Photochromism of single crystals composed of dioxazolylethene and dithiazolylethene

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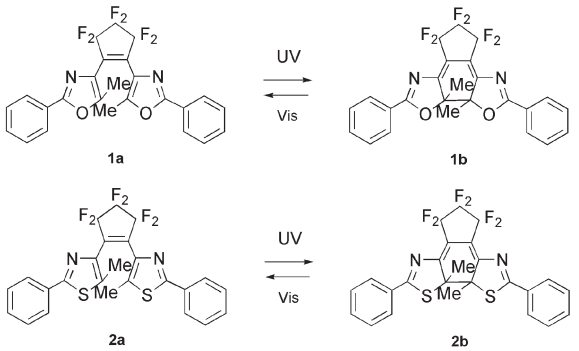
Although dioxazolylethene 1a did not show any photocoloration in the single crystalline phase, 1a displayed photochromism in the mixed crystal containing both 1a and dithiazolylethene 2a; the mixed crystal changed color from colorless to red, orange, and yellow upon irradiation with light of appropriate wavelengths.

Photochromism is referred to as a reversible transformation between two isomers having different absorption spectra by photoirradiation.[1,2] In quite a number of photochromic compounds, compounds which show photochromism in the crystalline phase are very rare.[3] Some diarylethene derivatives undergo thermally irreversible photochromic reactions even in the crystalline phase.[4,5] In these crystals, diarylethene molecules are fixed and packed in a photoactive antiparallel conformation and undergo effective photocyclization reactions. But when they are packed in a parallel conformation in crystals, they lose photoreactivity and show no photocoloration.

Recently, photochromism of two- or three-component diarylethene crystals has been reported.[6–8] Although multi-component photochromic crystals which exhibit various colors have potential for application to high-density memories and multi-color displays, it is not easy to prepare crystals composed of different kinds of molecules.[7] In general, molecules with different colors have quite different structures. Molecules with different structures cannot be mixed in the same single crystal. However, when each component molecule has a closely similar structure and unit cell dimensions, the system is anticipated to form fully miscible solid solutions.[9] In this study, single-crystalline photochromism of a mixed crystal composed of diarylethenes which have a similar geometrical structure, 1,2-bis(5-methyl-2-phenyloxazol-4-yl)perfluorocyclopentene (**1a**) and 1,2-bis(5-methyl-2-phenylthiazol-4-yl)perfluorocyclopentene (**2a**),[10] was examined (Scheme 1).

Colorless crystals were obtained by recrystallization from hexane solution of **1a** and **2a**, respectively. The single crystal of **1a** was rhombus-shaped and didn't show any photocoloration. The hexane solution of **1a** showed normal photochromic performance. Upon irradiation with 313 nm light, the colorless solution turned orange, in which maximum absorption was observed at 462 nm.

The single crystal of **2a** has a needle shape and turned a red color upon UV irradiation. Fig. 1 shows ORTEP drawings of **1a** and **2a**. X-ray crystallographic analysis showed that **1a** is packed in a parallel conformation and **2a** in an antiparallel one.[11,12] The difference in the photoreactivity of **1a** and **2a** in the homo-crystals is due to the difference in the conformation. In a previous report,[13] a dibenzothiophene derivative showed polymorphism, such as two types of photoreactive and photoinactive crystals depending on the recrystallization solvents. Although we tried recrystallization with various solvents such as ethanol, cyclohexane, diisopropyl ether and toluene, we could not obtain any photoactive **1a** crystal.



Scheme 1 Photochromism of compounds **1** and **2** in hexane solution.

