Dyes and Pigments 84 (2010) 25–35

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

The effect of substituent position upon unsymmetrical isomeric diarylethenes bearing a methoxy group

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A R T I C L E I N F O

Article history:
Received 31 March 2009
Received in revised form
13 June 2009
Accepted 18 June 2009
Available online 15 July 2009

Keywords:
Photochromism
Unsymmetrical diarylethene
Methoxy substituent position effect
Photochemistry
Fluorescent switch
Electrochemistry

A B S T R A C T

Three unsymmetrical isomeric photochromic diarylethenes bearing a methoxy group at either the *para-*, *meta-* or *ortho-*positions on one terminal benzene ring were synthesized and their optical and electrochemical properties investigated. Each of the compounds exhibited high photo-reactive sensitivity and functioned as a fluorescent photo-switch both in solution and in PMMA film. The molar absorption coefficients of both of the open-ring and closed-ring isomers decreased when the methoxy group was attached at any of the three positions on the terminal benzene ring whereas the cycloreversion quantum yield gradually increased in going from the *para-* to *meta-* to the *ortho-*position of substitution. Oxidation waves were clearly observed at 0.55, 0.74 and 0.58 V from cyclic voltammograms for some compounds but not for others at these voltages.

1. Introduction

Photochromic compounds are receiving more interest due to their potential applications in photonic devices such as optical memories, photo-switches, and full color displays [1–3]. Many types of photochromic compounds have been reported [4–6], the most promising candidates of which are diarylethene derivatives bearing two thiophene/benzothiophene rings. These diarylethene derivatives are so promising because they satisfy most of the requirements for the production of an optoelectronic device, including high thermal stability of both isomers, fatigue resistance, high sensitivity, and high reactivity in the solid state [7–14].

The photochromic properties of the diarylethenes depend on several factors, such as the nature of the heteroaryl moieties, the conformation of the open-ring isomer, electron donor/acceptor substituents, and the π-conjugation length of the heteroaryl groups, among others [15]. For example, diarylethenes with thiophene/benzothiophene moieties exhibit excellent thermal stability and fatigue resistance [7], but those with pyrrole rings are thermally unstable and return to the open-ring isomers even in the dark [16]. The *anti*-parallel conformation of the open-ring isomer of the thermally stable thiophene system with the rings in C_2 symmetrical arrangement can undergo an effective photocyclization reaction by a conrotatory mechanism. On the other hand, the parallel conformation of the open-ring isomer with the rings in an arrangement with mirror symmetry is photochemically inactive [17–20]. Electron-donating substituents can increase the absorption coefficients and decrease the cycloreversion quantum yields of diarylethenes, while electron-withdrawing groups do not affect the cycloreversion quantum yield but can shift the absorption maxima to longer wavelengths [21]. The longer the π-conjugation length of the heteroaryl groups, the lower the cycloreversion quantum yields of diarylethenes [22,23]. Among these factors, the effect of electron donor/acceptor substituents is the most important one for the design of a photoactive diarylethene with tunable properties. Diarylethenes bearing phenyl groups are the most common class of examples because they can be rapidly substituted by different electron-donating/withdrawing substituents at different positions of the benzene ring, which influences the optoelectronic properties of those diarylethenes [24].

Most publications to date have been concerned with the substituent effects on the photochromic properties of diarylethene compounds [10,25–30]. The majority of the research work has been devoted to the development of these molecules and investigative studies into their fundamental properties, and the results obtained have contributed to a broad understanding of the effects of substituents on the photochromism of diarylethenes. Although many publications concerning the substituent effect have been reported, reports on the influence of substituent position are rare. To the best of our knowledge, only a few publications concerning

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doi:10.1016/j.dyepig.2009.06.018

the substituent position effect on the optoelectronic properties of diarylethenes have been published [31–35]. Previously, the focus has been on the effect of electron-withdrawing groups, such as fluorine or chlorine atoms, and it has been found that these halide substituents and their positions have a significant effect on the properties of the diarylethene compounds [31–34].

The methoxy group is a strongly electron-donating substituent and has a large effect on the photochromic properties of the diarylethene system. For instance, the introduction of methoxy groups to the reactive positions (2- and 2′-positions of the thiophene rings) renders the cycloreversion quantum yield extraordinarily small [36,37]. As far as we are aware, there is only one study on the effect of the methoxy substituent position on the properties of the diarylethenes, in this case, on those bearing a pyrazole unit [35]. There are, however, no reports on the effect of the position of the electron-donating methoxy substituent on the properties of dithienylethene derivatives. The different positions of the methoxy group on the terminal benzene ring should noticeably affect the photochromic properties due to its electron-donating ability and the additional steric hindrance in the diarylethene system. As described in previous reports [32,33], it could be found that the substituent position effect on the properties of unsymmetrical diarylethenes was more significant than that of symmetrical diarylethene analogues. Moreover, investigation of the substituent position effect on the properties of unsymmetrical diarylethenes was helpful to demonstrate the structure–property relationships of unsymmetrical isomeric diarylethenes. Therefore, we have synthesized three unsymmetrical isomeric diarylethenes in order to clarify these effects in this work. The synthesized diarylethenes are 1-(2-methyl-5-phenyl-3-thienyl)-2-[2-methyl-5-(4-methoxyphenyl)-3-thienyl]perfluorocyclopentene (**1o**), 1-(2-methyl-5-phenyl-3-thienyl)-2-[2-methyl-5-(3-methoxyphenyl)-3-thienyl]perfluorocyclopentene (**2o**), and 1-(2-methyl-5-phenyl-3-thienyl)-2-[2-methyl-5-(2-methoxyphenyl)-3-thienyl]perfluorocyclopentene (**3o**) of which, **2o** and **3o** are new compounds. The photochromic process of the diarylethenes is shown in Fig. 1. Although diarylethene **1o** has been reported previously [38,39], it is presented here for comparison with those of other two diarylethene compounds.

2. Materials and methods

2.1. Experimental section

General: All solvents used were spectroscopic grade and 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. The elemental analyses were measured with a PE CHN 2400. The melting point determination was performed on a WRS-1B melting point apparatus. The absorption spectra were measured using an Agilent 8453 UV/VIS spectrometer. The absorptivity values of the closed-ring isomers **1c**–**3c** are determined by UV–VIS spectrometer after isolating by HPLC (silica column, hexane). In the photostationary state, all of their conversions from the open-ring isomers to the closed-ring isomers were larger than 95%. Photoirradiation was carried out using an 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 quantum yields were determined by comparison of the reaction yields of the diarylethenes in hexane with the known yield of the compound 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene (compound **4**, as shown in Fig. 1) in hexane ($\Phi_{o-c} = 0.59$, $\Phi_{o-c} = 0.013$) [12]. Fluorescent spectra were measured using a Hitachi F-4500 spectrophotometer. Crystal data (Table 1) from the diarylethene **2o** were collected on a Bruker SMART APEX2 CCD area-detector. Electrochemical examinations were performed in a one-compartment cell by using a Model 263 potentiostat–galvanostat (EG&G Princeton Applied Research) under computer control at room temperature. Platinum-electrodes (diameter 0.5 mm) served as working electrode and counter electrode. Platinum wire served as a 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 4.0×10^{-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. 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, then spin coating the homogeneous solution on a glass substrate ($20 \times 10 \times 1$ mm^3) at 1500 rpm.

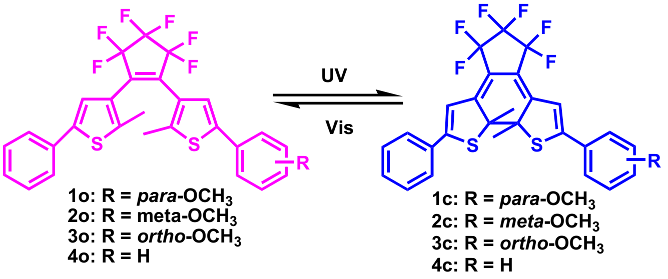

Fig. 1. Photochromism of diarylethenes **1**, **2**, **3** and **4**

Suitable crystals of **2o** 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 294(2) K using MoK\a radiation. The structures were solved by direct methods and refined by full-matrix least-squares procedures on F^2 by full-matric least-aquares techniques using SHELXTL-97 program. All nonhydrogen atoms were refined anisotropically. Crystallographic data for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as

Table 1
Crystal data and structure refinement for **2o**.

