

Substituent position effect on the properties of new unsymmetrical isomeric diarylethenes having a chlorine atom

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Abstract

Three new unsymmetrical photochromic diarylethenes bearing a chlorine atom at *para*-, *meta*- and *ortho*-position of one terminal benzene ring, namely {1-(2-methyl-5-phenyl-3-thienyl)-2-[2-methyl-5-(4-chlorophenyl)-3-thienyl]}perfluorocyclopentene (*para* **1o**), {1-(2-methyl-5-phenyl-3-thienyl)-2-[2-methyl-5-(3-chlorophenyl)-3-thienyl]}perfluorocyclopentene (*meta* **2o**), and {1-(2-methyl-5-phenyl-3-thienyl)-2-[2-methyl-5-(2-chlorophenyl)-3-thienyl]}perfluorocyclopentene (*ortho* **3o**), have been synthesized. The substituent position effect on their properties, including photochromism, fluorescence both in solution and in PMMA amorphous film and their electrochemical properties were investigated in detail. The results elucidated that the chlorine atom and its substituent position had a remarkable effect on the absorption characteristics, photochromic reactivity, fluorescence, as well as the electrochemical performances of these diarylethene compounds. For diarylethenes **1**, **2** and **3**, the cycloreversion quantum yields were gradually increased when the chlorine atom was attached to the *para*-, *meta*- and *ortho*-positions of the one terminal benzene rings; but their molar absorption coefficients both of their open-ring and closed-ring isomers were remarkably decreased. The fluorescent properties of *para*-substituted diarylethene embedded in poly(methyl methacrylate) (PMMA) amorphous film showed good fluorescent switches (quenched to 28%). Furthermore, the cyclic voltammograms experiments elucidated that the electrochemical properties of these diarylethene derivatives were also remarkably dependent on the chlorine atom position effect, which may be attributed to the different electron-inducing ability and steric effect when the chlorine atom was substituted on the different position of the terminal benzene ring.

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Keywords: Photochromism; Unsymmetrical diarylethene; Substituent position effect; Optical and electrochemical properties

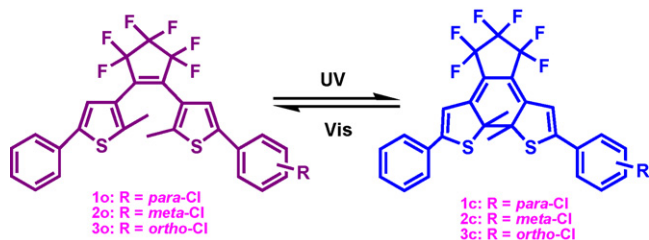
1. Introduction

The design and synthesis of photochromic molecules is an area of hotspot research because of the potential application in photonic devices, such as memory media and optical switching [1]. Photochromic compounds, such as spiropyrans [2], azobenzene [3], fulgides [4], and diarylethenes [5], have been extensively investigated. Among all types of these photochromic compounds, diarylethenes are the most promising candidates for technological applications because they usually satisfy all the fundamental requirements for the production of a device, mainly due to their excellent thermal stability of the respective isomers,

notable fatigue resistance, photochromic sensitivity, and high reactivity in the solid state [5].

Aiming at the potential application, some workers have considerably noticed the design of diarylethene derivatives with tunable optoelectronic properties [6]. Up to date, some research groups have devoted to the development of these molecules and investigative studies of their fundamental properties, and the results obtained have contributed to a broad understanding of the photochromism of diarylethenes [7]. As far as we know, although the majority of the research work reported to date has paid much attention to the substituent effect on the properties of diarylethene [8], very little work on the substituent position effect has been reported. In a previous paper, we reported the substituent position effect on the optoelectronic properties of three symmetrical photochromic diarylethenes bearing fluorine atoms of both terminal benzene rings. We found that the position of

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Scheme 1. Photochromism of diarylethenes **1**, **2** and **3**.

fluorine atom had a remarkable effect on molar absorption coefficient of the closed-ring isomers of diarylethenes, quantum yields of cyclization and cycloreversion reactions, fluorescence intensity, as well as oxidation potential [9]. We have also reported the electron-donating methoxyl group position effect on the properties of diarylethenes with a pyrazole unit and found that introduction of methoxyl group at different position of the terminal benzene ring could strongly influence the optical and electrochemical properties [10]. These results are very interesting and important, and they also encourage us to do a series of the consecutive research works in the near future for the sake of exploring the mechanism of the substituent position effect.

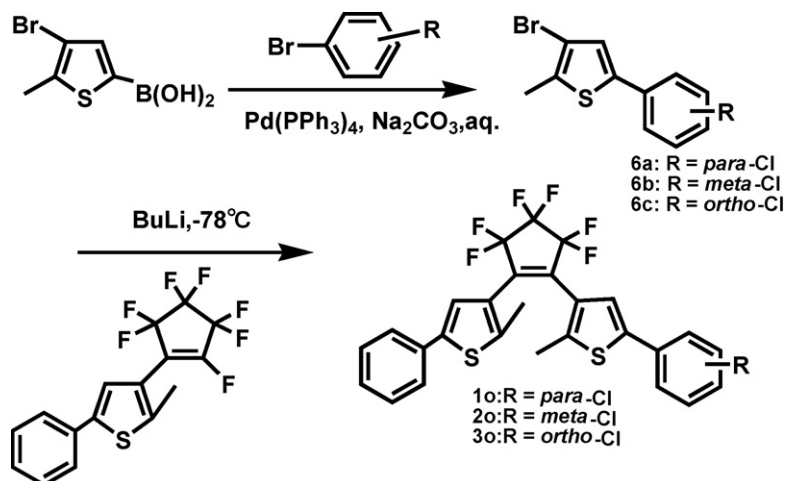
For chlorine atom, it has some unique natures differing from other electron-donating and electron-withdrawing substituents, such as resonance effect, inductive effect and its steric hindrance effect at *ortho*-position of the terminal benzene ring. The chlorine atom is working as an electron-donating character in the resonance effect, but it is working as an electron-withdrawing character in the inductive effect. We predicted that diarylethenes with a chlorine atom at the different position of the terminal benzene ring would have distinguishable characteristics due to its different electron-inducing ability and steric hindrance effect in the different photochromic isomeric diarylethene system. In this paper, in order to testify the correctness of our prediction, we have synthesized three new unsymmetrical isomeric diarylethene derivatives, namely {1-(2-methyl-5-phenyl-3-thienyl)-2-[2-methyl-5-(4-chlorophenyl)-3-thienyl]}perfluorocyclopentene (*para* **1o**), {1-(2-methyl-5-phenyl-3-thienyl)-2-[2-methyl-5-(3-chlorophenyl)-3-thienyl]}perfluorocyclo-

ntene (*meta* **2o**), and {1-(2-methyl-5-phenyl-3-thienyl)-2-[2-methyl-5-(2-chlorophenyl)-3-thienyl]}perfluorocyclopentene (*ortho* **3o**). Scheme 1 shows the molecular structures and photochromic schemes of diarylethenes **1**, **2** and **3**, which are discussed in this paper.

