Available online at www.sciencedirect.com
SCIENCE DIRECT
Tetrahedron 60 (2004) 6155–6161
Tetrahedron

Synthesis and photochromic properties of novel yellow developing photochromic compounds

Shizuka Takami* and Masahiro Irie*

Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, and 'Nanotechnology Support Project' of the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan, Hakozaki 6-10-1, Higashi-ku, Fukuoka 812-8581, Japan

Received 15 March 2004; revised 16 April 2004; accepted 14 May 2004

Available online 11 June 2004

Abstract—Two 1-thiazolyl-2-thienylcyclopentene derivatives, **1a** and **2a**, and a 1-thiazolyl-2-vinylcyclopentene derivative **3a** have been synthesized in an attempt to obtain photochromic compounds which change the color from colorless to yellow, and have low photocycloreversion quantum yields and high absorption coefficients of the colored isomers. All of these compounds underwent reversible photochromic reactions. Compounds **1a** and **2a** in toluene solutions changed the color upon 313 nm light irradiation from colorless to orange and pink, in which absorption maxima were observed at 494 nm (ε=10,000 M^{-1} cm^{-1}) and 525 nm (ε=8500 M^{-1} cm^{-1}), respectively. On the other hand, the colorless toluene solution of **3a** turned yellow upon irradiation with 313 nm light, in which the absorption maximum was observed at 416 nm (ε=17,100 M^{-1} cm^{-1}). The photocyclization/cycloreversion quantum yields of **3** were 0.19 and 0.0014, respectively. The conversion from the open- to the closed-ring isomer of **3** in the photostationary state under irradiation with 313 nm light was close to 100%.

1. Introduction

Photochromic compounds have attracted much attention because of their potential ability for optical memory, photo-optical switching and display devices.[1,2] Among them diarylethenes with heterocyclic aryl groups, such as thiophene or benzothiophene groups, are the most promising candidates for the applications[3–8] because of their fatigue resistant and thermally irreversible photochromic performance.[9,10] For the application to a full color display it is indispensable to prepare red and yellow developing diarylethene derivatives. Several attempts have been conducted to shift the absorption maximum of the closed-ring isomer to shorter wavelengths by introduction of thiazole rings as the aryl group. When the thiophene rings of 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentenes[11] are replaced with thiazole rings, the absorption maximum of the closed-ring isomer shifts from 575 nm (blue) to 525 nm (red).[12,13] Another approach to further shift the absorption band to shorter wavelength (yellow) is to attach the thiophene rings to the ethene moiety at the 2-position.[13–15] Very recently, oxazolylfulgides and 2,3-bis(2,3,5-trimethyl-3-thienyl)maleic imidine have been reported as yellow photochromic dyes.[16,17] These colored isomers are, however, photochemically unstable and the photocycloreversion quantum yields are rather high. For a full color display it is strongly desired to develop yellow photochromic compounds which have low photocycloreversion quantum yields and thermal stability at room temperature. In previous papers, we showed that introduction of alkoxy groups at the reactive carbons of diarylethene derivatives remarkably suppresses the photocycloreversion quantum yields.[6,12,18] Furthermore, the rational correlations between the substitution and the photocycloreversion quantum yields have been demonstrated based on an ab initio MO calculation.[19] In this study, we have synthesized two 1-thiazolyl-2-thienylcyclopentene derivatives **1a** and **2a**, and a 1-thiazolyl-2-vinylcyclopentene derivative **3a** having methoxy substituents to obtain yellow photochromic compounds having a low photocycloreversion quantum yield (Scheme 1).

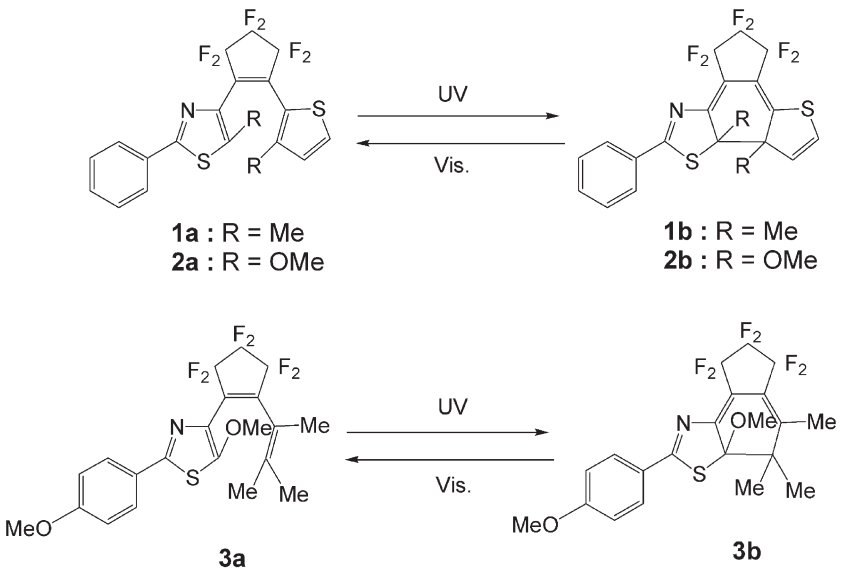
2. Results and discussion

2.1. Synthesis and photochromic properties of 1-thiazolyl-2-thienylcyclopentene derivatives

4-Thiazolyl[12,13] and 2-thienyl[14,15] chromophores were chosen as the aryl groups of diarylethenes to shift the absorption maxima of the closed-ring isomers to shorter

