Photochromic and Fluorescent Properties of a Diarylethene Dimer

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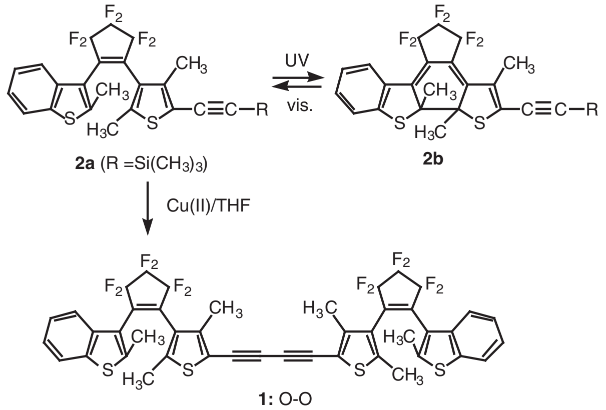
A diarylethene dimer connected with a diyne **1** (O–O) was synthesized. Upon irradiation with 350-nm light the colorless hexane solution of **1** (O–O) changed to a dark-blue solution, in which absorption maximum was observed at 574 nm. The color is due to the formation of the isomer having one closed-ring form **1** (O–C). **1** (O–C) emitted red fluorescence at 720 nm and the intensity reversibly changed along with the photochromic reaction.

Photochromic compounds have attracted much attention because of their potential ability for photonics devices, such as optical memory media and photo-optical switches.[1–4] Among various types of photochromic compounds, diarylethene derivatives are the most promising compounds for the application because of their thermally irreversible and fatigue resistant photochromic performance.[5,6] Upon irradiation with UV light the open-ring form isomer converts to the closed-ring one, which has a well-separated absorption band in the visible wavelength region.

Although many diarylethene derivatives have been reported, compounds which exhibit fluorescent emission from the closed-ring isomer are very rare.[7–10] An example is 1,2-bis(2-methyl-1-benzothiophen-3-yl)hexafluorocyclopentene derivative, which gives very weak fluorescence from the closed-ring isomer.[8,11] Fluorescent photochromic compounds, which reversibly change the fluorescence intensity along with the photochromic reaction, are useful for optical memory media[12] as well as fluorescent probes.

In this study, we have prepared a diarylethene dimer **1** (O–O) connected with a diyne and studied the photochromic as well as fluorescent properties. **1** (O–O) was synthesized from 1-(2-methylbenzothiophen-3-yl)-2-(2,4-dimethyl-5-trimethylsilylethynylthiophen-3-yl)hexafluorocyclopentene (**2**) by a one-pot procedure.[13] **2** was deprotected by KOH and then homo-coupling reaction in THF under Cu(II) catalysis gave **1** (O–O). Colorless amorphous **1** (O–O) was obtained with 86% yield.


2a (R =Si(CH$_3$)$_3$)

2b

1: O-O

Figure 1 shows the absorption spectral change of **1** (O–O) (3.2×10^{-5} M) in hexane by photoirradiation. Upon irradiation with 350-nm light an absorption band around 570 nm increased and reached the photostationary state. The color of the solution changed from colorless to dark-blue, in which absorption maximum was observed at 574 nm. When the dark-blue solution was irradiated with visible light ($\lambda > 550$ nm), the spectrum returned back to the original one with retention of the isosbestic points at 298, 320, and 374 nm.

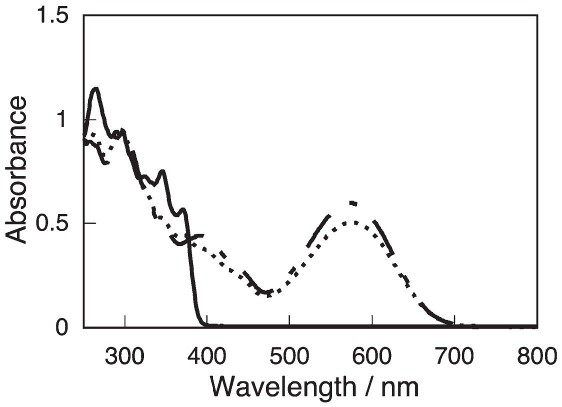


Figure 1. Absorption spectral change of **1** in hexane (3.2×10^{-5} M) by photoirradiation: O–O (solid line), **1** in the photostationary state under irradiation with 350-nm light (dotted line), and O–C (broken line).

