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Photochromic reactivity of a dithienylethene dimer

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Abstract

Photochromic reactivity of a dithienylethene dimer, 5-(2-(3,4-dimethyl-2-thienyl))-3,3,4,4,5,5-hexafluorocyclopent-1-enyl-2-(2-(2,4-dimethyl-3-thienyl))-3,3,4,4,5,5-hexafluorocyclopent-1-enyl-3,4-dimethylthiophene, was studied in solution as well as in the crystalline phase. In solution two kinds of closed-ring form isomers were reversibly produced upon irradiation with ultraviolet light, while in the crystalline phase only one kind of closed-ring form isomer was produced. The different reactivity was attributed to the difference in the distance between two reactive centers in the crystal.

Keywords: Photochromic reactivity; Dithienylethene dimer; Ultraviolet light

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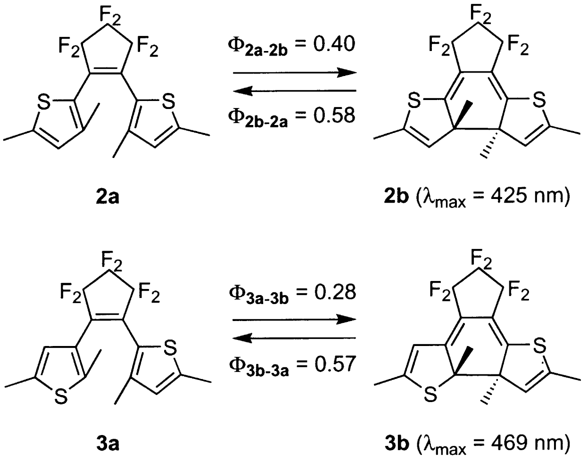
1. Introduction

Light-induced reversible isomerization between two forms having different absorption spectra is referred to photochromism [1], and compounds which are capable of these reactions are called photochromic compounds. Photochromic compounds, in general, undergo thermally reversible photoreactions. Photogenerated isomers return to the initial isomers in the dark. Such thermally reversible photochromic compounds cannot be applied to optoelectronic devices, such as optical memory, photo-optical switching and display [2]. Recently several thermally irreversible photochromic compounds, such as furylfulgides [3], diarylethenes [4], and phenoxynaphthacenequinone [5] have been developed. Among the compounds, diarylethenes with heterocyclic aryl groups are the most promising photochromic compounds for the applications because of their high fatigue resistance. Diarylethenes undergo the photochromic reactions (Scheme 1) [4].

The open-ring form isomer has two conformations, anti-parallel and parallel ones, and the conrotatory cyclization can proceed only from the anti-parallel conformation [6]. The parallel conformer cannot undergo the photocyclization. Upon irradiation with ultraviolet light, the open-ring anti-parallel conformer converts to the closed-ring form isomer and changes the color. The open-ring isomer has absorption in the ultraviolet region, while the closed-ring isomer has it in the visible region. Upon irradiation with visible light the colored closed-ring isomer returned to the initial colorless open-ring isomer.

When thiophene rings are attached to the ethene moiety at 2-position as the aryl groups, the absorption spectrum of the closed-ring isomer shows a blue shift in comparison with that of the dithienylethene with 3-thienyl groups. The blue shift is attributed to that π-conjugation in the closed-ring isomer is localized in the cyclohexadiene structure [7]. π-Conjugation structures and the quantum yields of cyclization and cycloreversion reactions are dependent on the substitution position of the thiophene rings [7].



A symmetrical dithienylethene dimer, in which two bis(3-thienyl)ethene moieties are connected by a covalent

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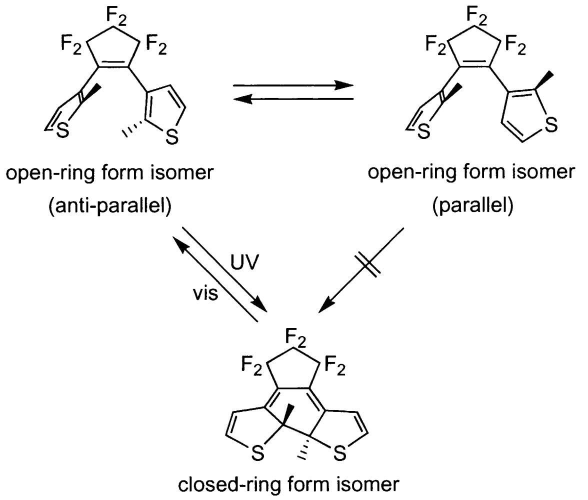


Scheme 1.

bond, was synthesized and the photochromic performance was studied by Peters and Branda [8]. In the dimer only one of the dithienylethene units was found to undergo the photocyclization.

