

Photochromism of Diarylethene Maleimide Derivatives

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Diarylmaleimide derivatives having an indole ring, *N*-cyanomethyl-2-[2-methoxy-1-benzothiophen-3-yl]-3-[2-methyl-1-octadecylindol-3-yl]maleimide or *N*-cyanomethyl-2-[2-ethoxy-1-benzothiophen-3-yl]-3-[2-methyl-1-octadecylindol-3-yl]maleimide, were synthesized in an attempt to shift the photosensitive wavelength longer such that it becomes longer than 450 nm. The derivatives underwent the photocyclization reaction upon irradiation with 450–550 nm light in hexane solution and the photogenerated closed-ring isomers returned to the initial open-ring isomers upon irradiation with light longer than 600 nm.

Diarylethenes having heterocyclic aryl groups undergo thermally irreversible and fatigue-resistant photochromic reactions.[1–3] So far, various types of diarylethene derivative with different kinds of ethene moiety have been synthesized, such as 1,2-diarylperfluorocyclopentenes,[4] 2,3-diarylmaleic anhydrides,[5–7] and 2,3-diarylmaleimides.[8–12] Although the absorption spectra of 1,2-diarylperfluorocyclopentenes are localized in the UV region, the spectra of 2,3-diarylmaleic anhydrides and 2,3-diarylmaleimides extend to visible regions longer than 400 nm. The latter compounds undergo reversible photochromic reactions upon irradiation with light longer than 400 nm. Both maleic anhydride and maleimide derivatives are prepared by acid–base and aldol condensation reactions, and diarylethenes that have a non-symmetrical aryl can be synthesized without any difficulty.

For the applications in near-field optical memory media,[13,14] it is desirable to develop photochromic compounds that have a sensitivity in a wavelength region longer than 400 nm for both directions, cyclization and cycloreversion reactions, because UV light can not pass through the glass fiber tip of a near-field microscope. For near-field memory media, in which writing and erasing are carried out by irradiation with 488 nm (Ar ion laser) and 633 nm (He–Ne laser) light, respectively, we have synthesized new diarylmaleimide derivatives and have examined the effect of an indole substituent on their absorption bands and photochromic reactivity.

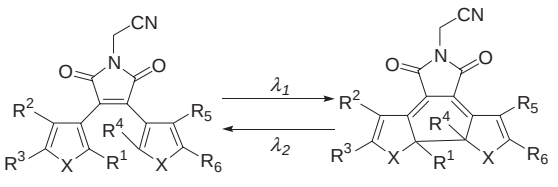


Chart 1.

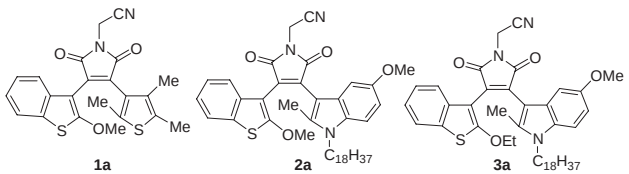
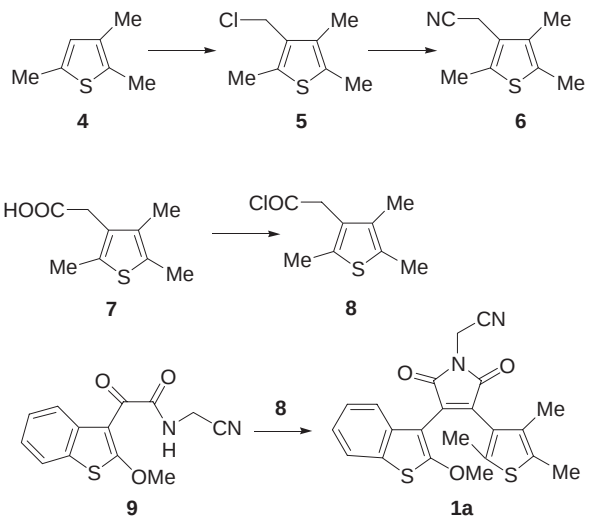


Chart 2.

Results and Discussion

Synthesis. Non-symmetrical diarylmaleimide derivatives **1a**–**3a** were prepared by the method shown in Schemes 1 and 2. The structures **1a**–**3a** were determined by ^{1}H NMR spectroscopy, and mass spectrum and elemental analyses.

