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Synthesis and Photochemical Reactions of Photochromic Terarylene Having a Leaving Methoxy Group

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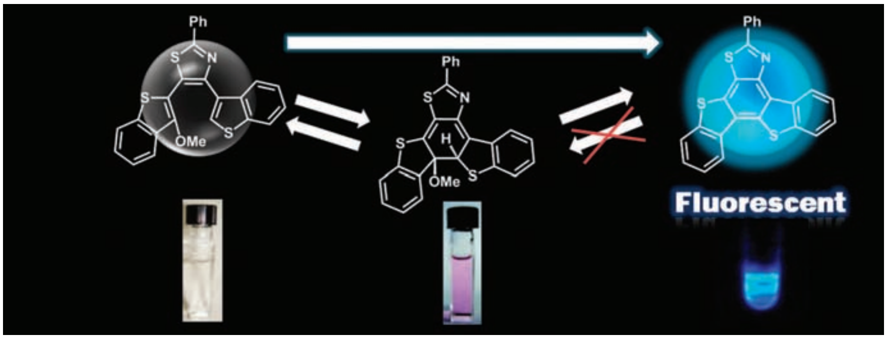
ABSTRACT



Photochromic terarylene having a methoxy group and hydrogen as the leaving units at the photochemical reaction center carbon atoms has been synthesized. This molecule shows irreversible photochemical reaction affording a highly fluorescent condensed aromatic molecule.

Recently, considerable interest has been focused on organic photochromic molecules whose molecular structure changes upon absorption of light.[1] Some of them have been practically used as light modulating materials, which change their colors under sunlight and bleach spontaneously in dark conditions.[2] Since the discovery of photochromic diarylethene[3] and fulguides[4] that hardly show spontaneous thermal bleaching at room temperature, these "P-type" photochromic molecules have been expected to be used as the active materials for future rewritable data storage.[5] Especially, photochromic diarylethene shows unique properties suitable for practical materials, i.e., high fatigue durability and relatively high photochromic coloration reactivity even in the solid state.[6] Some photochromic fluorescent molecules have been proposed based on diarylethene by connecting fluorescent units with the diarylethene backbone, and their clear reversible fluorescence modulation has been useful as the fluorescence-mode recording material.[7] One of the authors has studied some fluorescent diarylethene molecules and demonstrated their fluorescence switching even at the single molecule level and also the possibility of 3D high-density recording.[8] However, there is still a serious problem in using

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(1) *Photochromism*; Brown, G. H., Ed.; Wiley-Interscience: New York, 1971.

(2) *Organic Photochromic and Thermochromic Compounds*; Crano, J. C., Guglielmetti, R. J., Eds.; Plenum Press: New York, 1999.

(3) (a) Irie, M. *Chem. Rev.* **2000**, *100*, 1685. (b) Irie, M.; Mohri, M. *J. Org. Chem.* **1988**, *53*, 803. (c) Nakamura, S.; Irie, M. *J. Org. Chem.* **1988**, *53*, 6136.

(4) (a) Heller, H. G.; Oliver, S. *J. Chem. Soc., Perkin Trans. 1* **1981**, 197. (b) Yokoyama, Y. *Chem. Rev.* **2000**, *100*, 1717.

(5) *Photoreactive Materials for Ultrahigh-Density Optical Memory*; Irie, M., Ed.; Elsevier: Amsterdam, 1994.

