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Fluorescence Photoswitching of a Diarylethene by Irradiation with Single-Wavelength Visible Light

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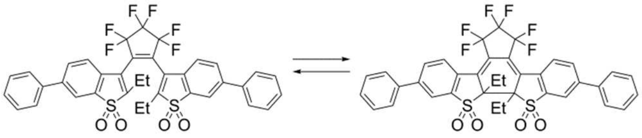
Supporting Information Placeholder

ABSTRACT: Photoswitchable turn-on mode fluorescent molecules have been so far successfully used in super-resolution fluorescence microscopies. Here, we report on fluorescence photoswitching of 1,2-bis(2-ethyl-6-phenyl-1-benzothiophene-1,1-dioxide-3-yl)perfluorocyclopentene (**1**) by irradiation with single-wavelength visible ($420\ \mathrm{nm} < \lambda < 470\ \mathrm{nm}$) light, the wavelength of which is longer than the 0-0 transition of open-ring isomer **1a**, without UV light excitation. By absorbing very weak hot bands or Urbach tails **1a** underwent a cyclization reaction to produce fluorescent closed-ring isomer **1b**. Both cyclization and cycloreversion reactions of **1** took place with the visible light in the far off-resonance region of the absorption edge. Based on numerical simulations of the formation process of **1b** from **1a** by irradiation with 450 nm light, weak absorption coefficients at 450 nm in *n*-hexane and CCl_4 were estimated to be 0.084 and 0.19 $M^{-1}\ cm^{-1}$, respectively. The reversible fluorescence photoswitching with the single visible light is advantageously applicable to super-resolution fluorescence imaging in biological systems.

Recently, considerable efforts have been paid to develop molecular photoswitches, which are capable to modulate physical and chemical properties of materials as well as biological activities upon photoirradiation.[1-9] Among them photoswitchable fluorescent molecules attract special interests because of their possible applications to ultrahigh density optical memory media[10-12] and super-resolution fluorescence microscopies.[12-16] The reversibly photoswitchable fluorescent molecules have been constructed by combining both photochromic and fluorescent chromophores in a molecule.[10,11] These molecules are initially fluorescent, while the fluorescence is quenched by an energy or an electron transfer mechanism when the photochromic unit undergoes the photoisomerization reaction. The turn-off mode fluorescence switching can be applied to optical memory media, but is hardly applicable to super-resolution fluorescence imaging, such as PALM (photoactivated localization microscopy) and STORM (stochastic optical reconstruction microscopy), because the imaging techniques require a dark back ground to detect single fluorescent molecules.[17] Turn-on mode fluorescent molecules are favorable for the super-resolution microscopies. A new type of photoswitchable fluorescent molecules, which have no fluorophore unit but exhibit turn-on mode fluorescence upon photoirradiation, have recently been developed.[18] They are sulfone derivatives of 1,2-bis(2-methyl-1-benzothiophen-3-yl)perfluorocyclopentene. When the methyl groups at 2- and 2′-poistions are replaced with short alkyl chains, and aryl groups are substituted at 6- and 6′-positions, the diarylethene derivatives were found to increase the fluorescence quantum yield of the closed-ring isomers up to ~ 0.9 and the absorption coefficient up to ~ $6 \times 10^4\ M^{-1}\ cm^{-1}$.[19] The derivatives have been successfully applied to super-resolution fluorescence microscopies, such as PALM and STORM[20-22] and RESOLFT (reversible saturable (switchable) optical linear fluorescence transitions) microscopy.[23]

During the course of study on the above photoswitchable diarylethenes we have discovered unprecedented photoreactions of 1,2-bis(2-ethyl-6-phenyl-1-benzothiopehne-1,1-dioxide-3-yl)perfluorocyclopentene (**1**). Upon irradiation with single-wavelength visible light **1** underwent reversible photoisomerization reactions and showed fluorescence photoswitching.



