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# Photochromism of diarylethene derivatives having cyclohexyl and cyclohexenyl groups in single-component crystals and a two-component mixed crystal

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ABSTRACT

Diarylethene derivatives **1a** having two cyclohexyl groups and **2a** having a cyclohexyl and a cyclohexenyl group formed a mixed crystal composed of almost equal amounts of the two components, and underwent photochromism in the mixed crystal as well as in the single-component crystals.

Photochromism is defined as a photoinduced reversible transformation of a chemical species between two isomers having different absorption spectra.[1] Although various types of photochromic molecules have been reported so far, molecules which show photochromic reactivity in the crystalline state are rare.[2–7] In addition, most photochromic crystals undergo thermally reversible photochromic reactions and photogenerated isomers return to the initial isomers in the dark. In contrast to them, diarylethene derivatives having heterocyclic aryl rings undergo thermally irreversible and fatigue-resistant photochromic reactions not only in solution but also in the single-crystalline phases.[8] They undergo photocyclization and photocycloreversion reactions in the crystal lattices by alternate irradiation with ultraviolet (UV) and visible light, and show reversible color changes between colorless and colored states. The photogenerated color and the quantum yield of the photoreaction vary depending on the molecular conformation in the crystal as well as on the chemical structure of the diarylethene molecule.[9]

Several examples of two- or three-component diarylethene mixed crystals which contain different kinds of diarylethene derivatives have been reported.[10] If the diarylethene components exhibit different absorption spectra, the photoreaction of each component can be selectively controlled by irradiation with light of appropriate wavelength, and the crystals show multicolor photochromism. A successful example of multicolor photochromic crystals is a three-component crystal composed of dioxazolyl-, dithiazolyl-, and dithienylethene derivatives, closed-ring isomers of which exhibit yellow, red, and blue, respectively.[10e] The molecules are quite similar in the geometrical structure except the difference in the atoms in the heterocyclic aryl rings. The similarity in the geometrical structures helps the formation of well-mixed crystals, and the crystal shows multicolor photochromism.

Based on the above strategy utilizing the similarity in the molecular geometrical structure, we tried to prepare another multi-component photochromic crystal by using diarylethene derivatives **1** and **2** having cyclohexyl and cyclohexenyl groups (Scheme 1). We expected that **1** and **2** form mixed crystals with **3** having two phenyl groups[11] because the geometry and size of the molecules are similar to each other. In addition, **3** having conjugative phenyl groups is known to turn blue upon UV irradiation, while **1** and **2** are expected to exhibit red color. Unfortunately, both **1** and **2** did not form mixed crystals with **3**, but we succeeded in the preparation of a two-component mixed crystal composed of almost equal amounts of **1** and **2**. We report on photochromic reactions of **1** and **2** in the single-component crystals and the two-component mixed crystal.

The syntheses of open-ring isomers **1a** and **2a** were performed according to Scheme 2. The details are described in the Supplementary data. First, 1-(4-bromo-5-methylthiophen-2-yl)cyclohexanol (**5**)[12] was prepared by a reaction of lithiated 3,5-dibromo-2-methylthiophene (**4**) with cyclohexanone. Then, **5** was reduced by adding $LiAlH_4$ under the presence of $AlCl_3$ to be transformed

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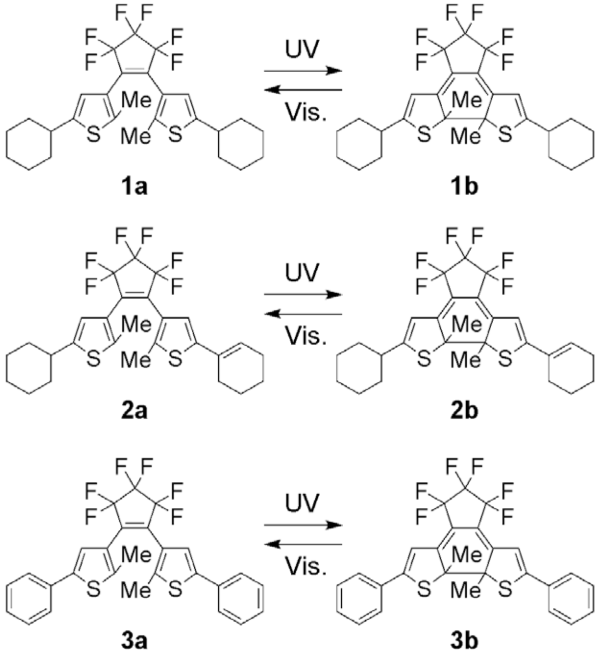


