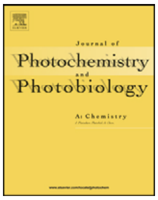
Journal of Photochemistry and Photobiology A: Chemistry 214 (2010) 230–240

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

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



Synthesis and the effect of substituent position upon unsymmetrical isomeric diarylethenes bearing a pyrrole unit

Gang Liu[a,b], Shouzhi Pu[b,*], Xiaomei Wang[a,*]

[a] College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, PR China
[b] Jiangxi Key Laboratory of Organic Chemistry, Jiangxi Science & Technology Normal University, Nanchang 330013, PR China

ARTICLE INFO

Article history:
Received 7 April 2010
Received in revised form 27 June 2010
Accepted 2 July 2010
Available online 8 July 2010

Keywords:
Photochromism
Diarylethene
Pyrrole group
Substituent position effect
Photochemical and electrochemical property

ABSTRACT

Four unsymmetrical diarylethenes bearing a pyrrole moiety were synthesized, and the structures of two isomeric compounds were determined by single-crystal X-ray diffraction analysis. The properties of these compounds, including photochromism, fluorescence and electrochemical properties of these diarylethenes were also investigated systematically. Each of the four diarylethene derivatives exhibited good photochromism and functioned as an effective fluorescent photoswitch both in solution and in PMMA films. The absorption maxima, the quantum yields of cyclization and cycloreversion, and the fluorescence quantum yields of the open-ring isomers increased whereas the emission peaks decreased evidently when the methoxy group was attached at any of the three positions on the terminal benzene ring. Compared with the analogous diarylethenes bearing a pyrazole moiety, the introduction of the pyrrole moiety could increase the absorption maxima and decrease the cycloreversion quantum yields significantly. Cyclic voltammograms testified that methoxy group and its substituted position could effectively modulate the electrochemical behaviours of these diarylethene derivatives.

1. Introduction

Photochromic compounds have been extensively investigated for their potential applications in erasable optical memories and photoswitches [1–3]. Among the photochromic compounds hitherto reported, diarylethenes are regarded as the best candidates for such devices, because of their advantages such as a high efficiency of photoisomerization, sufficient thermal stability of both the open-ring and the close-ring isomers, remarkable resistance to photo-fatigue, and ease monitoring by using UV–vis spectroscopy [4–7].

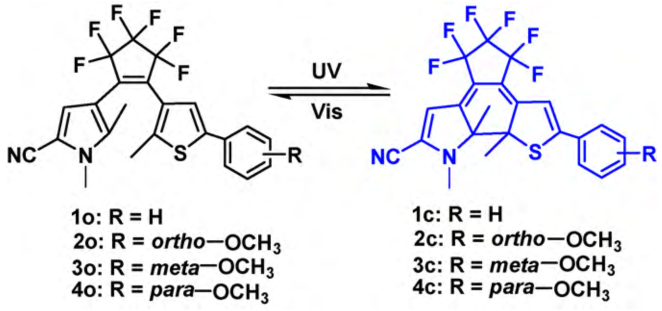
The photochromic process of diarylethenes is based on a reversible transformation between the open-ring isomer with a hexatriene structure and the closed-ring isomer with a cyclohexadiene structure, according to the Woodward-Hoffmann rule [8]. The open and closed isomers of diarylethenes differ from each other not only in their absorption spectra but also in various physical and chemical properties such as refractive index [9,10], oxidation/reduction potentials [11–13], and chiral properties [14–16], among others. These molecular property changes are of great interest because of their potential applications in photonic apparatus such as optical memories [1,17–20], multi-stable photoswitches [3,21–24], and full color displays [25].

On the one hand, the distinguishable features of diarylethenes mainly depended on the categories of heteroaryl moieties and their substitution positions [26]. For instance, diarylethenes bearing thiophene/benzothiophene moieties show good thermal stability and remarkable fatigue resistance [1], but those bearing pyrrole groups are thermally unstable and return to the open-ring isomers even in the dark [27]. The electron-donating substituents of the bis(3-thienyl)ethene diarylethenes could be effective to increase the absorption coefficient of the closed-ring isomers and decrease the cycloreversion quantum yield [28,29], however, those attached bis(2-thienyl)ethene diarylethenes could increase the maxima absorption of the open-ring isomers and reduce the cyclization quantum yield [30]. Previously, most of the heteroaryl moieties have been thiophene or benzothiophene rings, with just a few reports concerning other heteroaryl moieties such as furan [31], thiazole [32,33], indole [34,35], and so on. Pyrrole is an attractive aryl unit due to its biological characteristics [36,37], and its structure is similar to those of thiophene and furan. However, diarylethene derivatives with a pyrrole unit hitherto reported is very rare. As far as we are aware, there are only a few examples of photochromic diarylethenes bearing a pyrrole unit. Uchida et al. [27] reported a symmetrical diarylethene bearing two pyrrole groups that showed thermally unstable and reverted to the open-ring form even at room temperature in the dark. In a previous paper, we synthesized two isomeric hybrid diarylethenes bearing both pyrrole and thiophene moieties and investigated their photochromic features, indicating that the hybrid diarylethenes had

---

* Corresponding authors. Tel.: +86 791 3831996; fax: +86 791 3831996.
E-mail address: pushouzhi@tsinghua.org.cn (S. Pu).

1010-6030/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jphotochem.2010.07.001



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

good thermal stability and fatigue resistance in the solid medium [26].

On the other hand, electron donor/acceptor substituents and their substitution positions have also a significant effect on the photochromic properties of diarylethene derivatives [38,39]. So far, many publications concerning the substituent effect have been reported, but reports on the effect of substituent position are rare [40]. Previously, we reported the electron-donating methoxy substituent position effect not only on the properties of unsymmetrical photochromic dithienylethene derivatives, but also on those of unsymmetrical photochromic hybrid diarylethenes bearing both pyrazole and thiophene moieties [40–43]. The results indicated that the substituent position of methoxy group had a significant effect on the properties of these diarylethene compounds. However, there existed a great difference between the methoxy substituent effect of the isomeric dithienylethene derivatives and those of the isomeric diarylethenes bearing both pyrazole and thiophene moieties. That is to say, the substituent position effect of the same functional group is remarkable different from each other for different photochromic diarylethene systems. The result give us valuable insight and encourage us to explore the methoxy substituent position effect on the properties of hybrid photochromic diarylethenes bearing both pyrrole and thiophene moieties. Therefore, we have synthesized four hybrid diarylethenes bearing both pyrrole and thiophene moieties in order to clarify these effects in this work. The synthesized diarylethenes are 1-(2-cyano-1,5-dimethyl-4-pyrryl)-2-[2-methyl-5-phenyl-3-thienyl]perfluorocyclopentene (**1o**), 1-(2-cyano-1,5-dimethyl-4-pyrryl)-2-[2-methyl-5-(2-methoxyphenyl)-3-thienyl]perfluorocyclopentene (**2o**), 1-(2-cyano-1,5-dimethyl-4-pyrryl)-2-[2-methyl-5-(3-methoxyphenyl)-3-thienyl]perfluorocyclopentene (**3o**), and 1-(2-cyano-1,5-dimethyl-4-pyrryl)-2-[2-methyl-5-(4-methoxyphenyl)-3-thienyl]perfluorocyclopentene (**4o**) of which, **1o**, **2o** and **3o** are new compounds. The photochromic process of the diarylethenes is shown in Scheme 1. Although diarylethene **4o** has been reported previously [26], it is presented here for comparison with those of other three diarylethene compounds.

2. Experimental

2.1. General

NMR spectra were recorded on a Bruker AV400 (400 MHz) spectrometer with $CDCl_3$ as the solvent and tetramethylsilane as an internal standard. Infrared spectra (IR) were performed using a Bruker Vertex-70 spectrometer. Elemental analysis was measured with an elemental analyzer labeled the PE 2400 CHN analyzer. Melting point was taken on a WRS-1B melting point apparatus. Absorption spectra were measured using an Agilent 8453 UV/VIS spectrophotometer. Fluorescence spectra were measured using a Hitachi F-4500 fluorimeter. 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. 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 1.0×10^{-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.

Suitable crystals of **3o** and **4o** 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 Mo Kα radiation. The structures were solved by direct methods and refined by full-matrix least-squares procedures on F^2 by full-matrixc least-squares techniques using SHELXTL-97 program. All non-hydrogen atoms were refined anisotropically. Crystallographic data for of the structures in this paper have been deposited with in the Cambridge Crystallographic Data Centre as supplemental publication CCDC 762279 for **3o** and CCDC 639786 for **4o**. 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

2.2.1. 3-Bromo-5-phenyl-2-methylthiophene (*6a*)

Compound **6a** was prepared by reacting 3-bromo-2-methyl-5-thienylboronic acid [43] (3.1 g, 14.0 mmol) with bromobenzene (2.20 g, 14.0 mmol) in the presence of $Pd(PPh_3)_4$ (0.27 g, 0.23 mmol) and Na_2CO_3 (6.36 g, 60.0 mmol) in tetrahydrofuran (THF) (80 mL containing 10% water). After refluxing for 15 h, the product was extracted with ether. The organic layer was dried over $MgSO_4$, filtrated and evaporated. The crude product was purified by column chromatography on SiO_2 using hexane as the eluent and 3.0 g of **6a** obtained as a yellowish solid 83% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 2.34 (s, 3H, $-CH_3$), 7.02 (s, 1H, thiophone-H), 7.20 (d, J = 8.0 Hz, 1H, benzene-H), 7.29 (t, J = 8.4 Hz, 2H, benzene-H), 7.42 (d, J = 8.0 Hz, 2H, benzene-H).

2.2.2. 3-Bromo-5-(2-methoxyphenyl)-2-methylthiophene (*6b*)

Compound **6b** was prepared by an analogous method similar to that used for to **6a** and obtained as a buff solid in 68% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 2.41 (s, 3H, $-CH_3$), 3.91 (s, 3H, $-OCH_3$), 6.95–6.99 (m, 2H, benzene-H), 7.27 (s, 1H, thiophene-H), 7.30 (s, 1H, benzene-H), 7.54 (d, 1H, J = 8.0 Hz, benzene-H).

