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Single-Crystalline Photochromism of Diarylethene Mixtures

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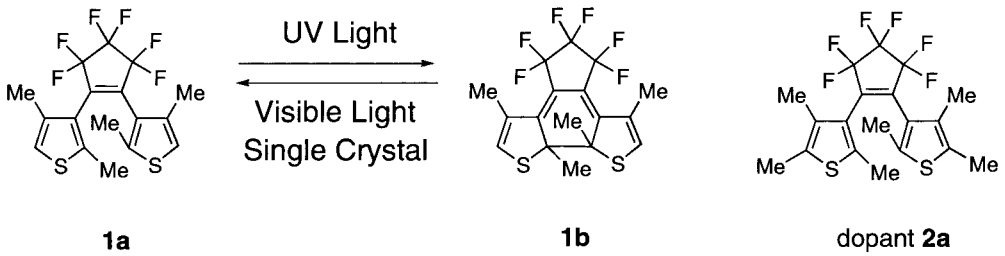
Crystal structures of 1,2-bis(2,4-dimethyl-3-thienyl)perfluorocyclopentene **1a**,1,2-bis(2,4,5-trimethyl-3-thieny)perfluorocyclopentene **2a** and their mixture were determined by X-ray crystal structure analysis and their photochromic reactivities were compared. In the crystal of **1a**, 17 mol% of molecules adopted a photoactive anti-parallel conformation and underwent photochromism. The crystal of **2a** was not photochromic, because the dithienylethenes are packed in a photochemically inactive anti-parallel conformation. In the co-crystal of **1a** and **2a**, **2a** adopted a photoactive anti-parallel conformation and the ratio of molecules in a photoactive conformation increased to 27 mol%. In the co-crystal, the spectrum of the closed-ring form isomers, **1b** and **2b**, generated by UV irradiation was broader and blue-shifted by ca. 10 nm in comparison with that of the **1a** homocrystal.

Some of dithienylperfluorocyclopentene derivatives undergo thermally stable photochromic reactions not only in solution but also in the single-crystalline phase.[1] The single crystals show a highly efficient and fatigue-resistant photochromic performance.[2] In a previous paper,[3] it has been shown that the single crystal of 1,2-bis(2,4-dimethyl-3-thienyl)perfluorocyclopentene, **1a**, undergoes reversible photocoloration (Scheme 1). Compound **1a** converted to red-colored closed-ring isomer **1b** by irradiation with UV light, and the red color disappeared by irradiation with visible light in the crystalline phase. The preliminary X-ray analysis of **1a** suggested that the crystal contains a disordered structure of anti-parallel and parallel conformers, although the atom positions could not be determined.[3]

The photocyclization reactions of diarylethene derivatives proceed only in a conrotatory mode.[4] Therefore, parallel conformers are photochemically inactive. The efficiency of photocoloration is dependent on the ratio of photoactive anti-parallel to photoinactive parallel conformers. Several attempts to increase the ratio, such as introduction of bulky isopropyl substituents into the 2-position of the thiophene ring[5] or inclusion into cyclodextrin cavities, have been reported.[6] Here, we have examined the ratio of the two conformers in the co-crystals of **1a** and 1,2-bis(2,4,5-trimethyl-3-thienyl)perfluorocyclopentene **2a.** The conformation of the molecules in the co-crystal is considered to be different from the conformations in the homocrystals of **1a** or **2a**.[7] We report on the structures of crystals **1a** and **2a** and of their co-crystal and on the photochromic performance.

Results and Discussion

Crystal Structure Analyses. All crystallographic data for crystals of **1a** and **2a**, and for the co-crystal of **1a** and **2a** are listed in Table 1. The crystal system and space group of the crystal of **1a** was Orthorhombic, *Pbcn* and $Z = 4$. Figure 1 shows the crystal structure viewed along the *b* and *c* axes. Viewed along the *b* axis, the molecules are in a herringbone arrangement and are oriented to two directions. The double bond of the cyclopentene ring C5=C5^{i} (2-fold rotation symmetry operation; i = 2-x, y, −0.5-z) inclines 23.9° or −23.9° from the *c* axis. Figure 2 shows the molecular structure of **1a**. A half of each molecule is crystallographically independent because the molecule is on a crystallographic 2-fold axis passing through the midpoints between C5=C5^{i} and between C7...C7^{i}. The puckering displacement disordered the 5-membered perfluorocyclopentene rings. The 2,4-dimethyl-3-thienyl groups were also disordered by 180° rotation around C2–C5 and C2^{i}–C5^{i} bonds, which join the thiophene group and the perfluorocyclopentene ring. The ratio of the two disordered forms A/B was 0.59(1)/0.41(1). The ratio was not dependent on the crystallization conditions (solvents and temperature).



