Pergamon

Tetrahedron 57 (2001) 4559–4565

TETRAHEDRON

Substituent effect on the photochromic reactivity of bis(2-thienyl)perfluorocyclopentenes

Kingo Uchida,[a,*] Toyokazu Matsuoka,[a] Seiya Kobatake,[b] Tadatsugu Yamaguchi[c] and Masahiro Irie[b,*]

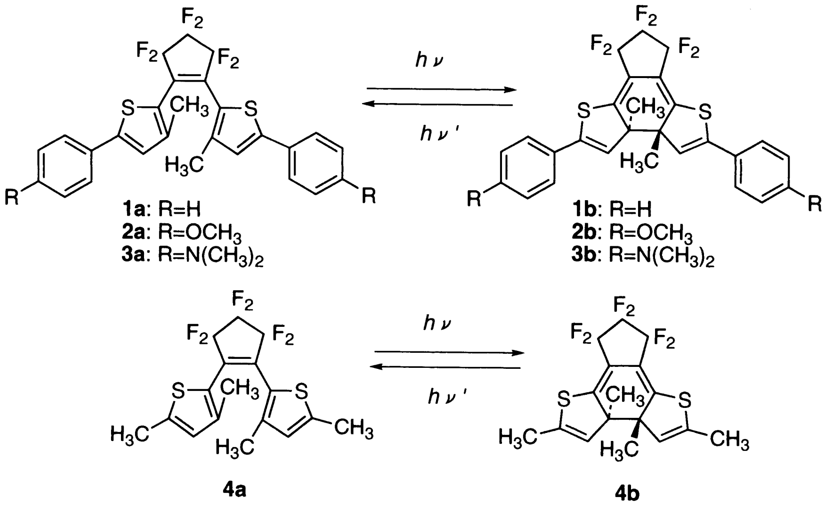
[a]*Department of Materials Chemistry, Faculty of Science and Technology, Ryukoku University, Seta, Otsu 520-2194, Japan*
[b]*Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University and CREST, Japan Science and Technology Corporation (JST), 6-10-1 Hakozaki, Fukuoka 812-8581, Japan*
[c]*Department of Applied Materials Science, College of Engineering, Osaka Prefecture University, 1-1 Gakuen-cho, Sakai, Osaka 599-8531, Japan*

Received 13 February 2001; accepted 3 April 2001

Abstract—Substituent effect on the photochromic reactivity of bis(2-thienyl)perfluorocyclopentenes was examined. Introduction of phenyl groups having electron-donating substituents on the *para*-position of the phenyl ring to the 5-position of the thiophene rings shifted the absorption bands of the open-ring isomers to longer wavelengths and reduced the quantum yield of the cyclization reactions. The substitution with *p*-(*N*,*N*-diethylamino)phenyl groups prohibited the cyclization reaction. The absorption spectra of the closed-ring isomers were not influenced by the substitution. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

Photochromic diarylethenes that undergo thermally irreversible and fatigue-resistant photo-cyclization and photo-cycloreversion reactions have been developed.[1,2] So far, furan, thiophene, and benzothiophene rings were connected to the ethene moiety at the 3-position. The 1,2-bis(3-thienyl)ethene derivatives convert to the cyclohexadiene derivatives with the absorption bands at longer wavelengths by photo-irradiation. The elongation of the conjugation length of the aryl groups by the introduction of phenylene or 2,4-thienylene rings in the 1,2-bis(3-thienyl)ethene framework showed the red-shift of the visible absorption bands of the closed-ring isomers.[3]

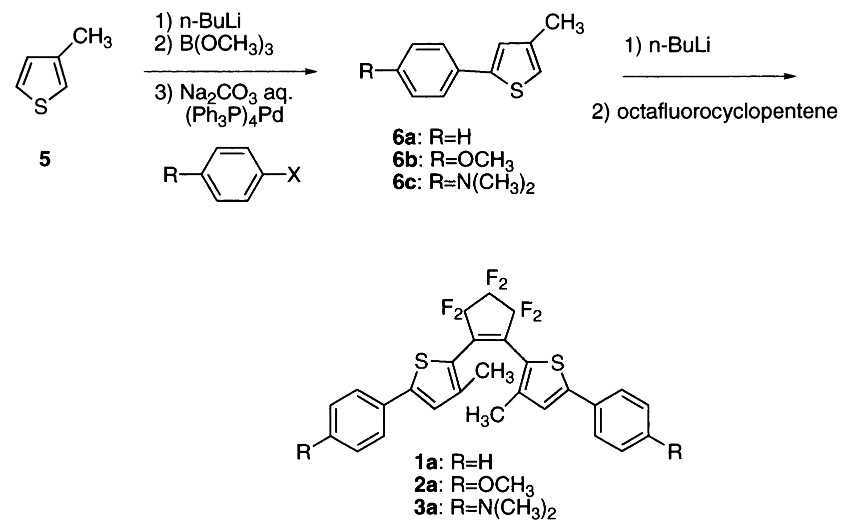


Scheme 1.

