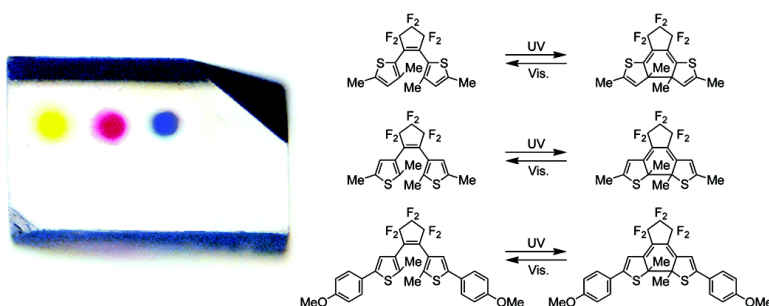


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Multicolor Photochromism of Two- and Three-Component Diarylethene Crystals

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Abstract: Novel photochromic single crystals composed of three different kinds of diarylethenes, 1,2-bis-(3,5-dimethyl-2-thienyl)perfluorocyclopentene (**1a**), 1,2-bis(2,5-dimethyl-3-thienyl)perfluorocyclopentene (**2a**), and 1,2-bis(2-methyl-5-*p*-methoxyphenyl-3-thienyl)perfluorocyclopentene (**3a**), have been prepared. The three-component crystals turned yellow, orange, red, purple, blue, green, or black upon irradiation with light of appropriate wavelengths. The colors of the crystals were thermally stable in the dark and completely bleached by irradiation with visible light. Such multicolored photochromic crystals have potential for the application to optoelectronic devices, such as multifrequency three-dimensional optical memory media or full-color displays.

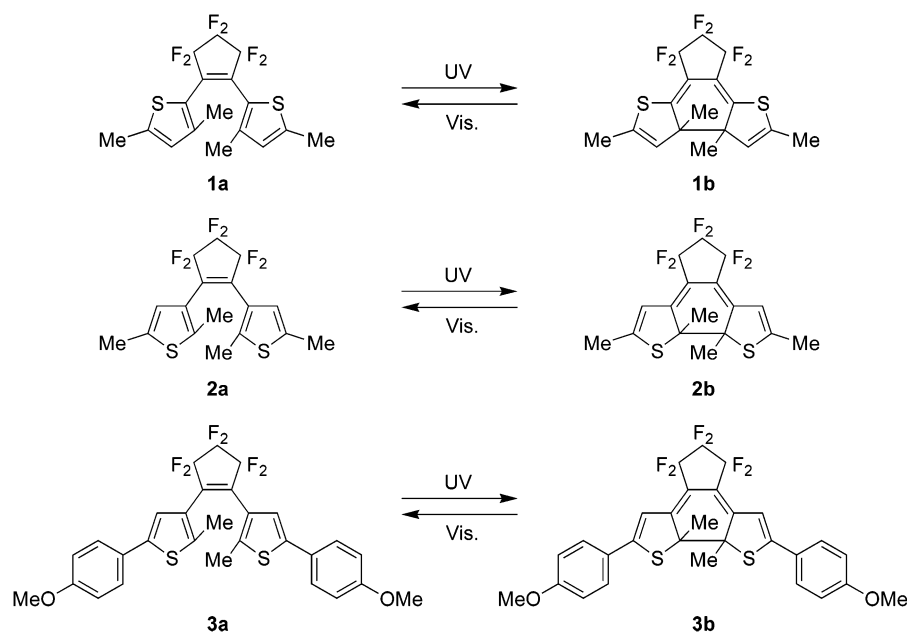
Introduction

Photochromism is referred as a reversible transformation between two isomers having different absorption spectra by photoirradiation.¹ Photochromic compounds have attracted much attention because of their potential application to optoelectronic devices such as rewritable optical memory media and optical switches.^{2–5} Although a large number of photochromic compounds have been thus far synthesized and studied, compounds which show photochromic reactivity in a crystalline phase are rare.^{6–14} In most cases, the photogenerated isomers are thermally unstable and return to the initial colorless isomers in the dark. This is a serious drawback for the application of photochromic crystals to optoelectronic devices.

Recently, we have found that some of diarylethene derivatives undergo thermally stable and photoreversible photochromic reactions in the single-crystalline phase.^{15–30} Upon irradiation with ultraviolet light, colorless single crystals of diarylethenes turn yellow, red, blue, or green, depending on the molecular structure. These colors are due to photogenerated closed-ring isomers, which are thermally stable in the dark. Upon irradiation with visible light, the colored crystals are completely bleached and return to the initial colorless ones.

In usual one-component photochromic systems, they interconvert between only two states, “colorless” and “colored”. On the other hand, in multicomponent systems composed of different kinds of photochromic compounds, reversible multi-mode switching between more than two states could be realized by the combination of two states of each component. In a two-component system, for example, four states ($2^2 = 4$) could be

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Scheme 1. Photochromism of Compounds **1**, **2**, and **3**

produced, and eight states ($2^3 = 8$) in a three-component system. The multicomponent or multicolored systems of diarylethenes have been reported for the first time by Lehn et al.³¹ They demonstrated that absorption properties of the multicomponent 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.³² Although these systems exhibit multicolors, photocoloration/decocoloration cycles, photocoloration efficiency, resolution of the colored images, and stability of the colored state are limited. Ideal systems are multicolored single crystals because of their high durability, high efficiency of photocoloration, and molecular-scale high resolution.

As a consequence of examining a great variety of combinations of single-crystalline photochromic diarylethenes, we found that 1,2-bis(3,5-dimethyl-2-thienyl)perfluorocyclopentene (**1a**),^{16,17} 1,2-bis(2,5-dimethyl-3-thienyl)perfluorocyclopentene (**2a**),¹⁸ and 1,2-bis(2-methyl-5-*p*-methoxyphenyl-3-thienyl)perfluorocyclopentene (**3a**)³⁰ formed three-component single crystals, of which the closed-ring isomers exhibit different colors, such as yellow, red, and blue, respectively. The system is based on previous two-component crystals.²⁸ Here, we report on the preparation procedures of two- or three-component crystals composed of **1a**, **2a**, and **3a** by recrystallization and their photochromic performances (Scheme 1).

