Photochemistry

# Conformational Control of Photochromic Reactivity in a Diarylethene Single Crystal**

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Photochromism is the result of reversible photoisomerization between two isomers that have distinct absorption spectra.[1,2] The two isomers differ from one another not only in their absorption spectra but also in various physical and chemical

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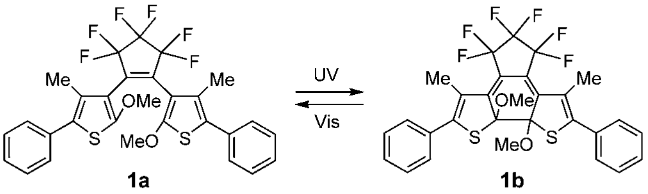
properties, such as refractive index, dielectric constant, oxidation–reduction potential, and geometric structure. Among a number of photochromic compounds, diarylethenes with heterocyclic aryl groups such as thiophene or benzothiophene are the most promising candidates for applications in optical memories and switches, owing to their *thermally irreversible* and fatigue-resistant photochromic performance.[3,4]

Photochemical reactions in the crystalline state have been intensively investigated since the pioneering work of Schmidt and co-workers in the early 1960s.[5–11] Although many photochromic compounds have been reported already, compounds that exhibit photochromism in the crystalline state are rare.[12,13] Typical photochromic compounds such as spiropyran and azobenzene are not photochromic in the crystalline phase, as large geometric structural changes are prohibited in crystals. However, some diarylethene derivatives can exhibit photochromism even in the single-crystalline phase.[14–16] Depending on the particular structure, diarylethene crystals turn yellow, red, blue, or green upon irradiation with UV light. The color of the crystal is thermally stable, and never returns to the initial colorless state in the dark. Diarylethene derivatives are the only photochromic chromophores that exhibit *thermally irreversible* photochromism in the single-crystalline phase.[17]

Recently, our group prepared alternating nanolayered or mosaic structures composed of two kinds of diarylethene derivatives and examined their photochromic performance.[18] When the cocrystals were irradiated with UV light, only one of the derivatives underwent photochromism. As a result, the irradiated co-crystals consisted of an alternating layered structure of open- and closed-ring isomers, or of a three-dimensional alternating alignment structure of open- and closed-ring isomers. During the course of our studies into single-crystalline photochromism, we found that crystals of 1,2-bis(2-methoxy-4-methyl-5-phenyl-3-thienyl)perfluorocyclopentene (**1a**) have a novel molecular-packing structure in which two different conformations are alternately packed. Herein we report single-crystalline photochromism and the important role that conformation plays in photochromic reactivity.

Single crystals of **1a** were obtained by recrystallization from acetone. The crystals have well-developed (001), ($\bar{1}01$), ($00\bar{1}$), and ($10\bar{1}$) surfaces. Other surfaces are not well-developed and were not determined. The crystals of **1a** turned blue upon irradiation at a wavelength of 366 nm (Scheme 1). To confirm that the blue color is a result of the closed-ring isomer **1b**, the blue-colored crystal was dissolved in hexane. The solution in hexane showed a visible absorption maximum at 617 nm, which is the same as that of the isolated closed-ring isomer **1b**. The blue color of the crystal disappeared upon irradiation with visible light ($\lambda > 500$ nm). The crystal of **1a** underwent photochromism.



***Scheme 1.*** Photochromic isomerization of diarylethene **1a** to the closed-ring structure **1b**.

The color of the crystal was observed with a polarizing microscope in which the polarizer and analyzer were set in parallel with each other. The UV-irradiated, colored crystal was placed on the sample stage and rotated. Viewed from the (001) surface at a given starting angle, the crystal showed a strong blue color. Upon rotation by 90°, the color of the crystal disappeared; the blue color reappeared at a rotation of 180°. The clear dichroism indicates that the photogenerated closed-ring isomers are regularly oriented in the crystal and that the photochromic reaction takes place in the crystal lattice.[14]

The crystal and molecular structures of **1a** were determined by X-ray crystallographic analysis. The crystal belongs to a monoclinic system with space group $P2_1/c$, and $Z = 8$ (Experimental Section). The two diarylethene conformers A and B are independent in the crystal. Figure 1 shows ORTEP renderings of the two conformers. The two geometric structures are different from each other, but in either case the molecules are arranged in an antiparallel orientation. Figure 2 shows the molecular packing diagrams viewed from the *b* and *c* axes. Blue- and red-rendered structures represent conformers A and B, respectively. In the crystal, the two conformations are alternately packed in layered structures with a layer thickness of $\approx 1$ nm.

