

Efficient synthesis and photochromic properties of 2,3-position hybrid diarylethene derivatives

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Abstract—An efficient synthetic method was proposed to synthesize some 2,3-position hybrid diarylethene derivatives. In these compounds, one of thiophene rings was attached to the ethylene moiety at 2-position, the other at 3-position. These asymmetric diarylethenes are sensitive at wavelengths in the region of 400 and 500 nm. They can undergo thermally irreversible and fatigue-resistant photochromic reactions in solution, some of them even in the solid state. Substituent effects on their photochromism were examined.
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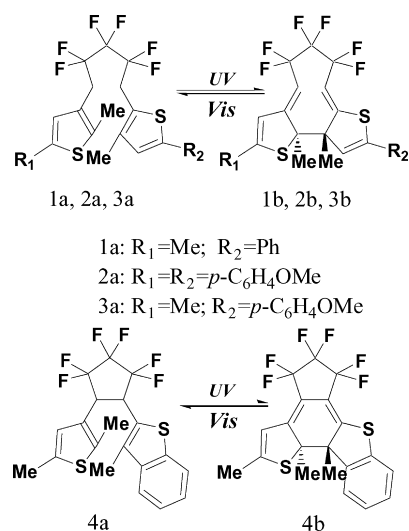
1. Introduction

To increase the storage density in the region of far field optical recording, one of the practical approaches to minimize the mark length is to decrease writing and reading laser wavelength. Research interests in short wavelength optical storage have been growing considerably in recent years.^{1,2} Photochromic diarylethenes have attracted considerable attention in the field of optical data storage and switches due to their thermal stability of both isomers and high fatigue resistance.³ However, most diarylethenes reported have absorption at 550–750 nm wavelength regions. Developing diarylethene derivatives sensitive at a wavelength around 500 nm or even shorter for short-wavelength recording is very important.

As well known, the absorption spectrum is dependent on the substituent effects and the π -conjugation length in a diarylethene molecule.^{4–7} In bis(2-thienyl)ethane, the π -conjugation in closed-ring form is localized in a cyclohexadiene structure, shifting the absorption to shorter wavelength, as compared with the closed-ring form of bis(3-thienyl)ethane where the π -conjugation extends throughout the whole molecule.⁵ Diarylethene with a hybrid structure of bis(2-thienyl)ethane and bis(3-thienyl)ethane has a spectrum matching with the short-wavelength laser (400–500 nm).⁶ However, these compounds have not been paid much attention. It is feasible to develop 2,3-position hybrid diarylethene derivatives for short-wavelength recording.

In this paper, we have prepared several asymmetric diarylethene derivatives (Scheme 1). These compounds

have a hybrid structure with one of the thiophene rings attached to the ethylene moiety at 2-position, the other at 3-position. An efficient synthetic method has been proposed based on the experimental results, and the photochromic properties of these compounds both in solution and in solid state have also been investigated.



Scheme 1.

2. Results and discussion

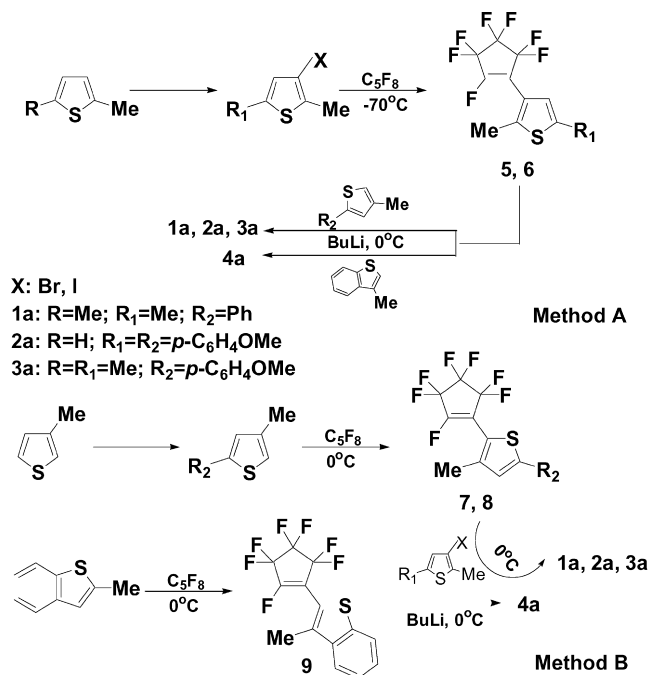
2.1. Synthesis of asymmetric diarylperfluorocyclopentene derivatives

1-(2,5-Dimethyl-3-thienyl)-2-(3-methyl-5-phenyl-2-thienyl)perfluorocyclopentene (**1a**), 1-[3-methyl-5-(*p*-methoxyphenyl)-2-thienyl]-2-[2-methyl-5-(*p*-methoxyphenyl)-3-thienyl]

Keywords: 2,3-position hybrid diarylethene; photochromic; crystal; short-wavelength recording.