**Scheme 1.** Photochromism of diarylethenes **1** having two cyclohexyl groups, **2** having a cylcohexyl and a cyclohexenyl group, and **3** having two phenyl groups.

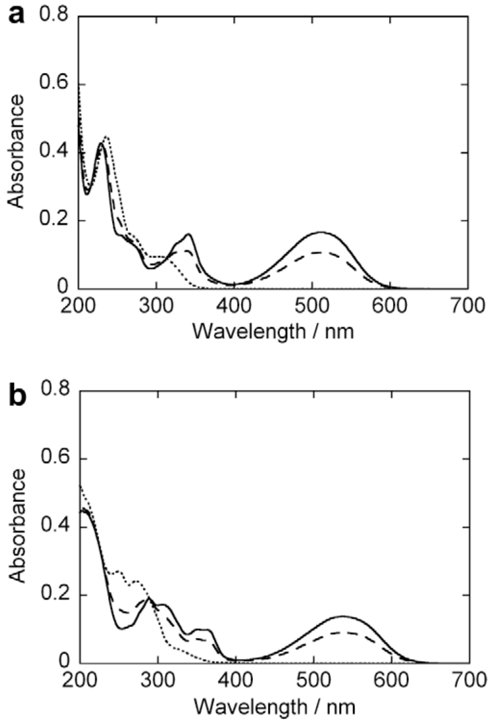
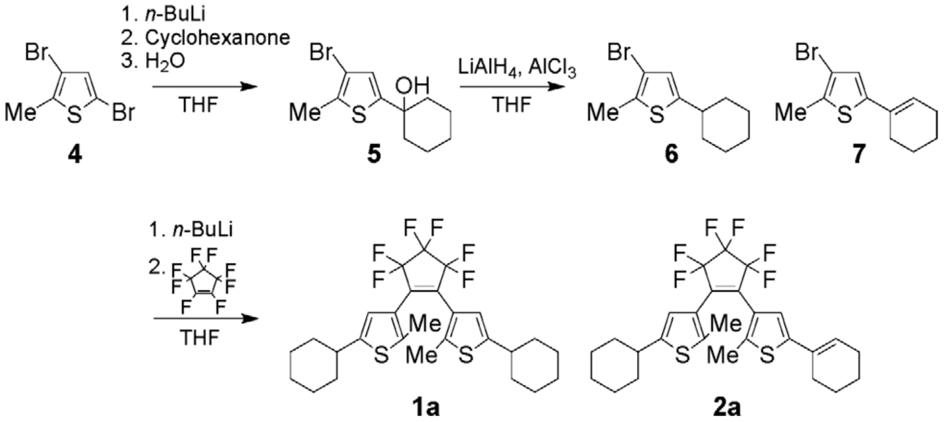


**Figure 1.** Absorption spectra of **1** (a, $1.90 \times 10^{-5}$ M) and **2** (b, $1.32 \times 10^{-5}$ M) in hexane. Dotted lines: open-ring isomers **1a** and **2a**, solid lines: closed-ring isomers **1b** and **2b**, dashed lines: photostationary states under irradiation with 300 nm light.