2.2.3. 3-Bromo-5-(3-methoxyphenyl)-2-methylthiophene (*6c*)

Compound **6c** was prepared by an analogous method similar to that used for to **6a** and obtained as a buff solid in 72% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 2.41 (s, 3H, $-CH_3$), 3.83 (s, 3H, $-OCH_3$), 6.83 (d, 1H, J = 8.0 Hz, benzene-H), 7.03 (s, 1H, thiophene-H), 7.09 (t, 2H, J = 4.0 Hz, benzene-H), 7.27 (t, 1H, J = 8.0 Hz, benzene-H).

2.2.4. 3-Bromo-5-(4-methylphenyl)-2-methylthiophene (*6d*)

Compound **6d** was prepared by an analogous method similar to that used for to **6a** and obtained as a buff solid in 72% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 2.40 (s, 3H, $-CH_3$), 3.83 (s, 3H, $-OCH_3$), 6.85 (d, 2H, $J = 8.8$ Hz, benzene-H), 6.99 (s, 1H, thiophene-H), 7.43 (d, 2H, $J = 8.8$ Hz, benzene-H).

*2.2.5. 3-Bromo-1,5-dimethyl-2-pyrrolecarbonitrile (**8**)*

To a stirred solution of 1,5-dimethyl-2-pyrrolecarbonitrile (**7**) (3.0 g, 25.0 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 yellowish 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 yellowish solid of 4.2 g in 85% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 2.30 (s, 3H, $-CH_3$), 3.68 (s, 3H, $-CH_3$), 6.74 (s, 1H, pyrrole-H).

*2.2.6. 2-Cyano-1,5-dimethyl-4-pyrryl-perfluorocyclopentene (**9**)*

To a stirred THF solution (80 mL) of compound **8** (4.0 g, 20.1 mmol) was added dropwise a 2.5 M *n*-BuLi/hexane solution (8.8 mL, 22 mmol) at −78 °C under nitrogen atmosphere. Stirring was continued for 30 min at −78 °C, octafluorocyclopentene (C_5F_8) (2.8 mL, 20.5 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 3.6 g compound **9** obtained as yellowish solid in 57% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 2.32 (s, 3H, $-CH_3$), 3.72 (s, 3H, $-CH_3$), 6.98 (s, 1H, pyrrole-H).

*2.2.7. 1-(2-Cyano-1,5-dimethyl-4-pyrryl)-2-[2-methyl-5-phenyl-3-thienyl]perfluorocyclopentene (**1o**)*

To a stirred anhydrous THF (80 mL) of compound **6a** (0.7 g, 2.5 mmol) was added dropwise a 2.5 M *n*-BuLi/hexane solution (1 mL, 2.5 mmol) at −78 °C under argon atmosphere. After 30 min, 15 mL THF containing compound **9** (0.8 g, 2.5 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 white solid in 36% yield. M.p. 140.2–141.2 °C; Anal. Calcd for $C_{23}H_{16}F_6N_2S$ (%): C, 59.22; H, 3.46; N, 6.01. Found C, 59.27; H, 3.51; N, 6.03; ^1H NMR (400 MHz, $CDCl_3$): δ 1.77 (s, 3H, $-CH_3$), 1.96 (s, 3H, $-CH_3$), 3.61 (s, 3H, $-CH_3$), 6.93 (s, 1H, pyrrole-H), 7.23 (s, 1H, thiophene-H), 7.39 (t, 1H, $J = 8.0$ Hz, benzene-H), 7.53–7.56 (m, 2H, benzene-H), 7.54 (d, 2H, $J = 7.6$ Hz, benzene-H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 10.7, 13.9, 32.4, 76.1, 76.4, 76.6, 76.7, 104.9, 109.4, 112.03, 125.0, 125.4, 127.4, 128.5, 132.7, 135.4, 139.7, 142.0; IR (ν, KBr, cm^{-1}): 756, 845, 987, 1097, 1183, 1277, 1334, 1385, 1548, 1624, 2221, 2372, 2920, 3125, 3450.

*2.2.8. 1-(2-Cyano-1,5-dimethyl-4-pyrryl)-2-[2-methyl-5-(2-methoxyphenyl)-3-thienyl]perfluorocyclopentene (**2o**)*

Diarylethene **2o** was prepared by an analogous method similar to that used for diarylethene **1o** using 3-Bromo-5-(2-methoxyphenyl)-2-methylthiophene (**6b**) instead of **6a**, and was obtained as a solid 0.45 g in 43% yield. M.p. 98.7–99.8 °C; Anal. Calcd for $C_{24}H_{18}F_6N_2OS$ (%): Calcd C, 58.06; H, 3.65; N, 5.64. Found C, 58.01; H, 3.69; N, 5.59; ^1H NMR (400 MHz, $CDCl_3$): δ 1.74 (s, 3H, $-CH_3$), 1.97 (s, 3H, $-CH_3$), 3.59 (s, 3H, $-CH_3$), 3.92 (s, 3H, $-OCH_3$), 6.95 (s, 1H, pyrrole-H), 6.97–7.02 (m, 2H, benzene-H), 7.26–7.28 (m, 1H, benzene-H), 7.41 (s, 1H, thiophene-H), 7.58–7.60 (m, 1H, benzene-H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 11.3, 14.2, 33.0, 55.6, 76.7, 77.0, 77.2, 77.4, 105.4, 110.2, 111.3, 111.8, 113.0, 113.7, 118.9, 121.1, 122.3, 124.8, 124.9, 127.8, 138.9, 134.8, 136.1, 137.6, 140.7, 155.6; IR (ν, KBr, cm^{-1}): 739, 845, 898, 987, 1030, 1054, 1115, 1128, 1184, 1278, 1335, 1384, 1436, 1482, 1599, 1656, 2218, 2372, 2923, 3130, 3450.

*2.2.9. 1-(2-Cyano-1,5-dimethyl-4-pyrryl)-2-[2-methyl-5-(3-methoxyphenyl)-3-thienyl]perfluorocyclopentene (**3o**)*

Diarylethene **3o** was prepared by an analogous method similar to that used for diarylethene **1o** using 3-Bromo-5-(3-methoxyphenyl)-2-methylthiophene (**6c**) instead of **6a**, and was obtained as a solid 0.48 g in 40% yield. M.p. 156.7–158.2 °C; Anal. Calcd for $C_{24}H_{18}F_6N_2OS$ (%): Calcd C, 58.06; H, 3.65; N, 5.64. Found C, 58.11; H, 3.61; N, 5.66; ^1H NMR (400 MHz, $CDCl_3$): δ 1.76 (s, 3H, $-CH_3$), 1.95 (s, 3H, $-CH_3$), 3.61 (s, 3H, $-CH_3$), 3.86 (s, 3H, $-OCH_3$), 6.87 (s, 1H, pyrrole-H), 6.86 (d, 1H, $J = 6.2$ Hz, benzene-H), 7.06 (s, 1H, thiophene-H), 7.14 (d, 1H, $J = 7.7$ Hz, benzene-H), 7.56 (s, 1H, benzene-H), 7.30 (t, 1H, $J = 7.8$ Hz, benzene-H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 11.3, 14.5, 33.1, 55.4, 76.7, 77.0, 77.3, 77.3, 105.5, 109.9, 111.4, 112.9, 113.3, 116.1, 118.1, 118.8, 122.8, 126.0, 130.1, 134.53, 136.0, 140.4, 142.3, 160.1; IR (ν, KBr, cm^{-1}): 688, 780, 975, 1049, 1103, 1189, 1272, 1332, 1434, 1581, 1606, 1643, 2217, 2957.

*2.2.10. 1-(2-Cyano-1,5-dimethyl-4-pyrryl)-2-[2-methyl-5-(4-methoxyphenyl)-3-thienyl]perfluorocyclopentene (**4o**)*

Diarylethene **4o** was prepared by an analogous method similar to that used for diarylethene **1o** using 3-Bromo-5-(4-methoxyphenyl)-2-methylthiophene (**6d**) instead of **6a**, and was obtained as a solid 0.41 g in 38% yield. M.p. 143.9–144.5 °C; Anal. Calcd for $C_{24}H_{18}F_6N_2OS$ (%): Calcd C, 58.06; H, 3.65; N, 5.64. Found C, 58.10; H, 3.59: N, 5.62; ^1H NMR (400 MHz, $CDCl_3$): δ 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, $CDCl_3$): δ 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 (ν, KBr, cm^{-1}): 630, 743, 822, 845, 895, 985, 1031, 1056, 1108, 1183, 1256, 1335, 1399, 1442, 1466, 1514, 1553, 1611, 2219, 2840, 3128.

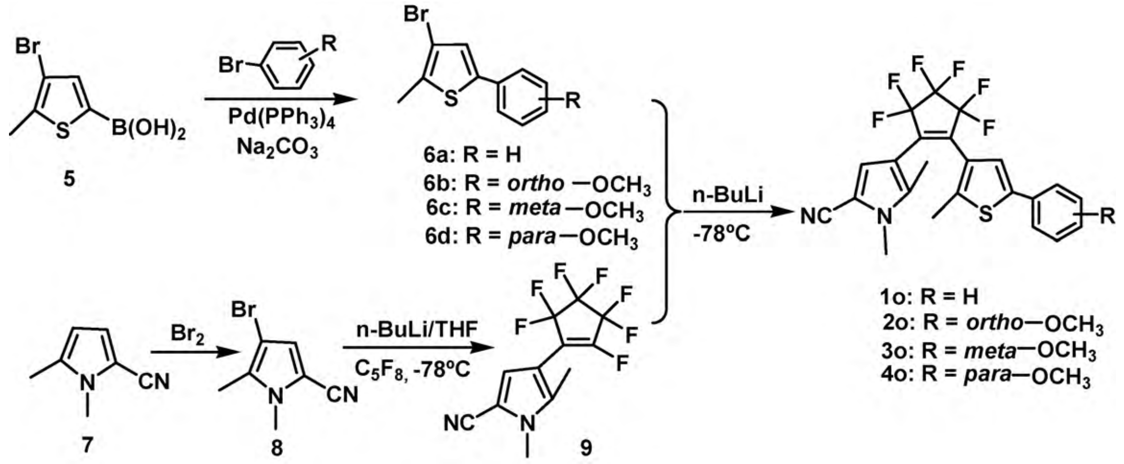
3. Results and discussion

3.1. Discussion of the synthetic strategy

The synthesis method of diarylethenes **1o**–**4o** is shown in Scheme 2. Suzuki coupling of four bromobenzene derivatives with a thiophene boronic acid [43] gave the compounds **6a**–**6d**. 2-Cyano-1,5-dimethyl-4-pyrryl-perfluorocyclopentene (**9**) was derived originally from 1,5-dimethyl-2-pyrrolecarbonitrile (**7**) according to the same method reported previously [26]. Finally, compounds **6a**–**6d** were lithiated separately and then coupled with compound **9** to give diarylethenes **1o**–**4o**, respectively. The structures of **1o**–**4o** were confirmed by NMR, IR, and elemental analysis.

