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Substituent position effect on the optoelectronic properties of photochromic diarylethenes

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Abstract—Photochromic diarylethenes bearing fluorine atoms at the *ortho*-, *meta*-, or *para*-position of both terminal phenyl rings have been synthesized. Effect of the substituent positions on their optoelectronic properties, including photochromism in solution, fluorescence, and electrochemical properties were investigated for the first time. The results indicated that the position of the fluorine substituent had remarkable impacts on molar absorption coefficient of the closed-ring forms of diarylethenes, quantum yields of the cyclization and cycloreversion reactions, fluorescence intensity, as well as the oxidation potential.

Photochromic compounds, such as spirobenzopyrans, azobenzenes, fulgides, and diarylethenes, have been extensively investigated for their potential applications in erasable optical memories, displays, and optical switches.[1] Among such compounds, diarylethenes with derivatives bearing thiophene or benzothiophene ring systems are regarded as the best candidates for applications because of their good thermal stability of both forms, remarkable fatigue resistance, rapid response, and high reactivity in the solid state.[2–6] In particular, diarylethenes with thiophene ring systems bearing terminal phenyl groups have been of considerable interest, because the hydrogen atoms attached to the terminal phenyl groups can be substituted by many other electron-donating groups or electron-withdrawing groups, which inevitably influence the optoelectronic properties of corresponding diarylethenes.[7]

To date, several publications concerning substituent effect on the photochromic performance of diarylethene have been reported. Pu et al.[7] and Irie et al.[8] reported the effect of the substituents at *para*-positions of the terminal phenyl groups on the photochromic property and the photochemical reactivity. The results showed that electron-donating substituents of the bis(3-thienyl)ethane diarylethenes could be effective to increase the absorption coefficient of the closed-ring forms and decrease the cycloreversion quantum yield; while electron-donating substituents of the bis(2-thienyl)ethane diarylethenes could be effective to increase the maxima absorption of the open-ring forms and reduce the cyclization quantum yield. Morimitsu et al.,[9] Takami and Irie[10] revealed that bulky alkoxy substituents at 2-and 2′-positions of the thiophene rings would strongly suppress the cycloreversion quantum yield and decrease the thermal stability of the colored closed-ring isomers at high temperature. Recently, Tanifuji et al.[11] reported the effect of the radical substituents on the photochromic reactivity of bis(3-benzothiophene)perfluorocyclopentene. In this letter, diarylethene derivatives bearing imino nitroxide and nitronyl nitroxide have been synthesized and these radical substituents reducing the quantum yields of both cyclization and cycloreversion reactions are presented.

To summarize, it can be easily concluded that these publications can be classified into two categories. One elucidated that different substituents at the same position (*para*-position) of the terminal phenyl rings affected the photochromic and photochemical properties of diarylethenes. The other mainly explained that different substituents at the same position (2- or 3-position) of the thiophene rings affected the photochromic performance of diarylethenes. Yamamoto et al.[12] had investigated photochromism of diarylethenes bearing carboxyl groups at the *ortho*-, *meta*-, and *para*-positions of both terminal phenyl groups. But, they particularly emphasized the effect of the intermolecular hydrogen bonding

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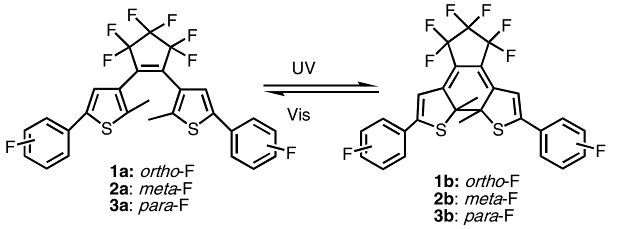
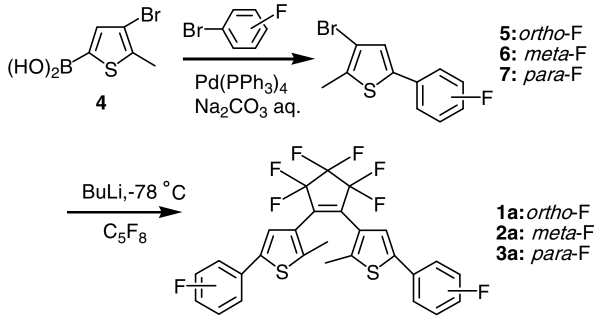
on the photochromic performance of these diarylethenes in the single-crystalline phase. Up to now, there is no report on the substituent position effect of the same functional group on the optoelectronic properties of diarylethenes.

