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# Effects of substitution on the optoelectronic properties of photochromic diarylethenes bearing a pyrrole moiety

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## ABSTRACT

Five diarylethenes bearing a pyrrole moiety were synthesized in order to investigate the effects of the substituents on the properties of these compounds. The structures of three of the diarylethenes were determined by single-crystal X-ray diffraction analysis. All of the diarylethene derivatives exhibited notable photochromism and functioned as effective fluorescent photo-switches in solution and in poly(methyl methacrylate) films. The absorption maxima and the quantum yields of cyclization and cycloreversion increased whereas the emission peaks and the emission intensities decreased evidently when the electron-withdrawing/donating substituent was attached at the *para*-position on the terminal benzene ring. Cyclic voltammograms indicated that the electron-withdrawing/donating substituents decreased the bang gaps of the open-ring isomers but enhanced those of the closed-ring isomers, compared with the unsubstituted parent diarylethene. The properties of these diarylethene derivatives were significantly different from each other, which might be attributed to the different substituent effects.

## 1. Introduction

Photochromic materials have attracted much attention as highly promising candidates for optical memories and photo-switches [1,2]. During the past several decades, there have been some achievements in the synthesis of new families of organic photochromic molecules [3–5]. Among various photochromic molecules, diarylethenes with heterocyclic aryl rings are regarded as the best candidates for photoelectronic applications mainly due to the excellent thermal stability of the respective isomers, notable fatigue resistance, rapid response and high reactivity in the solid state [6,7].

Diarylethenes bearing terminal phenyl groups have raised considerable interest in the last few years because the properties of the phenyl-substituted diarylethene derivatives can be further modified by suitable functionalization of the aromatic rings with electron-donating groups or electron-withdrawing groups [8–11]. For example, some reports indicated that the introduction of electron-donating substituents to bis(3-thienyl)ethene diarylethenes increased the absorption coefficient of the closed-ring isomers and decreased the cycloreversion quantum yield [10], but the same substituents on bis(2-thienyl)ethene diarylethenes increased the absorption maxima of the open-ring isomers and decreased the cyclization quantum yield [11]. Moreover, Bertarelli et al. demonstrated that the strong electron-donating substituents directly linked to the 5,5′-position of the diarylethene moieties gave rise to an increase in the change of the refractive index [12]. Tanifuji et al. reported the effect of radical substituents on the photochromic reactivity of bis(3-benzothiophene)perfluorocyclopentene [13], and Yamaguchi et al. investigated the substituent effect on the photochromic properties of diarylethenes bearing two benzofuran aryl groups [14]. Previously, we have reported that different substituents and the substituted-position had a significant effect on the properties of diarylethenes such as their photochromism, fluorescence, and electrochemical properties [15–21].

Apart from the fact that various functional substituents have notable effects on the photochromic features of diarylethenes, assorted heteroaryl moieties can also notably affect photochromic properties. A change in heteroaryl group can result in remarkable modification of the optical and electrochemical properties of each type of diarylethene molecule [22–25]. For instance, diarylethenes with thiophene or benzothiophene moieties exhibit excellent thermal stability and outstanding fatigue resistance [1,2], whereas symmetrical diarylethenes with two pyrrole rings are thermally unstable and return to the open-ring isomer, even in the dark [26].

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Diarylethenes bearing a pyrazole unit have a relatively high cycloreversion quantum yield [27], whereas dithienylethenes bearing bulky alkoxy groups at 2- and 2′-positions of the thiophene rings have a very small cycloreversion quantum yield [28]. Kawai et al. reported the triangular terthiophene derivatives which showed reversible photochromic reactions with high cyclization quantum yields [29]. Yamaguchi et al. developed a new type of 6π conjugated photochromic system with a bis(2,3′-benzothienyl) unit which demonstrated efficient photochromism and thermal stability for the colored isomers [30]. Yokoyama et al. and Branda et al. independently synthesized a new class of photochromic compounds based on a modified hexatriene skeleton [24,31]. This novel molecular scaffold offers the chance to decorate photoresponsive systems with a wide range of functional groups without sacrificing the photochromic behavior.

As described above, it can be concluded that most of the heteroaryl diarylethenes bear thiophene or benzothiophene rings, with just a few reports concerning other heteroaryl moieties such as furan, thiazole, indole, and so on. Pyrrole is an attractive aryl unit due to its biological characteristics [32], and its structure is similar to those of thiophene and furan. However, reports of diarylethene derivatives with a pyrrole unit are rare. As far as we know, there are only a few examples of photochromic diarylethenes bearing a pyrrole unit [26,33]. This present work a series of five unsymmetrical diarylethenes bearing a pyrrole moiety and different substituents at the *para*-position of the terminal phenyl ring was synthesized. Each of the diarylethene derivatives showed notable photochromism both in solution and in the solid state. Their photochromic scheme is shown in Fig. 1.

## 2. Experimental

### 2.1. General

All solvents were purified by distillation before use. NMR spectra were recorded on a Bruker AV400 (400 MHz) spectrometer with $CDCl_3$ as the solvent and tetramethylsilane as an internal standard. IR spectra were performed on a Bruker Vertex-70 spectrometer. Elemental analyses were determined with a PE CHN 2400 analyzer. Melting points were measured on a WRS-1B melting point apparatus. 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 light wavelength was isolated by the use of the appropriate filters. Fluorescence spectra were measured using a Hitachi F-4500 spectrophotometer. 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 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.

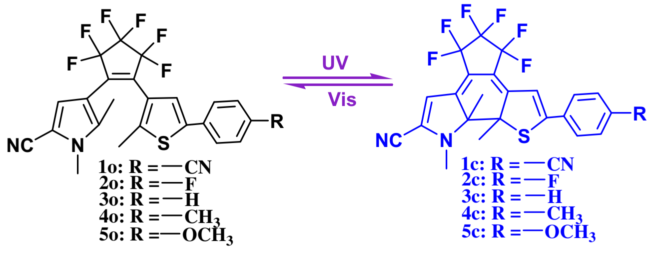

**Fig. 1.** Photochromism of diarylethenes **1**–**5**.

Suitable crystals of **2o**, **4o** and **5o** were obtained by slow evaporation of a hexane solution. All the measurements were collected by a Bruker SMART APEX II CCD diffractometer using a MULTI scan technique at room temperature 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. Further details on the crystal structure investigation have been deposited with The Cambridge Crystallographic Data Centre as supplementary publication CCDC 762280 for **2o**, 762281 for **4o**, and 639785 for **5o**. 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**–**5o** was shown in Fig. 2. Suzuki coupling of the five bromobenzene derivatives with a thiophene boronic acid [34,35] gave the alkylphenylthiophene derivatives (**7a**–**7e**). 1-(2-Cyano-1,5-dimethyl-4-pyrryl)perfluorocyclopentene (**10**) [33] was synthesized by bromination and lithiation reactions from 5-cyano-1,2-dimethylpyrrole. Finally, compounds **7a**–**7e** were separately lithiated and then coupled with compound **10** to give diarylethenes **1o**–**5o**, respectively.

#### 2.2.1. 3-Bromo-2-methyl-5-(4-cyanophenyl) thiophene (*7a*)

Compound **7a** was prepared by reacting 3-bromo-2-methyl-5-thienylboronic acid (**6**) [34,35] (5.0 g; 22.6 mmol) with 4-bromobenzonitrile (4.11 g, 22.6 mmol) in the presence of $Pd(PPh_3)_4$ (0.6 g) and $Na_2CO_3$ (6.4 g, 60 mmol) in tetrahydrofuran (THF) (80 mL, containing 10% water). After refluxing for 15 h at 70 °C, the reaction mixture was allowed to slowly warm to the room temperature and then extracted with ether. The organic layer was collected and dried over $MgSO_4$, filtrated and evaporated. The crude product was purified by column chromatography on $SiO_2$ using hexane as the eluent resulting in 4.46 g of **7a** being obtained as a pale yellow solid in 71% yield. M.p. 79–80 °C; Anal. Calcd for $C_{12}H_8BrNS$ (%): C, 51.81; H, 2.90; N, 5.04. Found C, 51.99; H, 3.01; N, 4.96; $^1H$ NMR (400 MHz, $CDCl_3$, TMS): δ 2.41 (s, 3H, $-CH_3$), 7.03 (s, 1H, thienyl-H), 7.06 (t, 2H, $J = 8.0$ Hz, phenyl-H), 7.44–7.48 (m, 2H, phenyl-H); IR (ν, KBr, $cm^{-1}$): 808, 829, 1013, 1067, 1164, 1329, 1465, 1504, 1604, 2224, 2919.

