Excited State Energy Migration and Photochromic Reaction in 1,2-Bis(2,4-dimethyl-3-thienyl)perfluorocyclopentene Single Crystal

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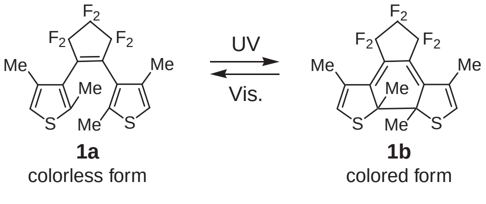
An excited state energy migration was found to compete with a photocyclization reaction in the single crystal of 1,2-bis(2,4-dimethyl-3-thienyl)perfluorocyclopentene.

Photochromic diarylethenes belong to the most promising photochromic compounds because of thermal stability of both isomers and fatigue-resistant property.[1] Some diarylethene derivatives can undergo photochromism even in the single-crystalline phase.[2] The colored forms of diarylethenes are stable in the crystals even at 100 °C. Such thermally irreversible crystalline photochromic materials are potentially applicable to various optoelectronic devices, such as holographic and three-dimensional optical recording memories and displays.[3–7]

In the course of study on single-crystalline photochromism of diarylethenes, we prepared a binary co-crystal composed of two types of diarylethenes.[8,9] Both diarylethenes can undergo photochromism in the home-crystals phase. However, in the co-crystals only one diarylethene selectively undergoes a photocyclization reaction to give the closed-ring isomer upon irradiation with ultraviolet light. This suggests that an excited state energy migration takes place in the crystal. The purpose of this paper is to examine the excited state energy migration in a single-component crystal of 1,2-bis(2,4-dimethyl-3-thienyl)perfluorocyclopentene (**1a**) (Scheme 1).

In solution, diarylethenes have two stable conformations with the aryl rings in mirror symmetry (named parallel conformation) and C_2 symmetry (named antiparallel conformation) in almost equal amounts, and they interconvert with each other in solution. The interconversion rate between the two conformations is much slower than the lifetime of photoexcited states.[10] The conrotatory cyclization can proceed only from the antiparallel conformation.[11] Diarylethenes in crystal cannot undergo the thermal interconversion between the two conformers. The photocyclization reactivity of diarylethenes in the crystalline phase depends on the distance between the reactive carbon atoms. When the distance is longer than 4.2 Å, the photocyclization cannot take place. When the distance is shorter than 4.2 Å, efficient photocyclization reactions take place.[12]



Scheme 1.

The diarylethenes in the crystal of **1a** have two or three conformations, which cannot interconvert with each other. X-ray crystallography indicates that the crystal system and space group of the crystal of **1a** are orthorhombic, *Pbcn*, and $Z = 4$.[13] A half of each molecule is crystallographically independent because the molecule is on a crystallographic 2-fold axis. The 2,4-dimethyl-3-thienyl groups are disordered by 180° rotation around a single bond, which joins the thiophene group and the perfluorocyclopentene ring, as shown in Figure 1. The ratio of the two disordered forms A/B was determined to be 0.59(1)/0.41(1). The ratio was constant even if the crystallization conditions such as recrystallization solvents and temperature were changed.

There are two possibilities of conformational distributions in the crystal. Table 1 shows a content of their conformers in the crystal. Case 1 has three conformers in the ratio of 34% (AA), 49% (AB), and 17% (BB). Case 2 consists of two conformers in the ratio of 59% (AA) and 41% (BB). The presence or absence of AB conformer cannot be determined by X-ray crystallography. Conformer AB is in the parallel conformation. Conformers AA and BB are in the antiparallel conformations. The distances between the reacting carbon atoms of AA and BB conformers are 5.35 and 3.91 Å, respectively. This indicates that the photocyclization reaction can proceed only from the photoactive antiparallel conformer (BB). If there is no excited state energy migration in the crystal, the photocyclization quantum yield cannot exceed 0.17 for case 1 or 0.41 for case 2. To know the presence

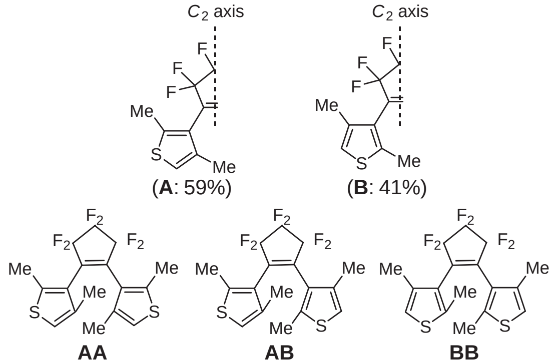


Figure 1. Conformations of **1a** in the crystal.

