

# Synthesis and photochromic reactivity of a diarylethene dimer linked by a phenyl group

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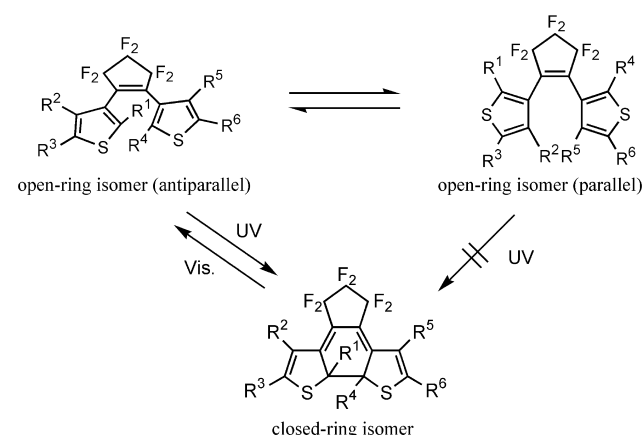
**Abstract**—A diarylethene dimer linked by a phenyl group was synthesized and the photochromic behavior was examined. Upon irradiation with ultraviolet light ( $\lambda=313$  nm), a hexane solution of the diarylethene dimer (**1a**) turned purple blue. Upon further prolonged irradiation the color changed to blue. The purple–blue and blue colors are due to the formation of a dimer having one open- and one closed-ring forms (**1b**) and a dimer having two closed-ring forms (**1c**), respectively. Both **1b** and **1c** returned to **1a** by irradiation with visible light ( $\lambda>500$  nm). The photochromic reactivity was evaluated by measuring quantum yields of the photocyclization and photocycloreversion reactions. The photocyclization quantum yield was 0.50. The cycloreversion quantum yield from **1c** to **1b** (0.0026) was lower than that from **1b** to **1a** (0.0094).

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## 1. Introduction

Light-induced reversible transformation is referred as photochromism.<sup>1–2</sup> Although a large number of photochromic compounds have been so far reported, compounds that undergo thermally stable photochromic reactions are limited to diarylethenes,<sup>3–6</sup> fulgides,<sup>7–9</sup> and phenoxy-naphthacenequinones.<sup>10–14</sup> Diarylethenes with heterocyclic

aryl rings are the most promising for the optoelectronic devices, such as optical memory,<sup>15–17</sup> photooptical switching,<sup>18–20</sup> and display,<sup>21–23</sup> because of their thermal irreversibility and fatigue-resistant properties.<sup>4,5</sup> The opening isomers of diarylethenes in solution have two conformations, antiparallel and parallel, in almost equal amounts.<sup>24,25</sup> The interconversion rate between the two conformations is much slower than the lifetime of photoexcited states. Therefore, both conformers are photoexcited independently. Among the two conformers, only the antiparallel conformer has a chance to be converted to the closed-ring isomer (Scheme 1).<sup>26</sup>