In this paper, we have examined the photochromic behavior of a non-symmetric dithienylethene dimer **1a**, which has two types of dithienylethene units with 2- and 3-thienyl groups in one molecule, 5-(2-(3,4-dimethyl-2-thienyl))-3,3,4,4,5,5-hexafluorocyclopent-1-enyl-2-(2-(2,4-dimethyl-3-thienyl))-3,3,4,4,5,5-hexafluorocyclopent-1-enyl-3,4-dimethylthiophene, in hexane as well as in the crystalline phase. In crystal the reactivity is expected to be influenced by the crystal lattice [9,10]. The characteristic reactivity in the crystalline phase has been studied based on the structural analysis using X-ray crystallography [11].

2. Experimental

2.1. Photochemical reaction

Hexane of spectroscopic grade was distilled before use. Absorption spectra in a solution were measured with a Hitachi U-3500 absorption spectrophotometer. Photoirradiation was carried out using a USHIO USH-500D 500 W high-pressure mercury lamp or USHIO 500 W xenon lamp as the light source. Monochromatic light was obtained by passing the light through a Ritsu MC-20L monochrometor. Absorption spectra in the crystalline phase were measured using a Leica DMLP polarizing microscope connected with a Hamamatsu PMA-11 detector. The polarizer and analyzer were set parallel to each other.

2.2. X-ray crystal structure analysis

Good quality crystals were selected for the X-ray diffraction study. The data collection was performed on a Bruker SMART1000 CCD-based diffractometer (50 kV, 40 mA) with Mo Kα radiation. The crystal was cooled at 113 K using a cryostat (RIGAKU GN2). The data collection was performed as follows: the data covered a hemisphere of the reciprocal space by combining four sets of runs; each frame covered 0.3° in ω for 30 s exposure time. The crystal-to-detector distance was 5.118 cm. Crystal decay was monitored by repeating the 50 initial frames at the end data collection and analyzing the duplicate reflections. Data reduction was performed using SAINT software, which corrects for Lorentz and polarization effects, and decay. The cell constants were calculated by the global refinement. The structure solved by direct methods using SHELXS-86 [12] and refined by full least-squares on F^2 using SHELXL-97 [13]. The positions of all hydrogen atoms were calculated geometrically and refined by the riding model. Disordered part with small occupancy was refined isotropically and the bond lengths and geometry were restrained in the refinement.

2.3. Synthesis and characterization of the compounds

^{1}H NMR spectrum was recorded on a JEOL GSX 400 spectrometer (400 MHz). Tetramethylsilane (TMS) was used as an internal standard. Mass spectrum was taken with a Shimadzu GCMS-QP5050A gas chromatograph-mass spectrometer. The melting point was measured using a Laboratory Devices MEL-TEMP II.

To a 200 ml THF solution containing 3-bromo-2,4-dimethylthiophene (2.89 g, 15 mmol) was added 10 ml of a 1.6 N *n*-BuLi hexane solution (16 mmol) at −78 °C under argon atmosphere, and the solution was stirred for 1 h at the low temperature. Then, a THF solution (50 ml) of 2-(2,3,3,4,4,5,5-heptafluorocyclopent-1-en-1-yl)-3,4-dimethylthiophene (4.9 g, 16 mmol) was slowly added to the reaction mixture at −78 °C, and the mixture was stirred for 3 h at the temperature. The reaction was stopped by the addition of methanol. The product was extracted with ether. The organic layer was dried over $MgSO_4$, filtered, and evaporated. The residue was purified by column chromatography (silica gel, ethyl acetate) to afford 1-(3,4-dimethyl-2-thienyl)-2-(2,4-dimethyl-3-thienyl)perfluorocyclopentene (2.2 g, 37%) and 5-(2-(3,4-dimethyl-2-thienyl))-3,3,4,4,5,5-hexafluorocyclopent-1-enyl-2-(2-(2,4-dimethyl-3-thienyl))-3,3,4,4,5,5-hexafluorocyclopent-1-enyl-3,4-dimethylthiophene (**1a**) (1.43 g, 14%): mp 113.8–114.4 °C (α-**1a**) and 113.0–113.8 °C (β-**1a**). The phase transition point from β-**1a** to α-**1a** was 84.9–86.1 °C; ^{1}H NMR ($CDCl_3$) δ 1.50 (s, 3H), 1.55 (s, 3H), 1.83 (s, 3H), 2.00 (s, 3H), 2.07 (s, 3H), 2.25 (s, 3H), 6.75 (s, ^{1}H), 7.13 (s, ^{1}H); MS m/z (M^+) 680. Anal. Calcd. for $C_{28}H_{20}F_{12}S_3$: C, 49.41; H, 2.96. Found: C, 49.36; H, 2.95.

