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# The effect of the cyano group position upon unsymmetrical isomeric diarylethenes bearing a pyrrole unit

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ABSTRACT

Four photochromic diarylethenes bearing a pyrrole moiety were synthesized, and the structures of two of the new isomeric compounds were determined by single-crystal X-ray diffraction analysis. Each of the diarylethene derivatives exhibited good photochromism both in solution and in poly(methyl methacrylate) films, which their photoconversion ratios from open-ring to closed-ring isomers were larger than 89% in hexane at photostationary state. They also functioned as effective fluorescent photoswitches both in hexane and in poly(methyl methacrylate) films. The absorption maxima, cyclization/cycloreversion quantum yields, and fluorescence quantum yields increased whereas the molar absorption coefficients and the emission peaks decreased notably when the cyano group was attached at any of the three positions on the terminal benzene ring. Cyclic voltammograms indicated that the introduction of cyano group decreased the band-gap of the open-ring isomer and increased that of the closed-ring isomer. The cyano group and its -substituted position can availably modulate the optical and electrochemical behaviours of these diarylethene derivatives.

## 1. Introduction

Photochromic molecules attract much attention from fundamental as well as practical points of view because of their potential for applications to optical devices, such as optical memories and switches [1–3]. Among the photochromic compounds, diarylethenes are regarded as the best candidates for such devices, owing to its excellent thermal stability, fatigue resistance, and easy monitoring using UV–vis spectroscopy [4,5]. As components of molecular electronics, it is desirable to develop various types of molecular switch devices with diarylethene compounds. During the past decades, there have been important achievements in the synthesis of new families of organic photochromic molecules [3,6,7].

Generally, most of the diarylethene derivatives show very large spectral shifts upon photoisomerization from the open-ring to closed-ring isomers [1]. The open-ring isomer is colourless in most cases, while the closed-ring isomer shows some colours such as yellow, red, or blue. The open-ring and closed-ring isomers differ from each other not only in their absorption but also in various physical and chemical properties such as $\pi$-conjugation length [8], refractive indices [9,10], geometrical structures [11,12], and chiral properties [13,14]. The photochromic characteristics of diarylethenes strongly depend on the kind of the heteroaryl moieties and the electron donor/acceptor substituents. The nature of the heteroaryl moieties greatly influences the photo-reactivity and the distinguishable features of diarylethenes. For instance, diarylethenes with thiophene or benzothiophene moieties exhibit excellent thermal stability [1,5,15], whereas symmetrical diarylethene bearing pyrrole groups is thermally unstable and returns to the open-ring isomers even in the dark [16]. Moreover, diarylethenes with benzofuran moieties have outstanding fatigue resistance and small photoconversion ratio [17], whereas diarylethenes bearing both thiazole and benzene moieties have relatively weak fatigue resistance [18]. For the diarylethene derivatives reported, most of the heteroaryl moieties have been thiophene or benzothiophene rings, with just a few reports on other heteroaryl moieties such as thiazole [19,20], oxazole [21], indole [22,23], and so on. Pyrrole is an attractive aryl unit due to its biological characteristics and has been applied in biosensors widely [24,25]. However, diarylethene derivatives with a pyrrole unit hitherto reported is very rare. Uchida et al. [16] reported a symmetrical diarylethene bearing two pyrrole groups that showed thermally unstable and reverted to the open-ring form even at room temperature in the dark. In a previous paper, we synthesized two isomeric hybrid diarylethenes bearing both pyrrole and thiophene moieties and investigated their photochromic features, indicating that the hybrid diarylethenes had good thermal stability and fatigue resistance in the solid medium [26]. On the other hand, electron

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donor/acceptor substituents and their substitution positions have also a significant effect on the photochromic properties of diarylethene derivatives [27,28], which can be used for the fine tuning of the optoelectronic properties of diarylethene compounds. 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 maxima absorption of the open-ring isomers and reduce the cyclization quantum yield [31]. In addition, Morimitsu et al. revealed that bulky alkoxy substituents at 2- and 2′-position of thiophene rings could extraordinarily decrease the cycloreversion quantum yield and the thermal stability of the colored closed-ring isomer at high temperature [32].

Although there are many reports concerning the substituent effects on the properties of diarylethenes, studies on the substituent position effect are extremely rare. Previously, we reported the electron-withdrawing cyano group position effect not only on the properties of unsymmetrical dithienylethenes with thiophene moieties [33], but also on those of symmetrical dithienylethenes [34]. Similarly, we also studied the electron-donating methoxy substituent position effect on the properties of different diarylethene systems [35–39]. The results revealed that the substituent position had a significant effect on the properties of these diarylethene compounds, and there existed a notable difference in the substituent position effect of the same functional group for different photochromic diarylethene systems. In this work, we have synthesized four hybrid photochromic diarylethenes bearing both pyrrole and thiophene moieties (**1o**–**4o**) in order to better understand the cyano substituent position effect on the properties of these compounds. The synthesized diarylethenes are 1-(2-cyano-1,5-dimethyl-4-pyrryl)-2-[2-methyl-5-phenyl-3-thienyl]perfluorocyclopentene (**1o**), 1-(2-cyano-1,5-dimethyl-4-pyrryl)-2-[2-methyl-5-(2-cyanophenyl)-3-thienyl]perfluorocyclopentene (**2o**), 1-(2-cyano-1,5-dimethyl-4-pyrryl)-2-[2-methyl-5-(3-cyanophenyl)-3-thienyl]perfluorocyclopentene (**3o**), and 1-(2-cyano-1,5-dimethyl-4-pyrryl)-2-[2-methyl-5-(4-cyanophenyl)-3-thienyl]perfluoro cyclopentene (**4o**) of which, **2o**, **3o** and **4o** are new compounds. Although diarylethene **1o** has been reported previously [37], it is presented here for comparison with those of other three diarylethene compounds. All of these diarylethenes showed good photochromism both in solution and in poly(methyl methacrylate) (PMMA) amorphous films. The photochromic scheme of diarylethenes **1o**–**4o** is shown in Fig. 1.

