Photochromism of Dithiazolylethenes Having Methoxy Groups at the Reaction Centers

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Photochromic dithiazolylethenes [1,2-bis(5-methoxy-2-phenylthiazol-4-yl)perfluorocyclopentene (**1a**) and (5-methoxy-2-phenylthiazol-4-yl)-2-(5-methyl-2-phenylthiazol-4-yl)perfluorocyclopentene (**2a**)] having methoxy substituents at the reaction centers were synthesized and their photochromic reactivity was compared with 1,2-bis(5-methyl-2-phenylthiazol-4-yl)perfluorocyclopentene (**3a**), which has methyl substituents at the reaction centers. All dithiazolylethene derivatives underwent reversible photocyclization reactions from the open-ring forms **1a**, **2a**, and **3a** to the closed-ring forms **1b**, **2b**, and **3b**, respectively. The photocyclization quantum yields of **1a** and **2a** were only slightly lower than that of **3a**, while the photocycloreversion quantum yields of **1b** and **2b** dramatically decreased relative to that of **3b** by factors of 100 and 10, respectively. Absorption maxima of dithiazolylethene derivatives **1b**, **2b**, and **3b** showed a hypsochromic shift as much as 50–80 nm relative to that of dithienylethene derivatives. This is explained by the difference in the HOMO–LUMO band gap between the two systems.

Introduction

Photochromic compounds have attracted much attention due to their potential applications in optical memory media and photo-optical switching devices.[1] In particular, diarylethenes with heterocyclic aryl groups, such as thiophene or benzothiophene groups, are the most promising candidates for applications, because they undergo fatigue resistant and thermally irreversible photochromic reactions.[2] Several attempts to control the photocyclization and photocycloreversion quantum yields by the introduction of various substituents to the diarylethenes have been reported.[3] When electron-donating groups are introduced at the *para*-positions of the phenyl groups of 1,2-bis(2,4-dimethyl-5-phenylthiophen-3-yl)perfluorocyclopentene, the photocycloreversion quantum yields decrease.[4] Methoxy substitution at the reaction centers of 1,2-bis(2-methyl-5-phenylthiophen-3-yl)perfluorocyclopentene has been reported to decrease the photocycloreversion quantum yield by a factor of 10^3.[5] Such a low photobleaching quantum yield could be useful in the production of, for example, memory cards, write-once memory media and color dosimeters.[6]

Dithiazolylethene[7] has a structure isoelectronic with dithienylethene, and both exhibit thermally irreversible photochromic reactions.[2][7a] Recently, we found that the position of substitution of the thiazole rings in the perfluorocyclopentene moiety strongly affected the absorption spectra.[7a] The absorption maximum of the closed-ring form of 1,2-bis(4-methyl-2-phenylthiazol-5-yl)perfluorocyclopentene shifted to a shorter wavelength relative to that of 1,2-bis(5-methyl-2-phenylthiazol-4-yl)perfluorocyclopentene.[7a] Although the photochromic reactivity of dithiazolylethene derivatives is of great interest, very little work on their photochromic reactions has been reported. In this paper, the photochromic properties of dithiazolylethene derivatives having methoxy substituents at the reaction centers has been examined, in order to probe the substituent effects of methoxy groups on the photocyclization/cycloreversion quantum yields. The photochromic reactivity of dimethoxy-substituted **1** and monomethoxy-substituted **2** was also compared with that of 1,2-bis(5-methyl-2-phenylthiazol-4-yl)percyclopentene (**3**) which has methyl substituents at the reaction centers (Scheme 1).

