Photochemical & Photobiological Sciences

PAPER

Cite this: *Photochem. Photobiol. Sci.*, 2015, **14**, 765

# The effect of a "push–pull" structure on the turn-on fluorescence of photochromic thio-ketone type diarylethenes

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Received 21st August 2014, Accepted 16th January 2015

DOI: 10.1039/c4pp00320a

www.rsc.org/pps

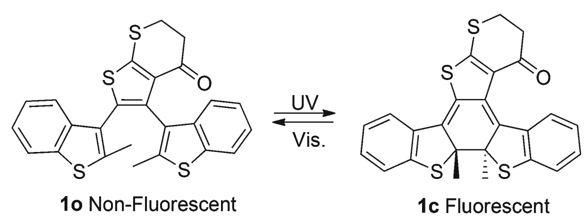
A series of diarylethene compounds with a thiophene bridging unit have been synthesized to investigate the relationship between molecular structure and photochromic properties. In particular, the fluorescence properties related to compound **1** were investigated. The results showed that a six-membered ring carrying an electron-donating sulfur atom and an electron-withdrawing carbonyl group is necessary to form a "push–pull" system for the fluorescence of **1**.

## Introduction

The fluorescence of photochromic materials can be modulated through photochromic reactions. Recently, these compounds have received a great deal of attention due to their potential application in optical memory[1–10] and biological labeling.[11–24] Among various photochromic materials, fluorescent diarylethenes have been of considerable interest because the two isomers that reversibly interconvert to each other under UV and visible light irradiation are thermally stable and fatigue resistant.[1] In the last decade, numerous diarylethene molecules capable of both photochromic and fluorescence switching have been reported.[25,26] The most widely used synthetic strategy for designing these molecules is coupling of a diarylethene backbone with a fluorophore, because diarylethenes are, in general, weakly fluorescent. In these compounds, fluorophore fluorescence is quenched by the ring-closed state of diarylethenes through a FRET process.[7,10,13,14,27–33]

Conversely, diarylethenes can be designed to emit strong fluorescence in the ring-closed state without the aid of external fluorophores.[34–43] Irradiation with external UV and visible light can modulate fluorescence by initiating a reversible change between the non-fluorescent ring-open state and the fluorescent ring-closed state of diarylethenes. Because of their simple structure, the turn-on mode diarylethenes can be readily prepared and used in various applications, including super-resolution fluorescence imaging applications such as PALM (photoactivatable localization microscopy) or STORM (stochastic optical reconstruction microscopy).[44–48]

In our previous study, we reported a novel turn-on fluorescent diarylethene derivative, **1** (Scheme 1), containing a fused six-membered ring with sulfur and carbonyl groups as the bridge unit of the non-fluorescent 2,3-bis(2-methylbenzothiophen-3-yl)thiophene (**BTT**).[35] Because of its significant fluorescence switching properties under alternating UV and visible light irradiation, the compound was successfully applied to live cell imaging. To provide insights into the relationship between molecular structure and photochromic properties, including fluorescence of diarylethene **1**, a series of derivatives (compounds **2** to **11**) were synthesized, and their photophysical properties were studied. The investigation studied the effects of ring size, sulfur atoms, carbonyl groups, and benzothiophene groups, as shown in Fig. 1. The results are described herein.




**Scheme 1** Photochromism of **1**.

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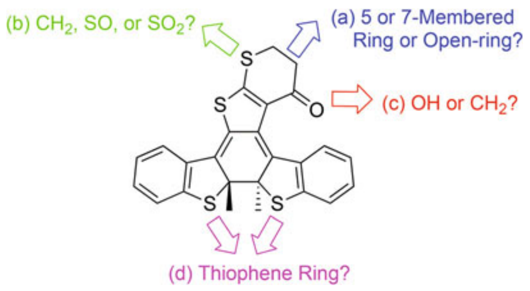