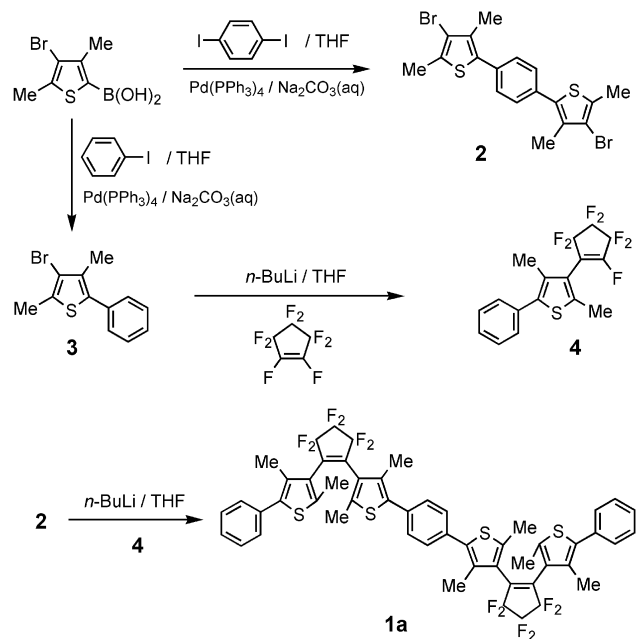


**Scheme 1.** Photochromic reaction of diarylethene. Two conformations in open-ring isomers are in equilibrium.

**Keywords:** diarylethene; photochromism; quantum yield; dimer; color change.

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Recently, we have reported photochromic behavior of a dimer, a trimer, and a tetramer of 1,2-bis(2,4-dimethyl-3-thienyl)perfluorocyclopentene connected with ethynylene.<sup>27</sup> Intramolecular excited energy migration to photoactive antiparallel conformers in the oligomers was found to enhance the photocyclization quantum yield. Such diarylethene oligomers are considered to be a model of conducting polymers which can photochemically switch the conductivity.<sup>28–30</sup> Although various types of diarylethene dimers connected with single bond,<sup>31</sup> phenylene,<sup>32</sup> ethynylene,<sup>27</sup> and diyne<sup>33</sup> were synthesized, in most cases only one of the diarylethenes can convert to the closed-ring form upon ultraviolet irradiation. When the one open- and one closed-ring form dimer is irradiated with ultraviolet light, the intramolecular excited energy transfer from the open-ring form unit to the closed-ring form one prohibits the formation of the two closed-ring form dimer. In this study we attempted to prepare a diarylethene dimer, which



Scheme 2. Synthetic route of diarylethene dimer **1a**.

can convert both diarylethene units into the closed-ring forms. Two diarylethene units were connected with a phenyl group, which suppresses the energy transfer to some extent.<sup>34</sup>

## 2. Results and discussion

### 2.1. Synthesis

Diarylethene dimer **1a** was synthesized according to a method described in Scheme 2. Compounds **2** and **4** were synthesized from 3-bromo-2,4-dimethyl-5-boronic acid. Compound **2** was prepared by a Suzuki coupling reaction of the boronic acid with diiodobenzene to be obtained in 29% yield. Compound **4** was prepared by reacting octafluorocyclopentene with **3**, which was given by a Suzuki coupling reaction of the boronic acid with iodobenzene. Diarylethene dimer **1a** was obtained by a coupling reaction of **2** with **4** and was purified by high performance liquid chromatography (HPLC) with silica gel column using hexane/ethyl acetate (99:1). The structure of the product was identified by <sup>1</sup>H NMR spectrum, mass spectrum, and elemental analysis, as described in Section 4.

### 2.2. Photochromism in hexane

Upon irradiation with 313 nm light the colorless hexane solution of **1a** turned purple–blue. Upon further prolonged irradiation the color changed to blue. The absorption spectral change is shown in Figure 1. The open-ring isomer **1a** has an absorption maximum at 271 nm. Upon irradiation with ultraviolet light for 1 min, the new absorption band appeared at 570 nm. When the solution was further irradiated with ultraviolet light, the peak shifted to 580 nm. The spectral shift suggests that a dimer having one open- and one closed-ring forms (**1b**) further converts to a dimer having two closed-ring forms (**1c**) upon prolonged ultraviolet light irradiation.

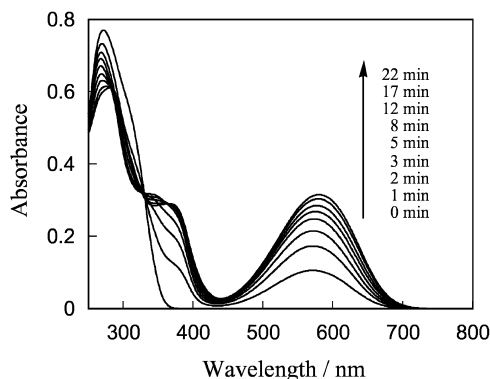


Figure 1. Absorption spectral change of **1a** in hexane upon irradiation with 313 nm light: [**1a**]= $1.8 \times 10^{-5}$  mol/L.

