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Single-crystalline photochromism of diarylethenes: reactivity–structure relationship†

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Photochromic reactivity of diarylethenes in the single-crystalline phase was found to be controlled by the distance between the reactive carbon atoms in the antiparallel conformation.

Photochromism is referred as a photochemically reversible transformation of a chemical species between two isomers having different absorption spectra.[1] Although many photochromic compounds have been so far reported, compounds which exhibit thermally stable photochromic reactivity in the single-crystalline phase are very rare.[2] In most cases, the photogenerated isomers are unstable and return to the initial isomers even in the dark. Recently, we have found that some photochromic diarylethene derivatives undergo thermally stable and fatigue resistant photochromic reactions.[3–9] The photochromic crystals are potentially useful for applications to optoelectronic devices such as optical memories, photoswitching, display, and actuators.[8,9]

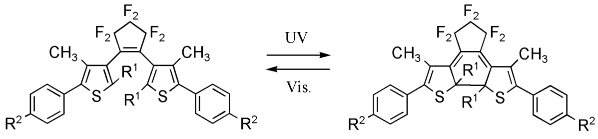
Diarylethenes in solution have two conformations; antiparallel and parallel ones. The photocyclization reaction can proceed only from the antiparallel conformation. In crystals, most diarylethenes are packed in the antiparallel conformation. This means that most diarylethenes should undergo photochromic reactions in the single-crystalline phase. However, this is not always the case. For example, 1,2-bis(2-methyl-1-benzothiophen-3-yl)perfluorocyclopentene, in which the distance of the reactive carbon atoms in the antiparallel conformation is 0.435 nm, is photochemically inactive in the crystalline phase. On the other hand, the 6,6′-dinitro derivative having a distance of 0.384 nm shows photochromic reactivity.[4] It is essential to investigate the details of the distance–reactivity relationship in the diarylethene single-crystalline photochromism.

The following diarylethenes with isopropyl and/or methoxy substituents were synthesized and their reactivity in the single-crystalline phase was examined (Scheme 1).

Diarylethenes **1a**–**4a** undergo photochromic reactions in hexane in a similar manner. The cyclization quantum yields in hexane were determined to be 0.46 (**1a**),[10] 0.48 (**2a**),[10] 0.49 (**3a**)[11] and 0.45 (**4a**). No significant difference in the quantum yields were observed. Single crystals of **1a** turned blue upon irradiation with ultraviolet light.[8] The absorption maximum of the colored isomer **1b** was observed at 630 nm in the crystal. The blue colored crystal returned to the initial colorless crystal upon irradiation with visible light ($\lambda > 500$ nm). Crystal **2a** did not show any color change upon irradiation with ultraviolet light. The introduction of methoxy groups at the *para*-position of the phenyl groups suppressed the photochromic reactivity in the crystalline phase. However, crystal **4a**,‡ which has isopropyl substituents at the reacting carbons, underwent photochromism in the crystalline phase. The crystal changed color from colorless to green as shown in Fig. 1. The color disappeared upon irradiation with visible light ($\lambda > 500$ nm).

To ascertain the substituent effects of methoxy and isopropyl groups, **3a** was prepared and the reactivity was examined in the single-crystalline phase. **3a** did not show any color change upon irradiation with ultraviolet light. The difference in the reactivity among **1a**–**4a** in the crystalline phase cannot be interpreted by simple electronic effects.

Fig. 2 shows the polarized absorption spectra of a photogenerated colored crystal of **4a**. In the measurement, the



1a: $R_1 = CH_3$, $R_2 = H$
2a: $R_1 = CH_3$, $R_2 = OCH_3$
3a: $R_1 = CH(CH_3)_2$, $R_2 = H$
4a: $R_1 = CH(CH_3)_2$, $R_2 = OCH_3$

1b: $R_1 = CH_3$, $R_2 = H$
2b: $R_1 = CH_3$, $R_2 = OCH_3$
3b: $R_1 = CH(CH_3)_2$, $R_2 = H$
4b: $R_1 = CH(CH_3)_2$, $R_2 = OCH_3$

Scheme 1

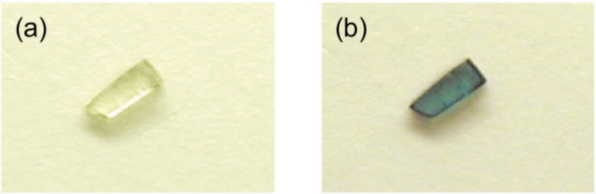


Fig. 1 Photographs of crystal **4a** before (a) and after (b) photoirradiation with ultraviolet light.

