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# The photochromism of unsymmetrical diarylethene isomers with an electron-withdrawing cyano substituent

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ABSTRACT

Three unsymmetrical isomeric diarylethenes bearing an electron-withdrawing cyano group were synthesized and their structures determined using single-crystal X-ray diffraction analysis. Each of the compounds displayed excellent photochromism in solution, in PMMA film, as well as in the crystalline phase. The isomeric compounds also functioned as a fluorescence switch in PMMA films. The cyclization quantum yield and the absorption maxima of both the ring-opened and ring-closed isomers increased in the order: *ortho*- < *meta*- < *para*-substitution of the cyano group. Compared with the unsubstituted parent compound, the cycloreversion quantum yield decreased whereas the molar absorption coefficient of the ring-opened and the ring-closed isomers increased significantly when the cyano group was attached at any of the three positions on the terminal benzene ring. Cyclic voltammetry studies indicated that the position of cyano substitution had a marked effect on the electrochemical behaviours of these isomeric diarylethenes.

## 1. Introduction

The exploration of photochromic diarylethenes with good optical and electromagnetic properties for molecule-scale information processing has become an active research area of organic chemistry [1], mainly due to their potential applications in photonic devices such as erasable memory media [2], optical switching [3–5], and full color displays [6]. Among the diarylethene derivatives hitherto reported, diarylethenes with heterocyclic aryl groups, especially those bearing two thiophene or benzothiophene rings, are the most promising candidates for these applications because of their excellent thermally irreversible photochromic property, remarkable fatigue-resistance, and high sensitivity [2,3,7–10].

Diarylethenes bearing phenyl groups have been of particular interest in the last few years because the phenyl group can increase the absorption coefficient of the photochromic molecule and the conversion at the photostationary state [11]. Moreover, the optoelectronic properties of the phenyl-substituted diarylethene derivatives can be further modified by suitable functionalization of the aromatic rings with electron-donating or electron-withdrawing groups [12–15]. To date, many reports concerning the substituent effect on the properties of diarylethene derivatives have been reported. For instance, some reports demonstrated that the introduction of electron-donating groups to bis(3-thienyl)ethene diarylethenes increases the absorption coefficient of the ring-closed isomers and decreases the cycloreversion quantum yield. Therefore, substitution with various functional groups could be an effective way to increase the maxima absorption of the ring-opened isomers and to reduce the cyclization quantum yield [16–18]. Moreover, Irie et al. demonstrated that the cycloreversion quantum yield was strongly suppressed by the introduction of electron-donating methoxy groups at the reactive 2- and 2′-positions of the thiophene rings [19,20]. Yamaguchi et al. investigated the substituent effect on the photochromic properties of diarylethenes bearing two benzofuran aryl groups [21], and Tanifuji et al. reported the effect of the radical substituents on the photochromic reactivity of bis(3-benzothiophene)perfluorocyclopentene [22]. In previous work, we also illustrated that different substituents had a significant effect on the properties of diarylethene derivatives, including their photochromism, fluorescence and electrochemical properties [23–26].

Apart from the fact that various functional groups have significant effects on the photochromic properties of diarylethenes, the position of the substituent can affect photochromic properties significantly, which can be used for the fine tuning of the optoelectronic properties of diarylethene compounds. Previously, the current authors focused on the effects of electron-donating methoxy groups or halide substituents [27–34]. This paper concerns the effect of the position of the cyano substitution on diarylethenes. The cyano group is a strongly electron-withdrawing substituent and has a distinguishable effect on the photochromic

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features of diarylethenes comparing with the effect of electron-donating group [16]. We synthesized three unsymmetrical isomeric diarylethenes bearing a cyano group in order to elucidate these effects. The three isomeric compounds (**1**, **2** and **3**) showed favorable photochromic properties in solution, in PMMA film as well as in the single crystalline phase.

## 2. Materials and methods

### 2.1. Experimental

General: Melting point was taken on a WRS-1B melting point apparatus. NMR spectra were recorded on a Bruker AV400 (400 MHz) spectrometer with $CDCl_3$ as the solvent and tetramethylsilane as an internal standard. Elemental analysis was performed with the PE 2400 CHN analyzer. Mass spectra were measured with an Agilent MS Trap VL spectrometer. Infrared spectra (IR) were recorded on a Bruker Vertex-70 spectrometer. Fluorescent spectra were measured using a Hitachi F-4500 spectrophotometer. Absorption spectra were measured using an Agilent 8453 UV/VIS spectrophotometer. Photoirradiation 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. The relative quantum yields were determined by comparing the reaction yield with the known yield of the compound 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene in hexane ($\Phi_{o-c} = 0.59$, $\Phi_{c-o} = 0.013$) [35]. 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 tetrafuoroborate ((TBA) $BF_4$) and $4.0 \times 10^{-3}$ mol/L dithienylethene. 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.

Suitable crystals of **1o**–**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 at room temperature using MoK\a 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 nonhydrogen atoms were refined anisotropically. Crystallographic data of the structures have been deposited in the Cambridge Crystallographic Data Centre as supplemental publication CCDC 751281 for **1o**, CCDC 615594 for **2o** and CCDC 722282 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 1223 336033 or e-mail:deposit@ccdc.cam.ac.uk).

### 2.2. Synthesis

#### 2.2.1. Synthesis of 3-bromo-2-methyl-5-(2-cyanophenyl)thiophene *5a*

Compound **5a** was prepared by reacting 3-bromo-2-methyl-5-thienylboronic acid (**4**) [30] (4.0 g; 18.2 mmol) with 1-bromo-2-cyanobenzene (3.31 g; 18.2 mmol) in the presence of $Pd(PPh_3)_4$ (caution: light sensitive, air sensitive; avoid strong oxidizing agents; 0.4 g) and $Na_2CO_3$ (6.40 g; 60 mmol) in tetrahydrofuran (THF) (80 mL, containing 10% water) for 15 h at 70 °C. The product **5a** was purified by column chromatography on $SiO_2$ using hexane as the eluent and 3.04 g obtained as baby yellow solid in 60% yield. $^1$H NMR (400 MHz, $CDCl_3$) δ 2.42 (s, 3H, $-CH_3$), 7.14 (d, 2H, J = 8.8 Hz, phenyl-H), 7.24 (s, 1H, thienyl-H), 7.27 (s, 1H, phenyl-H), 7.53 (d, 1H, J = 8.0 Hz, phenyl-H).