Keywords: Photochromic compound; Yellow color; Photochromism; Quantum yields.
* Corresponding authors. Tel.: +81-92-642-4132; fax: +81-92-642-3568; e-mail addresses: takami@cstf.kyushu-u.ac.jp; irie@cstf.kyushu-u.ac.jp

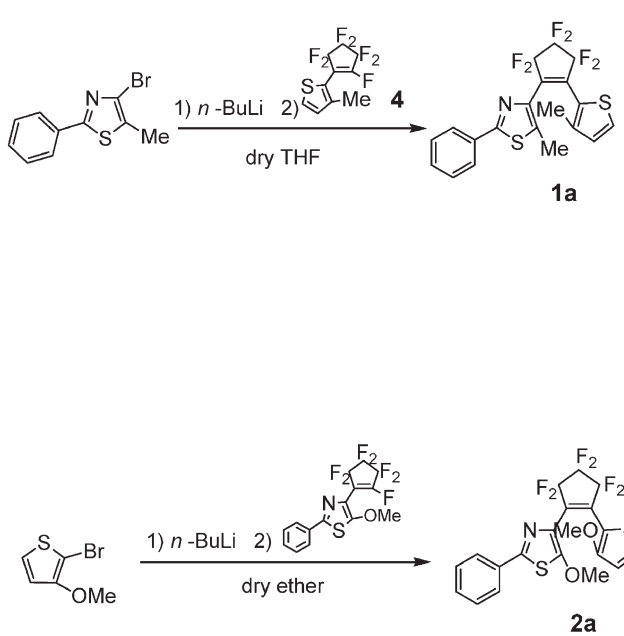
0040–4020/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2004.05.029



Scheme 1.

wavelengths. In order to reduce the photocycloreversion quantum yield, methoxy substituents were introduced at the reactive carbons. According to the above molecular design principle, compounds **1a** and **2a** were constructed. Compound **1a** was synthesized by the reaction of 4-bromo-5-methyl-2-phenylthiazole[12] with 1-(3-methyl-2-thienyl)octafluorocyclopentene (**4**) by bromine-lithium exchange followed by nucleophilic displacement of fluoride. A colorless solid was obtained in 14% yield. **2a** was synthesized by the reaction of 2-bromo-3-methoxythiophene[20] with 1-(5-methoxy-2-phenyl-4-thiazolyl)octafluorocyclopentene[12] in dry ether as a colorless solid. Both compounds were purified by column chromatography (hexane/AcOEt) and characterized by ^{1}H NMR spectroscopy, MS, and elemental analysis. (Scheme 2).

Figure 1 shows the absorption spectral change of **1** (3.3×10^{-5} M) in toluene by UV irradiation. Upon irradiation with 313 nm light, the colorless solution turned orange, in which a visible absorption band was observed at 494 nm (ε=10,000 M^{-1} cm^{-1}). The orange color is due to the closed-ring isomer **1b**. When the orange solution was irradiated with visible light (λ>440 nm), the spectrum readily returned back to the original one. The colored isomer was stable in the dark at room temperature and could be isolated by high performance liquid chromatography (HPLC, ethyl acetate/hexane=1/9 as the eluent). The structure of **1b** was analyzed with ^{1}H NMR spectroscopy, MS, and elemental analysis. All data agreed well with the closed-ring isomer **1b**. The conversion from **1a** to **1b** in the photostationary state under irradiation with 313 nm light was 69%.



Scheme 2.

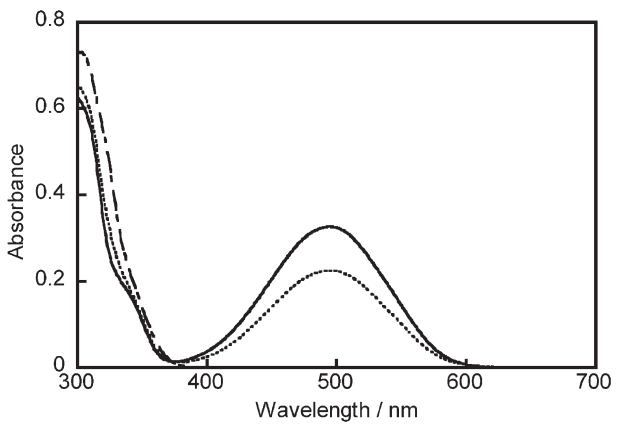


Figure 1. Absorption spectra of compound **1** (3.3×10^{-5} M) in toluene: (dashed line) open-ring isomer **1a**, (solid line) closed-ring isomer **1b**, and (dotted line) in the photostationary state under irradiation with 313 nm light.

