

Photochromic properties of 1,2-bis (6-substitute-2-methyl-1-benzofuran-3-yl) ethene derivatives

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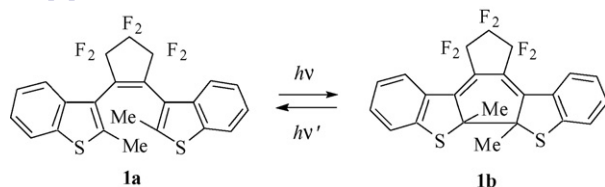
Abstract

1,2-Bis(1-benzofuran-3-yl)perfluorocyclopentene derivatives having iodo, phenyl, 2,4-diphenylphenyl, nitro, and formyl substituents at the 6 position of the benzofuran ring were synthesized. The photoreactivities of these compounds were studied in terms of the measured quantum yields and the conversions in the photostationary state. The mono- and bis-2,4-diphenylphenyl derivatives showed photochromism in an amorphous phase. © 2007 Elsevier B.V. All rights reserved.

Keywords: Photochromism; Diarylethene; Benzofuran; Substitute effect

1. Introduction

Various types of photochromic compounds have so far been synthesized in an attempt to apply them to optoelectronic devices [1–4]. Among these compounds, diarylethene derivatives are the most promising candidates for such applications because of their fatigue resistance and thermal irreversibility properties [2]. 1,2-Bis(2-methyl-1-benzothiophen-3-yl)perfluorocyclopentene (**1a**) is a representative diarylethene compound that fulfills the requirements for optical memory media [5].



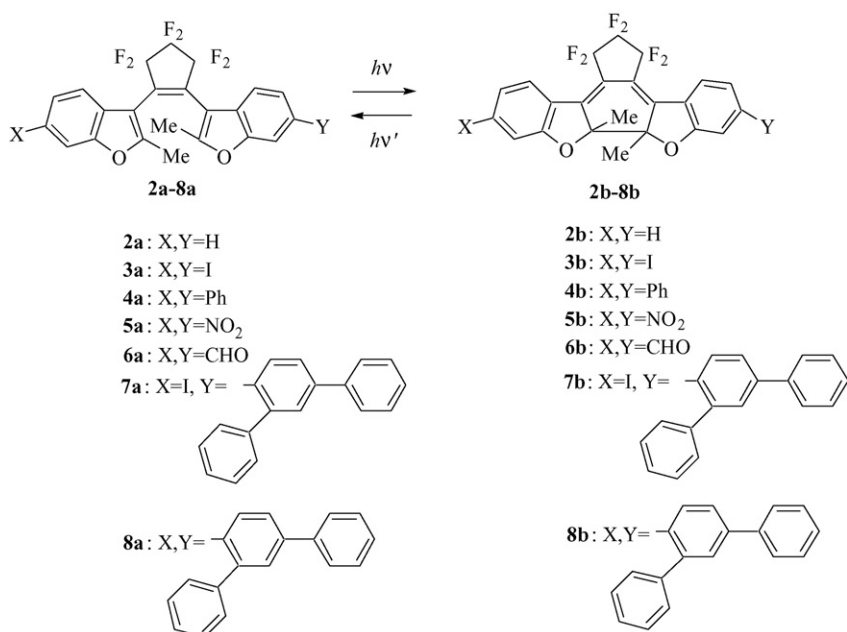
Some analogues of **1** have already been reported because of their superior properties such as thermal stability and fatigue resistance [6–18]. When formyl and iodo groups are substi-

tuted at the 6 position of benzothiophene rings, these analogues can be used precursors in amorphous studies [11]. When nitro groups are substituted at the 6 position of benzothiophene rings, the compound shows photochromism in a single crystal upon alternate irradiation with UV and visible lights [6].

Recently, we have synthesized 1,2-bis(2-methyl-1-benzofuran-3-yl)perfluorocyclopentene (**2a**) [14,15] and have observed that it undergoes photochromism in solution or in the single-crystalline phase upon irradiation with UV and visible light. **2a** is a thermally irreversible and fatigue-resistant compound [14]. The absorption maximum wavelength of **2b** (469 nm) is shorter than that of **1b** (517 nm) in hexane, and replacement of benzothiophene groups with benzofuran groups increases the cyclization quantum yield. To expand our study to the field of amorphous and single-crystalline materials, we have to prepare 1,2-bis(2-methyl-1-benzofuran-3-yl)perfluorocyclopentene analogues. In this work, 1,2-bis(2-methyl-1-benzofuran-3-yl)perfluorocyclopentene derivatives having iodo, phenyl, 2,4-diphenylphenyl, nitro, and formyl substituents at the 6 position of the benzofuran rings were synthesized. Also, amorphous photochromic compounds having a 2,4-phenylphenyl substituent at the 6 position were synthesized to elucidate the photochromic properties in a solution as well as in the

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amorphous phase.



