1a**):53 (**2a**):15 (**3a**) was obtained. X-ray analysis proved that **1a** and **3a** are packed in the crystal lattice of **2a**. The mixed crystal **1a**/**2a**/**3a** changed color from colorless to yellow, red, and blue upon irradiation with light of appropriate wavelengths.

Introduction

Photochromism is defined as a reversible transformation between two isomers having different absorption spectra by photoirradiation.[1,2] Although many photochromic compounds have been reported thus far, compounds which show photochromic reactivity in the crystalline phase are rare.[3−14] In addition, in many cases of single-crystalline photochromism, photogenerated isomers are thermally unstable, and the thermal instability prevents detailed crystallographic analysis of the photoproducts. Recently, we found that some diarylethene derivatives undergo thermally irreversible photochromic reactions even in the crystalline phase.[15−28] Upon irradiation with UV light, colorless single crystals turn yellow, red, blue, or green, depending on their molecular structures of diarylethenes. Colored forms are stable in the crystals even at 100 °C and never return to the initial colorless forms in the dark. The colors disappear by irradiation with visible light. The coloration/decoloration cycles can be repeated more than 10^4 times while maintaining the crystallinity. The photochromic crystals showing thermally irreversible and fatigue-resistant characters have promising potential for optoelectronic devices such as rewritable optical memory media, optical switches, and color displays.

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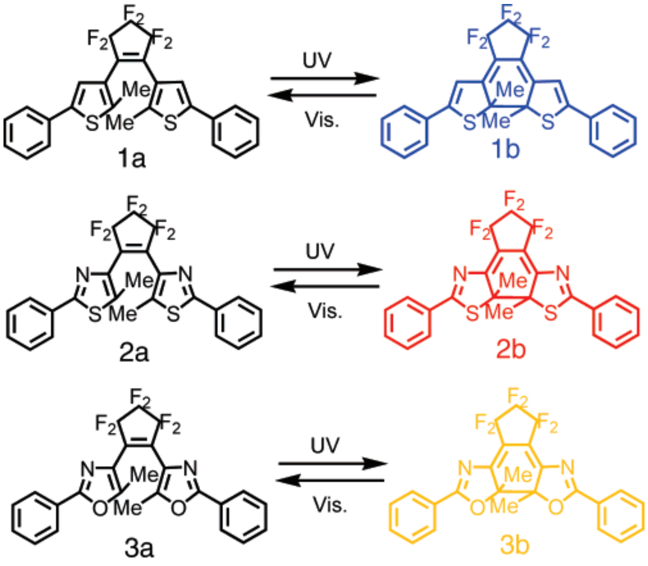
Scheme 1



Various types of multicomponent crystals have been prepared, and their photochromic performance have been examined.[23,25−27] These crystals exhibit various colors (yellow, red, blue, green, and black) upon irradiation with light of appropriate wavelengths, and the colors return to colorless upon irradiation with visible light. For example, a mixed crystal composed of 1,2-bis(2,5-dimethyl-3-thienyl)perfluorocyclopentene, 1,2-bis(3,5-dimethyl-2-thienyl)perfluorocyclopentene, and 1,2-bis[2-methyl-5-(4-methoxyphenyl)-3-thienyl]perfluorocyclopentene turned blue, red and yellow upon irradiation with appropriate wavelengths of light.[25,26] Although clear full-color change was observed upon photoirradiation, the content of the blue component was very low (<0.5%). Very recently, we succeeded in preparing two-component single crystals composed of almost equal amounts of 1,2-bis(5-methyl-2-phenyl-4-thiazolyl)perfluorocyclopentene (**2a**) and 1,2-bis(5-methyl-2-phenyl-4-oxazolyl)perfluorocyclopentene (**3a**), which are very similar in molecular structures.[29] The mixed crystal changed color from colorless to yellow, orange, and red upon irradiation with light of appropriate wavelengths, whereas **3a** did not show any photochromism in the homo-crystal.[29] In this paper, we describe single-crystalline photochromism of mixed crystals composed of 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene (**1a**),[20,22] **2a**[30,31] and **3a**[29] in almost equal amounts (Scheme 1). The three diarylethene derivatives having similar geometrical structures but different colors in the closed-ring isomers could readily mix with each other in a single crystal. The three-component crystal exhibited full colors upon photoirradiation.

Results and Discussion

Photochromism of Mixed Crystal 1a/2a. A colorless crystal was obtained by recrystallization of a mixture of **1a** and **2a** (**1a**/**2a** = 25/75 in molar ratio) from ethanol. The crystal shape was needle, which is similar to that of crystal **2a**. The composition ratio of **1a** and **2a** in the crystal was determined by HPLC using hexane/AcOEt (98/2 in v/v) as the eluent. The composition ratio of **1a** and **2a** in the crystal was 23:77 in molar ratio, which is almost the same as the feed ratio of **1a** and **2a**. The crystal is named as **1a/2a-α**. To confirm that both **1a** and **2a** are included in the crystal lattice, we carried out X-ray crystallographic analysis of the crystal. The crystallographic data are shown in Table 1. The crystal has a unit cell of monoclinic $P2_1/n$. As expected, the lattice parameters in the crystal are similar to those of homo-crystal **2a**.[32] Figure 1 shows the final molecular structure. The molecular structure of **1a** is expressed as a disordered structure of **2a**. In other words, **2a** is replaced with **1a** in the same sites of the crystal lattice of **2a**. The distance between the reacting carbon atoms was determined to be 3.43 Å, which is short enough for the reaction to take place in the crystal.[24] The site occupancy factor for **1a** was determined to be 17%, which is slightly less than the value determined by HPLC. When the feed ratio of **2a** was higher than that of **1a**, only a needle-like crystal was obtained.

