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In Situ Preparation of Highly Fluorescent Dyes upon Photoirradiation

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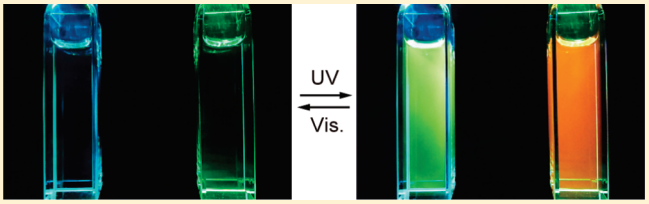
Supporting Information

ABSTRACT: Photoswitchable or photoactivatable fluorescent dyes are potentially applicable to ultrahigh density optical memory media as well as super-resolution fluorescence imaging when the dyes are highly fluorescent and have large absorption coefficients. Here, we report on highly fluorescent photochromic dyes, which are initially nonluminous in solution under irradiation with visible light but activated to emit green or red fluorescence upon irradiation with ultraviolet (UV) light. The dyes **5a**−**9a** are sulfone derivatives of 1,2-bis(2-ethyl-6-phenyl(or thienyl)-1-benzothiophen-3-yl)perfluorocyclopentene. It was found that substitution of phenyl or thiophene rings at 6 and 6′ positions of the benzothiophene-1,1-dioxide groups is effective to increase the fluorescence quantum yields of the closed-ring isomers over 0.7 and absorption coefficients over 4×10^4 M^{-1} cm^{-1}. The phenyl-substituted derivatives **5a**−**7a** undergo photocyclization reactions to produce yellow closed-ring isomers **5b**−**7b**, which emit brilliant green fluorescence at around 550 nm ($\Phi_F = 0.87-0.88$) under irradiation with 488 nm light. Any absorption intensity change of the closed-ring isomers was not observed even after 100 h storage in the dark at 80 °C. The closed-ring isomers slowly returned to the initial open-ring isomers upon irradiation with visible ($\lambda > 480$ nm) light. The ring-opening quantum yields ($\Phi_{C\rightarrow O}$) were measured to be $(1.6-4.0) \times 10^{-4}$. When the phenyl substituents are replaced with thiophene rings, such as compounds **8a** and **9a**, the absorption bands of the closed-ring isomers shift to longer than 500 nm. The closed-ring isomers exhibit brilliant red fluorescences at around 620 nm ($\Phi_F = 0.61-0.78$) under irradiation with 532 nm light. The ring-opening reactions are very slow ($\Phi_{C\rightarrow O} < 1 \times 10^{-5}$). The fluorescence lifetimes of these sulfone derivatives were measured to be around 2−3 ns, which is much longer than the value of the closed-ring isomer of 1,2-bis(2-methyl-1-benzothiophen-3-yl)perfluorocyclopentene ($\tau_F = 4$ and 22 ps). The closed-ring isomer **8b** in 1,4-dioxane exhibits excellent fatigue resistant property under irradiation with visible light ($\lambda > 440$ nm) superior to the stability of Rhodamine 101 in ethanol.



INTRODUCTION

Fluorescence is the most convenient tool to detect small amounts of molecules. Even single molecules can be detected using the fluorescence.[1−7] To make use of the high sensitivity, various types of fluorescent molecules have been developed and widely applied to microanalysis,[8,9] bioimaging,[10−16] and memory media.[17−21] Fluorescence spectra and/or intensity changes by external stimuli, such as chemicals, electrons (or holes), or photons, are adopted for the analysis and the imaging. When the fluorescence can be switched on and off upon photoirradiation, the fluorescence modulation is potentially applied to ultrahigh density optical memory media[17−21] and also to super-resolution fluorescence imaging.[14,16,22] It is strongly desired to explore for highly fluorescent dyes, which can be efficiently and instantaneously prepared or activated upon photoirradiation.

The photoswitchable fluorescent dyes can be designed and constructed by combining both photochromic and fluorescent chromophores in a molecule. On the basis of this idea, various fluorescent photochromic molecules have been synthesized.[17,18,20,21,23−28] Even limited to molecules having a photochromic diarylethene derivative as a photoswitching unit, a number of derivatives having a fluorescent unit, such as triphenyl imidazole,[29] anthracene,[17,28,30,31] perylenebisimide,[20,21,25,32] or 4,4-difluoro-8-(4′-iodophenyl)-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-*s*-indacene,[26] have been prepared. In these fluorescent photochromic molecules, the fluorescence is switched off by energy transfer or electron transfer processes when the diarylethene unit converts from the open- to the closed-ring isomer. Initially the molecules are fluorescent, while they convert to nonfluorescent states upon irradiation with UV light. The fluorescent switching from fluorescent to nonfluorescent states can be applied to optical memory media but is hardly applicable to super-resolution fluorescence imaging, such as PALM (photoactivatable localization microscopy) or STORM (stochastic optical reconstruction microscopy), because the imaging method requires initial dark background.[11,12,33]

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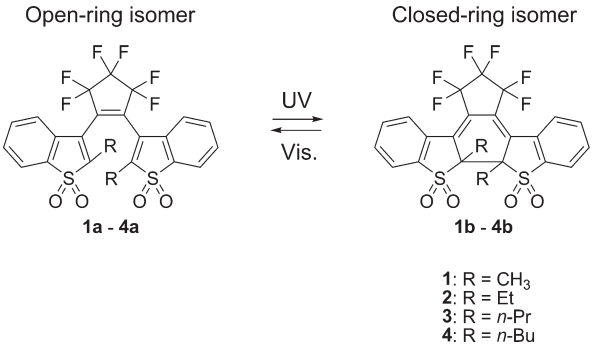
Scheme 1. Photochromism of Diarylethenes 1−4[a]



[a] The closed-ring isomers are fluorescent.

