Photochromism of Diarylethenes Linked by Hydrogen Bonds in the Single-Crystalline Phase

Satoshi Yamamoto, Kenji Matsuda, and Masahiro Irie*[a]

Abstract: Photochromic diarylethenes, which bear carboxyl groups at the *ortho*, *meta*, or *para* positions of both terminal phenyl groups, have been synthesized. The diarylethenes adopt linear chain structures as a result of hydrogen bonding in the crystalline phase, and the crystals exhibit photochromic properties. The absorption maximum of the photogenerated closed-ring isomer of the *para*-substituted derivative shows an 80 nm bathochromic shift in comparison with that of the *ortho*-substituted derivative. The maximum of the closed-ring isomer of the *meta*-substituted derivative is located in between those of the *para*- and *ortho*-substituted derivatives. The shifts can be attributed to the differences in conformation among the derivatives, arising from the restrictions imposed by the hydrogen-bonded chains.

Keywords: diarylethene · photochromism · hydrogen bonding · X-ray analysis

Introduction

Photochromic compounds inherently exhibit two different chemical forms, which are reversibly interconverted upon irradiation with light of appropriate wavelength.[1] Various types of photochromic compounds, such as spirobenzopyrans, azobenzenes, fulgides, and diarylethenes, have hitherto been developed. Among such compounds, diarylethenes show characteristic properties, including thermal stability of both isomers and fatigue-resistant performance.[2] The open-ring isomer of the diarylethene undergoes photocyclization to produce the closed-ring isomer upon irradiation with UV light, and the closed-ring isomer reverts to the open-ring isomer upon irradiation with visible light.

Some diarylperfluorocyclopentene derivatives having thiophene or benzothiophene rings are known to undergo photochromic reactions even in the single-crystalline phase.[3] An antiparallel conformation of the aryl groups and a short distance between the reactive carbons are essential for the reaction to take place in the crystalline phase.[4] The color and the photocycloreversion reactivity of the closed-ring isomers are dependent on the conformation of the molecule in the crystal.[5] The closed-ring isomer photogenerated in the crystal generally shows a bathochromic shift with respect to the closed-ring isomer in solution.[6]

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Hydrogen-bonded networks represent one of the most convenient methods for constructing supramolecular architectures.[7] The direction-specific character of hydrogen-bonding is successfully utilized to construct double helices, ring structures, and nanotubes.[8, 9] The geometry of the photogenerated closed-ring isomers in the crystals reflects the crystal packing of the open-ring isomers.[3] Therefore, if desired, crystal packing could be designed on the basis of hydrogen-bonded supramolecular assemblies, and the spectroscopic properties of the photochromic crystal would be controlled. Herein, we report on the synthesis and photochromic performance of intermolecularly hydrogen-bonded diarylethenes. The effect of the hydrogen bonding on the photochromic performance has been studied in the crystalline phase.

Results and Discussion

Molecular design and synthesis: When molecules have two carboxyl groups that cannot participate in intramolecular hydrogen bonding, the formation of hydrogen-bonded linear chain structures in aprotic solvents as well as in the crystal may be anticipated. 1,2-Bis(2-methyl-5-phenyl-3-thienyl)hexafluorocyclopentene, which is known to undergo photochromic reaction even in the crystalline phase,[3d] was chosen as the photochromic core and carboxyl groups were introduced at the *ortho*, *meta*, and *para* positions of both of the terminal phenyl groups (Scheme 1). As reference compounds, diarylethenes **4a–6a** bearing formyl substituents, which are similar in size but have less hydrogen-bonding character as compared to carboxyl groups, were also prepared.

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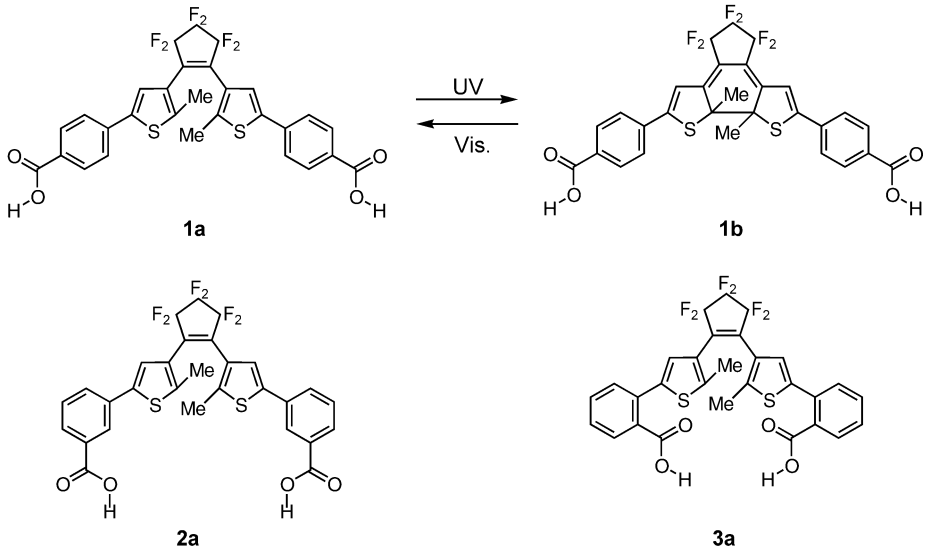


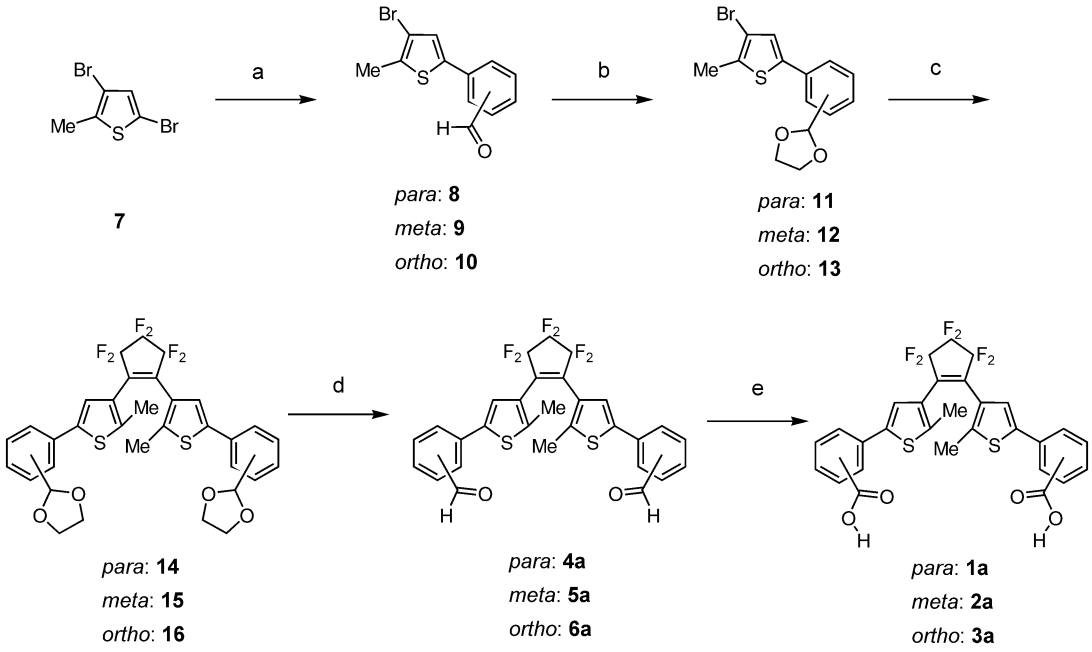
Scheme 1. Photochromic diarylethenes having intermolecular hydrogen-bonding sites.

