

# A photoresponsive laser dye containing photochromic dithienylethene units

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Received (in Cambridge, UK) 8th January 2001, Accepted 20th February 2001

First published as an Advance Article on the web 29th March 2001

A novel molecule, containing two photochromic dithienylethene moieties linked to a fluorescent bis(phenylethynyl)anthracene residue has been prepared, and shows a reversible change in its fluorescence quantum yield from 0.001 to 0.83, and a corresponding increase in laser emission intensity, on exposure to UV light.

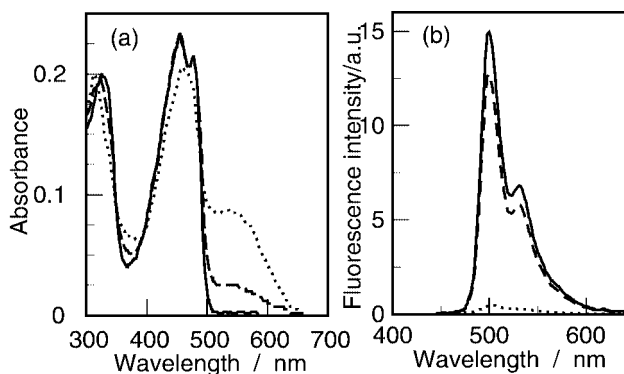
Dithienylethenes are the most promising photochromic compounds among various photochromic compounds for the photoelectronic applications, such as optical memory media and photoswitching devices, because of their fatigue resistant and thermally irreversible properties.<sup>1–4</sup> Although several dithienylethene derivatives have been reported to exhibit reversible fluorescence intensity changes upon photoisomerization,<sup>5–11</sup> the fluorescence quantum yields ( $\Phi_f$ ) of the molecules were relatively small. In the present work, a highly fluorescent dithienylethene was prepared and its photoresponsive laser emission was demonstrated.

9,10-Bis(2-phenylethynyl)anthracene was chosen as the fluorescence unit, because its  $\Phi_f$  is high ( $\Phi_f = 1$ ) and its emission spectrum overlaps with the characteristic absorption band of the closed-ring isomer of 1,2-bis(2,5-dimethyl-3-thienyl)perfluorocyclopentene.<sup>12</sup> The two photochromic dithienylethene units, 1-(2,5-dimethyl-3-thienyl)-2-(2,4-dimethyl-5-bromo-3-thienyl)perfluorocyclopentene, were connected to the fluorescent unit, 9,10-bis(4-bromo-phenylethynyl)anthracene by Pd(0) catalyzed cross-coupling reaction to obtain **1a** shown in Scheme 1. The molecular structure and purity of **1a** were confirmed by elemental analysis, <sup>1</sup>H-NMR and mass analysis.<sup>13</sup>

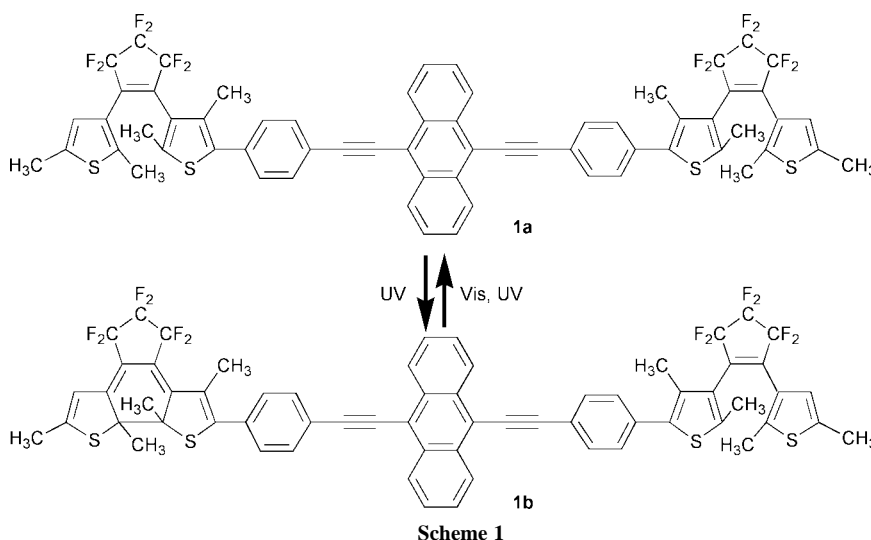
Fig. 1 shows optical absorption spectral change of **1a** in THF solution upon photoisomerization. By irradiation with 313 nm light the absorption bands at 340 nm decreased along with the increase of a new absorption band between 500 and 650 nm. The original absorption spectrum was recovered by irradiation with visible light ( $\lambda > 500$  nm). Fig. 1 also shows the

