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Synthesis and chlorine atom position effect on the properties of unsymmetrical photochromic diarylethenes

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Abstract

Unsymmetrical photochromic diarylethenes **1o**–**4o** have been synthesized, which diarylethenes **1o**–**3o** have a chlorine atom at *ortho*-, *meta*- and *para*-position of the terminal phenyl ring, respectively. The substituent position effect of chlorine atom on their properties, including photochromism both in solution and in the single crystalline phase and their electrochemical properties were investigated in detail. The results elucidated that the chlorine atom and its substituted position had significantly affected on the absorption characteristics, photochromic reactivity as well as the electrochemical performances of these diarylethene compounds. When the chlorine atom was introduced into the phenyl ring of these diarylethene systems, the cycloreversion quantum yields were effectively depressed; but, the molar absorption coefficients of the open-ring isomer and the differences of oxidation potential onsets between the open- and closed-ring isomers of these diarylethenes were significantly increased. Moreover, the position of the chlorine atom had also influenced evidently the above optical and electrochemical features.

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Keywords: Photochromism; Diarylethene; Synthesis; Photochemical and electrochemical property

1. Introduction

Photochromism is referred to as a reversible photoisomerization process induced at least in one direction by an electromagnetic radiation between two isomers having different absorption spectra [1]. Generally, photochromic compounds are classified into two categories, *i.e.*, thermally reversible compounds and thermally irreversible compounds [2]. Although various types of photochromic compounds have been reported to date, compounds that undergo thermally irreversible photochromic reactions are limited to diarylethenes [3], fulgides [4] and phenoxynaphthacenequinones [5], etc. Among these photochromic compounds, diarylethene derivatives bearing two thiophene or benzothiophene rings are the most promising candidates for optoelectronic devices such as optical memories, photoswitches and full-color displays, because of their excellent thermal stability in both isomers, remarkable fatigue resistance, and rapid response and high reactivity in the solid state [3a-d,6].

In this field, the majority of research work reported has been devoted to the development and fundamental properties of diarylethenes and some contents concerning substituent effect on their photochromic performance have also been reported. Irie et al. [7] and Pu 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. They revealed that electron-donating substituents attached bis(3-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. Tanifuji et al. [9] reported the effect of the radical substituents on the photochromic reactivity of bis(3-benzothiophene)perfluorocyclopentene. Morimitsu et al. [10], Takami and Irie [11] demonstrated that bulky alkoxy substituents at 2-and 2′-positions of the thiophene rings could strongly sup-

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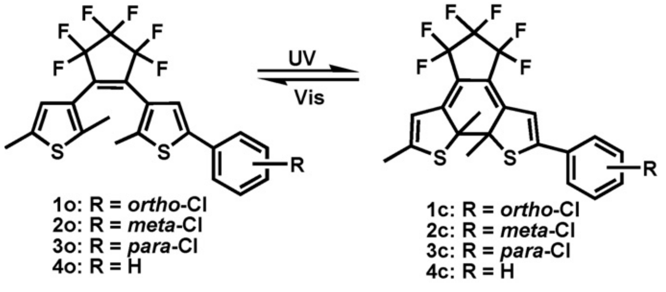
press the cycloreversion quantum yield and decrease the thermal stability of the colored closed-ring isomers at high temperature. Recently, Yamaguchi and Irie [12] reported that the bulky alkyl chains at 2-positions of benzothiophene and/or benzofuran rings increased the cyclization quantum yield and induced bathochromic shifts of the absorption spectra of the closed-ring isomers. From these publications, it can be easily drawn a conclusion that different substituent at the same position (*para*-position) of the terminal phenyl rings affects on the photochromic and photochemical properties of diarylethenes, or different substituents at the same position (2- or 3-position) of the heterocyclic aryl rings affects on the photochromic performance of diarylethenes. Yamamoto et al. [13] 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. Up to date, investigative studies concerning of the substituent position effect of the same functional group on the optoelectronic properties of diarylethenes are 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 remarkable impacts 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 [14]. 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 [15]. These results are very interesting and important, and they also enlighten us do a series of consecutive research works in the near future. In this paper, in order to elucidate the chlorine atom position effect on the optoelectronic characteristics of diarylethene derivatives, we have developed four unsymmetrical photochromic diarylethenes, *i.e.*, {1-(2,5-dimethyl-3-thienyl)-2-[2-methyl-5-(2-chlorophenyl)-3-thienyl]}perfluorocyclopentene (**1o**), {1-(2,5-dimethyl-3-thienyl)-2-[2-methyl-5-(3-chlorophenyl)-3-thienyl]}perfluorocyclopentene (**2o**), {1-(2,5-dimethyl-3-thienyl)-2-[2-methyl-5-(4-chlorophenyl)-3-thienyl]}perfluorocyclopentene (**3o**) and {1-(2,5-dimethyl-3-thienyl)-2-(2-methyl-5-phenyl-3-thienyl)}perfluorocyclopentene (**4o**). The four compounds show favorable photochromic performance in solution as well as in the single crystalline phase. The photochromic scheme of diarylethenes **1–4** which are discussed in this work is shown in Scheme 1.

2. Results and discussion

2.1. Synthesis of the diarylethene derivatives

The synthesis route for diarylethenes **1o**–**4o** is shown in Scheme 2. Suzuki coupling of four bromobenzene derivatives with thiophene boronic acid (**5**) [16] gave chlorophenylthiophene derivatives (**6a–6c**) and 3-bromo-2-methyl-5-phenylthiophene (**6d**). 2,5-dimethyl-3-thienylperfluorocyclopentene (**8**) was prepared according to the same procedure described previously [17]. Finally, compounds **6a–6d** was separately lithiated and then coupled with compound **8** to give diarylethenes **1o**–**4o**, respectively. The structures of **1o**–**4o** were confirmed by NMR, IR, and mass spectrometry, elemental analysis, and X-ray crystallographic analysis (Section 4).