**Fig. 1** Relationship between fluorescence and structure.

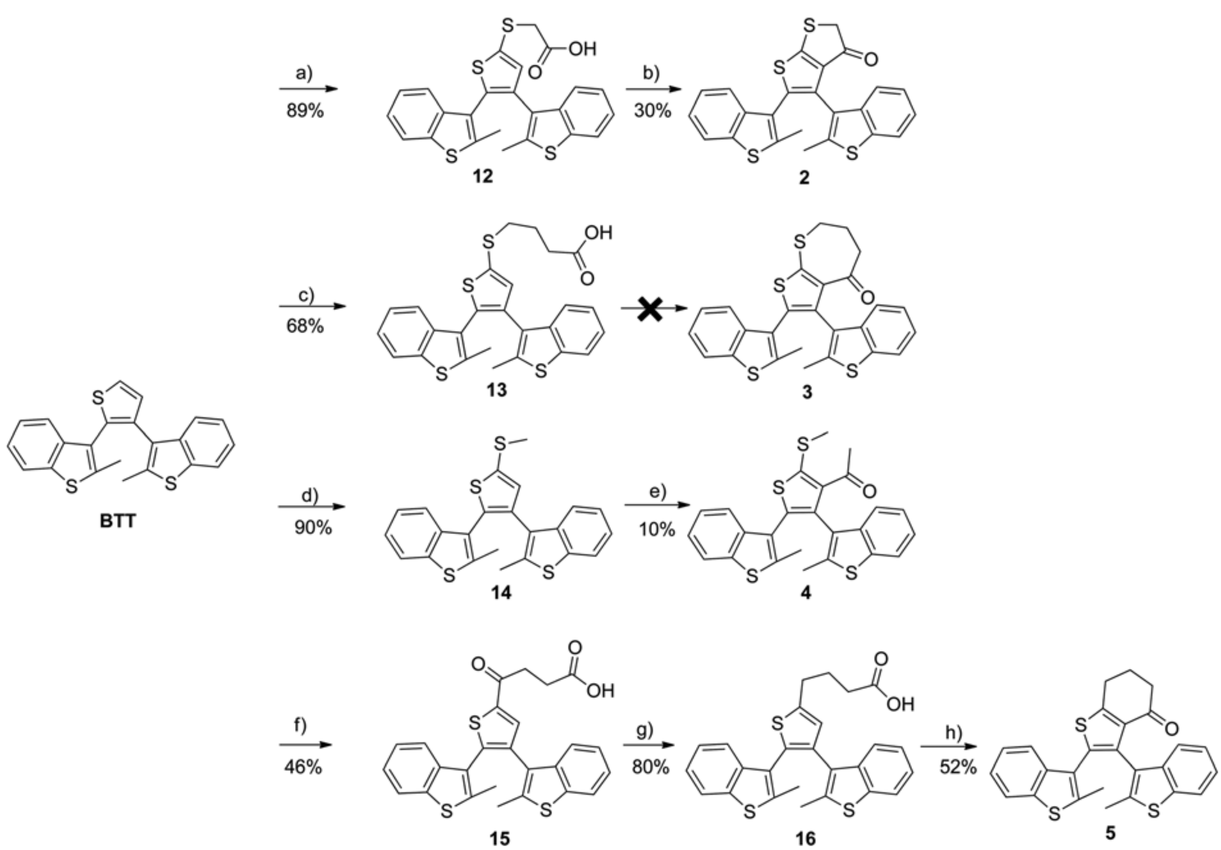
## Results and discussion

### Synthesis

To investigate the ring size effect of fluorescent compound **1**, syntheses of five- and seven-membered ring derivatives (compounds **2** and **3**) were studied, as outlined in Scheme 2. The open-ring acids, **12** and **13**, were easily prepared from **BTT** (2,3-bis(2-methylbenzothiophen-3-yl)thiophene) in high yields. However, intramolecular Friedel–Crafts acylation reactions to prepare **2** and **3** were not successful. Only a five-membered ring compound, **2**, was obtained in low yield after heating with methanesulfonic acid at 100 °C. Unfortunately, **2** decomposed rapidly under ambient conditions, and its photophysical properties could not be investigated in detail. Although it showed photochromism under UV and visible light irradiation, **2** was not fluorescent.

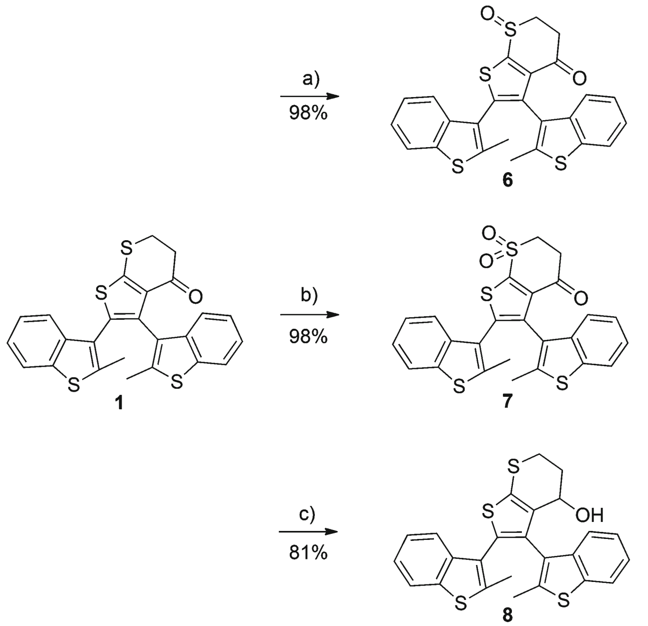
Compounds **4** and **5** were also prepared according to Scheme 2. For **4**, acetylation of methylthio compound **14** resulted in a mixture of derivatives with different numbers of acetyl groups. Chromatographic separation of the mixture gave **4** in 10% yield.

The sulfoxide and sulfone derivatives **6** and **7** were prepared according to Scheme 3. The most reactive sulfur atom in a non-aromatic ring of **1** was selectively oxidized by either *m*-chloroperoxybenzoic acid (*m*-CPBA) or hydrogen peroxide with sodium tungstate. Sulfoxide **6** was obtained in high yield from *m*-CPBA oxidation of **1**. Further oxidation of **6** to **7** by *m*-CPBA produced undesired sulfur atom oxidation products. However, oxidation of **1** by $H_2O_2$ in aqueous THF catalyzed by sodium tungstate gave sulfone **7** in near quantitative yield.[49] Structures **6** and **7** were identified by $^1$H-NMR. The two methylene protons on the beta carbon from the carbonyl groups of **6** and **7** appeared in the regions of 3.63–3.50 and 3.86–3.74 ppm, respectively, due to the stronger electron-withdrawing effect of the sulfone compared to the sulfoxide group. Interestingly, the two protons on the alpha carbon of **6** were in a diastereotopic relationship due to the chiral center of the sulfoxide group.




**Scheme 2** (a) *n*-BuLi, THF, −78 °C; then, $S_8$, −78 °C; then, $BrCH_2COOH$, $Et_3N$; (b) $CH_3SO_3H$, 100 °C; (c) *n*-BuLi, THF, −78 °C; then, $S_8$, −78 °C; then, $BrCH_2CH_2CH_2COOH$, $Et_3N$; (d) *n*-BuLi, THF, −78 °C; then MeSSMe, −78 °C; (e) AcCl, $AlCl_3$, $CH_2Cl_2$; (f) succinic anhydride, $AlCl_3$, $CH_2Cl_2$; (g) Zn–$HgCl_2$, toluene/conc. HCl; (h) TFAA, toluene.




Scheme 3 (a) *m*-CPBA, $CH_2Cl_2$; (b) $NaWO_2$–$H_2O$, $H_2O_2$, THF; (c) $NaBH_4$, THF–EtOH.

These protons appeared separately at 3.63–3.50 and 2.88–2.77 ppm. However, the two protons in **7** were observed in the 3.40–3.20 ppm region. Compound **8** was easily obtained by reducing **1** with $NaBH_4$.

