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Citation	Bulletin of the Chemical Society of Japan, 91(2); 153-157
Issue Date	2017-11
Type	Journal Article
Textversion	author
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DOI	10.1246/bcsj.20170322

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Tatsumoto Nakahama, Daichi Kitagawa, Hikaru Sotome, Syoji Ito, Hiroshi Miyasaka, Seiya Kobatake. (2017). Solid-State Fluorescence Behavior Induced by Photochemical Ring-Opening Reaction of 1,2-Bis(3-methyl-5-phenyl-2-thienyl)perfluorocyclopentene. *Bulletin of the Chemical Society of Japan*. 91, 153-157. <https://doi.org/10.1246/bcsj.20170322>

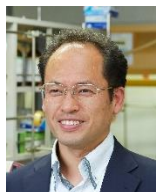
Solid-state fluorescence behavior induced by photochemical ring-opening reaction of 1,2-bis(3-methyl-5-phenyl-2-thienyl)perfluorocyclopentene

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Seiya Kobatake received Ph.D. degree from Osaka City University in 1996. He started his academic carrier as a postdoctoral researcher. In 2000, he was a research associate at Kyushu University. He moved to Osaka City University as associate professor in 2004 and has been a full professor since 2011. His current research focuses on photochromism of diarylethenes and their application.

Abstract

Crystals consisting of the closed-ring form of 1,2-bis(3-methyl-5-phenyl-2-thienyl)perfluorocyclopentene underwent a photochemical ring-opening reaction accompanying crystal fragmentation upon irradiation with visible light. The open-ring form crystal produced by the ring-opening reaction exhibited green fluorescence, whereas open-ring form crystals produced by recrystallization exhibit orange or yellow fluorescence depending on the polymorphic forms. The fluorescence quantum yield of the photogenerated open-ring form crystal was larger than that in *n*-hexane. The open-ring form exhibits different fluorescence colors depending on the intermolecular interaction in different states.

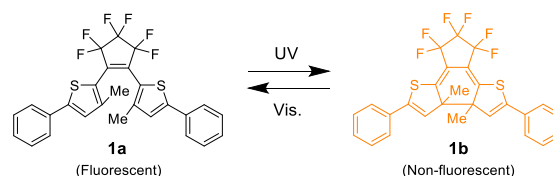
1. Introduction

Organic solid-state fluorescent materials are of significant interest for applications such as organic light-emitting diodes¹ and sensory materials.² However, the development of such applications suffers from fluorescence quenching at high concentration or in the aggregated state. In 2001, Tang's group found that a series of silole derivatives exhibits no fluorescence in dilute solution but exhibits strong fluorescence in the aggregated state due to restriction of intramolecular rotations.^{3,4} They termed the process aggregation-induced enhanced emission (AIEE) because the fluorescence emission was induced by aggregate formation.⁵ AIEE has attractive characteristics to investigate the fluorescence emission from practically useful solid aggregated states. Many researchers have worked on the design and synthesis of new AIEE molecules, which has resulted in the development of various molecules with AIEE character, such as tetraphenylethylene⁶⁻⁸ and cyanostilbene.⁹⁻¹¹ The investigation of new types of molecules with AIEE character continues to be an important challenge in the field of the organic fluorescent materials.

Photochromic diarylethenes have attracted much attention

for application to optical memory media, switching devices, and display materials because of excellent characteristics such as rapid response, high thermal stability of both isomers, high fatigue-resistance properties, and high reactivity in the solid state.¹² The fluorescence properties of some diarylethene crystals have been examined as potential organic solid-state fluorescent materials. 1,2-Bis(3-methyl-2-thienyl)perfluorocyclopentene, which undergoes reversible photochromic reactions in the single-crystalline phase, exhibits turn-off mode fluorescence switching in the crystalline state.^{13,14} Turn-on mode fluorescence switching in a crystal has been accomplished using diarylethenes with benzo[b]thiophene-*S,S*-dioxide groups.¹⁵