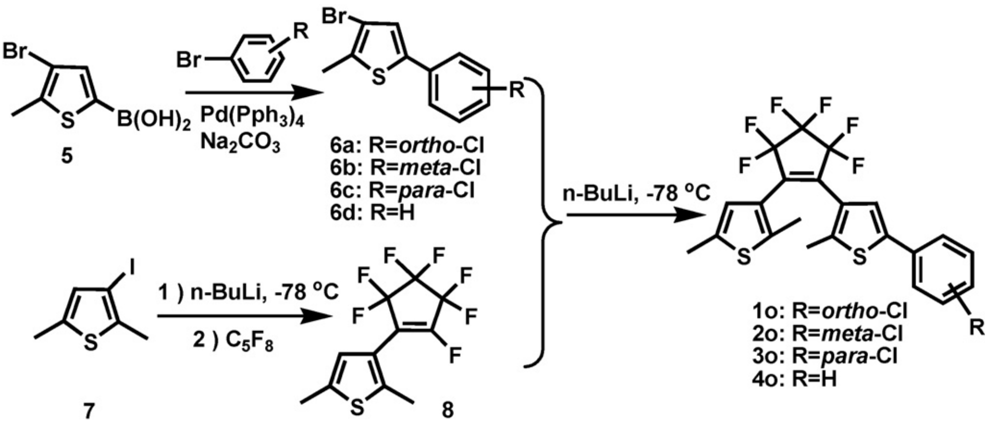


Scheme 1. Photochromism of diarylethenes **1–4.**

2.2. Photochromic reactions in hexane solution

The photochromic reactivity of diarylethenes **1–4** was examined in hexane, and their absorption spectral changes induced by alternating irradiation with UV and visible light were shown in Fig. 1. As shown in Fig. 1(A), the colorless solution containing the open-ring isomer **1o**, which shows the maximum absorption at 269 nm, turned magenta 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 530 nm. The conversion from **1o** to **1c** was 91% under irradiation with 297 nm light in the photostationary state, separated and detected by LC chromatography. Upon irradiation with visible light of wavelength longer than 450 nm, the colored solution returned to their original colorless form. Just as diarylethene **1o**, compounds **2o**–**4o** also show photochromism in hexane solution (Fig. 1(B)–(D)). The absorption characteristics of **2–4** were similar to that of diarylethene **1**. Upon irradiation with 297 nm light, absorption bands in the visible region appeared and the solutions turned magenta as a result of the cyclization reactions to produce **2c–4c**; all the solutions of **2c–4c** can be decolorized by irradiating them with visible light of wavelength longer than 450 nm induced the cycloreversion reactions to reproduce **2o–4o**. In the photostationary state, the conversion from the open-ring isomer to the closed-ring isomer was 95% for **2**, 98% for **3** and 83% for **4**, respectively.

Table 1 shows the absorption maxima and their coefficients of the open- and closed-ring isomers, and the cyclization and cycloreversion quantum yields of diarylethenes **1–4**. The data in Table 1 shows that the chlorine atom position effect on the absorption properties and photo-reactivity of both open-ring and closed-ring isomers of diarylethenes **1–3** are very significant. The absorption characteristics and photochromic reactivity of diarylethenes **1–3** displayed a well regular change.



Scheme 2. Synthetic route for diarylethenes **1o**–**4o.**

Among diarylethenes **1**–**3**, the absorption maxima and the molar absorption coefficients of the open- and closed-ring isomers and the cyclization quantum yield of the *para*-substituted derivative (compound **3**) are the biggest; while those of the *ortho*-substituted derivative (compound **1**) are the smallest. The values of the *meta*-substituted derivative (compound **2**) are in between those of the *para*- and *ortho*-substituted derivatives. These data shows a relatively remarkable increase with the chlorine atom substituting hydrogen atom of the benzene ring from at *ortho*- to at *para*-position. The absorption maxima of **3o** and **3c** are 25 and 11 nm longer than those of **1o** and **1c** in hexane, and the cyclization quantum yield of diarylethene **3** is 0.18 larger than that of diarylethene **1**. However, the changing trend of the cycloreversion quantum yield showed a minor decreasing trend with the chlorine atom substituting hydrogen atom of the benzene ring from at *ortho*- to at *para*-position. Among **1**–**3**, the