Scheme 1.

Table 1. Crystallographic Data

	1a	Crystal of mixture **1a** and **2a**[a)]	**2a**
Empirical formula	$C_{17}H_{14}F_6S_2$	$(C_{17}H_{14}F_6S_2)_{0.86}(C_{19}H_{18}F_6S_2)_{0.14}$	$C_{19}H_{18}F_6S_2$
MW	396.40		424.45
F(000)	808	817	1744
Temperature/K	111(2)	111(2)	306
Crystal size/mm	0.4 × 0.3 × 0.3	0.5 × 0.2 × 0.2	0.5 × 0.3 × 0.15
Crystal system	Orthorhombic		Monoclinic
Space group	*Pbcn*		*C*2/*c*
Z	4		8
a / Å	11.539(1)	11.331(3)	24.341(3)
b / Å	14.323(1)	14.636(3)	13.110(2)
c / Å	10.083(1)	10.272(2)	14.876(2)
β / °			121.327(2)
V / Å^3	1666(1)	1704(1)	4055(1)
Density calcd /g cm^{-3}	1.580	1.561	1.391
θ range for data collection / °	2.27 to 27.48	2.27 to 27.58	1.84 to 27.52
Reflections collected	9155	8420	20565
Independent reflections	1865	1866	4597
Refinement method		full matrix	
No. of restrains/parameters	151/25	155/26	302/20
Goodness-of-fit on F^2	1.081	1.053	1.041
$R1$ [$I > 2\sigma(I)$]	0.048	0.083	0.059
$wR2$ for all data	0.135	0.201	0.143
largest diff. peak and hole / eÅ^{-3}	0.37, −0.34	0.44, −0.38	0.33, −0.28

a) The crystal was obtained from methanol solution including **1** and **2** in ratio 8:2.

Therefore, in the crystal, three types of conformers coexist in the following combinatorial ratio: AA/AB/BB = 0.34/0.49/0.17 (i.e. A×A/2×A×B/B×B). Scheme 2 shows the ratio and conformations. Among the three conformers, only conformer BB shows a photoactive anti-parallel conformation. In the conformer BB, the distance between two reactive carbons C1B...C1B^{i} is 3.91(1) Å. Conformer AB is in the photoinactive parallel conformation. Although conformer AA is in the anti-parallel conformation, the conformer was photochemically inactive because the distance between C1A...C1A^{i} (5.35(1) Å) is too long for the molecule to undergo the photocyclization reaction.

The crystal and molecular structures of **2a** are shown in Figs. 3 and 4, respectively. The crystal system and space group were Monoclinic, *C*2/*c*, *Z* = 8. The perfluorocyclopentene was disordered in the ratio A/B = 0.35(1)/0.65(1) at room temperature. Although the molecule adopts an anti-parallel conformation, the distance between the reactive carbons, C1 and C10, was 5.17(1) Å, which is too long for the molecule to undergo photocyclization. In fact the crystal **2a** did not show any photochromism by irradiation with UV light.

Co-crystals of **1a** and **2a** were produced from methanol solutions by re-crystallization. When the molar ratio **2a**/**1a** in the solution was less than 3/7, crystals having a regular shape were obtained. When the ratio is higher than 3/7, the crystal quality became poor and could not be used for the X-ray analysis. For the X-ray structure analysis, the crystal obtained from the solution containing **2a**/**1a** = 1/4 was used. The crystal system and space group were the same as those for crystal **1a**. The unit cell volume was larger than that of crystal **1a**. The crystal packing was almost the same as that for the crystal **1a**, as shown in Fig. 5. Figure 6 shows the molecular structures of both molecules. The 2,4-dimethyl-3-thienyl groups of **1a** were disordered by 180° rotation around C2–C5 and C2^{i}–C5^{i} bonds. Although the molecular structure was very similar to the crystal structure of **1a**, a new atom C10C was observed, which could be assigned to 5-position methyl group of 2,4,5-trimethylthiophene group of dopant **2a**. The C10C atom located at the position was 1.37(4) Å far from C4B. With regard to C10C, in the least-square refinement no restraint for the geometry and thermal displacement factors was used.