#### 2.2.2. 3-Bromo-5-2-methyl-(4-fluorophenyl)thiophene (*7b*)

Compound **7b** was prepared by a method similar to that used for **7a**. The crude product was purified by column chromatography on $SiO_2$ using petroleum ether as eluent to give **7b** (2.54 g, 75%) as a yellow solid. M.p. 61–63 °C; Anal. Calcd for $C_{11}H_8BrFS$ (%): C, 48.73; H, 2.97. Found C, 48.91; H, 2.84; $^1H$ NMR (400 MHz, $CDCl_3$, TMS): δ 2.45 (s, 3H, $-CH_3$), 7.18 (s, 1H, thienyl-H), 7.50 (t, $J = 7.6$ Hz, 1H, phenyl-H), 7.56 (d, 1H, $J = 8.0$ Hz, phenyl-H), 7.73 (d, 1H, $J = 8.0$ Hz, phenyl-H), 7.79 (s, 1H, phenyl-H); IR (ν, KBr, $cm^{-1}$): 789, 818, 837, 945, 1011, 1098, 1158, 1243, 1277, 1303, 1326, 1375, 1469, 1516, 1541, 1602, 1885, 2917.

#### 2.2.3. 3-Bromo-2-methyl-5-phenyl-thiophene (*7c*)

Compound **7c** was prepared by a method similar to that used for **7a**. The crude product was purified by column chromatography on $SiO_2$ using hexane as eluent to give **7c** (2.54 g, 83%) as a pale yellow

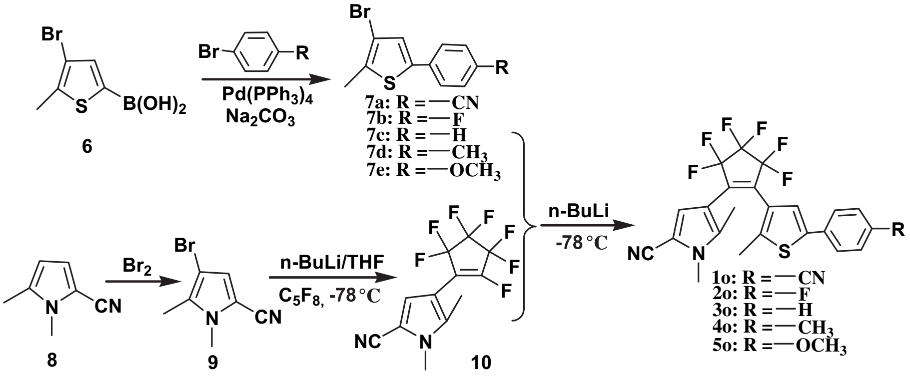

**Fig. 2.** Synthetic route for diarylethenes **1o**–**5o**.

solid. M.p. 66–68 °C; Anal. Calcd for $C_{11}H_9BrS$ (%): C, 52.19; H, 3.58. Found C, 52.34; H, 3.43; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 2.34 (s, 3H, $-CH_3$), 7.02 (s, 1H, thienyl-H), 7.20 (d, 1H, $J = 8.0$ Hz, phenyl-H), 7.29 (t, 2H, $J = 8.4$ Hz, phenyl-H), 7.42 (d, 2H, $J = 8.0$ Hz, phenyl-H); IR ($\nu$, KBr, $cm^{-1}$): 754, 792, 827, 904, 946, 1007, 1032, 1072, 1155, 1326, 1443, 1467, 1498, 1537, 2918.

### 2.2.4. *3-Bromo-2-methyl-5-(4-methylphenyl)thiophene (**7d**)*

Compound **7d** was prepared by a method similar to that used for **7a**. The crude product was purified by column chromatography on $SiO_2$ using petroleum ether as eluent to give **7d** (2.94 g, 83%) as a pale yellow solid. M.p. 67–68 °C; Anal. Calcd for $C_{12}H_{11}BrS$ (%): C, 53.94; H, 4.15. Found C, 54.09; H, 4.03; $^1H$ NMR (400 MHz, $CDCl_3$, TMS): $\delta$ 2.37 (s, 3H, $-CH_3$), 2.41 (s, 3H, $-CH_3$), 7.01 (s, 1H, thienyl-H), 7.19 (d, 2H, $J = 8.0$ Hz, phenyl-H), 7.38 (d, 2H, $J = 8.0$ Hz, phenyl-H); IR ($\nu$, KBr, $cm^{-1}$): 784, 807, 944, 1007, 1019, 1120, 1162, 1274, 1309, 1327, 1374, 1442, 1511, 2852, 2915.

### 2.2.5. *3-Bromo-2-methyl-5-(4-methoxyphenyl)thiophene (**7e**)*

Compound **7e** was prepared by a method similar to that used for **7a**. The crude product was purified by column chromatography on $SiO_2$ using petroleum ether as eluent to give **7e** (2.51 g, 76%) as a pale yellow solid. M.p. 107–108 °C; Anal. Calcd for $C_{12}H_{11}BrOS$ (%): C, 50.90; H, 3.92. Found C, 50.72; H, 4.04; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 2.41 (s, 3H, $-CH_3$), 3.91 (s, 3H, $-OCH_3$), 6.95–6.99 (m, 2H, phenyl-H), 7.27 (s, 1H, thienyl-H), 7.30 (s, 1H, phenyl-H), 7.54 (d, 1H, $J = 8.0$ Hz, phenyl-H); IR ($\nu$, KBr, $cm^{-1}$): 797, 818, 946, 1033, 1111, 1161, 1179, 1255, 1288, 1309, 1455, 1541, 1603, 2917.

### 2.2.6. *3-Bromo-1,5-dimethyl-2-pyrrolecarbonitrile (**9**)*

To a stirred solution of 1,5-dimethyl-2-pyrrolecarbonitrile (**8**) (3.01 g, 25.00 mmol) in acetic acid (100 mL) at 0 °C was slowly added $Br_2$/acetic acid ($v/v = 29/40$) solution. The reaction mixture was stirred overnight at this temperature. After pouring the reaction mixture into a beaker containing some water, a large quantity of yellow precipitate was produced. The precipitate was washed by water, filtered and dried, and then purified by silica gel column chromatography using hexane as the eluent. Compound **8** was obtained as a pale yellow solid (4.21 g) with a yield of 85%. M.p. 124–125 °C; Anal. Calcd for $C_7H_7BrN_2$ (%): C, 42.24; H, 3.54; N, 14.07. Found C, 42.05; H, 3.62; N, 14.23; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 2.30 (s, 3H, $-CH_3$), 3.68 (s, 3H, $-CH_3$), 6.74 (s, 1H, pyrrole-H); IR ($\nu$, KBr, $cm^{-1}$): 717, 811, 1045, 1133, 1175, 1334, 1375, 1410, 1470, 1529, 2214, 2953, 3130.

### 2.2.7. *2-Cyano-1,5-dimethyl-4-pyrryl-perfluorocyclopentene (**10**)*

To a stirred THF solution (80 mL) of compound **9** (4.02 g, 20.10 mmol) was added dropwise a 2.5 M *n*-BuLi/hexane solution (8.80 mL, 22.00 mmol) at −78 °C under nitrogen atmosphere. Stirring was continued for 30 min at −78 °C, octafluorocyclopentene ($C_5F_8$) (2.80 mL, 20.51 mmol) was slowly added and the reaction mixture was stirred for 2.0 h at this low temperature. The reaction was quenched by water. The product was extracted with diethyl ether. The organic layer was washed with 1 M aqueous HCl and water, and then dried over anhydrous $MgSO_4$, filtrated and evaporated *in vacuo*. The crude product was purified by column chromatography on silica gel using petroleum ether as the eluent to give 3.62 g compound **10** obtained as a pale yellow solid in 57% yield. M.p. 101–103 °C; Anal. Calcd for $C_{12}H_7F_7N_2$ (%): C, 46.17; H, 2.26; N, 8.97. Found C, 46.39; H, 2.11; N, 9.12; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 2.32 (s, 3H, $-CH_3$), 3.72 (s, 3H, $-CH_3$), 6.98 (s, 1H, pyrrole-H); IR ($\nu$, KBr, $cm^{-1}$): 845, 890, 974, 1031, 1155, 1203, 1281, 1330, 1372, 1488, 1547, 1696, 2219, 3450.