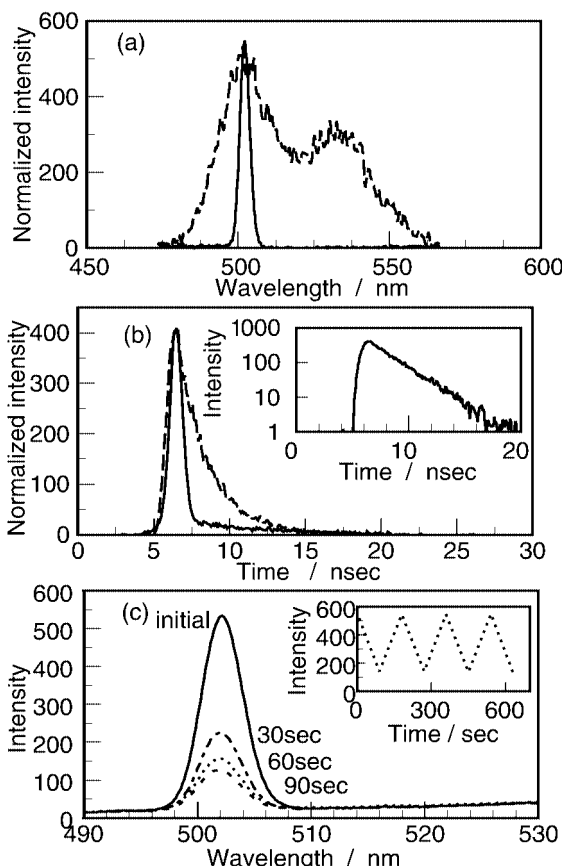
absorption spectrum of the isolated photo-product. It should be noted that there was only one photo-product in the HPLC analysis although **1** has two dithienylethene units. On the basis of the <sup>1</sup>H-NMR, the photo-product was assigned to the ring closed form **1b** in which one of the two dithienylethene units is in the closed-ring form.<sup>13</sup> Upon excitation of **1b**, excitation energy transfer from the excited open-ring unit to the closed-ring unit is considered to suppress further photo-cyclization of **1b**.

Fig. 1(b) shows the fluorescence emission spectrum of **1** in THF solution. The emission profile is similar to that of the bis(phenylethynyl)anthracene unit. The fluorescence intensity decreased upon irradiation with 313 nm light and almost disappeared in the isolated **1b**. The original emission spectrum



**Fig. 1** (a) Absorption spectra of **1a** (solid line), **1b** (dotted line) and the photostationary state under irradiation with 313 nm light (broken line) in THF solution (**1a**:  $\epsilon_{455\text{nm}} = 50500 \text{ M}^{-1} \text{ cm}^{-1}$ ). (b) Fluorescence spectra of **1a** (solid line), **1b** (dotted line) and the photostationary state under irradiation with 313 nm light (broken line) in THF solution (excitation wavelength = 450 nm). (Irradiation of 313 nm light induces both cyclization and cycloreversion reactions.)





**Fig. 2** Wavelength domain (a) and time domain (b) emission profiles of **1a** in (solid line) and outside (broken line) of the laser cavity. (Inset of (b): logarithmic decay of the spontaneous emission.) (c) Emission spectra of **1a** in the laser cavity, before UV irradiation (solid line), and after UV light irradiation for 30, 60 and 90 s (PSS). (Inset of (c): repetitive change of laser intensity with the alternative irradiation cycles of UV and visible light.)

was recovered by visible light irradiation. The fluorescence quantum yields,  $\phi_f$ , of **1a** and **1b** were determined, by using 9,10-bis(phenylethynyl)anthracene as a reference, to be  $\phi_f = 0.83$  and  $\phi_f < 0.001$ , respectively.

