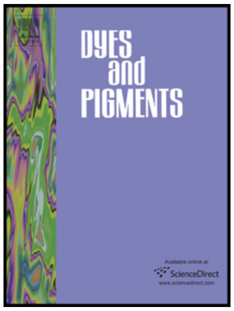


Syntheses and photochromism of new isomeric diarylethenes bearing an indole moiety

Chunhong Zheng, Shouzhi Pu, Zhiyi Pang, Bing Chen, Gang Liu, Yanfeng Dai

PII: S0143-7208(13)00130-7
DOI: 10.1016/j.dyepig.2013.04.003
Reference: DYPI 3902

To appear in: *Dyes and Pigments*

Received Date: 22 January 2013
Revised Date: 4 April 2013
Accepted Date: 6 April 2013

Please cite this article as: Zheng C, Pu S, Pang Z, Chen B, Liu G, Dai Y, Syntheses and photochromism of new isomeric diarylethenes bearing an indole moiety, *Dyes and Pigments* (2013), doi: 10.1016/j.dyepig.2013.04.003.

Highlights for manuscript

- Isomeric diarylethenes bearing an indole moiety were synthesized > They displayed high fluorescence efficiency and remarkable fatigue resistance > The effects of the indole ring and the methoxy position played a very important role.

Graphical Abstract

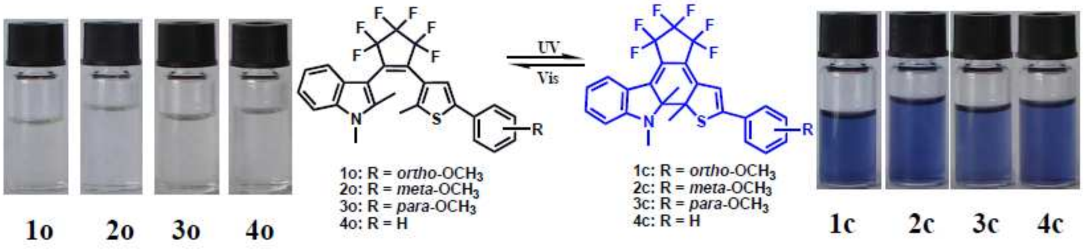
Syntheses and photochromism of new isomeric diarylethenes bearing an indole moiety

Chunhong Zheng[a], Shouzhi Pu[b, a]*, Zhiyi Pang[b], Bing Chen[b], Gang Liu[b], Yanfeng Dai[a]

[a]*Department of Chemistry, Nanchang University, Nanchang 330031, PR China*

[b]*Jiangxi Key Laboratory of Organic Chemistry, Jiangxi Science & Technology Normal University, Nanchang 330013, PR China*

***Corresponding author:** E-mail address: pushouzhi@tsinghua.org.cn (S. Pu); Tel./Fax: +86-791-83831996.



A new class of isomeric diarylethenes bearing an indole moiety was synthesized and the effects of the methoxy substituent position on their photochemical and electrochemical properties were investigated. The results indicated that the electron-donating methoxy group and its substituted position had a significant effect on the photochromic behaviors of these isomeric diarylethene derivatives.

Syntheses and photochromism of new isomeric diarylethenes bearing an indole moiety

Chunhong Zheng[a], Shouzhi Pu[b, a]*, Zhiyi Pang[b], Bing Chen[b], Gang Liu[b], Yanfeng Dai[a]

[a]*Department of Chemistry, Nanchang University, Nanchang 330031, PR China*

[b]*Jiangxi Key Laboratory of Organic Chemistry, Jiangxi Science & Technology Normal University, Nanchang 330013, PR China*

***Corresponding author:** E-mail address: pushouzhi@tsinghua.org.cn (S. Pu); Tel./Fax: +86-791-83831996.

Abstract—Four new photochromic diarylethenes, each bearing an indole moiety, were synthesized and three of their structures were determined by single-crystal X-ray diffraction analysis. Under alternating irradiation with UV and visible light, the compounds showed favorable photochromism in hexane, PMMA films and the crystalline phase. The cyclization quantum yield gradually increased and the molar absorption coefficients of the closed-ring isomers decreased going from the *ortho*- to *meta*- to the *para*-position of the substitution. The absorption maxima showed little change when the methoxy group was attached at any of the three positions on the terminal benzene ring. Each of the compounds displayed high fluorescence efficiency and remarkable fatigue resistance in both solution and PMMA films by photoirradiation. Of particular note, their fluorescent modulation efficiency could be achieved ca. 90% in solid media. Cyclic voltammograms testified that the methoxy group and its substituted position could effectively modulate the electrochemical behaviors of these diarylethenes.

Keywords: Photochromism; Diarylethene; Indole moiety; Methoxy group position effect; Fluorescence; Electrochemistry.

1. Introduction

Photochromic compounds have attracted much attention because of their potential application in photonic devices, such as optical memory media and photo-optical switches [1-3]. Diarylethenes derivatives are the most promising candidates among various photochromic molecules, because of their excellent thermal stability and outstanding fatigue resistance [4-7]. In order to acquire ideal photochromic properties, chemists usually expand the library of diarylethenes by either altering the central bridge or the two aryl units.

In the past several decades, significant advancement has been made in the synthesis of novel photochromic diarylethene systems [8-11]. It has been revealed that the nature of the aryl moieties can heavily influence the physicochemical properties of the photochromic diarylethenes during the process of cyclization and cycloreversion reactions induced by photoirradiation. For example, diarylethenes with thiophene or benzothiophene moieties exhibit excellent thermal stability and outstanding fatigue resistance [3,4], whereas dipyrrolyl-perfluorocyclopentene groups are thermally unstable and return to the open-ring isomer even in the dark [12]. Diarylethenes with two thiazole moieties have a high cyclization quantum yield [13,14], whereas diarylethenes with a pyrazole unit have a relatively high cycloreversion quantum yield [15]. Apart from the fact that the heteroaryl moieties have influenced the photochromic characteristics of diarylethene derivatives, the substituents and their substituted positions have also notably influenced their photochromic properties [16-19]. In particular, the properties of diarylethenes with terminal phenyl groups could be further modified by introduction of electron-donating or electron-withdrawing groups to the terminal benzene rings [20,21]. For instance, introduction of electron-donating substituents to bis(2-thienyl)ethene diarylethenes increased the absorption maxima of the open-ring isomers and decreased their cyclization quantum yield [20], and the same substituents on bis(3-thienyl)ethene diarylethenes increased the absorption coefficient of the closed-ring isomers and decreased the cycloreversion quantum yield [21]. An alkoxy group, as a strong electron-donating substituent, played a key role in the photochromic systems. Irie et al. revealed that the introduction of alkoxy groups at the reactive carbon sites in diarylethenes remarkably suppressed the cycloreversion quantum yields [17,22,23]. We found that the methoxy group and its substituted positions at the terminal phenyl groups had a significant effect on the properties of the diarylethenes with different photochromic skeletons [24-26]. However, its substituted position effect on the photochromic properties of diarylethenes with an indole moiety has never yet been reported.

To date, many reports have focused on the synthesis of photochromic diarylethenes with different heteroaryl units including thiophene, benzothiophene, thiazole, pyrrole, pyrazole, oxazole, furan, benzofuran, indene, benzene, naphthalene, pyridine and benzo[b]silole among others [27-39]. Indole has the structure of benzene fused with pyrrole and its 2-substituted forms are well known to exhibit strong fluorescence [40-43]. The indole ring system is probably the most ubiquitous heterocycle in nature [44]. However, the indole moiety is rarely used in diarylethenes [45-48], due to its high aromatic stabilization energy, which results in low thermal stability of the closed-ring forms [47,48]. Recently, we found that thermal fading of the closed-ring isomer could be significantly suppressed by the introduction of a low aromatic stabilization energy (ASE) aryl unit [49]. Based on this idea, in order to improve the thermal stability of diarylethenes with an indole moiety and investigate the methoxy substituted position effect on their properties, we have synthesized four new hybrid photochromic diarylethenes with both indole and thiophene moieties in this work, three of which are isomeric compounds with a methoxy at *ortho*-, *meta*- and *para*-positions of the terminal benzene ring. The synthesized diarylethenes are

1-(1,2-dimethylindol-3-yl)-2-[2-methyl-5-(2-methoxyphenyl)-3-thienyl]perfluorocyclopentene (**1o**), 1-(1,2-dimethylindol-3-yl)-2-[2-methyl-5-(3-methoxyphenyl)-3-thienyl]perfluorocyclopentene (**2o**), 1-(1,2-dimethylindol-3-yl)-2-[2-methyl-5-(4-methoxyphenyl)-3-thienyl]perfluorocyclopentene (**3o**) and 1-(1,2-dimethylindol-3-yl)-2-(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene (**4o**). The photochromic scheme of diarylethenes **1o–4o** is described in Fig. 1.

<Fig. 1>

2.1. General methods

Chemical reagents were purchased from Acros Corp. and used without further purification. All solvents used were spectroscopic grade and were purified by distillation before use. Reactions were monitored by analytical thin-layer chromatography on plates coated with 0.25 mm silica gel 60 F254. HPLC analysis was performed by an Agilent 1200 instrument fitted with a ZORBAX SIL column (5 µm particle size, 4.6 mm, 25 cm). Melting points were measured with a WRS-1B melting point apparatus. Infrared spectra were recorded on a Bruker Vertex-70 spectrometer. NMR spectra were obtained with a Bruker AV-400 spectrometer with teramethyl silane (TMS) as interal reference and $CDCl_3$ as solvent. Elemental analysis was measured with a PE CHN 2400 analyzer. Absorption spectra were obtained with an Agilent 8453 UV/Vis spectrometer. Photo-irradiation was carried out with an SHG-200 UV lamp, a CX-21 ultraviolet fluorescence analysis cabinet, and a BMH-250 visible lamp. The required wavelength was isolated by the use of the appropriate light filters. Fluorescence properties were measured with a Hitachi F-4500 spectrophotometer.