Results and Discussion

1,2-Bis(5-methoxy-2-phenylthiazol-4-yl)perfluorocyclopentene (**1a**) and 1-(5-methoxy-2-phenylthiazol-4-yl)-2-(5-methyl-2-phenylthiazol-4-yl)perfluorocyclopentene (**2a**) were synthesized by the reaction of 4-bromo-5-methoxy-2-

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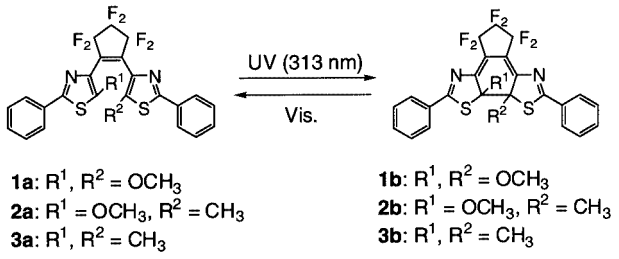
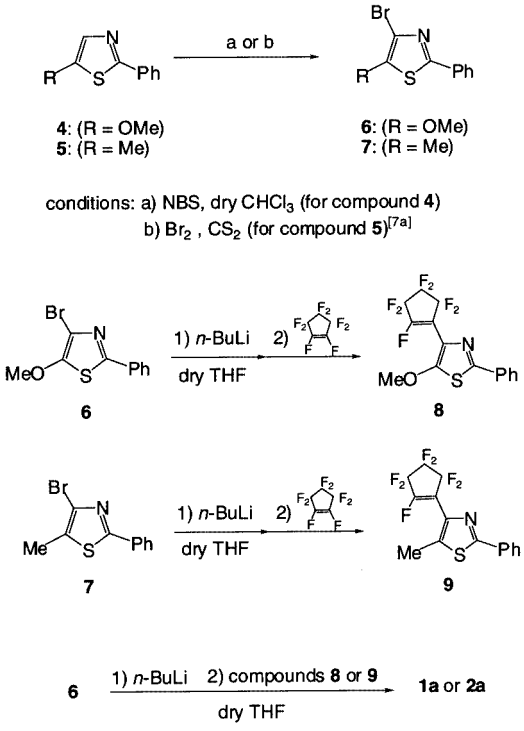


1a: R^1, $R^2 = OCH_3$
2a: $R^1 = OCH_3$, $R^2 = CH_3$
3a: R^1, $R^2 = CH_3$

1b: R^1, $R^2 = OCH_3$
2b: $R^1 = OCH_3$, $R^2 = CH_3$
3b: R^1, $R^2 = CH_3$

Scheme 1

phenylthiazole (**6**) with monosubstituted perfluorocyclopentenes **8** and **9**, respectively, by bromine−lithium exchange followed by nucleophilic displacement of fluoride, as illustrated in Scheme 2. Dithiazolylethenes **1a** and **2a** were characterized by ^{1}H NMR spectroscopy, MS, and elemental analysis. Dithiazolylethene **3a** was also prepared,[7a] in order to compare its reactivity with dimethoxy-substituted **1** and monomethoxy-substituted **2**.



Scheme 2

Figure 1 shows the spectral changes of compound **1** dissolved in toluene ($1.3\cdot10^{-5}$ M). The toluene solution of **1a** has an absorption maximum at 322 nm. Upon irradiation with 313 nm light the colorless solution of the open-ring form turned purple, showing an absorption maximum at 555 nm. The purple color is due to the closed-ring form, **1b**. The colored product was isolated by HPLC (silica gel; ethyl acetate/hexane, 1:3 as the eluent), and the structure of **1b** was confirmed by ^{1}H NMR spectroscopy, MS, and elemental analysis. All data were in good agreement with the closed-ring form **1b**. The purple color was bleached by irradiation with visible light ($\lambda > 480$ nm), however, the photobleaching rate of **1b** was much slower than that of **3b**. The red color of **3b** was bleached rapidly by irradiation with visible light for 1 min,[7a] while it took more than 1 h for the purple color of **1b** to be bleached. The conversion from the open- to the closed-ring form by irradiation with 313 nm light was almost 100% in the photostationary state. In the ^{1}H NMR spectrum of **1a** in $CDCl_3$, the resonance of the methoxy proton was observed at $\delta = 3.84$ ppm. Upon irradiation with 313 nm light, this signal decreased in intensity, while a new singlet appeared at $\delta = 3.57$ ppm.This new singlet was assigned to the methoxy protons attached to the photogenerated sp^3 carbon of compound **1b**. Figure 2 shows ^{1}H NMR spectra of the methoxy protons of **1** in $CDCl_3$ before and after photo-irradiation with 313 nm light. This indicates that the closed-ring form has a single structure with two methoxy groups in the trans position, as predicted theoretically.[8]

