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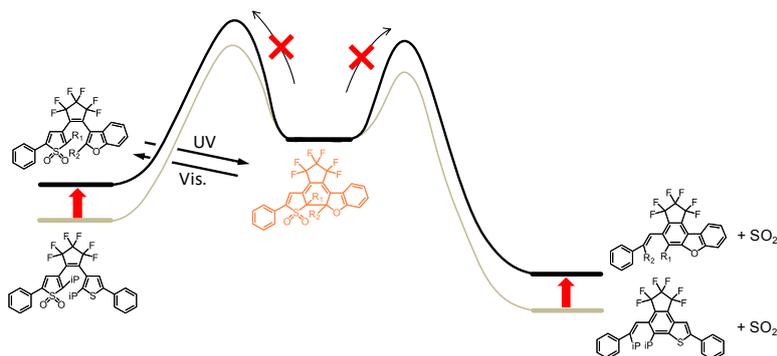Placed on: Osaka City University

Graphical Abstract

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Department of Applied Chemistry, Graduate School of Engineering, Osaka City University,
3-3-138 Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan

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3-3-138 Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan
∗ *Corresponding author. Tel. & fax: +81-6-6605-2797; e-mail: kobatake@a-chem.eng.osaka-cu.ac.jp*

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ABSTRACT

Diarylethenes having a benzofuryl group and their thiophene-*S*,*S*-dioxidized diarylethenes were synthesized and their optical properties and thermal stability were investigated. Upon oxidation of the thiophene ring, the optical properties such as absorption maxima, photocycloreversion quantum yields, and conversion from the open-ring isomer to the closed-ring isomer have changed. On the other hand, the thermal stability of the closed-ring isomers of the *S*,*S*-dioxidized diarylethenes is significantly higher than those of thiophene-*S*,*S*-dioxidized diarylethenes having a phenylthienyl group instead of a benzofuryl group. The high thermal stability of the closed-ring isomer was quantitatively discussed based on ground state energies obtained by quantum chemical calculations.
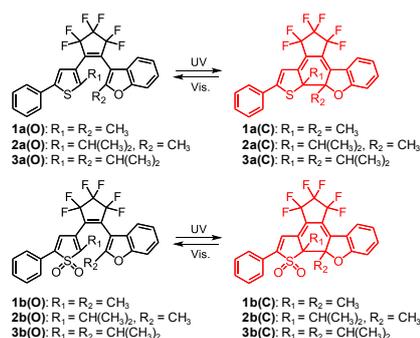
1. Introduction

A lot of photochromic compounds have been so far synthesized and investigated because they have a potential for use in application such as ophthalmic lenses,[1] optical memories,[2] photooptical switches,[3] displays,[4] nonlinear optics,[5] and photoresponsive actuators.[6] Especially, diarylethene derivatives are one of the representative photochromic compounds and can modulate physicochemical properties such as conductivity, dielectric constant, refractive index, and fluorescence according to photochromic reactions.[7,8] Furthermore, in recent studies, thiophene oxidized diarylethenes have attracted much attention because they have different properties from non-oxidized diarylethenes. For example, Kim and Ahn and coworkers have reported that while non-oxidized diarylethenes show no fluorescence at room temperature, diarylethenes having dioxidized benzothienyl groups as both aryl groups showed a strong fluorescent property in the closed-ring isomer.[9–11] Irie and coworkers have reported that the oxidized diarylethenes introducing ethyl groups at the reactive carbons showed much larger fluorescence quantum yields (Φ_f = 0.6-0.9) in the closed-ring isomer.[12,13] Kawai and coworkers have also reported that oxidized terarylenes showed relatively high fluorescence properties (Φ_f = 0.34-0.36).[14] These turn-on mode fluorescence switching systems are expected for application to optical recording media and biological systems.

On the other hand, we have reported the thermal irreversible reaction in the closed-ring isomer of diarylethenes having a dioxidized phenylthienyl group.[15,16] The closed-ring isomers of thiophene-*S*,*S*-dioxidized diarylethenes with secondary alkyl substituents at the reactive positions were found to undergo thermal bleaching reactions to produce byproducts. The rate of the thermal bleaching reactions can be controlled by the bulkiness of the substituent at the reactive positions and the introduction of methyl groups at the 4-position of the thiophene rings. Such materials can be used in application such as light-starting irreversible thermosensors. Thus, the investigation of novel oxidized diarylethenes is of great interest for making new functional photochromic materials.

Here, we have synthesized diarylethenes having a benzofuryl group (**1a−3a**) and their thiophene-*S*,*S*-dioxidized diarylethenes (**1b−3b**) as shown in **Scheme 1**. The photochromic reaction behavior and thermal stability of the closed-ring isomers are discussed in this paper.