2. Experimental

2.1. General

The solvents used were spectrograde and were purified by distillation before use. Absorption spectra were measured using a spectrophotometer (Shimadzu, UV-2100). The quantum yields were determined by comparing the reaction rates of the diarylethene derivatives in hexane against that of furylfulgide in toluene. Fluorescence spectra were measured with a Hitachi F-3010 fluorescence spectrophotometer. The fluorescence quantum yield was determined using anthracene, according to the method already reported [19]. A mercury lamp (Ushio, 500 W) was used as the light source. Light of appropriate wavelength was isolated by passing it through a monochromator (RITSU MC-10N) or through L-29, Y-44 and UV-D36C filters. ¹H NMR data was recorded on a Gemini 200 (200 MHz) spectrometer with CDCl₃ as solvent and tetramethylsilane as an internal standard. The mass spectrum was taken using a Shimadzu GCMS-QP5050A gas chromatography-mass spectrometer. X-ray crystallographic analysis was carried out using a Bruker SMART CCD X-ray diffractometer. HPLC was carried out on a Shimadzu LC-10AD liquid chromatography system coupled with a Shimadzu SPD-10AV spectrophotometric detector. A silica gel column (Wako Wakosil-5SIL) was used to analyze diarylethene isomers.

2.2. Synthesis

2.2.1. Preparation of 1,2-bis(2-methyl-6-iodo-1-benzofuran-3-yl)perfluorocyclopentene (**3a**)

Iodine (1.2 g, 4.0 mmol) and ortho periodic acid (0.39 g, 1.5 mmol) were added to a stirred solution of **2a** (1.9 g, 4.3 mmol) in acetic acid (150 ml), sulfuric acid (3 ml), and water

(7 ml), and the mixture was stirred for 3 h at 70 °C. The reaction mixture was poured into 500 ml of ice water. The mixture was extracted with ethyl acetate, and the organic layer was washed with water, an aqueous solution of sodium bicarbonate, and aqueous solution sodium thiosulfate, and dried over magnesium sulfate. The solvent was evaporated, and the residue was purified by column chromatography (silica, hexane) to give **3a** (1.67 g) in 57% yield.

3a: colorless crystal—mp 137–138 °C; ¹H NMR (CDCl₃, 200 MHz) δ 2.06 (s, 6H, CH₃), 7.15 (d, *J*=7.8 Hz, 2H), 7.49 (dd, *J*=7.8 Hz, 1.4 Hz, 2H), 7.77 (d, *J*=1.4 Hz, 2H). Ms(EI) (*m/z*) 688(*M*⁺). Anal. found: C 40.23, H 1.74%. Calcd. for C₂₃H₁₂F₆I₂O₂: C 40.14, H 1.76%.

2.2.2. Preparation of 1,2-bis(2-methyl-6-phenyl-1-benzofuran-3-yl)perfluorocyclopentene (**4a**)

Phenylboronic acid (0.60 g, 4.0 mmol), tetrakis(triphenylphosphine)paradium(0) salt (175 mg, 0.15 mmol), sodium carbonate (2.5 g) and water (10 ml) were added to a solution of **3a** (0.48 g, 1.1 mmol) in THF (10 ml). The reaction mixture was heated under reflux for 3 h. The reaction mixture was poured into water, extracted with diethyl ether, washed with water, dried over magnesium sulfate, and concentrated. The residue was purified by column chromatography (silica, hexane) to give **4a** (0.358 g) in 55% yield.

4a: colorless crystals—mp 167–168 °C; ¹H NMR (CDCl₃, 200 MHz) δ 2.13 (s, 6H, CH₃), 7.34–7.55 (m, 10H), 7.58–7.63 (m, 6H). Ms(EI) (*m/z*) 588(*M*⁺). Anal. found: C 71.61, H 3.74%. Calcd. for C₃₅H₂₂F₆O₂: C 71.43, H 3.77%.

2.2.3. Preparation of 1,2-bis(2-methyl-6-nitro-1-benzofuran-3-yl)perfluorocyclopentene (**5a**)

To a solution of acetic acid (60 ml) and acetic anhydrous (5 ml) was added **2a** (2.8 g, 6.4 mmol) at 10 °C. Fuming nitrate (3 ml) was slowly added to the solution while the

temperature was maintained below 10 °C. The mixture was stirred overnight at room temperature. Cold water was added to the mixture. The solution was neutralized and extracted with ethyl acetate. The organic layer was dried over magnesium sulfide, filtrated, and concentrated. The residue was purified by column chromatography on silica gel using hexane/chloroform (1:1) as the eluent to give **5a** (1.89 g) in 57% yield.