To confirm photogeneration of **1b** and **1c**, the photogenerated colored solution was analyzed by HPLC with a silica gel column using hexane and ethyl acetate (99:1) as the eluent. The elution peaks were detected at 328 nm, which is the isosbestic point, as can be seen from Figure 1. The opening form dimer **1a** was eluted at 22 min. The photogenerated colored solution gave the three peaks at 18, 20, and 22 min. Because the peak at 22 min is assigned to be **1a**, the peaks at 18 and 20 min are due to **1b** or **1c**. Each peak was isolated and analyzed by mass spectrometer and

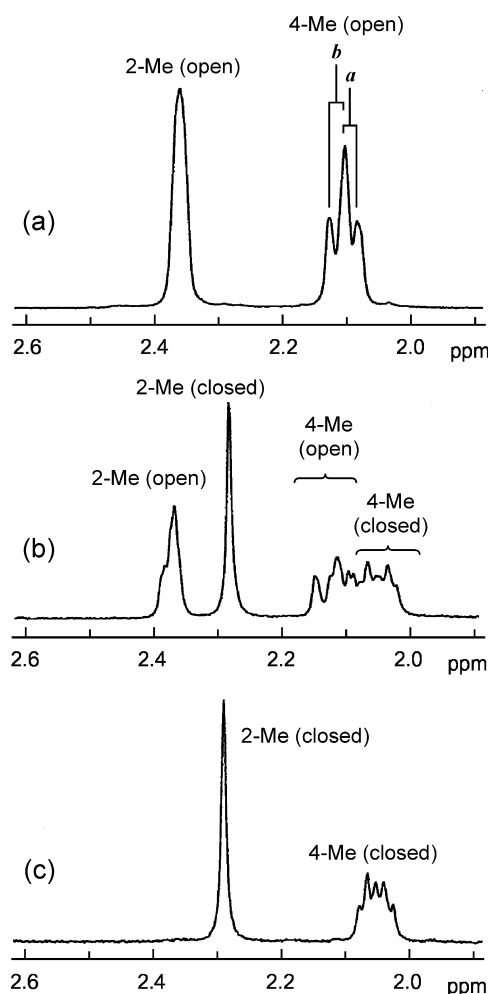
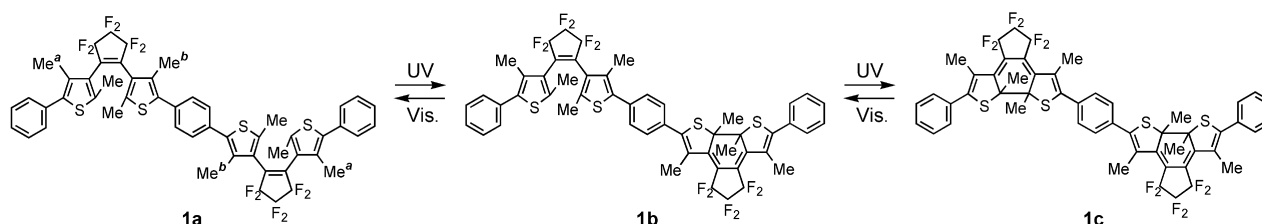


Figure 2. <sup>1</sup>H NMR spectra of **1a** (a), **1b** (b), and **1c** (c) in the range of 1.9–2.6 ppm.



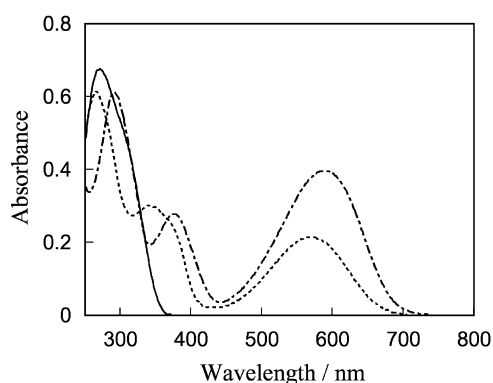
**Scheme 3.** Photochromic reaction of diarylethene dimer (**1a/1b/1c**).

$^1\text{H}$  NMR spectroscopy. The three compounds showed the same molecular weight ( $m/z=1018$ ).

**Figure 2** shows expanded  $^1\text{H}$  NMR spectra of three isomers in the range of 1.9–2.6 ppm. The signal at 2.36 ppm in **Figure 2(a)** is assigned to be 2-methyl protons of the thiophene rings of **1a**.<sup>35</sup> The three peaks at 2.08, 2.10, and 2.12 ppm in **Figure 2(a)** are assigned to 4-methyl protons of the thiophene rings. Diarylethenes have two conformations, antiparallel and parallel ones, in almost equal amounts. The 4-methyl protons in the conformations have different chemical shifts. Therefore, methyl protons *a* and *b*, shown in **Scheme 3**, are splitted to two peaks. Consequently three peaks with the ratio of 1:2:1 appeared in the NMR signals of the 4-methyl protons.

