Photochromism of a Diarylethene Trimer in a Bulk Amorphous Phase

Arisa Tomari, Tadatsugu Yamaguchi,* Naotaka Sakamoto, Yuji Fujita, and Masahiro Irie*†
Chemical and Textile Industry, Fukuoka Industrial Technology Center,
3-2-1 Kamikoga, Chikushino, Fukuoka 818-8540
†*Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University,*
6-10-1Hakozaki, Higashi-ku, Fukuoka 812-8581

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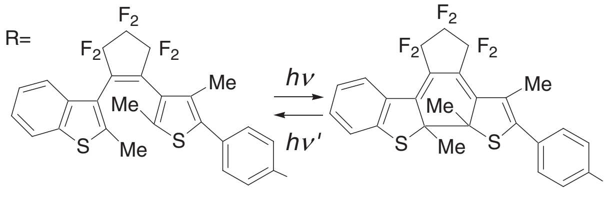
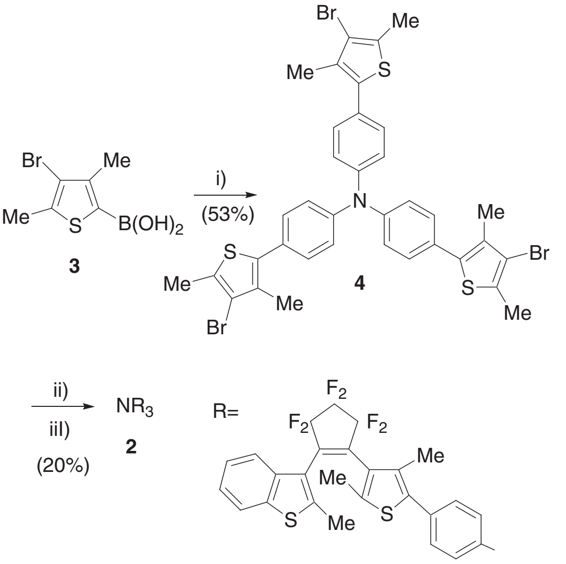
A photochromic compound having three diarylethene units was synthesized and its photochromic performance was examined in hexane solution as well as in a bulk amorphous phase. The compound formed a stable amorphous solid with T_g of 120 °C and the solid exhibited a reversible color change upon irradiation with UV and visible light.

Photochromism has attracted considerable attention because its potential ability for applications to molecular devices, such as optical memories and switches.[1] Among various thermally irreversible compounds diarylethene derivatives are the most promising compounds because of their fatigue resistant property.[2,3] For practical applications it is indispensable to disperse them in solid polymer matrices. However, miscible dye concentration is limited and dyes tend to segregate after long-term storage. A bulk amorphous solid is ideal from the viewpoint of high concentration and stability.[4,5] It has been reported previously that some diarylethene derivatives form bulk amorphous soilds.[4–10] But mostly the glass transition temperatures (T_g's) are below 100 °C and the photochromic reactivity is inefficient. Only a few compounds, such as 2,4-diphenylbenzene,[4] triphenylamine,[5] and spirobifluorene derivatives,[10] exhibit T_g above 100 °C. In this communication, a photochromic compound having three diarylethene units was synthesized in order to prepare the bulk amorphous solid with high T_g and high reactivity.

1: RNMe$_2$
2: NR$_3$



Diarylethene trimer **2** was synthesized according to Scheme 1. Compound **3**[11] was reacted with tris(4-bromophenyl)amine to give compound **4**. The coupling reaction of **4** with (2-methylbenzothiophen-3-yl)heptafluorocyclopenthene gave a trimer **2**. A diarylethene monomer **1** was also synthesized as a reference compound. The synthetic route of **1** was the same as that for **2**. 4-Bromo-*N*, *N*-dimethylaniline was used instead of tris(4-bromophenyl)amine.