(6) (a) Kaneuchi, Y.; Kawai, T.; Hamaguchi, M.; Yoshino, K.; Irie, M. *Jpn. J. Appl. Phys.* **1997**, *36*, 3736. (b) Kawai, T.; Koshido, T.; Katsumi, Y. *Appl. Phys. Lett.* **1995**, *67*, 795. (c) Tanio, N.; Irie, M. *Jpn. J. Appl. Phys.* **1994**, *33*, 1550. (d) Biteau, J.; Chaput, F.; Lahlil, K.; Boilot, J.-P.; Tsivgoulis, G. M.; Lehn, J.-M.; Darracq, B.; Marois, C.; Lé vy, Y. *Chem. Mater.* **1998**, *10*, 1945–1950. (e) Kawai, T.; Fukuda, N.; Gröschl. D.; Kobatake, S.; Irie, M. *Jpn. J. Appl. Phys.* **1999**, *38*, L1194. (f) Tanio, N.; Irie, M. *Jpn. J. Appl. Phys.* **1994**, *33*, 3942. (g) Kim, M.-S.; Kawai, T.; Irie, M. *Chem. Lett.* **2001**, 702. (h) Kim, M.-S.; Maruyama, H.; Kawai, T.; Irie, M. *Chem. Mater.* **2003**, *15*, 4539. (i) Irie, M.; Uchida, K.; Eriguchi, M.; Tsuzuki, H. *Chem. Lett.* **1995**, 899.

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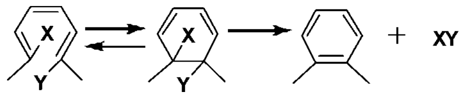
fluorescent photochromic molecules as practical optical recording materials. That is, the excitation light for the fluorescence readout usually induces photochromic bleaching or coloration reactions, and recorded information would easily be destroyed. To the best of our knowledge, the nondestructive readout capability and reversible fluorescence-mode recording have never been achieved simultaneously in the photomemory molecules.

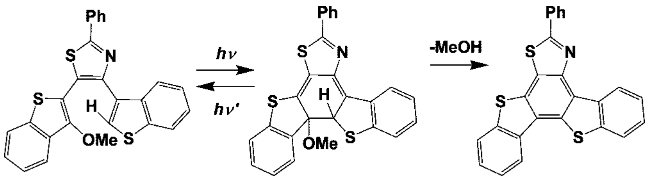
Because of the difficulty to achieve the nondestructive read-out capability, some write-once optical memory systems based on the organic fluorescence molecules have recently been reported. Irie et al.[9] and Misawa et al.[10] have individually studied fluorescence-mode write-once molecular memory systems. In both systems, the emission properties of the acid-sensitive fluorescent molecules are modulated by photoacid generation reactions. That is, the information is stored as the local acidity and readout with the modulated fluorescence signal. Because of irreversibility of the photoacid generation, they performed as the write-once memory, and nondestructive readout could be achieved. In these systems, however, the long-range diffusion of acid in the polymer matrix causes degradation of the stored information, while the short-range diffusion of acid is essentially required. This problem comes from the bimolecular nature of these systems. It is thus required to develop new unimolecular recording systems whose fluorescent nature can be irreversibly modulated by light irradiation.

In the present study, we propose novel photoresponsive fluorescent molecules, whose backbone structure is illustrated in Scheme 1. The hexatriene analogues having leaving groups X- and Y- are expected to show pericyclization reactions with relatively high efficiency and to give stable condensed aromatic moiety after liberation of the X−Y molecule. We here synthesized compound **1**, whose molecular structure is shown in Scheme 2.

Scheme 1



Scheme 2



1a **1b** **1c**

Compound **1** is a derivative of "triangle terarylene" which the authors have recently proposed as photochromic molecules having fairly high quantum yields in the photochemical cyclization reaction (60−70%) and high photochromic reactivity even in the solid states.[11] The methoxy group (CH_3O-) and hydrogen (H−) are introduced as the leaving units at the carbon atoms of the photochemical reaction center. Compound **1** would be converted to the benzo[1,2-b:3,4-b′]bis-[1]-benzothiophene structure, which has been reported as a luminescent molecule.[12] If a diarylethene structure with hexafluoro cyclopentene is used, the elimination of the fluorine would be induced.[13] In this letter, we report the synthesis and photochemical properties of compound **1**.