The synthetic procedure leading to **1a–6a** is shown in Scheme 2. Suzuki coupling of three isomeric bromobenzaldehydes with thiophene boronic acid gave formylphenylthiophene derivatives (**8–10**). After protection of compounds **8–10** with ethylene glycol, they were lithiated and then coupled with octafluorocyclopentene to give diarylethene derivatives (**14–16**). Deprotection gave formyl-substituted diarylethene derivatives (**4a–6a**). Jones oxidation of the formyl-substituted derivatives (**4a–6a**) afforded carboxyl-substituted diarylethenes (**1a–3a**). The structures of **1a–6a** were confirmed by ^{1}H NMR spectroscopy, mass spectrometry, elemental analysis, and UV/Vis spectroscopy.

Compounds **1a–3a** are anticipated to form intermolecular hydrogen-bonded chains in solution in aprotic solvents as well as in the crystalline phase. Intramolecular hydrogen-bonding is essentially precluded because of the strained conformation.

Photochromic behavior of compounds 1–6 in protic or aprotic solvents: The photochromic reactivity of diarylethenes **1–6** was examined in ethanol solution. Figure 1 shows the changes in the absorption spectra upon photoirradiation. Upon irradiation with 313 nm light, the colorless solutions containing **1a–6a** turned blue or purple. These colors could be attributed to the formation of the closed-ring isomers. Upon irradiation with 578 nm light, the colored solutions reverted to their original colorless forms. Table 1 shows the absorption maxima of the open- and closed-ring isomers in ethanol. When the substituents are in the same positions, the absorption maxima of diarylethenes bearing carboxyl groups are similar to those of the derivatives bearing formyl groups.

Table 1 also shows the maxima in aprotic cyclohexane. The absorption maxima in ethanol and cyclohexane are similar. In other words, $\Delta\lambda_{max}$ is small, except in the case of the *ortho*-substituted derivative **3b**, for which a considerable spectral



Scheme 2. Synthetic scheme used to obtain **1a–6a**. Reagents and conditions: a) i) *n*BuLi, ii) tri-*n*-butyl borate, iii) $Pd(PPh_3)_4$, *o*-, *m*-, and *p*-bromobenzaldehydes, Na_2CO_3, THF, H_2O, 48–64%. b) ethylene glycol, *p*-toluenesulfonic acid monohydrate, benzene, 96%. c) i) *n*BuLi, ii) octafluorocyclopentene, THF, 72–76%. d) PPTS, acetone, 96–98%. e) Jones' reagent, acetone, 70–87%.

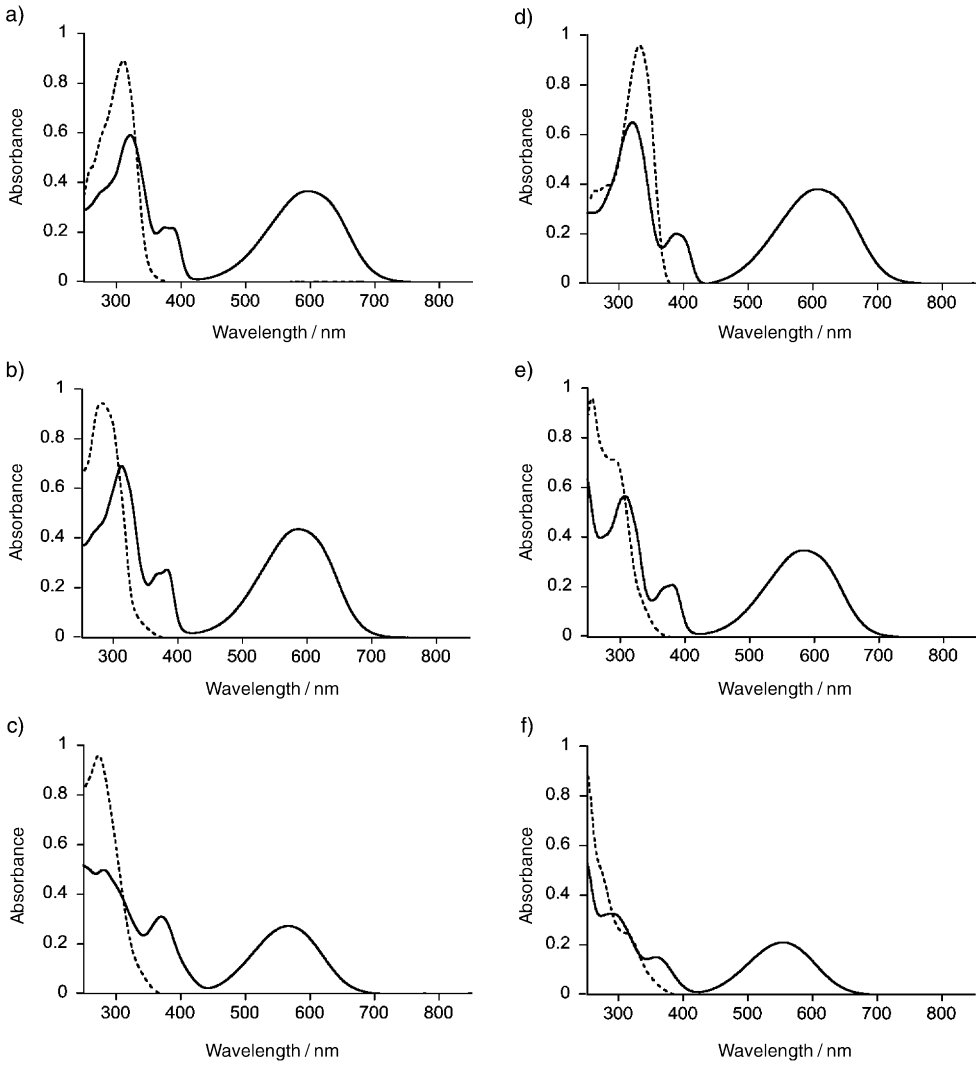


Figure 1. Photochromic spectral changes of **1a–6a** in ethanol solution before (dotted line) and after (solid line) photoirradiation with light of wavelength 313 nm: a) **1a**; b) **2a**; c) **3a**; d) **4a**; e) **5a**; f) **6a**.