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perfluorocyclopentene (**2a**), 1-(2,5-dimethyl-3-thienyl)-2-[3-methyl-5-(*p*-methoxyphenyl)-2-thienyl]perfluorocyclopentene (**3a**), and 1-(2,5-dimethylthien-3-yl)-2-(3-methylbenzo[*b*]thien-2-yl)perfluorocyclopentene (**4a**) were synthesized by the elimination reaction of mono-substituted perfluorocyclopentene with organolithium compounds according to the literature.⁸ Two methods could be applied to synthesize the asymmetric diarylethene derivatives as shown in Scheme 2.



Scheme 2.

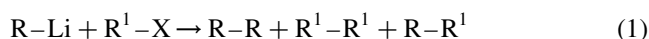
Method A synthesized the target compounds by using mono-substituted (3-thienyl)perfluorocyclopentenes while Method B using mono-substituted (2-thienyl)perfluorocyclopentenes. All the compounds were prepared by these methods to make a comparison. It was experimentally found that Method A is more effective than B. By analyzing the experimental results, we found the total yields were mainly determined by the metal–hydrogen exchange or metal–halogen exchange in the last reaction step. The total yields and the last step yields of them are summarized in Table 1. The total yields in Method A were based on starting materials 2-methylthiophene or 2,5-dimethyl-thiophene while in Method B based on 3-methylthiophene or 3-methylbenzo[*b*]thiophene. In Method B, lithiated thiophene derivatives are formed by the replacement of combined halogen by lithium. In a metal–halogen exchange reaction of an organolithium reagent and an alkyl halide, Wurtz coupling is a major side reaction,⁹ as shown in reaction Eq. (1). It can give direct coupling product R–R and R¹–R¹ or a cross-coupling product R–R¹. It was found that reactive heterocyclic aryl halides also followed by a Wurtz coupling during lithium–halogen exchange, leading to low concentration of lithiated thiophene derivatives. As a result, the yields of target compounds were remarkably decreased. On the other hand, lithiated thiophene derivatives formed by the replacement of combined

Table 1. The yields of Methods A and B (%)

Methods	1a	2a	3a	4a
A	75/44.3	85/21.8	78/34.0	84/43.4
B	45/19.1	43/6.8	40/9.7	49/31.3

The last step yield/total yield.

hydrogen by lithium in Method A created few by-products.



2.2. Photochromic properties of the asymmetric diarylethenes in solution

The spectral changes of **1a**, **2a**, **3a**, and **4a** in hexane exposed to UV light are shown in Figures 1–4. Upon irradiation with 365 nm light the colorless hexane solutions of **1a**, **3a**, **4a** turned to orange. The photogenerated orange closed-ring isomers have their absorption maxima at 468, 468, 466 nm, respectively. Upon visible light irradiation ($\lambda > 420$ nm) the orange color disappeared and the absorption bands of the open-ring forms were restored. On the other hand, the colorless hexane solution of **2a** turned to red when irradiated with 365 nm light. A new band appeared at 506 nm which is ascribable to the closed-ring form **2b**. This band disappeared upon irradiation with light of wavelength > 450 nm and the absorption band of open-ring form were restored. The absorption maxima of the open-ring and closed-ring forms of **1–4** and their absorption coefficients in hexane are summarized in Table 2.

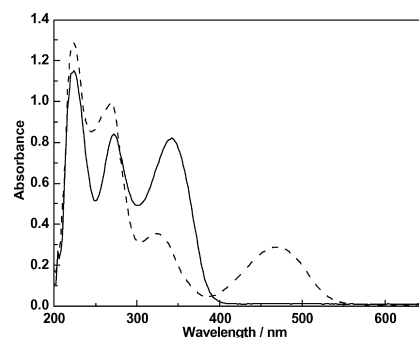


Figure 1. Absorption spectra of **1** in hexane (4.37×10^{-5} mol L⁻¹): (—) before photoirradiation and (---) after irradiation with 365 nm at room temperature.

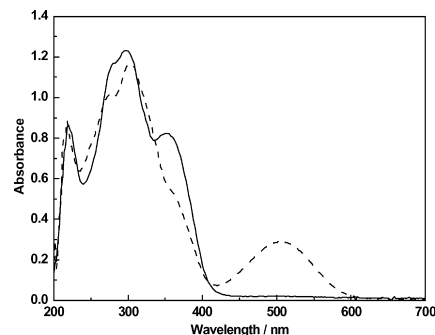
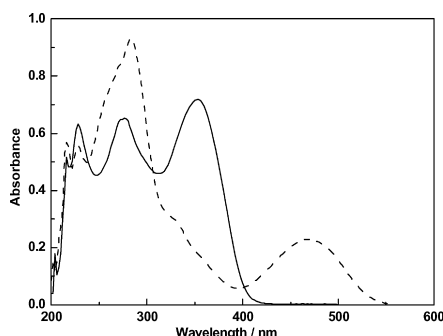
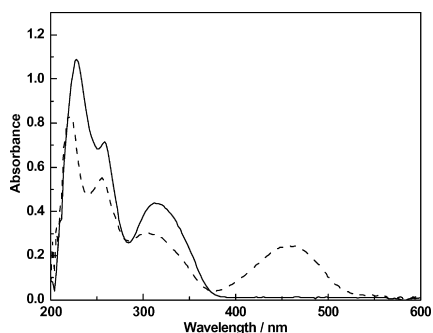