2. Materials and methods

2.1. Experimental

General: The solvents were purified by distillation before use. NMR spectra were recorded on Bruker AV400 (400 MHz) spectrometer with CDCl_3 as the solvent and tetramethylsilane as an internal standard. IR spectra were performed using Bruker Vertex-70 spectrometer. The elemental analysis was measured with PE CHN 2400. Melting point was determined by WRS-1B melting point determination apparatus. The absorption spectra were measured using an Agilent 8453 UV/vis spectrometer. Photo-irradiation was carried out using SHG-200 UV lamp, CX-21 ultraviolet fluorescence analysis cabinet and BMH-250 visible lamp. Light of appropriate wavelength was isolated by different light filters. The quantum yields were determined by comparing the reaction yields of the diarylethenes in hexane against 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene in hexane [11]. Fluorescence spectra were measured using a Hitachi F-4500 spectrophotometer. 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 0.5 mm) served as working electrode and counter electrode. Platinum wire served as a quasireference 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 0.1 mol/L tetrabutylammonium tetrafluoroborate ($(\text{TBA})\text{BF}_4$) 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.

Scheme 2. Synthetic route for diarylethenes **1o**, **2o** and **3o**.

2.2. Synthesis of diarylethenes

The synthesis route for diarylethenes **1o**, **2o** and **3o** was shown in Scheme 2. Suzuki coupling of three bromobenzene derivatives with thiophene boronic acid (**5**) [10b,12] gave chlorophenylthiophene derivatives (**6a–6c**). They were lithiated and then coupled with (2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene to give unsymmetrical diarylethene derivatives **1o**, **2o** and **3o**, respectively. The structures of **1o**, **2o** and **3o** were confirmed by NMR, IR, and elemental analysis.

2.2.1. 3-Bromo-5-(4-chlorophenyl)-2-methylthiophene (**6a**)

Compound **6a** was prepared by reacting 3-bromo-2-methyl-5-thienylboronic acid [13,11b] (2.21 g, 10.0 mmol) with 1-bromo-4-chlorobenzene (1.92 g, 10.0 mmol) in the presence of Pd(PPh₃)₄ (0.27 g, 0.23 mmol) and Na₂CO₃ (6.36 g; 60 mmol) in tetrahydrofuran (THF) (80 mL containing 10% water). After refluxing for 15 h, the product was extracted with ether. The organic layer was dried over MgSO₄, filtrated, and evaporated. The crude product was purified by column chromatography on SiO₂ using hexane as the eluent and 2.52 g of **6a** obtained as buffer oil in 88% yield. ¹H NMR (400 MHz, CDCl₃, TMS): δ 2.44 (s, 3H, –CH₃), 7.11 (s, 1H, thienyl-H), 7.35, 7.37 (d, *J* = 8.0, 2H, aryl-H), 7.44, 7.46 (d, *J* = 8.0, 2H, aryl-H).

2.2.2. 3-Bromo-5-(3-chlorophenyl)-2-methylthiophene (**6b**)

Compound **6b** was prepared by a method similar to that used for **6a** and obtained as buffer solid in 89% yield. ¹H NMR (400 MHz, CDCl₃, TMS): δ 2.42 (s, 3H, –CH₃), 7.12 (s, 1H, thienyl-H), 7.24–7.32 (m, 2H, aryl-H), 7.49 (s, 1H, aryl-H).

2.2.3. 3-Bromo-5-(2-chlorophenyl)-2-methylthiophene (**6c**)

Compound **6c** was prepared by a method similar to that used for **6a** and obtained as buffer solid in 81% yield. ¹H NMR (400 MHz, CDCl₃, TMS): δ 2.44 (s, 3H, –CH₃), 7.18 (s, 1H, thienyl-H), 7.25–7.28 (q, 2H, aryl-H), 7.44–7.47 (q, 2H, aryl-H).

2.2.4. {1-[2-Methyl-5-phenyl-3-thienyl]-2-[2-methyl-5-(4-chlorophenyl)-3-thienyl]}perfluorocyclopentene (**1o**)

To a stirred solution of **6a** (1.27 g, 4.40 mmol) in 30 mL THF was added dropwise a 2.4 mol/L *n*-BuLi/hexane solution (1.83 mL, 4.40 mmol) at –78 °C under nitrogen atmosphere. Stirring was continued for 30 min at –78 °C. (2-Methyl-5-phenyl-3-thienyl)perfluorocyclopentene (1.62 mL, 4.40 mmol) [14] was slowly added to the reaction mixture at –78 °C, and the mixture was stirred for 2.0 h at this low temperature. The reaction was quenched by water. The product was extracted with ether. The organic layer was washed with 1 M aqueous NaCl and water. The organic layer was dried over MgSO₄, filtrated and evaporated. The crude product was purified by column chromatography on silica gel using hexane as the eluent and 1.15 g of **1o** obtained as solid in 47% yield. ¹H NMR (400 MHz, CDCl₃, TMS): δ 1.89 (s, 6H, –CH₃), 7.19 (s, 2H, thiophene-H), 7.22 (d, 1H, *J* = 8.0, benzene-H), 7.27–7.32 (m, 4H, benzene-H), 7.40 (d, 2H, *J* = 8.0, benzene-H), 7.47 (d, 2H, *J* = 8.0, benzene-H);

¹³C NMR (100 MHz, CDCl₃, TMS): δ 13.53, 121.37, 121.80, 124.60, 124.99, 125.79, 126.94, 128.00, 130.84, 132.28, 132.72, 139.92, 140.65, 141.33; IR (ν, KBr, cm^{–1}) 753, 818, 897, 987, 1054, 1104, 1187, 1271, 1337, 1443, 1470, 1501, 1552, 1601, 1625, 2916; Anal. Calcd for C₂₇H₁₇ClF₆S₂ (%): Calcd C, 58.43; H, 3.09. Found C, 58.94; H, 3.07; mp: 128.6–129.0 °C.

2.2.5. {1-[2-Methyl-5-phenyl-3-thienyl]-2-[2-methyl-5-(3-chlorophenyl)-3-thienyl]}perfluorocyclopentene (**2o**)

Compound **2o** was prepared by a method similar to that used for **1o** and used solution of **6b** (1.27 g, 4.40 mmol) then 1.27 g of **2o** obtained as solid in 52% yield. ¹H NMR (400 MHz, CDCl₃, TMS): δ 1.96 (s, 3H, –CH₃), 1.97 (s, 3H, –CH₃), 7.26 (s, 1H, thiophene-H), 7.28 (t, 1H, *J* = 6.0, benzene-H), 7.29 (s, 1H, thiophene-H), 7.32 (t, 2H, *J* = 8.0, benzene-H), 7.37–7.42 (m, 3H, benzene-H), 7.53 (d, 2H, *J* = 8.0, benzene-H), 7.55 (s, 1H, benzene-H); ¹³C NMR (100 MHz, CDCl₃, TMS): δ 14.56, 122.38, 123.28, 123.77, 125.64, 127.84, 127.97, 129.03, 130.25, 135.00, 135.06; IR (ν, KBr, cm^{–1}) 758, 784, 853, 898, 979, 992, 1055, 1112, 1137, 1187, 1272, 1339, 1439, 1469, 1552, 1594, 1628, 2913, 3065; Calcd for C₂₇H₁₇ClF₆S₂ (%): Calcd C, 58.43; H, 3.09. Found C, 58.14; H, 3.17; mp: 118.6–119.0 °C.