	Compound **2o**
Formula	$C_{28}H_{20}F_6OS_2$
Formula weight	550.56
Temperature	294(2)
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions *a* (Å)	9.836(2)
b (Å)	11.798(3)
c (Å)	11.906(3)
α (o)	72.888(4)
β (o)	79.706(4)
γ (o)	80.866(4)
Volume (Å^3)	1290.9(5)
Z	2
Reflections collected	6620
Reflections observed	4524
Number of parameters	391
μ (mm^{-1})	0.270
Density (calcd.) (g/cm^3)	1.416
Goodness-of-fit on F^2	1.003
Radiation (Å)	0.71073
Final R_1[I > 2s(I)]	0.0510
wR_2[I > 2s(I)]	0.1044
R_1 (all data)	0.1299
wR_2 (all data)	0.1348

supplemental publication CCDC 671213. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: þ44 0 1223 336 033 or e-mail: deposit@ccdc.cam.ac.uk).

2.2. Synthesis

The synthesis route for the diarylethenes **1o**, **2o** and **3o** is shown in Fig. 2. Suzuki coupling of the three bromobenzene derivatives with a thiophene boronic acid [40,41] gave the methoxyphenylthiophene derivatives (**7a**, **7b** and **7c**). They were lithiated and coupled to (2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene [26,42] to give the unsymmetrical diarylethene derivatives **1o, 2o** and **3o**, respectively. The structures of **1o**, **2o** and **3o** were confirmed by NMR, IR, and elemental analysis.

2.2.1. Synthesis of 3,5-dibromo-2-methylthiophene *5*

Bromine in acetic acid (v/v = 29/40) 69.0 mL was slowly added to a stirred solution of 2-methylthiophene (24.0 g, 244.8 mmol) in acetic acid (100 mL) at 0 °C. The reaction mixture was stirred overnight at this temperature. The reaction was quenched by the addition of water 30 mL. The mixture was neutralized to pH $\geq$ 9.0 with Na_2CO_3 solid and extracted with ether. The ether extract was dried, filtrated, and concentrated. The residue was purified by distillation *in vacuo*. Compound **5** (50.7 g) [40,41] was obtained as a colorless oil in 81.2% yield. B.p. 100 °C; ^{1H} NMR (400 MHz, $CDCl_3$, TMS): δ 2.94 (s, 3H), 7.61 (s, 1H).

2.2.2. Synthesis of 3-bromo-2-methyl-5-thienylboronic acid *6*

n-Butyl lithium in hexane (1.6 mol/L, 40.6 mL, 65.0 mmol) was added to a stirred solution of **5** (16.3 g, 63.7 mmol) in dry ether (150 mL) at -78 °C under nitrogen atmosphere. After stirring for 30 min, boric acid tri-butyl ester (18.8 mL) was quickly added to the reaction mixture. The ensuing mixture was warmed to room temperature and then quenched with 4% aq. HCl (10 mL). The mixture was extracted with 4% aq. NaOH (100 mL), the basic extract was collected and neutralized by with 10% HCl. The solid residue was washed, filtrated, and dried. Compound **6** (12.0 g) [40,41,43] was obtained as a yellowish solid in 85.5% yield. M.p. 229–230 °C; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 2.51 (s, 3H), 4.59 (s, 2H), 7.33 (s, 1H).

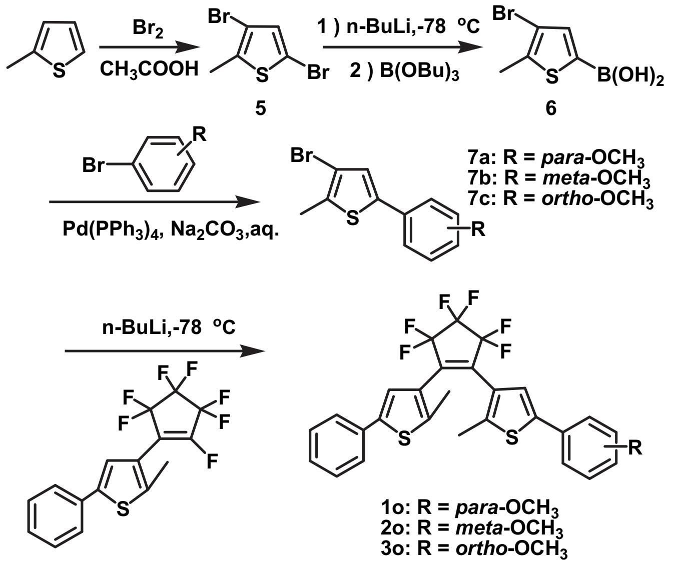

Fig. 2. Synthetic route for diarylethenes **1**, **2** and **3**.

2.2.3. 3-Bromo-2-methyl-5-(4-methoxyphenyl)thiophene *7a*

Compound **7a** was prepared by reacting compound **6** (5.0 g; 22.6 mmol) with 4-bromoanisole (4.23 g; 22.6 mmol) in the presence of tetrakis(triphenylphosphine)palladium(0) [$Pd(PPh_3)_4$ ed. Note: caution: irritant; air sensitive; light sensitive; incompatible with oxidants] (0.8 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 crude product was distillated *in vacuo* and purified by column chromatography on SiO_2 using hexane as the eluent. Compound **7a** (5.01 g) [40] was obtained as a yellowish solid in 78.3% yield.

M.p. 105–106 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 2.40 (s, 3H, $-CH_3$), 3.83 (s, 3H, $-CH_3$), 6.85 (d, 2H, J = 8.8 Hz, phenyl-H), 6.99 (s, 1H, thienyl-H), 7.43 (d, 2H, J = 8.8 Hz, phenyl-H).

2.2.4. 3-Bromo-2-methyl-5-(3-methoxyphenyl)thiophene *7b*

Compound **7b** [40] was prepared by an analogous method to **7a** and was obtained as a buff solid (4.82 g) in a 75.3% yield.

B.p. 221 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 2.41 (s, 3H), 3.83 (s, 3H), 6.83 (d, 1H, J = 8.0 Hz, phenyl-H), 7.03 (s, 1H, thienyl-H), 7.09 (t, 2H, J = 4.0 Hz, phenyl-H), 7.27 (t, 1H, J = 8.0 Hz, phenyl-H).

2.2.5. 3-Bromo-2-methyl-5-(2-methoxyphenyl)thiophene *7c*

Compound **7c** [40] was prepared by an analogous method similar to that used for to **7a** and was obtained as a buff solid (4.49 g) in 70.2% yield.

B.p. 172 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 2.41 (s, 3H, $-CH_3$), 3.91 (s, 3H, $-CH_3$), 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).