3.2. Photochromic behaviours of diarylethenes

The photochromic behaviours of diarylethenes **1**–**4** induced by photoirradiation at room temperature were measured both in hexane (2.0×10^{-5} mol/L) and in PMMA amorphous film (10%, w/w). In hexane, the absorption spectral changes of diarylethene **1** induced by alternating irradiation with UV light and visible light with appropriate wavelength are shown in Fig. 1. Diarylethene **1o** exhibited



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

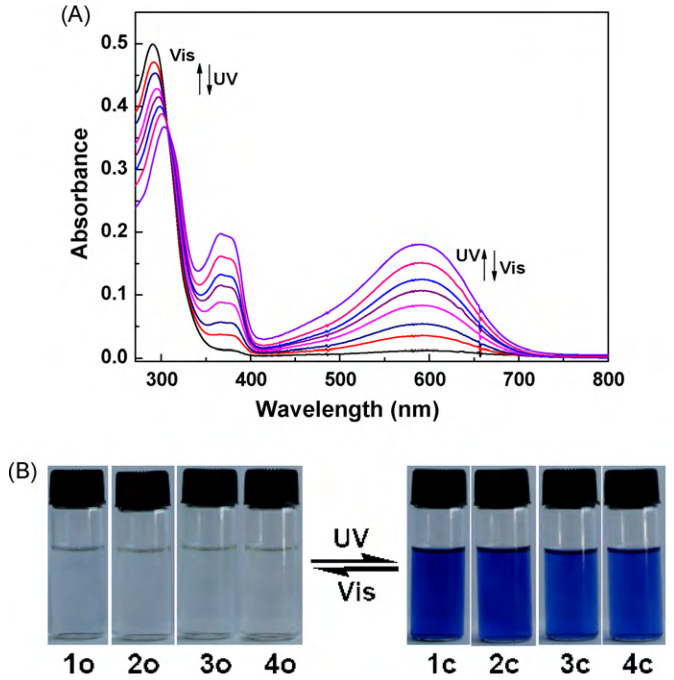


Fig. 1. Absorption spectral changes of diarylethene **1** and the color changes of diarylethenes **1**–**4** upon alternating irradiation with UV and visible light in hexane (2.0×10^{-5} mol/L) at room temperature: (A) spectral changes for compound **1** and (B) color changes for compounds **1**–**4**.

a sharp absorption peak at 290 nm in hexane, which was arisen from $\pi \rightarrow \pi^*$ transition [44]. Upon irradiation with 297 nm light, a new visible absorption band centered at 584 nm emerged while the original peak at 290 nm decreased, indicating the formation of the closed-ring isomer **1c**. This could be seen with the naked eye, as the colorless solution of **1o** turned blue. Alternatively, the blue colored solution could be bleached to colorless upon irradiation with visible light ($\lambda > 450$ nm), indicating **1c** was returning to the initial state **1o**. The coloration–decoloration cycle could be repeated more than 20 times and a clear isosbestic point was observed at 308 nm. Diarylethenes **2**–**4** showed analogous photochromism similar to diarylethene **1** in hexane. Upon irradiation with 297 nm light, absorption bands in visible region appeared and the solutions containing **2o**–**4o** turned blue as a result of the cyclization reactions to produce the closed-ring isomers **2c**–**4c**, which the absorption maxima were observed at 594, 589 and 592 nm, respectively. The color changes of diarylethenes **1**–**4** upon photoirradiation in hexane are also shown in Fig. 1. The blue colored solutions of **2c**–**4c** can be decolorized upon irradiation with visible light ($\lambda > 450$ nm) again, due to the compounds returning to the open-ring isomers **2o**–**4o**, respectively. In the photostationary state, the isosbestic points for diarylethenes **2**, **3** and **4** were observed at 330, 318 and 320 nm, respectively. In addition, the photoconversion ratios of the four derivatives were analyzed by HPLC in the photostationary state, which the value was 90% for **1**, 91% for **2**, 89% for **3**, and 94% for **4**, respectively (Table 1).

For practical applications in optical devices, it is very important that photochromic materials can keep good photochromism in a polymer film, such as the PMMA film [18]. The PMMA films were prepared by dissolving 10 mg diarylethene sample and 100 mg polymethylmethacrylate (PMMA) into chloroform (1 mL), with the aid of ultrasound, and then the homogeneous solution was spin-coated on a quartz substrate (10 mm × 10 mm × 1 mm). In PMMA amorphous film, diarylethenes **1**–**4** also showed similar photochromism as in solution. The absorption spectral change of diarylethene **1** and the color changes of diarylethenes **1**–**4** are shown in Fig. 2. Compared to those in hexane, the maximum absorption peaks of both the ring-opened and the ring-closed iso-

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

Compound	$\lambda_{o,max}$/nm[a] (ε/L mol^{-1} cm^{-1})		$\lambda_{c,max}$/nm[b] (ε/L mol^{-1} cm^{-1})		Φ[c]		Conversion at PSS in hexane
	Hexane	PMMA film	Hexane	PMMA film	Φ_{o-c}	Φ_{c-o}	
1	290 (2.49×10^4)	302	584 (1.00×10^4)	607	0.20	0.054	90%
2	308 (2.23×10^4)	314	594 (1.11×10^4)	614	0.25	0.088	91%
3	293 (2.04×10^4)	307	589 (9.36×10^3)	607	0.22	0.072	89%
4	296 (2.83×10^4)	307	592 (1.15×10^4)	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 (Φ_{o-c}) and cycloreversion reaction (Φ_{c-o}), respectively.

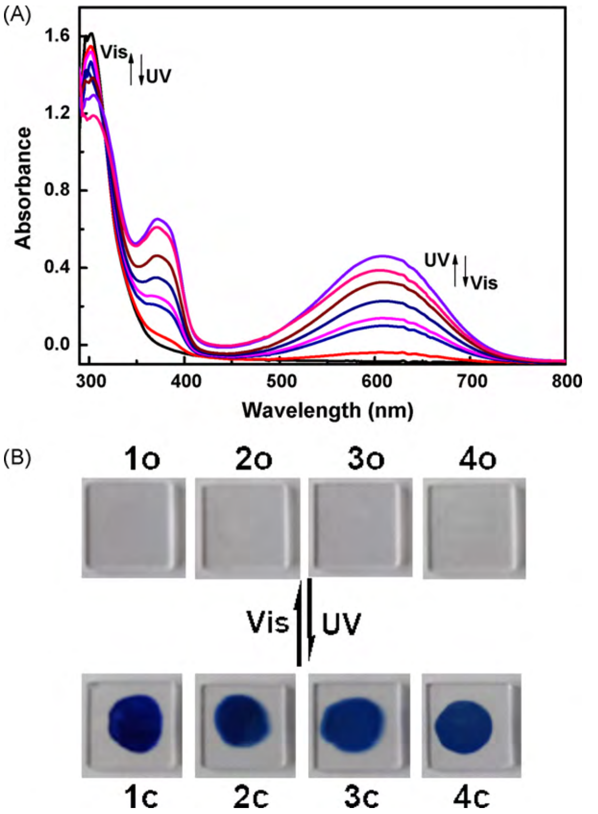


Fig. 2. Absorption spectral changes of diarylethene **1** and the color changes of diarylethenes **1**–**4** upon alternating irradiation with UV and visible light in PMMA film (10% w/w) at room temperature: (A) spectral changes for compound **1** and (B) color changes for compounds **1**–**4**.

mers of diarylethenes **1**–**4** in PMMA film are at longer wavelengths than those in hexane. The red shift values of the absorption maxima of the open-ring isomers are 12 nm for **1o**, 6 nm for **2o**, 14 nm for **3o**, and 11 nm for **4o**, and those of the closed-ring isomers are 23 nm for **1c**, 20 nm for **2c**, 18 nm for **3c**, and 22 nm for **4c**, respectively. The red shift phenomena are consistent with those of the reported studies of most of the diarylethenes [40,41,45], which may be attributed to the polar effect of the polymer matrix and the stabilization of molecular arrangement in solid state [46,47].