Results and Discussion

Photochromism of One-Component Crystals 1a, 2a, and 3a. Compounds **1a**, **2a**, and **3a** undergo photochromic reactions not only in solution but also in a single-crystalline phase.^{16–18,30} One-component single crystals **1a**, **2a**, and **3a** were prepared by recrystallization from hexane. Upon irradiation with ultraviolet light, the colorless crystals **1a**, **2a**, and **3a** turned yellow, red, and blue, respectively. These colors are due to photoge-

nerated closed-ring isomers **1b**, **2b**, and **3b**. Absorption maxima of the photogenerated closed-ring isomers in the crystals were 450, 535, and 630 nm for the crystals **1a**, **2a**, and **3a**, respectively. The colors were thermally stable in the dark and bleached by irradiation with visible light ($\lambda > 450$ nm).

Two-Component Crystals 1a/2a. Molecular structures of **1a** and **2a** resemble each other, in which thienyl rings are attached to the perfluorocyclopentene rings at 2-position for **1a** and 3-position for **2a**. Crystals **1a** and **2a** are isomorphous because both belong to the same space group and have similar molecular packing structures.^{33,34} Therefore, **1a** and **2a** are expected to form solid solutions in various composition ratios.³⁵ The colors of the closed-ring isomers **1b** and **2b** are different (**1b**: yellow, **2b**: red). The two-component crystals are anticipated to exhibit various colors, yellow, red, or orange, upon irradiation with UV light.

When the mixtures of **1a** and **2a** were recrystallized from hexane, two types of colorless crystals were obtained. One has a crystal shape similar to that of one-component crystal **2a** (α),¹⁸ and the other has a shape similar to that of the one-component crystal **1a** (β). Figure 1 shows the relationship between the feed ratio of **1a** and **2a** in the hexane solution and the composition ratio in the crystals obtained. The composition ratios of the crystals were determined by HPLC. In the solution containing 20 mol % of **1a**, only crystals having a crystal shape similar to that of crystal **2a** (α) were obtained. The crystals were mainly composed of **2a** and included a small molar amount (<3 mol %) of **1a**. When the feed ratio of **1a** was increased (from 33 to 50 mol %), both two-component crystals **1a/2a- α** and **- β** were obtained from the same batches. At 33 mol %, the composition ratios were **1a:2a** = 4:96 for the crystal **1a/2a- α** , and 87:13 for the crystal **1a/2a- β** . Above 60 mol % of **1a** in the solution, only

(33) X-ray crystallographic data of **1a**: $C_{17}H_{14}F_6S_2$, $M = 396.40$, $T = 123$ K, monoclinic, space group $P2_1/c$, $a = 12.014(1)$ Å, $b = 17.360(2)$ Å, $c = 16.257(2)$ Å, $\beta = 92.319(2)^\circ$, $V = 3387.7(5)$ Å³, $Z = 8$.

(34) X-ray crystallographic data of **2a**: $C_{17}H_{14}F_6S_2$, $M = 396.40$, $T = 115$ K, monoclinic, space group $P2_1/c$, $a = 17.144(1)$ Å, $b = 8.772(1)$ Å, $c = 11.227(1)$ Å, $\beta = 92.949(1)^\circ$, $V = 1686.2(2)$ Å³, $Z = 4$; also see ref 18c.

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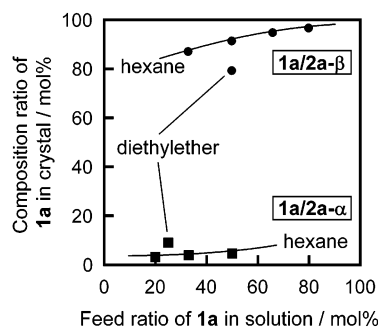


Figure 1. Relationship between feed ratio of **1a** and **2a** in hexane or diethyl ether solution and composition ratio in two-component crystals **1a/2a** obtained. Squares and circles show crystals **1a/2a-α** and **-β**, respectively.

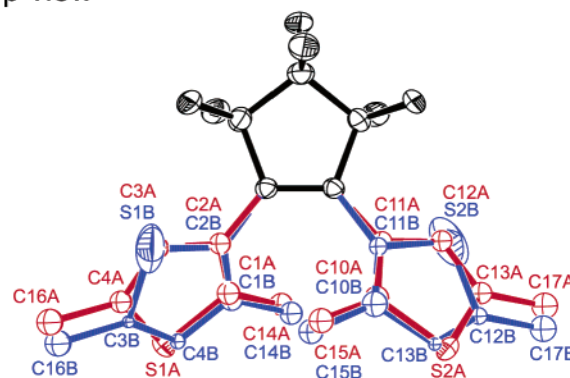
Table 1. Crystal Data and Structure Refinements for **1a/2a-α** and **1a/2a-β**

	1a/2a-α	1a/2a-β
formula	C ₁₇ H ₁₄ F ₆ S ₂	C ₁₇ H ₁₄ F ₆ S ₂
formula weight	396.40	396.40
temperature/K	123(2)	123(2)
crystal system	monoclinic	monoclinic
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> /Å	17.136(2)	12.096(1)
<i>b</i> /Å	8.778(8)	17.406(2)
<i>c</i> /Å	11.208(1)	16.336(1)
α /deg	90	90
β /deg	92.493(2)	92.669(2)
γ /deg	90	90
<i>V</i> /Å ³	1684(3)	3436(5)
<i>Z</i>	4	8
$\rho_{\text{calcd.}}$ /g cm ⁻³	1.563	1.533
μ /mm ⁻¹	0.375	0.367
<i>F</i> (000)	808	1616
θ range/deg	1.19 to 27.71	1.69 to 28.23
reflections collected	9307	19929
independent reflections	3587	7297
no. of restraints/parameters	64/214	128/605
goodness-of-fit on <i>F</i> ²	1.053	1.097
<i>R</i> ₁ (<i>I</i> > 2 σ (<i>I</i>))	0.0361	0.0459
<i>wR</i> ₂ (all data)	0.1009	0.1536
largest diff. peak/hole [e Å ⁻³]	0.348/−0.407	0.419/−0.461

crystal **1a/2a-β** was obtained. At 66 mol %, the composition ratio was **1a:2a** = 95:5. As the feed ratios of **1a** in the solution were increased, the composition ratios of **1a** in crystals **1a/2a-α** and **-β** increased. Judging from the crystal shapes, crystal **1a/2a-α** is considered to include **1a** in the crystal lattice of **2a**, and crystal **1a/2a-β** includes **2a** in the crystal lattice of **1a**. Figure 1 also shows the composition ratios of crystals obtained in diethyl ether solutions. Recrystallization of a mixture of **1a** and **2a** (25:75) from diethyl ether yielded crystal **1a/2a-α**, in which composition ratio was **1a:2a** = 9:91. When the feed ratio of **1a** was increased (50 mol %), crystal **1a/2a-β**, which includes as much as 21 mol % of **2a**, was obtained.

