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Thermally Irreversible Photochromic Systems. Reversible Photocyclization of 1,2-Bis(thiazolyl)perfluorocyclopentenes

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Abstract: Diarylethenes having thiazole rings, 1,2-bis(thiazol-4'-yl)perfluorocyclopentenes and 1,2-bis(thiazol-5'-yl)perfluorocyclopentenes, were synthesized. The binding positions of the thiazole rings to the perfluorocyclopentene moiety strongly affected the absorption spectra. The absorption maxima of the open- and closed-ring forms of 1,2-bis(5'-methyl-2'-phenylthiazol-4'-yl)perfluorocyclopentene were observed at 300 nm and 525 nm, respectively, while the maxima of 1,2-bis(4'-methyl-2'-phenylthiazol-5'-yl)perfluorocyclopentene shifted to 363 nm (open-ring form) and 406 nm (closed-ring form).

INTRODUCTION

There has been considerable interest in the synthesis of new photochromic compounds for photonics device.[1] We have so far synthesized various kinds of diarylethenes that undergo reversible photocyclization reactions.[2] Theoretical consideration based on a molecular orbital theory revealed that the thermal stability of both isomers of diarylethenes is attained by introducing aryl groups, which have low aromatic stabilization energy.[3] The theoretical prediction was confirmed by the synthesis of diarylethenes with various types of aryl groups.[4-8] When the aryl groups are furan, thiophene, or benzothiophene rings, which have low aromatic stabilization energy, the closed-ring forms are thermally stable and don't return to the open-ring forms in the dark. On the other hand, photogenerated closed-ring forms of diarylethenes with phenyl or indole rings, which have rather high aromatic stabilization energy, are thermally unstable.

In this paper, we report on the photochromic properties of bis(thiazolyl)perfluorocyclopentene derivatives **(1)-(5)**, and the effects of the binding position of the thiazole rings to the perfluorocyclopentene moiety on the absorption spectra (Scheme 1). Thiazole is a heterocyclic ring which has low aromatic stabilization energy. The diarylethenes having thiazole rings are expected to undergo thermally irreversible photochromic reactions.

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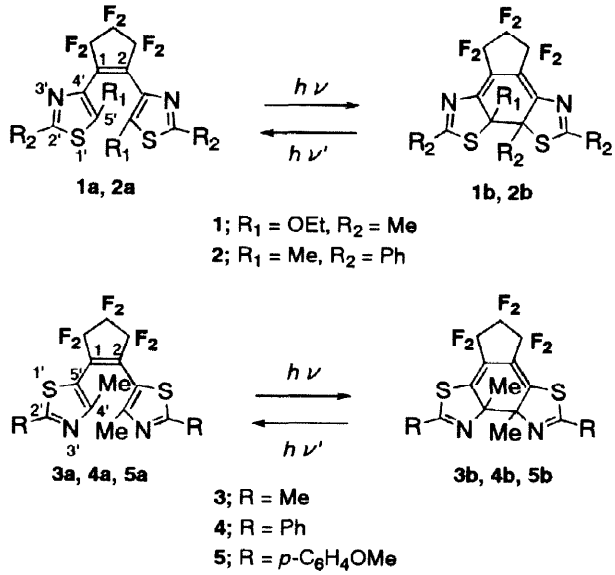


Scheme 1.

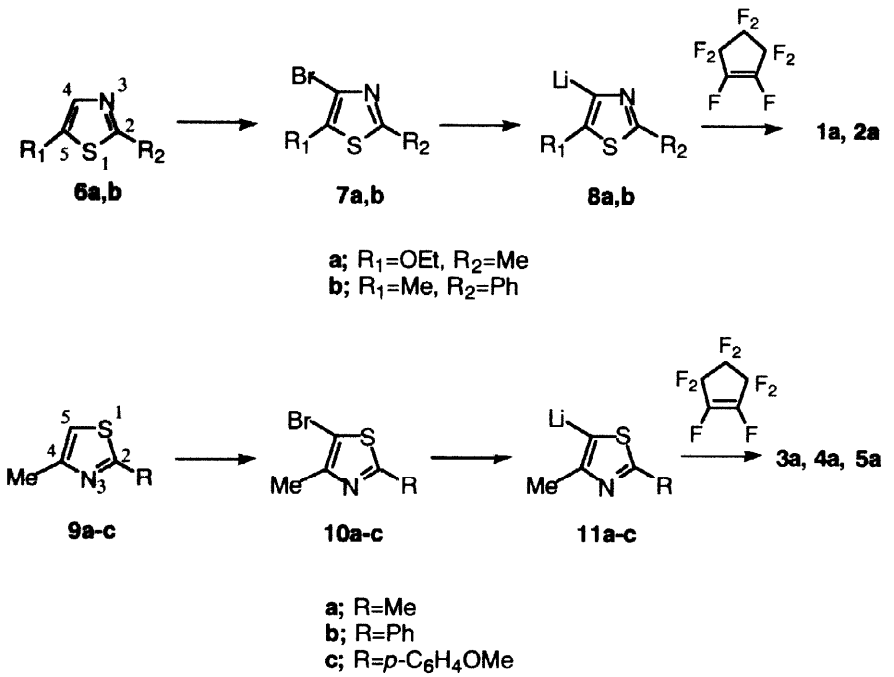
RESULTS AND DISCUSSION

Synthesis and Photochromic Properties of 1,2-Bis(thiazol-4'-yl)perfluorocyclopentene Derivatives:

1,2-Bis(5'-ethoxy-2'-methylthiazol-4'-yl)perfluorocyclopentene **1a** and 1,2-bis(5'-methyl-2'-phenylthiazol-4'-yl)perfluorocyclopentene **2a** were prepared by addition elimination reactions of perfluorocyclopentene with appropriate 2-lithiothiazoles as illustrated in Scheme 2. Ethoxy substituents were introduced at 5' positions of the thiazole rings of **1a** to increase the reactivity at 5' positions. Figure 1 shows the absorption spectral change of a hexane solution of **1a** (λ_{max} 323 nm) by irradiation with ultraviolet (334 nm) light. Upon irradiation the absorption at 323 nm decreased and the colorless hexane solution changed to a red solution, in which a visible absorption was observed at 474 nm. Figure 2 shows the spectral change of a hexane solution of **2a** (λ_{max} 300 nm) irradiated with 313 nm light. The absorption maximum of the photogenerated closed-ring form **2b** is observed at 525 nm. The fractions of the closed-ring forms in the photostationary state under above irradiation conditions were 0.87 and 0.97 for **1b** and **2b**, respectively.

Upon visible light irradiation (λ >400 nm) the red color disappeared and the absorption bands at 323 nm (**1a**) and 300 nm (**2a**) of the open-ring forms were restored. The coefficient ε at the absorption maximum of **2b** (525 nm) was 1.0 x 10^4 M^{-1} cm^{-1} and that of **1b** (474 nm) was 4.7 x 10^3 M^{-1} cm^{-1}. The ε of **2b** is twice as large as that of **1b**. Introduction of phenyl groups at 2'-positions to the thiazole rings of 1,2-bis(thiazol-4'-yl)perfluorocyclopentene derivatives is effective to increase the absorption coefficient, which is similar as observed for 1,2-bis(thiophen-3'-yl)perfluorocyclopentene derivatives.[9] The phenyl substituent was also effective to shift the absorption band of the closed-ring form to a longer wavelength.

Figures 3a and 3b show NMR spectra of methyl protons of **2** in $CDCl_3$ before and after photoirradiation with 313 nm light. Before irradiation, a Me-Ar signal was observed at 2.10 ppm. After UV irradiation, a new signal appeared at 2.03 ppm along with the decrease of the original signal intensity. The fact that only one methyl signal appeared at a higher field after photoirradiation indicates that the closed-ring form has a single structure with two methyl groups in the trans position, that is predicted theoretically.[3]



Scheme 2.

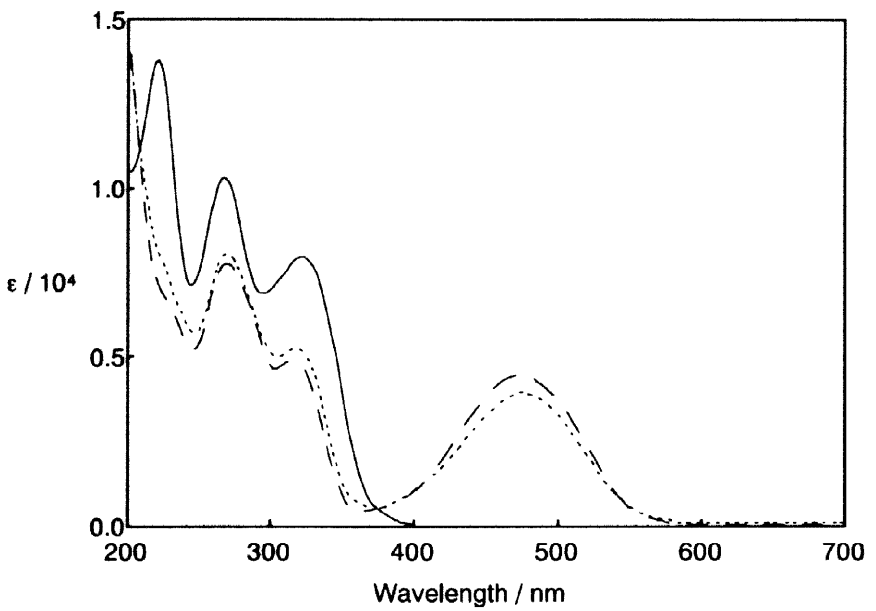


Figure 1. Absorption spectra of **1a** (——), **1b** (— — —), and in the photostationary state (·····) under irradiation with 334 nm light in hexane.

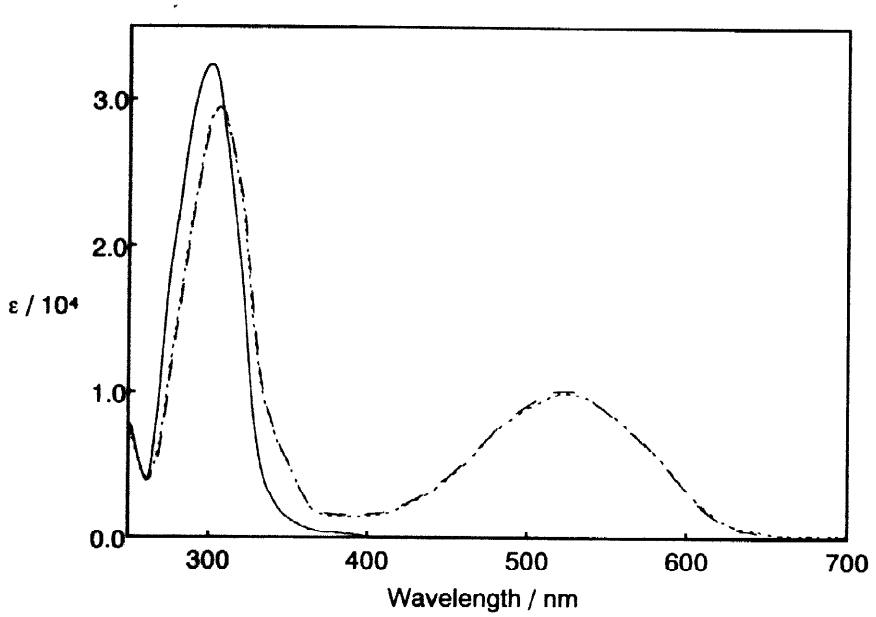


Figure 2. Absorption spectra of **2a** (———), **2b** (— — —), and in the photostationary state (·····) under irradiation with 313 nm light in hexane.