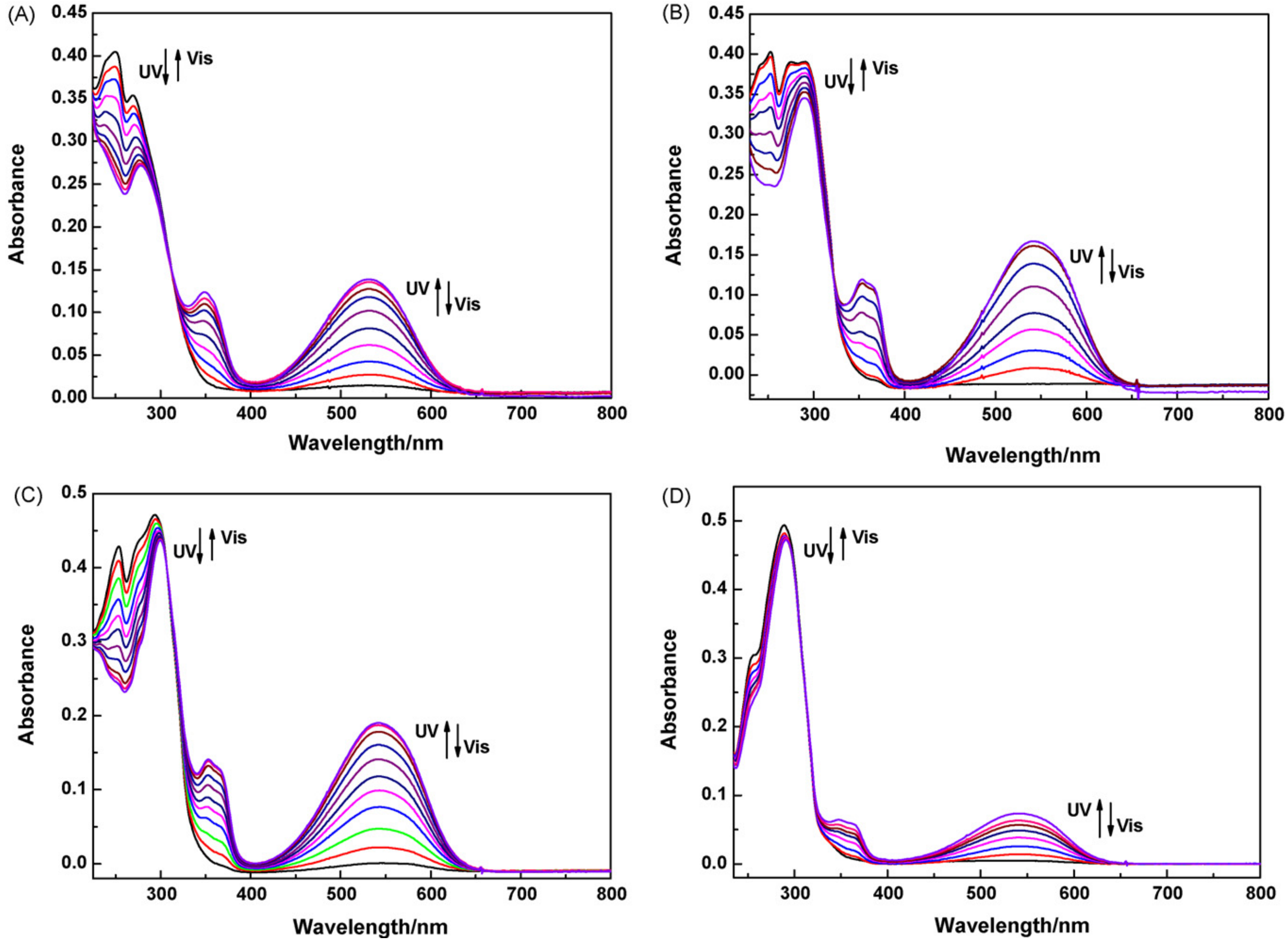


Fig. 1. Absorption spectral changes of diarylethenes **1**–**4** in hexane solution ($C = 2.0 \times 10^{-5}$ mol/L) at room temperature: (A) **1**, (B) **2**, (C) **3**, and (D) **4**.

Table 1
Absorption characteristics and photochromic reactivity of diarylethenes **1**–**4** 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}	
			$\Phi_{o\text{–}c}$	$\Phi_{c\text{–}o}$
1	269, 1.77×10^4	530, 6.95×10^3	0.50	0.014
2	275, 1.95×10^4	541, 8.35×10^3	0.52	0.011
3	294, 2.36×10^4	542, 9.51×10^3	0.68	0.0086
4	289, 2.47×10^4	541, 3.68×10^3	0.53	0.119

[a] Absorption maxima of open-ring forms.
[b] Absorption maxima of closed-ring forms.
[c] Quantum yields of cyclization reaction ($\Phi_{o\text{–}c}$) and cycloreversion reaction ($\Phi_{c\text{–}o}$), respectively.

cycloreversion quantum yield of **3** is the smallest ($\Phi_{c\text{–}o} = 0.0086$) and that of **1** is the biggest ($\Phi_{c\text{–}o} = 0.014$). Compared to compounds **1**–**3**, the absorption characteristic and photo-reactivity of non-chlorine atom derivative (compound **4**) is evidently different. Among the four compounds, the cycloreversion quantum yield and the molar absorption coefficient of its open-ring isomer are the biggest ($\Phi_{c\text{–}o} = 0.119$, $\varepsilon = 2.47 \times 10^4$ L mol cm^{-1}), but the molar absorption coefficient of its closed-ring isomer is the smallest ($\varepsilon = 3.68 \times 10^3$ L mol cm^{-1}). As described previously, it can be drawn a conclusion that the cycloreversion quantum yield could be effectively depressed and the molar absorption coefficient could be significantly enhanced when the chlorine atom was introduced into the benzene ring of diarylethene systems. The result is remarkably distinguished from those reported in our previous papers [14,15]. The electron-withdrawing fluorine substituent position does not affect significantly on the molar absorption coefficient of symmetrical dithienylethene derivatives [14]; while the electron-donating methoxyl substituent position can effectively enhance the cycloreversion quantum yield of unsymmetrical diarylethenes bearing a pyrazole unit [15].

2.3. Crystal structures and photochromic reactions in the crystalline phase

Colorless crystals of **1o**–**4o** suitable for X-ray analysis were obtained by the slow evaporation in hexane. In order to know better the relationship between the conformation and the photochromic reactivity of diarylethenes **1o**–**4o** in the crystalline phase, final structural confirmations of **1o**–**4o** were provided by X-ray crystallographic analysis. Table 2 shows the X-ray crystallographic analysis data and Fig. 2 shows the ORTEP drawings of the single crystals **1o**–**4o**. In previous papers [18], we reported the structures determinations of **1o** and **3o** by X-ray crystallography (Fig. 2(A) and (F)). The molecules of the two compounds are packed in a photoactive *anti*-parallel conformation, and the distances between the reactive carbon atoms (C5...C13 for **1o** and C5...C8 for **3o**) are 3.582 (4) Å (**1o**) and 3.612 (6) Å (**3o**). As shown in Fig. 2(B)–(E), for diarylethene **2o**, there were four independent molecules in the asymmetric unit and all of them were packed in a photoactive *anti*-parallel conformation in the crystalline phase, which can undergo photo-cyclization reaction [19]. The intramolecular distances between the two reactive carbon atoms for molecules I–IV are 3.665 (6), 3.750 (5), 3.753 (3) and 3.677 (5) Å, respectively (Table 3). Fig. 2(G) shows the ORTEP drawing of **4o**, indicating that it also packed