X-ray Crystallographic Analysis of Crystal 1a/2a. To confirm that both **1a** and **2a** are included in the crystal lattice, we carried out X-ray crystallographic analysis of two-component crystals **1a/2a-α** and **-β**. A crystal **1a/2a-α** was obtained by recrystallization in a diethyl ether solution of **1a** and **2a** (25:75). The composition ratio in the crystal was **1a** and **2a** = 9:91. The crystallographic data are shown in Table 1. As expected, the crystal has the same crystal system, space group, and unit cell dimensions as those of crystal **2a**.^{18c,34} The diarylethene molecule was crystallographically independent in this crystal. For the refinement, the coordinates of the open-ring isomer **2a**

Top view



Side view

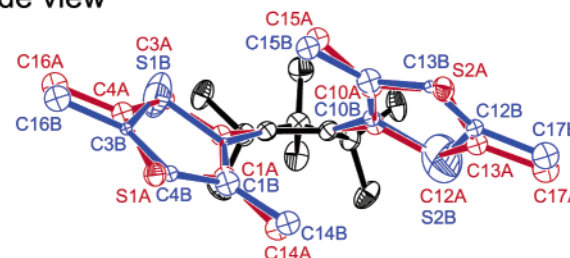


Figure 2. Molecular structures of two-component crystal **1a/2a-α**. Blue and red lines show **1a** and **2a**, respectively. The ellipsoids are drawn at 50% probability level. Disordered perfluorocyclopentene ring and hydrogen atoms are omitted for clarity. Site occupancy factor for dopant **1a** is 8%.

were used as an initial model. After the first least-squares refinement, two new electron peaks were observed near C3A and C12A of **2a**. The peaks were assigned to the sulfur atoms of the 2-thienyl rings of **1a** as S1B and S2B, and the molecular structure of **1a** was constructed. Because of the low composition ratio of **1a**, bond lengths of the thiophene rings of **1a** were restrained in the least-squares refinement. Using the model, the full-matrix least-squares refinement converged well (*R*₁ = 0.0361). The final molecular structures are shown in Figure 2. The molecular structure of **1a** was expressed as a disordered structure in crystal **2a**. In other words, **2a** was replaced with **1a** in the same sites of the crystal lattice of **2a**. The site occupancy factor for **1a** was 8%, which is consistent with the composition ratio determined by HPLC. Both **1a** and **2a** have photoreactive antiparallel conformations, and the distances between reactive carbon atoms were short enough for the photocyclization reaction to take place in the crystalline phase (3.57 Å for **1a**, 3.54 Å for **2a**).²⁹

Colorless crystal **1a/2a-β** was obtained by recrystallization of a mixture (**1a:2a** = 33:67) from hexane. The composition ratio of the crystal was **1a:2a** = 87:13. The crystal structure was determined by X-ray crystallographic analysis. The crystallographic data are shown in Table 1. This crystal had the same crystal system, space group, and cell parameters as those of one-component crystal **1a**.³³ In this crystal, two types of crystallographically independent molecules were observed, named as molecules A and B. After the first least-squares refinement, large electron density peaks appeared near the carbon atoms C4A and C13A (molecule A), C21A and C30A (molecule B) in the 2-thienyl rings of **1a**. These peaks were assigned to sulfur atoms S1B and S2B (molecule A), and S3B and S4B (molecule B) of the 3-thienyl rings of **2a**. The molecular structures of **2a** were observed as disordered struc-