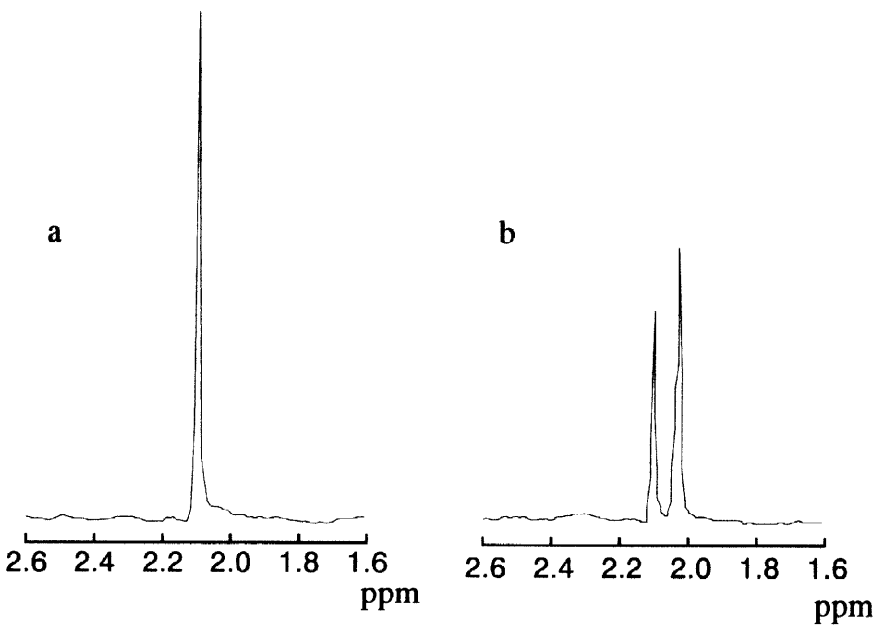


Figure 3. NMR spectra (300 MHz) of **2** in $CDCl_3$: (a) before irradiation; (b) in the photostationary state under irradiation with UV light ($300 < \lambda < 380$ nm).

Synthesis and Photochromic Properties of 1,2-Bis(thiazol-5'-yl)perfluorocyclopentene Derivatives:

1,2-Bis(2',4'-dimethylthiazol-5'-yl)perfluorocyclopentene **3a**, 1,2-bis(4'-methyl-2'-phenylthiazol-5'-yl)perfluorocyclopentene **4a**, and 1,2-bis[2'-(*p*-methoxyphenyl)-4'-methylthiazol-5'-yl]perfluorocyclopentene **5a** were synthesized by the similar method used for 1,2-bis(thiazol-4'-yl)perfluorocyclopentenes as illustrated in Scheme 2. Although compound **4a** has already been synthesized by Tanaka and his co-workers[10], the detailed

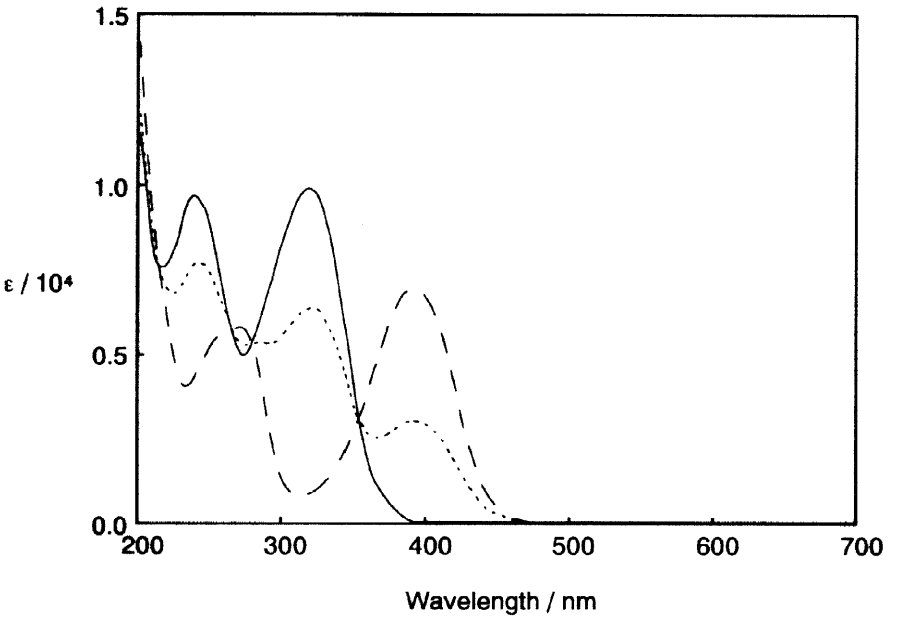


Figure 4. Absorption spectra of **3a** (——), **3b** (— — —), and in the photostationary state (·····) under irradiation with 366 nm light in hexane.