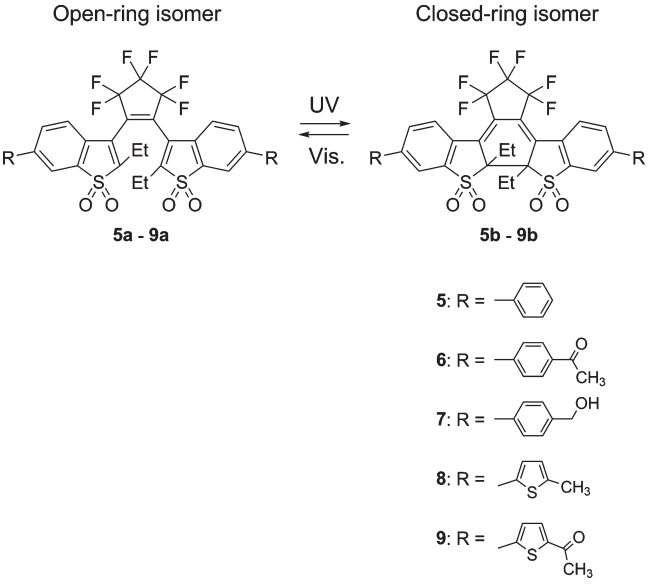
Another type of fluorescent photochromic diarylethenes is sulfone derivatives of 1,2-bis(2-methyl-1-benzothiophen-3-yl)-perfluorocyclopentene.[34,35] They are initially nonluminous and dark in solution under irradiation with visible ($\lambda > 400$ nm) light, while they are activated to emit blue fluorescence upon UV irradiation. Although the sulfone derivatives fulfill the PALM (or STORM) switching requirement to produce fluorescent dyes in the dark background, the quantum yields and the absorption coefficients are too low to be practically used for the ultrahigh density optical memory media and the PALM fluorescence imaging, both of which are, in principle, based on detection of single molecules. Our aim is to create photoswitchable fluorescent dyes, which have the fluorescence quantum yields close to 0.9 and high absorption coefficients[36] by chemical modification of the sulfone derivatives.

RESULTS AND DISCUSSION

1,2-Bis(2-methyl-1-benzothiophene-1,1-dioxide-3-yl)perfluorocyclpentene (**1a**) (Scheme 1) is known to undergo a reversible photochromic reaction and exhibit fluorescence in the closed-ring isomer **1b**.[34,35] **1a** is instantaneously activated to the fluorescent isomer **1b** upon UV irradiation. The fluorescence quantum yield and peak fluorescence wavelength were found to vary depending on alkyl substituents at the reactive carbons.[37] When the methyl substituents of **1a** are replaced with ethyl, propyl, and butyl substituents, such as compounds **2a**, **3a**, and **4a**, the peak wavelength shifts to longer wavelength region from 490 nm (**1b**) to 498 nm (**2b**), 500 nm (**3b**), and 499 nm (**4b**), and the yield increases from 0.01 (**1b**) to 0.12 (**2b**), 0.09 (**3b**), and 0.08 (**4b**) in ethyl acetate upon excitation at 398 nm. Among the four substituents, ethyl substituents are the most effective to increase the fluorescence quantum yield. Although the reason of the substituent effect is not known at the present stage of research, we employed ethyl substituents in the following experiments.

The fluorescence quantum yields and the absorption coefficients of the closed-ring isomers of 1,2-bis(2-alkyl-1-benzothiophene-1,1-dioxide-3-yl)perfluorocyclopentenes[34,35,37] and a polymer derivative[38] are insufficiently low.[36,39] To increase the quantum yield, we examined various substituent effects not only at the reactive carbons but also at other parts of the molecule and found that substitution of phenyl or thiophene rings at 6 and 6′ positions of the benzothiophene-1,1-dioxide groups was effective to dramatically increase the yield and the absorption coefficient.

Scheme 2. Photochromism of Diarylethenes 5−9 Having Phenyl and Thiophene Substituents



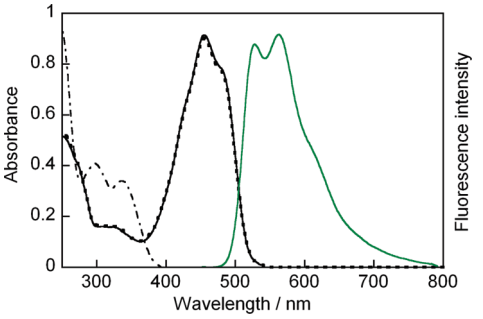


Figure 1. Absorption spectra of **5a** (black dashed line), **5b** (black solid line), and photostationary state under irradiation with 313 nm light (black dotted line) in 1,4-dioxane (2.0×10^{-5} M) and fluorescence spectrum of **5b** (green solid line) under irradiation with 488 nm light.

Phenyl- or thiophene-substituted derivatives **5a**−**9a** (Scheme 2) were prepared, and their fluorescent properties were examined. Suzuki−Miyaura coupling reaction using a 6,6′-diiodo derivative of **2a** was employed to prepare the derivatives. The details of the synthetic procedures are described in the Experimental Section.