to 3-bromo-5-cyclohexyl-2-methylthiophene (**6**).[13] On this reaction, 3-bromo-5-cyclohexenyl-2-methylthiophene (**7**) was also generated as a dehydrated by-product. **6** and **7** could not be separated by flash column chromatography, and were obtained as a mixture in the molar ratio of **6**:**7** = 4:1. The characterization of **6** and **7** in the mixture was confirmed by NMR spectroscopy. Finally, the mixture of **6** and **7** was lithiated and coupled with octafluorocyclopentene. On a TLC analysis of the reaction mixture, two major products were found to be photochromic. They were separated by flash column chromatography and identified to be **1a** having two cyclohexyl groups and **2a** having a cyclohexyl and a cyclohexenyl group by $^1$H NMR, MS, and elemental analysis.[14,15]

**1** and **2** underwent photochromism in solution. Figure 1 shows absorption spectra of **1** and **2** in hexane. Upon irradiation with UV light, colorless solutions of the open-ring isomers **1a** and **2a** turned red and reddish purple, respectively. These color changes are due to the generation of the closed-ring isomers **1b** and **2b**. **1b** and **2b** exhibit absorption maxima at 512 and 538 nm, respectively. The maximum of **2b** showed a bathochromic shift in comparison with that of **1b** by as much as 26 nm. The shift means that the olefin moiety in the cyclohexenyl group in **2b** participates in the π conjugation of the central photochromic backbone. The conversion ratios from the open- to the closed-ring isomers under irradiation with 300 nm light were 64% and 65% for **1** and **2**, respectively. The colored states were stable in the dark at room temperature and bleached by irradiation with visible light ($\lambda > 440$ nm).

Slow evaporation of a methanol solution of **1a** afforded colorless plate-like crystals. The crystal structure was determined by X-ray crystallographic analysis. The crystal belongs to a triclinic crystal system with a space group $P\overline{1}$ and $Z = 8$.[16] An asymmetric unit in the unit cell contains four **1a** molecules shown in ORTEP drawings in Figure 2a. The four molecules in Figure 2a adopt different conformations concerning the cyclohexane rings. The thiophene rings of the four molecules are fixed in anti-parallel orientations, and the distances between the reacting carbons are