1,2-Bis(3-methyl-5-phenyl-2-thienyl)perfluorocyclopentene also undergoes reversible photochromic reactions from the open-ring isomer (**1a**) to the closed-ring isomer (**1b**) in *n*-hexane and exhibits turn-off mode fluorescence switching with a fluorescence quantum yield (Φ_f) of 0.017 in the open-ring form in *n*-hexane (Scheme 1).¹⁶ In addition, **1a** has two polymorphic forms (crystals **1a- α** and **1a- β**), which exhibit strong orange and yellow fluorescence ($\Phi_f = 0.52$ and 0.50, respectively).¹⁷ Therefore, diarylethene **1a** has AIEE characteristics. However, crystals **1a- α** and **1a- β** do not undergo photocyclization reaction. Here, we have investigated the photochemical reactivity of crystal **1b** and the characteristic fluorescence emission induced by the photochemical ring-opening reaction of crystal **1b** upon irradiation with visible light (>500 nm). The fluorescence colors, quantum yields, and lifetimes in various states are discussed here.



Scheme 1. Photochromic reaction of diarylethene **1a/1b**.

2. Experimental

General. ^1H NMR spectra were conducted using a Bruker AV-300N spectrometer at 300 MHz. Deuterated chloroform (CDCl_3) was used as the solvent and tetramethylsilane (TMS) as an internal standard. High-performance liquid chromatography (HPLC) was performed using a Hitachi L-7150/L-2400 HPLC system equipped with a Kanto Chemical Mightysil Si 60 column. Powder X-ray diffraction profiles were recorded on a Rigaku MiniFlex II diffractometer using $\text{CuK}\alpha$ radiation ($\lambda = 1.54184 \text{ \AA}$). Single crystal X-ray crystallographic analysis was conducted using a Rigaku AFC/Mercury CCD diffractometer with $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) monochromated by graphite. The crystal structures were solved by a direct method using SIR92 and refined by the full-matrix least-squares method for F^2 with anisotropic displacement parameters for non-hydrogen atoms using SHELXL-97. Absorption spectra were measured with a JASCO V-560 absorption spectrophotometer. Photoirradiation in solution was conducted using a 200 W mercury-xenon lamp (Moritex MUV-202) as a light source. Monochromatic light was obtained by passing the light through a monochromator (Jobin Yvon H10 UV) and glass filters. Fluorescence spectra were measured with a JASCO FP-8300 fluorescence spectrophotometer. Fluorescence quantum yields were also determined with a JASCO FP-8300 fluorescence spectrometer equipped with a JASCO ILF-835 integrating sphere.

Fluorescence lifetime. Fluorescence lifetimes were measured using a time-correlated single-photon-counting (TCSPC) system. The experimental setup for the TCSPC has been described previously.¹⁸ Briefly, a Ti:sapphire oscillator (Spectra-Physics, Tsunami) was utilized as a pulsed light source. The operation wavelength, pulse width, and repetition rate were set to 800 nm, 70 fs, and 80 MHz, respectively. The fundamental frequency of the laser was converted to the second harmonic (400 nm) using a type I beta barium borate (BBO) crystal and this was used to excite the samples. The repetition rate was reduced down to 8 MHz using an electrooptic modulator (Conoptics, Model 350) and the excitation intensity to the sample was typically $2.2 \mu\text{W}$ at 8 MHz. The detection of fluorescence at the magic angle configuration was attained by utilizing a film polarizer and a Babinet-Soleil compensator. The fluorescence was detected using a photomultiplier tube (Hamamatsu Photonics, R3809U-50) equipped with a pre-amplifier (Hamamatsu Photonics, C5594) and a TCSPC module (PicoQuant, PicoHarp 300). For wavelength selection, a monochromator (Princeton Instruments, Acton 2150) was placed in front of the photomultiplier tube. Crystalline sample was retained with a pair of glass plates. For solution sample, 1 cm path length quartz cells were used. The typical response time of the system was determined to be 40 ps full width at half maximum by detecting scattered photons from a colloidal solution and scratched glass plate.