2.2.6. {1-[2-Methyl-5-phenyl-3-thienyl]-2-[2-methyl-5-(2-chlorophenyl)-3-thienyl]}perfluorocyclopentene (**3o**)

Compound **3o** was prepared by a method similar to that used for **1o** and used solution of **6c** (1.27 g, 4.40 mmol) then 0.57 g of **2o** obtained as liquid in 23% yield. ¹H NMR (400 MHz, CDCl₃, TMS): δ 2.00 (s, 3H, –CH₃), 2.02 (s, 3H, –CH₃), 7.28 (s, 1H, thiophene-H), 7.29 (s, 1H, thiophene-H), 7.27 (d, 1H, *J* = 8.0, benzene-H), 7.40 (t, 3H, *J* = 8.0, benzene-H), 7.46 (t, 2H, *J* = 4.0, benzene-H), 7.55 (d, 3H, *J* = 8.0, benzene-H); ¹³C NMR (100 MHz, CDCl₃, TMS): δ 13.50, 121.44, 124.00, 124.61, 124.73, 126.01, 126.47, 126.87, 126.94, 127.98, 128.08, 129.22, 129.52, 130.07, 131.17, 131.37, 132.33, 137.00, 141.22; IR (ν, KBr, cm^{–1}) 757, 844, 889, 988, 1052, 1116, 1192, 1274, 1337, 1441, 1596, 2918; Calcd for C₂₇H₁₇ClF₆S₂ (%): Calcd C, 58.43; H, 3.09. Found C, 58.04; H, 2.95.

3. Results and discussion

3.1. Photochromism of diarylethenes

The photochromic behaviors of diarylethenes **1**, **2** and **3** were examined both in hexane (2.0 × 10^{–5} mol/L) and in PMMA amorphous film, and their absorption spectral changes induced by photoirradiation at room temperature are shown in Figs. 1 and 2. As shown in Fig. 1(A), the colorless solution containing the open-ring isomer **1o**, which showed the maximum absorption at 289 nm, turned blue upon irradiation with 297 nm light. The color changes could be attributed to the formation of the closed-ring isomer **1c**, in which the maximum absorption peak was observed at 577 nm. Upon irradiation with visible light of wavelength longer than 450 nm, the colored solution

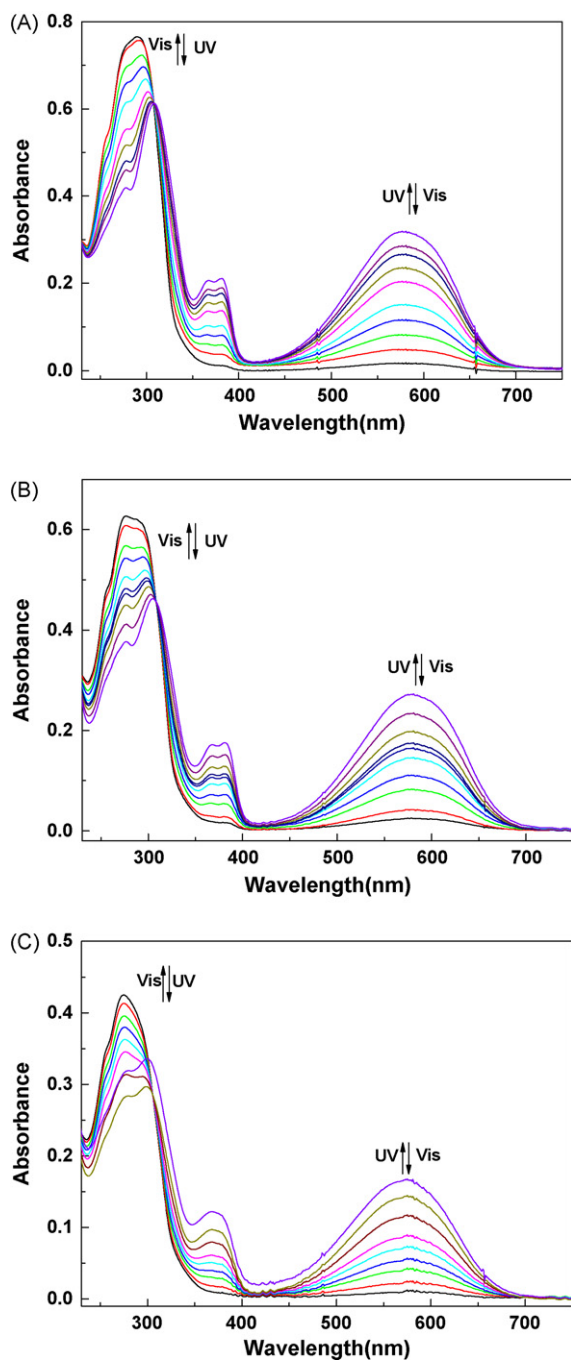


Fig. 1. Absorption spectral changes of diarylethenes **1**, **2** and **3** in hexane ($c = 2.0 \times 10^{-5}$ mol/L) at room temperature: (A) **1**, (B) **2** and (C) **3**.

returned to their original colorless form. Just as diarylethene **1**, compounds **2** and **3** also show photochromism in hexane solution (Fig. 1(B) and (C)). Upon irradiation with 297 nm light, absorption bands in the visible region appeared and the solutions of **2o** and **3o** turned blue as a result of the cyclization reactions to produce **2c** and **3c**. All the solutions of **2c** and **3c** can be decolorized upon irradiation with visible light ($\lambda > 450$ nm) attributable to reproducing the open-ring isomers **2o** and **3o**.

The photochromic properties of diarylethenes **1**, **2** and **3** are summarized in Table 1. From these data, it can be easily seen that the chlorine atom position effect on the absorption

maxima of both open-ring isomers and closed-ring isomers of diarylethenes **1**, **2** and **3** are not significant, however, the effect on the quantum yields and the molar absorption coefficients are more remarkable. Among compounds **1**, **2** and **3**, the cyclization quantum yield of **2** are the biggest ($\Phi_{o-c} = 0.72$); while that of **3** are the smallest ($\Phi_{o-c} = 0.50$). In hexane, the molar absorption coefficients of both the open-ring isomer and the closed-ring isomer of the *para*-substituted derivative (compound **1**) are the biggest; while those of the *ortho*-substituted derivative (compound **3**) are the smallest. The molar absorption coefficients of the *meta*-substituted derivative (compound **2**) are in between

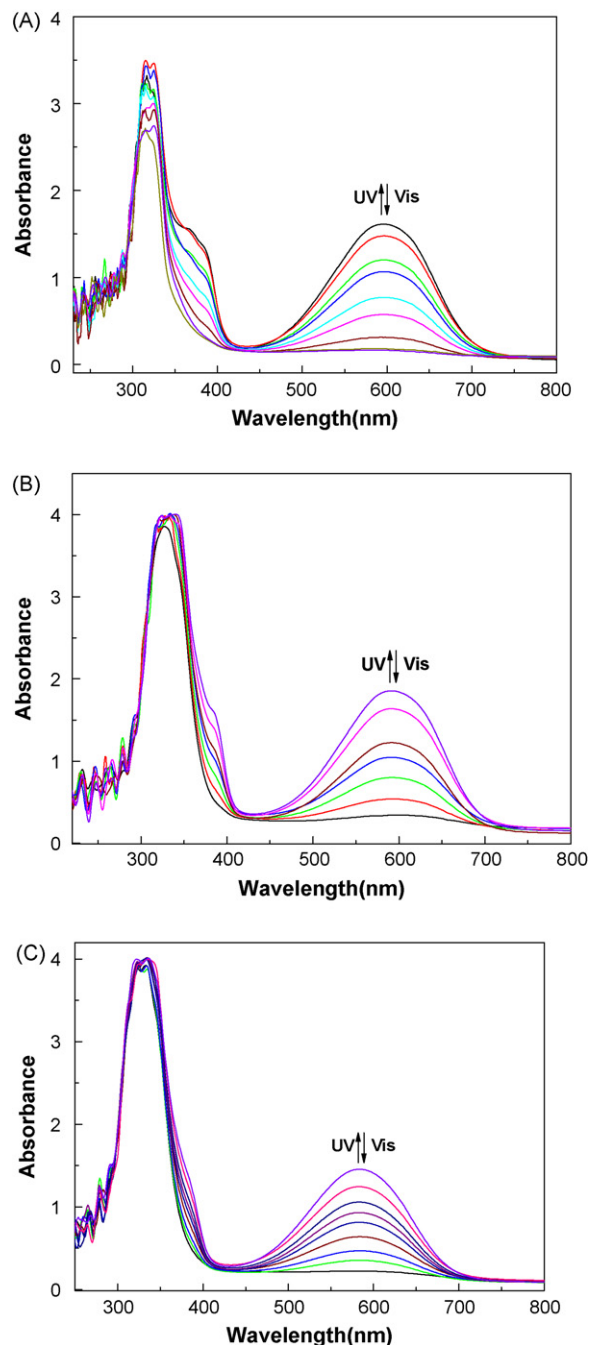


Fig. 2. Absorption spectral changes of diarylethenes **1**, **2** and **3** in PMMA film at room temperature: (A) **1**, (B) **2** and (C) **3**.