At 50 mol % of **2a** in the feed solution, two types of crystals were obtained from the same batch by recrystallization from ethanol. Figure 2 shows photographs of the crystals obtained from the 1/1 batch. The shape of the needle crystal was similar to that of crystal **2a**, and HPLC measurement showed that the composition ratio of the crystal was 33:67 in molar ratio for **1a**:**2a**. On the other hand, the shape of the other block crystal was similar to that of crystal **1a**, and the composition ratio of the crystal was 73:27 in molar ratio for **1a**:**2a**. Upon irradiation with UV light, the crystals changed to red-purple (needle-shaped crystal) and blue-purple (block-shaped crystal), respectively. Crystals **1a** and **2a** show red and blue colors under the same conditions.

The block crystal named as **1a/2a-**β was analyzed by X-ray crystallography. The crystallographic data are also shown in Table 1, and the final molecular structures are shown in Figure S1. The crystal has a unit cell of triclinic $P\bar{1}$. In this crystal, two types of crystallographically independent molecules are observed, named as molecules A and B. Although the crystal system, space group, and cell parameters are different from those of crystal **1a**, the crystal packing is the same as that of crystal **1a**.[33] The site occupancy factor for **1a** was determined to be 69%, which is almost the same as the composition ratio determined by HPLC. Both **1a** and **2a** are proved to have photoreactive antiparallel conformations. When the feed ratio of **1a** was higher than that of **2a**, only a block-shaped crystal was obtained, which is similar to that of crystal **1a**.

Figure 3 summarizes the relationship between the feed content of **1a** and **2a** in the ethanol solution and the composition content in the crystals obtained. As shown in Figure 3, it formed two kinds of mixed crystals. One mixed crystal contained 0−33 mol % **1a** in the crystal lattice of **2a** (corresponding to red squares). The other mixed crystal contained 0−27 mol % **2a** in the crystal lattice of **1a** (corresponding to blue circles). The composition ratio of **1a** or **2a** in the two-component crystal is higher than that reported in a previous paper.[29] This is ascribed to very similar geometrical structures of **1a** and **2a**. Thermal properties of the mixed crystals were studied by measuring the melting

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(32) Crystal data for **2a**: $C_{25}H_{16}F_6N_2S_2$, MW = 522.52, monoclinic, space group $P2_1/n$, a = 7.236(2) Å, b = 25.752(8) Å, c = 12.611(4) Å, β = 102.432(5)°, V = 2295.0(12)Å^3, Z = 4. CCDC-282860.

(33) Crystal data for **1a**: $C_{27}H_{18}F_6S_2$, MW = 520.23, monoclinic, space group $P2_1/c$, a = 18.704(2) Å, b = 11.801(1) Å, c = 21.338(2) Å, β = 95.468(2)°, V = 4688(1)Å^3, Z = 8; also see ref 20.

Table 1. Crystal Data and Structure Refinements for **1a/2a-**α, **1a/2a-**β, and **1a/2a/3a**

compound	**1a/2a-**α[a]	**1a/2a-**β[b]	**1a/2a/3a**[c]
formula	$C_{25.46}H_{16.46}F_6N_{1.54}S_2$ (**1a**/**2a** = 23/77)[d]	$C_{26.46}H_{17.46}F_6N_{0.54}S_2$ (**1a**/**2a** = 73/27)[d]	$C_{25.63}H_{16.63}F_6N_{1.37}S_{1.7}O_{0.30}$ (**1a**/**2a**/**3a** = 32/53/15)[d]
temp/K	123	123	123
crystal system	monoclinic	triclinic	monoclinic
space group	$P2_1/n$	$P\bar{1}$	$P2_1/n$
unit cell dimensions			
a/Å	7.091(3)	11.808(3)	7.288(3)
b/Å	24.868(12)	13.568(3)	25.792(10)
c/Å	12.256(6)	14.917(3)	12.586(5)
α/deg	90.00	81.763(3)	90.00
β/deg	102.575(5)	82.255(3)	102.519(6)
γ/deg	90.00	82.303(3)	90.00
V/Å	2109.3(17)	2327.5(8)	2309.4(15)
Z	4	4	4
D_{calcd}/(g/cm^{-3})	1.644	1.487	1.487
θ range/deg	1.64 to 24.72	1.39 to 26.37	1.84 to 25.38
μ/mm^{-1}	0.324	0.292	0.269
F(000)	1064	1064	1054
reflections collected	16348	24011	15777
independent reflection	3605	9266	3999
no.restraints/parameters	4/317	0/632	1/327
GOF on F^2	1.104	1.038	1.306
R1 [$I > 2\sigma(I)$]	0.0710	0.0444	0.0724
wR2 (all data)	0.1775	0.1105	0.1694
largest diff. peak/hole [e·Å^{-3}]	0.41 −0.42	0.66 −0.33	0.70 −0.55

[a] The crystal was obtained from ethanol solution including **1a** and **2a** in ratio 25:75. [b] The crystal was obtained from ethanol solution including **1a** and **2a** in ratio 50:50. [c] The crystal was obtained from ethanol solution including **1a**, **2a**, and **3a** in ratio 22:32:46 (corresponds to entry 5 in Table 2). [d] The composition ratio in the mixed crystal was determined by HPLC analysis.