2.2.6. 1-(2-methyl-5-phenyl-3-thienyl)-2-[2-methyl-5-(4-methoxyphenyl)-3-thienyl]perfluorocyclopentene (*1o*)

3-bromo-2-methyl-5-(4-methoxyphenyl)thiophene (**7a**) (1.39 g, 4.9 mmol) in anhydrous THF was added dropwise to a 2.4 mol/L *n*-BuLi hexane solution (2.04 mL) at -78 °C under an argon atmosphere. Stirring was continued for 30 min and (2-Methyl-5-phenyl-3-thienyl)perfluorocyclopentene (1.79 g, 4.9 mmol) was slowly added to the reaction mixture at -78 °C and stirred for 2 h at this temperature. The reaction was quenched with 20 mL water. The mixture was warmed to room temperature and extracted with ether. The organic layer was collected and washed with 1 M aq. NaCl 30 mL and then water 50 mL. The organic layer was dried over $MgSO_4$, filtrated and evaporated. The crude product was purified by column chromatography on silica gel using hexane as the eluent resulting in 1.03 g of **1o** being obtained in 38% yield. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.94 (s, 3H, $-CH_3$), 1.96 (s, 3H, $-CH_3$), 3.84 (s, 3H, $-OCH_3$), 6.92 (d, 2H, J = 8.0 Hz, benzene-H), 7.16 (s, 2H, thiophene-H), 7.29 (d, 1H, J = 8.0 Hz, benzene-H), 7.38 (d, 2H, J = 8.0 Hz, benzene-H), 7.48 (d, 2H, J = 8.0 Hz, benzene-H), 7.55 (d, 2H, J = 8.0 Hz, benzene-H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 14.54, 55.41, 114.24, 114.42, 114.48, 114.75, 121.85, 125.52, 125.57, 125.63, 126.04, 126.80, 126.95, 127.70, 127.82, 127.90, 128.80, 128.93, 129.01, 130.28, 132.26, 138.47, 141.94, 158.90; IR (ν, KBr, cm^{-1}) 756, 822, 897, 950, 988, 1034, 1053, 1112, 1180, 1253, 1273, 1338, 1441, 1466, 1515, 1609, 2837, 2919; Anal. Calcd for $C_{28}H_{20}F_6OS_2$ (%):C, 61.08; H, 3.66. Found: C, 60.97; H, 3.77.

2.2.7. 1-(2-methyl-5-phenyl-3-thienyl)-2-[2-methyl-5-(3-methoxyphenyl)-3-thienyl]perfluorocyclopentene (*2o*)

Diarylethene **2o** was prepared by an analogous method to that used for compound **1o** using 3-bromo-2-methyl-5-(3-methoxyphenyl)thiophene (**7b**) instead of **7a**, and was obtained as a solid 1.27 g in 47% yield. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.89 (s, 3H, $-CH_3$), 1.90 (s, 3H, $-CH_3$), 3.77 (s, 3H, $-OCH_3$), 6.77–6.79 (m, 1H, benzene-H), 6.98 (s, 1H, thiophene-H), 7.03 (t, 1H, J = 8.0 Hz, benzene-H), 7.07 (t, 1H, J = 8.0 Hz, benzene-H), 7.22 (s, 1H, thiophene-H), 7.24 (d, 2H, J = 8.0 Hz, benzene-H), 7.32 (t, 2H, J = 8.0 Hz, benzene-H), 7.47 (d, 2H, J = 8.0 Hz, benzene-H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 13.09, 13.52, 54.33, 110.18, 110.31, 112.36, 117.18, 121.40, 121.66, 122.09, 124.59, 124.77, 125.11, 126.89, 127.99, 128.78, 129.04, 132.31, 133.62, 140.25, 140.35, 141.04, 141.25, 159.03; IR (ν, KBr, cm^{-1}) 774, 800, 890, 990, 1051, 1115, 1167, 1192, 1273, 1337, 1433, 2433, 1468, 1499, 1581, 1602, 2835, 2917, 3001; Anal. Calcd for $C_{28}H_{20}F_6OS_2$ (%): C, 61.08; H, 3.66. Found: C, 61.02; H, 3.67; m.p.: 86.7–87.6 °C.

*2.2.8. 1-(2-methyl-5-phenyl-3-thienyl)-2-[2-methyl-5-(2-methoxyphenyl)-3-thienyl]perfluorocyclopentene (**3o**)*

Diarylethene **3o** was prepared by an analogous method similar to **1o** using 3-bromo-2-methyl-5-(2-methoxyphenyl)thiophene (**7c**) instead of **7a**, and was obtained as a liquid 0.97 g in 36% yield. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): 1.94 (s, 3H, $-CH_3$), 1.97 (s, 3H, $-CH_3$), 3.90 (s, 3H, $-OCH_3$), 6.95–7.01 (m, 2H, benzene-H), 7.22 (s, 1H, thiophene-H), 7.25 (s, 1H, thiophene-H), 7.29 (t, 2H, J = 8.0 Hz, benzene-H), 7.35–7.40 (m, 3H, benzene-H), 7.53–7.55 (m, 2H, benzene-H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 14.52, 55.54, 111.49, 111.62, 111.72, 120.82, 120.90, 121.03, 121.82, 122.55, 124.67, 125.11, 125.49, 125.62, 127.85, 127.89, 128.27, 128.76, 133.37, 142.08, 155.52, 157.133; IR (ν, KBr, cm^{-1}) 753, 895, 988, 1026, 1053, 1116, 1191, 1271, 1338, 1437, 1464, 1499, 1600, 2838, 2919, 3065; Anal. Calcd for $C_{28}H_{20}F_6OS_2$ (%): C, 61.08; H, 3.66. Found: C, 61.14; H, 3.59.

3. Results and discussion

3.1. Photochromism of diarylethenes

The photochromic behaviours of diarylethenes **1**, **2** and **3** were examined both in solution and in PMMA films. The changes in the absorption spectra of diarylethenes **1**, **2** and **3** induced by alternating irradiation with UV and visible light in hexane and in PMMA films are shown in Figs. 3 and 4, respectively. In hexane, the colorless solution containing diarylethene **1o** exhibits a sharp absorption peak at 288 nm, due to a $\pi \rightarrow \pi^*$ transition [44]. Upon irradiation with 297 nm light, a new absorption band in the visible region centered at 578 nm emerged while the original peak at 288 nm was 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. Alternatively, the blue solution could be bleached to colorless upon irradiation with visible light ($\lambda > 450$ nm), indicating **1c** was returning to the initial state **1o** (Fig. 3A). The coloration–decoloration cycles could be repeated more than 100 times and a clear isosbestic point was observed at 316 nm. As with diarylethene **1**, compounds **2** and **3** also show good photochromism in hexane (Fig. 3B and C). Upon irradiation with 297 nm light, absorption bands in the visible region appeared and the solutions of **2o** and **3o** turned blue due to the cyclization reactions leading to the closed-ring isomers **2c** and **3c**. These compounds had absorption maxima in the visible region at 577 and 583 nm, respectively. The blue-colored solutions of **2c** and **3c** can be decolorized upon irradiation with visible light ($\lambda > 450$ nm) again, due to the compounds returning to the open-ring forms **2o** and **3o**. This also causes the absorption maxima at 278 and 279 nm, respectively, to reappear. After repeating 100 coloration–decoloration cycles, the isosbestic points for diarylethenes **2** and **3** were observed at 311 and 318 nm. In PMMA films, diarylethenes **1**, **2** and **3** also showed similar photochromism as in hexane, and their spectral changes are shown in Fig. 4. The distortion of the spectra in the UV region is attributed to UV light being absorbed by the glass substrate and high concentration of diarylethene sample in the PMMA films [45] leading to a non-linear absorption response. Compared to those in hexane, the maximum absorption peaks of both the open-ring and the closed-ring isomers of diarylethenes **1**, **2** and **3** in PMMA film are at longer wavelengths than those in hexane. The red shift of the absorption maxima of the open-ring isomers are 36 nm for **1o**, 47 nm for **2o** and 46 nm for **3o**, and those of the closed-ring isomers are 18 nm for **1c**, 13 nm for **2c** and 14 nm for **3c**, respectively. The red shift phenomena may be attributed to