Materials. 1,2-Bis(3-methyl-5-phenyl-2-thienyl)perfluorocyclopentene (**1a**) was prepared by the method described previously.¹⁶ The diarylethene closed-ring form (**1b**) was isolated by HPLC (silica-gel column) using *n*-hexane/ethyl acetate (97:3) as the eluent.

3. Results and Discussion

Characterization of crystal 1b. Single crystal **1b** was fabricated by recrystallization from *n*-hexane/acetone. Single crystal X-ray crystallographic analysis was successfully performed and the results are summarized in Table 1. Crystal **1b** is monoclinic and belongs to the $P2_1/c$ space group. The crystal structure of crystal **1b** in an asymmetric unit and the molecular

packing diagram are shown in Figure 1. Crystal **1b** has four molecules in a unit cell and one molecule in the asymmetric unit. Molecule **1b** has a relatively planar structure compared with molecule **1a** in crystals **1a- α** and **1a- β** . In the crystal, two phenyl rings of adjacent molecules have parallel face-to-face stacking and the face-to-face distance is approximately 3.5 Å, which is sufficiently short for π - π intermolecular interaction, as shown in Figure 2.

Table 1. X-ray crystallographic data for crystal **1b**.

Formula	$\text{C}_{27}\text{H}_{18}\text{F}_6\text{S}_2$
Formula weight	520.53
Temperature	150 (2) K
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions	$a = 8.4417(8) \text{ \AA}$ $b = 13.9459(12) \text{ \AA}$ $c = 19.7795(19) \text{ \AA}$ $\beta = 91.572(6)^\circ$
Volume	$2327.7(4) \text{ \AA}^3$
Z	4
Density	1.485 g cm^{-3}
Goodness-of-fit on F^2	1.023
$R(I > 2\sigma(I))$	$R_1 = 0.0551$
$R(\text{all data})$	$wR_2 = 0.1248$

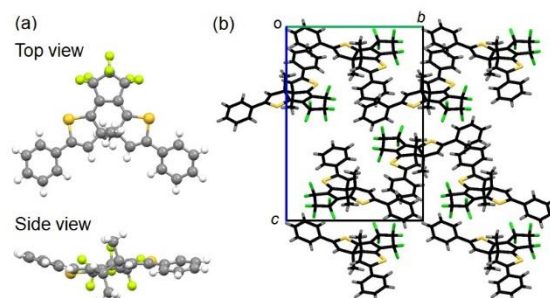


Figure 1. (a) Molecular structure and (b) packing diagram of **1b** in crystalline **1b**.

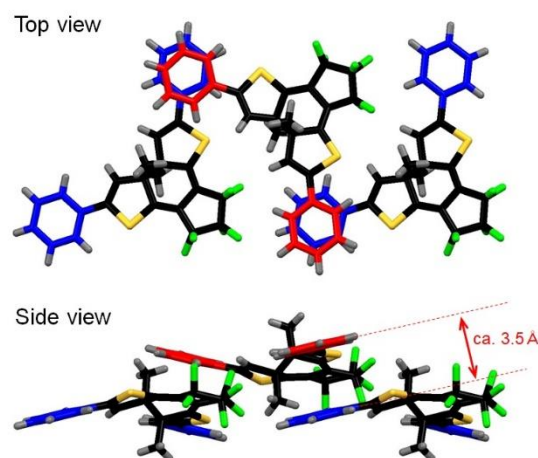


Figure 2. Molecular packing of crystal **1b** viewed from the top and side. The phenyl rings shown in red and blue indicate π - π intermolecular interaction

Ring-opening reaction of 1b in crystal 1b. Figure 3 shows

optical micrographs of crystal **1b** before and after irradiation with visible light. Crystal **1b** is orange colored before photoirradiation, whereas upon irradiation with visible light, the color became yellow. The photogenerated yellow solid material was confirmed to consist of the open-ring isomer **1a** from measurement of the absorption spectrum of a solution in *n*-hexane. Here, the photogenerated open-ring form crystal is called crystal **1a'**. In addition, crystal **1b** was rapidly fragmented simultaneously, as shown in Movie S1. The fragmentation is ascribed to the strain generated by the geometrical structure change of diarylethene molecules due to the photochemical ring-opening reaction from the closed-ring form to the open-ring form in the crystalline phase.^{19,20} The molecules in crystal **1b** have face-to-face π - π intermolecular interaction. The movement of the phenylthienyl groups by the photochemical ring-opening reaction may result in the loss of π - π intermolecular interaction. Consequently, the photochemical ring-opening reaction of **1b** in the crystal generates strain in the crystal.