1a **1b**

Figure 1 shows an absorption spectrum of **1a** and absorption and fluorescence spectra of **1b** in 1,4-dioxane. Upon irradiation with UV (365 nm) light, **1a** readily converted to **1b**, which exhibits fluorescence. The photobleaching process of **1b** is also shown in Fig. 1. **1b** reverted back to initial **1a** upon irradiation with 450 nm light. The cycloreversion reaction was followed by measuring the fluorescence of **1b**, because the fluorescence intensity is proportional to the amount of **1b** and a small amount of **1b** can be detected by the fluorescence. Although the fluorescence considerably decreased, noticeable intensity of fluorescence ascribed **1b** remained even after prolonged irradiation with 450 nm light. The absorption band of **1a** locates shorter than 400 nm and the 0-0 transition is around 400 nm. Therefore, **1a** has no apparent absorption at 450 nm. This means that all closed-ring **1b** isomers are expected to completely revert back to open-ring **1a** isomers by irradiation with 450 nm light. But, a small amount of **1b** survived. This result indicates that 450 nm light induces the cyclization reaction of **1a** in addition to the cycloreversion reaction, though there is no apparent absorption of **1a** at the wavelength.

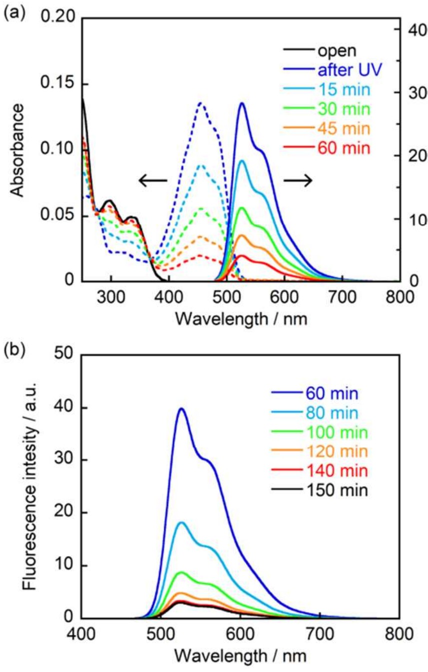


Figure 1. (a) Absorption and fluorescence spectral changes of **1** in 1,4-dioxane (3.2×10^{-6} M) upon irradiation with UV light (365 nm) and subsequent monochromatic 450 nm light. The solid black line showed the absorption spectrum of **1a**. Dashed lines showed the absorption spectra of **1b**. (b) Fluorescence spectral changes of **1b** in 1,4-dioxane upon prolonged irradiation with monochromatic 450 nm light. The fluorescence intensity after irradiation with 450 nm for 150 min was the same as the intensity after irradiation for 140 min.

In order to elucidate the unprecedented result we investigated following two mechanisms. One of possible mechanisms is that anti-Stokes Raman scattering lines induce the photoreactions. The Stokes Raman scattering of *n*-hexane has strong lines at around 2900 cm^{-1}, while the Raman scattering of carbon tetrachloride (CCl_4) has no notable lines longer than 790 cm^{-1} (see Fig. S1). In these two solvents we measured the threshold wavelength of light, which can induce the photocyclization reaction of **1a**. According to this anti-Stokes Raman scattering mechanism, the reaction threshold wavelength in *n*-hexane is expected to be longer than the wavelength in CCl_4. Figure 2 shows the fluorescence increase in the photostationary state under irradiation with monochromatic 500, 488, 480, 471, 468, 465, 460, 450, and 440 nm light (see Fig. S2). The fluorescence intensity correlates to the amount of the photogenerated **1b**, because the fluorescence quantum yields of **1b** in CCl_4 and *n*-hexane are almost similar, as shown in Table 1. The threshold wavelength in CCl_4 was observed at 471 nm, while the wavelength in *n*-hexane shifted to 460 nm. The shorter wavelength shift of the reaction threshold in *n*-hexane contradicts the anti-Stokes Raman scattering mechanism. The absence of oxygen effect also excludes the contribution of triplet states in CCl_4.

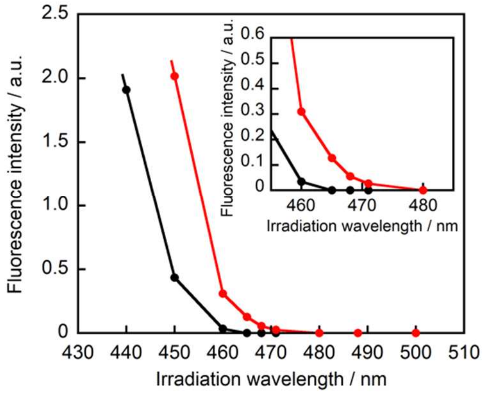


Figure 2. Fluorescence intensity of **1** in the photostationary state in *n*-hexane (black) and CCl_4 (red) under irradiation with monochromatic 500, 488, 480, 471, 468, 465, 460, 450, and 440 nm light. The excitation wavelength for the fluorescence was 450 nm.