The photochromic parameters of compounds **1**–**4** are summarized in Table 1. It could be seen from these data that the methoxy substituent position had a significant effect on the photochromic properties of these diarylethene derivatives, including the absorption maxima, molar absorption coefficients, and quantum yields of cyclization and cycloreversion. As shown in Table 1, the unsubstituted parent diarylethene **1** has the smallest absorption maxima and the smallest cyclization and cycloreversion quantum yields among these diarylethene derivatives. When introduction of the electron-donating methoxy group into the terminal benzene ring, the absorption maxima and the quantum yields of diarylethenes **2**–**4** increased at some extent. For isomeric diarylethenes **2**–**4**, the absorption maxima of both the open-ring isomer and the closed-ring isomer of the *ortho*-substituted derivative **2** are at the longest wavelength in hexane; while those of the *meta*-substituted derivative **3** are the shortest. The result is in good agreement with that reported for the methoxy substituent in a previous work [40], but it 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 [48–50]. For isomeric diarylethenes **2**–**4**, the molar absorption coefficients of both of the open-ring and the closed-ring isomers varied with the same trend in hexane, *i.e.*, they decreased in the order of *para*- > *ortho*- > *meta*-substituent by the methoxy group. Therefore, the molar absorption coefficients of both the open-ring and the closed-ring isomers of the *para*-substituted derivative **4** are the biggest; while those of the *meta*-substituted derivative **3** are the smallest. The values of the *ortho*-substituted derivative **2** are in between those of the *para* and *meta*-substituted derivatives. As shown in Table 1, the cyclization quantum yields of diarylethenes **1**–**4** 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 [42]. The cyclization and cycloreversion quantum yields of these three isomeric diarylethene derivatives showed an analogous changing trend similar to that of their molar absorption coefficients, *i.e.*, they also decreased in the order of *para*- ($\Phi_{o-c,4}=0.44$, $\Phi_{c-o,4}=0.10$) > *ortho*- ($\Phi_{o-c,2}=0.25$, $\Phi_{c-o,2}=0.088$) > *meta*-substituent ($\Phi_{o-c,3}=0.22$, $\Phi_{c-o,3}=0.072$) by the methoxy group. This varying pattern is different from those of isomeric diarylethenes reported previously [40–43]. In addition, the pyrrole moiety has also a significant effect on the photochromic properties of diarylethenes **1**–**4**. When replacing the pyrrole moiety with the thiophene moiety in the same molecular skeleton of photochromic diarylethenes, the absorption maxima and the molar absorption coefficients of both of the open-ring and closed-ring isomers decreased remarkably, and the absorption maxima of their closed-ring isomers showed so big hypsochromic shift that they exhibited the purple colors in hexane [41]. Similarly, when replacing the pyrrole moiety with the pyrazole unit, the molar absorption coefficients and the quantum yields of cyclization and cycloreversion increased significantly, but the absorption maxima decreased clearly [42], compared with pyrrole moiety. The result indicates that the substituent position effect of methoxy group is remarkable different from each other for diarylethenes bearing different aryl moiety.

The thermal stabilities of the open-ring and closed-ring isomers of unsymmetrical diarylethenes **1**–**4** were tested in hexane both at room temperature and at 80 °C. Storing these solutions in the dark and then exposing them to air for more than 10 days at room temperature and at 80 °C, respectively, we found that no changes in the UV/vis spectra of diarylethenes **1**–**4** were observed. The result indicated that the thermal stability of these unsymmetrical diarylethenes **1**–**4** was much better than that of the symmetrical diarylethene bearing two pyrrole moieties [27].

Colorless crystals of **3o** and **4o**, suitable for X-ray analysis, were obtained by the slow evaporation of hexane solutions. The X-ray crystallographic analysis data are listed in Table 2. Their ORTEP drawings of the single crystals **3o** and **4o** are shown in Fig. 3. The molecules of both diarylethenes **3o** and **4o** crystallize with an approximate C_2 symmetry with the photoactive *anti*-parallel conformation in the crystalline phase, which can undergo photocyclization [51,52]. Both the two molecules include four planar rings, which can form three dihedral angles between every two adjacent planar rings. The dihedral angles of diarylethenes **3o** and **4o** are listed in Table 3. From these data, it could be clearly seen that all dihedral angles of the *meta*-substituted derivative **3** are bigger than those of the *para*-substituted derivative **4**. The reason may be attributed to the molecular stereo-structure of methoxy group at different position. The distance between the two reactive C atoms is 3.681(2) Å for **3o** and 3.539(6) Å for **4o** (Table 3), which is close enough for the photocyclization to take place [52–54]. In fact, the crystals **3o** and **4o** showed good photochromism in accordance with the expected analysis (Fig. 4). Upon irradiation with 297 nm light, the colorless crystal of **3o** and **4o** turned blue quickly, as a result of the formation of the closed-ring isomers **3c** and **4c**. Alternatively, the blue colored crystals **3c** and **4c** returned

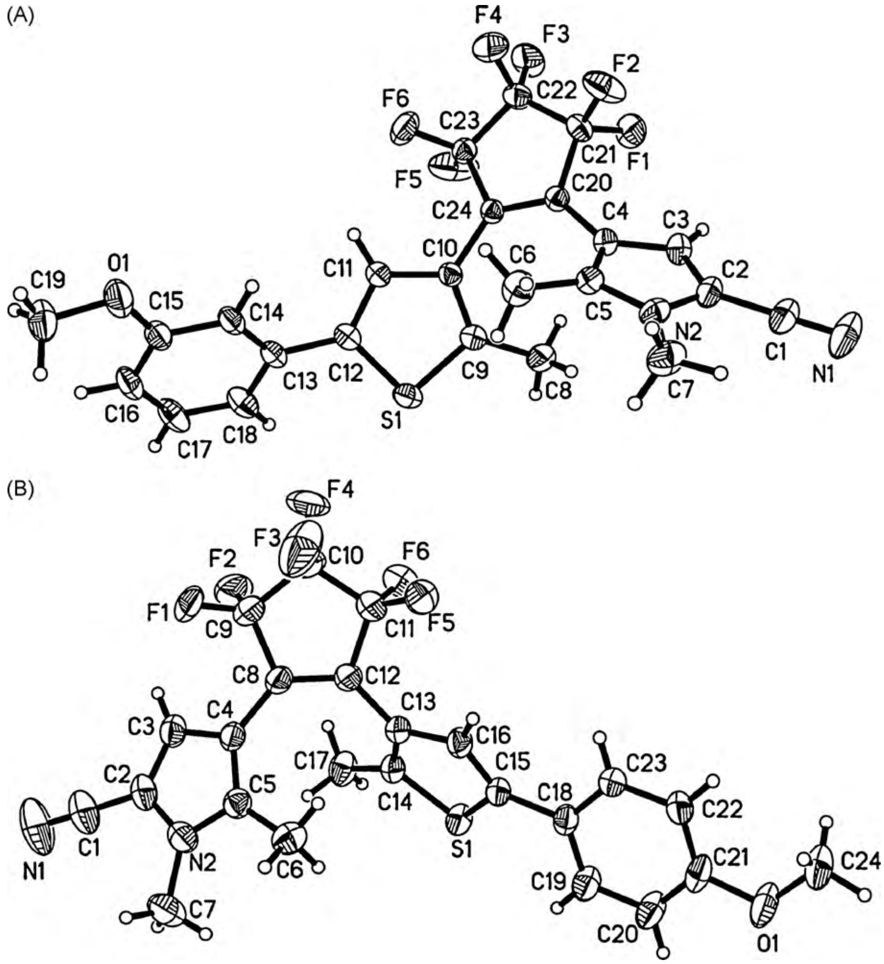


Fig. 3. ORTEP drawings of crystals **3o** and **4o**, showing 30% probability displacement ellipsoids: (A) **3o** and (B) **4o**.

Table 2
Crystal data and structure refinements for diarylethenes **3o** and **4o**.

	Compound **3o**	Compound **4o**
Formula	$C_{24}H_{18}F_6N_2OS$	$C_{24}H_{18}F_6N_2OS$
Formula weight	496.46	496.46
Temperature	294(2)	291(2)
Crystal system	Triclinic	Monoclinic
Space group	P-1	P2(1)/c
Unit cell dimensions		
a (Å)	8.8364(18)	23.120(3)
b (Å)	11.236(2)	8.9474(11)
c (Å)	11.943(2)	11.4416(13)
α (°)	91.277(3)	90.00
β (°)	108.206(3)	101.835(1)
γ (°)	92.082(4)	90.00
Volume (Å^3)	1124.9(4)	2316.6(5)
Z	2	4
Reflections collected	5769	36076
Reflections observed	3957	12597
Number of parameters	330	967
μ (mm^{-1})	0.213	0.202
Density (calcd.) (g/cm^3)	1.466	1.509
Goodness-of-fit on F^2	1.016	1.038
Radiation (Å)	0.71073	0.71073
Final R_1 $[I>2s(I)]$	0.0473	0.0537
wR_2 $[I>2s(I)]$	0.1116	0.1364
R_1 (all data)	0.0795	0.0715
wR_2 (all data)	0.1313	0.1524

Table 3
Distances between the reacting carbon atoms (d, Å) and dihedral angles (θ,°) of diarylethenes **3o** and **4o**.

Compound	d (Å)		θ (°)[a]		
			θ_1	θ_2	θ_3
3o	C5…C9	3.681(2)	46.5(3)	47.0(3)	33.0(3)
4o	C5…C14	3.539(6)	38.5(5)	45.3(5)	23.7(5)

[a] θ_1, dihedral angle between the cyclopentene ring the pyrrole ring; θ_2, dihedral angle between the cyclopentene ring and the thiophene ring; θ_3, dihedral angle between the thiophene ring and the adjacent benzene ring.

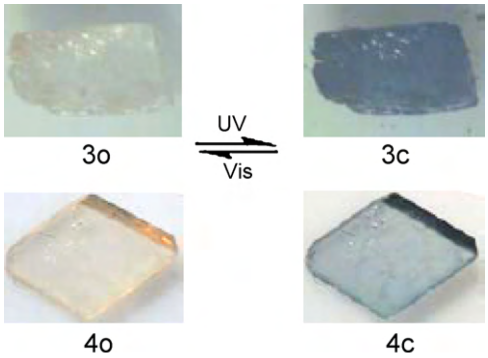


Fig. 4. Photographs of photochromic processes for diarylethenes **3** and **4** in the crystalline phase.