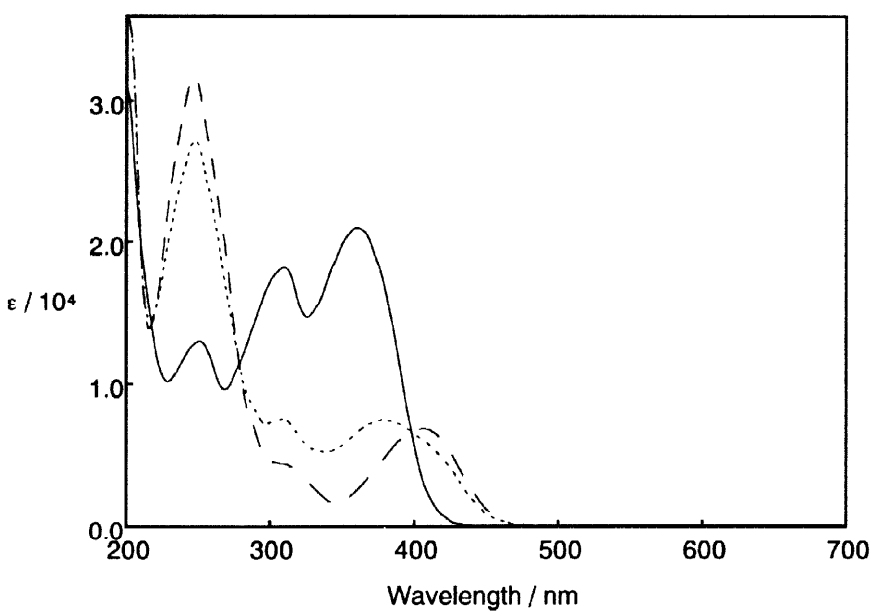


Figure 5. Absorption spectra of **4a** (——), **4b** (— — —), and in the photostationary state (·····) under irradiation with 366 nm light in hexane.

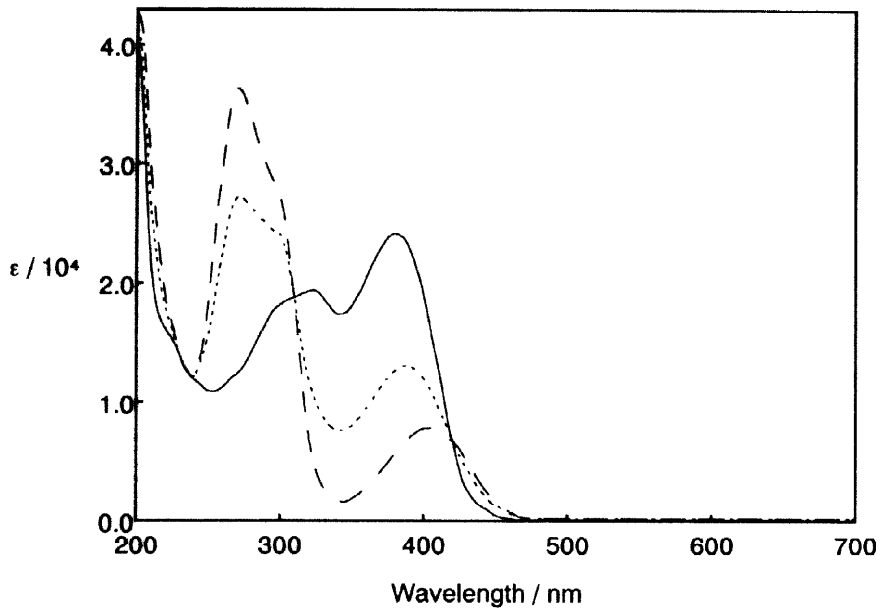


Figure 6. Absorption spectra of **5a** (———), **5b** (— — —), and in the photostationarystate (·····) under irradiation with 366 nm light in hexane.

photochromic behavior has not yet been revealed. The spectral changes of hexane solutions of **3a** (λ_{max} 320 nm), **4a** (λ_{max} 363 nm), and **5a** (λ_{max} 380 nm) are shown in Figs. 4, 5, and 6. Upon irradiation with 366 nm light the hexane solution turned yellow. The photogenerated yellow closed-ring forms have their absorption maxima at 391 nm (**3b**), 406 nm (**4b**), and 402 nm (**5b**), respectively. The conversions to their closed-ring forms in the photostationary states under 366 nm light irradiation were determined to be 0.48 (**3b**), 0.73 (**4b**) and 0.68 (**5b**).

Thermal stability of the closed-ring forms **3b**, **4b**, and **5b** was measured at 70°C in toluene. As described in the introductory part, diaryethenes having aryl groups with low aromatic stabilization energy undergo thermally irreversible photochromic reactions. This predicts that the photogenerated closed-ring forms **3b**, **4b**, and **5b** are thermally stable and hardly return to the open-ring forms. As expected, the photogenerated closed-ring forms were stable and keep the absorption intensity constant for more than 40 h at 70°C. Upon irradiation with visible light ($\lambda > 400$ nm) the yellow solutions became colorless and the initial absorptions were restored.

As can be seen from the solid line spectra in Figs. 4, 5, and 6, the absorption maxima of the open-ring forms of the derivatives shift to longer wavelengths from 320 nm (**3a**) to 380 nm (**5a**) and the absorption coefficients ε increase from 1.0 x 10^4 M^{-1} cm^{-1} (**3a**) to 2.4 x 10^4 M^{-1} cm^{-1} (**5a**) with an extension of π -conjugation length of the substituents on the 2'-positions of thiazole rings.

On the other hand, the absorption maxima of the closed-ring forms were not affected by the phenyl and *p*-methoxyphenyl substitutions. The different substitution effect of the phenyl groups to the absorption spectra of the closed- and open-ring forms is explained as follows. In the open-ring forms, the phenyl and *p*-methoxyphenyl substituents are in the π -conjugation chain extending throughout the molecule, while in the closed-ring forms the π -electrons in the central hexadiene structure have no significant interaction with those of the side arm phenyl groups. It is inferred from our previous results that sulfur lone pairs and sp^3 carbons that were produced by ring-closure reaction disconnect the π -conjugation. Table 1 summarized the absorption maxima and the

coefficients of these derivatives.