In this study, we have synthesized three diarylethenes, 1,2-bis(2-methyl-5-(2-fluorophenyl)thiophen-3-yl)-perfluorocyclopentene (*ortho* **1a**), 1,2-bis(2-methyl-5-(3-fluorophenyl)thiophen-3-yl)perfluorocyclopentene (*meta* **2a**), and 1,2-bis(2-methyl-5-(4-fluorophenyl)thiophen-3-yl)perfluorocyclopentene (*para* **3a**), which have fluorine groups at the *ortho*-, *meta*-, and *para*-positions of both terminal phenyl groups. And we investigate the effect of substituent position on the optoelectronic properties of photochromic diarylethenes based on the absorption spectra, fluorescence, and electrochemical properties. To the best of our knowledge, this is the first report on the effect of the same substituent at the different positions (*ortho*-, *meta*-, and *para*-position) of the terminal phenyl rings on the optoelectronic properties of photochromic diarylethenes. Scheme 1 shows diarylethenes **1a**–**3a**, which are discussed in this letter. Diarylethenes **1a** and **2a** are new compounds, and compound **3a** reported by us in a previous paper.[7]

The synthetic route for diarylethene **1a**, **2a**, and **3a** is shown in Scheme 2. Suzuki coupling of three isomeric bromobenzenes with thiophene boronic acid (**4**)[13] gave fluorophenylthiophene derivatives (**5**–**7**). They were lithiated and then coupled with octafluorocyclopentene to give fluorine-substituted diarylethene derivatives (**1a**–**3a**). The structures of compounds **1a**–**3a**[14] were confirmed by melting point, ^{1}H NMR and ^{19}F NMR spectroscopy, mass spectrometry, and UV–vis spectroscopy.



Scheme 1. Photochromism of diarylethenes **1a**–**3a**.



Scheme 2. Synthetic route for the target compounds.

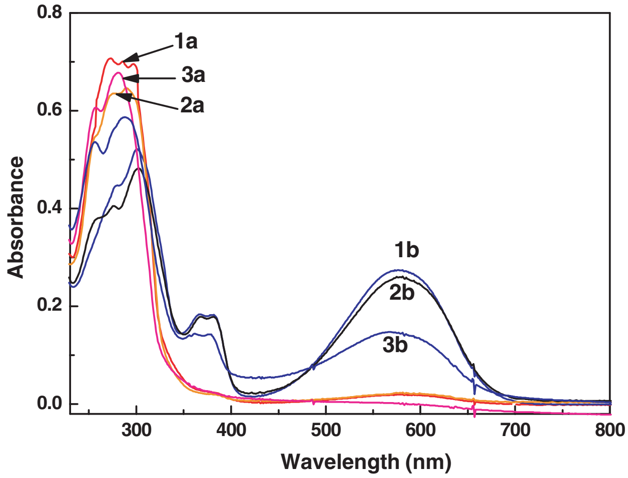


Figure 1. Absorption spectra of diarylethenes **1a**–**3a** in hexane solution ($C = 2.0 \times 10^{-5}$ mol/L).

In hexane solution, the photochromic reactivity of diarylethenes **1**–**3** was examined. Figure 1 shows their absorption spectral changes upon photoirradiation. Upon irradiation with 313 nm light, all of the colorless solutions containing **1a**–**3a** turned blue. The color changes could be attributed to the formation of the closed-ring forms. Upon irradiation with visible light ($\lambda > 500$ nm), the colored solutions returned to their original colorless forms. Their absorption spectral properties are summarized in Table 1. The quantum yields of diarylethenes **1**–**3** were measured in hexane using 1,2-bis(2-methyl-5-phenyl-thiophen-3-yl)perfluorocyclopentene as reference,[15] and the results are also shown in Table 1. From these data, we can see that the substituent position effect on the molar absorption coefficient of open-ring forms and the maxima wavelengths of both open-ring forms and closed-ring forms are not significant. However, the effect on the molar absorption coefficient of closed-ring forms and the quantum yields are more remarkable. Among compounds **1**–**3**, the maxima absorptions of the open-ring and closed-ring forms of the *meta*-substituted derivative are the biggest ($\lambda_{o,max} = 290$ nm, $\lambda_{c,max} = 579$ nm), but its quantum yields of cyclization and cycloreversion reactions are the smallest ($\Phi_{o-c} = 0.43$, $\Phi_{c-o} = 0.012$); while those of the *para*-substituted derivative are the smallest and the biggest, respectively. The values of the *ortho*-substituted derivative are in between those of the *para*- and *meta*-substituted derivatives. In addition, the molar absorption