#### 2.2.2. Synthesis of 3-bromo-2-methyl-5-(3-cyanophenyl)thiophene *5b*

Compound **5b** was prepared by an analogous method similar to that used for to **5a** and was obtained as a buff colored solid (3.21 g) in 59% yield. $^1$H NMR (400 MHz, $CDCl_3$) δ 2.43 (s, 3H, $-CH_3$), 6.96 (t, 1H, J = 8.0 Hz, phenyl-H), 7.13 (s,1H), 7.21 (d, H, J = 5.6 Hz, phenyl-H), 7.29 (s, 1H, phenyl-H), 7.53 (t, 1H, J = 6.8 Hz, phenyl-H).

#### 2.2.3. Synthesis of 3-bromo-2-methyl-5-(4-cyanophenyl)thiophene *5c*

Compound **5c** was prepared by an analogous method similar to that used for to **5a** and was obtained as a buff colouredsolid (3.57 g) in 61% yield.$^1$H NMR (400 MHz, $CDCl_3$) δ 2.41 (s, 3H, $-CH_3$), 7.03 (s, 1H, thienyl-H), 7.06 (t, 2H, J = 8.0 Hz, phenyl-H), 7.48 (t, 2H, J = 6.2 Hz, phenyl-H).

#### 2.2.4. Synthesis of 1-(2,5-dimethyl-3-thienyl)-2-[2-methyl-5-(2-cyanophenyl)-3-thienyl] perfluorocyclopentene *1o*

Compound **5a** (2.0 g, 7.2 mmol) in anhydrous THF was added dropwise to a 2.5 mol/L *n*-BuLi solution (3.1 mL) at −78 °C under an argon atmosphere. Stirring was continued for 30 min and (2,5-dimethyl-3-thienyl)perfluorocyclopentene [31,32,36] (2.19 g, 7.2 mmol) was slowly added to the reaction mixture at −78 °C and stirred for 1 h at this temperature. Then, the reaction was allowed to slowly warn to the room temperature and stirred there for 1 h. The reaction was quenched with 10 mL distilled water. The mixture was extracted with ether. The organic layer was collected and dried over $MgSO_4$, filtered and evaporated. The crude product was purified by column chromatography on silica gel using petroleum ether as the eluent resulting in 1.56 g of **1o** being obtained as white solid in 45% yield. M.p. 104.6–105 °C; MS *m/z* (M + 1) 484.58; $^1$H NMR (400 MHz, $CDCl_3$): δ 1.91 (s, 3H, $-CH_3$), 1.97 (s, 3H, $-CH_3$), 2.45 (s, 3H, $-CH_3$), 6.8 (s, 1H, thienyl-H), 7.15 (d, 1H, J = 8.0 Hz, phenyl-H), 7.10 (t, 1H, J = 8.0 Hz, phenyl-H), 7.20 (d, 1H, J = 5.6 Hz, phenyl-H), 7.44 (s, 1H, thienyl-H), 7.58 (t, 1H, J = 7.6 Hz, phenyl-H); $^{13}$C NMR (400 MHz, $CDCl_3$): δ 14.58, 15.00, 55.59, 112.1, 121.0, 121.9, 125, 126.9, 128.0, 130.7, 131.8, 136.0, 137.5, 139.5, 142.2, 156.0; IR (ν, KBr, $cm^{-1}$): 735, 772, 822, 860, 898, 986, 1051, 1103, 1188, 1274, 1336, 1441, 1555, 1594, 1637, 2225, 2927. Anal. Calcd. for $C_{23}H_{15}F_6NS_2$ (%): C, 57.14; H, 3.13. Found: C, 57.67; H, 3.54.

#### 2.2.5. Synthesis of 1-(2,5-dimethyl-3-thienyl)-2-[2-methyl-5-(3-cyanophenyl)-3-thienyl] perfluorocyclopentene *2o*

Compound **2o** was prepared by an analogous method similar to that used for to **1o** and was obtained as a white solid (1.66 g) in 48% yield. M.p. 138.8–138.9 °C; MS *m/z* (M + 1) 484.77; $^1$H NMR (400 MHz, $CDCl_3$): δ 1.90 (s, 3H, $-CH_3$), 1.97 (s, 3H, $-CH_3$), 2.45 (s, 3H, $-CH_3$), 6.75 (s, 1H, thienyl-H), 7.02 (t, 2H, J = 8.0 Hz, phenyl-H), 7.24 (d, 1H, J = 10.0 Hz, phenyl-H), 7.28 (s, 1H, thienyl-H), 7.35 (m, 2H, J = 8.0 Hz, phenyl-H); $^{13}$C NMR (400 MHz, $CDCl_3$): δ 14.25, 14.41, 15.07, 112.4, 114.5, 121.2, 123.4, 124.5, 126.1, 130.5, 135.5, 137.9, 139.8, 140.5, 141.8, 161.9, 164.4; IR (ν, KBr, $cm^{-1}$): 732, 798, 856, 892, 981, 1051, 1110, 1189, 1270, 1336, 1446, 1602, 2228, 2924. Anal. Calcd. for $C_{23}H_{15}F_6NS_2$ (%): C, 57.14; H, 3.13. Found: C, 57.38; H, 3.29.

#### 2.2.6. Synthesis of 1-(2,5-dimethyl-3-thienyl)-2-[2-methyl-5-(4-cyanophenyl)-3-thienyl] perfluorocyclopentene *3o*

Compound **3o** was prepared by an analogous method similar to that used for to **1o** and was obtained as a white solid (1.73 g) in 50%

yield. M.p. 149.0–149.5 °C; MS *m/z* (M + 1) 484.39; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 1.85 (s, 3H, $-CH_3$), 1.90 (s, 3H, $-CH_3$), 2.36 (s, 3H, $-CH_3$), 6.68 (s, 1H, thienyl-H), 7.02 (d, 2H, $J = 8.0$ Hz, phenyl-H), 7.08 (s, 1H, thienyl-H), 7.42–7.45 (m, 2H, phenyl-H); $^{13}$C NMR (400 MHz, $CDCl_3$): $\delta$ 14.25, 14.35, 15.07, 115.8, 116.1, 122.5, 124.5, 126.1, 127.3, 129.7, 137.8, 139.7, 140.9, 141.1, 161.3, 163.7; IR (ν, KBr, cm$^{-1}$): 742, 831, 887, 986, 1049, 1105, 1185, 1273, 1338, 1440, 1489, 1560, 1604, 2223, 2924. Anal. Calcd. for $C_{23}H_{15}F_6NS_2$ (%): C, 57.14; H, 3.13. Found: C, 57.35; H, 3.41.