5a: colorless crystal—mp 171–172 °C; ¹H NMR (CDCl₃, 200 MHz) δ 2.20 (s, 6H, CH₃), 7.52 (d, *J* = 8.6 Hz, 2H), 8.16 (dd, *J* = 8.6 Hz, 2.0 Hz, 2H), 8.33 (d, *J* = 2.0 Hz, 2H). Ms(EI) (*m/z*) 526(*M*⁺). Anal. found: C 52.39, H 2.38, N 5.14%. Calcd. for C₂₃H₁₂F₆N₂O₄: C 52.48, H 2.30, N 5.32%.

2.2.4. Preparation of 1,2-bis(2-methyl-6-formyl-1-benzofuran-3-yl)perfluorocyclopentene (**6a**)

To a solution of **2a** (2.18 g, 5.0 mmol) in nitrobenzene (8 ml) was added dichloromethyl methyl ether (7.5 mmol) and anhydrous aluminum chloride (2.80 g) at 0 °C and the solution was stirred for 15 h at room temperature under argon atmosphere. Water was poured into the reaction mixture and then the product was extracted with ethyl acetate, washed with water, dried with magnesium sulfate, and concentrated. After evaporation of nitrobenzene in a vacuum, column chromatography (chloroform) gave diformyl compound **6a** (1.60 g) in 65% yield.

6a: colorless crystals—mp 139–140 °C; ¹H NMR (CDCl₃, 200 MHz) δ 2.18 (s, 4.2H, CH₃), 2.21 (s, 1.8H), 7.52 (d, *J* = 8.6 Hz, 0.6H), 7.55 (d, *J* = 8.2 Hz, 1.4H), 7.75 (dd, *J* = 8.2 Hz, 1.2 Hz, 1.4H), 7.85 (dd, *J* = 8.6 Hz, 1.4 Hz, 0.6H), 7.90–7.92 (m, 2H), 9.92 (s, 0.6H), 10.04 (s, 1.4H). Ms(EI) (*m/z*) 492(*M*⁺). Anal. found: C 60.68, H 2.98%. Calcd. for C₂₅H₁₄F₆O₄: C 60.98, H 2.87%.

2.2.5. Preparation of 1-(2-methyl-1-benzofuran-3-yl)-2-(2-methyl-6-(2,4-diphenylphen-1-yl)-1-benzofuran-3-yl)perfluorocyclopentene (**7a**) and 1,2-bis(2-methyl-6-(2,4-diphenylphen-1-yl)-1-benzofuran-3-yl)perfluorocyclopentene (**8a**)

2,4-Diphenylphenylboronic acid (0.877 g, 3.19 mmol), tetrakis(triphenylphosphine)paradium salt (0.166 g, 0.14 mmol), sodium carbonate (2.5 g) and water (10 ml) were added to a solution of **3a** (0.978 g, 1.41 mmol) in THF (10 ml). The reaction mixture was heated under reflux for 24 h. The reaction mixture was poured into water, extracted with diethyl ether, washed with water, dried over magnesium sulfate, and concentrated. The residue was purified by column chromatography (silica, hexane) to give **7a** (0.220 g) in 20% yield and **8a** (0.370 g) in 29% yield.

7a: colorless crystals—mp 193 °C; ¹H NMR (CDCl₃, 200 MHz) δ 1.99 (s, 3H), 2.00 (s, 3H), 6.88–6.90 (m, 1H), 7.03–7.19 (m, 9H), 7.28–7.45 (m, 5H), 7.57–7.68 (m, 4H). Ms(EI) (*m/z*) 790(*M*⁺). Anal. found: C 62.29, H 3.19%. Calcd. for C₄₁H₂₅F₆O₂: C 62.54, H 3.31%.

8a: colorless crystals—mp 147 °C; ¹H NMR (CDCl₃, 200 MHz) δ 1.96 (s, 6H, CH₃), 6.87–6.89 (m, 2H), 7.09–7.17 (m, 14H), 7.28–7.46 (m, 8H), 7.58–7.61 (m, 8H). Ms(FAB)

(*m/z*) 892(*M*⁺). Anal. found: C 79.30, H 4.28%. Calcd. for C₅₉H₃₈F₆O₂: C 79.36, H 4.29%.