**Figure 2(c)** shows  $^1\text{H}$  NMR spectrum of an isomer eluted at 18 min by HPLC. Only one peak at 2.29 ppm is assigned to be 2-methyl protons in the closed-ring form unit. There is no more signal at 2.36 ppm corresponding to the 2-methyl protons in the open-ring form unit. The multi peaks at 2.0–2.1 ppm, which are due to different configurations and conformations, are assigned to 4-methyl protons.<sup>35</sup> Therefore, the isomer is assigned to **1c**.

**Figure 2(b)** shows the  $^1\text{H}$  NMR spectrum of an isomer eluted at 20 min by HPLC. The methyl protons of the product showed multi signals. In the NMR spectrum there existed characteristic signals at 2.28 and 2.37 ppm. The signal at 2.28 ppm is assigned to the 2-methyl protons of the closed-ring form unit. The signal at 2.37 ppm is assigned to the 2-methyl protons of the open-ring form unit. The ratio of the signals at 2.28 and 2.37 ppm is 1:1. The complex signals at the range of 2.0–2.2 ppm are assigned to the 4-methyl protons of the open- and closed-ring form units. Therefore, the isomer is assigned to **1b**.

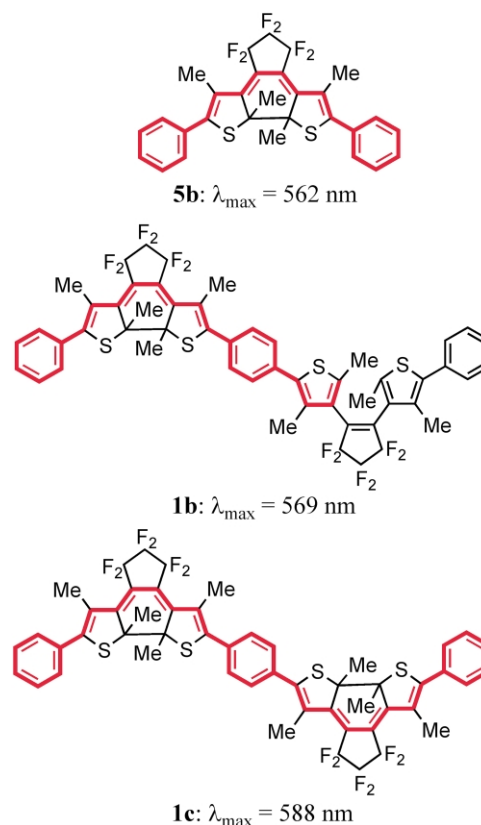


**Figure 3.** Absorption spectra of **1a** (—), **1b** (---), and **1c** (· · ·) in hexane:  $[1]=1.6\times 10^{-5}$  mol/L.

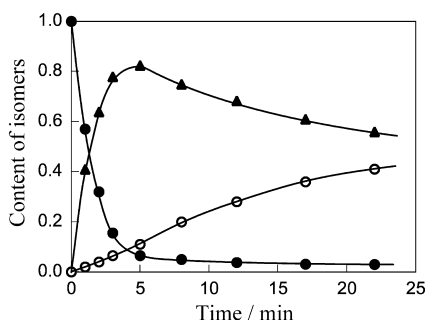
**Figure 3** shows absorption spectra of **1a**, **1b**, and **1c** in hexane under the same concentration. Compound **1a** has an absorption maximum at 271 nm. The  $\epsilon$  value at 271 nm was determined to be  $42700\text{ M}^{-1}\text{ cm}^{-1}$ . Compound **1b** has characteristic absorption maxima at 265, 342, and 569 nm. The  $\epsilon$  value at 569 nm was determined to be  $13500\text{ M}^{-1}\text{ cm}^{-1}$ . Compound **1c** has an absorption maximum at 588 nm ( $\epsilon=25000\text{ M}^{-1}\text{ cm}^{-1}$ ), which is longer than that of **1b**. The  $\epsilon$  value of **1c** at the longest wavelength was almost twice as large as that of **1b**. The absorption spectral shift of **1c** is ascribed to long  $\pi$ -conjugation by the two closed-ring forms of the diarylethene units. This indicates that two closed-ring form units in **1c** are connected by  $\pi$ -conjugation.