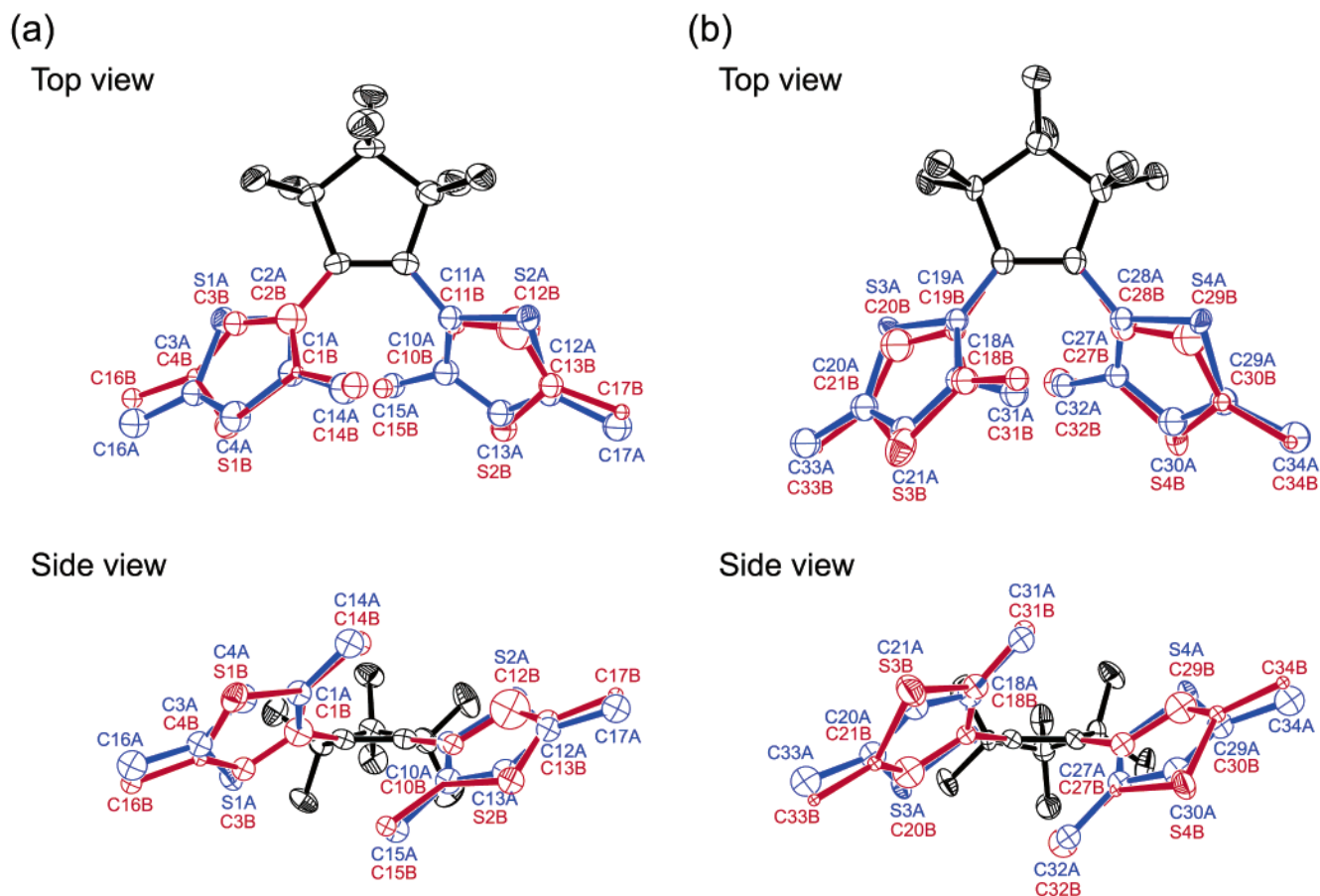


Figure 3. Molecular structures of two-component crystal **1a/2a- β** . (a) Molecule A and (b) molecule B. Blue and red lines show **1a** and **2a**, respectively. The ellipsoids are drawn at 50% probability level. Disordered perfluorocyclopentene rings and hydrogen atoms are omitted for clarity. Site occupancy factors for dopant **2a** are 16 and 13% on molecule A and B, respectively.

tures in crystal **1a** as shown in Figure 3. The site occupancy factors for **2a** were 16 and 13% for molecules A and B, respectively. This is consistent with the composition determined by HPLC measurement. Both **1a** and **2a** had photoreactive antiparallel conformations, and the distances between reactive carbon atoms were short enough for the photocyclization reaction: 3.61 Å (C1A–C10A in molecule A) and 3.49 Å (C18A–C27A in molecule B) in **1a**, and 3.49 Å (C1B–C10B in molecule A) and 3.51 Å (C18B–C27B in molecule B) in **2a**.²⁹

Photochromic Behavior of Crystal 1a/2a. According to the above X-ray crystallographic data, both **1a** and **2a** are anticipated to undergo photochromic reactions in the two-component crystals **1a/2a- α** and **- β** . First, photochromic behavior of crystal **1a/2a- α** , which included as much as 4 mol % of **1a** in the crystal lattice of **2a**, was examined. The colorless crystal **1a/2a- α** turned orange upon irradiation with 405-nm light. Figure 4a shows the absorption spectrum. This spectrum has two bands around 450 and 535 nm. This spectrum is composed of the spectra of the photogenerated closed-ring isomers **1b** and **2b**, indicating that both **1a** and **2a** underwent photocyclization reactions in the crystal. By partially bleaching with 578-nm light, the orange crystal turned yellow. The absorption spectrum is shown in Figure 4b. The spectrum in Figure 4b is the same as that of UV-irradiated one-component crystal **1a**. The bleached band is assigned to **2b**. The colorless crystal **1a/2a- α** turned red upon irradiation with 370-nm light. Figure 4c shows the absorption spectrum of the photoirradiated crystal. Relatively large absorp-

tion around 535 nm indicates that **2b** was predominantly produced upon irradiation with 370-nm light. The orange, yellow, and red colors were completely bleached upon irradiation with visible light ($\lambda > 450$ nm), and the crystal **1a/2a- α** returned to a colorless state. Thus, the crystal **1a/2a- α** exhibited multicolor changes from colorless to yellow, red, or orange upon irradiation with light of different wavelengths.

To confirm that the photochromic reactions of both components take place in the crystal lattice, absorption anisotropy of the photogenerated closed-ring isomers **1b** and **2b** in two-component crystal **1a/2a- α** was measured under polarized light. Figure 5 shows the polarized absorption spectra of **1b** and **2b** in the crystal **1a/2a- α** at a certain angle (30°), where the maximum absorption was observed, and its perpendicular angle (120°). These spectra were obtained upon UV irradiation and partial bleaching.³⁶ The absorption bands ($\lambda_{\text{max}} = 450$ nm for **1b** and $\lambda_{\text{max}} = 535$ nm for **2b**) correspond to the long-axis electronic transitions of the closed-ring isomers.^{18a} The polar plots shown in Figure 5 indicate that both absorption bands of **1b** and **2b** have large anisotropy in the same direction. This suggests that photochromic reactions of **1a** and **2a** take place in the crystal lattice and that the long-axis directions of the photogenerated closed-ring isomers **1b** and **2b** are the same. This is consistent with the above X-ray crystallographic analysis.

Next, photochromic behavior of crystal **1a/2a- β** , which included 13 mol % of **2a** in the crystal lattice of **1a**, was

(36) The wavelengths of the irradiated light are 405 and 578 nm for **1b** and 370 and 458 nm for **2b**.

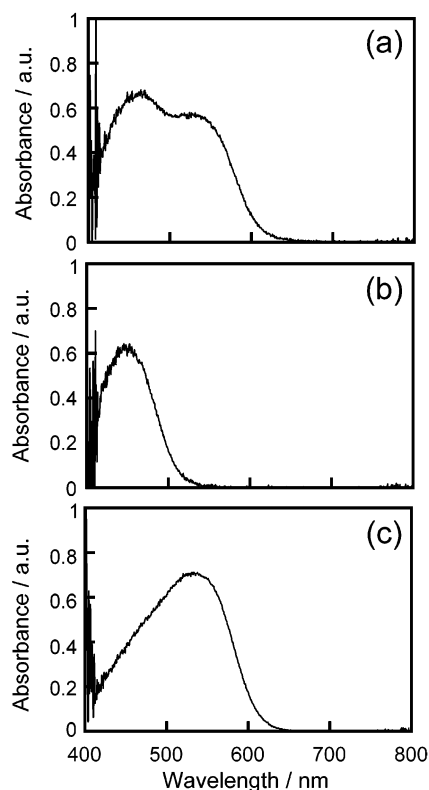


Figure 4. Absorption spectra of two-component crystal **1a/2a- α** irradiated with 405-nm light (a), both 405- and 578-nm light (b), and 370-nm light (c). The spectra were measured on (011) face.