Table 1. Absorption maxima of the open- and closed-ring isomers in ethanol and cyclohexane.

	λ_{max} (open) in ethanol [nm]	λ_{max} (closed) in cyclohexane [nm]	λ_{max} (closed) in ethanol [nm]
1	312	598	600
2	278	584	580
3	273	567	546
4	330	605	601
5	289	585	581
6	270	553	549

shift ($\Delta\lambda_{max} = 21$ nm) is observed between the protic and aprotic solvents. When a small amount of ethanol was added dropwise to a solution of **3b** in cyclohexane, a bathochromic shift of the maximum was observed. This finding suggests that hydrogen bonding affects the conformation of the closed-ring isomer of *ortho* derivative **3b**. In the cases of the *para* and *meta* derivatives **1b** and **2b**, no solvent dependence was observed. This indicates that the contribution from intermolecular hydrogen bonding is negligible for **1b** and **2b** in solution.

The packing diagrams of diarylethenes 1–3 in the crystalline phase: Diarylethenes **1a–6a** formed clear colorless single crystals upon recrystallization from appropriate solvents. Their molecular structures and crystal packing were determined by X-ray crystallographic analysis. Table 2 shows the X-ray crystallographic data at 123 K. These single crystals of the open-ring isomers did not contain any solvent.

Figure 2 shows the packing diagrams of carboxyl-substituted diarylethenes **1a–3a**. One-dimensional hydrogen-bonded chains were observed in their single crystals. The distances between carbonyl oxygen and hydroxyl oxygen O···H–O in **1a–3a** were 2.61 Å, 2.63 Å, and 2.64 Å, respectively. These sufficiently short distances indicate that the carboxyl-substituted diarylethenes form hydrogen-bonded arrays with adjacent molecules in the crystals. The chains have twofold helical symmetry and the position of substitution changes the pitch. The zigzag chain of *ortho* derivative **3a** shows the shortest pitch.

Figure 3 shows ORTEP drawings of the molecular structures of **1a–3a**. The numbering of the atoms is the same for all three molecules. Each of the compounds **1a–3a** was found to be packed in an antiparallel conformation in the crystal. The distances between the reactive carbon atoms, C1–C10, are 3.49 Å (**1a**), 3.52 Å (**2a**), and 3.59 Å (**3a**), which are short enough for the reaction to take place in the single-crystalline phase (Table 3).[4] The angles between the planes of the phenyl and thiophene rings are quite different among these compounds. The angles C3-C4-C16-C17 were found to be 32.5° (**1a**), 11.9° (**2a**), and −51.9° (**3a**), respectively. The angles in **1a** and **3a** thus differ by more than 84°. In *meta*-substituted **2a**, the phenyl and thiophene rings are coplanar.

Formyl-substituted diarylethenes (**4a–6a**) are also packed in an antiparallel conformation in their single crystals. The distances between the reactive carbon atoms were found to be 3.65 Å (**4a**), 3.54 Å (**5a**), and 3.66 Å (**6a**). In these derivatives, intermolecular hydrogen bonding was not discerned. The angles between the planes of the phenyl and thiophene rings, C3-C4-C16-C17, were found to be similar, at 25° (**4a**), 33.9° (**5a**), and 33.7° (**6a**).

Table 2. Crystallographic data of **1a**–**6a**.

	1a (*para*)	**2a** (*meta*)	**3a** (*ortho*)	**4a** (*para*)	**5a** (*meta*)	**6a** (*ortho*)
recrystallization solvent	2-propanol/THF	methanol	acetonitrile/THF	acetonitrile	acetonitrile	acetonitrile
empirical formula	$C_{29}H_{18}F_6S_2O_4$	$C_{29}H_{18}F_6S_2O_4$	$C_{29}H_{18}F_6S_2O_4$	$C_{29}H_{18}F_6S_2O_2$	$C_{29}H_{18}F_6S_2O_2$	$C_{29}H_{18}F_6S_2O_2$
formula weight	608.55	608.55	608.55	576.55	576.55	576.55
temperature [K]	123	123	123	123	123	123
crystal system	monoclinic	monoclinic	triclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$C2/c$	P-1	$C2/c$	$P2_1$	$C2/c$
a [Å]	15.561	23.694	8.379	25.936	8.3543(18)	17.057
b [Å]	12.833	8.488	11.003	9.198	13.106(3)	8.4761
c [Å]	14.501	13.483	14.809	10.368	11.347(3)	18.152
α [°]	90	90	91.154	90	90	90
β [°]	116.235	100.279	95.179	100.825	93.389(4)	104.260
γ [°]	90	90	110.575	90	90	90
volume [Å^3]	2597.5(5)	2668(3)	1271.0(8)	2429.4(12)	1240.3(5)	2543.5(8)
Z	4	4	2	4	2	4
goodness-of-fit on F^2	0.910	1.127	0.986	1.065	1.098	1.008
data/restraints/parameters	5551/0/380	2862/0/219	5270/0/372	2531/0/167	3536/1/354	2674/0/204
$R1$ [$I > 2\sigma(I)$]	0.0448	0.0659	0.0706	0.0777	0.0488	0.0392
$wR2$ (all data)	0.1250	0.1903	0.1976	0.2373	0.1293	0.1071

