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Syntheses and Photochromic Properties of Diarylethenes with a Naphthalene and a Thiophene Ring

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Two types of diarylethene, each of which contains a naphthalene and a thiophene ring, were synthesized, and their photochromic properties were studied. The photochromic properties are dependent on the bridge position of the

Introduction

Photochromic compounds have been vigorously studied because they are expected to be photomemory materials. Diarylethene is the one of the most attractive photochromic molecules because of its high fatigue resistance and the thermal irreversibility of its photochromism.^[1] A highly effective photochromic reaction is an essential feature for molecular photomemory, and an extremely high photocyclization reaction quantum yield has recently been found by fixing the conformation of a diarylethene with a bridging moiety (i.e., cyclophan-1-ene)^[2] or through intramolecular hydrogen bonding.^[3] However, to the best of our knowledge, despite attempts to control the cycloreversion quantum yields by changing the substituents,^[4] photon-quantitative reactions (when the quantum yield is almost 1.0 in solution) have not yet been reported. A highly efficient photochromic reaction and the thermal stability of both photoisomers are essential for photomemory. High thermal irreversibility can be achieved by using different diarylethene aromatic rings,^[1] and dithienylethenes, in which both aromatic rings are thiophene rings, were first developed by Irie and co-workers and are promising candidates for photomemory and photoswitching devices.^[5-10] Thiophene has a low aromatic stabilization energy compared with that of benzene; hence, the energy difference between the aromatic dithienylethene open form and the nonaromatic closed form is smaller than that of stilbene.^[1] Diarylethenes with two naphthalene rings have also been synthesized and show thermally irreversible photochromism.^[11] However, only one basic diarylethene structure with both a thiophene and a naphthalene ring has

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thiophene ring. The cycloreversion of one of the closed forms of some of the diarylethenes occurred almost photon quantitatively, and the photochromic reactions were thermally irreversible, at least at room temperature.

been reported.^[12] These facts prompted us to develop diarylethenes with both a thiophene and a naphthalene ring and to investigate their photochromic properties.

Results and Discussion

The diarylethenes with a thiophene and a naphthalene ring have been synthesized as shown in Scheme 1. We prepared four diarylethenes of two types: two are bridged at the 3-position of the thiophene ring (1a and 2a), and two are bridged at the 2-position (3a and 4a). The ¹H NMR spectrum of 1a at room temperature revealed that there were two conformations of the open ring form present in a 1:1 ratio. These conformations are assignable to the antiparallel and parallel conformations, according to a previous study.^[1] The antiparallel form is photoactive, and the parallel form is photoinactive; therefore, the existence of the parallel conformation may decrease the photocyclization quantum yield. Four stable conformations of 2a were observed by ¹H NMR spectroscopy. DFT calculations (B3LYP/6-31G*) for 2a with the Spartan program^[13] indicated that two of the conformations were antiparallel and the others were parallel (Figure 1). The DFT calculations revealed that the ratio of antiparallel to parallel conformations was 4:6. Different conformations were not indicated by the ¹H NMR spectra of 3a and 4a; the rotational barrier may be too low to show separate ¹H NMR spectra.

Figure 2 shows the absorption spectral changes of the diarylethenes 1a/1b, 2a/2b, 3a/3b, and 4a/4b in n-hexane. The colorless solutions turned red or yellow upon UV irradiation, and new absorption maxima appeared in the visible region. The colors and spectra returned to their initial states after irradiation in the visible region. The spectral changes of 3a/3b and 4a/4b were much smaller than those of 1a/1b and 2a/2b, as shown in Figure 2. The conversions at the photostationary state under irradiation with 313 nm light

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Scheme 1. Synthesis of diarylethenes composed of a thiophene and a naphthalene ring.



Figure 1. Four stable conformations of **2a** obtained by DFT calculations (B3LYP/6-31G*) with Spartan '08: (a) and (b) have antiparallel conformations, and (c) and (d) have parallel conformations. The calculated ratio was (a)/(b)/(c)/(d) = 0.16/0.24/0.33/0.27.

were estimated by HPLC analyses.^[14] The ratios of the photoisomers were determined by measuring the corresponding absorption areas at the isosbestic points. The results are summarized in Table 1. For instance, the conversion of **3a**/ **3b** was only 12.6%, which implies that the photostationary state of **3a/3b** at 313 nm consisted of 87.4% of the open form and 12.6% of the closed form. The extinction coefficients of the open form **3a** and the closed form **3b** were almost the same at 313 nm; therefore, one can consider that the cyclization quantum yield is quite low compared to the cycloreversion quantum yield or vice versa. The quantum yields of the diarylethene cyclization and cycloreversion reactions were measured and are shown in Table 1.^[15] The quantum yields for the photocyclization reactions were measured at 313 nm, and those for the cycloreversions were obtained by means of visible light (517 or 435 nm).



