

Photochromic Reactions of Diarylethenes in Single Crystals with Intermolecular O–H...N Hydrogen-Bonding Networks

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Abstract: The crystal structures and photochromic performance of a single crystal of a diarylethene derivative possessing carboxyl groups, 1,2-bis(5-carboxyl-2-methyl-3-thienyl)perfluorocyclopentene (**1a**), and cocrystals of **1a** with 4,4'-, 2,4'-, and 2,2'-bipyridines were examined. In crystal **1a**, a discrete cyclic structure was observed, in which four **1a** molecules are linked

through hydrogen bonds between the carboxyl groups. In the homocrystal, photoreactive and photoinactive conformers of **1a** exist in the ratio of 1:1. In the cocrystals of **1a** with bipyridines,

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O–H...N-type hydrogen bonds between **1a** and pyridyl groups were formed, and all **1a** molecules are fixed in a photoreactive conformation. Both the homocrystal **1a** and the cocrystals showed photochromic performances, and color variation from bluish-violet to cyan was observed, depending on the conformation of the packed diarylethene molecules.

Introduction

Photochromism is defined as a photoinduced reversible transformation between two isomers that have different absorption spectra.^[1] Photochromic compounds have attracted much attention because of their potential applicability to opto-electronic or photonic devices, such as optical-memory media and optical switches.^[2] Several compounds that show photochromic reactivities in the crystalline phase have also been reported.^[3–11] However, in most of these compounds, photogenerated colored isomers in the crystals are thermally unstable, and the colored crystals return to their initial colorless forms in the dark. This thermal instability is a serious drawback for practical applications.

Recently, we developed diarylethene single crystals that undergo thermally stable and fatigue-resistant photochromic reactions.^[12–21] Upon irradiation with UV light, the diarylethene molecules in the single crystals undergo photocyclization to yield corresponding closed-ring isomers, and the colorless crystals turn yellow, red, blue, or green, depending on the chemical structures of the molecules. These colors are

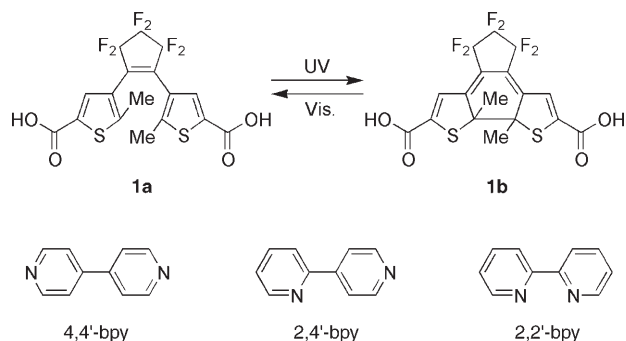
thermally stable and do not fade in the dark. Upon irradiation with visible light, the colored crystals return to their initial colorless forms. Coloration/decoulation cycles can be repeated many times by alternate irradiation with UV and visible light.^[13b] In addition, the photochromic diarylethene crystals exhibit characteristic properties that reflect both their crystal and molecular structures. The photogenerated colored crystals exhibit dichroism under polarized light, which originates from the regular alignment of molecules within the crystals.^[13] The accumulation of molecular structural changes accompanying the reactions induces photoreversible, nanoscale morphological changes in the crystal surfaces.^[18] Photocyclization and photocycloreversion quantum yields strongly depend on the molecular conformations in the crystals.^[19] Photochromic diarylethene crystals have potential for applications to photoactive devices, such as three-dimensional optical-memory media,^[17,22] optical switches,^[23] color displays,^[20] and photodriven nanoactuators.^[18] For these applications, however, rational strategies for the precise control of crystal structures and photochromic properties of diarylethene crystals must be established.

In crystal engineering,^[24] the essential tools to design and construct desired structures are intermolecular noncovalent bonds, such as hydrogen bonds,^[25] metal-coordinating bonds,^[26] and aromatic–aromatic interactions.^[27] The hydrogen-bonding interaction has been recognized as one of the most useful tools to construct various types of supramolecular architectures of organic molecules, because of its comparative robustness, directional-specific character, and diversi-

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ty. Here, we report the development of a crystal-engineering strategy for photochromic diarylethenes based on intermolecular hydrogen-bonding interactions. A diarylethene derivative **1** possessing two carboxyl groups at the 5-positions of thiophene rings was synthesized (Scheme 1). This diaryle-



Scheme 1. Diarylethene **1** (**1a**: open-ring isomer, **1b**: closed-ring isomer) and bipyridines 4,4'-bpy, 2,4'-bpy, and 2,2'-bpy.

there is anticipated to form hydrogen bonds between the carboxyl groups in the homocrystal and to cocrystallize with compounds that possess pyridyl groups by intermolecular O–H...N-type hydrogen-bonding interactions.^[28] Such interactions are useful for the hybridization of different types of functional molecules into a crystal. We prepared a single crystal of **1a** and cocrystals of **1a** with 4,4'-, 2,4'-, and 2,2'-bipyridines (4,4'-bpy, 2,4'-bpy, and 2,2'-bpy; Scheme 1), and examined their crystal structures and photochromic performance.

Results and Discussion

Photochromism of **1 in solution:** Figure 1 shows absorption spectral changes of **1** in acetonitrile. The acetonitrile solution of the open-ring isomer **1a** was colorless; **1a** has no absorption in the visible region. Upon irradiation with UV light, the colorless solution turned violet. This color change indicates that **1a** underwent a photocyclization reaction to form the closed-ring isomer **1b** by UV irradiation. The colored isomer **1b** was isolated by HPLC, and its molecular structure was characterized by NMR spectroscopy, mass spectrometry, and absorption-spectral measurement. Isomer **1b** has an absorption maximum at 586 nm in the visible region and this compound was thermally stable

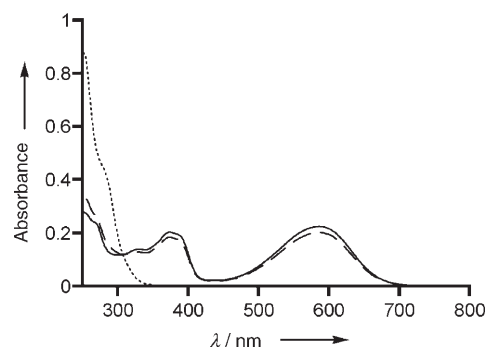


Figure 1. Absorption spectra of diarylethene **1** in acetonitrile (3.5×10^{-5} M): **1a** (.....), **1b** (—), and **1** in the photostationary state under irradiation with 300 nm light (---).

in the dark (see Supporting Information). Upon irradiation with visible light ($\lambda > 450$ nm), the violet solution of **1b** was completely bleached, and the absorption spectrum returned to that of **1a**. The coloration/decoloration cycles could be repeated many times by alternate irradiation with UV and visible light. The conversion ratio from **1a** to **1b** by irradiation with 300 nm light was 90%, as determined from the absorption spectral change shown in Figure 1. Thus, the diarylethene **1** underwent the thermally irreversible and photochemically reversible photochromic reactions.