### 2.2.8. *1-[2-Methyl-5-(4-cyanophenyl)-3-thienyl]-2-(2-cyano-1,5-dimethyl-4-pyrryl)perfluorocyclopentene (**1o**)*

To a stirred anhydrous THF (70 mL) of compound **7a** (0.59 g, 2.12 mmol) was added dropwise a 2.5 M *n*-BuLi/hexane solution (0.95 mL) at −78 °C under argon atmosphere. After 30 min, 15 mL THF containing compound **10** (0.66 g, 2.30 mmol) was added and the reaction mixture was stirred for 2 h at this low temperature. The reaction was allowed to slowly warm to the room 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 0.39 g compound **1o** as a colorless solid in 38% yield. M.p. 180–181 °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, 8.63; $^1H$ 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, $cm^{-1}$): 744, 824, 897, 980, 1057, 1119, 1194, 1269, 1333, 1436, 1552, 1606, 2219.

### 2.2.9. *1-[2-Methyl-5-(4-fluorophenyl)-3-thienyl]-2-(2-cyano-1,5-dimethyl-4-pyrryl)perfluorocyclopentene (**2o**)*

Diarylethene **2o** was prepared by an analogous method similar to that used for diarylethene **1o** using **7b** instead of **7a**, and was obtained as a colorless solid 0.39 g in 34% yield. M.p. 161–163 °C; 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, $CDCl_3$): $\delta$ 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, 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, $CDCl_3$): $\delta$ 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 ($\nu$, KBr, $cm^{-1}$): 741, 807, 828, 894, 987, 1056, 1095, 1183, 1231, 1275, 1335, 1397, 1469, 1513, 1548, 1623, 2221, 3123.

### 2.2.10. *1-[2-Methyl-5-phenyl-3-thienyl]-2-(2-cyano-1,5-dimethyl-4-pyrryl)perfluorocyclopentene (**3o**)*

Diarylethene **3o** was prepared by an analogous method similar to that used for diarylethene **1o** using **7c** instead of **7a**, and was obtained as a yellow solid 0.47 g in 36% yield. M.p. 140–142 °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.

### 2.2.11. *1-[2-Methyl-5-(4-methylphenyl)-3-thienyl]-2-(2-cyano-1,5-dimethyl-4-pyrryl)perfluorocyclopentene (**4o**)*

Diarylethene **4o** was prepared by an analogous method similar to that used for diarylethene **1o** using **7d** instead of **7a**, and was obtained as a colorless solid 0.37 g in 40% yield. M.p. 135–137 °C; Anal. Calcd for $C_{24}H_{18}F_6N_2S$ (%): C, 59.99; H, 3.78, N, 5.83. Found C, 59.94; H, 3.81; N, 5.72; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 1.68 (s, 3H, $-CH_3$), 1.87 (s, 3H, $-CH_3$), 2.30 (s, 3H, $-CH_3$), 3.54 (s, 3H, $-CH_3$), 6.88 (s, 1H, pyrrole-H), 7.13 (d, 3H, $J = 7.6$ Hz, phenyl-H), 7.36 (d, 2H, $J = 8.0$ Hz, phenyl-H); $^{19}F$ NMR (400 MHz, $CDCl_3$): $\delta$ 131.71 (2F), 110.36 (2F), 109.84 (2F). $^{13}C$ NMR (400 MHz, $CDCl_3$): $\delta$ 11.1,11.3, 14.5, 21.2, 33.1, 105.5, 110.0, 112.9, 118.8, 120.2, 122.0, 125.5, 125.9, 129.7, 130.5, 136.0, 138.0, 139.8, 142.6; IR ($\nu$, KBr, $cm^{-1}$): 740, 808, 844, 894, 982, 1055, 1111, 1192, 1262, 1332, 1436, 1551, 1642, 225, 2919, 3129.

### 2.2.12. *1-[2-Methyl-5-(4-methoxyphenyl)-3-thienyl]-2-(2-cyano-1,5-dimethyl-4-pyrryl)perfluorocyclopentene (**5o**)*

Diarylethene **5o** was prepared by an analogous method similar to that used for diarylethene **1o** using **7e** instead of **7a**, and was obtained as a colorless solid 0.41 g in 38% yield. M.p. 144–145 °C; Anal. Calcd for $C_{24}H_{18}F_6N_2OS$ (%): C, 58.06; H, 3.65; N, 5.64. Found C, 58.10; H, 3.59; N, 5.62; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 1.69 (s, 3H, $-CH_3$), 1.87 (s, 3H, $-CH_3$), 3.53 (s, 3H, $-CH_3$), 3.77 (s, 3H, $-OCH_3$), 6.84 (s, 1H, pyrrole-H), 6.86 (s, 2H, benzene-H), 7.04 (s, 1H, thiophene-H), 7.38 (d, 2H, $J = 8.4$ Hz, benzene-H); $^{13}C$ NMR (400 MHz, $CDCl_3$): $\delta$ 11.2, 14.4, 30.8, 32.9, 55.4, 105.5, 110.1, 112.8, 114.5, 116.2, 118.8, 121.5, 125.9, 126.2, 126.9, 135.9, 139.3, 142.5, 159.7; IR ($\nu$, KBr, $cm^{-1}$): 743, 822, 845, 895, 985, 1031, 1056, 1108, 1183, 1256, 1335, 1399, 1442, 1466, 1514, 1553, 1611, 2219, 2840, 3128.

## 3. Results and discussion

### 3.1. *Photochromism in solution and solid medium*

The photochromic behavior of diarylethenes **1**–**5** induced by photoirradiation at room temperature was measured in hexane ($2.0 \times 10^{-5}$ mol/L) and in PMMA amorphous films (10%, w/w) as well as the color of diarylethenes **1**–**5**, induced by alternating irradiation with UV and visible light of appropriate wavelength. The changes in the absorption spectra of diarylethene **1** and the color changes of diarylethenes **1**–**5** in hexane induced by alternating irradiation with UV light and visible light at appropriate wavelength are shown in Fig. 3. The absorption maximum of the colorless compound **1o** was observed at 312 nm ($\varepsilon$, $8.82 \times 10^3$ L/mol cm). Upon irradiation with 297 nm UV light, the colorless solution of **1o** turned blue with a new visible absorption band centered at 603 nm ($\varepsilon$, $3.32 \times 10^3$ L/mol cm), indicating the formation of the closed-ring isomer **1c**. Alternatively, the blue-colored solution bleached completely to colorless upon irradiation with visible light ($\lambda > 500$ nm), indicating that **1c** returned to the initial state **1o**. The coloration–decoloration cycle could be repeated more than 100 times and a clear isosbestic point was observed at 335 nm. Just like diarylethene **1**, upon irradiation with 297 nm light, the absorption bands of compounds **2**–**5** in the visible region appeared and the solutions turned blue as a result of the cyclization reaction leading to the production of the closed-ring isomers **2c**–**5c** (Fig. 3). Their absorption maxima in the visible region were observed at 586 nm for **2**, 584 nm for **3**, 592 nm for **4**, and 592 nm for **5**, respectively. All the blue-colored solutions of **2c**–**5c** could be decolorized upon irradiation with visible light of wavelength greater than 500 nm again, due to the conversion of the compounds to the open-ring isomers **2o**–**5o**. After repeating 100 coloration–decoloration cycles, the isosbestic points of compounds **2**–**5** were observed at 308, 308, 313, and 320 nm, respectively. In addition, the photoconversion ratios of the five derivatives were analyzed by HPLC in the photostationary state, with the value of 96% for **1**, 89% for **2**, 90% for **3**, 90% for **4**, and 94% for **5**, respectively (Table 1). In PMMA films, diarylethenes **1**–**5** also showed similar photochromism to that in hexane, and the changes in the absorption spectra of diarylethene **1** and the color changes of diarylethenes **1**–**5** are shown in Fig. 4. A 10 mg sample of each diarylethene **1**–**5** and 100 mg of poly(methyl