## 3. Results and discussion

### 3.1. Discussion of the synthetic stragegy

The synthesis route for the diarylethenes **1o**, **2o** and **3o** is shown in Fig. 1. Suzuki coupling of the three bromobenzene derivatives with a thiophene boronic acid [30] gave the cyanophenylthiophene derivatives (**5a**, **5b** and **5c**). They were lithiated and coupled to (2,5-dimethyl-3-thienyl)perfluorocyclopentene [31,32,36] to give the unsymmetrical diarylethene derivatives **1o, 2o** and **3o**, respectively. The structures of **1o**, **2o** and **3o** were confirmed by NMR, IR, and mass spectrometry, elemental analysis, and X-ray crystallographic analysis.

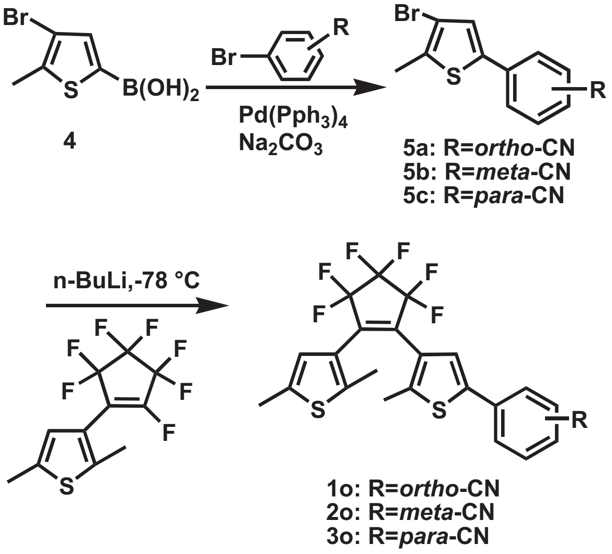

**Fig. 1.** Synthetic route for diarylethenes **1o**–**3o**.

### 3.2. Photochromic behaviours

The photochromic scheme of diarylethenes **1**, **2** and **3** is shown in Fig. 2.

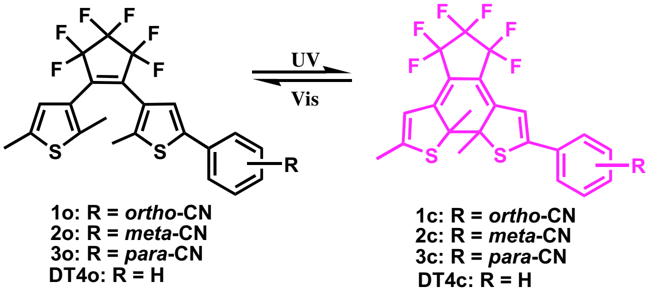

**Fig. 2.** Photochromism of diarylethenes **1**–**3**.

The photochromic behaviours of diarylethenes **1**, **2** and **3** induced by photoirradiation at room temperature were measured both in hexane and in PMMA films. In hexane, the absorption spectrum and color changes of diarylethenes **1**, **2** and **3** induced by alternating irradiation with UV light and visible light at appropriate wavelength are shown in Fig. 3. The absorption maximum of compound **1** was observed at 272 nm ($\varepsilon = 3.08 \times 10^4$ L mol$^{-1}$ cm$^{-1}$) in hexane, as the result of a $\pi$–$\pi^*$ transition [37]. This colorless solution turned purple and a new absorption band centered at 539 nm ($\varepsilon = 1.77 \times 10^4$ L mol$^{-1}$ cm$^{-1}$) appeared when it was irradiated with 297 nm violet light, resulting from a ring-closure reaction and the production of the ring-closed isomer **1c**. Upon irradiation with visible light ($\lambda > 450$ nm), the colored **1c** underwent a cycloreversion reaction to the initial colorless ring-opened isomer **1o**. Just like diarylethene **1**, compounds **2** and **3** also show good photochromism in hexane (Fig. 3). Upon irradiation with 297 nm light, absorption bands in the visible region appeared and the solutions of **2o** and **3o** turned purple due to the cyclization reactions, leading to the production of the ring-closed isomers **2c** and **3c**. Their absorption maxima in the visible region were observed at 544 and 552 nm, respectively. The purple-colored solutions of **2c** and **3c** can be decolorized upon irradiation with visible light ($\lambda > 450$ nm) again, due to the conversion of the compounds back to the ring-opened isomers **2o** and **3o**. This reversion also causes the reappearance of the absorption maxima at 295 and 312 nm, respectively. At the photostationary state, the isosbestic points for diarylethenes **1**, **2** and **3** were observed at 333, 331 and 341 nm, respectively.

In amorphous PMMA films, diarylethenes **1**, **2** and **3** also showed similar photochromism as in hexane, and their spectral and color changes are shown in Fig. 4. The PMMA films were prepared by dissolving 10 mg of diarylethene sample and 100 mg of polymethylmethacrylate (PMMA) in chloroform (1 mL) with the aid of ultrasound, and the homogeneous solution was spin-coated on a quartz substrate ($20 \times 10 \times 1$ mm$^3$) at 1500 rpm. Compared to those in hexane, the maximum absorption peaks of both the ring-opened and the ring-closed isomers of diarylethenes **1** and **2** in PMMA film are at longer wavelengths than those in hexane. The red shift phenomena are consistent with those of the reported studies of most of the diarylethenes [23,28–31,38], which may be attributed to the polar effect of the polymer matrix and the stabilization of molecular arrangement in solid state [39,40]. However, for diarylethene **3**, the absorption maxima of both its ring-opened and ring-closed isomers in PMMA film are at shorter wavelengths than those in hexane. The blue shift of its ring-opened isomer is 25 nm, and that of its ring-closed isomer is only one nanometer. To out best knowledge, this is a unique diarylethene example that its absorption maximum shows a blue shift in the solid state comparing to that in solution. The reason for this blue shift is not clear and further investigation is in progress.