Another possible mechanism is that the photoreaction is induced by absorbing very weak hot bands[24] or Urbach tails.[25-28] To verify the hot band mechanism the photoreactions induced upon irradiation with 450 nm was examined in detail. The reversible photocyclization/photocycloreversion reactions between open-ring isomer **1a** and closed-ring isomer **1b** are expressed as follows. We assumed that the reversible photoisomerizations are induced by irradiation with single-wavelength (λ) light.

Open-ring isomer **1a** $\underset{\lambda}{\overset{\lambda}{\rightleftarrows}}$ Closed-ring isomer **1b** (1)

$$\frac{\mathrm{d}C_\mathrm{B}}{\mathrm{d}t} = (\Phi_\mathrm{AB}\varepsilon_\mathrm{A}C_\mathrm{A} - \Phi_\mathrm{BA}\varepsilon_\mathrm{B}C_\mathrm{B})F \qquad (2)$$

$$F = \frac{1-10^{-(\varepsilon_\mathrm{A}C_\mathrm{A}+\varepsilon_\mathrm{B}C_\mathrm{B})d}}{\varepsilon_\mathrm{A}C_\mathrm{A}+\varepsilon_\mathrm{B}C_\mathrm{B}} \times \frac{10^3 I_0}{d}$$

, where Φ_{AB}, Φ_{BA}, ε_A, ε_B, C_A, C_B, d, and I_0 are the cyclization quantum yield, the cycloreversion quantum yield, the absorption coefficient of **1a** at λ, the absorption coefficient of **1b** at λ, the concentration of **1a** (M), the concentration of **1b** (M), the cell length (cm), and the light intensity (einstein/$cm^2 \cdot s$), respectively. When $\varepsilon_A C_A + \varepsilon_B C_B << 1$, the formation of the closed-ring isomers upon irradiation with single-wavelength (λ) light is expressed as follows, where C_o is the total concentration of **1a** and **1b**.

$$C_\mathrm{B} = \frac{\Phi_\mathrm{AB}\varepsilon_\mathrm{A}}{\Phi_\mathrm{AB}\varepsilon_\mathrm{A}+\Phi_\mathrm{BA}\varepsilon_\mathrm{B}}C_\mathrm{o}\left(1-e^{-(\Phi_\mathrm{AB}\varepsilon_\mathrm{A}+\Phi_\mathrm{BA}\varepsilon_\mathrm{B})\times 10^3 I_0 t}\right) \qquad (3)$$

In the photostationary state,

$$\frac{C_\mathrm{B}}{C_\mathrm{o}} = \frac{\Phi_\mathrm{AB}\varepsilon_\mathrm{A}}{\Phi_\mathrm{AB}\varepsilon_\mathrm{A}+\Phi_\mathrm{BA}\varepsilon_\mathrm{B}} \qquad (4)$$

Table 1. Photochemical and photophysical properties of **1**.

Solvent	*n*-Hexane	CCl_4	1,4-Dioxane
Φ_F	0.92	0.89	0.87
Φ_{AB}	0.42	0.50	0.62
Φ_{BA}	1.3×10^{-3}	6.6×10^{-4}	5.9×10^{-4}
$\varepsilon_{A\ (450\ nm)}$ / M^{-1} cm^{-1}	0.084	0.19	0.39
$\varepsilon_{B\ (450\ nm)}$ / M^{-1} cm^{-1}	4.5×10^4	4.3×10^4	4.5×10^4
Conversion (C_B / C_0) [a]	6.0×10^{-4}	3.4×10^{-3}	9.1×10^{-3}

[a] The ratio of photogenerated closed-ring isomer **1b** in the photostationary state under irradiation with 450 nm light.

