Fluorescence Switching of a Diarylethene Derivative Having Oxazole Rings

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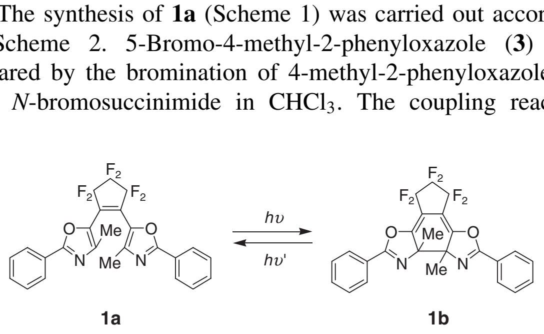
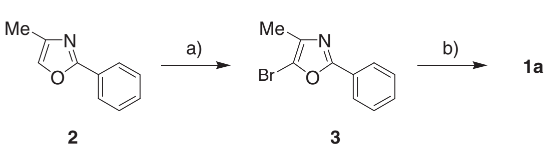
A diarylethene derivative, in which oxazole rings are attached to the ethene moiety at the 5-position, was synthesized, and its photochromic and fluorescent properties were examined. The derivative undergoes photochromism in solution and the open-ring isomer exhibits strong fluorescence. The fluorescence intensity was found to reversibly change along with the photochromism.

Various types of diarylethene derivatives have been synthesized and their optical absorption as well as emission properties has been so far examined. Diarylethenes undergo reversible photoisomerization between two isomers (open- and closed-ring isomers) having different optical properties. The optical absorption of the closed-ring isomer strongly depends on the kind and the connected position of the heteroaryl moieties.[1–9] Among many kinds of heteroaryl moieties, oxazole derivatives have characteristic properties such as fluorescent, laser emissive properties, and pH sensitivity.[10] In a previous study, we reported diarylethene derivatives having oxazole rings, 1,2-bis(5-methyl-2-phenyloxazol-4-yl)perfluorocyclopentene,[11] in which oxazole rings are attached to the ethene moiety at 4-position. Although the absorption maximum of the closed-ring isomer is shorter than 500 nm, the maximum is still in the visible region and the UV-irradiated solution was orange. To further shift the maximum to UV region, we have prepared 1,2-bis(4-methyl-2-phenyloxazol-5-yl)perfluorocyclopentene, in which oxazole rings are attached to the ethene moiety at 5-position, and examined its photochromic performance and fluorescent property.

The synthesis of **1a** (Scheme 1) was carried out according to Scheme 2. 5-Bromo-4-methyl-2-phenyloxazole (**3**) was prepared by the bromination of 4-methyl-2-phenyloxazole (**2**) with *N*-bromosuccinimide in $CHCl_3$. The coupling reaction between **3** and octafluorocyclopentene gave **1a** in 66% yield. **1a** was characterized by ^1H NMR, MS, and elemental analysis.[12] Detail synthetic procedures were described in Supporting Information.[13]



Scheme 1. Photochromism of dioxazolylethene **1**.



Scheme 2. a) NBS, $CHCl_3$, 92%; b) *n*-BuLi, octafluorocyclopentene, THF, 66%.

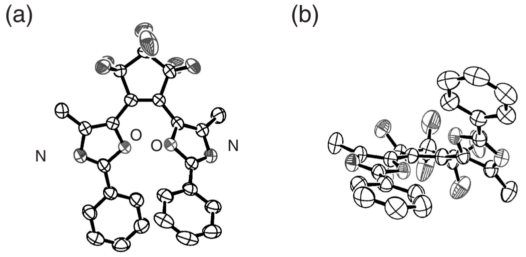


Figure 1. ORTEP drawings of **1a** showing 50% probability displacement ellipsoids: a) top view and b) side view. The CF_2 groups in the cyclopentene ring were disordered. Hydrogen atom and the disordered structure are omitted for clarify.

The molecular structure in crystal was determined by the X-ray crystallographic analysis.[14] A crystal of **1a** was obtained by recrystallization from hexane solution. The ORTEP drawings of **1a** are shown in Figure 1. **1a** is packed in a parallel conformation and the oxazole rings are attached to ethene moiety at the 5-position. As expected from the parallel conformation, the crystal did not show any photochromism. But, the crystal exhibited strong fluorescence.