On the other hand no appreciable residual peak was found around C4A. This indicates that the 2,4,5-trimethylthiophene group is ordered and the molecules are in the photoreactive anti-parallel conformation in the co-crystal of **1a** and **2a**. The ratio of occupancy factor **1a**A/**1a**B/**2a** for a disordered thienyl group was 0.53(1)/0.33(1)/0.14(1). This means that in the crystal the combinatorial ratio of conformers **1a**AA/**1a**AB/**1a**BB/**2a** is 0.33/0.40/0.13/0.14. The ratio shows that **2a** was included in the crystal as much as 14%. Based on the occupancy factors, 27% of molecules are in the photoreactive anti-parallel conformation (13% **1a**BB and 14% **2a**) in the crystal (Scheme 2). The result shows that doping of **2a** is effective to increase the ratio of the photoactive conformers. In other words, the crystal structure of **1a** acts as a template to change the conformation of **2a** from the photochemically inactive conformation in **2a** homocrystal to the photoactive conformation.

Absorption Spectra of Closed-Ring form 1b and 2b in Hexane Solution. The closed-ring forms **1b** and **2b** were thermally stable and could be isolated in the dark. Figure 7 shows absorption spectra of the closed-ring isomers **1b** and **2b** in hexane. The absorption spectra of **1b** and **2b** have the maximum at λ = 531 nm (ε = 5400 M^{-1} cm^{-1}) and 529 nm (ε = 6100 M^{-1} cm^{-1}), respectively.[8] The absorption spectra of **1b**

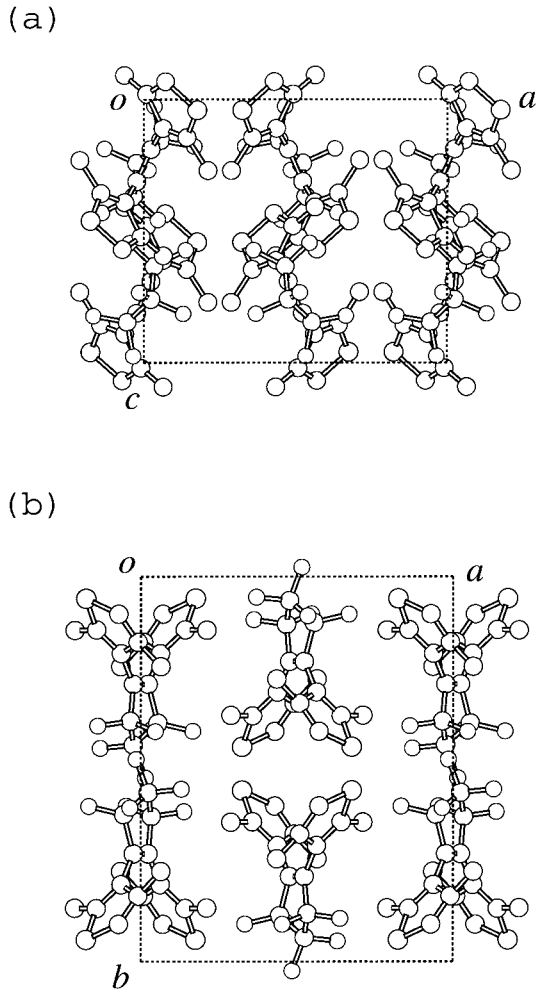


Fig. 1. Crystal structure of **1a** viewed along (a) the *b* axis and (b) the *c* axis. The disordered structures of the perfluorocyclopentene and the 2,4-dimethylthiophene groups are omitted to represent only photoactive conformers.

