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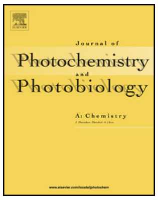

The effect of the fluorine atom position upon isomeric photochromic diarylethenes bearing a pyrrole unit

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ABSTRACT

A new class of isomeric diarylethenes bearing a pyrrole moiety have been synthesized, and their properties including photochromism, fluorescence, and electrochemical properties have been discussed systematically. Each of the diarylethenes exhibited evident photochromism and functioned as a remarkable fluorescent switch in both solution and PMMA films. Their photoconversion ratios were larger than 90%, and the fluorescent modulation efficiencies were greater than 88% in the photostationary state. The absorption maxima, quantum yields of cyclization and cycloreversion, and band-gaps of the closed-ring isomers increased whereas the emission intensity and band-gaps of the open-ring isomers greatly decreased when the fluorine atom was attached at any of the three positions on the terminal benzene ring. Cyclic voltammograms suggested that the oxidation onsets and band-gaps of the open-ring isomers were much bigger than those of the closed-ring isomers. The fluorine atom and its substituted position could availably modulate their optical and electrochemical behaviors.

1. Introduction

Various types of photochromic organic compounds, including stilbene [1], azobenzenes [2], furylfulgides [3,4], spirooxazines [5], and diarylethenes [6,7], have been so far developed from the view points of fundamental organic photochemistry and practical applications such as light-modulating and optical recording materials. During the past several decades, there have been important achievements in the synthesis of new families of organic photochromic molecules [8–10]. Among these molecules, diarylethenes with heterocyclic aryl rings are regarded as the best candidates for photoelectronic applications because of their excellent thermal stability, remarkable fatigue resistance, and high coloration sensitivity [11,12].

The photochromic process of diarylethenes is based on a reversible transformation between the open-ring isomer with a hexatriene structure and the closed-ring isomer with a cyclohexadiene structure, according to the Woodward–Hoffmann rule [11]. The open-ring isomer has two conformations, *anti*-parallel and parallel conformations, which exchange even at room temperature [13]. In general, the diarylethene undergoes a photocyclization reaction if it is orientated in an *anti*-parallel array and if the distance between two reactive carbon atoms on the aryl moiety is within 0.42 nm [14]. The photochromic characteristics of diarylethenes mainly depend on several factors, including the conformations of open-ring isomers, the categories of heteroaryl moieties, the electron donor/acceptor substituents, as well as the conjugation length of heteroaryl systems [15–24]. Particularly, the categories of heteroaryl moieties and substituents on the reactive position greatly influence the photoreactivity of diarylethene derivatives. On the one hand, the nature of the heteroaryl moieties greatly influences the photo-reactivity and the distinguishable features of diarylethenes. For instance, diarylethenes with benzofuran moieties have outstanding fatigue resistance and small photoconversion ratio [15], whereas diarylethenes bearing both thiazole and benzene moieties have relatively weak fatigue resistance [24]. Unsymmetrical diarylethenes bearing pyrrole groups exhibited excellent thermal stability and strong fluorescence switch [23], whereas symmetrical diarylethenes bearing two pyrrole groups were thermally unstable and returned to the open-ring isomers even in the dark [25]. Moreover, pyrazole derivatives had a big absorption maxima and high cycloreversion quantum yield [26], whereas oxazole derivatives had a small absorption maxima and showed good pH sensitivity and strong fluorescence switch [27]. On the other hand, the electron donor/acceptor substituents and their substituted positions have also a significant effect on the properties of diarylethene derivatives [23,28]. For instance, the electron-donating substituents of the bis(3-thienyl)ethene diarylethenes could be effective to increase the absorption coefficient of the closed-ring isomers and decrease the cycloreversion quantum yield [29,30]. However, those attached bis(2-thienyl)ethene diarylethenes could increase the absorption maxima of the open-ring isomers and reduce the cyclization quantum yield [31].

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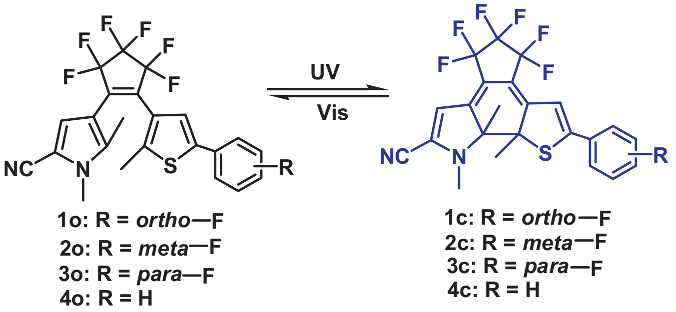


Scheme 1. Photochromism of diarylethenes **1**–**4**.

Pyrrole is an attractive aryl unit due to its biological characteristics [28], and its structure is similar to those of thiophene and furan. However, reports of diarylethene derivatives with a pyrrole unit are very rare [23,32]. Previously, we have reported the effect of methoxy/cyano substituent position on the properties of unsymmetrical diarylethenes with a pyrrole unit [23,33]. We have also investigated the effect of fluorine atom position on the properties of dithienylethenes [18,20]. The results indicated that the substituent position had a significant effect on the properties of these diarylethene derivatives. However, as far as we are aware, the effect of fluorine atom position on the properties of diarylethenes with a pyrrole unit has not hitherto been reported. In order to realize this idea, we have synthesized four hybrid diarylethenes bearing both pyrrole and thiophene moieties in this work. The synthesized diarylethenes are 1-[2-methyl-5-(2-fluorophenyl)-3-thienyl]-2-(2-cyano-1,5-dimethyl-4-pyrryl)perfluorocyclopentene (**1o**), 1-[2-methyl-5-(3-fluorophenyl)-3-thienyl]-2-(2-cyano-1,5-dimethyl-4-pyrryl) perfluorocyclopentene (**2o**), 1-[2-methyl-5-(4-fluorophenyl)-3-thienyl]-2-(2-cyano-1,5-dimethyl-4-pyrryl) perfluorocyclopentene (**3o**), and 1-(2-methyl-5-phenyl-3-thienyl)-2-(2-cyano-1,5-dimethyl-4-pyrryl)perfluorocyclopentene (**4o**) of which, **1o**, **2o**, and **3o** are new compounds. The photochromic process of these derivatives is shown in Scheme 1. Although diarylethene **4o** has been reported previously [23,33], it is presented here for comparison with those of other three diarylethene derivatives.