Suitable crystals of **2o**, **3o**, and **4o** were obtained by slow evaporation of corresponding solutions of these diarylethenes (**2o** in diethyl ether, **3o** in chloroform, and **4o** in chloroform-hexane cosolvent system). All the measurements were collected by a Bruker SMART APEX II CCD diffractometer using a MULTI scan technique at room temperature using Mo Kα radiation. The structures were solved by direct methods and refined by full-matrix least-squares procedures on F^2 by full-matrix least-squares techniques using SHELXTL-97 program. Further details on the crystal structure investigation have been deposited with The Cambridge Crystallographic Data Centre as supplementary publication CCDC 918112 for **2o**, 918113 for **3o**, and 918114 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

The synthetic route for diarylethenes **1o–4o** is shown in Fig. 2. First, Suzuki coupling of bromobenzene and three bromobenzene derivatives with thiophene boronic acid gave the phenylthiophene and methoxyphenylthiophene derivatives **6a–d**, which were lithiated and reacted with perfluorocyclopentene to give compounds **7a–d**. Then, brominated 1,2-dimethylindole **8** to give 3-bromo-1,2-dimethylindole **9**. Finally, compound **9** was lithiated and then separately coupled with compound **7a–d** to give diarylethene derivatives **1o–4o**. The structures of **1o–4o** were confirmed by elemental analysis, NMR, and IR spectroscopy. The PMMA films were prepared by dissolving 10 mg diarylethene sample and 100 mg polymethylmethacrylate (PMMA) in chloroform (1 mL) with the aid of ultrasound; then the homogeneous solution was spin-coated on a quartz substrate (10 mm × 10 mm × 1 mm).

<Fig. 2>

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

Compound **6a** was prepared by reacting 3-bromo-2-methyl-5-thienylboronic acid [50] (4.2 g, 19.0 mmol) with 1-bromo-2-methoxybenzene (3.91 g, 20.9 mmol) in the presence of $Pd(PPh_3)_4$ (0.73 g, 0.63

mmol) and Na_2CO_3 (2 mol L^{-1}, 10 mL) in tetrahydrofuran (THF) (80 mL) for 18 h at 343 K. The reaction was allowed to cool to room temperature. After being extracted with ether, the organic layer was dried over $MgSO_4$, filtered, and concentrated. The crude product was purified by column chromatography on silica gel using petroleum ether as eluent to afford 3.87 g of **6a** visible as a buff solid with a 72% yield. ^{1}H 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).

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

Compound **6b** was prepared according to the method used for **6a**. The crude product was purified by column chromatography on silica gel using petroleum ether as eluent to afford **6b** visible as a buff solid with a 74% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.41 (s, 3H, $-CH_3$), 3.83 (s, 3H, $-CH_3$), 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).

*2.2.3 3-Bromo-5-(4-methoxyphenyl)-2-methylthiophene (**6c**)*

Compound **6c** was prepared according to the method used for **6a**. The crude product was purified by column chromatography on silica gel using petroleum ether as eluent to afford **6c** visible as a buff solid with a 76% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.40 (s, 3H, $-CH_3$), 3.83 (s, 3H, $-CH_3$), 6.90 (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-5-phenyl-2-methylthiophene (**6d**)*

Compound **6d** was prepared according to the method used for **6a**. The crude product was purified by column chromatography on silica gel using petroleum ether as eluent to afford **6d** visible as a yellow buff solid with a 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.28 (s, 3H, $-CH_3$), 6.84 (s, 1H, phenyl-H), 7.12 (s, 1H, thienyl-H), 7.33-7.35 (d, 2H, *J* = 8.0 Hz, phenyl-H), 7.56-7.58 (d, 2H, *J* = 8.0 Hz, phenyl-H).

*2.2.5 1-[2-Methyl-5-(2-methoxyphenyl)-3-thienyl]perfluorocyclopentene (**7a**)*

To a stirred THF solution (50 mL) of compound **6a** (2.67 g, 9.44 mmol) was added dropwise a 2.5 M n-BuLi/hexane solution (3.8 mL, 9.5 mmol) at 195 K under argon atmosphere. Stirring was continued for 30 min at 195 K, octafluorocyclopentene (C_5F_8) (1.3 mL, 9.56 mmol) was slowly added and the reaction mixture was stirred for 2 additional hours at this temperature. The reaction was quenched by addition of water. After being extracted with ether, the organic layer was washed with water. The crude product was purified by column chromatography on silica gel using petroleum ether as eluent to afford 1.52 g of compound **7a** visible as a yellow oil with a 41% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.41 (s, 3H, $-CH_3$), 3.92 (s, 3H, $-CH_3$), 6.98-7.01 (m, 2H, phenyl-H), 7.29-7.31 (t, 1H, phenyl -H), 7.43 (s, 1H, thienyl -H), 7.57 (d, 1H, *J* = 8.6 Hz, phenyl-H).

*2.2.6 1-[2-Methyl-5-(3-methoxyphenyl)-3-thienyl]perfluorocyclopentene (**7b**)*

Compound **7b** was prepared according to the method used for **7a**. The crude product was purified by column chromatography on silica gel using petroleum ether as eluent to afford **7b** visible as a yellow oil with a 48% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.33 (s, 3H, $-CH_3$), 3.77 (s, 3H, $-CH_3$), 6.75 (d, 1H, *J* = 8.2 Hz, phenyl-H), 6.95 (s, 1H, thienyl-H), 7.01 (s, 2H, phenyl-H), 7.19 (t, 1H, *J* = 8.1 Hz, phenyl-H).

*2.2.7 1-[2-Methyl-5-(3-methoxyphenyl)-3-thienyl]perfluorocyclopentene (**7c**)*

Compound **7c** was prepared according to the method used for **7a**. The crude product was purified by column chromatography on silica gel using petroleum ether as eluent to afford **7c** visible as a buff solid with a 35% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.42 (s, 3H, $-CH_3$), 3.85 (s, 3H, $-CH_3$), 6.92 (d, 2H, *J*

= 8.6 Hz, phenyl-H), 7.00 (s, 1H, thienyl-H), 7.45 (d, 2H, *J* = 8.7 Hz, phenyl-H).

*2.2.8 1-(2-Methyl-5phenyl-3-thienyl)perfluorocyclopentene (**7d**)*

Compound **7d** was prepared according to the method used for **7a**. The crude product was purified by column chromatography on silica gel using petroleum ether as eluent to afford **7d** visible as a buff solid with a 55% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.51 (s, 3H, $-CH_3$), 7.24 (s, 1H, thienyl-H), 7.31 (t, 1H, *J* = 6.8 Hz, phenyl-H), 7.39 (t, 2H, *J* = 7.2 Hz, phenyl-H), 7.54 (d, 2H, *J* = 7.8 Hz, phenyl-H).

*2.2.9 3-Bromo-1,2-dimethylindole (**9**)*

To a stirred THF solution (60 mL) of compound **8** (2.18 g, 15 mmol) at room temperature was slowly added N-bromosuccinimide (**NBS**) (3.0 g, 16.86 mmol). After the stirring was continuted for 24 h, the mixture was poured into water slowly. After being extracted with ether, the organic layer was washed with water. Then the organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated. The crude product was purified by column chromatography on silica gel using petroleum ether as eluent to afford 2.3 g of compound **9** visible as a white solid with a 68% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.45 (s, 3H, $-CH_3$), 3.71 (s, 3H, $-CH_3$), 7.15 (t, 1H, *J* = 7.26 Hz, phenyl-H), 7.21 (t, 1H, *J* = 7.42 Hz, phenyl-H), 7.26 (d, 1H, *J* = 7.59 Hz, phenyl-H), 7.49 (d, 1H, *J* = 7.76 Hz, phenyl-H).

*2.2.10 1-(1,2-Dimethylindol-3-yl)-2-[2-methyl-5-(2-methoxyphenyl)-3-thienyl]perfluorocyclopentene (**1o**)*

To a stirred anhydrous THF (30 mL) of compound **9** (0.22 g, 1 mmol) was added dropwise a 2.5 M n-BuLi/hexane solution (0.4 mL, 1 mmol) at 195 K under argon atmosphere. After 30 min, THF (2 mL) containing compound **7a** (0.40 g, 1 mmol) was added and the reaction mixture was stirred for 2 h at this temperature. The reaction was allowed to warm to room temperature and quenched by addition of water. The product was extracted with diethyl ether. Then the combined organic layers were dried over

$MgSO_4$, filtered and concentrated. The crude product was purified by column chromatography on silica gel using petroleum ether/trichloromethane (v/v = 9/1) as the eluent to afford 0.22 g of compound **1o** visible as a red solid with a 42% yield. mp 99-100 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 1.71 (s, 3H, $-CH_3$), 1.91 (s, 3H, $-CH_3$), 3.56 (s, 3H, $-CH_3$), 3.81 (s, 3H, $-CH_3$), 6.86-6.93 (m, 2H, phenyl-H), 7.08 (t, 1H, J = 7.2 Hz, phenyl-H), 7.16-7.22 (m, 3H, phenyl-H), 7.45 (s, 1H, thienyl-H), 7.52 (d, 1H, J = 7.8 Hz, phenyl-H), 7.58 (d, 1H, J = 8.0 Hz, phenyl-H); IR (KBr, υ, cm^{-1}): 747, 786, 842, 895, 985, 1047, 1118, 1161, 1273, 1401, 1455, 1622, 1667, 2843, 3201.

