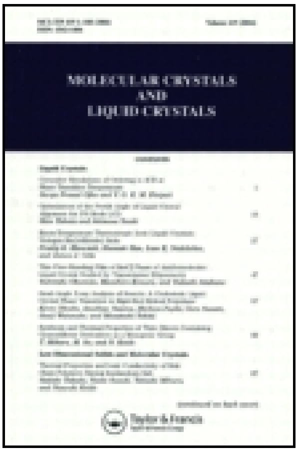

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Photochromism of Single Crystalline Diaruthenes

Masahiro Irie [a] , Thorsten Lifka [a] & Kingo Uchida [a]

[a] Faculty of Engineering, Kyushu University, Hakozaki 6-10-1, Higashi-ku, Fukuoka, 812, Japan

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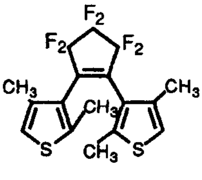
PHOTOCHROMISM OF SINGLE CRYSTALLINE DIARYLETHENES

MASAHIRO IRIE, THORSTEN LIFKA, and KINGO UCHIDA
Faculty of Engineering, Kyushu University,
Hakozaki 6-10-1, Higashi-ku, Fukuoka 812, Japan

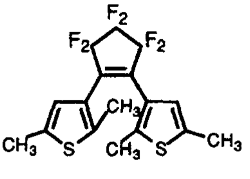
Abstract Dithienylperfluorocyclopentenes were found to undergo reversible photocyclization in the crystalline phase. Both the open-form colorless and photogenerated closed-ring colored isomers were thermally stable even at 100 ℃. Coloration / decoloration cycles could be repeated more than 100 times with keeping the crystal shape. Regular alignment of the colored isomers in the crystal was evidenced by the absorption measurement under linearly polarized light.

INTRODUCTION

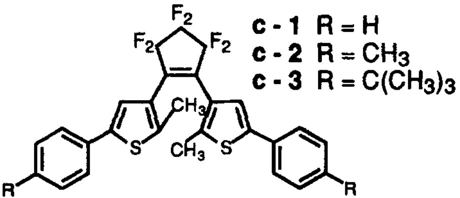
Recently we have developed a new class of photochromic compounds named "diarylethenes", which undergo thermally irreversible and fatigue resistant photochromic reactions.[1-10] When the compounds have thiophene or benzothiophene aryl groups, both isomers, initial colorless and photogenerated colored isomers, are thermally stable even at 200 ℃, and coloration / decoloration cycles can be repeated more than ten thousands time with keeping adequate photochromic performance. The compounds are potentially useful for various opto-electric devices, such as optical memory media and photo-optical switching devices.[1,5,9,10] During the course of study of substituted dithienylperfluorocyclopentenes we found that following diarylethenes undergo photochromic reactions in the single crystalline phase.[2]



a



b



c - 1 R = H
c - 2 R = CH_3
c - 3 R = $C(CH_3)_3$

c- 1,2,3

Although a great number of photochromic compounds have been so far reported, compounds which show photochromism in a crystalline phase are very rare, and in most crystalline photochromic systems the photogenerated colored isomers are thermally unstable at room temperature. We report here photochromic diarylethenes, which are stable in both isomer states even at 100 ℃ and show photoreactivity in the single crystalline phase.

RESULTS AND DISCUSSION

Upon exposure to 313 nm light the powder of compound **a** changed from white to red, and the red color disappeared by irradiation with visible light (> 450 nm). 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 **a** was used. The absorption maximum of the colored form was observed at 530 nm, which is almost similar to the closed-ring form of **a** in hexane solution (λmax = 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) without destruction of the crystal shape.

The photoreactivity in the crystalline phase was further confirmed by measuring the absorption spectrum 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 lattice. X-Ray analysis revealed that the two peaks reflect the scattered arrow-shaped packing of the molecules in the crystal.

When the thiophene rings have only two methyl groups (compounds

a and **b**), the dithienylethenes underwent photochromism in the crystalline phase. However, bis(2,4,5-trimethylthiphen-3-yl)perfluorocyclopentene having three methyl groups in the thiophene rings did not show any photochromic reactivity in the crystalline phase, though the reactivity in hexane solution is very similar to compounds **a** and **b**. X-Ray analysis of the crystal structure showed that compounds **a** and **b** have an anti-parallel conformation, while the above non-reactive dithienylethene has a parallel conformation in the crystalline phase. The molecules in the parallel conformation can not undergo conrotatory photocyclization reactions. The reactivity difference is dependent upon the conformation in the crystal.

Single crystals of **c-1**, **2** and **3** turned blue by irradiation with 366 nm light. The absorption maxima were similar to the closed-ring forms in hexane (λmax = 580 nm). Although the coloration quantum yields of these three compounds were very similar each other in hexane solution (Table 1), the reactivity strongly depended on the substituent R in the crystalline phase. When the substituent R is H or $C(CH_3)_3$, the crystals showed very quick coloration upon irradiatlon with 366 nm light. On the other hand, the crystal slowly turned blue and the degree of coloration remained low when R is CH_3. The crystal structure of **c-2** suppressed the photocyclization. In all cases the thermally stable blue color can be bleached completely by exposing the crystals to visible light (> 500 nm). From X-ray analysis of the crystal structures we tentatively attribtited the difference in the coloration

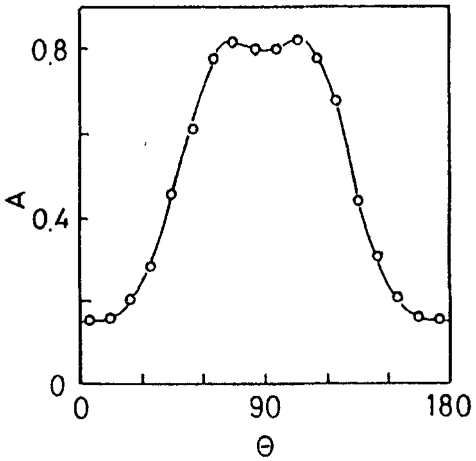


Figure 1. Rotation angle dependence of the absorption intensity of a photogenerated single crystal **a** at 530 nm.

Table 1 Quantum yield of compund **c-1**, **2**, and **3** in hexane solution.

R	$\Phi_{open \rightarrow close}$ at 313 nm	$\Phi_{close \rightarrow open}$ at 492 nm
H	0.68	0.013
CH_3	0.65	0.0097
$C(CH_3)_3$	0.70	0.011

behavior among compounds **c-1**, **2** and **3** to different molecular packing by the substituent R.

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