

Article

Multicolor Photochromism of Two-Component Diarylethene Crystals Containing Oxidized and Unoxidized Benzothiophene Groups

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Abstract: Preparing mixed crystals composed of two or more components is one of the useful approaches to not only modifying the physical properties and chemical reactivity of molecular crystals but also creating their novel functionality. Here we report preparation and photoresponsive properties of two-component mixed crystals containing photochromic bis(benzothienyl)ethene derivatives that show different colors in the closed-ring forms depending on the oxidation state of the benzothiophene groups. The similarity in the molecular structures of the two diarylethenes, which are different from each other only in the oxidation state of the benzothiophene groups, allowed the formation of two-component mixed crystals by recrystallization from mixed solutions containing the two compounds. Irradiating the mixed crystals with light of appropriate wavelengths induced the selective photoisomerization of the two diarylethenes, leading to multicolor photochromic performance, such as colorless, orange, yellow, and red. Such molecular crystals with multiresponsive functions can find potential applications in multistate optical recording and multicolor displays. The present results demonstrate that combining differently oxidized diarylethene derivatives is an effective strategy for preparing multicomponent mixed crystals with finely tuned composition and desired photoresponsive properties.

Keywords: diarylethene; mixed crystals; photochromism; X-ray crystallographic analysis

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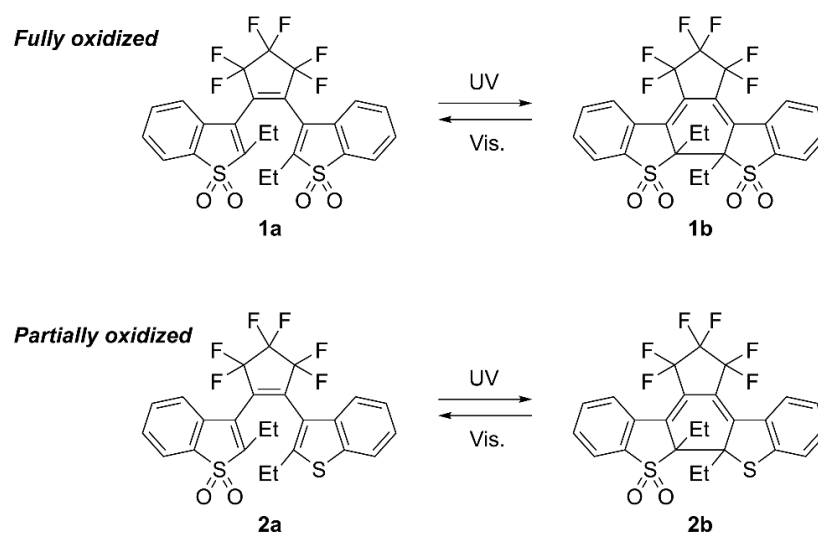
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1. Introduction

Photochromic molecules undergo photoreversible interconversion between two isomeric forms with different colors [1,2]. Although various types of photochromic molecules have so far been developed, molecules that show photochromic responses in crystals are relatively rare. Diarylethene derivatives undergo thermally irreversible and photochemically reversible photochromic reactions not only in solution but also in single crystals [3–6]. Upon irradiation with ultraviolet (UV) light, diarylethene molecules in crystals undergo cyclization isomerization to form closed-ring isomers, and the crystals change their colors, such as yellow, red, blue, or green, depending on the chemical structures of the component molecules. Upon irradiation with visible light, the photogenerated colors are completely bleached, and the crystals revert to the original colorless states. The diarylethene crystals are excellent in the resistance against photofatigue: as a conspicuous example, it has been reported that the coloration and decoloration cycles were repeated over 30,000 times by alternate irradiation with UV and visible light [7]. Additionally, diarylethene crystals show reversible shape changes upon photoirradiation and convert photoenergy into mechanical energy [8–13]. These photoresponsive diarylethene crystals can find potential applications in optical memory media, optical switches, displays, and light-driven actuators.