Scheme 1. Synthesis of triphenylamine derivative **2**. i) tris(4-bromophenyl) amine, Pd(PPh$_3$)$_3$, THF, Na$_2$CO$_3$, ii) *n*-BuLi, THF, iii) (2-methylbenzothiophen-3-yl)heptafluorocyclopentene.

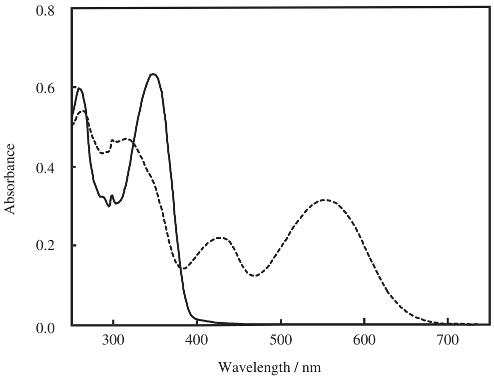


Figure 1. Absorption spectra of **2O–O–O** (solid line) and in the photostationary state (dashed line) under irradiation with 334-nm light in hexane (1.72 × 10^{-5} mol/L).

Figure 1 shows the absorption spectral change of **2** in hexane. At the photostationary state upon irradiation with 334-nm light, the three open-ring isomers **2O–O–O**, which showed the maxima at 350 nm (ε: 3.63 × 10^4 M^{-1}cm^{-1}), was transformed into the mixture of three kinds of closed-ring isomers, producing a mixture of **2C–O–O** (54%), **2C–C–O** (41%), and **2C–C–C** (5%), where **C** and **O** mean the closed and open-ring form isomers, respectively. The three isomers were isolated by HPLC (column: Wakosil 5SIL; eluent: hexane/ethyl acetate = 98/2). All three isomers gave the same absorption maximum at 559 nm, but the absorption coefficient increased with the increasing number of the closed-ring form, i.e., **2C–O–O** (ε: 1.29 × 10^4 M^{-1}cm^{-1}), **2C–C–O** (ε: 2.34 × 10^4 M^{-1}cm^{-1}) and **2C–C–C** (ε: 3.66 × 10^4 M^{-1}cm^{-1}). Upon irradiation with light of wavelength longer than 550-nm light, the closed-ring isomers returned to the original **2O–O–O**.

Just as for **2**, compound **1O** underwent photochromism upon irradiation with UV and visible light in hexane solution. **1O** showed the absorption maximum ($\varepsilon_{\max}$ $2.34 \times 10^4\,\mathrm{M^{-1}cm^{-1}}$) at 300 nm. Upon irradiation with 313-nm light, the diarylethene transformed into the closed-ring isomer **1C** ($\varepsilon_{\max}$ 1.79×10^4 $\mathrm{M^{-1}cm^{-1}}$) at 560 nm. In the photostationary state, the conversion ratio from the open- to the closed-ring isomers was 91%. The cyclization and cycloreversion quantum yields of **1** were determined to be 0.52 and 0.080 in hexane, respectively.

The cyclization and cycloreversion quantum yields were measured for compounds **2** and the effect of the energy transfer was examined. The quantum yield measurement was carried out by the same procedure as used in Ref. 12. The isomers formed upon irradiation with UV light were measured by HPLC. The cyclization/cycloreversion quantum yields between **2O–O–O** and **2C–O–O** were similar to the values for **1**. However, the cyclization quantum yields of **2C–O–O** and **2C–C–O** were strongly suppressed by the energy transfer to the closed-ring forms as shown below. The quantum yield from **2C–O–O** to **2C–C–O** was 1/16 of the quantum yield from **2O–O–O** to **2C–O–O**. It further decreased to a half for the reaction from **2C–C–O** to **2C–C–C**. The energy transfer between diarylethene units is considered to decrease the conversion to the closed-ring isomer in trimer **2**.

