Photochromic and fluorescent properties of bisfurylethene derivatives†

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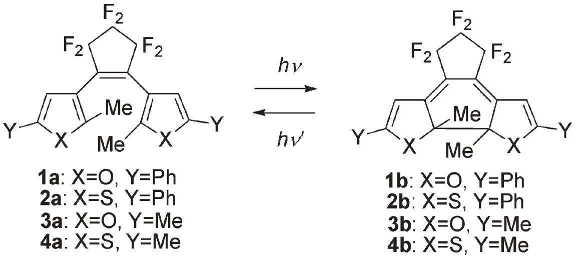
Photochromic diarylethenes having furan units (**1** and **3**) were synthesized and their photochromic performances were compared with those having thiophene units. The cyclization quantum yields of both derivatives in hexane are similar. In contrast, the cycloreversion quantum yield of the derivative having furan units (**1**) is much larger than that having thiophene units (**2**) in hexane. The difference is attributed to the conformation of the closed-ring isomers. Although **2a** and **4a** do not show any fluorescence, **1a** and **3a** exhibit fluorescence. Photochromism in the single crystalline phase was also observed for **1** and **3**. Upon irradiation with 313 nm light, the colorless crystals **1** and **3** changed to violet and yellow, respectively.

Introduction

Photochromism has attracted considerable attention because of its potential ability for applications to molecular devices, such as optical memories and switches.[1,2] Among various types of photochromic compounds, diarylethene derivatives are the most promising candidates for the applications because of their fatigue resistant property.[3] Although many diarylethene derivatives have been so far synthesized, most of them are composed of thiophene or benzothiophene heteroaryl groups.[3–8] Theoretical calculation predicts that 1,2-bis(3-furyl)ethene derivatives[9] will also undergo thermally irreversible photochromic reactions. However, diarylethenes having furan units have not been studied in detail yet. Recently, we have reported the synthesis of 1,2-bis(2-alkyl-1-benzofuran-3-yl)ethene derivatives,[10,11] and showed that they undergo thermally irreversible and fatigue resistant photochromic reactions.



It is known that diarylethene derivatives having furan units, such as 1-(9-anthryl)-2-(2-furyl)ethene,[12] give efficient fluorescence in cyclohexane. It has been reported that the fluorescence intensity can be modulated by the photochromism of diarylethene derivatives.[13–17] In this work, we have synthesized diarylethenes having furan rings, **1** and **3**, and compared their photochromic and fluorescent performances with those of diarylethenes having thiophene rings, **2** and **4**.[13,14]

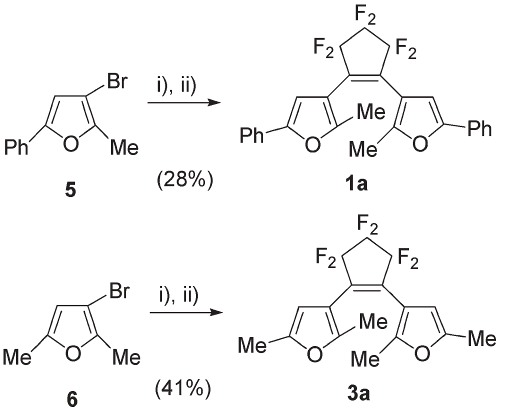
Results and discussion

Synthesis of bisfurylethenes 1a and 3a

Diarylethenes **1a** and **3a** were synthesized according to the general procedure for diarylethene derivatives (Scheme 1). The coupling reaction of 3-bromo-2-methyl-5-phenylfuran (**5**) with octafluorocyclopentene in dry THF gave **1a** in 28% yield. The reaction of 3-bromo-2,5-dimethylfuran (**6**) with octafluorocyclopentene in dry THF gave **3a** in 41%.

Photochromic reactions in hexane solution

Fig. 1(a) shows the absorption spectral change of **1** in hexane. Upon irradiation with 313 nm light, the open-ring isomer **1a**, which shows a maximum at 285 nm, was transformed into the closed-ring isomer **1b**, which has an absorption maximum at 525 nm. The conversion from the open to the closed-ring isomer was 92% under irradiation with 313 nm light. Upon irradiation with light of wavelength longer than 480 nm, the closed-ring isomer returned to the original open-ring isomer.