3. Results and discussion

3.1. Synthesis of diarylethene derivatives **3a–8a**

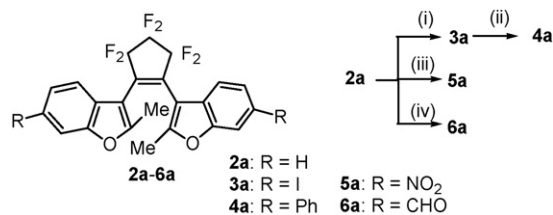
Diarylethene **3a** was synthesized by iodination of **2a** according to the procedure described in Scheme 1. Compound **3a** was converted into **4a** by Suzuki coupling with phenylboronic acid in THF. **5a** having two nitro moieties was synthesized from **2** following by the same procedure in Ref. [6] (Scheme 1). **2a** was formylated by dichloromethyl methyl ether to give **6a**. Diarylethenes **7a** and **8a** were synthesized by a Suzuki coupling reaction of the diiodo derivative **3a** with a boronic acid derivative of 2,4-diphenylbenzene.

The structure of **3a** was determined by X-ray crystallographic analysis as shown below. A single crystal of **3a** was obtained by recrystallization from chloroform. The ORTEP drawing of the diarylethene **3a** is shown in Fig. 1 [20]. The **3a** single crystal adopted a monoclinic space group *P2₁/c*. The ORTEP drawing of **3a** indicates that **3a** has two iodine moieties that are connected at the 6 position of 2-methylbenzofuran units, which is the same as the results of the iodination of **1**. The two benzofuran rings are oriented in parallel, and do not undergo photochromism in the crystalline phase [16].

4a–6a were not analyzed by X-ray crystallography, because no single crystal was obtained. **4a** has two phenyl moieties that are connected at the 6 position of 2-methylbenzofuran units, because the reaction is the same one which **1** was introduced to benzene units. The structure of **4a** having two benzene units was determined by ¹H NMR spectroscopy, mass spectroscopy and elemental analysis.

The structures of **5a** and **6a** were estimated by ¹H NMR spectroscopy. The assignments of proton signals are summarized in Fig. 2.

Iodine, nitro, and formyl groups are known as electron-withdrawing substituents. In the figure, the proton of the 7 position of benzofuran rings has the lowest value among all aromatic protons, because it is next to electron-withdrawing substituents. The same tendency was observed for the protons of the 5 position of benzofuran rings. The protons of the 5 position were coupled with the 4 position and the 7 position protons. These results show that **5a** and **6a** have the two nitro and formyl moieties that are connected at the 6 position of 2-methylbenzofuran units, respectively.



Scheme 1. Reagents and conditions: (i) HIO₃, I₂, AcOH, Ac₂O, 70 °C; (ii) PhB(OH)₂, Pd(PPh₃)₄, reflux; (iii) HNO₃, AcOH, Ac₂O, r.t.; (iv) CHCl₂OCH₃, AlCl₃, PhNO₂, r.t.

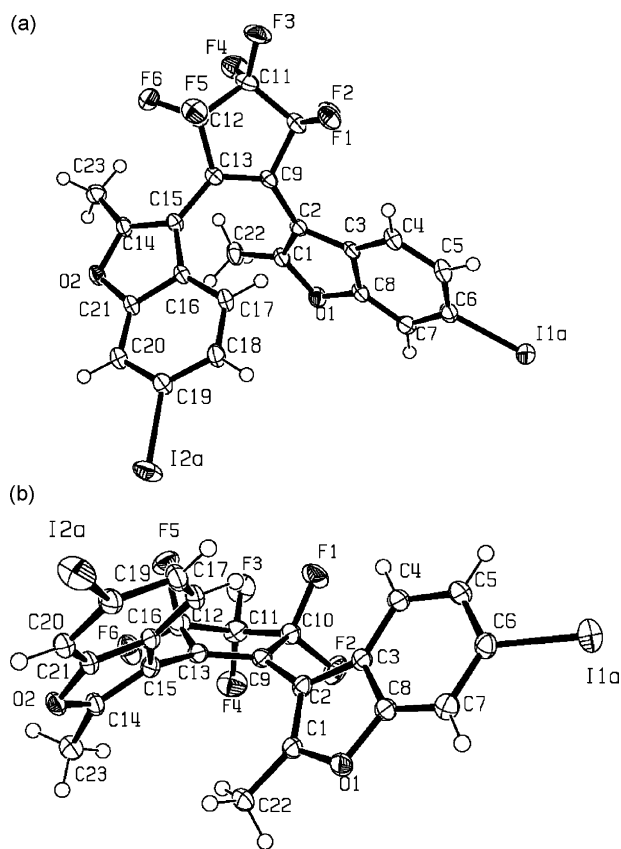


Fig. 1. ORTEP drawings of top (a) and side (b) views of **3a**, showing 50% probability displacement ellipsoids.

