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Substituent position effect on the properties of isomeric photochromic diarylethenes bearing chlorine atoms

Congbin Fan, Shouzhi Pu *, Gang Liu, Tianshe Yang

Jiangxi Key Laboratory of Organic Chemistry, Jiangxi Science & Technology Normal University, Nanchang 330013, PR China

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Abstract

Three new isomeric photochromic diarylethenes, namely 1,2-bis[2-methyl-5-(4-chlorophenyl)-3-thienyl]perfluorocyclopentene (**1o**), 1,2-bis[2-methyl-5-(3-chlorophenyl)-3-thienyl]perfluorocyclopentene (**2o**), and 1,2-bis[2-methyl-5-(2-chlorophenyl)-3-thienyl]perfluorocyclopentene (**3o**) which bear two chlorine atoms at the *para*-, *meta*-, and *ortho*-position of both terminal phenyl groups, have been synthesized. The substituent position effect of chlorine atoms on their optoelectronic properties, including photochromic behavior and fluorescence, both in solution and in PMMA amorphous film, and electrochemical properties were investigated in detail. The results elucidated that the chlorine atoms and their substituent positions had a significant effect on the optoelectronic properties of these compounds. These diarylethene derivatives bearing two chlorine atoms have shown good photochromic behavior and fluorescent switching both in solution and in PMMA film. For diarylethenes **1**–**3**, the cycloreversion quantum yields were gradually increased when the chlorine atom was attached to the *para*-, *meta*- and *ortho*-positions of the two terminal benzene rings; but, their absorption maxima, cyclization quantum yields and the molar absorption coefficients both of their open-ring and closed-ring isomers were remarkably decreased one by one. Furthermore, the clear oxidation waves of diarylethenes **1c**, **2c** and **3c** were observed at 1.01, 0.92 and 0.98 V by performing the cyclic voltammograms experiments.

Keywords: Photochromism; Diarylethene; Chlorine atom position effect; Optoelectronic property

1. Introduction

Photochromic compounds have attracted much attention because of their potential application to photonic devices, such as optical memories and switches [1]. Up to date, photochromic compounds, such as spirobenzopyrans [2], azobenzene [3], fulgides [4], and diarylethenes, have been extensively investigated for their potential applications in erasable optical recording, color displays, and photoswitches. Among such compounds, diarylethenes with heterocyclic aryl groups are the most promising candidates for those applications described above, mainly due to the excellent thermal stability of the respective isomers, notable fatigue resistance, and high reactivity in the solid state [5]. Diarylethene compounds can undergo a reversible cyclization/cycloreversion photoreaction upon alternating irradiation with UV and visible light. The two isomers of diarylethenes differ from each other not only in their absorption spectra, but in many physical and chemical properties, such as geometry structure [5a], refractive index [6], as well as oxidation/reduction potential, etc. [7]. By far, many dithienylethenes derivatives and their fundamental properties were reported [8]. The majority of the research work reported to date has been 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 [9]. Furthermore, diarylethenes bearing phenyl groups on the end are of special interest, because the end group can be substituted by electron-donating group or electron-withdrawing group. These groups inevitably influence the properties of corresponding diarylethenes.

Recently, several publications concerning substituent effect on the photochromic performance of diarylethene have been reported. Pu et al. [10] and Irie et al. [11] reported the effect of the substituents at *para*-positions of the terminal phenyl groups on the photochromic property and the photochemical reactivity. They revealed that electron-donating substituents attached bis(3-

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* Corresponding author. Tel.: +86 791 3805183; fax: +86 791 3805212.
E-mail address: pushouzhi@tsinghua.org.cn (S. Pu).

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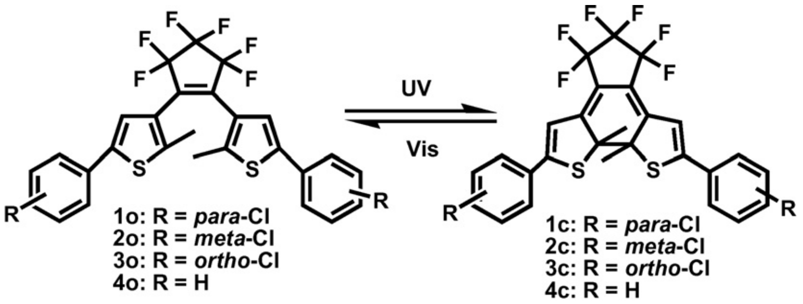


Scheme 1. Mechanistic rationale of the photochromic property of diarylethenes **1**–**4**.

thienyl)ethane diarylethenes could be effective to increase the absorption coefficient of the closed-ring forms and to decrease the cycloreversion quantum yield; while electron-donating substituents attached bis(2-thienyl)ethane diarylethenes could be an effective way to increase the maxima absorption of the open-ring forms and to reduced the cyclization quantum yield. Morimitsu et al. [12] and Takami and Irie [13] revealed that bulky alkoxy substituents could decrease the thermal stability of the colored closed-ring isomers at high temperature. Tanifuji et al. [14] reported the effect of the radical substituents on the photochromic reactivity of bis(3-benzothiophene)perfluorocyclopentene. Yamamoto et al. [15] had ever investigated photochromism of diarylethenes bearing carboxyl groups at the *ortho*-, *meta*- and *para*-positions of both terminal phenyl groups. But, they especially emphasized the effect of the intermolecular hydrogen bonding on the photochromic performance of these diarylethenes in the single-crystalline phase. However, investigation concerning of the substituent position effect of the same functional group on the optoelectronic properties of diarylethenes is very rare.

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 phenyl rings. We found that the position of 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 [16]. 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 positions of the terminal phenyl ring could strongly influence the optical and electrochemical properties [17]. These results are very interesting and important, and they also enlighten us do a series of the consecutive research works in the near future. In this paper, we have synthesized three new isomeric diarylethene derivatives, namely 1,2-bis[2-methyl-5-(4-chlorophenyl)-3-thienyl]perfluorocyclopentene (*para* **1o**), 1,2-bis[2-methyl-5-(3-chlorophenyl)-3-thienyl]perfluorocyclopentene (*meta* **2o**), and 1,2-bis[2-methyl-5-(2-chlorophenyl)-3-thienyl]perfluorocyclopentene (*ortho* **3o**). In order to compare their properties with that of diarylethene compound with no chlorine atom, we have also synthesized 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene (**4o**). Although photochromic behavior of compound **4** was reported by Irie et al. [5d], its fluorescence and electrochemical properties had not been reported. The photochromic scheme of the four diarylethene derivatives is shown in Scheme 1.