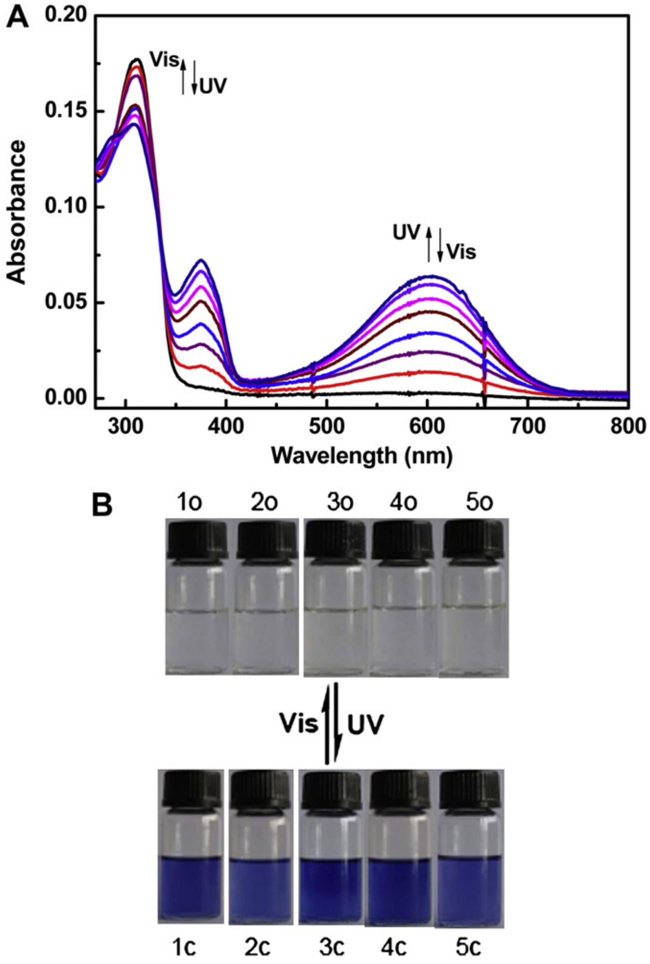

**Fig. 3.** Absorption spectral change of diarylethene **1** and color changes of diarylethenes **1**–**5** upon alternating irradiation with UV and visible light in hexane ($2.0 \times 10^{-5}$ mol/L) at room temperature: (A) spectral changes for compound **1** and (B) color changes for compounds **1**–**5**.

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

| Compound | $\lambda_{o,max}$/nm[a] ($\varepsilon$, L/mol cm) | | $\lambda_{c,max}$/nm[b] ($\varepsilon$, L/mol cm) | | $\Phi$[c] | | Conversion at PSS in hexane |
|---|---|---|---|---|---|---|---|
| | Hexane | PMMA film | Hexane | PMMA film | $\Phi_{o-c}$ | $\Phi_{c-o}$ | |
| **1** | 312 ($8.82 \times 10^3$) | 319 | 603 ($3.32 \times 10^3$) | 622 | 0.41 | 0.20 | 96% |
| **2** | 290 ($2.11 \times 10^4$) | 312 | 586 ($7.19 \times 10^3$) | 614 | 0.26 | 0.098 | 89% |
| **3** | 290 ($2.49 \times 10^4$) | 302 | 584 ($1.00 \times 10^4$) | 607 | 0.20 | 0.054 | 90% |
| **4** | 291 ($2.34 \times 10^4$) | 302 | 592 ($6.02 \times 10^3$) | 608 | 0.22 | 0.090 | 90% |
| **5** | 296 ($2.83 \times 10^4$) | 307 | 592 ($1.15 \times 10^4$) | 614 | 0.44 | 0.10 | 94% |

[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.

methacrylate) (PMMA) were dissolved in chloroform (1 mL) with the aid of ultrasound, and the homogeneous solution was spin-coated on a quartz substrate (10 mm × 10 mm × 1 mm). Upon irradiation with 297 nm light, the colorless diarylethene **1o**/PMMA film turned blue, of which the absorption maxima was observed at 622 nm; while the colors of other four diarylethene/PMMA films changed from colorless to blue with the appearance of a new broad absorption band centered at 614, 607, 608 and 614 nm, respectively, which was assigned to the formation of the closed-ring isomers **2c**–**5c**. All colored diarylethene/PMMA films reverted to colorless upon irradiation with visible light ($\lambda > 500$ nm). As has been observed for most of the reported diarylethenes [36,37], the maximum absorption peaks of both the open-ring and the closed-ring isomers for diarylethenes **1**–**5** in PMMA film were at longer wavelengths than those in hexane. The red shifts of the absorption maxima of the open-ring isomers were 7 nm for **1o**, 22 nm for **2o**, 12 nm for **3o**, 11 nm for **4o**, and 11 nm for **5o**, respectively, and those of the closed-ring isomers were 19 nm for **1c**, 28 nm for **2c**, 23 nm for **3c**, 16 nm for **4c** and 22 nm for **5c**, respectively. The red shift phenomena is ascribed to the polar effect of the polymer matrix in the amorphous solid state [38,39].

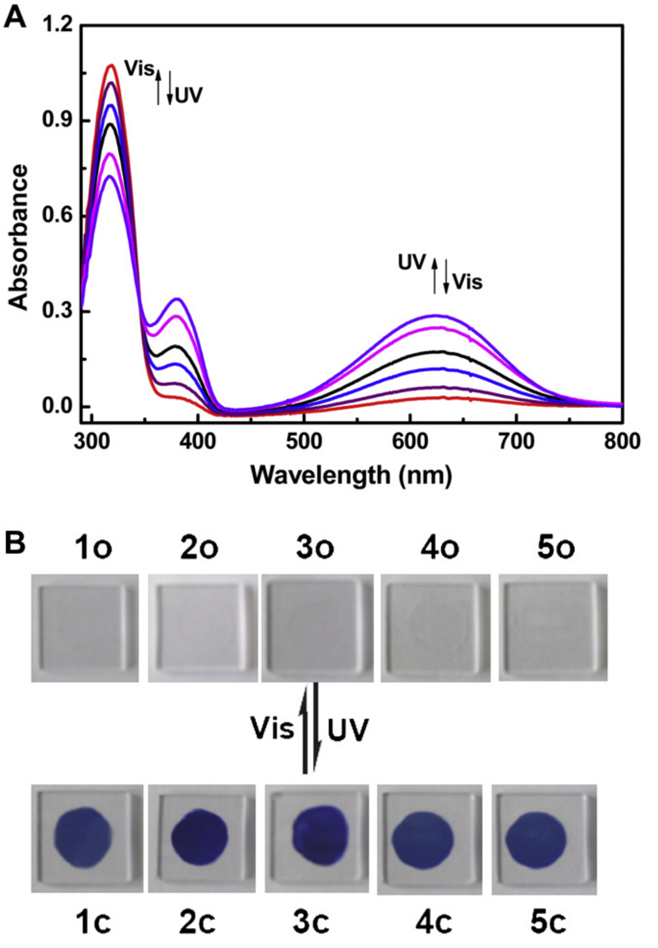

**Fig. 4.** Absorption spectral change of diarylethene **1** and color changes of diarylethenes **1**–**5** upon alternating irradiation with UV and visible light in PMMA films (10%, w/w) at room temperature: (A) spectral changes for compound **1** and (B) color changes for compounds **1**–**5**.

The photochromic features of diarylethenes **1**–**5** in hexane and in PMMA films are summarized in Table 1. The results showed that different substituents at the *para*-positions of the benzene ring had a significant effect on the photochromic features of diarylethenes **1**–**5** such as the absorption maxima, molar absorption coefficients, and quantum yields. Among these five compounds, the absorption maximum of the unsubstituted parent compound **3** was at the shortest wavelength in hexane and in a PMMA film. Replacing the hydrogen atom at the *para*-position of the terminal benzene ring with either an electron-withdrawing substituent (cyano or fluorine group, such as in compound **1** or **2**) or with an electron-donating group (methyl or methoxy group, such as in compound **4** or **5**) resulted in a red shift in the absorption maxima, the magnitude of which increased with electron-withdrawing and electron-donating ability. Thus, the stronger the electron-withdrawing/donating ability of the substituent is, the longer the absorption maximum of diarylethene is achieved in both open-ring and closed-ring isomers. For instance, the absorption maximum of **1** was longer than that of diarylethene **2** due to the stronger electron-withdrawing ability of the cyano group as compared to a fluorine atom. The result is consistent with that of diarylethene derivatives bearing a six-membered aryl unit [18]. When substituting with the electron-withdrawing group (cyano or fluorine group, such as in compound **1** or **2**) in the same diarylethene system, the molar absorption coefficients decreased notably, compared with the unsubstituted parent compound **3**. However, the strong electron-donating methoxy group could effectively enhance the molar absorption coefficient of diarylethene **5**, both for its open-ring and closed-ring isomers. The quantum yields of the unsubstituted parent compound **3** were 0.20 for the cyclization reaction and 0.054 for the cycloreversion reaction, were the smallest among the five diarylethene derivatives. When replacing the hydrogen atom at the *para*-position of the terminal benzene ring with an electron-withdrawing substituent (cyano or fluorine group, such as compound **1** or **2**), the quantum yields increased to some extent with the increase in the electron-withdrawing ability. Similarly, when replacing the hydrogen atom with an electron-donating substituent (methyl or methoxy group, such as compound **4** or **5**), the values also increased with the increase in the electron-donating ability. Compared to that of the unsubstituted parent compound **3**, the cyclization quantum yields of diarylethenes **1** and **5**, which had a strong electron-withdrawing/donating substituent, were twofold higher. Furthermore, for diarylethenes **1**–**5**, all of the cyclization quantum yields were higher than their respective cycloreversion quantum yields (Table 1). The result is quite different from that of diarylethenes bearing a pyrazole moiety whose cyclization quantum yields were much smaller than their respective cycloreversion quantum yields [27]. In addition, diarylethenes bearing a pyrrole unit have a larger absorption maximum of the closed-ring isomers compared with diarylethenes bearing thiophene, thiazole or pyrazole unit [17,27,40].