Keywords: photochromism; diarylethene; substituent effect; spectral shift; quantum yield.

[*] Corresponding authors. Fax: +81(0)77-543-7483; e-mail: uchida@chem.ryukoku.ac.jp

PII: S0040-4020(01)00389-1



Scheme 2.

The absorption characteristic is dependent on the connection positions of the aryl groups.[4] When the thiophene rings are attached to the ethene moiety at the 2-position, the elongation of the conjugation length shifts the absorption bands of the open-ring isomers to longer wavelengths, while the shift of the closed-ring isomers is insignificant.[4–8] Herein we have synthesized 1,2-bis(3-methyl-5-phenyl-2-thienyl)perfluorocyclopentene **1a**, 1,2-bis[3-methyl-5-(*p*-methoxyphenyl)-2-thienyl]perfluorocyclopentene **2a** and 1,2-bis[3-methyl-5-(*p*-*N*,*N*-diethylaminophenyl)-2-thienyl]-perfluorocyclopentene **3a** and compared the photochromic performance with 1,2-bis(3,5-dimethyl-2-thienyl)perfluorocyclopentene **4a** (Scheme 1).[3]

2. Results and discussion

2.1. Synthesis of 1,2-bis(3-methyl-5-phenyl-2-thienyl)-perfluorocyclopentene (1a), 1,2-bis[3-methyl-5-(*p*-methoxyphenyl)-2-thienyl]perfluorocyclopentene (2a) and 1,2-bis[3-methyl-5-(*p*-*N*,*N*-diethylaminophenyl)-2-thienyl]perfluorocyclopentene (3a)

The 1,2-bis(2-thienyl)perfluorocyclopentene derivatives, 1,2-bis(3-methyl-5-phenyl-2-thienyl)perfluorocyclopentene (**1a**), 1,2-bis[3-methyl-5-(*p*-methoxyphenyl)-2-thienyl]perfluorocyclopentene (**2a**), and 1,2-bis[3-methyl-5-(*p*-*N*,*N*-diethylaminophenyl)-2-thienyl]perfluorocyclopentene (**3a**) were prepared by the method shown in Scheme 2.

The hexane solution of **1a** is colorless and the absorption maximum was observed at 370 nm (ε: 2.28×10^4 M^{-1} cm^{-1}; 1 M=1 mol dm^{-3}). Introduction of the phenyl rings on the 5-positions of the thiophene moieties shifted the absorption maximum by as much as 34 nm and the absorption coefficient was twice as large as that of 1,2-bis(3,5-dimethyl-2-thienyl)perfluorocyclopentene **4a** (λ_{max}: 336 nm; ε: 1.3×10^4 M^{-1} cm^{-1}).[8] Fig. 1 shows the absorption spectral change of **1a**. Upon irradiation with UV light, the hexane solution turned yellow, in which the absorption maximum was observed at 438 nm (ε: 5.25×10^3 M^{-1} cm^{-1}). The spectrum of the isolated closed-ring isomer **1b** is also shown in Fig. 1. The photo-generated 438 nm band is due to the closed-ring isomer **1b**. Isomer **4b** has the absorption maximum at 425 nm (ε: 5.8×10^3 M^{-1} cm^{-1}), which is similar to **1b**.[4]

Fig. 2 illustrates the absorption spectral change of the

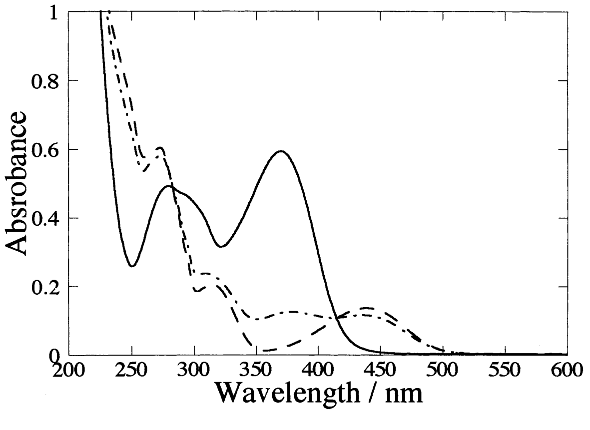


Figure 1. Absorption spectra of hexane solutions of **1a** (2.63×10^{-5} M^{-1} cm^{-1}) (solid line), **1b** (broken line), and the photostationary state (broken-dotted line; the population ratio of **1a** to **1b** is 18:82) under irradiation with 366 nm light.

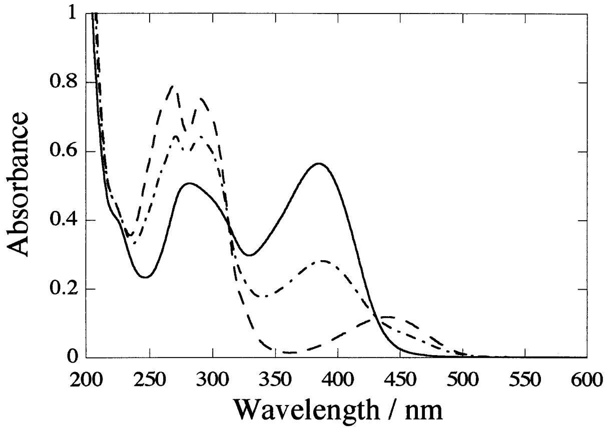


Figure 2. Absorption spectra of hexane solutions of **2a** (2.22×10^{-5} M^{-1} cm^{-1}) (solid line), **2b** (broken line), and the photostationary state (broken-dotted line; the population ratio of **2a** to **2b** is 47:53) under irradiation with 366 nm light.