The photochromic parameters of diarylethenes **1**, **2** and **3** are summarized in Table 1. These data showed that the cyano substituent position had a remarkable effect on the photochromic properties of these isomeric diarylethenes, including the absorption maxima, molar absorption coefficients, and quantum yields of cyclization and cycloreversion reactions. For these three isomeric diarylethene derivatives, the absorption maxima of both the ring-opened and the ring-closed isomers varied with the same trend in hexane, *i.e.*, they increased in the order of *ortho-* < *meta-* < *para*-substitution. Therefore, the absorption maxima of the ring-opened isomer and the ring-closed isomer of diarylethene **3** are the longest; while those of **1** are the shortest. The result is quite different from those reported for electron-donating methoxy groups, where the absorption maximum of diarylethene bearing the *ortho*-substituted methoxy group is the longest, and that of

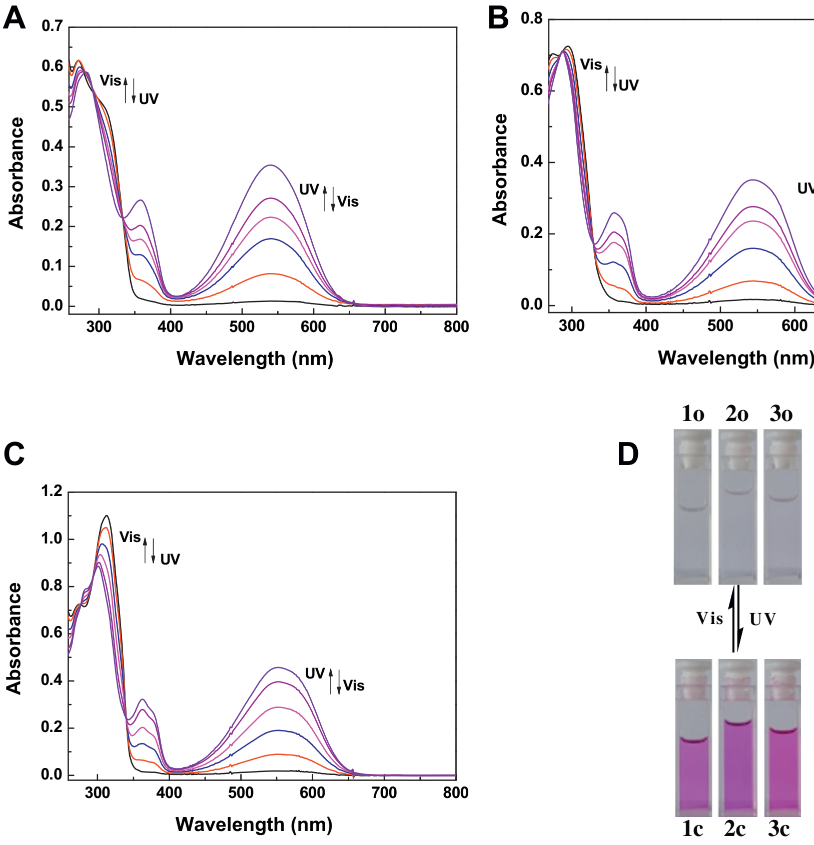

**Fig. 3.** Absorption spectral and color changes of diarylethenes **1**–**3** by photoirradiation in hexane ($2.0 \times 10^{-5}$ mol/L) at room temperature: (A) spectral changes for **1**, (B) spectral changes for **2**, (C) spectral changes for **3**, (D) color changes for **1**–**3**.

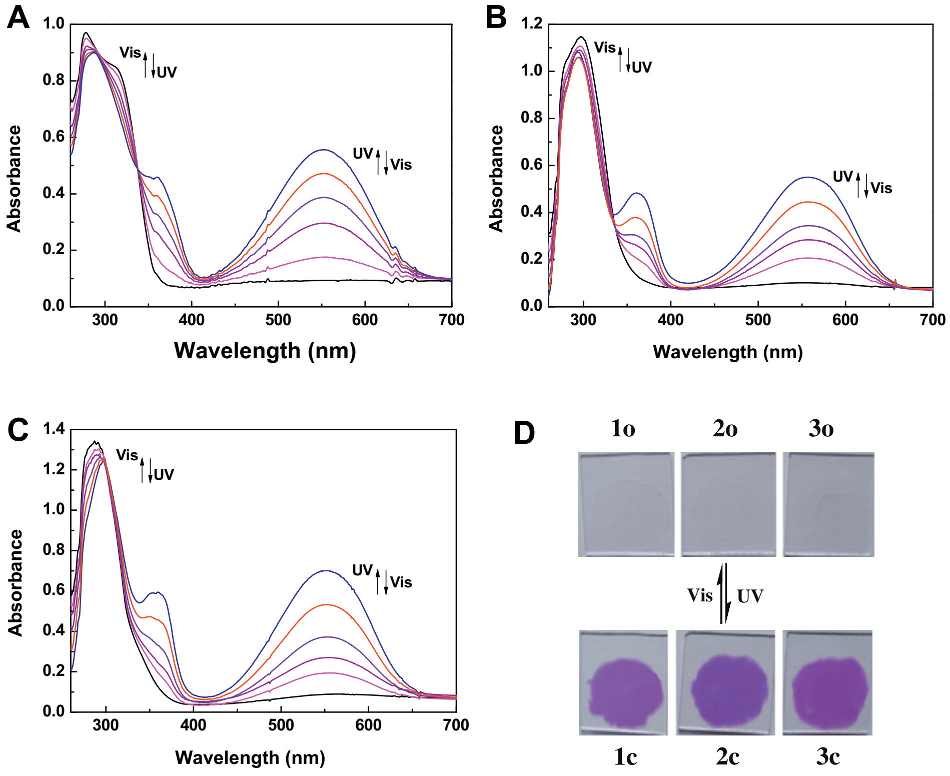

**Fig. 4.** Absorption spectral and color changes of diarylethenes **1**–**3** by photoirradiation in PMMA film (10%, w/w) at room temperature: (A) spectral changes for **1**, (B) spectral changes for **2**, (C) spectral changes for **3**, (D) color changes for **1**–**3**.