### 3.2. Photochromism in the crystalline phase

Among diarylethenes **1o**–**5o**, single crystals of diarylethenes **2o**, **4o** and **5o** were obtained by slow evaporation of hexane solutions. To gain a deeper understanding of the relationship between the conformation and the photochromism of these diarylethene derivatives in the crystalline phase, their structural confirmations were provided by X-ray crystallographic analysis. The ORTEP drawings of the single crystals of **2o**, **4o** and **5o** are shown in Fig. 5, and the X-ray crystallographic analysis data are listed in Table 2. For compound **2o**, there were two independent molecules in the asymmetric unit and both of them adopted an approximate $C_2$ symmetry with the photoactive *anti*-parallel conformation in the crystalline phase, which could undergo photocyclization [7,41,42]. The two planar aryl moieties exhibited similar geometries in each molecule, with dihedral angles between the cyclopentene ring and the adjacent aryl rings of 33.8° for N1/C17–C20 and 52.8° for S1/C1–C4 in one molecule and 34.5° for N3/C40–C43 and 50.5° for S4/C24–C27 in the other. The distances between the potentially photoactive C atoms (C4…C18 and C27…C41) in each molecule were 3.570 and 3.582 Å, respectively, which were close enough for the cyclization reaction [43,44]. The distances between the reacting carbon atoms $d$ (Å) and dihedral angles $\theta$ (°) of diarylethenes **4o** and **5o** were also measured as shown in Table 3. The distance between the potentially photoactive carbon atoms (C5…C9) in crystal **4o** was 3.566 Å, and that (C1…C13) in crystal **5o** was 3.539 Å. From the data, it could be concluded that all molecules of crystals **2o**, **4o** and **5o** were fixed in an *anti*-parallel mode in the crystalline phase and the distances of the two reactive carbon atoms were less than 4.2 Å, which were close enough for the photocyclization reaction, indicating that they could be expected to undergo photochromism in the single crystalline phase. In fact, the crystals of **2o**, **4o** and **5o** underwent photochromic reaction, in accordance with the expected ring closure, to form **2c**, **4c** and **5c** upon irradiation with UV light. The color changes of crystals **2o**, **4o** and **5o** upon photoirradiation in the crystalline phase are indicated in Fig. 6. Upon irradiation with 297 nm light, the colorless crystals of **2o**, **4o** and **5o** turned blue quickly. When these colored crystals were dissolved in hexane, the solution turned blue and the absorption maximum was observed at the same wavelength as that of their respective closed-ring isomer in solution. Alternatively, the blue-colored crystals returned to colorless upon irradiation with the appropriate wavelength visible light ($\lambda > 500$ nm). Furthermore, these crystals exhibited remarkable fatigue resistance greater than 100 cyclization/cycloreversion repeated cycles and their closed-ring isomers remained stable for more than 100 days in the dark at room temperature. As such, they could be potentially used for the construction of certain optoelectronic devices [6,45].

### 3.3. Fluorescence of diarylethenes

The fluorescent properties of diarylethenes **1o**–**5o** in solution ($5.0 \times 10^{-5}$ mol/L) and in PMMA films (10%, w/w) were measured at room temperature using a Hitachi F-4500 spectrophotometer. The fluorescence emission spectra of **1o**–**5o** are illustrated in Fig. 7. In hexane, the emission peaks of diarylethenes **1o**–**5o** were observed at 416, 415, 439, 430 and 426 nm when excited at 340 nm, and were observed at 416, 412, 423, 415, and 422 nm when excited at 350 nm in PMMA films. When comparing samples in hexane to those in PMMA films, the emission peaks of diarylethenes **2o**–**5o** consistently exhibited a hypsochromic shift with values of 3 nm for **2o**, 16 nm for **3o**, 15 nm for **4o**, and 4 nm for **5o**, respectively. The result is completely contrary to those reported previously [16,34,36,46]. Among diarylethenes **1o**–**5o**,

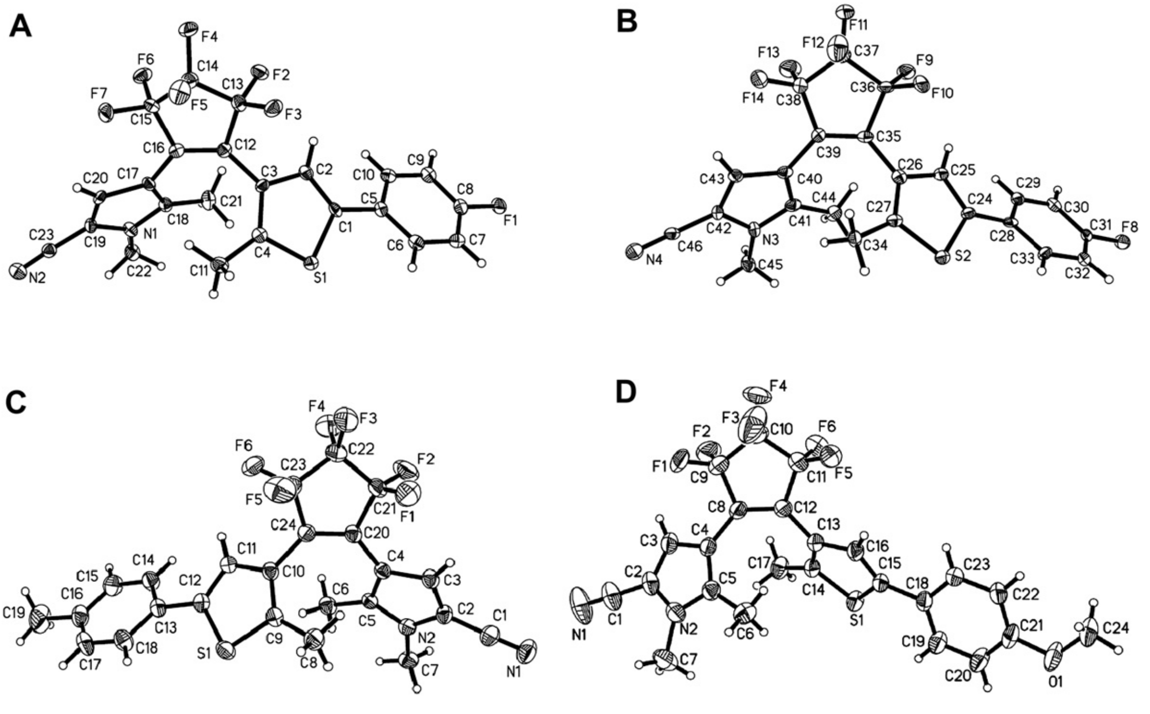

**Fig. 5.** ORTEP drawings of crystals **2o**, **4o** and **5o**, showing about 30% probability displacement ellipsoids: (A) **2o(I)**, (B) **2o(II)**, (C) **4o**, and (D) **5o**.