Figure 2. Absorption spectra of **2** in hexane (5.52×10^{-5} mol L⁻¹): (—) before photoirradiation and (---) after irradiation with 365 nm at room temperature.

Table 2. Absorption maxima and coefficients of **1**, **2**, **3**, and **4**; and the quantum yields in hexane

	λ_{\max}^a (nm) ($\epsilon/L \text{ mol}^{-1} \text{ cm}^{-1}$)	$\Phi_{a \rightarrow b}$ 365 nm	λ_{\max}^b (nm) ($\epsilon/L \text{ mol}^{-1} \text{ cm}^{-1}$)	$\Phi_{b \rightarrow a}$ 450 nm
1	224 (2.6×10^4)	0.28	468 (6.6×10^3)	0.013
2	296 (2.2×10^4)	0.40	506 (5.3×10^3)	0.024
3	352 (1.7×10^4)	0.71	468 (5.3×10^3)	0.065
4	228 (3.3×10^4)	0.57	466 (7.3×10^3)	0.15

^a Open-ring form.^b Closed-ring form.**Figure 3.** Absorption spectra of **3** in hexane ($1.81 \times 10^{-5} \text{ mol L}^{-1}$): (—) before photoirradiation and (---) after irradiation with 365 nm at room temperature.**Figure 4.** Absorption spectra of **4** in hexane ($3.32 \times 10^{-5} \text{ mol L}^{-1}$): (—) before photoirradiation and (---) after irradiation with 365 nm at room temperature.

As shown in Table 2, the closed-ring isomers **1b**, **3b**, and **4b** have the same absorption maximum at around 468 nm although their 2-thienyl groups are different. On the other hand, **2b** and **3b** have the same 2-thienyl groups, but the absorption maximum of **2b** shows red shift in comparison with **3b**, owing to the introduction of electron-donating substituent to its 3-thienyl group. It indicates that the absorption characteristics of the closed isomers of 2,3-position hybrid diarylethenes derivatives are determined by the properties of 3-thienyl groups. The closed-ring form of 2,3-position hybrid diarylethene has a hexatriene conjugation structure in which the π -conjugation extends from cyclohexadiene to 3-thienyl moieties. The 2-thienyl moieties cut off the extending of π -conjugation and thus do not affect the absorption spectra of the closed-ring isomer at longer wavelength. Absorption characteristic of closed-ring form of 2,3-position hybrid diarylethene is expected to be adjusted by altering the properties of 3-thienyl group.

2.3. Quantum yield

The quantum yields of cyclization and cycloreversion reactions of **1–4** were measured at room temperature. The quantum yields were determined by comparing the reaction yield of the 2,3-position hybrid diarylethenes against Aberchrome⁵⁴⁰ in hexane. The intensity of monochromatic radiation in measuring quantum yields of photoreaction $A \rightarrow B$ and $B \rightarrow A$ was about $4.05 \times 10^{-8} \text{ Ein s}^{-1} \text{ cm}^{-1}$ (365 nm) and $6.16 \times 10^{-9} \text{ Ein s}^{-1} \text{ cm}^{-1}$ (450 nm), respectively. The results are also summarized in Table 2.

2.4. Thermal stability and fatigue-resistant property

Thermal stability and fatigue-resistant are indispensable properties for practical applications. The thermal stability of the open-ring forms and the closed-ring forms of **1–4** were investigated by storing hexane solutions at 40°C in the dark at the presence of air for more than 3 months. In all cases no change was observed in the UV/Vis spectra. Also, no decomposition was detected when the compounds were exposed in air for more than half a year.

The fatigue resistant properties of **1a**, **3a**, and **4a** were measured in hexane in the present of air by irradiated with 254 and 365 nm wavelength light, respectively. Upon irradiation with 365 nm light the absorbance of the closed-ring forms of the compounds did not change after 1000 cyclization/cycloreversion cycles. However, upon irradiation with 254 nm light the photochromic performance of **1a**, **3a**, and **4a** decreased to about 89, 81, and 99%, respectively after 200 cycles. It is considered that the degradation is due to the formation of epoxide which is presumed to be the origin of the by-product.^{10,11} The photon of 254 nm has a higher energy and can easily generate singlet oxygen in the presence of oxygen. The photo-generated singlet oxygen could react with the 2-thienyl group of closed-ring form to produce a thiophene-endoperoxide. Benzothiophene has a much lower reactivity to singlet oxygen.¹² Therefore compound **4a** with a benzo [*b*]thiophene-2-yl group has a better fatigue resistant. In addition, other decomposition products could be easily induced by higher energy light. And further study on photolysis is currently in progress.