Table 1

Absorption characteristics and photochromic reactivity of diarylethenes **1**, **2** and **3** both in hexane ($c = 2.0 \times 10^{-5}$ mol/L) and in PMMA film (10%, w/w)

Compound	$\lambda_{\max,o}^a/nm$ ($\epsilon/L \text{ mol}^{-1} \text{ cm}^{-1}$)		$\lambda_{\max,c}^b/nm$ ($\epsilon/L \text{ mol}^{-1} \text{ cm}^{-1}$)		Φ^c	
	Hexane	PMMA film	Hexane	PMMA film	Φ_o	Φ_c
1	289/ 3.85×10^{-4}	325	577/ 1.60×10^{-4}	597	0.67	0.012
2	276/ 3.15×10^{-4}	325	581/ 1.35×10^{-4}	590	0.72	0.015
3	275/ 2.10×10^{-4}	329	575/ 0.85×10^{-4}	584	0.50	0.036

^a Absorption maxima of open-ring isomers.^b Absorption maxima of closed-ring isomers.^c Quantum yields of open-ring (Φ_o) and closed-ring isomers (Φ_c), respectively.

those of the *para*- and *ortho*-substituted derivatives. Compared to those of **3o** and **3c** ($\epsilon_{3o} = 2.10 \times 10^{-4} \text{ L mol}^{-1} \text{ cm}^{-1}$; $\epsilon_{3c} = 0.85 \times 10^{-4} \text{ L mol}^{-1} \text{ cm}^{-1}$), the molar absorption coefficient of **1o** and **1c** are almost twofold larger ($\epsilon_{1o} = 3.85 \times 10^{-4} \text{ L mol}^{-1} \text{ cm}^{-1}$; $\epsilon_{1c} = 1.60 \times 10^{-4} \text{ L mol}^{-1} \text{ cm}^{-1}$), indicating that a significant decrease with the chlorine atom attached to the terminal phenyl ring from *para*- to *ortho*-position. However, the cycloreversion quantum yields of diarylethenes **1**, **2** and **3** showed a contrary changing trend against the molar absorption coefficient. It increased along with the chlorine atom attached to the benzene ring from *para*- to *ortho*-position. Among **1**, **2** and **3**, the cycloreversion quantum yield of **1** is the smallest ($\Phi_{c-o} = 0.012$) and that of **3** is the biggest ($\Phi_{c-o} = 0.036$). Compared to diarylethenes **1**, **2** and **3**, the photochromic behavior of non-chlorine atom derivative (1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene, **4**) is evidently different. The photochromic parameters of compound **4** are mainly located in between those of the *para*- and *meta*-position chlorine substituted derivatives, with the exception of its cyclization

quantum yield ($\Phi_{o-c} = 0.59$) [11]. This is different from that of symmetrical diarylethene systems reported previously [15]. For the symmetrical diarylethenes bearing two chlorine atoms, the photochromic parameters of compound **4** are mainly located in between those of the *meta*- and *ortho*-position chlorine substituted derivatives, with the exception of its molar absorption coefficient, indicating that the chlorine atom position effect on photochromic behaviors is strengthened evidently. It was notable that the molar absorption coefficient and the cyclization quantum yield increased effectively when the chlorine atom was introduced into the *para*- or *meta*-position of the terminal benzene ring in diarylethene system; however, all photochromic parameters except the cycloreversion quantum yield decreased remarkably when the chlorine atom was introduced into the *ortho*-position of the terminal benzene ring. This result is in agreement well with that reported in Ref. [15], indicating that the trend of chlorine atom position effect on the photochromic behaviors of unsymmetrical diarylethene systems is the same as that of symmetrical diarylethene systems. However, the result is remarkably distinguished from those reported in

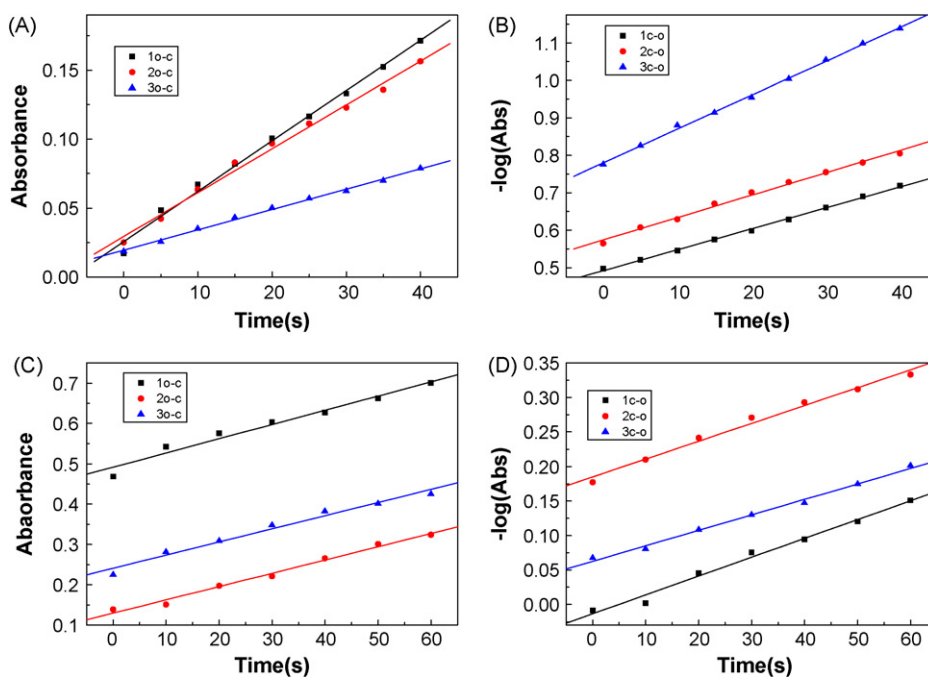


Fig. 3. The cyclization/cycloreversion kinetics of diarylethenes **1**, **2** and **3** both in hexane ($c = 2.0 \times 10^{-5}$ mol/L) and in PMMA films: (A) cyclization kinetics in hexane ($\lambda = 297$ nm), (B) cycloreversion kinetics in hexane ($\lambda > 450$ nm), (C) cyclization kinetics in PMMA film ($\lambda = 313$ nm), (D) cycloreversion kinetics in PMMA film ($\lambda > 450$ nm).

our other previous papers [9,10]. The electron-withdrawing fluorine substituent position does not affect significantly on the photochromic behaviors of symmetrical diarylethene derivatives [9]; while the electron-donating methoxyl substituent position can effectively enhance the cycloreversion quantum yield of unsymmetrical diarylethenes bearing a pyrazole unit [10].