1a(O): $R_1 = R_2 = CH_3$
2a(O): $R_1 = CH(CH_3)_2$, $R_2 = CH_3$
3a(O): $R_1 = R_2 = CH(CH_3)_2$

1a(C): $R_1 = R_2 = CH_3$
2a(C): $R_1 = CH(CH_3)_2$, $R_2 = CH_3$
3a(C): $R_1 = R_2 = CH(CH_3)_2$

1b(O): $R_1 = R_2 = CH_3$
2b(O): $R_1 = CH(CH_3)_2$, $R_2 = CH_3$
3b(O): $R_1 = R_2 = CH(CH_3)_2$

1b(C): $R_1 = R_2 = CH_3$
2b(C): $R_1 = CH(CH_3)_2$, $R_2 = CH_3$
**3b(C)**: $R_1 = R_2 = CH(CH_3)_2$

Scheme 1. Photochromic diarylethenes used in this work.

2. Results and Discussion

2.1. Photochromic reaction behavior

Diarylethenes **1a−3a** and thiophene-*S*,*S*-dioxidized diarylethenes **1b−3b** showed reversible photochromic reactions upon alternating irradiation with ultraviolet (UV) and visible light. In their diarylethenes, the photocyclization and photocycloreversion reactions can be repeated for several cycles. **Fig. 1** shows the absorption spectral changes of diarylethenes **1a−3a** and thiophene-*S*,*S*-dioxidized diarylethenes **1b−3b** in *n*-hexane. The open-ring isomers **1a(O)−3a(O)** have absorption maxima around 250 nm. Upon irradiation with 313 nm light, the colorless solution turned to red-purple, in which the visible absorption maxima were observed at 525, 542, and 552 nm for **1a(C)**, **2a(C)**, and **3a(C)**, respectively. These spectral changes are ascribed to the photoisomerization from the open-ring isomers to the closed-ring isomers. The colored solution returned to the initial colorless solution by irradiation with visible light (> 500 nm) and the absorption spectra returned to those of **1a(O)−3a(O)**. After the oxidation of the thiophene ring, the open-ring isomers **1b(O)−3b(O)** have absorption maxima around 340 nm. Upon irradiation with 313 nm light, the color of the solution changed from colorless to yellow-orange, in which the visible absorption maxima were observed at 470, 479, and 491 nm for **1b(C)**, **2b(C)**, and **3b(C)**, respectively. This is due to the photochromic reaction from the open-ring isomer to the closed-ring isomer. Upon irradiation with visible light (> 500 nm), the solution colors and absorption spectra returned to the initial states.
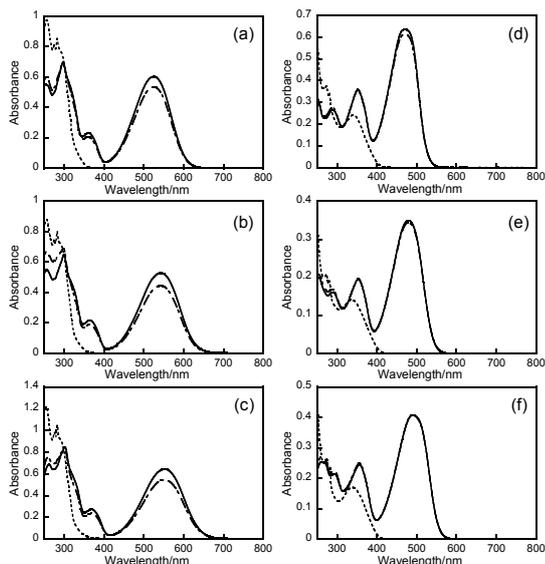
Fig. 1. Absorption spectra of **1a** (a), **2a** (b), **3a** (c), **1b** (d), **2b** (e), and **3b** (f) in *n*-hexane: open-ring isomer (O) (- - -), closed-ring isomer (C) (–), and the photostationary solution upon irradiation with 313 nm light (– — –).

In order to compare the photoreactivity before and after the oxidation of the thiophene ring, the molar absorption coefficient (ε), the photocyclization quantum yield ($\Phi_{o \to c}$), the photocycloreversion quantum yield ($\Phi_{c \to o}$), and the conversion from the open-ring isomer to the closed-ring isomer were determined as shown in **Table 1**. By the oxidation of the thiophene ring, the absorption maxima of the closed-ring isomers **1b(C)−3b(C)** were blue-shifted in comparison with those of **1a(C)−3a(C)**. Although the photocyclization quantum yields scarcely changed, the photocycloreversion quantum yields significantly decreased by a factor of $10-10^2$ upon the oxidation. Moreover, the conversion from the open-ring isomer to the closed-ring isomer increased up to 96-100% upon the oxidation.