2.5. Photochromism in single crystals

The single crystals of **1a–4a**^{† 13} were obtained by recrystallization from hexane. The ORTEP drawings and

[†] Selected crystals data for **1a**, **2a**, **4a**. Compound **1a**: $\text{C}_{22}\text{H}_{16}\text{F}_6\text{S}_2$, MW=458.47, triclinic, $P\bar{1}$ (No. 2), $a=8.640(5) \text{ \AA}$, $b=11.444(5) \text{ \AA}$, $c=11.945(3) \text{ \AA}$, $\alpha=103.79(3)^\circ$, $\beta=96.08(3)^\circ$, $\gamma=111.55(3)^\circ$, $V=1042.1(8) \text{ \AA}^3$, $Z=2$, $F(000)=468$, $D_c=1.461 \text{ g/cm}^3$, $\mu(\text{Mo K}\alpha)=0.314 \text{ mm}^{-1}$, $R[I \geq 2\sigma(I)]=0.0438$, $wR2$ (all data)=0.1054, 3029 data, 3617 unique. CCDC reference number 204278. Compound **2a**: $\text{C}_{29}\text{H}_{22}\text{F}_6\text{O}_2\text{S}_2$, MW=580.59, monoclinic, $P2_1/n$ (No. 14), $a=17.983(8) \text{ \AA}$, $b=12.475(2) \text{ \AA}$, $c=24.095(4) \text{ \AA}$, $\alpha=90.00^\circ$, $\beta=91.676(19)^\circ$, $\gamma=90^\circ$, $V=5403(3) \text{ \AA}^3$, $Z=8$, $F(000)=2384$, $D_c=1.427 \text{ g/cm}^3$, $\mu(\text{Mo K}\alpha)=0.264 \text{ mm}^{-1}$, $R[I \geq 2\sigma(I)]=0.0595$, $wR2$ (all data)=0.1266, 5265 data, 9506 unique. CCDC reference number 195030. Compound **4a**: $\text{C}_{20}\text{H}_{14}\text{F}_6\text{S}_2$, MW=432.43, monoclinic, $P2_1/c$ (No. 14), $a=19.168(6) \text{ \AA}$, $b=9.0086(17) \text{ \AA}$, $c=11.495(4) \text{ \AA}$, $\alpha=90.00^\circ$, $\beta=106.10(3)^\circ$, $\gamma=90^\circ$, $V=1907.0(9) \text{ \AA}^3$, $Z=4$, $F(000)=880$, $D_c=1.506 \text{ g/cm}^3$, $\mu(\text{Mo K}\alpha)=0.338 \text{ mm}^{-1}$, $R[I \geq 2\sigma(I)]=0.0725$, $wR2$ (all data)=0.1442, 2411 data, 3368 unique. CCDC reference number 204279.