Table 2
Crystal data for diarylethenes **1o**–**4o**

	Compound			
	1o	**2o**	**3o**	**4o**
Formula	$C_{22}H_{15}ClF_6S_2$	$C_{22}H_{15}ClF_6S_2$	$C_{22}H_{15}ClF_6S_2$	$C_{22}H_{16}F_6S_2$
Formula weight	492.91	492.91	492.91	458.47
Temperature (K)	294 (2)	294 (2)	294 (2)	291 (2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*P*21/*n*	*P*21/*c*	*P*21/*c*	*P*21/*c*
Unit cell dimensions				
a (Å)	6.9539 (12)	12.046 (2)	21.232 (3)	13.586 (3)
b (Å)	21.661 (4)	49.471 (9)	9.0912 (13)	18.419 (4)
c (Å)	14.543 (2)	15.429 (3)	11.1534 (17)	8.6071 (17)
α (°)	90.00	90.00	90.00	90.00
β (°)	94.278 (3)	106.687 (3)	98.243 (2)	105.440 (2)
γ (°)	90.00	90.00	90.00	90.00
Volume (Å^3)	2184.5 (6)	8808.0 (3)	2130.6 (5)	2076.2 (7)
Z	4	16	4	4
Density (calcd.) (g/cm^3)	1.499	1.487	1.537	1.467
Goodness-of-fit on F^2	1.062	1.039	1.008	1.019
Final *R* indices [$I/2\sigma(I)$]				
R_1	0.0403	0.0750	0.0395	0.0350
wR_2	0.0996	0.1664	0.0975	0.0948
R indices (all data)				
R_1	0.0732	0.2249	0.0761	0.0408
wR_2	0.1185	0.2233	0.11144	0.1011

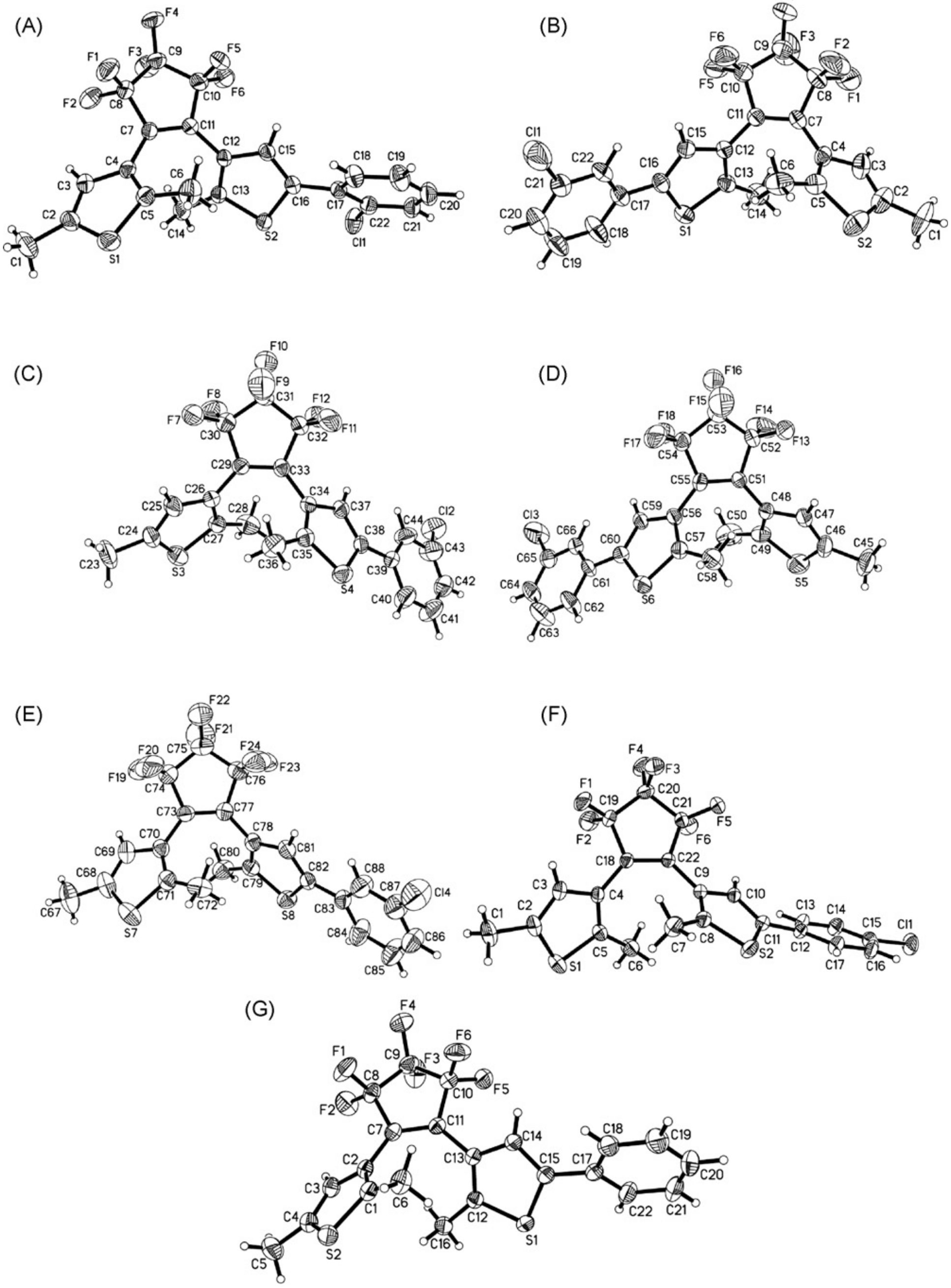


Fig. 2. ORTEP drawings of crystals **1o**–**4o**, showing 35% probability displacement ellipsoids: (A) **1o**, (B) **2o**—molecule I, (C) **2o**—molecule II, (D) **2o**—molecule III, (E) **2o**—molecule IV, (F) **3o**, and (G) **4o**.