The $^1\text{H NMR}$ spectrum of **6a** in CDCl_3 (200 MHz) shows that the open-ring of form diarylethene has two atropo conformers [2,15]. One conformer has two aromatic rings in mirror symmetry (in parallel orientation) and the other in C_2 symmetry (in antiparallel orientation). The methyl signals of antiparallel and parallel conformers were observed at 2.18 and 2.21 ppm, respectively. The intensity rate of the two signals indicated that the relative population ratio of the antiparallel and parallel conformers was 70:30.

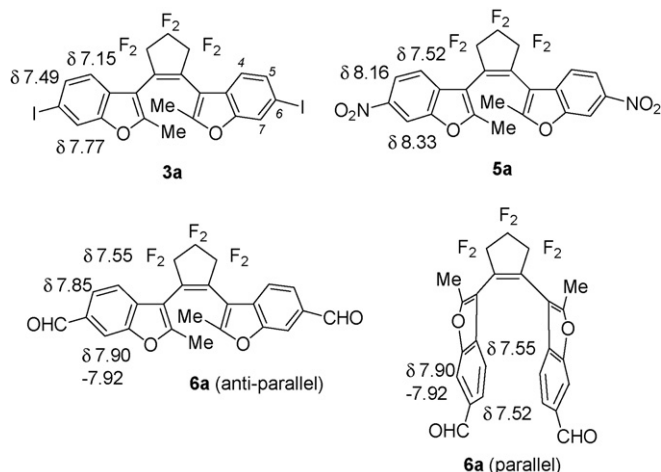


Fig. 2. $^1\text{H NMR}$ assignments of **3a**, **5a**, **6a** (antiparallel) and **6a** (parallel).

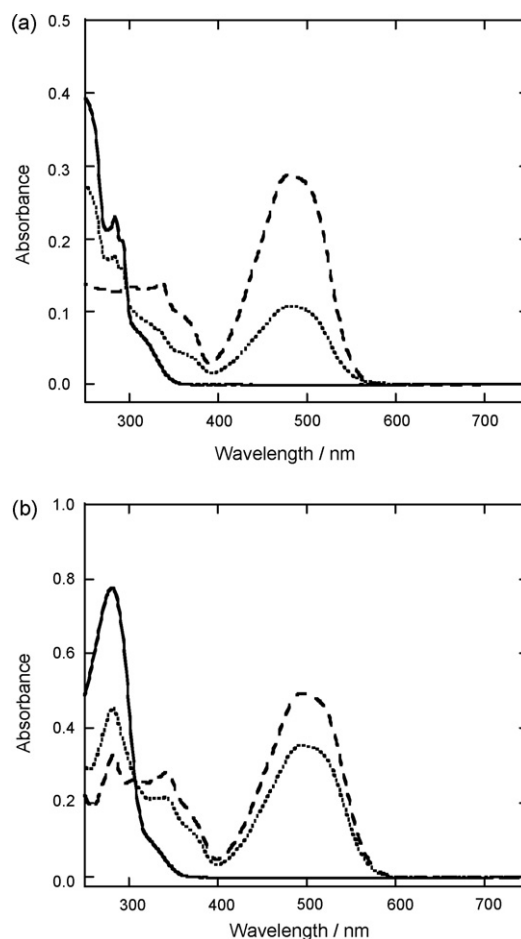


Fig. 3. (a) Absorption spectra of **3a** (1.2×10^{-5} mol/L) (solid line), **3b** (dashed line), and the photostationary state (dotted line) under irradiation with 313 nm light in hexane. (b) Absorption spectra of **4a** (1.9×10^{-5} mol/L) (solid line), **4b** (dashed line), and the photostationary state (dotted line) under irradiation with 313 nm light in hexane.

3.2. Photochromism of 1,2-bis(benzofuranyl)ethene derivatives **3a–6a**

Compounds **3a**, **4a**, **5a** and **6a** exhibited photochromism in hexane solution. Fig. 3(a) shows the absorption spectral change of **3a** in hexane under irradiation with 313 nm light. **3a** has an absorption maximum at 284 nm (ϵ , $1.91 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$). Upon irradiation with 313 nm light, the colorless solution of **3a** turned orange, in which a visible absorption band was observed at 480 nm. The red color is due to the closed-ring forms. The conversion from **3a** to **3b** in the photostationary state under irradiation with 313 nm light was 37%. The color disappeared after irradiation with visible light ($\lambda > 440$ nm). The colored isomer was isolated by HPLC, and the absorption characteristic was examined. The absorption coefficient of **3b** at 480 nm was $2.40 \times 10^{-4} \text{ M}^{-1} \text{ cm}^{-1}$, as shown in Table 1.