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

| 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] | |
|---|---|---|---|---|---|---|
| | Hexane | PMMA film | Hexane | PMMA film | $\Phi_{o-c}$ | $\Phi_{c-o}$ |
| 1 | 272 ($3.08 \times 10^4$) | 278 | 539 ($1.77 \times 10^4$) | 554 | 0.45 | 0.028 |
| 2 | 295 ($3.62 \times 10^4$) | 297 | 544 ($1.76 \times 10^4$) | 557 | 0.46 | 0.041 |
| 3 | 312 ($5.50 \times 10^4$) | 287 | 552 ($2.29 \times 10^4$) | 551 | 0.54 | 0.037 |

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

**Table 2**
Crystal data and structure refinements for diarylethenes **1o**–**3o**.

| | Compound **1o** | Compound **2o** | Compound **3o** |
|---|---|---|---|
| Formula | $C_{23}H_{15}F_6NS_2$ | $C_{23}H_{15}F_6NS_2$ | $C_{23}H_{15}F_6NS_2$ |
| Formula weight | 483.48 | 483.48 | 483.48 |
| Temperature | 296(2) | 294(2) | 291(2) |
| Crystal system | Triclinic | Monoclinic | Monoclinic |
| Space group | P-1 | P21/c | P21/c |
| Unit cell dimensions $a$ (Å) | 8.588(3) | 16.598(4) | 21.4209(19) |
| $b$ (Å) | 11.536(4) | 8.7178(18) | 9.1529(8) |
| $c$ (Å) | 13.043(5) | 17.250(4) | 11.2875(10) |
| $\alpha$ (o) | 99.488(4) | 90 | 90 |
| $\beta$ (o) | 107.867(4) | 116.899(4) | 102.1450(10) |
| $\gamma$ (o) | 109.715(4) | 90 | 90 |
| Volume (Å$^3$) | 1104.6(7) | 2226.1(8) | 2163.5(3) |
| $Z$ | 2 | 4 | 4 |
| Reflections collected | 8462 | 10978 | 15950 |
| Reflections observed | 4080 | 3935 | 4010 |
| Number of parameters | 292 | 346 | 322 |
| $\mu$ (mm$^{-1}$) | 0.302 | 0.299 | 0.308 |
| Density (calcd.) (g/cm$^3$) | 1.454 | 1.443 | 1.484 |
| Goodness-of-fit on $F^2$ | 1.031 | 1.02 | 1.038 |
| Radiation (Å) | 0.71073 | 0.71073 | 0.71073 |
| Final $R_1$[I > 2s(I)] | 0.0438 | 0.0443 | 0.035 |
| $wR_2$[I > 2s(I)] | 0.1139 | 0.1098 | 0.0976 |
| $R_1$ (all data) | 0.0571 | 0.0988 | 0.0470 |
| $wR_2$ (all data) | 0.1246 | 0.1396 | 0.1077 |

*para*-substituted methoxy group is the shortest [30,31]. The molar absorption coefficients of the ring-opened isomers **1o**–**3o** also clearly increased in the order of *ortho*- < *meta*- < *para*-substitution by the cyano group. Among the ring-closed isomers **1c**–**3c**, the molar absorption coefficient of the *para*-substituted derivative **3c** is the highest in hexane; while that of the *meta*-substituted derivative **2c** is the lowest. As shown in Table 1, the cyclization quantum yields of diarylethenes **1**–**3** are much higher than their respective cycloreversion quantum yields. This is completely different from unsymmetrical diarylethenes bearing a pyrazole unit whose cyclization quantum yields are lower than their respective cycloreversion quantum yields [33]. For diarylethenes **1**–**3**, the cyclization quantum yield increases in the order of *ortho*- ($\Phi_{o-c,1} = 0.45$) < *meta*- ($\Phi_{o-c,2} = 0.46$) < *para*-substitution ($\Phi_{o-c,3} = 0.54$) by the cyano group. However, the trend in the cycloreversion quantum yield is different. The cycloreversion quantum yield of the *meta*-substituted derivative **2** is the highest ($\Phi_{c-o,2} = 0.041$), that of the *ortho*-substituted derivative **1** is the lowest ($\Phi_{c-o,1} = 0.028$), and the *para*-substituted derivative **3** is intermediate ($\Phi_{c-o,3} = 0.037$). This pattern of variation is different from those of isomeric diarylethenes reported in previous work [31,32]. When substituting with the methoxy group in the same diarylethene system, the cyclization and cycloreversion quantum yields decreased evidently, and other photochromic parameters were also very different [31], compared with cyano substitution. However, the cyclization quantum yields increased and the cycloreversion quantum yields decreased significantly when substituting with chlorine atom in the same position of diarylethene system [32], compared with cyano substitution. The unsubstituted parent compound, namely 1-(2,5-dimethyl-3-thienyl)-2-(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene (**DT4**, as shown in Fig. 2), show quite different photochromic properties. The molar absorption coefficients of **DT4** ($\varepsilon_o = 2.47 \times 10^4$ L mol$^{-1}$ cm$^{-1}$, $\varepsilon_c = 3.68 \times 10^3$ L mol$^{-1}$ cm$^{-1}$) are much lower than that of **1**, **2** and **3**; while the cycloreversion quantum yield of **DT4** ($\Phi_{c-o} = 0.119$) is higher [32]. The result demonstrates that the photochromic features of diarylethenes can be effectively controlled by the introduction of the electron-withdrawing cyano group on the terminal benzene ring. Compared to the symmetric analogue, 1,2-bis(2-methyl-5-(4-cyanophenyl)-3-thienyl)perfluorocyclopentene [41], the cycloreversion quantum yields of the isomeric derivatives are higher, but their molar absorption coefficients and the absorption maxima are much lower.

Single crystals **1o**, **2o** and **3o**, suitable for X-ray analysis, were obtained by slow evaporation of hexane solutions. To gain a deeper understanding of the relationship between the conformation and the photochromism of these isomeric diarylethene derivatives in the crystalline phase, the structural conformations of diarylethenes **1o**, **2o** and **3o** were confirmed 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. 5. For diarylethene **1o**, the molecule crystallizes with an approximate $C_2$ symmetry with the photoactive *anti*-parallel conformation in the crystalline phase, which can undergo photocyclization [7,42–44]. The molecule includes four planar rings, which can form three dihedral angles between every two adjacent planar rings. The dihedral angles between the hexafluorocyclopentene ring and the two thiophene rings are 45.7(6)° for S1/C6–C9 and 52.3(6)° for S2/C18–C21, and that between the thiophene ring and the linked benzene ring is 37.5(6)°. In hexafluorocyclopentene ring, the distances clearly show that the C1–C5 bond (1.341(3) Å) is a double bond, being significantly shorter than other carbon–carbon single bonds (1.508(4) Å to 1.526(4) Å) of the ring. Two symmetrical thiophene moieties are linked by the C1=C5 double bond, with both of them attached to the ethylene group *via* the 2-position of the thiophene ring. The two methyl groups are located on opposite sides of the double bond, reflected in the torsion angles C5–C1–C7–C6 [−44.3(4)°] and C1–C5–C19–C18 [−53.5(4)°], 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 [45–47]. The intermolecular distance between the two reactive C atoms (C6...C18) is 3.664(3) Å.