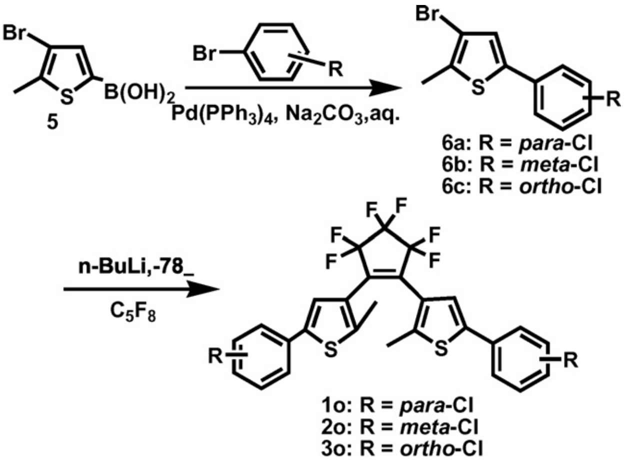
2. Results and discussion

2.1. Synthesis of diarylethene derivatives

The synthesis route for diarylethenes **1o**, **2o** and **3o** is shown in Scheme 2. Suzuki coupling of four bromobenzene derivatives with thiophene boronic acid (**5**) [18] gave chlorophenylthiophene derivatives (**6a**–**6c**). They were lithiated and then coupled with octafluorocyclopentene to give chlorine-substituted diarylethene derivatives (**1o**–**3o**). Compound **4o** was synthesized according to the same procedures reported by Irie et al. [5d]. The structures of **1o**, **2o**, **3o**, and **4o** were confirmed by NMR, IR, mass spectrometry, and elemental analysis (see Section 4).

2.2. Photochromism of diarylethenes

The photochromic behaviors of diarylethenes **1**–**4** induced by photoirradiation at room temperature were examined both in hexane and in PMMA amorphous film. The changes in the absorption spectra of diarylethenes **1**–**4** induced by alternating irradiation with UV and visible light in hexane are shown in Fig. 1. As shown in Fig. 1(A), the colorless solution containing the open-ring isomer **1o**, which shows the maximum absorp-



Scheme 2. Synthetic route for diarylethenes **1o**–**3o**.

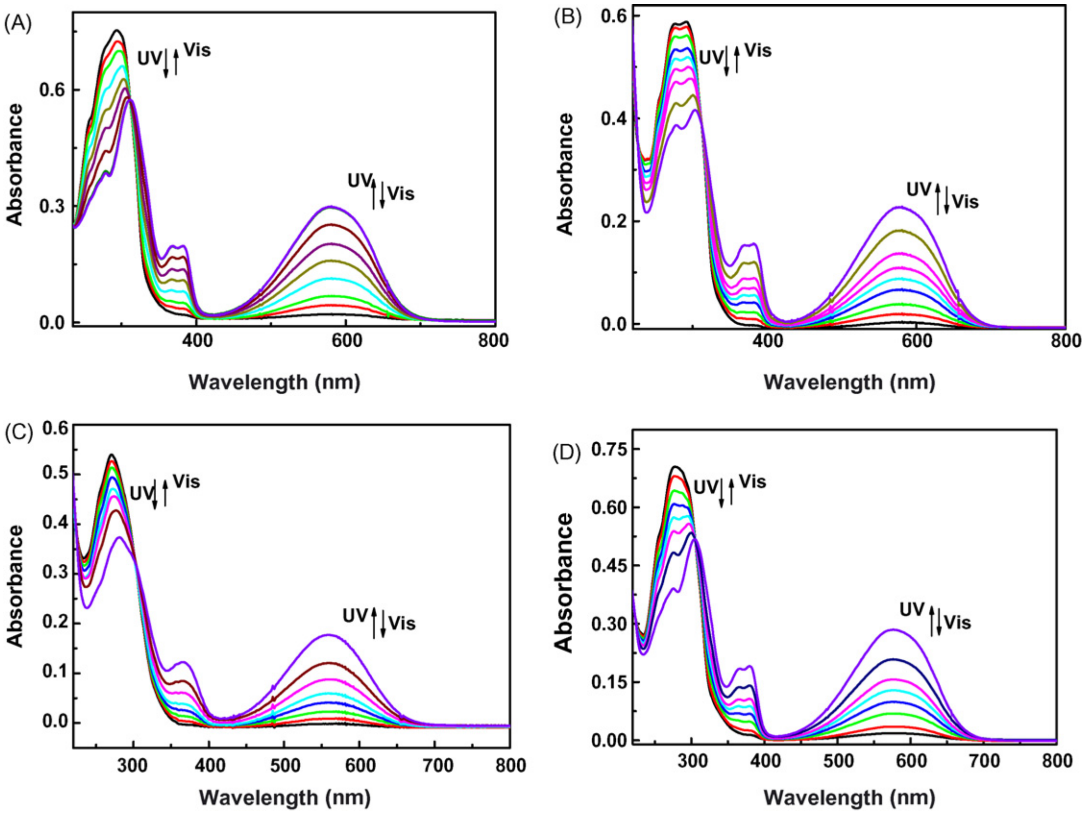


Fig. 1. Absorption spectral changes of diarylethenes **1**–**4** in hexane solution ($C = 2.0 \times 10^{-5}$ mol/L) at room temperature: (A) **1**, (B) **2**, (C) **3**, and (D) **4**.

tion at 294 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 absorption maximum was observed at 581 nm. Upon irradiation with visible light of wavelength longer than 450 nm, the colored solution returned to their original colorless form. Just as diarylethene **1**, compounds **2**–**4** also show photochromism in hexane solution (Fig. 1(B)–(D)). Upon irradiation with 297 nm light, absorption bands in the visible region appeared and the solutions of **2o** and **4o** turned blue as a result of the cyclization reactions to produce **2c** and **4c**; but the solution of **3o** turned to magenta (Fig. 2). All the solutions of **2c**, **3c** and **4c** can be decolorized upon irradiation with visible light ($\lambda > 450$ nm) attributable to reproducing the open-ring isomers **2o**, **3o** and **4o**. As shown in Fig. 2, the color changes of compound **3** differ from those of **1** and **2** during photochromic process, which may be attributed to the steric hindrance of *ortho*-chlorine group. The extent of the conjugation in the closed-ring isomers **3c** is much weaker than those of **1c** and **2c** because the thiophene–phenyl bond rotation is strained by the *ortho*-steric hindrance in **3c**, resulting in the blue-shifted absorption maximum of **3c** in comparison with those of **1c** and **2c**.