Thiophene ring-substituted derivatives such as **9** to **11** were designed and synthesized according to Scheme 4. The effects of thiophene and benzo[*b*]thiophene substituents on photochromic properties were investigated.

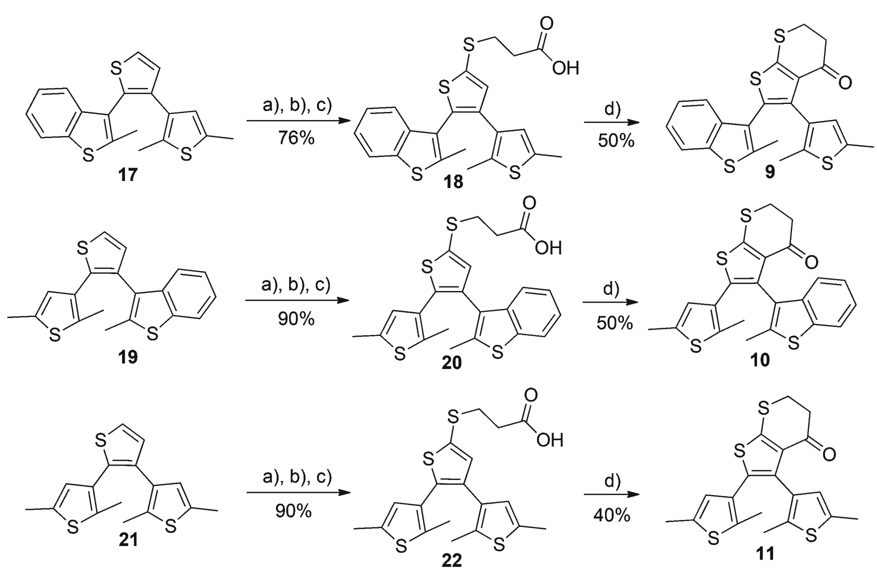
The open form of diarylethene has two different parallel (p-) and anti-parallel (ap-) conformations. The ratio of conformations can be determined by $^1$H NMR if signals are properly differentiated.[50] Compound **9** revealed a typical $^1$H-NMR spectrum of two conformers. As shown in Fig. 2(a), the thienyl-H peak for **9** splits into two peaks at 6.45 ppm for the ap-conformer and 6.08 ppm for the p-conformer. Their relative intensity was calculated to be 45 : 55. Conversely, only a single sharp peak was observed at 6.12 ppm in the $^1$H-NMR spectra of **10** (Fig. 2(b)). This result is likely due to fast rotation of the thienyl group in **10** at room temperature. In compound **9**, steric interaction between the carbonyl and thienyl groups might slow down rotation of the thienyl group, shown in the $^1$H-NMR spectra of the two conformers.

### Photophysical properties

The photophysical properties of diarylethenes **4–11** were investigated in ethyl acetate ($c = 1.0 \times 10^{-5}$ M) at room temperature. Fig. 3 shows changes in the absorption spectra in ethyl acetate induced by irradiation with UV light (312 nm). Most of the compounds showed a broad band near 515–570 nm, representing ring-closed isomer formation upon UV irradiation. The reddish color of the solutions disappeared after irradiation with visible light because of the ring opening reaction.

The photochromic properties of these compounds are summarized in Table 1. The results show that the electronic nature of the bridging unit had a significant effect on the photochromic features of diarylethenes, including absorption maxima, molar absorption coefficients, and quantum yields of the photoreaction.

The ring-opening reaction quantum yields of compounds **4**, **9**, and **11** were larger than their ring-closing reaction quantum yields. Conversely, other compounds showed a reversed quantum yield effect. The major structural difference between the two compound groups with different quantum yield effects lies in the aryl substituent at the 3-position of the bridging




Scheme 4 (a) *n*-BuLi, THF, −78 °C; (b) $S_8$, −78 °C; (c) $BrCH_2CH_2COOH$, $Et_3N$; (d) TFAA, toluene.

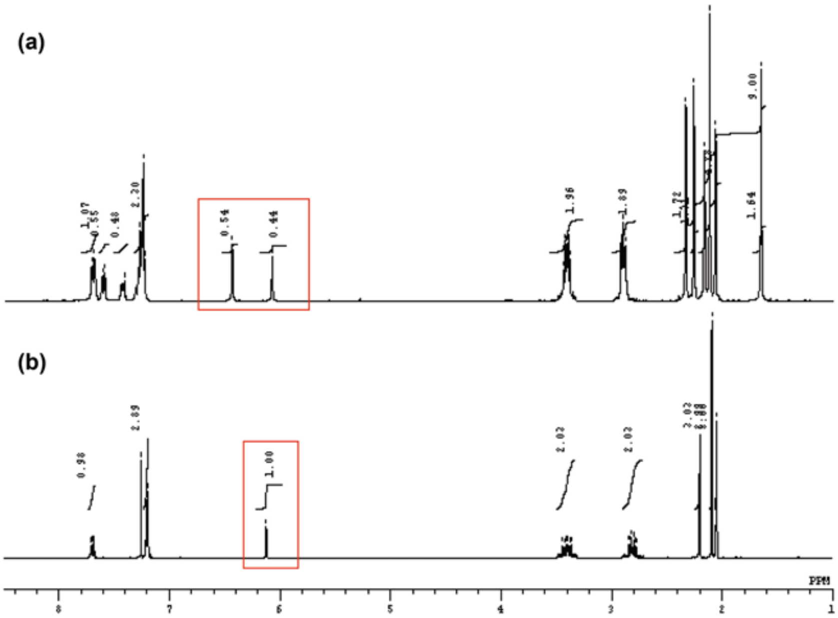



Fig. 2 $^{1}H$ NMR spectra of **9** (a) and **10** (b).

thiophene unit. Compounds with a dimethylthiophene substituent instead of methylbenzo[*b*]thiophene at the 3-position, such as **9** and **11**, underwent more efficient photochemical ring-opening reactions compared with the ring-closing reactions. This effect cannot be explained by the steric repulsion between carbonyl and the 3-position substituent, and HOMO/LUMO orbital symmetry was thought to have a role in the effect. The HOMOs/LUMOs of ring-closed forms of **9** (**9c**) and **10** (**10c**), which had different photochemical quantum yield effects, were obtained from a density functional theory calculation at the B3LYP/6-31G(d) level. The HOMO/LUMO of **1c** was also calculated for comparison.