The synthetic procedure is illustrated in the Supporting Information. To dibromo phenyl thiazole, benzothiophene derivatives having a hydrogen and a methoxy group at the α- and β-carbon atoms, respectively, were connected by the Pd-catalyzed coupling reactions. Chemical characterization of **1a** was performed with ^{1}H NMR and MS spectra as summarized in the Supporting Information (Figure S1). Photochemical reactivity of **1a** was studied in acetone and in hexane as high and low polarity solvents, respectively.

The original colorless acetone solution of **1a** was observed to turn yellow in color after UV-light irradiation of 365 nm in wavelength. A fair amount of yellow precipitates formed after a few minutes of UV-light irradiation. Acetone was removed from the yellow solution, and the residue was washed with acetone and hexane many times. The yellow solid was thus separated. ^{1}H NMR and HRMS measurements of the residue were carried out, and the formation of **1c** was identified as presented in the Supporting Information (Figure S2). This suggests that the photoreaction of **1a** generated **1c**. **1c** did not return to the original **1a** by irradiation of light or heating.

NMR measurement was also performed after UV-light irradiation in d_6-acetone solution of **1a** to confirm the conversion of **1a** to **1c**. Since the solution contained a small amount of yellow precipitates after the UV-light irradiation, ^{1}H NMR signals in the aromatic region were rather diffused. Nevertheless, the signal of the methoxy proton of **1a** (4.0 ppm) was apparently decreased, and that of methanol (3.3 ppm, s, 3H) was clearly observed after the UV-light irradiation, indicating elimination of CH_3OH during formation of **1c**. No ^{1}H signals other than those of **1a** and methanol were observed in the aliphatic region. The ratio of **1a** and

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(7) (a) Koshido, T.; Kawai, T.; Yoshino, K. *Synth. Met.* **1995**, *73*, 257. (b) Tsivgoulius, G. M.; Lehn, J.-M. *Chem. Eur. J.* **1996**, *2*, 1399. (c) Takeshita, M.; Irie, M. *Chem. Lett.* **1998**, 1123. (d) Ern, J.; Benz, A. T.; Martin, H.-D.; Mukamel, S.; Tretiak, S.; Tsyganenko, K.; Kuldova, K.; Trommsdorff, H. P.; Kryschi, C. *J. Phys. Chem. A* **2001**, *105*, 1741. (e) Fukaminato, T.; Kobatake, S.; Kawai, T.; Irie, M. *Proc. Jpn., Acad. B* **2001**, *77*, 30. (f) Tsujioka, T.; Irie, M. *Appl. Opt.: Information Processing* **1998**, *37*, 4419.

(8) (a) Irie, M.; Fukaminato, T.; Sasaki, T.; Tamai, N.; Kawai, T. *Nature* **2002**, *420*, 759. (b) Fukaminato, T.; Sasaki, T.; Kawai, T.; Tamai, N.; Irie, M. *J. Am. Chem. Soc.* **2004**, *126*, 14843. (c) Kawai, T.; Sasaki, T.; Irie, M. *Chem. Commun.* **2001**, 711.

(9) Kawai, T.; Konishi, T.; Matsuda, K.; Irie, M. *Jpn. J. Appl. Phys.* **2001**, *40*, 5145.

(10) Mizuno, T.; Yamasaki, K.; Misawa, H. *Jpn. J. Appl. Phys.* **2006**, *44*, 1640.

methanol was typically 3:1, although signal intensity in the aromatic region could not be analyzed because of the diffused signals.