Effect of Binding Positions of the Thiazolyl Groups to the Perfluorocyclopentene Moiety:

In order to know the effect of binding position of the thiazole ring to the perfluorocyclopentene moiety, photochromic behavior of compounds **2** and **4**, that have same phenyl substituents at 2'-positions of thiazole rings, were compared. When the thiazolyl groups were bound to the perfluorocyclopentene moiety at 5'-positions, the maximum of the closed-ring form **4b** (λ_{max} 406 nm) shifted to a shorter wavelength in comparison with the closed form **2b** (λ_{max} 525 nm), in which the thiazolyl groups were bound at 4'-positions. The blue shift observed for **4b** suggests that the π-electrons in the central hexadiene structure have no significant interaction with those of the side arm phenyl groups.[11] In **2b**, π -conjugation is extended to the phenyl substituents. This explains the longer absorption band of **2b**.

The open-form **4a**, on the other hand, gave an absorption band at a longer wavelength compared with **2a**. The π-conjugation in the open-ring form **4a** extends throughout the molecule, while in **2a** the π-electrons in the central hexatriene structure have no significant interaction with those of the side arm phenyl groups.

Quantum Yield:

The quantum yields of cyclization and ring-opening reactions of **1-5** were measured in hexane solution at room temperature. Mercury lines and the light from Xe lamp, which were isolated with a monochrometer, were used to induce the reactions. The results are summarized in Table 1.

Table 1. Absorption maxima and their coefficients of the open-ring and closed-ring forms of bis(thiazolyl)ethenes, and quantum yields of cyclization and ring-opening reactions in hexane.

	λ_{max} / nm (ε_{max} / $M^{-1}cm^{-1}$)	$\Phi_{a\rightarrow b}$		λ_{max} / nm (ε_{max} / $M^{-1}cm^{-1}$)	$\Phi_{b\rightarrow a}$
1a	323 (8.5×10^3)	0.14 (366 nm)	**1b**	474 (4.7×10^3)	0.04 (492 nm)
2a	300 (3.4×10^4)	0.32 (313 nm)	**2b**	525 (1.0×10^4)	0.02 (492 nm)
3a	320 (1.0×10^4)	0.16 (366 nm)	**3b**	391 (7.0×10^3)	0.07 (420 nm)
4a	363 (2.1×10^4)	0.22 (366 nm)	**4b**	406 (7.0×10^3)	0.01 (420 nm)
5a	380 (2.4×10^4)	0.19 (366 nm)	**5b**	402 (7.7×10^3)	0.02 (430 nm)

In order to shed light on the effect of binding positions of the thiazolyl groups to the perfluorocyclopentene moiety on the quantum yields, the yields of **2** and **4** were compared. The cyclization quantum yield of **2a** is 0.32, while that of **4a** is 0.22. The structure of **2a**, in which the thiazolyl groups are bound at 4'-positions to the perfluorocyclopentene moiety, is favorable for the cyclization reaction. In the structure, the β position to S atom in the thiazole ring is bound to perfluorocyclopentene moiety. 1,2-Bis(2',4'-dimethyl-5'-phenylthiophen-3'-yl)perfluorocyclopentene, in which β position to S atom in the thiophene ring is bound to perfluorocyclopentene moiety, is known to have a very high quantum yield of cyclization reaction (0.46).[11] The reactivity difference of **2a** and **4a** is considered to reflect the difference of the electron density in the reactive carbon and the conformation of the thiazole ring in the open-ring forms. The ring-opening quantum yields of **2b** and **4b** are 0.02 and 0.01, respectively. These values are similar to those of dithienylethene derivatives.[9]

Next, the quantum yields of **3**, **4**, and **5** were compared to reveal the substituent effect on the thiazole

ring. The cyclization quantum yield were affected by the phenyl and *p*-methoxyphenyl substitutions. The quantum yields of **3a** and **4a** are 0.16 and 0.22, respectively. Introduction of phenyl groups to the thiazole rings increased the yield. However, introduction of methoxy groups to the *p*-positions of the phenyl substituents reduced the yield (**5a**, $\Phi_{a\rightarrow b} = 0.19$). The ring-opening quantum yield was also dependent on the aryl substituents. Introduction of phenyl or *p*-methoxyphenyl groups at the 2'- positions of the thiazole rings decreased the ring-opening quantum yield from 0.07(**3b**) to 0.01(**4b**) and 0.02(**5b**).

Fatigue Resistant Property:

Fatigue resistance, i.e., how many times photo-cyclization and ring-opening reaction cycles can be repeated without loss of performance, is an important photochromic property.[12] Hexane solutions of compounds **2**, **3**, and **4** (in thin cells with light pass length of 2 mm) were irradiated alternatively with 366 nm light for 45 s and visible light ($\lambda > 420$ nm) for 60 s in the presence of air. The irradiation times, 45 s and 60 s, were long enough for these compounds to convert to the photostationary state and to the complete photobleached state, respectively. Figure 7 shows the results. The absorption intensity at the wavelengths of their λ_{max} in closed-ring forms remained constant even after 3400 photo-cyclization / ring-opening reaction cycles. This indicates that the bis(thiazolyl)perfluorocyclopentenes have a fatigue resistant property irrespective of the substitution position of the thiazole rings to the perfluorocyclopentene moiety. Thiazole rings are useful for constructions of fatigue resistant and thermally irreversible photochromic diarylethenes.

