# Photochromism of Furylfulgide in a Single-crystalline Phase

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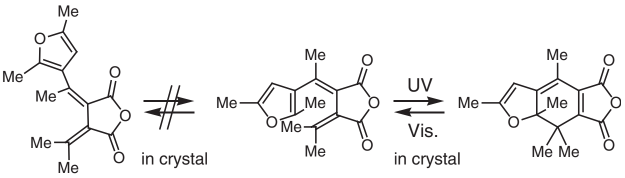
(*E*)-2,5-Dimethyl-3-furylethylidene(isopropylidene)succinic anhydride (***1E***) was found to undergo photochromism in the single-crystalline phase. Upon irradiation with 366-nm light, the single crystal turned red. When the photogenerated colored crystal was observed under polarized light, the red color intensity changed by rotating the crystal. The colored crystal was stable at room temperature.

Photochromism is referred as a reversible transformation between two isomers upon photoirradiation.[1,2] Photochromic compounds are classified into two categories, T-type (thermally reversible) and P-type (thermally irreversible). Spiropyrans and azobenzenes belong to T-type photochromic compounds, while furylfulgides and diarylethenes belong to P-type compounds. The P-type compounds are applicable to optical memory, photooptical swiching and displays.[3–8] Photochromic compounds such as spiropyran and azobenzene do not show any photochromism in the single-crystalline phase, because large geometrical structure changes are required for the photochromism and such structure changes are prohibited in the crystals. Recently, we have reported thermally irreversible and fatigue-resistant photochromic diarylethene crystals.[9–11] The photocyclization/cycloreversion reactions of the diarylethenes were found to proceed efficiently in the crystal lattice.[12]

Fulgides change the color from colorless or yellow to red or blue upon exposure to ultraviolet (UV) light, and the red or blue color disappears upon visible light irradiation. Some phenylfulgides were reported to show photochromism in the crystalline states,[13,14] whereas no detailed information is available. The phenylfulgides are thermally unstable and belong to the T-type category. Heller developed thermally irreversible photochromic furylfulgides.[15] In solution the closed-ring isomer is stable even at 100 °C. Upon UV light irradiation, photocyclization is competed with *E*–*Z* isomerization.

Here we report thermally irreversible crystalline photochromism of furylfulgide (***1E***). The fulgide crystal undergoes photochromism inside the crystal without the *E*–*Z* photoisomerization. There are some papers for photocoloration of thermally irreversible furylfulgide crystals.[16,17] Following results have confirmed that the photochromic reaction of the fulgide crystal proceeds not only on the crystal surface but also inside the crystal.



**1*Z*** **1*E*** **1*C***

A plate single crystal having hexagonal surface (Figure 1) was obtained by recrystallization from a hexane solution of *E* isomer (***1E***). X-ray crystallographic analysis of this crystal was similar to the data reported previously:[16,18] monoclinic, $P2_1/n$, $T = 123(2)$ K, $a = 12.538(4)$ Å, $b = 7.639(2)$ Å, $c = 14.567(4)$ Å, $\beta = 109.135(4)°$, $V = 1318.0(6)$ Å$^3$, $Z = 4$, $R1 = 0.0406$ ($I > 2\sigma(I)$). Figure 1 shows photographs of the crystal (crystal size: $1.0 \times 0.5 \times 0.5$ mm$^3$) observed under polarized light. The observation was carried out on a surface of (010) of crystal ***1E***. Polarizer and analyzer in a polarizing microscope were set in parallel each other. The crystal of ***1E*** was pale yellow. When the crystal was observed under polarized light, the crystal was colorless at a certain angle ($\theta = 0°$). When the crystal was rotated as much as 90° ($\theta = 90°$), the crystal changed to yellow. The yellow color is due to the absorption tail to 450 nm. Figure 2 shows a packing diagram of ***1E*** viewed from the surface of (010). The electronic transition of the longest wavelength absorption band in ***1E*** is directed at the long axis of the fulgide molecule. Upon irradiation with 366-nm light (intensity: 12 mW cm$^{-2}$) for ca. 5 s, the crystal color turned red. At the angle of $\theta = 90°$, the crystal was red, as shown in Figure 1d. The color became weak when the crystal was rotated as much as 90° ($\theta = 0°$). The red color has an absorption anisotropy. The electronic transition moment of the red color absorption band of ***1C*** is directed at the same as that of ***1E***.