## 2. Experimental

### 2.1. General

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 open-ring to closed-ring isomers at photostationary state were measured using an Agilent 1100 HPLC chromatographic analyzer. Fluorescence spectra were measured using a Hitachi F-4500 fluorimeter. Photo-irradiation was carried out using a SHG-200 UV lamp, 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 tetrabutylammonium tetrafluoroborate ($(TBA)BF_4$) and $1.0 \times 10^{-3}$ mol/L dithienylethene 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. The PMMA films were prepared by dissolving 10 mg sample of each diarylethene **1**–**4** and 100 mg of poly (methyl methacrylate) into 1.0 mL chloroform with aid of ultrasound, then spin coating the homogeneous solution on a quartz substrate (20 mm × 20 mm × 1 mm) at 1500 rpm.

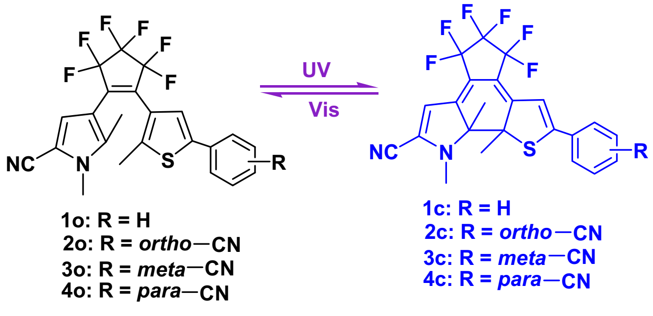


**Fig. 1.** Photochromism of diarylethenes **1**–**4**.

Suitable crystals of **2o** and **3o** were obtained by slow evaporation of a hexane solution. All the measurements were made on a Bruker SMART APEX II CCD diffractometer using a MULTI scan technique using Mo Kα radiation. The structures were solved by direct methods and refined by full-matrix least-squares procedures on $F^2$ by full-matrix least-squares techniques using SHELXTL-97 program. All non-hydrogen atoms were refined anisotropically. Crystallographic data for the structures of the two diarylethenes in this paper have been deposited in the Cambridge Crystallographic Data Centre as supplemental publication CCDC 764125 for **2o** and CCDC 764126 for **3o**. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 0 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

### 2.2. Synthesis

The synthesis method of diarylethenes **1o**–**4o** was shown in Fig. 2. Suzuki coupling of the four bromobenzene derivatives with a thiophene boronic acid [27] gave the alkylphenylthiophene derivatives (**5a**–**d**) [24,28]. 1-(2-cyano-1,5-dimethyl-4-pyrryl)perfluorocyclopentene (**6**) [17] was synthesized by bromination and lithiation reactions from 5-cyano-1,2-dimethylpyrrole. Finally, compounds **5a**–**d** were separately lithiated and then coupled with compound **6** to give diarylethenes **1o**–**4o**, respectively.

#### 2.2.1. 1-(2-Cyano-1,5-dimethyl-4-pyrryl)-2-[2-methyl-5-phenyl-3-thienyl]perfluorocyclopentene (*1o*)

To a stirred anhydrous THF (80 mL) of compound **5a** (0.54 g, 2.12 mmol) [24] was added dropwise a 2.5 M *n*-BuLi/hexane solution (0.95 mL, 2.38 mmol) at −78 °C under argon atmosphere. After 30 min, 15 mL THF containing compound **6** (0.66 g, 2.30 mmol) [17] 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 0.35 g

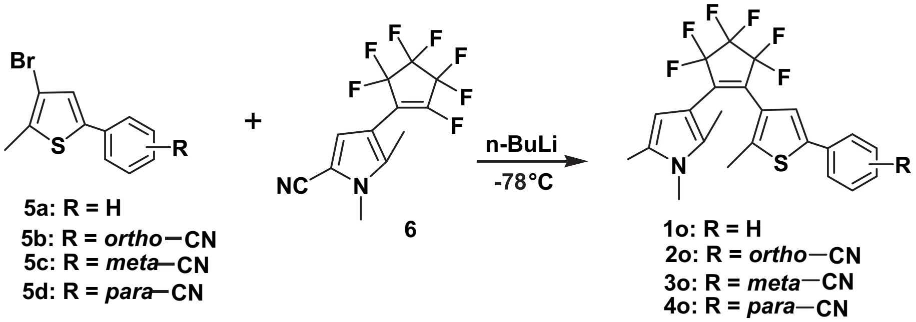
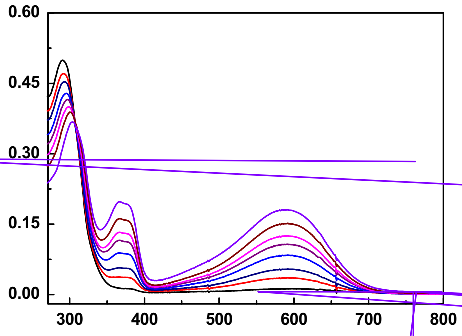


**Fig. 2.** Synthetic route for diarylethenes **1**–**4**.

compound **1o** as a colourless solid in 36% yield. M.p. 140.2–141.2 °C; 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, $CDCl_3$): $\delta$ 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, $CDCl_3$): $\delta$ 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 ($\nu$, KBr, $cm^{-1}$): 756, 845, 987, 1097, 1183, 1277, 1334, 1385, 1548, 1624, 2221, 2372, 2920, 3125, 3450.

### 2.2.2. *Synthesis of diarylethenes **2o**–**4o***

Diarylethenes **2o**–**4o** were prepared by an analogous method similar to that used for diarylethene **1o**. Compound **2o**: colorless solid, yield: 52%; M.p. 137.3–138.5 °C; Anal. Calcd for $C_{24}H_{15}F_6N_3S$ (%): C, 58.65; H, 3.08; N, 8.55. Found C, 58.71; H, 3.03; N, 8.49; $^1H$