**Table 2**
Crystal data for diarylethenes **2o**, **4o** and **5o**.

| | Compound | | |
|---|---|---|---|
| | **2o** | **4o** | **5o** |
| Formula | $C_{23}H_{15}F_7N_2S$ | $C_{24}H_{18}F_6N_2S$ | $C_{24}H_{18}F_6N_2OS$ |
| Formula weight | 484.43 | 480.46 | 496.46 |
| Temperature | 113(2) | 294(2) | 291(2) |
| Crystal system | Orthorhombic | Triclinic | Monoclinic |
| Space group | Pca2(1) | P-1 | P2(1)/c |
| Unit cell dimensions $a$ (Å) | 16.626(3) | 8.058(3) | 23.120(3) |
| $b$ (Å) | 6.3555(13) | 8.805(3) | 8.9474(11) |
| $c$ (Å) | 38.695(8) | 15.818(6) | 11.4416(13) |
| $\alpha$ (°) | 90.00 | 90.194(7) | 90.00 |
| $\beta$ (°) | 90.00 | 98.116(7) | 101.835(1) |
| $\gamma$ (°) | 90.00 | 96.102(7) | 90.00 |
| Volume (Å$^3$) | 4088.8(14) | 1104.6(7) | 2316.6(5) |
| $Z$ | 8 | 2 | 4 |
| Density (calcd.) (g/cm$^3$) | 1.574 | 1.445 | 1.509 |
| Goodness-of-fit on $F^2$ | 1.089 | 1.043 | 1.038 |
| Final $R_1[I > 2s(I)]$ | 0.0674 | 0.074 | 0.0537 |
| $wR_2[I > 2s(I)]$ | 0.1502 | 0.1996 | 0.1364 |
| $R_1$ (all data) | 0.0828 | 0.1066 | 0.0715 |
| $wR_2$ (all data) | 0.1610 | 0.2212 | 0.1524 |

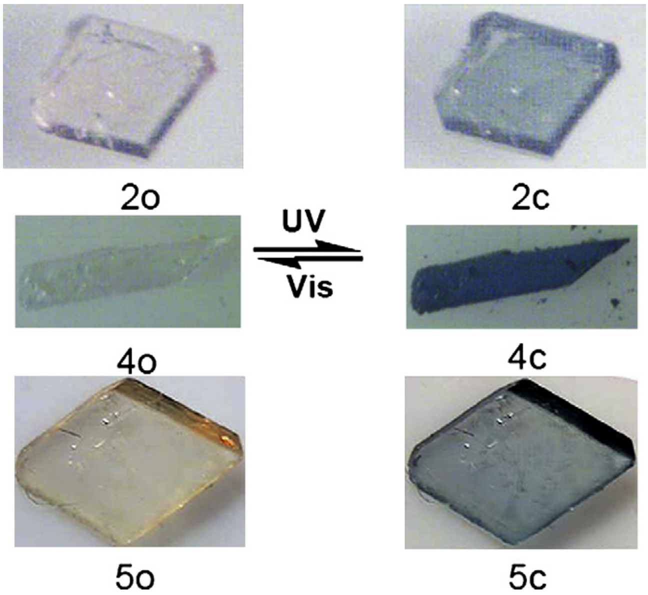

**Fig. 6.** Photographs of photochromic processes of diarylethenes **2**, **4** and **5** in the crystalline phase.

the emission peak of the unsubstituted parent diarylethene **3o** was at the longest wavelength and its emission intensity was the strongest in hexane and in PMMA films. When the hydrogen atom at the *para*-position of the terminal benzene ring was replaced with either an electron-withdrawing or with an electron-donating substituent, both the emission peak and the emission intensity decreased notably with the increase in the electron-withdrawing or electron-donating ability. The result was different from diarylethene derivatives bearing a thiazole moiety [40]. For diarylethenes bearing a thiazole moiety, the emission peak was shifted to a longer wavelength when replacing the hydrogen atom with an electron-donating substituent, while it was shifted to a shorter wavelength when replacing with an electron-withdrawing substituent. Moreover, when going from electron-withdrawing to electron-donating groups, the emission peaks of these diarylethenes were shifted to a longer wavelength in hexane (from 416 to 430 nm), and their emission intensities were significantly increased at a lower concentration ($5.0 \times 10^{-5}$ mol/L). Therefore, the electron-donating group could be effective to increase the emission peak and the emission intensity of diarylethenes bearing a pyrrole moiety. The result is quite different from that of diarylethenes bearing a biphenyl moiety where the electron-donating group could be effective to increase the emission intensity but decrease the emission peak [8]. In addition, by using anthracene (0.27 in acetonitrile) as the reference, the fluorescence quantum yields of the open-ring isomers of **1o**–**5o** were determined to be 0.047, 0.028, 0.010, 0.013, and 0.025, respectively. The result indicated that the unsubstituted parent diarylethene **3** had the smallest fluorescence quantum yield. Replacing the hydrogen atom at the *para*-position of the terminal benzene ring with an electron-withdrawing substituent (such as in compound **1** or **2**) or with an electron-donating substituent (such as in compound **4** or

**Table 3**
Distances between the reacting carbon atoms $d$ (Å) and dihedral angles $\theta$ (°) of diarylethenes **2o**, **4o** and **5o**.

| Compound | $d$ (Å) | | $\theta$ (°)[a] | | |
|---|---|---|---|---|---|
| | | | $\theta_1$ | $\theta_2$ | $\theta_3$ |
| **2o(I)** | C4…C18 | 3.570 | 33.8 | 52.8 | 29.1 |
| **2o(II)** | C27…C41 | 3.582 | 34.5 | 50.5 | 28.6 |
| **4o** | C5…C9 | 3.566 | 37.2 | 53.2 | 26.4 |
| **5o** | C1…C13 | 3.539 | 38.5 | 45.3 | 23.7 |

[a] $\theta_1$, Dihedral angle between the cyclopentene ring and 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.

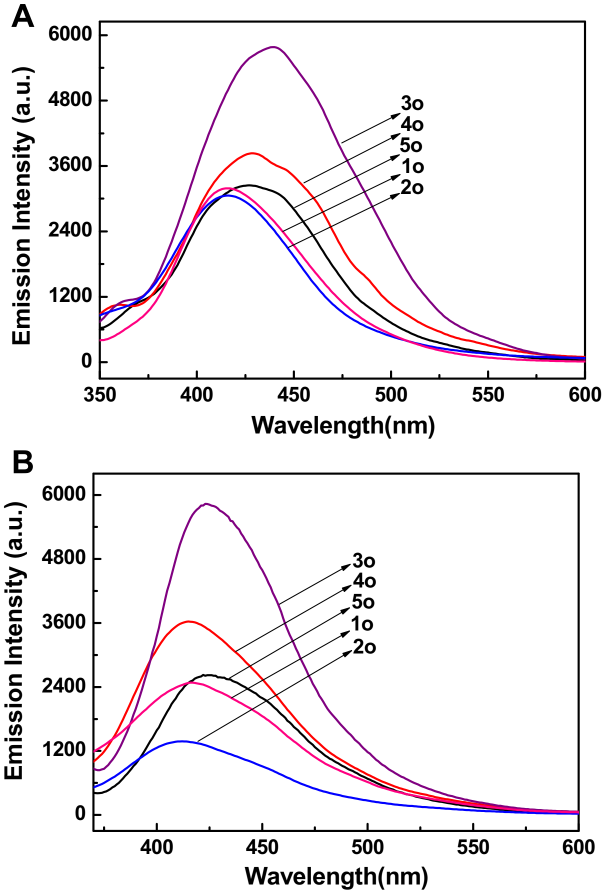

**Fig. 7.** Fluorescence emission spectra of diarylethenes **1**–**5** both in hexane solution ($5.0 \times 10^{-5}$ mol/L) and in PMMA films (10%, w/w) at room temperature: (A) emission spectra in hexane, excited at 340 nm and (B) emission spectra in PMMA films, excited at 350 nm.