These results are similar to those of the thiophene-*S*,*S*-dioxidized diarylethenes having a phenylthienyl group.[9]

Table 1
Optical properties of diarylethenes in *n*-hexane

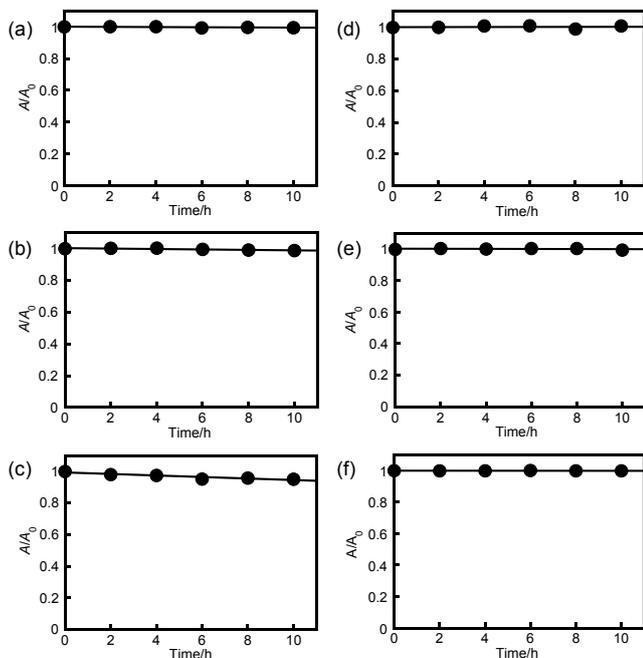|	open-ring isomer		closed-ring isomer		$\Phi_{o \to c}$	$\Phi_{c \to o}$	Conv./ %
	λ_{max}/nm	ε/M^{-1}cm^{-1}	λ_{max}/nm	ε/M^{-1}cm^{-1}			
1a	257	29400	525	18100	0.39	0.088	89
2a	256	23400	542	14000	0.52	0.20	84
3a	255	27000	552	14400	0.51	0.14	84
1b	341	7200	470	19000	0.39	0.0066	96
2b	337	8400	479	20700	0.39	0.0028	98
3b	339	8500	491	20300	0.30	0.0024	~100

2.2. Thermal stability of the closed-ring isomer

The closed-ring isomers of diarylethenes having bulky substituents at the reactive carbons, such as isopropyl or isobutyl groups, show thermal cycloreversion reaction to the open-ring isomers.[17–23] On the other hand, the closed-ring isomers of the thiophene-*S*,*S*-dioxidized diarylethenes having secondary alkyl groups at the reactive positions undergo a thermally irreversible reaction to produce byproducts. Byproducts are produced by elimination of the sulfonyl group and rearrangement of the secondary alkyl group from the closed-ring isomer upon heating as shown in **Scheme 2**.[15,16] The photogenerated closed-ring isomer (**4b(C)**) of the oxidized diarylethene having isopropyl groups at the reactive positions (**4b(O)**) formed three byproducts upon heating.
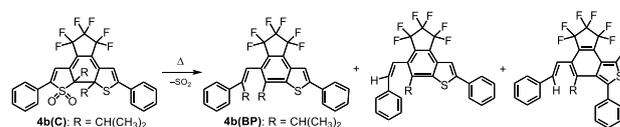
Scheme 2. Thermal byproducts formation of thiophene-*S*,*S*-dioxidized diarylethene closed-ring isomer **4b(C)**.

Here, we investigated the thermal reaction behavior of the closed-ring isomers **1a(C)−3a(C)** and **1b(C)−3b(C)**. **Fig. 2** shows the absorbance changes of the colored solutions of **1a(C)−3a(C)** and **1b(C)−3b(C)** in toluene at 110 °C. Before the oxidation, **1a(C)** and **2a(C)** did not show any decoloration even after 10 h. On the other hand, the absorbance of **3a(C)** slightly decreased. This is due to the introduction of bulky isopropyl substituents at both reactive carbons. After the oxidation of a thiophene ring, **1b(C)−3b(C)** caused less thermal decoloration reaction even after 10 h at 110 °C, regardless of the introduction of bulky isopropyl substituents at the reactive carbons. These results are different from those of the thiophene-*S*,*S*-dioxidized diarylethenes having the phenylthienyl group. This is ascribed to the introduction of a benzofuryl group instead of a phenylthienyl group.

Fig. 2. Absorbance change of **1a(C)** (a), **2a(C)** (b), **3a(C)** (c), **1b(C)** (d), **2b(C)** (e), and **3b(C)** (f) in toluene at 110 °C.

In order to quantitatively discuss the thermal stability of the closed-ring isomer of diarylethenes, the energy difference (ΔH) between the open- and closed-ring isomers in the ground states and the energy difference ($\Delta H'$) between the closed-ring isomer and the total energy of byproduct and SO_2 were calculated by density functional theory (DFT) at the B3LYP/6-31G(d) level. The energy of SO_2 was calculated to be -1440317.2 kJ mol^{-1}. For comparison, the ΔH and $\Delta H'$ values of the thiophene-S,S-dioxidized diarylethene having a phenylthienyl group (**4b**) were also calculated. **Table 2** shows ground state energies of the open-ring isomer (**O**), the closed-ring isomer (**C**), the byproduct (**BP**), and their energy differences (ΔH and $\Delta H'$). In our previous work, it was clarified that diarylethenes having ΔH value over about 60 kJ mol^{-1} exhibit the thermal cycloreversion reaction at 100 °C.[16] Before the oxidation, the ΔH values of **1a–3a** are 37.90, 61.01, and 88.95 kJ mol^{-1}, respectively. These values suggest that only the closed-ring isomer **3a(C)** shows the thermal cycloreversion reaction at 100 °C, which is consistent with the experimental results. After the oxidation, the ΔH values of **1b–3b** are much smaller than 60 kJ mol^{-1}, which means that the closed-ring isomers of the thiophene-S,S-dioxidized diarylethenes **1b(C)–3b(C)** cannot undergo thermal cycloreversion reactions at 100 °C. This is also consistent with the experimental results.