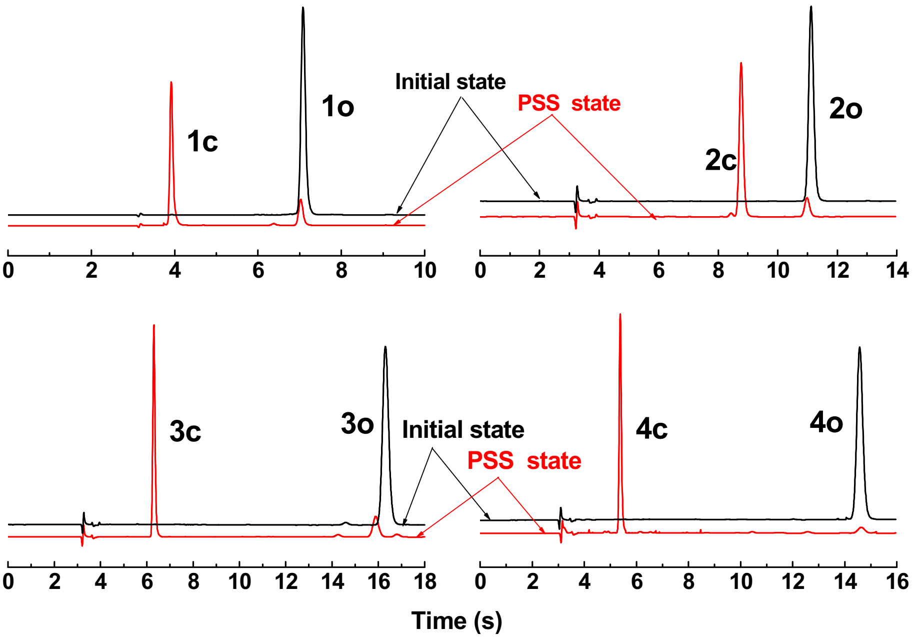


**Fig. 4.** The photoconversion ratios of diarylethenes **1**–**4** at photostationary state in hexane by HPLC method.

NMR (400 MHz, CDCl$_3$): $\delta$ 1.83 (s, 3H, –CH$_3$), 2.10 (s, 3H, –CH$_3$), 3.63 (s, 3H, –CH$_3$), 6.98 (s, 1H, pyrrole-H), 7.41 (s, 1H, thiophene-H), 7.47 (t, 1H, $J$ = 7.6 Hz, phenyl-H), 7.57 (d, 1H, $J$ = 7.8 Hz, phenyl-H), 7.63 (t, 1H, $J$ = 7.2 Hz, phenyl-H), 7.76 (d, 1H, $J$ = 7.8 Hz, phenyl-H). $^{13}$C NMR (400 MHz, CDCl$_3$): $\delta$ 12.9, 15.8, 34.5, 107.1, 110.9, 112.1, 114.3, 119.6, 120.1, 127.7, 129.3, 129.6, 131.1, 134.4, 135.5, 137.7, 138.1, 138.7, 144.2; IR ($\nu$, KBr, cm$^{-1}$): 545, 578, 632, 655, 685, 763, 823, 835, 851, 895, 983, 1056, 1116, 1187, 1274, 1332, 1385, 1438, 1492, 1553, 1595, 1633, 2222. Compound **3o**: colorless solid, yield: 44%; M.p. 183.6–184.4 °C; Anal. Calcd for $C_{24}H_{15}F_6N_3S$ (%): C, 58.65; H, 3.08; N, 8.55. Found C, 58.71; H, 3.02; N, 8.62; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 1.80 (s, 3H, –CH$_3$), 2.00 (s, 3H, –CH$_3$), 3.64 (s, 3H, –CH$_3$), 6.93 (s, 1H, pyrrole-H), 7.32 (s, 1H, thiophene-H), 7.54 (t, 1H, $J$ = 8.0 Hz, phenyl-H), 7.60 (d, 1H, $J$ = 7.8 Hz, phenyl-H), 7.78 (d, 1H, $J$ = 7.8 Hz, phenyl-H), 7.83 (s, 1H, phenyl-H). $^{13}$C NMR (400 MHz, CDCl$_3$): $\delta$ 12.8, 15.9, 34.4, 107.2, 111.3, 114.1, 114.9, 119.6, 120.2, 125.5, 127.9, 130.4, 131.0, 131.3, 132.5, 135.9, 137.2, 141.2, 143.3; IR ($\nu$, KBr, cm$^{-1}$): 454, 545, 619, 633, 649, 679, 705, 740, 754, 793, 840, 850, 893, 981, 1057, 1111, 1137, 1194, 1274, 1336, 1384, 1397, 1431, 1459, 1490, 1581, 1599, 1639, 2219. Compound **4o**: yellow solid, yield: 38%; M.p. 180.1–181.1 °C; Anal. Calcd for $C_{24}H_{15}F_6N_3S$ (%): C, 58.65; H, 3.08; N, 8.55. Found C, 58.69; H, 3.05; N, 8.48; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 1.81 (s, 3H, –CH$_3$), 2.00 (s, 3H, –CH$_3$), 3.62 (s, 3H, –CH$_3$), 6.90 (s, 1H, pyrrole-H), 7.35 (s, 1H, thiophene-H), 7.42–7.45 (m, 4H, phenyl-H); $^{13}$C NMR (400 MHz, CDCl$_3$): $\delta$ 11.4, 14.6, 33.0, 105.8, 109.8, 111.3, 112.7, 118.5, 118.8, 124.7, 125.8, 126.7, 132.9, 135.8, 137.4, 140.2, 142.6; IR ($\nu$, KBr, cm$^{-1}$): 503, 744, 824, 897, 980, 1057, 1119, 1194, 1269, 1333, 1436, 1552, 1606, 2219.