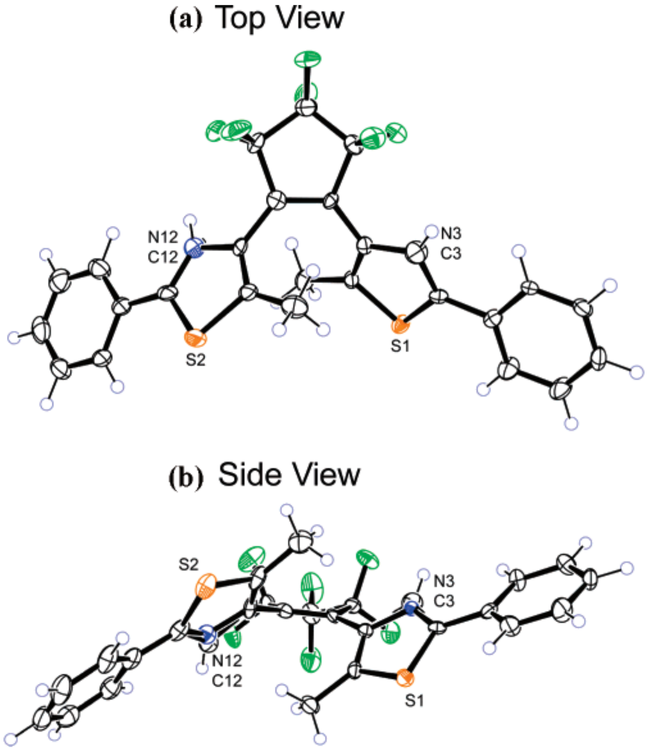

Figure 1. ORTEP drawings of top (a) and side views (b) of mixed crystal **1a/2a-**α showing the 50% probability displacement ellipsoids. Site occupancy factor for **1a** is 17%.

point of the crystals. The melting points of pure **1a** and **2a** were determined to be 139 and 155 °C, respectively. The melting points of **1a/2a-α** crystal decrease with increasing the content of **1a** (0−33 mol %) as shown in Figures S2 and S3. A similar melting point change for **1a/2a-**β crystal was also observed. The melting point of **1a**/**2a**-β (91/9) was measured to be 135 °C. Using the method developed for binary systems, the phase diagram of **1a** and **2a** was constructed.[34,35] The phase diagram is typical for conventional two-component crystals (Figure S3).

Photochromic behavior of crystal **1a**/**2a**-α, which included as much as 23 mol % **1a** in the crystal lattice of **2a**, was examined. Figure 4 shows the absorption spectra. Upon irradiation with 370-nm light, the colorless crystal **1a**/**2a**-α changed to red-purple. By partially bleaching with 458-nm light, the red-purple crystal turned blue as shown in Figure 4b. The spectrum in Figure 4b is the same as that of UV-irradiated crystal **1a**. On the other hand, by partially bleaching with 692-nm light, the red-purple crystal turned red as shown in Figure 4c. The spectrum in Figure 4c is the same as that of UV-irradiated crystal **2a**. The purple, blue, and red colors were completely bleached upon irradiation with visible light (λ > 450 nm). Thus, the crystal **1a**/**2a**-α exhibits multicolor photochromism.

To confirm that the photochromic reactions of both components took place in the crystal lattice, the absorption anisotropy of the photogenerated closed-ring isomers **1b** and **2b** in the mixed crystal **1a**/**2a**-α was measured. Figure 5 shows the polarized absorption spectra of **1b** and **2b** in the crystal **1a**/**2a**-α at a certain angle (0°, where the maximum absorption was observed) and its perpendicular angle (90°). These spectra were obtained upon UV irradiation and partial bleaching. The anisotropy of the absorption bands (λ_{max} = 600 nm for **1b** and λ_{max} = 550 nm for **2b**) correspond to the long-axis directions of the photogenerated closed-ring isomers **1b** and **2b**. The absorption anisotropy of **1b** and **2b** in the mixed crystal **1a**/**2a**-α is in the same direction. This indicates that **1a** is packed in a manner similar to that of **2a** in the crystal **1a**/**2a**-α, and

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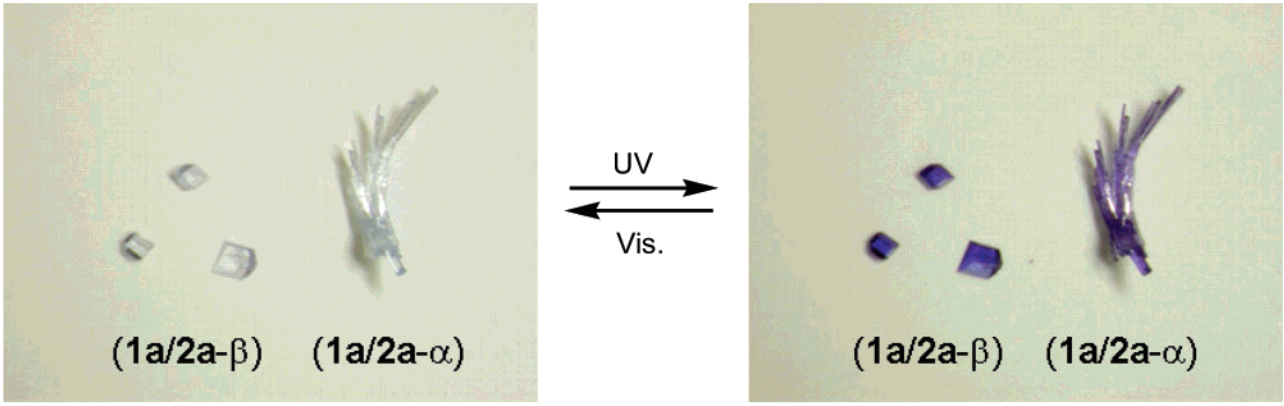

Figure 2. Photographs of mixed crystals **1a**/**2a**-α and -β obtained from the same batch.