Figure 2 shows the absorption spectral changes of **2** (2.4×10^{-5} M) in toluene by UV irradiation. The absorption maximum of the photogenerated closed-ring isomer **2b** was observed at 525 nm. The absorption maximum is 31 nm longer than that of **1b** (494 nm). The pink color is due to the closed-ring form **2b** and bleached by irradiation with visible

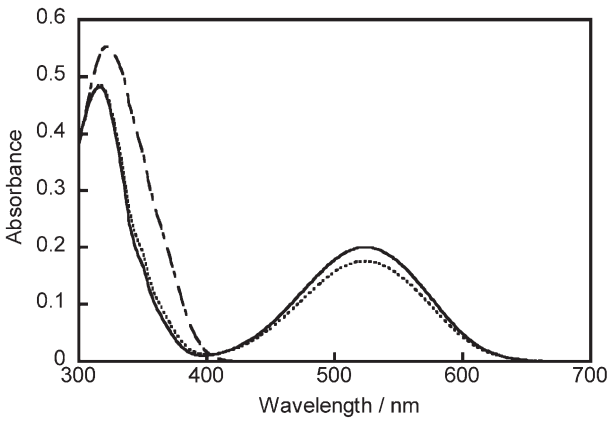


Figure 2. Absorption spectra of compound **2** (2.4×10^{-5} M) in toluene: (dashed line) open-ring isomer **2a**, (solid line) closed-ring isomer **2b**, and (dotted line) in the photostationary state under irradiation with 313 nm light.

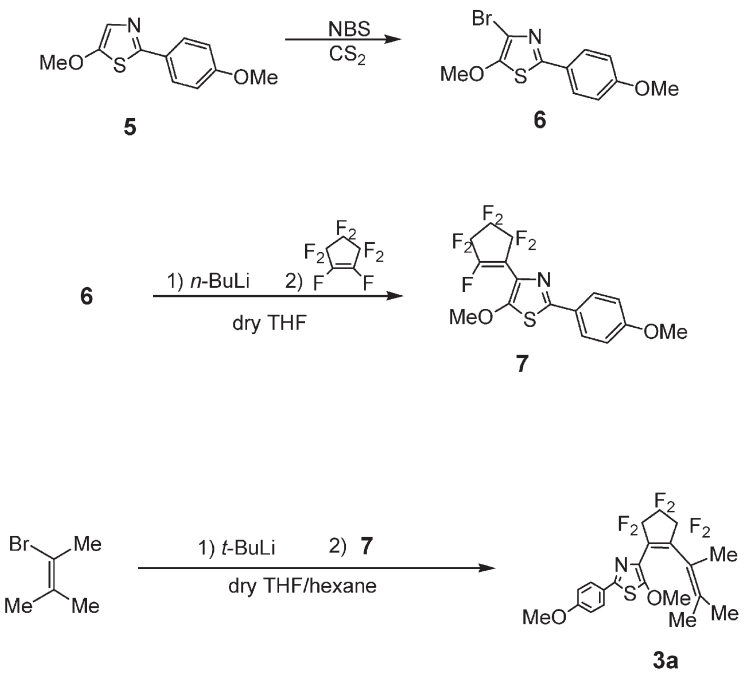
light ($\lambda>440$ nm). The structure of isolated colored product was analyzed by ^{1}H NMR spectroscopy, MS, and elemental analysis. All data agreed well with the closed-ring isomer **2b**. The photobleaching rate of **2b** was slower than that of **1b**. The absorption coefficient of **2b** is 8500 M^{-1} cm^{-1}, which is less than that of **1b**. The conversion from the open-ring to the closed-ring isomer by irradiation with 313 nm was 89%.

The photocyclization/cycloreversion quantum yields were measured in toluene at 25 °C. The photocyclization quantum yields of **1a** and **2a** were determined to be 0.36 and 0.26, respectively. The methoxy substitution scarcely affected the cyclization reaction. On the other hand, the photocycloreversion quantum yield was strongly suppressed by the methoxy substituents. The photocycloreversion quantum yield of **2b** (0.012) was decreased as much as 10 times in comparison with that of **1b** (0.12). The hypsochromic shifts of **1b** and **2b** are not large enough to exhibit yellow color. Therefore, the 2-thiophene group[14,15] was replaced with an ethylene unit to further shift the absorption band of the closed-ring isomer to shorter wavelengths.

2.2. Synthesis and photochromic properties of a 1-thiazolyl-2-vinylcyclopentene derivative

Recently, novel photochromic compounds having a thiophene and a 2-butene or stryl unit have been reported by Branda et al. [21] and Yokoyama et al.[22,23] The colorless solutions of these compounds turned to yellow by irradiation with UV light. The absorption maximum of the closed-ring isomer of 1-(1,2-dimethylpropenyl)-2-(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene (**8**) is reported to be 450 nm in dichloromethane.[21] When the thiophene ring is replaced with a thiazole ring, the absorption maximum of the closed-ring isomer is expected to shift to a wavelength shorter 450 nm. In other words, the closed-ring isomer would not give yellow color. In order to obtain yellow colored closed-ring isomer, it is required to introduce substituents[24,25] which shift the band to longer wavelengths. We designed a derivative **3a**, which has methoxy substituents at the *para*-position of the phenyl ring and 5-position of the thiazole ring. Both methoxy substituents are effective to induce bathochromic shift.[6,12,18,24] The methoxy group at the 5-position is also known to decrease the photocycloreversion quantum yield. The synthesis was performed according to Scheme 3. 5-Methoxy-2-(4-methoxyphenyl)thiazole **5** was obtained from *N*-(4-methoxybenzoyl) glycine methyl ester as a yellow solid in 80% yield. Compound **3a** was synthesized by the coupling reaction of **7** and 2-bromo-3-methyl-2-butene,[26] and was purified by HPLC. The structures of all compounds were confirmed by ^{1}H NMR, mass spectroscopy, and elemental analysis.