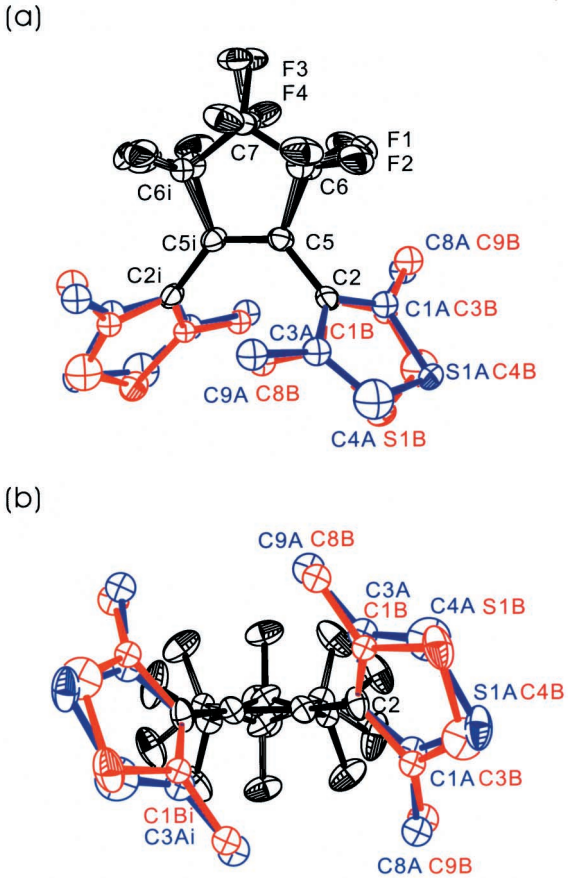
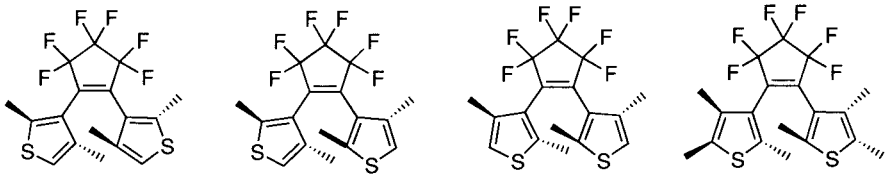


Fig. 2. Molecular structure of **1a**; (a) the best view, (b) viewed along the best molecular plane. Ellipsoids are drawn by 50% probability. A 2,4-dimethylthiophene ring is disordered in the ratio A:B = 0.59:0.41. The red lines represent photoactive conformer B.

and **2b** in hexane are very similar to each other.

Photochromic Behavior of Crystal of 1a. The single crystal of **1a** showed photochromic reactivity; the crystal turned from transparent to red by irradiation with UV light and the color disappeared by irradiation with visible light. The spectral change of the single crystal upon irradiation with 366 nm is shown in Fig. 8a. The spectrum of the (010) face was measured using linearly polarized light. Upon irradiation with UV light, a broad absorption band appeared around 550 nm. The absorption band is attributable to photo-generated closed-ring isomer **1b** in the crystal. As described above, **1a** molecules are in herringbone arrangement and they incline +/− 23.9° to the *b* axis. The electronic transition moment of the photo-generated closed-ring isomer is expected to align along the two directions and the polar plot should have four maxima, as observed previously.[3]

Photochromic Behavior of Co-crystal of 1a and 2a. The co-crystal of **1a** and **2a** was also photochromic. However, the crystal became violet after UV irradiation. Figure 9 shows a photograph of **1a** and the co-crystal of **1a** and **2a** after UV irradiation. Figure 8b shows the spectrum of the photogenerated closed-ring isomers, **1b** and **2b** in the co-crystal. The absorption maximum was observed at 560 nm and the band tail extended to 700 nm. To determine the absorption characteristics of the band, red visible light (> 670 nm) was irradiated to the colored crystal. The absorption band in the longer wavelength region decreased faster than the band in the shorter wavelength region. Upon prolonged irradiation with $\lambda > 670$ nm light, the band in the longer wavelength region almost disappeared and the remaining spectrum was similar to that of **1b** (Fig. 10). The absorption maximum was shifted from 560 nm to 550 nm by the irradiation. The inhomogeneous bleaching of the spectrum indicates that the absorption band in the longer wavelength region is attributable to the closed-ring form isomer **2b**. In hexane solution, the closed-ring forms **1b** and **2b** have very similar absorption spectra (Fig. 7). In the co-crystal of **1a** and **2b**, the absorption of the photogenerated closed-ring form **2b** was red-shifted. The X-ray structure analysis study of 1,2-bis(2,5-dimethyl-3-thienyl)perfluorocyclopentene proved that the red-shift is attributable to the molecular distortion.[9] In the co-crystal, photogenerated **2b** is considered to be in the distorted form in comparison with **1b** because of the large molecular size of the two extra methyl groups of **2b**.



	1aAA (anti-parallel) non reactive	**1**aAB (parallel) non reactive	**1**aBB (anti-parallel) reactive	**2** (anti-parallel) reactive
Crstyal **1**	34%	49%	17%	
Crystal of the mixure	33%	40%	13%	14%

Scheme 2.