Table 1. Absorption spectral properties of diarylethenes **1**–**3** in hexane at 2.0×10^{-5} mol/L

Compound	$\lambda_{o,max}$ (nm)[a] (ε/L mol^{-1} cm^{-1})	$\lambda_{c,max}$ (nm)[b] (ε/L mol^{-1} cm^{-1})	Φ[c]	
			Φ_{o-c}	Φ_{c-o}
1	286 (3.5×10^4)	577 (1.4×10^4)	0.54	0.015
2	290 (3.2×10^4)	579 (1.3×10^4)	0.43	0.012
3	281 (3.4×10^4)	570 (7.3×10^3)	0.58	0.025

[a] Absorption maxima of open-ring forms.

[b] Absorption maxima of closed-ring forms.

[c] Quantum yields of cyclization reaction (Φ_{o-c}) and cycloreversion reaction (Φ_{c-o}), respectively.

coefficient of closed-ring forms of the *ortho*-substituted derivative is the biggest, while that of the *para*-substituted derivative is the smallest.

The fluorescence spectra of diarylethenes **1a**–**3a** ($C = 2.0 \times 10^{-5}$ mol/L) in hexane at room temperature are illustrated in Figure 2. As shown in this figure, the hexane solutions of diarylethenes **1a**, **2a**, and **3a** showed relatively strong fluorescence at 340, 348, and 348 nm when excited at 290 nm. The fluorescence maxima of the three compounds were observed at 340 and 348 nm, indicating that the substituent position effect on the fluorescence peak was not significant. However, the fluorescence intensities of diarylethenes **1a**, **2a**, and **3a** changed dramatically along with the substituent position. The values increased rapidly from *ortho*-substituted to *para*-substituted diarylethene derivative. Among them, the relative fluorescence intensity of *ortho*-substituted derivative is the weakest, and that of *para*-substituted derivative is the strongest. The values of the *meta*-substituted derivative are located in between those of the *ortho*- and *para*-substituted derivatives. Upon irradiation with 313 nm light, their fluorescence intensity decreased along with the photochromism from open-ring form to closed-ring form, suggesting that all of the closed-ring forms of the three diarylethenes showed no fluorescence or their fluorescence was very weak.[16] In addition, the optimal fluorescence spectra of diarylethenes **1a**, **2a**, and **3a** were at 340, 351, and 348 nm when excited at 289, 293, and 285 nm, respectively.

The concentration dependent fluorescence spectrum of diarylethene **1a** was measured in hexane at room temperature, as shown in Figure 3. When the solutions at 2.0×10^{-5}, 5.0×10^{-5}, and 1.0×10^{-4} mol/L were excited at 290 nm, the maximum emission arose at 340, 347, and 354 nm, respectively. When the concentration increased to 1.0×10^{-3} mol/L, the hexane solution showed no fluorescence. As shown in Figure 3, it can be seen easily that the fluorescence spectra depended heavily on the concentration. It gave a systematic red shift and the relative fluorescence intensity decreased dramatically when the concentration increased. The self-quench phenomenon may be resulted from the formation of excimers and/or exciplexes in high concentration solution so that deactivation effect takes place during the excited-state lifetime.[17] Furthermore, the concentration effect on the fluorescence spectra of diarylethenes **2a** and **3a** were also studied, and the results are summarized in Table 2. These results exhibited that all fluorescence of the three compounds are remarkable concentration dependent. The fluorescence peak showed a systematic red shift and the relative fluorescence intensity decreased remarkably upon increasing the concentration. The results also demonstrated that molecular aggregation and fluorescence quench may occur when the concentration increases.[18]

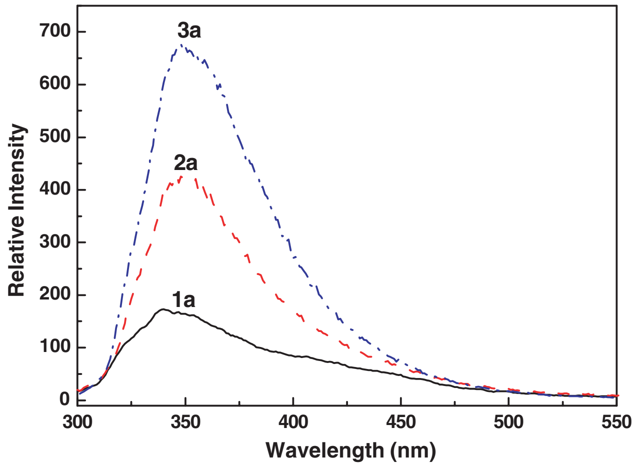


Figure 2. Fluorescence spectra of diarylethenes **1a**–**3a** in hexane solution ($C = 2.0 \times 10^{-5}$ mol/L) at room temperature, excited at 290 nm.