2. Experimental

2.1. General method

NMR spectra were recorded on a Bruker AV400 (400 MHz) spectrometer with $CDCl_3$ as the solvent and tetramethylsilane as an internal standard. Infrared spectra (IR) were performed using a Bruker Vertex-70 spectrometer. Elemental analysis was measured with an elemental analyzer labeled the PE 2400 CHN analyzer. Melting point was taken on a WRS-1B melting point apparatus. Absorption spectra were measured using an Agilent 8453 UV/VIS spectrophotometer. Photoconversion ratios from the open-ring to the closed-ring isomers in the photostationary state were measured using an Shimadzu HPLC 10AVP chromatographic analyzer. Fluorescence spectra were measured using a Hitachi F-4500 fluorimeter. Photo-irradiation was carried out using an SHG-200 UV lamp, a CX-21 ultraviolet fluorescence analysis cabinet, and a BMH-250 visible lamp. The required wavelength was isolated by the use of the appropriate filters. 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 the working electrode and counter electrode. Platinum wire served as a quasireference electrode. It was calibrated using an internal ferrocene (Fc/Fc+) standard with a formal potential of $E_{1/2}$ = +0.35 V *versus* platinum wire. The typical electrolyte was acetonitrile (5 mL) containing 0.1 mol L^{-1} tetrabutylammonium tetrafluoroborate ($(TBA)BF_4$) and 1.0×10^{-3} mol L^{-1} diarylethene sample. All solutions were deaerated by bubbling with a dry argon stream and maintained at a slight argon overpressure during electrochemical experiments. Solvents used were spectroscopic grade and were purified by distillation.

2.2. Synthesis

The synthesis route for diarylethenes **1o**–**4o** is shown in Scheme 2. Compounds (**5a**–**5d**) [18] were separately lithiated and then coupled with 1-(2-cyano-1,5-dimethyl-4-pyrryl) perfluorocyclopentene (**6**) [23] to give diarylethenes **1o**–**4o**, respectively.

2.2.1. Synthesis of 1-[2-methyl-5-(2-fluorophenyl)-3-thienyl]-2-(2-cyano-1,5-dimethyl-4-pyrryl)perfluorocyclopentene (**1o**)

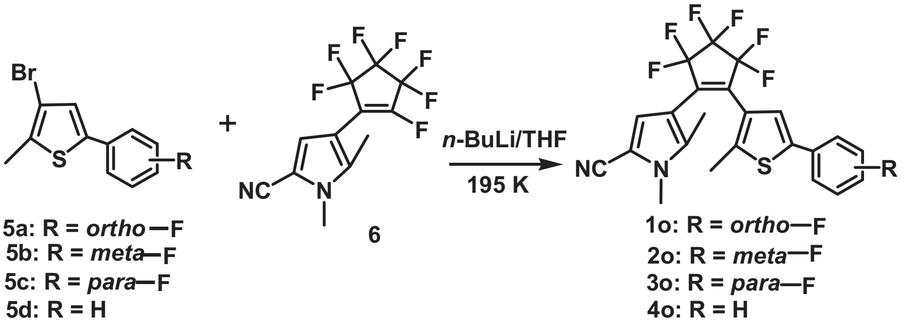
To a stirred anhydrous THF (80 mL) of compound **5a** (0.76 g, 2.82 mmol)[18] was added dropwise a 2.5 mol L^{-1} *n*-BuLi/hexane solution (1.20 mL, 3.00 mmol) at 195 K under argon atmosphere. After 30 min, 15 mL THF containing compound **6** (0.86 g, 2.75 mmol) [23] was added and the reaction mixture was stirred for 2 h at this low temperature and quenched by water. The product was extracted with diethyl ether, and then dried with $MgSO_4$, filtered, and evaporated *in vacuo*. The crude product was purified by column chromatography using petroleum ether as the eluent to give 0.51 g compound **1o** as a colorless solid in 38% yield. M.p. 342–343 K; anal. calcd. for $C_{23}H_{15}F_7N_2S$ (%): C, 57.02; H, 3.12; N, 5.78. Found C, 57.11; H, 3.04; N, 5.88; ^1H NMR (400 MHz, $CDCl_3$): δ 1.77 (s, 3H, $-CH_3$), 2.01 (s, 3H, $-CH_3$), 3.61 (s, 3H, $-CH_3$), 6.93 (s, 1H, pyrrole-H), 7.13 (d, 1H, J = 8.0 Hz, phenyl-H), 7.17 (s, 1H, thiophene-H), 7.26–7.29 (m, 1H, phenyl-H), 7.37 (s, 1H, phenyl-H), 7.37 (t, 1H, J = 6.8 Hz, phenyl-H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 11.3, 14.3, 33.0, 41.1, 105.6, 111.0, 112.9, 116.6, 118.8, 121.3, 124.6, 126.0, 128.3, 129.3, 135.1, 141.2, 157.8, 160.3; IR (ν, KBr, cm^{-1}): 757, 842, 896, 984, 1054, 1110, 1187, 1273, 1332, 1383, 1436, 1482, 1551, 1635, 2216, 2920.

2.2.2. Synthesis of 1-[2-methyl-5-(3-fluorophenyl)-3-thienyl]-2-(2-cyano-1,5-dimethyl-4-pyrryl)perfluorocyclopentene (**2o**)

Diarylethene **2o** was prepared by a method similar to that used for diarylethene **1o** using 3-bromo-2-methyl-5-(3-fluorophenyl)thiophene (**5b**) instead of **5a**, and was obtained as a colorless solid 0.44 g in 40% yield. M.p. 403–404 K; anal. calcd. for $C_{23}H_{15}F_7N_2S$ (%): C, 57.02; H, 3.12; N, 5.78. Found C, 57.09; H, 3.06; N, 5.87; ^1H NMR (400 MHz, $CDCl_3$): δ 1.77 (s, 3H, $-CH_3$), 1.96 (s, 3H, $-CH_3$), 3.60 (s, 3H, $-CH_3$), 6.85 (d, 1H, J = 6.8 Hz, phenyl-H), 6.92 (s, 1H, pyrrole-H), 7.06 (s, 1H, thiophene-H), 7.12 (d, 1H, J = 7.8 Hz, phenyl-H), 7.21 (s, 1H, phenyl-H), 7.28 (t, 1H, phenyl-H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 11.3, 14.5, 33.0, 55.4, 105.5, 109.9, 111.4, 112.9, 113.3, 118.1, 118.8, 122.8, 125.9, 130.1, 134.6, 135.9, 140.4, 142.3, 160.1; IR (ν, KBr, cm^{-1}): 740, 777, 842, 900, 983, 1032, 1056, 1114, 1137, 1185, 1274, 1335, 1384, 1441, 1488, 1585, 1612, 1656, 2222, 2370, 2921.