The closed-ring form isomers **1b** and **1c** were separated by HPLC (hexane and ethyl acetate with silica gel column) from hexane solution containing **1a**, which was irradiated with 334 nm for 1 day. **1b**: mp 114.2–115.0 °C; ^{1}H NMR ($CDCl_3$) δ 1.32 (s, 1.5H, anti-parallel), 1.34 (s, 1.5H, parallel), 1.50 (s, 1.5H, parallel), 1.52 (s, 1.5H, anti-parallel), 1.63 (s, 1.5H, anti-parallel), 1.66 (s, 1.5H, parallel), 1.86 (d, $J = 1.2$ Hz, 1.5H, anti-parallel), 1.87 (d, $J = 1.2$ Hz, 1.5H, parallel), 2.10 (s, 1.5H, parallel), 2.16 (d, $J = 1.5$ Hz, 1.5H, anti-parallel), 2.36 (s, 1.5H, anti-parallel), 2.42 (d, $J = 2.1$ Hz, 1.5H, parallel), 5.78 (d, $J = 1.5$ Hz, 0.5H, parallel), 5.79 (d, $J = 1.5$ Hz, 0.5H, anti-parallel), 6.82 (s, 0.5H, anti-parallel), 6.83 (s, 0.5H, parallel); MS *m/z* (M^+) 680. Anal. Calcd. for $C_{28}H_{20}F_{12}S_3$: C, 49.41; H, 2.96. Found: C, 49.51; H, 2.92.

3. Results and discussion

3.1. Photochromic reactions in solution

1a has two reactive units in one molecule. One part is bis(2-thienyl)ethene and the other part has (2-thienyl) and (3-thienyl) aryl groups. **1a** was synthesized by the reaction of 2-(2,3,3,4,4,5,5-heptafluorocyclopent-1-en-1-yl)-3,4-dimethylthiophene with lithiated 3-bromo-2,4-dimethylthiophene. As mentioned above, the closed-ring isomer of bis(2-thienyl) ethene has its absorption maximum at the shorter wavelength than that of 1-(2-thienyl)-2-(3-thienyl)ethene. Fig. 1 shows the spectral change of **1** by photoirradiation in hexane. Upon irradiation with 334 nm light, the colorless solution of **1a** turned yellow, in which a visible absorption band was observed at 457 nm. The yellow color completely disappeared by irradiation with visible light ($\lambda > 450$ nm).

Two kinds of colored products were isolated by HPLC. The ratio of the two products was approximately 10:1. The structure of the major product was determined by ^{1}H NMR, absorption spectroscopy, and X-ray crystallographic analysis. ^{1}H NMR measurement revealed that the proton at 5-position of 2,4-dimethyl-3-thienyl group shifts from 6.75 to 6.82 ppm and the proton at 5-position of 3,4-dimethyl-2-thienyl group shifts from 7.13 to 5.78 ppm in the major colored product. These results suggest the participation of 3,4-dimethyl-2-thienyl group in the photochromic reaction. The absorption maximum (456 nm) and the molar absorption coefficient (4.3×10^3 M^{-1} cm^{-1}) of the major product were similar to those of **2b** (425 nm and 5.8×10^3 M^{-1} cm^{-1}). The major product was recrystallized from ethyl acetate solution to form rectangular red crystals. The molecular structure in the crystals was determined by X-ray crystallographic analysis and shown in Fig. 2 and Table 1. The structure shows that the cyclization reaction took place at bis(2-thienyl)ethene moiety and the product was assigned to **1b**.