The properties and reactivity of molecular crystals vary strongly depending on not only the chemical structures of the component molecules but also their crystal structures. Various crystal-engineering approaches utilizing noncovalent interactions, such as hydrogen bond, metal-coordinating bond, halogen bond, π - π interaction and so on, have been applied to control the conformation and packing structure of the molecules in the crystals and obtain targeted properties and reactivity [14,15]. Preparing nonstoichiometric mixed crystals that contain two or more components is also a promising methodology to precisely tailor the functionality of molecular crystals by combining the characteristics of the substances being mixed [16,17]. According to Kitaigorodsky's studies, the fundamental design guideline for preparing mixed crystals is based on the similarity in size and shape of the component molecules [18,19]. It has been reported that multicomponent mixed crystals can be prepared by using photochromic diarylethene derivatives. For example, bis(2-thienyl)ethene and bis(3-thienyl)ethene derivatives form two-component mixed crystals [20]. Although the two diarylethene molecules are different in the connecting position of the thienyl groups to the central hexafluorocyclopentene bridge, their entire molecular structures are quite similar to each other, leading to the miscibility of the two components in the crystal. The resulting mixed crystals exhibit multicolor photochromism by the combination of different colors of the closed-ring isomers. Multicolor photochromic crystals have also been prepared by mixing bis(3-thienyl)ethene, bis(4-thiazolyl)ethene, and bis(4-oxazolyl)ethene derivatives with different heteroaryl rings that are structurally similar to each other but exhibit distinctly different colors in the closed-ring forms [21,22]. In addition, the mixed-crystal approach has successfully been applied to improve photomechanical responses of photodeformable rod-like diarylethene crystals [10,23].

Here we propose a new strategy for preparing multicomponent mixed crystals using photochromic diarylethene derivatives having differently oxidized benzothiophene groups. Bis(benzothiophenyl)perfluorocyclopentene is one of the well-studied scaffolds of photochromic diarylethene [24,25]. The corresponding oxidized derivatives having benzothiophene *S,S*-dioxide also undergo reversible photochromism [26–31]. We chose diarylethenes **1a** and **2a** shown in Scheme 1 as components for the preparation of mixed crystals. The two compounds are different only in the oxidation state of the benzothiophene groups, that is, the presence or absence of the oxygen atoms on the sulfur atoms, and they show different colors in the closed-ring forms. The similarity in the molecular size and shape of the compounds allowed the formation of mixed crystals and the resulting crystals exhibited multicolor photochromism. The preparation and photochromic behaviors of the mixed crystals were examined.



Scheme 1. Photoisomerization of diarylethenes **1** and **2**.

2. Materials and Methods

2.1. General

The reagents and solvents for synthesis were commercially available and used without any purification. Spectroscopic-grade solvents (Kanto Chemical, Tokyo, Japan) were used for spectral measurement. **1a** was synthesized with reference to the previously reported method [29].

^1H and ^{13}C NMR spectroscopy in CDCl_3 was performed with ECX-400P (JEOL, Tokyo, Japan). Tetramethylsilane (TMS) was used as an internal standard. Mass spectrometry (MS) based on electron-impact (EI) ionization was performed with GCMS-QP2010Plus (Shimadzu, Kyoto, Japan). Elemental analysis (C, H, N, and S) was performed with Vario MICRO Cube (Elementar, Langensfeld, Germany). Differential scanning calorimetry (DSC) was performed with Q200 (TA Instruments, New Castle, USA).

X-Ray crystallographic analysis was performed with D8 QUEST (Bruker AXS, Massachusetts, USA). The radiation wavelength was $0.71073 \text{ \AA}$ (Mo K_α). The temperature of the crystals was controlled by a low-temperature controller (JAN 2-12, Japan Thermal Engineering, Sagami, Japan). The diffraction images were integrated with the Bruker APEX3 v2015.9-0 program. The cell parameters were determined by global refinement. The absorption correction was carried out using the multiscan method (SADABS). The structures were solved by the direct method and refined using the SHELX-2014 program [32]. CCDC 2217447, 2217448, and 2217449 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk).

UV-visible absorption spectra of solution samples were recorded with Hitachi, U-4100. Polarized absorption spectra of single crystals were measured using a polarizing microscope (DM2500P, Leica, Wetzlar, Germany) and a multichannel photodetector (C7473, Hamamatsu Photonics, Hamamatsu, Japan) according to the previously reported method [31].

Photoirradiation to solution samples was carried out using a 300 W xenon lamp (MAX-303, Asahi Spectra, Tokyo, Japan) with an optical band-pass filter (313 nm) or an optical long-pass filter ($>440 \text{ nm}$). Photoirradiation to single crystals was carried out using a 300 W xenon lamp (MAX-303, Asahi Spectra, Tokyo, Japan) with an optical band-pass filter (430 nm) or an LED irradiation system (CL-1501, LED head: CL-H1-365-9-1 for 365 nm, CL-H1-525-7-1 for 525 nm, Asahi Spectra, Tokyo, Japan).