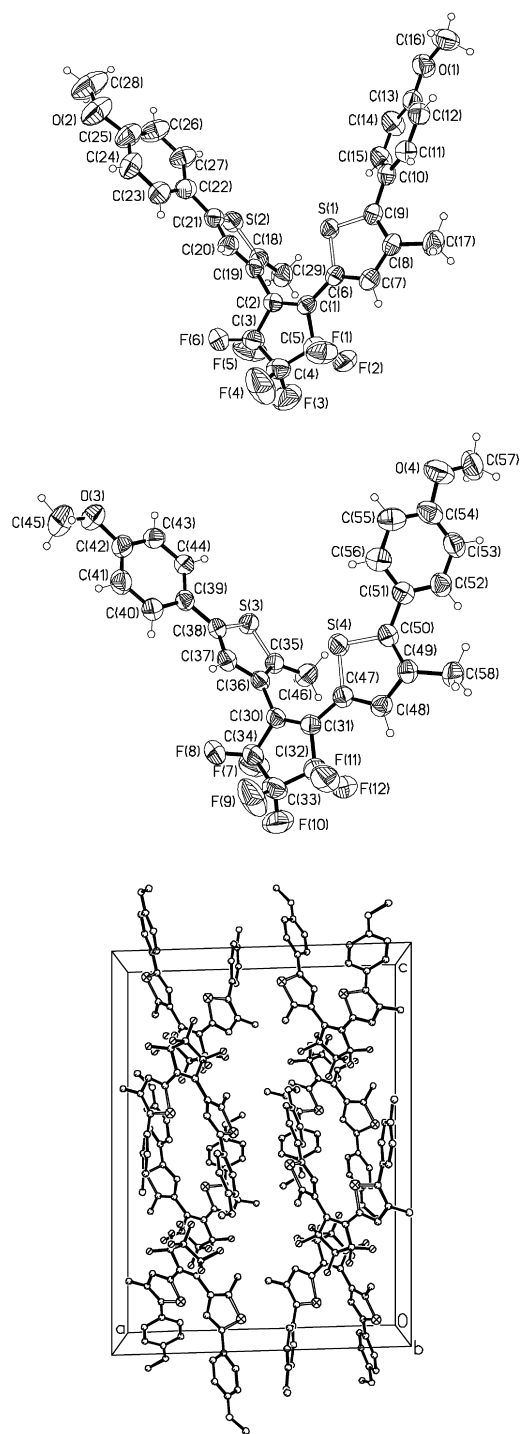


Figure 5. ORTEP drawing (with 35% probability ellipsoids) and packing view (along the *b* direction) of **2a**.

packing arrangements of **1a**, **2a**, and **4a** are displayed in Figures 5–7. The X-ray crystallographic study of **2a** shows that there are two independent molecules in an asymmetric unit cell. Both of them are packed in non-reactive parallel conformation.¹⁴ The distances between the reactive carbons of the two independent molecules were 5.884 Å (C8, C18) and 5.534 Å (C35, C49), respectively, which are above the upper limit of the critical distance for photocyclization in the solid state.¹⁵ As a result, the crystals of **2a** did not show any photochromic effect upon irradiation with UV light. On the other hand, it was observed that both **1a** and **4a** were

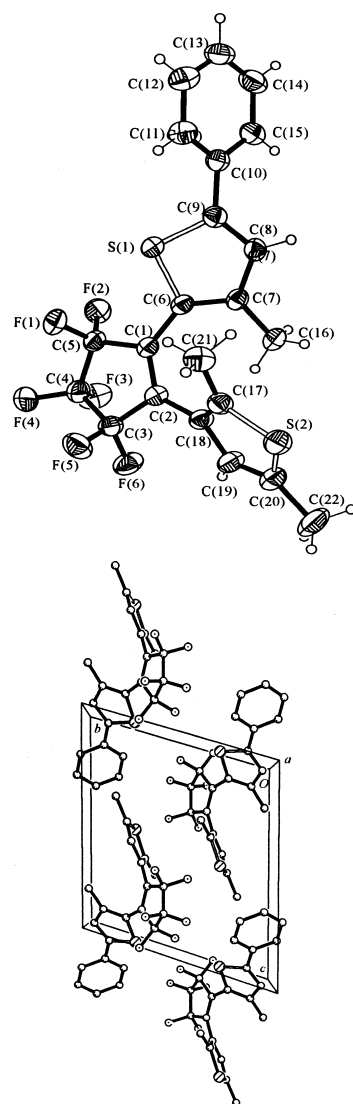


Figure 6. ORTEP drawing (with 35% probability ellipsoids) and packing view (along the *b* direction) of **1a**.

packed in photoactive antiparallel conformation, as well as **3a**.¹³ The distances between two reactive carbons of them (C7 and C17 for **1a**, C7 and C15 for **4a**) were 3.567 and 3.59 Å, respectively. Although distances of photoactive atoms of **1a**, **3a**, and **4a** are close enough for cyclization reaction,¹⁵ only **4a** shows photochromic reactivity in the crystalline state. Upon irradiation with 365 nm light, the pale yellow crystals of **4a** turned orange, and the orange color faded after irradiation with visible light. It was observed that the shape of the crystals of **4a** showed great morphological change in the course of photochromic reaction. Upon exposure to UV light, the surface of the crystal turned rough. After few minutes, the colored crystal was broken and separated into several parts. Owing to the different substituent positions of two thiophene rings, the closed-ring form of 2,3-position hybrid diarylethene has a twisted conformation. The crystal disintegration of **4a** is attributed to the large molecular structure change and large atomic and molecular motion during the photoisomerization. It demonstrates that the photochromic reaction is largely topochemically dominated and strictly controlled by