Figure 3 shows the absorption spectral change of **3** (2.5×10^{-5} M) in toluene by irradiation with UV light. The



Scheme 3.

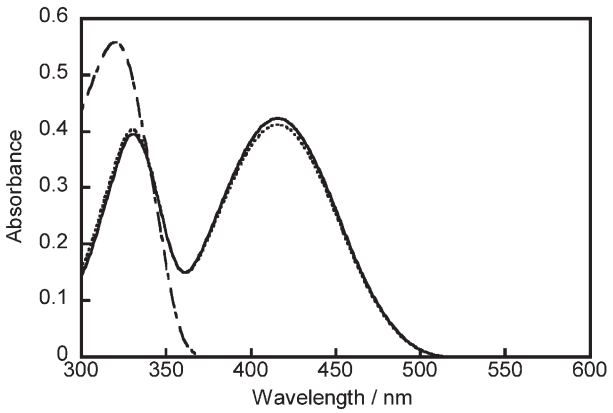


Figure 3. Absorption spectra of compound **3** (2.5×10^{-5} M) in toluene: (dashed line) open-ring isomer **3a**, (solid line) closed-ring isomer **3b**, and (dotted line) in the photostationary state under irradiation with 313 nm light.

spectrum of the isolated colored isomer is also shown in Figure 3. Upon irradiation with 313 nm light the colorless toluene solution of **3a** slowly turned yellow, in which absorption maxima were observed at 330 and 416 nm. It should be noted that any photochemical side product was not observed by HPLC analysis. The photostationary spectrum is almost the same as the colored isomer, indicating a high conversion from the colorless to the colored isomers by irradiation with 313 nm light. The yellow colored solution slowly returned back to the initial colorless solution upon prolonged irradiation with visible light. The colored isomer was stable in the dark at room temperature and could be isolated by HPLC (silica gel; ethyl acetate/hexane=2/8 as the eluent). The molecular characteristics of the yellow colored isomer was examined by ^{1}H NMR, mass spectrum, and elemental analysis. All analysis data agreed with that of the closed-ring isomer **3b**.

The cyclization quantum yield (313 nm) was determined to be 0.19. The quantum yield is slightly smaller than the values of **1a** and **2a**. On the other hand, the cycloreversion quantum yield was remarkably suppressed to 0.0014. Although the photocyclization/cycloreversion quantum yields of (**8**) are not reported, the conversion from the open- to the closed-ring isomer with 365 nm light at the photostationary state is reported to be 64%.[21] The low conversion suggests that the photocycloreversion quantum yield is rather high in comparison with **3**, in which the conversion as high as 100% is observed. The photocyclization and photocycloreversion quantum yields of **1**, **2** and **3** are summarized in Table 1. The photocycloreversion quantum yield of **3b** is 10 times smaller than that of **2b**.

Figure 4 shows the colors of the closed-ring isomers **1b**, **2b** and **3b** in toluene. The absorption band of **3b** (416 nm) showed hypochromic shift in compared with those of **1b**

Table 1. Absorption maxima and coefficients of the open- and closed-ring isomers of compounds **1**, **2**, and **3**, and the quantum yields in toluene

	λ max/nm (ε/M^{-1} cm^{-1})	$\Phi_{a\rightarrow b}$		λ max/nm (ε/M^{-1} cm^{-1})	$\Phi_{b\rightarrow a}$	Conversion (313 nm)
1a	302 (22300)	0.36 (300 nm)	**1b**	494 (10000)	1.2×10^{-1}(492 nm)	0.69
2a	321 (23000)	0.26 (313 nm)	**2b**	525 (8500)	1.2×10^{-2}(525 nm)	0.89
3a	320 (22500)	0.19 (313 nm)	**3b**	416 (17100)	1.4×10^{-3}(416 nm)	0.97

