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Synthesis, Photochromic, and Electrical Properties of Diarylethene Derivatives Having 9-Carbazolyl or 2-(1,3,4-Oxadiazolyl) Group as Carrier Mobilization Sites

Keita Tani,* Koji Kubono, Kazushige Hori, Kentaro Shoji, Goji Shiga, Muneyuki Yamamoto, and Tsuyoshi Tsujioka
Division of Natural Science, Osaka Kyoiku University, Asahigaoka, Kashiwara, Osaka 582-8582

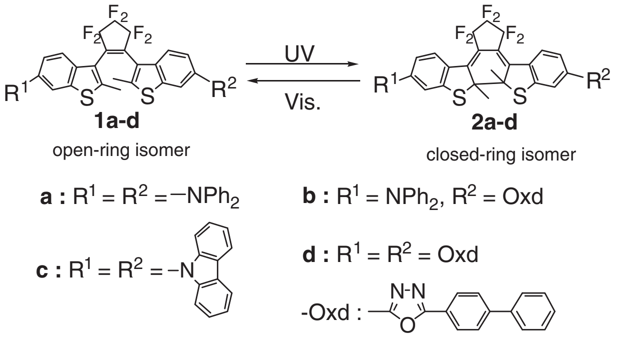
(Received July 12, 2011; CL-110593; E-mail: ktani@cc.osaka-kyoiku.ac.jp)

Diarylethene derivatives, **1c** and **1d**, having carrier mobilization sites have been synthesized. Their photochromic properties are examined both in solution and in thin film. Current–voltage characteristics at photostationary state of **1c** and **1d** showed drastic current increase compared with the corresponding open-ring isomers **1c** and **1d**, respectively.

Photochromism is a reversible change between two isomers by irradiation with appropriate light, whose absorption and emission spectra, refractive indexes, conductivities, and so on are different.[1] Therefore, much attention has been paid to photochromic systems due to potential application for optoelectronic devices such as optical data storage.[2] Of the many photochromic molecules available, diarylethene (DAE) derivatives are among the most striking candidates, as they show excellent fatigue resistance and thermal stability between open-ring and closed-ring isomers.[3]

Recently it has been reported by one of us (T. T.) that DAEs **1a** and **1b** having carrier mobilization sites showed not only photochromism but also interesting electrical behaviors.[4] However, the electrical properties of DAEs with carrier mobilization sites have not been fully investigated and the current–voltage (*I*–*V*) characteristics obtained in **1a** at photostationary state (PSS) was less than 18 µA/4 mm^2 with applied voltage of 15 V.[4a]

Here we report the synthesis, photochromic, and electrical properties of DAEs **1c** and **1d** having carbazole or 1,3,4-oxadiazole moiety as carrier mobilization sites as shown in Scheme 1, since carbazole and 1,3,4-oxadiazole derivatives show good hole-[5] and electron-mobilities,[6] respectively. The improvement of *I*–*V* characteristics is anticipated for **1c** and **1d**, because current will be controlled by two factors. One is the degree of π-conjugated extension in open- and closed-ring isomers and another is carrier mobilization sites directly attached to DAE, although carrier mobility is affected by many factors.[7]

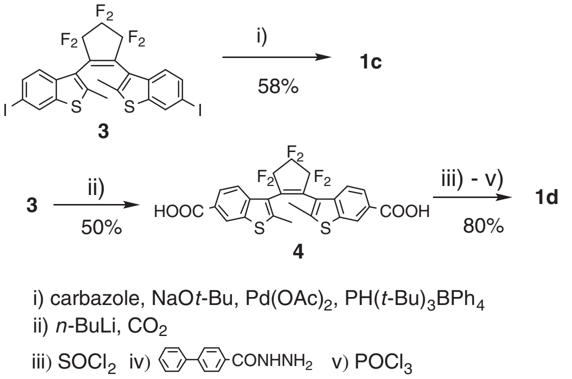


Scheme 1. Molecular structure of DAEs, **1c** and **1d**, and their corresponding closed-ring isomers.

The synthetic route of **1c** and **1d** is shown in Scheme 2. Iodobenzothiophene derivative **3**[8] was reacted with carbazole in the presence of sodium *tert*-butoxide, palladium acetate, and PH(*t*-Bu)$_3$BPh$_4$ to give **1c** in 58% yield. Treatment of **3** with butyllithium, then with dry ice afforded dicarboxylic acid **4**, which was converted to 1,3,4-oxadiazole derivative **1d** by cyclization of diacylhydrazides with phosphorus oxychloride.[9] The structures of DAEs, **1c** and **1d**, are confirmed by ^{1}H NMR and elemental analysis or high-resolution MS.[10]

From the measurement of ^{1}H NMR, DAEs synthesized here are in equilibrium between parallel conformation and anti-parallel conformation, whose assignment can be achieved by the comparison of the chemical shifts of methyl proton and aromatic protons[11] and the population of parallel and anti-parallel conformers for **1c** and **1d** are ca. 2:3.