The optimized structures of the closed-ring isomers of **1c**, **9c**, and **10c** are shown in Fig. 4. The HOMO electron density was distributed over the whole molecule, whereas the LUMO electron density was more localized on the thiophene bridge unit and its branches. As shown in the figure, the carbonyl group of **9c** does not interact with the dimethylthiophene substituents in the HOMO or LUMO because they are not in the proximal position. The carbonyl group in **10c** is positioned on top of the methylbenzo[*b*]thiophene substituent. Both the bottom orbital of the carbonyl and the top orbital of the benzo[*b*]thiophene unit are in the same orbital phase, indicating attraction between the two groups in the HOMO. The interaction was more significant in the LUMO. Side views of the HOMO and LUMO of **10c** clearly show the effect. This pi–pi attracting interaction in the excited state may increase the activation barrier proceeding to the open isomer from the photo-excited closed isomer of **10c**, lowering the ring-opening reaction quantum yield. The carbonyl group in **4** can rotate freely, resulting in ineffective interaction between the carbonyl and benzo[*b*]thiophene substituents.

### Fluorescence of diarylethenes

The fluorescence properties of diarylethenes **4–11** were measured in ethyl acetate at room temperature to investigate the difference compared with fluorescent compound **1**. Unfortunately, only the ring-closed form of **10** (**10c**) was found to be weakly fluorescent.

In the structure of fluorescent compound **1c**, the electron-withdrawing carbonyl group and the electron-donating sulfur atom constitute an electron "push–pull" system through the thiophene bridge unit.[38] This system may contribute to fluorescence. Compounds **5c–8c** do not experience the "push–pull" mechanism because these compounds lack either the carbonyl or sulfur atom, and fluorescence was not observed. For compounds **4c**, **9c**, and **11c**, the absence of fluorescence despite such a "push–pull" system may be due to the high $\Phi_{c-o}$. The photo-excited compounds relax rapidly toward a ring-open isomer without light emission, as expected from the high $\Phi_{c-o}$.[52,53]

Considering the "push–pull" mechanism, only **10c** is expected to be fluorescent. In fact, **10c** emits light upon UV excitation. However, its fluorescence intensity was weak. Fig. 5 shows the concentration-dependent fluorescence emission spectra of **10** at the photostationary state (black: $1 \times 10^{-5}$ M, red: $1 \times 10^{-4}$ M, blue: $1 \times 10^{-3}$ M) in ethyl acetate at room temperature. Upon 520 nm light excitation, **10c** exhibited a weak reddish fluorescence centered at 598 nm, which was 18 nm red-shifted compared with compound **1**. The fluorescence quantum yield of **10c** was less than 0.01.

In summary, a series of diarylethene compounds derived from the **BTT** structure have been synthesized to investigate the correlation between the molecular structure and photochromic properties including fluorescence. The results show