Figure 2. Absorption spectral changes of **1**, **2**, **3**, and **4** in *n*-hexane upon irradiation with 313 nm light.

Table 1. Conversions^[a] at 366 nm and quantum yields for photocyclization and cycloreversion reactions.

	Conversion [%][a]	$\Phi_{ m cyclization}$	$\Phi_{ m cycloreversion}$
1	30.8	0.34 (313 nm)	0.62 (517 nm)
2	34.5	0.32 (313 nm)	0.29 (517 nm)
3	12.6	0.25 (313 nm)	0.29 (435 nm)
4	21.7	0.23 (313 nm)	0.95 (435 nm)
9 ^[16]	_[b]	0.21 (280 nm)	0.13 (492 nm)
10 ^[16]	77	0.40 (366 nm)	0.58 (425 nm)

[a] Determined by HPLC. [b] Not reported.

As expected, the quantum yield of the cycloreversion reaction of the closed form of **4b** is quite high, 0.95, and is almost quantitative (Figure 2). On the other hand, that of **3b** is 0.29. In spite of the very low conversion, such a small quantum yield could be responsible for the wavelength-dependence of the quantum yield. The reasons for these remarkable quantum yields are still obscure, but it has been reported that dithienylethenes with thiophene rings connected at the 2-position tend to show high cycloreversion quantum yields.^[16] For example, Table 1 shows the quantum yields of the reported dithienylethenes **9** and **10**. Indeed, the quantum yield for the cycloreversion of **10** was much larger than that of **9**. Compounds **3a** and **4a** are

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bridged at the 2-position of the thiophene rings, and the diational $10-\pi$ -electron naphthalene rings may enhance the clo



Another important feature for organic photomemory is thermal irreversibility; hence, the thermal cycloreversion reactions of the closed forms 1b, 2b, 3b, and 4b were studied. Sealed toluene solutions of 1b, 2b, 3b, and 4b were stored at 100 °C in the dark. After 3 h of heating, no changes were observed in the absorption spectra of the photostationary states of 2a/2b, 3a/3b, and 4a/4b, but the absorption spectrum of 1a/1b changed slightly. Next, the thermal cycloreversion reaction rates of 1b were measured at various temperatures, and the activation energy was estimated from the Arrhenius plot (Figure 3). The activation energy and the pre-exponential factor of the thermal cycloreversion of 1b were 134 kJmol^{-1} and $6.3 \times 10^{13} \text{ s}^{-1}$, respectively, and the calculated half-life at 20 °C was ca. 250 years. Therefore, the photocyclization of 1b is thermally reversible, but it still has a long lifetime at ambient temperatures.



Figure 3. Arrhenius plot for the thermal cycloreversion of 1b in toluene.

Conclusions

Diarylethenes with both a thiophene and a naphthalene ring showed almost thermally irreversible photochromic properties. The photocycloreversion quantum yield for one diarylethene was almost photon quantitative, and the photocyclization reaction quantum yields were relatively low. If an extra bridge was formed, the conformation could be fixed in the photoactive antiparallel conformation, and the photocyclization reaction efficiency would be increased. Our future research will be the development of further cyclophan-1-ene systems with a thiophene and a naphthalene ring to obtain much more efficient photochromic compounds such as those we have already reported.^[2,17]

Experimental Section

General Remarks: Absorption spectra were measured with an absorption spectrophotometer (Hitachi, U-3310). ¹H NMR spectra were recorded with a JEOL-AL300 FT-NMR spectrometer at 300 MHz. All chemical shifts are given in ppm relative to that of tetramethylsilane (TMS), and coupling constants are given in Hz. Mass spectra were recorded with a JEOL JMS-GCMATE II spectrometer (EI, 70ev). Photoirradiation was performed with a 500 W super-high-pressure mercury lamp, and monochromic light was obtained by passing it through a monochromator (JOBIN YVON). The quantum yields were determined by a similar manner to that described previously.^[15]