The photochromic properties of diarylethenes **1**–**4** in hexane are summarized in Table 1. From these data, it can easily be seen that the chlorine atom position effect on the photochromic features (including absorption maxima, molar absorption coefficients, and quantum yields) of diarylethenes **1**–**4** are distinctly different. The photochromic behaviors of diarylethenes **1**–**3** displayed a well regular change in hexane. In hexane, the cyclization quantum yield, absorption maxima and molar absorption coefficients, both for the open-ring and for the closed-ring isomers of the *para*-substituted derivative (compound **1**) are the biggest; while those of the *ortho*-substituted derivative (compound **3**) are the smallest. These parameters of the *meta*-substituted derivative (compound **2**) are in between those of the

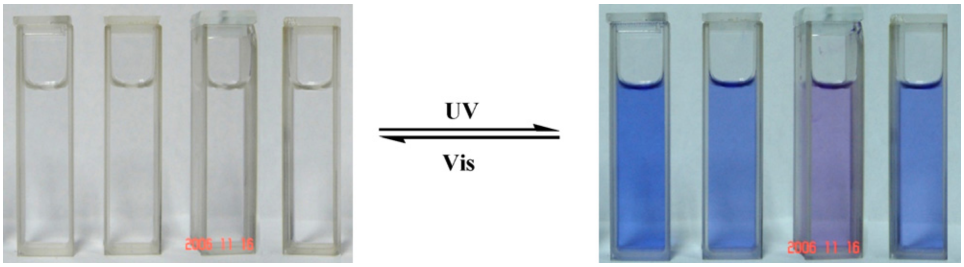


Fig. 2. Color changes of diarylethenes **1**–**4** (from left to right) upon alternating irradiation with UV–vis light in hexane solution.

Table 1
Absorption characteristics and photochromic reactivity of diarylethenes **1**–**4** in hexane at 2.0×10^{-5} mol/L and in PMMA film

Compounds	$\lambda_{max,o}$ [a], nm (ε, dm^3 mol^{-1} cm^{-1})		$\lambda_{max,c}$ [b], nm (ε, dm^3 mol^{-1} cm^{-1})		Φ[c]	
	Hexane	PMMA film	Hexane	PMMA film	$\Phi_{o\text{-}c}$	$\Phi_{c\text{-}o}$
1	294 (3.8×10^4)	322	581 (1.5×10^4)	598	0.77	0.012
2	292 (2.9×10^4)	317	581 (1.2×10^4)	591	0.71	0.019
3	271 (2.7×10^4)	315	560 (0.9×10^4)	573	0.45	0.052
4[d]	277 (3.5×10^4)	319	577 (1.4×10^4)	591	0.59	0.013

[a] Absorption maxima of open-ring isomers.

[b] Absorption maxima of closed-ring isomers.

[c] Quantum yields of open-ring ($\Phi_{o\text{-}c}$) and closed-ring isomers ($\Phi_{c\text{-}o}$), respectively.

[d] See Ref. [5d].

para- and *ortho*-substituted derivatives. Compared to those of **3o** and **3c**, the absorption maxima of **1o** and **1c** are red-shifted by 23 and 21 nm, respectively, and the molar absorption coefficients and cyclization quantum yield of **1** are twofold larger. The results showed a significant decrease with the chlorine atoms attached to the benzene rings from *para*- to *ortho*-position. However, the cycloreversion quantum yields of diarylethenes **1**–**3** showed a contrary changing trend against those of the above parameters. It increased along with the chlorine atoms attached to the benzene rings from *para*- to *ortho*-position. Among **1**–**3**, the cycloreversion quantum yield of **1** is the smallest ($\Phi_{c\text{-}o} = 0.012$) and that of **3** is the biggest ($\Phi_{c\text{-}o} = 0.052$). Compared to compounds **1**–**3**, the photochromic behavior of non-chlorine atom derivative (compound **4**) is evidently different. 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 coefficients [5d]. Therefore, it could be drawn a conclusion that the absorption maximum and the cyclization quantum yield increased effectively when the chlorine atoms were introduced into the *para*- or *meta*-positions of the two terminal benzene rings in diarylethene system; however, all photochromic parameters except the cycloreversion quantum yield decreased distinctly when the chlorine atoms were introduced into the *ortho*-positions of the two terminal benzene rings. The result is remarkably distinguished from those reported in our previous papers [16,17]. The electron-withdrawing fluorine substituent position does not affect significantly on the photochromic behaviors of symmetrical diarylethene derivatives [16]; while the electron-donating methoxyl substituent position can effectively enhance the cycloreversion quantum yield of unsymmetrical diarylethenes bearing a pyrazole unit [17].

In the PMMA amorphous film, diarylethenes **1**–**4** also showed good photochromism as similar as those in solution. Their photochromic properties of diarylethenes **1**–**4** in PMMA film are also summarized in Table 1. Upon irradiation 313 nm light, the colors of the four diarylethene/PMMA films changed from colorless to blue with the appearance of a new broad absorption band at 598, 591, 573, and 591 nm, respectively, which was assigned to the formation of the closed-ring isomers **1c**, **2c**, **3c**, and **4c**. All colored diarylethene/PMMA films can revert to colorless, upon irradiation with visible light ($\lambda > 450$ nm). From Table 1, we can easily see that the maximum absorption peaks of both the open-ring and the closed-ring isomers in PMMA film are longer than those in hexane solution. The red shift values of the absorption maxima of open-ring isomers are 28 nm for **1o**, 25 nm for **2o**, 43 nm for **3o**, and 41 nm for **4o**, and those of closed-ring isomers are 17 nm for **1c**, 10 nm for **2c**, 13 nm for **3c**, and 14 nm for **4c**, respectively. The red shift phenomena may be ascribed to the stabilization of molecular arrangement in solid state [19].

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. 3 and its packing diagram is shown in Fig. 4. As shown in Fig. 3, there are two independent molecules (molecules I and II) in the asymmetric unit. Both of them occupied approximately in C_2 symmetry and packed in a photoactive *anti*-parallel conformation in the crystalline phase, which can undergo photocyclization reaction [20]. In the hexafluorocyclopentene rings of the two molecules, the F atoms of the CF_2 groups are disordered and two distinct conformations were modeled. The site occupancies are 0.50:0.50 for the F atoms attached to C13–C15 for molecule I and C4–C42 for molecule II. In the hexafluorocyclopentene rings of the two molecules, the C12–C16 [1.346(7) Å] and C39–C43 [1.351(7) Å] bonds are clearly double bonds, while the other bonds in the ring are single bonds. The thiophene rings are linked by the C12═C16 and C39═C43 double bonds; the methyl groups are located on opposite sides of the double bond, and thus they are *trans* with respect to the double bond. Such a conformation is crucial for the compound to exhibit photochromic and photo-induced properties [21].