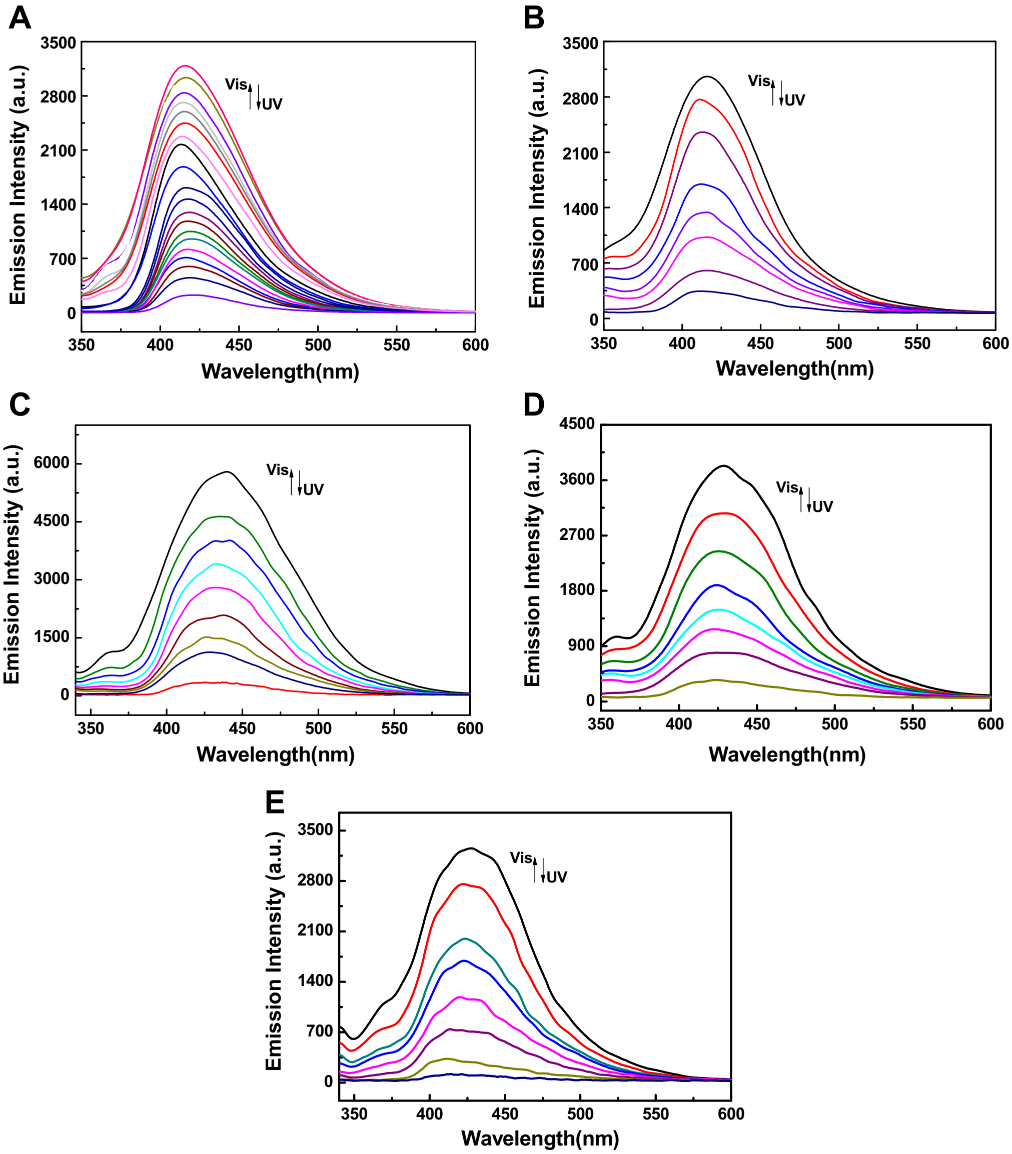

**Fig. 8.** Emission intensity changes of diarylethene **1**–**5** upon irradiation with 297 nm UV light at room temperature in hexane ($5.0 \times 10^{-5}$ mol/L).

**5**) resulted in an increase in the fluorescence quantum yield with the increase in either electron-withdrawing or electron-donating ability. Furthermore, the fluorescence quantum yields of diarylethenes **1** and **2** bearing an electron-withdrawing group were much higher than those of diarylethenes **4** and **5** bearing an electron-donating group.

As has been observed for most of the reported diarylethenes [33,47–51], diarylethenes **1**–**5** exhibited a very good fluorescent switch upon changing from open-ring isomers to closed-ring isomers by photoirradiation both in hexane and in PMMA films. When irradiated by UV light, the photocyclization reaction occurred and the emission intensity of diarylethenes **1o**–**5o** decreased significantly due to the production of the non-fluorescence closed-ring isomers **1c**–**5c**. The back irradiation by visible light with appropriate wavelength regenerated their open-ring isomers and recovered the original emission intensity. Figs. 8 and 9 showed the fluorescence changes of diarylethenes **1**–**5** in hexane ($5.0 \times 10^{-5}$ mol/L) and in PMMA films (10%, w/w), respectively. Upon irradiation with 297 nm light, the emission intensity of diarylethenes **1o** was quenched to *ca.* 7% in hexane and 28% in a PMMA film when arrived at the photostationary state. Therefore, the fluorescent modulation efficiency of diarylethene **1** was 93% in hexane and 72% in a PMMA film. Like diarylethene **1**, the fluorescent modulation efficiencies of diarylethenes **2**–**5** in hexane were 90% for **2**, 93% for **3**, 91% for **4**, and 96% for **5**, respectively, and those in PMMA films were 74% for **2**, 83% for **3**, 78% for **4**, and 76% for **5**, respectively, at the photostationary state. The results showed that the fluorescent modulation efficiencies of diarylethenes **1**–**5** in hexane were much greater than those in PMMA films. The fluorescent modulation efficiency of diarylethene **1** in hexane was about 21% higher than that in PMMA films. Similarly, the fluorescent modulation efficiency was increased by 16% for **2**, 10% for **3**, 13% for **4**, and 20% for **5** in hexane, respectively, compared with that in PMMA films. The result was completely contrary to those of the unsymmetrical diarylethene derivatives whose fluorescent modulation efficiencies in hexane are much lower than those in PMMA films [18,34,46]. However, our findings were in agreement with that of diarylethene derivatives bearing a thiazole moiety [40,52]. Compared with diarylethenes bearing two thiophene moieties [16,36,37], the fluorescent modulation efficiencies of diarylethenes

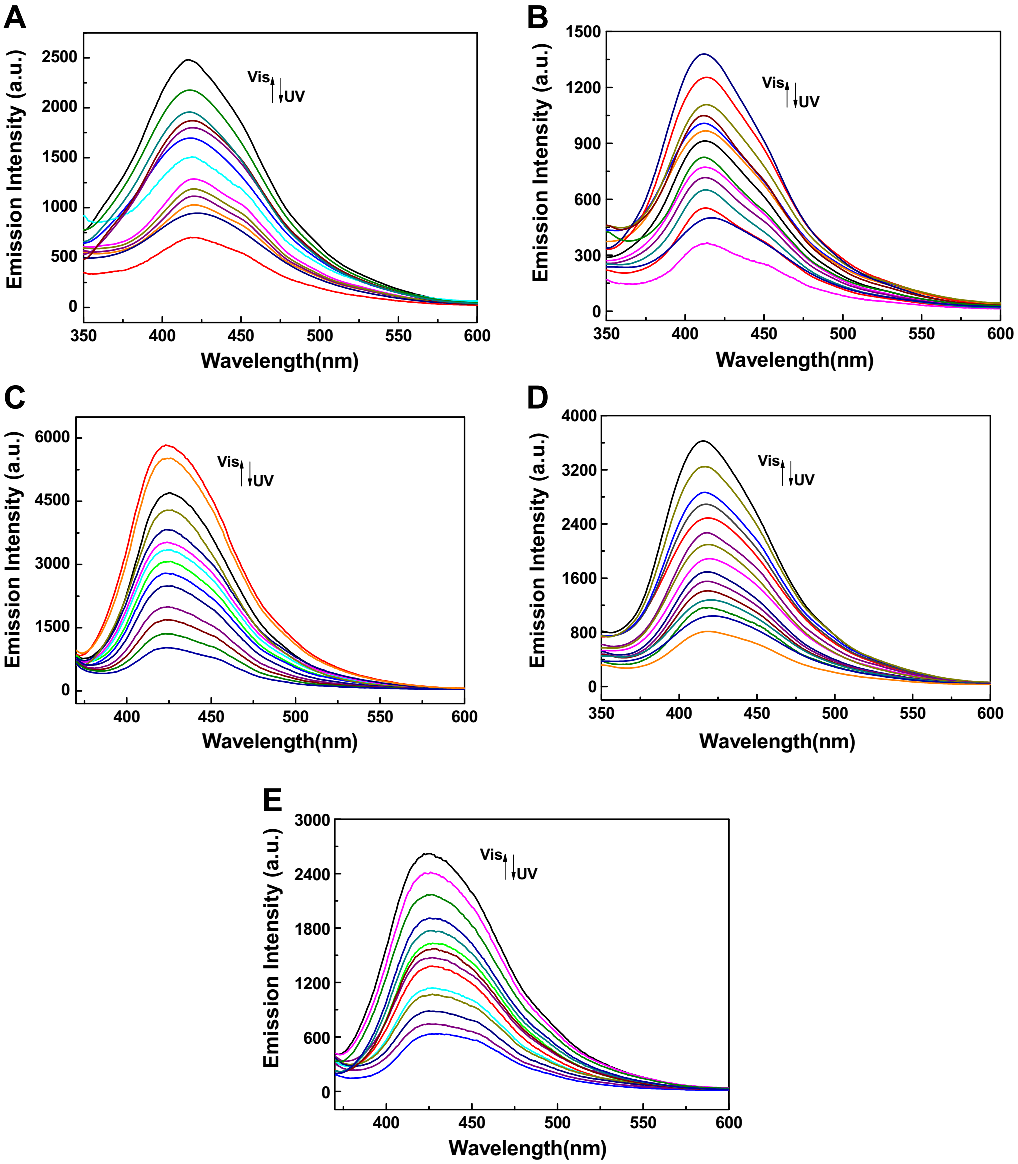

**Fig. 9.** Emission intensity changes of diarylethene **1**–**5** upon irradiation with 297 nm UV light at room temperature in PMMA films (10%, w/w), excited at 350 nm.