## 3. Results and discussion

### 3.1. Photochromic behaviours of diarylethenes

The photochromic behaviour of diarylethenes **1**–**4** induced by photoirradiation at room temperature was measured both in hexane ($2.0 \times 10^{-5}$ mol/L) 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. 3. Diarylethene **1o** exhibited a sharp absorption peak at 290 nm in hexane, which was arisen from $\pi \rightarrow \pi^*$ transition [40]. Upon irradiation with 297 nm light, a new visible absorption band centered at 584 nm emerged while the original peak at 290 nm decreased, indicating the formation of the closed-ring isomer **1c**. This could be seen with the naked eye, as the colorless solution of **1o** turned blue. Similarly, the blue colored solution could be bleached to colorless upon irradiation with visible light ($\lambda$ >450 nm), indicating **1c** was returning to the initial state **1o**. The coloration–decoloration cycle could be repeated more than 50 times and a clear isosbestic point was observed at 308 nm. Just like diarylethene **1**, diarylethenes **2o**–**4o** also showed excellent photochromism in hexane. In the photostationary state, the isosbestic points for diarylethenes **2**, **3** and **4** were observed at 335, 321 and 334 nm, respectively. When arrived at the photostationary state, the photoconversion ratios from open-ring to closed-ring isomers of the four derivatives were analyzed under UV irradiation in hexane solution by HPLC, and the results are shown in Fig. 4. From this

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

| Compound | $\lambda_{o,max}$/nm[a] ($\varepsilon$/L mol$^{-1}$ cm$^{-1}$) | | $\lambda_{c,max}$/nm[b] ($\varepsilon$/L mol$^{-1}$ cm$^{-1}$) | | $\Phi$[c] | | Conversion at PSS in hexane |
|---|---|---|---|---|---|---|---|
| | hexane | PMMA film | hexane | PMMA film | $\Phi_{o-c}$ | $\Phi_{c-o}$ | |
| **1** | 290 ($2.49 \times 10^4$) | 302 | 584 ($1.00 \times 10^4$) | 607 | 0.20 | 0.054 | 90% |
| **2** | 292 ($1.44 \times 10^4$) | 306 | 590 ($7.92 \times 10^3$) | 611 | 0.27 | 0.078 | 89% |
| **3** | 295 ($7.34 \times 10^3$) | 312 | 592 ($2.88 \times 10^3$) | 611 | 0.36 | 0.15 | 91% |
| **4** | 312 ($8.82 \times 10^3$) | 319 | 603 ($3.32 \times 10^3$) | 622 | 0.41 | 0.20 | 96% |

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

figure, it can be easily calculated the photoconversion ratios of diarylethenes **1**–**4** in the photostationary state, which their values are 90% for **1**, 89% for **2**, 91% for **3**, and 96% for **4** (Table 1).

The photochromic features of these compounds are summarized in Table 1. The results showed that the cyano substituent position had a significant effect on the photochromic properties of these diarylethene derivatives, including the absorption maxima, molar absorption coefficients, and quantum yields of cyclization and cycloreversion. Among these diarylethene derivatives, the unsubstituted parent diarylethene **1** has the smallest absorption maxima and quantum yields of cyclization and cycloreversion, but it has the biggest molar absorption coefficients of both the ring-opened and ring-closed isomers. When introduction of the electron-withdrawing cyano group into any position of the terminal benzene ring, the absorption maxima and the quantum yields of diarylethenes **2**–**4** increased to some extent, whereas their molar absorption coefficients showed a reverse trend. For isomeric diarylethenes **2**–**4**, the absorption maxima and the quantum yields of both the open-ring isomers and the closed-ring isomers varied with the same trend, *i.e.*, they increased in the order of *ortho*- < *meta*- < *para*-substituent by the cyano group. Therefore, both the absorption maxima and the quantum yields of cyclization and cycloreversion of the *para*-substituted derivative **4** are the biggest; while those of the *ortho*-substituted derivative **2** are the smallest. The values of the *meta*-substituted derivative **3** are in between those of the *para* and *ortho*-substituted derivatives. However, the molar absorption coefficients of diarylethenes **2**–**4** showed a different changing trend, compared with that of their absorption maxima and quantum yields. In hexane, they decreased in the order of *meta*- < *para*- < *ortho*-substituent by the cyano group. As a result, the molar absorption coefficients of both the open-ring and the closed-ring isomers of the *ortho*-substituted derivative **2** are the biggest; while those of the *meta*-substituted derivative **3** are the smallest. Compared to that of the diarylethene **2**, the molar absorption