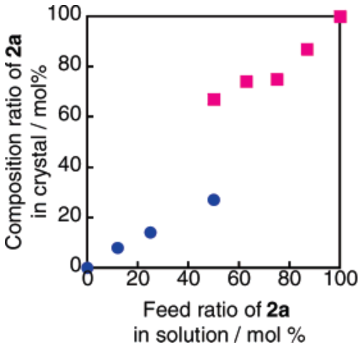

Figure 3. Relationship between content of **2a** in feed ethanol solution and composition content of **2a** in mixed crystal obtained. Red squares and blue circles show mixed crystals **1a**/**2a**-α and **1a**/**2a**-β, respectively.

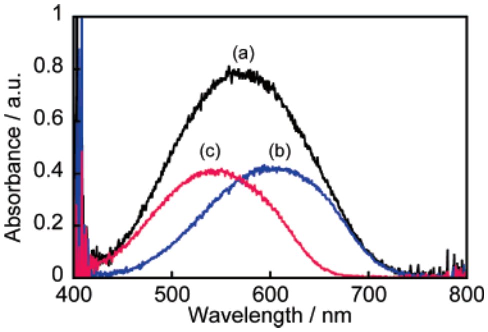

Figure 4. Absorption spectra of mixed crystal **1a**/**2a**-α irradiated with 370-nm light (a), 370- and 458-nm light (b), and 370- and 692-nm light (c). The absorption spectra were measured on (0−11) face.

both components undergo photochromic reactions in the crystal lattice. The photochromic reaction in the crystal lattice was further confirmed by in situ X-ray crystallographic analysis. The photogenerated closed-ring isomers were observed as disordered structures of **1a**/**2a**-α as shown in Figure S4. A similar photochromic reaction of crystal **1a**/**2a**-β was observed (Figures S6 and S7).

The possibility of energy migration and transfer in the photochromic reactions was examined for mixed crystals **1a**/**2a**-α (**1a**/**2a** = 76/24) and -β (**1a**/**2a** = 27/73). Figure 6 shows the time dependence of the conversion ratios from **1a** to **1b** and from **2a** to **2b** in the mixed crystals upon irradiation with 370-nm light. The composition ratios of **1b** and **2b** in the photoirradiated mixed crystals were monitored by HPLC. Upon irradiation of the mixed crystal **1a**/**2a**-α with 370-nm light, both **1a** and **2a** molecules underwent photochromic reactions. The conversion ratios of **1a** and **2a** to the closed-ring isomers **1b** and **2b** are similar to each other. This indicates that both **1a** and **2a** underwent efficient photochromic reactions upon irradiation with 370-nm light and that any appreciable energy migration and transfer do not take place in the crystal. A similar photochromic reaction was observed for the mixed crystal **1a**/**2a**-β. In both **1a**/**2a**-α and -β crystals, the closed-ring isomers **1b** and **2b** were equally efficiently produced upon irradiation with 370-nm light. The absence of energy migration and transfer is ascribed to very fast photocyclization reactions of the diarylethene derivatives.[36] Next, we tried to obtain three-component crystals of **1a**, **2a**, and **3a**.

Table 2. Relationship between Condition of Crystallization and Composition Ratio in Three-Component Crystal **1a**/**2a**/**3a** Obtained

entry	solvent	feed ratio in solution (**1a**:**2a**:**3a**)	composition ratio in crystal[a] (**1a**:**2a**:**3a**)
1	hexane	28:28:44 (4:4:6)	9:72:19
2	hexane	38:24:38 (6:4:6)	15:66:19
3	hexane	42:23:35 (7:4:6)	15:67:18
4	ethanol	38:24:38 (6:4:6)	72:27:1
5	ethanol	22:32:46 (3:4:6)	32:53:15
6	ethanol	17:33:50 (2:4:6)	24:55:21
7	ethanol	19:38:43 (2:4:4)	24:65:11

[a] Determined by HPLC analylsis.

Photochromism of Mixed Crystal 1a/2a/3a. In a previous paper,[29] we have reported that **3a** can sit in the crystal lattice of **2a** and that colorless two-component crystal **2a**/**3a** turned yellow, orange, or red by irradiation with light of different wavelengths. Furthermore, **1a** can sit in the crystal lattice of **2a** as described above. Therefore, it is anticipated that three-component crystals can be prepared by mixing these three diarylethene derivatives **1a**, **2a**, and **3a**. To obtain the three-component crystal with high content of each molecule, crystallization conditions have been carefully examined. When the feed ratio of **2a** and **3a** was 4:6 in molar ratio (in hexane), mixed crystals containing both components in high content were obtained.[29] Thus, we fixed the ratio of **2a** to **3a** as 4:6 and changed the ratio of **1a** in recrystallization solutions.

Crystallization solvents, the feed ratio of three compounds, and the composition ratio of the crystals obtained are summarized in Table 2. Three-component crystals **1a**/**2a**/**3a** with various compositions were prepared from hexane or ethanol