2.2. Synthesis of **2a**

To a dichloromethane solution (20 mL) of 1,2-bis(2-ethyl-3-benzo[*b*]thienyl)perfluorocyclopentene [33] (1.0 g, 2.0 mmol) was added *m*-chloroperoxybenzoic acid (0.62 g, 3.6 mmol) and the mixture was stirred for 8 h at room temperature. The resulting mixture was washed with aqueous NaHCO_3 and aqueous $\text{Na}_2\text{S}_2\text{O}_3$ and then extracted with dichloromethane. The organic layer was dried over MgSO_4 , filtered, and concentrated in vacuo. The residue was purified by silica gel column chromatography (hexane: ethyl acetate = 80:20 $\rightarrow$ 0:100) to afford **2a** as a white solid (0.57 g, 1.1 mmol, 53%). ^1H NMR (400 MHz, CDCl_3 , TMS) δ 7.77 (1H, d, 8.0 Hz, Ar-H), 7.72–7.67 (1.66H, m, Ar-H), 7.63–7.51 (4.66H, m, Ar-H), 7.42–7.24 (5.30H, m, Ar-H), 7.16 (0.66H, d, $J = 7.6 \text{ Hz}$, Ar-H), 2.82–2.67 (3.64H, m, CH_2), 2.55–2.43 (2H, m, CH_2), 2.32–2.22 (1H, m, CH_2), 1.39 (1.98H, t, $J = 7.6 \text{ Hz}$, CH_3), 1.35 (1.98H, t, $J = 7.6 \text{ Hz}$, CH_3), 1.00 (3H, t, $J = 7.6 \text{ Hz}$, CH_3), 0.77 (3H, t, $J = 7.6 \text{ Hz}$, CH_3); ^{13}C NMR (100 MHz, CDCl_3 , TMS) δ 151.58, 150.74, 147.80, 147.23, 138.31, 138.16, 137.90, 137.64, 135.73, 135.29, 133.71, 133.23, 130.32, 130.25, 130.16, 129.55, 125.12, 125.02, 124.85, 124.77, 124.71, 123.44, 123.40, 123.36, 122.88, 122.59, 122.47, 121.91, 121.85, 121.81, 121.70, 121.68, 121.66, 121.64, 116.75, 116.55, 30.95, 23.13, 19.20, 18.62, 15.93, 15.58, 12.01, 11.20; MS (EI) m/z 528 [M] $^+$; anal. C 56.66, H 3.43, N 0.00, S 11.81%, calcd for $\text{C}_{25}\text{H}_{18}\text{F}_6\text{O}_2\text{S}_2$, C 56.81, H 3.43, N 0.00, S 12.13%; mp (DSC) 112°C . NMR spectra of **2a** are shown in Figure

S1 in the supplementary material. The NMR spectra contain signals of antiparallel and parallel conformers of the open-ring isomer **2a** [3,4]. The purity (>99%) of **2a** after recrystallization from diethyl ether was confirmed by analytical HPLC, as shown in Figure S2.

3. Results and Discussion

3.1. Photochromism of **1** and **2** in Solution

The photochromism of the diarylethenes in solution was examined. Figure 1 shows the absorption spectra of **1** and **2** in ethyl acetate. The open-ring isomers **1a** and **2a** have no optical absorption in the visible-wavelength region, and the solutions were colorless. Upon irradiation with 313 nm light, the colorless solutions of **1a** and **2a** turned yellow and red, respectively, because of the photoinduced formation of the corresponding closed-ring isomers **1b** and **2b**. The absorption maxima of **1b** and **2b** in the visible-wavelength region are located at 412 nm and 519 nm, respectively. **1b** has the absorption maximum at a wavelength shorter than **2b**. The oxidation of the benzothiophene groups leads to a significant hypsochromic shift of the absorption wavelength of the closed-ring isomer [26–28]. The photogenerated colors were stably kept in the dark at room temperature. Upon irradiation with visible ($\lambda > 440$ nm) light, the yellow and red colors of the closed-ring isomers were completely bleached, and the absorption spectra reverted to the original spectra of the open-ring isomers. Thus, the two diarylethenes undergo photochromism and show different colors in the closed-ring forms, reflecting the difference in the oxidation state of the benzothiophene groups.

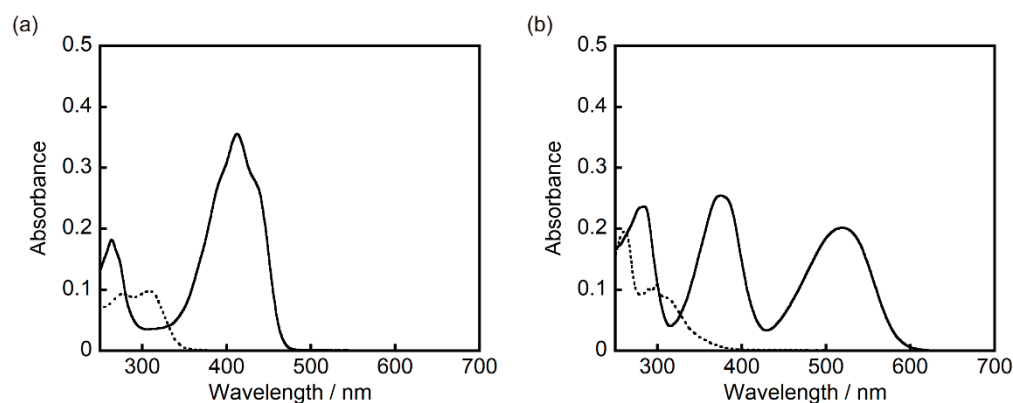


Figure 1. Absorption spectra of **1** (a) and **2** (b) in ethyl acetate (2.0×10^{-5} M). Dotted lines: open-ring isomers **1a** and **2a**, solid lines: photostationary states under irradiation with 313 nm light.