Figure 2a shows the absorption spectral change of **1** by photoirradiation in hexane. **1a** has absorption maxima at 287 and 373 nm. Upon irradiation with $\lambda > 380$-nm light, the absorption bands decreased and a new band appeared at 252 nm. In contrast to typical photochromism of diarylethene derivatives, the absorption spectrum showed a hypsochromic shift. The photogenerated isomer was isolated by HPLC (Wako, Wakosil 5SIL; hexane/ethyl acetate = 80/20 as the eluent) and found to be closed-ring isomer **1b** by NMR and MS.[15] The closed-ring isomer **1b** gave the absorption maxima at 252 and 353 nm. From the spectrum of **1b**, the conversion from **1a** to **1b** in the photostationary state was estimated to be 63% under irradiation with longer than 380-nm light. The absorption spectrum of **1b** almost returned to that of **1a** upon irradiation with 254-nm light. The cyclization and cycloreversion quantum yields of **1** in hexane were determined by using the standard procedure.[16] The absorption maxima, coefficients, and quantum yields are summarized in Table 1.

Upon irradiation with 365-nm light, the hexane solution of **1a** exhibited relatively intense blue-green fluorescence. Figure 2b shows the fluorescence spectral change of **1** along with the photochromic reaction in hexane. The fluorescence maximum of **1a** was observed at 470 nm. The fluorescence quantum yield was 19% by excitation with 365-nm light. This

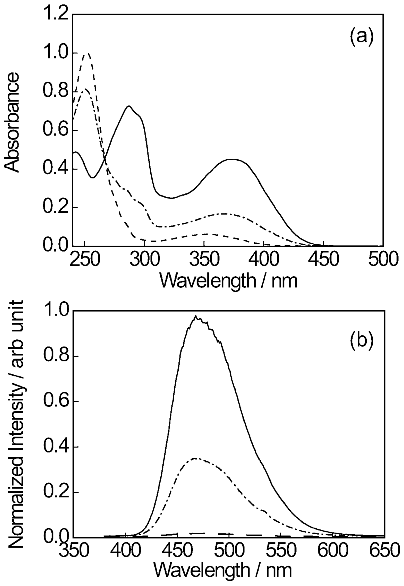


Figure 2. (a) Absorption and (b) fluorescence spectral change of **1** in hexane (2.7×10^{-5} mol dm^{-3}, $\lambda_{\text{exc}} = 267$ nm) by photoirradiation: **1a** (—), **1** in the photostationary state under irradiation with $\lambda > 380$-nm light (– · · –), and **1b** (– –).

Table 1. Absorption maxima, coefficients, and quantum yields of **1** in hexane

	λ_{max}/nm	ε/M^{-1} cm^{-1}	$\Phi_{\text{open}\rightarrow\text{closed}}$	$\Phi_{\text{closed}\rightarrow\text{open}}$
1a	287	27000	0.10[a]	—
	373	17000		
1b	252	38000	—	0.33[b]
	353	2400		

[a]Measured at 373 nm. [b]Measured at 252 nm.

value is much higher than that of the other fluorescent diarylethene derivatives so far reported.[8,9,17] Upon irradiation with $\lambda > 380$-nm light, the fluorescence of **1a** decreased and the emission was reduced to 38% of the initial intensity in the photostationary state and the value showed good agreement with the conversion estimated from the absorption spectra. The closed-ring isomer **1b** isolated by HPLC was nonfluorescent. Upon irradiation with 254-nm light the fluorescence almost returned to the initial intensity. This cycle could be repeated many times.

In conclusion, dioxazolylethene **1a** was synthesized and its photochromic and fluorescent properties were examined. The compound exhibited a reversible photochromic reaction in solution. The absorption band of **1** was shifted to a shorter wavelength upon the photocyclization reaction. The open-ring isomer **1a** gave relatively intense fluorescence ($\Phi_f = 0.19$). The fluorescence was reversibly switched by alternate irradiation with $\lambda > 380$-nm and 254-nm light.

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12 **1a**: pale yellow crystals: mp 147.8–149.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.27 (s, 6H), 7.36–7.46 (m, 6H), 7.91–7.93 (m, 4H); MS m/z 490 (M^+). Anal. Calcd for $C_{25}H_{16}F_6O_2N_2$: C, 61.23; H, 3.29; N, 5.71%. Found: C, 61.28; H, 3.30; N, 5.75%.
13 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/.
14 Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-688564. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge).
15 **1b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.32 (s, 6H), 7.39–7.46 (m, 6H), 7.92–7.98 (m, 4H); MS m/z 490 (M^+).
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