*2.2.11 1-(1,2-Dimethylindol-3-yl)-2-[2-methyl-5-(3-methoxyphenyl)-3-thienyl]perfluorocyclopentene (**2o**)*

Compound **2o** was prepared according to the method used for **1o**. The crude product was purified by column chromatography on silica gel using petroleum ether/trichloromethane (v/v = 9/1) as eluent to afford **2o** visible as a colorless crystal with a 52% yield. mp 102-103 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 1.75 (s, 3H, $-CH_3$), 2.01 (s, 3H, $-CH_3$), 3.63 (s, 3H, $-CH_3$), 3.84 (s, 3H $-OCH_3$), 6.84 (d, 1H, J = 8.2 Hz, phenyl-H), 7.03 (s, 1H, thienyl-H), 7.12 (d, 1H, J = 6.9 Hz, phenyl-H), 7.15 (d, 1H, J = 7.9 Hz, phenyl-H), 7.22 (t, 1H, J = 7.3 Hz, phenyl-H), 7.26-7.32 (m, 3H, phenyl-H), 7.61 (d, 1H, J = 7.9 Hz, phenyl-H); IR (KBr, υ, cm^{-1}): 692, 751, 781, 845, 976, 996, 1047, 1119, 1183, 1268, 1338, 1401, 1454, 1534, 1618, 1668, 2840, 3192.

*2.2.12 1-(1,2-Dimethylindol-3-yl)-2-[2-methyl-5-(4-methoxyphenyl)-3-thienyl]perfluorocyclopentene (**3o**)*

Compound **3o** was prepared according to the method used for **1o**. The crude product was purified by column chromatography on silica gel using using petroleum ether/trichloromethane (v/v = 9/1) as eluent to afford **3o** visible as a colorless crystal with a 47% yield. mp 205-206 °C; ^1H NMR (400 MHz,

$CDCl_3$): δ 1.74 (s, 3H, -CH_3), 2.01 (s, 3H, -CH_3), 3.64 (s, 3H, -CH_3), 3.84 (s, 3H, -CH_3), 6.91 (d, 2H, *J* = 8.7 Hz, phenyl-H), 7.14 (s, 1H, thienyl-H), 7.20-7.29 (m, 3H, phenyl-H), 7.45 (d, 2H, *J* = 8.7 Hz, phenyl-H), 7.62 (d, 1H, *J* = 8.0 Hz, phenyl-H); IR (KBr, υ, cm^{-1}): 744, 812, 842, 895, 974, 1041, 1104, 1183, 1272, 1334, 1401, 1455, 1512, 1622, 1667, 2837, 3200.

*2.2.13 1-(1,2-Dimethylindol-3-yl)-2-(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene (**4o**)*

Compound **3o** was prepared according to the method used for **1o**. The crude product was purified by column chromatography on silica gel using using petroleum ether/trichloromethane (v/v = 9/1) as eluent to afford **4o** visible as a colorless crystal with a 47% yield. mp 160-161 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 1.76 (s, 3H, -CH_3), 2.00 (s, 3H, -CH_3), 3.62 (s, 3H, -CH_3), 7.14 (t, 1H, *J* = 6.8 Hz, phenyl-H), 7.20-7.30 (m, 3H, phenyl-H), 7.35 (s, 1H, thienyl-H), 7.37 (t, 2H, *J* = 7.2 Hz, phenyl-H), 7.53 (d, 2H, *J* = 7.6 Hz, phenyl-H), 7.61 (d, 1H, *J* = 8.0 Hz, phenyl-H); IR (KBr, υ, cm^{-1}): 689, 749, 811, 842, 893, 974, 998, 1044, 1107, 1184, 1272, 1335, 1401, 1454, 1625, 1667, 3209.

3. Results and discussion

3.1 Photochromism of diarylethenes in hexane and PMMA films

The photochromic behaviors of diarylethenes **1–4** induced by photoirradiation was measured in both hexane (2.0×10^{-5} mol L^{-1}) and PMMA films (10%, w/w) at room temperature. The absorption spectral change of diarylethene **1** and color changes of diarylethenes **1**–**4** induced by alternating irradiation with UV and visible light in hexane and in PMMA films are shown in Fig. 3. In hexane, the absorption maximum of diarylethene **1o** was observed at 263 nm due to a π-π^* transition. Upon irradiation with 297 nm light, a new absorption band centered at 583 nm emerged due to the formation of the closed-ring isomer **1c**. This could easily be seen with the naked eye, as the colorless solution of **1o** turned blue. In the reverse reaction, the blue colored solution was entirely bleached to become colorless upon irradiation with visible light (λ > 500 nm), indicating that **1c** was returning to the initial state **1o**. Diarylethenes **2–4** exhibited analogous photochromism similar to diarylethene **1** in hexane. Upon irradiation with 297 nm light, the solutions containing **2o–4o** turned blue as a result of the cyclization reactions to produce the closed-ring isomers **2c–4c**, for which the absorption maxima were observed at 583, 583 and 582 nm, respectively. The blue colored solutions of **2c–4c** could again be bleached by irradiation with visible light because the compounds returned to the open-ring isomers **2o–4o**, respectively. In the photostationary state, the isosbestic points for diarylethenes **1–4** were observed at 331, 324, 313 and 336 nm, respectively. The photoconversion ratios of **1–4** from open-ring to closed-ring isomers in hexane were analyzed by HPLC in the photostationary state, with the values being 62% for **1**, 71% for **2**, 68% for **3** and 64% for **4** (Table 1). In PMMA amorphous films, diarylethenes **1–4** also showed similar photochromism as observed in hexane (Fig. 3). As the results obtained for most of the reported diarylethenes show, the maximum absorption peaks of diarylethenes **1–4** in PMMA films shifted at a longer wavelength than that of hexane. The red shift values of the absorption maxima of the closed-ring isomers are 22 nm for **1o**, 22 nm for **2o**, 20 nm for **3o** and 20 nm for **4o**, respectively. The red shift phenomena may be attributed to the polar effect of the polymer matrix and the stabilization of molecular arrangement in solid state [51,52].

The photochromic parameters of compounds **1–4** are summarized in Table 1. Although the absorption maxima did not greatly change when the methoxy group was attached at any of the three positions on the terminal benzene ring, other photochromic features including molar absorption coefficients, cyclization and cycloreversion quantum yields were heavily dependent on the methoxy substituted position of the terminal benzene ring. As shown in Table 1, the unsubstituted parent diarylethene **4** has the biggest molar absorption coefficient and the smallest cyclization and cycloreversion quantum yields among these derivatives. Upon introduction of the methoxy group into any of the three positions on the terminal benzene ring, the molar absorption coefficients decreased and the quantum yields of diarylethenes **1–3** increased to some extent. For the isomeric compounds **1–3**, the cyclization quantum yield gradually increased as the molar absorption coefficients of the closed-ring isomers decreased going from the *ortho*- to *meta*- to the *para*-position of substitution. However, the molar absorption coefficients of the open-ring isomers decreased in order of *meta*- > *ortho*- > *para*-substituent by the methoxy group. Among these isomeric derivatives, the molar absorption coefficients of the *para*-substituted derivative **3** are the smallest both for its open-ring and closed-ring isomers, however, its cyclization quantum yield is the biggest ($\Phi_{o-c,3} =$ 0.48). The cycloreversion quantum yields of isomeric diarylethenes **1–3** are almost constant (0.41~0.42), but greater than that of the unsubstituted parent derivative **4** ($\Phi_{o-c, 4} =$ 0.33). This result indicated that introduction of electron-donating methoxy group in the terminal benzene ring could significantly enhance the cyclorerversion quantum yield of diarylethenes with an indole unit, but its substituted position hardly influenced their cycloreversion quantum yields. Compared with the analogous diarylethenes with a pyrazole moiety [15], the absorption maxima of the closed-ring isomers of diarylethenes with an indole moiety showed a hypsochromic shift, and their cycloreversion quantum yields decreased markedly. When replacing the thiophene or phenylthiophene moiety with the indole unit in the same molecular skeleton of photochromic diarylethenes, the cycloreversion quantum yields increased significantly [24,26]. Similarly, when replacing the pyrrole moiety with the indole unit, both the cyclization quantum yields and the cycloreversion yields increased whereas the photoconversion ratios in the photostationary state decreased remarkably [25]. These results suggest that the indole moiety has a significant effect on the photochromic properties of the diarylethene derivatives.

The thermal stability of both the open-ring and closed-ring isomers of diarylethenes **1–4** were tested in hexane at room temperature and 341 K. Storing these solutions in the dark and then exposing them to air for more than 60 hrs at room temperature and at 341 K, respectively, resulted in no changes in the observed UV/vis spectra for diarylethenes **1–4**. This result showed that the thermal stability of these unsymmetrical diarylethenes was much better than that of the symmetrical diarylethenes with two indole moieties [47]. In addition, the fatigue resistance of diarylethenes **1–4** was examined in both hexane and PMMA amorphous films at room temperature, and the result is presented in Fig. 4. As depicted in Fig. 4, the coloration and de-coloration cycles of **1–4** could repeat 50 times in hexane with the degradation of 16% for **1c**, 12% for **2c**, 18% for **3c** and 14% for **4c**, while repeating 200 times in PMMA films with the degradation of 14% for **1c**, 10% for **2c**, 21% for **3c** and 21% for **4c**, respectively. Among these four derivatives, therefore, the fatigue resistance of the *meta*-substituted derivative **2** is the strongest and that of the *para*-substituted derivative **3** is the weakest in both solution and solid medium.