Photochromism. The diarylethene **1a** includes thiophene and benzothiophene. Figure 1 shows the photochromic reaction of **1** in hexane. Upon irradiation with 445 nm light, **1a** changed to **1b**, which shows a new peak at 550 nm. The conversion ratio from the open- to the closed-ring isomers was 80% in the photostationary state under irradiation with 445 nm light. The closed-ring isomer **1b** returned to **1a** upon irra-



Scheme 1.

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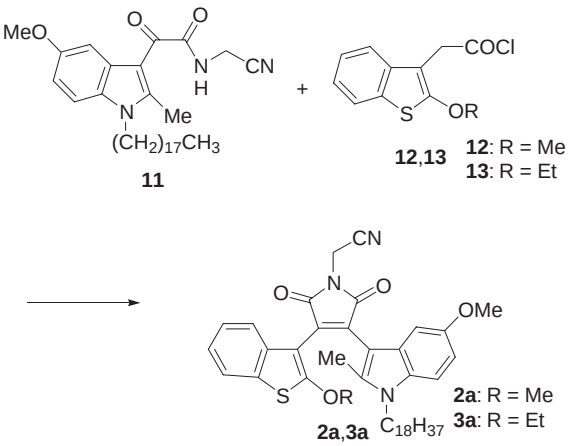

Scheme 2.

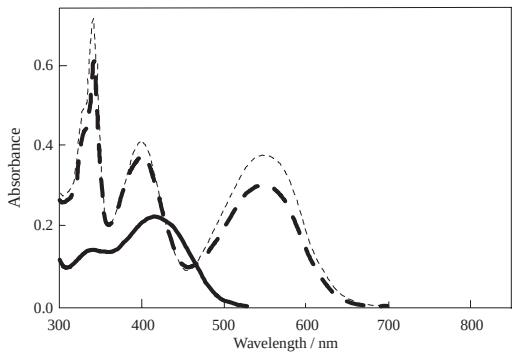

Fig. 1. Absorption spectra of **1a** (solid line), **1b** (dotted line), and **1** in photostationary state (dashed line) under irradiation with 445 nm light in hexane ($c = 5.1 \times 10^{-5}$ M).

diation with 550 nm light. The conversion ratio was strongly suppressed when the irradiation wavelength was shifted from 445 nm to 488 nm.

To increase the sensitivity at 488 nm, we replaced the thiophene ring with a 5-methoxyindole. Two types of diarylethene, **2a** and **3a**, with a 5-methoxyindole ring were prepared.

The diarylethene **2a** includes 5-methoxy-2-methyindole and 2-methoxy-1-benzothiophene. Figure 2 shows the spectra of **2a** before and after irradiation with 488 nm light in hexane. Upon irradiation with 488 nm light, the open-ring isomer **2a** converted to the closed-ring isomer **2b**. The conversion ratio was 87% in the photostationary state under irradiation with 488 nm light. Upon irradiation with 633 nm light, the closed-ring isomer **2b** returned to **2a**. The absorption spectral change of the ethoxy derivative **3** was similar to that of **2** in hexane, as shown in Fig. 3.

Table 1 summarizes the absorption maxima of the open- and closed-ring isomers in hexane and their coefficients. The diarylethene **1b**, which is of the thiophene–benzothiophene type, has an absorption band at 550 nm. The absorption band of **2b** and **3b** shifted to longer wavelengths, that is, 662 nm and 661 nm, respectively, with the introduction of 5-methoxy-2-methylindole. However, the cyclization/cycloreversion quantum yields dramatically decreased with the introduction of 5-methoxyindole. No appreciable difference in cyclization/cycloreversion quantum yield was observed between **2** and **3**.

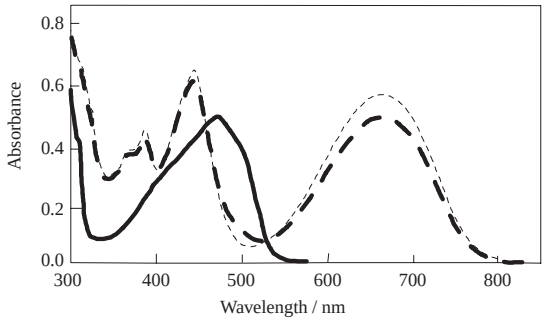

Fig. 2. Absorption spectra of **2a** (solid line), **2b** (dotted line), and **2** in photostationary state (dashed line) under irradiation with 488 nm light in hexane ($c = 6.1 \times 10^{-5}$ M).