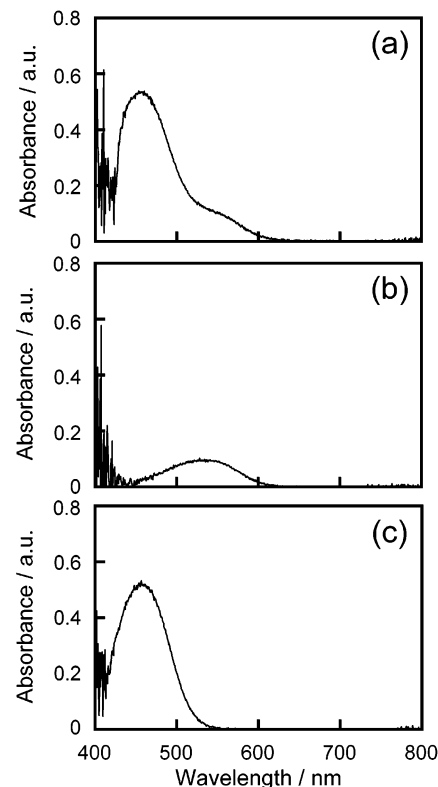


Figure 6. Absorption spectra of two-component crystal **1a/2a- β** irradiated with 370-nm light (a), both 370- and 458-nm light (b), and 405-nm light (c). The spectra were measured on (010) face.

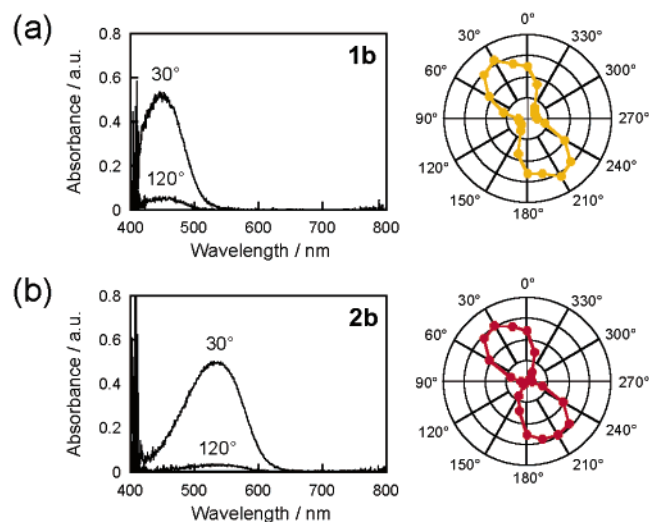


Figure 5. Polarized absorption spectra and polar plots of absorbance of photogenerated closed-ring isomers in two-component crystal **1a/2a- α** . (a) **1b** and (b) **2b**. Absorbance is plotted at 450 and 535 nm for **1b** and **2b**, respectively. The spectra were measured on (011) face.

examined. Upon irradiation with 370-nm light, the colorless crystal **1a/2a- β** turned yellow. Figure 6a shows the absorption spectrum of the colored crystal. The spectrum had not only a large band around 450 nm but also a small shoulder around 540 nm. Upon irradiation with 458-nm light, the 450-nm band disappeared, and only the 535-nm band remained as shown in Figure 6b. Upon irradiation with 405-nm light, the colorless crystal turned also yellow. The absorption spectrum of the crystal irradiated with 405-nm light is shown in Figure 6c. The spectrum has a large band similar to that of the photogenerated

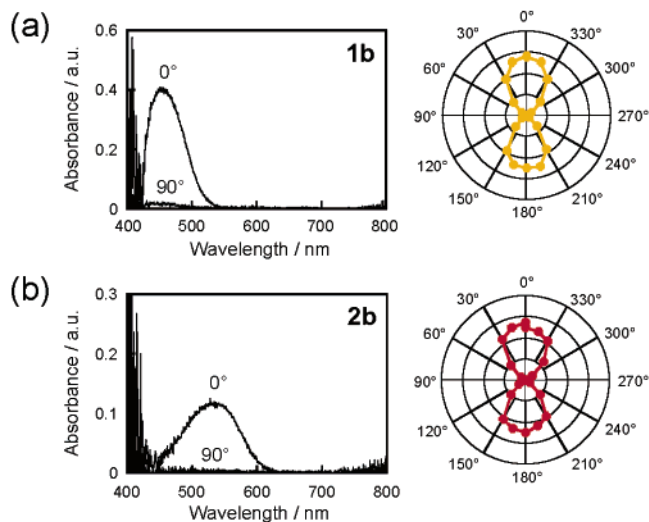


Figure 7. Polarized absorption spectra and polar plots of absorbance of photogenerated closed-ring isomers in two-component crystal **1a/2a- β** . (a) **1b** and (b) **2b**. Absorbance is plotted at 450 and 535 nm for **1b** and **2b**, respectively. The spectra were measured on (010) face.

closed-ring isomer **1b** in one-component crystal **1a**. The yellow color was completely bleached upon irradiation with visible light ($\lambda > 450$ nm).

Figure 7 shows the polarized absorption spectra of **1b** and **2b** in crystal **1a/2a- β** and the polar plots of the absorbance at 450 and 535 nm for **1b** and **2b**, respectively. The direction of the absorption anisotropy of **2b** in crystal **1a/2a- β** was the same as that of **1b**, that is, the long-axis electronic transition moments of the photogenerated closed-ring isomers **1b** and **2b** were parallel to each other. This indicates that **1a** is replaced with

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) ^a	composition ratio in crystals (1a : 2a : 3a) ^b
1	methanol	0.4:1:0.5	3.3:96.6:0.1
2	ethanol	0.4:1:0.5	2.1:97.8:0.1
3	2-propanol	0.4:1:0.5	1.6:98.2:0.2
4	acetonitrile	0.4:1:0.5	2.4:97.4:0.2
5	acetonitrile	0.4:1:1	3.5:96.4:0.1
6	acetonitrile	0.1:1:0.5	1.9:97.7:0.4

^{a,b} Molar ratio.

2a in the same site of crystal lattice of **1a**, and supports the above X-ray crystallographic analysis.

Three-Component Crystal 1a/2a/3a. As described above, **1a** can sit in the crystal lattice of **2a**. In our recent contribution,²⁸ we also reported that **3a** can sit in the crystal lattice of **2a** and that colorless two-component crystal **2a/3a** turned red, blue, or purple by irradiation with light of different wavelengths. The crystal lattice of **2a** is considered to provide the sites where **1a** and **3a** can sit. It is worthwhile to note that photogenerated **1b**, **2b**, and **3b** exhibit three primary colors, yellow, red, and blue. We tried to prepare three-component crystals composed of **1a**, **2a**, and **3a**, and observe multicolor changes by photoirradiation.

