Photochromism of Single Crystalline Diarylethenes

Masahiro Irie,* Kingo Uchida, Takeshi Eriguchi, and Hirohisa Tsuzuki†
Institute of Advanced Material Study, Kyushu University, Kasuga-Koen 6-1, Kasuga, Fukuoka 816
†*Center of Advanced Instrumental Analysis, Kyushu University, Kasuga-Koen 6-1, Kasuga, Fukuoka 816*

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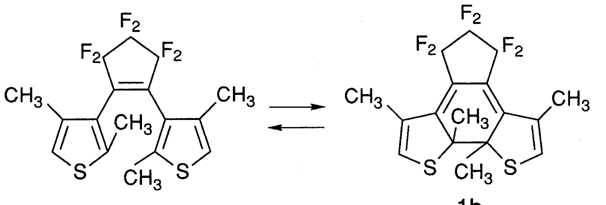
1,2-Bis(2,4-dimethy-3-thienyl)perfluorocyclopentene was found to undergo a reversible photochromic reaction in a single crystalline phase with rotation of the thiophene rings. Both the open-ring colorless and the photogenerated red isomers were thermally stable even at 100℃. Coloration/decoloration cycles could be repeated more than 100 times without destruction of the crystal shape. Regular alignment of the photogenerated colored isomers in the crystal was evidenced by the absorption measurement under linearly polarized light.

Although a great number of photochromic compounds have been reported,[1] compounds which undergo photochromic reactions in a crystalline phase are rare. Typical examples so far reported are N-salicylideneanilines,[2] 2-(2',4'-dinitrobenzyl)-pyridine,[3] diphenylmaleonitrile[4] and triarylimidazole dimer.[5] In most cases, the photogenerated colored isomers are thermally unstable and readily return to the initial colorless isomers at ambient temperature. When both isomers are thermally stable in the crystalline phase, the compound can be potentially applied to many photonic devices.[6] We report here on a new class of photochromic compounds that are stable in both isomeric states, and show photoreactivity in the crystalline phase.

Diarylethenes with heterocyclic rings are known to undergo thermally irreversible and fatigue resistant photochromic reactions, provided that the heterocyclic rings are thiophene or benzothiophene rings.[7] During the course of study of substituted dithienylperfluorocyclopentenes[8] we found that compound **1** undergo a photochromic reaction in the polycrystalline state.[9] On exposure to 313 nm light the powder changed from white to red, and the red color disappeared by irradiation with visible light (λ > 450 nm).



1a 1b

In order to judge whether the reaction takes place in the real crystalline phase or in the surface defects we examined the reaction in a single crystal. A plate form single crystal grown in a methanol solution of **1a** was used. The single crystal turned red by irradiation with 313 nm light. The absorption maximum of the colored form was observed at 530 nm, which is almost similar to the closed-ring form **1b** in hexane solution (λ max = 527 nm). The red color remained stable up to the melting temperature (Tm = 133℃) and thermal decoloration was not discerned at room temperature. The thermally stable red color was readily bleached by irradiation with 530 nm light. The coloration / decoloration cycle could be repeated many times (more than 100 times with keeping the adequate photochromic performance) without destruction of the crystal shape. The photochromic behavior suggests that the reversible cyclization reaction takes place in the crystalline phase.

The photoreactivity in the crystalline phase was further confirmed by measuring the absorption spectra under linearly polarized light. A colorless crystal was irradiated with 313 nm light and placed on the stage of a polarizing microscope. The polarizer and the analyzer were set in parallel each other. When the sample stage was turned, the red color intensity dramatically changed. Figure **1** shows the rotation angle dependence of the absorption intensity at 530 nm. Two peaks were observed in the intensity, and the red color was strongly reduced at 0 and 180 degrees. This result clearly indicates that the photogenerated colored isomers regularly align in the crystal. When compound **1** was dispersed in polystyrene film (1 wt %), the colored isomers showed a constant absorption intensity at any angle.

Figure **2** shows a crystal packing diagram determined by X-ray analysis.[10] The cyclopentene planes of the molecules are placed in perpendicular to the ac-plane, and half of the cyclopentene planes tilt at as much as +30.2 degree from the c-axis and the other half at - 30.2 degree. The closed-ring form is considered to have a coplanar structure and the electronic transition moment is nearly parallel to the cyclopentene planes. The two peaks shown in Fig. **1** reflect the ordering of the molecules. In fact, the crystal plane analysis revealed that the flat plane of the thin plate crystal corresponds to ac-plane.