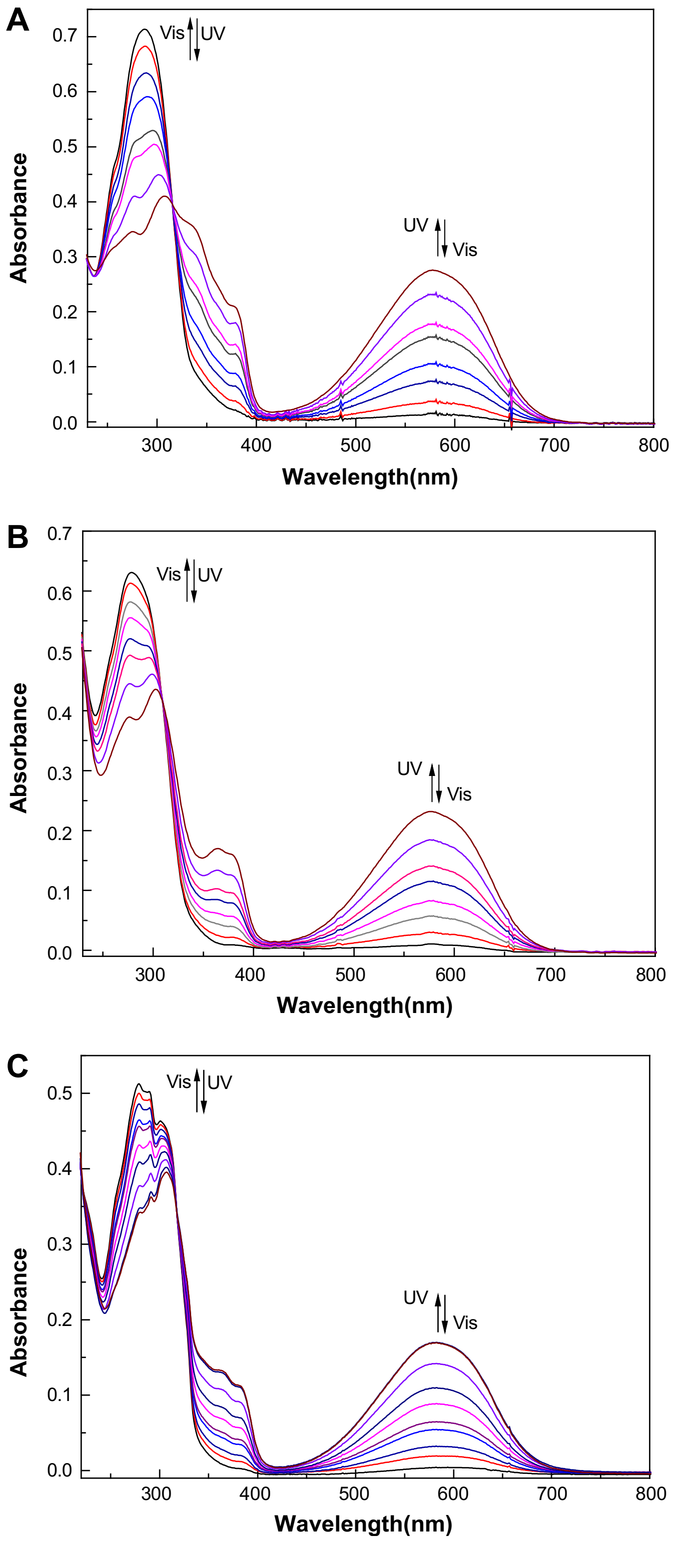

Fig. 3. Absorption spectral changes of diarylethenes **1**, **2** and **3** in hexane solution (2.0×10^{-5} mol/L) at room temperature. *(A)* **1**, *(B)* **2**, and *(C)* **3**.

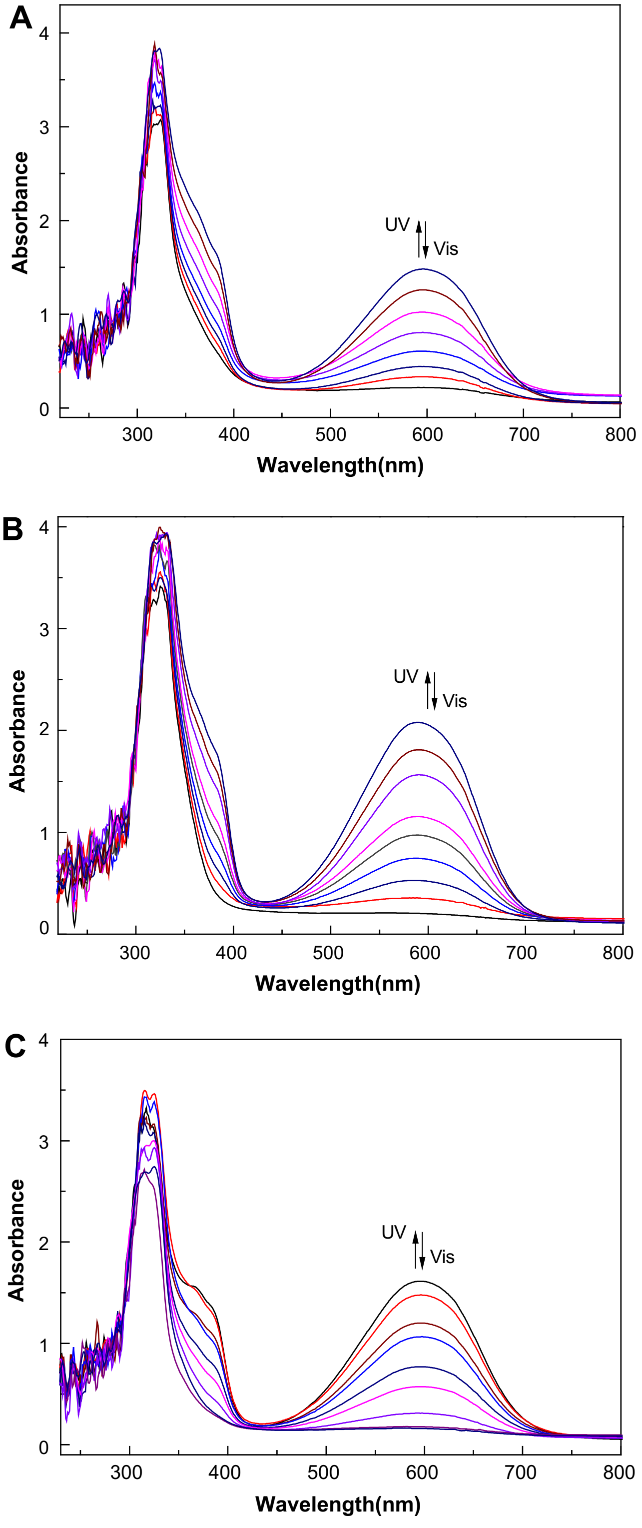

Fig. 4. Absorption spectral changes of diarylethenes **1**, **2** and **3** in PMMA (10% w/w) amorphous films at room temperature. *(A)* **1**, *(B)* **2**, and *(C)* **3**.

the polar effect of the polymer matrix and the stabilization of molecular arrangement in solid state [46].

The absorption spectral parameters of diarylethenes **1**, **2** and **3** both in hexane and in PMMA films are summarized in Table 2. The cyclization and cycloreversion quantum yields of diarylethenes **1**, **2** and **3** are also included in Table 2 and were determined by comparison of their reaction yields in hexane to 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene (compound **4**) in identical conditions [12]. The results show that the methoxy substituent position had a significant effect on the photochromic features of diarylethenes, including the absorption maxima, molar absorption coefficients, and quantum yields. Among these three isomeric compounds, the absorption maximum of the *ortho*-substituted derivative **3c** is at the longest wavelength both in hexane and in a PMMA film; while that of *meta*-substituted derivative **2c** is the shortest, although the *para*-substituted derivative is the same with experimental error. These results are consistent with the differences being due to the different Hammett effects, where the Hammett substituent constants are 0.12 for *meta*-methoxy, −0.27 for *para*-methoxy and −0.39 for *ortho*-methoxy [47]. The result is quite different from those reported for chlorine substituents where the absorption maximum of diarylethene with the *ortho*-substituted chlorine atom is the shortest, and that of *para*- or *meta*-substituted derivatives is the longest [32–34]. As shown in Table 2, the molar absorption coefficients of diarylethenes **1**, **2** and **3** changed with a regular trend in hexane, *i.e.*, it decreased from *para*- to *meta*- to the *ortho*-position. Therefore, the molar absorption coefficients of both the open-ring isomer and the closed-ring isomer of **1** are the biggest; while those of **3** are the smallest. However, the cycloreversion quantum yield increases from **1** ($\Phi_{o-c} = 0.014$) to **3** ($\Phi_{o-c} = 0.035$). This is in good agreement with previous reports [33]. The trend in the cyclization quantum yield is, however, irregular. The cyclization quantum yield of the *para*-substituted derivative **1** is the biggest ($\Phi_{o-c} = 0.68$), that of the *meta*-substituted derivative **2** is the smallest ($\Phi_{o-c} = 0.58$), and the *ortho*-substituted derivative **3** is in between ($\Phi_{o-c} = 0.60$). The unsubstituted parent compound **4** is quite different. The molar absorption coefficient of the closed-ring isomer **4c** ($\varepsilon = 1.4 \times 10^4\ \mathrm{L\ mol^{-1}\ cm^{-1}}$) is higher than all **1**, **2** and **3**; while the cycloreversion quantum yield of compound **4** ($\Phi_{o-c} = 0.013$) is lower [12]. This indicates that the photochromic properties of diarylethenes can be effectively modulated by the introduction of the electron-donating methoxy group into the terminal benzene ring. Compared to symmetric analogue, 1,2-bis[2-methyl-5-(4-methoxyphenyl)-3-thienyl]perfluorocyclopentene (compound **5**) [48], the cyclization/cycloreversion quantum yields of the isomeric derivatives are greater, but their molar absorption coefficients are decreased.