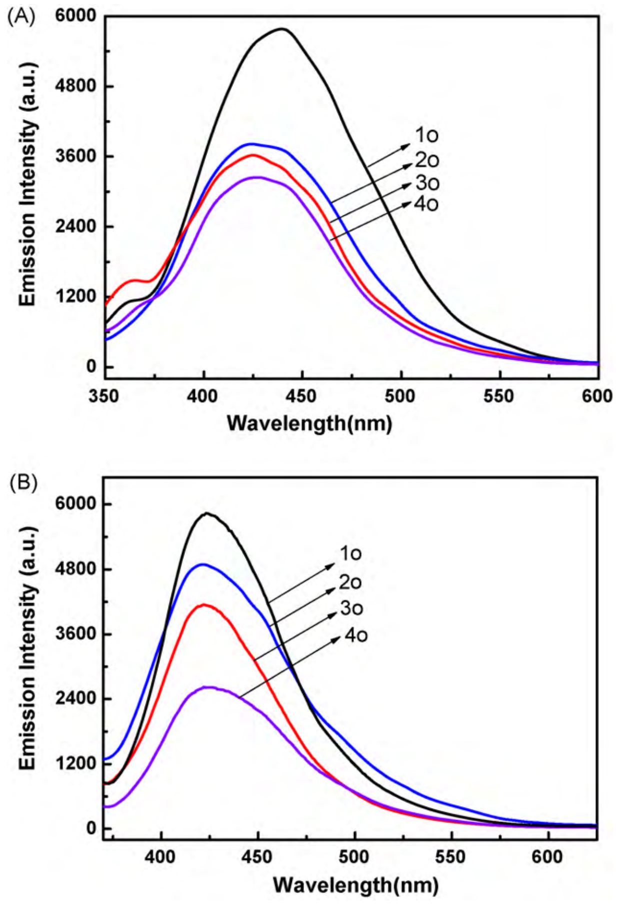


Fig. 5. Fluorescence emission spectra of diarylethenes **1**–**4** both in hexane solution (5.0×10^{-5} mol/L) and in PMMA films (10%, w/w) at room temperature: (A) emission spectra in hexane, excited at 340 nm and (B) emission spectra in PMMA films, excited at 350 nm.

to colorless and reproduce **3o** and **4o** upon irradiation with visible light ($\lambda > 500$ nm). After 500 repeat cycles, the two isomeric diarylethenes still showed good photochromism by alternating irradiation with UV and visible light in the single crystalline phase. So, they can be potentially used for the construction of certain optoelectronic devices [55,56].

3.3. Fluorescence of diarylethenes

Fluorescent properties can be useful not only in molecular scale optoelectronics [57], but in digital fluorescence photoswitches [58]. The fluorescence emission spectra of **1o**–**4o** in hexane (5.0×10^{-5} mol/L) and in PMMA films (10%, w/w) at room temperature are illustrated in Fig. 5. In hexane, the emission peaks of diarylethenes **1o**–**4o** were observed at 439, 425, 425 and 426 nm when excited at 340 nm, and were observed at 424, 422, 422 and 422 nm when monitored at 350 nm in PMMA films. When comparing samples in hexane to those in PMMA film, the emission peaks of diarylethenes **1o**–**4o** consistently exhibit a hypsochromic shift with values of 15 nm for **1o**, 3 nm for **2o**, 3 nm for **3o**, and 4 nm for **4o**. The result is contrary to those reported previously [40,41,48,49]. Among isomeric diarylethenes **2o**–**4o**, the emission intensity of the *ortho*-substituted derivative **2o** is the strongest and that of the *para*-substituted derivative **4o** is the smallest both in hexane and in PMMA film, which may be attributed to the steric hindrance of *ortho*-methoxy group in addition to its strong electron-donating nature [40]. This is in good agreement with those of the unsymmetrical diarylethenes bearing a pyrazole unit [42], however, its completely contrary to those of the unsymmetrical dithienylethene derivatives whose the emission intensity of the *ortho*-substituted derivative is the smallest and that of the *para*-substituted derivative is the strongest both in hexane and in PMMA film [41]. Compared to isomeric diarylethenes **2o**–**4o**, the unsubstituted parent diarylethene **1o** showed the strongest emission intensity and the lowest energy emission peak both in hexane and in PMMA film. The results showed that the electron-donating group could be effective to reduce the emission peak and weaken the fluorescent intensity of diarylethenes bearing a pyrrole unit. The fluorescence quantum yields of the open isomers of **1o**, **2o**, **3o**, and **4o** were determined to be 0.010 0.024, 0.044, and 0.025, respectively, using anthracene (0.27 in acetonitrile) as the reference. From the data, we can see that the unsubstituted parent diarylethene **1** has the smallest fluorescence quantum yield. That is to say, the introduction of electron-donating methoxy group in the terminal benzene ring can significantly enhance the fluorescence quantum yield of diarylethenes bearing a pyrrole unit.

As has been observed for most of the reported diarylethenes [40–43,58–62], diarylethenes **1**–**4** exhibited relatively strong fluorescence switch on changing from open-ring isomers to closed-ring isomers. When irradiated by UV light, the photocyclization was occurred and the fluorescence of diarylethenes **1**–**4** effectively was quenched, due to producing the non-fluorescence closed-ring isomers. The back irradiation by appropriate wavelength visible light regenerated their respective open-ring isomers and recovered the original emission spectra. During the process of photoisomerization, the fluorescent spectral changes of diarylethene **1**–**4** in hexane solutions (5.0×10^{-5} mol/L) and in PMMA films (10%, w/w) are shown in Figs. 6 and 7, respectively. Upon irradiation with 297 nm light, the samples arrived at the photostationary sate, resulting in the emission intensities of diarylethenes **1o**–**4o** being quenched to *ca.* 7% for **1**, 7% for **2**, 12% for **3**, and 4% for **4**. That is to say, the fluorescent modulation efficiencies of diarylethenes **1**–**4** at photostationary state were 93% for **1**, 93% for **2**, 88% for **3**, and 96% for **4**. The result is well consistent with the photoconversion ratios of diarylethenes **1**–**4** in the photostationary state. To some extent, the fluorescent modulation efficiency depends on the photoconversion ratio of diarylethenes. The greater the photoconversion ratio is, the bigger the fluorescent modulation efficiency is achieved in the photostationary state. Therefore, the fluorescent modulation efficiency of the *para*-substituted derivative **4** is the biggest and the *meta*-substituted derivative **3o** is the smallest among isomeric diarylethenes **2**–**4** in hexane. Similarly, their emission intensities decreased to the photostationary state upon irradiation with 313 nm light in PMMA films, where the emission intensities of diarylethenes **1**–**4** were quenched to *ca.* 17% for **1**, 28% for **2**, 19% for **3**, and 24% for **4**, respectively. Therefore, the fluorescent modulation efficiencies of diarylethenes **1**–**4** in hexane were much higher than those in PMMA film. This is completely contrary to those of the unsymmetrical dithienylethene derivatives whose fluorescent modulation efficiencies in hexane are much lower than those in PMMA film [40,41]. Compared with those reported diarylethenes [40,41,48,49], the fluorescent modulation efficiencies of diarylethenes **1**–**4** were significantly enhanced both in the liquid and solid media. This indicated that diarylethenes bearing a pyrrole unit have the potential use as fluorescent modulation switches [6,63]. 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 light 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 and fluorescence modulation switches.

The concentration dependence on the florescence spectrum of diarylethenes **1o** was measured in hexane at room tempera-

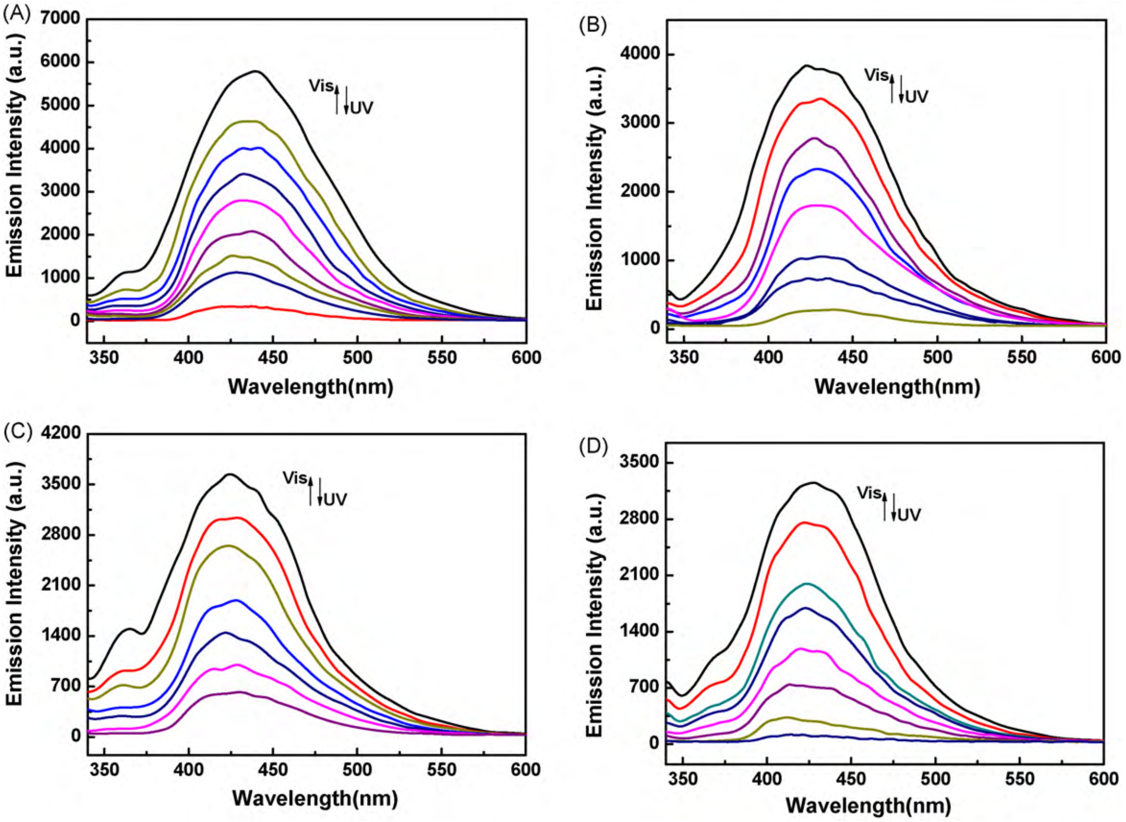


Fig. 6. Emission intensity changes of diarylethene **1**–**4** by photoirradiation at room temperature in hexane (5.0×10^{-5} mol/L), excited at 340 nm.