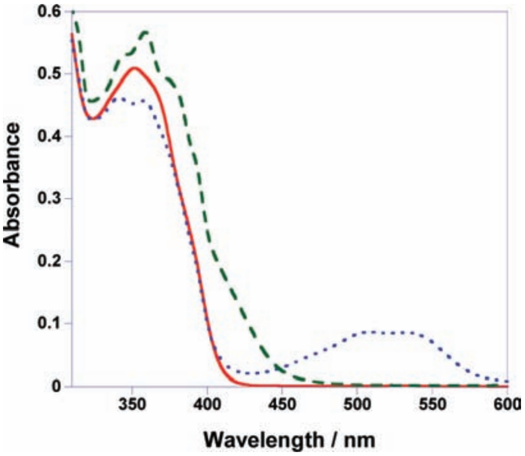

Figure 1. Changes of the absorption spectrum of **1a** in hexane solution: (red —) original state (**1a**), (blue ----) after UV irradiation (**1b** + **1a**), (green — — —) after acid addition (**1c** + **1a**).

We also studied photoreactivity of **1a** in hexane as a low polarity solvent. Figure 1 shows the changes in the absorption spectra of the hexane solution of **1a** (4.8×10^{-5} mol dm^{-3}) upon light irradiation. The colorless **1a** solution turned to red upon UV-light irradiation. This red solution showed an absorption band at 530 nm. The red solution returned to the original state **1a** quasi-reversibly upon visible light irradiation. An isosbestic point at 395 nm was observed in the photocoloration and the photobleaching reactions, indicating the photochemical reactions consisting of well-defined two components. The visible absorption band at about 500 nm is typical for the ring-closed form of the terarylene derivatives, and Scheme 2 shows the ring-closed form isomer **1b** as a possible structure of the red component. We assumed **1b** and evaluated its $\pi-\pi^*$ wavelength by the quantum-chemical calculation. The TD-DFT calculation in B3LYP/6-31G for **1b** predicted a visible absorption band of 504 nm, which agreed well with the experimental observation. The evaluated HOMO and LUMO distributions and also the stable geometries of **1a** and **1b** are given in the Supporting Information (Figure S5). For the calculation, the Gaussian03[14] suite of programs was used. The photochemical reaction from **1a** to **1b** would be specified as the pericyclization reaction typical for the terarylene derivatives, whose photochemical quantum yields are typically about 60%.[11] The isosbestic point was maintained during the first several minutes of UV-light irradiation and visible light irradiation, and further UV-light irradiation resulted in the irreversible reaction, which was characterized to be the elimination reaction from **1b** to **1c**. Indeed, the red colored hexane solution gradually changed to yellow, and thus the separation of **1b** from the red solution failed.

The hexane solution containing the red compound changed to yellow immediately after addition of TFA. This reaction was completed within less than one minute even after exposure to TFA vapor, which suggests progress of the acid-catalyzed elimination reaction. The yellow precipitate was also collected and identified to be **1c** by ^{1}H NMR and MS measurements. As shown in Figure 1, the hexane solution did not show any absorption band in the visible region after the addition of TFA, indicating a complete reaction of **1b** to **1c**. In the hexane solution, **1b** seemed to be relatively stable, and the acid-catalyzed elimination of the methoxy group resulted in **1c**. These changes of color upon the photochemical and acid-catalyzed reactions are presented in the Supporting Information (Figure S3).

The absorption spectrum of **1c** showed a characteristic bathochromic shift from that of **1a**, and the threshold wavelength of the absorption band of **1c** was slightly longer than that of **1a**. As summarized in the Supporting Information (Figure S4), the TD-DFT calculation of the B3LYP/6-31G(d) level supported this small bathochromic shift of **1c** in comparison with **1a**. That is, absorption peak wavelengths of **1a** and **1c** were calculated to be 295 and 380 nm, respectively. The fused aromatic ring structure of **1c** would be responsible for this bathochromic shift.