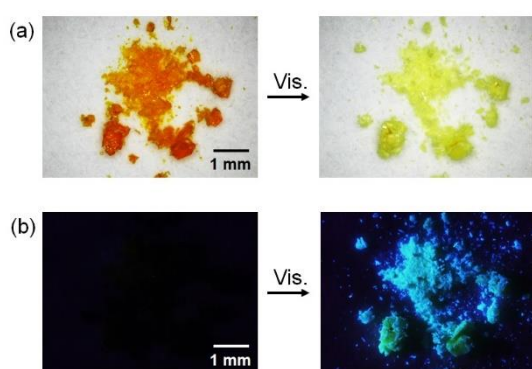


Figure 3. Optical micrographs of crystal **1b** observed (a) under white light and (b) under excitation at 365 nm before and after irradiation with visible light.

Figure 4 shows diffuse reflection spectra for the powdered crystals of **1b** before and after irradiation with visible light. Before irradiation with visible light, a broad band was observed in the region of 400–600 nm. The band disappeared by the ring-opening reaction upon irradiation with visible light and a band around 400 nm appeared. The absorption bands are similar to those of **1a** and **1b** in *n*-hexane. Crystal **1a'** produced by the ring-opening reaction of **1b** in the crystal did not undergo the photocyclization reaction from the open-ring form to the closed-ring form upon irradiation with UV light. No reaction has already been observed for **1a** crystals produced by recrystallization from acetone (crystal **1a- α**) and *n*-hexane (crystal **1a- β**), which gives two polymorphic crystals,¹⁷ whereas **1a** undergoes reversible photochromic reactions in *n*-hexane.¹⁶

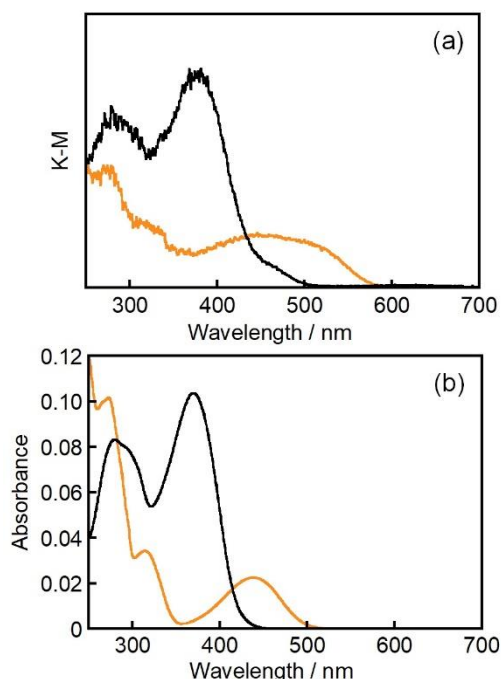


Figure 4. (a) Diffuse reflection spectra for powdered crystals of **1b** (orange) and **1a'** (black). (b) Absorption spectra of **1a** (black) and **1b** (orange) in *n*-hexane (4.5×10^{-6} M).