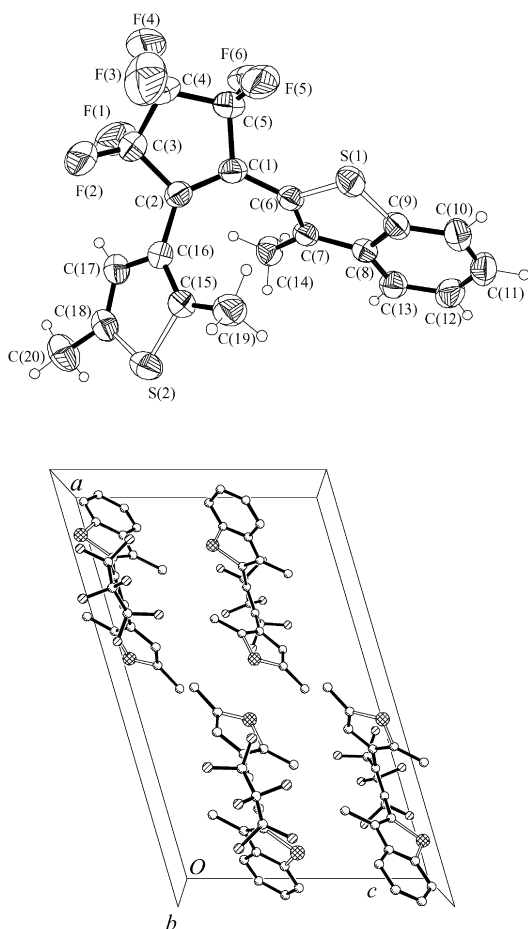


Figure 7. ORTEP drawing (with 35% probability ellipsoids) and packing view (along the *b* direction) of **4a**.

the packing arrangement of molecules. When the open-ring form converts to the closed-ring form, the disrotatory cyclization of the two thiophene rings requires atomic or molecular movement and favorable arrangement. Molecules with elongated shape like those phenyl and 4-anisole-containing ones (**1a**, **2a**, **3a**, but not **4a**) would not be favored to have molecular motions. And more atomic motions would be needed in these molecules during isomerization, which would be strongly prohibited by the packing in densely packed crystalline solid-phase.

3. Conclusion

Four kinds of 2,3-position hybrid diarylethene derivatives were prepared by two methods. It was experimentally found that a higher yield could be obtained from the method using mono-substituted (3-thienyl)perfluorocyclopentene. The absorption spectra of the closed-ring forms of the compounds were located at wavelengths in the region of 400 and 500 nm. They exhibited thermally irreversible and fatigue-resistant photochromic effects in solution, some of them even in the solid state. The study on the photochromic reactivity of the compounds in crystalline state showed that photochromic reactions were topochemically dominated and controlled by the packing arrangement of molecules. These 2,3-position hybrid diarylethenes have potential

application in rewritable short-wavelength optical data storage.

4. Experimental

4.1. Materials and apparatus

4-Methyl-2-phenylthiophene, 4-methyl-2-(*p*-methoxyphenyl)thiophene and 3-bromo-2-methyl-5-(*p*-methoxyphenyl)thiophene were prepared by using palladium-catalyzed Suzuki coupling of thiopheneboronic acid and bromobenzene (or bromoanisole) according to literature method.^{5,8} The necessary chemicals were purchased from commercial sources. Solvents were purified by standard methods.

The contents of carbon, hydrogen and nitrogen were carried out on an elemental analyzer (Carbo Erba 1106). ¹H NMR spectra were performed on a NMR spectrometer (Bruker AM500, 500.13 MHz) in CDCl₃ solution using TMS as internal standard. IR spectra were recorded on Nicolet (PE 2000) FT-IR spectrophotometer using KBr discs in the range 4000–400 cm⁻¹. MS spectra were recorded on a ZAB-HS apparatus. Melting points were determined on an XT-4 melting point apparatus. X-ray crystallographic analysis was measured with a Bruker P4 diffractometer equipped with graphite monochromatized Mo K α radiation at 295 K. Steady absorption spectra were measured with a HP8452A diode array spectrophotometer. Photo-irradiation was carried out using an UV lamp (SHG-200) and 150 W xenon arc lamp. Light of appropriate wavelength was isolated by a monochromator. The light intensity was determined by Aberchrome⁵⁴⁰ actinometry.

4.1.1. (2,5-Dimethyl-3-thienyl)perfluorocyclopentene (**5**).

To a stirred THF solution (50 mL) containing 3-iodo-2,5-dimethylthiophene (3.0 g, 12.5 mmol) was slowly added 7.8 mL of BuLi hexane solution (1.6 M, 12.5 mmol) under nitrogen atmosphere at -70°C , and the solution was stirred for 1 h. Then perfluorocyclopentene (2.64 g, 12.5 mmol) was added. And the mixture was stirred for 3 h at this temperature. A dilute HCl aqueous solution was added to the reaction mixture. The mixture was extracted with ether three times. The combined organic layer was dried with MgSO₄, filtered and evaporated in vacuo. The residue was purified by column chromatography on silica gel (hexane) to give 3.08 g of **5** in 81% yield.

Pale yellow oil, ¹H NMR (500 MHz, CDCl₃): 2.39 (s, 3H); 2.43 (s, 3H); 6.73 (s, 1H, Ar). Calcd for C₁₁H₇SF₇: C, 43.43; H, 2.32%. Found: C, 43.37; H, 2.13%.