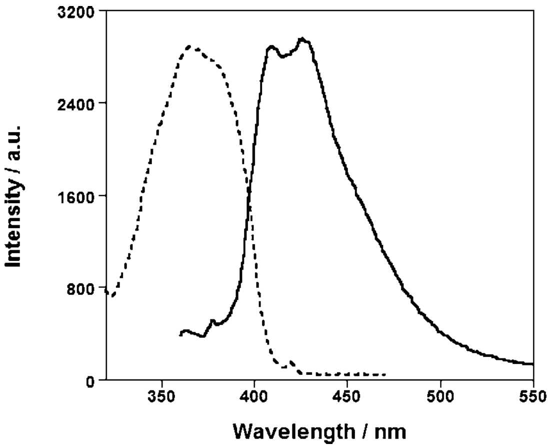

Figure 2. Emission (—) and excitation (---) spectra of **1c** in toluene solution (4.8×10^{-5} mol dm^{-3}) obtained with excitation at 320 nm and detection at 430 nm, respectively.

Optical properties of **1c** were examined in toluene after careful treatment with hexane for removing **1a**. Figure 2 shows fluorescence emission and excitation spectra of **1c** in the toluene solution (6.75×10^{-6} mol dm^{-3}) under nitrogen atmosphere. **1c** showed a characteristic emission peak at 420 nm. The peak wavelength of the excitation spectrum at about 360 nm agreed well with that of the absorption spectrum. **1c** showed a relatively high fluorescence quantum yield of 10% at ambient temperature in toluene. Fluorescence of **1c** can thus be measured under excitation at 400−410 nm where **1a** showed no absorbance. **1c** is expected to show fairly high stability in fluorescent emission because of its stable condensed aromatic structure with the 26π electron system. If **1a** would be used in the write-once memory systems, 365 nm UV laser light would be available for recording as it induces photochemical reaction to **1c** in the hydrophilic medium, and 405 nm violet laser-light could be used for readout of the memory as it excites the fluorescence emission of **1c** but not any photochemical reaction of **1a**; thus, nondestructive readout memory should be achieved.

In summary, we synthesized a new photoresponsive molecule having a terarylene type structure and a methoxy group as the leaving unit, which shows a relatively high fluorescence quantum yield after UV-light irradiation, indicating the possibility of future application to an active material in write-once type optical data-storage systems.

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Supporting Information Available: Synthetic scheme, TD-DFT calculation data, and spectral data (NMR and MS). This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) (a) Kawai, T.; Iseda, T.; Irie, M. *Chem. Commun.* **2004**, 72. (b) Kawai, S.; Nakashima, T.; Atsumi, K.; Sakai, T.; Harigai, M.; Imamoto, Y.; Kamikubo, H.; Kataoka, M.; Kawai, T. *Chem. Mater.* **2007**, *19*, 3479. (c) Nakagawa, T.; Atsumi, K.; Nakashima, T.; Hasegawa, Y.; Kawai, T. *Chem. Lett.* **2007**, *36*, 372. (d) Nakashima, T.; Atsumi, K.; Kawai, S.; Nakagawa, T.; Hasegawa, Y.; Kawai, T. *Eur. J. Org. Chem.* **2007**, *19*, 3212. (e) Nakashima, T.; Goto, M.; Kawai, S.; Kawai, T. *J. Am. Chem. Soc.* **2008**, *130*, 14570. (f) Nakagawa, T.; Hasegawa, Y.; Kawai, T. *J. Phys. Chem. A* **2008**, *112*, 5096. (g) Nakashima, T.; Miyamura, K.; Sakai, T.; Kawai, T. *Chem. Eur. J.* **2009**, *14*, in press. (h) Kutsunugi, Y.; Kawai, S.; Nakashima, T.; Kawai, T. *New J. Chem.* **2009**, in contribution.

(12) Zander, M. *Z. Naturforsch.* **1985**, *40a*, 497.

(13) (a) Higashiguchi, K.; Matsuda, K.; Kobatake, S.; Yamada, T.; Kawai, T.; Irie, M. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 2389. (b) Higashiguchi, K.; Matsuda, K.; Yamada, T.; Kawai, T.; Irie, M. *Chem. Lett.* **2000**, *12*, 1358.

(14) *Gaussian 03*, revision B.03; Gaussian, Inc.: Pittsburgh, PA, 2003. See Supporting Information for the full reference.