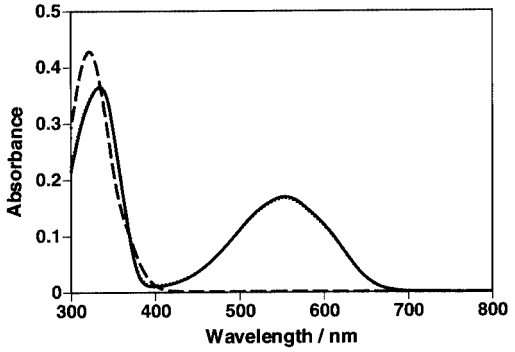


Figure 1. Absorption spectra of a toluene solution of dimethoxy-substituted **1** ($1.3\cdot10^{-5}$ M): (dashed line) open-ring form **1a**, (solid line) closed-ring form **1b**, and (dotted line) in the photostationary state under irradiation with 313 nm

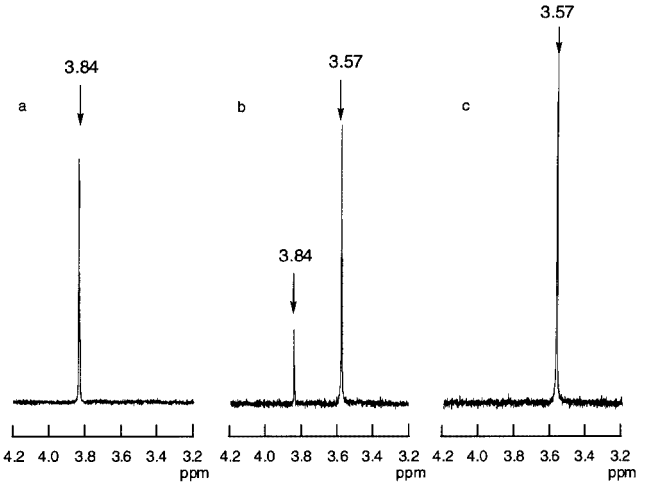


Figure 2. ^{1}H NMR spectra (200 MHz) of **1** in $CDCl_3$: (a) before irradiation; (b) after 10 min under irradiation with 313 nm; (c) at the photostationary state under irradiation with 313 nm

Figure 3 shows the spectral changes of compound **2** dissolved in toluene ($1.2\cdot10^{-5}$ M). Similar color and spectral changes to those of compound **1** were observed. The red-

purple color due to the ring-closed form **2b** appeared upon irradiation with 313 nm light and was bleached by irradiation with visible light ($\lambda > 480$ nm) for 5 min. The photocycloreversion efficiency of **2b** was intermediate between those of **1b** and **3b**. On photobleaching the spectrum converted back into the original one yielding an isosbestic point at 323 nm. The conversion from the open-ring to the closed forms by irradiation with 313 nm light was almost 96%. In the ^{1}H NMR spectrum of **2a** in $CDCl_3$, the resonances due to the methoxy and methyl protons at the reaction centers were observed at $\delta = 3.84$ and 2.19 ppm, respectively. Upon irradiation with 313 nm light new singlet signals corresponding to **2b** appeared at $\delta = 3.40$ and 2.12 ppm along with the decrease in intensity of the original signals.