1-(2,3,3,4,4,5,5-Heptafluoro-1-cyclopenten-1-yl)-2-methylnaphthalene (6):^[2] To a flame-dried 1000 mL round-bottomed flask, 1bromo-2-methylnaphthalene (5; 25.0 g 114 mmol) and dry tetrahydrofuran (THF, 220 mL) were added, and the solution was cooled to -70 °C in a dry-ice-acetone bath under an Ar atmosphere. To this solution, a 1.6 N nBuLi in hexane solution (89.0 mL) was added dropwise, and the mixture was stirred for 30 min at this temperature. A dry THF (30 mL) solution of 1,2,3,3,4,4,5,5-octafluorocyclopentene (15.2 g, 114 mmol) was added dropwise, and the mixture was stirred for 2 h at the same temperature; the bath was then removed, and the mixture was stirred at room temperature overnight. Methanol and brine were added to the solution, and the organic layer was separated and washed with brine twice. The mixture was dried with MgSO₄, and the solvent was evaporated in vacuo. Recrystallization (MeOH) of the residue afforded 6 (19.8 g, 59.1 mmol) as colorless prisms in 52.1% yield; m.p. 61.8-63.2 °C. ¹H NMR (300 MHz, CDCl₃): δ = 2.43 (s, 3 H), 7.48 (d, J = 8 Hz, 1 H), 7.47–7.55 (m, 3 H), 7.86–7.92 (m, 2 H) ppm. HRMS (EI): calcd. for C₁₆H₉F₇ [M]⁺ 334.0592; found 334.0592.

2,4-Dimethyl-3-[3,3,4,4,5,5-hexafluoro-2-(2-methyl-1-naphthalenyl)-1-cyclopenten-1-yllthiophene (1a): To a flame-dried 200 mL round-bottomed flask, 3-bromo-2,4-dimethylthiophene (7a; 1.0 g 5.24 mmol)^[16] and dry THF (50 mL) were added, and the solution was cooled to -70 °C in a dry-ice-acetone bath under an Ar atmosphere. To this solution, a 1.6 N *n*BuLi in hexane solution (3.9 mL) was added dropwise, and the mixture was stirred for 30 min at this temperature. A dry THF (30 mL) solution of 6 (1.59 g, 4.80 mmol) was added dropwise, and the mixture was stirred for 2 h at the same temperature; the bath was then removed, and the mixture was stirred at room temperature overnight. Methanol and brine were added to the solution, and the organic layer was separated and washed with brine twice. The mixture was dried with MgSO₄, and the solvent was evaporated in vacuo. The residue was subjected to silica gel column chromatography, and the hexane eluate was evaporated in vacuo. Recrystallization (MeOH) of the residue afforded 1a (0.65 g, 1.54 mmol) as colorless prisms in 32% yield; m.p. 113.0–115.0 °C. ¹H NMR (300 MHz, CDCl₃): δ = 1.91 (s, 1.5 H), 2.15 (s, 1.5 H), 2.16 (s, 1.5 H), 2.42 (s, 1.5 H), 2.43 (s, 3 H), 6.50 (s, 0.5 H), 6.60 (s, 0.5 H), 7.28 (d, J = 9 Hz, 1 H), 7.42–7.51 (m, 2 H), 7.75–7.80 (m, 3 H) ppm (parallel/antiparallel 1:1). HRMS (EI): calcd. for C₂₂H₁₆F₆S [M]⁺ 426.0877; found 426.0878.

2,4-Dimethyl-3-[3,3,4,4,5,5-hexafluoro-2-(2-methyl-1-naphthalenyl)-1-cyclopenten-1-yl]-5-phenylthiophene (2a): To a flame-dried Date: 05-05-14 17:56:46

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200 mL round-bottomed flask, 3-bromo-2,4-dimethyl-5-phenylthiophene (7b; 0.80 g, 3.0 mmol)^[18] and dry THF (65 mL) were added, and the solution was cooled to -70 °C in a dry-ice-acetone bath under an Ar atmosphere. To this solution, a 1.6 N nBuLi in hexane solution (2.2 mL) was added dropwise, and the mixture was stirred for 30 min at this temperature. A dry THF (30 mL) solution of 6 (1.19 g, 3.55 mmol) was added dropwise, and the mixture was stirred for 2 h at the same temperature; the bath was then removed, and the mixture was stirred at room temperature overnight. Methanol and brine were added to the solution, and the organic layer was separated and washed with brine twice. The mixture was dried with MgSO₄, and the solvent was evaporated in vacuo. The residue was subjected to silica gel column chromatography, and the hexane eluate was evaporated in vacuo. Recrystallization (MeOH) of the residue afforded 2a (0.65 g, 1.29 mmol) as colorless prisms in 43% yield; m.p. 113.0–114.5 °C. ¹H NMR (300 MHz CDCl₃): $\delta = 1.93$ (s, 1.5 H), 2.17 (s, 0.75 H), 2.17 (s, 0.75 H), 2.21 (s, 1.5 H), 2.44 (s, 0.75 H), 2.44 (s, 0.75 H), 2.46 (s, 1.5 H), 2.46 (s, 1.5 H), 7.14-7.16 (m, 1 H), 7.26–7.35 (m, 4.5 H), 7.43–7.52 (m, 2 H), 7.78–7.81 (m, 3.5 H) ppm (a mixture of several conformations). HRMS (EI): calcd. for C₂₈H₂₀F₆S [M]⁺ 502.1190; found 502.1190.