Figure 1 shows the absorption spectra of **5a** (λ_{1max}, 298 nm; ε, 2.0×10^4 M^{-1} cm^{-1}; λ_{2max}, 336 nm; ε, 1.7×10^4 M^{-1} cm^{-1}), **5b** (λ_{max}, 456 nm; ε, 4.6×10^4 M^{-1} cm^{-1}), and photostationary state under irradiation with 313 nm light in 1,4-dioxane. **5b** was isolated from the photostationary solution using HPLC. **5a** has no absorption in the visible region ($\lambda > 400$ nm). Upon irradiation with UV light ($\lambda = 313$ nm), a new absorption appears at 456 nm. The new absorption is ascribed to the closed-ring isomer **5b**. The photocyclization quantum yield was determined to be 0.42.

The closed-ring isomer **5b** exhibits brilliant green fluorescence at around 550 nm. The fluorescence excitation spectrum agrees to the absorption spectrum of **5b**. The fluorescence quantum yield was measured to be 0.87 in 1,4-dioxane upon excitation at 488 nm. The quantum yield is extremely high and 7 times larger

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Table 1. Photophysical Properties of 2, 5−9 in 1,4-Dioxane[a]

	open-ring isomer **a**		closed-ring isomer **b**			
	λ_{max}/nm (ε/10^4 M^{-1} cm^{-1})	$\Phi_{O\rightarrow C}$	λ_{max}/nm (ε/10^4 M^{-1} cm^{-1})	$\Phi_{C\rightarrow O}$	Φ_F	τ_F/ns
2	275 (0.52), 310 (0.52)	0.28 [b,c]	414 (1.8)	0.18 [b,d]	0.22	1.2
5	298 (2.0), 336 (1.7)	0.42 [c]	456 (4.6)	4.0×10^{-4} [f]	0.87	3.0
6	267 (4.1), 300 (3.2)	0.51 [c]	456 (4.7)	3.6×10^{-4} [f]	0.87	2.8
7	301 (2.2), 340 (1.9)	0.43 [c]	463 (5.0)	1.6×10^{-4} [f]	0.88	2.9
8	330 (2.6), 374 (2.6)	0.21 [e]	506 (6.2)	$<1.0 \times 10^{-5}$ [f]	0.78	2.6
9	363 (4.1)	0.32 [e]	485 (6.3)	$<1.0 \times 10^{-5}$ [f]	0.61	1.9

[a] λ_{max}, absorption maximum; ε, absorption coefficient; $\Phi_{O\rightarrow C}$, cyclization quantum yield; $\Phi_{C\rightarrow O}$, cycloreversion quantum yield; Φ_F, fluorescence quantum yield; τ_F, fluorescence lifetime. [b] **1** was used as a reference.[35] [c] Under irradiation with 313 nm light. [d] Under irradiation with 405 nm light. [e] Under irradiation with 365 nm light. [f] Under irradiation with 488 nm light.

than the value of **2b** in ethyl acetate. The closed-ring isomer **5b** has a large absorption coefficient and is thermally stable. Any absorption intensity decrease was not observed even after 100 h storage in the dark at 80 °C. The absorption at 456 nm and the fluorescence at around 550 nm decrease and return to the initial state upon irradiation with visible (λ > 480 nm) light. The ring-opening quantum yield ($\Phi_{C\rightarrow O}$) of **5b** was measured to be 4.0×10^{-4}, which is much lower than the value of **1b** ($\Phi_{C\rightarrow O}$ = 0.061) and **2b** ($\Phi_{C\rightarrow O}$ = 0.18).[35] Solvent dependence of the fluorescence quantum yield was also measured. The yields were determined to be 0.89 (in dichloromethane), 0.79 (in THF), and 0.76 (in ethanol). Although the yield has a tendency to decrease with increasing solvent polarity, the high yield still remains even in polar ethanol.

The highly fluorescent and thermally stable dye is instantaneously prepared from the open-ring isomer **5a** upon irradiation with UV light. The open-ring isomer has no absorption in the visible region (λ > 400 nm), which means that the solution is initially dark under irradiation with 488 nm light. Upon UV irradiation, a new visible absorption due to the closed-ring isomer appears and excitation of the band by irradiation with 488 nm light exhibits brilliant fluorescence. Therefore, the signal ratio between the fluorescent state and dark background becomes huge.

Similar fluorescence behavior was observed for **6** and **7** having acetophenone and benzylalcohol substituents, respectively (see Figures S1 and S2). The acetyl group is reported to be effective to increase the fluorescence quantum yield,[35] and the hydroxy group is useful to introduce a reactive tag to proteins and others. Contrary to the expectation, increase in the fluorescence quantum yield was not observed by the acetyl modification. The absorption coefficients, cyclization/cycloreversion quantum yields, and fluorescence quantum yields of **6** and **7** are summarized in Table 1.

