Reversible Fluorescence Intensity Change of a Diarylethene

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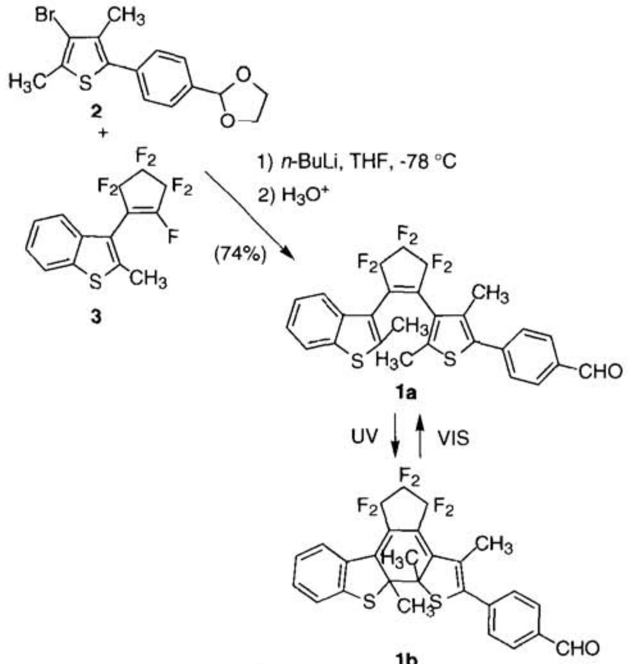
A photochromic diarylethene **1** reversibly changed the fluorescence intensity by alternate irradiation with 330 ± 30 nm and > 460 nm light.

Switching of chemical and physical properties of photochromic compounds by photoirradiation has been widely studied.[1] Among them, switching of fluorescent property is of interest from the view point of applications to fluorescent probes.[2] Photochromic compounds such as fulgides,[3,4] dihydroazulene,[5] thioxanthene derivatives[6] and dithienylethene with oligothiophene aryl groups[7] are reported to change the fluorescence intensity by photoirradiation.

Here we describe the fluorescent property of a diarylethene which is composed of thiophene and benzothienylethene aryl groups. The compound reversibly changed the fluorescence intensity by alternate irradiation with UV and visible light.



Scheme 1.

Preparation of the fluorescent diarylethene **1** is shown in Scheme 1. Coupling of thiophene derivative **2**[8] and benzothiophene derivative **3**[8] in the presence of *n*-BuLi in THF at -78 ℃, followed by hydrolysis of acetal moiety by hydrochloric acid afforded the open-ring form **1a**[9] in 74% yield. The open-ring form **1a** and the closed ring form **1b** were isolated by HPLC (SiO_2, eluent: hexane/AcOEt (4:1)). Both isomers were thermally stable in the dark for more than one month at room temperature.

Figure 1 shows the absorption spectral change of **1** in hexane-AcOEt (10:1) upon irradiation with 313 nm light. The absorption spectra of the open-ring form **1a** and the closed ring form **1b** are shown as dashed and dotted lines, respectively. The absorption maximum of **1a** was observed at 315 nm (ε, 16000 $M^{-1}cm^{-1}$) and those of **1b** at 410 (ε, 4000 $M^{-1}cm^{-1}$) and 540 nm (ε, 8900 M^{-1} cm^{-1}). The closed-ring form **1b** increased by irradiation with 313 nm light and the conversion from **1a** to **1b** at photostationary state was 90%. The spectrum returned to the original one by irradiation with visible light (>460 nm).

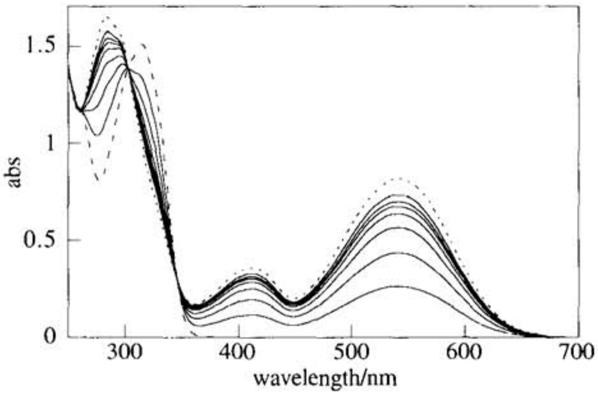


Figure 1. Absorption spectral change of **1** (9.3 x 10^{-5} mol dm^{-3}, in hexane-AcOEt (10:1)) by irradiation with 313 nm light. The spectra were taken every 1 min up to 7 min irradiation. Dashed and dotted lines show the spectra of **1a** and **1b**, respectively.