For molecule I, the dihedral angles between the hexafluorocyclopentene ring and the two thiophene rings are 43.7(6)° for S1/C7–C10 and 50.2(6)° for S2/C18/C17/C20–C21, and those between the thiophene rings and the adjacent benzene rings are 17.3(6)° for C1–C6 and 22.5(6)° for C22–C27. The orientations of the methyl groups at C10 and C18 are defined by the torsion angles C12–C9–C10–C11 [0.9(9)°] and C16–C17–C18–C19 [−1.3(9)°]. The intramolecular distance between the two reactive C atoms (C10 and C18) is 3.657(5) Å. 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 Å [5g,22]. Similarly, for molecule II, the dihedral angles between the central cyclopentene ring and

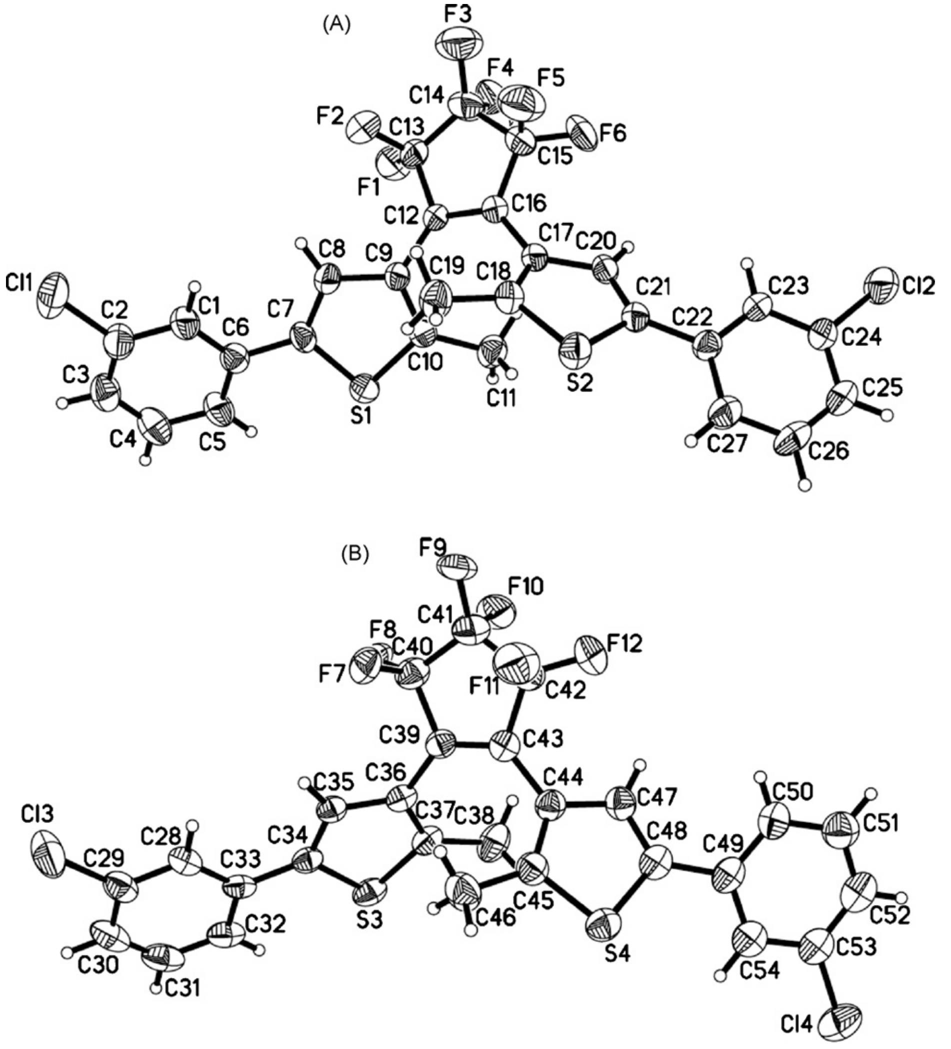


Fig. 3. ORTEP drawings of diarylethene **2o**, showing 35% probability displacement ellipsoids: (A) molecule I and (B) **2o** molecule II.

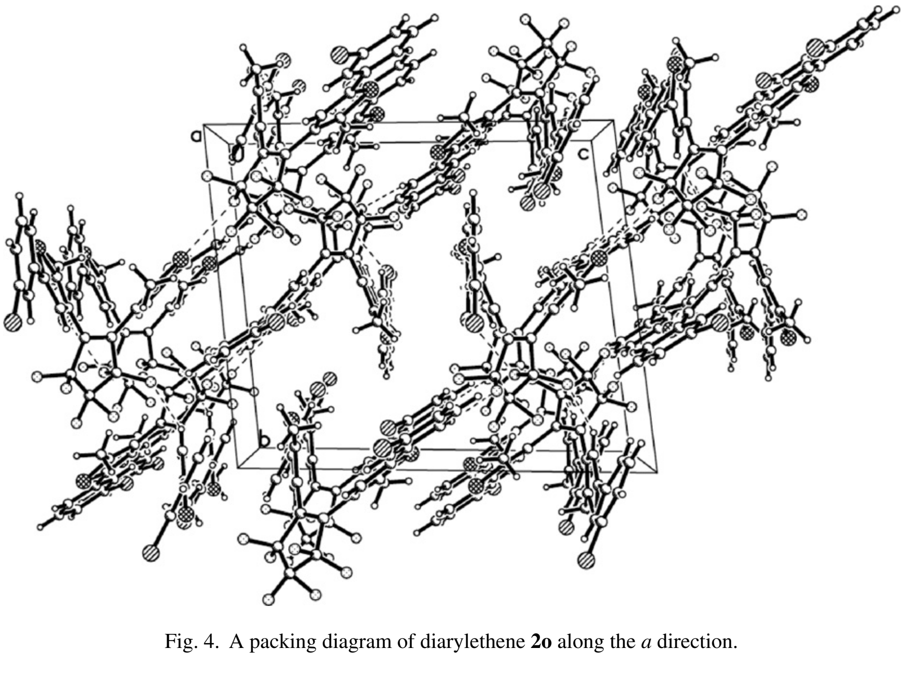


Fig. 4. A packing diagram of diarylethene **2o** along the *a* direction.

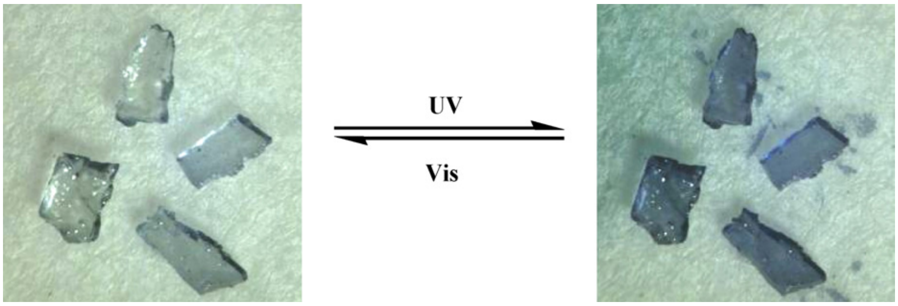


Fig. 5. Photographs of photochromic processes of diarylethene **2** in the crystalline phase.

thiophene rings are 48.4(4)° for S3/C34–C37 and 44.2(4)° for S4/C45/C44/C47–C48. The distance between the two reactive C atoms (C37. . .C45) is 3.549(7) Å, which again is less than the value of 4.2 Å, allowing photochromism. The orientations of the methyl groups at C37 and C45 are defined by the torsion angles C39–C36–C37–C38 [−2.8(9)°] and C43–C44–C45–C46 [−4.4(9)°].