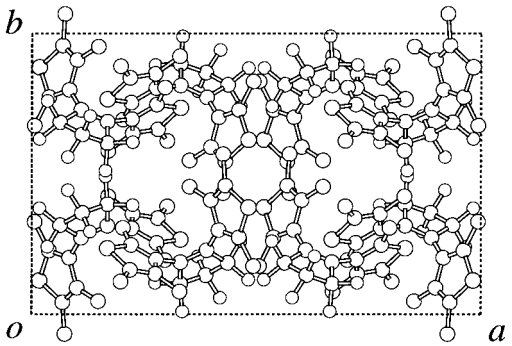


Fig. 3. Crystal structure of **2a** viewed along the *c* axis. The disordered structures of the perfluorocyclopentene rings are omitted for clarity.

Conclusion

The crystal **1a** showed single crystalline photochromism. The crystal **1a** contains three kinds of conformers: photoactive anti-parallel, non-reactive anti-parallel, and non-reactive parallel conformers. Because of the similarity of the molecular shape, **1a** cocrystallized with a small amount of **2a** to give the co-crystal of **1a** and **2a**. Upon UV irradiation, the crystal showed a broader absorption band in the longer wavelength region than that of the crystal of **1a**. The absorption band at longer wavelength region was attributed to the closed-ring form **2b** by selective bleaching experiment. The absorption spectrum of **2b** was appreciably red-shifted in comparison with the spectrum in hexane solution. The shift was attributed to the distortion of the molecular structure of the closed-ring isomer **2b**.

Experimental

Preparation of 1,2-Bis(2,4,5-trimethyl-3-thienyl)perfluorocyclopentene 2a. 3-Iodo-2,4,5-trimethythiophene (20 g, 79 mmol) was dissolved in distilled THF (273 mL). To the solution 1.6 M butyllithium hexane solution (54.5 mL, 87 mmol) was added over 1 hour at −78 °C. The white slurry was stirred for 1 hour at −78 °C. Perfluorocyclopentene (5.4 mL, 40 mmol) was added at −78 °C. The solution was stirred for 1.5 hours. The reaction was quenched by water and the cooling bath was removed. The organic layer was washed by brine and dried with $MgSO_4$ and evaporated. Silica-gel chromatography (eluent: hexane) and crystallization from methanol afforded **2a** (9.0 g, yield 55%): mp 121–124 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.89 (s, 3H), 2.22 (s, 3H), 2.23 (s, 3H); Anal. calcd for $C_{19}H_{18}F_6S_2$: C 53.76, H 4.27%; found: C 53.73, H 4.27%.

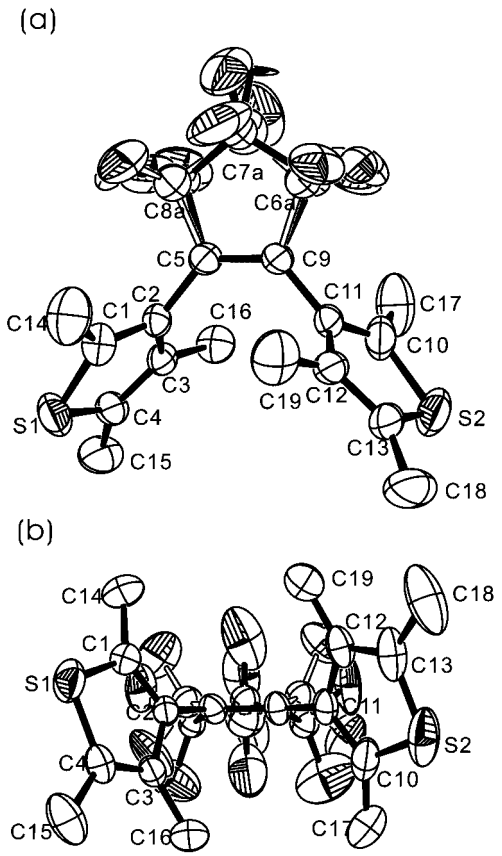


Fig. 4. Molecular structure of **2a**. The meanings of (a) and (b) are the same in Fig. 2. Ellipsoids are drawn by 30% probability. The molecule adopts non-reactive anti-parallel conformation. Distance between the reaction points, C1 and C10 is 5.17(1) Å.

Preparation of 2b: the Closed-Ring Form of 2a. 100 mg of **2a** was dissolved in methanol (30 mL). The solution was irradiated with 313 nm light for 2 hours. After methanol was removed in the dark, a crystalline mixture of **2a** and **2b** was obtained. Dark red plate-like single crystals of **2b** were collected by hand.