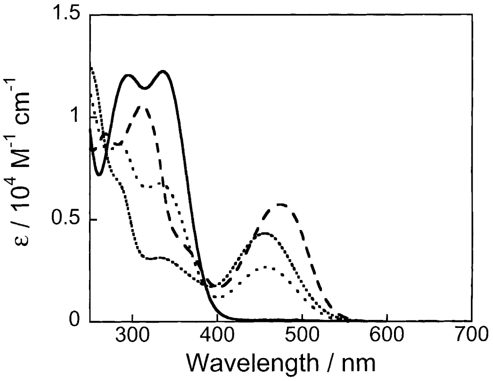


Fig. 1. Absorption spectra of **1a** (—), **1b** (· · ·), **1c** (- - -), and **1** in the photostationary state under irradiation with 334 nm (· · ·) in hexane.

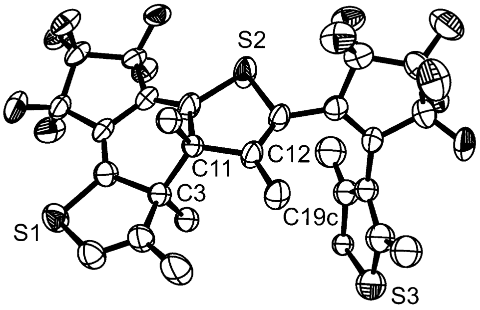


Fig. 2. ORTEP drawing of closed-ring isomer **1b** showing 50% probability displacement ellipsoids. 2,4-Dimethyl-3-thienyl group of parallel conformation and perfluorocyclopentene were disordered. Therefore, one side was omitted for clarity. Hydrogen atoms were also omitted for clarity.

^{1}H NMR measurement and X-ray crystallographic analysis could not be carried out for the minor product because of its small amount. Only absorption spectral analysis was carried out. The absorption maximum (475 nm) and the molar absorption coefficient (5.7×10^3 M^{-1} cm^{-1}) of the minor product were similar to those of **3b** (469 nm and 4.5×10^3 M^{-1} cm^{-1}). The molecular structure of the compound was estimated from the absorption spectrum to be the closed-ring isomer of 1-(2-thienyl)-2-(3-thienyl)ethene moiety, **1c**.

Fig. 1 shows the spectra of the isolated closed-ring form isomers **1b** and **1c**. The molar ratio of **1a**:**1b**:**1c** in the photostationary state under irradiation with 334 nm light was 9.0:13:1.0. Both **1b** and **1c** converted back to **1a** by irradiation with visible light ($\lambda > 450$ nm). Formation of the closed-ring isomer, in which both dithienylethene units are

Table 1
Crystallographic parameters for **1b**

Formula	$C_{28}H_{20}F_{12}S_3$
Formula weight	680.62
Crystal color	Red
Crystal system	Orthorhombic
Space group	*Pbca*
a (Å)	15.859(3)
b (Å)	20.073(3)
c (Å)	36.083(6)
$\alpha = \beta = \gamma$ (°)	90
V (Å^3)	11486(3)
Z	16
$D_{\text{calcd.}}$ (g cm^{-3})	1.574
R_1	0.0810
wR_2	0.2208

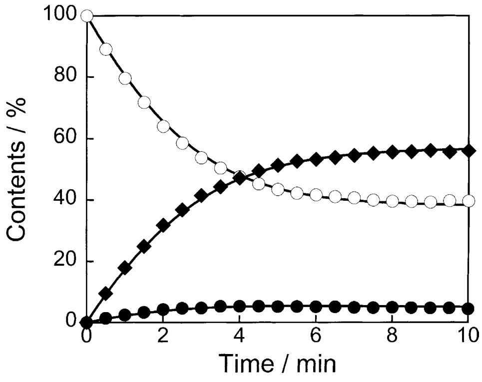


Fig. 3. Decay of **1a** (open circles) and formation of **1b** (filled diamonds) and **1c** (filled circles) upon irradiation with 334 nm light. The initial concentration of **1a** was 0.41 mM. The solid lines were least-square fits of the concentration of **1a**, **1b**, and **1c** calculated based on Eqs. (1)–(3) (see text).

in the closed-ring form, **1d**, was not discerned. This result agreed to the observation for the symmetric dimer [8].