Figure 3 shows the formation of **1b** from pure **1a** in *n*-hexane and in CCl_4 upon irradiation with 450 nm light. To detect a very small amount of **1b**, less than 10^{-7} M, fluorescence was used to measure the concentrations of **1b** (see SI). The formation curves were analyzed according to eq. (3). The curves are well reproduced by using the equation. Based on the analysis the conversion ratios in the photostationary state in *n*-hexane and CCl_4 under irradiation with 450 nm light were determined to be 0.060% and 0.34%, respectively. It is possible to estimate the weak absorption coefficients of **1a**, $\varepsilon_{A,}$ at 450 nm from the photostationary conversion ratios. The cyclization and cycloreversion quantum yields, Φ_{AB} and $\Phi_{BA,}$ and absorption coefficients of **1b**, ε_B, were measured by independent experiments.[19c,d] Table 1 shows the weak absorption coefficients at 450 nm estimated from eq. (4) along with the quantum yields of cyclization and cycloreversion reactions, and the fluorescence quantum yields in *n*-hexane and CCl_4. The absorption coefficient at 450 nm in 1,4-dioxane can also be estimated from Fig. 1. The fluorescence intensity obtained after irradiating **1b** with 450 nm light for 150 min, as shown in Fig. 1b, agreed to the intensity generated by irradiating **1a** with 450 nm light for 60 min. The coefficient in 1,4-dioxane, 0.39 M^{-1} cm^{-1}, was larger than the values in *n*-hexane (0.084 M^{-1} cm^{-1}) and CCl_4 (0.19 M^{-1} cm^{-1}). Although the absorption coefficients were very low, the formation of **1b** was clearly observed upon irradiation with 450 nm light. This is attributed to very low cycloreversion quantum yields of **1b**, Φ_{BA}: less than ~ 10^{-3}, in these solvents.

Eq. (4) also indicates that the light intensity does not influence the conversion ratios in the photostationary state. Figure 3 also shows the formation of **1b** upon irradiation with low (1/4) intensity light. Even when the irradiation intensity was decreased to 1/4, the conversion ratios in the photostationary state were the same as those of full intensity light.

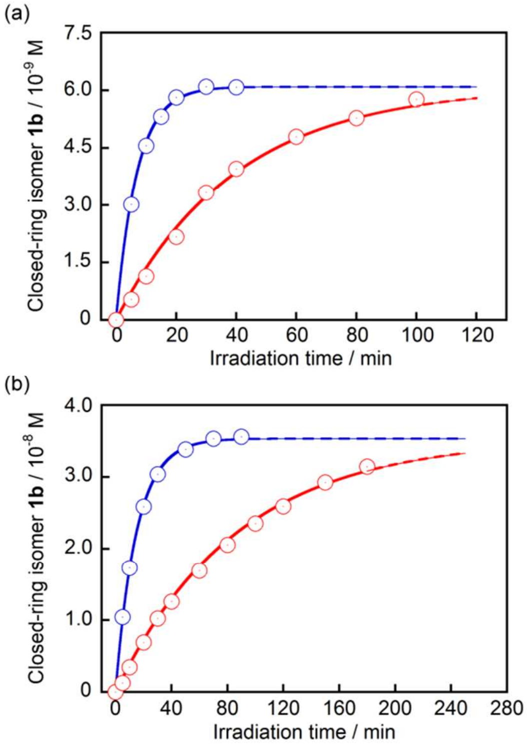


Figure 3. Formations of closed-ring isomer **1b** from pure **1a** (1.0×10^{-5} M) in *n*-hexane (a) and CCl_4 (b) upon irradiation with monochromatic 450 nm light. The two formation curves were measured by changing the light intensity, 100% (blue) and 25% (red), respectively. Solid lines were simulated by using eq (3).