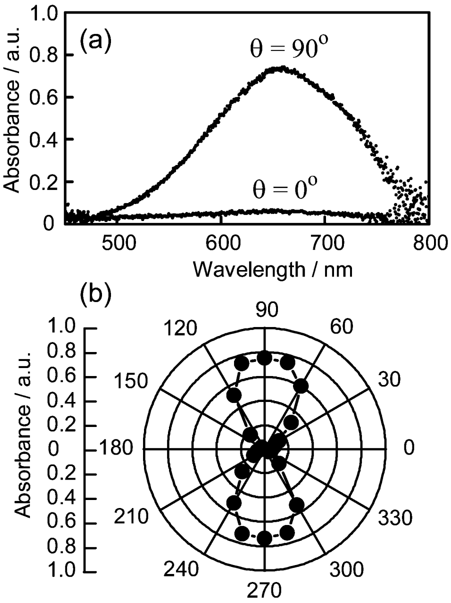


Fig. 2 (a) Polarized absorption spectra of the photogenerated colored crystal of **4a** and (b) polar plots of the absorbance at 655 nm.

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† Electronic supplementary information (ESI) available: X-ray crystallographic data for **2a**, **3a** and **4a**. See http://www.rsc.org/suppdata/cc/b2/b208419h/

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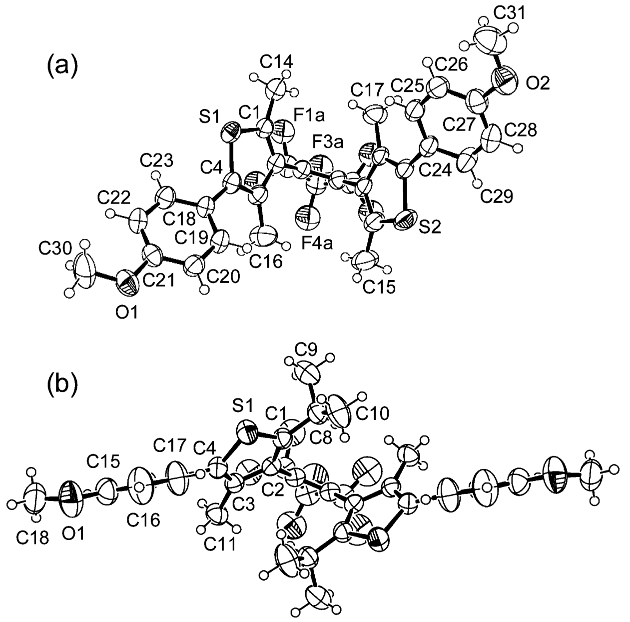

Fig. 3 ORTEP drawings of **2a** (a) and **4a** (b) showing 50% probability displacement ellipsoids. The fluorinated cyclopentene rings were disordered. Only the major structures are illustrated for clarity.

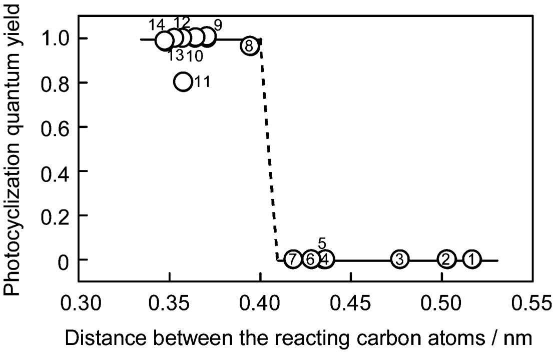

Fig. 4 Relationship between the photocyclization quantum yield and the distance between the reacting carbons. 1: 1,2-bis(2,4,5-trimethyl-3-thienyl)perfluorocyclopentene, 2: 1,2-bis(2,4-dimethyl-5-methoxyphenyl-3-thienyl)perfluorocyclopentene, 3: 1,2-bis(2-methyl-6-formylbenzothiophen-3-yl)perfluorocyclopentene, 4: 1,2-bis(2-isopropyl-4-methyl-5-phenyl-3-thienyl)perfluorocyclopentene, 5: 1,2-bis(2-methylbenzothiophen-3-yl)perfluorocyclopentene, 6: 1-(2-methylbenzothiophen-3-yl)-2-(2,6-dimethylbenzothiophen-3-yl)perfluorocyclopentene, 7: 1,2-bis(2,6-dimethylbenzothiophen-3-yl)perfluorocyclopentene, 8: 1,2-bis(2,4-dimethyl-5-phenyl-3-thienyl)perfluorocyclopentene, 9: 1,2-bis(2-ethyl-5-phenyl-3-thienyl)perfluorocyclopentene, 10: 1,2-bis(2-methyl-5-tolyl-3-thienyl)perfluorocyclopentene, 11: 1,2-bis(2,5-dimethyl-3-thienyl)perfluorocyclopentene, 12: 1,2-bis(2-methyl-5-*tert*-butylphenyl-3-thienyl)perfluorocyclopentene, 13: 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene, 14: 1,2-bis(2-methyl-5-methoxyphenyl-3-thienyl)-perfluorocyclopentene.