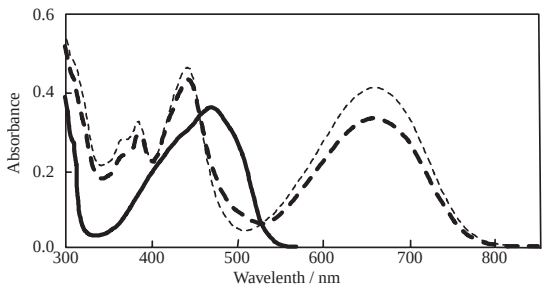

Fig. 3. Absorption spectra of **3a** (solid line), **3b** (dotted line), and **3** in photostationary state (dashed line) under irradiation with 488 nm light in hexane ($c = 4.4 \times 10^{-5}$ M).

Table 1. Absorption Characteristics and Photoreactivities of Diarylmaleimide Derivatives **1–3** in Hexane

Compound	$\varepsilon/10^3$ dm^3 mol^{-1} cm^{-1}		Quantum yield	
	Open form	Closed-ring form	Cyclization	Cycloreversion
1	4.3 (414 nm)	7.3 (550 nm)	0.24 (445 nm)	0.075 (550 nm)
2	8.3 (470 nm)	10.1 (662 nm)	0.046 (500 nm)	0.032 (660 nm)
3	8.3 (470 nm)	9.5 (661 nm)	0.057 (500 nm)	0.035 (660 nm)

Solvent Effects. Photochromic reactivity was found to depend on solvent polarity. Figure 4 shows the conversion ratios of **2** in a solution of hexane and benzene. The conversion ratio was strongly affected by solvent polarity. The conversion ratio of 87% in hexane decreased to 18% in benzene. Solvent polarity does not affect the ratio of the parallel conformation to the anti-parallel conformation of the diarylethene **2** in the ground state. This was confirmed by ^{1}H NMR measurements.

The solvent effect is explained by an intramolecular charge transfer (TICT).[15] When a compound is photoexcited to the first excited singlet state, the compound can take two conformations: planar and twisted. In polar solvents, photoexcitation induces a intramolecular charge transfer from the donor benzo[b]thiophene and indole rings to the electron acceptor maleimide moiety. The charge-separated polarized state prefers the twisted conformation, from which photocyclization cannot proceed.

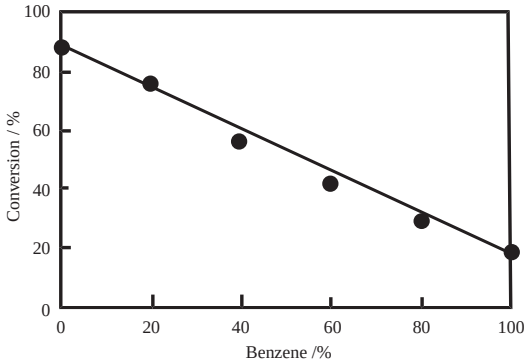

Fig. 4. Relationship between conversion and solvent change of **2a** (●).

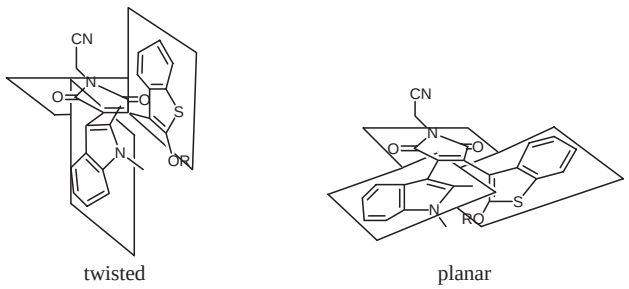

Chart 3.

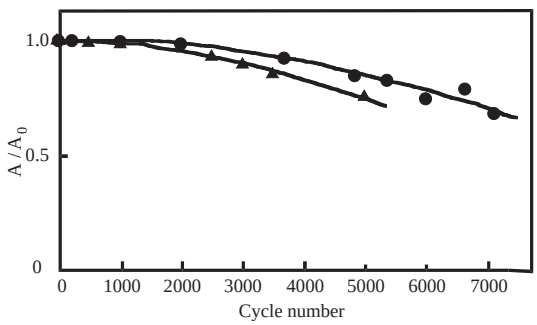

Fig. 5. Fatigue resistances of **2a** (▲) and **3a** (●) in hexane solution in air.

Photocyclization can proceed only from the anti-parallel and planar conformations. The increase of twisted conformation in a polar solvent led to a decrease in the conversion ratio from the open- to the closed-ring isomers.