Scheme 1 Synthesis of the diarylethenes **1a** and **3a**. *Reagents and conditions*: i) n-butyllithium (1.1 eq), THF at −78 °C, ii) octafluorocyclopentene (0.5 eq) at 78 °C.

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† Electronic supplementary information (ESI) available: ORTEP drawings of **1a** and **3a**, photographs of single crystals of **1** and **3**, and fluorescence spectra of **3**. See DOI: 10.1039/b611294c

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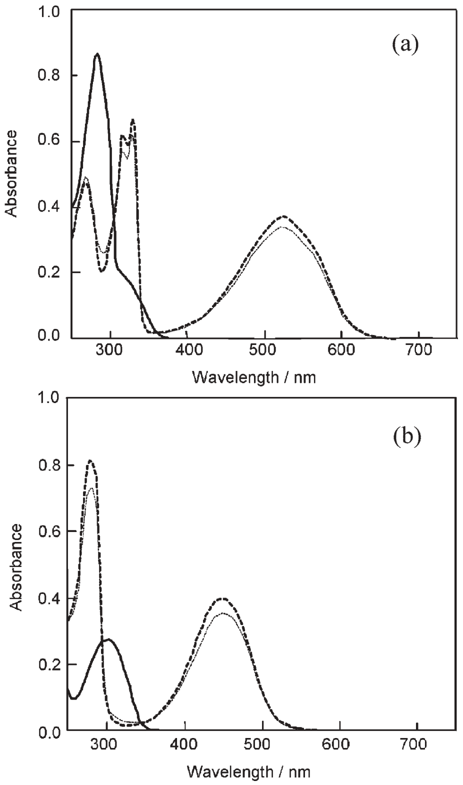

Fig. 1 (a) Absorption spectra of **1a** (solid line), **1b** (dashed line) and in the photostationary state (dotted line) under irradiation with 313 nm light in hexane ($c = 2.2 \times 10^{-5}$ mol L^{-1}). (b) Absorption spectra of **3a** (solid line), **3b** (dashed line) and in the photostationary state (dotted line) under irradiation with 313 nm light in hexane–ethyl acetate 9 : 1 solution ($c = 4.6 \times 10^{-5}$ mol L^{-1}).

The coloration/decoloration cycles of **1** could be repeated more than 150 times in hexane under argon atmosphere. It is reported that **2** decomposes in less than 200 cycles under the same conditions and produces a by-product.[3,20] Similar by-product (λ_{max} = 470 nm) formation was observed for **1**.

Although the closed-ring isomer was stable at 60 °C for 3 h in toluene solution in the presence of air, the closed-ring isomer started to decompose at 80 °C. The decomposition was not observed under argon atmosphere.

Fig. 1(b) shows the absorption spectral change of **3** by photoirradiation in a mixed solution (hexane–ethyl acetate = 9 : 1). The mixed solvent was used for the purification of the product. At the photostationary state under irradiation with 313 nm light, 90% of the open-ring isomer **3a** converted to the closed-ring isomer **3b**. Upon irradiation with 440 nm light, the closed-ring isomer returned to the open-ring isomer. Under argon atmosphere the decomposition was not observed at 80 °C for 3h in toluene. However the closed-ring isomer **3b** readily decomposed in the presence of air. We could not exchange the mixed (hexane–ethyl acetate) solution for hexane solution.

Table 1 shows the absorption maxima and their coefficients of the open- and closed-ring isomers, and the cyclization and cycloreversion quantum yields of **1–4**. The absorption maximum wavelength of **1b** is 50 nm shorter than that of **2b** in hexane. The absorption maximum of **3b** is 56 nm shorter than that of **4b**. A similar bathochromic shift is also observed for the closed-ring isomer of 1,2-bis(2-methyl-1-benzofuran-3-yl)perfluorocyclopentene.[10]

Enhancement of absorption coefficient was observed for **1b** (ε =16500 for **1b** and ε = 15600 for **2b**). Theoretical calculation for the absorption spectra of the closed-ring isomer **1b** and **2b** was carried out with Gaussian 03.[21] The calculated wavelengths of **1b** and **2b** are 557.59 nm (f = 0.4604) and 594.83 nm (f = 0.4306), respectively. The calculated absorption wavelength maxima correlate well with the experimental ones. Similar enhancement of absorption coefficient was observed for **3b** (ε = 8700 for **3b** and ε = 8000 for **4b**).