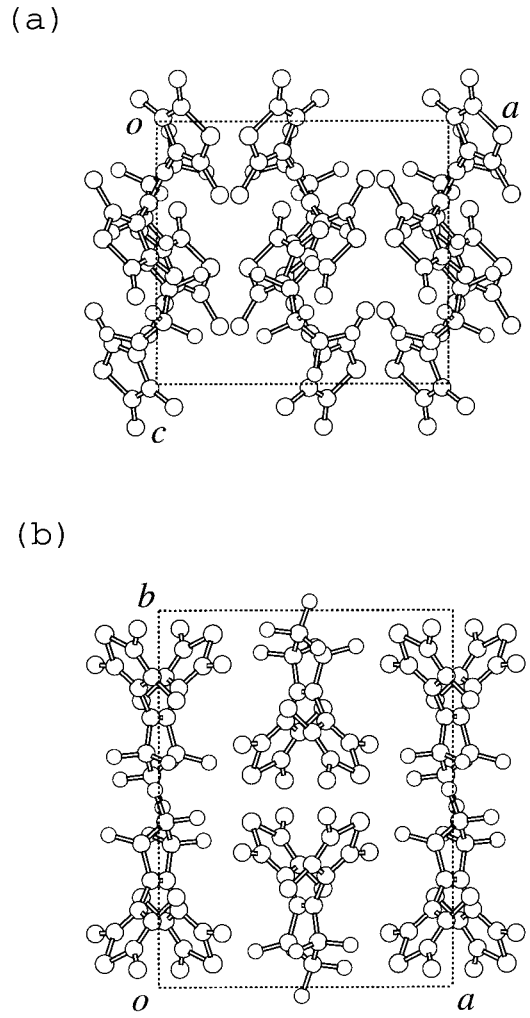


Fig. 5. Crystal structure of the co-crystal of **1a** and **2a** viewed along (a) the *b* axis and (b) the *c* axis. The disordered structures of the perfluorocyclopentenes and the 2,4-dimethylthiophene groups of **1a** are omitted to represent only photoactive conformers. Methyl groups at 5-position of 2,4,5-trimethylthiophene in **2a** are accommodated in the space surrounded by the thiophene rings.

Crystallization. Preparation of compound **1a** has been reported.[8] All crystals used for X-ray analyses were obtained from the methanol solution. For microscope observation, the crystal of **1a** and the co-crystal of **1a** and **2a** were prepared from isopropyl ether. Although the crystal structures of the crystal **1a** and co-crystal did not depend on these crystallization solvents, isopropyl ether gave crystals with well-developed (010) faces.

Absorption Spectra Measurements of Single Crystals. A microscope (Leica DMLP polarizing microscope) equipped with a CCD detector (Hamamatsu photonics, PMA-11) was used for the measurements of the absorption spectra of the single crystals. The microscope had two light sources, a halogen lamp for observation and a 75 W Xe-lamp for irradiation. The polarizer and analyzer were set in parallel to each other. The crystals with well-developed (010) faces were used. The bleaching experiment of the co-crystal of **1a** and **2a** was carried out as follows; after the co-crystal was colored with UV light, the crystal was bleached by irradiating with the visible light from the halogen lamp passed through a R-67 cut-off glass.