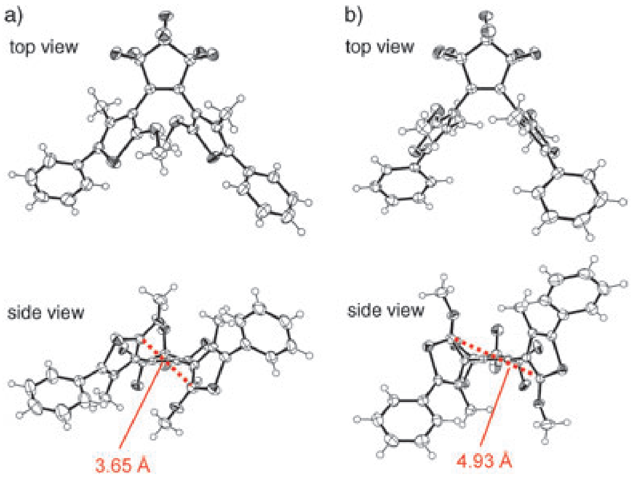


***Figure 1.*** ORTEP renderings of a) conformer A, and b) conformer B in crystals of **1a** with 50% probability displacement ellipsoids. Distances between reactive carbon atoms are indicated, and highlighted with dashed lines.

Our group previously reported that the photocyclization reactivity of diarylethenes in the single-crystalline phase is controlled by the distance between the reactive carbon atoms in the antiparallel orientation.[19] If the distance exceeds 4.2 Å, the photocyclization reaction does not take place. However, if distance is shorter than 4.0 Å, the diarylethenes can undergo an efficient photocyclization reaction. The

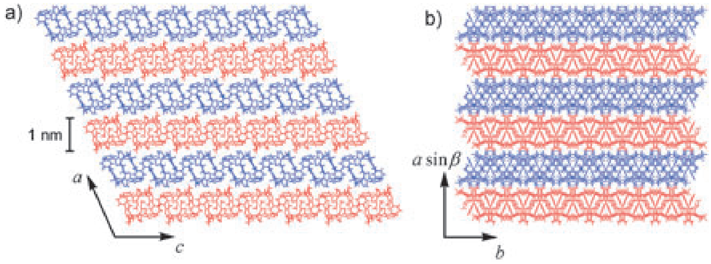


*Figure 2.* Molecular-packing diagrams of **1a** viewed from a) the *b* axis and b) the *c* axis. Blue- and red-colored molecules show photoactive and photo-inactive diarylethene conformers A and B, respectively.

distance dependence of photochromic reactivity is similar to the observation of photochemical C–C bond formation in the crystalline phase reported by Schmidt and co-workers.[5] As shown in Figure 1, conformer A has a distance of 3.65 Å between the reactive carbon atoms, whereas the analogous distance in conformer B is 4.93 Å.

Thin microcrystals of diarylethene **1a** were prepared by sublimation on a thin glass plate by heating at 104 °C. The typical crystal size was ≈ $10 \times 10 \times 5\ \mu m^3$. Crystal shapes and reversible color changes were similar to those of crystals obtained from a solution in acetone. Microcrystals were irradiated at 366 nm (≈ $26\ mW\,cm^{-2}$). The molar ratio of open- to closed-ring isomers (**1a**/**1b**) after irradiation with UV light was determined by HPLC (silica gel column, hexane/ethyl acetate (98:2) as eluent). Figure 3 shows the time dependence of the conversion ratio for the photocyclization reaction in the crystal. Upon irradiation at 366 nm, **1a** was efficiently converted into closed-ring isomer **1b** by as much as 50 % after irradiation for 4 h. This indicates that half the molecules packed in the crystal undergo the photochromic reaction.

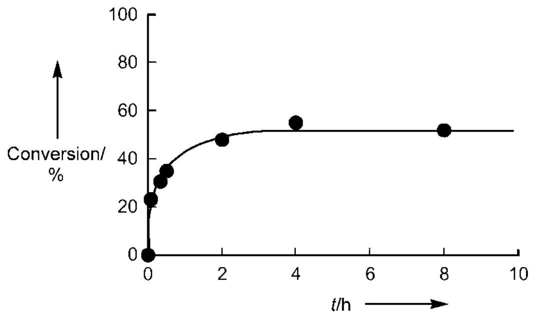


*Figure 3.* The progress of the photocyclization reaction over time in the diarylethene microcrystal of **1a** by irradiation at $\lambda = 366$ nm.

Single crystals of **1a** were prepared by recrystallization from acetone, and were used for X-ray crystallography in situ. An appropriate size for crystallographic analysis was obtained by cutting the crystals to final dimensions of ≈ $0.3 \times 0.2 \times 0.05\ mm^3$. A single crystal was then irradiated with UV light. A high conversion ratio for such a thick crystal cannot be expected, owing to the inner-filter effect of absorption.[20] After irradiation at 366 nm (≈ $5\ mW\,cm^{-2}$) for 5 h, the closed-ring isomer **1b** was detected by X-ray diffractometry. The space group was not changed, and the unit-cell dimensions were similar to those initially determined (Experimental Section). The molecular structure is shown in Figure 4. The positions of the sulfur atoms, the reactive carbon atoms, and the methoxy groups in the closed-ring isomer were obtained only from conformer A. No peak that corresponds to the closed-ring isomer of conformer B was observed. This result indicates that only conformer A underwent the photochromic reaction upon irradiation with UV light, and that conformer B remained inactive. The difference in the distance between the reactive carbon atoms explains the different reactivity of the two conformers. The conversion saturation at 50 % shown in Figure 3 is also explained by the selective photoreaction. The conformational difference controls the reactivity, as observed for chiral organic salts.[21]