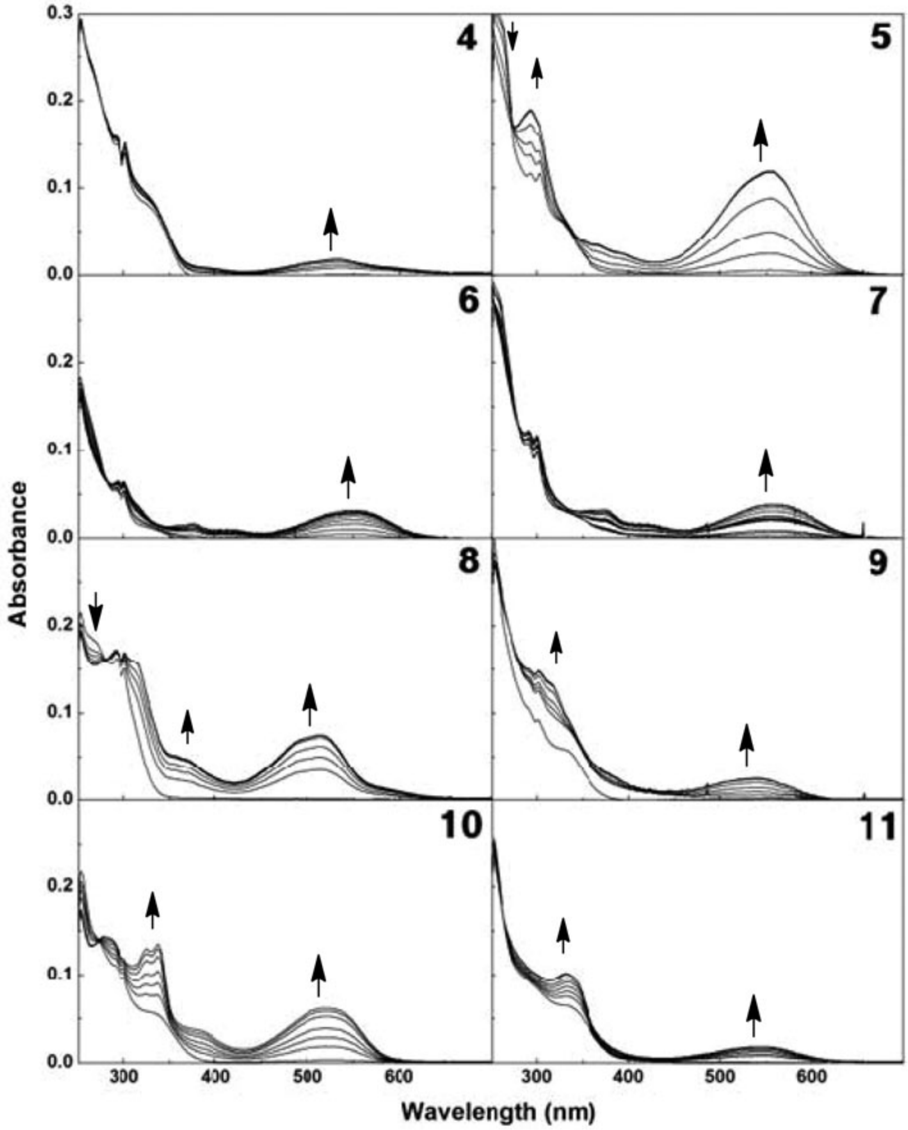



**Fig. 3** Absorption spectra for compounds **4–11** ($1.0 \times 10^{-5}$ M) in ethyl acetate at room temperature. Arrows indicate the changes upon irradiation with UV light (312 nm).

**Table 1** Photophysical properties of diarylethene derivatives

| | AP : P[a] | $\Phi_{o-c}$[b,c] | $\Phi_{c-o}$[b,d] | Conversion at PSS (%) | $\lambda_{max}$ (nm)/$\varepsilon$ ($10^3$ $M^{-1}$ $cm^{-1}$) Open-ring | Closed-ring |
|---|---|---|---|---|---|---|
| **1** | 65 : 35 | 0.25 | 0.17 | 50 | 252/27.2 | 520/12.8 |
| **4** | —[e] | 0.15 | 0.64 | 11 | 253/28.5 | 532/16.4 |
| **5** | 65 : 35 | 0.34 | 0.13 | 60 | 253/32.2 | 552/19.8 |
| **6** | 62 : 38 | 0.11 | 0.07 | 34 | 252/18.4 | 554/9.41 |
| **7** | 63 : 37 | 0.14 | 0.07 | 27 | 252/29.5 | 570/13.7 |
| **8** | —[e] | 0.30 | 0.20 | 43 | 252/21.5 | 515/17.4 |
| **9** | 55 : 45 | 0.22 | 0.35 | 9 | 253/30.8 | 539/13.9 |
| **10** | — | 0.13 | 0.068 | 68 | 253/17.5 | 520/9.12 |
| **11** | — | 0.23 | 0.52 | 42 | 253/25.8 | 544/4.29 |

[a] Antiparallel (ap-) to parallel (p-) ratio. Observed in $^1$H NMR spectra in $CDCl_3$ ($5.0 \times 10^{-3}$ M). [b] **BTF6** was used as a reference.[41,51] [c] Cyclization quantum yield measured at 312 nm in ethyl acetate. [d] Ring opening quantum yield in ethyl acetate measured at $\lambda_{max}$ of the closed-ring isomer. [e] Not determined due to complex peaks.

that a six-membered ring carrying an electron-donating sulfur atom and an electron-withdrawing carbonyl group is necessary to form a "push–pull" system for the fluorescence of **1**. The turn-on fluorescence during diarylethene photocyclization can be achieved by a simple modification of the molecular structure and electronic properties of the bridge unit. This study may provide a new strategy for improving the photophysical properties of compound **1** and may aid in designing new fluorescent diarylethenes.

# Experimental

### General

All reagents and spectrograde solvents were purchased from Sigma-Aldrich. Flash column chromatography was performed

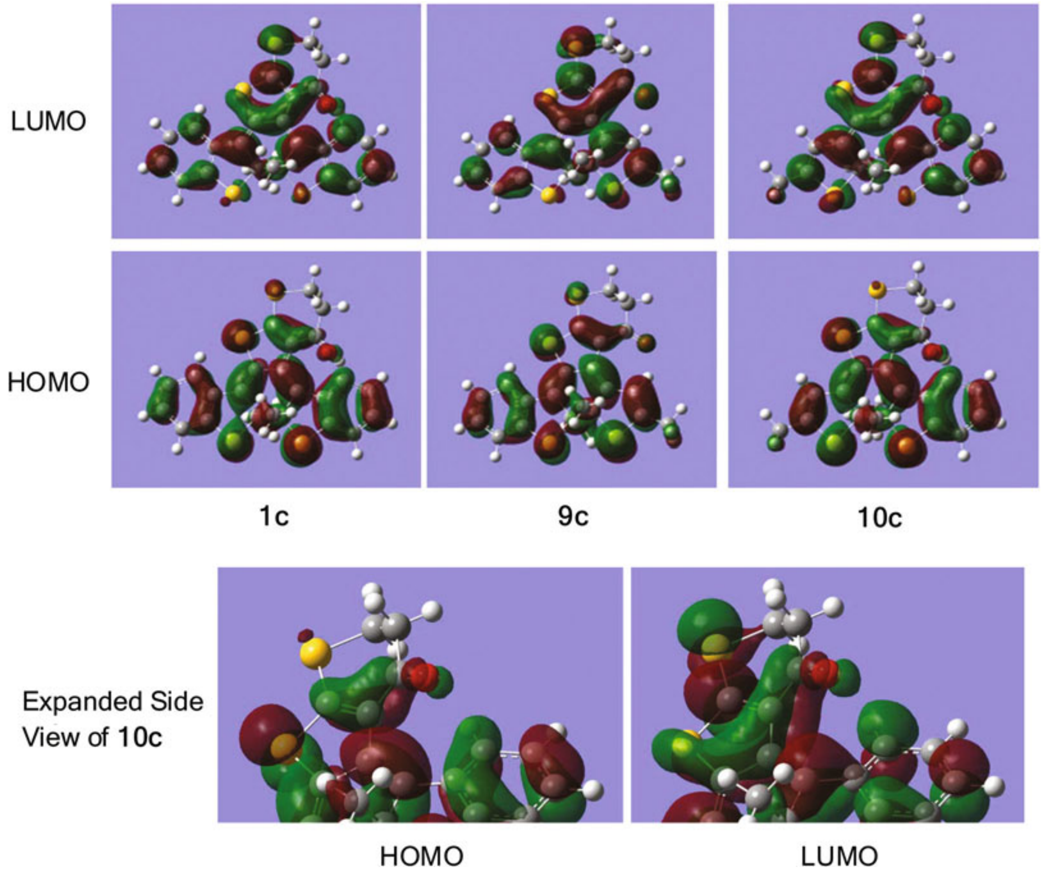



Fig. 4 HOMO and LUMO of **1**, **9**, and **10**.