2.2.3. Synthesis of 1-[2-methyl-5-(4-fluorophenyl)-3-thienyl]-2-(2-cyano-1,5-dimethyl-4-pyrryl)perfluorocyclopentene (**3o**)

Diarylethene **3o** was prepared by a method similar to that used for diarylethene **1o** using 3-bromo-2-methyl-5-(4-fluorophenyl)thiophene (**5c**) instead of **5a**, and was obtained as a colorless solid 0.39 g in 34% yield. M.p. 434–435 K; anal. calcd. for $C_{23}H_{15}F_7N_2S$ (%): C, 57.02; H, 3.12; N, 5.78. Found C, 57.07; H, 3.08; N, 5.86; ^1H NMR (400 MHz, $CDCl_3$): δ 1.71 (s, 3H, $-CH_3$), 1.88 (s, 3H, $-CH_3$), 3.55 (s, 3H, $-CH_3$), 6.86 (s, 1H, pyrrole-H), 7.02 (t,



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

2H, $J = 8.4$ Hz, phenyl-H), 7.10 (s, 1H, thiophene-H), 7.42–7.45 (m, 2H, phenyl-H). ^{13}C NMR (400 MHz, CDCl$_3$): δ 11.3, 14.5, 77.0, 33.1, 105.5, 109.9, 112.9, 115.9, 116.1, 118.8, 122.5, 126.0, 127.3, 127.4, 129.5, 135.9, 140.3, 141.4, 161.3, 163.8; IR (ν, KBr, cm^{-1}): 741, 807, 828, 894, 987, 1056, 1095, 1183, 1231, 1275, 1335, 1397, 1469, 1513, 1548, 1623, 2221, 3123.

*2.2.4. Synthesis of 1-(2-methyl-5-phenyl-3-thienyl)-2-(2-cyano-1,5-dimethyl-4-pyrryl)perfluorocyclopentene (**4o**)*

Diarylethene **4o** was prepared by the reported method [23] using 3-bromo-2-methyl-5-phenyl-thiophene (**5d**) as raw materials, and was obtained as a yellow solid 0.47 g in 36% yield. M.p.

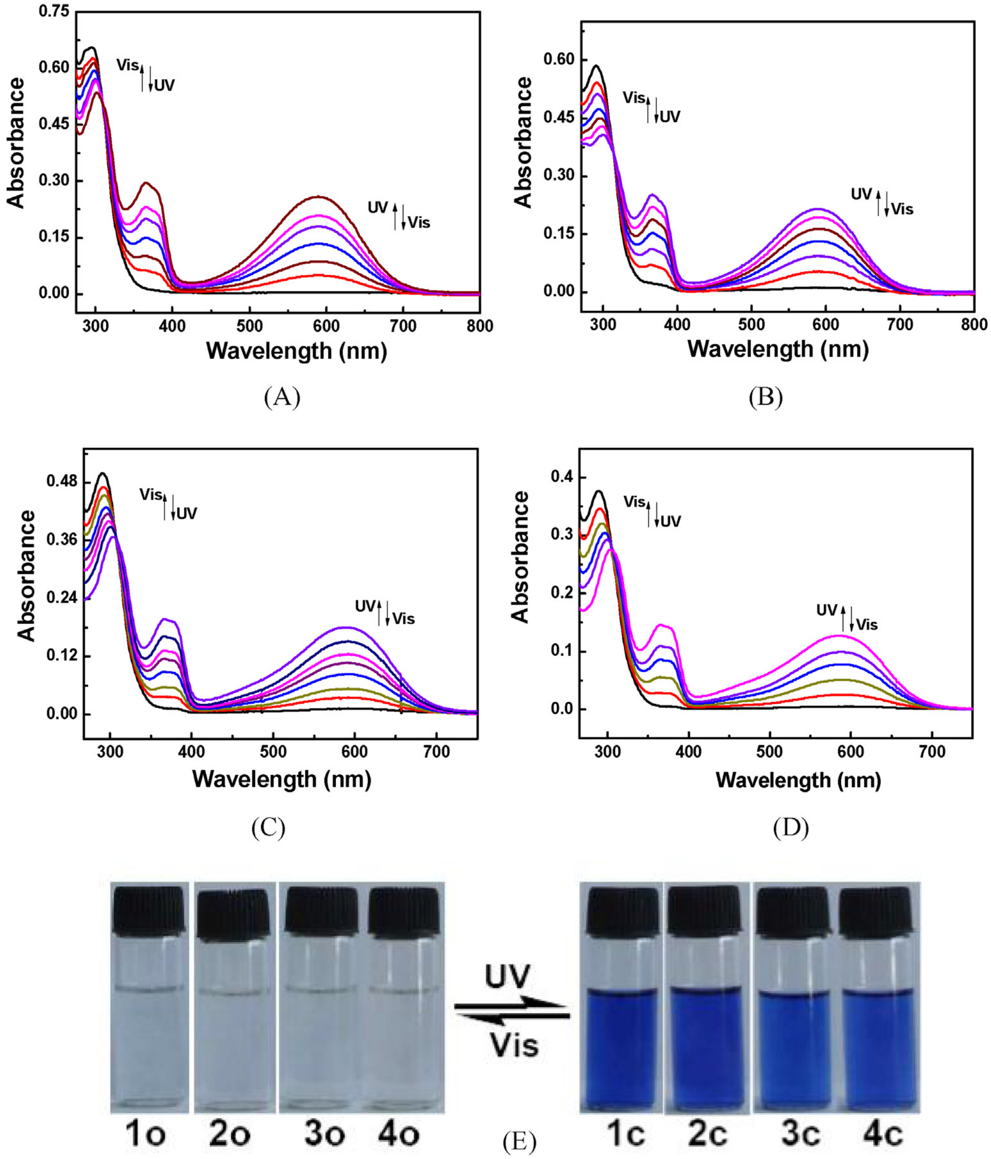


Fig. 1. Absorption spectral and color changes of diarylethenes **1**–**4** upon alternating irradiation with UV and visible light in hexane (2.0×10^{-5} mol L^{-1}) at room temperature: (A) spectral changes for **1**, (B) spectral changes for **2**, (C) spectral changes for **3**, (D) spectral changes for **4**, and (E) color changes for **1**–**4**.