3.2. Single-Component Crystals of **1a** and **2a**

The crystal structures of single-component crystals of **1a** and **2a** were examined by X-ray crystallographic analysis. The crystal of **1a** having two oxidized benzothiophene groups was prepared by recrystallization from acetone. The crystal parameters are summarized in Table 1. The crystal has a monoclinic unit cell with a space group of $C2/c$ and $Z = 4$, which is the same as that of the crystal of **1a** recrystallized from ethyl acetate [31]. The asymmetric unit in the unit cell is a half of the **1a** molecule with a C_2 symmetry. The **1a** molecule in the crystal is fixed in a photoreactive antiparallel conformation, and the distance between the reacting carbon atoms C3 and C3' (D) is 4.03 Å, as shown in Figure 2a. This fulfills the requirement for the diarylethene molecule to undergo photoisomerization in the crystal [34]. Indeed, the crystal underwent photochromism, as described later.

Table 1. Crystal data for single-component crystals of **1a** and **2a** and a two-component mixed crystal **1a·2a** (**1a:2a** = 85:15).

	1a	2a	1a·2a
Crystallization solvent	Acetone	Diethyl ether	Acetone
Formula	C ₂₅ H ₁₈ F ₆ O ₄ S ₂	C ₂₅ H ₁₈ F ₆ O ₂ S ₂	C ₂₅ H ₁₈ F ₆ O _{3.57} S ₂
Formula weight	560.51	528.51	553.60
T/K	223 (2)	100 (2)	223 (2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	C2/c	P2 ₁ /c	C2/c
a/Å	15.0346 (11)	13.1649 (8)	15.0533 (5)
b/Å	15.1774 (11)	10.5410 (6)	15.1878 (5)
c/Å	10.7072 (7)	16.5297 (10)	10.6375 (3)
β/°	107.706 (2)	99.859 (2)	107.8093 (13)
V/Å ³	2327.5 (3)	2260.0 (2)	2315.47 (13)
Z	4	4	4
R ₁ (I > 2σ(I))	0.0328	0.0571	0.0529
wR ₂ (all data)	0.0906	0.1265	0.1420
CCDC No.	2217447	2217448	2217449

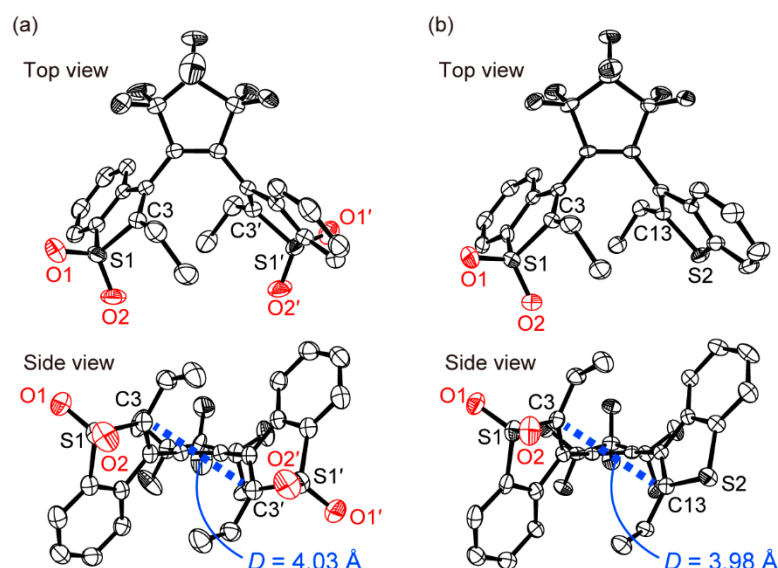


Figure 2. Molecular structures in single-component crystals of **1a** (a) and **2a** (b) determined by X-ray crystallographic analysis. The crystals of **1a** and **2a** were prepared by recrystallization from acetone and diethyl ether, respectively. The ellipsoids are shown at 50% probability level. The hydrogen atoms are omitted for clarity. *D* is the distance between the reacting carbon atoms.