Colorless crystals of **2o,** suitable for X-ray analysis, were obtained by slow evaporation of a hexane solution. To better understand the relationship between the conformation and the photochromic reactivity of diarylethene **2o** in the crystalline phase, structural confirmation was obtained by X-ray crystallography. An ORTEP drawing of diarylethene **2o** is shown in Fig. 5 and a corresponding packing diagram is shown in Fig. 6, indicating that the molecule crystallizes with an approximate C_2 symmetry with the photoactive *anti*-parallel conformation in the crystalline phase, which can undergo the photocyclization [13,49,50]. The hexafluorocyclopentene ring of this molecule was disordered evenly over two distinct conformations. In the perfluorocyclopentene ring of diarylethene **2o**, the distances clearly indicate that the C12–16 bond (1.346(4) Å) is a double bond, being significantly shorter than other carbon-carbon single bonds (1.495(5) to 1.518(5) Å) of the ring. Two symmetrical thiophene moieties are linked by the C12=C16 double bond, with both of them attached to the ethylene group *via* the 3-position of the thiophene ring. The two methyl groups are located on opposite sides of the double bond, reflected in the torsion angles C12–C16–C17–C18 [−50.8(6)°] and C10–C9–C12–C16 [−47.6(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 [51]. The dihedral angles between the hexafluorocyclopentene ring and the two

Table 2
Absorption characteristics and the photochromic reactivity of the diarylethenes **1**, **2** and **3** in hexane (2.0×10^{-5} mol/L) and in PMMA films (10% w/w).

Compound	$\lambda_{\max,\,o}$[a]/nm (ε/dm^3 mol^{-1} cm^{-1})		$\lambda_{\max,\,c}$[b]/nm (ε/dm^3 mol^{-1} cm^{-1})		Φ[c]	
	Hexane	PMMA film	Hexane	PMMA film	Φ_{o-c}	Φ_{o-c}
1	288 nm (3.57×10^4)	324	578 nm (1.38×10^4)	596	0.68	0.014
2	278 nm (3.17×10^4)	325	577 nm (1.16×10^4)	590	0.58	0.024
3	279 nm (2.56×10^4)	325	583 nm (8.47×10^3)	597	0.60	0.035

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

thiophene rings are 45.8(6)° for S1/C7–C10 and 52.2(3)° for S2/C18/C17/C20/C21, and those between the thiophene rings and the adjacent benzene rings are 18.9(6)° for the unsubstituted ring and 26.9(8)° for the ring with the methoxy substituent. The intramolecular distance between the two reactive C atoms (C10⋯ C18) is 3.623(2) Å. This distance indicates that the crystal can be expected to undergo photochromism in the crystalline phase, because photochromic reactivity usually occurs when the distance between these C atoms is less than 4.2 Å [12,52,53].

The crystal of **2o** exhibited photochromic reaction, in accordance with the expected ring closure, to form the closed-ring isomer **2c**. The color change upon photoirradiation is shown in Fig. 7. Upon irradiation with 313 nm light, the colorless crystal **2o** quickly turned blue. When the blue crystal was dissolved in hexane, an intense absorption maximum was observed at 577 nm, the same as that of the closed-ring isomer **2c** prepared in solution. Alternatively, the blue-colored crystals reverted to colorless upon irradiation with the appropriate visible light ($\lambda > 450$ nm). Furthermore, the diarylethene crystal exhibited remarkable fatigue resistance (larger than 200 cyclization/cycloreversion repeat cycles) and its closed-ring isomer remained stable for more than one year in the dark at room temperature. Thus, these crystals will be a promising candidate for optoelectronic applications, such as high density three-dimensional optical recording media and optical switch materials [8,54].

3.2. *Photochromic cyclization-cycloreversion kinetics of diarylethenes **1–3***

The photochromic cyclization and cycloreversion kinetics of diarylethenes **1**, **2** and **3** both in hexane and in PMMA film were investigated by irradiation with UV light (297 nm, cyclization reaction) and visible light ($\lambda > 500$ nm, cycloreversion reaction), as shown in Fig. 8. The concentrations of all solutions were 2.0×10^{-5} mol/L. All absorption data were collected at the absorption maxima of the appropriate diarylethenes. As shown in Fig. 8A and C, the relationship between absorbance and exposure time (*A vs. t*) exhibits linearity (linear correction factors> 0.99) upon irradiation with 297 nm light in hexane or 313 nm light in a PMMA film, indicating that the photocyclization reactions of the diarylethenes are zeroth order reactions. The slopes of the *A vs. t* lines gave the rate constants k_{o-c}. The cycloreversion kinetic curves in hexane and in PMMA film are shown in Fig. 8B and D, respectively, which can be plotted according to eq. (1) [40,55].

$$Kt = \ln\frac{A_\infty - A_0}{A_\infty - A_t} \tag{1}$$

These data also are clearly linear, suggesting that the cycloreversion processes of diarylethenes **1**, **2** and **3** is a first order reaction both in hexane and in PMMA film. Of the three compounds, the k_{o-c} (3.38×10^{-3}) of diarylethene **3** is the biggest and its k_{c-o} (5.5×10^{-3}) is the smallest in hexane, which is consistent with it having the biggest cyclization and the smallest cycloreversion quantum yields, suggesting that the rate constant is direct proportional to the quantum yield of the photoirradiation reaction [33]. In PMMA amorphous film, the k_{c-o} of diarylethenes **1**, **2** and **3** showed an increasing trend from the *para*- to *meta*- to the *ortho*-position, but that of k_{c-o} was irregular. The photoirradiation reaction kinetics in a solid medium are, however, influenced by

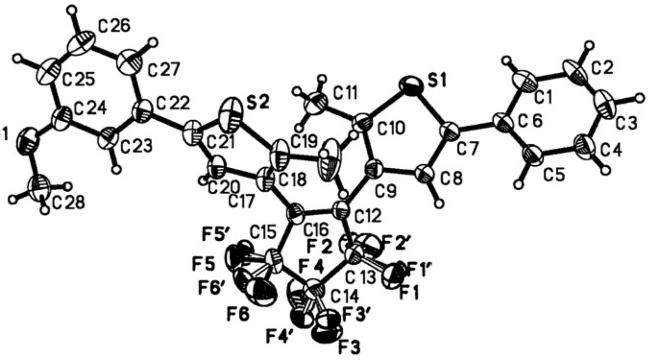

Fig. 5. ORTEP drawing of **2o**, showing 35% probability displacement ellipsoids.