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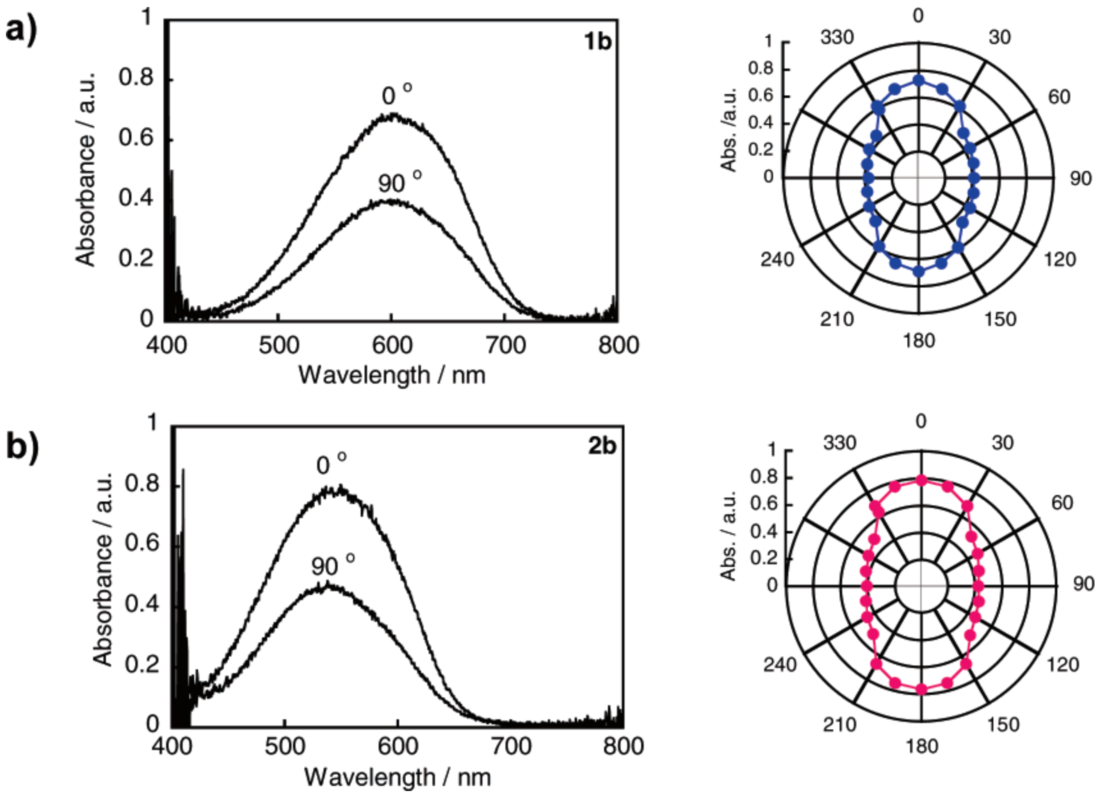

Figure 5. Polarized absorption spectra and polar plots of absorbance of photogenerated closed-ring isomers, **1b** (a) and **2b** (b), on (0−11) face in mixed crystal **1a**/**2a**-α. Absorbance is plotted at 600 and 550 nm for **1b** and **2b**, respectively.

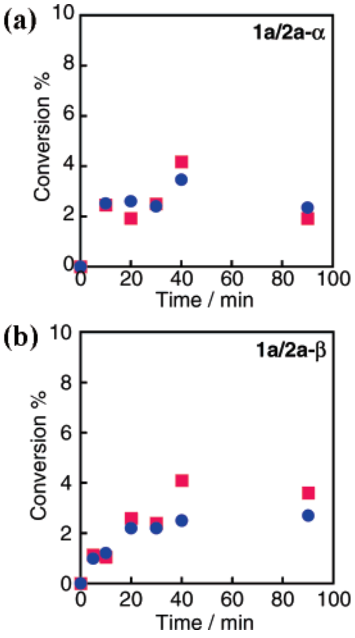

Figure 6. Time dependence of conversion from open- to closed-ring isomers in mixed crystals **1a**/**2a**-α (a) and **1a**/**2a**-β (b) upon irradiation with 370-nm light. Blue circles and red squares indicate conversion from **1a** to **1b**, and from **2a** to **2b**, respectively.

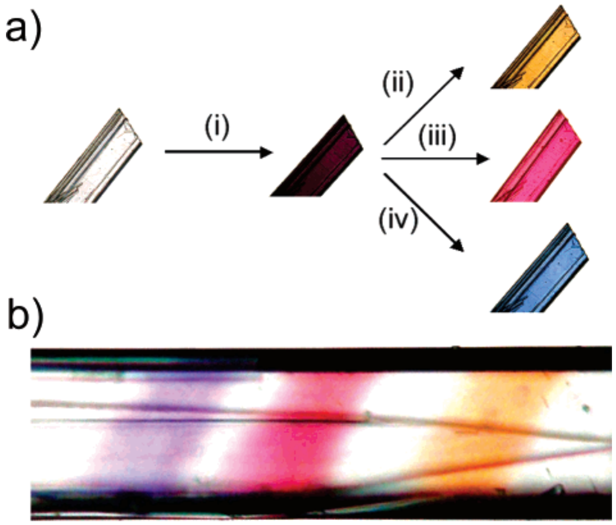

Figure 7. (a) Photographs of three-component crystal **1a**/**2a**/**3a** upon UV and visible light irradiation. (i) The wavelengths of irradiation with 370-nm for black, (ii) > 620-nm for yellow, (iii) 435-nm and >690-nm for red, (iv) 435-nm for blue. (b) Photograph of partially colored three-component crystal **1a**/**2a**/**3a**.

solution. At the feed ratio of **1a**:**2a**:**3a**, which is 4:4:6 in hexane, two kinds of crystals are obtained from the same batch (entry 1). One has a needle-type shape which is similar to the shape of crystal **2a**. The composition ratio of the crystal was determined to be 9:72:19 in molar ratio for **1a**:**2a**:**3a**. The content of the minor components is much higher than that observed in a previous paper.[26] The high contents of each of the three molecules are attributed to the similar geometrical structures of **1a**, **2a**, and **3a**. Another type of crystal is a plate type, which is similar to that of the crystal of **3a**. The crystal did not show any photochromic reaction. This agrees with the fact that the homo-crystal of **3a** is photochemically inactive.[29] When the feed ratio of the **1a** content in hexane solution increases, the composition ratio of the molecule in the obtained crystal increases. In particular, we obtained a three-