X-ray diffraction. Single-crystal X-ray crystallographic analysis of crystal **1a'** was performed. However, it could not be accomplished due to the lack of crystallinity after the ring-opening reaction. The crystal may contain invisible cracking by the photoinduced crystal fragmentation. Therefore, powder X-ray diffraction measurement was performed. Figures 5a and b show X-ray powder diffraction patterns for crystals **1b** and **1a'**. For comparison, Figures 5c–e show the patterns calculated for crystals **1b**, **1a- α** ,¹⁷ and **1a- β** .¹⁷ The diffraction pattern of crystal **1b** was consistent with that calculated for a single crystal of **1b**. In contrast, the diffraction pattern of crystal **1a'** was not consistent with those of crystals **1b**, **1a- α** , and **1a- β** , which indicates that crystal **1a'** has a crystal structure that is different from those of crystals **1a- α** and **1a- β** . Thus, a new polymorphic form of **1a** was produced by the ring-opening reaction of crystal **1b**.

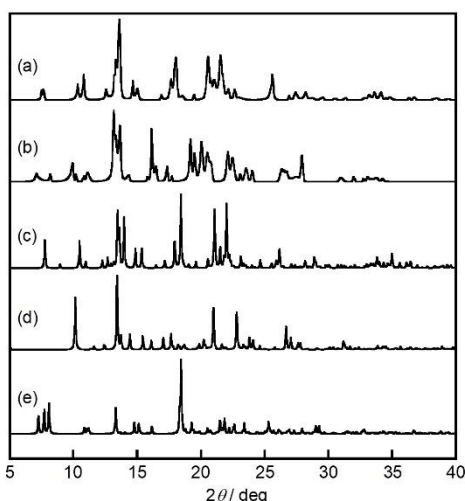


Figure 5. Powder X-ray diffraction patterns for (a) crystal **1b** at 300 K and (b) crystal **1a'** at 300 K, and calculated patterns for (c) crystal **1b** at 150 K, (d) **1a-α** at 200 K, and (e) **1a-β** at 200 K. The calculated patterns were obtained using parameters determined from single-crystal X-ray crystallographic analysis of **1b**, **1a-α**, and **1a-β**.

Fluorescence spectra. As shown in Figure 3b, crystal **1b** exhibited no fluorescence upon excitation at 365 nm. On the contrary, after irradiation with visible light, the crystal exhibited green fluorescence (Figure 3b). In the initial process upon irradiation with visible light, the fluorescence spectrum was observed around 530 nm (Figure S1). Upon continuous irradiation with visible light, the fluorescence maximum wavelength (λ_{flu}) was shifted to the shorter wavelength. Finally, λ_{flu} was observed at 491 nm with Φ_f of 0.15. The shift of λ_{flu} is ascribed to quenching by reabsorption to **1b** in the low photoreaction conversion. The influence of the reabsorption decreased in the higher photoreaction conversion. Table 2 summarizes the optical properties of crystals **1b** and **1a'**. For comparison, the optical properties of **1a** in the crystal (crystals **1a-α** and **1a-β**) and in *n*-hexane are also shown in Table 2. Φ_f for crystal **1a'** was larger than that in *n*-hexane. This indicates that **1a** in crystal **1a'** also has AIEE character as well as **1a** in crystals **1a-α** and **1a-β**. λ_{flu} of crystal **1a'** is different from those of crystals **1a-α** (λ_{flu} = 601 nm) and **1a-β** (λ_{flu} = 570 nm) and that in *n*-hexane (λ_{flu} = 480 nm). These results indicate that diarylethene **1a** exhibits four different fluorescence colors, i.e. blue, green, yellow, and orange, depending on the crystalline state or the solvent solution, as shown in Figure 6. This is the first example that the diarylethene itself exhibits multiple fluorescent colors when in the different states.

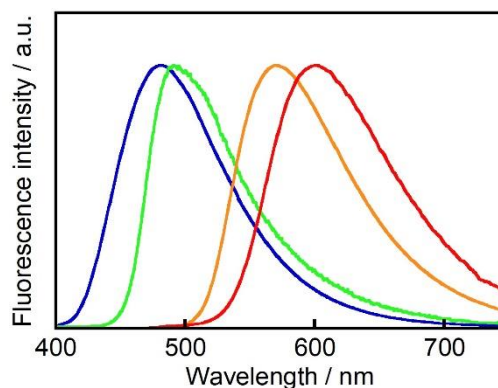


Figure 6. Fluorescence spectra of **1a** in *n*-hexane (4.5×10^{-6} M) (blue), crystal **1a'** (green), crystal **1a-α** (red), and crystal **1a-β** (orange).