**Scheme 2.** Syntheses of **1a** and **2a**.

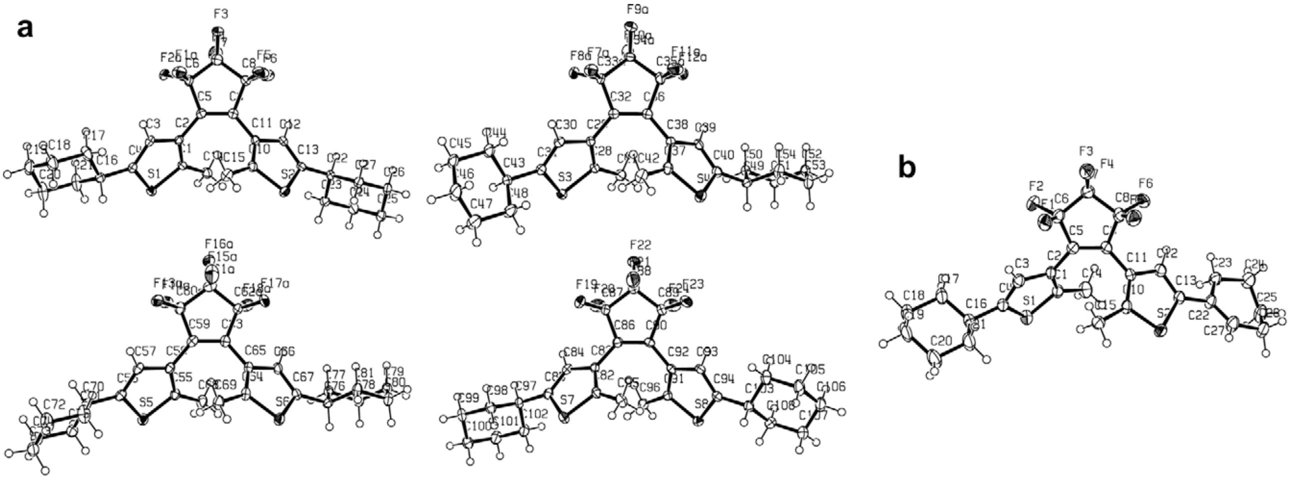


**Figure 2.** ORTEP drawings for single-component crystals of **1a** (a) and **2a** (b).

3.465–3.501 Å. This fulfills the requirement for diarylethene derivatives to undergo photochromic reactions in the crystalline state.[9] Single crystals of **2a** were grown by recrystallization from hexane. The crystal of **2a** is triclinic $P\overline{1}$ with $Z = 2$.[16] Figure 2b shows an ORTEP drawing of **2a**. C22–C27 is the olefin double bond in the cyclohexenyl group. **2a** molecule also adopts an anti-parallel conformation, and the distance between the reacting carbons is 3.493 Å. The crystal of **2a** is also expected to show photochromic reactivity.

Photochromism of the single-component crystals of **1a** and **2a** was examined. Upon irradiation with UV light ($\lambda = 365$ nm), the colorless single crystals of **1a** and **2a** turned red and reddish purple, respectively. Figure 3 shows polarized absorption spectra of the colored crystals. Absorption maxima for **1b** and **2b** in the colored crystals are located at 525 and 550 nm, respectively. Anisotropy in polar plots of the absorbance reflects the regular orientation of the photogenerated closed-ring isomers in the crystals and means that photocyclization reactions in both the crystals of **1a** and **2a** proceed in the single-crystalline phase.[17] The colored crystals were bleached by visible irradiation ($\lambda > 440$ nm).

We tried to prepare mixed crystals composed of **1a** and **3a** or composed of **2a** and **3a**. Unfortunately, upon recrystallization from mixed hexane solutions, the molecules crystallized separately and did not yield mixed crystals, probably due to the difference in the planarity between the cyclohexyl and phenyl groups or due to the difference in the solubility to the solvent. However, we found that **1a** and **2a** form a mixed crystal composed of almost equal amounts of the two components. The mixed crystal was prepared by recrystallization of a 1:1 (molar ratio) mixture of **1a** and **2a** from methanol. The composition ratio of the crystal was found to be **1a**:**2a** = 53:47 by HPLC analysis. Molecular structures of **1a** and **2a** are quite similar to each other except that **2a** has the olefin moiety in the cyclohexenyl group. This enables the formation of mixed crystals composed of **1a** and **2a** in almost equal amounts. According to X-ray crystallographic analysis, the mixed crystal has the same unit cell as that of the single-component crystal of **2a**, triclinic $P\overline{1}$ with $Z = 2$.[16] On the refinement of the molecular structure, however, high peaks of residual electron density were observed around the cyclohexenyl group in **2a**. These peaks were assigned to the carbon atoms in the cyclohexyl group in **1a,** which is incor-

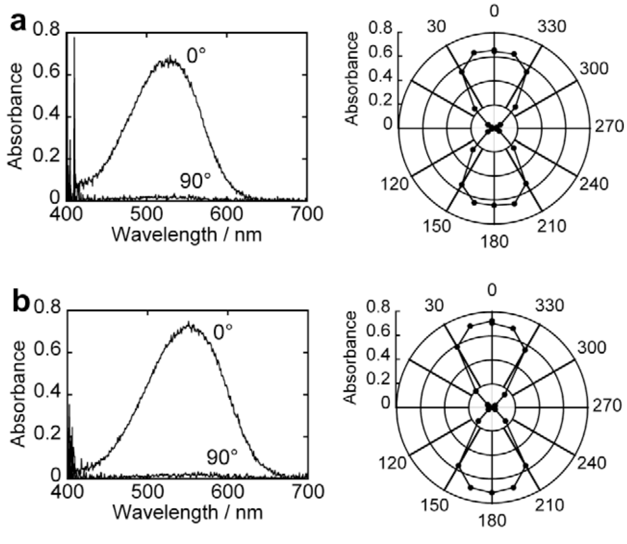


**Figure 3.** Polarized absorption spectra and polar plots of the absorbance for UV-irradiated single-component crystals of **1a** (a) and **2a** (b).