Generally, the color and the absorption band changes are mainly dependent on the π-conjugation length in molecular structure [22a]. 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 [18b,23]. Crystal of **2o** showed photochromic reaction, in accordance with the expected ring closure, to produce **2c**. Their color changes upon photoirradiation are shown in Fig. 5. Upon irradiation with 297 nm light, the colorless crystal of **2o** turned to blue quickly. When the blue crystal was dissolved in hexane, the solution immediately turned blue, and a new broad absorption band was appeared at visible light region. Alternatively, the blue colored solution reverted to the colorless one upon irradiation with appropriated wavelength visible light ($\lambda > 450$ nm). Furthermore, this diarylethene crystal exhibited remarkable fatigue resistance and its color remained stable very long time (> 1 year) in the dark. 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. [24].

2.3. Fluorescence of diarylethenes

Fluorescent properties can be useful not only in molecular-scale optoelectronics, but for digital photoswitching of fluorescence [25]. The fluorescence modulation is a particularly intriguing approach due to the stabilization of diarylethene and versatility in materials selection [26]. Until now, many diarylethene derivatives and their fluorescent properties have been reported [23a,27]. In this work, the fluorescence properties of the four diarylethenes both in solution and in PMMA film were measured using a Hitachi F-4500 spectrophotometer. The fluorescence emission spectra of **1o**, **2o**, **3o** and **4o** (5.0×10^{-5} mol/L) at room temperature are illustrated in Fig. 6. The result showed that all of them exhibited good fluorescence both in hexane solution and in PMMA film. In hexane, emission peaks of diarylethenes **1o**, **2o**, **3o**, and **4o** were observed at 416, 418, 404, and 414 nm when excited at 290 nm; while those of the four compounds were observed at 433, 435, 423, and 461 nm when exited at 300 nm in PMMA film. Compared to those in hexane, the emission peaks of the four 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 17 nm for **1**, 17 nm for **2**, 19 nm for **3**, and 47 nm for **4**, respectively. Among **1**–**3**, the emission intensity of **3o** is the biggest and that

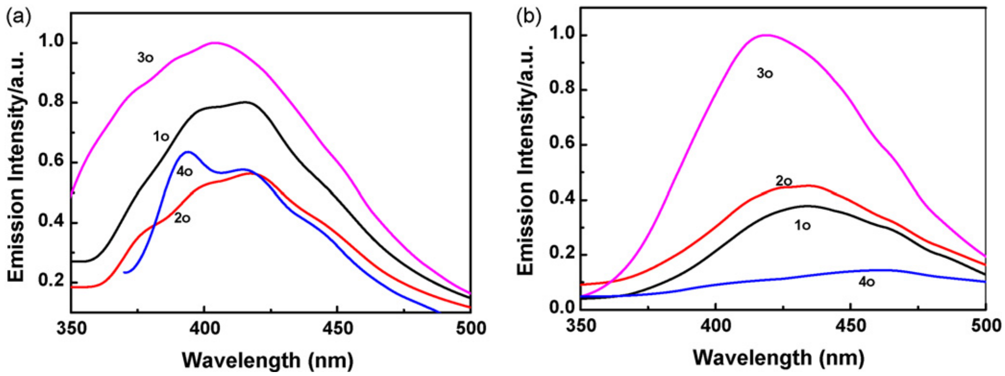


Fig. 6. Fluorescence emission spectra of diarylethenes **1**–**4** both in hexane solution (5.0×10^{-5} mol/L) and in PMMA film (10%, w/w) at room temperature: (A) emission spectra in hexane, excited at 290 nm; (B) emission spectra in PMMA film, excited at 300 nm.

of **2o** is the smallest in hexane; however, the emission intensity of **3o** is the biggest and that of **1o** is the smallest in PMMA film. Compared to compounds **1**, **2** and **3**, diarylethene **4** exhibited dual fluorescence peaks (394 and 414 nm) in hexane and very weak fluorescence in PMMA film. Thus, it is clear that the position of the substituent on the phenyl group has a significant effect not only on the emission intensity, but also on the position of the emission peak. Among the four diarylethene derivatives, the emission peak of diarylethene **3** is the shortest and its relative emission intensity is the strongest both in solution and in PMMA film. This phenomenon also may be ascribed to the steric hindrance of *ortho*-chlorine group and the special nature of chlorine atom, such as resonance and polar effect. On the one hand, the thiophene–phenyl bond rotation is strained by *ortho*-steric hindrance. On the other hand, the chlorine atom is working as an electro-donating character in the resonance effect, but it is working as an electro-withdrawing character in the polar effect.

As has been observed for most of the reported diarylethenes [28], diarylethenes **1**–**4** exhibited a relatively strong fluorescence switches along with the photochromism from open-ring isomers to closed-ring isomers. When irradiated by UV light, the photocyclization reaction was occurred and the emission intensity of diarylethenes **1**–**4** decreased significantly, due to producing the non-fluorescence closed-ring isomers. The back irradiation by appropriate wavelength visible light regenerated their open-ring isomers and recovered the original emission intensity. During the process of photoisomerization, the four compounds exhibited changes in their fluorescence in hexane (5.0×10^{-5} mol/L) as shown in Fig. 7. Upon irradiation with 297 nm light, the emission intensities of diarylethenes **1o**, **2o**, **3o**, and **4o** were decreased by photocyclization. The emission intensities of **1**–**4** in a photostationary state were quenched to *ca.* 42, 61, 65, and 66%, respectively. Similarly, the emission intensity changes of diarylethenes **1**–**4** in PMMA film (10%, w/w) during the process of photoisomerization are shown in Fig. 8. Upon irradiation with 300 nm light at room temperature, their emission intensities decreased remarkably along with the photoisomerization from open-ring isomers to closed-ring isomers when excited at 300 nm. When arrived at photostationary state, the emission intensities of diarylethenes **1**–**4** were quenched to *ca.* 44, 28, 24, and 73%, respectively. Therefore, the fluorescence switching of diarylethenes **2** and **3** showed more significant than that of diarylethenes **1** and **4** in PMMA film. The incomplete cyclization reaction and the existence of parallel conformations of diarylethenes **1o**, **2o**, **3o**, and **4o** may be the main cause for the moderate change in fluorescence induced by photoirradiation. 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 [29]. Therefore, these diarylethene compounds could be potentially applied to optical memory with fluores-