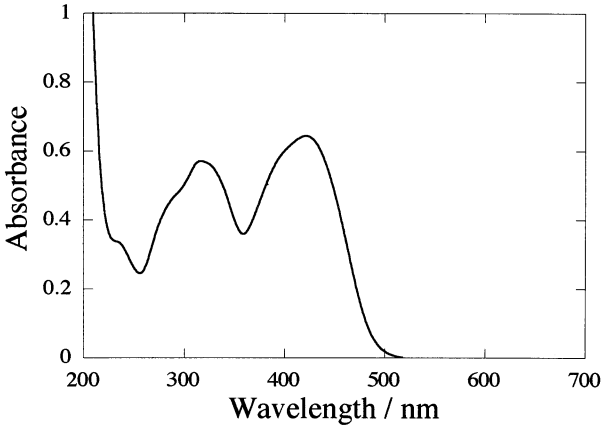


Figure 3. Absorption spectrum of hexane solutions of **3a** (2.87×10^{-5} M^{-1} cm^{-1}).

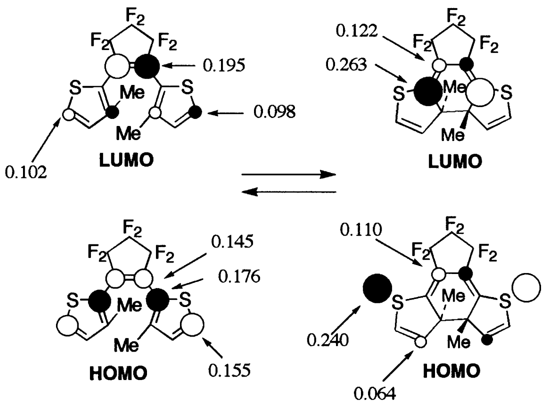


Figure 4. HOMO and LUMO orbitals and their electron densities of the 1,2-bis(3-methyl-2-thienyl)perfluorocyclopentene backbone.

hexane solution of **2a** (λ_{max}: 385 nm; ε: 2.53×10^4 M^{-1} cm^{-1}). Upon irradiation with 366 nm light, the absorption band at 385 nm decreased accompanied with the formation of a yellow color in which an absorption shoulder was observed around 450 nm. The spectrum of the isolated closed-ring isomer is also shown in Fig. 2. The closed-ring isomer showed the absorption maximum at 440 nm (ε: 5.3×10^3 M^{-1} cm^{-1}). The spectral shift by the introduction of the *p*-methoxyphenyl rings was negligible.[9]

In order to confirm that the spectral changes are due to the photo-cyclization and photo-cycloreversion, the photochromic reaction was also monitored by ^{1}H NMR spectra.[1,5] The methyl signals of **2a** were observed at 2.23 ppm in $CDCl_3$. Upon UV irradiation, a new signal appeared at 1.96 ppm, which is attributable to the methyl signal of the closed-ring isomer **2b**. The signal disappeared under visible light irradiation.

Fig. 3 shows the absorption spectrum of **3a**. The absorption band (λ_{max}: 421 nm; ε: 2.59×10^4 M^{-1} cm^{-1}) shifted by as much as 85 nm in comparison with **4a**. No spectral change was observed upon irradiation with any wavelength. The result indicates that the introduction of *N*,*N*-diethylamino groups causes the red-shift of the absorption band of open-ring isomers, enhances the absorption coefficients, and reduces the cyclization quantum yield. This substituent effect is in contrast to the effect observed in bis(5-phenyl-3-thienyl)perfluorocyclopentenes, in which the absorption maximum of the closed-ring isomers shows a remarkable red-shift by the introduction of electron-donating groups.[3]

To explain the red-shift of the absorption bands of **1a**, **2a** and **3a**, we calculated the electron densities of HOMO and LUMO orbitals of open-and closed-ring isomers of 1,2-bis(3-methyl-2-thienyl)perfluorocyclopentene by using the MOPAC program of the CAChe system. The calculated results are shown in Fig. 4. In the open-ring isomer, the electron densities at 5-positions are relatively high. Introduction of electron-donating substituents will destabilize the HOMO orbital, resulting in the bathochromic shift of the absorption bands of the open-ring isomer. On the other hand, the electron density at 5-positions of the closed-ring isomer is almost zero. Therefore, the introduction of electron-donating substituents does not affect the absorption band of the closed-ring isomers at longer wavelengths.