in an *anti*-parallel conformation in the crystalline phase. The intramolecular distance between the two reactive carbon atoms for **4o** is 3.555 (4) Å. From Fig. 2, one can easily see that both of the methyl groups attached to the reactive carbon atoms in each molecule are located on opposite sides of the double bonds and thus *trans* with respect to the double bond. Such a conformation is crucial for the compound to exhibit photochromic and photo-induced properties [20]. All distances between the potentially reactive carbon atoms and dihedral angles between the two adjacent planar rings of **1o**–**4o** are summarized in Table 3. As shown in Fig. 2 and Table 3, all molecules of crystals **1o**–**4o** are fixed in an *anti*-parallel mode in the crystalline phase and the distances of the two reactive carbon atoms are less than 4.2 Å which is close enough for the reaction to take place, indicating that they can be expected to undergo photochromism in the single crystalline phase.

Generally, the color and the absorption band changes are mainly dependent on the π-conjugation length in molecular structure [21]. 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

Table 3
Distances between the reacting carbon atoms *d* (Å) and dihedral angles θ (°) of diarylethenes **1o–4o**

Compound	*d* (Å)		θ (°)[a]		
			θ_1	θ_2	θ_3
1o	C5. . .C13	3.582 (4)	41.0 (5)	52.1 (5)	39.9 (5)
2o	C5. . .C13	3.665 (6)	46.0 (7)	54.0 (7)	10.4 (7)
	C27. . .C35	3.750 (5)	49.8 (6)	58.2 (5)	9.3 (6)
	C49. . .C57	3.753 (3)	51.8 (4)	54.1 (4)	5.3 (4)
	C71. . .C79	3.677 (5)	44.5 (3)	56.7 (3)	7.2 (3)
3o	C5. . .C8	3.612 (6)	40.9 (5)	41.2 (5)	27.8 (4)
4o	C1. . .C12	3.555 (4)	42.4 (7)	44.3 (7)	39.0 (7)

[a] θ_1, Dihedral angle between the cyclopentene ring and 2,5-dimethylthiophene ring; θ_2, dihedral angle between the cyclopentene ring and the thiophene ring attached to a benzene ring; θ_3, dihedral angle between the thiophene ring and the adjacent benzene ring.

resulting in displaying remarkable different color [22]. Crystals of **1o–4o** shows photochromic reaction, in accordance with the expected ring closure, to form **1c–4c**. Their color changes upon photo-irradiation are shown in Fig. 3. Upon irradiation with 297 nm light, the colorless crystal of **1o–4o** turned to magenta quickly. When the magenta crystal was dissolved separately in hexane, the solution immediately turned to magenta, and a new broad absorption band was appeared at visible light region, which was the same as that of the closed-ring isomer **1c–4c**, respectively. Alternatively, the magenta colored solution reverted to the colorless one upon irradiation with appropriated wavelength visible light ($\lambda > 450$ nm). Furthermore, these diarylethenes crystals exhibited remarkable fatigue resistance and their colors remained stable very long time in the dark. So, these crystals will be the promising candidates for optoelectronic applications, such as high density three-dimensional optical recording media, optical switches and color displays, etc. [23].

2.4. Electrochemical properties

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 for optoelectronic device applications [24]. Besides their excellent photochromic performance, the electrochemical behaviors of diarylethenes also attract much attention [25]. The electrochemical properties of diarylethenes are being used for molecular switches and can be potentially applied to molecular-scale electronic switches. Recently, the electrochemical reaction of diarylethenes has received considerable attention in reports of electrochemical ring opening and closing [26]. In order to investigate the chlorine atom position effect on the electrochemical characteristics of diarylethenes, we carried out electrochemical examinations by linear sweep method under the same experimental conditions using diarylethenes **1o–4o**, respectively. The method and experimental details were described in Section 4. The typical electrolyte was acetonitrile (5 mL) containing 0.15 mol/L $LiClO_4$ and 4×10^{-3} mol/L diarylethene sample. All solution were deaerated by a dry argon stream and maintained at a slight argon overpressure during electrochemical experiments. The anodic polarization curves of the open-ring and the closed-ring isomers of diarylethenes **1–4** were shown in Fig. 4. It can be clearly seen from Fig. 4 that the oxidation of **1o**, **1c**, **2o**, **2c**, **3o**, **3c**, **4o** and **4c** was initiated at 1.05, 0.38, 1.16, 0.40, 0.96, 0.32, 1.01 and 0.89 V, respectively. These data together with those shown in Fig. 4 show that the oxidation onsets of the open-ring isomers of diarylethenes **1–4** are higher than those of the corresponding closed-ring isomers, indicating that the electronic-withdrawing effect of the chlorine atom is more significant in the closed-ring isomer. Moreover, the difference of oxidation onset between the open- and closed-ring isomers of diarylethenes **1–4** ($\Delta V_{o\text{–}c}$) was 0.67 for **1**, 0.76 for **2**, 0.64 for **3**, and 0.12 V for **4**, respectively. It can be drawn a conclusion that the chlorine atom and its substituted position have greatly affected on the electrochemical performances of these diarylethene compounds. For *ortho*-, *meta*- and *para*-position substitution of the chlorine atom, the oxidation potential onset showed a remarkable difference with $\Delta V_{o\text{–}c}$ greater than 0.6 V for diarylethenes **1–3**. On the other hand, the oxidation potential

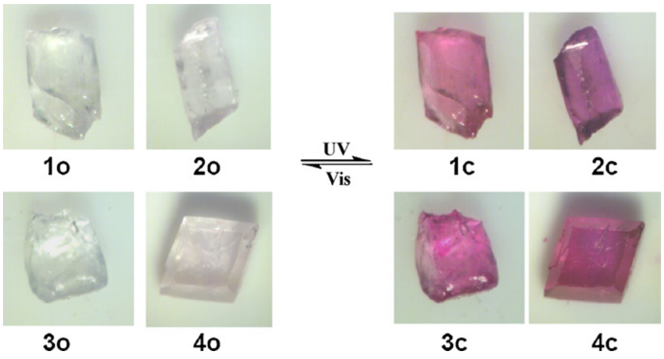


Fig. 3. Photographs of photochromic processes of diarylethenes **1–4** in the crystalline phase.