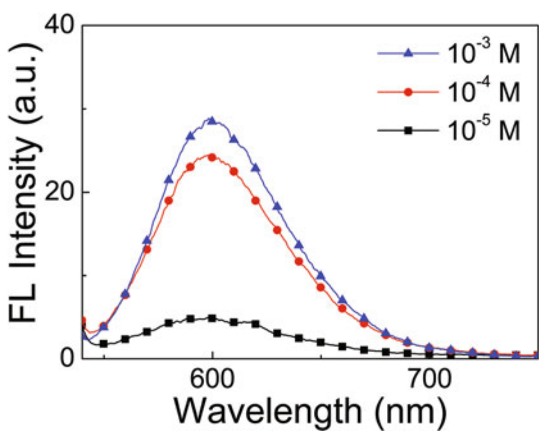



Fig. 5 Concentration-dependent fluorescence emission spectra of **10** at its photostationary state (black: 1 × $10^{-5}$ M, red: 1 × $10^{-4}$ M, blue: 1 × $10^{-3}$ M) in ethyl acetate at room temperature.

using Merck silica gel 60 (70–230 mesh). Melting points were determined with a Laboratory Devices Mel-Temp 3.0 melting point apparatus. The $^{1}$H and $^{13}$C NMR spectra were recorded using a JEOL JNM-AL300 spectrometer at 300 and 75 MHz in $CDCl_3$, respectively, with tetramethylsilane as the internal reference. High-resolution mass spectrometry (HRMS) spectra were recorded with a JEOL JMS-700 spectrometer. Fourier transform infrared (FTIR) spectroscopy measurements were performed using a JASCO FTIR-4200 instrument. HPLC was performed using a Young Lin SP-930D liquid chromatograph coupled with a Young Lin UV-730D spectrophotometric detector. UV absorption spectra were recorded on a Shimadzu UV-3100 spectrophotometer in spectroscopy grade ethyl acetate. Fluorescence spectra were recorded in spectroscopy grade ethyl acetate on a Fluoro Max-2 spectrophotometer equipped with a 150 W ozone-free xenon lamp. UV and visible irradiation was performed with standard lamps used to visualize TLC plates (VL6L; 312 nm, 8 mW $cm^{-2}$) and a 400 W tungsten lamp. The samples were placed in a glass chamber maintained at room temperature. Photochromic changes as a function of time were monitored using a 500 W xenon lamp (Newport-74000) equipped with a monochromator (Newport-66921).

### Synthesis of diarylethenes

**1-(4,5-Bis(2-methylbenzo[*b*]thiophen-3-yl)-2-(methylthio)-thiophen-3-yl)ethanone (4).** Acetyl chloride (0.05 mL, 0.6 mmol) was added dropwise to a stirring solution of $AlCl_3$ (0.17 g, 1.3 mmol) in dry $CH_2Cl_2$ (5 mL) at 0 °C and stirred at 0 °C for 1 h under a nitrogen atmosphere. A solution of **14** (0.27 g, 0.6 mmol) in dry $CH_2Cl_2$ (5 mL) was added to the mixture and kept for 10 min at that temperature. Then the reaction mixture was poured into ice water, and extracted with $CH_2Cl_2$. The organic layer was washed with water, followed by brine solution and dried over $MgSO_4$. This organic layer was filtered off and concentrated to give the crude product, which was purified by column chromatography (stationary phase: silica gel 60–120, mobile phase: hexane) to give **4** as a white powder. Yield: 30 mg, 10%. M.p.: 85.0–88.7 °C. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.7–7.65 (m, 1.81H, Ar–H), 7.60–7.56 (m, 0.75H, Ar–H), 7.42–7.40 (m, 0.69H, Ar–H), 7.36–7.28 (m, 2.46H, Ar–H), 7.15–7.08 (m, 1.04H, Ar–H), 6.96–6.94 (m, 0.35H, Ar–H), 2.65 (s, 2.95H, CO*CH*$_3$–*H*), 2.42 (s, 1.07H), 2.04 (s, 1.04H), 1.96 (s, 1.80H), 1.82 (s, 2.01H), 1.76 (s, 1.17H), 1.71 (s, 1.71H). $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 194.68, 141.08, 140.31, 140.18, 138.72, 137.84, 137.75, 135.12, 131.56, 127.53, 124.61, 124.30, 124.02, 123.97, 123.88, 123.73, 122.11, 122.09, 122.04, 121.85, 121.64, 28.44, 28.40, 18.42, 18.37, 15.13, 15.01, 14.90, 14.76.