The cyclization quantum yields for **1** and **2** are similar (0.53 and 0.59). In contrast, the cycloreversion quantum yield for **1** (0.077) is much larger than that of **2** (0.013). The cycloreversion quantum yield is known to depend on the conformations of the closed-ring isomer. When the conformation is coplanar and π-conjugation extends throughout the molecule, the quantum yield decreases. To know the origin of the relatively large quantum yield, X-ray crystallographic analysis of the closed-ring form **1b** was carried out as shown in Fig. 2.[22] The torsion angle of **1b** (C2a–C12–C16–C18a: 23.8°) is much larger than that of **2b** (C6b–C6a–C3b–C3a: −3.4°).[18] The large torsion angle of **1b** suggests that the lack of coplanarity of the closed-ring isomer **1b**. This may contribute to the higher cycloreversion quantum yield of **1**.

Fluorescent properties in hexane solution

Fig. 3(a) shows the fluorescence spectra of **1** in hexane (c = 2.0×10^5 M). The excitation wavelength is 313 nm. The solid line represents the fluorescence in the open isomer. The dashed line represents the fluorescence at the photostationary state under irradiation with 313 nm light. Although **2a** is non-fluorescent, **1a** exhibits fluorescence (λ_{em} = 438 nm). The fluorescence quantum yield[23] and the fluorescence life time are 0.03 and 1.19 ns, respectively. The fluorescence intensity reversibly changed upon irradiation with 313 nm and visible (>480 nm) light.

Table 1 Absorption characteristics and photoreactivity of diarylethene derivatives **1**, **2**, and **4** in hexane and **3** in hexane–ethyl acetate 9 : 1 solution

	$\varepsilon/10^4$ dm^3 mol^{-1} cm^{-1}		Quantum yield	
Compound	**a**	**b**	Cyclization	Cycloreversion
1	3.87 (285 nm)	1.65 (525 nm)	0.53 (313 nm)	0.077 (517 nm)
2[a]	3.56 (280 nm)	1.56 (575 nm)	0.59 (313 nm)	0.013 (492 nm)
3	0.61 (302 nm)	0.87 (449 nm)	0.35 (313 nm)	0.32 (436 nm)
4	0.53[b] (303 nm)	0.80[b] (505 nm)	0.40 (313 nm)	0.12 (505 nm)

[a] Ref. 18 data. [b] Ref. 19 data.

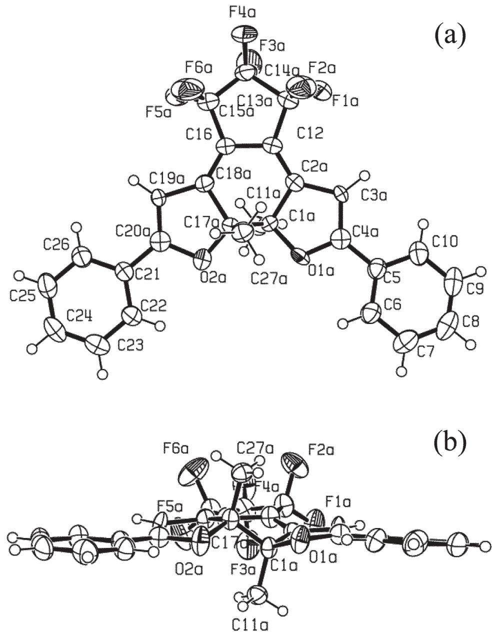

Fig. 2 ORTEP drawings of **1b**: (a) top view and (b) side view. The ellipsoid represents 50% displacement of atoms.