3.2 Crystal structures and photochromism in the crystalline phase

To better understand the photochromic behavior in the crystalline phase, the final structural confirmations of diarylethenes **2o**, **3o** and **4o** were provided by X-ray crystallographic analysis. The X-ray crystallographic analysis data are listed in Table 2, and their ORTEP drawings are shown in Fig. 5. The molecules of the three single crystals crystallized with a C_2 symmetry in the photoactive *anti*-parallel conformation in the crystalline phase. Such a conformation is crucial for the compound to exhibit photochromism [53]. There are four planar rings in the three crystal molecules, which can form three dihedral angles between every two adjacent planar rings. The dihedral angles in diarylethenes **2o–4o** are summarized in Table 3. Compared to the *meta*-substituted derivative **2o**, the *para*-substituted derivative **3o** has a smaller dihedral angle between the thiophene ring and the adjacent benzene ring. The reason may be attributed to the steric-structure of methoxy group at different positions in the terminal benzene ring. The distance between the two reactive carbon atoms is 3.689 Ǻ for **2o** (C1…C19), 3.777 Ǻ for **3o** (C1…C19) and 3.772 Ǻ for **4o** (C1…C18), respectively (Table 3). Based on the empirical rule that the molecule undergoes the photocyclization reaction if the molecule is fixed in an *anti*-parallel mode and the distance between reacting carbon atoms on the aryl rings is less than 4.2 Å [54,55], the three crystals should exhibit photochromism by photoirradiation in the single crystalline phase. In fact, the crystals **2o–4o** showed favorable photochromism, in accordance with the expected ring closure, to form **2c–4c** upon irradiation with UV light. As shown in Fig. 6, the colorless crystal of **2o–4o** turned green upon irradiation with 297 nm light, and the colored crystals reverted to a colorless state upon irradiation with visible light (λ > 500 nm). After 200 repeat cycles, the three crystals still exhibited favorable photochromism in the crystalline phase. Therefore, they can potentially be used for the construction of certain optoelectronic devices [55].

3.3 Fluorescence of diarylethenes

Fluorescence can be useful in molecular scale optoelectronics and digital fluorescence photoswitches, and the fluorescence features of many diarylethenes have been extensively reported [56-60]. The fluorescence emission spectra of diarylethenes **1–4** in both hexane (2.0×10^{-5} mol L^{-1}) and PMMA films (10%, w/w) were evaluated at room temperature, and the results are shown in Fig. 7. In hexane, the emission peaks of diaryelthenes **1o–4o** were observed at 421, 421, 423 and 425 nm when excited at 350 nm, and were observed at 441, 443, 445 and 440 nm when monitored at 350 nm in PMMA films. When comparing samples in hexane to those in PMMA films, the emission peaks of **1o–4o** consistently displayed an evident bathochromic shift with values of 20 nm for **1o**, 22 nm for **2o**, 22 nm for **3o** and

15 nm for **4o**. The result is in agreement with the same molecular skeleton with thiophene or phenylthiophen moieties [24,26]. Among the four derivatives, the emission intensity of the unsubstituted parent diarylethene **4o** was the strongest in both hexane and PMMA films. This result indicated that the electron-donating methoxy group could decrease the fluorescent intensity of diarylethenes with an indole unit. This was in agreement with the methoxy-substituted diarylethenes containing a pyrrole moiety [25]. For the isomeric compounds **1–3**, the emission intensity gradually decreased going from the *meta*- to *ortho*- to the *para*-position of substitution. As a result, the emission intensity of the *para*-substituted derivative **3o** is the weakest in both hexane and PMMA films.

<Fig. 7>

In general, for photochromic diaryelthene derivatives, the initial fluorescence open-ring isomer is switched off after the photocyclization reaction due to the formation of the non-fluorescence closed-ring isomers. The fluorescence can be readily restored upon visible light irradiation. As has been observed for most of the reported diarylethenes [61-63], diarylethenes **1–4** exhibited evident fluorescent switches in addition to the photochromism from the open-ring isomers to the closed-ring isomers by photoirradiation in both hexane and PMMA films. During the process of photoisomerization, the fluorescent spectral changes of diarylethenes **1–4** in hexane (2.0×10^{-5} mol L^{-1}) and in PMMA films (10%, w/w) are shown in Figs. 8 and 9, respectively. Upon irradiation with 297 nm light, the emission intensity of diarylethenes **1o–4o** in hexane was quenched to ca. 30% for **1**, 27% for **2**, 27% for **3** and 29% for **4** when arrived at the photostationary state (Figs. 8). Similarly, the emission intensity of **1o–4o** was quenched to ca. 10% for **1**, 10% for **2**, 14% for **3** and 13% for **4** in PMMA films when arrived at the photostationary state (Figs. 9). That is to say, the fluorescent modulation efficiency of the four derivatives in hexane was 70% for **1**, 73% for **2**, 73% for **3** and 71%

for **4**, and that in PMMA films was 90% for **1**, 90% for **2**, 86% for **3** and 87% for **4**. The data indicated that diarylethenes with an indole moiety exhibited relatively high fluorescent modulation efficiency in both solution and solid media by photoirradiation, especially in solid media. This characteristic is ideal for practical applications in optical devices, such as optical recording media and fluorescent switches [64,65].

< Fig. 8 >

< Fig. 9 >

3.4 Electrochemistry of diarylethenes

The electrochemical reactions are being used for molecular switching and also can potentially be applied to molecular-scale electronic switches [66,67]. Electrocyclic reactions induced by electrochemical reduction or oxidation have been reported [40,68-71]. Herein, we investigated the electrochemical properties of **1–4** by cyclic voltammetry (CV). Their electrochemical characteristics are summarized in Table 4, which is converted into Fig. 10. The methoxy group could effectively modulate the electrochemical behaviors of these diarylethene derivatives. The oxidation onset potential of the unsubstituted parent diarylethene **4o** is the highest, whereas that of **4c** is the lowest. The oxidation onset potentials of **1o–3o** were observed at +1.17, 1.10 and 1.09 V, and those of **1c–3c** were observed at +1.22, 1.25 and 1.17 V, respectively. These results indicated that the oxidation process of the open-ring isomers **1o–3o** occurred at a lower potential, as compared with that of the corresponding closed-ring isomers **1c–3c**.

< Fig. 10 >

<Table 4>

According to the reported method [72,73], the Highest Occupied Molecular Orbitals (HOMO) and the

Lowest Unoccupied Molecular Orbitals (LUMO) energy levels could be estimated by using the energy level of ferrocene as a reference. Based on the HOMO and LUMO energy level, the band-gap (E_g) of each compound could be calculated approximately. The data showed that the band-gaps increased in order of **1** < **2** < **3** (*ortho*- < *meta*- < *para*-). When introducing the methoxy group into the terminal benzene ring at *meta*- or *para*- positions, the band-gaps of **2** and **3** increased significantly, compared with the unsubstituted parent diarylethene **4**. The results suggested that the methoxy group and its substituted position have a significant effect on the electrochemical properties of these diarylethenes but further work is required to quantify the effects.

Conclusion

In conclusion, four unsymmetrical diarylethenes with an indole moiety have been synthesized, and their photochemical and electrochemical properties have been investigated systematically. The results suggested that the methoxy group and its substituted position had a significant effect on the properties of these diarylethene derivatives. The effected properties include photochromism, fluorescence and electrochemistry and could be effectively modulated by the methoxy group and its substituted position at the terminal benzene ring. Furthermore, the indole moiety induced some new characteristics that were distinguishable from those of the reported diarylethenes with thiophene, pyrazole or pyrrole rings. The results will be helpful in understanding the methoxy substituent position effect on the properties of diarylethenes with an indole moiety and for the synthesis of new diarylethenes with tunable photochromic behaviors.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (21162011, 21262015), the Project of Jiangxi Advantage Sci-Tech Innovative Team (20113BCB24023), the Project of Jiangxi

Youth Scientist, and the Project of the Science Funds of Jiangxi Education Office (KJLD12035, GJJ11026, GJJ12587).

References

[1] Dürr H, Bouas–Laurent H. Photochromism, molecules and systems. Amsterdam: Elsevier;1990.

[2] Kawata S, Kawata Y. Three–dimensional optical data storage using photochromic materials. Chem Rev 2000;100:1777–88.

[3] Irie M. Photochromism: memories and switches–Introduction. Chem Rev 2000;100:1683–4.

[4] Irie M. Diarylethenes for memories and switches. Chem Rev 2000;100:1685–716.

[5] Tian H, Yang SJ. Recent progresses on diarylethene based photochromic switches. Chem Soc Rev 2004;33:85–97.

[6] Tian H, Wang S. Photochromic bisthienylethene as multi-function switches. Chem Commun 2007:781–92.

[7] Tian H, Feng YL. Next step of photochromic switches? J Mater Chem 2008;18:1617–22.

[8] Pu SZ, Zheng CH, Le ZG, Liu G, Fan CB. Substituent effects on the properties of photochromic diarylethenes. Tetrahedron 2008;64:2576–85.

[9] Kutsunugi Y, Coudret C, Micheau JC, Kawai T. Photomodulation of the proton affinity and acid gated photochromism of a novel dimethylaminophenyl thiazole diarylethene. Dyes Pigm 2012; 92, 838–46.

[10] Wu Y, Chen SJ, Yang YH, Zhang Q, Xie YS, Tian H, Zhu WH. A novel gated photochromic reactivity controlled by complexation/dissociation with BF_3. Chem Commun 2012;48:528–30.

[11] Yang YH, Xie YS, Zhang Q, Nakatani K, Tian H, Zhu WH. Aromaticity-Controlled Thermal Stability of Photochromic Systems Based on a Six-Membered Ring as Ethene Bridges: Photochemical and Kinetic Studies. Chem Eur J 2012;18:11685–94.

[12] Uchida K, Matsuoka T, Sayo K, Iwamoto M, Hayashi S, Irie M. Thermally reversible

photochromic systems. Photochromism of a dipyrrolyl perfluorocyclopentene. Chem Lett 1999:835–6.

[13] Morinaka K, Ubukata T, Yokoyama Y. Structurally versatile novel photochromic bisarylindenone and its acetal: Achievement of large cyclization quantum yield. Org Lett 2009;11: 3890–3.