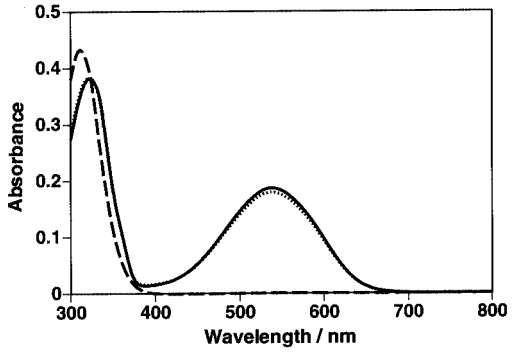


Figure 3. Absorption spectra of a toluene solution of monomethoxy-substituted **2** ($1.2\cdot10^{-5}$ M): (dashed line) open-ring form **2a**, (solid line) closed-ring form **2b**, and (dotted line) in the photostationary state under irradiation with 313 nm

Table 1 summarizes absorption maxima and absorption coefficients of the open- and closed-ring isomers **1**−**3** in toluene. The absorption maxima of the open-ring (**1a**−**3a**) and closed-ring (**1b**−**3b**) forms were dependent on the number of methoxy substituents at the reaction centers. The absorption maximum of dimethoxy-substituted **1** (**1a**: λ_{max} = 322 nm, **1b**: λ_{max} = 555 nm) showed a bathochromic shift of as much as about 20 nm relative to the maximum of **3** (**3a**: λ_{max} = 305 nm, **3b**: λ_{max} = 534 nm). Additionally, the absorption coefficient of **1** is slightly lower than that of **3**. The absorption maxima and coefficients of monomethoxy-substituted **2** were intermediate between those of **1** and **3**. Dithienylethene derivatives have also been reported to exhibit a bathochromic shift of the absorption maximum and a decrease of the absorption coefficient when methoxy substituents were introduced to the reaction centers.[5]

The photocyclization and photocycloreversion quantum yields of **1**−**3** shown in Table 1 were measured in toluene at 25 °C with fulyl fulgide[9] as a reference. The photocyclization quantum yields were measured by irradiation with 313 nm light, while the photocycloreversion quantum yields were measured by irradiation at the absorption maxima. A cyclization quantum yield as high as 0.42 was observed for **3a**, but this decreased to 0.29 when methoxy groups were introduced at the reaction centers of the dithiazolylethenes. Dimethoxy-substituted derivative **1a** and monomethoxy-substituted derivative **2a** gave similar cyclization quantum yields. In contrast, the photocycloreversion quantum yield dramatically decreased when methoxy groups were introduced at the reaction centers. The cycloreversion quantum yields of **1b** and **2b** were $3.3\cdot10^{-4}$ and $4.0\cdot10^{-3}$, which are respectively 100 and 10 times smaller than that of **3b** ($1.7\cdot10^{-2}$). It should be noted that no degradation of the test solution was observed by HPLC analysis during the photocyclization and cycloreversion experiments of **1**. This means that no photochemical side-reaction having a quantum yield higher than 10^{-6} takes place in the photochemistry of **1**. Additionally, we measured the thermal stability of the ring-closed isomer **1b** at 100 °C in toluene. It was found that the closed-ring form **1b** was thermally stable at 100 °C for 48 h. The methoxy substituent effect on the quantum yields for the photocycloreversion reactions is similar to that observed for the dithienylethene derivatives. The introduction of methoxy groups is considered to affect the electronic structures[10] of the excited states of **1b** and **2b**.

The absorption spectra of closed-ring forms **1b**, **2b**, and **3b** of dithiazolylethene derivatives containing imine C=N moieties (absorption maxima of **1b**: 544 nm, **2b**: 531 nm, and **3b**: 525 nm in hexane) showed a hypsochromic shift of as much as about 50−80 nm relative to their dithienylethene analogues[5] (absorption maxima of dimethoxy-substituted: 625 nm, monomethoxy-substituted: 600 nm, and dimethyl-substituted: 575 nm in hexane). In order to investigate this difference in the absorption maxima, molecular orbital calculations both for **3b** and for the closed-ring form of 1,2-bis(2-methyl-5-phenylthiophen-3-yl)percyclopentene (**10**) were undertaken using standard MOPAC software with CNDO/S parameterization.[11] Although the conformations of **3b** and **10** were similar (as judged by the dihedral angle between phenyl and aryl groups), a considerable difference between the HOMO states was observed. The orbital profiles of HOMO and LUMO based on the CNDO/S parameterization are illustrated in Figure 4. In