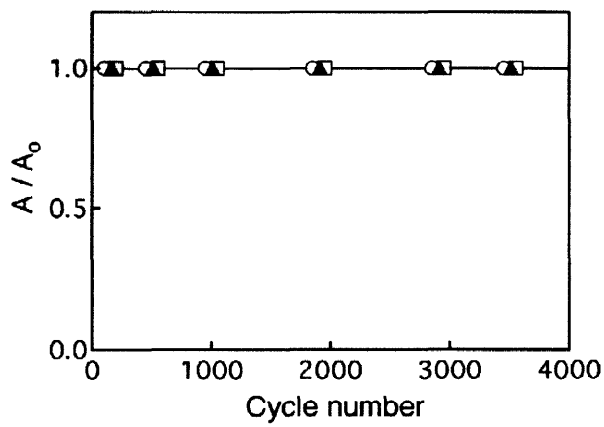


Figure 7. Fatigue resistant property of **2a** (—○—), **3a** (—▲—), and **4a** (—□—) in hexane solution in the presence of air. Initial absorbance of the samples was fixed to 0.3.

Conclusion

A series of diarylethenes having thiazole rings were synthesized to compare the photochromic properties of 1,2-bis(thiazol-4'-yl)perfluorocyclopentenes and 1,2-bis(thiazol-5'-yl)perfluorocyclopentene. The binding positions of the thiazole rings to the perfluorocyclopentene moiety strongly affected the absorption spectra. When the thiazole ring was substituted at 5'-position, the maximum of the closed-ring form shifted to shorter wavelength in comparison with the bis(thiazol-4'-yl)perfluorocyclopentenes.

EXPERIMENTAL SECTION

Compound **6a**, **6b**, **9a**, and **9b** were prepared according to literature methods.[13-17] ^{1}H NMR spectra were recorded on a Varian Gemini-200 (200 MHz) spectrometer with $CDCl_3$ as the solvent and tetramethylsilane as an internal standard. Mass spectra (EI, 75 eV) were measured with a JEOL JMS-01-SG-2 mass spectrometer. The absorption spectra were recorded on a Hitachi U-3410 spectrophotometer. Photoirradiation was carried out by using an USHIO 1000 W high-pressure mercury lamp and an USHIO 500 W Xe lamp as the exciting light source. Mercury lines at 280, 313, 334, and 366 nm, and the light (420, 430, 492 nm) from Xe lamp were isolated by passing the light through a monochrometer (Ritsu MC-10N). Quantum yields were determined by comparing the reaction rates of the diarylethenes in hexane with that of 2-[1-(2,5-dimethyl-3-furyl)ethylidene]-3-isopropylidenesuccinic anhydride (furyl fulgide) in toluene[18,19]. The samples were not degassed. The concentrations of the solutions were adjusted so that the absorbance at the irradiation wavelength is 0.60 for the ring-closure reactions and less than 0.2 for the ring-opening reactions. For the ring-closure reactions, the absorption increases of the closed-ring forms in the very initial isomerization step (less than 10%), where the change of the absorbed light intensity is negligible (less than 4%), were followed to determine the quantum yields. The ring-opening quantum yields were measured from the absorption decreases of the closed-ring forms. Experiments were carried always out more than 3 times and the average values were shown in Table 1. The experimental errors among them were less than 10%.

Closed-ring forms were separated by HPLC in the dark in order to estimate the absorption coefficients. After measurements of the absorption spectra of the closed-ring forms in hexane, the solutions were irradiated with visible light to convert all of them to the open-ring forms. From the ratios of the absorbances of the closed-ring forms and the open-ring forms, whose absorption coefficients were previously determined by normal method, the absorption coefficients of the closed-ring forms were determined.

4-bromo-5-ethoxy-2-methylthiazole (7a).

N-Bromosuccimide (4.0 g, 22.5 mmol) and benzoylperoxide (533 mg, 2.2 mmol) were added to a stirred solution of 5-ethoxy-2-methylthiazole (**6a**[13], 2.00 g, 11.4 mmol) in 50 ml of carbon tetrachloride. After stirring for 24 h at ambient temperature, 10 ml of 5N NaOH aqueous solution was added to quench the reaction. The reaction mixture was extracted with chloroform (100 ml). The combined organic layer was extracted with ethyl acetate. The organic layer was dried ($MgSO_4$), filtered and evaporated in vacuo. The residue was distilled under reduced pressure to give 3.31 g of 4-bromo-5-ethoxy-2-methylthiazole **7a** in 75% yield.

7a: colorless oil; bp 150-151 ℃ / 38 mmHg; ^{1}H NMR($CDCl_3$) δ 1.43 (t, 3H,CH_3-), 2.60 (s, 3H, ArMe), 4.13 (q, 2H, -CH_2-).; MS m/z (relative intensity), 223 (M^+, ^{81}Br, 100), 222 (52.2), 221 (M^+, ^{79}Br, 87.8), 59 (85.8). Anal. Calcd for C_6H_8NOSBr: C, 32.43; H, 3.60; N, 6.31. Found: C, 32.27; H, 3.76; N, 6.24.

1,2-Bis(5'-ethoxy-2'-methylthiazol-4'-yl)perfluorocyclopentene (1a).