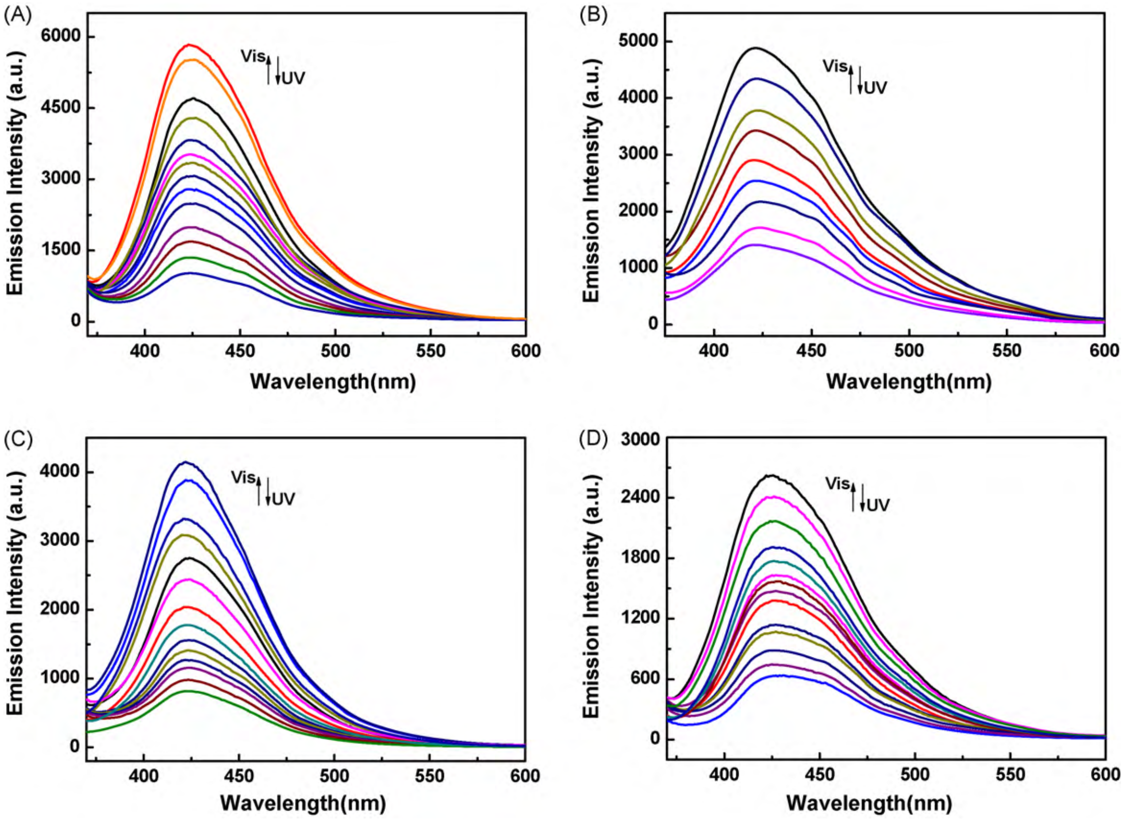


Fig. 7. Emission intensity changes of diarylethene **1**–**4** by photoirradiation at room temperature in PMMA film (10%, w/w), excited at 350 nm.

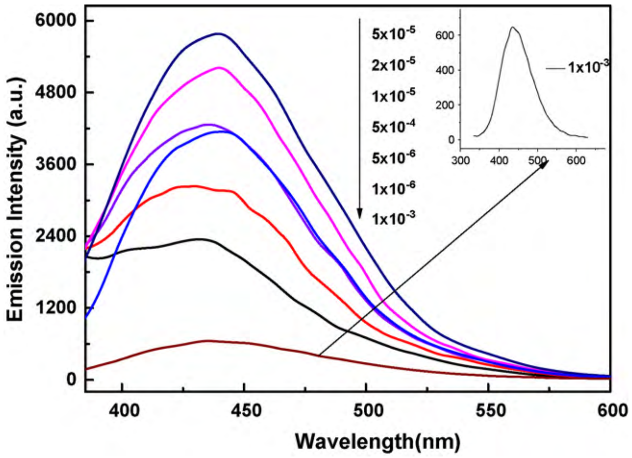


Fig. 8. Emission spectral changes of diarylethene **1o** in various concentrations in hexane at room temperature, excited at 340 nm.

ture and the result is shown in Fig. 8. When the concentration of diarylethene **1o** in hexane was increased from 1.0×10^{-6} to 5.0×10^{-5} mol/L, the emission peak showed a clear bathochromic shift from 427 to 439 nm when excited at 340 nm, and the emission intensity increased dramatically with the increase of the concentration. However, when the concentration increased further from 5.0×10^{-5} to 1.0×10^{-3} mol/L, the emission peak shifted slightly along the longer wavelength direction, and the emission intensity decreased remarkably. The hexane solution showed very weak fluorescence when the concentration arrived at 1.0×10^{-3} mol/L. Just like diarylethene **1o**, compounds **2o**–**4o** showed similar fluorescent properties depending on the concentration employed. The results are summarized in Table 4. The result elucidated that diarylethenes **1o**–**4o** exhibited a significant concentration effect on their fluorescent properties. The emission peaks of diarylethenes **1o**–**4o** showed an evident bathochromic shift along with the increase of concentration. However, the emission intensities of them showed a remarkable initial increase with subsequent dramatic decrease with the increase of concentration. The strongest and the smallest values were obtained at 5.0×10^{-5} and 1.0×10^{-3} mol/L, respectively. The fluorescent quenching of diarylethenes **1o**–**4o** at higher concentration may be ascribed to the molecular aggregation [64].

3.4. Electrochemistry of diarylethenes

The electrochemical properties of diarylethenes can be potentially applied to molecular scale electronic switches [65]. The oxidative cyclization and cycloreversion and the reductive electrochemical cyclization of some diarylethene derivatives have been reported [12,13,66,67]. Cyclic voltammograms (CV) were performed on the diarylethenes **1**–**4** under identical experimental conditions at a scanning rate of 50 mV s^{-1}. The CV curves of diarylethenes **1**–**4** are shown in Fig. 9. The oxidation onsets of **1o**–**4o** were observed at +1.63, 1.43, 1.51, and 1.31 V, and those of **1c**–**4c** were observed at +0.72, 1.15, 0.98, and 0.79 V, respectively. The result indicated that the oxidation process of the open-ring isomers **1o**–**4o** occurs at higher potentials than that of the corresponding closed-ring isomers **1c**–**4c**. This is in accordance with the theory that longer conjugation length generally leads to less positive potentials, with the addition of each heterocyclic ring [66]. After cyclization reaction, the π-conjugation of the ring-closed isomer extends across the perfluorocyclopentene ring causing a lower oxidation onset. Moreover, there are great differences amongst the electronic current and polarization curve shapes between the open-ring and closed-ring isomers of diarylethenes **1**–**4** at the scanned voltage region. The difference of oxidation onset between the open-ring and closed-ring isomers of diarylethenes **1**–**4** ($\Delta V_{\text{o–c}}$) was 0.91 V for **1**, 0.28 V for **2**, 0.53 V for **3**, and 0.52 V for **4**. Compared to isomeric diarylethenes **2**–**4**, the unsubstituted parent diarylethene **1** showed the biggest $\Delta V_{\text{o–c}}$, indicating that the electron-donating group could be effective to decrease the $\Delta V_{\text{o–c}}$ of these diarylethene derivatives.

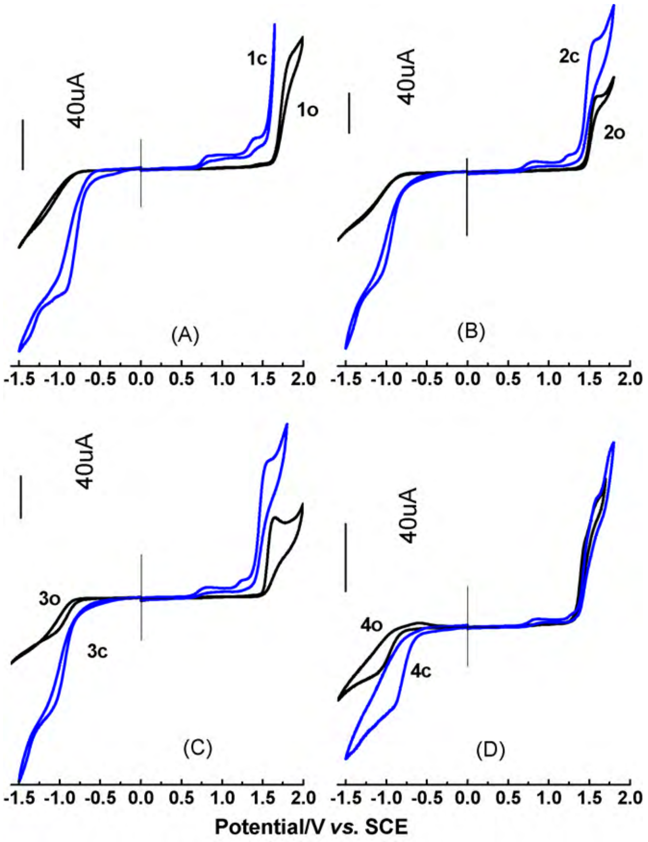


Fig. 9. Cyclic voltammograms (second scan) of diarylethene **1**–**4** in acetonitrile with the scanning rate of 50 mV s^{-1}: (A) **1**, (B) **2**, (C) **3**, and (D) **4**.

Table 4
The effect of concentration on the fluorescence spectra of diarylethenes **1**–**4** at room temperature in hexane, monitored at 340 nm.