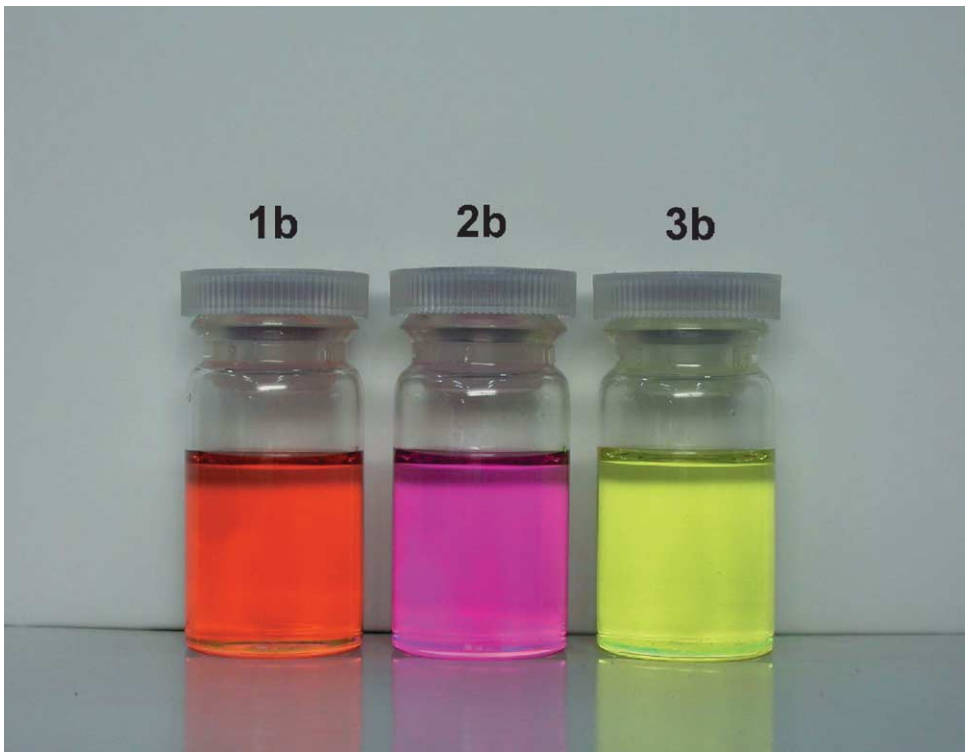


Figure 4. Toluene solutions of compounds **1**, **2**, and **3** under irradiation with 313 nm: orange (**1b**), pink (**2b**), and yellow colors (**3b**).

(494 nm) and **2b** (525 nm). This is ascribed to shorter π-conjugation length of **3b** in comparison with **1b** and **2b**. More interestingly, the absorption coefficient of **3b** is 17,100 M^{-1} cm^{-1}, which is much larger than that of **1b** (10,000 M^{-1} cm^{-1}) and **2b** (8500 M^{-1} cm^{-1}). The value, is also much larger than the absorption coefficients of the closed-ring isomers of yellow developing diarylethenes,[7] such as 1,2-bis(3-methyl-2-thienyl)perfluorocyclopentene (6870 M^{-1} cm^{-1} at 432 nm in 3-methylpentane),[27] 1,2-bis(3,5-dimethyl-2-thienyl)perfluorocyclopentene (5800 M^{-1} cm^{-1} at 425 nm in hexane),[14,28,29] 1,2-bis(3-methyl-5-phenyl-2-thienyl)perfluorocyclopentene (5250 M^{-1} cm^{-1} at 438 nm in hexane),[14,28,29] 1,2-bis(2,4-dimethyl-5-thiazolyl)perfluorocyclopentene (7000 M^{-1} cm^{-1} at 390 nm in hexane)[13] and 1,2-bis(2-methyl-4-phenyl-5-thiazolyl)perfluorocyclopentene (7000 M^{-1} cm^{-1} at 406 nm in hexane)[13]. The large absorption coefficient of **3b** is due to the methoxy group at the *para*-position of the phenyl ring.[24]

3. Conclusion

New photochromic compounds **1a**, **2a** and **3a** were synthesized in an attempt to obtain yellow developing photochromic compounds with low photocycloreversion quantum yields and large absorption coefficients of the closed-ring isomers. The toluene solution of **3a** turned yellow by irradiation with 313 nm, showing an absorption maximum at 416 nm (ε=17,100 M^{-1} cm^{-1}). The absorption coefficient of the closed-ring isomer **3b** was much larger than those of **1b** and **2b**. The photocyclization/cycloreversion quantum yields of **3** were determined to be 0.19 and 0.0014, respectively. Compound **3** is a useful candidate as a yellow photochromic dye.

4. Experimental

HPLC was performed on a Hitachi L-7100 liquid chromatography coupled with a Hitachi L-7400 spectrophotometeric detector. ^{1}H NMR spectra were recorded on a Varian Gemini 200 instrument. Mass spectra were measured with a Shimadzu GCMS-QP5050A gas chromatography-mass spectrometer. Absorption spectra were measured on a Hitachi U-3500 absorption spectrophotometer. Photoirradiation was carried out using an Ushio 500 W superhigh-pressure mercury lamp or an Ushio 500 W xenon lamp. Monochromatic light was isolated by passing the light through a cut off filter (UV-27) and monochromator (Ritsu MC-10N). The quantum yields were determined by comparing the reaction rate of the photochromic compounds in toluene against furyl fulgide in toluene.[30,31] The samples were not degassed. The quantum yield measurement was carried out three times and average values were adopted as the quantum yields.