The fluorescence quantum yield of a diarylethene derivative having a furan unit (0.47) is reported to be larger than that of the corresponding thienyl derivative (0.28) in cyclohexane.[12] The quantum yield of the furyl derivative **1a** (0.03) is larger than that of the thienyl derivative **2a** (non-fluorescent) in hexane. The thiophene ring is more flexible than the furan ring. The flexibility difference is considered to affect the non-radiative process and the quantum yield. The fluorescence intensity reversibly changed upon irradiation with 313 nm and visible (>480 nm) light. Although **4a** is non-fluorescent, **3a** also exhibits fluorescence. The fluorescence maximum is 382 nm in hexane solution (excitation wavelength: 313 nm). The fluorescence quantum yield is 0.03 (313 nm).[23]

Single crystalline photochromism

2 is known to show photochromism in a single-crystalline phase.[18] Just like **2**, **1** undergoes photochromism in the single crystalline phase. The ORTEP drawing of **1a** indicates that **1a** is packed in a photoactive anti-parallel conformation in the crystal[24] and the distance between the reactive carbon atoms is 0.354 nm. The distance is shorter than the value of 0.42 nm which allows a photochromic reaction in the crystal. Upon irradiation with 365 nm for 3 s, the crystal turned violet, which absorbs at 546 nm. Fig. 4(a) shows the polarized absorption spectra of the colored crystal **1**. By rotating the sample under polarized light, the absorption intensity ratio at 546 nm changed. The order parameter of 0.84 (546 nm) indicates that the closed-ring isomers are regularly orientated in the crystal. Fig. 4(b) showed the polar plot at 546 nm.

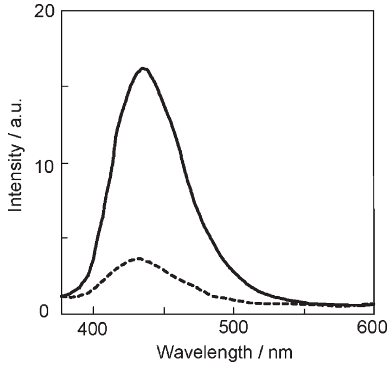

Fig. 3 Fluorescence spectra of **1a** (solid line) and in the photostationary state under irradiation with 313 nm light (dashed line) in hexane ($c = 2.0 \times 10^{-5}$ M).

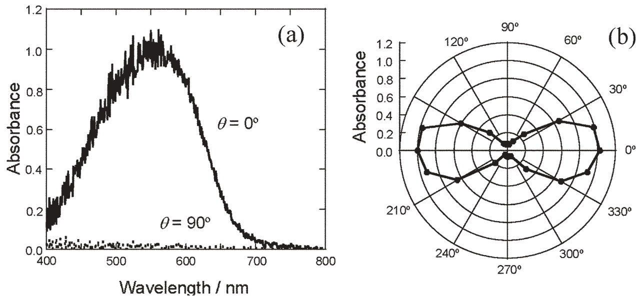

Fig. 4 (a) Absorption spectra of a single crystal **1** after irradiation with 365 nm light. (b) Polar absorption plot at 546 nm of a single crystal of **1** after irradiation with 365 nm light.

3 also undergoes photochromism in the single crystalline phase. Upon irradiation with 365 nm for 3 s, the crystal turned yellow, which absorbs at 450 nm. Fig. 5(a) and (b) show the polarized absorption spectra of **3** and the polar plots at 450 nm. The ORTEP drawing of **3a** indicates that the crystal has two molecules in the asymmetric unit.[25] The molecules have furan rings in a photoactive anti-parallel conformation, and the distances between the reactive carbon atoms are determined to be 0.354 and 0.374 nm, which are short enough for the molecule to undergo photochromism in the single crystalline phase. The coloration/decoloration cycles of the crystals **1** and **3** could be repeated more than 100 times without destruction.

Conclusions

Diarylethenes having furan units (**1a** and **3a**) were synthesized and their photochromic and fluorescent performances were examined in solution as well as in the single crystalline phase.

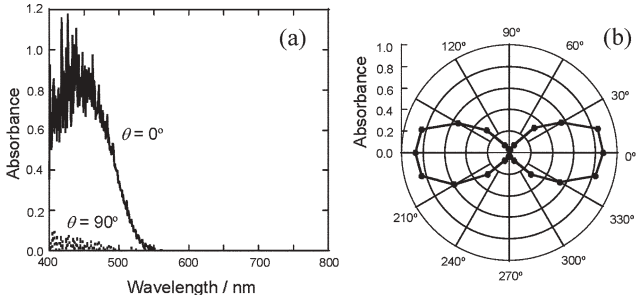

Fig. 5 (a) Absorption spectra of a single crystal **3** after irradiation with 365 nm light. (b) Polar absorption plot at 450 nm of a single crystal of **3** after irradiation with 365 nm light.