[14] Fukumoto S, Nakashima T, Kawai T. Photon-quantitative reaction of a dithiazolylarylene in solution. Angew Chem Int Ed 2011;50:1565–8.

[15] Pu SZ, Yang TS, Xu JK, Chen B. Syntheses and properties of new photochromic diarylethene derivatives having a pyrazole unit. Tetrahedron Lett 2006;47:6473–7.

[16] Zheng CH, Pu SZ, Xu JK, Luo MB, Huang DC, Shen L. Synthesis and the effect of alkyl chain length on optoelectronic properties of diarylethene derivatives. Tetrahedron 2007;63: 5437–49.

[17] Morimitsu K, Shibata K, Kobatake S, Irie M. Dithienylethenes with a Novel Photochromic Performance. J Org Chem 2002;67:4574–8.

[18] Pu SZ, Yang TS, Xu JK, Chen B. Substituent position effect on the optoelectronic properties of photochromic diarylethenes. Tetrahedron Lett 2006;47:3167–71.

[19] Liu G, Pu SZ, Wang XM, Liu WJ, Fan CB. The effect of the cyano group position upon unsymme trical isomeric diarylethenes bearing a pyrrole unit. Dyes Pigm 2011;90:89–99.

[20] Uchida K, Matsuoka T, Kobatake S, Yamaguchi T, Irie M. Substituent effect on the photochromic reactivity of Bis(2-thienyl)perfluorocyclepentenes. Tetrahedron 2001;57:4559–65.

[21] Irie M, Sakemura K, Okinaka M, Uchida K. Photochromism of dithienylethenes with electron-donating substituents. J Org Chem 1995;60:8305–9.

[22] Takami S, Irie M. Synthesis and photochromic properties of novel yellow developing photochromic compounds. Tetrahedron 2004;60:6155–61.

[23] Takami S, Kawai T, Irie M. Photochromism of dithiazolylethenes having methoxy groups at the reaction centers. Eur J Org Chem 2002;3796–800.

[24] Pu SZ, Fan CB, Miao WJ, Liu G. The effect of substituent position upon unsymmetrical isomeric diarylethenes bearing a methoxy group. Dyes Pigm 2010;84:25–35.

[25] Liu G, Pu SZ, Wang XM. Synthesis and the effect of substituent position upon unsymmetrical isomeric diarylethenes bearing a pyrrole unit. J Photochem Photobiol A 2010;214:230–40.

[26] Pu SZ, Liu WJ, Miao WJ. Photochromism of new unsymmetrical isomeric diarylethenes bearing a methoxyl group. J Phys Org Chem 2009;21:1–11.

[27] Irie M, Miyatake O, Uchida K. Blocked photochromism of diarylethenes. J Am Chem Soc 1992;114:8715–16.

[28] Liu G, Pu SZ, Wang XM. Photochromism of new 3,5-position hybrid diarylethene derivatives bearing both thiophene and thiazole moieties. Tetrahedron 2010;66:8862–71.

[29] Uchida K, Ishikawa T, Takeshita M, Irie M. Thermally irreversible photochromic systems. Reversible photocyclization of 1,2-Bis(thiazolyl)perfluorocyclopentenes. Tetrahedron 1998;54:6627–38.

[30] Tian H, Chen BZ, Tu HY, Müllen K. Novel bisthienylethene-based photochromic tetraazaporphyrin with photoregulating luminescence. Adv Mater 2002:14:918–923.

[31] Nakashima T, Goto M, Kawai S, Kawai T. Photomodulation of ionic interaction and reactivity: Reversible photoconversion between imidazolium and imidazolinium. J Am Chem Soc 2008;130:14570–5.

[32] Shibata K, Kuroki L, Fukaminato T, Irie M. Fluorencence switch of a diarylethene derivative having oxazole rings. Chem Lett 2008;37:832–3.

[33] Sysoiev D, Fedoseev A, Kim Y, Exner Thomas E, Boneberg J, HuhnT. Leiderer P, Scheer E, Groth U, Steiner Ulrich E. Synthesis and photoswitching studies of difurylperfluorocyclopentenes with extended π-systems. Chem Eur J 2011;17:6663–72.

[34] Yamaguchi T, Irie M. Photochromism of Bis(2-alkyl-1-benzofuran-3-yl)perfluorocyclopentene derivatives. J Org Chem 2005;25:10323–8.

[35] Yamaguchi T. Irie M. Photochromism of diarylethene derivatives having an indene unit. Tetrahedron Lett 2006;47:1267–9.

[36] Yamaguchi T, Hosaka M, Ozeki T, Morimoto M, Irie M. Photochromism of diarylethene derivatives bearing a benzo[b]silole unit. Tetrahedron Lett 2011;52:5601–4.

[37] Pu SZ, Fan CB, Miao WJ, Liu G. New photochromic diarylethenes with a six-membered aryl unit. Tetrahedron 2008;64:9464–70.

[38] Uchida K, Nakamura S, Irie M. Photochromism of dinaphthylethene derivatives. Stability of the closed-ring forms. Res Chem lntermed 1995;10:861–76.

[39] Pu SZ, Yan PJ, Liu G, Miao WJ, Liu WJ. New photochromic diarylethenes bearing a pyridine moiety. Tetrahedron Lett 2011;52:143–7.

[40] Öhrn A, Karlström G. Simulations of the absorption and fluorescence of indole in aqueous solution and at a nonpolar/polar interface. J Phys Chem A 2007;111:10468–77.

[41] Yagi K, Irie M. Fluorescence property of photochromic diarylethenes with indole groups. Bull Chem Soc Jpn 2003;76:1625–28.

[42] Liang YC, Dvornikov AS, Rentzepis PM. Photochemistry of photochromic 2-indolylfulgides with substituents at the 1'-position of the indolylmethylene moiety. J Photochem Photobiol A 2001;146:83–93.

[43] Kaletaş BK, Williams R, König B, Cola LD. Strong fluorescence enhancement of 2-bromo-3-(1H-indol-3-yl)maleimide upon coordination to a Lewis-acidic metal complex. Chem Commun 2002:776–7.

[44] Humphrey GR, Kuethe JT. Practical methodologies for the synthesis of indoles. Chem Rev 2006;106:2875–911.

[45] Moriyama Y, Matsuda K, Tanifuji N, Irie S, Irie M. Electrochemical cyclizatio cycloreversion reactions of diarylethenes. Org Lett 2005;7:3315–8.

[46] Yagi K, Soong CF, Irie M. Synthesis of fluorescent diarylethenes having a 2,4,5-triphenylimidazole chromophore. J Org Chem 2001;66:5419–23.

[47] Nakayama Y, Hayashi K, Irie M. Thermally irreversible photochromic systems. Reversible photocyclization of 1,2-diselenenylethene and 1,2-diindolylethene derivatives. J Org Chem 1990;55:2592–6.

[48] Irie M. Photochromic diarylethenes for photonic devices. Pure & Appl Chern 1996;68:1367–71.

[49] Liu G, Pu SZ, Wang RJ. Photochromism of Asymmetrical diarylethenes with a pyrrole unit: Effects of aromatic stabilization energies of aryl rings. Org Lett 2013;15:980–3.

[50] Gilat SL, Kawai SH, Lehn J-M. Synthesis and chlorine atom position effect on the properties of unsymmetrical photochromic diarylethenes. Chem Eur J 1995;1:275–84.

[51] Kasatani K, Kambe S, Irie M. Photochromic reaction and fluorescence of dithienylethenes in the solid state. J Photochem Photobiol A 1999;122:11–5.

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

[53] Woodward RB, Hoffmann R. The conservation of orbital symmetry. Verlag Chemie, GmbH, Weinheim, Germany, 1970.

[54] Ramamurthy V, Venkatesan K. Photochemical reactions of organic crystals. Chem Rev 1987;87:433–81.

[55] Kobatake S, Uchida K, Tsuchida E, Irie M. Single-crystalline photochromism of diarylethenes: reactivitye structure relationship. Chem Commun 2002:2804–5.

[56] Chen BZ, Wang MZ, Wu YQ, Tian H. Reversible near-infrared fluorescence switch by novel photochromic unsymmetrical-phthalocyanine hybrids based on bisthienylethene. Chem Commun 2002:1060–1.

[57] Jiang GY, Wang S, Yuan WF, Jiang L, Song YL, Tian H, Zhu DB. Highly fluorescent contrast for rewritable optical storage based on photochromic bisthienylethene-bridged naphthalimide dimer. Chem Mater 2006;18:235–7.

[58] Zou Q, Li X, Zhang JJ, Zhou J, Sun BB, Tian H. Unsymmetrical diarylethenes as molecular keypad locks with tunable photochromism and fluorescence via Cu^{2+} and CN^- coordinations. Chem Commun 2012;48:2095–7.

[59] Liu HH, Chen Y. Construction of multilevel fluorescent switch using photochromic diarylethene and fluorescent dye. Dyes Pigm 2011;89:212–6.

[60] Uno K, Niikura H, Morimoto M, Ishibashi Y, Miyasaka H, Irie M. In situ preparation of highly fluorescent dyes upon photoirradiation. J Am Chem Soc 2011;133:13558–64.

[61] Suzuki Y, Yokoyama K. Design and synthesis of intramolecular charge transfer-based fluorescent reagents for the highly-sensitive detection of proteins. J Am Chem Soc 2005;127:17799–802.

[62] Irie M, Fukaminato T, Sasaki T, Tamai N, Kawai T. Organic chemistry: A digital fluorescent

molecular photoswitch. Nature 2002;420:759–60.

[63] Giordano L, Jovin TM, Irie M, Jares-Erijman EA. Diheteroarylethenes as thermally stable photoswitchable acceptors in photochromic fluorescence resonance energy transfer (pcFRET). J Am Chem Soc 2002;124:7481–9.