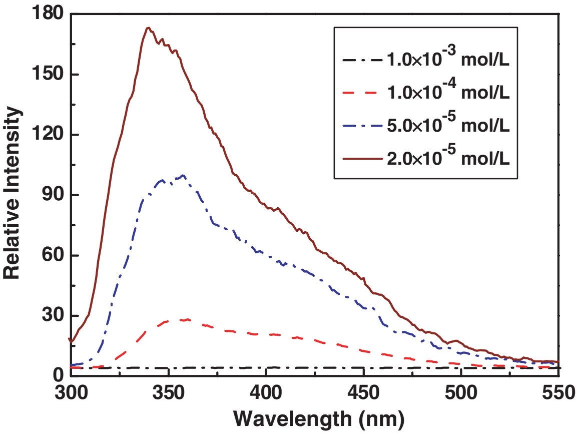


Figure 3. Fluorescence spectra of diarylethene **1a** in various concentrations in hexane at room temperature, monitored at 290 nm.

The electrochemical properties of diarylethene are being used for molecular switching and also can be potentially applied to molecular-scale electronic switches. The oxidative cyclization and cycloreversion of some diarylethene derivatives had been reported.[19–21] In order to investigate the substituent position effect on the electrochemical properties of diarylethenes, we performed electrochemical examinations by linear sweep method under the same experimental conditions using diarylethenes **1a**, **2a**, and **3a**, respectively. Electrochemical examinations were performed in a one-compartment cell by using a Model 263 potentiostat–galvanostat (EG&G Princeton Applied Research) under computer control at room temperature. Platinum-electrodes (diameter

Table 2. The concentration effect on the fluorescence spectra of diarylethenes **1a**–**3a** at room temperature in hexane, monitored at 290 nm

Concentration (mol/L)	$\lambda_{\text{em,max}}$ (Relative intensity)		
	1a	**2a**	**3a**
2.0×10^{-5}	340 (173.18)	348 (425.50)	348 (677.50)
5.0×10^{-5}	347 (97.49)	354 (208.70)	352 (231.90)
1.0×10^{-4}	354 (28.08)	361 (8.39)	362 (16.78)
1.0×10^{-3}	—[a]	—	401 (7.69)

[a] No fluorescence spectrum peak.

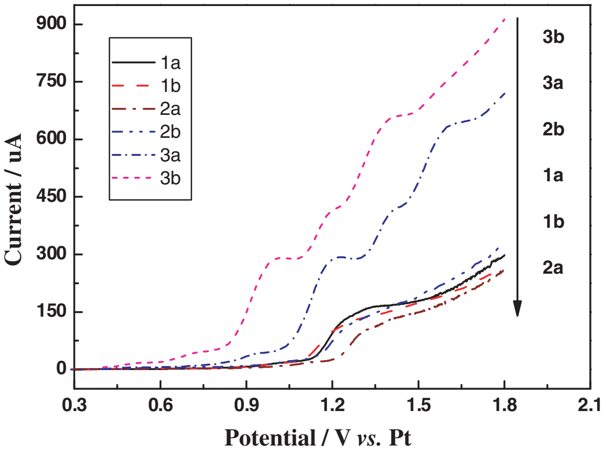


Figure 4. The anodic polarization curves of diarylethene **1**–**3**.