The above phenyl-substituted derivatives can be excited using 488 nm laser light and exhibit green fluorescence. Another useful laser light locates at 532 nm. To shift the absorption bands of the closed-ring isomer to longer than 500 nm, the phenyl substituent was replaced with thiophene substituent as compounds **8a** and **9a**. Figure 2 shows the absorption spectra of **8a** (λ_{1max}, 330 nm; ε, 2.6×10^4 M^{-1} cm^{-1}; λ_{2max}, 374 nm; ε, 2.6×10^4 M^{-1} cm^{-1}), **8b** (λ_{max}, 506 nm; ε, 6.2×10^4 M^{-1} cm^{-1}), and photostationary state under irradiation with 365 nm light in 1,4-dioxane. The photostationary spectrum overlaps with that of **8b**. **8a** has no absorption longer than 450 nm. Upon irradiation with UV light (λ = 365 nm), a new absorption appears at 506 nm. The new

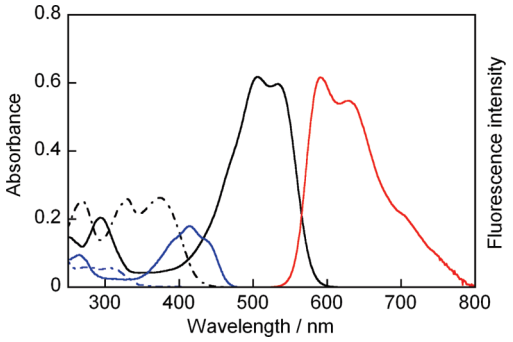


Figure 2. Absorption spectra of **8a** (black dashed line), **8b** (black solid line), and photostationary state under irradiation with 365 nm light in 1,4-dioxane (1.0×10^{-5} M) and fluorescence spectrum of **8b** (red solid line) under irradiation with 532 nm light. The photostationary spectrum overlaps with the spectrum of **8b**. The absorption spectra of **2a** (blue dashed line) and **2b** (blue solid line) in 1,4-dioxane (1.0×10^{-5} M) were also shown as a reference.

absorption is ascribed to the closed-ring isomer **8b**. The photocyclization quantum yield was determined to be 0.21. The closed-ring isomer exhibits brilliant red fluorescence at around 620 nm under irradiation with 532 nm light. The fluorescence quantum yield was measured to be 0.78 in 1,4-dioxane. The closed-ring isomer is thermally as well as photochemically stable and hardly returns to the initial state. Any absorption intensity change of the closed-ring isomer was not observed even after 100 h storage in the dark at 80 °C.

The acetyl thiophene-substituted derivative **9b** also exhibits brilliant red fluorescence upon irradiation with 532 nm light, and the fluorescence quantum yield was measured to be 0.61, which is lower than the value of the methyl thiophene derivative **8b**. Although the ring-opening reactions of these thiophene-substituted derivatives **8b** and **9b** are very slow under irradiation with visible light (λ > 480 nm), the absorption at around 500 nm is substantially bleached. The ring-opening quantum yields were estimated to be less than 1×10^{-5}.

Figure 3 shows photographs of fluorescence changes of 1,4-dioxane solutions containing **5** and **8** upon irradiation with 365 nm light under irradiation with 488 nm blue light (left-side solution containing **5**) and 532 nm green light (right-side solution containing **8**). Before irradiation with UV light, both solutions are dark, and any luminescence was not observed. Upon 365 nm light irradiation, brilliant green and red fluorescences instantaneously appeared. These fluorescences are

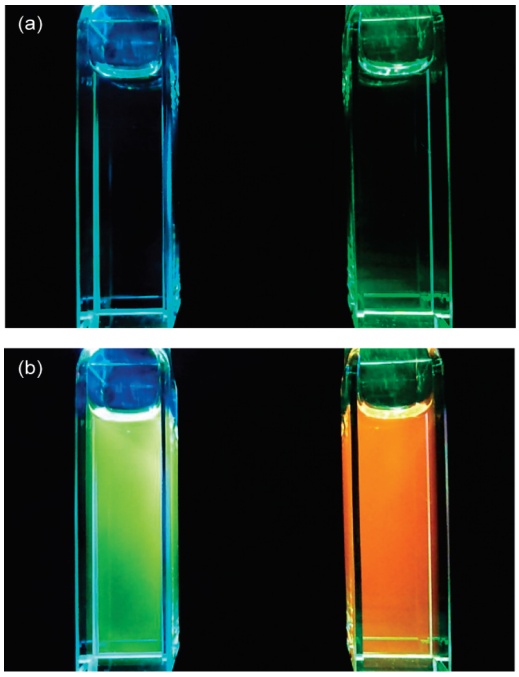


Figure 3. Photographs of 1,4-dioxane solutions containing **5** and **8** before (a) and after (b) irradiation with 365 nm light under irradiation with 488 nm blue light (left-side solution containing **5**) and 532 nm green light (right-side solution containing **8**).

attributed to the formation of **5b** and **8b** upon irradiation with 365 nm light.

Another characteristic feature of these sulfone derivatives having phenyl or thiophene substituents is fatigue resistant property. Figure 4 shows the decrease of the absorption maxima of **5b** and **8b** in 1,4-dioxane upon irradiation with visible light ($\lambda > 440$ nm) and weak 365 nm light. The 365 nm light was applied to convert photogenerated open-ring isomers to the closed-ring isomers. The decay curves of absorbances of Rhodamine 101 in ethanol and fluorescein in water are also shown as references. Any appreciate decay of the absorbance was not observed for **8b**, while appreciable decrease was observed in the absorbances of **5b** and Rhodamine 101 upon irradiation with visible light ($\lambda > 440$ nm). The absorption band of fluorescein disappeared in less than 2 h under the present illumination condition. The fatigue resistant property of **8b** is excellent and superior to the stability of Rhodamine 101, while the stability of **5b** is moderate.