3.2. Kinetic study in solution

Fig. 3 shows the time dependence of the formation of **1b** and **1c**. A hexane solution containing **1a** was irradiated with 334 nm light, and the concentration changes of **1a**, **1b** and **1c** were monitored by HPLC. The formation of **1b** was about 7.6 times faster than that of **1c** at the initial stage of photoirradiation, and in the photostationary state the amount of **1b** was about 13 times larger than that of **1c**. The time course of formation of **1b** and **1c** was analyzed based on Scheme 2.

$$\frac{\mathrm{d}C_{\mathbf{1a}}}{\mathrm{d}t} = (-k_{\mathbf{1a}-\mathbf{1b}}C_{\mathbf{1a}} + k_{\mathbf{1b}-\mathbf{1a}}C_{\mathbf{1b}} - k_{\mathbf{1a}-\mathbf{1c}}C_{\mathbf{1a}} + k_{\mathbf{1c}-\mathbf{1a}}C_{\mathbf{1c}})F \qquad (1)$$

$$\frac{\mathrm{d}C_{\mathbf{1b}}}{\mathrm{d}t} = (k_{\mathbf{1a}-\mathbf{1b}}C_{\mathbf{1a}} - k_{\mathbf{1b}-\mathbf{1a}}C_{\mathbf{1b}})F \qquad (2)$$

$$\frac{\mathrm{d}C_{\mathbf{1c}}}{\mathrm{d}t} = (k_{\mathbf{1a}-\mathbf{1c}}C_{\mathbf{1a}} - k_{\mathbf{1c}-\mathbf{1a}}C_{\mathbf{1c}})F \qquad (3)$$

$$F = \frac{1-10^{-A}}{A}, \quad A = \varepsilon_{\mathbf{1a}}C_{\mathbf{1a}} + \varepsilon_{\mathbf{1b}}C_{\mathbf{1b}} + \varepsilon_{\mathbf{1c}}C_{\mathbf{1c}}$$

$$k_{\mathbf{1a}-\mathbf{1b}} = \varepsilon_{\mathbf{1a}}\Phi_{\mathbf{1a}-\mathbf{1b}}I_0, \quad k_{\mathbf{1b}-\mathbf{1a}} = \varepsilon_{\mathbf{1b}}\Phi_{\mathbf{1b}-\mathbf{1a}}I_0,$$

$$k_{\mathbf{1a}-\mathbf{1c}} = \varepsilon_{\mathbf{1a}}\Phi_{\mathbf{1a}-\mathbf{1c}}I_0, \quad k_{\mathbf{1c}-\mathbf{1a}} = \varepsilon_{\mathbf{1c}}\Phi_{\mathbf{1c}-\mathbf{1a}}I_0$$