0.5 mm) served as working electrode and counter electrode. Platinum wire served as a quasi-reference electrode. It was calibrated using the ferrocene (Fc/Fc+) redox couple, which has a formal potential $E_{1/2} = +0.35$ V versus platinum wire. The typical electrolyte was acetonitrile (5 mL) containing 0.15 mol/L $LiClO_4$ and 4.0×10^{-3} mol/L dithienylethene. All solutions were deaerated by a dry argon stream and maintained at a slight argon overpressure during electrochemical experiments. Figure 4 shows the anodic polarization curves of **1a**, **1b**, **2a**, **2b**, **3a**, and **3b**. We can see from Figure 4 that *ortho*- and *para*-fluorine substituted diarylethenes (compounds **1** and **2**) showed similar electrochemical behavior both in closed-ring and open-ring forms. The oxidation potential onsets of **1a**, **1b**, **2a**, and **2b** initiated at 1.14, 1.11, 1.22, and 1.15 V, respectively. In sharp contrast to **1** and **2**, the oxidation potentials of **3a** and **3b** decreased significantly to 0.97 and 0.79 V, respectively. Moreover, the great difference of the open-ring form and closed-ring form of compound **3** was observed up to 0.18 V. Furthermore, the anodic current densities of **3a** and **3b** were much higher than that of **1a**, **1b** and **2a**, **2b** at given applied potentials. On the other hand, similar phenomenon was observed when the oxidation potentials of **1a**, **2a**, and **3a** are all higher that those of **1b**, **2b**, and **3b**.

These phenomena described above strongly suggested that substituent position of fluorine atom at phenyl ring had significant effect on the optoelectronic properties of diarylethenes. The main reason for these may be ascribed to the electro-withdrawing nature of fluorine atom at *para*-position of the terminal phenyl groups. For *meta*-position substituent fluorine atom of diarylethene **2**, the electro-withdrawing effect is not remarkable. For *ortho*-position substituent fluorine atom of diarylethene **1**, the electro-withdrawing effect, together with its steric effect plays a main role so that the compositive effect is similar to that of diarylethene **2**.[22]

In conclusion, three diarylethenes bearing fluorine atoms at the *ortho*-, *meta*-, and *para*-positions of both terminal phenyl groups were synthesized. The effect of different substitution positions of fluorine atoms on the optoelectronic properties of diarylethenes was investigated for the first time. The results showed that the optoelectronic performances of diarylethenes, including molar absorption coefficient, photochromic quantum yields, fluorescence intensity, and electrochemical property, etc., were significantly dependent on the effect of the substituent position. The oxidation potential differences of the open-ring and closed-ring forms of the *ortho*-, *meta*-, and *para*-substituted diarylethene derivatives were 0.03, 0.07, and 0.18 V, respectively. The reason may be attributed to the different electro-withdrawing effects when the fluorine atom was substituted on the different positions of the terminal phenyl groups. The *para*-position of the terminal phenyl groups of diarylethene on these performances is the most significant. The present results are useful for the designation of efficient photoactive and excellent characteristic diarylethene compounds.

Acknowledgments

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14. Selected data for **1**–**3**: compound **1a**: mp = 106.3–107.3 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 1.98 (s, 6H), 7.12–7.19 (m, 6H), 7.44 (s, 2H), 7.54–7.58 (m, 2H); ^{19}F NMR (400 MHz, $CDCl_3$): δ 110.05 (4F), 113.60 (2F), 113.78 (2F); MS *m*/*z* (M) 556; compound **2a**: mp = 145.9–146.8 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 1.97 (s, 6H), 6.98–7.02 (t, 2H, $J = 8.0$ Hz), 7.22 (s, 2H), 7.29 (s, 2H), 7.30–7.38 (m, 4H); ^{19}F NMR (400 MHz, $CDCl_3$): δ 110.00 (4F), 112.30 (2F), 131.77 (2F); MS *m*/*z* (M) 556;

compound **3a**: mp = 69–71 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.96 (s, 6H), 7.06–7.13 (t, 4H, $J = 8.4$ Hz), 7.21 (s, 2H), 7.49–7.52 (t, 4H, $J = 6.8$ Hz); ^{19}F NMR (400 MHz, $CDCl_3$): δ 110.05 (4F), 113.69, 131.79; MS *m*/*z* (M) 556; compound **1b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.18 (s, 6H), 6.89 (s, 2H), 7.20–7.22 (d, 4H, $J = 8.0$ Hz), 7.37–7.40 (t, 2H, $J = 6.4$ Hz), 7.45–7.49 (t, 2H, $J = 8.0$ Hz); MS *m*/*z* (M) 556; compound **2b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.23 (s, 6H), 6.69 (s, 2H), 7.13–7.17 (t, 2H, $J = 8.0$ Hz), 7.28 (s, 2H), 7.39–7.43 (m, 4H); MS *m*/*z* (M) 556; compound **3b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.17 (s, 6H), 6.61 (s, 2H), 7.10–7.14 (t, 4H, $J = 7.2$ Hz), 7.53–7.59 (t, 4H, $J = 6.8$ Hz); MS *m*/*z* (M) 556.

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