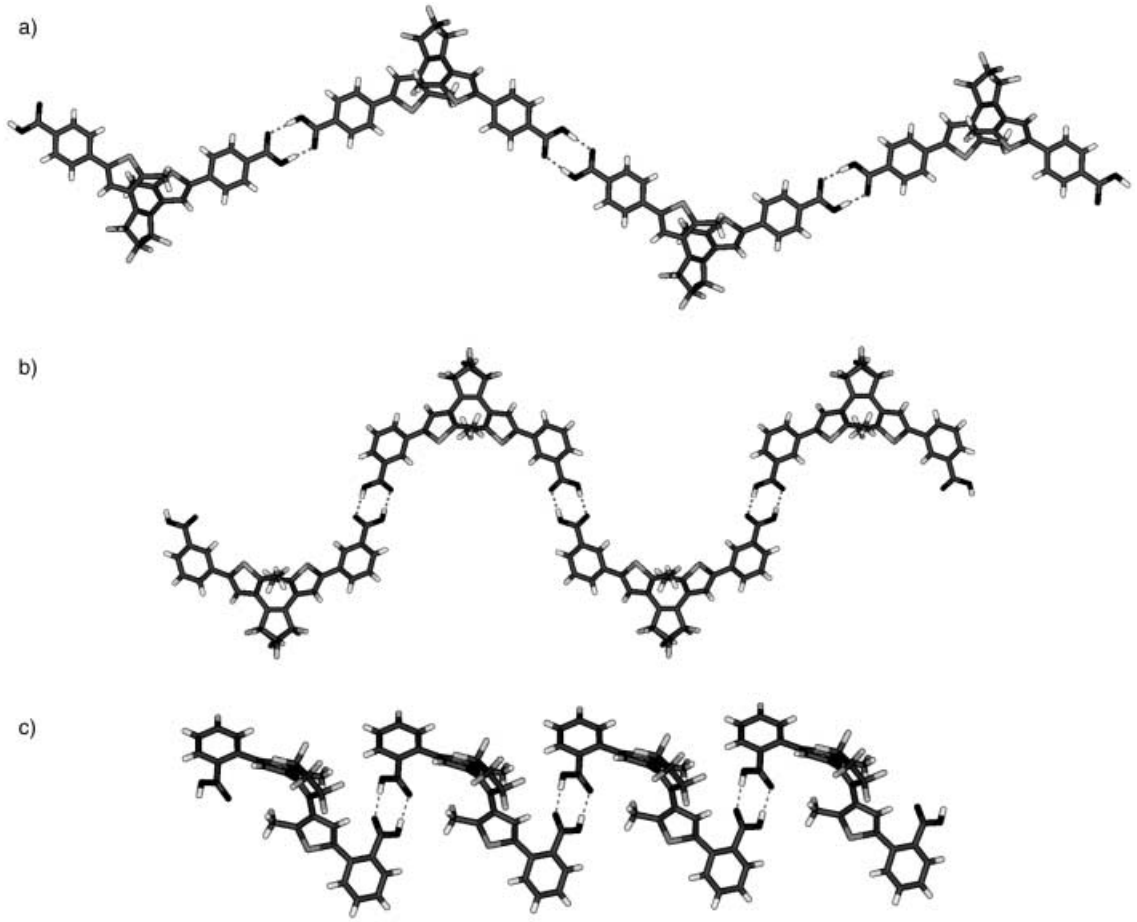


Figure 2. X-ray structures of one-dimensional linear chains of carboxyl-substituted diarylethenes: a) **1a**; b) **2a**; c) **3a**.

Photochromism of diarylethenes 1a–6a in the single-crystalline phase: Compounds **1a–3a** were found to undergo photochromic reactions in the single-crystalline phase. Upon irradiation with 366 nm light, the single crystals turned blue or reddish purple. These color changes are due to the generation of the closed-ring isomers **1b–3b**. The colors disappeared

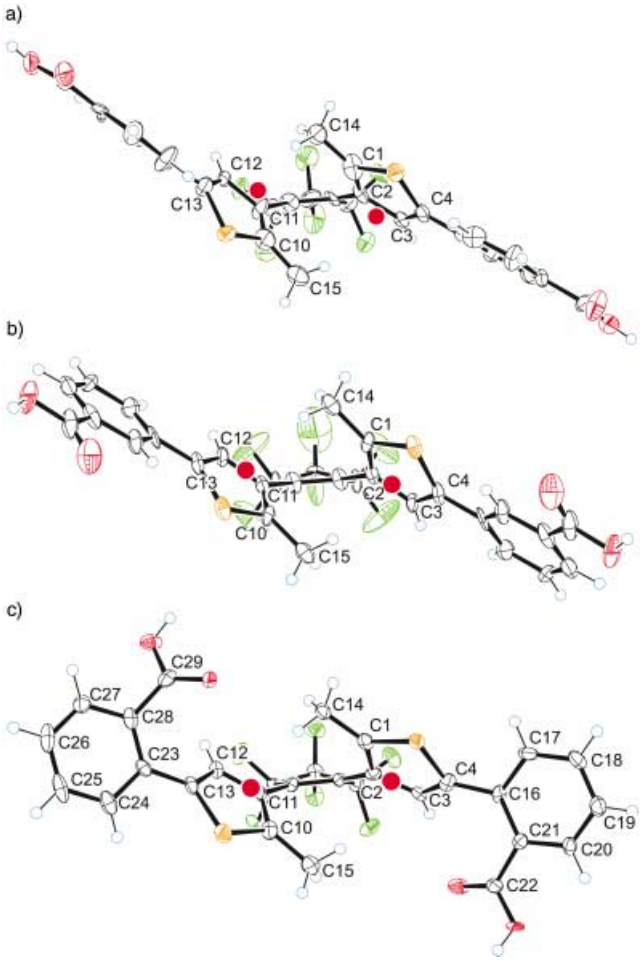


Figure 3. ORTEP drawings of a) **1a**, b) **2a**, and c) **3a**. The hexafluorocyclopentene unit is located below the plane of the paper, away from the viewer. The red circles indicate the positions of the sulfur atoms that appear in the UV-irradiated crystal.

Table 3. Distances between the reactive carbons and torsion angles between the planes of the thiophene and phenyl rings, as obtained from X-ray data, along with the absorption maxima of the photogenerated closed-ring isomers in the single-crystalline phase.

	Distance between the reactive carbons [Å][a]	Torsion angle [°][b]	Absorption maxima [nm]
1a	3.49	32.5[c]	640
2a	3.52	11.9	600
3a	3.59	−51.9[c]	560
4a	3.65	25	605
5a	3.54	33.9[c]	610
6a	3.66	33.7	605

[a] The distance C1−C10. [b] The angle C3-C4-C16-C17. [c] The two angles in the molecules are different in these compounds. The other torsion angles are 23.7° (**1a**), −40.5° (**3a**), and 33.6° (**5b**).

upon irradiation with visible light ($\lambda > 500$ nm). The coloration/decoloration cycles could be repeated many times without loss of integrity of the crystals.