The closed-ring isomer (**5b**) of 1,2-bis(2,4-dimethyl-5-phenyl-3-thienyl)perfluorocyclopentene has an absorption maximum at 562 nm.<sup>36</sup> Red shifts as much as 7 and 26 nm for **1b** and **1c**, respectively, are ascribed to the extension of  $\pi$ -conjugation, as shown in **Figure 4**.

**Figure 5** shows a time-course of the formation of the two isomers (**1b** and **1c**) under the same condition as **Figure 1**.



**Figure 4.** Longest absorption wavelength of closed-ring forms.



**Figure 5.** Change in the content of the isomers, **1a** (●), **1b** (▲), and **1c** (○), in the photocyclization reaction of **1a** in hexane upon irradiation with 313 nm light:  $[1a]=1.8 \times 10^{-5}$  mol/L.

Upon irradiation with 313 nm light, the amount of **1a** decreased. At the same time the amount of two isomers, **1b** and **1c**, having closed-ring form units increased. The amount of **1b** reached maximum after 5 min of photoirradiation. After 22 min of photoirradiation, the ratio of **1a**, **1b**, and **1c** was 3:56:41.

### 2.3. Quantum yield

The photocyclization and cycloreversion quantum yields of **1** were measured in hexane at room temperature. The quantum yield measurement was carried out as follows. The dimer **1a** was dissolved in hexane and the solution was irradiated with ultraviolet light ( $\lambda=328$  nm). A 500 W Xenon lamp was used as the light source and the irradiated wavelength ( $\lambda=328$  nm) was isolated by passing the light through a monochromator and a band pass filter. The rates of the photoreactions were followed by measuring the ratio change of **1a**, **1b**, and **1c** by HPLC. The irradiated hexane solution was passed through HPLC and the ratio of **1a**, **1b**, and **1c** was analyzed by setting the monitoring wavelength to the isobestic point ( $\lambda=328$  nm). The light intensity was calibrated by the photoreaction of furylfulgide in hexane solution. The quantum yield measurement was carried out three times and average values were adopted as the quantum yield. The error of the relative quantum yields was less than 5%.

Upon irradiation with 328 nm light, **1b** is produced at first following the decrease of **1a**. At the early stage of the photoreaction, the formation of **1c** is negligible. When the conversion reaches more than 90%, **1c** is gradually produced. The photocyclization quantum yields were determined at the early stage of the photoreaction,<sup>27,37</sup> where the formation of **1c** is negligible. The quantum yield of **1a** to **1b** was determined to be 0.50. The quantum yield of a monomeric diarylethene, 1,2-bis(2,4-dimethyl-5-phenyl-3-thienyl)perfluorocyclopentene (**5a**), has been determined to be 0.46.<sup>36</sup> Diarylethene dimer has four conformations: A–A, A–P, P–A, and P–P (A: antiparallel conformation, P: parallel conformation). Among them only one conformation, which has both parallel conformations (P–P) is photoinactive and other three conformations can undergo the photocyclization reaction if the energy migration between two diarylethene units at the excited state takes place efficiently. On the basis of the assumption that the cyclization quantum yield of each diarylethene unit in the antiparallel conformation is 0.92 and that the energy transfer

from inactive P to photoactive A takes place efficiently in the dimer, the cyclization quantum yield is expected to increase up to around 0.69 ( $0.92 \times 3/4$ ).<sup>27</sup> However, only slight increase in the cyclization quantum yield was observed (from 0.46 to 0.50). This indicates that the energy transfer through a phenyl group from the parallel conformation unit to the antiparallel conformation unit is not efficient.