2.2. Quantum yield

The quantum yields of cyclization and cycloreversion reactions of **1** and **2** were measured in hexane at room temperature. Light of appropriate wavelength was isolated by passing light from mercury and Xe lamps through a monochromator, and this was used to induce the reactions. The results are summarized in Table 1. The cyclization quantum yield was found to depend on the introduction of the substituents.[9] The quantum yield of the cyclization reaction of **1a** was determined to be 0.17, while the yield of **2a** decreased to 0.045. Compared with the yield of **4a** (ϕ= 0.40), the cyclization reactivity is low. In the case of 1,2-bis(3-thienyl)ethenes, whose thiophene rings are attached to the ethene moiety at the 3-positions, such as diarylethenes having oligothiophenes,[9] the cycloreversion quantum yields was strongly suppressed by the introduction of long

Table 1. Absorption maxima and their coefficients for the open-ring and closed-ring isomers of bis(2-thienyl)perfluorocyclopentenes, and the quantum yields of photo-induced cyclization and cycloreversion reactions in hexane

	λ_{max}/nm (ε_{max}/M^{-1} cm^{-1})	$\Phi_{a\to b}$		λ_{max}/nm (ε_{max}/M^{-1} cm^{-1})	$\Phi_{b\to a}$
1a	370 (2.28×10^4)	0.17 (366 nm)[a]	**1b**	438 (5.25×10^3)	0.48 (440 nm)[a]
2a	385 (2.53×10^4)	0.045 (366 nm)	**2b**	440 (5.30×10^3)	0.40 (440 nm)[a]
3a	421 (2.59×10^4)	0.00	**3b**	–	–
3a	450 (2.65×10^4)[b]	0.14 (366 nm)[a–c]	**3b**	318 (4.49×10^4)[b]	0.32 (440 nm)[a,b]
4a	336 (1.3×10^4)	0.40 (366 nm)[a]	**4b**	425 (5.8×10^3)	0.58 (425 nm)[a]

[a] Quantum yields were measured at the wavelengths.
[b] Obtained in acetonitrile solution.
[c] Measured in the presence of CF_3COOH.

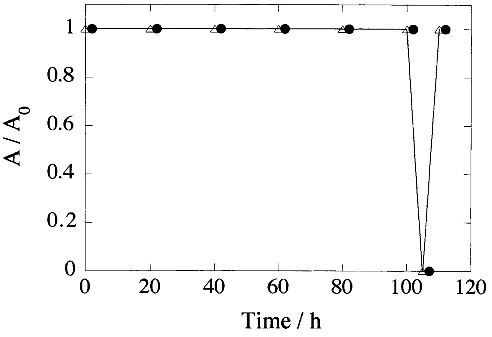


Figure 5. Thermal stability of the closed-ring isomers **1b** (●) and **2b** (△).

π-conjugated aryl groups. In a similar manner, the introduction of substituted phenyl groups is considered to suppress the cyclization quantum yield. Introduction of electron-donating *N*,*N*-diethylamino groups finally suppressed the photo-cyclization reaction. The reactivity was dependent on the electron-donating character of the substituents. This is attributable to the contribution of a twisted intramolecular charge transfer (TICT) character of the derivative.[10]

2.3. Fluorescence quantum yield

1,2-Bis(3-methyl-2-thienyl)perfluorocyclopentenes **1a**, **2a**, and **3a** exhibited fluorescence. The fluorescence quantum yields were measured using anthracene (ϕ_f=0.29) as a reference in hexane solution at room temperature. The excitation wavelength was 366 nm. The fluorescence quantum yields for **1a**, **2a**, and **3a** were determined to be 0.017, 0.038, and 0.039, respectively. No fluorescence was observed for closed-ring isomers **1b**, **2b**, and **3b**. This may be due to the non-conjugated structure of the closed-ring isomers.

2.4. Thermal stability of the closed-ring isomers

Fig. 5 illustrates the thermal stability of the closed-ring isomers, **1b** and **2b**, in a decalin solution at 80°C in the presence of air. The value of A/A_0 was plotted against the storage time in the dark, where A_0 is the initial absorbance at the absorption maximum of the closed-ring forms and A is the absorbance after *t* hours at 80°C. As can be seen in Fig. 5, the absorption intensity of the photo-generated closed-ring isomers **1b** and **2b** remained stable for 100 h. Upon irradiation with visible light (λ>480 nm), the color disappeared and colorless isomers **1a** and **2a** were regenerated. These results indicate that the photochromic reactivity was completely maintained after the heating.

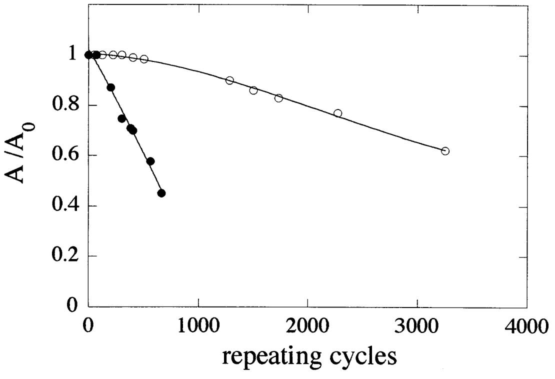


Figure 6. Fatigue-resistant property of diarylethene **1** [in ethanol (○); in hexane (●)].