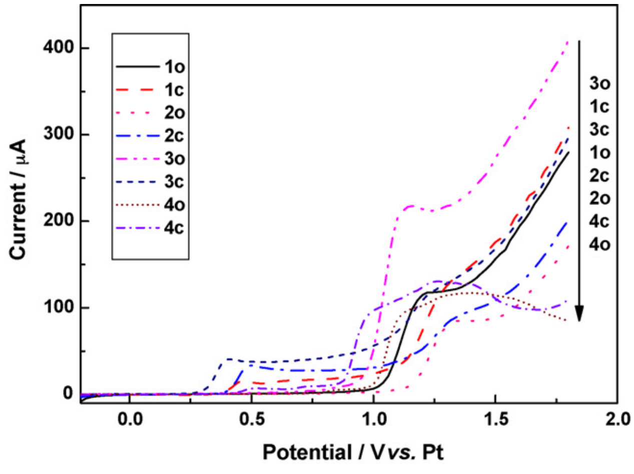
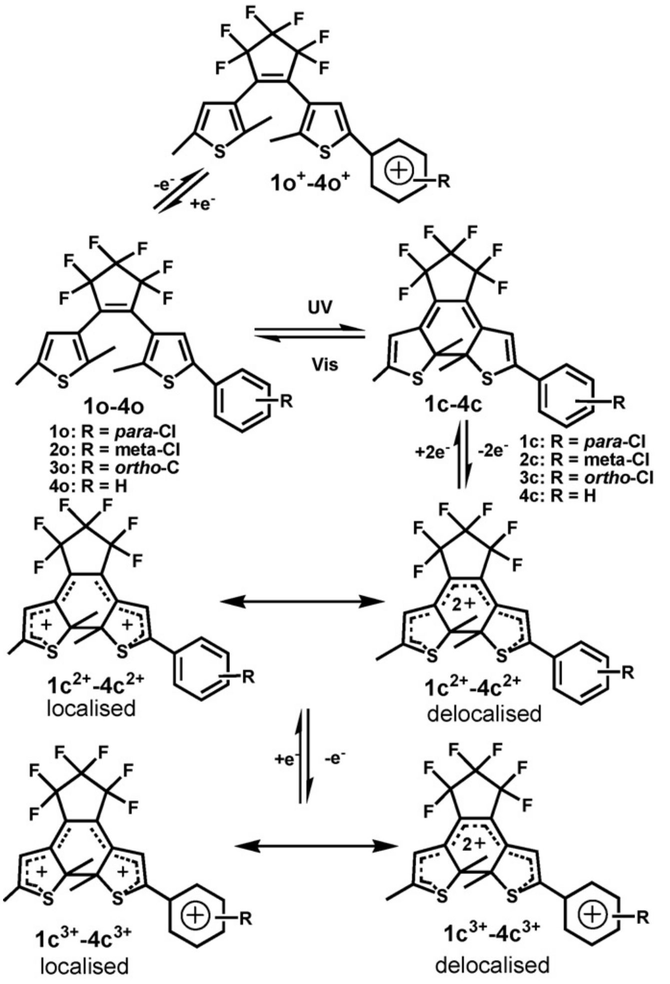


Fig. 4. The anodic polarization curves of diarylethenes **1–4**.



Scheme 3. Redox and photochemical processes observed for diarylethenes **1**–**4**.

onsets of **4o** and **4c** were similar to each other when the chlorine atom was substituted by a hydrogen atom ($\Delta V_{\text{o–c}} = 0.12$ V). Among these four compounds, the $\Delta V_{\text{o–c}}$ of *meta*-position derivative (**2**) is the biggest and that of non-chlorine atom substituted derivative (**4**) is the smallest. The result is evidently different from those reported in our previous papers [14,15]. When the weak electron-withdrawing chlorine atom was substituted by the fluorine atom, the $\Delta V_{\text{o–c}}$ of *para*-position derivative is the biggest ($\Delta V_{\text{o–c}} = 0.18$ V) and that of *ortho*-position derivative is the smallest ($\Delta V_{\text{o–c}} = 0.03$ V) [14]; while the $\Delta V_{\text{o–c}}$ of *meta*-position derivative is the biggest ($\Delta V_{\text{o–c}} = 0.24$ V) and that of *para*-position derivative is the smallest ($\Delta V_{\text{o–c}} = 0.05$ V) when the chlorine atom was substituted by the strong electron-donating methoxyl groups in diarylethenes with a pyrazole unit [15]. The great differences were possible contributed to the different diarylethene systems and the effect of different substitutes with different electron-withdrawing or electron-donating ability. A detailed explanation requires further examination.