Mixed crystals containing **1a** and **2a** were prepared by recrystallization of a mixture of **1a** and **2a** from hexane. Fig. 2 shows the feed ratio dependence on the composition of the mixed crystals. When the content of **1a** is less than 60% in hexane, the crystal shape is needle or long plate and similar to that of the single crystal of **2a**. Reasonable amounts of both components can be included in the mixed crystals. Fig. 3 shows the photochromism of mixed crystal **1a**/**2a** obtained in hexane solution containing **1a** and **2a** with feed ratio 6 : 4. The composition ratio of **1a** and **2a** in the crystal was 30 : 70. The colorless crystal turned red upon irradiation with 405 nm light. The absorption maximum was observed at 547 nm. When the colorless mixed crystal **1a**/**2a** was irradiated with 370 nm light and bleached by 633 nm light, it

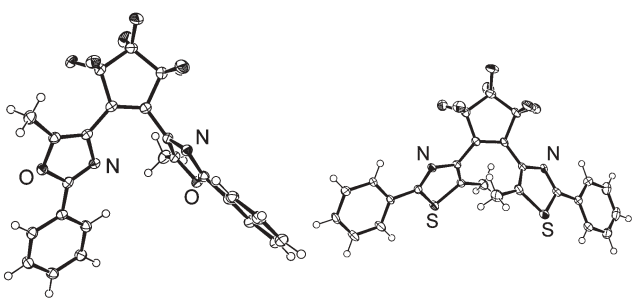


Fig. 1 Molecular structures of single crystals **1a** and **2a**.

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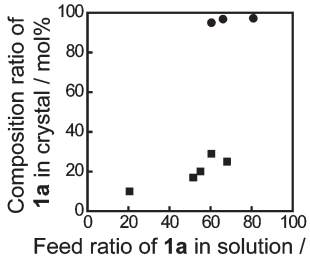

Fig. 2 Relationship between the feed ratio of **1a** and **2a** in hexane solution and the composition ratio of the two-component crystal **1a/2a**. ■: needle- or long plate-shaped crystal. ●: rhombus-shaped crystal.[14]

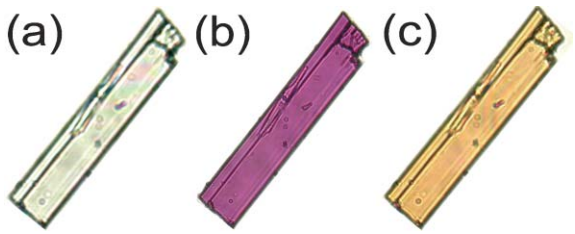

Fig. 3 Photographs of mixed crystal **1a/2a** (a) before photoirradiation, (b) after irradiation with 405 nm light, (c) after irradiation with 370 nm and 633 nm light.

turned yellow *via* orange. The absorption band has a maximum at 472 nm. To establish the origin of the red and yellow colors, the red and yellow colored crystals were dissolved in hexane, and the absorption spectra were measured. The spectra were the same as those of the closed-ring isomers **2b** and **1b**. The results indicate that the red and yellow colors of the crystal are due to **2b** and **1b**.

Fig. 4 shows the polarized absorption spectra of **1b** and **2b** in the crystal **1a/2a** at a certain angle (0°), where the maximum absorption was observed, and the spectra at the perpendicular angle (90°). The high intensity absorption bands (λ_{max} = 450 nm for **1b** and λ_{max} = 550 nm for **2b**) correspond to the long-axis absorption of the photogenerated closed-ring isomers **1b** and **2b**. Absorption bands of **1b** and **2b** showed large anisotropy in the

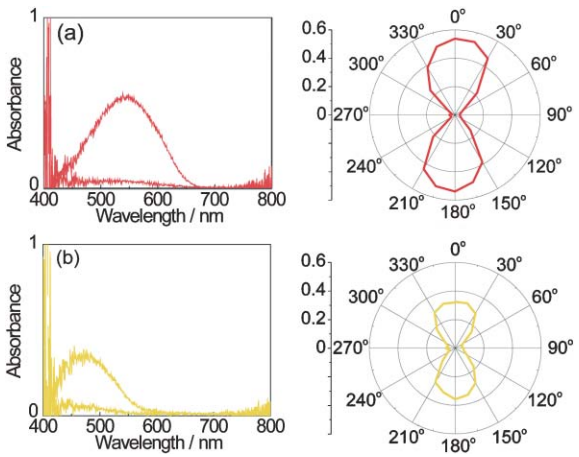

Fig. 4 Polarized absorption spectra and polar plots of absorbance of photogenerated closed-ring isomers, **2b** (a) and **1b** (b), on (0, −1, 0) face in mixed crystal **1a/2a**. Absorbance is plotted at 550 nm and 450 nm for **2b** and **1b**, respectively.