Next, we discuss the $\Delta H'$ values for the thiophene-S,S-dioxidized diarylethenes. The $\Delta H'$ values of **1b**, **2b**, and **3b** were estimated to be 148.22, 179.51, and 198.94 kJ mol^{-1}, respectively, by the DFT calculation. These values are smaller than 214.56 kJ mol^{-1} for **4b** that undergoes the thermal bleaching reaction to produce byproducts.[15,16] The relationships between the $\Delta H'$ values and the logarithm of the rate constant (k) at 100 °C and activation energy (E_a) for the thermal byproduct formation of the thiophene-S,S-dioxidized diarylethenes have been reported previously as shown in **Fig. 3**.[16] The relationships are expressed as follows:

$$\log(k/\text{s}^{-1}) = 0.114 \times (\Delta H'/\text{kJ mol}^{-1}) - 27.8$$

$$(E_a/\text{kJ mol}^{-1}) = -0.968 \times (\Delta H'/\text{kJ mol}^{-1}) + 329$$

Table 2
Energy gap (ΔH) calculated between the open- and closed-ring isomers and energy gap ($\Delta H'$) calculated between the dioxidized closed-ring isomer and the byproduct.

	ΔH/kJ mol^{-1}	$\Delta H'$/kJ mol^{-1}
1a	37.90	
2a	61.01	
3a	88.95	
1b	-25.89	148.22
2b	6.48	179.51
3b	38.82	198.94
4b	57.31	214.56
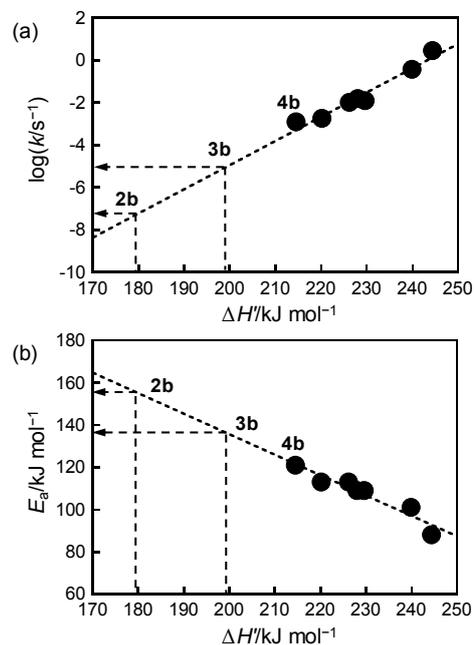
Fig. 3. Relationship between $\Delta H'$ and the logarithm of k at 100 °C (a) and the activation energy (b) for the thermal byproduct formation of the oxidized diarylethenes.

From these relationships with the $\Delta H'$ values, the k values at 100 °C and the E_a values of **2b** and **3b** were calculated to be $k = 1.3 \times 10^{-11}$ s^{-1} and $E_a = 186$ kJ mol^{-1} for **1b**, $k = 4.6 \times 10^{-8}$ s^{-1} and $E_a = 155$ kJ mol^{-1} for **2b**, and $k = 7.6 \times 10^{-6}$ s^{-1} and $E_a = 136$ kJ mol^{-1} for **3b** as shown in **Table 3**. Compared with the values for **4b** ($k = 1.2 \times 10^{-3}$ s^{-1} and $E_a = 121$ kJ mol^{-1}), the k value decreased by a factor of 10^2–10^8 and the E_a value became significantly large. This is due to the decrease in aromatic stabilization energy by the introduction of the benzofuryl group instead of the phenylthienyl group, which results in the destabilization of the open-ring isomer and the byproduct in the ground state as shown in **Fig. 4**. As a result, the closed-ring isomer **1b(C)–3b(C)** could not cause the thermal bleaching reaction even at 110 °C. Thus, the thermal reaction behavior of the closed-ring isomer could be explained by the quantum chemical calculations.

Table 3
The rate constant and activation energy of the thermal byproduct formation for **2b(C)**, **3b(C)**, and **4b** at 100 °C.