$$\begin{tikzcd}
\mathbf{1O} \arrow[r, shift left, "\Phi_{313}= 0.52"] & \mathbf{1C} \arrow[l, shift left, "\Phi_{517}= 0.080"]
\end{tikzcd}$$

$$\begin{tikzcd}
\mathbf{2O\text{-}O\text{-}O} \arrow[r, shift left, "\Phi_{313}= 0.47"] & \mathbf{2C\text{-}O\text{-}O} \arrow[l, shift left, "\Phi_{517}= 0.092"] \arrow[d, shift left, "\Phi_{313}= 0.029"] \\
\mathbf{2C\text{-}C\text{-}C} \arrow[r, shift left, "\Phi_{517}= 0.060"] & \mathbf{2C\text{-}C\text{-}O} \arrow[l, shift left, "\Phi_{313}= 0.015"] \arrow[u, shift left, "\Phi_{517}= 0.075"]
\end{tikzcd}$$

Compound **2** formed a transparent amorphous solid. The melting temperature of **2** was 292 °C. The crystals were heated above the melting temperatures and then slowly cooled. In the second run of differential scanning calorimetry (DSC) measurement a peak due to the crystalline state disappeared and a clear shift of the base line was observed at 120 °C (Figure 2). From the threshold temperature, T_g was evaluated to be 120 °C. The amorphous film was prepared on a quartz slide glass by a spin-coating method. The film thickness was 80 nm.

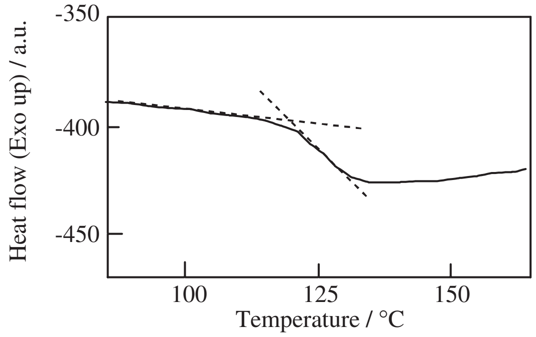


Figure 2. DSC profile of **2O–O–O** at 2nd and subsequent heating scans. (temperature scan rate 10 °C/min, sample weight = 10.0 mg)

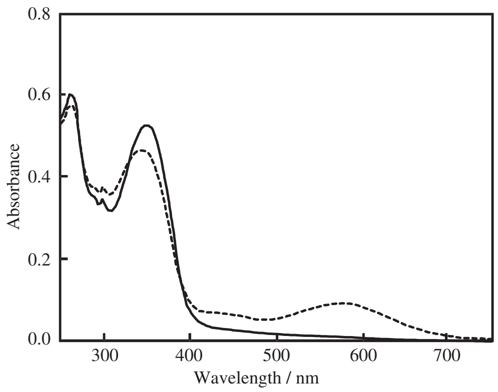


Figure 3. Absorption spectra of **2O–O–O** (solid line) and in the photostationary state (dashed line) under irradiation with 334-nm light in bulk amorphous phase (film thickness = 80 nm).

Figure 3 shows the absorption spectral change of **2** in the bulk amorphous phase. Upon irradiation with 334-nm light, the colorless film of **2** turned violet, in which visible absorption band was observed at 580 nm. At the photostationary state upon irradiation with 334-nm light, the **2O–O–O** was transformed into the mixture of two kinds of closed-ring isomers, producing a mixture of **2C–O–O** (26%), **2C–C–O** (1%). The violet color disappeared by irradiation with >550-nm light.

In conclusion, a new type of photochromic compound having three diarylethene units was synthesized and the photochromic reactivity was examined in hexane solution as well as in a bulk amorphous solid. The compound underwent photochromic reactions in the bulk amorphous phase.