In addition, the redox and photochemical processes for diarylethenes **1**–**4** are summarized in Scheme 3. It is clear from the reversibility at higher scan rates that the oxidation process (**1o**–**4o** → $\mathbf{1o^+}$–$\mathbf{4o^+}$) is reversible. As shown in Fig. 4, The oxidation waves of diarylethenes **1o**–**4o** were observed at 1.18, 1.30, 1.10, and 1.20 V, respectively, which were assigned to the unique oxidation of the chlorophenyl groups of diarylethenes **1o**–**4o** ($\mathbf{1o^+}$, $\mathbf{2o^+}$, $\mathbf{3o^+}$ and $\mathbf{4o^+}$, Scheme 3). Compared to those of diarylethenes **1o**–**4o**, the first oxidation waves of **1c**–**4c** observed at 0.46, 0.48, 0.39 and 0.50 V were assigned to the thienyl ring followed by formation of the closed-ring form **1c**–**4c**, which undergoes intramolecular electron transfer from the phenyl-substituted groups to form +2 valence particles ($\mathbf{1c^{2+}}$, $\mathbf{2c^{2+}}$, $\mathbf{3c^{2+}}$ and $\mathbf{4c^{2+}}$, Scheme 3) [26b]. The second oxidation waves of **1c**–**4c** observed at 1.27, 1.32, 1.21 and 1.24 V were assigned to form +3 valance particle ($\mathbf{1c^{3+}}$, $\mathbf{2c^{3+}}$, $\mathbf{3c^{3+}}$, $\mathbf{4c^{3+}}$, Scheme 3), although the oxidation waves of **1c**–**4c** are unconspicuous (Fig. 4).

3. Conclusions

In the present work, four unsymmetrical diarylethenes were synthesized and their structures were established by X-ray crystallographic analysis. All derivatives undergo good photochromism both in solution and in the single crystalline phase. The absorption characteristics, photochromic reactivity and electrochemical properties of these compounds were significantly dependent on the substituent position effect of the chlorine atom attached to the terminal phenyl rings. In comparison of those of diarylethenes **1**–**3**, which contained a chlorine atom at *ortho-, meta-* and *para*-position of the terminal phenyl ring, respectively, the cycloreversion quantum yield of the non-chlorine atom substituted derivative **4** was increased remarkably, but its molar absorption coefficients and the difference of oxidation potential onsets between the open- and closed-ring isomers were significantly decreased. The results of this study are useful for the design of efficient photoactive and good photochromic diarylethene derivatives.

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 recorded on Bruker Vertex-70 spectrometer and mass spectra were measured with Agilent MS Trap VL spectrometer. The absorption spectra were measured using a 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 wavelengths was isolated by different light filters. The quantum yields were determined by comparing the reaction yields of the dithienylethenes in hexane against 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene in hexane [7c]. 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 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 a diarylethene sample (C = 4 × 10^{-3} mol/L). 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**–**4o** was shown in Scheme 2 and experimental details were carried out as following.

4.2.1. 3-Bromo-2-methyl-5-(2-chlorophenyl)thiophene (6a)

Compound **6a** was prepared by reacting 3-bromo-2-methyl-5-thienylboronic acid **(5)** [16b] (2.21 g, 10.0 mmol) with 1-bromo-2-chlorobenzene (1.92 g, 10.0 mmol) in the presence of $Pd(PPh_3)_4$ (0.40 g) and Na_2CO_3 (3.18 g, 30.0 mmol) in tetrahydrofuran (THF) (40 mL containing 10% water) for 15 h at 70 °C. **6a** was purified by column chromatography on SiO_2 using hexane as the eluent and 2.34 g obtained as buffer oil in 81% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.44 (s, 3H, –CH_3), 7.18 (s, H, thienyl–H), 7.25–7.47 (m, 4H, phenyl–H).

4.2.2. 3-Bromo-2-methyl-5-(3-chlorophenyl)thiophene (6b)

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, $CDCl_3$): δ 2.42 (s, 3H, –CH_3), 7.12 (s, 1H, thienyl–H), 7.24–7.32 (m, 2H, phenyl–H), 7.49 (s, 1H, phenyl–H).

4.2.3. 3-Bromo-2-methyl-5-(3-chlorophenyl)thiophene (6c)

6c was prepared by a method similar to that used for **6a** and obtained as buffer solid in 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.44 (s, 3H, –CH_3), 7.109 (s, 1H, thienyl–H), 7.36 (d, J = 8.4, 2H, phenyl–H), 7.445 (d, J = 8.4, 2H, phenyl–H).

4.2.4. 3-Bromo-2-methyl-5-phenylthiophene (6d)

6d was prepared by a method similar to that used for **6a** and obtained as buff solid in 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.28 (s, 3H, –CH_3), 6.84 (s, 1H, phenyl–H), 7.12 (s, 1H, thienyl–H), 7.34 (d, 2H, J = 8.0 Hz, phenyl–H), 7.57 (d, 2H, J = 8.0 Hz, phenyl–H).

4.2.5. (2,5-Dimethyl-3-thienyl)perfluorocyclopentene (8)

To a stirred solution of 3-iodo-2,5-dimethylthiophene (**7**) (18.20 g, 76.5 mmol) in THF was added dropwise a 1.6 mol/L *n*-BuLi/hexane solution (50 mL, 80 mmol) at −78 °C under argon atmosphere. Stirring was continued for 30 min at this low temperature. Perfluorocyclopentene (10.3 mL, 76.5 mmol) was added to the reaction mixture, and the mixture was stirred for another 2 h at −78 °C, then the reaction was warned spontaneously to the room temperature. The reaction was stopped by the addition of methanol (5 mL). The product was extracted with ether. The organic layer was washed with 1 M HCl aqueous solution and water, respectively. 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 15.3 g of **8** obtained as yellow oil in 66% yield. ^{19}F NMR (376 MHz, $CDCl_3$) δ 108.53 (2F), 117.84 (2F), 128.22 (1F), 129.90 (2F). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.28 (s, 3H, –CH_3), 2.234 (s, 3H, –CH_3), 6.54 (s, 1H, thienyl–H).