	k/s^{-1} at 100 °C	$E_a/\text{kJ mol}^{-1}$
1b(C)	1.3×10^{-11} [a]	186 [a]
2b(C)	4.6×10^{-8} [a]	155 [a]
3b(C)	7.6×10^{-6} [a]	136 [a]
4b(C)	1.2×10^{-3} [b]	121 [b]

a) Calculated values. b) Experimental values.
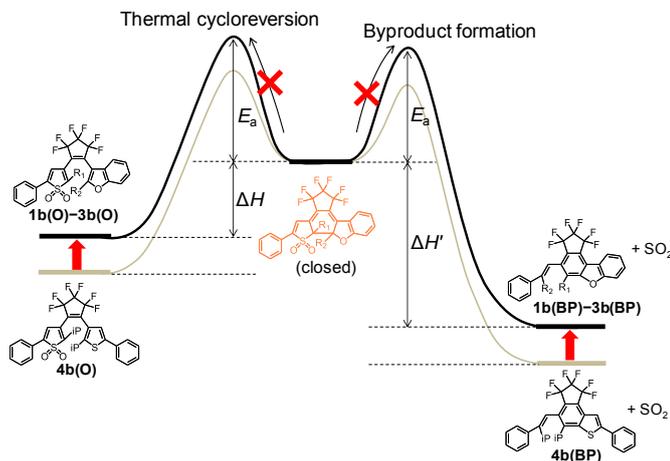
Fig. 4. Schematic energy diagram of the oxidized diarylethene system in the ground state.

3. Conclusion

We have synthesized diarylethenes having a benzofuryl group (**1a−3a**) and their thiophene-*S*,*S*-dioxidized diarylethenes (**1b−3b**) and investigated their optical properties and the thermal stability of the closed-ring isomers. Upon oxidation of the thiophene ring, the absorption maxima of the closed-ring isomers were blue-shifted. The photocycloreversion quantum yields decreased by a factor of $10-10^2$, whereas the photocyclization quantum yields scarcely changed. Moreover, the conversion from the open-ring isomer to the closed-ring isomer increased up to 96-100%. The diarylethene closed-ring isomers **1b(C)−3b(C)** have high thermal stability, which is predicted from the ΔH and $\Delta H'$ values obtained from the DFT calculations. These results provide new knowledge for molecular design of diarylethenes with a desired thermal stability.

4. Experimental Section

4.1. General.

Solvents used were spectroscopic grade and purified by distillation before use. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on a Bruker AV-300N spectrometer with tetramethylsilane as the internal standard. Infrared spectra (IR) were recorded on a JASCO FT/IR-410 spectrometer. High-resolution mass spectra (HRMS) were obtained on a Bruker FT-ICR/solariX mass spectrometer. UV-vis absorption spectra were measured with a JASCO V-560 absorption spectrometer. Photoirradiation in solution was conducted using a 200 W mercury−xenon lamp (Moritex MUV-202) as a light source. Monochromatic light was obtained by passing the light through a monochromator (Jobin Yvon H10 UV) and glass filters. The heating of the sample for the thermal cycloreversion was carried out using a constant temperature chamber ESPEC ST-110. The sample in an optical quartz cell was degassed and sealed off under vacuum. High-performance liquid chromatography (HPLC) was carried out using a HITACHI HPLC system equipped with a Kanto Chemical Mightysil Si 60 column. The difference in energy in the ground states was calculated using Spartan'14 computational software. The molecular structures were fully optimized at the B3LYP/6-31G(d) level of theory, and vibrational frequencies for all optimized species were computed at the same level to confirm each stationary point to be a minimum.

4.2. Materials.

Diarylethenes **1a−3a** and thiophene-*S*,*S*-dioxidized diarylethenes **1b−3b** were synthesized as shown in **Scheme 3**. Compounds **5−12** were prepared by similar methods according to the procedures described in the literature.[24-26]
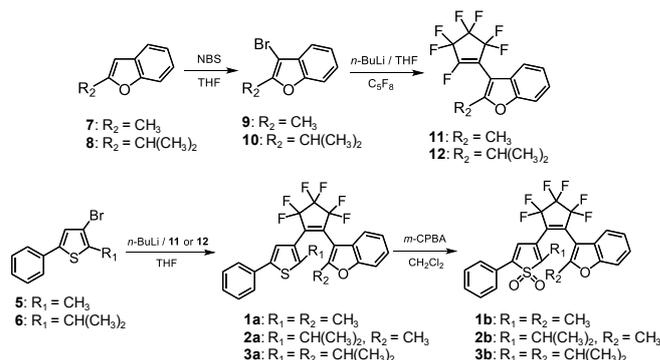
Scheme 3. Synthetic routes of diarylethenes and thiophene-*S*,*S*-dioxidized diarylethenes.

4.2.1. 1-(2-Methyl-3-benzofuryl)-2-(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene (1a)