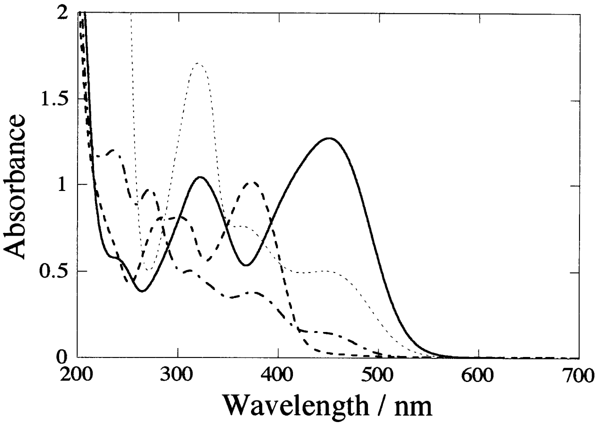


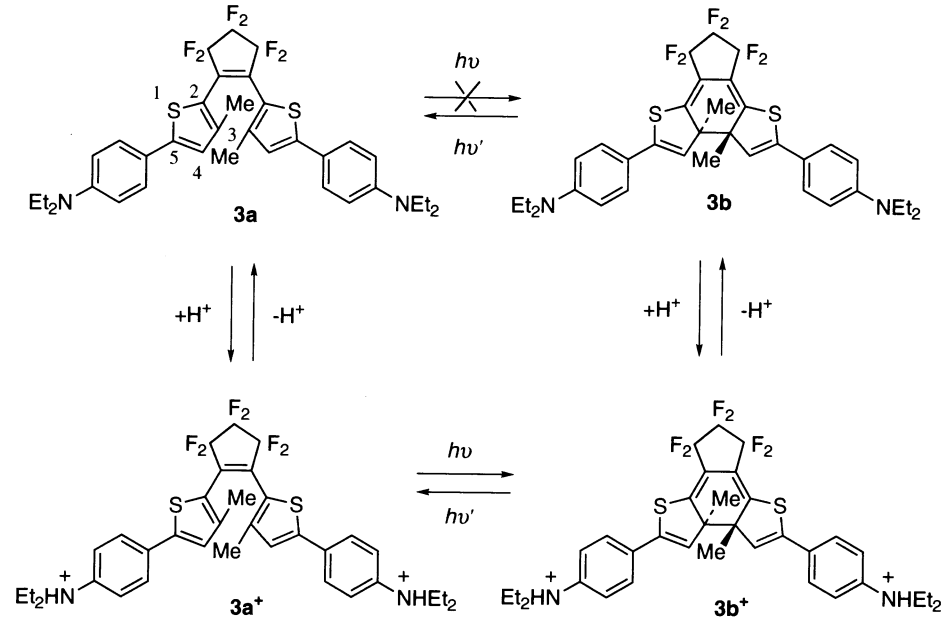
Figure 7. Gated photochromic system of diarylethene **3**. Solid line is the spectrum of **3a** in acetonitrile (4.8×10^{-5} M, 3.0 ml). Addition of trifluoroacetic acid (5.1 mg) generated **3a**$^+$ and changed the spectrum to that shown by the broken line. After UV irradiation the spectrum generated is shown by the broken-dotted line (the population ratio of **3a**$^+$ to **3b**$^+$ is 40:60). Following addition of triethylamine (8.5 mg) in the dark the spectrum shifted to that given by the dotted line. Visible light (λ>450 nm) irradiation regenerated the spectrum illustrated by the original solid line.

2.5. Fatigue-resistant property

Fatigue resistance, the number of times that photo-cyclization and cycloreversion reactions can be repeated without loss of performance, is an indispensable property for practical applications. Hexane and ethanol solutions of compound **1** (in thin cells with light pass length of 2 mm) were irradiated alternatively with 366 nm light for 10 s and visible light (λ>450 nm) for 40 s, and the absorption intensity at the wavelength of λ_{max} of the open-ring isomer (370 nm in hexane, 379 nm in ethanol) was plotted against the cycles, as shown in Fig. 6. The irradiation times were sufficiently long for the compound to convert to the photo-stationary state and to the photo-bleached state, respectively. The photochromic performance was maintained over 99% after 400 cyclization/cycloreversion cycles in ethanol, and then gradually declined.

2.6. Gated photochromic reaction of 3 by addition of acid[11,12]

Electron-donating *N*,*N*-diethylamino groups on phenyl rings prohibited the photo-cyclization reaction of bis(2-thienyl)-ethenes. Fig. 7 shows the absorption spectral change of **3a** by the addition of trifluoroacetic acid in acetonitrile. The spectral change indicates that the electron-donating character of the diethylamino groups disappeared with the protonation. The protonated **3a** underwent a normal photochromic reaction upon irradiation with UV (366 nm) and visible (λ>450 nm) light, as shown in Fig. 7. The quantum yield of the cyclization reaction of protonated **3a** was 0.14. The formed protonated closed-ring isomer **3b** returned to a neutralized form by the addition of triethylamine. The deprotonated **3b** underwent a cycloreversion reaction (ϕ= 0.32) upon irradiation with 440 nm light (Scheme 3).