Fig. 3(b) shows the absorption spectral change of **4a** in hexane upon irradiation with 313 nm light. **4a** has an absorption maximum at 284 nm (ϵ , $4.08 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$). Upon irradiation with 313 nm light, the colorless solution of **4a** turned red, in which a visible absorption band was observed at 495 nm. The

Table 1
Absorption maxima, coefficients of open- and closed-ring forms, and quantum yields of cyclization and cycloreversion reactions in hexane solution of **2–8**

Compound	ε ($\times 10^4$ dm ³ mol ⁻¹ cm ⁻¹)		Quantum yield	
	a	b	Cyclization	Cycloreversion
2	1.00 (274 nm)	1.44 (469 nm)	0.38 (313 nm)	0.35 (469 nm)
3	1.91 (284 nm)	2.40 (480 nm)	0.37 (313 nm)	0.22 (480 nm)
4	4.08 (281 nm)	2.59 (495 nm)	0.63 (313 nm)	0.14 (495 nm)
5	2.52 (298 nm)	1.59 (489 nm)	0.55 (313 nm)	0.25 (489 nm)
6	3.20 (289 nm)	1.56 (494 nm)	0.52 (313 nm)	0.32 (494 nm)
7	2.93 (292 nm)	2.30 (492 nm)	0.43 (313 nm)	0.18 (490 nm)
8	5.66 (290 nm)	3.20 (500 nm)	0.29 (313 nm)	0.13 (490 nm)

conversion from **4a** to **4b** in the photostationary state under irradiation was 72%. The color disappeared after irradiation with visible light ($\lambda > 440$ nm).

Similarity to **4a**, **5a** and **6a** show photochromism in hexane. Fig. 4(a) shows the absorption spectral change of **5a** in hexane upon irradiation with 313 nm light. Upon irradiation with 313 nm light, the colorless solution of **5a** turned red, in which a visible absorption band was observed at 489 nm. The conversion

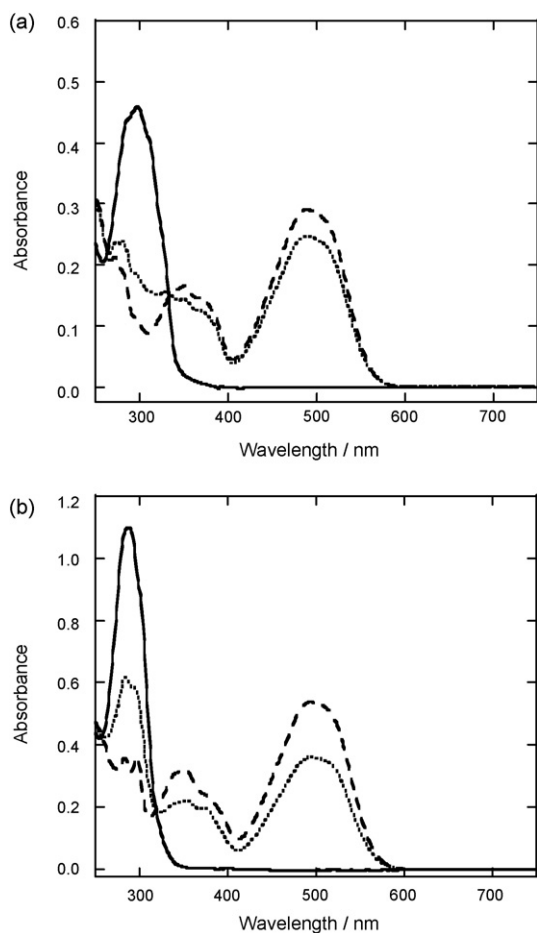


Fig. 4. (a) Absorption spectra of **5a** (1.9×10^{-5} mol/L) (solid line), **5b** (dashed line), and the photostationary state (dotted line) under irradiation with 313 nm light in hexane. (b) Absorption spectra of **6a** (3.4×10^{-5} mol/L) (solid line), **6b** (dashed line), and the photostationary state (dotted line) under irradiation with 313 nm light in hexane.

from **5a** to **5b** in the photostationary state under irradiation was 84%.

Fig. 4(b) shows the absorption spectral change of **6a** in hexane upon irradiation with 313 nm light. Upon irradiation with 313 nm light, the colorless solution of **6a** turned red, in which a visible absorption band was observed at 494 nm. The conversion from **6a** to **6b** in the photostationary state under irradiation was 67%.