3,5-Dimethyl-2-[3,3,4,4,5,5-hexafluoro-2-(2-methyl-1-naphthalenyl)-1-cyclopenten-1-yl]thiophene (3a): To a flame-dried 500 mL round-bottomed flask, 2,4-dimethylthiophene (8a; 1.12 g, 10.0 mmol),^[19] N,N,N',N'-tetramethylethylenediamine (TMEDA; 1.8 mL 11.7 mmol), and dry diethyl ether (130 mL) were added, and the solution was cooled to 0 °C in an ice bath under an Ar atmosphere. To this solution, a 1.6 N nBuLi in hexane solution (7.6 mL) was added dropwise, and the mixture was heated to reflux for 45 min. The mixture was cooled to -70 °C, and a dry diethyl ether (70 mL) solution of 1 (3.3 g, 9.0 mmol) was added dropwise at this temperature, and the mixture was stirred for 2 h at the same temperature; the bath was then removed, and the mixture was stirred at room temperature overnight. Methanol and brine were added to the solution, and the organic layer was separated and washed with brine twice. The mixture was dried with MgSO₄, and the solvent was evaporated in vacuo. The residue was subjected to silica gel column chromatography, and the hexane eluate was evaporated in vacuo. Recrystallization (n-hexane) of the residue afforded **3a** (0.65 g, 1.29 mmol) as colorless prisms in 43% yield; m.p. 66.9–68.7 °C. ¹H NMR (300 MHz CDCl₃): δ = 2.16 (s, 3 H), 2.17 (s, 3 H), 2.37 (s, 3 H), 6.40 (s, 1 H), 7.37 (d, J = 8 Hz, 1 H), 7.44-7.48 (m, 2 H), 7.58-7.62 (m, 1 H), 7.81-7.86 (m, 2 H) ppm. HRMS (EI): calcd. for C₂₂H₁₆F₆S [M]⁺ 426.0877; found 426.0870.

2-[3,3,4,4,5,5-Hexafluoro-2-(2-methyl-1-naphthalenyl)-1-cyclopenten-1-yl]-3-methyl-5-phenylthiophene (4a): To a flame-dried 300 mL round-bottomed flask, 4-methyl-2-phenylthiophene (8b; 1.00 g, 5.7 mmol),^[20] TMEDA (1.0 mL, 6.5 mmol), and dry diethyl ether (60 mL) were added, and the solution was cooled to 0 °C in an ice bath under an Ar atmosphere. To this solution, a 1.6 N nBuLi in hexane solution (4.2 mL) was added dropwise, and the mixture was heated to reflux for 1 h. The mixture was cooled to -70 °C, and at this temperature, a dry diethyl ether (70 mL) solution of 1 (2.1 g, 6.3 mmol) was added dropwise, and the mixture was stirred for 2 h at the same temperature; the bath was then removed, and the mixture was stirred at room temperature overnight. Methanol and brine were added to the solution, and the organic layer was separated and washed with brine twice. The mixture was dried with MgSO₄, and the solvent was evaporated in vacuo. The residue was subjected to silica gel column chromatography, and the hexane eluate was evaporated in vacuo. Recrystallization (*n*-hexane) of the residue afforded **4a** (0.56 g, 1.15 mmol) as colorless prisms in 20% yield; m.p. 74.4–76.5 °C. ¹H NMR (300 MHz CDCl₃): δ = 2.21 (s, 3 H), 2.41 (s, 3 H), 6.92 (s, 1 H), 7.21–7.28 (m, 4 H), 7.38 (d, *J* = 8 Hz, 1 H), 7.43–7.51 (m, 2 H), 7.64 (d, *J* = 8 Hz, 1 H), 7.81–7.87 (m, 2 H) ppm. HRMS (EI): calcd. for C₂₇H₁₈F₆S [M]⁺ 488.1033; found 488.1041.

Supporting Information (see footnote on the first page of this article): NMR spectra of **1a–4a** and HPLC charts for the open forms and the photostationary states of diarylethenes **1–4**.

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Diarylethenes with a Naphthalene and a Thiophene Ring



Photochromism



Thermally irreversible photochromic diarylethenes with a naphthalene and a thiophene ring are synthesized, and their photochromic properties are studied. The quantum yield for the photocycloreversion of one diarylethene is very high. Except for one example, both photoisomers of the diarylethenes are thermally stable at ambient temperature; hence, they are candidates for molecular photomemory.

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Syntheses and Photochromic Properties of Diarylethenes with a Naphthalene and a Thiophene Ring

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