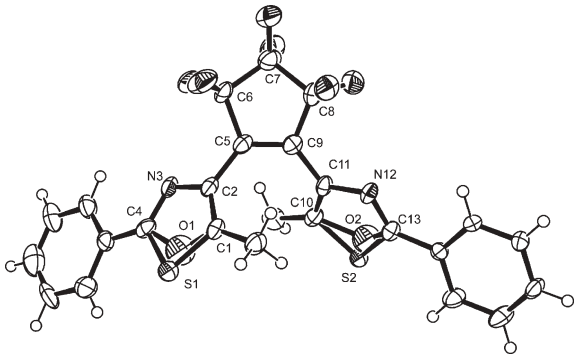

Fig. 5 Molecular structure of mixed crystal **1a/2a** (**1a** : **2a** = 17 : 83). Site occupancy factor for **1a** is 15%.

same direction. These red and yellow colors were completely bleached upon irradiation with visible light (λ > 460 nm) and the crystal returned to colorless.

X-ray crystallographic analysis was carried out for **1a/2a** crystal with composition ratio 17 : 83. The crystal has the same crystal system, space group, and unit cell dimensions as those of crystal **2a**.[15] The molecular structure is shown in Fig. 5. Both molecules are packed in an antiparallel conformation and the distance between the reacting carbon atoms, C(1)–C(10), was determined to be 3.48 Å, which is close enough for the photoreaction. These results indicate that **1a** is fitted into the packing template of single crystal **2a** in the mixed crystal **1a/2a**.

In conclusion, we prepared photochromic single crystals composed of **1a** and **2a**. Although homo-crystal of **1a** is photochemically inactive because of its parallel conformation, in the mixed crystal **1a/2a**, **1a** changed its conformation to photoactive antiparallel. By changing the wavelength of the irradiating light, the mixed crystal **1a/2a** selectively underwent photochromic reaction and the colorless crystal turned red, orange and yellow.

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11 Crystal data for **1a**: $C_{25}H_{16}F_6N_2O_2$, MW = 490.40, monoclinic, space group $P2_1/c$, a = 11.618(3), b = 17.791(5), c = 10.274(3) Å, α = 90, β = 95.773(5), γ = 90°, V = 2112.8(10) Å^3, Z = 4, D_c = 1.542 g cm^{-3}, μ(Mo-Kα) = 0.298 mm^{-1}, 11879 reflections measured, 4256 unique

(R_{int} = 0.0372) were used in all calculations. The final $wR(F^2)$ was 0.0939 (all data). CCDC 282862. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b512873k.
12 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), b = 25.752(8), c = 12.611(4) Å, α = 90, β = 102.432(5), γ = 90°, V = 2295.0(12) Å^3, Z = 4, D_c = 1.512 g cm^{-3}, μ(Mo-Kα) = 0.0143 mm^{-1}, 11529 reflections measured, 4662 unique (R_{int} = 0.0143) were used in all calculations. The final $wR(F^2)$ was 0.1530 (all data). CCDC 282860. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b512873k.
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14 When the recrystallizing solution contained excess **1a**, rhombus-shaped crystals were obtained. When the feed ratio of **1a** was 60 mol%, both rhombus- and needle- or long plate-shaped crystals were obtained from the same batch.
15 Crystal data for mixed crystal **1a**/**2a**: $(C_{25}H_{16}F_6N_2O_2)_{16}$-$(C_{25}H_{16}F_6N_2S_2)_{84}$, monoclinic, space group $P2_1/n$, a = 7.202(2), b = 25.771(7), c = 12.589(4) Å, α = 90, β = 102.302(4), γ = 90°, V = 2282.7(11) Å^3, Z = 2, D_c = 1.474 g cm^{-3}, μ(Mo-Kα) = 1.9 mm^{-1}, 12804 reflections measured, 4782 unique (R_{int} = 0.0253) were used in all calculations. The final $wR(F^2)$ was 0.1530 (all data). CCDC 282861. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b512873k.