Figure 1 shows the absorption spectral changes from open-ring isomer **1c** to the photostationary state (PSS) upon irradiation with 365 nm light. The colorless toluene solution of **1c** turns violet and new absorption appears around 420 and 550 nm,



i) carbazole, NaO*t*-Bu, Pd(OAc)$_2$, PH(*t*-Bu)$_3$BPh$_4$
ii) *n*-BuLi, CO$_2$
iii) SOCl$_2$ iv) CONHNH$_2$ v) POCl$_3$

Scheme 2. Synthetic route of DAEs, **1c** and **1d**.

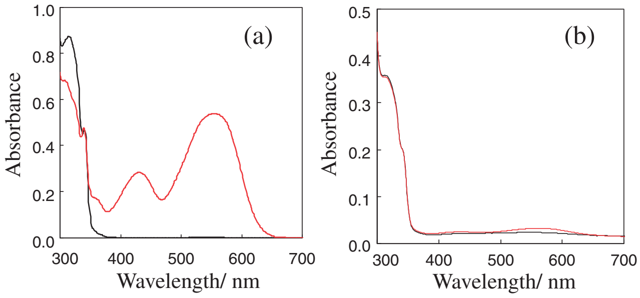


Figure 1. (a) Absorption spectra of **1c** in toluene (3.93 × 10^{-5} M) (black line) and at the PSS by photoirradiation with 365 nm (red line) and (b) that in thin film (black line) and at the PSS by photoirradiation with 365 nm (red line).

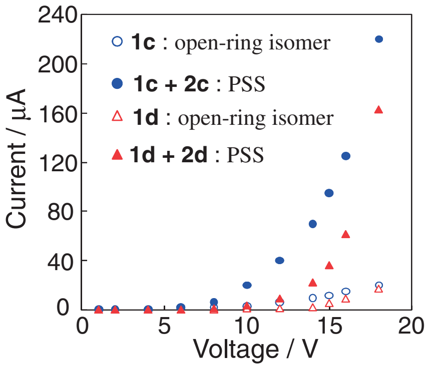


Figure 2. Current–voltage characteristics of a photochromic device with DAEs, **1c** and **1d**, for open-ring isomer and PSS.

which is due to the formation of closed-ring isomer **2c** as shown in Figure 1(a). The violet solution thus obtained returned to colorless upon irradiation with visible light (500–600 nm) to give open-ring isomer **1c**. Similar photocyclization and cycloreversion was observed for **1d**.[12] On the other hand, the efficiency of photochromic interconversion in thin film (30 nm thickness) of **1c** was very low and only a small amount (ca. 3%) of closed-ring isomer existed at the PSS upon irradiation with 365 nm, as shown in Figure 1(b). DAE **1d** also hardly changed from open-ring isomer to closed-ring isomer in the thin film at the PSS similar to **1c**.

The X-ray crystal structure of **1c** was examined to get some clues of this lower efficiency of ring closing reaction of **1c** in thin film state. The molecular structure of **1c** in the crystal[13] is shown in Figure S1.[14] It revealed that the distance between two carbon atoms in ring closure were 0.55 nm. This suggests that a considerable fraction of the film state seems to be fixed in photoinactive stereochemistry.[15]

Current–voltage characteristics of DAEs, **1c** and **1d**, are measured by using the device structure as shown in Figure S2.[14] The DAE layers were of the same thickness of 30 nm and they were changed into the PSS by UV irradiation with 365 nm. Although the ratio of closed-ring isomer at the PSS of DAEs determined by measurement of the absorption spectrum change was very low as shown in Figure 1(b), applied-voltage dependence of the current was measured.[16] Figure 2 clearly shows that the current is drastically increased with the increase of applied voltage at the PSS, while it sluggishly increased for open-ring isomers. It is noted that the current obtained for PSS (**1c** + **2c**) was more than 80 µA/4 mm^2 with applied voltage of 15 V, which was superior to that obtained for **1a**.[4a] The ratio of the current of **1c** and **1d** in the ON (PSS) and OFF (open-ring isomer) with applied voltage of 8 V was ca. 10. However, these values were lower than the recently reported highest value of ca. 10^3 by Meerholz[17] probably due to a very small portion of closed-ring isomer at PSS in thin film.