n-BuLi (1.6 M solution in *n*-hexane) (0.32 mL, 0.51 mmol) was slowly added to a stirred dry THF solution (5.0 mL) containing compound **5** (120 mg, 0.46 mmol) at −78 °C under argon atmosphere. After the mixture has been stirred for 2 h, compound **11** (150 mg, 0.46 mmol) in dry THF was added to the mixture. The reaction was further stirred at −78 °C for 2 h, and the reaction was allowed to slowly warm up to room temperature. The reaction was quenched by the addition of water. The product was extracted with diethyl ether. The organic layer was dried over MgSO$_4$, filtered, and concentrated. The crude product was purified by column chromatography on silica gel (*n*-hexane/ethyl acetate = 9:1) and by HPLC (*n*-hexane/ethyl acetate = 98:2) to give 68 mg of **1a** in 47% yield as a colorless crystal. mp 155-156 °C. ^{1}H NMR (300 MHz, CDCl$_3$, TMS) δ = 1.88 (s, 3H, CH$_3$), 2.13 (s, 3H, CH$_3$), 7.1-7.6 (m, 10H, Aromatic H). ^{13}C NMR (75 MHz, CDCl$_3$) δ = 13.5, 14.9, 105.7, 111.2, 120.2, 122.5, 123.8, 124.7, 125.8, 126.4, 128.1, 129.2, 133.4, 141.5, 142.5, 154.3, 156.3. IR (v, KBr, cm^{-1}): 432, 474, 544, 575, 694, 756, 798, 841, 891, 926, 987, 1065, 1126, 1192, 1273, 1338, 1435, 1458, 1597, 1635, 2854, 2920, 2958, 3024, 3070. HRMS (MALDI) m/z = 478.0819 (M$^+$). Calcd for C$_{25}$H$_{16}$F$_6$OS = 478.0821.

4.2.2. 1-(2-Methyl-3-benzofuryl)-2-(2-isopropyl-5-phenyl-3-thienyl)perfluorocyclopentene (2a)

n-BuLi (1.6 M solution in *n*-hexane) (0.73 mL, 1.2 mmol) was slowly added to a stirred dry THF solution (5.0 mL) containing compound **6** (300 mg, 1.1 mmol) at −78 °C under argon atmosphere. After the mixture has been stirred for 2 h, compound **11** (350 mg, 1.1 mmol) in dry THF was added to the mixture. The reaction was further stirred at −78 °C for 2 h, and the reaction was allowed to slowly warm up to room temperature.

The reaction was quenched by the addition of water. The product was extracted with diethyl ether. The organic layer was dried over MgSO$_4$, filtered, and concentrated. The crude product was purified by column chromatography on silica gel (*n*-hexane/ethyl acetate = 9:1) and by HPLC (*n*-hexane/ethyl acetate = 98:2) to give 120 mg of **2a** in 23% yield as a colorless crystal. mp 103-104 °C. ^{1}H NMR (300 MHz, CDCl$_3$, TMS) δ = 0.78 (d, *J* = 6.8 Hz, 6H, CH$_3$), 2.13 (s, 3H, CH$_3$), 2.71 (sept, *J* = 6.8 Hz, 1H, CH), 7.2-7.6 (m, 10H, Aromatic H). ^{13}C NMR (75 MHz, CDCl$_3$) δ = 13.4, 25.0, 29.3, 105.3, 111.2, 119.9, 121.9, 123.2, 123.8, 124.7, 125.8, 126.9, 128.0, 129.1, 129.2, 133.7, 142.5, 154.3, 155.3, 156.0. IR (*v*, KBr, cm^{-1}): 432, 513, 552, 575, 690, 752, 798, 849, 922, 991, 1057, 1122, 1192, 1269, 1335, 1458, 1597, 1643, 2870, 2931, 2970, 3024, 3066. HRMS (MALDI) *m/z* = 506.1132 (M$^+$). Calcd for C$_{27}$H$_{20}$F$_6$OS = 506.1134;

4.2.3. 1-(2-Isopropyl-3-benzofuryl)-2-(2-isopropyl-5-phenyl-3-thienyl)perfluorocyclopentene (3a)

n-BuLi (1.6 M solution in *n*-hexane) (1.0 mL, 1.6 mmol) was slowly added to a stirred dry THF solution (5.0 mL) containing compound **6** (400 mg, 1.4 mmol) at −78 °C under argon atmosphere. After the mixture has been stirred for 2 h, compound **12** (500 mg, 1.4 mmol) in dry THF was added to the mixture. The reaction was further stirred at −78 °C for 2 h, and the reaction was allowed to slowly warm up to room temperature. The reaction was quenched by the addition of water. The product was extracted with diethyl ether. The organic layer was dried over MgSO$_4$, filtered, and concentrated. The crude product was purified by column chromatography on silica gel (*n*-hexane/ethyl acetate = 95:5), HPLC (hexane/ethyl acetate = 98:2) and by recrystallization from hexane to give 220 mg of **3a** in 31% yield as a colorless crystal. mp 128-129 °C. ^{1}H NMR (300 MHz, CDCl$_3$, TMS) δ = 0.73 (d, *J* = 5.6 Hz, 6H, CH$_3$), 0.98 (d, *J* = 6.7 Hz, 6H, CH$_3$), 2.73 (sept, *J* = 6.8 Hz, 2H, CH), 7.20 (t, *J* = 1.3 Hz, 1H, Aromatic H), 7.2-7.6 (m, 9H, Aromatic H). ^{13}C NMR (75 MHz, CDCl$_3$) δ = 20.6, 25.0, 27.5, 29.2, 102.8, 111.4, 120.1, 122.2, 123.0, 123.7, 124.6, 125.9, 127.2, 128.0, 129.1, 133.8, 142.5, 154.4, 155.5, 163.3. IR (*v*, KBr, cm^{-1}): 420, 467, 505, 544, 567, 694, 752, 806, 856, 922, 995, 1053, 1076, 1119, 1265, 1342, 1458, 1566, 1635, 2877, 2939, 2974, 3028, 3066. HRMS (MALDI) *m/z* = 534.1444 (M$^+$). Calcd for C$_{29}$H$_{24}$F$_6$OS = 534.1447.