4.1. Compound data

4.1.1. 1-(5-Methyl-2-phenyl-4-thiazolyl)-2-(3-methyl-2-thienyl)perfluorocyclopentene (1a). To a stirring solution of 4-bromo-5-methyl-2-methylthiazole[12] (524 mg, 2.10 mmol) in dry THF (6 mL) was slowly added 1.6 M *n*-BuLi in hexane (1.30 mL, 2.20 mmol) at −80 °C under argon atmosphere. After the mixture had been stirred for 15 min at −80 °C, compound **4** (540 mg, 1.90 mmol) in dry THF (2 mL) was added. The reaction mixture was further stirred at −80 °C for 2 h, and then distilled water was added. The product was extracted with 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=1/9) to afford to 130 mg (14%) of **1a** as colorless needles: mp 107–108 °C. ^{1}H NMR ($CDCl_3$, 200 MHz): δ=1.80 (s, 3H), 1.98 (s, 3H), 6.86 (d, *J*=5.0 Hz, 1H), 7.44 (m, 5H), 7.88 (m, 2H). MS (*m*/*z*) 445 (M^+). Anal. Found: C, 53.96; H, 2.85; N, 3.00%. Calcd for $C_{20}H_{13}F_6NS_2$: C, 53.93; H, 2.94; N, 3.14%.

4.1.2. Closed-ring isomer for 1a (1b). Compound **1b** was isolated as an orange solid by passing a photostationary solution containing **1a** and **1b** thorough HPLC (ethyl acetate/hexane=1/9): ^{1}H NMR ($CDCl_3$, 200 MHz): δ=1.68 (s, 3H), 1.81 (s, 3H), 5.73 (d, *J*=6.0 Hz, 1H), 6.24 (d, *J*=6.0 Hz, 1H), 7.42–7.62 (m, 3H), 7.85–8.05 (m, 2H). MS (*m*/*z*) 445 (M^+). Anal. Found: C, 53.93; H, 2.95; N, 3.18%. Calcd for $C_{20}H_{13}F_6NS_2$: C, 53.93; H, 2.94; N, 3.14%.

4.1.3. 1-(5-Methoxy-2-phenyl-4-thiazolyl)-2-(3-methoxy-2-thienyl)perfluorocyclopentene (2a). To a stirring solution of 2-bromo-3-methoxythiophene[20] (500 mg, 2.6 mmol) in dry ether (25 mL) was slowly added 1.6 M *n*-BuLi in hexane (1.6 mL, 2.7 mmol) at −80 °C under argon atmosphere. After the mixture had been stirred for 15 min at −80 °C, 1-(5-methoxy-2-phenyl-4-thiazolyl)perfluorocyclopentene[12] (1.0 g, 2.8 mmol) in dry ether (10 mL) was added. The reaction mixture was further stirred at −80 °C for 1 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=2/8) and HPLC (ethyl acetate/hexane=2/8) to afford to 50 mg (4%) of **2a** as colorless plates: mp 133–134 °C. ^{1}H NMR ($CDCl_3$, 200 MHz). δ=3.59 (s, 3H), 3.81 (s, 3H), 6.80 (d, *J*=5.6 Hz, 2H), 7.35–7.50 (m, 5H), 7.70–7.80 (m, 2H). MS (*m*/*z*) 447 (M^+). Anal. Found: C, 50.58; H, 2.85; N, 3.10%. Calcd for $C_{20}H_{13}F_6NO_2S_2$: C, 50.31; H, 2.74; N, 2.93%.

4.1.4. Closed-ring isomer for 2a (2b). Compound **2b** was isolated as a red solid by passing a photostationary solution containing **2a** and **2b** thorough HPLC (ethyl acetate/hexane=2/8): ^{1}H NMR ($CDCl_3$, 200 MHz): δ=1.67 (s, 3H), 1.75 (s, 3H), 2.39 (s, 3H), 7.34–7.16 (m, 5H), 7.42–7.34 (m, 3H), 7.85–7.76 (m, 2H). MS (*m*/*z*) 447 (M^+). Anal. Found: C, 50.57; H, 2.76; N, 3.18%. Calcd for $C_{20}H_{13}F_6NO_2S_2$: C, 50.31; H, 2.74; N, 2.93%.

4.1.5. 1-[5-Methoxy-2-(4-methoxyphenyl)-4-thiazolyl]-2-(1,2-dimethylpropenyl)perfluoro-cyclopentene (3a). To a stirring solution of 2-bromo-3-methyl-2-butene[26] (210 mg, 1.4 mmol) in a mixed solvent of anhydrous hexane (13 mL) and THF (13 mL) was slowly added 1.5 M *t*-BuLi in heptane (1.1 mL, 1.7 mmol) at −80 °C under argon atmosphere. After the mixture had been stirred for 40 min at −80 °C, compound **7** (250 mg, 0.61 mmol) in a mixed solvent of anhydrous hexane (2.5 mL) and THF (2.5 mL)

was added. The reaction mixture was further stirred at −80 °C for 1 h, and the reaction was allowed to slowly warm to room temperature and stirred there for 1 h. The reaction was quenched with distilled water. The product was extracted with 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=2/8) to afford to 15 mg (5%) of **3a** as colorless needles: mp 93–94 °C. ^{1}H NMR ($CDCl_3$, 200 MHz): δ=1.49 (s, 3H), 1.75 (s, 3H), 1.93 (s, 3H), 3.86 (s, 3H), 4.01 (s, 3H), 6.93 (d, J=9.0 Hz, 2H), 7.71 (d, J=9.0 Hz, 2H). MS (*m*/*z*) 463 (M^+). Anal. Found: C, 54.30; H, 4.20; N, 3.18%. Calcd for $C_{21}H_{19}F_6NO_2S_2$: C, 54.42; H, 4.13; N, 3.02%.