The fluorescence lifetimes of **2b**, **5b**−**9b** were measured and are shown in Table 1. The derivatives having phenyl or thiophene substituents exhibit similar lifetimes of 2−3 ns, while the lifetime of **2b** is shorter (1.2 ns). These lifetimes are, however, much longer than the lifetime of 1,2-bis(2-methyl-1-benzothiophen-3-yl)perfluorocyclopentene (τ_F = 4 and 22 ps).[40,41]

To reveal the reason why the fluorescence quantum yields of the derivatives having phenyl or thiophene substituent are large, we estimated the fluorescence decay rate constant (k_f) and nonradiative decay rate constant (k_{nr}) on the basis of the fluorescence quantum yields and the lifetimes. The rate constants for unsubstituted derivative **2b** and **5b** having phenyl substituents were calculated to be 1.8×10^8 s^{-1} (k_f) and 6.5×10^8 s^{-1} (k_{nr}), and 2.9×10^8 s^{-1} (k_f) and 4.3×10^7 s^{-1} (k_{nr}), respectively.[42] Change in k_f is not significant by the substitution, but k_{nr} remarkably decreases in **5b**. The result indicates that

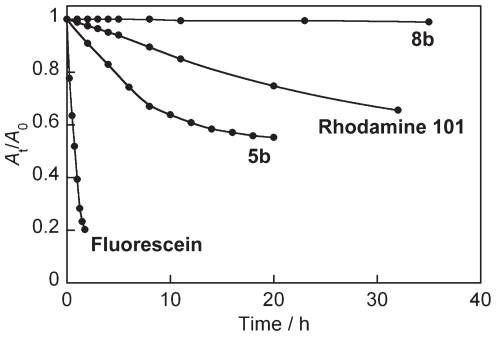


Figure 4. The absorbance changes of **5b** and **8b** in 1,4-dioxane solutions (4×10^{-6} M) upon irradiation with visible light ($\lambda > 440$ nm) and weak 365 nm light. The 365 nm light was applied to convert the photogenerated open-ring isomers to the closed-ring isomers. The absorbance changes of Rhodamine 101 in ethanol and fluorescein in water (4×10^{-6} M) were also shown as references.

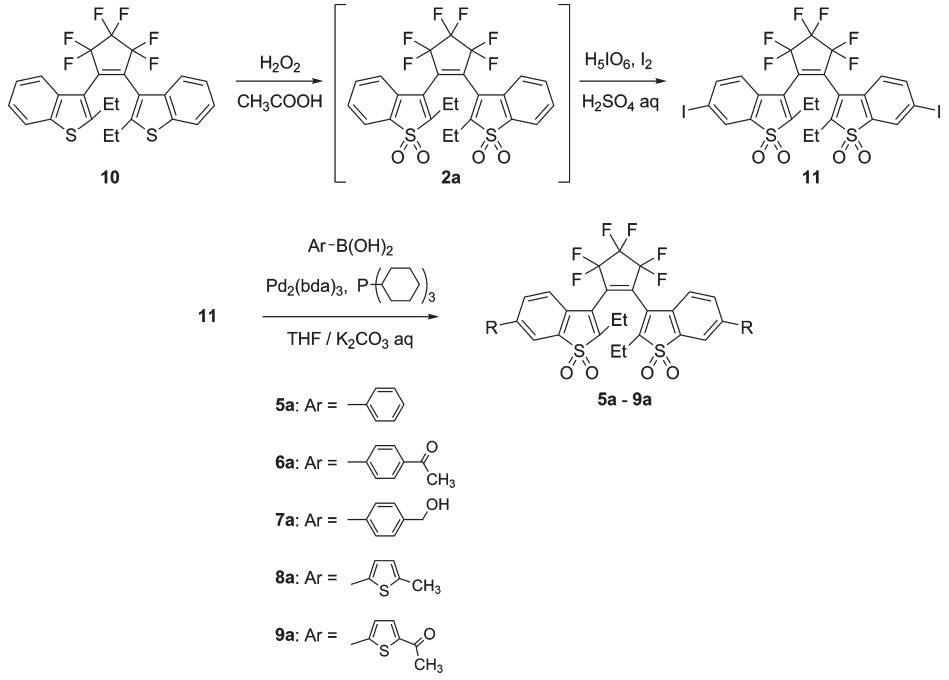
nonradiative decay processes including the cycloreversion reaction are strongly suppressed by the substitution, and this is the reason why the fluorescence quantum yield increases.

In conclusion, we have prepared diarylethene derivatives, which can be activated to fluorescent isomers upon irradiation with UV light. The isomers exhibit brilliant and fatigue resistant fluorescence upon irradiation with 488 or 532 nm light.

EXPERIMENTAL SECTION

General Procedures. Commercially available reagents and solvents for syntheses were of reagent grade and used without further purification. Solvents for spectral measurements were of spectroscopic grade. ^{1}H and ^{13}C NMR spectra were measured with a NMR spectrometer (Bruker, Avance 400). Tetramethylsilane was used as an internal standard. In the NMR data, (ap) and (p) indicate the proton signals of antiparallel and parallel conformations, respectively. Mass spectra were measured with a gas chromatography−mass spectrometer (Shimadzu, GCMS-QP2010Plus). Elemental analysis was carried out with an elemental micro analysis system (Elementar, Vario MICRO Cube). The closed-ring isomers were isolated from the photostationary solutions using HPLC (Hitachi L-2130 pump system, L-2420 detector, Wakosil 5SIL). Absorption and fluorescence spectra were measured with an absorption spectrophotometer (Hitachi, U-4100) and a fluorescence spectrophotometer (Hitachi, F-2500), respectively. Fluorescence spectra were corrected using the fluorescence of acridine orange as a reference.[43] Fluorescent quantum yields were measured with an absolute PL quantum yield measurement system (Hamamatsu, C9920-02G) and were confirmed by comparing the yields with those of reference samples, fluorescein and Rhodamine 6G. The absorption maxima were used as the excitation wavelengths of the fluorescence quantum yield measurement. For the measurement of the fluorescence time profiles, time-correlated single-photon counting (TCSPC) method using a picosecond Nd^{3+}:YAG laser (DPM-1000&SBR-5080-FAP, Coherent, 532 nm) with 8 MHz repetition rate and a femtosecond broad band Ti: Sapphire laser (SHG 450 nm) with 8 MHz repetition rate were employed. A photomultiplier tube (Hamamatsu Photonics, R3809U-50) with an amplifier (Hamamatsu Photonics C5594) and a counting board (PicoQuanta, PicoHarp 300) were used for the signal detection. The instrumental response function was estimated by the fwhm of the scattered light from a colloidal solution for the excitation light pulse. In the present measurements, it was 32 ps. Photoirradiation for photoreactions was carried out using a 500 W xenon lamp (Ushio, SX-UI501XQ) or a 300 W xenon lamp (Asahi spectra, MAX-302).