Scheme 3.

The reaction was also monitored by ^{1}H NMR spectroscopy in CD_3CN. In the ^{1}H NMR spectrum of **3a**, the signals were observed at 1.13, 1.79, 3.38, 6.70, 7.04, and 7.44 ppm. The signals at 1.13 and 3.38 ppm are due to the diethylamino groups; the signal at 1.79 ppm due to methyl groups on the thiophene rings; the signals at 6.70 and 7.44 ppm due to the aromatic protons of phenylene moieties; and the signal at 7.04 ppm due to aromatic protons on thiophene rings. By the addition of trifluoroacetic acid, these signals were shifted to 1.13, 1.84, 3.61, 7.53, 7.39, and 7.86 ppm, respectively. A large shift was observed for the signals of the ethene moiety (3.38 to 3.61 ppm), and phenylene moieties (6.70 to 7.53 and 7.44 to 7.86 ppm, respectively). These shifts indicate the formation of quaternary ammonium salt by protonation. Upon irradiation with 366 nm light, new signals were observed at 1.57 (s, 3H), 6.56 (s, 1H), 7.58 (d, 2H, J= 8.8 Hz), and 7.75 (d, 2H, J=8.8 Hz) ppm, respectively. They disappeared upon visible light (λ>430 nm) irradiation; therefore they were attributable to the photo-generated closed-ring isomer.

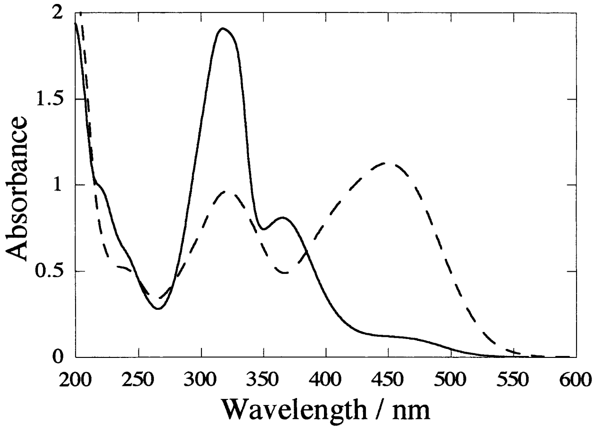


Figure 8. Absorption spectra of **3a** (4.26×10^{-5} M^{-1} cm^{-1}) (solid line) and **3b** (broken line) in acetonitrile.

Fig. 8 illustrates the absorption spectra of **3a** and **3b** in acetonitrile solution. The closed-ring isomer **3b** (λ_{max}: 318 nm; ε: 4.49×10^4 M^{-1} cm^{-1}) has the absorption band at shorter wavelength than that of **3a** (λ_{max}: 446 nm; ε: 2.65×10^4 M^{-1} cm^{-1}). This is the first diarylethene derivative that induces the hypsochromic spectral change upon photo-isomerization from the open- to closed-ring isomer. The photo-cyclization reaction requires the intermediate protonated form. This means that the recorded memory can be read many times based on the detection of the spectral change longer than 500 nm, where the closed-ring isomer has no absorption.

3. Conclusion

A series of bis(2-thienyl)perfluorocyclopentenes were synthesized to clarify the substituent effect of electron-donating groups on photochromic performance. The substitutions strongly affect the absorption spectra of open-ring isomers and the cyclization quantum yield.

4. Experimental

^{1}H NMR spectra were recorded on a Bruker DPX400 (400 MHz) spectrometer with $CDCl_3$ as the solvent and tetramethylsilane as an internal standard. The mass spectra (EI, 75 eV) were measured on a JEOL JMS-01-SG-2 mass spectrometer. The absorption spectra were measured using a Hitachi U-3410 spectrophotometer. Photo-irradiation was carried out using an USHIO 500 W high-pressure mercury and xenon arc lamp. Light of appropriate wavelength was isolated by passing the arc light through a monochromator (Ritsu MC-10N). The quantum yields were determined by comparing the reaction yields of the diarylethenes in hexane against furyl-fulgide in toluene.[13,14] The samples were not degassed.

4.1. Compound data

4.1.1. 4-Methyl-2-phenylthiophene (6a). To an ether solution (anhydrous, 40 ml) containing 3.0 g (30.6 mmol) of 3-methylthiophene (**5**), 19 ml (30.6 mmol) of 1.6N *n*-butyl lithium hexane solution was gradually added at 0°C. The solution was heated for 1 h under reflux. After cooling the solution to 0°C, 4.76 g (45.9 mmol) of trimethyl borate was gradually added. Then the solution was stirred for 1 h at room temperature, 20 w/w% Na$_2$CO$_3$ aqueous solution (32 ml), iodobenzene (6.20 g, 30.6 mmol), 50 ml of tetrahydrofuran, and 0.44 g of tetrakis(triphenylphosphine) palladium(0) were added and heated for 5 h under reflux with heavy stirring. After the heating was over, the reaction mixture was poured into the water, and the reaction mixture was extracted with ether three times. The combined organic layer was dried with MgSO$_4$, filtered and evaporated in vacuo. The residue was purified by column chromatography on silica gel (hexane) to give 5.04 g of 4-methyl-2-phenylthiophene (**6a**) in 89% yield.