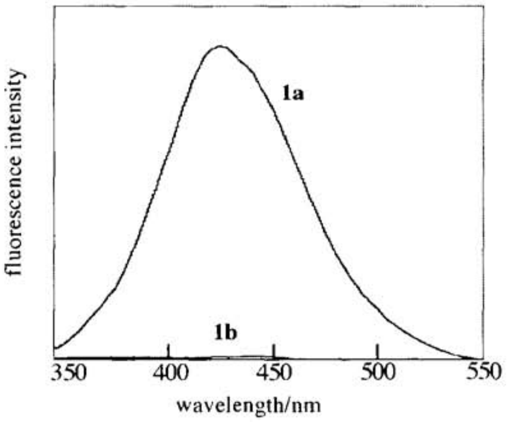


Figure 2 . Fluorescence spectra of **1a** and **1b** (9.3 x 10^{-5} mol dm^{-3}, in hexane-AcOEt (10:1)), excited at 301 nm).

The fluorescence spectra of the open-ring form **1a** and the closed-ring form **1b** excited at 301 nm which is the isosbestic point of these photoisomers are shown in Figure 2. The fluorescence maximum of **1a** was observed at 420 nm, while any fluorescence emission was not detected for **1b** in the wavelength. The fluorescence intensity decreased when **1a** converted to **1b** by UV irradiation and no fluorescence was observed above 600 nm. Under the fluorescent measurement conditions, formation of the closed-ring form **1b** was negligible.

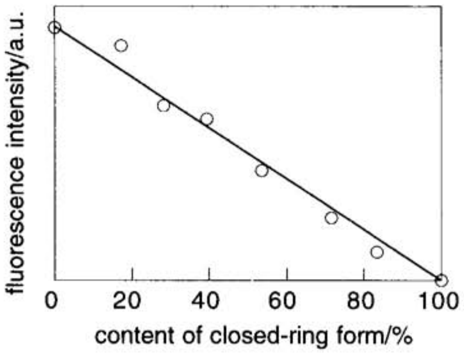


Figure 3. Content of the closed-ring form **1b** *vs.* fluorescence intensity at 420 nm ([**1**]=3.25×10^{-5} mol dm^{-3}, in AcOEt-hexane (10:1), excited at 301 nm).

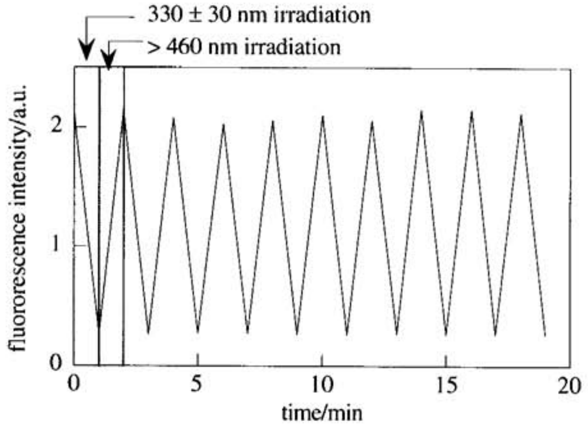


Figure 4. Fluorescence spectral change (at 420 nm) of **1** in hexane-AcOEt (10:1) by alternate irradiation with 330 ± 30 nm (1 min)and > 460 nm light (1 min).

Figure 3 shows **1b** content dependence of the fluorescence intensity. Linear relationship exists between the content of the closed-ring form and the fluorescence intensity. This linearity indicates that there is no energy transfer from the excited open-ring form to the closed-ring form under the present experimental conditions. The decrease in fluorescence intensity by irradiation with UV light is ascribed to the decrease of the fluorescent open-ring form **1a**.

Figure 4 shows the fluorescence intensity change at 420 nm (excitation : 301 nm) by alternate irradiation with UV (330±30 nm) and visible (>460 nm) light. The fluorescence intensity reversibly changed by alternate irradiation and this cycle could be repeated more than 100 times.

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References

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8 Preparation and spectral data of these compounds will be published elsewhere.

9 Selected data of **1a**: white powder from hexane; mp 162.0-163.2 °C, MS *m/z* 536 [M$^+$], ^{1}H NMR (in CDCl$_3$, 200 MHz, 20 °C) δ 1.95 (1.5H, s), 2.21 (1.5H, s), 2.24 (1.5H, s), 2.42 (3H, s), 2.50 (1.5H, s), 7.31-7.90 (8H, m), 9.93 (0.5H, s), 10.02 (0.5H, s). At 20 °C, two conformations of **1a**, the parallel and the anti-parallel conformations, were observed separately in NMR time scale and the ratio was 1:1, although these conformations exchange each other at room temperature.