413–414 K; anal. calcd. for $C_{23}H_{16}F_6N_2S$ (%): C, 59.22; H, 3.46; N, 6.01. Found C, 59.27; H, 3.51; N, 6.03; ^1H NMR (400 MHz, $CDCl_3$): δ 1.77 (s, 3H, $-CH_3$), 1.96 (s, 3H, $-CH_3$), 3.61 (s, 3H, $-CH_3$), 6.93 (s, 1H, pyrrole-H), 7.23 (s, 1H, thiophene-H), 7.39 (t, 1H, J = 8.0 Hz, benzene-H), 7.53–7.56 (m, 2H, benzene-H), 7.54 (d, 2H, J = 7.6 Hz, benzene-H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 10.7, 13.9, 32.4, 76.1, 76.4, 76.6, 76.7, 104.9, 109.4, 112.03, 125.0, 125.4, 127.4, 128.5, 132.7, 135.4, 139.7, 142.0; IR (ν, KBr, cm^{-1}): 756, 845, 987, 1097, 1183, 1277, 1334, 1385, 1548, 1624, 2221, 2372, 2920, 3125, 3450.

3. Results and discussion

3.1. Photochromic behaviors of diarylethenes

The photochromic behaviors of diarylethenes **1**–**4** induced by photoirradiation at room temperature were measured both in hexane (2.0×10^{-5} mol L^{-1}) and in PMMA amorphous films (10%, w/w). In hexane, the absorption spectral and color changes of diarylethene **1**–**4** induced by alternating irradiation with UV light and visible light with appropriate wavelength are shown in Fig. 1. Diarylethene **1o** exhibited a sharp absorption peak at 295 nm in hexane, which was arisen from $\pi \rightarrow \pi^*$ transition [34]. Upon irradiation with 297 nm light, a new visible absorption band centered at 589 nm emerged while the original peak at 295 nm decreased due to the formation of the closed-ring isomer **1c**. This could be seen with the naked eye, as the colorless solution of **1o** turned blue. Alternatively, the blue colored solution could be bleached to colorless upon irradiation with visible light ($\lambda > 450$ nm), indicating **1c** returned to the initial state **1o**. The coloration–decoloration cycle could be repeated more than 50 times and a clear isosbestic point was observed at 309 nm. As with diarylethene **1**, diarylethenes **2o**–**4o** also showed evident photochromism in hexane. Upon irradiation with 297 nm light, absorption bands in visible region appeared and the solutions containing **2o**–**4o** turned blue as a result of the cyclization reactions to produce the closed-ring isomers **2c**–**4c**, which the absorption maxima were observed at 587 nm for **2c**, 586 nm for **3c**, and 584 nm for **4c**. The blue colored solutions of **2c**–**4c** can be decolorized upon irradiation with visible light ($\lambda > 450$ nm) again because of reproducing the open-ring isomers **2o**–**4o**, respectively. In the photostationary state, the isosbestic point was observed at 335 nm for **2c**, 321 nm for **3c**, and 334 nm for **4c**. When arrived at the photostationary state, the photoconversion ratios from the open-ring to the closed-ring isomers of these derivatives were analyzed under UV irradiation in hexane by HPLC method, and the results are shown in Fig. 2. It can be easily calculated the photoconversion ratios of these diarylethene derivatives in the photostationary sate, with the value of 92% for **1**, 94% for **2**, 91% for **3**, and 90% for **4**, respectively (Table 1).

For practical applications in optical devices, it is very important that photochromic materials can keep good photochromism in a polymer film, such as the PMMA film [35]. The PMMA films were prepared by dissolving 10 mg diarylethene sample and 100 mg poly(methylmethacrylate) (PMMA) into chloroform (1.0 mL), with the aid of ultrasound, then spin coating the homogeneous solution on a quartz substrate (10 mm × 10 mm × 1 mm). The thickness of these PMMA films was determined to be *ca.* 20 μm. In PMMA amorphous films, diarylethenes **1**–**4** also showed similar photochromism as samples in solution. The absorption spectral and color changes of diarylethenes **1**–**4** are shown in Fig. 3. Compared to those in hexane, the maximum absorption peaks of both the open-ring and the closed-ring isomers of diarylethenes **1**–**4** in PMMA films are at a longer wavelength than that in hexane. The red shift values of the absorption maxima of the open-ring isomers are 16 nm for **1o**, 13 nm for **2o**, 13 nm for **3o**, and 12 nm for **4o**, and those of the closed-ring isomers are 36 nm for **1c**, 36 nm for **2c**, 23 nm for **3c**, and 23 nm for **4c**, respectively. The red shift phenomena are consistent with those of the reported diarylethenes [23,33], which may be attributed to the polar effect of the polymer matrix in the amorphous solid state [36,37].