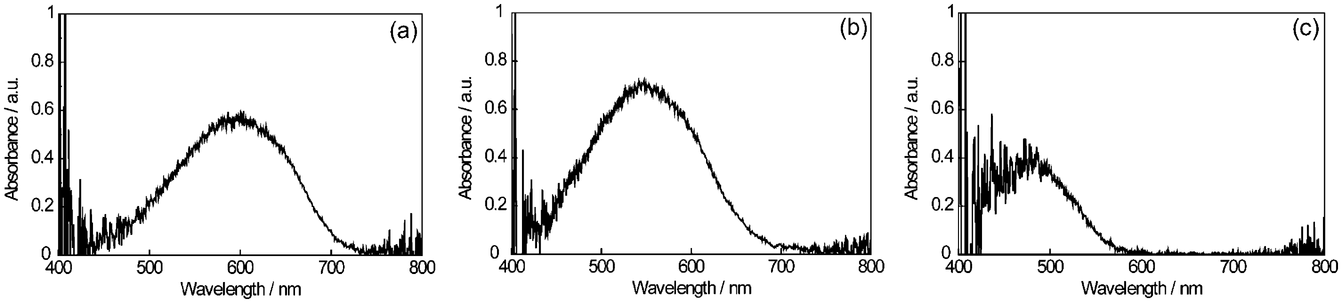

Figure 8. Absorption spectra of the photogenerated closed-ring isomers, **1b** (a), **2b** (b), and **3b** (c) in mixed crystal **1a**/**2a**/**3a** (entry 2).

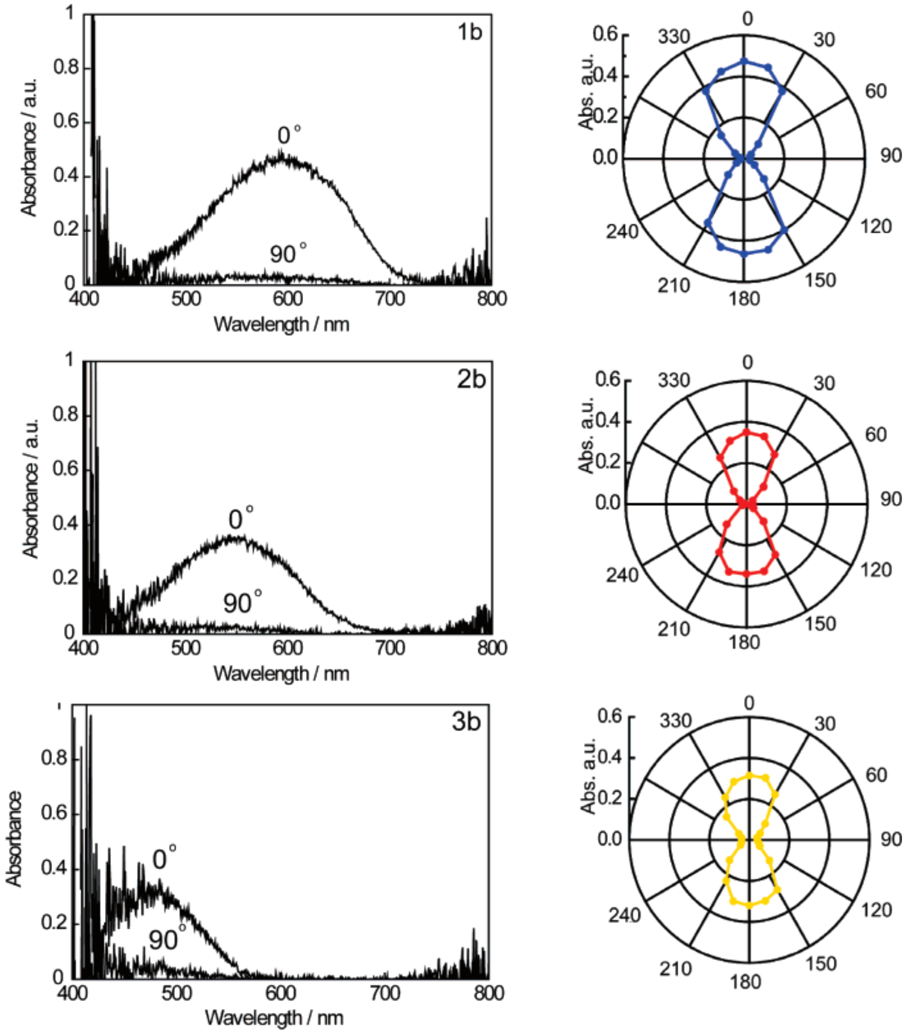

Figure 9. Polarized absorption spectra and polar plots of absorbance of photogenerated closed-ring isomers, **1b**, **2b**, and **3b**, on (0−10) face in three-component crystal **1a**/**2a**/**3a** (entry 2). Absorbance is plotted at 590, 540, and 480 nm for **1b**, **2b** and **3b**, respectively.

component crystal composed of **1a**/**2a**/**3a** in the ratio of 15/67/18 (entry 3).

When we used ethanol as a recrystallizaton solvent, the composition ratio of the crystals dramatically changed from those in hexane. This is ascribed to differences in solubility in ethanol. When we set the feed ratio **1a**/**2a**/**3a** to 6/4/6 in ethanol, similar to those for entry 2, block-shaped crystals were obtained (entry 4). The shape is similar to that of **1a**. The composition ratio was determined to be 72:27:1 in molar ratio for **1a:2a**:**3a**. When the feed ratio of **1a** was decreased, the composition ratio of the crystal changes to 32:53:15 for **1a**/**2a**/**3a** (entry 5). The shape of the crystal is similar to that of crystal **2a**. For **1a**:**2a**:**3a** in the feed ratio 2:4:6, the composition ratio is 24:55:21 (entry 6).