In the PMMA amorphous film, diarylethenes **1**, **2** and **3** also showed good photochromism (Fig. 2) as similar as that in solution. The photochromic properties of diarylethenes **1**, **2** and **3** in PMMA film are also summarized in Table 1. Upon irradiation 313 nm light, the colors of the three diarylethene/PMMA films changed from colorless to blue with the appearance of a new broad absorption band at 597, 590 and 584 nm, respectively, which was assigned to the formation of the closed-ring isomers **1c**, **2c** and **3c**. All colored diarylethene/PMMA films can revert to colorless upon irradiation with visible light ($\lambda > 450$ nm). From Table 1, it can be easily seen that the maximum absorption peak of the closed-ring isomer decreased with the chlorine atom attached to the terminal benzene ring from *para*- to *ortho*-position. The maximum absorption peaks of both the open-ring and the closed-ring isomers of diarylethenes **1**, **2** and **3** in PMMA film are longer than those in hexane solution. The red shift values of the absorption maxima of the open-ring isomers are 36 nm for **1o**, 49 nm for **2o** and 54 nm for **3o**, and those of the closed-ring isomers are 20 nm for **1c**, 9 nm for **2c** and 9 nm for **3c**, respectively. The red shift phenomena may be ascribed to the stabilization of molecular arrangement in solid state [16].

The photochromic cyclization and cycloreversion kinetics of diarylethenes **1**, **2** and **3** both in hexane and in PMMA films were investigated by alternating irradiation with UV–vis and visible light, as shown in Fig. 3. The concentrations of all solutions were 2.0×10^{-5} mol/L. All absorption data were collected at the maximum absorption peak. As shown in Fig. 3(A), it can be clearly seen that the relationships between absorbance and exposure time (A vs. t) show good linearity (linear correction factors > 0.99) upon irradiation with 297 nm in hexane, suggesting that the photochromic cyclization reactions of diarylethenes **1**, **2** and **3** should belong to zeroth order reaction. The slopes of the A versus t lines gave the zeroth order rate constant k_{o-c} . According to this method, all the k values for the cyclization process of diarylethenes **1**, **2** and **3** can be easily obtained and they are 3.64×10^{-3} , 3.18×10^{-3} and 1.48×10^{-3} mol/L s $^{-1}$, respectively. Similarly, those of diarylethenes **1**, **2** and **3** in PMMA film are 3.53×10^{-3} , 3.29×10^{-3} and 3.26×10^{-3} mol/L s $^{-1}$, respectively (Fig. 3(C)). During the cycloreversion processes of diarylethenes **1**, **2** and **3**, the relationships between $-\log(\text{Abs})$ and exposal time also show good linearity, indicating that the cycloreversion processes belong to first order reaction. From Fig. 3, the rate constant of the cycloreversion process (k_{c-o}) of diarylethenes **1–3** in hexane were calculated to be 5.59×10^{-3} , 5.97×10^{-3} and 9.03×10^{-3} s $^{-1}$, respectively (Fig. 3(B)), and those in PMMA film were calculated to be 2.73×10^{-3} , 2.59×10^{-3} and 2.24×10^{-3} s $^{-1}$, respectively (Fig. 3(D)). Of the three compounds, the k_{o-c} of diarylethene **3** is the smallest and its k_{c-o} is the biggest in hexane, which is well consistent with the smallest cyclization quantum and the biggest cyclore-

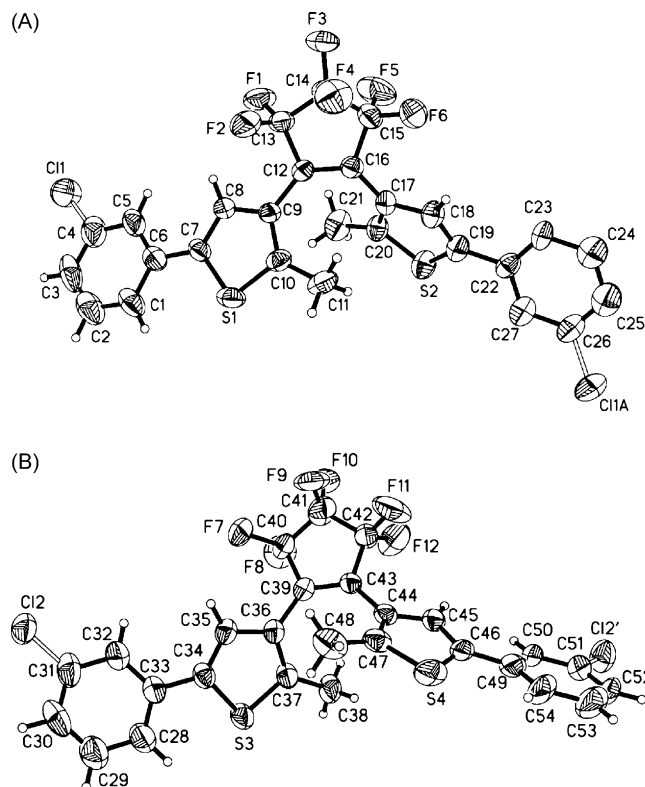


Fig. 4. ORTEP drawings of diarylethene **2o**, showing 35% probability displacement ellipsoids: (A) molecule I and (B) molecule II.

version quantum yield of diarylethene **3**, suggesting that the rate constant is direct proportioned to the quantum yield of photochemical reaction. However, the values both of k_{o-c} and k_{c-o} is no remarkable change in PMMA film. The possible reason is that the photochemical reaction kinetics may be influenced by many factors, such as molar absorption coefficient, quantum yield and environmental medium, etc.

Moreover, colorless crystal of **2o** suitable for X-ray analysis was obtained by the slow evaporation in hexane. In order to know better the relationship between the conformation and the photochromic reactivity of diarylethene **2o** in the crystalline phase, its structural confirmation was provided by X-ray crystallographic diffraction analysis. The ORTEP drawing is shown in Fig. 4 and its packing diagram is shown in Fig. 5. There are two independent molecules (molecule I and molecule II) in the asymmetric unit (Fig. 4) and they are packed in a photoactive *anti*-parallel conformation in the crystalline phase (Fig. 5), which can undergo photo-cyclization reaction [17]. It was found that the chlorine atom substituents randomly to the benzene rings of both wings of each molecule. They were named as C11 and C1A for molecule I and C12 and C12' for molecule II, and their occupancies were assigned to be 0.5 in the final refinement. In the hexafluorocyclopentene rings of the two molecules, the C12–C16 [1.355(8) Å] and C39–C43 [1.356(8) Å] bonds are clearly double bonds, while the other bonds in the two rings are single bonds. The four thiophene rings are linked by the C12=C16 and C39=C43 double bonds; the methyl groups are all located on opposite sides of the double bond, and thus they are *trans* with respect to the double bond. Such a conformation is crucial