The photoirradiated sample was analyzed with high performance liquid chromatography (HPLC, silicagel column, Wakosil 5SIL, eluent hexane/ethyl acetate (99:1)). When monitored at the isosbestic point of 320 nm, two peaks were observed. When the monitoring wavelength was shifted to 574 nm, at which wavelength only the closed-ring isomer absorbs, only one peak was observed in the HPLC chart. Diarylethenes have two conformations, with two aryl rings in anti-parallel (ap) and parallel (p) conformation.[14] The methyl protons of the O–O dimer showed simple ten signals.[14] The ratio of conformers were ap-ap:ap-p:p-p = 1:2:1. The spectrum of the isolated colored dimer showed complex seven signals, as shown in Figure 2.[15] In the NMR spectrum there existed a characteristic signal at 1.98 ppm assigned to one of the methyl protons of the open-ring form and characteristic signals 2.04 ppm assigned to two methyl protons of the closed-ring form. The ratio of the two signals was 1:2, which indicates that the colored isomer is an O–C dimer having both open-ring form O and closed-ring form C. The colored isomer was identified as O–C by ^{1}H NMR. The isomer in which both diarylethenes are in the closed-ring form (C–C) was not detected. Even after prolonged irradiation any other photoproduct was not discerned. The absence of the isomer having two closed-ring form isomer in the photoirradiated dimer agrees to the results observed in other dimers so far reported.[16,17] Excited energy transfer from the open- to the closed-ring isomers is considered to prohibit the formation of C–C dimer. The cyclization quantum yield of the dimer was measured to be 0.36. The conversion of the dimer to **1** (O–C) in the photostationary state reached 0.88.

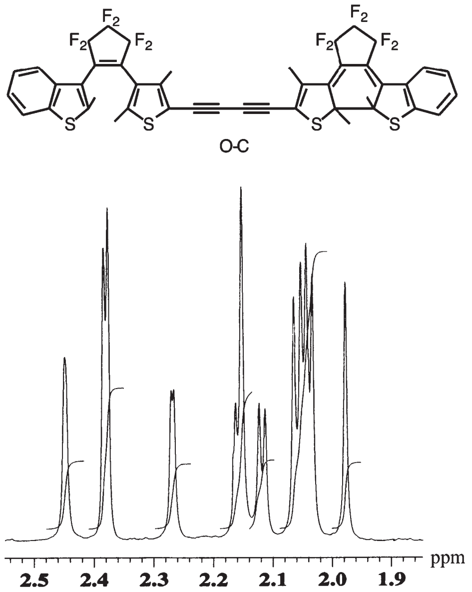


Figure 2. ^{1}H NMR methyl signals of the O–C.

Figure 3 shows the fluorescence spectra of dimer **1** (O–O and O–C) and **2** (R = Si(CH$_3$)$_3$) in hexane by irradiation with 313-nm light at room temperature. Although **2a** gives fluorescence at 410 nm, any fluorescence was not observed from **1** (O–O) by excitation at 313 nm. Upon irradiation with 313-nm light both **2a** and **1** (O–O) converted to the closed-ring isomers, **2b** and **1** (O–C). The closed-ring isomers **1** (O–C) gave red fluorescence at 720 nm by excitation at 574 nm, while any fluorescence was not detected from **2b**. The excitation spectrum of the red fluorescence agreed to the absorption spectrum of **1** (O–C).

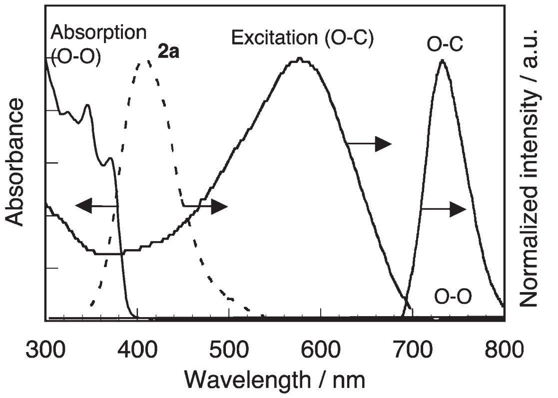


Figure 3. Absorption spectrum of **1** (O–O), fluorescence and excitation spectra of **1** (O–C) and fluorescence spectrum of **2a** in hexane at room temperature.