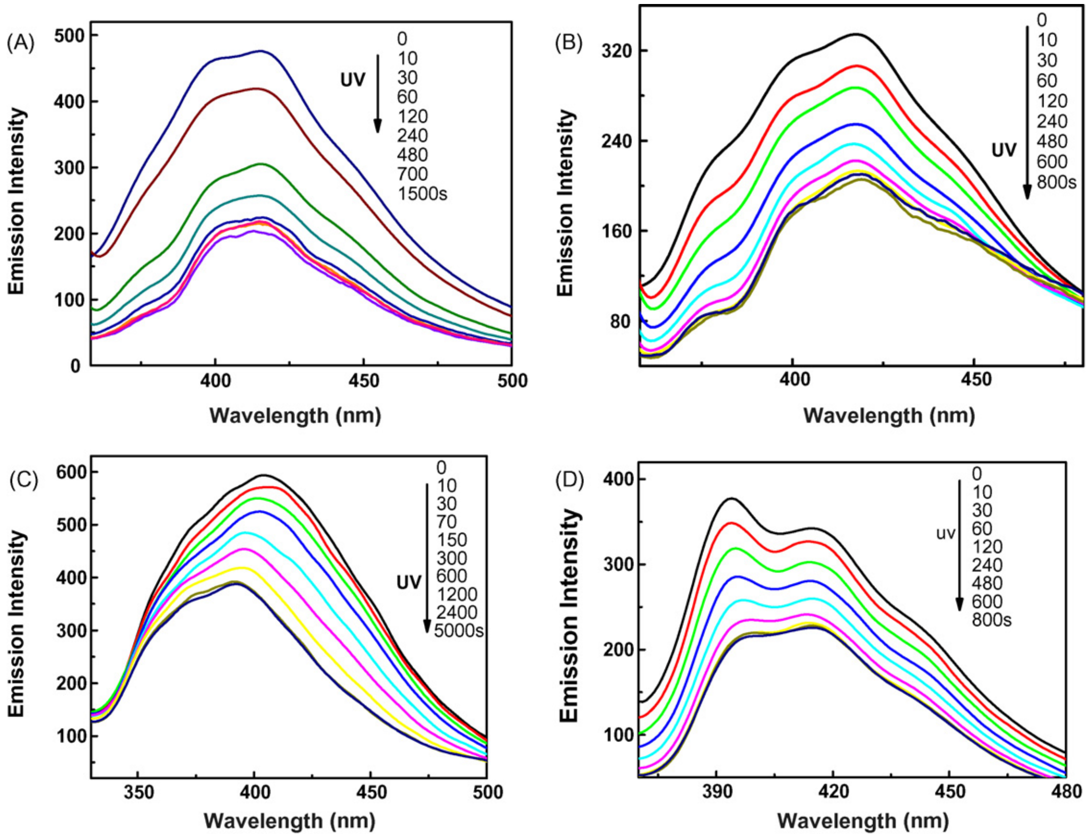


Fig. 7. Emission intensity changes of diarylethenes **1**–**4** in hexane (5.0×10^{-5} mol/L) upon irradiation with 297 nm UV light at room temperature, excited at 290 nm: (A) **1**, (B) **2**, (C) **3** and (D) **4**.

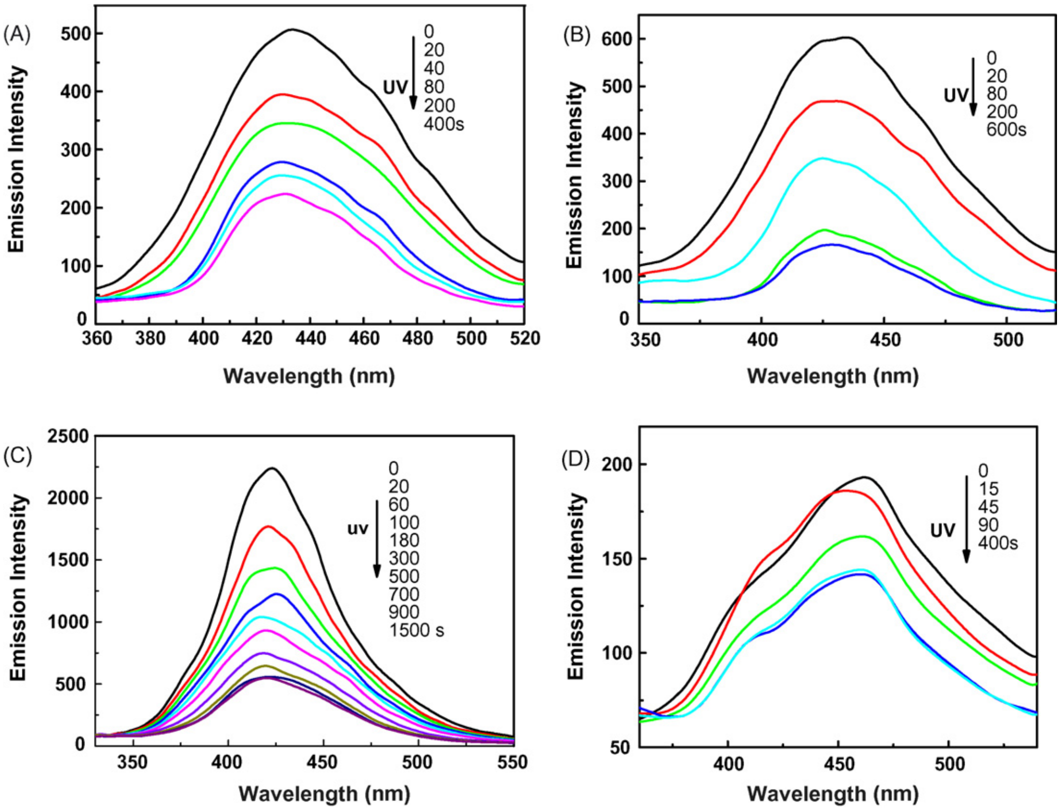


Fig. 8. Emission intensity changes of diarylethenes **1**–**4** in PMMA film (10%, w/w) upon irradiation with 313 nm UV light at room temperature, excited at 300 nm: (A) **1**, (B) **2**, (C) **3** and (D) **4**.

cence readout method and fluorescence modulation switches [30].