Scheme 3. Synthesis of Compounds 5a−9a



Wavelength of the light was selected using band-pass or cutoff optical filters and a monochromator (Ritsu, MC-10N). Typical intensity of 365 nm light used for the cyclization was 3−10 mW/cm^2. Photocyclization and photocycloreversion quantum yields were determined using furyl fulgide[44] as a reference.

Synthesis. Compounds **5a**−**9a** were prepared as shown in Scheme 3.

*1,2-Bis(2-ethyl-6-iodo-1-benzothiophen-1,1-dioxide-3-yl)perfluorocyclopentene (**11**).* A solution of 1,2-bis(2-ethyl-1-benzothiophen-3-yl)perfluorocyclopentene (**10**)[45] (4.0 g, 8.1 mmol) in acetic acid (200 mL) was heated to the boiling temperature (118 °C). Twenty milliliters of 50% hydrogen peroxide solution was slowly added to the solution, and the mixture was refluxed for 30 min. The resulting mixture was poured into cold water (200 mL) to give a precipitate. The precipitate was filtered, washed with distilled water several times, and dried in vacuo. The white powder product was added into cold sulfuric acid (80 mL), and the mixture was stirred vigorously at −5 °C for 20 min to dissolve the powder perfectly. Orthoperiodic acid (2.3 g, 10 mmol) and iodine (4.5 g, 18 mmol) were added to the solution, and the mixture was stirred at −5 °C for 2 h. After the pale green mixture turned dark purple, the mixture was warmed to 0 °C and further stirred for 2 h, and then carefully poured into cold ice water (160 mL). The mixture was extracted with chloroform (300 mL) three times. Additionally, the aqueous layer was extracted with ethyl acetate (200 mL) twice. The organic layer (chloroform and ethyl acetate) was washed with aqueous $NaHCO_3$, $Na_2S_2O_3$, and brine, dried over anhydrous $MgSO_4$, and evaporated in vacuo. The crude product was purified by silica gel column chromatography (hexane:ethyl acetate = 10:1 → 8:1) to give **11** (4.7 g, 5.8 mmol, 72% yield) as a white solid. **11**: mp 123−124 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.06 (t, J = 7.6 Hz, 3.4H (ap)), 1.39 (t, J = 7.6 Hz, 2.6H (p)), 2.29−2.37 (m, 1.7H (p)), 2.42−2.59 (m, 2.3H (ap)), 6.80 (d, J = 8.4 Hz, 0.9H (p)), 6.91 (d, J = 8.4 Hz, 1.1H (ap)), 7.79 (dd, J = 8.4 and 1.6 Hz, 0.9H (p)), 7.95 (dd, J = 8.4 and 1.6 Hz, 1.1H (ap)), 8.00 (d, J = 1.6 Hz, 0.9H (p)), 8.06 (d, J = 1.6 Hz, 1.1H (ap)); MS (EI) m/z (M^+) 812; ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.45, 11.68, 19.08, 19.24, 96.37, 122.68, 122.84, 123.49, 123.87, 128.67, 128.79, 131.30, 131.33, 136.94, 142.42, 142.76, 148.00, 148.48. Anal. Calcd for $C_{25}H_{16}F_6I_2O_4S_2$: C, 36.96; H, 1.99; S, 7.89. Found: C, 36.97; H, 1.91; S, 7.85.