Photochromic behavior of the mixed crystal **1a**/**2a**/**3a** (entry 2) was examined. By changing the wavelength of irradiating light, the mixed crystal **1a**/**2a**/**3a** underwent photochromic reactions, and the colorless crystal turned yellow, red, and blue. Figure 7a shows the color change of the mixed crystal upon irradiation with appropriate wavelengths of light. The colorless crystal turned purplish black upon irradiation with 370-nm light. Then, upon irradiation with >620-nm light, the color of the crystal turned yellow. On the other hand, by partially bleaching with light of wavelengths of 435- and >690-nm, it turned to

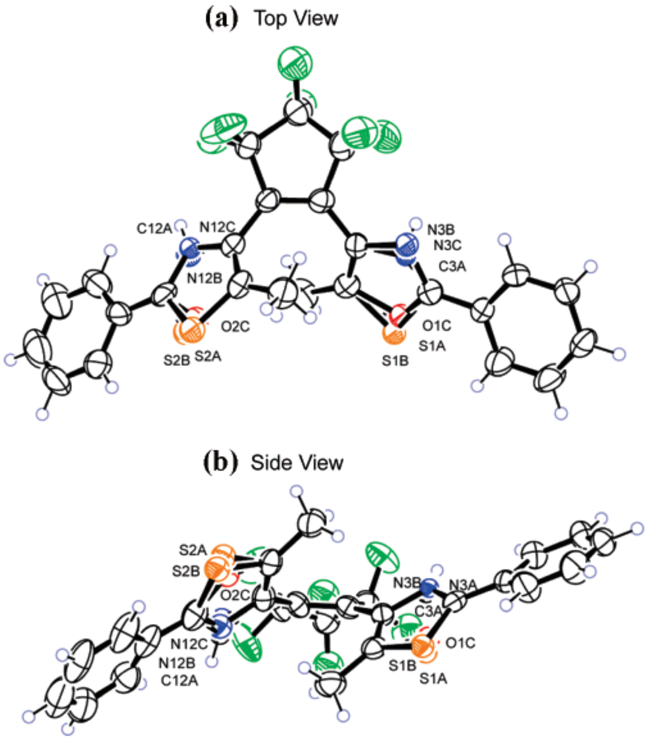

Figure 10. ORTEP drawings of top (a) and side views (b) of three-component crystal **1a**/**2a**/**3a** (entry 5) showing the 50% probability displacement ellipsoids. Site occupancy factors for **1a**, **2a**, and **3a** are 31, 48, and 21%, respectively.

red. When irradiated with 435-nm light, the black crystal turned blue. Figure 7b shows a photograph of the partially colored crystal.

The absorption spectra of the colors in the three-component mixed crystal **1a**/**2a**/**3a** are shown in Figure 8. These spectra are same as those of UV-irradiated crystal **1a** (blue), **2a** (red), and **3a** (yellow). (Although **3a** does not show photochromic reaction in the homo-crystal, the mixed crystal **2a**/**3a** changes color from colorless to yellow upon irradiation with appropriate wavelengths of light. The yellow absorption spectrum is similar to that observed in the mixed crystal **2a**/**3a**.[29])

Figure 9 shows the polarized absorption spectra of the closed-ring isomers **1b**, **2b**, and **3b** and the polar plots of the absorbance. The absorption bands ($\lambda_{\max} = 590$ nm for **1b**, $\lambda_{\max} = 540$ nm for **2b**, and $\lambda_{\max} = 480$ nm for **3b**) correspond to the long-axis absorption of the photogenerated closed-ring isomers **1b**, **2b**, and **3b**. The absorption anisotropy of the yellow, red, and blue colors in the mixed crystal **1a**/**2a**/**3a** is in the same direction. This indicates that **1a** and **3a** are packed in a manner similar to that of **2a** in the three-component crystal, and three components underwent photochromic reactions in the crystal lattice. The fact that all three component molecules (**1a**, **2a**, and **3a)** undergo photochromism in the crystal indicates that energy migration and transfer play a minor role in the single-crystalline photochromism of diarylethenes.

Single-crystal X-ray analysis was carried out for the crystal with composition ratio of 32:53:15 (**1a**:**2a**:**3a**) (entry 5). Disordered structures were observed for thiophene, thiazole, and oxazole rings. The crystal has the same crystal system, space group, and unit cell dimensions as those of crystal **2a**. Figure 10 shows the molecular structure of mixed crystal **1a**/**2a**/**3a**. According to the X-ray crystallographic analysis, **1a** and **3a** were found to be packed in the crystal lattice of **2a** of the mixed crystal **1a**/**2a**/**3a**, and the composition ratio was determined to be 31:48:21 (**1a**:**2a**:**3a**) for the crystal. The three component molecules are packed in antiparallel conformation, and the distance between the reacting carbon atoms was determined to be 3.51 Å, which is close enough for the photoreaction to take place. In a previous three-component system,[26] the structure of the minor content was not observed by X-ray analysis because of the small content. High content of the three component molecules in the crystal enabled us to confirm the three-component composition in the crystal by X-ray crystallographic analysis.

Conclusion

We have obtained two types of two-component crystals **1a**/**2a**-α and **1a**/**2a**-β. The former contains 0−33 mol % **1a** in the crystal lattice of **2a**, the latter contains 0−27 mol % **2a** in the crystal lattice of **1a**. Furthermore, we succeeded in preparing three-component mixed crystals **1a**/**2a**/**3a**. A crystal composed of three derivatives **1a**, **2a**, and **3a** in the molar ratio of 32:53:15 was obtained. According to X-ray analysis, **1a** and **3a** were proved to be packed in the crystal lattice of **2a** of the mixed crystal **1a**/**2a**/**3a**. The mixed crystal **1a**/**2a**/**3a** could change color from colorless to yellow, red, and blue upon irradiation with light of appropriate wavelengths.