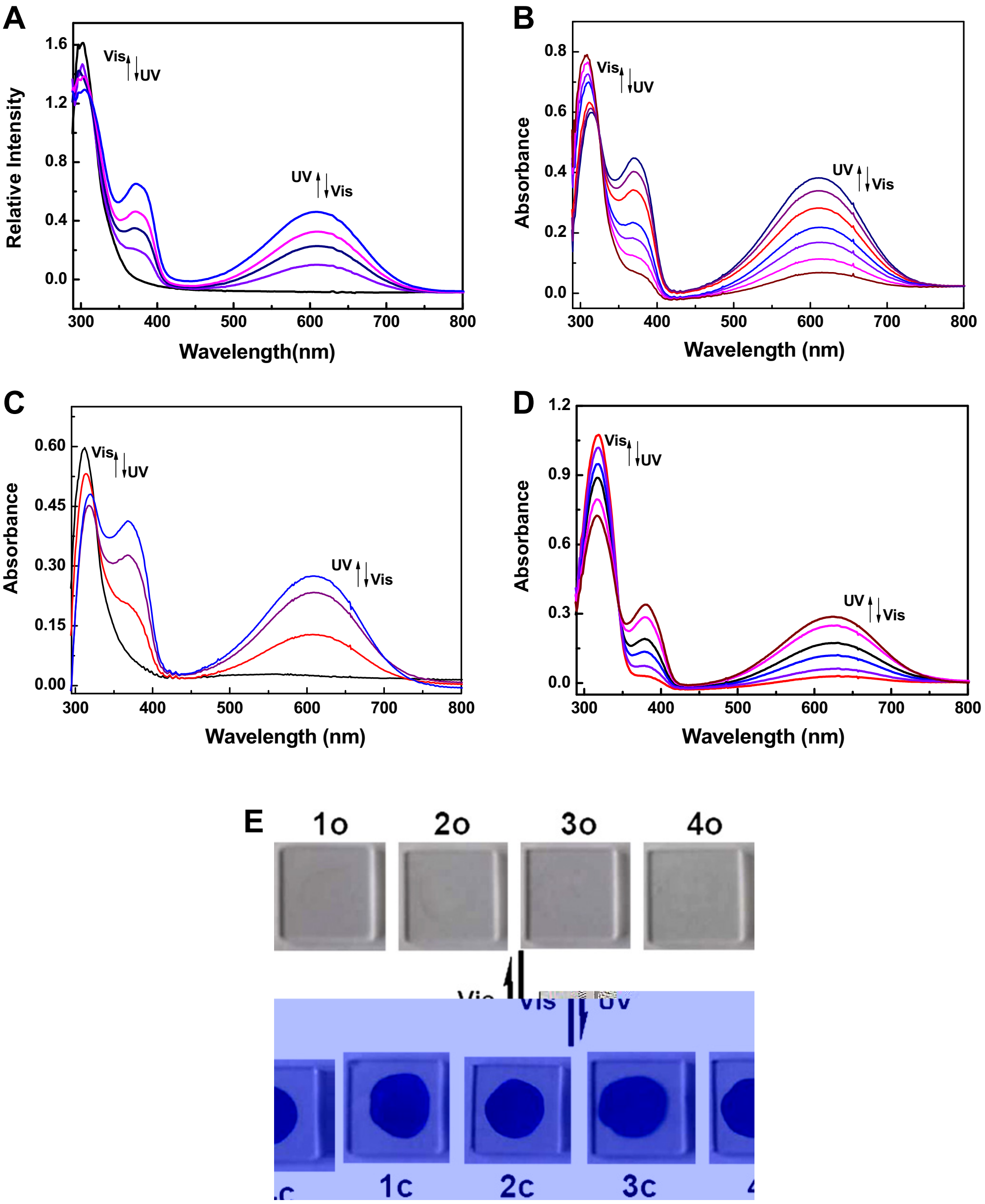


**Fig. 5.** Absorption spectral and color changes of diarylethenes **1**–**4** by photoirradiation in PMMA films (10%, w/w) at room temperature: (A) spectral changes for **1**, (B) spectral changes for **2**, (C) spectral changes for **3**, (D) spectral changes for **4**, (E) color changes for **1**–**4**.

coefficients of diarylethenes **3** and **4** were almost twofold lower. These varying patterns are quite different from those of isomeric diarylethenes bearing different substituents reported [33–39]. Furthermore, the pyrrole moiety has also a significant effect on the photochromic properties of diarylethenes **1**–**4**. When replacing the pyrrole moiety with the thiophene moiety in the same molecular skeleton of photochromic diarylethenes, the molar absorption coefficients and the cyclization quantum yields increased remarkably, and the absorption maxima of their closed-ring isomers showed so big hypsochromic shift that they exhibited the purple colours in hexane [33].

The thermal stabilities of the open-ring and closed-ring isomers of unsymmetrical diarylethenes **1**–**4** were tested in hexane both at room temperature and at 80 °C. Storing these solutions in hexane in the dark and then exposing them to air both at room temperature and at 80 °C for more than 72 h, we found that no changes in the UV/vis spectra of diarylethenes **1**–**4** were observed. That is to say, no decomposition was detected, which indicates that unsymmetrical diarylethenes bearing a pyrrole unit had better thermal stability than symmetrical ones bearing pyrrole units [16].

For practical applications in optical devices, it is very important that photochromic materials can keep good photochromism in a polymer film such as poly(methyl methacrylate) (PMMA) [41,42]. In PMMA amorphous films, diarylethenes **1**–**4** also showed similar photochromism to that in hexane solution, and their spectral and color changes are shown in Fig. 5. As has been observed for most of the reported diarylethenes [33,36,43,44], the maximum absorption peaks of both the open-ring and the closed-ring isomers in PMMA films are longer than those in hexane. The red shift values of the absorption maxima of the open-ring isomers are 12 nm for **1o**, 14 nm for **2o**, 17 nm for **3o**, and 7 nm for **4o**, and those of the closed-ring isomers are 23 nm for **1c**, 21 nm for **2c**, 19 nm for **3c**, and 19 nm for **4c**, respectively. The red shift phenomena may be attributed to the polar effect of the polymer matrix in solid state [45,46].

Single crystals of diarylethenes **2o** and **3o** were obtained by slow evaporation of hexane solutions. To gain a deeper understanding of the relation between the conformation and the photochromic behaviors of the two diarylethene derivatives in the crystalline phase, their final structural confirmations were provided by X-ray crystallographic analysis. The X-ray crystallographic analysis data are listed in Table 2. Their ORTEP drawings and photochromism induced by alternating irradiation with UV light and visible light in the crystalline phase are shown in Fig. 6 The molecules of both diarylethenes **2o** and **3o** crystallize with an appropriate $C_2$ symmetry

**Table 2**
Crystal data and structure refinements for diarylethenes **2o** and **3o**.

| | Compound **2o** | Compound **3o** |
|---|---|---|
| Formula | $C_{24}H_{15}F_6N_3S$ | $C_{24}H_{15}F_6N_3S$ |
| Formula weight | 491.45 | 491.45 |
| Temperature | 113 (2) | 113 (2) |
| Crystal system | Triclinic | Triclinic |
| Space group | *P* − 1 | *P* − 1 |
| Unit cell dimensions | 1090.1 (3) | 1093 (5) |
| *a* (Å) | 9.0882 (13) | 8.999 (17) |
| *b* (Å) | 9.1285 (12) | 11.24 (4) |
| *c* (Å) | 15.097 (3) | 12.62 (3) |
| $\alpha$ (°) | 76.237 (7) | 113.08 (6) |
| $\beta$ (°) | 85.251 (8) | 109.49 (5) |
| $\gamma$ (°) | 63.686 (7) | 90.20 (5) |
| Volume (Å$^3$) | 1090.1 (3) | 1093 (5) |
| *z* | 2 | 2 |
| Reflections collected | 10129 | 10272 |
| Reflections observed | 5087 | 5116 |
| Number of parameters | 311 | 312 |
| μ (mm$^{-1}$) | 0.217 | 0.217 |
| Density (calcd.) (g/cm$^3$) | 1.497 | 1.493 |
| Goodness-of-fit on $F^2$ | 1.016 | 1.060 |
| Final $R_1$ [$I > 2s(I)$] | 0.0358 | 0.0419 |
| $wR_2$ [$I > 2s(I)$] | 0.0960 | 0.1136 |
| $R_1$ (all data) | 0.0507 | 0.0612 |
| $wR_2$ | 0.1014 | 0.1249 |