First, crystallization conditions were examined. Table 2 shows crystallization solvents, feed ratio of the three compounds, and composition ratio of the crystals obtained. Upon slow evaporation of solvent, one-component crystals of **3a**, of which solubility was the poorest among the three compounds, were formed in early stage. The crystals **3a** did not include any amounts of **1a** and **2a** at all. After several days, a different type of crystal, the shape of which is similar to that of crystal **2a**, was obtained. The crystals were composed of **1a**, **2a**, and **3a**. The three-component crystals were not obtained from hexane solutions. The composition ratio of the crystals could be controlled by changing solvents and feed ratios as shown in Table 2.

Photochromic Behavior of Crystal 1a/2a/3a. The influence of the composition ratios on the coloration was examined. Upon irradiation with 405-nm light, the colorless crystals of the entries 2, 4, and 6 in Table 2 turned orange, pale green, and blue, respectively. Figure 8 shows the absorption spectra of the colored crystals. All spectra have broad bands which could be interpreted by the overlapping of the absorption spectra of all the photogenerated closed-ring isomers **1b**, **2b**, and **3b**. This indicates that all the components in the crystals underwent photocyclization reactions. The shape of the spectra is dependent on the composition of the crystals. As the composition ratio of **3a** was increased, the intensity of the absorption band due to **3b** got stronger. All these colors were completely bleached upon irradiation with visible light ($\lambda > 450$ nm), and the crystals returned to the initial colorless ones.

The photocoloration of the entry 4 crystal in Table 2 was carefully examined. Figure 9 shows absorption spectra of the crystal irradiated with 370-, 405-, and 417-nm light. Upon irradiation with 370-nm light, the colorless crystal turned yellowish red, in which the absorption band around 535 nm due to **2b** was observed as shown in Figure 9a. When irradiated with 405-nm light, the colorless crystal turned pale green. The absorption bands due to **1b** and **3b** appeared (Figure 9b). This indicates that the open-ring isomers **1a** and **3a** have the absorption bands at longer wavelength than **2a**. Upon irradiation

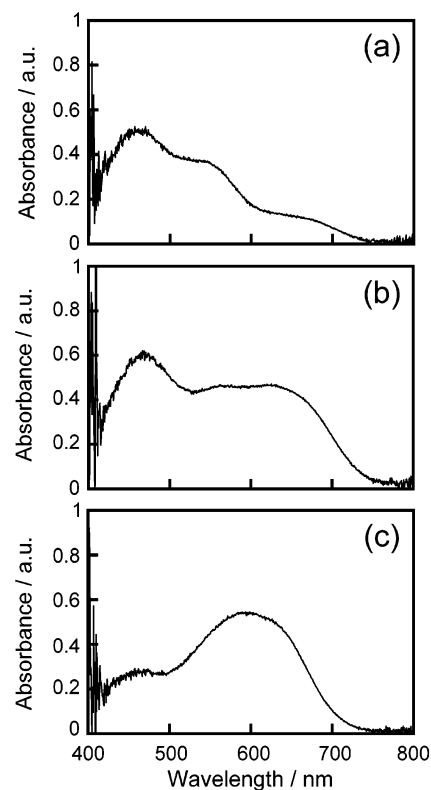


Figure 8. Absorption spectra of three-component crystal **1a/2a/3a** with various composition ratios irradiated with 405-nm light. (a) Entry 2; **1a**:**2a**:**3a** = 2.1:97.8:0.1, (b) entry 4; **1a**:**2a**:**3a** = 2.4:97.4:0.2, and (c) entry 6; **1a**:**2a**:**3a** = 1.9:97.7:0.4. The spectra were measured on (011) face.

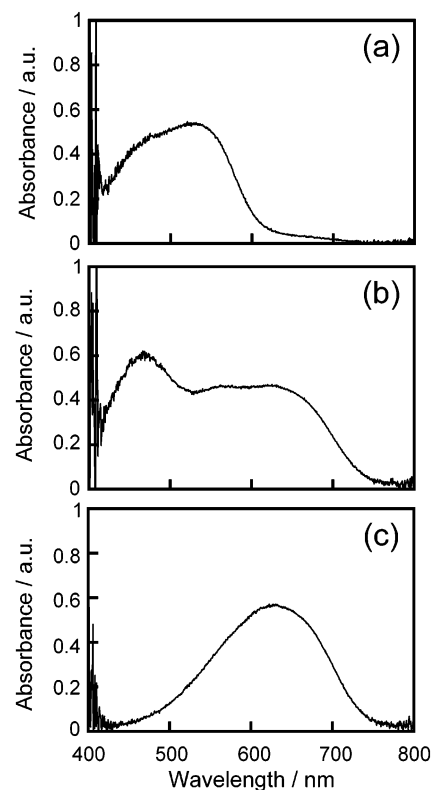


Figure 9. Absorption spectra of three-component crystal **1a/2a/3a** (entry 4; **1a**:**2a**:**3a** = 2.4:97.4:0.2) irradiated with 370-nm light (a), 405-nm light (b), and 417-nm light (c). The spectra were measured on (011) face.