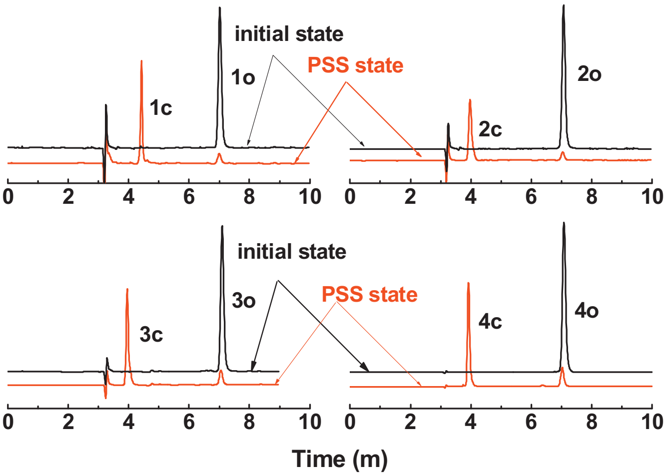


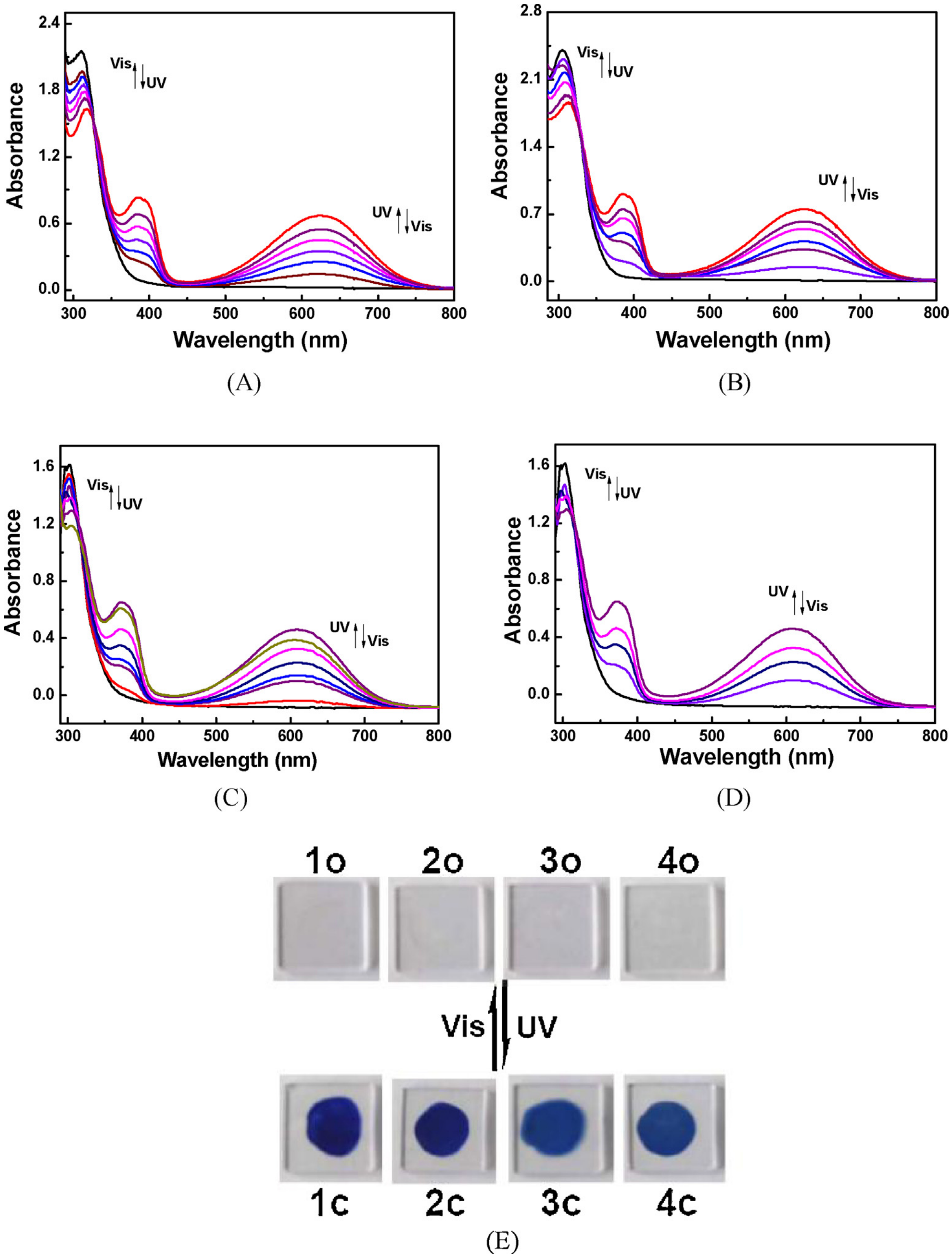
Fig. 2. The photoconversion ratios of diarylethenes **1**–**4** in hexane in the photostationary state by HPLC analysis.

The photochromic features of diarylethenes **1**–**4** in hexane and in PMMA films are summarized in Table 1. The results showed that the fluorine atom position had a significant effect on the photochromic properties of these diarylethene derivatives, including the absorption maxima, molar absorption coefficients, photoconversion ratios, and quantum yields of cyclization and cycloreversion. Among these derivatives, the unsubstituted parent diarylethene **4** had the smallest absorption maxima, quantum yields of cyclization and cycloreversion, as well as the photoconversion ratio. When introduction of the electron-withdrawing fluorine atom into any position of the terminal benzene ring, the values of these photochromic parameters of diarylethenes **1**–**3** clearly increased. The result is in good agreement with that of the reported diarylethenes bearing a methoxy group [23]. For isomeric diarylethenes **1**–**3**, the absorption maxima and molar absorption coefficients of both the open-ring and the closed-ring isomers varied with the same trend, *i.e.*, they decreased in the order of *ortho*- > *meta*- > *para*-substituent by the fluorine atom. Therefore, the absorption maxima and molar absorption coefficients of the *ortho*-substituted derivative **1** are the biggest; while those of the *para*-substituted derivative **3** are the smallest. The result is quite different from that of diarylethenes bearing a methoxy group, where the absorption maxima and molar absorption coefficients of the *meta*-substituted derivative are the smallest [23]. Furthermore, the cyclization quantum yields and the photoconversion ratios of these isomeric compounds varied with the same trend, *i.e.*, they decreased in the order of *meta*- > *ortho*- > *para*-substituent by the fluorine atom. However, the cycloreversion quantum yields showed a reverse changing trend, and they increased in the order of *meta*- < *ortho*- < *para*-substituent by the fluorine atom. Consequently, the *meta*-substituted derivative **2** had the biggest cyclization quantum yield and the smallest cycloreversion quantum yield, while the *para*-substituted derivative **3** had the smallest cyclization quantum yield and the biggest cycloreversion quantum yield. This varying pattern is different from those of isomeric diarylethenes reported previously [18,23]. In addition, for diarylethenes **1**–**4**, all of the cyclization quantum yields were higher than their respective cycloreversion quantum yields (Table 1), which is consistent with isomeric diarylethenes reported previously [23,33]. The results indicated that the categories of heteroaryl moieties and substituents greatly influenced

Table 1
Absorption spectral properties of diarylethenes **1**–**4** in hexane (2.0×10^{-5} mol L^{-1}) and in PMMA films (10 %, w/w) at room temperature.