The photocycloreversion reactions of **1c** to **1b** and **1a** was examined. The hexane solution of **1c** was irradiated with 570 nm light. At first, **1b** is produced upon irradiation with visible light. And then, **1a** is produced through **1b**. The photocycloreversion quantum yields were determined by fitting the experimental data by the least squares procedure. The quantum yields of **1c** to **1b** and **1b** to **1a** were determined to be 0.0026 and 0.0094, respectively. The difference of the two quantum yields is explained by the difference of the  $\pi$ -conjugation length in the closed-ring forms.<sup>38,39</sup> The very low cycloreversion quantum yield of **1c** is ascribed to large extension of  $\pi$ -conjugation, as shown in Figure 4. The antibonding nature in the excited singlet state of the central photogenerated carbon–carbon bond decreases with the extension of  $\pi$ -conjugation, and the weak antibonding character is considered to decrease the cycloreversion quantum yields.

### 3. Conclusion

A novel diarylethene dimer linked by a phenyl group (**1a**) was synthesized. Upon irradiation with 313 nm light, the hexane solution of the dimer turned purple blue. Upon prolonged photoirradiation, the color changed to blue. The initial open-ring form dimer changed to the dimer having one open- and one closed-ring forms (**1b**) and then further to the dimer having two closed-ring forms (**1c**). The diarylethene dimer was found to form **1c** being connected by  $\pi$ -conjugation through a phenyl ring. The cyclization quantum yield of the dimer was slightly larger than the value of the diarylethene monomer. The cycloreversion quantum yield of **1c** to **1b** was smaller than that of **1b** to **1a** because of the extension of  $\pi$ -conjugation.

### 4. Experimental

Absorption spectra were measured with an absorption spectrophotometer (Hitachi U-3410). <sup>1</sup>H NMR spectra were recorded on a Varian Gemini-200 (200 MHz) spectrometer. Mass spectra were measured with mass spectrometers (Shimadzu GCMS-QP5050A and JEOL GC-mate II). Photoirradiation was carried out by using an Ushio 500 W Xenon lamp as the exciting light source. Monochromatic light was isolated by passing the light through a cut-off filter (UV-27) and a monochromator (Ritsu MC-10N). HPLC was performed on a Shimadzu LC-6AD liquid chromatograph coupled with a Shimadzu SPD-10AV spectrophotometric detector. Silica gel columns (Wakosil 5SIL, Wako) were used to isolate various isomers. The quantum yields were determined as described in the literature.<sup>27,37</sup> The samples were not degassed.

## 4.1. Compound data

**4.1.1. 1,4-Bis(4-bromo-3,5-dimethyl-2-thienyl)benzene (2).** 4-Bromo-3,5-dimethylthiophene-2-boronic acid<sup>40</sup> (7.0 g; 30 mmol) was added into a flask containing THF (200 mL), 20 wt% Na<sub>2</sub>CO<sub>3</sub>(aq) (70 mL), 1,4-diiodobenzene (2.5 g; 7.6 mmol), and a small amount of Pd(PPh<sub>3</sub>)<sub>4</sub> (1.6 g; 1.4 mmol). The mixture was refluxed for 5 h at 70°C. The product was extracted with chloroform. The organic layer was dried over MgSO<sub>4</sub>, filtered, and concentrated. The residue was purified by HPLC with silica gel column and by recrystallization from chloroform to give 1.0 g of **2** in 29% yield as colorless crystals. Mp=183–184°C. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>, TMS) δ=2.30 (s, 6H, CH<sub>3</sub>), 2.44 (s, 6H, CH<sub>3</sub>), 7.43 (s, 4H, Ar). MS *m/z* (M<sup>+</sup>)=454, 456, 458 (1:2:1). Anal. calcd for C<sub>18</sub>H<sub>16</sub>Br<sub>2</sub>S<sub>2</sub>: C, 47.38; H, 3.53. Found: C, 47.49; H, 3.49.