The single-component crystal of **2a** suitable for X-ray analysis was prepared by recrystallization from diethyl ether. The recrystallization from acetone afforded no single crystals with good quality. The crystal has a monoclinic unit cell with *P2₁/c* and *Z* = 4 (Table 1), and the asymmetric unit is one molecule of **2a**. Figure 2b shows the molecular structure of **2a** in the crystal. The **2a** molecule also adopts an anti-parallel conformation that is quite similar to that of **1a**. The distance between the reacting carbon atoms C3 and C13 (*D*) is 3.98 Å, indicating that **2a** can also undergo photoisomerization in the crystal.

The photochromism of the single-component crystals was investigated. Upon irradiation with UV (λ = 365 nm) light, the colorless crystals of **1a** and **2a** turned yellow and red, respectively, as shown in Figure 3, because of the photoinduced formation of the corresponding closed-ring isomers **1b** and **2b**. Figure 3 also shows the polarized absorption spectra of the yellow and red crystals. The photogenerated closed-ring isomers **1b** and **2b** in the crystals have absorption bands with maxima at 450 nm and 535 nm, respectively. The absorption wavelength of **1b** is shorter than that of **2b**, as observed for the ethyl

acetate solutions. The polar plots of the absorbance of **1b** and **2b** show clear anisotropy, which originates from the regular orientation of the diarylethene molecules in the single crystals (Figure S3) [35]. Upon irradiation with visible ($\lambda > 440$ nm) light, the yellow and red crystal returned to the original colorless ones. Thus, **1** and **2** undergo reversible photochromism in the single-component crystals.

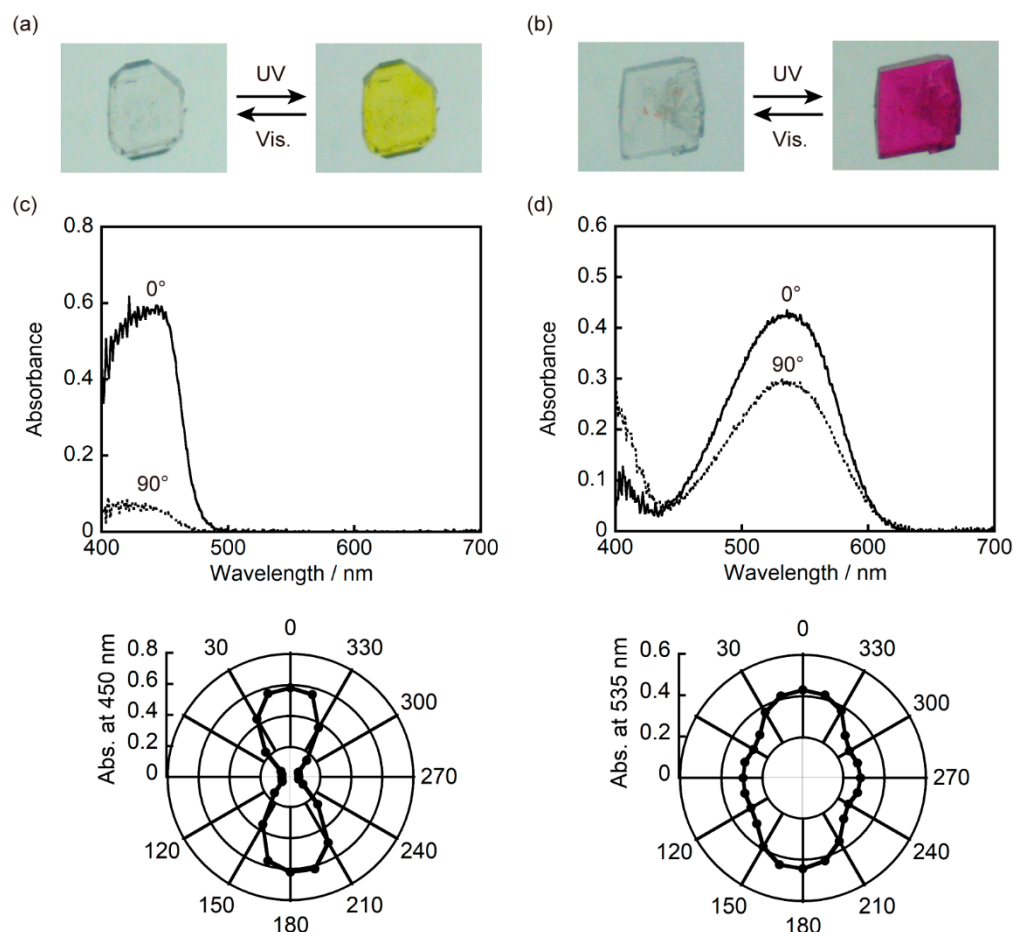


Figure 3. Photographs of photoinduced color changes of single-component crystals of **1a** (a) and **2a** (b). Polarized absorption spectra and polar plots of absorbance of the yellow **1a** crystal (c) and the red **2a** crystal (d) after irradiation with 365 nm light. The absorption spectra of the crystals of **1a** and **2a** were measured on $(-1\ 1\ 0)$ and $(1\ 1\ 1)$ faces, respectively (see Figure S3). The direction of 0° was set to the angle where the maximum absorbance was observed. In the polar plots the absorbance at 450 nm and 535 nm was monitored for the crystals of **1a** and **2a**, respectively.