4.1.6. Closed-ring isomer for 3a (3b). Compound **3b** was isolated as a yellow solid by passing a photostationary solution containing **3a** and **3b** thorough HPLC (ethyl acetate/hexane=3/7): ^{1}H NMR ($CDCl_3$, 200 MHz): δ=1.20 (s, 3H), 1.44 (s, 3H), 2.04 (s, 3H), 3.16 (s, 3H), 3.90 (s, 3H), 6.97 (d, J=9.0 Hz, 2H), 8.01 (d, J=9.0 Hz, 2H). MS (*m*/*z*) 463 (M^+). Anal. Found: C, 54.40; H, 4.10; N, 2.80%. Calcd for $C_{21}H_{19}F_6NO_2S_2$: C, 54.42; H, 4.13; N, 3.02%.

4.1.7. 1-(3-Methyl-2-thienyl)perfluorocyclopentene (4). To a solution of 2-bromo-3-methylthiophene (5.0 g, 28 mmol) in dry ether (60 mL) was added slowly 1.6 M *n*-BuLi in hexane (18 mL, 29 mmol) at −80 °C under argon atmosphere. After the mixture was stirred for 30 min at −80 °C, perfluorocyclopentene (3.8 mL, 28 mmol) in dry ether (2 mL) was added. The reaction mixture was further stirred at −80 °C for 1 h and then distilled water was added. The product was extracted with ether, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography (hexane) to afford 5.8 g (71%) of **4** as colorless oil: ^{1}H NMR (200 MHz, $CDCl_3$): δ=2.29 (d, J=3.4 Hz, 1H), 6.99 (d, J=5.2 Hz, 1H), 7.53 (d, J=5.2 Hz, 1H). MS (*m*/*z*) 290 (M^+). Anal. Found: C, 41.42; H, 1.76%. Calcd for $C_{10}H_5F_7S$: C, 41.39, H, 1.74%.

4.1.8. 5-Methoxy-2-(4-methoxyphenyl)thiazole (5). *N*-(4-methoxybenzoyl) glycine methyl ester[32,33] (10.0 g, 52 mmol) and phosphorus pentasulfide (10 g, 52 mmol) were rapidly added to dry chloroform (15 mL), and the mixture solution was stirred at 80 °C under argon atmosphere. After stirring for 1 h, white precipitate was deposited in the mixture solution. Then the mixture was refluxed for 24 h under argon atmosphere. The reaction mixture was poured in aqueous NaOH water, and extracted with dichloromethane. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography (ethyl acetate/hexane=3/7) to afford 8 g (80%) of **5** as a yellow solid. ^{1}H NMR (200 MHz, $CDCl_3$): δ=3.84 (s, 3H), 3.94 (s, 3H), 6.92 (d, J=9.0 Hz, 2H), 7.06 (s, 1H), 7.73 (d, J=9.0 Hz, 2H). MS (*m*/*z*) 221 (M^+). Anal. Found: C, 59.91; H, 5.25; N, 6.41%. Calcd for $C_{11}H_{11}NO_2S$: C, 59.71; H, 5.01; N, 6.33%.

4.1.9. 4-Bromo-5-methoxy-2-(4-methoxyphenyl)thiazole (6). *N*-bromosuccinimide (5.5 g, 31 mmol) was added to a stirred solution of **5** (6.9 g, 31.0 mmol) in dry chloroform (140 mL). The mixture was stirred at −80 °C for 1 h and room temperature for 1 h and extracted with ethyl acetate. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography (ethyl acetate/hexane=3/7) to afford 7.5 g (80%) of **6** as colorless crystals: mp 102–103 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ=3.85 (s, 3H), 4.02 (s, 3H), 6.93 (d, J=9.0 Hz, 2H), 7.75 (d, J=9.0 Hz, 2H). MS (*m*/*z*) 300 (M^+). Anal. Found: C, 44.21; H, 3.41; N, 4.63%. Calcd for $C_{11}H_{10}NO_2SBr$: C, 44.01; H, 3.36; N, 4.67%.

4.1.10. 1-[5-Methoxy-2-(4-methoxyphenyl)-4-thiazolyl]-perfluorocyclopentene (7). To a solution of **7** (1 g, 3.33 mmol) in dry THF (40 mL) was added slowly 1.6 M *n*-BuLi in hexane (2.0 mL, 3.2 mmol) at −80 °C under argon atmosphere. After the mixture was stirred for 15 min at −78 °C, perfluorocyclopentene (0.50 mL, 2.34 mmol) in dry THF (2 mL) was added. The reaction mixture was further stirred at −78 °C for 1 h and then distilled water was added. The product was extracted with ether, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography (ethyl acetate/hexane=3/7) to afford 870 mg (67%) of **7** as colorless needles: mp 77–78 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ=3.86 (s, 3H), 4.10 (s, 3H), 6.95 (d, J=8.8 Hz, 2H), 7.78 (d, J=8.8 Hz, 2H). MS (*m*/*z*) 413 (M^+). Anal. Found: C, 46.27; H, 2.63; N, 3.65%. Calcd for $C_{16}H_{10}NO_2SF_7$: C, 46.50; H, 2.44; N, 3.39%.