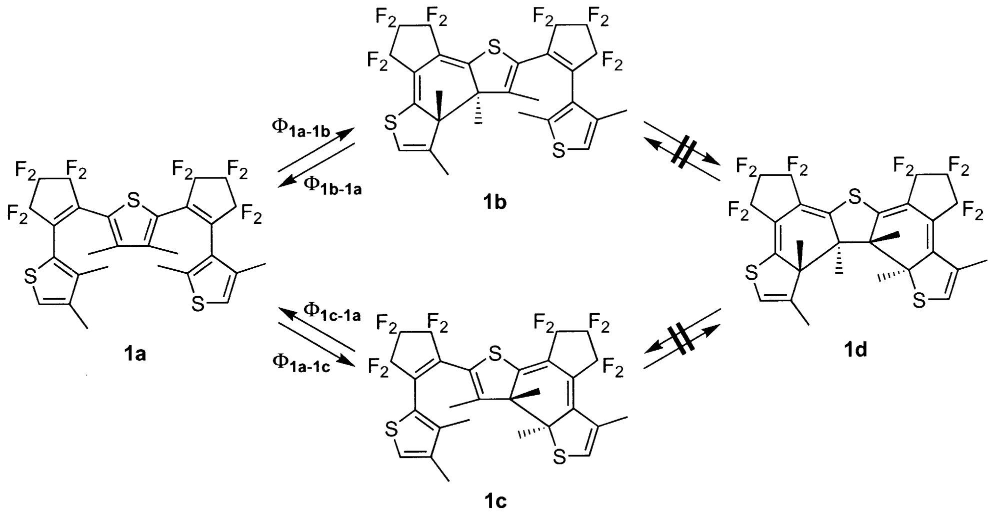
In these differential equations, I_0 is the intensity of light and $\Phi_{\mathbf{1a}-\mathbf{1b}}$, $\Phi_{\mathbf{1b}-\mathbf{1a}}$, $\Phi_{\mathbf{1a}-\mathbf{1c}}$, and $\Phi_{\mathbf{1c}-\mathbf{1a}}$ are the reaction quantum yields of **1a** to **1b**, **1b** to **1a**, **1a** to **1c**, and **1c** to **1a**, respectively. $\varepsilon_{\mathbf{1a}}$, $\varepsilon_{\mathbf{1b}}$, and $\varepsilon_{\mathbf{1c}}$ are the molar absorption coefficients of **1a**, **1b**, and **1c** at the irradiation wavelength (334 nm). $C_{\mathbf{1a}}$, $C_{\mathbf{1b}}$, and $C_{\mathbf{1c}}$ are the concentrations of **1a**, **1b**, and **1c**.

These differential equations were numerically solved and the results were fitted to the experimental data as shown in Fig. 3. The best-fitted curves are shown as solid lines in the figure. The parameters used are as follows: $\varepsilon_{\mathbf{1a}} = 1.2 \times 10^4\,\mathrm{M^{-1}\,cm^{-1}}$, $\varepsilon_{\mathbf{1b}} = 3.1 \times 10^3\,\mathrm{M^{-1}\,cm^{-1}}$, $\varepsilon_{\mathbf{1c}} = 7.4 \times 10^3\,\mathrm{M^{-1}\,cm^{-1}}$ (at 334 nm). The ratio of $\Phi_{\mathbf{1a}-\mathbf{1b}}:\Phi_{\mathbf{1b}-\mathbf{1a}}:\Phi_{\mathbf{1a}-\mathbf{1c}}:\Phi_{\mathbf{1c}-\mathbf{1a}}$ was calculated to be 5.9:16:1.0:15.

The quantum yields of cycloreversion reactions of **1b** and **1c** to **1a**, $\Phi_{\mathbf{1b}-\mathbf{1a}}$ and $\Phi_{\mathbf{1c}-\mathbf{1a}}$ were measured in hexane by irradiation with visible light at each absorption maximum. $\Phi_{\mathbf{1b}-\mathbf{1a}}$ and $\Phi_{\mathbf{1c}-\mathbf{1a}}$ were obtained to be 0.54 and 0.52, respectively. The ratio well agreed with the ratio obtained from the above simulation. Based on the values $\Phi_{\mathbf{1a}-\mathbf{1b}}$ and $\Phi_{\mathbf{1a}-\mathbf{1c}}$ were estimated to be 0.20 and 0.034, respectively.

3.3. Photochromic reaction in a single-crystalline phase

Two different kinds of crystals were obtained from the hexane solution of **1a**. The two kinds of crystals could be



Scheme 2.

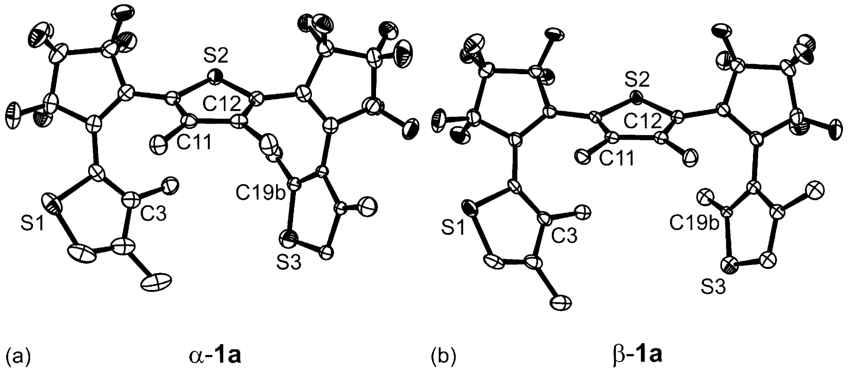


Fig. 4. ORTEP drawing of open-ring isomer α-**1a** (a) and β-**1a** (b) showing 50% probability displacement ellipsoids. 2,4-Dimethylthiophene group and perfluorocyclopentene were disordered. Therefore, one side was omitted for clarity. Hydrogen atoms were also omitted for clarity.