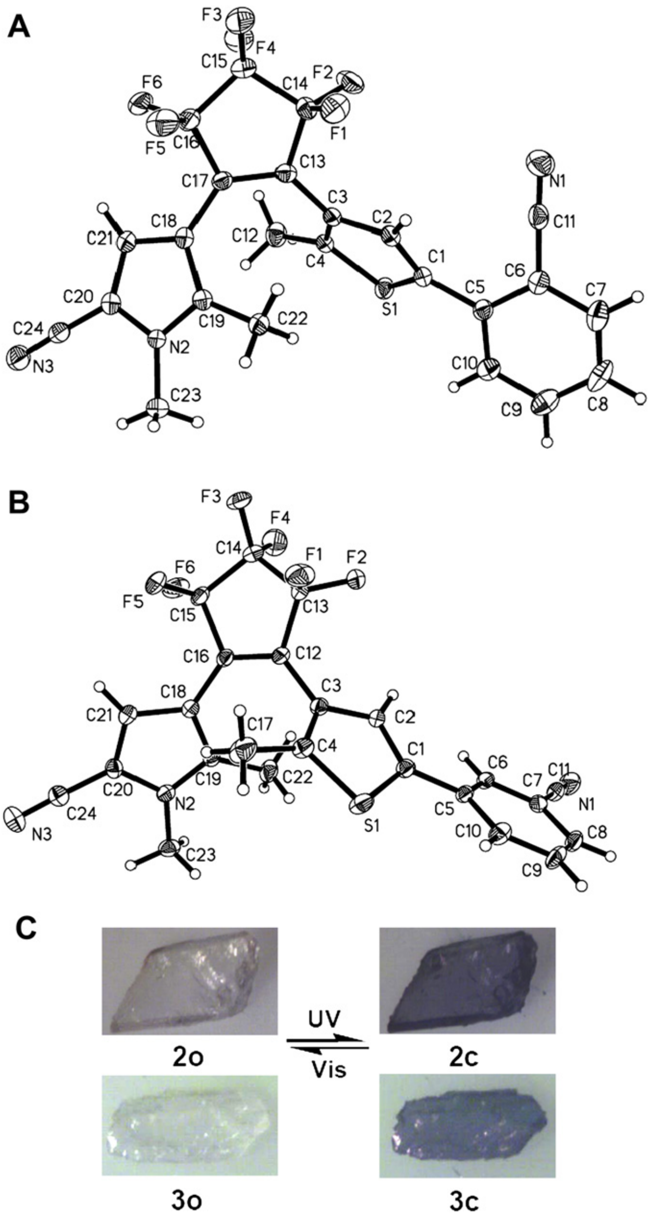


**Fig. 6.** ORTEP drawings of crystals **2o** and **3o** and their color changes by photoirradiation in the single crystalline phase: (A) ORTEP drawing of **2o**, (B) ORTEP drawing of **3o**, (C) color changes for crystals **2o** and **3o**.

**Table 3**
Distances between the reacting carbon atoms *d* (Å) and dihedral angles $\theta$ (°) of diarylethenes **2o** and **3o.**

| Compound | *d* (Å) | | $\theta$ (°)[a] | | |
|---|---|---|---|---|---|
| | | | $\theta_1$ | $\theta_2$ | $\theta_3$ |
| **2o** | C4...C19 | 3.520 (5) | 36.7 (3) | 56.6 (3) | 38.2 (3) |
| **3o** | C4...C19 | 3.629 (4) | 41.9 (6) | 60.3 (6) | 22.1 (6) |

[a] $\theta_1$, Dihedral angle between the cyclopentene ring and cyclopentene ring linked up with the pyrrole ring; $\theta_2$, dihedral angle between the cyclopentene ring and the thiophene ring; $\theta_3$, dihedral angle between the thiophene ring and the adjacent benzene ring.

with the photoactive *anti*-parallel conformation in the crystalline phase, which can undergo photocyclization [15,47]. For diarylethene **2o**, the distances clearly show that the C13–C17 bond (1.351 Å) in hexafluorocyclopentene ring is a double bond, being significantly shorter than other carbon-carbon single bonds (1.499 Å to 1.550 Å) of the ring. The thiophene and pyrrole moieties are linked by the C13=C17 double bond. The two methyl groups are located on opposite sides of the double bond, reflected in the torsion angles C13–C17–C18–C19 [−38.8(6)°] and C17–C13–C3–C4 [−52.5(6)°] and are thus *trans* with respect to the double bond. Such a conformation is crucial for the compound to exhibit photochromic and photo-induced properties [48]. The dihedral angles between the hexafluorocyclopentene ring and the two heteroaryl rings are 36.7 (3)° for N2/C18–C21 and 56.6(3)° for S1/C1–C4, and that between the thiophene ring and the linked benzene ring is 38.2(3)°. The corresponding data of compounds **3o** are summarized in Table 3. The distance between the two reactive C atoms is 3.520(5) Å for **2o** and 3.629(4) for **3o**, which is close enough for the photocyclization to take place [15,48,49]. In fact, the crystals **2o** and **3o** showed good photochromism in accordance with the expected analysis (Fig. 6). Upon irradiation with 297 nm light, the colorless crystal of **2o** and **3o** turned blue quickly, as a result of the formation of the closed-ring isomers **2c** and **3c**. Alternatively, the blue colored crystals **2c** and **3c** returned to colorless and reproduce **2o** and **3o** upon irradiation with visible light ($\lambda > 500$ nm). After 500 repeat cycles, the two isomeric diarylethenes still showed good photochromism by alternating irradiation with UV and visible light in the single crystalline phase. So, they can be potentially used for the construction of certain optoelectronic devices [50,51].