4.2.4. 1-(2-Methyl-3-benzofuryl)-2-(2-methyl-5-phenyl-1,1-dioxide-3-thienyl)perfluorocyclo-pentene (1b)

m-Chloroperbenzoic acid (*m*CPBA) (63 mg, 0.37 mmol) was added to a stirred dichloromethane solution (3.0 mL) containing **1a** (50 mg, 0.11 mmol). The reaction mixture was stirred overnight in the dark at room temperature. The reaction mixture was extracted with dichloromethane. The organic phase was dried over MgSO$_4$, filtered, and evaporated. The crude product was purified by column chromatography on silica gel (*n*-hexane/ethyl acetate = 9:1) and by HPLC (*n*-hexane/ethyl acetate = 95:5) to give 34 mg of **1b** in 64% yield as a pale yellow crystal. mp 99-100 °C. ^{1}H NMR (300 MHz, CDCl$_3$, TMS) δ = 1.83 (s, 3H, CH$_3$), 2.30 (s, 3H, CH$_3$), 6.80 (s, 1H, Aromatic H), 7.2-7.7 (m, 9H, Aromatic H). ^{13}C NMR (75 MHz, CDCl$_3$) δ = 9.3, 13.9, 105.3, 111.6, 119.7, 120.2, 124.4, 125.6, 126.4, 126.7, 129.5, 131.0, 141.9, 154.4. IR (*v*, KBr, cm^{-1}): 424, 463, 540, 687, 748, 795, 833, 876, 930, 991, 1057, 1084, 1138, 1192, 1277, 1311, 1342, 1431, 1585, 1624, 2854, 2920, 2989, 3032, 3070, 3093. HRMS (MALDI) *m/z* = 510.0718 (M$^+$). Calcd for C$_{25}$H$_{16}$F$_6$O$_3$S = 510.0719.

4.2.5. 1-(2-Methyl-3-benzofuryl)-2-(2-isopropyl-5-phenyl-1,1-dioxide-3-thienyl)perfluorocyclo-pentene (2b)

*m*CPBA (68 mg, 0.40 mmol) was added to a stirred dichloromethane solution (2.0 mL) containing **2a** (50 mg, 0.10 mmol). The reaction mixture was stirred overnight in the dark at room temperature. The reaction mixture was extracted with dichloromethane. The organic phase was dried over MgSO$_4$, filtered, and evaporated. The crude product was purified by column chromatography on silica gel (*n*-hexane/ethyl acetate = 85:15) and by HPLC (*n*-hexane/ethyl acetate = 95:5) to give 28 mg of **2b** in 53% yield as a pale yellow amorphous solid. ^{1}H NMR (300 MHz, CDCl$_3$, TMS) δ = 0.98 (d, *J* = 7.1 Hz, 6H, CH$_3$), 2.35 (s, 3H, CH$_3$), 2.68 (sept, *J* = 7.1 Hz, 1H, CH), 6.80 (s, 1H, Aromatic H), 7.2-7.7 (m, 9H, Aromatic H). ^{13}C NMR (75 MHz, CDCl$_3$) δ = 14.0, 19.7, 29.2, 104.8, 111.6, 119.2, 119.8, 122.8, 124.3, 125.5, 126.0, 126.3, 126.7, 129.5, 130.9, 142.1, 149.5, 154.3, 156.8. IR (*v*, KBr, cm^{-1}): 422, 486, 561, 596, 646, 688, 750, 800, 837, 864, 904, 928, 991, 1074, 1136, 1198, 1278, 1309, 1340, 1456, 1493, 1579, 2852, 2877, 2937, 2978, 3039, 3066. HRMS (MALDI) *m/z* = 538.1030 (M$^+$). Calcd for C$_{27}$H$_{20}$F$_6$O$_3$S = 538.1032.

4.2.6. 1-(2-Isopropyl-3-benzofuryl)-2-(2-isopropyl-5-phenyl-1,1-dioxide-3-thienyl)perfluorocyclo-pentene (3b)