To a dry THF solution (30 ml) of 3.0 g (13.5 mmol) of 4-bromo-5-ethoxy-2-methylthiazole (**7a**), 9.4 ml (15.0 mmol) of n-BuLi hexane solution (1.6 N) was added to form **8a** at -60℃ under a nitrogen atmosphere. After 45 min, 0.89 ml (6.9 mmol) of perfluorocyclopentene was added to the solution. After additional 30 min stirring at the temperature, the reaction was allowed to stand at ambient temperature. Then, hydrochloric acid was added. The reaction mixture was extracted with diethyl ether (30 ml x 3). The combined ether layer was dried ($MgSO_4$), filtered and evaporated in vacuo. The residue was purified by column chromatography on silica

gel (toluene / ethyl acetate = 1 / 19) to give 452 mg of 1,2-Bis(5'-ethoxy-2'-methylthiazol-4'-yl)perfluorocyclopentene **1a** in 7.3 % yield.

1a: mp 147-147.5 ℃; ^{1}H NMR($CDCl_3$) δ = 1.12 (t, 6H, Ar-O-CH_2-CH_3), 2.62 (s, 6H, 2Ar-Me), 3.87 (q, 4H, Ar-O-CH_2-CH_3).; MS m/z (relative intensity) 458 (M^+, 11.0), 413 (89.9), 59 (100). Anal. Calcd for $C_{17}H_{16}N_2F_6O_2S_2$: C, 44.53; H, 3.52; N, 6.11. Found: C, 44.27; H, 3.49; N, 6.19.

4-bromo-5-methyl-2-phenylthiazole (7b).

Bromine (0.44 ml, 10.2 mmol) was added to a stirred solution of 5-methyl-2-phenylthiazole (**6b**[14], 1.25 g, 4.92 mmol) in 30 ml of carbon disulfide cooled on ice bath. After 72 h stirring at ambient temperature, water was added to quench the reaction. The reaction mixture was extracted with chloroform (100 ml). The combined organic layer was washed with sodium thiosulfate aqueous solution, dried ($MgSO_4$), filtered and evaporated in vacuo. The residue was purified by column chromatography on silica gel (hexane / ethyl acetate = 9 / 1) to give 600 mg of 4-bromo-5-methyl-2-phenylthiazole **7b** in 48% yield.

7b: colorless oil; ^{1}H NMR($CDCl_3$) δ =2.49 (s, 3H, Ar-Me), 7.45 (m, 3H, Ph), 7.89 (m, 2H, Ph).; MS m/z (relative intensity) 255 (M^+, ^{81}Br, 100), 254 (53.3), 253 (M^+, ^{79}Br, 94.1). Anal. Calcd for $C_{10}H_8NSBr$: C, 47.24; H, 3.15; N, 5.51. Found: C, 47.27; H, 3.26; N, 5.29.

1,2-Bis(5'-methyl-2'-phenylthiazol-4'-yl)perfluorocyclopentene (2a).

To a dry THF solution (30 ml) of 600 mg (2.4 mmol) of 4-bromo-5-methyl-2-phenylthiazole (**7b**), 1.76 ml (2.8 mmol) of n-BuLi hexane solution (1.6 N) was added at -60℃ under a nitrogen atmosphere. After 45 min stirring, 0.16 ml (1.2 mmol) of perfluorocyclopentene was added to the solution. After additional 3h stirring at the temperature, the reaction mixture was allowed to stand at ambient temperature. Then, hydrochloric acid was added. The reaction mixture was extracted with diethyl ether (30 ml x 3). The combined ether layer was dried ($MgSO_4$), filtered and evaporated in vacuo. The residue was purified by column chromatography on silica gel (hexane / ethyl acetate = 9 / 1) to give 30 mg of 1,2-Bis(5'-methyl-2'-phenylthiazol-4'-yl)perfluorocyclopentene **2a** in 5% yield.

2a: colorless prisms; mp 148-150 ℃; ^{1}H NMR($CDCl_3$) δ = 1.65 - 2.03 (s, 6H, 2Me), 7.45 - 7.99 (m, 10H, Ar). ; MS m/z (relative intensity) 522 (M^+, 75.9), 59 (100). Anal. Calcd for $C_{25}H_{16}N_2F_6S_2$: C, 57.47; H, 3.07; N, 5.36. Found: C, 57.40; H, 3.11; N, 5.04.

5-bromo-2,4-dimethylthiazole (10a).

Bromine (4.4 ml, 102 mmol) was added to a stirred solution of 2,4-dimethylthiazole (**9a**[15], 9.66 g, 85.3 mmol) in 80 ml of carbon disulfide cooled on ice bath. After 48 h stirring at ambient temperature, water was added to quench the reaction. The reaction mixture was extracted with chloroform (100 ml). The combined organic layer was washed with sodium thiosulfate aqueous solution, dried ($MgSO_4$), filtered and evaporated in vacuo. The residue was distilled under reduced pressure to give 7.64 g of 5-bromo-2,4-dimethylthiazole **10a** in 47% yield.

10a: colorless oil; bp 100 ℃ / 100 mmHg; ^{1}H NMR($CDCl_3$) δ =2.33 (s, 3H, Ar-Me), 2.61 (s, 3H, Ar-Me).; MS m/z (relative intensity) 193 (M^+, ^{81}Br, 100), 192 (51.5), 191 (M^+, ^{79}Br, 92.9). Anal. Calcd for C_5H_6NBrS: C, 31.25; H, 3.13; N, 7.29. Found: C, 31.25; H, 3.23; N, 7.22.

1,2-Bis(2',4'-dimethylthiazol-5'-yl)perfluorocyclopentene (3a).

To a solution of 1.0 g(5.2 mmol) of 5-bromo-2,4-dimethylthiazole (**10a**) in 30 ml of dry THF, 3.7 ml (5.9 mmol) of n-BuLi hexane solution (1.6 N) was added at -60℃ under a nitrogen atmosphere. After 1h stirring, 0.35 ml (2.7 mmol) of perfluorocyclopentene was added to the solution. After additional 3 h stirring at -60℃, the

reaction was allowed to ambient temperature then hydrochloric acid was added. The reaction mixture was extracted with diethyl ether (30 ml x 3). The combined ether layer was dried ($MgSO_4$), filtered and evaporated in vacuo. The residue was purified by column chromatography on silica gel (hexane / ethyl acetate = 4 / 1) to give 125 mg of 1,2-Bis(2',4'-dimethylthiazol-5'-yl)perfluorocyclopentene **3a** in 12% yield.