*1,2-Bis(2-ethyl-6-phenyl-1-benzothiophen-1,1-dioxide-3-yl)perfluorocyclopentene (**5a**).* To a THF solution (10 mL) containing **11** (150 mg, 0.185 mmol) and phenylboronic acid (57 mg, 0.47 mmol) were added saturated aqueous K_2CO_3 (10 mL), tris(dibenzylideneacetone)-dipalladium(0) (30 mg, 0.033 mmol), and 18% tricyclohexylphosphine toluene solution (0.1 mL), and the mixture was stirred at room temperature for 20 min. The resulting mixture was neutralized with diluted hydrochloric acid and extracted with chloroform. The organic layer was evaporated in vacuo, and the residue was purified by silica gel column chromatography (hexane:ethyl acetate = 9:1 → 7:1) to give **5a** (126 mg, 0.177 mmol, 96% yield) as a white solid. **5a**: mp 199−200 °C; ^{1}H NMR (400 MHz, 1,4-dioxane-d_8) δ 1.04 (t, J = 7.6 Hz, 3.7H (ap)), 1.37 (t, J = 7.6 Hz, 2.3H (p)), 2.45−2.51 (m, 1.6H (p)), 2.59−2.70 (m, 2.4H (ap)), 7.34−7.50 (m, 8H), 7.62 (d, J = 7.2 Hz, 1.6H (p)), 7.67 (d, J = 7.2 Hz, 0.8H (p)), 7.71 (d, J = 7.2 Hz, 2.4H (ap)), 7.87 (d, J = 7.2 Hz, 1.2H (ap)), 8.16 (s, 0.8H (p)), 8.22 (s, 1.2H (ap)); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.64, 11.92, 19.17, 19.29, 121.05, 122.88, 123.08, 123.25, 123.34, 127.07, 127.11, 127.99, 128.07, 128.96, 129.04, 129.22, 129.29, 131.80, 132.17, 136.51, 138.08, 144.39, 144.52, 148.15, 148.56; MS (EI) m/z (M^+) 712. Anal. Calcd for $C_{37}H_{26}F_6O_4S_2$: C, 62.35; H, 3.68; S, 9.00. Found: C, 62.55; H, 4.02; S, 8.92.

*1,2-Bis(2-ethyl-6-(4-acetylphenyl)-1-benzothiophen-1,1-dioxide-3-yl)perfluorocyclopentene (**6a**).* To a THF solution (10 mL) containing **11** (150 mg, 0.185 mmol) and 4-acetylphenylboronic acid (74 mg, 0.45 mmol) were added saturated aqueous K_2CO_3 (10 mL), tris-(dibenzylideneacetone)dipalladium(0) (30 mg, 0.033 mmol), and 18% tricyclohexylphosphine toluene solution (0.1 mL), and the mixture was stirred at room temperature for 20 min. The resulting mixture was neutralized with diluted hydrochloric acid and extracted with chloroform. The organic layer was evaporated in vacuo, and the residue was purified by silica gel column chromatography (hexane:ethyl acetate = 8:2 → 6:4) to give **6a** (137 mg, 0.172 mmol, 93% yield) as a white solid. **6a**: mp 218−219 °C; ^{1}H NMR (400 MHz, 1,4-dioxane-d_8) δ 1.06 (t, J = 7.6 Hz, 3.9H (ap)), 1.38 (t, J = 7.6 Hz, 2.1H (p)), 2.46−2.52 (m, 1.4H (p)), 2.54 (s, 2.1H (p)), 2.58 (s, 3.9H (ap)), 2.61−2.70 (m, 2.6H (ap)), 7.37 (d, J = 8.0 Hz, 2H), 7.73 (m, 2.1H), 7.83 (d, J = 8.4 Hz, 2.6H (ap)), 7.94 (d, J = 8.0 Hz, 1.3H (ap)), 8.01 (d, J = 8.4 Hz, 1.4H (p)), 8.07 (d, J = 8.4

Hz, 2.6H (ap)), 8.24 (s, 0.7H (p)), 8.29 (s, 1.3H (p)); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.65, 11.87, 19.27, 19.37, 26.70, 121.19, 122.95, 123.20, 127.27, 127.34, 128.84, 129.21, 129.28, 132.04, 132.42, 136.68, 137.25, 142.30, 143.01, 143.15, 148.71, 149.25, 197.29,; MS (EI) m/z (M^+) 796. Anal. Calcd for $C_{41}H_{30}F_6O_6S_2$: C, 61.80; H, 3.79; S, 8.05. Found: C, 61.47; H, 3.52; S, 8.44.

*1,2-Bis(2-ethyl-6-(4-(hydroxymethyl)phenyl)-1-benzothiophen-1,1-dioxide-3-yl)perfluorocyclopentene (**7a**).* To a THF solution (10 mL) containing **11** (150 mg, 0.185 mmol) and 4-(hydroxymethyl)-phenylboronic acid (68 mg, 0.45 mmol) were added saturated aqueous K_2CO_3 (10 mL), tris(dibenzylideneacetone)dipalladium(0) (30 mg, 0.033 mmol), and 18% tricyclohexylphosphine toluene solution (0.1 mL), and the mixture was stirred at room temperature for 20 min. The resulting mixture was neutralized with diluted hydrochloric acid and extracted with chloroform. The organic layer was evaporated in vacuo, and the residue was purified by silica gel column chromatography (hexane:ethyl acetate = 6:4 → 2:8) to give **7a** (133 mg, 0.172 mmol, 93% yield) as a white solid. **7a**: mp 205−206 °C; ^{1}H NMR (400 MHz, 1,4-dioxane-d_8) δ 1.03 (t, J = 7.6 Hz, 3.9H (ap)), 1.37 (t, J = 7.6 Hz, 2.1H (p)), 2.40−2.50 (m, 1.4H (p)), 2.56−2.70 (m, 2.6H (ap)), 3.78−3.84 (m, 2H), 4.59 (d, J = 6.0 Hz, 1.4H (p)), 4.62 (d, J = 6.0 Hz, 2.6H (ap)), 7.34 (d, J = 8.0 Hz, 2H), 7.40 (d, J = 8.0 Hz, 1.4H (p)), 7.46 (d, J = 8.0 Hz, 2.6H (ap)), 7.61 (d, J = 8.0 Hz, 1.4H (p)), 7.70 (m, J = 8.0 Hz, 3.3H), 7.88 (d, J = 8.0 Hz, 1.3H (ap)), 8.17 (s, 0.7H (p)), 8.23 (s, 1.3H (ap)); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.65, 11.91, 19.17, 19.29, 64.70, 64.75, 120.94, 122.91, 123.12, 127.21, 127.27, 127.66, 127.72, 128.07, 131.69, 132.07, 136.53, 137.30, 141.92, 144.14, 148.14; MS (EI) m/z (M^+) 772. Anal. Calcd for $C_{39}H_{30}F_6O_6S_2$: C, 60.62; H, 3.91; S, 8.30. Found: C, 60.79; H, 3.94; S, 8.40.