Table 1. Content of three conformers in the crystal of **1a**[a]

	AA	AB	BB
Case 1	34%	49%	17%
Case 2	59%	—	41%

[a]Determined by X-ray crystallographic analysis.[13]

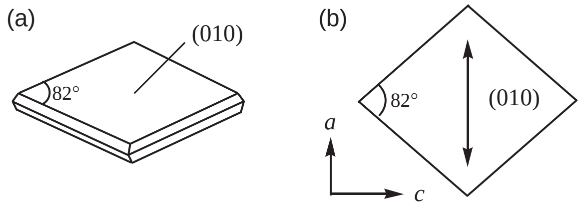


Figure 2. The shape of crystal **1a** (a) and the surface irradiated with polarized light (b). The arrow showed the transition-moment direction of visible absorption band of the closed-ring isomer.

of the excited state energy migration in the crystal, the photocyclization quantum yield of crystal **1a** was determined according to the method described in the literature.[14]

The (010) face of single crystal **1a** shown in Figure 2 was used for measuring photocyclization/cycloreversion quantum yields. Figure 3a shows absorption spectrum of the photoirradiated crystal of **1a**. The crystal turned red upon irradiation with 370 nm light. The absorption band appeared at 545 nm. The absorbance gradually increased by time upon ultraviolet light irradiation. During the measurement the conversion was less than 1%. The absorption coefficient of the photogenerated closed-ring isomer in the crystal was measured to be 5700 $M^{-1}\,cm^{-1}$ at 545 nm under polarized light. The rates of the photocyclization and cycloreversion reactions in the crystal was compared with that of 1,2-bis(2-ethyl-5-phenyl-3-thienyl)-perfluorocyclopentene (**2a**) and 1,2-bis(2,5-dimethyl-3-thienyl)-perfluorocyclopentene crystals as a reference, respectively.[14] Figure 3b shows the time-absorbance plots for the photocyclization. Based on the absorption coefficient and the rate of the photocyclization reactions, the photocyclization quantum yield ($\Phi_{o\rightarrow c}$) were determined to be 0.51. Table 2 shows the quantum yields in crystal and in hexane solution. The photocycloreversion quantum yield ($\Phi_{c\rightarrow o}$) was almost the same in crystal and in solution.

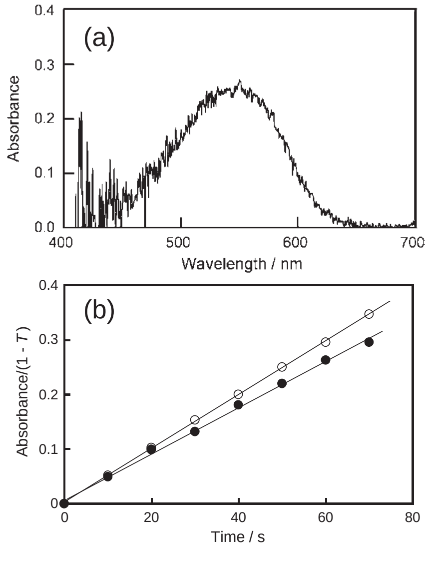


Figure 3. Absorption spectrum of the photoirradiated crystal of **1a** (a) and absorbance changes of crystals of **1a** at 545 nm (●) and **2a** at 630 nm (○) (b). *T* represents the transmittance in the crystal at 370 nm.

Table 2. Photocyclization and cycloreversion quantum yields of **1a/1b**

	In hexane[a]	In crystal
$\Phi_{o\rightarrow c}$	0.21 ± 0.02 (280 nm)[b]	0.51 ± 0.04 (370 nm)[b]
$\Phi_{c\rightarrow o}$	0.13 ± 0.02 (492 nm)[b]	0.12 ± 0.02 (533 nm)[b]

[a]Ref. 15. [b]Values in parenthesis show irradiation wavelength.

The photocyclization quantum yield of **1a** in hexane is 0.21.[15] This is due to the presence of the two stable conformers, of which only one conformer can be participated in the conrotatory photocyclization reaction. In the crystal, the quantum yield was much larger than that in the solution. The content of the photoactive BB conformer is less than 0.51 in both cases of 1 and 2 shown in Table 1. This indicates that the excited state energy migrates in crystal. The energy migration is considered to take place among the molecules with almost same energy level because the parallel and antiparallel conformers have very similar absorption spectra.[11]

In case 1, the content of the photoactive BB conformer is 0.17. Therefore, the excited state AA or AB conformers effectively transfer the energy to the BB conformer. The quantum yield of 0.51 means that the energy migration efficiency is estimated to be 86% under the assumption that the actual cyclization quantum yield of BB is 0.80.[14]

In case 2, the AB conformer is absent and the content of the photoactive conformer is 0.41. Therefore, the excited state AA conformer transfers the energy to the BB conformer. The quantum yield of 0.51 means the energy migration efficiency of 55%.

In conclusion, in both cases the excited state energy of the diarylethene molecules transfers to other diarylethene molecules in crystal. In other words, the photon energy absorbed by the AA or AB conformer is transferred to the reactive BB conformer in the crystal. The AA and AB conformers act as photosensitizers in the crystal.

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