**1**–**5** were significantly enhanced both in solution and in solid states. This indicated that diarylethenes bearing a pyrrole unit might have the potential use as fluorescent modulation switches [53,54].

### 3.4. Electrochemical properties of diarylethenes 1–5

The electrochemical properties of diarylethenes can be potentially applied to molecular scale electronic switches [55]. The oxidative cyclization and cycloreversion and the reductive electrochemical cyclization of some diarylethene derivatives have been reported [56–60]. Herein, cyclic voltammograms (CV) were performed on the diarylethenes **1**–**5** under identical experimental conditions at a scanning rate of 50 mV/s. Fig. 10 shows the CV curves of diarylethene **1**–**5** with the scanning rate of 50 mV/s. The oxidation onsets of **1o**–**5o** were observed at 1.71, 1.52, 1.63, 1.49, and 1.31 V, and those of **1c**–**5c** were observed at 0.79, 0.67, 0.72, 0.75, and 0.79 V, respectively. Therefore, the oxidation process of the open-ring isomers **1o**–**5o** occurred at higher potentials than the corresponding closed-ring isomers **1c**–**5c**. This is in accordance with the theory that longer conjugation length generally leads to less positive potentials, with the addition of each heterocyclic ring [9,61]. The difference of oxidation onset between the open-ring and closed-ring isomers of diarylethenes **1**–**5** ($\Delta V_{o-c}$) was 0.93 V for **1**, 0.85 V for **2**, 0.91 V for **3**, 0.74 V for **4**, and 0.52 V for **5**, respectively. This indicated that the difference of oxidation onsets of these diarylethenes gradually decreased (from 0.93 to 0.52 V) when going from electron-withdrawing to electron-donating groups. The $\Delta V_{o-c}$ of diarylethene **1** was the biggest and that of diarylethene **5** was the smallest.

According to the same method reported [19,62], the HOMO and LUMO energy level can also be estimated by using the energy level of ferrocene as reference. Based on the HOMO and LUMO energy level, the band gap ($E_g$, $E_g = \text{LUMO} - \text{HOMO}$) of each compound could be calculated approximately and the results were summarized in Table 4. From this table, it could be easily seen that the different substituents at the *para*-position of the benzene ring had a significant effect on the electrochemical properties of diarylethenes **1**–**5**. Among these diarylethene derivatives, the $E_g$ of the unsubstituted parent compound **3o** was the biggest and that of **3c**

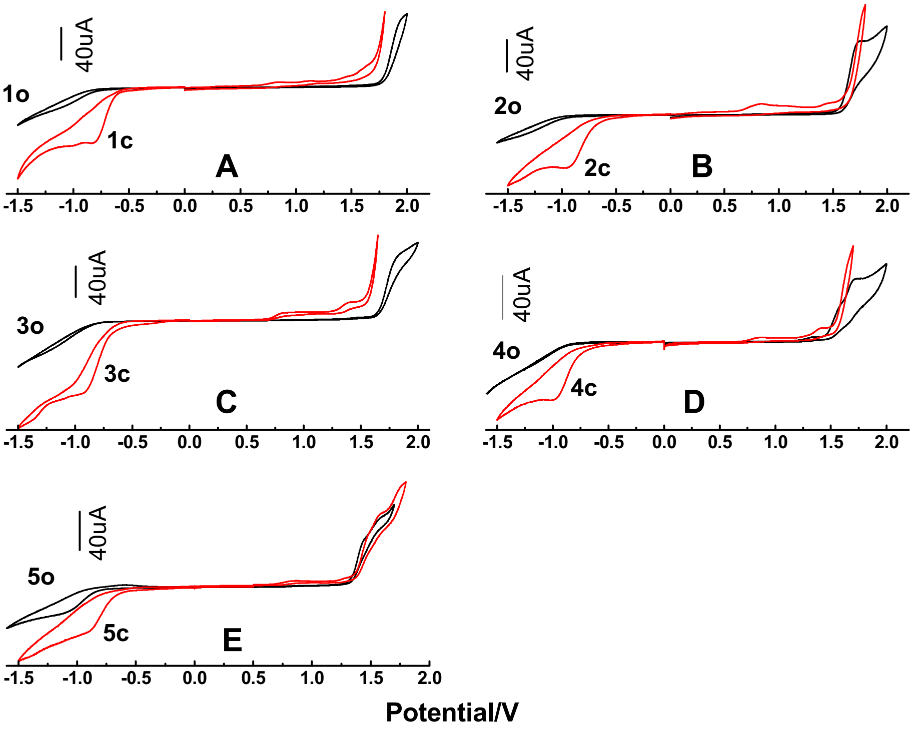

**Fig. 10.** Cyclic voltammetry (second scan) of diarylethene **1**–**5** in acetonitrile with the scanning rate of 50 mV/s: (A) **1**, (B) **2**, (C) **3**, (D) **4**, and (E) **5**.

was the smallest, implying that the charge transfer must be faster in **3c** compared to that in others [60]. Introducing either an electron-withdrawing or an electron-donating group into the terminal benzene ring of the same diarylethene skeleton resulted in a decrease in the $E_g$s of the open-ring isomers **1o**, **2o**, **4o**, and **5o** whilst those of the closed-ring isomers **1c**, **2c**, **4c**, and **5c** increased significantly, compared with the unsubstituted parent diarylethene **1**. Furthermore, the $E_g$s of diarylethenes **1** and **2** bearing an electron-withdrawing group were much higher than those of diarylethenes **4** and **5** bearing an electron-donating group. It should be noted here that calculation of the absolute HOMO and LUMO levels from the electrochemical data in combination with the energy gap is still in debate [63]. As shown in Fig. 10, there were great differences in the electronic current and polarization curve shapes between the open-ring and closed-ring isomers of diarylethenes **1**–**5** at the scanned voltage region. The results indicated that the different substituents might have a notable effect on the electrochemical characteristics of these diarylethenes bearing a pyrrole moiety but further work is required to quantify the effects.

**Table 4**
Electrochemical properties of diarylethenes **1**–**5** in acetonitrile.

| Compound | Oxidation | | Reduction | | Band gap |
|---|---|---|---|---|---|
| | $E_{onset}$ (V) | IP (eV) | $E_{onset}$ (V) | EA (eV) | $E_g$ |
| **1o** | 1.71 | −6.51 | −0.84 | −3.96 | 2.55 |
| **1c** | 0.79 | −5.59 | −0.69 | −4.11 | 1.48 |
| **2o** | 1.52 | −6.32 | −1.04 | −3.76 | 2.56 |
| **2c** | 0.67 | −5.47 | −0.75 | −4.05 | 1.42 |
| **3o** | 1.63 | −6.43 | −0.97 | −3.83 | 2.60 |
| **3c** | 0.72 | −5.52 | −0.63 | −4.17 | 1.35 |
| **4o** | 1.49 | −6.29 | −0.90 | −3.90 | 2.39 |
| **4c** | 0.75 | −5.55 | −0.75 | −4.05 | 1.50 |
| **5o** | 1.31 | −6.11 | −0.89 | −3.91 | 2.20 |
| **5c** | 0.79 | −5.59 | −0.77 | −4.04 | 1.55 |

## 4. Conclusions

In conclusion, five unsymmetrical diarylethenes bearing a pyrrole moiety were synthesized and the substituent effects on their photochemical and electrochemical features were discussed. All of them underwent remarkable photochromism both in solution and in PMMA films, and three compounds among them also underwent notable photochromism in the crystalline phase. Compared with the unsubstituted parent diarylethene **3**, the absorption maxima, the quantum yields of cyclization and cycloreversion of other diarylethenes bearing an electron-withdrawing/donating group at the *para*-position of the terminal benzene ring were notably increased. However, their fluorescence emission peaks, the emission intensities, and the $\Delta V_{o-c}$s were much lower than those of diarylethene **3**. The $E_g$s of the open-ring isomers of diarylethenes bearing an electron-withdrawing group were much higher than those of diarylethenes bearing an electron-donating group whereas that of the closed-ring isomers showed an inverse trend for these diarylethene derivatives. The properties induced by the introduction of the pyrrole moiety, which were different from those of diarylethenes bearing thiophene or pyrazole rings reported previously, may shed some lights on the further application of photochromic diarylethenes.

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