The colors of the crystals were analyzed under polarized light. Figure 4 shows polar plots of the (001) surface of a crystal of **3a**. Upon irradiation with 366 nm light the crystal

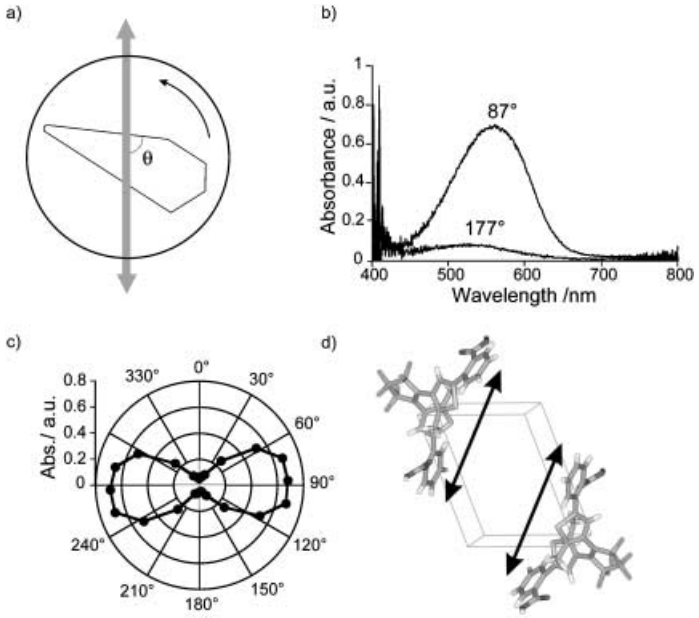


Figure 4. Absorption anisotropy of **3a**: a) the crystal shape and the direction of the polarizer, b) polarized absorption spectra of the (001) face, c) polar plot at 610 nm, d) packing diagrams of crystal **3a** projected onto the (001) face.

changed to a deep reddish-purple color. At a certain angle ($\theta = 87°$), the crystal showed strong absorption, and the absorption maximum was observed at 560 nm. When the crystal was rotated as much as 90°, the absorption intensity decreased but the position of the maximum was unchanged. The deep reddish-purple color reappeared upon rotation through 180°. The change in color intensity seen upon rotating the crystal sample indicates that the closed-ring isomers are regularly oriented in the crystal and that photochromic reaction had taken place in the crystal lattice. Upon irradiation with visible light ($\lambda > 500$ nm), the color disappeared. The direction of the transition moment, which was determined from the polarized absorption spectrum, is shown in Figure 4d, along with the crystal structure. The direction of the transition moment coincides with the long axis of the open-ring isomer of **3a**.

Figure 5 shows the polarized absorption spectra of photogenerated closed-ring isomers **1b–3b** (Figure 5a) and **4b–6b** (Figure 5b) at the angles of maximum color intensity.[10] The positions of the absorption maxima are listed in Table 3. It is inferred from the spectra that the substitution position strongly affects the position of the maximum in the case of carboxyl-substituted derivatives, while the effect is negligible in the case of formyl-substituted derivatives. The maximum of *para*-substituted **1a** (640 nm) shows an 80 nm bathochromic shift in comparison with that of *ortho*-substituted **3a** (560 nm). The fairly large spectral shift in the carboxyl-substituted derivatives is considered to reflect the difference in the angles between the planes of the phenyl and thiophene rings, as observed for the spectra of 1,2-bis(2-methyl-5-(4-methoxyphenyl)-3-thienyl)perfluorocyclopentene in the single-crystalline phase.[5]

To establish the precise structures of the colored closed-ring isomers photogenerated in the crystals, in situ X-ray crystallographic analyses were carried out. The red circles shown in

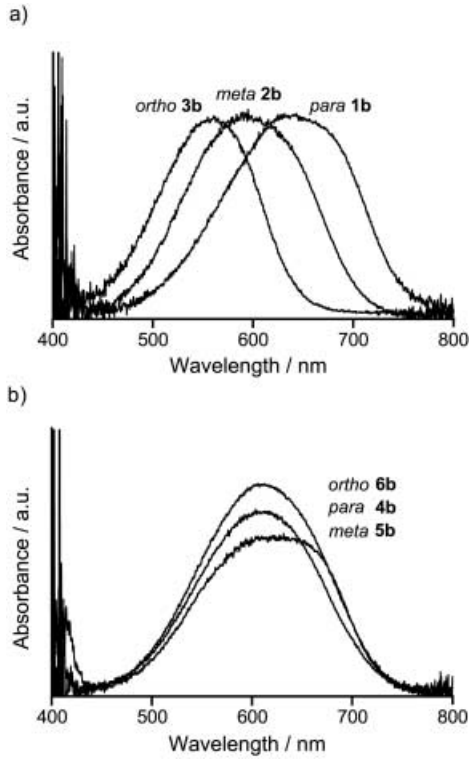


Figure 5. Photochromism in the single-crystalline phase: a) carboxyl-substituted diarylethene crystals **1b**–**3b**; b) formyl-substituted diarylethene crystals **4b**–**6b**.

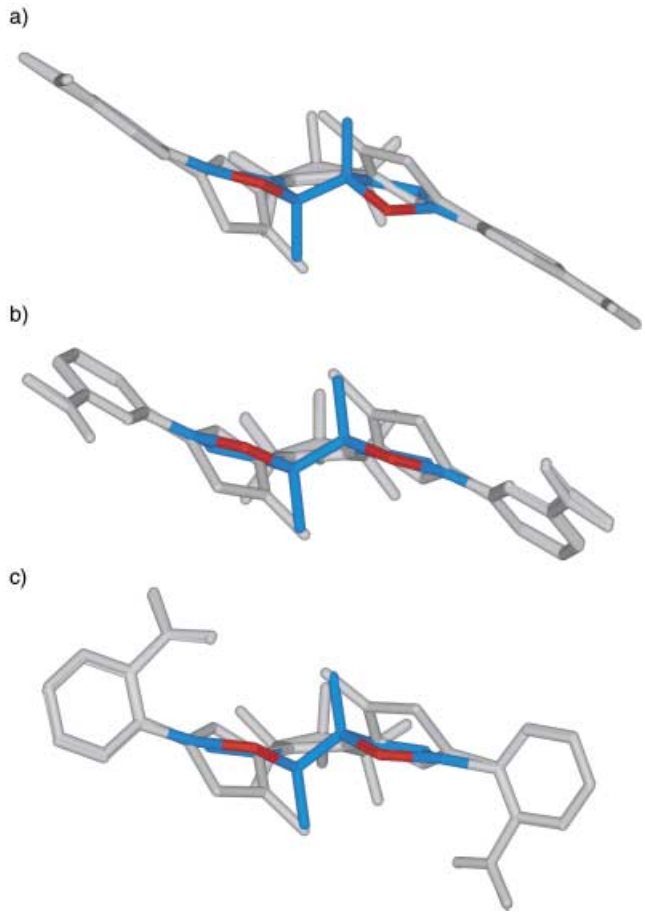


Figure 6. The calculated structures of the closed-ring isomers of a) **1b**, b) **2b**, and c) **3b** in the crystal. The coordinates of the sulfur atoms (red line) that appeared in the difference Fourier electron density maps of the UV-irradiated crystals were used for the calculations. Partial MM2 calculations were carried out on the thiophene and methyl moieties (blue line) with the rest of the structures being fixed. The open-ring isomers are overlaid. Hydrogen atoms have been omitted for clarity.