During the cyclization reaction the thiophene groups are required to rotate along C-C bond between thiophene and ethylene moieties.[11] Such a rotational motion is considered

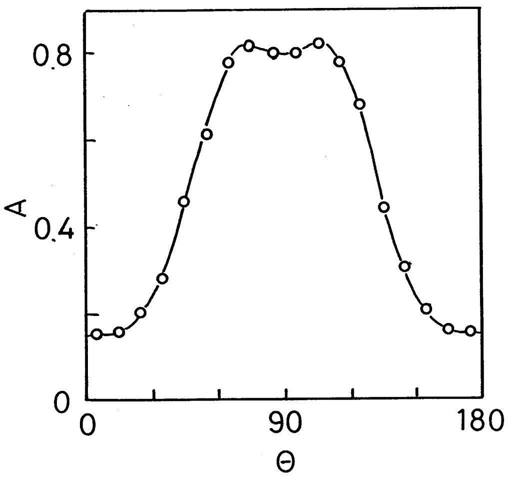


Figure 1. Rotation angle dependence of the absorption intensity of a photoirradiated single crystal **1** at 530 nm. The angle at which the intensity becomes minimum was arbitrarily assigned zero degree.

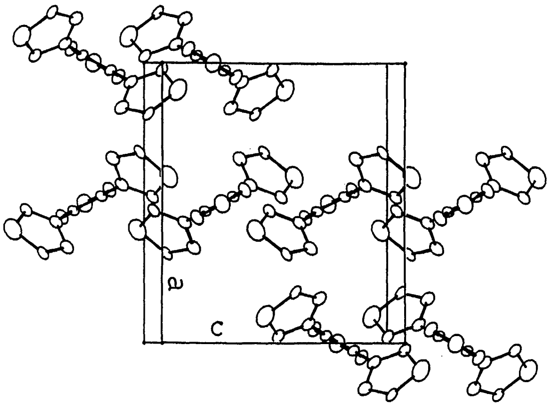


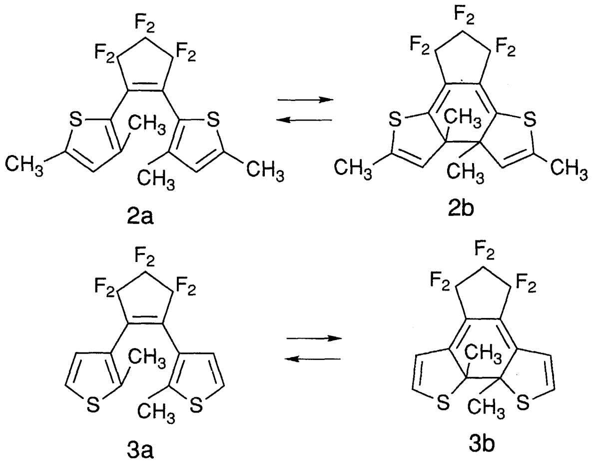
Figure 2. Crystal packing diagram of **1a** viewed down b-axis. Only the molecular frameworks are shown.

hardly to occur in crystals. X-ray crystallographic analysis indicates that adjacent molecules contact each other at the thiophene rings. Rotation of thiophene rings of a molecule is considered to reorganize the neighboring thiophene rings to some extent. Although at present the topotactic reorganization mechanism is not clear, cooperative rotation of the adjacent thiophene rings is one of possible mechanisms of the reaction.

The conversion from the open- to the closed-ring form in the crystal was measured by dissolving a photoirradiated thin plate crystal in hexane. The absorption spectrum indicated the conversion of 7.8%. The relatively low conversion is explained as follows. The ε values at 313 nm of the open-ring colorless and close-ring colored isomers are $1{,}200M^{-1}$ cm^{-1} and $3{,}500M^{-1}$ cm^{-1}, respectively, and ring-opening and cyclization quantum yields are almost similar. At longer wavelengths the ε value of the colored isomer is much larger than that of the colorless isomer. The overlapping of the absorption of the colored isomer at the photoirradiation wavelength and rather short penetration length of light (~10 μm) possibly limits the conversion of the whole crystal.

Whether a photochromic reaction occurs or not in the crystalline phase strongly depends on the molecular structure. When hydrogens at 5 and 5' positions of the thiophene moieties of **1a** were replaced with methyl groups, the reaction was no more observed. 1,2-Bis(2-methylbenzo[b]thiophen-3-yl)perfluorocyclopentene[8] was also photochemically inactive in crystal. On the other hand, following two diarylethenes, **2** and **3**, with two or less methyl groups were found to undergo photochromic reactions both in solution and in crystal.

In order to specify the structural prerequisite it is indispensable to further accumulate data on the correlation between the structure based on X-ray crystallography and the reactivity in crystal for various diarylethenes.



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References and Notes

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9 **1a**: colorless prism; mp 133 ℃. Anal. Found: C, 51. 46: H, 3.62%.Calcd for $C_{17}H_{14}F_6S_2$: C, 51. 51; H, 3.53%. MS(m/z) 396(M+); ^1H NMR (200 MHz, $CDCl_3$) 2.04(6H, s, $2CH_3$), 2.29(6H, s, $2CH_3$), 6.70(2H, s, 2 aromatic protons).
10 Crystal data : formula, $C_{17}H_{14}F_6S_2$; fw, 396.42 ; space group, *Pbca* (No. 61) ; a = 11.7380(8) Å, b = 14.5347(8) Å, c = 10.2772(9) Å ; V = 1753.4(2) Å ^{3}; Z = 4 ; D_{calcd} = 1.500 ; *R* (*R*w) = 0.102 (0.139). A total of 1465 independent reflections were used for the calculation.
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