According to Wondrazek *et al.*[26] and Kinoshita *et al.*[27] the absorption spectra (or the emission excitation spectra) of fluorescent dyes, such as coumarin 7 and rhodamine 6G, show an exponential frequency dependence in the far off-resonance region of the absorption tails at room temperature. The tails have been reported to obey the Urbach rule known in the absorption spectra of solid materials, as expressed by the following formula.[25-28]

$$\varepsilon(E) \propto \varepsilon(E_{00})\exp\left[-\frac{\sigma(E_{00}-E)}{k_{B}T}\right] \qquad (5)$$

, where ε, k_B, T, and σ are the absorption coefficient, the Boltzmann constant, the absolute temperature of the sample and the steepness parameter, respectively. As described above, very weak absorption coefficients at the wavelengths, where apparent absorption is absent, can be estimated from eq. (4) by measuring the conversion ratios in the photostationary state. The conversion ratios were measured by irradiation with monochromatic 440 nm, 435 nm and 429 nm light in addition to 450 nm light in *n*-hexane and CCl_4. The absorption coefficients estimated from eq. (4) were plotted in Fig. 4 along with the absorption tails of the open-ring isomer **1a**. As can be seen from Fig. 4 the coefficients obey the exponential frequency dependence at the wavelengths longer than ~ 415 nm (~ 24000 cm^{-1}). The σ values in *n*-hexane and CCl_4 were obtained to be around 0.7, which is slightly lower than the values observed for coumarin 7 and rhodamine 6G.

The exponential frequency dependence shown in Fig. 4 indicates that the unprecedented photoreactions induced with the visible light in the far off-resonance region of the absorption edge are caused by the absorption of hot bands or Urbach tails. The open-ring **1a** isomers in the vibrationally excited states undergo optical transition into electronically excited states by absorbing the very weak hot bands and the cyclization reaction from **1a** to **1b** takes place. At the same time, the visible light induces the cycloreversion reaction from **1b** to **1a**. After prolonged irradiation, the system reaches the photostationary state. Both cyclization and cycloreversion reactions can be induced by irradiation with single-wavelength visible ($420 < \lambda < 470$ nm) light. Although the absorption coefficients of **1a** at the visible-wavelength region are very small, the very low cycloreversion quantum yields of **1b**, less than ~ 10^{-3}, result in the presence of **1b** in the photostationary state.[29]

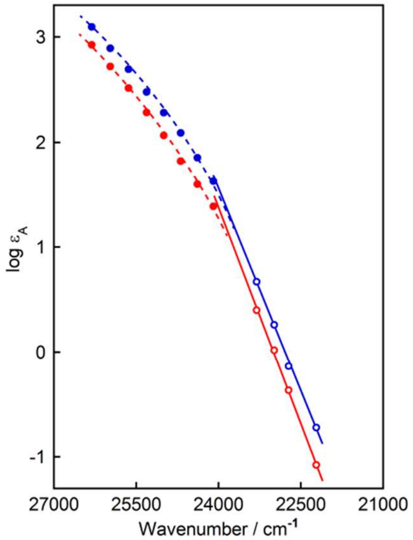


Figure 4. Logarithmic plot of molar absorption coefficients of **1a** (ε_A) in *n*-hexane (red) and CCl_4 (blue) obtained from absorption spectra of **1a** (closed circles) and fluorescence intensities of **1b** in the photostationary states under irradiation with monochromatic visible light (open circles).

In conclusion, reversible fluorescence photoswitching of **1** was induced by irradiation with single-wavelength visible light, the wavelength of which is longer than the 0-0 transition of **1a**. The visible light induces the photocyclization reaction of **1a** to produce fluorescent **1b**. A considerable amount of **1b** is produced when the cycloreversion quantum yield of **1b** is very low, less than $\sim 10^{-3}$. The cyclization reaction of **1a** with the visible light in the far off-resonance region of the absorption edge is ascribed to the electronical transition caused by the optical absorption of the very weak hot bands or the Urbach tails. The derivatives having the single-wavelength visible light sensitivity can be advantageously applicable to super-resolution fluorescence microscopies, such as PALM and STORM.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: ######/##########.

Experimental details and additional data (PDF)

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Notes

The authors declare no competing financial interests.

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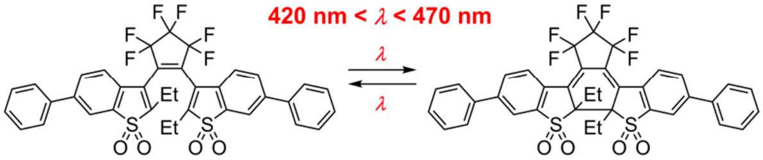
(29) Similar photoreactions have also been noticed at the single-molecule level in PALM/STORM experiments using diarylethene derivatives with very low cycloreversion quantum yields.[21,22]



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