2.4. Electrochemistry of diarylethenes

It was well known that diarylethene compounds underwent reversible photochromic reactions between colorless and colored isomers when stimulated by alternate irradiation with UV and visible light. Because of the remarkable differences in the nature of π-conjugation between the two isomers, these photoresponsive systems offer several choices of changes not only in optical properties but also in electrochemical properties, both of which are useful in optoelectronic device applications [31]. Besides their excellent photochromic performance, the electrochemical behaviors of diarylethenes were also attracted much attention [7b,32]. 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 had been reported [33]. In this work, we performed electrochemical examinations by cyclic voltammograms (CV) method under the same experimental conditions using diarylethenes **1o**, **2o**, **3o**, and **4o**, respectively. The typical electrolyte was acetonitrile (5 mL) containing 0.1 mol/L tetrabutylammonium tetrafuoroborate ((TBA)BF_4) 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.

When the CV measurement was carried out, besides photochromism, electrochromism was also observed with the closed-ring isomers of these diarylethenes during electrolysis. During the cyclic voltammetry experiments, we found that the colorless solutions containing diarylethene derivatives around the platinum electrode changed to colored solutions (compound **3** changed to magenta; other compounds changed to blue). This indicates that the open-ring isomers of these diarylethenes underwent oxidative cyclization to produce their closed-ring isomers, respectively, although no marked changes in the absorption spectra were detected because of the too small amount of the closed-ring isomers in solution. The colored solutions of the closed-ring isomers of these diarylethene compounds in photostationary state, which were obtained from the conversion of open-ring isomers upon irradiation with UV light, however, not decolorized back to a colorless solutions during the electrolysis, indicating that the closed-ring isomers cannot undergo oxidative cycloreversion. The results suggested that the cation radicals of the closed-ring isomers of these diarylethenes are more stable than those of the open-ring isomers and the oxidative cyclization is thermodynamically allowed [33a,d].

Fig. 9 shows the CV curves of diarylethenes **1**–**4** 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**, **3c**, **4o** and **4c** was initiated at 0.70, 0.61, 0.78, 0.73, 0.62, 0.57, 0.52 and 0.46 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 conju-

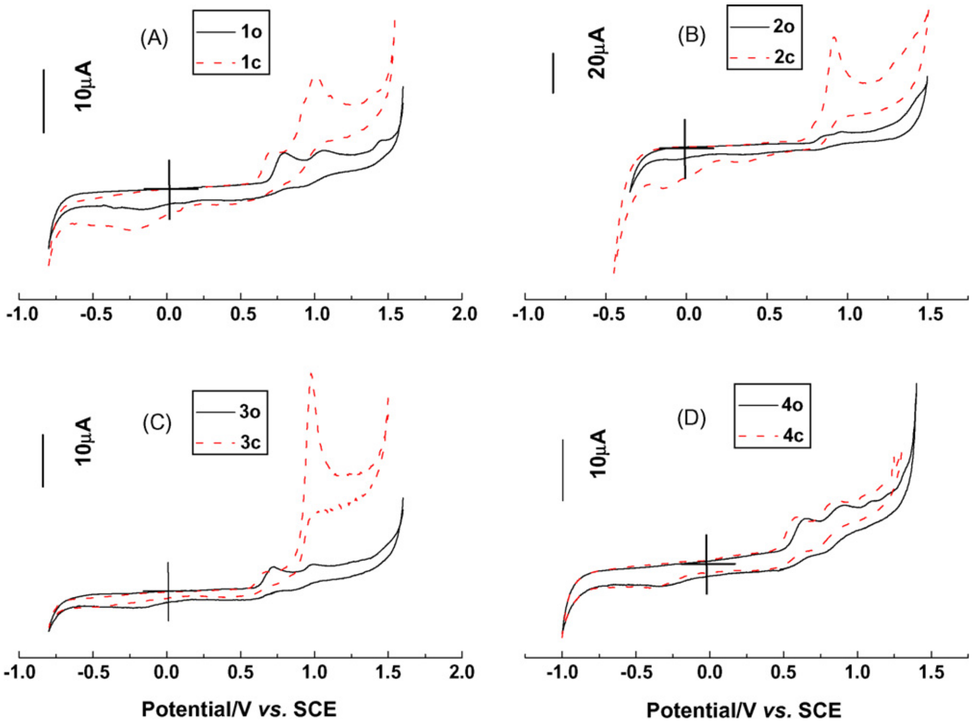


Fig. 9. Cyclic voltammetry (second scan) of diarylethenes **1**–**4** in acetonitrile at a scan rate of 50 mV/s: (A) **1**, (B) **2**, (C) **3** and (D) **4**.

gation length generally leads to less positive potentials, with the addition of each heterocyclic ring [10]. After cyclization reaction, the π-conjugation lengths of **1c**, **2c**, **3c**, and **4c** were much longer than those of **1o**, **2o**, **3o**, and **4o**, 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**–**3**, with the exception of diarylethene **4**. The closed-ring isomers of diarylethenes **1**–**3** show the distinct oxidation waves at 1.01, 0.92 and 0.98 V; however, all of their open-ring isomers show no oxidation waves at those voltages. Moreover, both the open-ring isomer and closed-ring isomer of diarylethene **4** showed no evident oxidation peak at a broad potential region varying from 0 to 1.40 V. All these electrochemical results indicated that the substitution of chlorine atoms on the two terminal benzene rings and the substituent position effect had a great effect on both the open-ring and closed-ring isomers of these diarylethene derivatives. This may be ascribed to the special nature of chlorine atom, such as resonance, polar and steric effect. The chlorine atom is working as an electro-donating character in the resonance effect, but it is working as an electro-withdrawing character in the polar effect. For different position substitution of chlorine atoms of diarylethenes **1**–**3**, different electro-inducing ability and steric effect induced to their distinguishable electrochemical properties described above. The detailed factors need further investigation.

3. Conclusions

Three new symmetrical diarylethenes bearing two chlorine atoms at the *para*-, *meta*-, or *ortho*-position of both terminal phenyl groups were synthesized. All of them exhibited good photochromism and fluorescent switching both in solution and in PMMA film. In hexane solution, the photochromic parameters of the *para*-substituted diarylethene, including the maximum absorption wavelength, the molar absorption coefficients and the cyclization yield, are the biggest; while those of the *ortho*-substituted derivative are the smallest. In PMMA film, the *meta*- and *ortho*-substituted diarylethene compounds showed relatively remarkable fluorescent switches and the conversions of their fluorescence emission intensity at the photostationary state arrived at 72 and 76%, respectively. In the crystalline phase, the molecule of the *meta*-substituted diarylethene packed in a photoactive *anti*-parallel conformation and the distance between the two reactive carbon atoms is less than 4.2 Å, resulting in good photochromism in the single-crystalline phase. In addition, the cyclic voltammograms results showed that different position substitution of chlorine atoms induced to the distinguishable electrochemical properties for these diarylethene derivatives. All results indicated that the substituent position effect of chlorine atom has a significant effect on the photochromic behavior, fluorescence and electrochemical characters of the diarylethene derivatives. This research work may be useful for the design and synthesis of efficient photoactive diarylethene derivatives with tunable properties.