The corresponding data of compounds **2o** and **3o** are summarized in Table 3. For diarylethenes **2o** and **3o**, both of them also adopt the *anti*-parallel conformation in the crystalline phase, and the distance between the two reactive C atoms is 3.552(6) Å for **2o** [48] and 3.594 (6) Å for **3o**. As a result, all molecules of crystals **1o**, **2o** and **3o** are fixed in an anti-parallel mode in the crystalline phase and the distances of the two reactive C atoms are less than 4.2 Å, which is close enough for the photocyclization reaction to take place [44,49,50]. In fact, the crystals of **1o**, **2o** and **3o** underwent photochromic reaction, in accordance with the expected ring closure, to form **1c**, **2c** and **3c** upon irradiation with UV light. Fig. 5 shows the color changes of crystals **1o**, **2o** and **3o** upon photoirradiation in the crystalline phase. When these colored crystals were dissolved in hexane, an intense absorption maximum was appeared at the same wavelength as that of their respective ring-closed isomer in solution. Alternatively, the purple-colored crystals

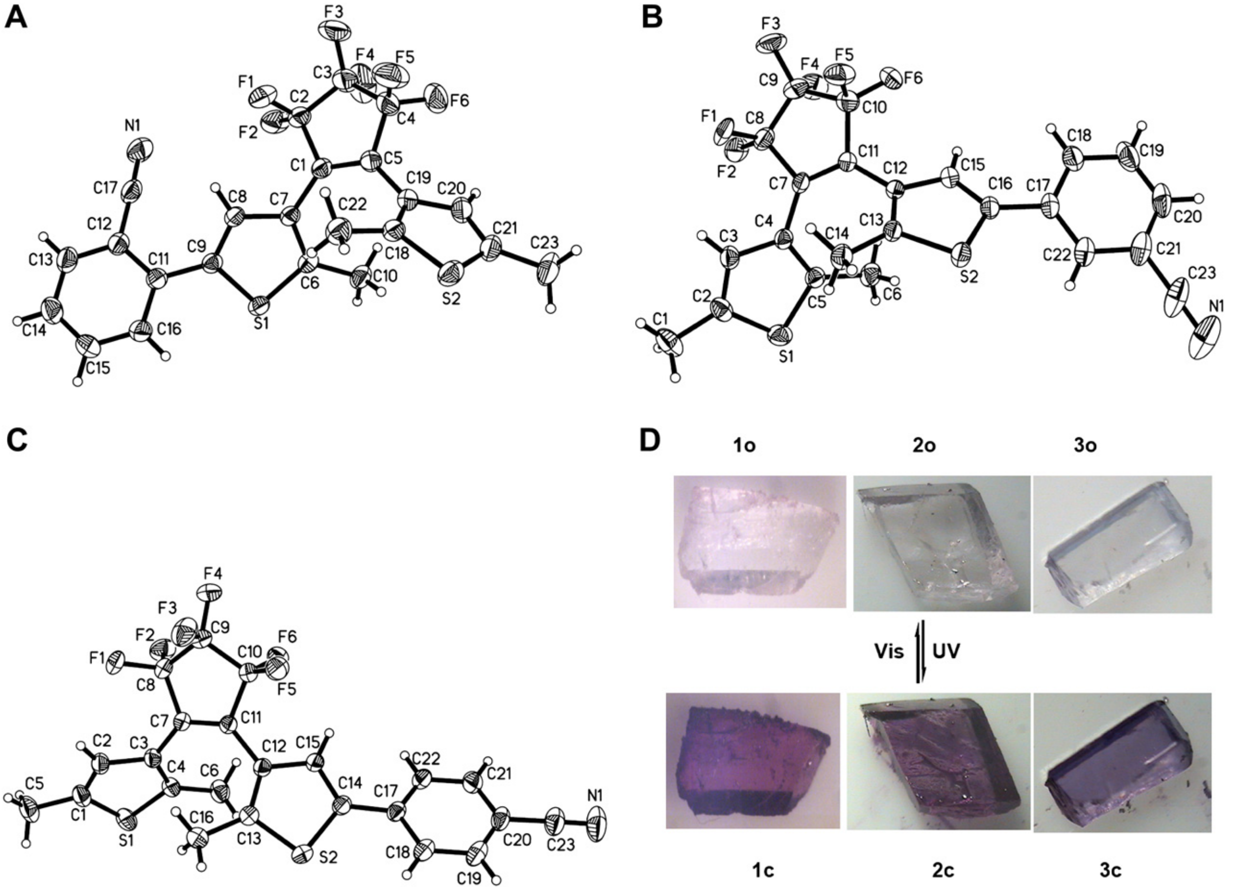

**Fig. 5.** ORTEP drawings of crystals **1o**–**3o** and their color changes by photoirradiation in the single crystalline phase: (A) ORTEP drawing of **1o**, (B) ORTEP drawing of **2o**, (C) ORTEP drawing of **3o**, (D) color changes for crystals **1**–**3**.

returned to colorless upon irradiation with the appropriate visible light ($\lambda > 450$ nm). Moreover, these photochromic crystals exhibited remarkable fatigue-resistance greater than 100 cyclization/cycloreversion repeated cycles and their ring-closed isomers remained stable for more than 300 days in the dark at room temperature. Therefore, they can be potentially used for the construction of certain optoelectronic devices [51].

### 3.3. Fluorescence of diarylethenes

Using a Hitachi F-4500 spectrophotometer, the fluorescence properties of diarylethenes **1o**, **2o** and **3o** both in solution ($2.0 \times 10^{-5}$ mol/L) and in amorphous PMMA films (10% w/w) were measured at room temperature. Because diarylethenes **2o** and **3o** show very faint fluorescence in solution, we herein only discuss the fluorescent property of diarylethene **1o** in hexane. In hexane, the emission peak of diarylethene **1o** was observed at 384 nm when excited at 300 nm. As shown in Fig. 6, the emission intensity of diarylethene **1o** was slightly decreased upon irradiation with 297 nm UV light. Irradiation by visible light at appropriate wavelengths regenerated the ring-opened isomer **1o** and restored the original emission spectrum. When reaching the photostationary state, the emission intensity of diarylethene **1** was quenched to *ca.* 88%. The lower fluorescent conversion may be mainly caused by the incomplete cyclization reaction and the existence of parallel conformations with relatively strong fluorescence [27–29].