This result indicates that the fluorescence at 720 nm is due to the closed-ring isomer **1** (O–C). The fluorescence intensity changed upon alternate irradiation with UV and visible light. The fluorescence spectral change of the red fluorescence observed at longer wavelength can be potentially applicable to fluorescence-readout optical memory.[18]

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References and Notes

1 G. H. Brown, in "Photochromism," Wiley-Interscience, New York (1971).
2 H. Dürr and H. Bouas-Laurent, in "Photochromism: Molecules and Systems," Elsevier, Amsterdam (1990).
3 Y. Hirschberg, *J. Am. Chem. Soc.*, **78**, 2304 (1954).
4 M. Irie, in "Photo-reactive Materials for Ultrahigh-Density Optical Memory," Elsevier, Amsterdam (1994).
5 M. Irie, *Chem. Rev.*, **100**, 1685 (2000).
6 M. Irie and K. Uchida, *Bull. Chem. Soc. Jpn.*, **71**, 985 (1998).
7 G. M. Tsivgoulius and J.-M. Lehn, *Chem.—Eur. J.*, **2**, 1399 (1996).
8 M.-S. Kim, T. Kawai, and M. Irie, *Chem. Lett.*, **2001**, 702.
9 T. Kawai, M.-S. Kim, T. Sasaki, and M. Irie, *Opt. Mater.*, **21**, 275 (2002).
10 A. Fernandez-Acebes and J.-M. Lehn, *Chem.—Eur. J.*, **5**, 3285 (1999).
11 T. Utsumi, T. Kawai, M. Hamaguchi, K. Yoshino, and M. Irie, *Jpn. J. Appl. Phys.*, **36**, 3736 (1997).
12 M. Irie, T. Fukaminato, T. Sasaki, N. Tamai, and T. Kawai, *Nature*, **420**, 759 (2002).
13 M. Takeshita, C. Choi, and M. Irie, *J. Chem. Soc., Chem. Commun.*, **1997**, 2265.
14 Selected data for **1** (O–O): colorless amorphous; UV–vis (hexane) $\lambda_{\max}$ (ε); 264 (35300), 290 (29000), 298 (29000), 324 (22500), 347 (22800), 371 (17200); ^{1}H NMR (400 MHz, CDCl$_3$, TMS) δ 1.92 (s, 1.5H), 1.96 (s, 1.5H), 2.10 (s, 1.5H), 2.13 (s, 1.5H), 2.21 (s, 1.5H), 2.24 (s, 1.5H), 2.35 (s, 3H), 2.37 (s, 3H), 2.41 (s, 1.5H), 2.43 (s, 1.5H), 7.50–7.80 (m, 8H); MS m/z 910 (M$^+$); Anal. Calcd C$_{44}$H$_{26}$F$_{12}$S$_4$: C, 58.01; H, 2.88%; Found. C, 58.33; H, 3.07%.
15 Selected data for **1** (O–C): blue amorphous; UV–vis (hexane) $\lambda_{\max}$ (ε); 256 (29200), 298 (28600), 350 (22700), 391 (13200), 574 (15500); ^{1}H NMR (400 MHz, CDCl$_3$, TMS) δ 1.98 (s, 1.5H), 2.04–2.08 (m, 6H), 2.13–2.18 (m, 4.5), 2.28 (s, 1.5H), 2.39 (s, 3H), 2.46 (s, 1.5H), 7.20–7.57 (m, 8H); FAB-HRMS Calcd C$_{44}$H$_{26}$F$_{12}$S$_4$: m/z 910.0726; Found. m/z 910.0707 (M$^+$).
16 A. Peters and N. R. Branda, *Adv. Mater. Opt. Electron.*, **10**, 245 (2000).
17 T. Kaieda, S. Kobatake, H. Miyasaka, M. Murakami, N. Iwai, Y. Nagata, A. Itaya, and M. Irie, *J. Am. Chem. Soc.*, **124**, 2015 (2002).
18 T. Tsujioka and M. Irie, *Appl. Opt.*, **37**, 4419 (1998).

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