### 3.2. Fluorescence of diarylethenes

Fluorescent properties can be useful in molecular-scale optoelectronics and digital photoswitching of fluorescence [52–54]. The fluorescence modulation is a particularly intriguing approach due to the stabilization of diarylethene and versatility in materials selection [55]. Until now, the fluorescent properties of many diarylethene derivatives have been extensively explored [33–40,56–60]. In this work, the fluorescence properties of the four diarylethenes in hexane solution and in PMMA films were measured using a Hitachi F-4500 fluorimeter at room temperature. The fluorescence emission spectra of diarylethenes **1o**–**4o** in hexane ($5.0 \times 10^{-5}$ mol/L) and in PMMA films (10%, w/w) at room temperature are illustrated in Fig. 7. In hexane, the emission peaks of diarylethenes **1o**–**4o** were observed at 439, 418, 419 and 415 nm when exited at 340 nm, and were observed at 424, 417, 414 and 414 nm in PMMA films when excited at 350 nm. Compared to those in hexane, the emission peaks of diarylethenes **1o**–**4o** in PMMA films consistently exhibit a hypsochromic shift with values of 15 nm for **1o**, 1 nm for **2o**, 5 nm for **3o**, and 1 nm for **4o**. The result is contrary to those reported previously [36,38,43]. Among isomeric diarylethenes **2o**–**4o**, the emission intensity of the *ortho*-substituted derivative **2o** is the strongest and that of the *meta*-substituted derivative **3o** is the smallest both in hexane and in PMMA film. The result is quite different from those of the similar unsymmetrical diarylethenes with an electron-donating methoxy group whose the emission intensity of the *ortho*-substituted derivative is the strongest and that of the *para*-substituted derivative is the smallest both in hexane and in PMMA film [37]. Compared to isomeric diarylethenes **2o**–**4o**, the unsubstituted parent diarylethene **1o** showed the strongest emission intensity and the lowest energy emission peak both in hexane and in PMMA film. The results showed that the electron-withdrawing cyano group could be effective to reduce the emission peak and weaken the fluorescent intensity of diarylethenes bearing a pyrrole unit. This is in good agreement with those of the unsymmetrical diarylethenes with the same skeleton and with an electron-donating methoxy group in the terminal benzene ring [37]. In addition, by using anthracene (0.27 in acetonitrile) as the reference, the fluorescence quantum yields of the open isomers of **1o**, **2o**, **3o**, and **4o** were determined to be 0.010, 0.051, 0.027, and 0.047, respectively. From the data, it can be easily concluded that the unsubstituted parent diarylethene **1** has the smallest fluorescence quantum yield. Therefore, the introduction of electron-withdrawing cyano group into any position of the terminal benzene ring can significantly improve the fluorescence quantum yield of diarylethenes bearing a pyrrole moiety.

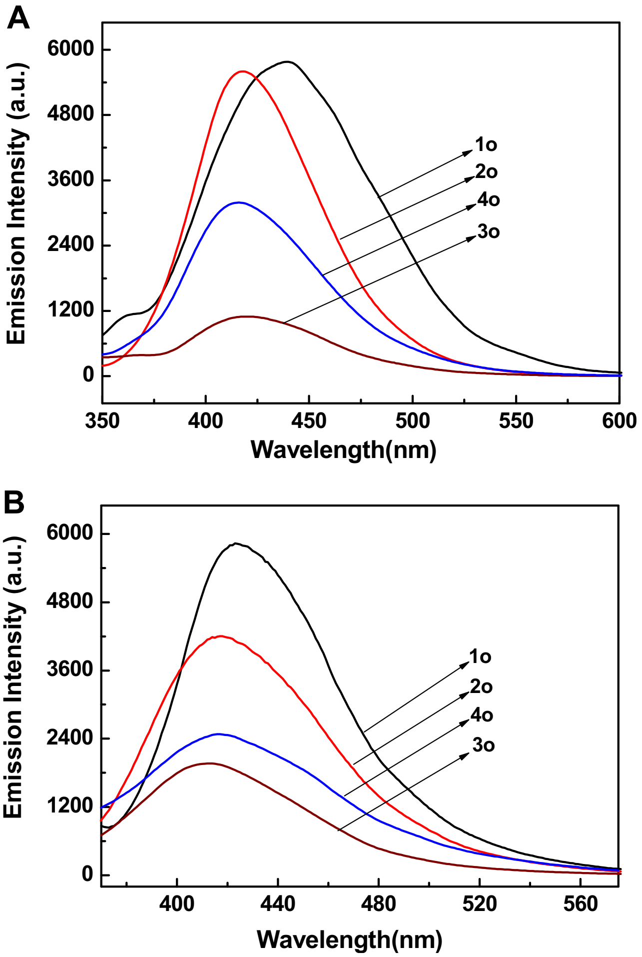


**Fig. 7.** Fluorescence emission spectra of diarylethenes **1**–**4** both in hexane solution ($5.0 \times 10^{-5}$ mol/L) and in PMMA films (10%, w/w) at room temperature: (A) emission spectra in hexane, excited at 340 nm; (B) emission spectra in PMMA films, excited at 350 nm.

Diarylethenes **1**–**4** exhibited an excellent fluorescent switch on changing from the open-ring isomers to closed-ring isomers by photoirradiation both in hexane and in PMMA film. When irradiated by UV light, the photocyclization reaction was occurred and the emission intensity of diarylethenes **1o**–**4o** decreased significantly due to producing the non-fluorescence closed-ring isomers **1c**–**4c**. The back irradiation by appropriate wavelength visible light regenerated their open-ring isomers **1o**–**4o** and recovered the original emission intensity. The fluorescence changes of diarylethenes **1**–**4** by photoirradiation in hexane ($5.0 \times 10^{-5}$ mol/L) and in PMMA films (10%, w/w) are showed in Figs. 8 and 9. Upon irradiation with UV light, the emission intensity of **1o** was quenched to *ca.* 7% in hexane and 17% in a PMMA film when arrived at the photostationary state. That is to say, its fluorescent modulation efficiency at photostationary