Fatigue Resistance. Fatigue resistance is an indispensable property for practical applications. Hexane solutions of **2a** and of **3a** were irradiated alternately with 488 nm light for 2 min and 633 nm light for 2 min in the presence of air.[9] The absorbance of the closed-ring isomer was plotted against the number of cycles (Fig. 5). Although both compounds showed fairly good fatigue resistances, the fatigue resistance of **3a**, which has an ethoxy substituent, was superior to that of **2a**, which has a methoxy group. The difference in fatigue resistance between **2** and **3** is explained as follows.

It has been reported that photooxidative degradation is dependent on the polymer structure for poly(methyl methacrylate), poly(ethyl methacrylate), poly(*n*-butyl methacrylate), and poly(hexyl methacrylate).[16] Photodegradation occurred most readily for poly(methyl methacrylate). The difference was attributed to the flexibility and the mobility of alkyl chains, which suppress the photodegradation. The ethoxy substituent was effective to suppress the photodegradation.

Thermal Stability. The thermal stabilities of both isomers are the most important requirement for optical memory devices. Indole derivatives are considered to be thermally unstable. The diarylethenes **2** and **3** are thermally stable for 10 days at 50 °C in hexane. The absorbance of the closed-ring isomers of **2b** and **3b** did not decrease even at 120 °C for 3 h in decaline.

Conclusion

We have demonstrated that diarylmaleimide derivatives having an indole ring could be synthesized in an attempt to shift the photosensitive wavelength such that it becomes longer than 450 nm. The derivatives underwent photocyclization upon irradiation with 488 nm light or >560 nm light in hexane.

Experimental

The solvents used were spectrograde and were purified by distillation before use. Absorption spectra were measured with an absorption spectrophotometer (Shimadzu UV-2400PC). A mercury lamp (Ushio, 500W) was used as a light source. Monochromic light was obtained by passing light through a Toshiba cutoff filter (UV-35) and a monochromator (Ritsu MC-10N) or through an O-56 filter. Quantum yield was determined by comparing the reaction yields of diarylethenes in hexane with the yield of furyl fulgide in toluene. The sample was not degassed. ^{1}H NMR spectra were recorded on a Varian Gemini-200 (200 MHz) spectrometer with $CDCl_3$ and with d_6-benzene as solvent and tetramethylsilane as internal standard. The mass spectra were measured on a Shimadzu GC-2010 mass spectrometer. Fatigue resistance was measured using an apparatus described in Ref. 9.

3-Chloromethyl-2,4,5-trimethylthiophene (5). Chloromethyl methyl ether (9.5 mL, 125 mmol) and zinc chloride (0.34 mL, 2.5 mmol) at room temperature were added to a stirred solution of 2,3,5-trimethylthiophene (3.16 g, 25 mmol) in dichloromethane (25 mL), and the reaction mixture was stirred for 1 h at room temperature. The reaction mixture was poured into water. Extraction with chloroform, drying with anhydrous magnesium sulfate, and evaporation of this mixture afforded crude 3-chloromethyl-2,4,5-trimethylthiophene (**5**). This compound was used for cyanation without further purification. **5**: Yellow liquid. bp 43–45 °C/2 mmHg. ^{1}H NMR ($CDCl_3$) δ 2.06 (s, 3H), 2.23 (s, 3H), 2.36 (s, 3H), 4.43 (s, 2H).

3-Cyanomethyl-2,4,5-trimethylthiophene (6). A mixture of **5**, benzene (5 mL), tetrabutylammnonium bromide (0.31 g, 0.96 mmol), and sodium cyanide (2.35 g, 48 mmol) in water (10 mL) was refluxed for 1 h. After cooling to ambient temperature, the reaction mixture was extracted with chloroform. The combined organic phase was dried with anhydrous magnesium sulfate, filtered, and evaporated in vacuo. The residue was purified by distillation in vacuo to give 6.82 g of **6** in 83% yield. **6**: Yellow crystals. mp. 61–62 °C. ^{1}H NMR ($CDCl_3$) δ 2.07 (s, 3H), 2.27 (s, 3H), 2.33 (s, 3H), 3.38 (s, 2H).

2,4,5-Trimethylthiophen-3-ylacetic acid (7). A mixture of compound **6** (0.20 g, 1.21 mmol) and 4 mL of concentrated hydrochloric acid was refluxed for 3 h. After cooling, the mixture

was extracted with chloroform. The extracts were dried over anhydrous magnesium sulfate and concentrated in vacuo to give 0.150 g of **7** in 62% yield. **7**: Yellow crystals. mp. 106–107 °C. ^{1}H NMR ($CDCl_3$) δ 2.00 (s, 3H), 2.22 (s, 3H), 2.28 (s, 3H), 3.35 (s, 2H).