Concentrations (mol/L)	$\lambda_{\text{em,max}}$ (emission intensity)			
	1o	**2o**	**3o**	**4o**
1.0×10^{-6}	427 (2338)	403 (3299)	401 (2426)	402 (2011)
5.0×10^{-6}	430 (3231)	408 (3928)	407 (2796)	409 (2300)
1.0×10^{-5}	435 (4276)	417 (5520)	421 (3383)	414 (2935)
5.0×10^{-5}	439 (5780)	425 (3810)	425 (3621)	426 (3242)
5.0×10^{-4}	441 (4138)	430 (2554)	427 (2492)	426 (2351)
1.0×10^{-3}	441 (637)	436 (274)	430 (333)	430 (499)

According to the same method reported previously [68–70], the Highest Occupied Molecular Orbitals (HOMO) and the Lowest Unoccupied Molecular Orbitals (LUMO) energy levels can be estimated by using the energy level of ferrocene as reference. Based on the HOMO and LUMO energy level, the band-gap (E_g) of each compound can be calculated approximately and the results are summarized in Table 5. These data showed that the band-gaps of the ring-closed isomers **1c**–**4c** are lower than those of their corresponding ring-opened isomers **1o**–**4o**. Among these compounds, the E_g of **1o** is the highest (E_g = 2.60 eV) and that of **1c** is the lowest (E_g = 1.35 eV), implying that the charge transfer must be faster in **1c** compared to that in others [71]. When introducing the methoxy group into the terminal benzene ring of the same diarylethene

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

Compounds	Oxidation		Reduction		Band gap
	E_{onset} (V)	IP (eV)	E_{onset} (V)	EA (eV)	E_g (eV)
1o	1.63	−6.43	−0.97	−3.83	2.60
1c	0.72	−5.52	−0.63	−4.17	1.35
2o	1.43	−6.23	−0.90	−3.9	2.33
2c	1.15	−5.95	−0.77	−4.03	1.92
3o	1.51	−6.31	−0.97	−3.81	2.48
3c	0.98	−5.78	−0.79	−4.01	1.77
4o	1.31	−6.11	−0.89	−3.91	2.20
4c	0.79	−5.59	−0.76	−4.04	1.55

skeleton, the band-gaps of the open-ring isomers **2o**–**4o** decreased, and those of the closed-ring isomers **2o**–**4o** increased significantly, compared with the unsubstituted parent diarylethene **1**. The results suggest that the methoxy group and its substituted position have a great effect on the electrochemical properties of these diarylethene compounds but further work is required to quantify these effects. It should be noted here that calculation absolute HOMO and LUMO levels from electrochemical data in combination with the energy gap is still in debate [70].

4. Conclusions

In summary, four unsymmetrical diarylethene derivatives bearing a pyrrole moiety were synthesized, and their photochemical and electrochemical properties were discussed systematically. All compounds undergo good photochromism both in solution and in PMMA films. In comparison of the unsubstituted parent diarylethene **1**, the absorption maxima, the quantum yields of cyclization and cycloreversion, and the fluorescence quantum yields of the open-ring isomers of diarylethenes **2**–**4** bearing a methoxy group at the *ortho*-, *meta*-, and *para*-position of the terminal benzene ring increased remarkably. However, the fluorescence emission peaks and the E_gs of the open-ring isomers of **2**–**4** were much lower than those of **1**. The methoxy group and its substituted position had a significant effect on the photochemical and electrochemical properties of these isomeric diarylethene derivatives. The pyrrole moiety induced new features which differed from those of diarylethenes bearing thiophene or pyrazole rings which had been reported previously. The results will be helpful for in understanding the substituent position effect on the properties of diarylethenes bearing a pyrrole moiety and for the synthesis of efficient photoactive diarylethenes with tunable properties.

Acknowledgements

This work was supported by Program for the NSFC of China (20962008, 50973077), New Century Excellent Talents in University (NCET-08-0702), the Key Scientific Project from Education Ministry of China (208069), National Natural Science Foundation of Jiangxi Province (2008GZH0020, 2009GZH0034) and the Youth Science Funds of the Education Office of Jiangxi, China (GJJ09302).

References

[1] M. Irie, Diarylethenes for memories and switches, Chem. Rev. 100 (2000) 1685–1716.
[2] S. Kawata, Three-dimensional optical data storage using photochromic materials, Chem. Rev. 100 (2000) 1777–1788.
[3] H. Tian, S.J. Yang, Recent progresses on diarylethene based photochromic switches, Chem. Soc. Rev. 33 (2004) 85–97.
[4] S.H. Chen, H.M.P. Chen, Y. Geng, D.J. Stephen, K.L. Marshall, T.N. Blanton, Novel glassy nematic liquid crystals for non-destructive rewritable optical memory and photonic switching, Adv. Mater. 15 (2003) 1061–1065.
[5] K. Uchida, A. Takata, M. Saito, A. Murakami, S. Nakamura, M. Irie, A novel photochromic film by oxidation polymerization of a bisbenzothienylethene with phenol groups, Adv. Mater. 15 (2003) 785–788.
[6] H. Tian, B.Z. Chen, H.Y. Tu, K. Müllen, Novel bisthienylethene-based photochromic tetraazaporphyrin with photoregulating luminescence, Adv. Mater. 14 (2002) 918–923.
[7] F.M. Raymo, M. Tomasulo, Electron and energy transfer modulation with photochromic switches, Chem. Soc. Rev. 34 (2005) 327–336.
[8] K. Matsuda, M. Irie, Diarylethene as a photoswitching unit, J. Photochem. Photobiol. C: Photochem. Rev. 5 (2004) 169–182.
[9] C. Bertarelli, A. Bianco, F. D'Amore, M.C. Gallazzi, G. Zerbi, Effect of substitution on the change of refractive index in dithienylethene: An ellipsometric study, Adv. Funct. Mater. 14 (2004) 357–363.
[10] E. Kim, Y.-K. Choi, M.-H. Lee, Photoinduced refractive index change of a photochromic diarylethene, Macromolecules 32 (1999) 4855–4860.
[11] G. Guirado, C. Coudret, M. Hliwa, J.-P. Launay, Understanding electrochromic processes initiated by dithienylcyclopentene cation-radicals, J. Phys. Chem. B 109 (2005) 17445–17459.
[12] W.R. Browne, J.J.D. de Jong, T. Kudernac, M. Walko, L.N. Lucas, K. Uchida, J.H. van Esch, B.L. Feringa, Oxidative electrochemical switching in dithienylcyclopentenes, part 1: effect of electronic perturbation on the efficiency and direction of molecular switching, Chem. Eur. J. 11 (2005) 6414–6429.
[13] W.R. Browne, J.J.D. de Jong, T. Kudernac, M. Walko, L.N. Lucas, K. Uchida, J.H. van Esch, B.L. Feringa, Oxidative electrochemical switching in dithienylcyclopentenes, part 2: effect of substitution and asymmetry on the efficiency and direction of molecular switching and redox stability, Chem. Eur. J. 11 (2005) 6430–6441.
[14] T. Okuyama, Y. Tani, K. Miyake, Y. Yokoyama, Chiral helicenoid diarylethene with large change in specific optical rotation by photochromism, J. Org. Chem. 72 (2007) 1634–1638.
[15] Y. Tani, T. Ubukata, Y. Yokoyama, Y. Yokoyama, Chiral helicenoid diarylethene with highly diastereoselective photocyclization, J. Org. Chem. 72 (2007) 1639–1644.
[16] K. Matsuda, S. Yamamoto, M. Irie, Diastereoselective cyclization of a diarylethene having a chiral *N*-phenylethylamide substituent in crystals, Tetrahedron Lett. 42 (2001) 7291–7293.
[17] C.C. Corredor, Z.-L. Huang, K.D. Belfield, Two-photon 3D data storage via fluorescence modulation of an efficient fluorene dye by a photochromic diarylethene, Adv. Mater. 18 (2006) 2910–2914.
[18] S.Z. Pu, H.H. Tang, B. Chen, J.K. Xu, W.H. Huang, Photochromic diarylethene for two-photon 3D optical storage, Mater. Lett. 60 (2006) 3553–3557.
[19] S.Z. Pu, F.S. Zhang, J.K. Xu, L. Shen, Q. Xiao, B. Chen, Photochromic diarylethenes for three-wavelength optical memory, Mater. Lett. 60 (2006) 485–489.
[20] S.Z. Pu, T.S. Yang, B. Yao, Y.L. Wang, M. Lei, J.K. Xu, Photochromic diarylethene for polarization holographic optical recording, Mater. Lett. 61 (2007) 855–859.
[21] H. Tian, Y.L. Feng, Next step of photochromic switches, J. Mater. Chem. 18 (2008) 1617–1622.
[22] J.J. Zhang, W.J. Tan, X.L. Meng, H. Tian, Soft mimic gear-shift with a multi-stimulus modified diarylethene, J. Mater. Chem. 19 (2009) 5726–5729.
[23] H. Tian, S. Wang, Photochromic bisthienylethene as multi-function switches, Chem. Commun. (2007) 781–792.
[24] Y.L. Feng, Y.L. Yan, S. Wang, W.H. Zhu, S.X. Qian, H. Tian, Photochromic thiophene oligomers based on bisthienylethene: syntheses, photochromic and two-photon properties, J. Mater. Chem. 16 (2006) 3685–3692.
[25] K. Higashiguchi, K. Matsuda, N. Tanifuji, M. Irie, Full-color photochromism of a fused dithienylethene trimer, J. Am. Chem. Soc. 127 (2005) 8922–8923.
[26] S.Z. Pu, G. Liu, L. Shen, J.K. Xu, Efficient synthesis and properties of isomeric photochromic diarylethenes having a pyrrole unit, Org. Lett. 9 (2007) 2139–2142.
[27] K. Uchida, T. Matsuoka, K. Sayo, M. Iwamoto, S. Hayashi, M. Irie, Thermally reversible photochromic systems. Photochromism of a dipyrrolylperfluorocyclopentene, Chem. Lett. (1999) 835–836.
[28] M. Irie, K. Sakemura, M. Okinaka, K. Uchida, Photochromism of dithienylethenes with electron-donating substituents, J. Org. Chem. 60 (1995) 8305–8309.
[29] S.Z. Pu, C.H. Zheng, Z.G. Le, G. Liu, C.B. Fang, Substituent effects on the properties of photochromic diarylethene, Tetrahedron 64 (2008) 2576–2585.
[30] K. Uchida, T. Matsuoka, S. Kobatake, T. Yamaguchi, M. Irie, Substituent effect on the photochromic reactivity of bis(2-thienyl)perfluorocyclopentenes, Tetrahedron 57 (2001) 4559–4565.
[31] X.D. Deng, L.S. Liebeskind, A contribution to the design of molecular switches: novel acid-mediated ring-closing-photochemical ring-opening of 2,3-bis(heteroaryl)quinones, J. Am. Chem. Soc. 123 (2001) 7703–7704.
[32] K. Uchida, T. Ishikawa, M. Takeshita, M. Irie, Thermally irreversible photochromic systems. Reversible photocyclization of 1,2-bis(thiazolyl)perfluorocyclopentenes, Tetrahedron 54 (1998) 6627–6638.
[33] S. Takami, M. Irie, Synthesis and photochromic properties of novel yellow developing photochromic compounds, Tetrahedron 60 (2004) 6155–6161.
[34] K. Yagi, M. Irie, Fluorescence property of photochromic diarylethenes with indole groups, Bull. Chem. Soc. Jpn. 76 (2003) 1625–1628.
[35] K. Yagi, C.F. Soong, M. Irie, Synthesis of fluorescent diarylethenes having a 2,4,5-triphenylimidazole chromophore, J. Org. Chem. 66 (2001) 5419–5423.
[36] K. Abu-Rabeah, B. Polyak, R.E. Ionescu, S. Cosnier, R.S. Marks, Synthesis and characterization of a pyrrole-alginate conjugate and its application in a biosensor construction, Biomacromolecules 6 (2005) 3313–3318.
[37] T. Bando, H. Sugiyama, Synthesis and biological properties of sequence-specific DNA-alkylating pyrrole–imidazole polyamides, Acc. Chem. Res. 39 (2006) 935–944.