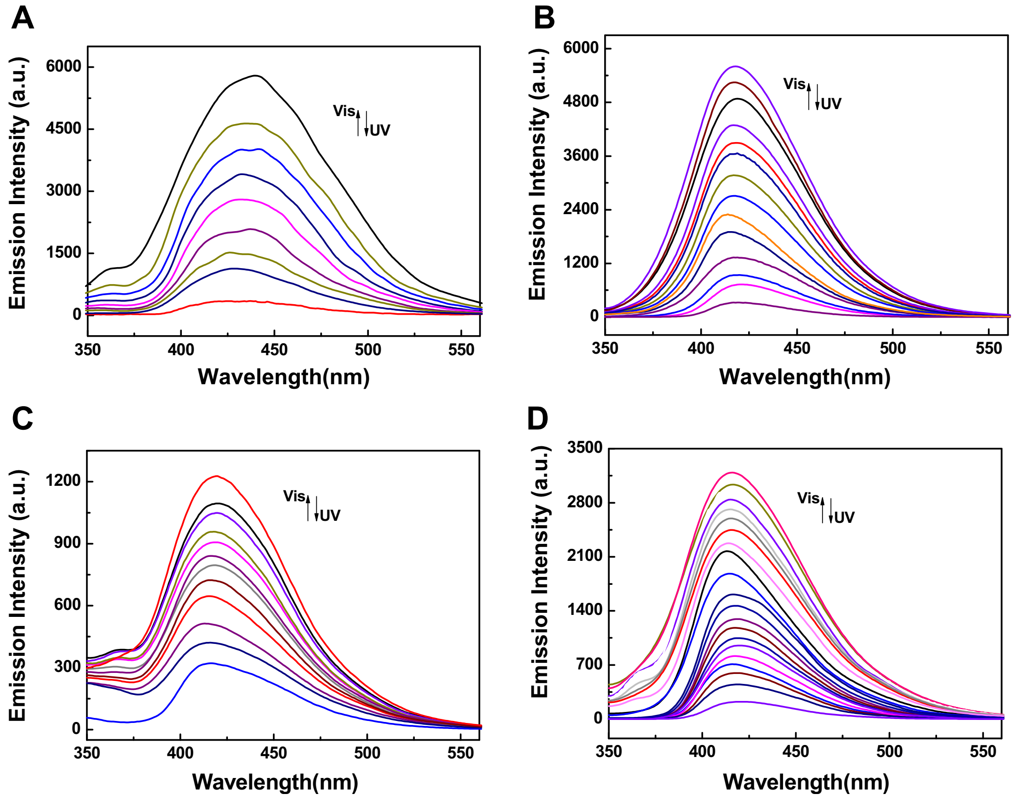


**Fig. 8.** Emission intensity changes of diarylethenes **1**–**4** upon irradiation with 297 nm UV light at room temperature in hexane ($5.0 \times 10^{-5}$ mol/L), excited at 340 nm: (A) **1**, (B) **2**, (C) **3**, and (D) **4**.

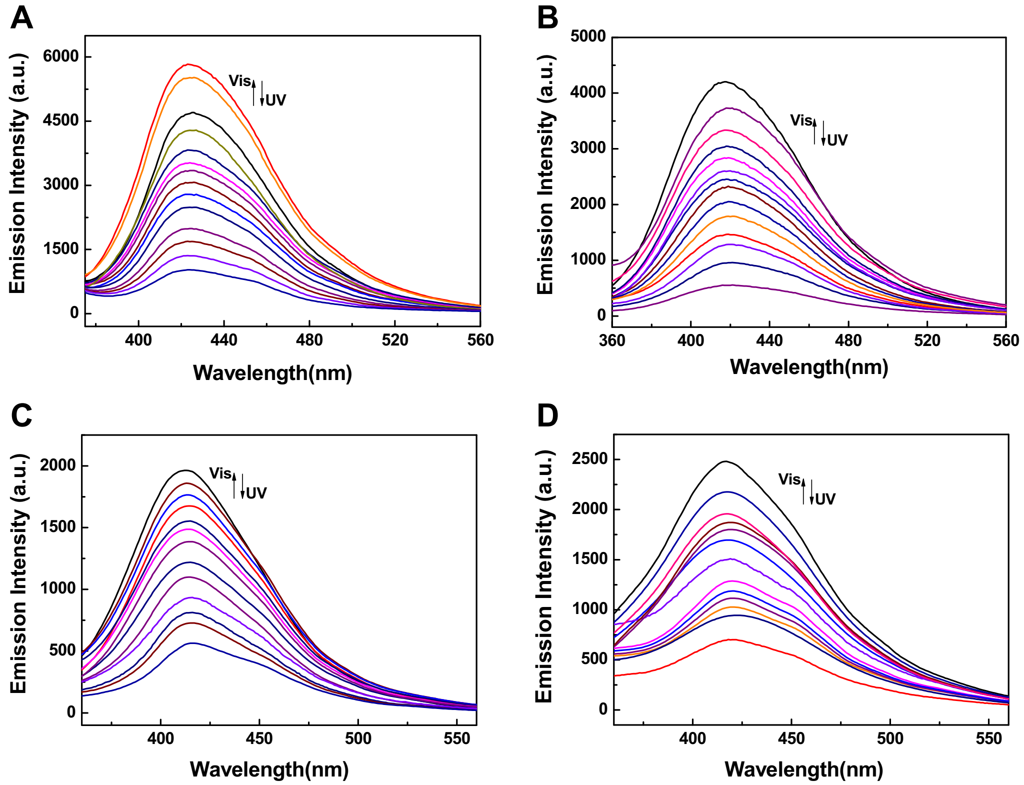


**Fig. 9.** Emission intensity changes of diarylethenes **1**–**4** upon irradiation with 297 nm UV light at room temperature in PMMA films (10%, w/w), excited at 350 nm: (A) **1**, (B) **2**, (C) **3**, and (D) **4**.

different, compared with the cyano group [37]. The results suggest that the cyano group and its -substituted position have a great effect on the electrochemical properties of these diarylethene compounds but further work is required to quantify these effects.

## 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 substituents on the properties of these compounds. It has been demonstrated that electron-withdrawing cyano substituent and its -substituted position have a significant effect on the photochemical and electrochemical properties of these diarylethene derivatives. Compared with the unsubstituted parent diarylethene **1**, diarylethenes **2**–**4** bearing a cyano group at the *ortho*-, *meta*- and *para*-position of the terminal benzene ring have larger absorption peaks, quantum yields of cyclization and cycloreversion, fluorescence quantum yields, and the oxidation onsets, however, they have smaller molar absorption coefficients and emission peaks. In addition, the introduction of the pyrrole moiety increased the absorption maxima and the cycloreversion quantum yields whereas decreased the molar absorption coefficients and the cyclization quantum yields significantly, compared with the analogous dithienylethene derivatives. The results may shed some lights on the further application of photochromic diarylethenes bearing a pyrrole moiety.

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