Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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Version of record first published: 31 Aug 2006

To cite this article: Seiya Kobatake, Masakazu Morimoto & Masahiro Irie (2005): Nanolayered Structures in Photochromic Crystal of 1,2-Bis(2-methyl-5-p-methoxyphenyl-3-thienyl)perfluorocyclopentene, Molecular Crystals and Liquid Crystals, 431:1, 523-527

To link to this article: http://dx.doi.org/10.1080/15421400590947306

Mol. Cryst. Liq. Cryst., Vol. 431, pp. 223/[523]–227/[527], 2005

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400590947306

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Nanolayered Structures in Photochromic Crystal of 1,2-Bis(2-methyl-5-p-methoxyphenyl-3-thienyl) perfluorocyclopentene

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*A photochromic diarylethene, 1,2-bis(2-methyl-5-p-methoxyphenyl-3-thienyl)-perfluorocyclopentene (***1a***), forms four kinds of polymorphic crystals by recrystallization from the hexane solution. X-ray crystallographic analysis of the needle crystals among four polymorphic forms indicated that the diarylethene is orientated into herringbone nanolayered structures. The crystal exhibited photochromism upon photoirradiation. Alternate nanolayered structures composed of open- and closed-ring isomers were formed by irradiation with polarized visible light after irradiation with ultraviolet light.*

Keywords: diarylethene; nanolayered structure; photochromism; single crystal

INTRODUCTION

Photochromic compounds which exhibit the photochromic reactivity in the crystalline phase are very rare [1]. In most cases photogenerated

This work was partly supported by Grants-in-Aid for Scientific Research on Priority Areas (417) (15033252), Young Scientists (A) (16685014), Scientific Research (S) (15105006), and the 21st Century COE Program from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

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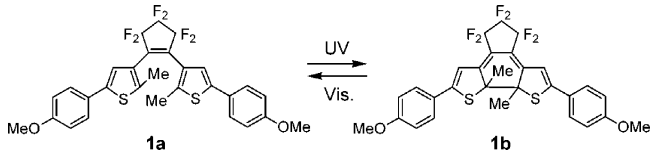
isomers in the crystal are thermally unstable [2–6]. We found that some diarylethene derivatives undergo photochromism in the single-crystalline phase and the photogenerated colored isomers are stable in the dark [7–13]. Thermally irreversible and fatigue resistant photochromic crystals can be potentially applied to various optoelectronic devices, such as holographic and three-dimensional optical recording memories [14–17].

During the course of study of single-crystalline photochromism, we found that 1,2-bis(2-methyl-5-*p*-methoxyphenyl-3-thienyl)perfluorocyclopentene (**1a**) forms four polymorphic crystals when recrystallized from the hexane solution [18]. This paper is focused on photochromism and a packing diagram of the needle crystals among four polymorphic forms. The diarylethene in the crystals was packed in herringbone structures.



RESULTS AND DISCUSSION

X-ray Crystallographic Analysis

When diarylethene **1a** was recrystallized from the hexane solution, four different shapes of crystals were obtained. X-ray crystallographic analysis of the crystals indicated that they are polymorphic forms. One of them has needle shapes. The needle crystals had a space group of monoclinic $P2_1/c$ and $Z = 4$ [18]. The unit cell volume was 2620.1(9) Å^3. Figure 1 shows ORTEP drawing of **1a**. The photocyclization reactivity in the crystal depends on the distance between the reactive carbon atoms [19]. When the distance is larger than 4.2 Å, the photocyclization reaction does not take place in the crystalline phase. However, when the distance is shorter than 4.0 Å, the diarylethenes can undergo an efficient photocyclization reaction. The distance between the reactive carbon atoms of **1a** in the crystal was 3.59 Å. The distance was shorter enough for the photocyclization reaction to take place in the crystalline phase.

Figure 2 shows a molecular packing diagram of **1a** in the crystal. The long axes of two diarylethene molecules in layers A and B are perpendicular to each other. The diarylethenes in the same direction are packed in layered structures. In other words, the crystal has herringbone structures.

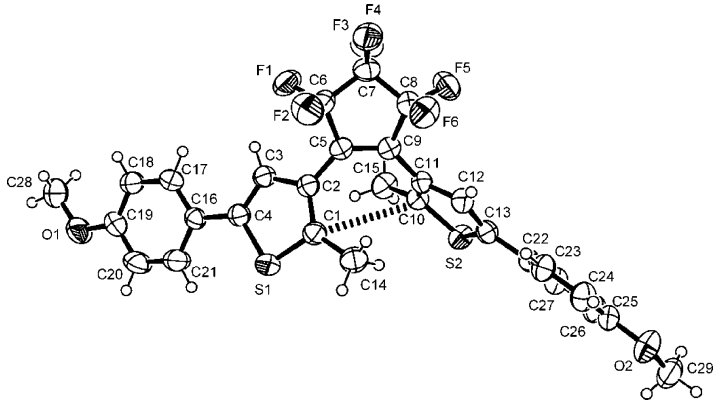


FIGURE 1 ORTEP drawing of **1a**. The ellipsoids are drawn at 50% probability level. The distance between the reactive carbon atoms, C1–C10, shown by a dashed line was 3.59 Å.