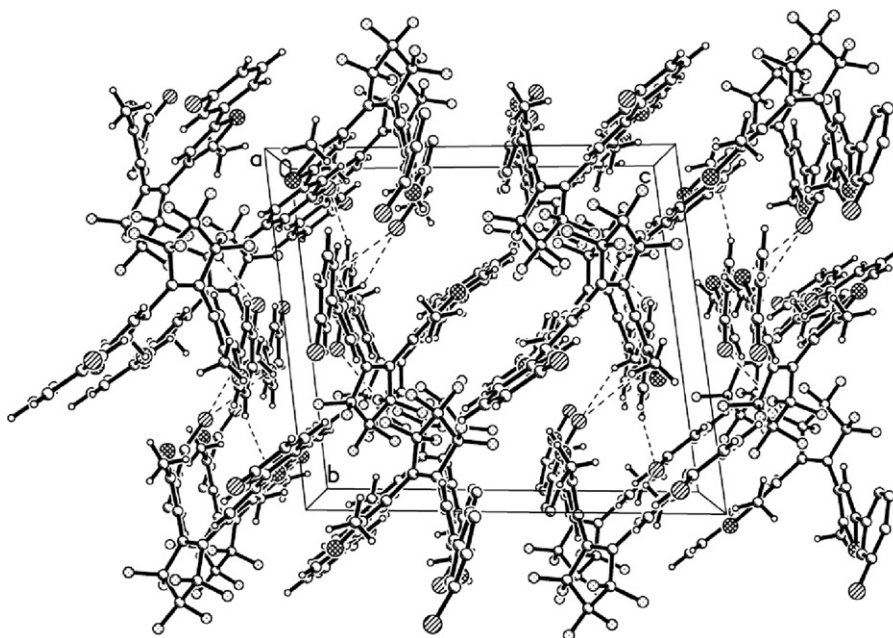


Fig. 5. A packing diagram of diarylethene **2o** along the *a* direction.

for the compound to exhibit photochromic and photo-induced properties [18].

For molecule I, the dihedral angles between the hexafluorocyclopentene ring and the two thiophene rings are $48.4(4)^\circ$ for S1/C7–C10 and $45.0(4)^\circ$ for S2/C20/C17–C19, and those between the thiophene rings and the adjacent benzene rings are $5.9(4)^\circ$ for C1–C6 and $27.4(4)^\circ$ for C22–C27. The orientations of the methyl groups at C10 and C20 are defined by the torsion angles C12–C9–C10–C11 [$1.0(10)^\circ$] and C16–C17–C20–C21 [$4.2(12)^\circ$]. The intramolecular distance between the two reactive C atoms (C10...C20) is $3.550(3) \text{ \AA}$. This distance indicates that the crystal can be expected to undergo photochromism in the crystalline phase, because photochromic reactivity usually appears when the distance between the reactive C atoms is less than 4.2 \AA [19]. Similarly, for molecule II, the dihedral angles between the central cyclopentene ring and the two thiophene rings are $46.9(6)^\circ$ for S3/C34–C37 and $45.4(6)^\circ$ for S4/C47/C44–C46, and those between the thiophene rings and the adjacent benzene rings are $25.4(6)^\circ$ for C28–C33 and $13.0(6)^\circ$ for C49–C54. The distance between the two reactive C atoms (C37...C47) is $3.604(5) \text{ \AA}$, which again is less than the value of 4.2 \AA , allowing photochromism. The orientations of the methyl groups at C37 and C47 are defined by the torsion angles C39–C36–C37–C38 [$-2.0(11)^\circ$] and C43–C44–C47–C48 [$1.1(11)^\circ$]. Further details on the crystal structure investigation have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 651837 for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Centre, 12 Union Road, Cambridge CB21EZ, UK [fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk]).

Generally, the color and the absorption band changes are mainly dependent on the π -conjugation length in molecular

structure [20]. The arrangement described above was very beneficial to form the extended π -conjugation. The π -conjugation can extend throughout the whole molecule upon irradiation with UV light, and its absorption spectrum displays drastic changes resulting in displaying remarkable different color [11,21]. Crystals of **2o** showed photochromic reaction, in accordance with the expected ring closure, to form **2c**. Their color changes upon photo-irradiation are shown in Fig. 6. Upon irradiation with 297 nm light, the colorless crystal of **2o** turned to blue quickly. When the blue crystal was dissolved separately in hexane, the solution immediately turned to blue, and a new broad absorption band was appeared at visible light region, which was the same as that of the closed-ring isomer **2c**. Alternatively, the blue colored solution reverted to the colorless one upon irradiation with appropriated wavelength visible light ($\lambda > 450 \text{ nm}$). Furthermore, the diarylethene crystal exhibited remarkable fatigue resistance (larger than 200 cyclization/cycloreversion repeat cycles) and its colors remained stable very long time in the dark (larger than 1 year). So, this crystal will be the promising candidates for optoelectronic applications, such as high density three-dimensional optical recording media, optical switches and color displays, etc. [5b,20,22].

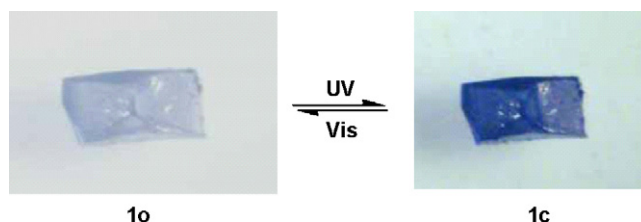


Fig. 6. Photographs of photochromic processes of diarylethene **2** in the crystalline phase.

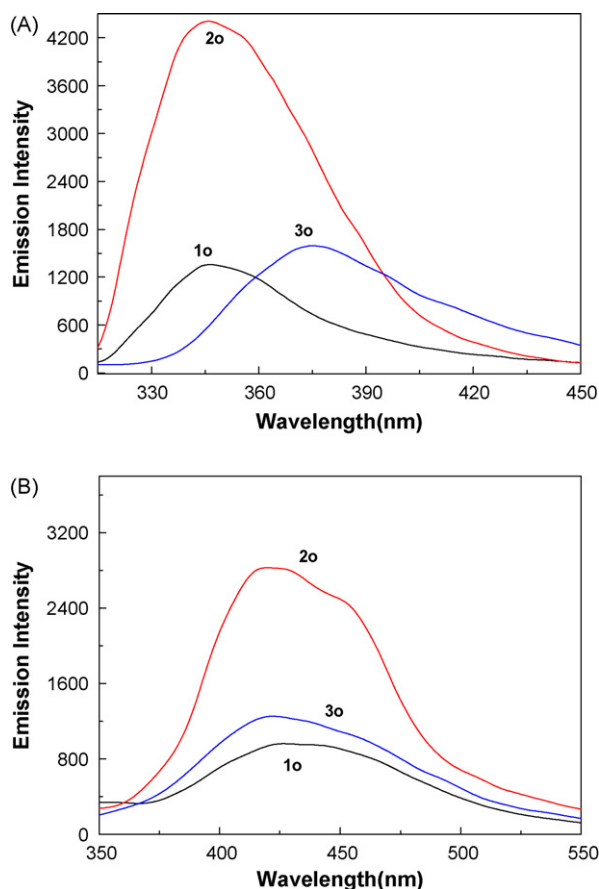


Fig. 7. Fluorescence emission spectra of diarylethenes **1**, **2** and **3** both in hexane ($c = 2.0 \times 10^{-5}$ mol/L) and in PMMA film (10%, w/w) at room temperature: (A) emission spectra in hexane, excited at 290 nm and (B) emission spectra in PMMA film, excited at 300 nm.