3a: pale yellow prisms; mp 80-81 ℃; ^{1}H NMR($CDCl_3$) δ = 1.65 - 2.13 (s, 6H, 2Me), 2.70 (s, 6H, 2Me).; MS m/z (relative intensity) 398 (M^+, 88.9), 324 (100). Anal. Calcd for $C_{15}H_{12}N_2F_6S_2$: C, 45.16; H, 3.01; N, 7.02. Found: C, 45.36; H, 3.11; N, 7.04.

2-phenyl-5-bromo-4-methylthiazole (10b).

Bromination of **9b**[16,17] (1.19 g, 6.8 mmol) was carried out by a similar procedure as used for **10a.** The crude product was purified by column chromatography on silica gel (ethyl acetate) to give 1.41 g of 2-phenyl-5-bromo-4-methylthiazole **10b** in 82% yield.

10b: colorless prisms; mp 60-61 ℃; ^{1}H NMR($CDCl_3$) δ =2.44 (s, 3H, Ar-Me), 7.40-7.56 (m, 5H, Ph).; MS m/z (relative intensity) 255 (M^+, ^{81}Br, 89.7), 253 (M^+, ^{79}Br, 100), 175 (84.8). Anal. Calcd for $C_{10}H_8NBrS$: C, 47.24; H, 3.15; N, 5.51. Found: C, 47.37; H, 3.28; N, 5.46.

1,2-Bis(4'-methyl-2'-phenylthiazol-5'-yl)perfluorocyclopentene (4a).

This compound was prepared from 1.0 g (3.9 mmol) of 2-phenyl-5-bromo-4-methyl-thiazole (**10b**) by a similar procedure as used for **3a.** After the purification, 382 mg of 1,2-Bis(4'-methyl-2'-phenylthiazol-5'-yl)perfluorocyclopentene **4a** was obtained in 38% yield.

4a: mp 107-109 ℃; ^{1}H NMR($CDCl_3$) δ = 1.59 - 2.13 (s, 6H, 2Me), 7.44 - 7.96 (m, 10H, Ar).; MS m/z (relative intensity) 522 (M^+, 88.1), 386 (42.4), 59 (100). Anal. Calcd for $C_{25}H_{16}N_2F_6S_2$: C, 57.47; H, 3.07; N, 5.36. Found: C, 57.51; H, 3.02; N, 5.28.

2-(*p*-methoxyphenyl)-4-methylthiazole (9c).

2-(*p*-methoxyphenyl)-4-methylthiazole (**9c**) was synthesized from 5.0 g of benzamide (33 mmol) by a same procedure as used for **9a.** The obtained crude product was distilled under reduced pressure to give 2.36 g of 2-(*p*-methoxyphenyl)-4-methylthiazole **9c** in 35% yield.

9c: bp 168-170 ℃ / 7 mmHg; ^{1}H NMR($CDCl_3$) δ =2.50 (s, 3H, Ar-Me), 4.85 (s, 3H, Ar-O-Me), 6.80 (s, 1H, Ar-H), 6.91-8.80 (dd, 4H, Ph-H).; MS m/z (relative intensity) 205 (M^+, 100). Anal. Calcd for $C_{11}H_{11}NOS$: C, 64.39; H, 5.37; N, 6.83. Found: C, 64.51; H, 5.40; N, 6.85.

2-(*p*-methoxyphenyl)-5-bromo-4-methylthiazole (10c).

Bromination and followed purification of **9c** (600 mg, 2.9 mmol) were carried out by a similar procedure as used for **10b** to give 752 mg of 2-(*p*-methoxyphenyl)-5-bromo-4-methylthiazole **10c** in 91% yield.

10c: ^{1}H NMR($CDCl_3$) δ =2.45 (s, 3H, Ar-Me), 4.86 (s, 3H, Ar-O-Me), 6.92-8.83 (dd, 4H).; MS m/z (relative intensity) 285 (M^+, ^{81}Br, 85.6), 283 (M^+, ^{79}Br, 100), 203 (43.6), 162 (86.1). Anal. Calcd for $C_{11}H_{10}NBrOS$: C, 46.48; H, 3.52; N, 4.93%. Found: C, 46.61; H, 3.50; N, 4.85.

1,2-Bis[2'-(*p*-methoxyphenyl)-4'-methylthiazol-5'-yl]perfluorocyclo-pentene (5a).

This compound was prepared from 350 mg (1.2 mmol) of 5-bromo-2-(*p*-methoxyphenyl)-4-methylthiazole (**10c**) by a similar procedure as used for **3a.** After the purification, 144 mg of 1,2-bis[2'-(*p*-methoxyphenyl)-4'-methylthiazol-5'-yl]perfluorocyclopentene **5a** was obtained in 20% yield.

5a: yellow needles; mp 135-136 ℃; ^{1}H NMR($CDCl_3$) δ = 2.13 - 2.48 (s, 6H, 2Me), 3.85 (s, 6H, 2Me), 6.91-8.90 (m, 8H).; MS m/z (relative intensity) 582 (M^+, 89.2), 581 (100). Anal. Calcd for $C_{27}H_{20}N_2F_6O_2S_2$: C, 55.66; H, 3.46; N, 4.80. Found: C, 55.66; H, 3.50; N, 4.83.

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