Single crystal of **1a:** Upon slow evaporation of an acetonitrile solution of **1a**, colorless single crystals were obtained. The X-ray analysis of the crystal was performed to determine the crystal structure. The crystallographic data are listed in Table 1. The crystal has a triclinic crystal system, and the space group is $P\bar{1}$. The crystal contains not only **1a** molecules, but also acetonitrile molecules, which were used as the crystallization solvent. Two **1a** molecules and one acetonitrile molecule are crystallographically independent, and four **1a** molecules and two acetonitrile molecules are included in a unit cell. Figure 2a shows the ORTEP drawing

Table 1. Crystal data for crystals **1a**, **1a**·4,4'-bpy, **1a**·2,4'-bpy, and **1a**·2,2'-bpy.

	1a	1a ·4,4'-bpy	1a ·2,4'-bpy	1a ·2,2'-bpy
formula	(C ₁₇ H ₁₀ F ₆ O ₄ S ₂) ₂ ·(C ₂ H ₃ N)	(C ₁₇ H ₁₀ F ₆ O ₄ S ₂) ₂ ·(C ₁₀ H ₈ N ₂) ₂ ·(CHCl ₃)	(C ₁₇ H ₁₀ F ₆ O ₄ S ₂)·(C ₁₀ H ₈ N ₂)·(H ₂ O)	(C ₁₇ H ₁₀ F ₆ O ₄ S ₂) ₂ ·(C ₁₀ H ₈ N ₂)·(C ₂ H ₃ N) ₃
formula weight	953.79	1344.48	630.57	1192.09
<i>T</i> [K]	123(2)	123(2)	123(2)	173(2)
crystal system	triclinic	monoclinic	monoclinic	triclinic
space group	$P\bar{1}$	$C2/c$	$P2_1/c$	$P\bar{1}$
<i>a</i> [Å]	8.6813(16)	32.497(12)	13.837(6)	13.757(5)
<i>b</i> [Å]	15.432(3)	6.560(3)	17.399(8)	14.835(5)
<i>c</i> [Å]	16.190(3)	27.587(10)	11.553(5)	15.571(5)
α [°]	67.980(3)	90	90	65.960(4)
β [°]	85.426(3)	101.033(6)	108.329(7)	77.956(5)
γ [°]	77.874(3)	90	90	64.847(5)
<i>V</i> [Å ³]	1965.9(6)	5772(4)	2640(2)	2624.7(15)
<i>Z</i>	2	4	4	2
ρ_{calcd} [g cm ⁻³]	1.611	1.547	1.586	1.508
goodness-of-fit on F^2	1.043	1.087	1.041	1.029
data/restraints/parameters	7851/0/559	5944/9/430	5914/0/391	10232/1/723
R_1 [$I > 2\sigma(I)$]	0.0350	0.0739	0.0340	0.0678
wR_2 (all data)	0.0985	0.1881	0.0948	0.1933

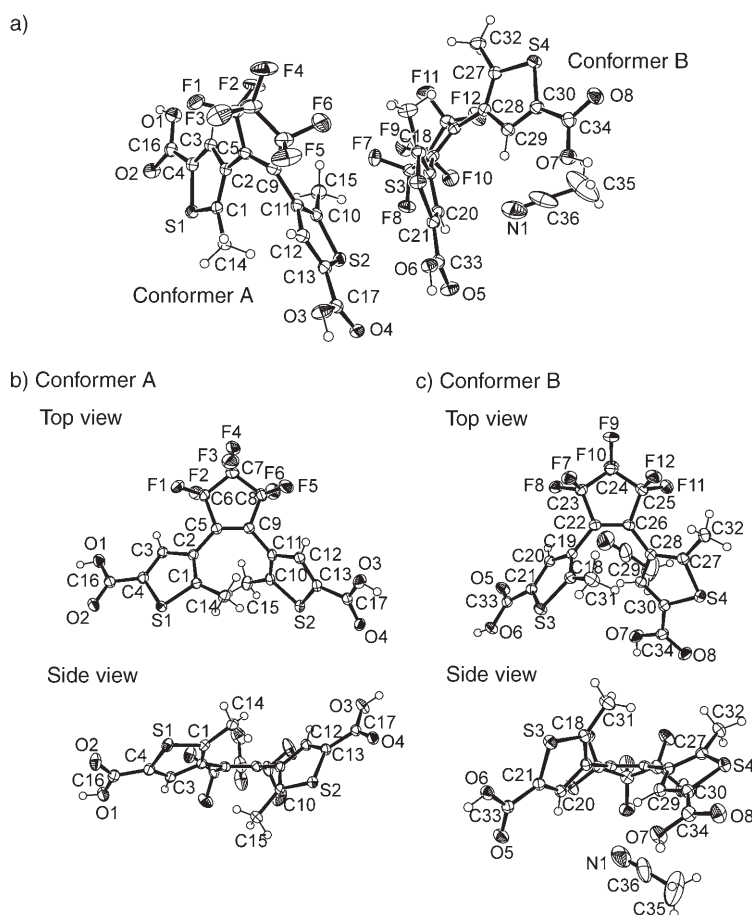


Figure 2. ORTEP drawings for crystal **1a**: **1a** and acetonitrile molecules in the asymmetric unit (a), detailed views of the photoreactive antiparallel conformer A (b) and the photoinactive parallel conformer B (c) of **1a**. The ellipsoids are drawn at 50% probability level.