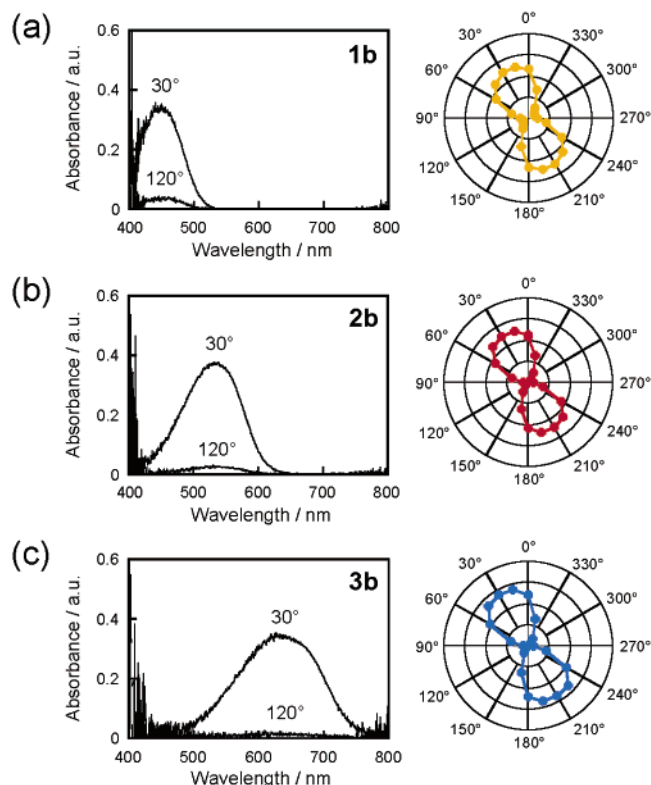


Figure 10. Polarized absorption spectra and polar plots of photogenerated closed-ring isomers in three-component crystal **1a/2a/3a**. (a) **1b**, (b) **2b**, and (c) **3b**. Absorbance is plotted at 450, 535, and 630 nm for **1b**, **2b**, and **3b**, respectively. The spectra were measured on (011) face.

with 417-nm light, however, the colorless crystal turned blue, and the absorption band due to **1b** was not detected as shown in Figure 9c. Although the long-wavelength light caused the cyclization reaction from **1a** to **1b**, the yellow color of **1b** was also bleached by the light. The color of the three-component crystal **1a/2a/3a** was dependent on the wavelength of the irradiated light. All these colors were completely bleached upon irradiation with visible light ($\lambda > 450$ nm).

X-ray crystallographic analysis of the three-component crystals **1a/2a/3a** showed that the crystal had the same unit cell as that of one-component crystal **2a**.^{18c,34} However, the molecular and packing structures of **1a** and **3a** were not discerned because of their small contents in the crystals. To know the molecular arrangement of the three components and their reactivity in the crystal, the anisotropy of the polarized absorption spectra was measured. The absorption spectra of the photogenerated closed-ring isomers **1b**, **2b**, and **3b** in the crystal were obtained by irradiation with light of selective wavelengths.³⁷ Figure 10 shows the polarized absorption spectra of **1b**, **2b**, and **3b** and the polar plots of the absorbance. The absorption anisotropy of the yellow, red, and blue colors are in the same direction. This result clearly indicates that both **1a** and **3a** certainly sit in the crystal lattice of **2a**³⁸ and that all three components underwent photochromic reactions in a single-crystalline phase.³⁹

Full-Color Display. The possible application of the three-component crystal **1a/2a/3a** to a full-color display was examined. By controlling the irradiating wavelengths of light, the

(37) The wavelengths of the irradiated light are 405 and 578 nm for **1b**, 370, 458, and 692 nm for **2b**, and 405 and 492 nm for **3b**.

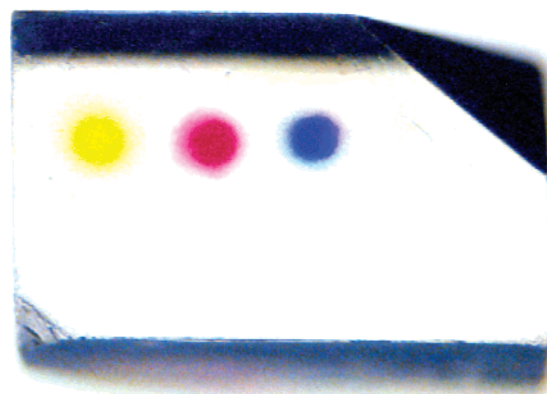


Figure 11. Photograph of partially colored three-component crystal **1a/2a/3a**: (left) yellow, (center) red, and (right) blue. The wavelengths of the irradiated light are 405 and 578 nm for yellow, 370 and 458 nm for red, and 405 and 492 nm for blue.

colorless crystal exhibited yellow, red, and blue colors. Figure 11 shows a photograph of the partially colored crystal. The intensity of the three colors could be modulated by careful control of the wavelengths of irradiated light. The combination of “ON” and “OFF” states of the each primary color gave eight colors ($2^3 = 8$), such as colorless, yellow, red, blue, orange, purple, green, or black. Figure 12 shows absorption spectra of the colors. Such a multicolored photochromic crystal has potential for the application to a new type of photofunctional devices, such as photoswitchable full-color displays.

Conclusions

Two- or three-component photochromic single crystals composed of diarylethenes **1a**, **2a**, and **3a** were prepared, and multicolor changes upon irradiation with light of different wavelengths were demonstrated. The crystal **2a** served as a host including **1a** or **3a** or both in its crystal lattice. The colorless two-component crystal **1a/2a** photoreversibly turned yellow, red, or orange. The three-component crystal **1a/2a/3a** exhibited yellow, red and blue colors by irradiation with light of appropriate wavelengths. Such multicolored photochromic diarylethene crystals have potential for the application to multi-frequency three-dimensional optical memory media and photoswitchable full-color displays.

Experimental Section

General. Solvents used were spectroscopic grade and purified by distillation before use. Absorption spectra in a single-crystalline phase were measured using a Leica DMLP polarizing microscope connected with a Hamamatsu PMA-11 photodetector. Polarizer and analyzer were set in parallel to each other. Photoirradiation was carried out using a 75-W xenon lamp or a 100-W halogen lamp as the light sources attached to the microscope. The wavelength of the light used for the photo-

(38) The solubility of **3a** with large methoxyphenyl groups into crystal **2a** was much less than that of **1a**. The polarized absorption anisotropy of the photogenerated closed-ring isomer **3b** in the two-component crystal **2a/3a** (see ref 28) and the three-component crystal **1a/2a/3a** clearly showed that **3a** is substitutionally incorporated in the **2a** host crystals. Pentacene guest molecules are known to be substitutionally incorporated in naphthalene or anthracene host crystals by replacement of two host molecules with one guest molecule. (Brillante, A.; Craig, D. P. *J. Chem. Soc., Faraday Trans. II* **1975**, *71*, 1457–1472.)

(39) The photocyclization reaction in the diarylethene crystals takes place in less than 10 ps. (Miyasaka, H.; Nobuto, T.; Itaya, A.; Tamai, N.; Irie, M. *Chem. Phys. Lett.* **1997**, *269*, 281–285.) Therefore, the energy transfer from **2a** to low-concentration **1a** or **3a** is negligible.