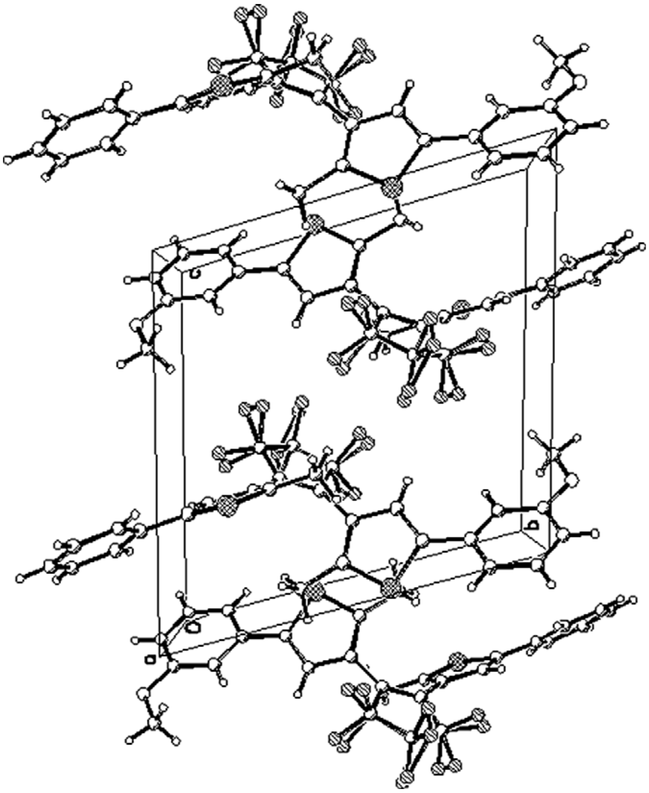

Fig. 6. A packing diagram of diarylethene **2o**, viewed along the *a* axis.

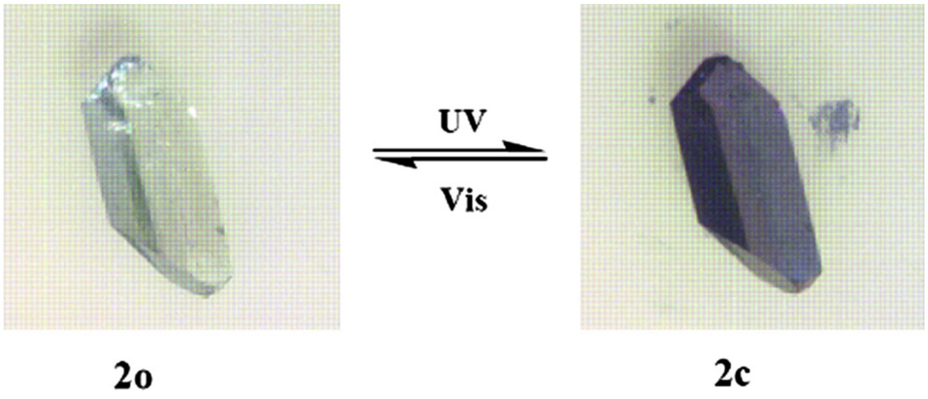

Fig. 7. Photographs of photochromic processes of diarylethene **2** in the crystalline phase.

many interfering factors, such as molar absorption coefficient, quantum yield and the polymer medium [33].

3.3. Fluorescence of diarylethenes

The fluorescence spectra of the diarylethenes **1o**, **2o** and **3o** in hexane (2.0×10^{-5} mol/L) and in PMMA amorphous films (10% w/w) at room temperature are shown in Fig. 9. In hexane, the emission peaks of diarylethenes **1o**, **2o** and **3o** were observed at 419, 403 and 399 nm when excited at 340 nm, 350 nm and 350 nm, respectively, and were observed at 441, 437, and 433 nm when exited at 300 nm in PMMA films. Compared to those in hexane, the emission peaks of diarylethenes **1o**, **2o** and **3o** exhibit a bathochromic shift in PMMA film consistently across their maxima absorption wavelengths with values of 21 nm for **1**, 34 nm for **2**, and 34 nm for **3**. Among the three isomeric diarylethene derivatives, the emission intensity of **3o** is the strongest and that of **1o** is the smallest, however, the emission peak of **3o** is at higher energy and that of **1o** is the lowest both in hexane and in PMMA film. The strongest emission intensity and the highest energy emission peak of diarylethene **3o** may be attributed to the steric hindrance of *ortho*-methoxy group in addition to its strong electron-donating nature. On the one hand, the thiophene-phenyl bond rotation is hindered by the steric hindrance. On the other hand, the electron-donating *ortho*-methoxy group enhances the fluorescent efficiency [25,32,40].

As has been observed for most of the reported diarylethenes [25,27,54,56], diarylethenes **1**, **2** and **3** exhibited a relatively strong fluorescent switch on changing from the open-ring isomers to

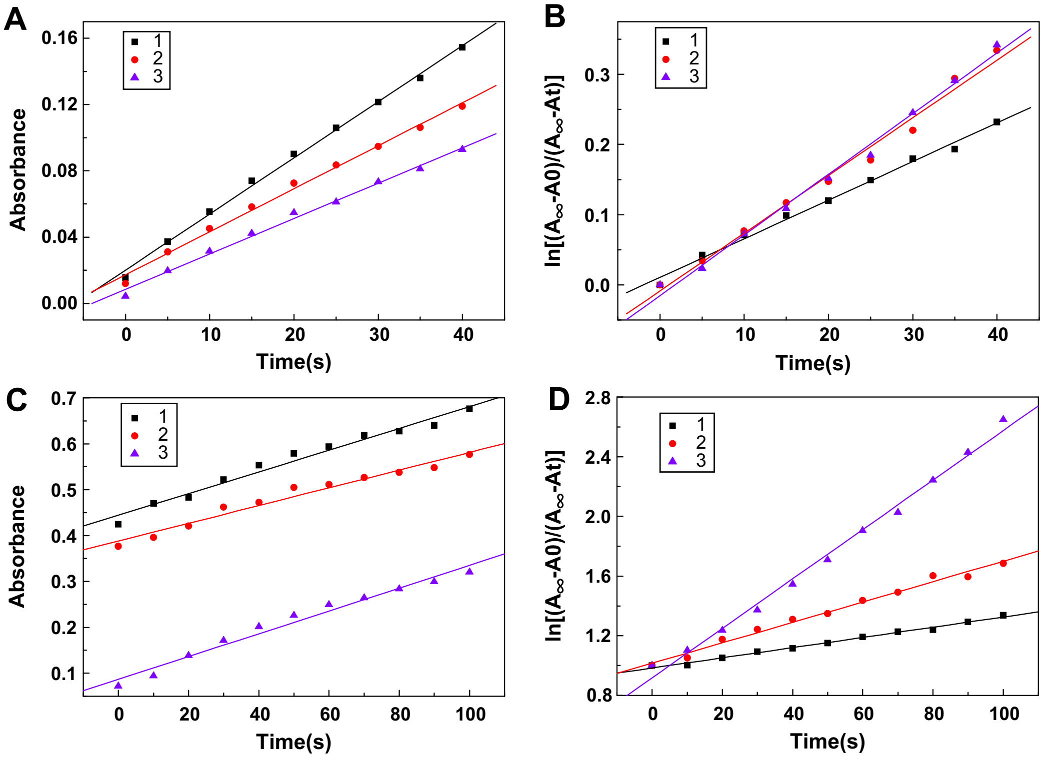

Fig. 8. The cyclization/cycloreversion kinetics of diarylethenes **1**, **2** and **3** in hexane (2.0×10^{-5} mol/L) and in PMMA films. *(A)* Cyclization kinetics in hexane upon irradiation with UV light ($\lambda = 297$ nm), *(B)* Cycloreversion kinetics in hexane upon irradiation with visible light ($\lambda > 450$ nm). *(C)* Cyclization kinetics in PMMA films upon irradiation with UV light ($\lambda = 313$ nm), *(D)* Cycloreversion kinetics in PMMA films upon irradiation with visible light ($\lambda > 450$ nm).