4. Experimental

4.1. 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 Agilent 8453 UV/VIS spectrometer. Photoirradiation was carried out using SHG-200 UV lamp, CX-21 ultraviolet fluorescence analysis cabinet and BMH-250 visible lamp. Light of appropriate wavelengths 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 (**4o**) in hexane [5d]. Fluorescence spectra were measured using a Hitachi F-4500 spectrophotometer, and the breadths of excitation and emission slits were both 10 nm. 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 tetrafuoroborate ($(TBA)BF_4$) 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.

4.2. Synthesis

The synthesis method of diarylethenes **1o**–**3o** was shown in Scheme 2 and experimental details were carried out as following.

4.2.1. 3-Bromo-5-(4-chlorophenyl)-2-methylthiophene (*6a*)

Compound **6a** was prepared by reacting 3-bromo-2-methyl-5-thienylboronic acid [18] (2.21 g, 10.0 mmol) with 1-bromo-4-chlorobenzene (1.92 g, 10.0 mmol) in the presence of $Pd(PPh_3)_4$ (0.27 g, 0.23 mmol) and Na_2CO_3 (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 $MgSO_4$, filtrated, and evaporated. The crude product was purified by column chromatography on SiO_2 using hexane as the eluent and 2.52 g of **6a** obtained as buffer oil in 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 2.44 (s, 3H, $-CH_3$), 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).

4.2.2. 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. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 2.42 (s, 3H, $-CH_3$), 7.12 (s, 1H, thienyl–H), 7.24–7.32 (m, 2H, aryl–H), 7.37,7.39 (d, $J = 8.0$, 1H, aryl-H), 7.49 (s, 1H, aryl–H).

4.2.3. 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. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 2.44 (s, 3H, $-CH_3$), 7.18 (s, 1H, thienyl–H), 7.25–7.28 (q, 2H, aryl–H), 7.44–7.47 (q, 2H, aryl–H).

4.2.4. 1,2-Bis[2-methyl-5-(4-chlorophenyl)-3-thienyl]-perfluorocyclopentene (*1o*)

To a stirred solution of **6a** (1.72 g, 6.8 mmol) in 30 mL THF was added dropwise a 2.5 M *n*-BuLi/hexane solution (2.73 mL, 6.81 mmol) at −78 °C under nitrogen atmosphere. Stirring was continued for 30 min at −78 °C. C_5F_8 (0.46 mL, 3.41 mmol) 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 $MgSO_4$, filtrated and evaporated. The crude product was purified by column chromatography on silica gel using hexane as the eluent and 1.11 g of **1o** obtained as solid in 56% yield. mp 202.0–202.6 °C; Anal. Calcd for $C_{27}H_{17}Cl_2F_6S_2$ (%): Calcd C, 55.02; H, 2.74. Found C, 55.94; H 2.55; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.95 (s, 6H, $-CH_3$), 7.26 (s, 2H, thienyl–H), 7.34, 7.36 (d, 4H, $J = 8.0$, aryl–H), 7.45, 7.47 (d, 4H, $J = 8.0$, aryl–H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 14.58, 122.72, 125.92, 126.79, 129.18, 131.78, 133.77, 141.01, 141.63; IR (ν, KBr, cm^{-1}) 727, 820, 887, 986, 1053, 1102, 1187, 1260, 1335, 1404, 1469, 1501, 1552, 1619, 2914.

4.2.5. 1,2-Bis[2-methyl-5-(3-chlorophenyl)-3-thienyl]-perfluorocyclopentene (*2o*)

2o was prepared by a method similar to that used for **1o** and 1.23 g of **2o** obtained as solid in 61% yield. mp: 129.4–129.5 °C; Anal. Calcd for $C_{27}H_{17}Cl_2F_6S_2$ (%): Calcd C, 55.02; H, 2.74. Found C, 55.30; H, 2.49; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.89 (s, 6H, $-CH_3$), 7.22 (s, 2H, thienyl–H), 7.22–7.27 (m, 4H, aryl–H), 7.33, 7.35 (d, 2H, $J = 8.0$, aryl–H), 7.45 (s, 2H, aryl–H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 13.57, 122.15, 122.73, 124.60, 124.88, 126.85, 129.23, 133.95, 139.67, 140.99; IR (ν, KBr, cm^{-1}) 780, 872, 975, 1054, 1113, 1190, 1274, 1337, 1439, 1569, 1595, 1629, 2916.

4.2.6. 1,2-Bis[2-methyl-5-(2-chlorophenyl)-3-thienyl]-perfluorocyclopentene (*3o*)

3**o** was prepared by a method similar to that used for **1o** and 0.65 g of **3o** obtained as solid in 33% yield. mp: 112.6–113.1 °C; Anal. Calcd for $C_{27}H_{17}Cl_2F_6S_2$ (%): Calcd C, 55.02; H, 2.74. Found C, 55.86; H, 2.54; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.97 (s, 6H, $-CH_3$), 7.21 (s, 2H, thienyl–H), 7.23, 7.25 (d, 4H, $J = 8.0$, aryl–H), 7.39–7.42 (m, 4H, aryl–H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 13.26, 123.91, 126.01, 126.44, 128.06, 109.53, 130.06, 131.17, 131.34, 137.02, 141.53; IR (ν, KBr, cm^{-1}) 758, 888, 988, 1050, 1104, 1195, 1273, 1339, 1436, 1461, 1492, 1553, 1632, 2914, 3063.

4.2.7. 1,2-Bis(2-methyl-5-phenyl-3-thienyl)-perfluorocyclopentene (*4o*)

4o was prepared by the same method as that reported by Irie et al. [5d].

4.3. Crystallography

Crystal data diarylethenes **2o** was collected by a Bruker SMART APEX2 CCD area-detector equipped with graphite monochromatized Mo Kα radiation at room temperature ($\lambda = 0.71073$ Å). The linear absorption coefficient μ of diarylethenes **2o** for Mo Kα radiation was 4.71 cm^{-1}. Direct phase determination yielded the positions of all non-hydrogen atoms. All non-hydrogen atoms were subjected to anisotropic refinement. All hydrogen atoms were generated geometrically with C–H bond distances of 0.93–0.96 Å according to criteria described in the SHELXTL manual. They were included in the refinement with Uiso(H) = 1.2 Ueq(C) or 1.5 Ueq(methyl C). Further details on the crystal structure investigation have been deposited with The Cambridge Crystallographic Data Centre as supplementary publication number CCDC 646343 for **2o**, These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223-336033.

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