3.3. Two-Component Mixed Crystals Containing **1a** and **2a**

Two-component mixed crystals of **1a** and **2a** were prepared by recrystallization from mixed solutions containing the two compounds. A mixture of **1a** and **2a** was dissolved into acetone, and the solvent was slowly evaporated at room temperature. After several days, colorless single crystals were obtained. The composition ratio of the crystals was analyzed by HPLC (Figure S4). Table 2 shows the relationship between the feed ratio of **1a** and **2a** in solution and the composition ratio in the crystal. The crystals contained both **1a** and **2a**, and the composition ratio varied depending on the feed ratio. With increasing the feed ratio of **2a** in solution, the composition ratio of **2a** in the crystal increased. When the content of **2a** in the feed solution was increased over 50%, the quality of the mixed crystals obtained became poor, suggesting that the crystal lattice deteriorated. DSC measurements show that the melting points of the mixed crystals are lower than that of the single-component crystal of **1a** (Figure S5).

Table 2. Feed ratio of **1a** and **2a** in solution and composition ratio of **1a** and **2a** in two-component mixed crystals, which was determined by HPLC. The mixed crystals were prepared by recrystallization from acetone.

Entry	Feed Ratio in Solution (1a:2a)	Composition Ratio in Crystal (1a:2a)
1	90:10	97:3
2	70:30	85:15
3	50:50	53:47

X-Ray crystallographic analysis of the two-component mixed crystal was carried out. Figure 4 shows the X-ray crystal structure of the two-component mixed crystal with a composition ratio of **1a:2a** = 85:15 (entry 2 in Table 2). The crystallographic parameters are listed in Table 1. The cell parameters and overall crystal structure of the mixed crystal were very similar to those of the single-component crystal of **1a**. However, we noticed meaningful alteration in the occupancy parameter of the oxygen atoms (O1 and O2) on the oxidized benzothiophene groups. The single-component crystal of **1a** showed full occupancy (100%) at the oxygen sites, while the occupancy of the oxygen atoms in the mixed crystal decreased down to 89%, indicating that the **2a** molecules, in which one of the two benzothiophene groups is unoxidized, are substitutionally incorporated into the crystal lattice of **1a**. The occupation of **2a** at the molecular sites in the crystal lattice of **1a** decreased the occupancy parameter of the oxygen atoms in the X-ray crystal structure. Considering the 89% occupancy of the oxygen atoms and the C_2 symmetry of the diarylethene molecule in the crystal lattice of **1a**, the ratio of **1a** and **2a** in the mixed crystal is calculated to be 78:22, which is approximately consistent with the ratio measured by HPLC. In addition, the X-ray crystallographic structure means that **2a** molecules in the mixed crystal adopt the photoreactive antiparallel conformation in the same way as **1a** molecules.

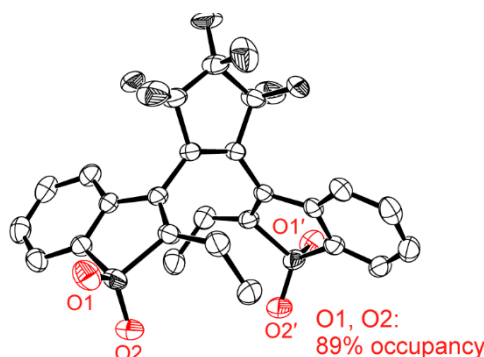


Figure 4. Molecular structure in a two-component mixed crystal containing **1a** and **2a** (entry 2 in Table 2) determined by X-ray crystallographic analysis. The crystal was prepared by recrystallization of a mixture of **1a** and **2a** with a molar ratio of **1a:2a** = 70:30 from acetone. The composition ratio of the crystal was **1a:2a** = 85:15 as determined by HPLC. According to the X-ray analysis, the occupancy parameter of the oxygen atoms (O1 and O2) was 89%.