**2,3-Bis(2-methylbenzo[*b*]thiophen-3-yl)-thieno[2,3-*b*]cyclohexanone (5).** To a solution of **16** (0.10 g, 0.22 mmol) in toluene (3 mL) at 0 °C was added trifluoroacetic anhydride (0.06 mL, 0.44 mmol) at 0–5 °C. The mixture was warmed to 25 °C and monitored by TLC until ring closure was complete (*ca.* 12 h). The reaction mixture was cooled to 0–5 °C and quenched into cold $H_2O$ (3 mL, 5 °C) keeping the temperature at <25 °C. The mixture was stirred for 30 min and the layers were separated. The organic layer was washed with brine and dried over $MgSO_4$. This organic layer was concentrated to give the crude product, which was purified by column chromatography (stationary phase: silica gel 60–120, mobile phase: 10% ethyl acetate in hexane) to give **5** as a white solid. Yield: 50 mg, 52%. M.p.: 139.1–142.9 °C. HRMS (FAB$^+$): *m*/*z* 444.0680 (M$^+$) (requires *m*/*z* 444.0676). $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.83–7.52 (m, 3.51H, Ar–H), 7.39–7.11 (m, 4.04H, Ar–H), 6.82 (d, 045H, *J* = 7.9 Hz, Ar–H), 3.08–2.94 (m, 2.0H, $CH_2CH_2$*CH*$_2$–*H*), 2.76–2.70 (m, 2.0H, $CH_2CH_2$*CH*$_2$–*H*), 2.42–2.36 (m, 1.14H, $CH_2CH_2$*CH*$_2$–*H*), 2.22–2.12 (m, 3.19H, $CH_2CH_2$*CH*$_2$–*H* and $CH_3$), 1.92–1.79 (m, 3.68H, $CH_3$). $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 197.96, 141.95, 141.08, 139.90, 139.43, 137.92, 136.49, 134.13, 133.48, 130.38, 129.98, 127.06, 126.60, 125.98, 125.76, 125.14, 124.68, 124.29, 123.81, 122.35, 121.80, 38.71, 29.74, 23.47, 14.79, 14.38.

**2,3-Bis(2-methylbenzo[*b*]thiophen-3-yl)-5,6-dihydro-4*H*-thieno[2,3-*b*]thiopyran-4-one-7-oxide (6).** *m*-CPBA (57 mg, 0.33 mmol) was added to a stirring solution of **1** (100 mg, 0.22 mmol) in dry $CH_2Cl_2$ (5 mL) in an ice bath. The mixture was stirred for 1.5 h in an ice bath and quenched by the successive addition of the aqueous solutions of 10% $Na_2S_2O_3$ and 10% $NaHCO_3$, and the reaction mixture was extracted with $CH_2Cl_2$. The organic layer was washed with water, followed by brine solution and dried over $MgSO_4$. This organic layer was filtered off and concentrated to give the crude product, which was purified by column chromatography (stationary phase: silica gel 60–120, mobile phase: 50% ethyl acetate in hexane) to give **6** as a yellow powder. Yield: 105 mg, 98%. M.p.: 137.6–140.5 °C. HRMS (FAB$^+$): *m*/*z* 478.0030 (M$^+$) (requires *m*/*z* 478.0190). $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.69–7.56 (m, 2.69H, Ar–H), 7.36–7.18 (m, 3.53H, Ar–H), 7.16–6.93 (m, 2.26H, Ar–H), 3.63–3.50 (m, 3.0H, $CH_2$*CH*$_2$–*H*), 2.88–2.77 (m, 1.0H, $CH_2$*CH*$_2$–*H*), 2.40 (s, 1.15H, p-$CH_3$), 2.21–2.18 (m, 1.15H, p-$CH_3$), 1.86–1.82 (m, 3.69H, ap-$CH_3$). Ratio of p/ap = 38/62. $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 187.10, 186.78, 139.61, 138.81, 138.36, 137.69, 137.53, 135.22, 134.86, 125.86, 125.73, 124.69, 124.58, 124.35, 124.26, 124.00, 123.81, 123.64, 123.51, 122.31, 122.16, 122.09, 121.98, 121.83, 121.53, 49.35, 48.79, 30.94, 30.54, 29.67, 15.15, 15.01.

**2,3-Bis(2-methylbenzo[*b*]thiophen-3-yl)-5,6-dihydro-4*H*-thieno[2,3-*b*]thiopyran-4-one-7,7-dioxide (7).** A solution of $NaWO_2 \cdot 2H_2O$ (7.3 mg, 0.5 mmol) in water (0.3 mL) was added to a stirring solution of **1** (20 mg, 0.04 mmol) in THF (4 mL) under an ice bath. 30% $H_2O_2$ (1 mL) was added to the mixed solution slowly and then heated to 60 °C for 2 h. The mixture was cooled and quenched by the addition of the aqueous solutions of 10% $Na_2S_2O_3$, and the reaction mixture was extracted with ethyl acetate. The organic layer was washed with water, followed by brine solution and dried over $MgSO_4$. This organic layer was filtered off and concentrated to give the crude product, which was purified by column chromatography (stationary phase: silica gel 60–120, mobile phase: 50% ethyl acetate in hexane) to give **7** as yellow powder. Yield: 21 mg, 98%. M.p.: 230.6–233.0 °C. HRMS (EI$^+$): *m*/*z* 494.0122 (M$^+$) (requires *m*/*z* 494.0139). $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.71–7.56 (m, 2.66H, Ar–H), 7.37–7.21 (m, 3.70H, Ar–H), 7.15–7.08 (m, 1.14H, Ar–H), 7.03–6.93 (m, 0.70H, Ar–H), 3.86–3.74 (m, 2.0H, $CH_2$*CH*$_2$–*H*), 3.40–3.20 (m, 2.0H, $CH_2$*CH*$_2$–*H*), 2.40 (s, 1.07H, p-$CH_3$), 2.19 (s, 1.07H, p-$CH_3$), 1.85 (s, 1.84H, ap-$CH_3$), 1.83 (s, 1.83H, ap-$CH_3$). Ratio of p/ap = 37/63. $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 185.09, 148.75, 142.81, 140.39, 139.43, 139.36, 139.03, 137.79, 137.52, 136.89, 134.60, 134.83, 124.72, 124.38, 124.29, 124.22, 123.97, 123.75, 123.65, 123.56, 122.08, 121.82, 121.70, 121.50, 53.42, 51.89, 37.51, 15.16, 14.99.