of the crystallographically asymmetric unit. In the crystal, two different types of conformers of **1a** exist. The one (conformer A) is fixed in a photoreactive antiparallel conformation, and the other (conformer B) is fixed in a photoinactive parallel conformation.^[29] It has been proved that the photochromic reactivity of diarylethene derivatives in the single-crystalline phase is controlled by the molecular conformations in the crystals.^[19] If the molecule is fixed in an antiparallel mode and the distance between reacting carbon atoms on the aryl rings is less than 4.2 Å, the molecule undergoes the photocyclization reaction.^[19c] The photocyclization reaction does not proceed from the parallel conformation.^[13b] Figure 2b and c show detailed views of the conformers A and B, respectively. The conformer A has an antiparallel conformation, and the distance between reactive carbon atoms, C1 and C10, is 3.56 Å, which is short enough for the photocyclization reaction to take place in the crystalline phase.^[19c] On the other hand, the conformer B has a photoinactive parallel conformation, and the distance between reactive carbon atoms, C18 and C27, is 4.52 Å. The ratio of the conformers A to B is 1:1, therefore, only 50% of the diarylethene molecules in the crystal can undergo photochromic reactions.

In addition, a unique molecular assembly was observed in crystal **1a**, as shown in Figure 3. Four **1a** molecules are linked by hydrogen-bonding interactions between the carboxyl groups to form a discrete macrocyclic structure. Two of the participating molecules are the photoreactive antiparallel conformer A, and the other two are the photoinactive parallel conformer B. The interaction motif of the carboxyl groups is the same as that observed in the benzoic acid dimer.^[30]

Cocrystals of 1a with bipyridines: Diarylethene **1a** possessing two carboxyl acid groups is anticipated to form stoichiometric cocrystals with bipyridine derivatives through intermolecular O–H...N-type hydrogen-bonding interactions.^[28] Cocrystallization with different molecules may change the molecular conformation, the molecular packing structure, and the photochromic performance of the diarylethene. We attempted to prepare cocrystals of **1a** with 4,4'-, 2,4'-, and 2,2'-bipyridines (4,4'-bpy, 2,4'-bpy, and 2,2'-bpy) and examined the crystal structures and photochromic performance of the crystals.

A 1:1 (molar ratio) mixture of **1a** and 4,4'-bpy was dissolved in chloroform, and the solution was recrystallized by slow evaporation of the solvent. Colorless crystals with a

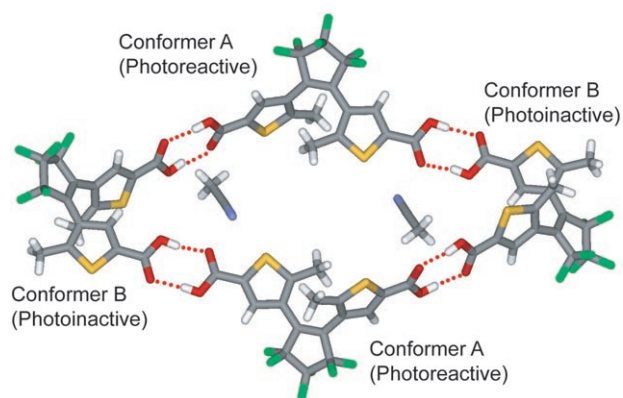


Figure 3. Hydrogen-bonding network in crystal **1a**. Red dotted lines indicate O–H...O hydrogen-bonding interactions.

platelike shape were obtained. The X-ray crystallographic data of the crystal are listed in Table 1. The unit cell is monoclinic $C2/c$, which is different from that of crystal **1a**. One **1a** molecule, one 4,4'-bpy molecule, and one half of a chloroform molecule (crystallization solvent) are crystallographically independent, and the unit cell includes eight **1a** molecules, eight 4,4'-bpy molecules, and four chloroform molecules. The crystal is composed of **1a**, 4,4'-bpy, and chloroform in the molar ratio of 2:2:1. Figure 4 shows the ORTEP drawing of the asymmetric unit in the crystal. The **1a** molecule has a photoreactive antiparallel conformation,^[29] and the distance between reactive carbon atoms, C1 and C10, is 3.51 Å, which is short enough for the photocyclization reaction to take place in the crystalline phase.^[19c]

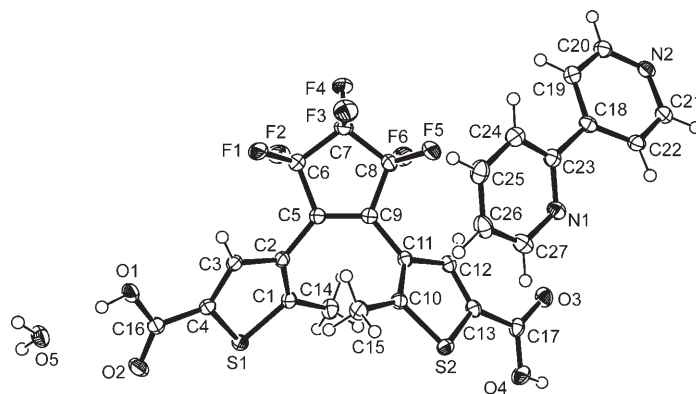


Figure 6. ORTEP drawing for cocystal **1a**·2,4'-bpy. The ellipsoids are drawn at 50% probability level.

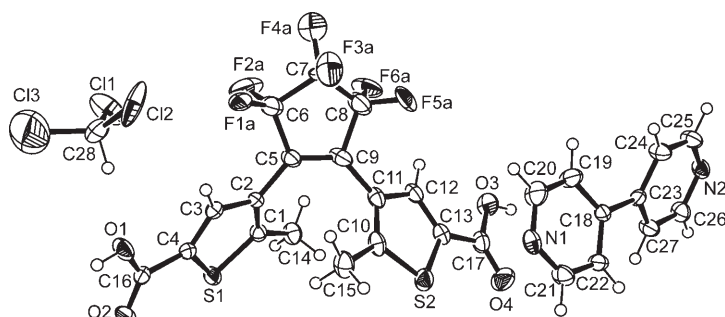


Figure 4. ORTEP drawing for cocystal **1a**·4,4'-bpy. The ellipsoids are drawn at 50% probability level.