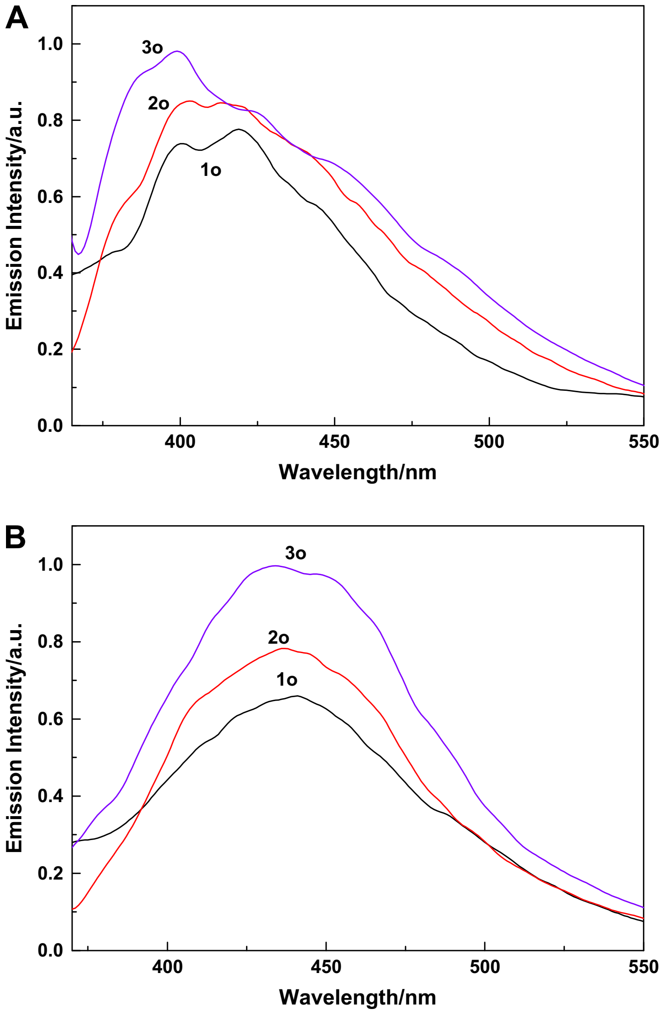

Fig. 9. Fluorescence emission spectra of diarylethenes **1**, **2** and **3** both in hexane solution (2.0×10^{-5} mol/L) and in PMMA films (10%, w/w) at room temperature: (A) Emission spectra in hexane, excited at 340 nm, 350 nm and 350 nm, respectively. (B) Emission spectra in PMMA films, excited at 300 nm.

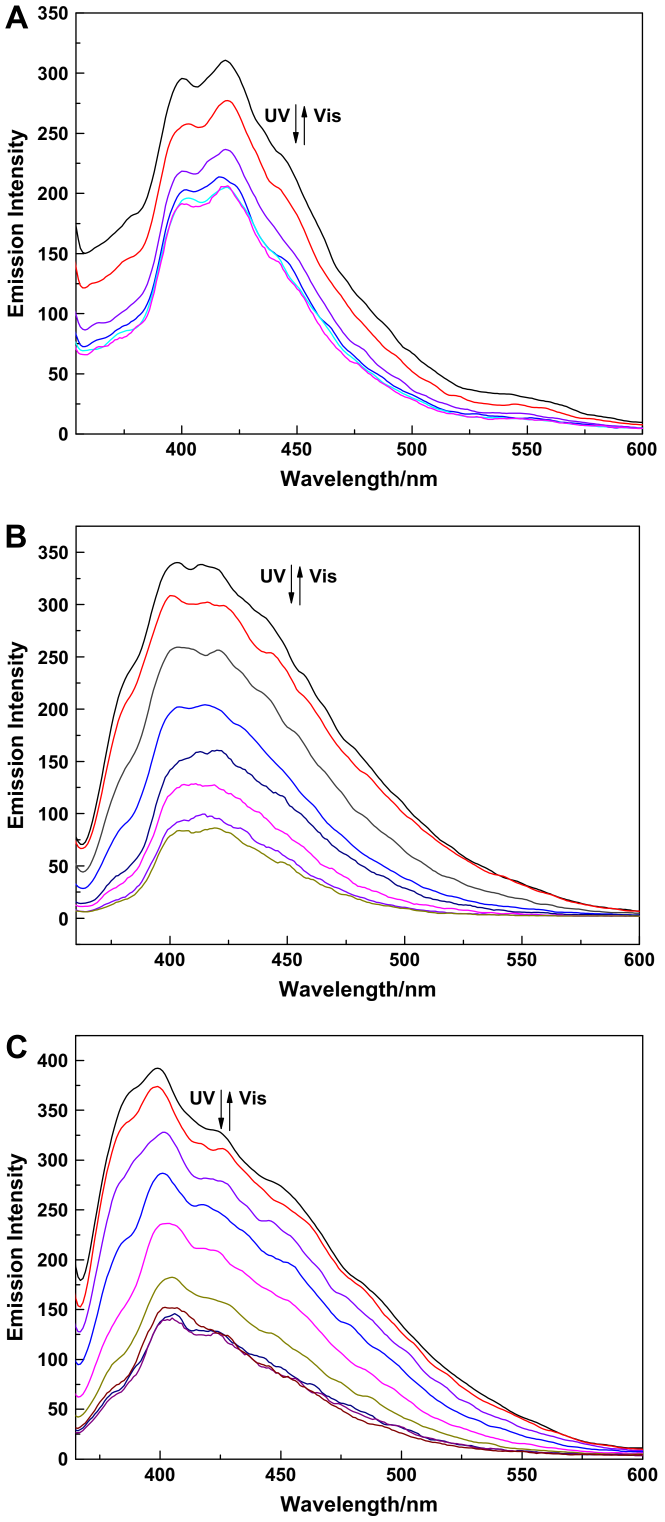

Fig. 10. Change in the intensity of the fluorescence spectra of diarylethenes **1**, **2** and **3** in hexane solution (2.0×10^{-5} mol/L) upon irradiation with 297 nm UV light at room temperature, excited at 340 nm, 350 nm, and 350 nm respectively. *(A)* **1**, *(B)* **2**, and *(C)* **3**.

closed-ring isomers by photoirradiation both in hexane and in PMMA film. When irradiated with UV light, the fluorescence of the samples was effectively quenched. Irradiation by appropriate wavelength visible light regenerated the open-ring isomers **1o**, **2o**, and **3o** and recovered the original emission spectra. During the process of photoisomerization, the three isomeric compounds exhibited changes in their fluorescence in hexane as shown in Fig. 10. On irradiation with 297 nm UV light the samples arrived at the photostationary state, resulting in the emission intensities of diarylethenes **1**, **2** and **3** being quenched to *ca.* 66%, 25% and 35%, respectively. Similarly, the emission intensity changes of diarylethenes **1**, **2**, and **3** in PMMA film during the process of photoisomerization are shown in Fig. 11. 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.* 38%, 22%, and 25%, respectively. Therefore, the fluorescent switching efficiency of **1** was much weaker than those of **2** and **3** both in hexane and in PMMA film. The incomplete cyclization reaction and the existence of parallel conformations of **1** may be the cause for the smaller change in fluorescent intensity induced by photoirradiation [32,33]. In addition, the "on" and "off" state of the fluorescence was measured by changing the power of the UV and visible light. The average "on" and "off" times shortened with increasing power, indicating that the switching effect is indeed photochemical [44]. Therefore, these diarylethene compounds could be potentially applied to optical memory with fluorescence readout method or a fluorescent modulation switch [57,58]. Varying the position of the methoxy group changes the fluorescent properties and may be useful for increasing selectivity in their application as the fluorescent photo-switches.