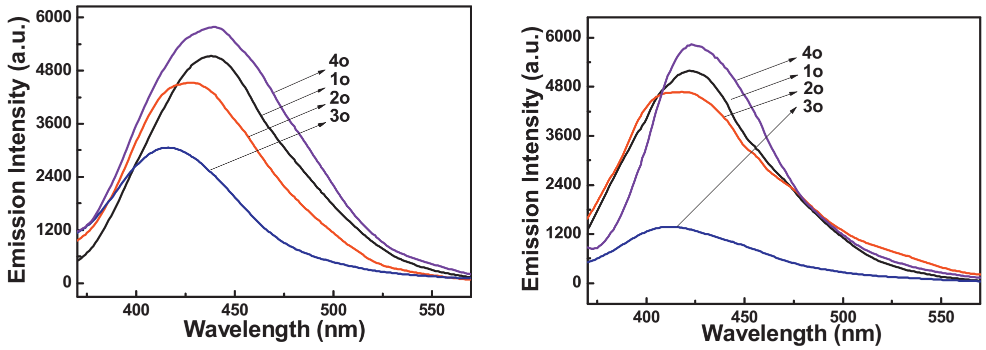
Compound	$\lambda_{o,max}$/nm[a] (ε/L mol^{-1} cm^{-1})		$\lambda_{c,max}$/nm[b] (ε/L mol^{-1} cm^{-1})		Φ[c]		Photoconversion ratios at PSS
	Hexane	PMMA film	Hexane	PMMA film	Φ_{o-c}	Φ_{c-o}	
1	295 (3.29×10^4)	311	589 (1.41×10^4)	625	0.33	0.072	92%
2	291 (2.93×10^4)	304	587 (1.15×10^4)	623	0.40	0.067	94%
3	290 (2.11×10^4)	303	586 (7.19×10^3)	609	0.26	0.098	91%
4	290 (2.49×10^4)	302	584 (1.00×10^4)	607	0.20	0.054	90%

[a] Absorption maxima of open-ring isomers.
[b] Absorption maxima of closed-ring isomers.
[c] Quantum yields of cyclization reaction (Φ_{o-c}) and cycloreversion reaction (Φ_{c-o}), respectively.



(A) (B) (C) (D) (E)

Fig. 3. Absorption spectral and color changes of diarylethenes **1**–**4** upon alternating irradiation with UV and visible light in PMMA films (10%, w/w) at room temperature: (A) spectral changes for **1**, (B) spectral changes for **2**, (C) spectral changes for **3**, (D) spectral changes for **4**, and (E) color changes for **1**–**4**.



(A) (B)

Fig. 4. Emission spectra of diarylethenes **1**–**4** in hexane (5.0×10^{-5} mol L^{-1}) and in PMMA films (10%, w/w) at room temperature: (A) emission spectra in hexane, excited at 340 nm; (B) emission spectra in PMMA films, excited at 350 nm.

the optoelectronic properties of diarylethenes. For example, when replacing the pyrrole moiety with the thiophene moiety in the same molecular skeleton of photochromic diarylethenes, the photochromic parameters including the absorption maxima, molar absorption coefficients, and the cycloreversion quantum yields decreased, but the cyclization quantum yields increased evidently [18]. When replacing the fluorine atom with the methoxy group in the same molecular skeleton, the absorption maxima and the cycloreversion quantum yields increased significantly [10].

The thermal stabilities of the open-ring and the closed-ring isomers of **1**–**4** were tested in hexane both at room temperature and at 342 K. Storing these solutions in hexane in the dark and then exposing them to air both at room temperature and at 342 K for more than 72 h, no changes in their UV/vis spectra were observed, suggesting that no decomposition was detected. The result indicates that these unsymmetrical diarylethenes bearing a pyrrole unit are thermal stable.