Figure 5 shows a hydrogen-bonding network in cocystal **1a**·4,4'-bpy. An infinite linear-chain structure is observed, in

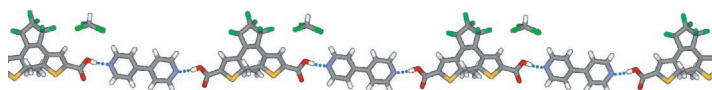


Figure 5. Hydrogen-bonding network in cocystal **1a**·4,4'-bpy. Blue dotted lines indicate O–H...N hydrogen-bonding interactions.

which **1a** and 4,4'-bpy molecules are linked alternately through O–H...N-type hydrogen bonds between the carboxyl groups of **1a** and the nitrogen atoms of 4,4'-bpy. Notably, all **1a** molecules in this cocystal are fixed in a photoreactive antiparallel conformation.

An acetonitrile solution containing **1a** and 2,4'-bpy in the molar ratio of 1:1 afforded, upon slow evaporation of the solvent over a period of several days, colorless single crystals with a platelike shape. The crystallographic data of the crystal are shown in Table 1. The crystal has a unit cell of monoclinic $P2_1/c$. One **1a** molecule, one 2,4'-bpy molecule, and one water molecule are crystallographically independent. Acetonitrile molecules are not incorporated in this crystal. The unit cell includes four molecules of each component in the molar ratio of 1:1:1. The ORTEP drawing of the asymmetric unit is shown in Figure 6. The **1a** molecule adopts a

photoreactive antiparallel conformation,^[29] and the distance between reactive carbon atoms, C1 and C10, is 3.44 Å. The molecule meets the requirements for the photocyclization reaction to take place in the crystalline phase.^[19c]

Figure 7 shows a hydrogen-bonding network in the cocystal **1a**·2,4'-bpy. Unlike cocystal **1a**·4,4'-bpy, a two-dimensional hydrogen-bonding sheet, in which **1a**, 2,4'-bpy, and water molecules are involved, is observed. In this sheet, **1a** and water molecules are linked alternately through O–H...O-type hydrogen bonds to form one-dimensional chain structures. Furthermore, these linear chains are connected by O–H...N-type hydrogen bonds between 2,4'-bpy and **1a** or water to form the two-dimensional sheet. The 4-position nitrogen of the pyridyl ring is an acceptor for the carboxyl group of the **1a** molecule, whereas the 2-position nitrogen accepts the hydroxyl group of the water molecule. In this hydrogen-bonding sheet, all **1a** molecules are fixed in a photoreactive antiparallel conformation.

A cocystal of **1a** and 2,2'-bpy was prepared by recrystallization of a 1:1 (molar ratio) mixture of the components from acetonitrile. Colorless crystals with a platelike shape

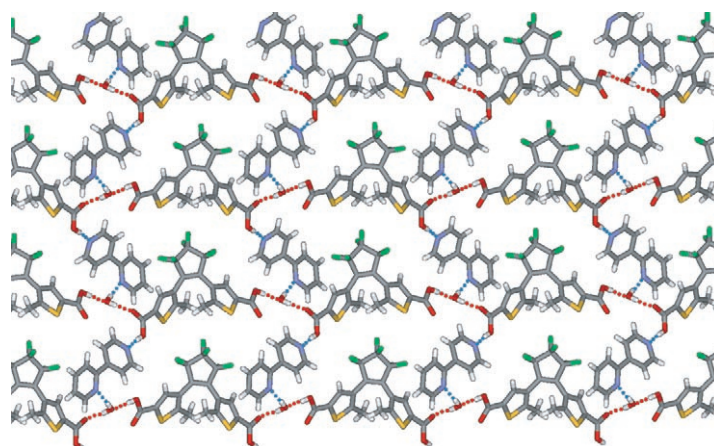


Figure 7. Hydrogen-bonding network in cocystal **1a**·2,4'-bpy. Red and blue dotted lines indicate O–H...O and O–H...N hydrogen-bonding interactions, respectively.

were obtained. The X-ray crystallographic data of the crystal are listed in Table 1. The unit cell of the crystal is triclinic $P\bar{1}$. Two **1a** molecules, one 2,2'-bpy molecule, and three acetonitrile molecules are crystallographically independent. The crystal comprises **1a**, 2,2'-bpy, and acetonitrile in the molar ratio of 2:1:3. Figure 8 shows the ORTEP drawing of the asymmetric unit in the crystal. Both of the **1a** molecules in the asymmetric unit are fixed in the photoreactive antiparallel conformation,^[29] and the distances between reactive carbon atoms are 3.57 Å (C1 and C10) and 3.56 Å (C18 and C27), which are short enough for the molecules to undergo photocyclization reactions.^[19c]

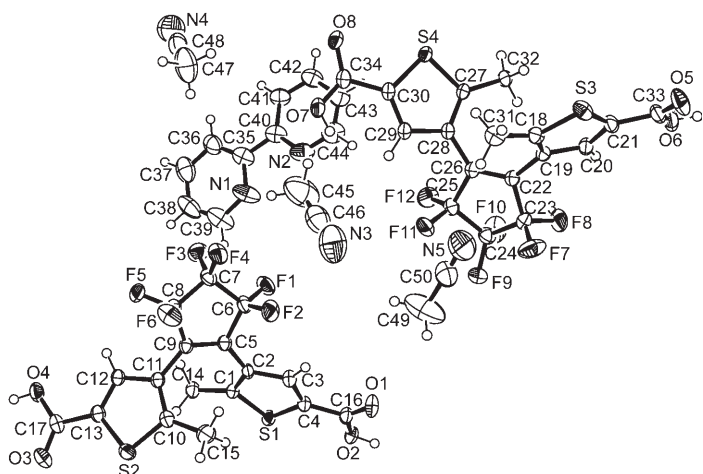


Figure 8. ORTEP drawing for cocrystal **1a**·2,2'-bpy. The ellipsoids are drawn at 50% probability level.