separated by their appearance. One crystal was colorless and showed photochromic reactivity in the single-crystalline phase (α phase) [11]. The other crystal was non-photochromic and gave a strong emission (β phase). The crystal structures of both crystals were determined by X-ray crystallographic analysis. Fig. 4a and b and Table 2 show the molecular structures of α-**1a**, β-**1a** and the structural data, respectively. Two crystals showed different torsion angles of three thiophene rings, and therefore, different distances between the reactive carbons. Although both distances of reactive carbons of β-**1a**, 3.48 and 3.83 Å, are short enough, less than 4.2 Å, for the reaction, the photocyclization reaction was not observed.

The single-crystalline α-**1a** was irradiated with weak 415 nm light for 50 h. Then, the crystal was dissolved in hexane and the photo-products were analyzed by HPLC. Only one photo-product was detected and the conversion to the product was around 3%. From the retention time the product was assigned to **1b**. In the crystal a selective cyclization reaction took place.

In the α-**1a** crystal the distances of C(3)–C(11) and C(12)–C(19b), which are considered to be reactive carbon atoms, were 3.50 and 4.03 Å, respectively. Although both distances are short enough for the reaction to take place, the distance C(3)–C(11) is much shorter than that of C(12)–C(19b). In the crystal the short-distance carbons C(3)–C(11) predominantly react to produce only one closed-ring isomer. The reactivity difference in the two reactive sites can be explained as follows. Upon irradiation with 415 nm light, the excited energy delocalizes throughout the molecule. Although the two reactive sites, C(3)–C(11) and C(12)–C(19b), have similar reaction probability, in the crystal the distance is different and controls the reactivity. The short-distance carbons C(3)–C(11) have higher reactivity than the other long-distance carbons C(12)–C(19b) [4]. Therefore, C(3)–C(11) carbons reacted predominantly.[1]

Table 2
Crystallographic parameters for **1a**

Compound	α-**1a**	β-**1a**
Formula	$C_{28}H_{20}F_{12}S_3$	$C_{28}H_{20}F_{12}S_3$
Formula weight	680.62	680.62
Crystal color	Colorless	Yellow
Crystal system	Monoclinic	Monoclinic
Space group	*Cc*	$P2_1/c$
a (Å)	10.1047(11)	13.0792(12)
b (Å)	15.0140(16)	14.3724(13)
c (Å)	18.503(2)	16.4496(15)
β (°)	94.288(2)	112.772(2)
V (Å^3)	2799.3(5)	2851.2(5)
Z	4	4
$D_{\mathrm{calcd.}}$ (g cm^{-3})	1.615	1.586
R_1	0.0363	0.0486
wR_2	0.0865	0.1375

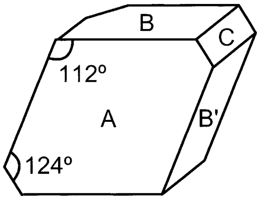


Fig. 5. Shape of single crystal α-**1a**.

The selective formation of **1b** in the crystal was also confirmed by measuring the absorption spectrum using polarized light. A rhombus-shaped single crystal, α-**1a**, was used for the measurement. The crystal shape of α-**1a** consists of eight surfaces, with two parallelograms (A), four rectangles (B and B′) and two squares (C) as illustrated in Fig. 5. Surfaces A, B, B′, and C correspond to planes of (0 0 1), (1 −1 0), (1 1 0), and (0 1 0), respectively. Upon irradiation with 366 nm light, the crystal turned red at a certain angle ($\theta = 0^\circ$ of Fig. 6(a)). When the crystal was

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[1] Disorder was observed for the right-side 2,4-dimethylthiophene in both α-**1a** and β-**1a** crystals. The disorder indicated that only 40% of the molecules are in photochemically active conformation in α-**1a** crystal. This is additional reason why the formation of **1c** was strongly suppressed.