References and Notes

1 H. Dürr and H. Bouas-Laurent, "Photochromism Molecules and Systems," Elsevier, Amsterdam (1990).
2 M. Irie, "Photo-Reactive Materials for Ultrahigh-Density Optical Memory," Elsevier, Amsterdam (1994).
3 M. Irie, *Chem. Rev.*, **100**, 1685 (2000).
4 M. Kim, T. Kawai, and M. Irie, *Chem. Lett.*, **2001**, 702.
5 M. Fukudome, K. Kamiyama, T. Kawai, and M. Irie, *Chem. Lett.*, **2001**, 70.
6 T. Kawai, N. Fukuda, D. Groschl, S. Kobatake, and M. Irie, *Jpn. J. Appl. Phys., Part 2*, **38**, L1194 (1999).
7 H. Utsumi, D. Nagahara, H. Nakano, and Y. Shirota, *J. Mater. Chem.*, **10**, 2436 (2000).
8 S. Takami, T. Kawai, and M. Irie, *Eur. J. Org. Chem.*, **2002**, 3796.
9 T. Yamaguchi, K. Nomiyama, M. Isayama, and M. Irie, *Adv. Mater.*, **16**, 643 (2004).
10 H. Tian, B. Chen, and P.-H. Liu, *Chem. Lett.*, **2001**, 990.
11 T. Yamaguchi, T. Inagawa, H. Nakazumi, S. Irie, and M. Irie, *J. Mater. Chem.*, **11**, 2453 (2001).
12 T. Kaieda, S. Kobatake, H. Miyasaka, M. Nurakami, N. Iwai, Y. Nagata, A. Itaya, and M. Irie, *J. Am. Chem. Soc.*, **124**, 2015 (2002).
13 **4**: brown liquid; ^{1}H NMR (200 MHz) δ 2.29 (s, 9H), 2.43 (s, 9H), 7.16–7.19 (m, 6H), 7.29–7.33 (m, 6H). EIMS m/z 809 (M$^+$).
14 **1O**: brown crystals; mp 178–179 °C; ^{1}H NMR (200 MHz) δ 1.87 (s, 1.6H), 2.12 (s, 1.6H), 2.17 (s, 1.6H), 2.39 (s, 1.4H), 2.41 (s, 1.4H), 2.43 (s, 1.4H), 2.93 (s, 3H), 2.97 (s, 3H), 6.62–6.73 (m, 2H), 7.07–7.32 (m, 6H), 7.59–7.77 (m, 2H). EIMS m/z 551 (M$^+$); Anal. Calcd for $C_{28}H_{23}F_6NS_2$: C 60.97, H 4.20, N 2.54%. Found: C 60.94, H 4.21, N 2.52%.
15 **2O–O–O**: brown crystals; mp. 292 °C; ^{1}H NMR (200 MHz) δ 1.88 (s, 4.8H), 2.15 (s, 4.8H), 2.19 (m, 4.8H), 2.41 (s, 8.4H), 2.47 (s, 4.2H), 6.94–7.36 (m, 18H), 7.61–7.64 (m, 3H), 7.74–7.77 (m, 3H). Anal. Calcd for $C_{78}H_{51}F_{18}NS_6$: C 60.97, H 3.35, N 0.91%. Found: C 61.10, H 3.52, N 0.84%. FABMS m/z: [M$^+$] 1535. **2C–O–O**: ^{1}H NMR(200 MHz) δ 1.90–1.91 (m, 5H), 2.08–2.22 (m, 13H), 2.41–2.47 (m, 9H), 6.94–7.63 (m, 22H), 7.74–7.84 (m, 2H). **2C–C–O**: ^{1}H NMR (200 MHz) δ 1.90–1.91 (m, 3H), 2.08–2.22 (m, 12H), 2.43–2.50 (m, 3H), 6.94–7.66 (brs, 23H), 7.73–7.85 (m, 1H). **2C–C–C**: ^{1}H NMR (200 MHz) δ 2.10–2.12 (m, 27H), 7.10–7.39 (m, 24H).

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