Table 1. Absorption maxima and coefficients of the open- and closed-ring isomers of dithiazolylethene, and the quantum yields in toluene

	λ max / nm (ε / $M^{-1}\cdot cm^{-1}$)	$\Phi_{a\rightarrow b}$		λ max / nm (ε / $M^{-1}\cdot cm^{-1}$)	$\Phi_{b\rightarrow a}$	Conversion (313 nm)
1a	322 (33000)	0.29 (313 nm)	**1b**	555 (13100)	$3.3\cdot10^{-4}$ (555 nm)	1.00
2a	311 (34500)	0.28 (313 nm)	**2b**	540 (15000)	$4.0\cdot10^{-3}$ (540 nm)	0.96
3a	305 (37000)	0.42 (313 nm)	**3b**	534 (14500)	$1.7\cdot10^{-2}$ (534 nm)	0.95

the HOMO states, the orbital profiles of the 3, 4, 5, and 6 positions of **3b** are significantly bigger than those of **10**. This means that electron density of **3b** is more localized than it is in **10**, at the 3, 4, 5, and 6 positions. The visible transitions of **3b** and **10** were also calculated by using CNDO/S. The HOMO−LUMO energy gap of **3b** is 5.86 eV, slightly higher than that (5.66 eV) of **10**. The hypsochromic shift of **3b** relative to **10** is attributable to the difference in the wavefunction of HOMO level, which is due to localization of the electrons at the central cyclohexadiene structure.

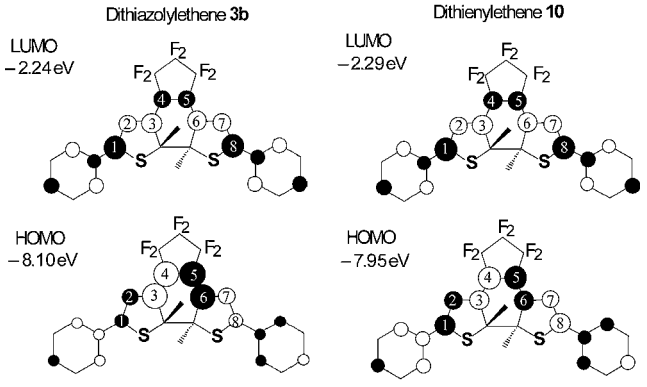


Figure 4. CNDO/S calculation[11] of HOMO and LUMO for dithienylethene **10** and dithiazolylethene **3b**

Conclusion

We have examined the photochromic reactivity of dithiazolylethene derivatives having methoxy substituents at the reaction centers. The quantum yields of photocycloreversion reaction were greatly diminished by the introduction of methoxy groups at the reactiong centers. Dimethoxy-substituted **1b** and monomethoxy-substituted **2b** showed, respectively, 100-fold and 10-fold smaller cycloreversion quantum yields than **3b**. In contrast, the cyclization quantum yields of **1a** and **2a** were scarcely affected by the substitution. Furthermore, it was found that the closed form **1b** was thermally stable at 100 °C for 48 h. The absorption maxima of the closed-ring forms of dithiazolylethene derivatives showed a hypsochromic shift of as much as 50−80 nm relative to the maximum of their dithienylethene analogues. The hypsochromic shift was explained by the difference in the HOMO−LUMO band gap between the two systems.

