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Photochromism of 1,2-Bis(5-*n*-alkyl-2-phenyloxazol-4-yl)perfluorocyclopentene Derivatives in Single-crystalline Phase

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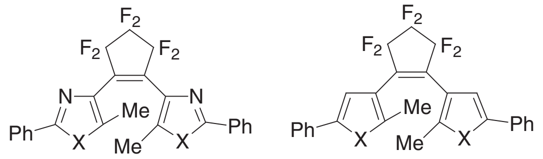
1,2-Bis(5-*n*-alkyl-2-phenyloxazol-4-yl)perfluorocyclopentenes were synthesized and their photochromic performance was examined in hexane solution as well as in single-crystalline phase.

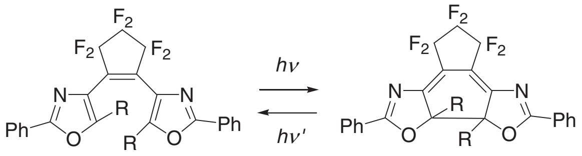
Photochromism has attracted considerable attention because of its potential ability for applications in molecular devices, such as optical memories and switches.[1,2] Among various thermally irreversible compounds, diarylethene derivatives are the most promising because of their fatigue resistance.[3–8] Some diarylethene derivatives undergo reversible photochromic reactions in single-crystalline phase. 1,2-Bis(5-methyl-2-phenyloxazol-4-yl)perfluorocyclopentene (**1a**) (Chart 1) shows normal photochromic performance in hexane solution, but its single crystal shows no photochromism.[9,10] Similar compounds, namely, 1,2-bis(5-methyl-2-phenylthiazol-4-yl)perfluorocyclopentene (**2a**),[9] 1,2-bis(2-methyl-5-phenyl-3-furanyl)perfluorocyclopentene (**3a**),[11] and 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene (**4a**),[12] show photochromism in hexane as well as in single-crystalline phase.

The reason why the single crystal of **1a** shows no photochromism in single-crystalline phase has not been clarified so far.[9,10] Long chains (such as ethyl, propyl, and butyl chains) of the substituent at the reaction positions in benzothiophene derivatives[13] play an important role in photochromism in single-crystalline phase. Here, we focused on the effect of the *n*-alkyl moiety on reactive carbon atoms. 1,2-Bis(5-*n*-alkyl-2-phenyloxazol-4-yl)perfluorocyclopentenes **5a**–**7a** were newly synthesized and their photochromic performance was evaluated in hexane solution as well as in single-crystalline phase (Scheme 1).



1a: X=O **2a**: X=S **3a**: X=O **4a**: X=S

Chart 1.



1a: R=Me
5a: R=Et
6a: R=*n*-Pr
7a: R=*n*-Bu

1b: R=Me
5b: R=Et
6b: R=*n*-Pr
7b: R=*n*-Bu

Scheme 1.

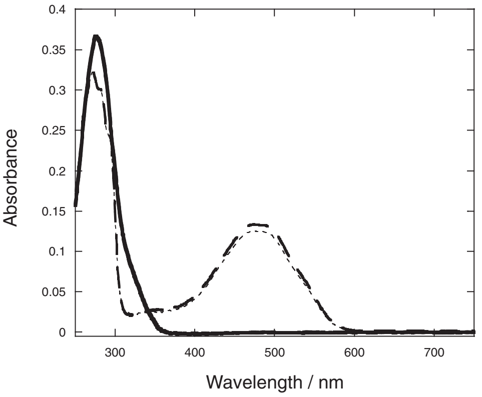


Figure 1. Absorption spectra of **5a** (solid line), **5b** (dashed line), and **5** in the photostationary state (dotted line) under irradiation with 313-nm light in hexane (9.9×10^{-6} mol L^{-1}).

Figure 1 shows the absorption spectral changes of **5** in hexane. Upon irradiation with 313-nm light, the colorless hexane solutions turned orange, in which the visible absorption maximum was observed at 474 nm. The orange color disappeared by irradiation with visible light ($\lambda > 440$ nm), and the absorption spectrum returned to that of the initial state. Just as **5**, diarylethenes **6** and **7** show photochromism in hexane (see Supporting Information; SI[20]).