Figure 3 indicate the positions of the photogenerated sulfur atoms, as ascertained from the difference Fourier electron density map.[11] The sulfur atoms moved from upper or lower positions to central ones. It is possible to estimate the structures of the photogenerated closed-ring isomers from the positions of the sulfur atoms. The structural optimizations were carried out by means of partial MM2 calculations of the thiophene and methyl moieties (C1, C2, C3, C4, C10, C11, C12, C13, C14, and C15 in Figure 3), with the assumption that the positions of the hexafluorocyclopentene ring, the carboxyphenyl groups, and the photogenerated sulfur atoms (S1′ and S2′) are fixed. The calculated structures are shown in Figure 6.

As can be seen from Figure 6, *para*-substituted derivative **1b** has the greatest coplanarity between the planes of the phenyl and thiophene rings, and π-conjugation is considered to extend throughout the molecule. In the case of the *ortho* derivative **3b**, the two rings are almost perpendicular. The shift in the absorption maximum from 560 nm (*ortho*-substituted derivative **3b**) to 640 nm (*para*-substituted derivative **1b**) can thus be ascribed to the difference in coplanarity between the phenyl and thiophene rings.

To confirm this assumption, theoretical calculations (INDO/S method) of the spectra were carried out, based on the estimated structures. The lowest-energy absorption peaks were calculated to appear at 492, 461, and 383 nm for **1b**, **2b**, and **3b**, respectively (Table 4). A coplanar configuration of the planes of the phenyl and thiophene rings gave rise to a longer wavelength absorption maximum. The result verified that the differences in position of the absorption maxima between the three derivatives are due to different conformations of the closed-ring isomers in the crystals.

Table 4. Calculated torsion angles of the photogenerated closed-ring isomers and calculated absorption maxima of photogenerated closed-ring isomers **1a**–**3b**.

	Calculated torsion angle [°][a]	Calculated absorption maxima [nm]
1b	−14.7[b]	492
2b	−25.8	461
3b	−93.5[b]	383

[a] The angle C3-C4-C16-C17. [b] The two angles in the molecules are different in these compounds. The other calculated torsion angles are −16.4° (**1a**) and −84.7° (**3a**).

Conclusion

Photochromic diarylethenes bearing carboxyl groups at the *ortho*, *meta*, and *para* positions of both terminal phenyl groups

have been synthesized. These derivatives have been found to form various types of linear polymers linked by hydrogen bonds in their crystals. The diarylethenes show photochromism in the crystalline state upon irradiation with light of appropriate wavelengths, and the absorption maxima of the closed-ring isomers show large differences, as much as 80 nm between the *para*- and *ortho*-substituted compounds. The large bathochromic shift of the *para*-substituted diarylethene can be ascribed to the coplanar conformation between the thiophene and phenyl rings that affects the π-conjugation length.

Experimental Section

General: All reactions were monitored by thin-layer chromatography carried out on 0.2 mm Merck silica gel plates (60 F-254). Column chromatography was performed on silica gel (Kanto Chemical, 63–210 mesh). ^{1}H NMR spectra were recorded on a Varian Gemini 200 instrument. Mass spectra were obtained on Shimadzu GCMS-QP 5050 A (EI) and JEOL JMS-GCmateII (FAB) mass spectrometers. Melting points were measured using a Laboratory Devices MEL-TEMP II apparatus and are uncorrected. Jones' reagent (1.94 M) was prepared as follows: H_2SO_4 (6.1 mL, 110 mmol) was added dropwise to an aqueous solution (10 mL) of CrO_3 (7.0 mg, 70 mmol) at 0 °C, and then distilled water (20 mL) was added. The synthesis of **5a** has been reported previously.[3n]

3-Bromo-5-(4-formylphenyl)-2-methylthiophene (*para* 8): A solution of *n*-butyllithium in hexane (1.6 M, 64.0 mL, 102 mmol) was added dropwise to a well-stirred solution of dibromo compound **7** (25.0 g, 98 mmol) in anhydrous THF (250 mL) under Ar at −78 °C, and stirring was continued at this temperature for 1 h. Tri-*n*-butyl borate (39.3 mL, 102 mol) was slowly added to the reaction mixture at −78 °C, and the mixture was stirred for 2 h at this temperature. Then, 4-bromobenzaldehyde (18.1 g, 98 mmol), $Pd(PPh_3)_4$ (3.2 g, 2.8 mmol), and a suspension of Na_2CO_3 (40 g) in water (160 mL) were successively added to the reaction mixture at room temperature. The mixture was stirred under reflux for 4.5 h, and then allowed to cool to room temperature. Diethyl ether was added, the organic layer was collected, and the aqueous layer was further extracted with diethyl ether. The combined organic layers were dried over $MgSO_4$, and the solvents were evaporated. Purification of the crude product by column chromatography (silica gel, $CHCl_3$) afforded phenylthiophene derivative **8** (13.3 g, 48 %) as a white solid. M.p. 114.1–114.7 °C; ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 2.44$ (s, 3H), 7.26 (s, 1H), 7.66 (d, $J = 8$ Hz, 4H), 7.88 (d, $J = 8$ Hz, 4H), 10.0 ppm (s, 1H); EI-MS: *m*/*z*: 280 $[M]^+$; elemental analysis calcd (%) for $C_{12}H_9BrOS$: C 51.26, H 3.23; found: C 51.36, H 3.23.

3-Bromo-5-(2-formylphenyl)-2-methylthiophene (*ortho* 10): A solution of *n*-butyllithium in hexane (1.6 M, 137 mL, 218 mmol) was added dropwise to a well-stirred solution of dibromo compound **7** (54.4 g, 213 mmol) in anhydrous THF (250 mL) under Ar at −78 °C, and stirring was continued at this temperature for 0.5 h. Tri-*n*-butyl borate (84 mL, 218 mol) was slowly added to the reaction mixture at −78 °C, and the mixture was stirred for 2 h at this temperature. Then, 2-bromobenzaldehyde (6.3 g, 218 mmol), $Pd(PPh_3)_4$ (1.2 g, 1.0 mmol), and a suspension of Na_2CO_3 (20 g) in water (80 mL) were successively added to the reaction mixture at room temperature. The mixture was stirred under reflux for 4.5 h, and then allowed to cool to room temperature. Diethyl ether was added, the organic layer was collected, and the aqueous layer was further extracted with diethyl ether. The combined organic layers were dried over $MgSO_4$, and the solvents were evaporated. Purification of the crude product by column chromatography (silica gel, $CHCl_3$) afforded phenylthiophene derivative **10** (4.1 g, 68 %) as a white solid. M.p. 69.5–70.2 °C; ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 2.47$ (s, 3H), 6.90 (s, 1H), 7.66 (t, $J = 7$ Hz, 2H), 7.59–7.67 (m, 1H), 7.98–8.02 (m, 1H), 10.22 ppm (s, 1H); EI-MS: *m*/*z*: $[M]^+$ 280; elemental analysis calcd (%) for $C_{12}H_9BrOS$: C 51.26, H 3.23; found: C 51.34, H 3.20.