*1,2-Bis(2-ethyl-6-(5-methylthiophen-2-yl)-1-benzothiophen-1,1-dioxide-3-yl)perfluorocyclopentene (**8a**).* To a THF solution (10 mL) containing **11** (150 mg, 0.185 mmol) and 5-methylthiophen-2-ylboronic acid (65 mg, 0.46 mmol) were added saturated aqueous K_2CO_3 (10 mL), tris(dibenzylideneacetone)dipalladium(0) (30 mg, 0.033 mmol), and 18% tricyclohexylphosphine toluene solution (0.1 mL), and the mixture was stirred at room temperature for 20 min. The resulting mixture was neutralized with diluted hydrochloric acid and extracted with chloroform. The organic layer was evaporated in vacuo, and the residue was purified by silica gel column chromatography (hexane:ethyl acetate = 10:1 → 7:3) to give **8a** (132 mg, 0.175 mmol, 95% yield) as a pale yellow solid. **8a**: mp 204−205 °C; ^{1}H NMR (400 MHz, 1,4-dioxane-d_8) δ 0.98 (t, J = 7.6 Hz, 3.9H (ap)), 1.34 (t, J = 7.6 Hz, 2.1H (p)), 2.37−2.69 (m, 10H), 6.76 (d, J = 3.6 Hz, 0.7H (p)), 6.81 (d, J = 3.6 Hz, 1.3H (ap)), 7.19 (d, J = 8.4 Hz, 0.7H (p)), 7.26 (d, J = 8.4 Hz, 1.3H (ap)), 7.32 (d, J = 3.6 Hz, 0.7H (p)), 7.41 (d, J = 3.6 Hz, 1.3H (ap)), 7.53 (dd, J = 8.0 and 1.6 Hz, 0.7H), 7.73 (dd, J = 8.0 and 1.6 Hz, 1.3H (ap)), 8.06 (d, J = 1.6 Hz, 0.7H (p)), 8.14 (d, J = 1.6 Hz, 1.3H (ap)); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.64, 11.92, 15.51, 15.55, 19.02, 19.21, 118.89, 118.94, 122.90, 123.20, 123.31, 123.38, 125.39, 125.46, 126.92, 127.01, 129.39, 129.67, 136.57, 136.63, 137.76, 137.83, 138.42, 142.51, 142.65, 147.51, 147.83; MS (EI) m/z (M^+) 752. Anal. Calcd for $C_{35}H_{26}F_6O_4S_4$: C, 55.84; H, 3.48; S, 17.04. Found: C, 56.13; H, 3.48; S, 17.35.

*1,2-Bis(2-ethyl-6-(5-acetylthiophen-2-yl)-1-benzothiophen-1,1-dioxide-3-yl)perfluorocyclopentene (**9a**).* To a THF solution (10 mL) containing **11** (150 mg, 0.185 mmol) and 5-acetylthiophen-2-ylboronic acid (76 mg, 0.45 mmol) were added saturated aqueous K_2CO_3 (10 mL), tris(dibenzylideneacetone)dipalladium(0) (30 mg, 0.033 mmol), and 18% tricyclohexylphosphine toluene solution (0.1 mL), and the mixture was stirred at room temperature for 20 min. The resulting mixture was neutralized with diluted hydrochloric acid and extracted with chloroform. The organic layer was evaporated in vacuo, and the residue was purified by silica gel column chromatography (hexane: ethyl acetate = 7:3 → 4:6) to give **9a** (134 mg, 0.166 mmol, 90% yield) as a white solid. **9a**: mp 251−252 °C; ^{1}H NMR (400 MHz, 1,4-dioxane-d_8) δ 1.03 (t, J = 7.6 Hz, 3.7H (ap)), 1.36 (t, J = 7.6 Hz, 2.3H (p)), 2.48−2.69 (s, 10H), 7.28 (d, J = 8.0 Hz, 0.8H (p)), 7.32 (d, J = 8.0 Hz, 1.2H (ap)), 7.56 (d, J = 4.0 Hz, 0.8H (p)), 7.64 (d, J = 4.0 Hz, 1.2H (ap)), 7.71−7.77 (m, 2.8H), 7.92 (d, J = 8.0 Hz, 1.2H (ap)), 8.24 (s, 0.8H (p)), 8.31 (s, 1.2H (ap)); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.62, 11.86, 19.25, 19.37, 26.61, 26.66, 119.80, 122.93, 123.04, 123.13, 123.41, 125.97, 126.01, 128.92, 129.02, 130.79, 131.09, 133.24, 133.28, 136.42, 136.48, 136.84, 136.88, 145.30, 145.37, 148.14, 148.18, 148.84, 149.28, 190.28; MS (EI) m/z (M^+) 808. Anal. Calcd for $C_{37}H_{26}F_6O_6S_4$: C, 54.94; H, 3.24; S, 15.86. Found: C, 55.09; H, 3.23; S, 15.99.

■ ASSOCIATED CONTENT

Supporting Information. Absorption and fluorescence spectra of **6**, **7**, and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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