Experimental Section

General Remarks: ^{1}H NMR spectra were recorded on a Varian Gemini 200 spectrometer. HPLC was performed on a Hitachi L-7100 liquid chromatograph coupled with a Hitachi L-7400 spectrophotometeric detector. A silica gel column [Si 60 250-20 (5μm)] was used. Mass spectra were taken with a Shimadzu GCMS-QP5050A gas chromatography-mass spectrometer. Absorption spectra were measured with a Hitachi U-3500 absorption spectrophotometer. Photoirradiation was carried out using USHIO 500-W superhigh-pressure mercury lamp or an USHIO 500-W xenon lamp. Monochromatic light was obtained by passing the light through a combination of Toshiba band-pass filter (UV-D33S) or sharp cut filter (Y-46, Y-47, and Y-48) and monochromator (Ritsu MC-10N). Elemental analyses were performed by the Microanalytical Laboratory at the Department of Chemistry, Faculty of Science, Kyushu University. The cyclization quantum yields were determined by comparing the photocyclization rate of furyl fulgide in toluene with a standard procedure.[9a] The cycloreversion quantum yields were also measured using furyl fulgide in toluene as a reference.[9b]

Materials: Compounds **5** and **7** were prepared according to methods reported previously.[7a] Spectroscopic grade solvents were purified by distillation before use. All reactions were monitored by thin-layer chromatography carried out on 0.2 mm Merck silica gel plates (60F-254). Column chromatography was performed on silica gel (Merck, 70−230 mesh).

5-Methoxy-2-phenylthiazole (4): *N*-benzoyl glycine methyl ester[12] (1.00 g, 5.18 mmol) and phosphorus pentasulfide (1.40 g, 6.30 mmol) were rapidly added to 15 mL of dry chloroform, and the mixture was stirred at 80 °C under an atmosphere of argon. After 1 h, white precipitate had formed. Then the mixture was refluxed for 24 h under an atmosphere of argon. The reaction mixture was poured into aqueous NaOH and extracted with dichloromethane. The organic layer was dried with $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography (ethyl acetate/hexane, 1:1) to afford 566 mg (57%) of **4** as a red oil: ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.96−3.95 (d, *J* = 2.2 Hz, 3 H), 7.12 (s, 1 H), 7.43−7.38 (m, 3 H), 7.82−7.78 (m, 2 H) ppm. MS *m*/*z* = 191 [M^+]. $C_{10}H_9NOS$ (191.3): calcd. C 62.80, H 4.74, N 7.32; found C 62.64, H 4.78, N 7.34.

4-Bromo-5-methoxy-2-phenylthiazole (6): *N*-bromosuccinimide (447 mg, 2.51 mmol) was added to a stirred solution of **4** (400 mg, 2.09 mmol) in dry chloroform (10 mL). The mixture was stirred at room temperature for 4 h and extracted with ethyl acetate. The organic layer was dried with $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography (ethyl acetate/hexane, 1:3) to afford 550 mg (97%) of **6** as colorless prisms: m.p. 71−72 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 4.03 (s, 3 H), 7.45−7.36 (m, 3 H), 7.85−7.76 (m, 2 H) ppm. MS *m*/*z* = 271 [M^+]. $C_{10}H_8BrNOS$ (269.0): calcd. C 44.46, H 2.98, N 5.18; found C 44.56, H 2.99, N 5.19.

1-(5-Methoxy-2-phenylthiazol-4-yl)perfluorocyclopentene (8): To a solution of **6** (500 mg, 1.85 mmol) in dry THF (5 mL) was slowly added dropwise *n*-butyllithium (1.22 mL, 1.6 M in hexane, 1.94 mmol) at −78 °C under an atmosphere of argon. After the mixture had been stirred for 15 min at −78 °C, perfluorocyclopentene (0.20 mL, 0.93 mmol) in dry THF (2 mL) was added. The reaction mixture was stirred at −78 °C for 2.5 h, and then distilled water was added. The product was extracted with diethyl ether, dried with $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography (ethyl acetate/hexane, 1:3) to afford 510 mg (72%) of **8** as colorless needles: m.p. 79−80 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 4.13 (s, 3 H), 7.48−7.40 (m, 3 H), 7.88−7.82 (m, 2 H) ppm. MS *m*/*z* = 383 [M^+]. $C_{15}H_8F_7NOS$ (383.0): calcd. C 47.00, H 2.10, N 3.65; found. C 47.25, H 2.08, N 3.66.