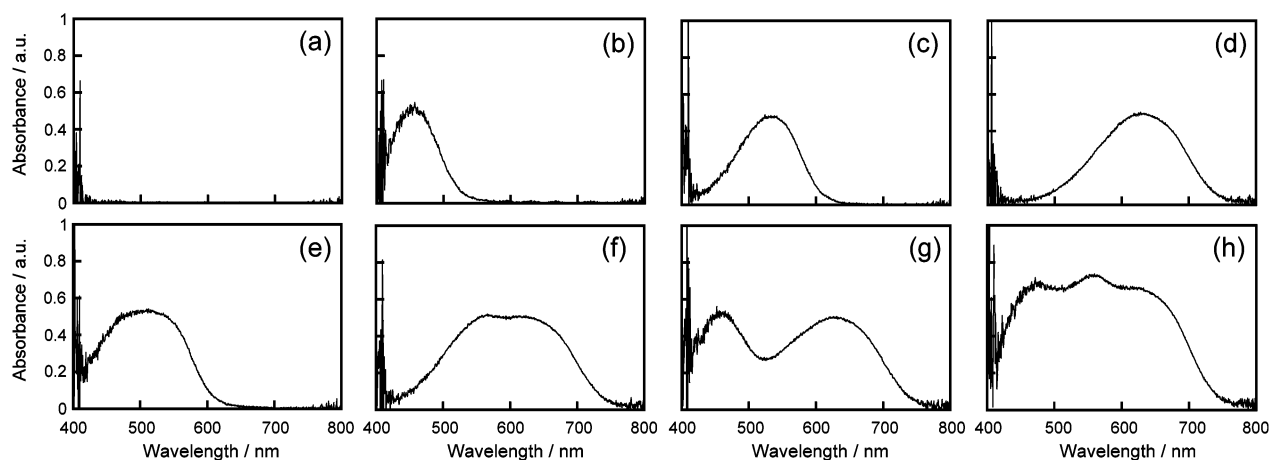


Figure 12. Absorption spectra of three-component crystal **1a/2a/3a** as a full-color display: (a) colorless, (b) yellow, (c) red, (d) blue, (e) orange, (f) purple, (g) green, and (h) black. The wavelengths of the irradiated light are 405 and 578 nm for yellow, 370, 458 and 692 nm for red, 405 and 492 nm for blue, 405, 578 and 692 nm for orange, 405 and 458 nm for purple, 405 and 545 nm for green, and 405 nm for black.

clization and photocycloreversion reactions in a single-crystalline phase was selected by passing the light through a band-pass filter or a cutoff filter.

Materials. 1,2-Bis(3,5-dimethyl-2-thienyl)perfluorocyclopentene (**1a**),¹⁷ 1,2-bis(2,5-dimethyl-3-thienyl)perfluorocyclopentene (**2a**),^{18a} and 1,2-bis(2-methyl-5-*p*-methoxyphenyl-3-thienyl)perfluorocyclopentene (**3a**)³⁰ were synthesized according to the methods described in the literature.

HPLC Measurement. The composition ratios of multicomponent crystals were measured by a HPLC system (pump: Shimadzu LC-6AD, UV detector: Shimadzu SPD-10AV) equipped with a silica gel column (Wako, Wakosil 5SIL), using hexane for crystal **1a/2a** or hexane/ethyl acetate (95:5) for crystal **1a/2a/3a** as the eluent.

General Procedure of X-ray Crystallographic Analysis. X-ray crystallographic analysis was performed using a Bruker SMART1000 CCD-based diffractometer (50 kV, 40 mA) with Mo K α radiation. The crystals were cooled to 123 K by cryostat (Rigaku GN2). The data were collected as a series of ω -scan frames, each with a width of 0.3°/frame. The crystal-to-detector distance was 5.118 cm. Crystal decay was monitored by repeating the 50 initial frames at the end data collection and analyzing the duplicate reflections. Data reduction was performed using SAINT software, which corrects for Lorentz and polarization effects, and decay. The cell constants were determined by the global refinement. The structures were solved by direct methods using SHELXS-86⁴⁰ and refined by full least-squares on F^2 using SHELXL-97.⁴¹ The positions of all hydrogen atoms were calculated geometrically and refined by the riding model. In least-squares refinements disordered structures were refined using geometrical restraints. For each disordered structure, occupancy factors were refined under a constraint such that the sum was 1.

Details of Crystal Structure Determination of 1a/2a- α . The crystal system and space group (monoclinic, $P2_1/c$) were determined unambiguously in the same way as for those of crystal **2a**.^{18c,34} A unit cell contains four molecules, and one molecule is crystallographically independent. Using the structure of **2a** as an initial model, the direct method of SHELXS-86 gave two electron density peaks near the carbon atoms C3A and C12A of the thiophene rings, which imply the presence

of dopant **1a**. The peaks were assigned as the sulfur atoms S1B and S2B of **1a**. After positioning the sulfur atoms, there is no other meaningful peak ($<0.34 \text{ e } \text{\AA}^{-3}$). Due to the closeness of atoms on the thiophene rings of **1a** and **2a**, carbon atoms, which belonged to the thiophene rings, were refined isotropically. Because of the low composition ratio of **1a**, bond lengths were restrained in the least-squares refinement. The perfluorocyclopentene ring was disordered due to puckering.

Details of Crystal Structure Determination of 1a/2a- β . The crystal system and space group (monoclinic, $P2_1/c$) were determined unambiguously, in the same way as for those of crystal **1a**.³³ A unit cell contains eight molecules and two molecules are crystallographically independent. Using the structure of **1a** as an initial model, the direct method of SHELXS-86 gave four electron density peaks near the carbon atoms C4A, C13A, C21A, and C30A of the thiophene rings, which imply the presence of dopant **2a**. The peaks were assigned as the sulfur atoms S1B, S2B, S3B, and S4B of **1a**. After positioning the sulfur atoms, there is no other meaningful peak ($<0.42 \text{ e } \text{\AA}^{-3}$). Due to the closeness of atoms on the thiophene rings of **1a** and **2a**, carbon atoms, which belonged to the thiophene rings, were refined isotropically. Because of the low composition ratio of **2a**, bond lengths were restrained in the least-squares refinement. The perfluorocyclopentene ring was disordered due to puckering.

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Supporting Information Available: Shapes of crystals **1a/2a- α** , **1a/2a- β** , and **1a/2a/3a**; measurements of polarized absorption spectra of colored crystals (PDF). 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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