Although **2a** and **4a** did not show any fluorescence, **1a** and **3a** exhibit fluorescence. **1** and **3** undergo photochromism in the single crystalline phase. The cycloreversion quantum yield for **1** is much larger than that of **2** in hexane. The closed-ring isomer **1b** has a less coplanar conformation, and this may contribute to the higher cycloreversion quantum yield of **1**.

Experimental

General

Solvents used were spectrograde and were purified by distillation before use. Absorption spectra were measured with a spectrophotometer (Hitachi, U-3410). The quantum yields were determined by comparing the reaction rates of the diarylethene derivatives in hexane against that of furylfulgide in toluene. The samples were not degassed. For solution measurements, a super-high pressure mercury lamp (Ushio, 500 W) was used as a light source. Light of appropriate wavelength was isolated by passing light through a monochromator (RITSU MC-10N) or through L-29 and Y-48 filters. Fluorescence spectra were measured with a Hitachi F-3010 fluorescence spectrophotometer. Fluorescence life times were measured with a time-resolved spectrofluorometer (Hamamatsu C4334-01, C5094, and C4792) excited with a pulsed N_2 laser. The pulse width was 600 ps and the wavelength was 337.1 nm. The decay curve was analyzed with the single-exponential fitting after deconvolution of the excitation light pulse profile. The goodness of the fit was judged with the reduced χ^2 value (0.68). Absorption spectra in the single crystalline phase were measured using an OPTI-POL 2POL (Nikon) polarizing microscope connected to a Hamamatsu PMA-11 detector. Photoirradiation for single crystal measurements was carried out using a 100 W mercury lamp (Nikon, C-SHG1 and LH-M100CB-1) as a light source. ^{1}H NMR spectra were recorded on a Gemini 200 spectrometer (200 MHz) at room temperature with $CDCl_3$ (chloroform-*d*) as solvent and tetramethylsilane as an internal standard. Mass spectra were measured with mass spectrometers (Shimadzu GCMS-QP5050A and JEOL GC-mate II). Good quality crystals (**1a**: 0.2 × 0.2 × 0.1 mm, **1b**: 0.1 × 0.1 × 0.05 mm, and **3a**: 0.1 × 0.05 × 0.05 mm) were selected for the X-ray diffraction study. The data collection was performed on a Bruker SMART 1000 CCD-based diffractometer (55 kV, 35 mA) with MoKα irradiation. HPLC was carried out on a Shimadzu LC-10AD liquid chromatograph coupled with a Shimadzu SPD-10AV spectrophotomeric detector. A silica gel column (Wako Wakosil-5SIL) was used to analyze diarylethene isomers.

1,2-Bis(3-(2-methyl-5-phenylfuryl))perfluorocyclopentene (1a)

To a stirred THF solution (20 ml) containing 3-bromo-2-methyl-5-phenylfuran (**3**)[26] (0.791 g, 3.33 mmol) was slowly added 2.29 ml of 1.6 M butyllithium hexane solution (3.66 mmol) at −78 °C, and the solution was stirred for 15 min at −78 °C. Then octafluorocyclopentene (0.221 ml, 1.66 mmol) was added slowly to the reaction mixture at −78 °C, and left to stand with stirring at −78 °C to 30 °C for 12 h. The reaction mixture was poured into concentrated sodium ammonium chloride solution and extracted with diethyl ether. The organic layer was dried over anhydrous magnesium sulfate and evaporated *in vacuo*. The crude product was purified by column chromatography on silica gel (hexane) to give 0.224 g of **1a** in 28% yield as colorless crystals; mp. 116–117 °C; ^{1}H NMR (200 MHz) δ 2.05 (6H, s), 6.71 (2H, s), 7.26–7.30 (2H, m), 7.37–7.41 (4H, m), 7.62–7.64 (4H, m). MS (FAB) 488.1231 (M^+, $C_{27}H_{18}F_6O_2$ requires 488.1211). Anal. Calcd for $C_{27}H_{18}F_6O_2$: C 66.40, H 3.71%. Found: C 66.21, H 3.72%.