The fluorescence lifetimes of **1a** in crystal **1a'** and *n*-hexane were compared. Figure 7 shows the fluorescence decay curves of **1a** in crystal **1a'** and in *n*-hexane. The fluorescence lifetime (τ) of **1a** in crystal **1a'** consisted of 0.19 ns (53%), 0.40 ns (46%), and 3.8 ns (1%) when the fluorescence was monitored at 540 nm. On the other hand, when the fluorescence was monitored at 600 nm, τ was observed to be 0.38 ns (80%), 1.4 ns (8%), and 4.7 ns (12%). These results indicate that the fluorescence consists of mainly two components, < 1 ns and 1–5 ns. **1a** in *n*-hexane also showed a decay curve with multiple components: 0.14 ns (93%) and 0.42 ns (7%). The components of τ for **1a** in *n*-hexane were consistent with the faster decay component for crystal **1a'**. These results indicate that the faster decay component in crystal **1a'** is due to the fluorescence of a single molecule. On the other hand, the lifetime of 1–5 ns does not exist for **1a** in *n*-hexane. The longer lifetime of 1–5 ns is close to those of crystals **1a-α** and **1a-β**. The molecules in the **1a-α** crystal have face-to-face π - π intermolecular interaction between phenyl rings (Figure S2). In crystals **1a-β** the molecules have edge-to-face π - π intermolecular interaction between phenyl rings (Figure S3). In spite of the different π - π intermolecular interactions, τ in crystals **1a-α** and **1a-β** are similar. It was previously reported that 1,2-bis(3-methyl-2-thienyl)perfluorocyclopentene showed two components of τ in a low concentration solution and in the crystalline phase. It was revealed that the longer τ was attributed to molecular aggregations, which exhibited a red-shifted fluorescence spectrum in comparison with that of monomer.¹⁴ It is possible that similar phenomena occurred with **1a** in *n*-hexane and with crystal **1a'**. τ of **1a** in the amorphous phase was observed to be 0.30 ns (46.4%), 0.84 ns (25.1%), 3.1 ns (21.6%),

Table 2. Absorption and fluorescence spectroscopic data for crystalline **1b**, **1a'**, **1a-α**, and **1a-β** and **1a** in *n*-hexane.

	λ_{abs} / nm	λ_{flu} / nm	$\Phi_f^{a)}$	τ_1 / ns	τ_2 / ns	τ_3 / ns
crystal 1b	445	—	—	—	—	—
crystal 1a' ^{b)}	377	491	0.15	0.19 (53%) ^{c)} 0.38 (80%) ^{d)}	0.40 (46%) ^{c)} 1.4 (8%) ^{d)}	3.8 (1%) ^{c)} 4.7 (12%) ^{d)}
crystal 1a-α ^{e)}	394, 509	601	0.52	1.9 (11%) ^{f)}	4.6 (89%) ^{f)}	—
crystal 1a-β ^{e)}	398, 505	570	0.50	1.9 (14%) ^{f)}	4.5 (86%) ^{f)}	—
1a in <i>n</i> -hexane	370 ^{g)}	480 ^{g)}	0.017 ^{g)}	0.14 (93%) ^{h)}	0.42 (7%) ^{h)}	—

a) Excited at 365 nm. b) A sample after the ring-opening reaction in 100% conversion in crystal **1b**. c) Excited at 400 nm and monitored at 540 nm. d) Excited at 400 nm and monitored at 600 nm. e) Ref. 17. f) Excited at 540 nm and monitored at 600 nm. g) Ref. 16. h) [**1a**] = 2.6×10^{-5} M. Excited at 400 nm and monitored at 500 nm.

and 5.6 ns (6.9%) when the fluorescence was monitored at 600 nm (Figure S4). The longer lifetime of 1–5 ns was observed even in the amorphous phase. Therefore, the slower decay component is ascribed to the condensed state.