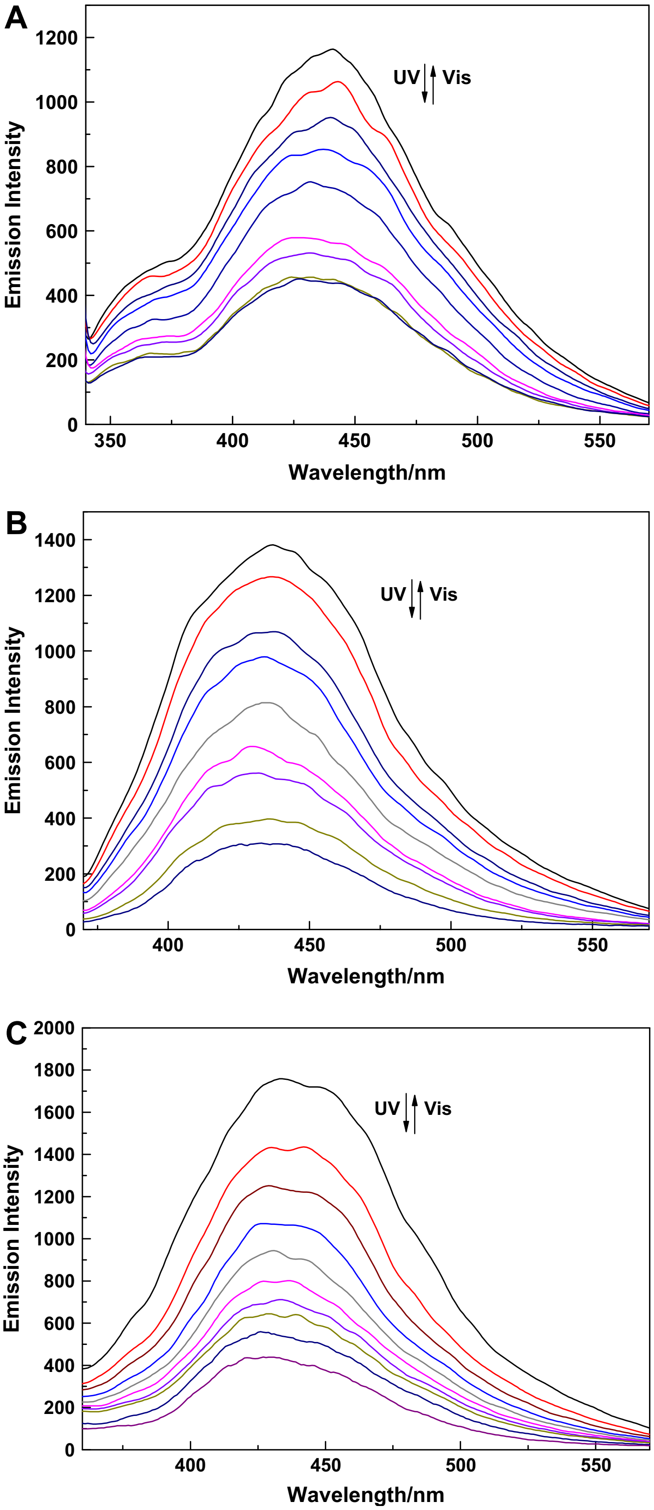

Fig. 11. Change in the intensity of the fluorescence spectra of diarylethenes **1**, **2**, and **3** in PMMA films upon irradiation with 313 nm light at room temperature, excited at 300 nm *(A)* **1**, *(B)* **2**, and *(C)* **3**.

3.4. Electrochemistry of diarylethenes

The photoresponsive system described here also allows for changes in the electrochemical properties, due to the differences in the π-conjugation of the two isomers of diarylethenes. This is may be useful for a photoelectronic device [59]. The oxidative cyclization and cycloreversion of some diarylethene derivatives had been reported [59–61].

Cyclic voltammograms (CV) were performed on the diarylethenes **1**, **2** and **3** under identical experimental conditions at 50 mV/s and are shown in Fig. 12. The onset of the oxidation waves for **1o**, **1c**, **2o**, **2c**, **3o** and **3c** were at 0.51, 0.29, 0.61, 0.45, 0.54 and 0.45 V, respectively. This shows that the oxidation process for the open-ring isomers **1o**, **2o** and **3o** occurs at higher potentials than in the corresponding closed-ring isomers **1c**, **2c** and **3c**. This is because the longer conjugation length of the closed-ring isomers generally leads to a less positive potential [30]. The cyclization reaction allows the π-conjugation to extend across the perfluorocyclopentene ring causing a lower oxidation onset. As shown in Fig. 12, the closed-ring isomers of diarylethenes **1**, **2** and **3** show distinct oxidation waves at 0.55, 0.74 and 0.58 V, but the open-ring isomers show no oxidation waves at these voltages. The new oxidation waves show that the closed-ring isomers of diarylethenes **1**, **2** and **3** have more complex electrochemical properties, due to the increased π-conjugation lengths. Among these isomeric compounds, the oxidation onset and the oxidation peak of *meta*-substituted derivative **2** are the highest, and those of *para*-substituted derivative **1** are the lowest. For the different positions of the methoxy group in the diarylethenes **1**, **2** and **3**, the electron-donating and steric effects induced are different and lead to distinguishable electrochemical properties. The results suggest that the methoxy group and its substituted position have a significant effect on the electrochemical properties of the three isomeric

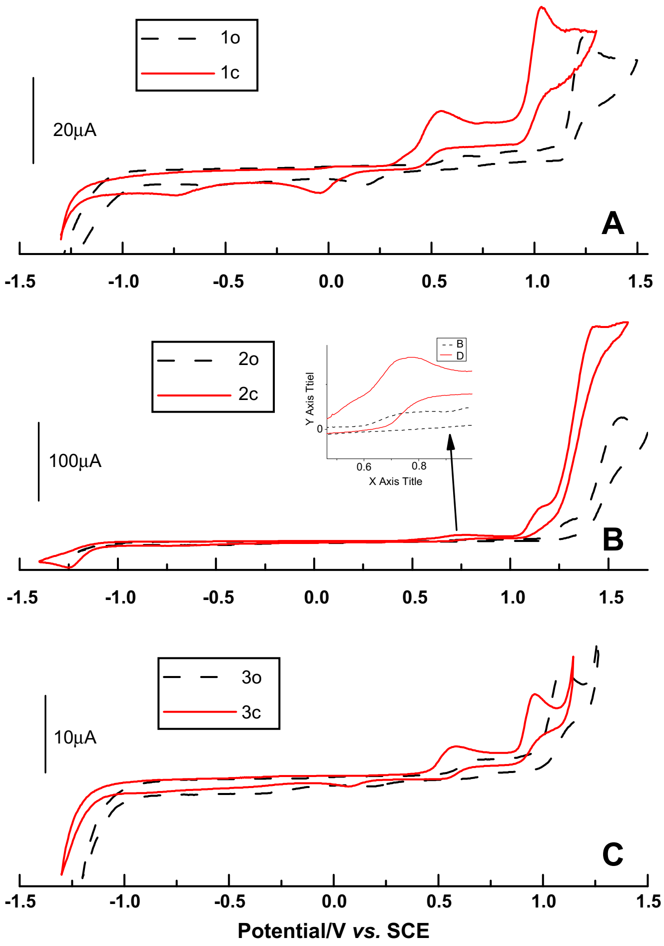

Fig. 12. Cyclic voltammetry (second scan) of diarylethenes **1, 2** and **3** in acetonitrile at a scan rate of 50 mV/s *(A)* **1**, *(B)* **2**, and *(C)* **3**.

diarylethene derivatives but further work is required to quantify these effects.

4. Conclusions

Three unsymmetrical isomeric diarylethenes bearing a methoxy group at the *para*-, *meta*-, and *ortho*-position of the terminal benzene ring were synthesized, and their photochemical and electrochemical properties were discussed systematically. The results showed that the electron-donating methoxy group at different positions of the terminal benzene ring had a significant effect on the optical and electrochemical properties of these diarylethene derivatives. The electron-donating methoxy group induced new characteristics which differed from those of diarylethene derivatives bearing chlorine atoms which have been reported previously. The results will be helpful in understanding the influence of the position of substituents in diarylethenes and for the synthesis of efficient photoactive diarylethene derivatives with tunable properties.

Acknowledgements

This work was supported by Program for New Century Excellent Talents in University (NCET-08-0702), the Project of Jiangxi Youth Scientist, National Natural Science Foundation of Jiangxi Province (2008GZH0020), the Key Scientific Project from Education Ministry of China (208069) and the Science Funds of the Education Office of Jiangxi, China (GJJ08365).

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