A single crystal of **5** was obtained by recrystallization in hexane. This single crystal of **5** turned brown upon irradiation with 366-nm light. Figure 2 shows the color change of the crystal under a polarized microscope. Before photoirradiation, the crystal was colorless (Figures 2a and 2b). Upon irradiation with 366-nm light, the crystal turned brown at a certain angle $\theta = 0°$ (Figure 2c). When the crystal was rotated by as much as 90° (Figure 2d), it turned pale yellow. The clear dichroism from brown to pale yellow indicates that the closed-ring isomer is regularly oriented in the crystal. Figure 2e shows the polarized absorption spectra of the crystal at $\theta = 0°$ (Figure 2c) and $\theta = 90°$ (Figure 2d). The maximum absorbance of the brown crystal at 500 nm appeared at $\theta = 0°$ and $\theta = 180°$. Similarly, the single-crystalline photochromism was observed in **6** and **7**.

To clarify the conformation of the single crystal, we analyzed single crystals of **5a**–**7a** by X-ray crystallography. Figure 3a shows an ORTEP drawing of a photochromic single crystal of **5a**.

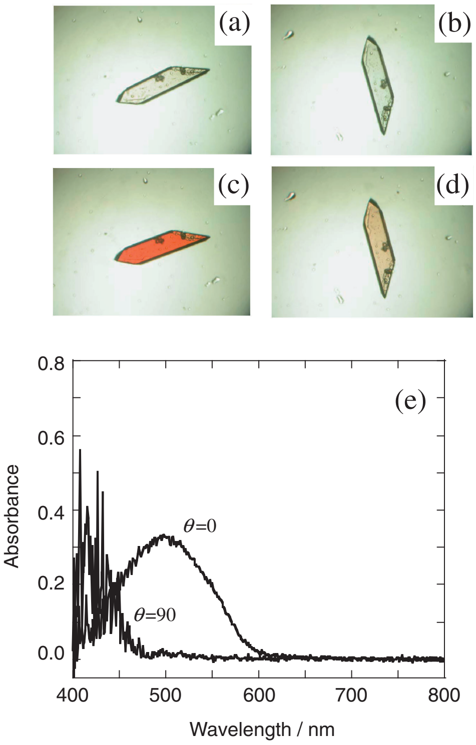


Figure 2. Photographs of single crystal of **5** under polarized light before (a: $\theta = 0°$; b: $\theta = 90°$) and after (c: $\theta = 0°$; d: $\theta = 90°$) irradiation with 366-nm light. (e) Polar absorption spectra of **5**.

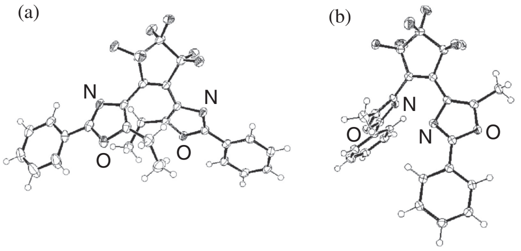


Figure 3. ORTEP drawings of (a) **5a** and (b) **1a**.

The ethyl derivative **5a** is packed in an antiparallel conformation in its crystal form. The distance between reactive carbon atoms is 0.374 nm, which is sufficiently close for conrotatory cyclization to occur. In general, an antiparallel conformation and a distance shorter than 0.42 nm are necessary for the reaction to take place.[14] The propyl derivative **6a** and the butyl derivative **7a** are packed in photoreactive antiparallel conformations in the crystal forms.[15–17] The distances between the reactive carbon atoms are 0.356 (for **6a**) and 0.349 nm (for **7a**).

Figure 3b shows an ORTEP drawing of a single crystal of **1a**.[9] **1a** is structurally packed in a twisted conformation in its crystal forms, and the distances between the reactive carbon atoms are 0.516 nm. This does not fulfill the requirement of photochromism in single-crystalline phase.

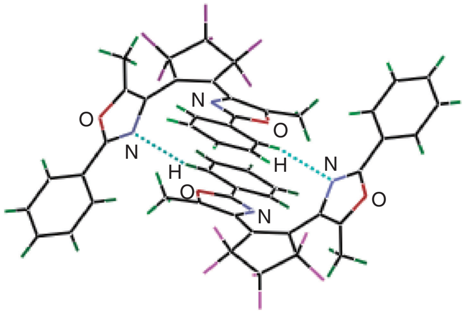


Figure 4. Molecular packing diagram of **1a**. The blue line indicates the intermolecular interaction (N···H–C).