[38] K. Yumoto, M. Irie, K. Matsuda, Control of the photoreactivity of diarylethene derivatives by quaternarization of the pyridylethynyl group, Org. Lett. 10 (2008) 2051–2054.

[39] S.Z. Pu, T.S. Yang, G.Z. Li, J.K. Xu, B. Chen, Substituent position effect on the optoelectronic properties of photochromic diarylethenes, Tetrahedron Lett. 47 (2006) 3167–3171.

[40] S.Z. Pu, C.B. Fan, W.J. Miao, G. Liu, The effect of substituent position upon unsymmetrical isomeric diarylethenes bearing a methoxy group, Dyes Pigments 84 (2010) 25–35.

[41] S.Z. Pu, W.J. Liu, W.J. Miao, Photochromism of new unsymmetrical isomeric diarylethenes bearing a methoxyl group, J. Phys. Org. Chem. 22 (2009) 954–963.

[42] S.Z. Pu, T.S. Yang, J.K. Xu, B. Chen, Syntheses and properties of new photochromic diarylethene derivatives having a pyrazole unit, Tetrahedron Lett. 47 (2006) 6473–6477.

[43] T.S. Yang, S.Z. Pu, B. Chen, J.K. Xu, Electron-donating methoxy group position effect on properties of a new unsymmetrical diarylethene derivatives having a pyrazole unit, Can. J. Chem. 85 (2007) 12–20.

[44] Z.X. Li, L.Y. Liao, W. Sun, C.H. Xu, C. Zhang, C.J. Fang, C.H. Yan, Reconfigurable cascade circuit in a photo- and chemical-switchable fluorescent diarylethene derivative, J. Phys. Chem. C 112 (2008) 5190–5196.

[45] S.Z. Pu, C.B. Fan, W.J. Miao, G. Liu, New photochromic diarylethenes with a six-membered aryl unit, Tetrahedron 64 (2008) 9464–9470.

[46] K. Kasatani, S. Kambe, M. Irie, Photochromic reaction and fluorescence of dithienylethenes in the solid state, J. Photochem. Photobiol. A 122 (1999) 11–15.

[47] M. Hoshino, F. Ebisawa, T. Yoshida, K. Sukegawa, Refractive index change in photochromic diarylethene derivatives and its application to optical switching devices, J. Photochem. Photobiol. A 105 (1997) 75–81.

[48] C.B. Fan, S.Z. Pu, G. Liu, T.S. Yang, Substituent position effect on the properties of isomeric photochromic diarylethenes bearing chlorine atoms, J. Photochem. Photobiol. A: Chem. 194 (2008) 333–343.

[49] C.B. Fan, S.Z. Pu, G. Liu, T.S. Yang, Substituent position effect on the properties of new unsymmetrical isomeric diarylethenes having a chlorine atom, J. Photochem. Photobiol. A: Chem. 197 (2008) 415–425.

[50] S.Z. Pu, L.S. Yan, Z.D. Wen, G. Liu, L. Shen, Synthesis and chlorine atom position effect on the properties of unsymmetrical photochromic diarylethenes, J. Photochem. Photobiol. A: Chem. 196 (2008) 84–93.

[51] S. Kobatake, K. Uchida, E. Tsuchida, M. Irie, Single-crystalline photochromism of diarylethenes: reactivity–structure relationship, Chem. Commun. (2002) 2804–2805.

[52] M. Morimoto, M. Irie, Photochromism of diarylethene single crystals: crystal structures and photochromic performance, Chem. Commun. (2005) 3895–3905.

[53] M. Morimoto, M. Irie, Photochromic reactions of diarylethenes in single crystals with intermolecular O–H···N hydrogen-bonding networks, Chem. Eur. J. 12 (2006) 4275–4282.

[54] V. Ramamurthy, K. Venkatesan, Photochemical reactions of organic crystals, Chem. Rev. 87 (1987) 433–481.

[55] M. Irie, T. Fukaminato, T. Sasaki, N. Tamai, T. Kawai, A digital fluorescent molecular photoswitch, Nature 420 (2002) 759–760.

[56] M. Berberich, A.-M. Krause, M. Orlandi, F. Scandola, F. Würthner, Toward fluorescent memories with nondestructive readout: photoswitching of fluorescence by intramolecular electron transfer in a diaryl ethene-perylene bisimide photochromic system, Angew. Chem. 120 (2008) 6718–6721.

[57] B. Gorodetsky, H.D. Samachetty, R.L. Donkers, M.S. Workentin, N.R. Branda, Reductive electrochemical cyclization of a photochromic 1,2-dithienylcyclopentene dication, Angew. Chem. Int. Ed. 43 (2004) 2812–2815.

[58] T. Fukaminato, T. Sasaki, T. Kawai, N. Tamai, M. Irie, Digital photoswitching of fluorescence based on photochromism of diarylethene derivatives at a single-molecule level, J. Am. Chem. Soc. 126 (2004) 14843–14849.

[59] H. Tian, B. Qin, R.X. Yao, X.L. Zhao, S.J. Yang, A single photochromic molecular switch with four optical outputs probing four inputs, Adv. Mater. 15 (2003) 2104–2107.

[60] S.Z. Xiao, T. Yi, Y.F. Zhou, Q. Zhao, F.Y. Li, C.H. Huang, Multi-state molecular switches based on dithienylperfluorocyclopentene and imidazo [4,5-f] [1,10] phenanthroline, Tetrahedron 62 (2006) 10072–10078.

[61] Y. Zou, T. Yi, S.Z. Xiao, F.Y. Li, C.Y. Li, X. Gao, J.C. Wu, M.X. Yu, C.H. Huang, Amphiphilic diarylethene as a photoswitchable probe for imaging living cells, J. Am. Chem. Soc. 130 (2008) 10750–15751.

[62] C. Zhang, H.-P. Zhou, L.-Y. Liao, W. Feng, W. Sun, Z.-X. Li, C.-H. Xu, C.-J. Fang, L.-D. Sun, Y.-W. Zhang, C.-H. Yan, Luminescence modulation of ordered upconversion nanopatterns by photochromic diarylethene: rewritable optical storage with nondestructive readout, Adv. Mater. 22 (2010) 633–637.

[63] B.Z. Chen, M.Z. Wang, Y.Q. Wu, H. Tian, Reversible near-infrared fluorescence switch by novel photochromic unsymmetrical-phthalocyanine hybrids based on bisthienylethene, Chem. Commun. (2002) 1060–1061.

[64] T. Fukaminato, T. Kawai, S. Kobatake, M. Irie, Fluorescence of photochromic 1,2-bis(3-methyl-2-thienyl)ethene, J. Phys. Chem. B 107 (2003) 8372–8377.

[65] D. Bonifazi, M. Scholl, F. Song, L. Echegoyen, G. Accorsi, N. Armaroli, F. Diederich, Exceptional redox and photophysical properties of a triply fused diporphyrin-C_{60} conjugate: novel scaffolds for multicharge storage in molecular scale electronics, Angew. Chem. Int. Ed. 42 (2003) 4966–4970.

[66] S.Z. Pu, T.S. Yang, J.K. Xu, L. Shen, G.Z. Li, Q. Xiao, B. Chen, Syntheses and optoelectronic properties of four photochromic dithienylethenes, Tetrahedron 61 (2005) 6623–6629.

[67] Y. Moriyama, K. Matsuda, N. Tanifuji, S. Irie, M. Irie, Electrochemical cyclization/cycloreversion reactions of diarylethenes, Org. Lett. 7 (2005) 3315–3318.

[68] C.H. Zheng, S.Z. Pu, J.K. Xu, M.B. Luo, D.C. Huang, L. Shen, Synthesis and the effect of alkyl chain length on optoelectronic properties of diarylethene derivatives, Tetrahedron 63 (2007) 5437–5449.

[69] F.C. Tsai, C.C. Chang, C.L. Liu, W.C. Chen, S.A. Jenekhe, New thiophene-linked conjugated poly(azomethine)s: theoretical electronic structure, synthesis, and properties, Macromolecules 38 (2005) 1958–1966.

[70] X.W. Zhan, Y.Q. Liu, X. Wu, S. Wang, D.B. Zhu, New series of blue-emitting and electron-transporting fluorene-based copolymers, Macromolecules 35 (2002) 2529–2537.

[71] E. Kim, M. Kim, K. Kim, Diarylethenes with intramolecular donor–acceptor structures for photo-induced electrochemical change, Tetrahedron 62 (2006) 6814–6821.