The photochromism of the two-component mixed crystals was examined. Figure 5a shows photographs of the photoinduced color changes in the mixed crystal with the composition ratio of **1a:2a** = 85:15 (entry 2 in Table 2). The crystal was colorless before photoirradiation. Upon irradiation with 365 nm light, the crystal turned orange, suggesting the photoinduced formation of the yellow closed-ring isomer **1b** and the red **2b**. Figure 5b shows an absorption spectrum of the orange crystal. The spectrum has two absorption maxima at around 450 nm and 535 nm, which are respectively ascribed to the closed-ring isomers **1b** and **2b**, indicating that both **1a** and **2a** underwent photocyclization reactions in the mixed crystal. The photochromic behavior of the mixed crystal upon irradiation with 365 nm light was altered by the composition ratio of the two components. As the ratio of **2a** increased, the relative absorption intensity of **2b** at 535 nm increased (Figure

S6). Upon irradiating the orange crystal with 525 nm light the crystal turned yellow (Figure 5a). In the yellow crystal, the long-wavelength absorption band of **2b** at 535 nm disappears, and there remains the band of **1b** at 450 nm (Figure 5d). This indicates that 535 nm light irradiation induces the selective cycloreversion reaction of **2b** in the mixed crystal. After that, irradiating the yellow crystal with 430 nm light induced the cycloreversion reaction of **1b** and the crystal reverted to the colorless state. Irradiating the colorless crystal with both 365 nm and 430 nm light induced the selective formation of **2b** and the crystal turned red, as shown in Figure 5a. In the red crystal, the absorption band of **2b** at 535 nm preferentially appears (Figure 5c). Thus, the mixed crystal underwent the selective photoisomerization of the two diarylethene components by irradiation with light of appropriate wavelengths, resulting in the multicolor photochromic performance, such as colorless, orange, yellow, and red. Such multicolor photochromic crystals are potentially applicable to multistate optical recording and multicolor displays.

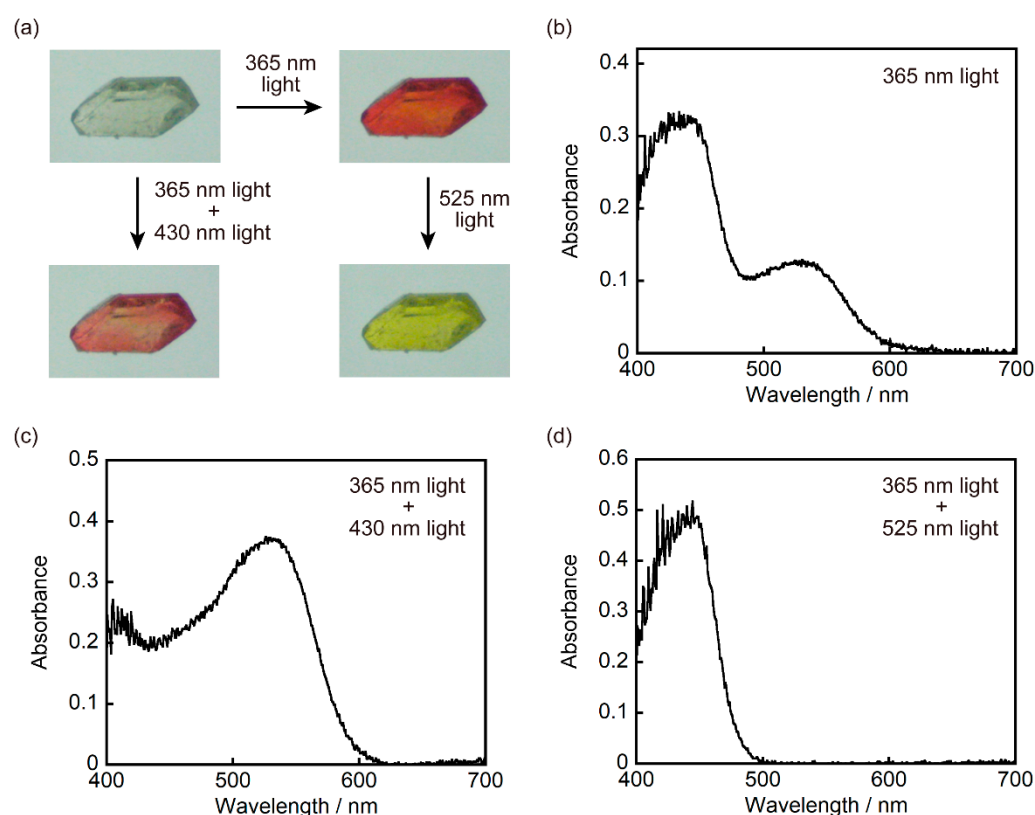


Figure 5. (a) Photographs of photoinduced color changes of a two-component mixed crystal with a composition ratio of **1a:2a** = 85:15 (entry 2 in Table 2). Absorption spectra of the two-component crystal irradiated with 365 nm light (b), irradiated with both 365 nm and 430 nm light (c), and irradiated with both 365 nm and 525 nm light (d). The absorption spectra were measured on (−1 1 0) face.