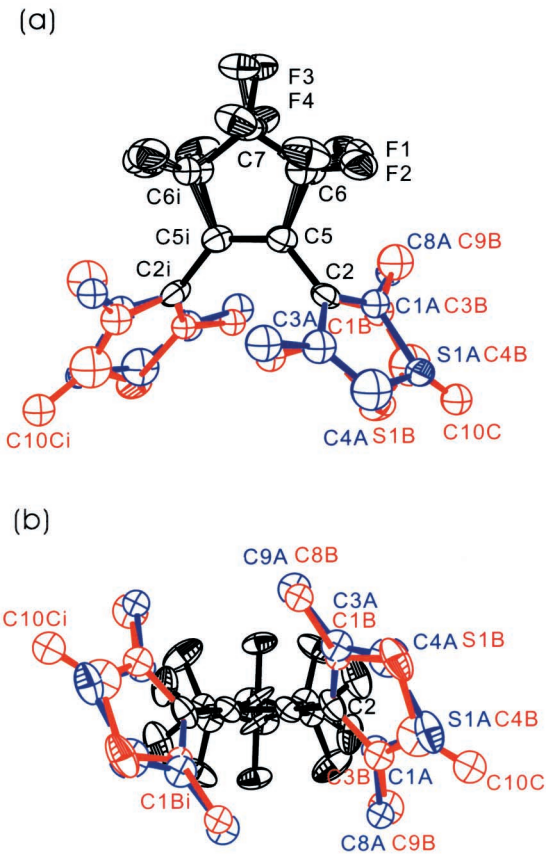


Fig. 6. Molecular structure of the co-crystal of **1a** and **2a**. Ellipsoids are drawn by 50% probability. A 2,4-dimethylthiophene ring of **1a** is disordered in the ratio A:B = 0.53:0.33. Occupancy factor of atom C10C belongs to a 2,4,5-trimethylthiophene ring of **2a** is 0.14. The red lines represent photoactive conformer B.

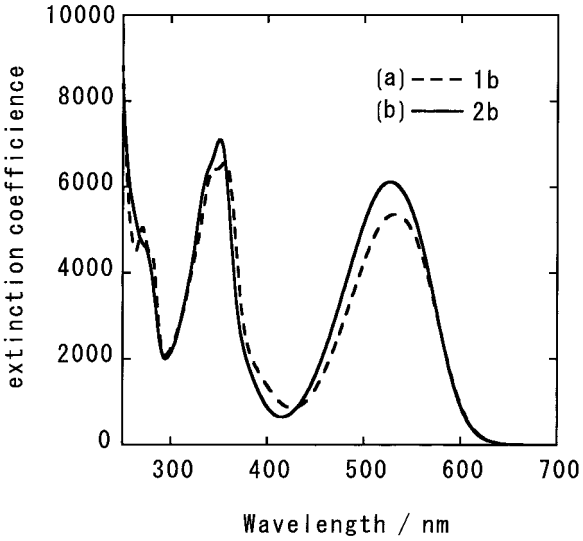


Fig. 7. Absorption spectra of the closed-ring forms (a) **1b** and (b) **2b** in hexane.

General Procedure of X-ray Crystal Structure Analyses. For X-ray diffraction intensity measurements, a Bruker

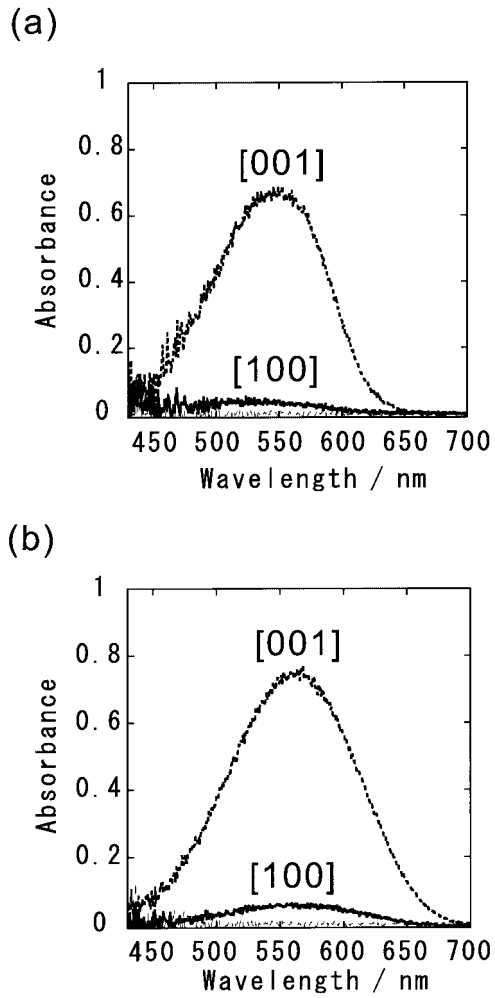


Fig. 8. Absorption spectra on (010) faces of (a) the crystal of **1a** and (b) the co-crystal of **1a** and **2a** after 366 nm irradiation. [001] and [100] represent the orientations of linearly polarized light.

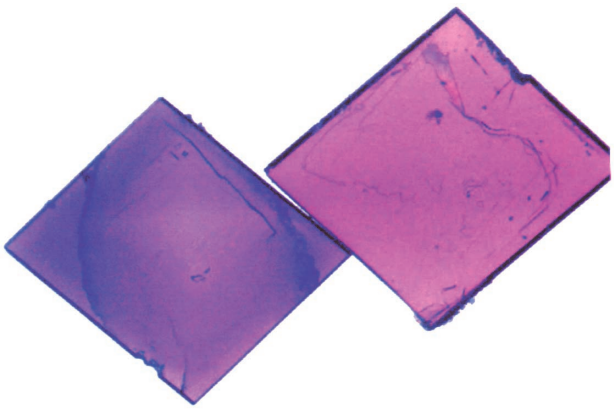


Fig. 9. Photograph of crystal **1a** (right) and the co-crystal of **1a** and **2a** (left) after UV irradiation. The crystal face is (010).