[64] Gerasimos M, Lehn T J-M, Photonic molecular devices: Reversibly photoswitchable fluorophores for nondestructive readout for optical memory. Angew Chem Int Ed Engl 1995;34:1119–22.

[65] Gerasimos M, Lehn T J-M, Photoswitched and functionalized oligothiophenes: Synthesis and photochemical and electrochemical properties. Chem Eur J 1996;2:1399–406.

[66] Bonifazi D, Scholl M, Song F, Echegoyen L, Accorsi G, Armaroli N, Diederich F. Exceptional redox and photophysical properties of a triply fused diporphyrin-C60 conjugate: novel scaffolds for multicharge storage in molecular scale electronics. Angew Chem Int Ed 2003;42:4966–70.

[67] Suzuki T, Nishida J-I, Tsuji T. Hexaphenylethane derivatives exhibiting novel electrochromic behavior. Angew Chem Int Ed Engl 1997;36:1329–31.

[68] Peters A, Branda NR. Electrochromism in photochromic dithienylcyclopentenes. J Am Chem Soc 2003;125:3404–5.

[69] Peters A, Branda NR. Electrochemically induced ring-closing of photochromic 1,2-dithienylcyclopentenes. Chem Commun 2003:954–5.

[70] Zhou XH, Zhang FS, Yuan P, Sun F, Pu SZ, Zhao FQ, Tung CH. Photoelectrochromic dithienylperfluorocyclopentene derivatives. Chem Lett 2004;33:1006–7.

[71] Yokojima S, Matsuda K, Irie M, Murakami A, Kobayashi T, Nakamura S. Characterization of cationic diarylethene by electron spin resonance and absorption spectras ratio of open/closed-ring isomers. J Phys Chem A 2006;110:8137–43.

[72] Tsai FC, Chang CC, Liu CL, Chen WC. Jenekhe SA. New thiophene-linkedconjugatedpoly(azomethine)s: Theoretical electronic structure, synthesis, and properties. Macromolecules 2005;38:1958–66.

[73] Zhan XW, Liu YQ, Wu X, Wang S, Zhu DB. New series of blue-emitting and electron-transporting fluorene-based copolymers. Macromolecules 2002;35:2529–37.

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

Compd	$\lambda_{o,max}$/nm[a] (ε/L mol^{-1} cm^{-1})		$\lambda_{c,max}$/nm[b] (ε/L mol^{-1} cm^{-1})		Φ[c]		PR[d] (%)
	Hexane	PMMA film	Hexane	PMMA film	$\Phi_{o\text{-}c}$	$\Phi_{c\text{-}o}$	
1	263 (2.40×10^4)	266	583 (1.49×10^4)	605	0.45	0.42	62
2	261 (2.52×10^4)	264	583 (1.27×10^4)	605	0.46	0.41	71
3	264 (2.14×10^4)	268	583 (1.26×10^4)	603	0.48	0.42	68
4	261 (3.01×10^4)	264	582 (1.57×10^4)	602	0.35	0.33	64

[a] Absorption maxima of open-ring isomers.

[b] Absorption maxima of closed-ring isomers.

[c] Quantum yields of cyclization reaction ($\Phi_{o\text{-}c}$) and cycloreversion reaction ($\Phi_{c\text{-}o}$), respectively.

[d] Photoconversion ratio from the open-ring to closed-ring isomers in the photostationary state.

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

	Compound **2o**	Compound **3o**	Compound **4o**
Formula	$C_{27}H_{21}F_6NOS$	$C_{27}H_{21}F_6NOS$	$C_{26}H_{19}F_6NS$
Formula weight	521.51	521.51	491.48
Temperature (K)	296(2)	296(2)	293(2)
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	P2(1)/c	P-1	C2/c
Unit cell dimensions			
a (Å)	10.5158(7)	9.3846(9)	29.671(3)
b (Å)	9.6720(6)	11.7086(11)	8.8587(5)
c (Å)	23.9488(15)	11.7682(11)	19.4976(11)
α (º)	90.00	82.5700(10)	90.00
β (º)	90.8710(10)	81.7930(10)	114.432(6)
γ (º)	90.00	71.3460(10)	90.00
Volume ($Å^3$)	2435.5(3)	1207.8(2)	4666.0(6)
Z	4	2	8
Density (calcd.) (g/cm^3)	1.422	1.434	1.399
Goodness-of-fit on $\boldsymbol{F}^2$	1.040	0.985	1.037
Final *R* indices [$I/2\sigma(I)$]			
R_1	0.0406	0.0627	0.0683
ωR_1	0.0995	0.1497	0.1766
R indices (all data)			
R_1	0.0602	0.0756	0.0981
ωR_1	0.1122	0.1633	0.2000

Table 3. Distance between the reacting carbon atoms *d* (Ǻ) and dihedral angles θ (º) of diarylethenes **2o**–**4o**.

Compound	*d* (Ǻ)		θ (º)[a]		
			θ_1	θ_2	θ_3
2o	C1…C19	3.689	46.2	50.5	32.2
3o	C1…C19	3.777	50.9	52.7	22.3
4o	C1…C18	3.772	50.5	53.2	32.9

[a] θ_1, Dihedral angle between the cyclopentene ring and 1,2-dimethylindole ring;

θ_2, dihedral angle between the cyclopentene ring and thiophene ring;

θ_3, dihedral angle between the thiophene ring and the adjacent benzene ring.

Table 4

Compd	Oxidation		Reduction		Band gap
	E_{onset} (V)	IP (eV)	E_{onset} (V)	EA (eV)	E_g
1o	1.17	-5.97	-0.59	-4.21	1.76
1c	1.22	-6.02	-0.48	-4.32	1.70
2o	1.1	-5.9	-0.92	-3.88	2.02
2c	1.25	-6.05	-0.84	-3.96	2.09
3o	1.09	-5.89	-0.99	-3.81	2.08
3c	1.17	-5.97	-0.93	-3.87	2.10
4o	1.19	-5.99	-0.83	-3.97	2.02
4c	1.11	-5.91	-0.69	-4.11	1.80

* The acetonitrile used as solvent was spectrograde and was purified by distillation prior to use.

Figures Captions:

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

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

Fig. 3. Absorption spectral change of diarylethene **1** and color changes of diarylethenes **1–4** upon alternating irradiation with UV and visible light at room temperature: (A) Spectral changes for **1** in hexane (2.0×10^{-5} mol L^{-1}); (B) Spectral changes for **1** in a PMMA film (10%, w/w); (C) Color changes for **1–4** both in hexane and PMMA films.

Fig. 4. Fatigue resistances of diarylethenes **1–4** in air atmosphere at room temperature: (A) In hexane; (B) In PMMA films. Initial absorptance of the sample was fixed to 1.0.

Fig. 5. ORTEP drawings of crystals **2o–4o**, showing 35% probability displacement in ellipsoids (H atoms were omitted for clarity): (A) **2o**; (B) **3o**; (C) **4o**.

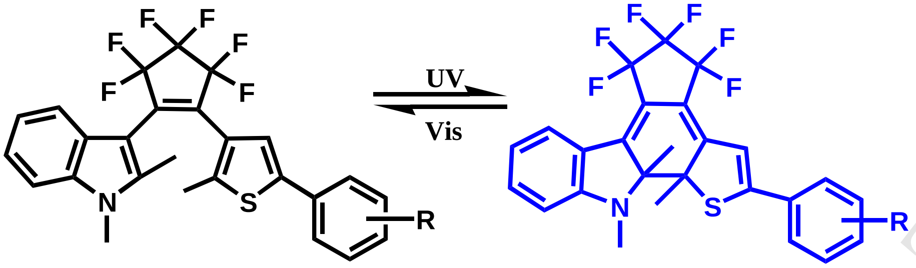
Fig. 6. Photographs of photochromic processes of diarylethenes **2–4** in the crystalline phase.

Fig. 7. Fluorescence emission spectra of diarylethenes **1–4** both in hexane (2.0×10^{-5} mol L^{-1}) and PMMA films (10%, w/w) at room temperature: (A) In hexane, excited at 350 nm; (B) In PMMA films, excited at 350 nm.

Fig. 8. Emission intensity changes of diarylethenes **1–4** upon irradiation with 297 nm UV light in hexane (2.0×10^{-5} mol L^{-1}) at room temperature, excited at 350 nm: (A) **1**; (B) **2**; (C) **3**; (D) **4**.

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

Fig. 10. The effect of the methoxy group and its substituted position on the electrochemical properties of diarylethenes **1–4**.