Photochromism in a Single-Crystalline Phase

Single crystal **1a** turned blue upon irradiation with 370-nm light. The photogenerated blue color is due to the formation of the closed-ring isomer **1b**. The photogenerated blue color of the crystals disappeared upon irradiation with visible light ($\lambda > 500$ nm). Figure 3 shows polarized absorption spectra of the colored crystal at a certain angle ($\theta = 45^\circ$). When the crystal was rotated as much as 90°, the absorbance of the crystal was not changed ($\theta = 135^\circ$). Well-defined absorption anisotropy was not observed as can be seen from Figure 3b. Molecules are packed in two different orientations, which are almost perpendicular to each other. This suggests that the diarylethenes in both layers A and B were converted to the closed-ring isomers.

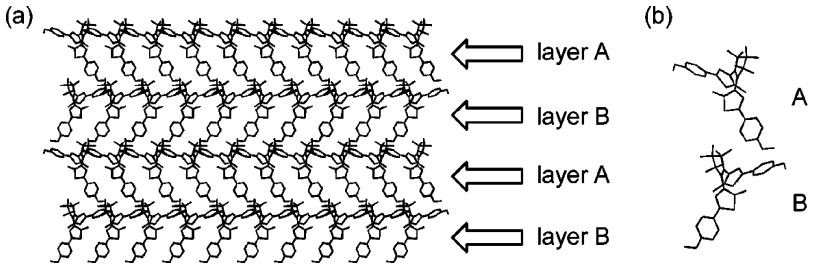


FIGURE 2 Molecular packing diagram viewed from the (100) face (a) and the typical molecular structures (b) of crystal **1a** in layers A and B.

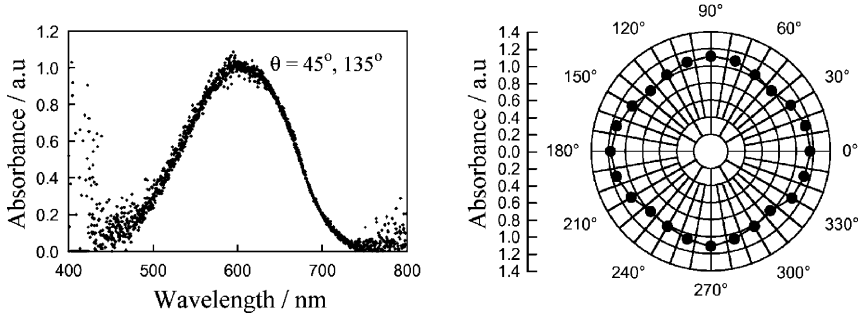


FIGURE 3 Polarized absorption spectra (left) and the polar plots of the absorbance at 600 nm (right) after irradiation with nonpolarized 370-nm light.

Partially Bleaching Reaction

As described above, the diarylethene molecules in the crystal are packed as shown in Figure 2. The long axes of the molecules are oriented perpendicularly to each other. This suggests that linearly polarized light can selectively bleach the closed-ring isomers. The colorless crystal was irradiated with 370-nm non-polarized light to give the blue-colored crystal. The diarylethenes in the layers A and B were converted to the closed-ring isomers. When the colored crystal was irradiated with linearly polarized light ($\lambda > 570$ nm) in the direction of 135°, the colored closed-ring isomers along the polarized light were preferentially bleached and the molecules oriented perpendicularly to the irradiated polarized light were hardly bleached. Figure 4 shows the polarized absorption spectra and the polar plots. The order

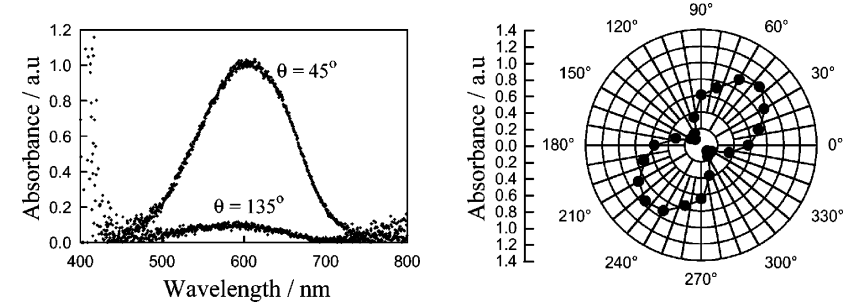


FIGURE 4 Polarized absorption spectra (left) and the polar plots of the absorbance at 600 nm (right) after irradiation with nonpolarized 370-nm light and then partial photobleaching upon irradiation with polarized visible light ($\lambda > 570$ nm).

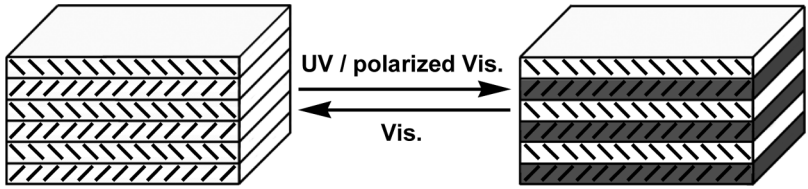


FIGURE 5 Schematic illustration for photochromism of single crystal **1a**. Black-indicated layers in the right side indicate the layers of the colored closed-ring isomers.

parameter $((A_{||} - A_{\perp})/(A_{||} + 2A_{\perp}))$ was determined to be 0.75 after the partial bleaching. The increase in the order parameter up to 0.75 suggests that the partially bleaching reaction took place under the polarized light. This indicates that molecules in only layer A returned to the initial colorless open-ring isomers and that the crystal was composed of alternate open- and closed-ring isomer nanolayered structures, as shown in Figure 5.

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