*m*CPBA (62 mg, 0.36 mmol) was added to a stirred dichloromethane solution (3.0 mL) containing **3a** (55 mg, 0.10 mmol). The reaction mixture was stirred overnight in the dark at room temperature. The reaction mixture was extracted with dichloromethane. The organic phase was dried over MgSO$_4$, filtered, and evaporated. The crude product was purified by column chromatography on silica gel (*n*-hexane/ethyl acetate = 85:15) and by HPLC (*n*-hexane/ethyl acetate = 95:5) to give 31 mg of **3b** in 53% yield as a pale yellow crystal. mp 111-112 °C. ^{1}H NMR (300 MHz, CDCl$_3$, TMS) δ = 0.95 (d, *J* = 6.9 Hz, 6H, CH$_3$), 1.27 (d, *J* = 6.9 Hz, 6H, CH$_3$), 2.6-2.9 (m, 2H, CH), 6.79 (s, 1H, Aromatic H), 7.3-7.7 (m, 9H, Aromatic H). ^{13}C NMR (75 MHz, CDCl$_3$) δ = 19.8, 20.9, 27.6, 29.2, 102.0, 111.8, 119.4, 119.7, 122.4, 124.2, 125.3, 126.4, 126.7, 129.5, 130.9, 142.1, 149.7, 154.4, 163.9. IR (*v*, KBr, cm^{-1}): 420, 488, 559, 596, 648, 688, 752, 802, 827, 870, 904, 937, 993, 1053, 1068, 1142, 1198, 1277, 1311, 1338, 1456, 1601, 2877, 2937, 2978, 3039, 3066. HRMS (MALDI) *m/z* = 566.1426 (M$^+$). Calcd for C$_{29}$H$_{24}$F$_6$O$_3$S = 566.1423.

Acknowledgments

References

1. Crano, J. C.; Flood, T.; Knowles, D.; Kumar, A.; Van Gemert, B. *Pure Appl. Chem.* **1996**, *68*, 1395–1398.
2. Irie, M.; Matsuda, K. In *Electron Transfer in Chemistry*; Balzani, V. Ed.; Wiley-VCH, Weinheim, 2001; pp. 215–242.
3. Irie, M. In *Molecular Switchings*; Feringa, B. L. Ed.; Wiley-VCH, Weinheim, 2001; pp. 37–62.
4. Delaire, J. A.; Nakatani, K. *Chem. Rev.* **2000**, *100*, 1817–1846.
5. Bechinger, C.; Ferrere, S.; Zaban, A.; Sprague, J.; Gregg, B. A. *Nature* **1996**, *383*, 608–610.

6. Kobatake, S.; Takami, S.; Muto, H.; Ishikawa, T.; Irie, M. *Nature* **2007**, *446*, 778–781.
7. Irie, M. *Chem. Rev.* **2000**, *100*, 1685–1716.
8. Irie, M.; Fukaminato, T.; Matsuda, K.; Kobatake, S. *Chem. Rev.* **2014**, *114*, 12174–12277.
9. Jeong, Y. C.; Han, J. P.; Kim, Y.; Kim, E.; Yang, S. I.; Ahn, K. H. *Tetrahedron* **2007**, *63*, 3173–3182.
10. Jeong, Y. C.; Yang, S. I.; Ahn, K. H.; Kim, E. *Chem. Commun.* **2005**, 2503–2505.
11. Jeong, Y. C.; Yang, S. I.; Kim, E.; Ahn, K. H. *Tetrahedron* **2006**, *62*, 5855–5861.
12. Uno, K.; Niikura, H.; Morimoto, M.; Ishibashi, Y.; Miyasaka, H.; Irie, M. *J. Am. Chem. Soc.* **2011**, *133*, 13558–13564.
13. Sumi, T.; Kaburagi, T.; Morimoto, M.; Une, K.; Sotome, H.; Ito, S.; Miyasaka, H.; Irie, M. *Org. Lett.* **2015**, *17*, 4802–4805.
14. Taguchi, M.; Nakagawa, T.; Nakashima, T.; Kawai, T. *J. Mater. Chem.* **2011**, *21*, 17425–17432.
15. Shoji, H.; Kobatake, S. *Chem. Commun.* **2013**, *49*, 2362–2364.
16. Shoji, H.; Kitagawa, D.; Kobatake, S. *New J. Chem.* **2014**, *38*, 933–941.
17. Chen, D. Z.; Wang, Z.; Zhang, H. H. *J. Mol. Struct. (Theochem)* **2008**, *859*, 11–17.
18. Kobatake, S.; Irie, M. *Chem. Lett.* **2003**, *32*, 1078–1079.
19. Morimitsu, K.; Shibata, K.; Kobatake, S.; Irie, M. *Chem. Lett.* **2002**, 572–573.
20. Morimitsu, K.; Shibata, K.; Kobatake, S.; Irie, M. *J. Org. Chem.* **2002**, *67*, 4574–4578.
21. Kobatake, S.; Uchida, K.; Tsuchida, E.; Irie, M. *Chem. Lett.* **2000**, 1340–1341.
22. Kitagawa, D.; Sasaki, K.; Kobatake, S. *Bull. Chem. Soc. Jpn.* **2011**, *84*, 141−147.
23. Shoji, H.; Kitagawa, D.; Kobatake, S. *Res.Chem. Intermed.* **2013**, *39*, 279−289.
24. Ortega, N.; Urban, S.; Beiring, B.; Glorius, F. *Angew. Chem. Int. Ed.* **2012**, *51*, 1710−1713.
25. Yamaguchi, T.; Irie, M. *J. Org. Chem.* **2005**, *70*, 10323−10328.
26. Ren, P.; Wang, R.; Pu, S.; Liu, G.; Fan, C. *J. Phys. Org. Chem.* **2014**, *27*, 183−190.