1o: R = *ortho*-OCH$_3$
2o: R = *meta*-OCH$_3$
3o: R = *para*-OCH$_3$
4o: R = H

1c: R = *ortho*-OCH$_3$
2c: R = *meta*-OCH$_3$
3c: R = *para*-OCH$_3$
4c: R = H

Fig. 1

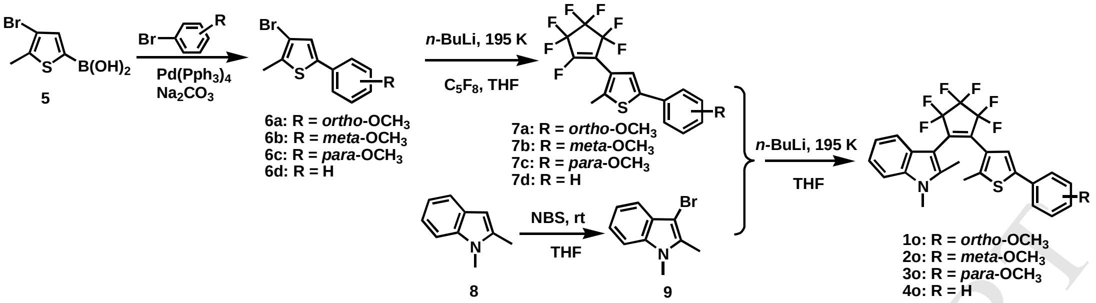
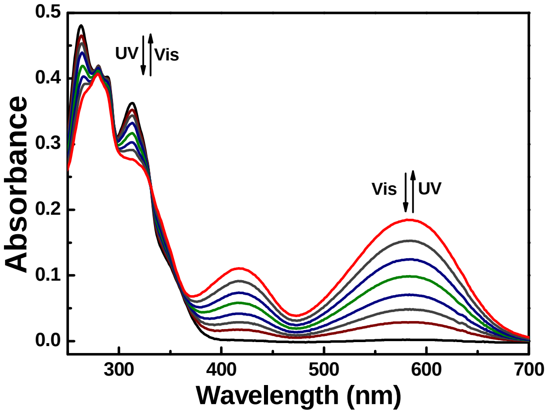
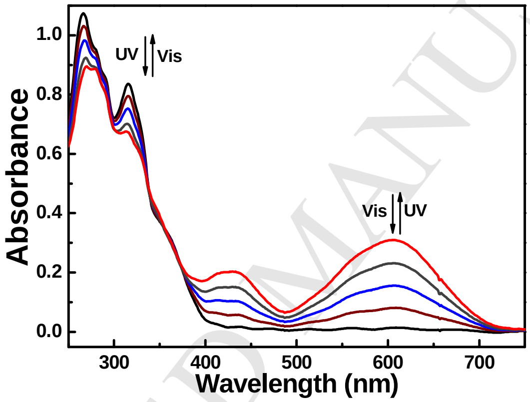

Br
B(OH)2
5
Br
R
Pd(Pph3)4
Na2CO3
Br
S
R
6a: R = ortho-OCH3
6b: R = meta-OCH3
6c: R = para-OCH3
6d: R = H
n-BuLi, 195 K
C5F8, THF
F
7a: R = ortho-OCH3
7b: R = meta-OCH3
7c: R = para-OCH3
7d: R = H
N
8
NBS, rt
THF
9
n-BuLi, 195 K
THF
1o: R = ortho-OCH3
2o: R = meta-OCH3
3o: R = para-OCH3
4o: R = H

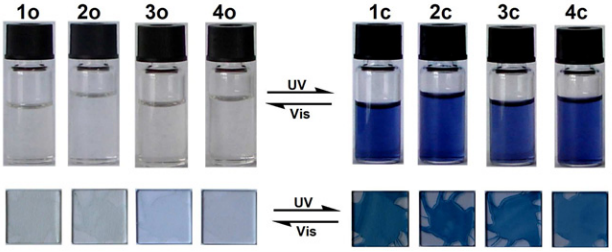
Fig. 2


0.5
0.4
0.3
0.2
0.1
0.0
Absorbance
300
400
500
600
700
Wavelength (nm)
UV
Vis
Vis
UV

(A)

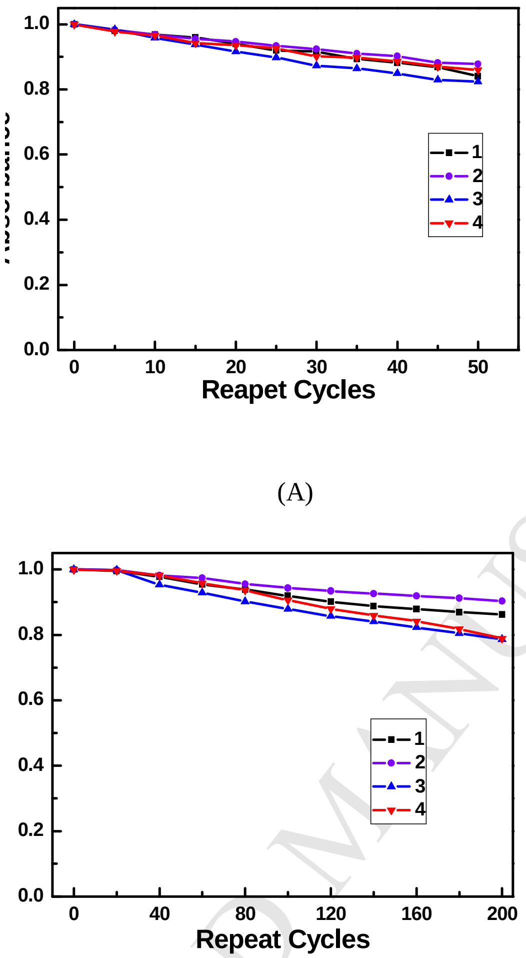

1.0
0.8
0.6
0.4
0.2
0.0
Absorbance
300
400
500
600
700
Wavelength (nm)
UV
Vis
Vis
UV

(B)


1o
2o
3o
4o
UV
Vis
1c
2c
3c
4c
UV
Vis

(C)

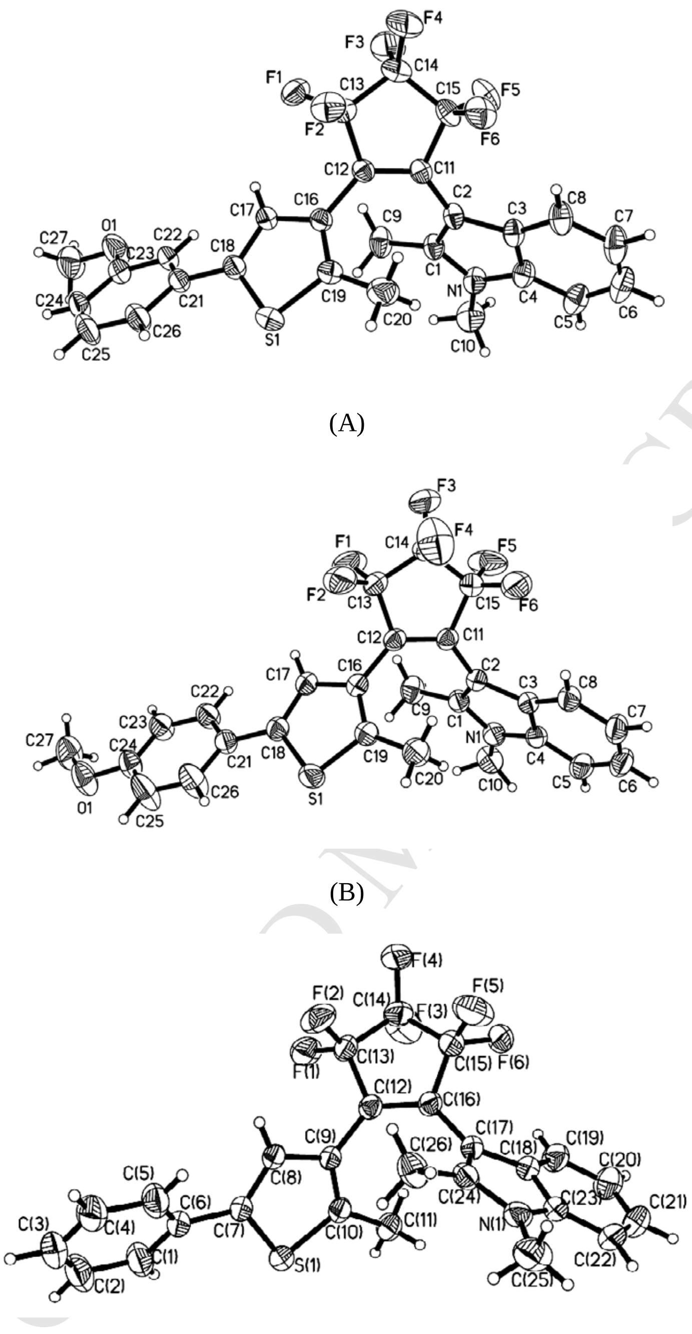
Fig. 3


1.0
0.8
0.6
0.4
0.2
0.0
0
10
20
30
40
50
Reapet Cycles
1
2
3
4
1.0
0.8
0.6
0.4
0.2
0.0
0
40
80
120
160
200
Repeat Cycles
1
2
3
4

(A)

(B)

Fig. 4


F4
F3
F1
C13
C14
C15
F5
F2
F6
C12
C11
C17
C16
C2
C3
C8
C7
C27
O1
C22
C18
C9
C23
C1
C24
C21
C19
N1
C4
C26
S1
C20
C5
C6
C25
C10
F3
F4
F1
C14
F5
F2
C13
C15
F6
C12
C11
C17
C16
C2
C3
C8
C22
C9
C1
C7
C23
C18
N1
C27
C24
C21
C19
C4
C20
C10
C5
C6
O1
C26
S1
C25
F(4)
F(2)
C(14)
F(3)
F(5)
C(13)
C(15)
F(6)
F(1)
C(12)
C(16)
C(17)
C(19)
C(9)
C(26)
C(18)
C(20)
C(5)
C(8)
C(24)
C(23)
C(6)
C(21)
C(3)
C(4)
C(7)
C(10)
C(11)
N(1)
C(1)
C(22)
C(2)
S(1)
C(25)

(A)

(B)

(C)