Figure 9 shows a hydrogen-bonding network in cocrystal **1a**·2,2'-bpy. The **1a** molecules are linked through S-shaped O–H···O-type hydrogen-bonding interactions between the carboxyl groups to form a parallel double-chain structure. The 2,2'-bpy molecules bind to the double chain through O–H···N-type hydrogen-bonding interactions. The 2-position nitrogen atoms on the 2,2'-bpy molecule are fixed in a *syn* conformation, and they face in the same direction. One of the nitrogen atoms acts as a hydrogen acceptor, but the other is not involved in the hydrogen bond. The bipyridine molecules break the hydrogen-bonding network in this crystal. It seems that the steric crowding around the nitrogen

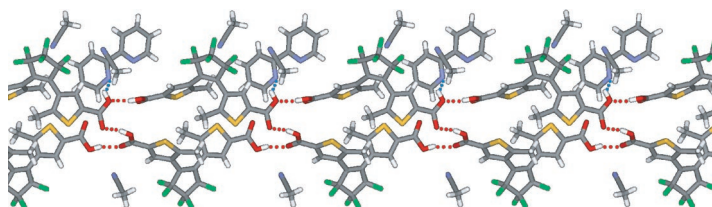


Figure 9. Hydrogen-bonding network in cocrystal **1a**·2,2'-bpy. Red and blue dotted lines indicate O–H···O and O–H···N hydrogen-bonding interactions, respectively.

atoms hinders the formation of infinite hydrogen-bonding networks. All **1a** molecules in the cocrystal are fixed in a photoreactive antiparallel conformation, as observed in cocrystals **1a**·4,4'-bpy and **1a**·2,4'-bpy. Cocrystallization with the bipyridine derivatives increased the proportion of photoreactive conformers in the crystals to 100%.

Photochromism of single crystal **1a and cocrystals with bipyridines:** The single crystal of **1a** and the cocrystals of **1a**·4,4'-bpy, **1a**·2,4'-bpy, and **1a**·2,2'-bpy underwent photochromic reactions. Upon irradiation with 370 nm light, crystals **1a**, **1a**·4,4'-bpy, and **1a**·2,2'-bpy turned bluish violet, on the other hand, crystal **1a**·2,4'-bpy turned cyan. The absorption spectra of the colored crystals are shown in Figure 10.

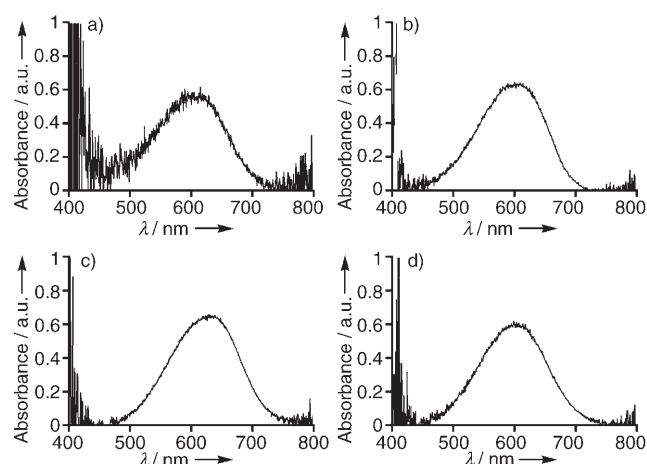


Figure 10. Absorption spectra of photogenerated colored crystals of **1a** (a), **1a**·4,4'-bpy (b), **1a**·2,4'-bpy (c), and **1a**·2,2'-bpy (d).

The absorption maxima of crystals **1a**, **1a**·4,4'-bpy, and **1a**·2,2'-bpy are located at 600 nm, whereas that of crystal **1a**·2,4'-bpy is shifted by as much as 30 nm to a longer wavelength of 630 nm. The photogenerated colors were thermally stable in the dark (see Supporting Information), and completely bleached by irradiation with visible light ($\lambda > 450$ nm).

To analyze the origin of the shift in absorption spectra, the photogenerated colored crystals were dissolved in acetonitrile, and absorption spectra of the solutions were compared. All solutions gave maximum at 586 nm, which is identical to that of the closed-ring isomer **1b**. This indicates that the color of the crystals is ascribed to **1b**. The color variation is attributed to the difference in molecular conformation of the diarylethene in the crystals.^[19d] The absorption spectrum is considered to reflect the π -conjugation length of the photogenerated closed-ring isomer **1b** in the crystals. Figure 11 shows the molecular structures of **1a** in crystals **1a**, **1a**·4,4'-bpy, **1a**·2,4'-bpy, and **1a**·2,2'-bpy. Parts a, b, and d of this figure (especially side views) show that the carbonyl groups of **1a** in crystals **1a**, **1a**·4,4'-bpy, and **1a**·2,2'-bpy, respectively, tilt against the molecular planes. On the other hand, in crystal **1a**·2,4'-bpy (Figure 11c), one of the carbonyl