Acknowledgements

This work was partially supported by the Ministry of Education, Science, Sports and Culture, Nanotechnology Support Project, Grant-in-Aid for Scientific Research (S) (No. 15105006) and the 21 Century COE program.

References and notes

1. Brown, G. H. *Photochromism*; Wiley: New York, 1971.
2. Dürr, H.; Bouas-Laurent, H. *Photochromism, Molecules and Systems*; Elsevier: Amsterdam, 1990.
3. Irie, M.; Fukaminato, T.; Sasaki, T.; Tamai, N.; Kawai, T. *Nature* **2002**, *420*, 759–760.
4. Matsuda, K.; Irie, M. *Chem. Eur. J.* **2001**, *7*, 3466–3473.
5. Morimoto, M.; Kobatake, S.; Irie, M. *J. Am. Chem. Soc.* **2003**, *125*, 11080–11087.
6. Morimitsu, K.; Shibata, K.; Kobatake, S.; Irie, M. *J. Org. Chem.* **2002**, *67*, 4574–4578.
7. Kawata, S.; Kawata, Y. *Chem. Rev.* **2000**, *100*, 1777–1788.
8. Nakatani, K.; Delaire, J. A. *Chem. Mater.* **1997**, *9*, 2682–2684.
9. Irie, M. *Chem. Rev.* **2000**, *100*, 1685–1716.
10. Irie, M.; Uchida, K. *Bull. Chem. Soc. Jpn* **1998**, *71*, 985–996.
11. Irie, M.; Lifka, T.; Kobatake, S.; Kato, N. *J. Am. Chem. Soc.* **2000**, *122*, 4871–4876.
12. Takami, S.; Kawai, T.; Irie, M. *Eur. J. Org. Chem.* **2002**, 3796–3800.
13. Uchida, K.; Ishikawa, T.; Takeshita, M.; Irie, M. *Tetrahedron* **1998**, *54*, 6627–6638.
14. Uchida, K.; Irie, M. *Chem. Lett.* **1995**, 969–970.

15. Uchida, K.; Kido, Y.; Yamaguchi, T.; Irie, M. *Bull. Chem. Soc. Jpn* **1998**, *71*, 1101–1108.
16. Matsushima, R.; Morikane, H.; Kohno, Y. *Chem. Lett.* **2003**, 302–303.
17. Luo, Q.; Li, X.; Jing, S.; Zhu, W.; Tian, H. *Chem. Lett.* **2003**, 1116–1117.
18. Shibata, K.; Kobatake, S.; Irie, M. *Chem. Lett.* **2001**, 618–619.
19. Guillaumont, D.; Kobayashi, T.; Kanda, K.; Miyasaka, H.; Uchida, K.; Kobatake, S.; Shibata, K.; Nakamura, S.; Irie, M. *J. Phys. Chem. A* **2002**, *106*, 7222–7227.
20. Demanze, F.; Yassar, A.; Garnier, F. *Macromolecules* **1996**, *29*, 4267–4273.
21. Peters, A.; Vitols, C.; Mcdonald, R.; Branda, N. R. *Org. Lett.* **2003**, *5*, 1183–1186.
22. Yokoyama, Y.; Nagashima, H.; Shrestha, S.; Yokoyama, Y.; Takada, K. *Bull. Chem. Soc. Jpn* **2003**, *76*, 355–361.
23. Shrestha, S.; Nagashima, H.; Yokoyama, Y.; Yokoyama, Y. *Bull. Chem. Soc. Jpn* **2003**, *76*, 363–367.
24. Irie, M.; Sakemura, K.; Okinaka, M.; Uchida, K. *J. Org. Chem.* **1995**, *60*, 8305–8309.
25. Irie, M.; Miyatake, O.; Sumiya, R.; Hanazawa, M.; Horikawa, Y.; Uchida, K. *Mol. Cryst. Liq. Cryst.* **1994**, *246*, 155.
26. Patel, B. A.; Kim, J.-I. I.; Bender, D. D.; Kao, L.-C.; Heck, R. F. *J. Org. Chem.* **1981**, *46*, 1061–1067.
27. Fukaminato, T.; Kawai, T.; Kobatake, S.; Irie, M. *J. Phys. Chem. B* **2003**, *107*, 8372–8377.
28. Uchida, K.; Irie, M. *J. Inf. Recording* **1998**, *24*, 101–104.
29. Uchida, K.; Matsuoka, T.; Kobatake, S.; Yamaguchi, T.; Irie, M. *Tetrahedron* **2001**, *57*, 4559–4565.
30. Yokoyama, Y.; Kurita, Y. *J. Synth. Org. Chem. Jpn* **1991**, *49*, 364–372.
31. Heller, H. G.; Langan, J. R. *J. Chem. Soc., Perkin Trans. 2* **1981**, 341–343.
32. Matsumura, E.; Shin, T.; Murao, S.; Kawano, T. *Agric. Biol. Chem.* **1985**, *49*, 973–979.
33. Storer, A. C.; Carey, P. R. *Biochemistry* **1985**, *24*, 6808–6818.