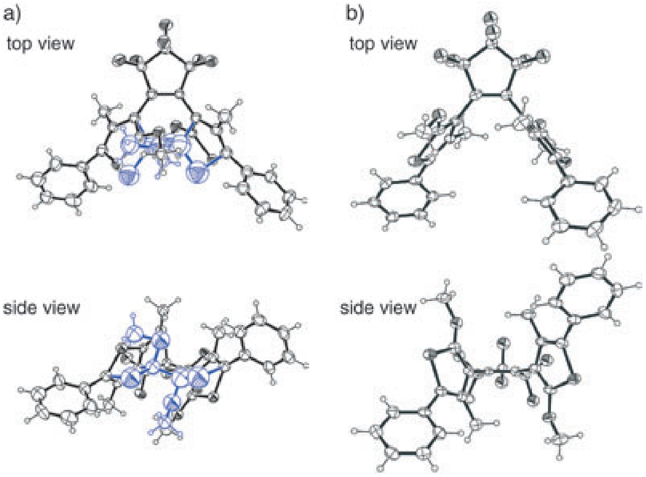


*Figure 4.* ORTEP renderings of a) conformer A and b) conformer B in photoirradiated crystals of **1a** with 30 % probability displacement ellipsoids. The photogenerated closed-ring isomer **1b** is indicated in blue. The conversion ratio obtained by X-ray crystallographic analysis was 8 %.

In conclusion, diarylethene **1a** is packed in two different conformations in the crystalline state, and the two conformers exhibit different photochemical reactivities. The periodic refractive index change in the crystal structure could be potentially useful in future photonic devices, such as one-dimensionally periodic photonic crystals and three-dimensional optical memory.[22]

## Experimental Section

Single crystals were observed with a Nikon E600POL polarizing microscope. Polarizer and analyzer were set in parallel with each other. Photoirradiation was carried out with a mercury short arc lamp (100 W). The wavelength ($\lambda = 366$ nm) was selected by passing the light through a band-pass filter. X-ray crystallographic analysis of single crystals was performed with a Bruker SMART CCD X-ray diffractometer or a Rigaku RAXIS X-ray diffractometer with $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) and a graphite monochromator. Crystal cell constants were calculated by global refinement. The structure was solved by direct methods with SHELXS86[23] and refined by full least-squares on $F^2$ with SHELXL97.[24]

**1a** (Synthesis details in the Supporting Information): m.p. 117.5–118.5 °C; UV/Vis (*n*-hexane): $\lambda_{max}$ ($\varepsilon$) = 288 nm (28 600 $\text{M}^{-1}\,\text{cm}^{-1}$); $^1$H NMR (200 MHz, $CDCl_3$/TMS): $\delta$ = 2.10 (s, 6 H; Me), 3.78 (s, 6 H; MeO), 7.2–7.5 ppm (m, 10 H; Ph); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 14.1 (Me), 61.3 (MeO), 110.2 (3-thienyl), 111.5 ($CF_2$), 116.0 ($CF_2$), 124.4 (5-thienyl), 127.1 (Ph), 128.6 (Ph), 129.1 (Ph), 130.5 (4-thienyl), 134.1 (Ph), 139.5 (C=C), 163.4 ppm (2-thienyl); FAB-HRMS: *m*/*z*: calcd for $C_{29}H_{22}F_6O_2S_2$ $[M]^+$: 580.0965; found: 580.0966.

Crystal data for **1a**: $C_{29}H_{22}F_6S_2O_2$; monoclinic; space group $P2_1/c$; $a = 24.036(5)$, $b = 10.017(2)$, $c = 24.141(6)$ Å, $\beta = 114.104(4)°$, $V = 5306(2)$ Å$^3$; $Z = 8$; $T = 123(2)$ K; $M = 580.61$; $\mu(\text{Mo}_{K\alpha}) = 0.269\ \text{mm}^{-1}$, 30 557 reflections measured, 11 264 independent reflections. Final $R_1$ $[I > 2\sigma(I)] = 0.0456$, $wR_2$ (all data) = 0.1202.

Crystal data for **1a**/**1b** (photoirradiated crystal): $C_{29}H_{22}F_6S_2O_2$; monoclinic; space group $P2_1/c$; $a = 24.040(7)$, $b = 9.929(3)$, $c = 24.191(7)$ Å, $\beta = 113.897(7)°$, $V = 5279(3)$ Å$^3$; $Z = 8$; $T = 123(2)$ K; $M = 580.61$; $\mu(\text{Mo}_{K\alpha}) = 0.271\ \text{mm}^{-1}$, 38 733 reflections measured, 12 116 independent reflections. Final $R_1$ $[I > 2\sigma(I)] = 0.0794$, $wR_2$ (all data) = 0.1690.

CCDC-253 671 (**1a**) and -253 672 (**1a**/**1b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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