3-Bromo-5-(4-(2,5-dioxolanyl)phenyl)-2-methylthiophene (*para* 11): A solution of **8** (8.2 g, 29 mmol), ethylene glycol (19.7 g, 310 mmol), and *p*-toluenesulfonic acid monohydrate (73 mg, 0.29 mmol) in benzene (300 mL) was refluxed for 7 h in an apparatus fitted with a Dean–Stark condenser. The reaction mixture was subsequently poured into aqueous sodium hydrogen carbonate solution, extracted with diethyl ether, and the combined extracts were washed with aqueous sodium hydrogen carbonate solution and water, dried ($MgSO_4$), and concentrated. Dioxolane **11** (9.1 g, 96 %) was obtained as a white solid. M.p. 117.5–119.6 °C; ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 2.42$ (s, 3H), 4.04–4.15 (m, 4H), 5.82 (s, 1H), 7.12 (s, 1H), 7.35–7.55 ppm (m, 4H); EI-MS: *m*/*z*: $[M]^+$ 326; elemental analysis calcd (%) for $C_{14}H_{13}BrO_2S$: C 51.70, H 4.03; found: C 51.83, H 4.03.

3-Bromo-5-(2-(2,5-dioxolanyl)phenyl)-2-methylthiophene (*ortho* 13): A solution of **10** (8.2 g, 29 mmol), ethylene glycol (19.7 g, 310 mmol), and *p*-toluenesulfonic acid monohydrate (73 mg, 0.29 mmol) in benzene (300 mL) was refluxed for 7 h in an apparatus fitted with a Dean–Stark condenser. The reaction mixture was subsequently poured into aqueous sodium hydrogen carbonate solution, extracted with diethyl ether, and the combined extracts were washed with aqueous sodium hydrogen carbonate solution and water, dried ($MgSO_4$), and concentrated. Dioxolane **13** (9.1 g, 96 %) was obtained as a colorless oil. ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 2.43$ (s, 3H), 3.99–4.23 (m, 4H), 5.87 (s, 1H), 7.06 (s, 1H), 7.36–7.43 (m, 3H), 7.70–7.75 (m, 1H); EI-MS: $[M]^+$ *m*/*z*: 326; elemental analysis calcd (%) for $C_{14}H_{13}BrO_2S$: C 51.70, H 4.03; found: C 51.83, H 4.03.

1,2-Bis(2-methyl-5-(4-(2,5-dioxolanyl)phenyl)thiophen-3-yl)hexafluorocyclopentene (*para* 14): A solution of *n*-butyllithium in hexane (1.6 M, 6.1 mL, 9.7 mmol) was added dropwise to a well-stirred solution of monobromo compound **11** (3.0 g, 9.3 mmol) in anhydrous THF (100 mL) under Ar at −78 °C, and stirring was continued at this temperature for 1 h. Then, a solution of octafluorocyclopentene (0.6 mL, 4.6 mmol) in anhydrous THF (5 mL) was added dropwise. The mixture was stirred for 6 h and allowed to warm to room temperature, whereupon saturated aqueous NH_4Cl solution was slowly added. The resultant mixture was then extracted with diethyl ether and the combined organic extracts were washed with brine and dried ($MgSO_4$). After removal of the solvent, column chromatography (silica gel; CH_2Cl_2/hexane, 1:1) of the residue afforded diarylethene **14** (2.36 g, 76 %) as white crystals. M.p. 128.4–129.4 °C; ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta =$ 1.96 (s, 6H), 4.01–4.19 (m, 8H), 5.83 (s, 2H), 7.29 (s, 2H), 7.47–7.58 ppm (m, 8H); FAB-MS: *m*/*z*: $[M+H]^+$ 665; elemental analysis calcd (%) for $C_{33}H_{26}F_6O_4S_2$: C 59.63, H 3.94; found: C 59.63, H 3.98.

1,2-Bis(2-methyl-5-(2-(2,5-dioxolanyl)phenyl)thiophen-3-yl)hexafluorocyclopentene (*ortho* 16): A solution of *n*-butyllithium in hexane (1.6 M, 5.1 mL, 8.1 mmol) was added dropwise to a well-stirred solution of monobromo compound **13** (2.5 g, 7.7 mmol) in anhydrous THF (50 mL) under Ar at −78 °C, and stirring was continued at this temperature for 0.5 h. Then, a solution of octafluorocyclopentene (0.5 mL, 3.9 mmol) in anhydrous THF (3 mL) was added dropwise. The mixture was stirred for 5 h and allowed to warm to room temperature, whereupon saturated aqueous NH_4Cl solution was slowly added. The resultant mixture was then extracted with diethyl ether and the combined organic extracts were washed with brine and dried ($MgSO_4$). After removal of the solvent, column chromatography (silica gel; CH_2Cl_2/hexane, 1:1) of the residue afforded diarylethene **16** (1.85 g, 72 %) as yellow crystals. M.p. 189.5–190.0 °C; ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 2.00$ (s, 3H), 3.97–4.20 (m, 8H), 5.80 (s, 2H), 7.26 (s, 2H), 7.30–7.45 (m, 6H), 7.75–7.77 ppm (m, 2H); FAB-MS: *m*/*z*: $[M+H]^+$ 665; elemental analysis calcd (%) for $C_{33}H_{26}F_6O_4S_2$: C 59.63, H 3.94; found: C 59.58, H 3.92.

1,2-Bis(2-methyl-5-(4-formylphenyl)-thiophen-3-yl)hexafluorocyclopentene (*para* 4a): A solution of diarylethene **14** (2.3 g, 2.7 mmol) in wet acetone (50 mL) containing pyridinium tosylate (3.9 g, 9.0 mmol) was refluxed for 16 h. The mixture was cooled to room temperature and water was added. The resultant mixture was then extracted with diethyl ether and the combined organic extracts were washed with brine and dried ($MgSO_4$). After removal of the solvent in vacuo, purification of the crude product by recrystallization afforded slightly yellow crystals of diarylethene **4a** (2.6 g, 98 %). M.p. 199.1–200.5 °C; ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 2.01$ (s, 6H), 7.45 (s, 1H), 7.71 (d, $J = 8$ Hz, 4H), 7.91 (d, $J = 8$ Hz, 4H), 10.02 ppm (s, 2H); FAB-MS: *m*/*z*: $[M+H]^+$ 577; elemental analysis calcd (%) for $C_{29}H_{18}F_6O_2S_2$: C 60.41, H 3.15; found: C 60.45, H 3.18.