**Table 3**
Distances between the reacting carbon atoms ($d$, Å) dihedral angles ($\theta$, °) of **1o**–**3o**.

| Compound | $d$ (Å) | | $\theta$ (°)[a] | | |
|---|---|---|---|---|---|
| | | | $\theta_1$ | $\theta_2$ | $\theta_3$ |
| **1o** | C8…C16 | 3.664(3) | 52.3(6) | 45.7(6) | 37.5(6) |
| **2o** [48] | C5…C13 | 3.552(6) | 45.8(5) | 44.0(5) | 24.4(3) |
| **3o** | C4…C13 | 3.594(6) | 42.3(8) | 41.1(8) | 23.8(8) |

[a] $\theta_1$, Dihedral angle between the hexafluorocyclopentene ring and 2,5-dimethylthiophene ring; $\theta_2$, dihedral angle between the hexafluorocyclopentene ring and the thiophene ring attached t a benzene ring; $\theta_3$, dihedral angel between the thiophene ring and the adjacent benzene ring.

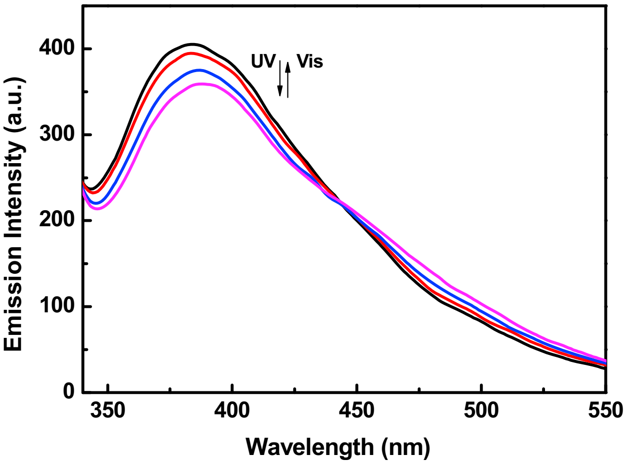

**Fig. 6.** Emission intensity changes of diarylethene **1** in hexane ($2.0 \times 10^{-5}$ mol/L) upon irradiation with 297 nm UV light at room temperature, excited at 300 nm.

In PMMA films, the emission peaks of diarylethenes **1o**, **2o** and **3o** were observed at 411, 407, and 413 nm when excited at 300 nm. Their emission intensity changes in PMMA films during the process of photoisomerization are shown in Fig. 7. As observed for most of the reported diarylethenes [34,52–56], diarylethenes **1**, **2** and **3** displayed a relatively strong fluorescence switch when they are converted from the ring-opened isomers to ring-closed isomers by photoirradiation in PMMA film. Upon irradiation with 313 nm light, their emission intensities decreased to the photostationary state, where the emission intensities of diarylethenes **1**, **2** and **3** were quenched to *ca.* 50%, 60%, and 54%, respectively. The result showed that the position of cyano substitution had a significant effect not only on the emission spectra but also on the fluorescence switching properties of diarylethenes **1**, **2** and **3**. This characteristic may be useful for increasing selectivity in their potential application as the fluorescence photo-switches. In addition, Compared to diarylethenes **1**–**3**, the analogues bearing an electron-donating methoxy group exhibited stronger emission intensity [31], and other analogues bearing a fluorine atom displayed stronger fluorescence switching property [38].

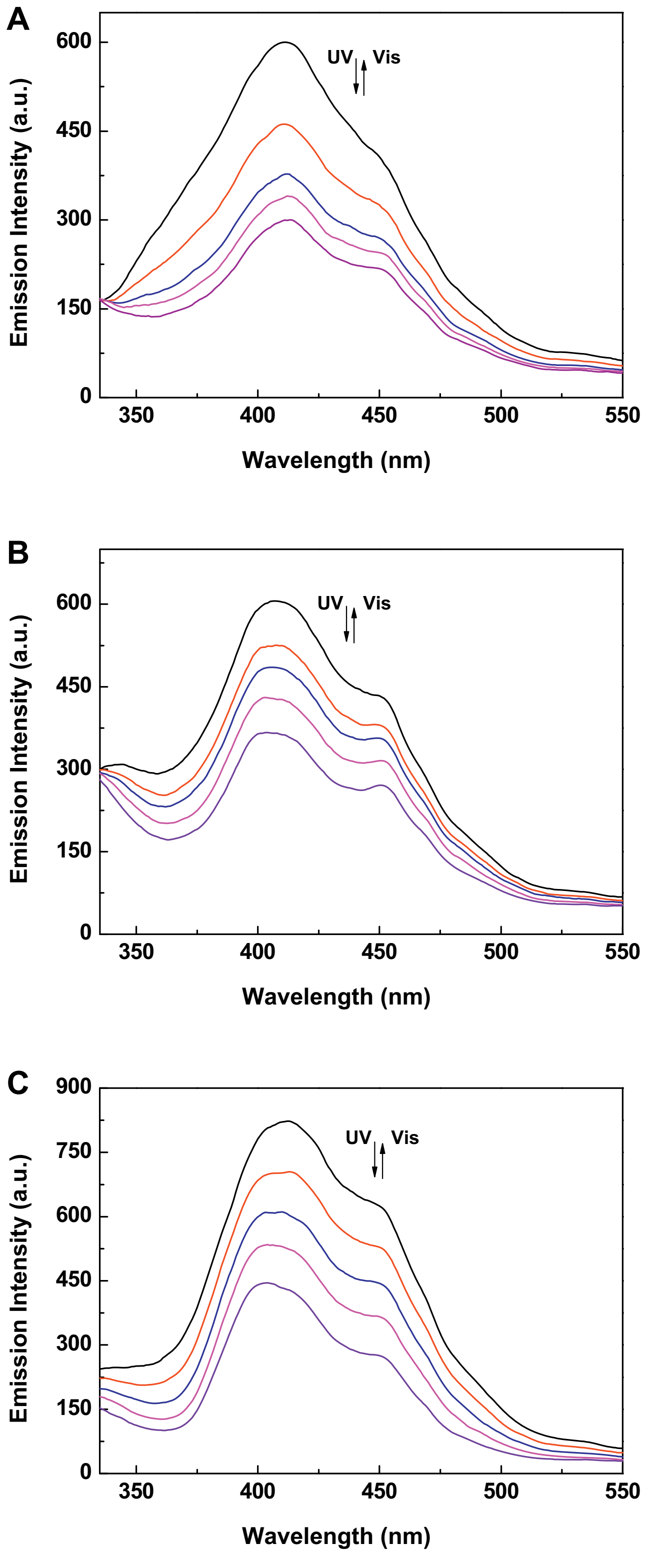

**Fig. 7.** Emission intensity changes of diarylethenes **1**–**3** in PMMA film (10%, w/w) upon irradiation with 313 nm UV light at room temperature, excited at 300 nm: (A) **1**, (B) **2**, and (C) **3**.