The strong fluorescence quenching in **1b** is attributed to the efficient energy transfer from the excited bis(phenylethynyl)anthracene to the closed-ring dithienylethene unit. Because of spectral overlapping of the emission band of **1a** at about 530 nm and the absorption band of **1b**, the excited state of the bis(phenylethynyl)anthracene unit is quenched by the closed-ring unit. The residual weak emission observed in isolated **1b** was considered to be the emission from a small amount of **1a** which was formed from **1b** during the fluorescence measurement.

The laser emission experiment of **1a** was carried out as follows. THF solution of **1a** (0.1 mM) in a quartz cuvette (10 × 10 mm) was placed in the cavity of a dye laser system (Laser Photonics, DL2S), which is composed of a front highly reflective mirror, a back grating reflector and a cylindrical lens for focusing the pumping beam from a pulsed N<sub>2</sub> laser (Hamamatsu Photonics, LN-203). The excitation laser power, the pulse width, the wavelength and the repetition frequency were 0.1 mJ, 600 psec, 337.1 nm, and 10 Hz, respectively. The

solution was stirred during the measurements. The emission was detected with a gated streak-scope system (Hamamatsu Photonics, C4334-01, C5094 and C4792). The emission from the laser cavity was detected by an analog integration mode, while its spontaneous emission was detected by a single-photon counting mode. Fig. 2(a) and (b) show emission spectra and the decay profile of **1a** placed inside and outside of the laser cavity, respectively. The emission of **1a** in the laser cavity showed a symmetrical narrow peak and any Stokes line typical for the spontaneous emission was not observed. The spontaneous emission decayed exponentially with a single lifetime of about 1.8 nsec, as shown in the inset of Fig. 2(b), while the emission from the laser cavity was dumped immediately with the excitation light pulse. The narrow and symmetrical emission profiles in the wavelength and the time domains are typical for the laser emission. Characteristic threshold of the laser emission was observed at about 0.08 mJ.

As shown in Fig. 2(c), the laser emission intensity dramatically decreased by irradiation with 313 nm light and it was recovered to the initial value by irradiation with visible light ( $\lambda > 500$  nm). The reversible intensity change was observed for several tenth cycles. The emission power remained stable after standing in the absence of UV light.

In conclusion, a photochromic dithienylethene having bis(phenylethynyl)anthracene changed the fluorescence intensity by photoisomerization of the dithienylethene units (between  $\phi_f = 0.83$  and  $< 0.001$ ). The dye exhibited a laser emission and the emission intensity was reversibly switched by alternative irradiations with 313 nm light and  $\lambda > 500$  nm light.

This work was partly supported by CREST (Core Research for Evolution Science and Technology) of Japan Science and Technology Corporation (JST) and also by Grant-in-Aid for Scientific Research on Priority Areas ('Molecular Synchronization', #11167263) from the Ministry of Education, Science, Sports and Culture, Japan.

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- 12 S. Kobatake, T. Yamada, K. Uchida and M. Irie, *J. Am. Chem. Soc.*, 1999, **121**, 2380.
- 13 **1a**: Anal. Found: C, 65.48; H, 3.98%. Calcd. for C<sub>64</sub>H<sub>42</sub>F<sub>12</sub>S<sub>4</sub>: C, 65.86; H, 3.63%. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>)  $\delta$  = 2.05 (s, 6H), 2.07 (s, 6H), 2.29 (s, 6H), 2.40 (s, 6H), 6.65 (s, 2H), 7.47 (d, 4H, *J* = 7.8 Hz), 7.67 (m, 4H), 7.80 (d, 4H, *J* = 7.8 Hz), 8.70 (m, 4H), MS (*m/z*) = 1166 (M<sup>+</sup>). **1b**: <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  = 2.05 (s, 3H), 2.07 (s, 3H), 2.16 (s, 3H), 2.19 (s, 3H), 2.22 (s, 3H), 2.23 (s, 3H), 2.29 (s, 3H), 2.40 (s, 3H), 6.07 (s, 1H), 6.65 (s, 1H), 7.46 (d, 2H, *J* = 7.8 Hz), 7.52 (d, 2H, *J* = 7.8 Hz), 7.64–7.72 (m, 4H), 7.77–7.86 (m, 4H), 8.65–8.75 (m, 4H), MS (*m/z*) = 1166 (M<sup>+</sup>).