1-(5-Methyl-2-phenylthiazol-4-yl)perfluorocyclopentene (9): Treatment of **7** under the same conditions as for the synthesis of **8** gave 500 mg (69%) of **9** as colorless plates. M.p. 71−72 °C. ^{1}H NMR

(200 MHz, $CDCl_3$): δ = 2.54 (d, *J* = 3 Hz, 1 H), 7.48−7.42 (m, 3 H), 7.94−7.86 (m, 2 H) ppm. MS *m/z* = 367 [M^+]. $C_{15}H_8F_7NS$ (383.0): calcd. C 49.05, H 2.20, N 3.81; found. C 49.23, H 2.18, N 4.11.

1,2-Bis(5-methoxy-2-phenylthiazol-4-yl)perfluorocyclopentene (1a): To a solution of **6** (540 mg, 2.00 mmol) in dry THF (8 mL) was added *n*-butyllithium (1.30 mL, 1.6 M in hexane, 2.10 mmol) at −78 °C under an atmosphere of argon. After the mixture had been stirred for 15 min at −78 °C, **8** (510 mg, 1.33 mmol) in dry THF (2 mL) was added. The reaction mixture was further stirred at −78 °C for 2.5 h, and then distilled water was added. The product was extracted with diethyl ether, dried with $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography (ethyl acetate/hexane, 3:7) and HPLC (ethyl acetate/hexane, 1:3) to afford 540 mg (68%) of **1a** as a colorless solid. A small portion of this product was recrystallized from hexane/ethyl acetate to give colorless needles: m.p. 142−142.5 °C. ^1H NMR (200 MHz, $CDCl_3$): δ = 3.84 (s, 6 H), 7.44−7.35 (m, 6 H), 7.84−7.74 (m, 4 H) ppm. MS *m/z* = 554 [M^+], 523 [M^+ − OMe]. $C_{25}H_{16}F_6N_2O_2S_2$ (554.1): calcd. C 54.15, H 2.91, N 5.05; found. C 54.25, H 2.97, N 5.10.

Closed-Ring Form for 1a (1b): Compound **1b** was isolated as a purple solid by passing a photostationary solution containg **1a** and **1b** thorough HPLC (ethyl acetate/hexane, 1:3): ^1H NMR (200 MHz, $CDCl_3$): δ = 3.57 (s, 6 H), 7.65−7.45 (m, 6 H), 8.05−7.98 (m, 4 H) ppm. MS *m/z* = 554 [M^+], 523 [M^+ − OMe]. $C_{25}H_{16}F_6N_2O_2S_2$ (554.1): calcd. C 54.15, H 2.91, N 5.05; found. C 54.32. H 2.95, N 5.07.

1-(5-Methoxy-2-phenylthiazol-4-yl)-2-(5-methyl-2-phenylthiazol-4-yl)perfluorocyclopentene (2a): To a solution of **6** (500 mg, 1.85 mmol) in dry THF (8 mL) was slowly added *n*-butyllithium (1.22 mL, 1.6 M in hexane, 1.94 mmol) at −78 °C under an atmosphere of argon. After the reaction mixture had been stirred at −78 °C for 15 min, **9** (480 mg, 1.31 mmol) in dry THF (2 mL) was added. The reaction mixture was further stirred at −78 °C for 2.5 h, and then distilled water was added. The product was extracted with diethyl ether, dried with $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography (ethyl acetate/hexane, 1:9) and HPLC (ethyl acetate/hexane, 1:4) to afford 260 mg (37%) of **2a** as a colorless solid. A small portion of this product was recrystallized from hexane/ethyl acetate to give colorless needles: m.p. 171−172 °C. ^1H NMR (200 MHz, $CDCl_3$): δ = 2.19 (s, 3 H), 3.84 (s, 3 H), 7.48−7.30 (m, 6 H), 7.70−7.64 (m, 2 H), 7.97−7.91 (m, 2 H) ppm. MS *m/z* = 538 [M^+]. $C_{25}H_{16}F_6N_2OS_2$ (538.1): calcd. C 55.76, H 2.99, N 5.20; found. C 55.83, H 3.09, N 5.23.