### 3.4. Electrochemistry of diarylethenes

Because of the differences in the π-conjugation of the two isomers of diarylethenes, the photoresponsive system described here also allows for changes in their electrochemical properties. To date, the oxidative cyclization and cycloreversion of diarylethene derivatives have been attracted much attention due to their potentially important applications in photoelectronic devices [57–61].

Cyclic voltammograms (CV) were performed on the diarylethenes **1**, **2** and **3** under identical experimental conditions at 50 mV/s and the results are shown in Fig. 8. The oxidation onsets of their ring-opened isomers **1o**, **2o** and **3o** were initiated at 1.83, 1.82 and 1.70 V, and those of their ring-closed isomers **1c**, **2c** and **3c**

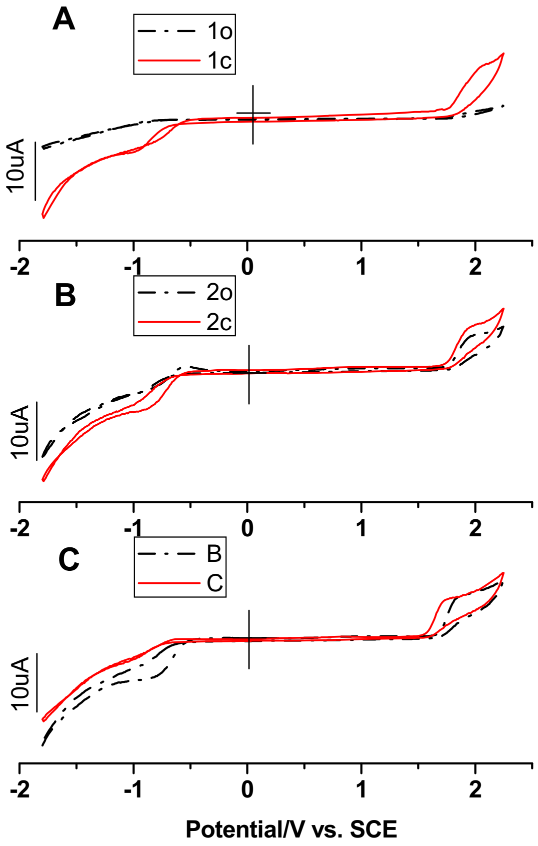

**Fig. 8.** Cyclic voltammetry (second scan) of diarylethenes **1**–**3** in acetonitrile at a scan rate of 50 mV/s: (A) **1**, (B) **2**, and (C) **3**.

**Table 4**
Electrochemical parameters of diarylethenes **1**–**3**.[a]

| Compound | Oxidation | | Reduction | | Band gap |
|---|---|---|---|---|---|
| | $E_{onset}$ (V) | IP (eV) | $E_{onset}$ (V) | EA (eV) | $E_g$ |
| **1o** | +1.83 | −6.63 | −0.84 | −3.96 | 2.67 |
| **1c** | +1.75 | −6.55 | −0.69 | −4.11 | 2.44 |
| **2o** | +1.82 | −6.62 | −0.64 | −4.16 | 2.46 |
| **2c** | +1.77 | −6.57 | −0.57 | −4.23 | 2.34 |
| **3o** | +1.70 | −6.50 | −0.61 | −4.19 | 2.31 |
| **3c** | +1.61 | −6.41 | −0.66 | −4.14 | 2.27 |

[a] The acetonitrile used as solvent was spectrograde and was purified by distillation before use.

were initiated at 1.75, 1.77 and 1.61 V, respectively. These data show that the oxidation process for the ring-opened isomers **1o**, **2o** and **3o** occurs at higher potentials than in the corresponding ring-closed isomers **1c**, **2c** and **3c**. This is because the longer conjugation length of the ring-closed isomers generally leads to a less positive potential [62]. After the cyclization reaction, the π-conjugation of the ring-closed isomer extends across the perfluorocyclopentene ring causing a lower oxidation onset. The results are in good agreement with those of the analogous diarylethenes bearing a methoxy group [31]. However, they are opposite to those of the analogues bearing a fluorine atom, for which the oxidation onsets of the ring-opened isomers are lower than those of the corresponding ring-closed isomers [38].

According to the reported methods [24,63,64], 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, as shown in Table 4. From this table, it can be easily concluded that the band-gaps of the ring-closed isomers **1c**, **2c** and **3c** are lower than those of their corresponding ring-opened isomers **1o**, **2o** and **3o**. Among these compounds, the $E_g$ of **3c** is the lowest ($E_g = 2.27$ eV), and that of **1o** is the highest ($E_g = 2.67$ eV). Compared with those of diarylethenes bearing a methoxy group that has the highest $E_g$ of 2.18 eV [31], the band-gaps of diarylethenes **1**, **2** and **3** are increased significantly, which may be attributed to the strong electron-withdrawing ability of the cyano group. Moreover, there exist clear differences among diarylethenes **1**, **2** and **3** not only in the shape of polarization curve but also in all electrochemical parameters. This is possibly because the different positions of the cyano group in the diarylethenes **1**, **2** and **3** lead to the different electron-withdrawing and steric effects. The results indicate that the cyano group and its substituted position have a great effect on the electrochemical properties of the three isomeric diarylethene compounds but further work is required to quantify these effects.

## 4. Conclusions

Three unsymmetrical isomeric diarylethenes bearing a cyano group at either the *para*-, *meta*-, or *ortho*-positions of the terminal benzene ring were synthesized, and their photochemical and electrochemical properties were investigated. It has been demonstrated that the electron-withdrawing cyano group and its substituted position have a significant effect on the properties of these isomeric diarylethene derivatives. The electron-withdrawing cyano group induced some new properties, which differed from those of diarylethene derivatives bearing methoxy group or halide substituents reported previously. These results will contribute to our understanding of the influence of the position of strong electron-withdrawing substituents in diarylethenes.

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