In conclusion, DAEs having carrier mobilization sites have been synthesized and current can be switched on the basis of the photochromic properties of DAEs. We are searching for DAEs linked with carrier mobilization sites, whose ring-closure reaction will occur much efficiently in thin film, to achieve high ON–OFF ratio.

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References and Notes

1 a) *Photochromism: Molecules and Systems*, ed. by H. Dürr, H. Bouas-Laurent, Elsevier, Amsterdam, **2003**. b) E. Kim, Y.-K. Choi, M.-H. Lee, *Macromolecules* **1999**, *32*, 4855. c) T. Kawai, T. Kunitake, M. Irie, *Chem. Lett.* **1999**, 905. d) G. M. Tsivgoulis, J.-M. Lehn, *Chem.—Eur. J.* **1996**, *2*, 1399. e) T. Fukaminato, T. Sasaki, T. Kawai, N. Tamai, M. Irie, *J. Am. Chem. Soc.* **2004**, *126*, 14843.

2 T. Tsujioka, M. Kume, Y. Horikawa, A. Ishikawa, M. Irie, *Jpn. J. Appl. Phys.* **1997**, *36*, 526.

3 M. Irie, *Chem. Rev.* **2000**, *100*, 1685.

4 a) A. Taniguchi, T. Tsujioka, Y. Hamada, K. Shibata, T. Fuyuki, *Jpn. J. Appl. Phys.* **2001**, *40*, 7029. b) T. Tsujioka, H. Kondo, *Appl. Phys. Lett.* **2003**, *83*, 937.

5 S. Grigalevicius, *Synth. Met.* **2006**, *156*, 1.

6 a) A. P. Kulkarni, C. J. Tonzola, A. Babel, S. A. Jenekhe, *Chem. Mater.* **2004**, *16*, 4556. b) J. Bettenhausen, P. Strohriegl, W. Brütting, H. Tokuhisa, T. Tsutsui, *J. Appl. Phys.* **1997**, *82*, 4957.

7 T. Tsujioka, M. Irie, *J. Photochem. Photobiol., C* **2010**, *11*, 1.

8 K. Matsuda, M. Irie, *Chem.—Eur. J.* **2001**, *7*, 3466.

9 A. B. Theocharis, N. E. Alexandrou, *J. Heterocycl. Chem.* **1990**, *27*, 1685.

10 ^{1}H NMR, elemental analysis or high-resolution mass spectral data and mp's of **1c** and **1d** are summarized in Supporting Information which is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

11 a) K. Uchida, Y. Nakayama, M. Irie, *Bull. Chem. Soc. Jpn.* **1990**, *63*, 1311. b) M. Irie, K. Sakemura, M. Okinaka, K. Uchida, *J. Org. Chem.* **1995**, *60*, 8305.

12 Details of the photochromic reaction of **1c** and **1d** will be reported elsewhere.

13 Crystal data for **1c** + 1/2 hexane, colorless plate (benzene–hexane), fw 841.9, triclinic, space group $P\bar{1}$, $a = 11.985(4)$ Å, $b = 13.707(3)$ Å, $c = 14.703(4)$ Å, $\alpha = 65.921(16)°$, $\beta = 69.76(2)°$, $\gamma = 81.86(2)°$, $V = 2069.0(11)$ Å^3, $Z = 2$, $D_{\mathrm{calcd}} = 1.352$ g cm^{-3}, $\mu(\mathrm{Mo}\,K\alpha) = 0.194$ mm^{-1}, Rigaku AFC7R diffractometer, 9487 independent reflections, and 4088 reflections with $I > 2.0\sigma(I)$, $R = 0.0687$, $wR_2 = 0.2839$. Crystallographic data of **1c** have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-838936.

14 Figures S1 and S2 are shown in Supporting Information which is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

15 S. Kobatake, K. Uchida, E. Tsuchida, M. Irie, *Chem. Commun.* **2002**, 2804.

16 Isomerization from closed-ring isomer to open-ring isomer by electric carrier injection was reported.[4b] However, current was measured immediately after modulating applied voltage and it did not change significantly, indicating the possibility of electric isomerization when measuring I–V characteristics would be low.

17 P. Zacharias, M. C. Gather, A. Köhnen, N. Rehmann, K. Meerholz, *Angew. Chem., Int. Ed.* **2009**, *48*, 4038.