6a: Colorless oil; ^{1}H NMR(CDCl$_3$) δ=2.29 (s, 3H), 6.85 (s, 1H), 7.13 (s, 1H), 7.25 (t, 1H, *J*=7.4 Hz), 7.36 (dd, 2H, *J*=7.4, 7.2 Hz), 7.58 (d, 2H, *J*=7.2 Hz); IR (KBr) 3040, 1590, 1495 cm^{-1}; MS (*m*/*z*) 174 (M$^+$). Found: C, 75.84; H, 5.82%. Calcd for $C_{11}H_{10}S$: C, 75.81; H, 5.78%.

4.1.2. 4-Methyl-2-(*p*-methoxyphenyl)thiophene (6b). 4-Methyl-2-(*p*-methoxyphenyl)thiophene (**6b**) was prepared from 3.00 g of 3-methylthiophene (30.6 mmol) and 7.16 g (30.6 mmol) of 4-iodoanisole by the same procedure as that used for **6a**. The crude product was purified by column chromatography on silica gel (hexane/chloroform=7/3) to give 1.55 g of **6b** in 25% yield.**6b**: Colorless prism, mp 56.4–57.9°C; ^{1}H NMR (CDCl$_3$) δ=2.27 (s, 3H), 3.83 (s, 3H), 6.79 (s, 1H), 6.90 (d, 2H, *J*=8.7 Hz), 7.01 (s, 1H), 7.50 (d, 2H, *J*=8.7 Hz); IR (KBr) 2940, 1605, 1550, 1245, 1150 cm^{-1}; MS (*m*/*z*) 204 (M$^+$). Found: C, 70.39; H, 6.05%. Calcd for $C_{12}H_{12}OS$: C, 70.54; H, 5.92%.

4.1.3. 4-Methyl-2-(*N*,*N*-diethylaminophenyl)thiophene (6c). 4-Methyl-2-(*N*,*N*-diethylaminophenyl)thiophene (**6c**) was prepared from 1.28 g of 3-methylthiophene (13.1 mmol) and 3.60 g (13.1 mmol) of *p*-*N*,*N*-diethylaminoiodobenzene by the same procedure as that used for **6a**. The crude product was purified by column chromatography on silica gel (hexane/chloroform=7/3) to give 1.33 g of **6c** in 41% yield.

6c: Pale yellow plates, mp 35.3–37.0°C; ^{1}H NMR (CDCl$_3$) δ=1.18 (t, 6H, *J*=7.0 Hz), 2.26 (s, 3H), 3.37 (q, 4H, *J*=7.0 Hz), 6.66 (d, 2H, *J*=8.9 Hz), 6.71 (s, 1H), 6.93 (s, 1H), 7.43 (d, 2H, *J*=8.9 Hz); IR (KBr) 2975, 1780 cm^{-1}; MS (*m*/*z*) 245 (M$^+$). Found: C, 73.25; H, 7.77; N, 5.68%. Calcd for $C_{15}H_{19}NS$: C, 73.43; H, 7.81; N, 5.71%.

4.1.4. 1,2-Bis(3-methyl-5-phenyl-2-thienyl)perfluorocyclopentene (*1a*). To a solution containing 5.04 g (27.1 mmol) of **6a** in 70 ml of ether anhydrous, 16.9 ml of *n*-butyl lithium hexane solution (1.6N, 27.1 mmol) was added at 0°C under an argon gas atmosphere. After the mixture was heated under reflux for 1 h, the reaction mixture was cooled to 0°C. Perfluorocyclopentene (2.87 g, 13.55 mmol) was added gradually and stirred for 1 h at this temperature. Methanol was added to the reaction mixture and extracted with ether three times. The combined ether layers were dried with MgSO$_4$, filtered and evaporated in vacuo. The residue was purified by column chromatography on silica gel (hexane) to give 4.93 g of 1,2-bis(3-methyl-5-phenyl-2-thienyl)perfluorocyclopentene (**1a**) in 30% yield.

1a: Pale yellow needles, mp 120.1–121.4°C; ^{1}H NMR (CDCl$_3$) δ=1.84 (s, 6H), 7.08 (s, 2H), 7.32 (t, 2H, *J*=7.2 Hz), 7.39 (dd, 4H, *J*=7.8, 7.4 Hz), 7.58 (d, 4H, *J*=7.2 Hz); IR (KBr) 1590, 1460 cm^{-1}; MS (*m*/*z*) 520 (M$^+$). Found: C, 62.21; H, 3.61%. Calcd for $C_{27}H_{18}F_6S_2$: C, 62.29; H, 3.49%.