In the excitation spectra, crystals **1a- α** and **1a- β** have a band from 500 nm to 600 nm (Figure S5). On the other hand, the excitation band of crystal **1a'** was not observed in the region of 500–600 nm, but was slightly shifted to the longer wavelength than that of **1a** in *n*-hexane. Thus, the large red-shifted fluorescence for crystals **1a- α** and **1a- β** is ascribed to the intermolecular π - π interactions. Contrastively, crystal **1a'** exhibited the slightly red-shifted fluorescence in comparison with **1a** in *n*-hexane, but it is not the major characteristics in crystal **1a'** compared with those in crystals **1a- α** and **1a- β** .

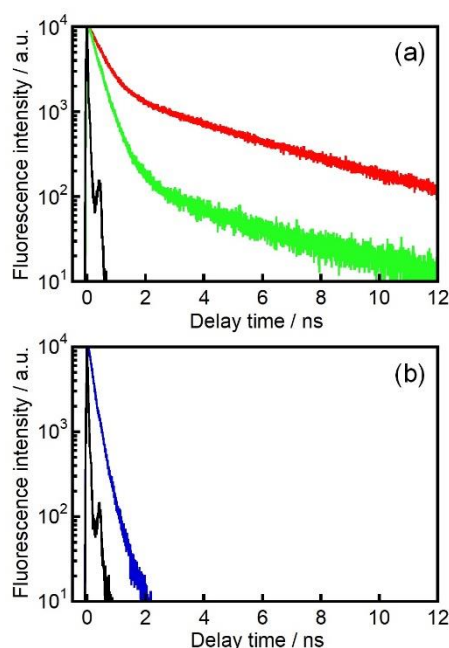


Figure 7. Fluorescence decay curve for (a) crystal **1a'** monitored at 540 nm ($\chi^2 = 1.16$) (green) and 600 nm ($\chi^2 = 1.17$) (red) and for (b) **1a** in *n*-hexane monitored at 500 nm ($\chi^2 = 1.16$) (blue).

4. Conclusion

We have fabricated crystals of diarylethene closed-ring form **1b** and demonstrated the change in the solid-state luminescence of the crystal induced by irradiation with visible light. Upon irradiation with visible light, **1b** in the crystal underwent the photochemical ring-opening reaction accompanying crystal fragmentation. The **1b** crystal exhibited no fluorescence at the initial state. However, after the ring-opening reaction, green fluorescence was observed with higher Φ_f than that in solution. This fluorescence color is different from those in crystals **1a- α** and **1a- β** and in *n*-hexane, but is ascribed to the difference in the intermolecular interaction between **1a** molecules.

This work was partly supported by JSPS KAKENHI Grant Numbers JP26107002 and JP26107013 in Scientific Research on Innovative Areas “Photosynergetics”, JP16H06505 in Scientific Research on Innovative Areas “Nano-Material Optical-Manipulation”, JP16K17896, JP26288009, JP16H03827, and JP15K13625. The authors also thank Nippon Zeon Co., Ltd. for providing octafluorocyclopentene.

Supporting Information

Additional fluorescence properties and molecular packings (PDF) and a movie of photoinduced fragmentation (Movie S1). This material is available on http://dx.doi.org/10.1246/bcsj.****.

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Graphical Abstract

Solid-state fluorescence behavior induced by photochemical ring-opening reaction of 1,2-bis(3-methyl-5-phenyl-2-thienyl)perfluorocyclopentene

Tatsumoto Nakahama, Daichi Kitagawa, Hikaru Sotome, Syoji Ito, Hiroshi Miyasaka and Seiya Kobatake

<Summary>

A crystalline diarylethene closed-ring form underwent the photochemical ring-opening reaction accompanying crystal fragmentation upon irradiation with visible light. The photogenerated open-ring form of the crystal exhibited green fluorescence, which is a different color from those of the open-ring form crystals produced by recrystallization and the open-ring form in *n*-hexane. The difference in the fluorescence color is ascribed to the difference in intermolecular interactions.

<Diagram>