**2,3-Bis(2-methylbenzo[*b*]thiophen-3-yl)-5,6-dihydro-4*H*-thieno[2,3-*b*]thiopyran-4-ol (8).** $NaBH_4$ (65 mg, 1.7 mmol) was added to a solution of **1** (80 mg, 0.17 mmol) in THF–EtOH (2 mL/1 mL) and refluxed for 24 h. The reaction mixture was cooled in an ice bath and quenched using MeOH (4 mL), extracted with ether. The organic layer was washed with water, followed by brine solution and dried over $MgSO_4$. This organic layer was filtered off and concentrated to give the crude product, which was purified by column chromatography (stationary phase: silica gel 60–120, mobile phase: 25% ethyl acetate in hexane) to give **8** as a greenish yellow powder. Yield: 65 mg, 81%. M.p.: 222.0–223.7 °C. HRMS (EI$^+$): *m*/*z* 464.0392 (M$^+$) (requires *m*/*z* 464.0397). $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.72–7.32 (m, 3.0H, Ar–H), 7.30–7.91 (m, 5.0H, Ar–H), 4.39 (broad, 1.0H, OH), 3.52–3.44 (m, 1.0H, *CH*OH–*H*), 2.96–2.89 (m, 1.0H, $CH_2$*CH*$_2$–*H*), 2.36–1.58 (m, 9.0H, $CH_2$*CH*$_2$–*H* and $CH_3$). $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 140.41, 138.26, 137.53, 133.91, 130.17, 124.19, 123.94, 123.92, 123.73, 122.50, 121.89, 121.73, 121.43, 61.10, 31.57, 30.06, 29.67, 29.34, 29.05, 22.64, 15.08, 14.12.

**3-(2,5-Dimethylthiophen-3-yl)-2-(2-methylbenzo[*b*]thiophen-3-yl)-5,6-dihydro-4-*H*-thieno[2,3-*b*]thiopyran-4-one (9).** Compound **9** was prepared by a method similar to that used for **5**

and was obtained as a yellow solid. Yield: 50%. M.p.: 85.7–87.6 °C. HRMS ($EI^+$): $m/z$ 426.0235 ($M^+$) (requires $m/z$ 426.0240). $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 7.70 (d, 1.0 H, $J$ = 5.8 Hz, Ar–H), 7.60 (d, 0.53H, $J$ = 6.8 Hz, Ar–H), 7.44–7.42 (m, 0.44H, Ar–H), 7.27–7.23 (m, 2.21H, Ar–H), 6.44 (s, 0.51H, Ar–H), 6.08 (s, 0.42H, Ar–H), 3.44–3.38 (m, 2.0H, $CH_2CH_2$–$H$), 2.92–2.88 (m, 2.0H, $CH_2CH_2$–$H$), 2.34 (s, 1.62H, $CH_3$), 2.26 (s, 1.25H, $CH_3$), 2.17 (s, 1.34H, $CH_3$), 2.12 (s, 1.50H, $CH_3$), 2.07 (s, 1.24H, $CH_3$), 1.65 (s, 1.73H, $CH_3$). $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 188.25, 152.13, 140.69, 139.99, 137.83, 136.38, 134.13, 133.95, 133.75, 133.67, 132.96, 131.10, 129.45, 127.19, 126.73, 124.25, 124.10, 123.85, 123.63, 122.23, 121.96, 121.90, 121.76, 39.64, 29.66, 15.21, 15.06, 14.93, 14.63, 14.05.

**2-(2,5-Dimethylthiophen-3-yl)-3-(2-methylbenzo[*b*]thiophen-3-yl)-5,6-dihydro-4-*H*-thieno[2,3-*b*]thiopyran-4-one (10).** Compound **10** was prepared by a method similar to that used for **5** and obtained as a yellow solid. Yield: 50%. M.p.: 184.5–186.9 °C. HRMS ($EI^+$): $m/z$ 426.0231 ($M^+$) (requires $m/z$ 426.0240). $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 7.71–7.63 (m, 1.0H, Ar–H), 7.20–7.19 (m, 3.0H, Ar–H), 6.12 (s, 1.0H, Ar–H), 3.44–3.36 (m, 2.0H, $CH_2CH_2$–$H$), 2.84–2.77 (m, 2.0H, $CH_2CH_2$–$H$), 2.20 (s, 3.0H, $CH_3$), 2.09 (s, 3.0H, $CH_3$), 2.05 (s, 3.0H, $CH_3$). $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 187.74, 150.80, 140.44, 137.60, 137.04, 135.54, 135.25, 133.28, 133.14, 131.70, 128.36, 127.77, 126.77, 123.71, 123.22, 121.97, 121.80, 39.36, 29.75, 14.94, 14.54, 14.09.

**2,3-Bis(2,5-dimethylthiophen-3-yl)-5,6-dihydro-4*H*-thieno-[2,3-*b*]thiopyran-4-one (11).** Compound **11** was prepared by a method similar to that used for **5** and obtained as a yellow solid. Yield: 40%. M.p.: 116.5–118.4 °C. HRMS ($EI^+$): $m/z$ 390.0237 ($M^+$) (requires $m/z$ 390.0240). $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 6.37 (s, 1.0H, Ar–H), 6.24 (s, 1.0H, Ar–H), 3.38–3.34 (m, 2.0H, $CH_2CH_2$–$H$), 2.87–2.84 (m, 2.0H, $CH_2CH_2$–$H$), 2.37 (s, 3.0H, $CH_3$), 2.30 (s, 3.0H, $CH_3$), 2.10 (s, 3.0H, $CH_3$), 1.88 (s, 3.0H, $CH_3$). $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 188.45, 150.56, 135.38, 135.03, 133.86, 133.78, 133.61, 132.77, 131.80, 131.43, 128.64, 127.41, 127.07, 39.63, 29.60, 15.25, 15.03, 13.93, 13.70.

## Acknowledgements

This work was supported by a grant from the Kyung Hee University in 2013 (KHU-20130571).

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