1,2-Bis(2-methyl-5-(2-formylphenyl)-thiophen-3-yl)hexafluorocyclopentene (*ortho* 6a): A solution of diarylethene **16** (900 mg, 1.4 mmol) in wet acetone (50 mL) containing pyridinium tosylate (1.36 g, 5.41 mmol) was refluxed for 24 h. The mixture was cooled to room temperature and water was added. The resultant mixture was then extracted with diethyl ether and the combined organic extracts were washed with brine and dried ($MgSO_4$).

After removal of the solvent in vacuo, purification of the crude product by recrystallization afforded colorless crystals of diarylethene **6a** (750 g, 96%). M.p. 178.5–180.0 °C; ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 1.98$ (s, 3H), 2.00 (s, 3H), 7.26–7.92 (m, 10H), 10.01 ppm (s, 2H); EI-MS: m/z: $[M]^+$ 576; elemental analysis calcd (%) for $C_{29}H_{18}F_6O_2S_2$: C 60.41, H 3.15; found: C 60.51, H 3.25.

1,2-Bis(2-methyl-5-(4-carboxylphenyl)thiophen-3-yl)hexafluorocyclopentene (*para* 1a): Jones' reagent (5.7 mL, 10.8 mmol) was added dropwise to a well-stirred solution of **4a** (1.5 g, 2.6 mmol) in acetone (120 mL) at room temperature, and stirring was continued for 5 h. 2-Propanol was then slowly added, the resultant mixture was extracted with diethyl ether, and the combined organic extracts were dried ($MgSO_4$). After removal of the solvent, column chromatography (silica gel; ethyl acetate) of the residue afforded diarylethene **1a** (2.4 g, 76%) as a white powder. M.p. 290 °C (dec.); ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 2.00$ (s, 6H), 7.70 (s, 2H), 7.78 (d, $J = 8$ Hz, 4H), 7.97 ppm (d, $J = 8$ Hz, 4H); FAB-MS: m/z: $[M]^+$ 608; elemental analysis calcd (%) for $C_{29}H_{18}F_6O_4S_2$: C 57.23, H 2.98; found: C 57.60, H 3.19.

1,2-Bis(2-methyl-5-(3-carboxylphenyl)thiophen-3-yl)hexafluorocyclopentene (*meta* 2a): Jones' reagent (6.0 mL, 12 mmol) was added dropwise to a well-stirred solution of **5a** (1.0 g, 1.8 mmol) in acetone (100 mL) at room temperature, and stirring was continued for 5 h. 2-Propanol was then slowly added, the resultant mixture was extracted with diethyl ether, and the combined organic extracts were dried ($MgSO_4$). After removal of the solvent, column chromatography (silica gel; ethyl acetate) of the residue afforded diarylethene **2a** (900 mg, 87%) as a white powder. M.p. 290 °C (decomp); ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 2.02$ (s, 6H), 7.52–7.61 (m, 4H), 7.89 (d, $J = 8$ Hz, 4H), 8.11 ppm (s, 2H); FAB-MS: m/z: $[M]^+$ 608; elemental analysis calcd (%) for $C_{29}H_{18}F_6O_4S_2$: C 57.23, H 2.98; found: C 57.41, H 3.15.

1,2-Bis(2-methyl-5-(2-carboxylphenyl)thiophen-3-yl)hexafluorocyclopentene (*ortho* 3a): Jones' reagent (2.0 mL, 4.0 mmol) was added dropwise to a well-stirred solution of **6a** (580 mg, 1.0 mmol) in acetone (50 mL) at room temperature, and stirring was continued for 14 h. 2-Propanol was then slowly added, the resultant mixture was extracted with diethyl ether, and the combined organic extracts were dried ($MgSO_4$). The solvent was removed and the resultant powder was washed with ethyl acetate. Diarylethene **3a** (425 mg, 70%) was obtained as a white powder. M.p. 255–256 °C; ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 1.93$ (s, 6H), 7.14 (s, 2H), 7.48–7.59 (m, 6H), 7.70 ppm (d, $J = 7$ Hz, 2H); EI-MS: $[M]^+$ m/z: 608; elemental analysis calcd (%) for $C_{29}H_{18}F_6O_4S_2$: C 57.23, H 2.98; found: C 57.23, H 3.18.

Photochemical measurements: Absorption spectra were measured on a Hitachi U-3500 spectrophotometer. Photoirradiation was carried out using a USHIO 500 W super high-pressure mercury lamp or a USHIO 500 W xenon lamp. Mercury lines of 313 nm and 578 nm were selected by passing the light through a combination of either a band-pass filter (UV-D33S) or a sharp-cut filter (Y-52) and a monochromator (Ritsu MC-20L). Single crystals were irradiated with light of wavelength 400 nm, obtained by passing the light from a xenon lamp through a combination of a UV-D33S band pass filter and a UV29 or a UV35 sharp-cut filter and monochromator. Changes in the absorption spectra in the single-crystalline phase were measured with a Leica DMLP polarizing microscope connected to a Hamamatsu PMA-11 photodetector. The polarizer and analyzer were set in parallel to each other. Photoirradiation was carried out using a 75 W xenon lamp or a 100 W halogen lamp as the light source, which was attached to the microscope.

X-ray crystallographic analysis: X-ray crystallographic analysis was carried out on a Bruker SMART1000 CCD-based diffractometer (50 kV, 40 mA) using Mo-K_α radiation. The data were collected as a series of ω-scan frames, each with a width of 0.3°/frame. The crystal-to-detector distance was 5.118 cm. Crystal decay was monitored by repeating the 50 initial frames at the end of the data collection and analyzing the duplicate reflections. Data reduction was performed using SAINTPLUS software,[12] which corrects for Lorentz and polarization effects, as well as for decay. The cell constants were calculated by global refinement. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using SHELXL software.[13] The positions of all hydrogen atoms were calculated geometrically and they were refined as a riding model. CCDC-204750 (**1a**), CCDC-204751 (**2a**), CCDC-200319 (**3a**), CCDC-204752 (**4a**), CCDC-194694 (**5a**), and CCDC-204753 (**6a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.a-c.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336033; or e-mail: deposit@ccdc.cam.ac.uk).

Simulation of the photogenerated closed-ring isomers: CS Chem3D (Cambridge Software) was used for partial MM2 optimizations. The structural optimizations were carried out by means of partial MM2 calculations of the thiophene and methyl moieties (C1, C2, C3, C4, C10, C11, C12, C13, C14, and C15), with fixed positions of the hexafluorocyclopentene and carboxyphenyl moieties and the photogenerated sulfur atoms (S1′ and S2′).

Calculation of absorption spectra: The INDO/S method as implemented in MOS-F (Fujitsu) was used for these calculations. Twenty molecular orbitals were taken into account in the calculations (default value). Coordination of the photogenerated closed-ring isomers obtained by MM2 calculation was assumed for this INDO/S calculation.

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