From the structural analysis of **1a**, we observed an interaction between oxazole and phenyl rings. Figure 4 shows the molecular packing diagrams of the crystal of **1a**. The intermolecular hydrogen bond N···H–C is present.[18] The N···H distance and the angle in the N···H–C interaction are 0.249 nm and 166.41°, respectively. The existence of the intermolecular interaction led to the twisted conformation, and it caused no photochromism in single-crystalline phase. It was reported that the single crystal of 2-methylpyrazine has N···H–C structures, and that the N···H distance and the angle in the N···H–C interaction are 0.244–0.272 nm and 152–163°, respectively.[19] The N···H distances for **5a**, **6a**, and **7a** were 0.381, 0.357, and 0.407 nm, respectively. The results revealed that there was no N···H–C interaction in the crystals of **5a**–**7a**. From the molecular packing diagrams of **5a**–**7a**, the alkyl moieties such as ethyl, propyl, and butyl groups were oriented parallel to the 2-phenyloxazole ring. The crystal packing diagrams of **1a** and **5a**–**7a** revealed that all the phenyl and oxazole rings as aryl moieties of the open-form diarylethene **1a** and **5a**–**7a** were almost located in the same plane (see SI[20]).

In Figure 4, there are two types of aryl moiety in the open-form diarylethene **1a**. One is a 2-phenyloxazole unit (A-unit), which has an intermolecular interaction on a nitrogen atom. The other is a 2-phenyloxazole unit (B-unit), which has an intermolecular interaction on a phenyl ring. The molecular packing diagram of **1a** shows that these A- and B-units pile each other from the view down the *c* axis (see SI[20]). The distance between the methyl group on A-unit and the oxazole ring on B-unit is 0.284 nm. If the methyl groups replace the bulky ethyl groups (such as **5a**), the oxazole ring on the B-unit is pushed by the ethyl group on A-unit. The bond between the B-unit and perfluorocyclopentene then rotates, the N···H bond is cleaved, and the crystal packing in **5a** is formed. It seems that the same mechanism works in the diarylethenes **6a** and **7a**.

In summary, we have synthesized the oxazole derivatives **5a**–**7a**, which showed photochromism in hexane as well as in single-crystalline phase. X-ray crystallography showed that these compounds were oriented in photoactive antiparallel conformations. We determined the reason why the methyl derivative **1a** showed no photochromism in single-crystalline phase. We also observed a N···H–C intermolecular interaction in the compound. The interaction led to the photoinactive conformation of the single crystal. These findings can greatly contribute to the study of photochromic oxazole derivatives.

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15 Crystal data for **5a**: $C_{27}H_{20}F_6N_2O_2$, $M_r = 518.45$, triclinic, space group $P\bar{1}$, $a = 9.8195(11)$ Å, $b = 11.5131(13)$ Å, $c = 11.9448(14)$ Å, $\alpha = 111.100(2)°$, $\beta = 103.269(2)°$, $\gamma = 92.253(2)°$, $V = 1215.1(2)$ Å^3, $Z = 2$, $D_{\mathrm{calcd}} = 1.417$ g cm^{-3}, $R_1 = 0.0588$ for 4936 observed reflections with $I > 2\sigma(I)$ from 13090 unique reflections. CCDC deposition number: 814585.

16 Crystal data for **6a**: $C_{29}H_{24}F_6N_2O_2$, $M_r = 546.50$, orthorhombic, space group $Pbcn$, $a = 20.8983(5)$ Å, $b = 11.6318(3)$ Å, $c = 10.6689(2)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 2593.45(10)$ Å^3, $Z = 4$, $D_{\mathrm{calcd}} = 1.400$ g cm^{-3}, $R_1 = 0.0547$ for 2288 observed reflections with $I > 2\sigma(I)$ from 15455 unique reflections. CCDC deposition number: 814583.

17 Crystal data for **7a**: $C_{31}H_{28}F_6N_2O_2$, $M_r = 574.55$, monoclinic, space group $P2_1/n$, $a = 9.6630(9)$ Å, $b = 25.974(2)$ Å, $c = 10.8475(10)$ Å, $\alpha = 90°$, $\beta = 90.825(2)°$, $\gamma = 90°$, $V = 2722.3(4)$ Å^3, $Z = 4$, $D_{\mathrm{calcd}} = 1.402$ g cm^{-3}, $R_1 = 0.0539$ for 4799 observed reflections with $I > 2\sigma(I)$ from 30280 unique reflections. CCDC deposition number: 814584.

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20 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.