***N*-Cyanomethyl-2-(2-methoxybenzothien-3-yl)-3-(2,4,5-trimethylthien-3-yl)maleimide (1a).** Oxalyl chloride (0.17 mL, 1.4 mmol) was added to a benzene solution (10 mL) containing 104 mg (0.55 mmol) of **8**. The mixture was stirred for 1 h, and refluxed for 1 h. After evaporating benzene and excess oxalyl chloride in vacuo, 10 mL of 1,2-dichloromethane solution containing 153 mg (0.55 mmol) of **9** and 5 mL of triethylamine was added dropwise. After stirring for 40 h at room temperature, the reaction mixture was extracted with chloroform (100 mL) following the addition of 50 mL of water. The organic phase was washed with 2 M hydrochloric acid, and dried over anhydrous magnesium sulfate, and evaporated in vacuo. The residue was purified by thin-layer chromatography on silica gel (hexane/ethyl acetate = 7/3) to give 77 mg of **1a** in 32% yield. **1a**: Orange crystals. mp. 171–172 °C. ^{1}H NMR ($CDCl_3$) δ 1.84 (s, 3H), 1.95 (s, 3H), 2.20 (s, 3H), 3.74 (s, 2H), 4.50 (s, 2H), 7.00–7.70 (m, 4H). Mass (EI) 422 (M^+).

***N*-Octadecyl-2-methyl-5-methoxyindole (10).** Commercial 60% sodium hydride (0.75 g, 19 mmol) in DMSO (21 mL) was added to 2-methyl-5-methoxyindole (15 mg, 9.3 mmol) with cooling in an ice bath, and then the mixture was stirred for 1 h at room temperature. This was then cooled in an ice bath, and octadecylbromide (3.5 g, 10 mmol) was added to the mixture. The reaction mixture was stirred for 3 h at room temperature and then poured into water. It has then extracted with hexane; the organic phase was dried over anhydrous magnesium sulfate and evaporated in vacuo. The mixture was purified by recrystallization with ethanol to give 2.9 g **10** in 75% yield. **10**: Yellow crystals. ^{1}H NMR ($CDCl_3$) δ 0.86–1.71 (m, 3H), 2.39 (s, 3H), 3.83 (s, 3H), 4.00 (t, J = 8 Hz, 2H), 6.15–7.25 (m, 4H).

***N*-Cyanomethyl-2-methyl-1-(*N*-octadecyl)indole-3-glycoxylamide (11).** A dichloromethane solution (130 mL) containing 78 mg (0.37 mmol) of aminoacetonitrile sulfate and 0.13 mL (0.96 mmol) of triethylamine was refluxed for 4 h. In another flask, 30 mg (0.24 mmol) of oxalyl chloride was added to a 1,2-dichloroethane solution (8 mL) of *N*-octadecyl-2-methyl-5-methoxyindole (**10**) (0.10 g, 0.24 mmol) and the mixture was refluxed for 3 h. To this reaction mixture, the dichloromethane solution was added, and the resulting mixture was stirred for 12 h at room temperature. The reaction mixture was extracted with chloroform, after the addition of 50 mL of 2 M hydrochloric acid. The organic phase was dried over anhydrous magnesium sulfate and evaporated in vacuo. The residue was recrystallized from ethyl acetate to give 96 mg of **11** in 77% yield. **11**: Yellow crystals. mp. 119–120 °C. ^{1}H NMR ($CDCl_3$) δ 0.70–1.82 (m, 35H), 2.65 (s, 3H), 3.83 (s, 3H), 4.00 (t, 2H), 4.23 (d, J = 8 Hz, 2H), 6.70–7.83 (m, 3H).