4.1.5. 1,2-Bis[3-methyl-5-(*p*-methoxyphenyl)-2-thienyl]-perfluorocyclopentene (2a). 1,2-Bis[3-methyl-5-(*p*-methoxyphenyl)-2-thienyl]perfluorocyclopentene (**2a**) was synthesized from **6b** (1.55 g, 7.59 mmol) by the same procedure as that used for **1a**. The crude product was purified by column chromatography on silica gel (hexane/chloroform=7/3) to give 520 mg of **2a** in 25% yield.**2a**: Pale yellow prisms, mp 130–131°C; ^{1}H NMR (CDCl$_3$) δ=2.23 (s, 6H), 3.84 (s, 6H), 6.91 (d, 4H, *J*=8.7 Hz), 7.05 (s, 2H), 7.50 (d, 4H, *J*=8.7 Hz); IR (KBr) 1605, 1510, 1250, 1305 cm^{-1}; MS (*m*/*z*) 580 (M$^+$). Found: C, 59.86; H, 3.98%. Calcd for $C_{29}H_{22}F_6O_2S_2$: C, 59.99; H, 3.82%.

4.1.6. 1,2-Bis[3-methyl-5-(*p*-*N*,*N*-diethylaminophenyl)-2-thienyl]perfluorocyclopentene (3a). 1,2-Bis[3-methyl-5-(*p*-*N*,*N*-diethylaminophenyl)-2-thienyl]perfluorocyclopentene (**3a**) was synthesized from **6c** (1.33 g, 5.42 mmol) by the same procedure as that used for **1a**. The crude product was purified by column chromatography on silica gel (hexane/chloroform=7/3) to give 180 mg of **3a** in 10% yield.

3a: Yellow prisms, mp 90–91°C; ^{1}H NMR (CDCl$_3$) δ=1.18 (t, 12H, *J*=7.0 Hz), 1.78 (s, 6H), 3.38 (q, 8H, *J*=7.0 Hz), 6.65 (d, 4H, *J*=8.7 Hz), 6.88 (s, 2H), 7.43 (d, 4H, *J*=8.6 Hz); IR (KBr) 2960, 1350 cm^{-1}; MS (*m*/*z*) 662 (M$^+$). Found: C, 64.31; H, 5.60; N, 4.03%. Calcd for $C_{35}H_{36}F_6N_2S_2$: C, 63.44; H, 5.44; N, 4.23%.

Acknowledgements

This work was supported by a Grant-in-Aid for Scientific Research © No. 12640567 from the Ministry of Education, Science, Sports, and Culture and by CREST of Japan Science and Technology Corporation (JST).

References

1. (a) Irie, M.; Mohri, M. *J. Org. Chem.* **1988**, *53*, 803. (b) Irie, M.; Uchida, K. *Bull. Chem. Soc. Jpn.* **1998**, *73*, 985. (c) Kawai, S. H.; Gilat, S. L.; Lehn, J.-M. *Chem. Eur. J.* **1995**, *1*, 285. (d) Tsivgoulis, G. M.; Lehn, J.-M. *Chem. Eur. J.* **1996**, *2*, 1399.
2. Crano, J. C.; Guglielmetti, R. *Main Photochromic Families, Organic Photochromic and Thermochromic Compounds*, 1; Plenum: New York, 1999.

3. Irie, M.; Sakemura, K.; Okinaka, M.; Uchida, K. *J. Org. Chem.* **1995**, *60*, 8305.
4. Uchida, K.; Irie, M. *Chem. Lett.* **1995**, 969.
5. Uchida, K.; Kido, Y.; Yamaguchi, T.; Irie, M. *Bull. Chem. Soc. Jpn.* **1998**, *73*, 1101.
6. Uchida, K.; Ishikawa, T.; Takeshita, M.; Irie, M. *Tetrahedron* **1998**, *54*, 6627.
7. Uchida, K.; Irie, M. *Journal of Information Recording* **1998**, *24*, 101.
8. Uchida, K.; Yamaguchi, T.; Irie, M. *The Reports of the Institute of Advanced Material Study, Kyushu University* **1996**, *10*, 23.
9. Irie, M.; Eriguchi, T.; Takada, T.; Uchida, K. *Tetrahedron* **1997**, *53*, 12263.
10. Irie, M.; Sayo, K. *J. Phys. Chem.* **1992**, *96*, 7671.
11. Yokoyama, Y.; Yamane, T.; Kurita, Y. *J. Chem. Soc., Chem. Commun.* **1991**, 1722.
12. Pina, F.; Melo, M. J.; Maestri, M.; Ballardini, R.; Balzani, V. *J. Am. Chem. Soc.* **1997**, *119*, 5556.
13. Yokoyama, Y.; Kurita, Y. *Nippon Kagaku Kaishi* **1992**, 998.
14. Yokoyama, Y.; Kurita, Y. *Synth. Org. Chem. Jpn.* **1991**, *49*, 364.