Closed-Ring Form for 2a (2b): Compound **2b** was isolated as a purple solid by passing a photostationary solution containg **2a**, **2b** thorough HPLC (ethyl acetate/hexane, 1:4): ^1H NMR (200 MHz, $CDCl_3$): δ = 2.12 (s, 3 H), 3.34 (s, 3 H), 7.26−7.62 (m, 6 H), 8.00−7.04 (m, 4 H) ppm. MS: *m/z* = 538 [M^+]. $C_{25}H_{16}F_6N_2OS_2$ (538.1): calcd. C 55.76, H 2.99, N 5.20; found. C 56.00, H 3.06, N 5.04.

Acknowledgments

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[1] [1a] *"Photochromism: Molecules and Switches": Chem. Rev.* **2000**, *100*, whole of issue 5. [1b] G. H. Brown, *Photochromism*, Wiley-Interscience: New York, **1971**. [1c] H. Dürr, H. Bouas-Laurent, *Photochromism: Molecules and Systems*, Elsevier: Amsterdam, **1990**. [1d] M. Irie, (Ed.), *Photo-reactive Materials for Ultrahigh Density Optical Memory*, Elsevier: Amsterdam, **1994**.

[2] [2a] M. Irie, *Chem. Rev.* **2000**, *100*, 1685−1716. [2b] M. Irie, K. Uchida, *Bull. Chem. Soc. Jpn.* **1998**, *71*, 985−996.

[3] [3a] M. Irie, T. Eriguchi, T. Takada, K. Uchida, *Tetrahedron* **1997**, *53*, 12263−12271. [3b] K. Uchida, E. Tsuchida, Y. Aoi, S. Nakamura, M. Irie, *Chem. Lett.* **1999**, 63−64. [3c] S. Kobatake, K. Uchida, E. Tsuchida, M. Irie, *Chem. Lett.* **2000**, 1340−1341.

[4] M. Irie, K. Sakemura, M. Okinaka, K. Uchida, *J. Org. Chem.* **1995**, *60*, 8305−8309.

[5] K. Shibata, S. Kobatake, M. Irie, *Chem. Lett.* **2001**, 618−619.

[6] [6a] S. Irie, T. Yamaguchi, H. Nakazumi, S. Kobatake, M. Irie, *Bull. Chem. Soc. Jpn.* **1999**, *72*, 1139−1142. [6b] S. Irie, M. Irie, *Bull. Chem. Soc. Jpn.* **2000**, *73*, 2385−2388.

[7] [7a] K. Uchida, T. Ishikawa, M. Takeshita, M. Irie, *Tetrahedron* **1998**, *54*, 6627−6638. [7b] S. Iwata, Y. Ishihara, C.-P. Qian, K. Tanaka, *J. Org. Chem.* **1992**, *57*, 3726−3727.

[8] S. Nakamura, M. Irie, *J. Org. Chem.* **1988**, *53*, 6136−6138.

[9] [9a] Y. Yokoyama, Y. Kurita, *J. Synth. Org. Chem. Jpn.* **1991**, *49*, 364−372. [9b] H. G. Heller, J. R. Langan, *J. Chem. Soc., Perkin Trans. 2* **1981**, 341−343.

[10] D. Guillaumont, T. Kobayashi, K. Kanda, H. Miyasaka, K. Uchida, S. Kobatake, K. Shibata, S. Nakamura, Irie, M. submitted for publication.

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[12] [12a] T. Miyazawa, T. Yamada, S. Kuwata, *Bull. Chem. Soc. Jpn.* **1984**, *57*, 3605−3606. [12b] K.-D. Ginzel, P. Brungs, E. Steckhan, *Tetrahedron* **1989**, *45*, 1691−1701.

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