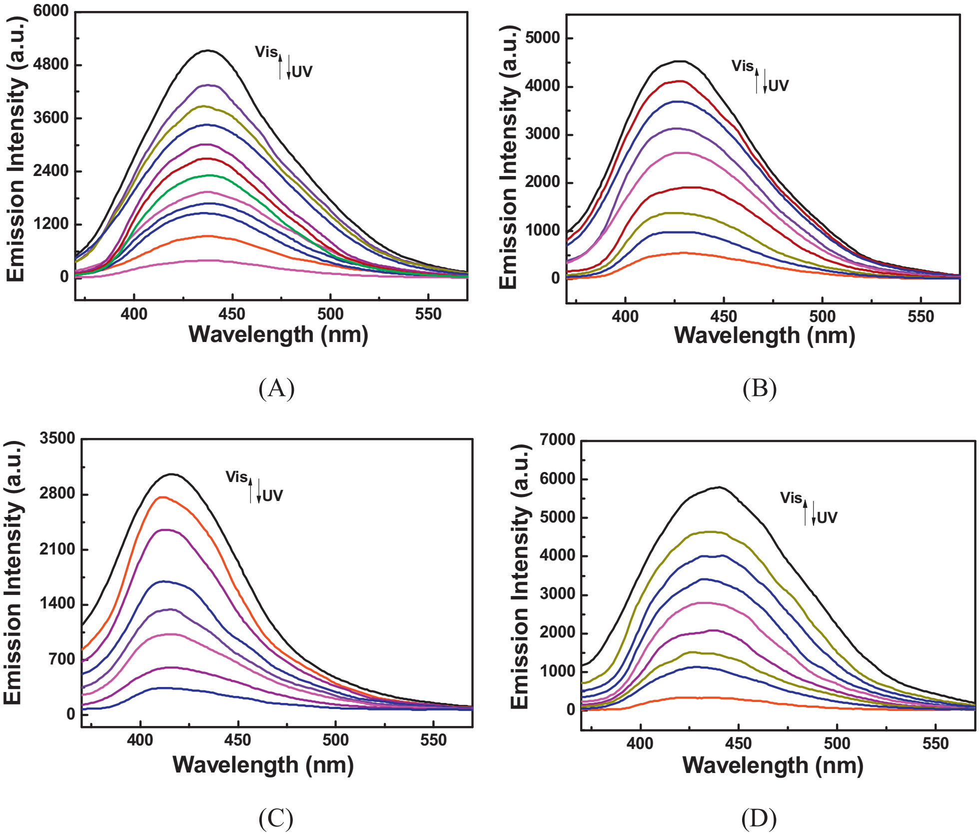
3.2. Fluorescence of diarylethenes

Fluorescent properties can be useful in molecular-scale optoelectronics and digital photoswitching of fluorescence [38–40]. The fluorescence modulation is a particularly intriguing approach due to the stabilization of diarylethene and versatility in materials selection [41]. In this work, the fluorescence properties of the four diarylethenes in hexane and in PMMA films were measured at room temperature. The fluorescence emission spectra of diarylethenes **1o**–**4o** in hexane (5.0×10^{-5} mol L^{-1}) and in PMMA films (10%, w/w) at room temperature are illustrated in Fig. 4, and the data are listed in Table 2. In hexane, the emission peaks of diarylethenes **1o**–**4o** were observed at 437, 426, 414, and 440 nm when excited at 340 nm, and were observed at 422, 416, 409, and 423 nm when monitored at 350 nm in PMMA films. Compared to samples in hexane, the emission peaks of diarylethenes **1o**–**4o** in PMMA films consistently exhibit a hypsochromic shift with the value of 15 nm for **1o**, 10 nm for **2o**, 5 nm for **3o**, and 17 nm for **4o**. This is completely contrary to those of the reported diarylethenes whose emission peaks in PMMA films are much longer than those in solution [18,42]. For the isomeric diarylethenes **1**–**3**, the emission peak and emission intensity varied with the same trend in both hexane and PMMA films, *i.e.*, they decreased in the order of *ortho*- > *meta*- > *para*-substituent by the fluorine atom. The result is in good agreement with that of the reported diarylethenes bearing a methoxy group [23]. However, it is quite different from that of diarylethenes bearing a thiophene moiety [18]. Compared to isomeric diarylethenes **1o**–**3o**, the unsubstituted parent diarylethene **4o** showed the biggest emission peak and the strongest emission intensity in both hexane and a PMMA film. The results indicated that the fluorine atom could be effective to decrease the emission intensity and shift the emission peak to a shorter wavelength direction, which may be attributed to the steric hindrance of the fluorine group and its electron-withdrawing nature. By using anthracene (0.27 in acetonitrile) as the reference, the fluorescence quantum yields of diarylethenes **1o**–**4o** were determined to be 0.033, 0.030, 0.028, and 0.010, respectively. The result indicated that introduction of electron-withdrawing fluorine group into any position of the terminal benzene ring could improve significantly the fluorescence quantum yields of the diarylethene derivatives.

Table 2
The fluorescent emission behaviors of diarylethenes **1**–**4** at room temperature in hexane (5.0×10^{-5} mol L^{-1}) and in PMMA films (10%, w/w).

Compound	$\lambda_{em,max}$ (emission intensity)		Fluorescent modulation efficiency (%)	
	Hexane	PMMA film	Hexane	PMMA film
1	437 (5127)	422 (5192)	92	91
2	426 (4524)	416 (4672)	88	79
3	414 (3057)	409 (1372)	90	74
4	440 (5779)	423 (5836)	93	83

As has been observed for most of the reported diarylethenes [18,22,23], diarylethenes **1**–**4** exhibited a notable fluorescent switch on changing from the open-ring to the closed-ring isomers. When irradiated by UV light, the photocyclization occurred and the fluorescence of diarylethenes **1o**–**4o** greatly quenched due to producing the non-fluorescence closed-ring isomers **1c**–**4c**. The back irradiation by appropriate wavelength visible light regenerated their respective open-ring isomers and recovered the original emission spectra. During the process of photoisomerization, the emission spectral changes of diarylethene **1**–**4** in hexane (5.0×10^{-5} mol L^{-1}) and in PMMA films (10%, w/w) are shown in Figs. 5 and 6, respectively. The intensity of the fluorescence decreased to 8% in hexane and 9% in a PMMA film of initial value by UV irradiation and recovered to the initial intensity upon visible light irradiation. Therefore, the fluorescent modulation efficiency of diarylethene **1** was 92% in hexane and 91% in PMMA film. Just like diarylethene **1**, the fluorescent modulation efficiencies of diarylethenes **2**–**4** were 88% for **2**, 90% for **3**, and 93% for **4** in hexane, and were 79% for **2**, 74% for **3**, and 83% for **4** in PMMA films when arrived at the photostationary state. For diarylethenes **1**–**4**, their fluorescent modulation efficiencies in hexane were much bigger than those in PMMA films. Compared with diarylethenes bearing two thiophene moieties [18,42,43], the fluorescent modulation efficiencies of diarylethenes **1**–**4** were significantly enhanced in both hexane and PMMA films. Therefore, diarylethenes bearing a



(A) (B) (C) (D)

Fig. 5. Emission intensity changes of diarylethenes **1**–**4** upon irradiation with 297 nm UV light at room temperature in hexane (5.0×10^{-5} mol L^{-1}), excited at 340 nm: (A) **1**, (B) **2**, (C) **3**, and (D) **4**.

pyrrole unit have one of the most promising candidates for fluorescent switching materials [44–48].