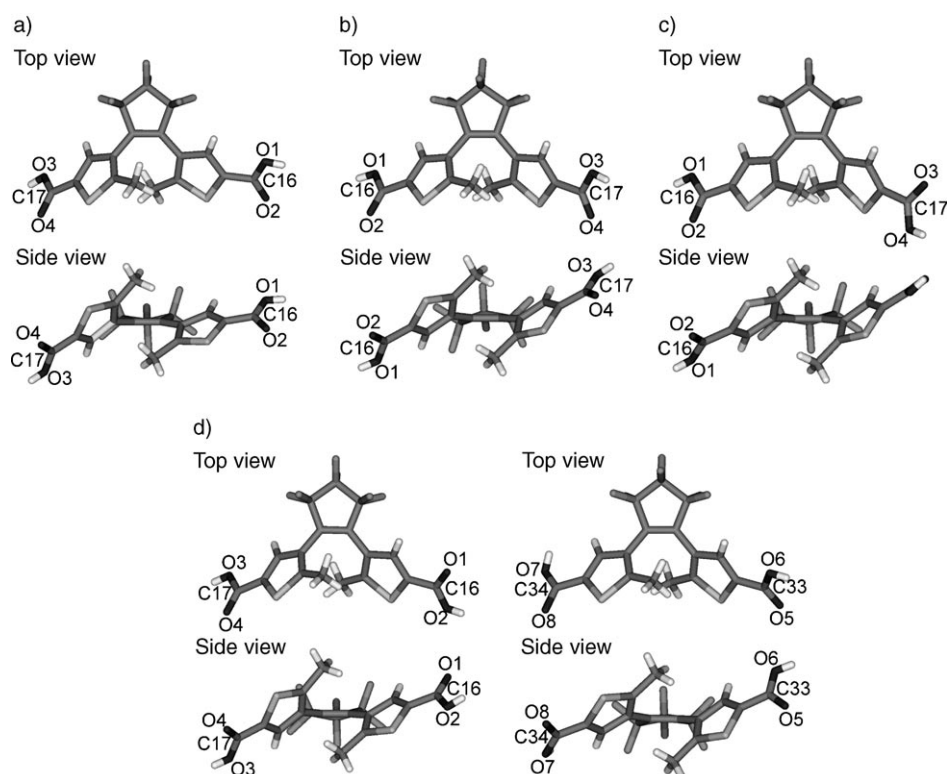


Figure 11. Molecular structures of diarylethene **1a** in crystals of **1a** (a), **1a**-4,4'-bpy (b), **1a**-2,4'-bpy (c), and **1a**-2,2'-bpy (d). In (a), only the photoreactive conformer A is shown. In (d), the two diarylethene molecules are crystallographically independent in the unit cell.

groups (C17=O3) has a coplanar conformation with respect to the molecular plane, and the other (C16=O2) tilts. During photocyclization reactions of dithienylethenes, the thiophene rings rotate, whereas the carboxyl groups at the 5-positions of the thiophene rings do not rotate.^[19b,d] Therefore, the photogenerated closed-ring isomers in crystal **1a**-2,4'-bpy have a planar structure and more extended π -conjugation than those in crystals **1a**, **1a**-4,4'-bpy, and **1a**-2,2'-bpy. This difference in molecular conformation and π -conjugation length explains why the absorption band of the former crystal was at longer wavelengths than those exhibited by the latter crystals.

Conclusion

The single crystal of diarylethene **1a** possessing two carboxyl groups and the cocrystals with three kinds of bipyridine derivatives, 4,4'-bpy, 2,4'-bpy, and 2,2'-bpy, were prepared and their crystal structures and photochromic performance were investigated. In crystal **1a**, a discrete macrocyclic assembly was observed, in which four **1a** molecules are linked through hydrogen bonds between the carboxyl groups. The crystal includes both photoreactive and photoinactive conformers of **1a** in the ratio of 1:1. In the cocrystals of **1a** with the bipyridines, O–H \cdots N hydrogen-bonding interactions between the carboxyl groups of **1a** and the pyridyl groups of

the bipyridines were observed. Self-assembled structures of a linear single chain, a two-dimensional sheet, and a parallel double chain were prepared. Cocrystallization with the bipyridines increased the proportion of photoreactive conformers to 100%. All crystals showed photochromism. The absorption spectra of UV-irradiated crystals reflected the molecular conformations of the diarylethene molecules in the crystals.

Experimental Section

General: Solvents used were of spectroscopic grade and were purified by distillation before use. The 4,4'-, 2,4'-, and 2,2'-bipyridines were purchased from Tokyo Kasei Kogyo and were purified by recrystallization from acetonitrile before use. ¹H NMR spectra were recorded by using a Bruker Avance 400 spectrometer (400 MHz). Tetramethylsilane (TMS) was used as an internal standard. Mass spectra were recorded by using a JEOL JMS-GCmate II GCMS system. Absorption spectra in solution were measured by

using a Hitachi U-3410 absorption spectrophotometer. Photoirradiation was carried out by using an Ushio 500 W super high-pressure mercury lamp. Monochromatic light was obtained by passing the light through a monochromator (Ritsu MV-10N). Absorption spectra in the single-crystalline phase were measured by using a Leica DMLP polarizing microscope connected to a Hamamatsu PMA-11 photodetector (see Supporting Information). Polarizer and analyzer were set in parallel to each other. Photoirradiation was carried out by using a 75 W xenon lamp or a 100 W halogen lamp. The wavelength of the light was selected by passing the light through band-pass filters or cut-off filters.

1,2-Bis(5-carboxyl-2-methyl-3-thienyl)perfluorocyclopentene (1a): 15% *n*BuLi hexane solution (3.2 mL, 5.2 mmol) was added to a dry THF solution (20 mL) containing 1,2-bis(5-carboxyl-2-methyl-3-thienyl)perfluorocyclopentene^[31] (1.3 g, 2.5 mmol) at –78 °C under argon atmosphere, and the reaction mixture was stirred for 2 h at this low temperature. An excess amount of solid CO₂ was added to the reaction mixture at –78 °C, and the mixture was stirred for 2 h at this temperature. A small amount of water was added to the mixture. The mixture was neutralized with HCl, and then was extracted with diethyl ether. The organic layer was dried over MgSO₄, filtrated, and concentrated. The residue was purified by silica gel column chromatography using hexane/ethylacetate (80:20 v/v) as the eluent to give **1a** (0.63 g, 56%) as crystals. ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 2.06 (s, 6H; CH₃), 7.79 ppm (s, 2H; thienyl proton); FAB-MS: *m/z*: 455.9 [*M*⁺]; elemental analysis calcd (%) for C₁₇H₁₀F₆O₄S₂ (455.99): C 44.74, H 2.21; found: C 45.10, H 2.26.

Closed-ring isomer of 1a (1b): Compound **1b** was isolated by subjecting a photostationary solution containing **1a** and **1b** to HPLC (Hitachi L-7100 pump system equipped with Hitachi L-7400 detector, silica gel column (Kanto, MightySil Si 60), hexane/ethyl acetate (70:30) as the eluent). Retention times for **1a** and **1b** were 42 and 29 min, respectively. ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 2.24 (s, 6H; CH₃), 6.97 ppm (s, 2H; olefinic proton); FAB-MS: *m/z*: 455.9 [*M*⁺]; UV/Vis (acetonitrile): λ_{max} (ϵ) = 586 (6.5 \times 10³), 374 nm (5.9 \times 10³ M⁻¹ cm⁻¹).