4.1.2. [2-Methyl-5-(*p*-methoxyphenyl)-3-thienyl]perfluorocyclopentene (6**).** The coupling reaction of 3-bromo-2-methyl-5-(*p*-methoxyphenyl)thiophene (3.5 g, 12.3 mmol) and perfluorocyclopentene (2.6 g, 12.3 mmol) was performed by the procedure as described for compound **5**. The crude product was purified by silica gel chromatography (hexane/chloroform=3/1) to give 3.56 g of **6** in 73% yield.

Pale blue solid, ¹H NMR (500 MHz, CDCl₃): 2.46 (s, 3H); 3.84 (s, 3H); 6.91 (d, *J*=8.6 Hz, 2H, Ar); 7.12 (s, 1H, Ar);

7.46 (d, 2H, $J=9.5$ Hz, Ar). Calcd for $C_{17}H_{11}SOF_7$: C, 51.53; H, 2.80%. Found: C, 51.48; H, 2.73%.

4.1.3. (3-Methyl-5-phenyl-2-thienyl)perfluorocyclopentene (7). To a stirred THF solution (50 mL) containing 4-methyl-2-phenylthiophene (3.0 g, 17.2 mmol) was slowly added 10.7 mL of BuLi hexane solution (1.6 M, 17.2 mmol) under nitrogen atmosphere at 0°C. 30 min later, perfluorocyclopentene (3.64 g, 17.2 mmol) was added gradually. The mixture was stirred for 2 h at this temperature. Then the reaction was stopped by the addition of a dilute HCl aqueous solution. The reaction mixture was extracted with ether three times. The combined organic layer was dried with $MgSO_4$, filtered and evaporated in vacuo. The residue was purified by column chromatography on silica gel (hexane) to give 3.65 g of **7** in 58% yield.

Yellow oil, 1H NMR (500 MHz, $CDCl_3$): 2.29 (s, 3H); 7.13 (s, 1H); 7.35–7.37 (m, 3H), 7.57 (d, 2H, $J=7.7$ Hz, Ar). Calcd for $C_{16}H_9SF_7$: C, 52.46; H, 2.48%. Found: C, 52.55; H, 2.35%.

4.1.4. [3-Methyl-5-(*p*-methoxyphenyl)-2-thienyl]perfluorocyclopentene (8). The coupling reaction of 4-methyl-2-(*p*-methoxyphenyl)thiophene (3.5 g, 17.2 mmol) and perfluorocyclopentene (3.64 g, 17.2 mmol) was performed by the procedure as described for compound **7**. The crude product was purified by silica gel chromatography (hexane/chloroform=3/1) to give 3.05 g of **8** in 45% yield.

Pale yellow prism, mp 61–62°C. 1H NMR (500 MHz, $CDCl_3$): 2.29 (s, 3H); 3.85 (s, 3H); 6.29 (d, $J=8.0$ Hz, 2H, Ar); 7.08 (s, 1H); 7.52 (d, $J=8.0$ Hz, 2H, Ar). Calcd for $C_{17}H_{11}SOF_7$: C, 51.52; H, 2.80%. Found: C, 51.66; H, 2.92%.

4.1.5. (3-Methylbenzo[*b*]thiophene-2-yl)perfluorocyclopentene (9). The coupling reaction of 3-methylbenzo[*b*]thiophene (2.0 g, 13.5 mmol) and perfluorocyclopentene (2.85 g, 13.5 mmol) was performed by the procedure as described for compound **7**. The crude product was purified by silica gel chromatography (hexane/chloroform=4/1) to give 3.53 g of **9** in 77% yield.

Pale yellow oil, 1H NMR (500 MHz, $CDCl_3$): 2.44 (s, 3H); 7.34–7.38 (m, 2H); 7.70–7.80 (m, 2H). Calcd for $C_{14}H_7SF_7$: C, 49.42; H, 2.07%. Found: C, 49.24; H, 1.97%.

4.1.6. 1-(2,5-Dimethyl-3-thienyl)-2-(3-methyl-5-phenyl-2-thienyl)perfluorocyclopentene (1a). *Method A.* To a stirred THF solution (10 mL) containing 4-methyl-2-phenylthiophene (0.1 g, 0.57 mmol) was slowly added 0.36 mL of BuLi hexane solution (1.6 M, 0.57 mmol) under nitrogen atmosphere at 0°C. 30 min later, compound **5** (0.17 g, 0.56 mmol) was added and the mixture was stirred for 2 h at this temperature. Methanol was added to stop the reaction. The reaction mixture was extracted with ether and evaporated in vacuo, then purified by column chromatography (hexane) to give 0.2 g of 1-(2,5-dimethylthiophene-3-yl)-2-(3-methyl-5-phenyl-2-thienyl)perfluorocyclopentene (**1a**) in 75% yield.