3.2. Fluorescence of diarylethenes

The fluorescence spectra of diarylethenes **1o**, **2o** and **3o** both in hexane (2.0×10^{-5} mol/L) and in PMMA amorphous films (10%, w/w) at room temperature are illustrated in Fig. 7. All of them showed good fluorescence both in hexane and in PMMA film. As shown in Fig. 7, we can clearly see that the hexane solutions of diarylethenes **1o**, **2o** and **3o** showed strong fluorescence at 346, 346 and 375 nm when excited at 290 nm; while those of the three compounds were observed at 422, 416 and 420 nm when excited at 300 nm in PMMA film. In hexane, the fluorescence quantum yields of diarylethenes **1**, **2** and **3** are 0.031, 0.079 and 0.028, respectively, which are inverse proportioned to their cyclization quantum yields [23]. Compared to those in hexane, the emission peaks of the three compounds showed a remarkable bathochromic shift in PMMA film, which is well consistent with those of their maxima absorption wavelengths. The red shift values of their emission peaks are 76 nm for **1**, 70 nm for **2**, and 45 nm for **3**, respectively. Among compounds **1o**, **2o**, and **3o**, the emission intensity of **2o** is the biggest and that of **1o** is almost equal to the emission intensity of **3o** both in hexane and in PMMA film. Thus, it is clear that the chlorine atom attached at different position on the terminal benzene ring

has a significant effect not only on the emission peak but also on the emission intensity.

As has been observed for most of the reported diarylethenes [24], diarylethenes **1**, **2** and **3** exhibited a relatively strong fluorescence switches along with the photochromism from open-ring isomers to closed-ring isomers in PMMA film. When irradiated by light of 313 nm, the photocyclization reaction was carried out and the non-fluorescent closed-ring isomers of these three compounds were produced. The back irradiation by appropriate wavelength visible light regenerated their open-ring isomers **1o**, **2o**, and **3o** and recovered the original emission spectra. During the process of photoisomerization, the three isomeric compounds exhibited changes in their fluorescence in hexane as shown in Fig. 8. Upon irradiation with 297 nm UV light, the emission intensities of diarylethenes **1o**, **2o** and **3o** were minor decreased by photocyclization. When arrived at the photostationary state, the emission intensities of diarylethenes **1**, **2** and **3** were quenched to ca. 95, 97 and 77%, respectively. The existence of parallel conformations and weakly fluorescent anti-parallel conformations of **1o**, **2o** and **3o** in hexane may be the main cause for the lower change in fluorescence induced by photoirradiation. Although diarylethenes **1**, **2** and **3** showed very weakly fluorescent switching in solution, they exhibited relatively strong fluorescent switching in the solid state. The emission intensity changes of diarylethenes **1**, **2**, and **3** in PMMA film during the process of photoisomerization are shown in Fig. 9. Upon irradiation with 313 nm light, their emission intensities decreased remarkably along with the photoisomerization from open-ring isomers to closed-ring isomers. Along with the photochromism from the open-ring isomers to the closed-ring isomers upon irradiation with 313 nm light, the value of $-\log(\text{int})$ and the exposal time showed good linearity during the period of starting irradiation. The rate constant k (the slope of $-\log(\text{int})$ vs. t) of fluorescence relative intensity of diarylethenes **1**, **2** and **3** in PMMA films were calculated to be 7.06×10^{-3} , 5.60×10^{-3} and 4.00×10^{-3} , respectively. When arrived at photostationary state, the emission intensities of diarylethenes **1**, **2** and **3** were quenched to ca. 28, 29, and 45%, respectively. The results are different from those of symmetrical diarylethene systems reported previously [15]. In that paper, the symmetrical diarylethenes bearing two chlorine atoms showed good fluorescence switches not only in hexane but also in PMMA film, the trends of chlorine atom position effect on the fluorescence switches are not the same as those of unsymmetrical diarylethene systems. In addition, we measured the “on” and “off” state of the switchable fluorescence by changing the power of the UV and visible light. The average “on” and “off” times shortened in proportion to the reciprocal power of the radiated light, indicating that the switching effect is indeed photochemical [26]. Therefore, these diarylethene compounds could be potentially applied to optical memory with fluorescence readout method and fluorescence modulation switches [24c,25]. The phenomena are useful for application as the fluorescence switches [26]. The fluorescence maxima of diarylethenes **1o**, **2o** and **3o** were observed at 346, 346 and 375 nm in hexane and 422, 416 and 420 nm in PMMA amorphous film, respectively. These indicated that the chlorine atom substituent position

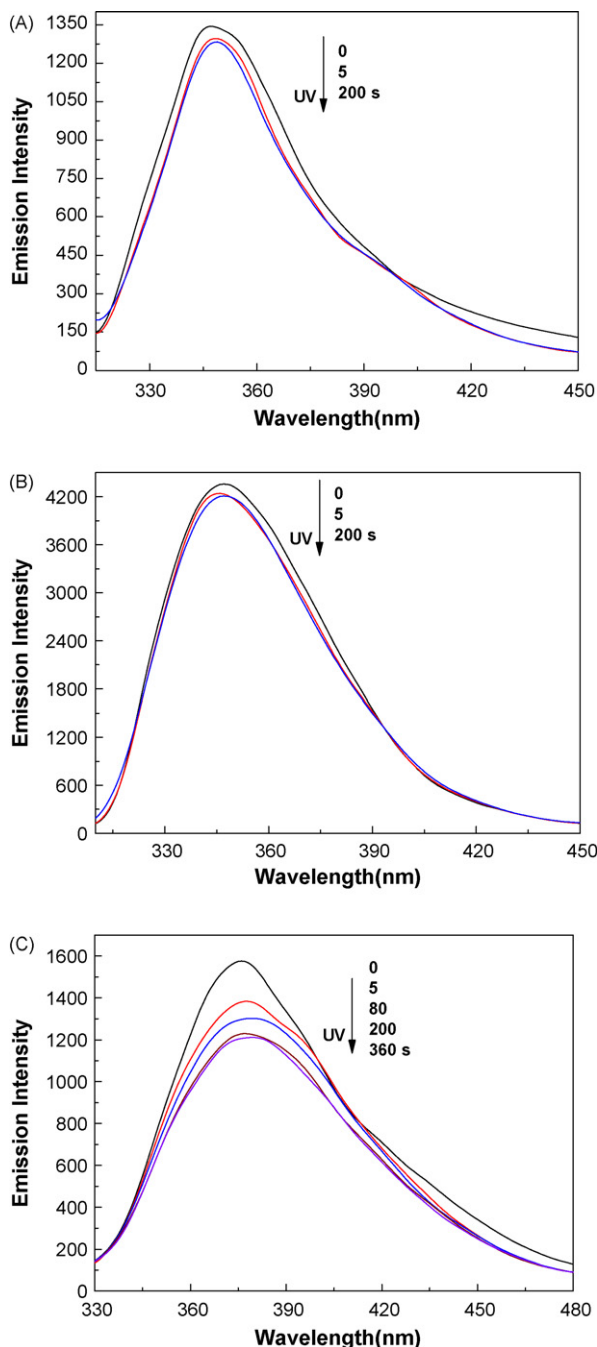


Fig. 8. Emission intensity changes of diarylethenes **1**, **2** and **3** in hexane ($c = 2.0 \times 10^{-5}$ mol/L) upon irradiation with 297 nm UV light at room temperature, excited at 290 nm: (A) **1**, (B) **2** and (C) **3**.

effect on the fluorescence peak is significant. The chlorine atom in different position show different fluorescence properties are useful for selectively application as the fluorescence switches.