1b: violet crystals; mp. 165–166 °C; ^{1}H NMR (200 MHz) δ 1.68 (6H, s), 6.30 (2H, s), 7.45–7.47 (6H, m), 7.78–7.80 (4H, m). MS *m*/*z* (M^+) 488.

1,2-Bis(3-(2,5-dimethylfuryl))perfluorocyclopentene (3a)

To a stirred THF solution (30 ml) containing 3-bromo-2,5-dimethyl-5-phenylfuran (**3**)[27] (3.6 g, 20.6 mmol) was slowly added 14.1 ml of 1.6 M butyllithium hexane solution (22.6 mmol) at −78 °C, and the solution was stirred for 15 min at −78 °C. Then octafluorocyclopentene (1.36 ml, 10.3 mmol) was added slowly to the reaction mixture at −78 °C, and left to stand with stirring at −78 °C to 30 °C for 12 h. The reaction mixture was poured into concentrated sodium ammonium chloride solution and extracted with diethyl ether. The organic layer was dried over anhydrous magnesium sulfate and evaporated *in vacuo*. The crude product was purified by column chromatography on silica gel (hexane) to give 1.53 g of **3a** in 41% yield as colorless crystals; mp. 39–40 °C; ^{1}H NMR (200 MHz) δ 1.90 (3H, s), 2.24 (3H, s), 6.00 (2H, s). MS *m*/*z* (M^+) 364. Anal. Calcd for $C_{17}H_{14}F_6O_2$: C 56.05, H 3.87%. Found: C 56.07, H 3.87%.

Acknowledgements

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22 *Crystal data* for **1b**: $C_{27}H_{18}F_6O_2$, MW = 488.41, monoclinic, space group *P*21/*n*, $a = 7.1697(3)$ Å, $b = 29.4835(11)$ Å, $c = 10.9137(5)$ Å, $\alpha = 90^\circ$, $\beta = 104.206(3)^\circ$, $\gamma = 90^\circ$, $V = 2236.47(16)$ Å^3, $Z = 4$, $D_c = 1.451$ g cm^{-3}, μ(Mo-Kα) = 0.124 mm^{-1}, $T = 203(2)$ K, $R_1 = 0.0534$ for 3381 observed reflections with $I > 2\sigma(I)$ from 5676 unique reflections. CCDC deposition number: 293125.

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24 *Crystal data* for **1a**: $C_{27}H_{18}F_6O_2$, MW = 488.41, triclinic, space group $P\bar{1}$, $a = 9.5522(17)$ Å, $b = 10.8168(19)$ Å, $c = 11.1672(19)$ Å, $\alpha = 88.607(3)^\circ$, $\beta = 86.743(3)^\circ$, $\gamma = 86.796(3)^\circ$, $V = 1149.9(3)$ Å^3, $Z = 2$, $D_c = 1.411$ g cm^{-3}, μ(Mo-Kα) = 0.121 mm^{-1}, $T = 298(2)$ K, $R_1 = 0.0405$ for 2736 observed reflections with $I > 2\sigma(I)$ from 3811 unique reflections. CCDC deposition number: 293126.

25 *Crystal data* for **3a**: $C_{17}H_{14}F_6O_2$, MW = 364.28, triclinic, space group $P\bar{1}$, $a = 11.196(4)$ Å, $b = 12.226(4)$ Å, $c = 13.502(5)$ Å, $\alpha = 75.000(5)^\circ$, $\beta = 77.462(5)^\circ$, $\gamma = 68.203(5)^\circ$, $V = 1642.5(10)$ Å^3, $Z = 4$, $D_c = 1.473$ g cm^{-3}, μ(Mo-Kα) = 0.141 mm^{-1}, $T = 298(2)$ K, $R_1 = 0.0783$ for 2331 observed reflections with $I > 2\sigma(I)$ from 6573 unique reflections. CCDC deposition number: 615568.

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