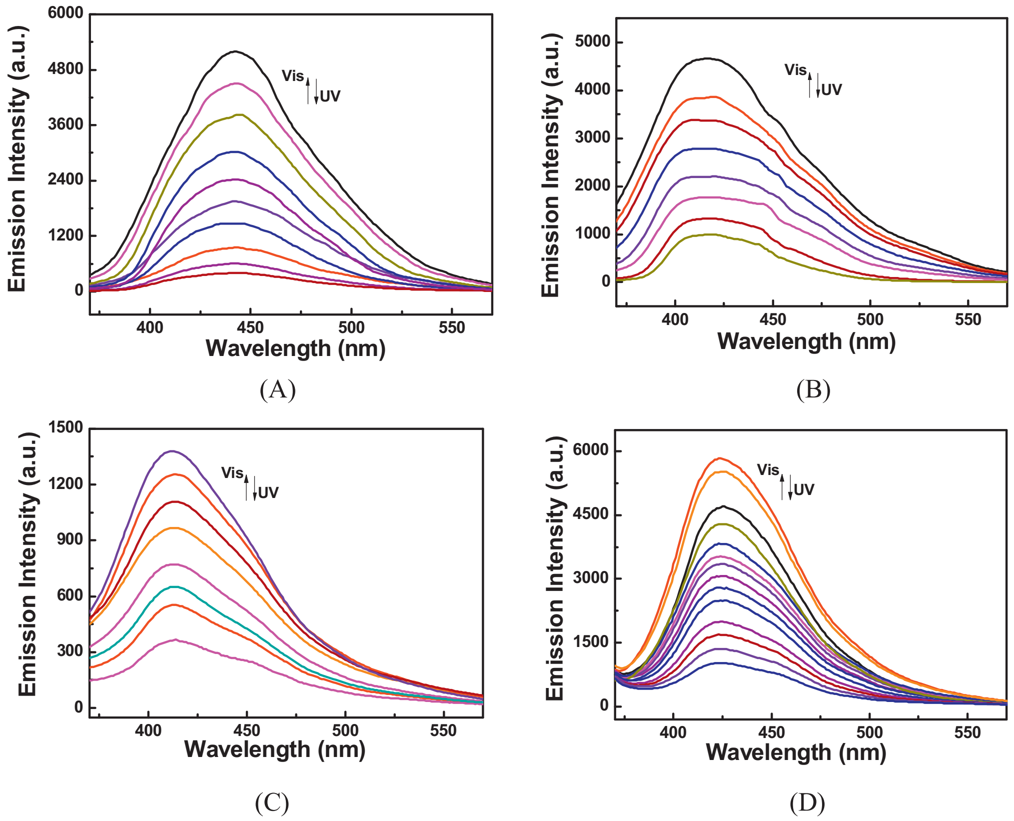
3.3. Electrochemistry of diarylethenes

The electrochemical properties of diarylethenes can be potentially applied to molecular scale electronic switches [49]. The oxidative cyclization and cycloreversion and the reductive electrochemical cyclization of some diarylethene derivatives have been reported [50–52]. Herein, cyclic voltammograms (CV) were performed on the diarylethenes **1**–**4** under identical experimental conditions at a scanning rate of 50 mV s^{-1}. The CV curves of diarylethenes **1**–**4** are shown in Fig. 7. The oxidation onsets of **1o**–**4o** were observed at +1.47, +154, +1.52, and +1.63 V, and those of **1c**–**4c** were observed at +0.61, +0.70, +0.67, and +0.72 V, respectively. Therefore, the difference of oxidation onset between the open-ring and the closed-ring isomers of diarylethenes **1**–**4** (ΔV_{o-c}) was 0.86 V for **1**, 0.84 V for **2**, 0.85 V for **3**, and 0.91 V for **4**. The result indicated that the oxidation process of the open-ring isomers **1o**–**4o** occurs at higher potentials than that of the corresponding closed-ring isomers **1c**–**4c**. This is in accordance with the theory that the longer conjugation length generally leads to a less positive potential [46,53]. After the cyclization reaction, the π-conjugation of the closed-ring isomers extends across the perfluorocyclopentene ring causing a lower oxidation onset. Compared to isomeric diarylethenes **1**–**3**, the unsubstituted parent diarylethene **4o** showed the biggest oxidation onsets both for the open-ring and the closed-ring isomers. The oxidation onsets of diarylethenes **1**–**3** notably decreased when the fluorine group was attached at any of the three positions on the terminal benzene ring.

Table 3
Electrochemical properties of diarylethenes **1**–**4** in acetonitrile.

Compound	Oxidation		Reduction		Band gap (E_g)
	E_{onset} (V)	IP (eV)	E_{onset} (V)	EA (eV)	
1o	1.47	−6.27	−1.04	−3.76	2.54
1c	0.61	−5.41	−0.88	−3.92	1.49
2o	1.54	−6.34	−1.05	−3.75	2.59
2c	0.70	−5.50	−0.91	−3.89	1.61
3o	1.52	−6.32	−1.04	−3.76	2.56
3c	0.67	−5.47	−0.75	−4.05	1.42
4o	1.63	−6.43	−0.97	−3.83	2.60
4c	0.72	−5.52	−0.63	−4.17	1.35

According to the reported method [54–56], the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO) energy levels can be estimated by using the energy level of ferrocene as reference. Based on the HOMO and LUMO energy level, the band-gap (E_g) of each compound can be calculated approximately and the data are summarized in Table 3. The result showed that the band-gaps of the closed-ring isomers **1c**–**4c** are much lower than those of the open-ring isomers **1o**–**4o**. Among these compounds, the E_g of **4o** is the highest (E_g = 2.60 eV) and that of **4c** is the lowest (E_g = 1.35 eV), implying that the charge transfer must be faster in **4c** compared to that in others [52]. Compared with the unsubstituted parent diarylethene **4**, the band-gaps of the open-ring isomers **1o**–**3o** decreased, and those of the closed-ring isomers **1c**–**3c** increased significantly. The results indicated that the fluorine atom and its substituted position had a great effect on the electrochemical properties of these diarylethene compounds but further work is required to quantify these effects. It should be noted here that calculation absolute HOMO and LUMO levels from



(A) (B)

(C) (D)

Fig. 6. Emission intensity changes of diarylethenes **1**–**4** upon irradiation with 297 nm UV light at room temperature in PMMA films (10%, w/w), excited at 350 nm: (A) **1**, (B) **2**, (C) **3**, and (D) **4**.

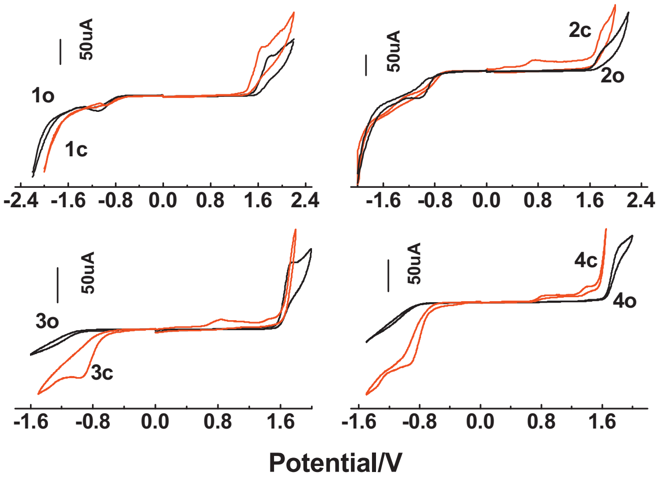


Fig. 7. Cyclic voltammetry (second scan) of diarylethene **1**–**4** in acetonitrile with the scanning rate of 50 mV s^{-1}.

electrochemical data in combination with the energy gap is still in debate [56].

4. Conclusions

In conclusion, four unsymmetrical diarylethenes based on the hybrid skeleton of thiophene and pyrrole moieties were synthesized in order to investigate the effects of the fluorine substituent position on their optical and electrochemical properties. The results showed that electron-withdrawing fluorine atom and its substituted position had a significant effect on the photochemical properties. In comparison of the unsubstituted parent diarylethene **4**, the absorption maxima, quantum yields of cyclization and cycloreversion, and band-gaps of the closed-ring isomers of these isomeric diarylethenes increased whereas their emission intensity and the band-gaps of the open-ring isomers decreased remarkably. The introduction of the pyrrole moiety induced new features which differed from those of diarylethenes bearing thiophene or pyrazole moieties. The results in this study will be useful for understanding the substituent position effect on the properties of diarylethenes bearing a pyrrole moiety and for the design of efficient photoactive isomeric diarylethene derivatives with tunable properties.

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