3.3. Electrochemistry of diarylethenes

Diarylethene compounds underwent reversible photochromic reactions between colorless and colored isomers when stimulated by alternate irradiation with UV and visible

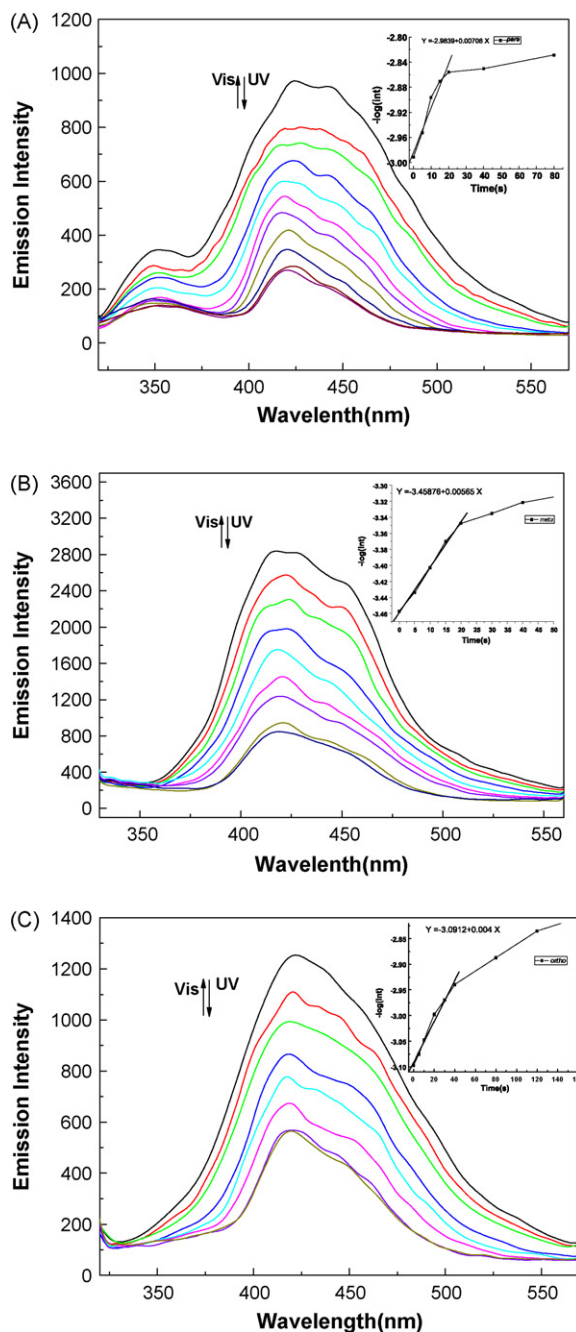


Fig. 9. Emission intensity changes of diarylethenes **1**, **2** and **3** in PMMA film (10%, w/w) upon irradiation with 313 nm light at room temperature, excited at 300 nm: (A) **1**, (B) **2** and (C) **3**. Inset figure shows the relationships between $-\log(\text{int})$ and the exposal time upon irradiation with 313 nm UV light.

light. Because of the remarkable differences in the nature of π -conjugation between the two isomers, these photoresponsive systems offer changes not only in optical properties but also in electrochemical properties, both of which are useful in optoelectronic device applications [25c,26]. The electrochemical properties of diarylethenes can be used for molecular switching and also can be potentially applied to molecular-scale electronic switches. The oxidative cyclization and cycloreversion of some diarylethene derivatives have been

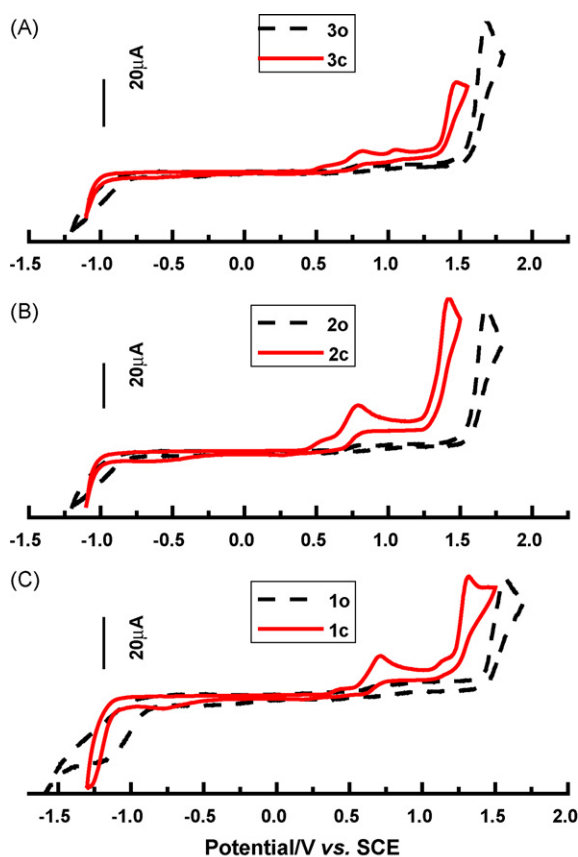


Fig. 10. Cyclic voltammetry (second scan) of diarylethenes **1**, **2** and **3** in acetonitrile at a scan rate of 50 mV/s: (A) **1**, (B) **2** and (C) **3**.

reported [27]. In this work, we performed electrochemical examinations by cyclic voltammograms (CV) method under the same experimental conditions using diarylethenes **1**, **2** and **3**, respectively. The typical electrolyte was acetonitrile (5 mL) containing 0.1 mol/L tetrabutylammonium tetrafluoroborate ((TBA)BF₄) and 4.0×10^{-3} mol/L diarylethene sample. All solutions were deaerated by a dry argon stream and maintained at a slight argon overpressure during electrochemical experiments.

Fig. 10 shows the CV curves of diarylethenes **1**, **2** and **3** with the scanning rate of 50 mV/s. From this figure, it can be clearly seen that the oxidation of **1o**, **1c**, **2o**, **2c**, **3o** and **3c** was initiated at 0.586, 0.350, 0.689, 0.425, 0.673 and 0.466 V, respectively. The result indicated that the oxidation onsets of the open-ring isomers were higher than those of the closed-ring isomers. This is in accordance with the theory that longer conjugation length generally leads to less positive potentials, with the addition of each heterocyclic ring [8b]. After cyclization reaction, the π -conjugation lengths of **1c**, **2c**, and **3c** were much longer than those of **1o**, **2o**, and **3o**, respectively. Moreover, there are great differences of the electronic current and polarization curve shapes between the open-ring and closed-ring isomers of diarylethenes **1**, **2** and **3**. The closed-ring isomers of diarylethenes **1**, **2** and **3** show the distinct oxidation waves at 0.70, 0.78 and 0.81 V, but all of their open-ring isomers show no oxidation waves at those

voltages. This is in agreement well with that of symmetrical diarylethenes bearing two fluorine atoms on the two terminal benzene rings reported previously [15]. The oxidation peaks of closed-ring isomers are increased when the chlorine atom attached to the terminal benzene ring from *para*- to *ortho*-position. This may be ascribed to the special nature of chlorine atom, such as resonance, inductive and steric effect. For different position substitution of chlorine atoms of diarylethenes **1**, **2** and **3**, different electron-inducing ability and steric effect induced to their distinguishable electrochemical properties described above. The detailed factors need further investigation.

4. Conclusions

Three new unsymmetrical diarylethenes bearing one chlorine atoms at the *para*-, *meta*-, or *ortho*-position of unilateral terminal benzene groups have been synthesized, and their photochromic and fluorescent properties both in solution and in PMMA film have been investigated. The results showed that the chlorine substituent position effect on photochromic and fluorescent properties of these diarylethenes is very remarkable. In addition, the cyclic voltammograms results showed that the closed-ring isomers of diarylethenes **1**, **2** and **3** show the distinct oxidation waves. The oxidation peaks of the closed-ring isomers are increased when the chlorine atom attached to the terminal benzene ring from *para*-, *meta*- to *ortho*-position. It is hoped that this work may be useful for the design and synthesis of efficient photoactive diarylethene derivatives with tunable properties.

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