polarizer and analyzer were set parallel each other. At $\theta = 0°$, strong absorption was observed at 655 nm, while at $\theta = 90°$ the absorption almost disappeared. The absorption intensity depends on the direction of electronic transition moments of the packed molecules. The order parameter $((A_{||} - A_{\perp})/(A_{||} + 2A_{\perp}))$ was estimated to be 0.84. The high order parameter indicates that the photochromic reaction took place in the crystal lattice.

X-Ray crystallographic analysis of the open-ring form crystals **1a**–**4a** was carried out to determine the precise conformation of molecules **1a**–**4a** in the crystalline phase.§ All diarylethenes were packed in the antiparallel conformation but had different distances between the reactive carbons. Fig. 3 shows ORTEP drawings of **2a** and **4a**. The distances between the reactive carbons for **1a**, **2a**, **3a** and **4a** were 0.396, 0.503, 0.436 and 0.387 nm, respectively. The distances for **1a** and **4a** were shorter than 0.40 nm, while the distances for **2a** and **3a** were larger than 0.43 nm. The single-crystalline photochromic reactivity depended on the distance between the reactive carbon atoms rather than polar and steric substituent effects.

Fig. 4 shows a correlation of the cyclization quantum yields of diarylethene crystals so far examined and the distances between the reactive carbon atoms of the diarylethenes in the crystals. When the distance is larger than 0.42 nm, the photocyclization reaction in crystals is suppressed.

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Notes and references

‡ *Selected data* for **4a**: needle crystals; mp = 142–143 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (d, *J* 6.7 Hz, 4H), 6.93 (d, *J* 6.7 Hz, 4H), 3.84 (s, 6H × 0.86), 3.83 (s, 6H × 0.14), 3.06 (septet, *J* 6.8 Hz, 2H × 0.14), 2.85 (septet, *J* 6.8 Hz, 2H × 0.86), 2.18 (s, 6H × 0.86), 1.29 (d, *J* 6.8 Hz, 6H × 0.14), 1.19 (d, *J* 6.8 Hz, 6H × 0.14), 1.19 (d, *J* 6.8 Hz, 6H × 0.86), 0.85 (d, *J* 6.8 Hz, 6H × 0.86) (the ratio of the antiparallel and parallel was estimated to be 86 : 14 by ^{1}H NMR spectroscopy); *m/z* (M^+) 664; Anal. Calc. for $C_{31}H_{26}F_6O_2S_2$: C, 63.24; H, 5.16. Found: C, 63.44; H, 5.24%.

§ *Crystal data*: for **2a**: $C_{31}H_{26}F_6O_2S_2$, T = 298(2) K, M = 608.64, monoclinic, space group $P2_1/c$, a = 12.564(3), b = 9.771(2), c = 23.797(5) Å, β = 96.368(4)°, V = 2903.2(10) Å^3, Z = 4, μ(Mo-Kα) = 0.249 mm^{-1}, 10956 reflections measured, 3545 independent reflections (R_{int} = 0.0592). Final $R1$ ($I > 2\sigma(I)$) = 0.0453, $wR2$(all data) = 0.1151. For **3a**: $C_{33}H_{30}F_6S_2$, M = 604.69, monoclinic, space group $C2/c$, a = 23.5746(4), b = 8.316(2), c = 19.233(4) Å, β = 127.235(3)°, V = 2998.4(9) Å^3, T = 298(2) K, Z = 4, μ(Mo-Kα) = 0.236 mm^{-1}, 6489 reflections measured, 2151 independent reflections (R_{int} = 0.0763). Final $R1$ ($I > 2\sigma(I)$) = 0.0440, $wR2$(all data) = 0.1152. For **4a**: $C_{35}H_{34}F_6O_2S_2$, T = 304(2) K, M = 664.74, monoclinic, space group $C2/c$, a = 13.567(1), b = 14.728(1), c = 18.098(1) Å, β = 111.948(1)°, V = 3353.9(5) Å^3, Z = 4, μ(Mo-Kα) = 0.222 mm^{-1}, 29012 reflections measured, 3887 independent reflections (R_{int} = 0.0334). Final $R1$ ($I > 2\sigma(I)$) = 0.0447, $wR2$(all data) = 0.1345. CCDC reference numbers 192542 (**2a**), 192543 (**3a**) and 192544 (**4a**). See http://www.rsc.org/suppdata/cc/b2/b208419h/ for crystallographic data in CIF or other electronic format.

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