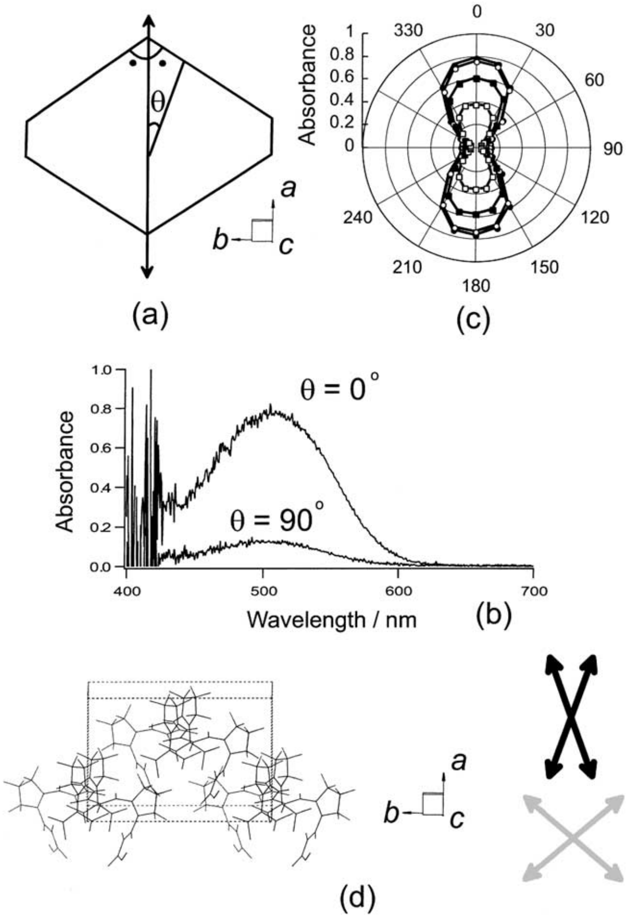

Fig. 6. Polarized absorption spectra of the colored crystal of the surface A: (a) direction of polarizer; (b) polarized absorption spectra; (c) the polar plots at 500 nm (filled circles), 520 nm (open circles), 540 nm (filled rectangles), and 560 nm (open rectangles); (d) packing diagrams of α-**1a**. The black arrows indicate the electronic transition moment vectors of 502 nm absorption for bis(2-thienyl)ethene and the gray arrows indicate the imaginary electronic transition moment vectors for (2-thienyl)(3-thienyl) ethene.

rotated as much as 90°, the color almost disappeared. Fig. 6 shows the polarized absorption spectra on surface A at 0° and 90° (b) and the polar plots at several wavelengths (c). The absorption maximum did not show any appreciable shift by the rotation of the sample. In addition, any shape change of the polar plots was not observed even if the monitory wavelength was shifted to longer wavelengths. These results indicate that the absorption spectrum has a single component.

Fig. 6(d) shows the packing diagrams of α-**1a** and expected electronic transition moment vectors on surface A. The black arrows indicate the transition moment vectors of **1b**, and gray arrows are the expected vectors of **1c**. The observed polar plots agree to the shape of the composite of two black arrows. The absorption spectrum of **1c** is supposed to have an absorption band longer than that of **1b**. The absence of the shape change of the polar plots at longer wavelengths also confirmed that **1c** is not formed in the crystal.

4. Conclusions

A non-symmetrical diarylethene dimer, 5-(2-(3,4-dimethyl-2-thienyl))-3,3,4,4,5,5-hexafluorocyclopent-1-enyl-2-(2-(2,4-dimethyl-3-thienyl))-3,3,4,4,5,5-hexafluorocyclopent-1-enyl-3,4-dimethylthiophene (**1a**) underwent photochromic reaction in hexane as well as in the crystalline phase. In solution both closed-ring isomers, in which bis(2-thienyl)ethene moiety (**1b**) or 1-(2-thienyl)-2-(3-thienyl)ethene moiety (**1c**) undergoes the cyclization reaction were produced, while in the crystalline phase only **1b** was detected. The X-ray crystallography and polarized absorption spectra also indicate that **1c** was not generated. The distance difference in the reactive carbons controlled the selectivity.

Acknowledgements

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