Table 1 shows the summary of the absorption maxima and absorption coefficients of open- and closed-ring isomers in hexane. The cyclization and cycloreversion quantum yields were also measured and included in Table 1. Compound **2b** showed an absorption maximum at 469 nm. The maximum shifted to 480 nm for **3b**. The longest absorption-maximum wavelength of 495 nm was observed for **4b**. The absorption maximum of the colored isomers shifted to longer wavelengths with increasing π -conjugation length. The absorption maxima of **5b** and **6b** also shifted to longer wavelengths after introducing electron-withdrawing substituents.

Theoretical calculation for the absorption bands of the closed-ring isomers **3b**, **5b**, and **6b** was carried out with Gaussian 03 [21]. The calculated wavelengths of **3b**, **5b**, and **6b** were 523.03 nm ($f=0.7358$), 545.99 nm ($f=0.4460$), and 533.03 nm ($f=0.4604$), respectively. The wavelength for **2b** was reported to be 492.06 nm ($f=0.3131$) [14]. The absorption wavelengths correlate well with the experimental absorption wavelengths.

Replacement of benzothiophene groups with benzofuran groups shifts the absorption maximum wavelength of the closed-ring isomer in hexane. The closed-ring isomer of 1,2-bis(2-methyl-6-phenyl-1-benzothiophen-3-yl)perfluorocyclopentene (**9**) [6] has an absorption at 543 nm, the absorption maximum wavelength of **4b** (495 nm) is 48 nm shorter than that of **9b**. The closed-ring isomer of 1,2-bis(2-methyl-6-nitro-1-benzothiophen-3-yl)perfluorocyclopentene (**10**) [18] has an absorption at 545 nm, and the absorption maximum wavelength of **5b** (489 nm) is 56 nm shorter than that of **10b**. Therefore, the absorption maximum wavelength of the 6-substituted benzofuran derivative is about 50 nm shorter than that of the 6-substituted benzothiophene derivative in hexane, as in the case of benzofuran and benzothiophene derivatives [14,15].

In Table 1, the cyclization quantum yield of **4** ($\Phi=0.63$) was higher than that of **2** ($\Phi=0.38$), whereas that of **3** ($\Phi=0.37$) was almost as the same as that of **2**. The cyclization

quantum yield of 1,2-bis(6-phenyl-2-methyl-1-benzothiopen-3-yl)perfluorocyclopentene (**9**) ($\Phi = 0.31$) [6] is twice as large as that of **4** ($\Phi = 0.63$). Replacement of benzothiophene group with benzothiophene group increased the cyclization quantum yield. The cycloreversion quantum yield of **4** ($\Phi = 0.14$) was as the same as that of **9** ($\Phi = 0.14$) [18]. The extension of π -conjugation length by the introduction of the phenyl group in the closed-ring isomer is considered to decrease the cyclization quantum yield.

The cyclization quantum yields of **5** and **6** were higher than that of **2**, whereas the cycloreversion quantum yields of **5** and **6** were lower than that of **2**. The cyclization/cycloreversion quantum yields of **5** and **6** are changed after introducing electron-withdraw substituents. The cyclization quantum yield of the 6-nitro benzofuran derivative **5** ($\Phi = 0.55$) is slightly larger than that of the 6-nitro benzothiophene derivative **10** ($\Phi = 0.43$) [6], and the cycloreversion quantum yield of **5** ($\Phi = 0.25$) is larger than that of **10** ($\Phi = 0.10$) [6].

3.3. Photochromism of amorphous diarylethenes **7** and **8**

As in the case of **4**, which has phenyl substituents at the 6 position of benzofuran units, **7** and **8** show photochromism in hexane. The hexane solutions of **7b** and **8b** show characteristic absorption bands at 492 and 500 nm, respectively. Under irradiation with 313 nm light, the conversions from open- to the closed-ring isomers are 79% and 57%, respectively. Upon irradiation with visible light (>460 nm), the red color disappear to produce **7a** and **8a**, which are colorless isomers. The photochromic characteristics of **7** and **8** were shown in Table 1. The absorption maximum wavelength of **8b** (500 nm) was 40 nm shorter than that of the closed-ring isomer of 1,2-bis(2-methyl-6-(2,4-diphenylphenyl)-1-benzothiophen-3-yl)perfluorocyclopentene (**11**) [11] (540 nm) in hexane. The cyclization quantum yield of the benzofuran derivative **8** ($\Phi = 0.29$) is smaller than that of the benzothiophene derivative **11** ($\Phi = 0.40$) [11]. This may contribute to increase fluorescence (**8**: Φ_{fl} (313 nm) = 0.028; **11**: Φ_{fl} (313 nm) = 0.011) [11] and non-radiative process.