Figure 6 shows the polarized absorption spectra of the orange two-component mixed crystal after 365 nm light irradiation. The absorption bands at 450 nm and 535 nm correspond to the electronic transitions of the closed-ring isomers **1b** and **2b**, the transition moment of which is parallel to the long axis of the molecule [35]. As shown in Figure 6, both the absorption bands of **1b** and **2b** show clear anisotropy in the same direction, indicating that the photoisomerization of **1a** and **2a** takes place in the crystal lattice and the long axes of the photogenerated **1b** and **2b** molecules are oriented to the same direction.

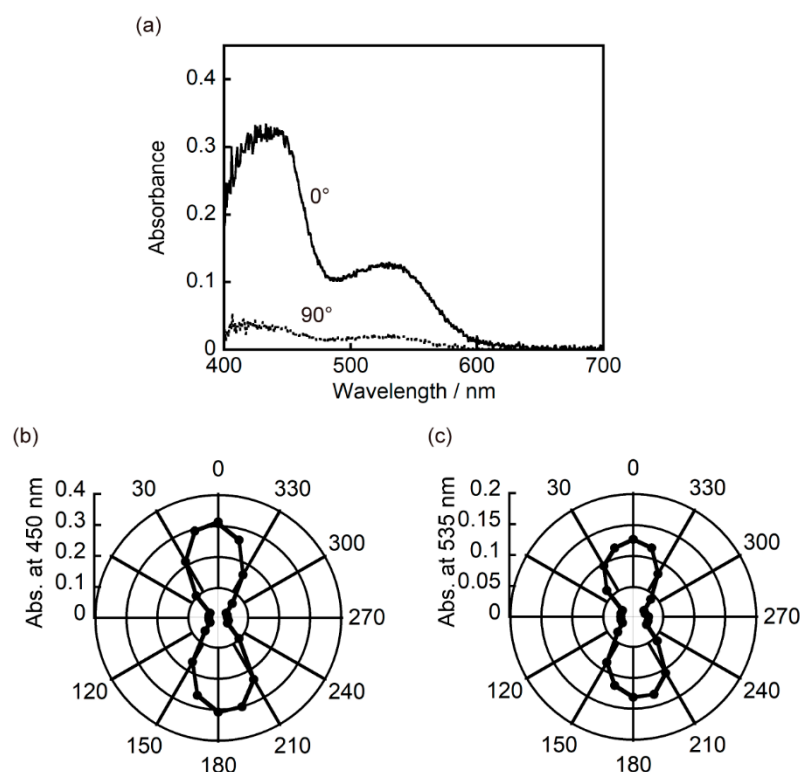


Figure 6. Polarized absorption spectra (a) and polar plots of absorbance (b,c) of an orange two-component mixed crystal (**1a:2a** = 85:15, entry 2 in Table 2) after irradiation with 365 nm light. The absorption spectra were measured on (−1 1 0) face. The direction of 0° was set to the angle where the maximum absorbance was observed. In the polar plots, the absorbance at 450 nm (b) and 535 nm (c) was monitored.

4. Conclusions

The diarylethene derivatives **1a** and **2a**, which are different from each other in the oxidation state of the benzothiophene groups and the color of the closed-ring isomer, formed the two-component mixed crystals by simple recrystallization from mixed solutions. The similarity in the molecular shape and size of the component diarylethenes enabled the formation of the mixed crystals, the composition ratio of which was controlled by the feed ratio in the mother solution. X-Ray crystallographic analysis revealed that **2a** is substitutionally incorporated as a dopant in the crystal lattice of **1a**. The mixed crystals exhibited photochromism and also underwent the selective photoisomerization of the two diarylethenes by appropriate light irradiation, resulting in the multicolor photochromic property. These results demonstrate that hybridizing diarylethene derivatives with different oxidation states into mixed crystals is useful for preparing molecular crystals with multiresponsive functions.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/cryst12121730/s1>, Figure S1: NMR spectra of **2a**; Figure S2: HPLC chromatogram of **2a**; Figure S3: Molecular packing diagrams of single-component crystals; Figure S4: HPLC chromatogram of mixed crystals; Figure S5: DSC curves of crystals; Figure S6: Absorption spectra of mixed crystals.

Author Contributions: Conceptualization, M.M.; methodology, M.M.; validation, R.N., Y.N. and M.M.; formal analysis, R.N., Y.N. and M.M.; investigation, R.N., Y.N. and M.M.; resources, R.N., Y.N. and M.M.; data curation, R.N., Y.N. and M.M.; writing—original draft preparation, R.N. and M.M.; writing—review and editing, R.N., Y.N. and M.M.; visualization, R.N., Y.N. and M.M.; supervision, M.M.; project administration, M.M.; funding acquisition, R.N. and M.M. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflicts of interest.

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