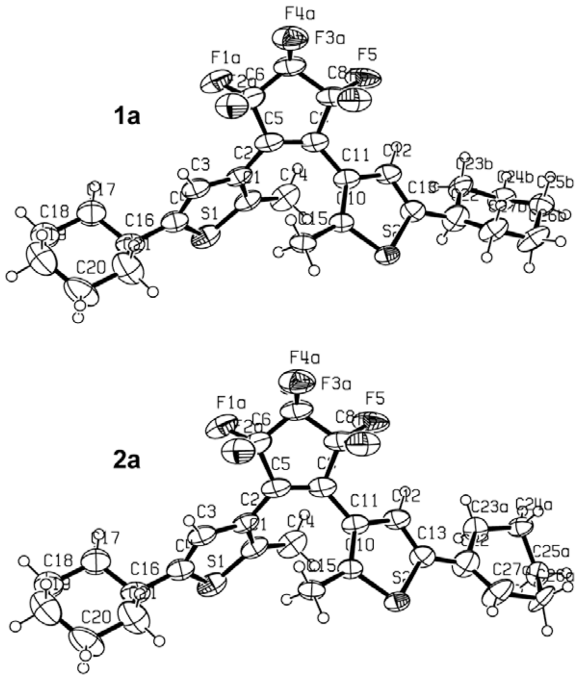


**Figure 4.** ORTEP drawings for **1a** and **2a** in two-component mixed crystal of **1a**·**2a**. The occupancy ratio is **1a**:**2a** = 59:41.

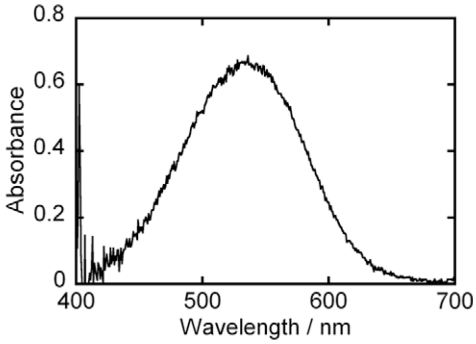


**Figure 5.** Absorption spectrum of UV-irradiated two-component mixed crystal of **1a**·**2a**.

porated into the crystal lattice of **2a**. The final molecular structures after the refinement are shown as ORTEP drawings in Figure 4. The cyclohexyl group in **1a** is observed as a disordered structure on the cyclohexenyl group in **2a**. The occupancy ratio of the cyclohexyl and cyclohexenyl groups is 59:41, which is consistent with the composition ratio determined from HPLC analysis.

Photochromism of the two-component mixed crystal composed of **1a** and **2a** was also examined. Upon irradiation with UV light ($\lambda$ = 340 nm), the colorless single crystal turned red. Figure 5 shows an absorption spectrum of the UV-irradiated colored crystal. The spectrum has a maximum at 535 nm, and is located between the spectra of the single-component crystals of **1a** and **2a**. HPLC analysis of the colored crystal revealed that both of the closed-ring isomers **1b** and **2b** were generated in the molar ratio of **1b**:**2b** = 57:43 by the UV irradiation. There is no remarkable selectivity in the photocyclization of **1a** and **2a** in the mixed crystal.

In conclusion, **1a** and **2a** formed a mixed crystal composed of almost equal amounts of the two components owing to the similarity in the molecular structures, and both underwent photochromism in the mixed crystal as well as in the single-component crystals.

## Acknowledgments

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## Supplementary data

Supplementary data (experimental and syntheses) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2009.02.139.