X-ray crystallographic analysis: X-ray crystallographic analysis was performed by using a Bruker SMART1000 CCD-based diffractometer (50 kV, 40 mA) with $\text{MoK}\alpha$ radiation. The crystals were cooled by cryostat (Rigaku GN2). The data were collected as a series of ω -scan frames, each with a width of 0.3° per frame. The crystal-to-detector distance was 5.340 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 by using SAINT software, which corrects for Lorentz and polarization effects, and decay. The cell constants were determined by the global refinement. The structures were solved by direct methods using SHELXS-86^[32] and refined by full least-squares on F^2 using SHELXL-97.^[33] The positions of all hydrogen atoms were calculated geometrically and refined by the riding model. CCDC-283550 (**1a**), CCDC-283551 (**1a-4,4'-bpy**), CCDC-283552 (**1a-2,4'-bpy**), and CCDC-283553 (**1a-2,2'-bpy**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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- [1] a) G. H. Brown, *Photochromism*, Wiley-Interscience, New York, **1971**; b) H. Dürr, H. Bouas-Laurent, *Photochromism: Molecules and Systems*, Elsevier, Amsterdam, **2003**.
- [2] a) M. Irie, *Photo-reactive Materials for Ultrahigh-Density Optical Memories*, Elsevier, Amsterdam, **1994**; b) A. Toriumi, S. Kawata, M. Gu, *Opt. Lett.* **1998**, *23*, 1924–1926; c) M. Irie, T. Fukaminato, T. Sasaki, N. Tamai, T. Kawai, *Nature* **2002**, *420*, 759–760; d) S. L. Gilat, S. H. Kawai, J.-M. Lehn, *Chem. Eur. J.* **1995**, *1*, 275–284; e) K. Matsuda, M. Irie, *J. Am. Chem. Soc.* **2001**, *123*, 9896–9897; f) T. Kawai, Y. Nakashima, M. Irie, *Adv. Mater.* **2005**, *17*, 309–314.
- [3] J. H. Golden, *J. Chem. Soc.* **1961**, 3741–3748.
- [4] a) K. Maeda, T. Hayashi, *Bull. Chem. Soc. Jpn.* **1970**, *43*, 429–438; b) M. Kawano, T. Sano, J. Abe, Y. Ohashi, *J. Am. Chem. Soc.* **1999**, *121*, 8106–8107.
- [5] K. Ichimura, S. Watanabe, *Bull. Chem. Soc. Jpn.* **1976**, *49*, 2220–2223.
- [6] A. M. Trozzolo, T. M. Leslie, A. S. Sarpotdar, R. D. Small, G. J. Ferraudi, T. DoMinh, R. L. Hartless, *Pure Appl. Chem.* **1979**, *51*, 261–270.
- [7] a) H. Sixl, R. Warta, *Chem. Phys.* **1985**, *94*, 147–155; b) A. Schmidt, S. Kababya, M. Appel, S. Khatib, M. Botoshansky, Y. Eichen, *J. Am. Chem. Soc.* **1999**, *121*, 11291–11299.
- [8] S. Kobatake, M. Irie, *Chem. Lett.* **2004**, 904–905.
- [9] D. G. Patel, J. B. Benedict, R. A. Kopelman, N. L. Frank, *Chem. Commun.* **2005**, 2208–2210.
- [10] a) E. Hadjoudis, M. Vittorakis, I. Moustakali-Mavridis, *Tetrahedron* **1987**, *43*, 1345–1360; b) K. Amimoto, H. Kanatomi, A. Nagakari, H. Fukuda, H. Koyama, T. Kawato, *Chem. Commun.* **2003**, 870–871.
- [11] Y. Mori, Y. Ohashi, K. Maeda, *Bull. Chem. Soc. Jpn.* **1989**, *62*, 3171–3176.
- [12] a) M. Irie, K. Uchida, *Bull. Chem. Soc. Jpn.* **1998**, *71*, 985–996; b) M. Irie, *Chem. Rev.* **2000**, *100*, 1685–1716; c) S. Kobatake, M. Irie, *Bull. Chem. Soc. Jpn.* **2004**, *77*, 195–210; d) M. Morimoto, M. Irie, *Chem. Commun.* **2005**, 3895–3905.
- [13] a) S. Kobatake, T. Yamada, K. Uchida, N. Kato, M. Irie, *J. Am. Chem. Soc.* **1999**, *121*, 2380–2386; b) S. Kobatake, M. Yamada, T. Yamada, M. Irie, *J. Am. Chem. Soc.* **1999**, *121*, 8450–8456; c) M. Irie, T. Lifka, S. Kobatake, N. Kato, *J. Am. Chem. Soc.* **2000**, *122*, 4871–4876; d) S. Kobatake, K. Shibata, K. Uchida, M. Irie, *J. Am. Chem. Soc.* **2000**, *122*, 12135–12141.
- [14] a) T. Yamada, S. Kobatake, K. Muto, M. Irie, *J. Am. Chem. Soc.* **2000**, *122*, 1589–1592; b) T. Yamada, S. Kobatake, M. Irie, *Bull. Chem. Soc. Jpn.* **2000**, *73*, 2179–2184; c) S. Kobatake, M. Morimoto, Y. Asano, A. Murakami, S. Nakamura, M. Irie, *Chem. Lett.* **2002**, 1224–1225.
- [15] a) T. Kodani, K. Matsuda, T. Yamada, S. Kobatake, M. Irie, *J. Am. Chem. Soc.* **2000**, *122*, 9631–9637; b) K. Matsuda, S. Yamamoto, M. Irie, *Tetrahedron Lett.* **2001**, *42*, 7291–7293; c) S. Yamamoto, K. Matsuda, M. Irie, *Org. Lett.* **2003**, *5*, 1769–1772; d) S. Yamamoto, K. Matsuda, M. Irie, *Angew. Chem.* **2003**, *115*, 1674–1677; *Angew. Chem. Int. Ed.* **2003**, *42*, 1636–1639; e) S. Yamamoto, K. Matsuda, M. Irie, *Chem. Eur. J.* **2003**, *9*, 4878–4886.