Compounds **7a** and **8a** exhibited melting temperatures of 193 and 147 °C, respectively. The glass transition states of **7a** and **8a** were obtained by a DSC method after the first melting and cooling cycles. Clear shifts, which were attributable to the glass-to-liquid transition of the materials, were observed at 68 and 60 °C.

Bulk amorphous thin films were prepared by spin coating an ethyl acetate solution of the **8a** on a quartz substrate. Fig. 5(a) and (b) shows the absorption spectral change of the bulk amorphous thin films of **7a** and **8a**. The thicknesses of the amorphous films are 290 and 70 nm, respectively. The visible absorption peak of **7b** can be observed at 506 nm, which is 14 nm longer than that of **7b** in hexane. Upon irradiation with 313 nm light, the colorless film of **7a** turned red owing to the formation of **7b**. The conversion from **7a** to **7b** in the photostationary state was estimated to be 18% for the amorphous film. Upon irradiation with visible light ($\lambda > 460$ nm), the red color disappeared

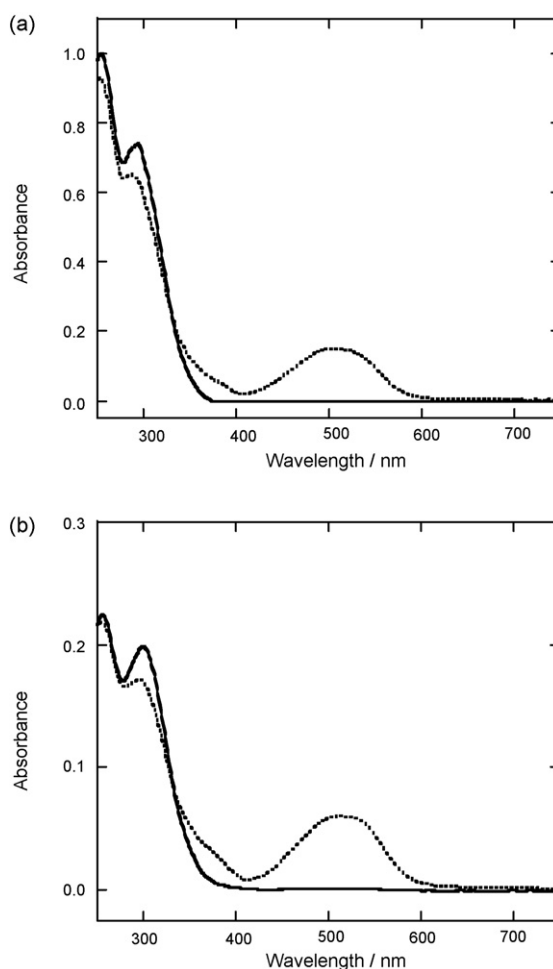


Fig. 5. (a) Absorption spectra of **7a** (solid line) and in the photostationary state (dotted line) under irradiation with 313 nm light in hexane (film thickness: 290 nm). (b) Absorption spectra of **8a** (solid line) and in the photostationary state (dotted line) under irradiation with 313 nm light in hexane (film thickness: 70 nm).

to produce the original colorless films. The same results were observed for **8**. The absorption peak of **8b** in the bulk amorphous phase was observed at 515 nm, which is 15 nm longer than that of **8b** in hexane. The conversion from **8a** to **8b** in the photostationary state was estimated to be 26% for the amorphous film. Although the diarylethene amorphous materials so far synthesized turned to blue or violet in the bulk amorphous phase, **7b** and **8b**, which have benzofuran rings, showed a red color in the bulk amorphous phase. The absorption maximum wavelength of **8b** (515 nm) is 48 nm shorter than that of **11b** (563 nm). The red color is indispensable for constructing a rewritable full color system.

In conclusion, we have synthesized diarylethene derivatives having 2-methyl-6-substitute-1-benzofuran rings. All benzofuran derivatives underwent photochromism in hexane solution. The data obtained are useful for constructing photochromic systems having 1,2-bis(6-substitute-1-benzofuran-3-yl)ethenes. The 2,4-diphenylphenyl derivatives (**7** and **8**) showed photochromism in an amorphous phase. The color of the amorphous films turned from colorless to red upon irradiation with 313 nm light.

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- [20] Crystallographic data (3a) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Center with supplementary publication numbers CCDC 638175. Copies of data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44 (0)1223 336033 or e-mail: deposit@ccdc.cam.ac.uk].
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