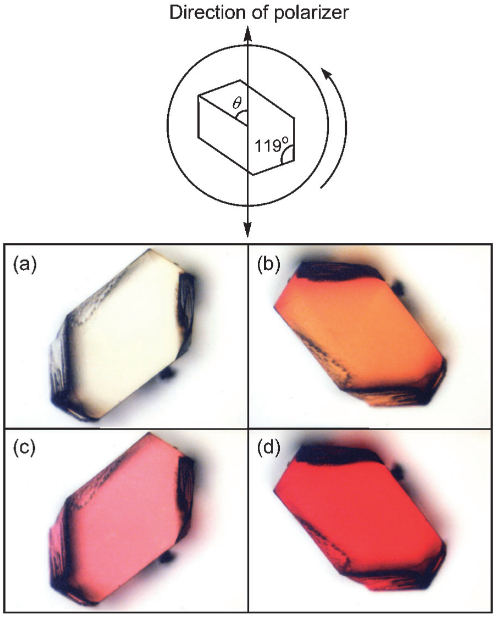


**Figure 1.** Photographs of crystal ***1E*** observed under polarized light: (a) before photoirradiation, $\theta = 0°$, (b) before photoirradiation, $\theta = 90°$, (c) after UV irradiation, $\theta = 0°$, (d) after UV irradiation, $\theta = 90°$.

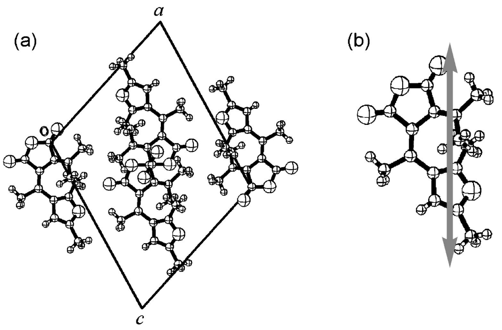


**Figure 2.** Packing diagram of crystal ***1E*** (a) and the molecular structure (b). The arrow showed long axis of the molecule.

The red colored crystal was dissolved in hexane, and then the solution was analyzed with high performance liquid chromatography (HPLC) (silica-gel column, hexane/ethyl acetate = 93:7). ***1Z***, ***1E***, and ***1C*** should be eluted at 12.1, 13.7, and 29.0 min, respectively. HPLC profile of the photoirradiated crystal indicated that only ***1C*** was produced (ca. 2% conversion after UV irradiation for 5 h). ***1Z*** was not observed.

To measure the absorption spectra in the single crystalline phase, a thin crystal was obtained by sublimation on thin glass plat. The polarizing absorption spectrum of crystal ***1E*** has a tail of 450 nm. Figure 3 shows polarizing absorption spectra of crystal ***1E*** and the photoirradiated crystal. The absorption maximum of the colored crystal appeared at 515 nm. The absorbance changed with rotating the crystal. The polar plot of the absorbance at 515 nm shows that the colored molecules are packed regularly in the crystal lattice. The red colored crystal returned to the colorless crystal by irradiation with visible light ($\lambda >$ 550 nm).

To confirm that the cyclization reaction takes place in the crystal bulk, the partly irradiated crystal was observed from side of the crystal. As can be seen from Figure 4, the cyclization reaction proceeded to the depth of more than 140 µm upon irradiation with 435-nm light. The polar plot and the photograph clearly indicate that the furylfulgide undergoes the photochromic reaction inside the crystal.

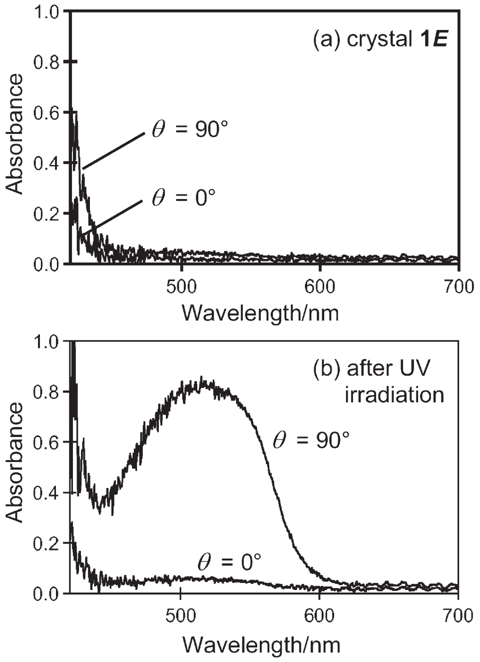


**Figure 3.** Polarized absorption spectra of crystal ***1E*** (a) and the UV-irradiated crystal (b).

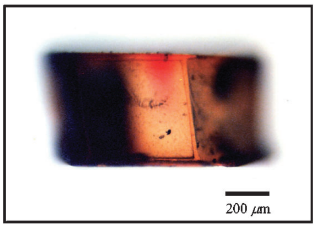


**Figure 4.** Photograph viewed from the side of the partly irradiated crystal. The cyclization reaction took place at the red-colored part of the crystal.

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