- [16] a) K. Matsuda, K. Takayama, M. Irie, *Chem. Commun.* **2001**, 363–364; b) K. Matsuda, K. Takayama, M. Irie, *Inorg. Chem.* **2004**, *43*, 482–489; c) K. Matsuda, Y. Shinkai, M. Irie, *Inorg. Chem.* **2004**, *43*, 3774–3776.
- [17] T. Fukaminato, S. Kobatake, T. Kawai, M. Irie, *Proc. Jpn. Acad. Ser. B* **2001**, *77*, 30–35.
- [18] M. Irie, S. Kobatake, M. Horichi, *Science* **2001**, *291*, 1769–1772.
- [19] a) K. Shibata, K. Muto, S. Kobatake, M. Irie, *J. Phys. Chem. A* **2002**, *106*, 209–214; b) T. Yamada, K. Muto, S. Kobatake, M. Irie, *J. Org. Chem.* **2001**, *66*, 6164–6168; c) S. Kobatake, K. Uchida, E. Tsuchida, M. Irie, *Chem. Commun.* **2002**, 2804–2805; d) M. Morimoto, S. Kobatake, M. Irie, *Chem. Eur. J.* **2003**, *9*, 621–627.
- [20] a) M. Morimoto, S. Kobatake, M. Irie, *Adv. Mater.* **2002**, *14*, 1027–1029; b) T. Yamada, S. Kobatake, M. Irie, *Bull. Chem. Soc. Jpn.* **2002**, *75*, 167–173; c) M. Morimoto, S. Kobatake, M. Irie, *J. Am. Chem. Soc.* **2003**, *125*, 11080–11087.
- [21] a) M. Morimoto, S. Kobatake, M. Irie, *Cryst. Growth Des.* **2003**, *3*, 847–854; b) M. Morimoto, S. Kobatake, M. Irie, *Photochem. Photobiol. Sci.* **2003**, *2*, 1088–1094; c) M. Morimoto, S. Kobatake, M. Irie, *Chem. Rec.* **2004**, *4*, 23–38; d) S. Kobatake, Y. Matsumoto, M. Irie, *Angew. Chem.* **2005**, *117*, 2186–2189; *Angew. Chem. Int. Ed.* **2005**, *44*, 2148–2151.
- [22] a) W. J. Tomlinson, E. A. Chandross, R. L. Fork, C. A. Pryde, A. A. Lamola, *Appl. Opt.* **1972**, *11*, 533–548; b) D. Psaltis, F. Mok, *Sci. Am.* **1995**, *273*, 52–58.
- [23] K. Nakatani, J. A. Delaire, *Chem. Mater.* **1997**, *9*, 2682–2684.
- [24] a) G. R. Desiraju, *Crystal Engineering: The Design of Organic Solids*, Elsevier, Amsterdam, **1989**; b) G. R. Desiraju, *Crystal Design: Structure and Function*, Wiley, Chichester, **2003**.
- [25] a) G. R. Desiraju, *Angew. Chem.* **1995**, *107*, 2541–2558; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2311–2327; b) M. C. Etter, *Acc. Chem. Res.* **1990**, *23*, 120–126; c) C. B. Aakeröy, K. R. Seddon, *Chem. Soc. Rev.* **1993**, *22*, 397–407.
- [26] a) N. Takeda, K. Umemoto, K. Yamaguchi, M. Fujita, *Nature* **1999**, *398*, 794–796; b) S. Leininger, B. Olenyuk, P. J. Stang, *Chem. Rev.* **2000**, *100*, 853–908; c) B. Moulton, M. J. Zaworotko, *Chem. Rev.* **2001**, *101*, 1629–1658.
- [27] a) C. A. Hunter, J. K. M. Sanders, *J. Am. Chem. Soc.* **1990**, *112*, 5525–5534; b) E. A. Meyer, R. K. Castellano, F. Diederich, *Angew. Chem.* **2003**, *115*, 1244–1287; *Angew. Chem. Int. Ed.* **2003**, *42*, 1210–1250; c) G. R. Desiraju, A. Gavezzotti, *J. Chem. Soc. Chem. Commun.* **1989**, 621–623; d) G. W. Coates, A. R. Dunn, L. M. Henling, D. A. Dougherty, R. H. Grubbs, *Angew. Chem.* **1997**, *109*, 290–293; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 248–251; e) C. Dai, P. Nguyen, T. B. Marder, A. J. Scott, W. Clegg, C. Viney, *Chem. Commun.* **1999**, 2493–2494.
- [28] a) C. B. Aakeröy, A. M. Beatty, B. A. Helfrich, *J. Am. Chem. Soc.* **2002**, *124*, 14425–14432; b) D. M. Shin, Y. K. Chung, I. S. Lee, *Cryst. Growth Des.* **2002**, *2*, 493–496; c) N. Shan, A. D. Bond, W. Jones, *Cryst. Eng.* **2002**, *5*, 9–24.
- [29] The open-ring isomer of diarylethene has two conformations with the aryl rings in mirror symmetry (parallel conformation) and C_2 symmetry (antiparallel conformation). According to the Woodward–Hoffmann rule, photoinduced electrocyclic reactions of 6π systems

- proceed in the conrotatory mode. The conrotatory photocyclization of diarylethene can proceed from the antiparallel conformation only. See: a) R. B. Woodward, R. Hoffmann, *The Conservation of Orbital Symmetry*, Verlag Chemie, Weinheim, **1970**; b) S. Nakamura, M. Irie, *J. Org. Chem.* **1988**, *53*, 6136–6138; c) K. Uchida, Y. Nakayama, M. Irie, *Bull. Chem. Soc. Jpn.* **1990**, *63*, 1311–1315; d) M. Irie, O. Miyatake, K. Uchida, *J. Am. Chem. Soc.* **1992**, *114*, 8715–8716.
- [30] L. Leiserowitz, *Acta Crystallogr. Sect. B* **1976**, *32*, 775–802.
- [31] A. Peters, N. R. Branda, *Chem. Commun.* **2003**, 954–955.
- [32] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **1990**, *46*, 467–473.
- [33] G. M. Sheldrick, *SHELXL-97, Program for Crystal Structure Refinement*, Universität Göttingen, Göttingen (Germany), **1997**.

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