4.2.6. {1-(2,5-dimethyl-3-thienyl)-2-[2-methyl-5-(2-chlorophenyl)-3-thienyl]}perfluorocyclopentene (1o)

To a stirred anhydrous THF containing **6a** (2.30 g, 8.0 mmol) was added dropwise a 2.5 mol/L *n*-BuLi/hexane solution (3.3 mL) at −78 °C under argon atmosphere. After the mixture has been stirred for 30 min, compound **8** (2.43 g, 8.0 mmol) in solvent of anhydrous THF was added. The reaction was further stirred at −78 °C for 2 h, and the reaction was allowed to slowly warn to the room temperature. The reaction was quenched with distilled water. The product was extracted with ether, dried with $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by column chromatography using petroleum ether as the eluent to afford to 2.51 g in 51% yield of **1o** as white solid. Melting point 80.8–81.9 °C; Anal. Calcd for $C_{22}H_{15}ClF_6S_2$ (%): Calcd C, 53.61; H, 3.07. Found C, 53.92; H, 3.37; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.89 (s, 3H, –CH_3), 1.98 (s, 3H, –CH_3), 2.43 (s, 3H, –CH_3), 6.75 (s, 1H, thienyl–H), 7.24 (s, 1H, thienyl–H), 7.28 (t, 2H, J = 7.4 Hz, phenyl–H), 7.16 (s, 2H, phenyl–H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.16, 14.21, 15.1, 124.4, 125.2, 127.0, 127.6, 129.0, 130.5, 131.1, 132.3, 132.4, 137.7, 137.8, 139.8, 142.3; IR (KBr, ν, cm^{-1}): 739, 764, 825, 855, 893, 983, 1049, 1115, 1191, 1273, 1336, 1442, 1487, 1630, 2919.

4.2.7. {1-(2,5-dimethyl-3-thienyl)-2-[2-methyl-5-(3-chlorophenyl)-3-thienyl]}perfluorocyclopentene (2o)

2o was prepared by a method similar to that used for **1o** and obtained as solid in 53% yield. Melting point 104.4–106.2 °C; Anal. Calcd for $C_{22}H_{15}ClF_6S_2$ (%): Calcd C, 53.61; H, 3.07. Found C, 53.83; H, 3.25; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.86 (s, 3H, –CH_3), 1.94 (s, 3H, –CH_3), 2.43 (s, 3H, –CH_3), 6.73 (s, 1H, thienyl–H), 7.26 (s, 1H, thienyl–H), 7.31 (t, 2H, J = 7.8 Hz, phenyl–H), 7.41 (d, 1H, J = 7.4 Hz, phenyl–H), 7.51 (s, 1H, phenyl–H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.2, 14.4, 15.1, 123.4, 123.7, 124.5, 124.6, 125.6, 126.2, 127.7, 130.2, 135.0, 135.2, 137.9, 139.8, 140.4, 141.9; IR (KBr, ν, cm^{-1}): 745, 776, 823, 836, 892, 977, 1051, 1108, 1189, 1273, 1336, 1445, 1492, 1571, 1594, 2924.

4.2.8. {1-(2,5-dimethyl-3-thienyl)-2-[2-methyl-5-(4-chlorophenyl)-3-thienyl]}perfluorocyclopentene (3o)

3o was prepared by a method similar to that used for **1o** and obtained as solid in 55% yield. Melting point 145.1–145.4 °C; Anal. Calcd for $C_{22}H_{15}ClF_6S_2$ (%): Calcd C, 53.61; H, 3.07. Found C, 53.35; H, 3.04; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.86 (s, 3H, –CH_3), 1.92 (s, 3H, –CH_3), 2.42 (s, 3H, –CH_3), 6.73 (s, 1H, thienyl–H), 7.23 (s, 1H, thienyl–H), 7.35 (d, 2H, J = 8.5 Hz, phenyl–H), 7.46 (d, 2H, J = 8.5 Hz, phenyl–H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.3, 14.5, 15.1, 122.9, 124.5, 124.6,126.2, 126.8, 129.2, 131.9, 133.7, 137.9, 139.8, 140.7, 141.5; IR (KBr, ν, cm^{-1}): 727, 819, 888, 984, 1049, 1103, 1187, 1265, 1336, 1440, 1489, 1550, 1622, 2922.

*4.2.9. {1-(2,5-dimethyl-3-thienyl)-2-(2-methyl-5-phenyl-3-thienyl)}perfluorocyclopentene (**4o**)*

4o was prepared by a method similar to that used for **1o** and obtained as solid in 57% yield. Melting point 89.0–90.1 °C; Anal. Calcd for $C_{22}H_{16}F_6S_2$ (%): Calcd C, 57.63; H, 3.52. Found C, 57.59; H, 3.47; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.90 (s, 3H, –CH_3), 1.96 (s, 3H, –CH_3), 2.45 (s, 3H, –CH_3), 6.75 (s, 1H, thienyl–H), 7.276 (s, 1H, thienyl–H), 7.32 (t, 1H, $J = 7.4$ Hz, phenyl–H), 7.40 (t, 2H, $J = 7.6$ Hz, phenyl–H), 7.556 (d, 2H, $J = 7.6$ Hz, phenyl–H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.7, 13.8, 14.5, 122.1, 124.1, 124.2, 125.1, 125.5, 127.3, 128.5, 133.0, 137.2, 139.2, 140.6, 141.5; IR (KBr, ν, cm^{-1}): 736, 759, 821, 890, 986, 1049, 1087, 1114, 1133, 1189, 1271, 1335, 1384, 1439, 1627.

4.2.10. Crystallography

Crystal data diarylethenes **1o–4o** were 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 **1o–4o** for Mo Kα radiation was 4.24, 4.20, 4.34 and 3.15 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 Uequiv. (C) or 1.5 Uequiv. (methyl C). Further details on the crystal structure investigation have been deposited with The Cambridge Crystallographic Data Centre as supplementary publication number CCDC 615590, 615589, 615588 and 641706 for **1o, 2o, 3o** and **4o**. 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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