Fig. 5

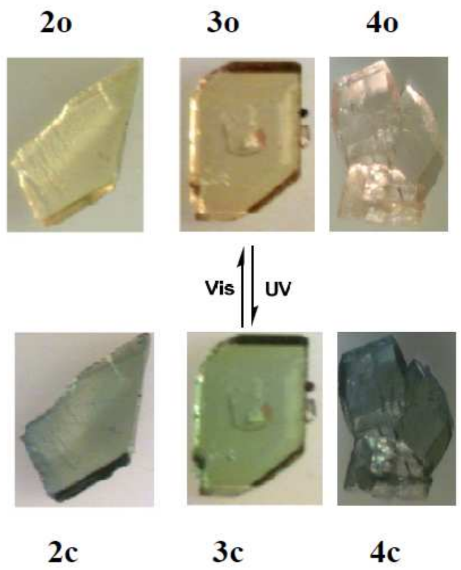
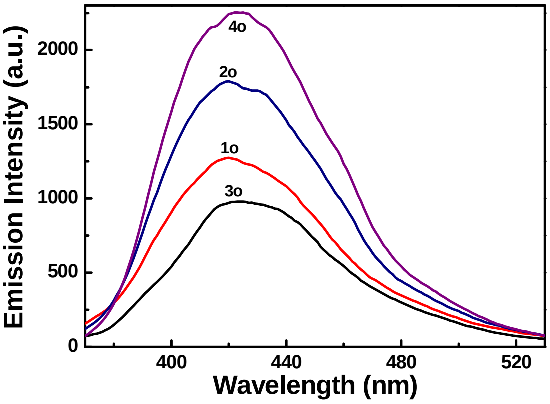
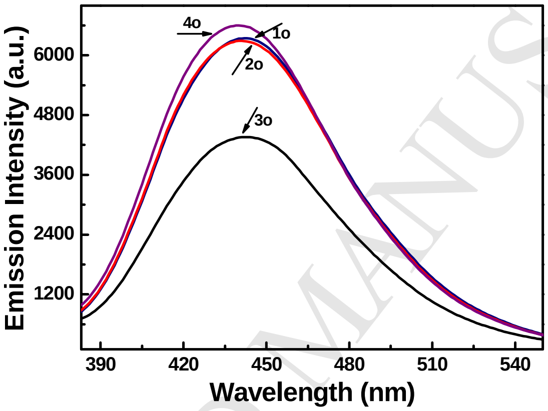


Fig. 6

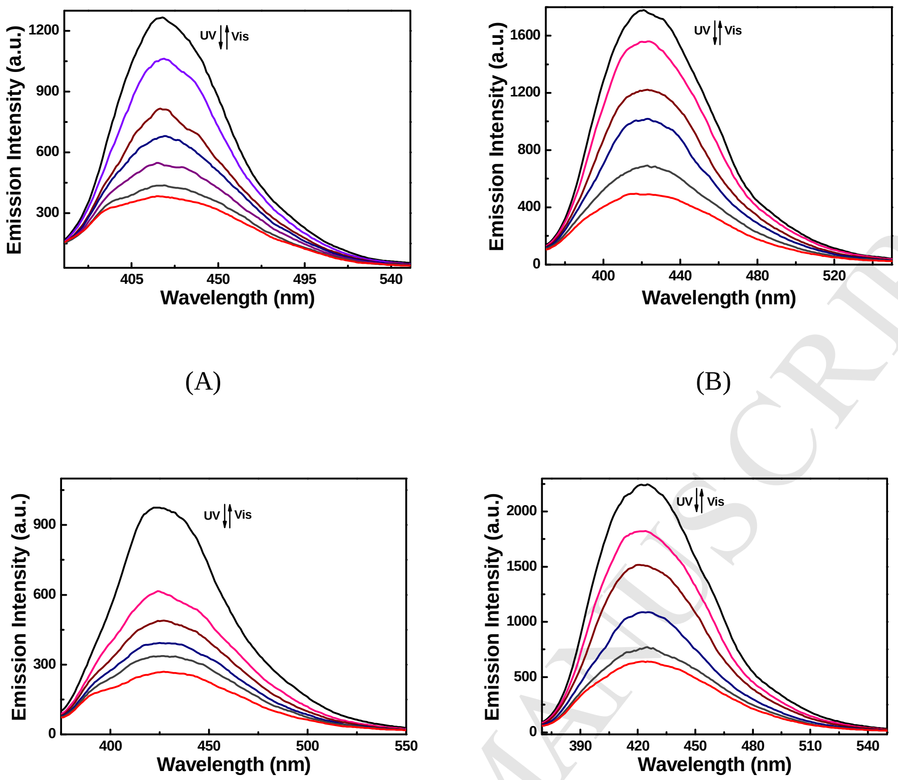

Emission Intensity (a.u.)
0
500
1000
1500
2000
400
440
480
520
Wavelength (nm)
4o
2o
1o
3o

(A)


Emission Intensity (a.u.)
1200
2400
3600
4800
6000
390
420
450
480
510
540
Wavelength (nm)
4o
1o
2o
3o

(B)

Fig. 7


Emission Intensity (a.u.)
1200
900
600
300
405
450
495
540
Wavelength (nm)
UV
Vis
Emission Intensity (a.u.)
1600
1200
800
400
0
400
440
480
520
Wavelength (nm)
UV
Vis
Emission Intensity (a.u.)
900
600
300
0
400
450
500
550
Wavelength (nm)
UV
Vis
Emission Intensity (a.u.)
2000
1500
1000
500
0
390
420
450
480
510
540
Wavelength (nm)
UV
Vis

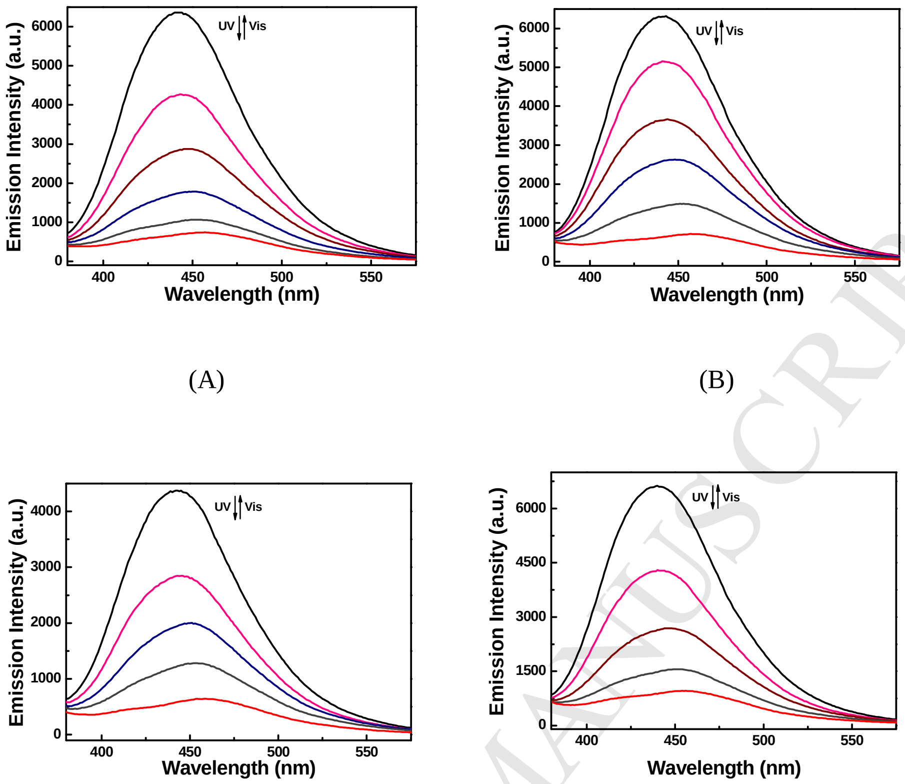
(A)

(B)

(C)

(D)

Fig. 8


Emission Intensity (a.u.)
Wavelength (nm)
UV
Vis
0
1000
2000
3000
4000
5000
6000
1500
4500
400
450
500
550

(A) (B)

(C) (D)

Fig. 9

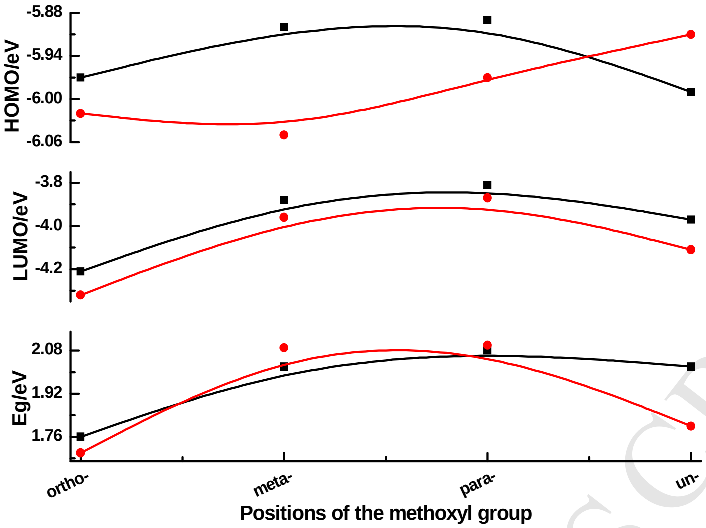

HOMO/eV
-5.88
-5.94
-6.00
-6.06
LUMO/eV
-3.8
-4.0
-4.2
Eg/eV
2.08
1.92
1.76
ortho-
meta-
para-
un-
Positions of the methoxyl group

Fig. 10

Table 4 Electrochemical properties of diarylethenes **1–4**.

Compd	Oxidation		Reduction		Band gap
	E_{onset} (V)	IP (eV)	E_{onset} (V)	EA (eV)	E_{g}
1o	1.17	-5.97	-0.59	-4.21	1.76
1c	1.22	-6.02	-0.48	-4.32	1.70
2o	1.1	-5.9	-0.92	-3.88	2.02
2c	1.25	-6.05	-0.84	-3.96	2.09
3o	1.09	-5.89	-0.99	-3.81	2.08
3c	1.17	-5.97	-0.93	-3.87	2.10
4o	1.19	-5.99	-0.83	-3.97	2.02
4c	1.11	-5.91	-0.69	-4.11	1.80

* The acetonitrile used as solvent was spectrograde and was purified by distillation prior to use.