***N*-Cyanomethyl-2-[2-methoxy-1-benzothiophen-3-yl]-3-[2-methyl-1-octadecylindol-3-yl]maleimide (2a).** A 0.14 mL (1.78 mmol) volume portion of oxalyl chloride was added to a benzene solution (14 mL) of 2-methoxy-1-benzothiophen-3-ylacetic acid (0.16 g, 0.71 mmol).[17] The mixture was stirred for 1 h, followed by 1 h of reflux. After benzene and excess oxalyl chloride were evaporated in vacuo, 5 mL of a 1,2-dichloromethane solution containing 0.375 mg (0.71 mmol) of **11** and 5 mL of triethylamine was added dropwise. After stirring for 40 h at room temperature, the reaction mixture was extracted with chloroform (100 mL) following the addition of 50 mL of water. The organic phase was washed with 2 M hydrochloric acid, dried over anhydrous magnesium sulfate, and evaporated in vacuo. The residue was purified by thin-layer chromatography on silica gel (hexane/ethyl acetate = 7/3) to give 0.342 mg of **2a** in 68% yield. **2a**: Orange crystals. mp. 73–74 °C. ^{1}H NMR ($CDCl_3$) δ 0.70–1.60 (m, 35H), 2.20 (s, 3H), 3.20 (s, 3H), 3.58 (s, 3H), 3.90 (t, J = 8 Hz, 2H), 4.53 (s, 2H), 6.36–7.55 (m, 7H). Mass (EI) 709 (M^+). Anal. Calcd for $C_{43}H_{55}N_3O_4S$: C, 72.74; H, 7.81; N, 5.92%. Found: C, 72.84; H, 7.84; N, 5.85%.

***N*-Cyanomethyl-2-[2-ethoxy-1-benzothiophen-3-yl]-3-[2-methyl-1-octadecylindol-3-yl]maleimide (3a).** **3a** was synthesized from **13**, which was produced from 100 mg (0.424 mmol) of 2-ethoxybenzothiophen-3-ylacetic acid and 229 mg (0.424 mmol) of **11** by the same procedure as that used for **2a**. The crude product was purified by thin-layer chromatography on silica gel (hexane/ethyl acetate = 7/3) to give 74 mg of **3a** in 24% yield. **3a**: Orange crystals. mp. 92–93 °C. ^{1}H NMR ($CDCl_3$) δ 0.72–1.60 (m, 38H), 2.20 (s, 3H), 3.20 (s, 3H), 3.58 (s, 3H), 4.12 (q, J = 8 Hz, 2H), 4.53 (s, 2H), 6.36–7.55 (m, 7H). Mass (EI) 723 (M^+). Anal. Calcd for $C_{44}H_{57}N_3O_4S$: C, 72.99; H, 7.94; N, 5.80%. Found: C, 73.15; H, 7.98; N, 5.76%.

References

1 M. Irie, *Chem. Rev.*, **100**, 1685 (2000).

2 M. Irie and K. Uchida, *Bull. Chem. Soc. Jpn.*, **71**, 985 (1998).

3 M. Irie, "Photo-Reactive Materials for Ultrahigh-Density Optical Memory," Elsevier, Amsterdam (1994).

4 M. Hanazawa, R. Sumiya, Y. Horikawa, and M. Irie, *J. Chem. Soc., Chem. Commun.*, **1992**, 206.

5 M. Irie and M. Mohri, *J. Org. Chem.*, **53**, 803 (1988).

6 Y. Nakayama, K. Hayashi, and M. Irie, *Bull. Chem. Soc. Jpn.*, **64**, 789 (1991).

7 T. Yamaguchi and M. Irie, *Chem. Lett.*, **2005**, 64.

8 T. Yamaguchi, K. Uchida, and M. Irie, *J. Am. Chem. Soc.*, **119**, 6066 (1997).

9 K. Uchida, Y. Kido, T. Yamaguchi, and M. Irie, *Bull. Chem. Soc. Jpn.*, **71**, 1101 (1998).

10 T. Yamaguchi, Y. Fujita, and M. Irie, *Chem. Lett.*, **2004**, 1398.

11 M. M. Krayushkin, V. Z. Shirinyan, L. I. Bereńkil, A. A. Shirnkin, A. Y. Martynkin, and B. M. Uzhinov, *Russ. J. Org. Chem.*, **38**, 1335 (2002).

12 H. Tian, C. Bingzhi, and P. Liu, *Chem. Lett.*, **2001**, 990.

13 D. G. Crowe, *Appl. Opt.*, **30**, 4480 (1991).

14 M. Hamano and M. Irie, *Jpn. J. Appl. Phys.*, **35**, 1764 (1996).

15 M. Irie and K. Sayo, *J. Phys. Chem.*, **96**, 7671 (1992).

16 H. Kaczmarek, A. Kamińska, and A. van Herk, *Eur. Polym. J.*, **36**, 767 (2000).

17 R. Salo and S. Jan, *Acta Chem. Scand.*, **24**, 304 (1970).