Experimental Section

General. The two-component crystals **1a**/**2a** and three-component crystal **1a**/**2a**/**3a** were prepared by recrystallization of a mixture of **1a**, **2a**, and **3a** from ethanol or hexane. The composition ratios of the mixed crystals were measured by a HPLC system (pump: Shimadzu LC-6AD, UV detector: Shimadzu SPD-10AV) equipped with a silica gel column (Kanto, Mightysil 5SIL), using hexane/ethyl acetate (98/2 in volume) as the eluent. A polarizing microscope (Leica DMLP) equipped with a CCD detector (Hamamatsu PMA-11) was used for the measurement of the absorption spectra of the single crystals. A 75-W Xe lamp (Ushio) was used as a light source for ultraviolet and visible light irradiation, respectively. Monochromatic light was obtained by passing the light through band-pass filters.

X-ray Crystallographic Analysis of Crystals 1a/2a-α and 1a/2a-*β*. The data collection was performed on a Bruker SMART1000 CCD-based diffractometer (60 kV, 30 mA) with Mo Kα 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 5.127 cm. Crystal decay was monitored by repeating the 50 initial frames at the end of data collection and by 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[37] and refined by full least-squares on F^2 using SHELXL-97.[38] The positions of all hydrogen atoms were calculated geometrically and refined by the riding model. The disordered part was refined isotropically.

To obtain the structure of the two-component crystal, the disordered structure was introduced with thiazole and thiophene rings, and each occupancy factor for the two disordering parts of the nitrogen atom of the thiazole and the hydrogen and carbon atoms of the thiophene was fixed to 0.5. Because the thiazole ring and thiophene ring are very similar structures, carbon and sulfur atoms which belonged to the thiazole and thiophene rings were refined identically. For each

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(37) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467−473.

(38) Sheldrick, G. M. *SHELXL-97*; Program for Crystal Structure Refinement; University of Göttingen: Göttingen, 1997.

disordered structure, occupancy factors were refined under a constraint such that the sum is 1. After the refinement of **1a/2a**-α and **1a**/**2a**-***β***, the largest residual electron densities are 0.41 e•A^{-3} and 0.66 e•A^{-3}, respectively. The residual electron density might be a result of the refinement of the disordered atoms with isotropic, rather than anisotropic, atomic displacement parameters. For **1a/2a**-α, the refined occupancy factor assigned to **1a** was converged to 0.17. This indicates that the ratio of **1a/2a** in the crystal **1a/2a**-α is 17/83. For **1a/2a**-*β*, the refined occupancy factor assigned to **2a** was converged to 0.33. This indicates that the ratio of **1a/2a** in the crystal **1a/2a**-*β* is 67/33. The crystal data of the two-component crystals **1a**/**2a**-α and **1a**/**2a**-*β* are deposited at the Cambridge Crystallographic Data Centre. (CCDC-628220 for **1a/2a**-α) and (CCDC-628221 for **1a/2a**-*β*).

Details of Crystal Structure Determination of Crystal 1a/2a/3a. X-ray crystallographic analysis of crystal **1a**/**2a**/**3a** was performed by the method similar to that described for crystals **1a/2a**-α and **1a/2a**-*β*. To obtain the structure of three-component crystal **1a**/**2a**/**3a**, the crystal structure **2a** was used as the initial model. After the first least-square refinement, the disordered structure was introduced with thiazole (or thiophene) and oxazole rings, and each occupancy factor for the two disordering parts of sulfur atoms of the thiazole or thiophene and oxygen atom of the oxazole was fixed to 0.5. For each disordered structure, occupancy factors were refined under a constraint that the sum is 1. The occupancy factor of sulfur and oxygen atoms in the unit cell of the crystal **1a**/**2a**/**3a** converged to 0.79 and 0.21, respectively. This indicates that 21% **3a** is included in the three-component crystal. For the two disordered structures of **1a** and **2a** or **3a**, occupancy factors were also refined under a constraint that the sum is 1. The occupancy factors of the carbon and hydrogen atoms in the thiophene ring (**1a**) and the nitrogen atoms in the thiazole and oxazole rings (**2a** and **3a**) converged to 0.28 and 0.72, respectively. This indicates that 28% **1a** is included in the three-component crystal. Therefore, the composition ratio (**1a**/**2a**/**3a**) was estimated to be 28:51:21. Finally, the three disordering parts of the thiophene ring (sulfur and carbon atoms), the thiazole ring (sulfur and nitrogen atoms), and the oxazole ring (oxygen and nitrogen atoms) were made, and occupancy factors were set to 0.28, 0.51, and 0.21, respectively. After the refinement of **1a**/**2a**/**3a**, the largest residual electron density is 0.70 e•A^{-3}. The occupancy factors converged to 0.312, 0.475, and 0.213, respectively. This means that 31.2% **1a** and 47.5% **2a**, and 21.3% **3a** are included in the three-component crystal **1a**/**2a**/**3a**. The crystal data of the three-component crystal **1a**/**2a**/**3a** are deposited at the Cambridge Crystallographic Data Centre (CCDC-628222).

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Supporting Information Available: ORTEP drawings of the mixed crystal **1a**/**2a**-*β*; phase diagram of the mixed crystal **1a**/**2a**; in situ X-ray crystallographic analysis of the mixed crystal **1a**/**2a**-α; absorption spectra and polarized absorption spectra and polar plots of absorbance of photogenerated closed-ring isomers in mixed crystal **1a**/**2a**-*β*. X-ray crystallographic data in form of a crystallographic information file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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