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12. Compound **5**: pale yellow crystals; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 1.26–1.86 (m, 10H, aliphatic H), 1.77 (s, 1H, OH), 2.36 (s, 3H, CH$_3$), 6.77 (s, 1H, thienyl H).
13. Compound **6**: pale yellow oil; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 1.26–2.66 (m, 11H, aliphatic H), 2.33 (s, 3H, CH$_3$), 6.57 (s, 1H, thienyl H). Compound **7**: pale yellow oil; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 1.26–2.66 (m, 8H, aliphatic H), 2.34 (s, 3H, CH$_3$), 6.07 (m, 1H, olefinic H), 6.70 (s, 1H, thienyl H).
14. Compound **1a**: colorless crystals; mp 115–116 °C; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 1.24–2.70 (m, 22H, aliphatic H), 1.81 (s, 6H, CH$_3$), 6.68 (s, 2H, thienyl H); MS (EI) *m*/*z* 532 (M$^+$); elemental Anal. Calcd for $C_{27}H_{30}F_6S_2$: C 60.88, H 5.68. Found: C 60.90, H 5.67. Compound **2a**: colorless crystals; mp 120–121 °C; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 1.25–2.71 (m, 19H, aliphatic H), 1.81 (s, 3H, CH$_3$), 1.85 (s, 3H, CH$_3$), 6.07 (m, 1H, olefinic H), 6.71 (s, 1H, thienyl H), 6.81 (s, 1H, thienyl H); MS (EI) *m*/*z* 530 (M$^+$); elemental Anal. Calcd for $C_{27}H_{28}F_6S_2$: C 61.11, H 5.32. Found: C 60.87, H 5.31.
15. Another photochromic compound, which was supposed to be a diarylethene derivative having two cyclohexenyl groups, 1,2-bis(5-cyclohexenyl-2-methyl-3-thienyl)perfluorocyclopentene, was detected on the TLC analysis, but could not be isolated because of the low yield and the instability of the compound. The compound decomposed during the isolation and purification process.
16. *Crystal data for* **1a**: $C_{27}H_{30}F_6S_2$, $M$ = 532.65, $T$ = 93(2) K, triclinic $P\overline{1}$, $a$ = 15.6169(12), $b$ = 16.5614(13), $c$ = 20.4041(16) Å, $\alpha$ = 91.6290(10)°, $\beta$ = 92.9890(10)°, $\gamma$ = 104.878(2)°, $V$ = 5088.6(7) Å$^3$, $Z$ = 8, $R_1$ ($I > 2\sigma$) = 0.0511, $wR_2$ (all data) = 0.1027. *Crystal data for* **2a**: $C_{27}H_{28}F_6S_2$, $M$ = 530.63, $T$ = 93(2) K, triclinic $P\overline{1}$, $a$ = 8.3804(14), $b$ = 11.4709(19), $c$ = 13.424(2) Å, $\alpha$ = 86.426(3)°, $\beta$ = 73.184(3)°, $\gamma$ = 87.983(3)°, $V$ = 1232.7(4) Å$^3$, $Z$ = 2, $R_1$ ($I > 2\sigma$) = 0.0545, $wR_2$ (all data) = 0.0965. *Crystal data for* **1a**·**2a**: $(C_{27}H_{30}F_6S_2)_{0.589}(C_{27}H_{28}F_6S_2)_{0.411}$, $M$ = 531.82, $T$ = 93(2) K, triclinic $P\overline{1}$, $a$ = 8.6118(13), $b$ = 11.4971(17), $c$ = 13.344(2) Å, $\alpha$ = 87.125(2)°, $\beta$ = 73.441(2)°, $\gamma$ = 83.191(2)°, $V$ = 1257.3(3) Å$^3$, $Z$ = 2, $R_1$ ($I > 2\sigma$) = 0.0754, $wR_2$ (all data) = 0.1922. Crystallographic data (excluding structure factors) for the structures in this Letter have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 714780–714782. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.Uk).
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