**4.1.2. 3-Bromo-2,4-dimethyl-5-phenylthiophene (3).** 4-Bromo-3,5-dimethylthiophene-2-boronic acid<sup>40</sup> (3.3 g; 14 mmol) was added into a flask containing THF (100 mL), 20 wt% Na<sub>2</sub>CO<sub>3</sub>(aq) (35 mL), iodobenzene (2.4 g; 12 mmol), and a small amount of Pd(PPh<sub>3</sub>)<sub>4</sub> (0.83 g; 0.72 mmol). The mixture was refluxed for 5 h at 70°C. The product was extracted with chloroform. The organic layer was dried over MgSO<sub>4</sub>, filtered, and concentrated. The residue was purified by silica gel column chromatography and by recrystallization from hexane to give 2.6 g of **3** in 83% yield as colorless crystals. Mp=33–35°C. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>, TMS) δ=2.25 (s, 3H, CH<sub>3</sub>), 2.42 (s, 3H, CH<sub>3</sub>), 7.2–7.5 (m, 5H, Ar). MS *m/z* (M<sup>+</sup>)=266, 268 (1:1). Anal. calcd for C<sub>12</sub>H<sub>11</sub>BrS: C, 53.94; H, 4.15. Found: C, 53.98; H, 4.16.

**4.1.3. 1-(2,4-Dimethyl-5-phenyl-3-thienyl)heptafluorocyclopentene (4).** Compound **3** (2.0 g; 7.4 mmol) was added into a flask containing dry THF (50 mL) at nitrogen atmosphere. The solution was cooled down at –78°C. And then 15% *n*-BuLi hexane solution (4.6 mL; 7.5 mmol) was added dropwise to the solution. The mixture was stirred for 2 h at the temperature. Octafluorocyclopentene (1.5 mL; 11 mmol) was added to the mixture. And then the mixture was stirred for 3 h at –78°C. The reaction mixture was quenched with water, and then was extracted with ether. The organic layer was dried over MgSO<sub>4</sub>, filtered, and concentrated. The residue was purified by silica gel column chromatography using hexane as the eluent to give 2.1 g of the product. Yield: 75%. Mp=63–64°C. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>, TMS) δ=2.11 (s, 3H, CH<sub>3</sub>), 2.39 (s, 3H, CH<sub>3</sub>), 7.2–7.5 (m, 5H, Ar). MS *m/z* (M<sup>+</sup>)=380. Anal. calcd for C<sub>17</sub>H<sub>11</sub>F<sub>7</sub>S: C, 53.69; H, 2.92. Found: C, 53.89; H, 2.94.

**4.1.4. Diarylethene dimer (1a).** Compound **2** (0.55 g; 1.2 mmol) was added into a flask containing dry THF (20 mL) at nitrogen atmosphere. The solution was cooled down at –78°C. And then 15% *n*-BuLi hexane solution (1.5 mL; 2.5 mmol) was added dropwise to the solution. The mixture was stirred for 3 h at the temperature. Compound **4** (1.0 g; 2.6 mmol) dissolved in dry THF (5 mL) was added to the mixture. And then the mixture was stirred for 3 h at –78°C. The reaction mixture was quenched with water, and then was extracted with chloroform. The organic layer was

dried over MgSO<sub>4</sub>, filtered, and concentrated. The residue was purified by silica gel column chromatography using hexane/ethyl acetate (99:1) as the eluent to give 0.47 g of the product. Yield: 38%. Mp=113–114°C. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>, TMS) δ=2.08–2.13 (m, 12H, CH<sub>3</sub>), 2.36 (s, 12H, CH<sub>3</sub>), 7.2–7.5 (m, 14H, Ar). HR-MS *m/z* (M<sup>+</sup>)=1018.1686 (calcd 1018.1665). Anal. calcd for C<sub>52</sub>H<sub>38</sub>F<sub>12</sub>S<sub>4</sub>: C, 61.28; H, 3.76. Found: C, 61.39; H, 4.07.

**4.1.5. Photoisomers of 1a (1b and 1c).** The hexane solution of **1a** was irradiated with 313 nm light. The blue colored solution was separated by HPLC (silica gel; hexane/ethyl acetate=99:1). **1b**: <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>, TMS) δ=2.0–2.2 (m, 12H, CH<sub>3</sub>), 2.28 (s, 6H, CH<sub>3</sub>), 2.37 (s, 6H, CH<sub>3</sub>), 7.2–7.5 (m, 14H, Ar). MS *m/z* (M<sup>+</sup>)=1018. **1c**: <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>, TMS) δ=2.0–2.1 (m, 12H, CH<sub>3</sub>), 2.29 (s, 12H, CH<sub>3</sub>), 7.43 (s, 10H, Ar), 7.49 (s, 4H, Ar). MS *m/z* (M<sup>+</sup>)=1018.

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