SMART1000 diffractometer (Mo $K\alpha$, 50 kV, 40 mA) with a CCD area detector was used. The crystal-to-detector distance was 5.1 cm. The crystal **1a** and the co-crystal of **1a** and **2a** were cooled at

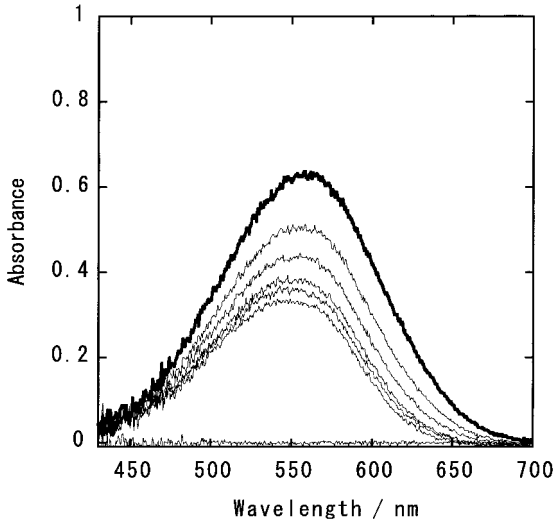


Fig. 10. Change of absorption spectra of the co-crystal of **1a** and **2a** during bleaching by irradiation with $\lambda > 670$ nm light.

111 K by the cryostat (Rigaku GN2). Every data collection was performed over a hemisphere of the reciprocal space. Every frame was taken by 0.3° rotation in ω axis. The first 50 frames and the last 50 frames were used for examination of crystal decay by analyzing the same reflections. Data reduction was performed using SAINT software, which corrects for Lorentz and polarization effects. The cell constants were determined by the global refinement. SADABS software was used for decay and absorption correction. The structures were solved by direct methods using SHELXS-86[10] and refined by full least-squares on F^2 using SHELXL-97.[11] The positions of all hydrogen atoms were calculated geometrically and refined by the riding model. In least-square refinements disordered structures were refined using geometrical restrains. No restraint was used for the displacement parameters. For each disordered structure, occupancy factors were refined under a constraint that the sum was 1. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition numbers 172330–172332. The data also were deposited as Document No. 75002 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Detail of Crystal Structure Determination of 1a. The crystal system and space group (Orthorhombic, *Pbcn*) were determined unambiguously. A unit cell contains four molecules and a half of each molecule is crystallographically independent. Direct method of SHELXS-86 gave the two highest electron density peaks on the thiophene ring, which indicated two possibilities for the position of the sulfur atom. Using a model without the disordered thiophene ring, least-square refinement afforded a non-positive definition on a carbon atom and an abnormal bond length on the thiophene ring. Therefore the disordered structure was introduced with the two thiophene rings related to each other with 180° rotation about C2–C5 bond. Due to the closeness of atoms on two thiophene rings, carbon atoms which belonged to the thiophene ring were refined isotropically. The perfluorocyclopentene ring was also disordered due to puckering. Although a perfluorocyclopentene ring rides on a crystallographic 2-fold axis, the perfluorocyclopentene ring should have local C_s symmetry. To satisfy this

requirement, each occupancy factor for the two disordering parts of the perfluorocyclopentene ring was fixed to 0.5. Atom C6A and C6B were refined isotropically because of the closeness between C6A and C6B.

Detail of Crystal Structure Determination of the Co-crystal of 1a and 2a. The structure of **1a** was used as the initial model without solving the structure. The same geometrical constrains were used for the refinement of **1a**. The highest residual electron density peak (height 0.76 eÅ^{-3}) appeared 1.32 Å far from atom C4B. The peak was assigned as the 4-position of methyl group C10C in 2,4,5-trimethylthiophene, dopant **2a**. After positioning of the C10C atom, there is no other meaningful peak ($<$ 0.47 eÅ^{-3}). For atom C10C, no restraints for the geometry and the thermal displacement factors were used. Occupancy factors were also refined under a constraint that the sum of the three occupancies for S1A, H4B, C10C is 1.

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