Method B. To a stirred anhydrous THF (10 mL) containing 0.14 g of 3-iodo-2,5-dimethylthiophene (0.58 mmol) was

added 0.36 mL of BuLi hexane solution (1.6 M, 0.58 mol) under nitrogen atmosphere at $-78^\circ C$. The mixture was stirred for 15 min. Then, compound **7** (0.21 g, 0.58 mmol) was added. The reaction mixture was stirred for 3 h at that temperature. Methanol was added to stop the reaction. The reaction mixture was extracted with ether and evaporated in vacuo, then purified by column chromatography (hexane) to give 0.12 g of **1a** in 45% yield.

Yellow prism, mp 82–83°C; 1H NMR (500 MHz, $CDCl_3$): 1.74 (s, 3H), 1.91 (s, 3H); 2.43 (s, 3H); 6.73 (s, 1H); 7.06 (s, 1H); 7.32 (t, $J=7.5$ Hz, 1H, Ar); 7.37 (t, $J=7.5$ Hz, 2H, Ar); 7.57 (d, $J=7.0$ Hz, 2H, Ar). IR (KBr): 2962, 1616, 1492, 1263 cm^{-1} ; MS (m/z) 426 (M^+); Calcd for $C_{22}H_{16}S_2F_6$: C, 57.63; H, 3.52%. Found: C, 57.88; H, 3.42%.

4.1.7. 1-[3-Methyl-5-(*p*-methoxyphenyl)-2-thienyl]-2-[2-methyl-5-(*p*-methoxyphenyl)-3-thienyl]perfluorocyclopentene (2a). 1-[3-Methyl-5-(*p*-methoxyphenyl)-2-thienyl]-2-[2-methyl-5-(*p*-methoxyphenyl)-3-thienyl]perfluorocyclopentene (**2a**) was prepared by the same procedure as that used for **1a**. Method A gave **2a** in 85% yield, and Method B gave **2a** in 43% yield.

Yellow prism, mp 103–104°C; 1H NMR (500 MHz, $CDCl_3$): $\delta=1.72$ (s, 3H), 2.32 (s, 3H), 3.85 (s, 3H), 3.86 (s, 3H), 6.90 (s, 1H), 6.91–6.97 (m, 4H, Ar), 6.99 (s, 1H, Ar), 7.33–7.50 (m, 4H, Ar). IR (KBr): 2958, 1608, 1514, 1251 cm^{-1} ; MS (m/z) 580 (M^+); calcd for $C_{29}H_{22}S_2O_2F_6$: C, 59.99; H, 3.82%. Found: C, 60.14; H, 3.75%.

4.1.8. 1-(2,5-Dimethyl-3-thienyl)-2-[3-methyl-5-(*p*-methoxyphenyl)-2-thienyl]perfluorocyclopentene (3a). 1-(2,5-Dimethyl-3-thienyl)-2-[3-methyl-5-(*p*-methoxyphenyl)-2-thienyl]perfluorocyclopentene (**3a**) was prepared by the same procedure as that used for **1a**. Method A gave **3a** in 78% yield, and Method B gave **3a** in 40% yield.

Yellow prism, mp 73–74°C 1H NMR (500 MHz, $CDCl_3$): $\delta=1.73$ (s, 3H), 1.91 (s, 3H), 2.43 (s, 3H), 3.84 (s, 3H), 6.90 (d, $J=8.6$ Hz, 2H), 6.73 (s, 1H), 6.94 (s, 1H), 7.49 (d, $J=8.6$ Hz, 2H). IR (KBr): 2957, 1608, 1512, 1257 cm^{-1} ; MS (m/z) 456 (M^+); calcd for $C_{23}H_{18}S_2OF_6$: C, 56.55; H, 3.71%. Found: C, 56.44; H, 3.92%.

4.1.9. 1-(2,5-Dimethylthien-3-yl)-2-(3-methylbenzo[*b*]thien-2-yl)perfluorocyclopentene (4a). 1-(2,5-Dimethylthien-3-yl)-2-(3-methylbenzo[*b*]thien-2-yl)perfluorocyclopentene (**4a**) was prepared by the same procedure as that used for **1a**. Method A gave **4a** in 84% yield, and Method B gave **4a** in 49% yield.

Yellow plate, mp 73–74°C; 1H NMR (500 MHz, $CDCl_3$): 1.84 (s, 3H); 1.95 (s, 3H); 2.42 (s, 3H); 6.76 (1H, Ar); 7.40–7.42 (m, 2H, Ar); 7.66 (t, $J=4.0$ Hz, 1H, Ar); 7.82–7.84 (m, 1H, Ar). IR (KBr): 2954, 1618, 1496, 1272 cm^{-1} ; MS (m/z) 432 (M^+); calcd for $C_{20}H_{14}S_2F_6$: C, 55.55; H, 3.26%. Found: C, 56.40; H, 3.33%.

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