## Electron-donating methoxyl group position effect on properties of diarylethene derivatives having a pyrazole unit

## Tianshe Yang, Shouzhi Pu, Bing Chen, Jingkun Xu

**Abstract:** New types of asymmetrical photochromic diarylethene derivatives having a pyrazole unit, namely 1-[1,3,5-trimethyl-1-pyrazol-4-yl],2-[2-methyl-5-(4-methoxylphenyl)-1-thien-3-yl]perfluorocyclopentene (**1a**), 1-[1,3,5-trimethyl-pyrazol-4-yl],2-[2-methyl-5-(3-methoxylphenyl)-1-thien-3-yl] perfluorocyclopentene (**2a**), 1-[1,3,5-trimethyl-pyrazol-4-yl],2-[2-methyl-5-(2-methoxylphenyl)-1-thien-3-yl]perfluorocyclopentene (**3a**), and 1-[1,3,5-trimethyl-pyrazol-4-yl],2-[2-methyl-5-phenyl-1-thien-3-yl]perfluorocyclopentene (**4a**), were synthesized. Their optical and electrochemical properties, such as photochromism, photochromic cyclization–cycloreversion kinetics, and fluorescence and electrochemical properties were investigated in detail. The results show that all of these compounds have good photochromism, high cycloreversion quantum yield, and relatively strong fluorescence. Their cyclization–cycloreversion processes were determined to be zeroth to first order reactions. The oxidations of diarylethenes **1a–4a** were initiated at 0.73, 1.11, 0.79, and 1.03 V, respectively. Furthermore, introduction of the electron-donating methoxyl group at different positions of the terminal phenyl ring was found to strongly influence these optical and electrochemical properties.

Key words: photochromism, diarylethene, electron-donating group, optical and electrochemical properties.

**Résumé :** On a effectué la synthèse de nouveaux types de dérivés diaryléthènes asymétriques et photochomiques comportant une unité pyrazole, soit le 1-[1,3,5-triméthyl-1-pyrazol-4-yl]-2-[2-méthyl-5-(4-méthoxyphényl)-1-thién-3-yl]perfluorocyclopentène (1a), le 1-[1,3,5-triméthyl-1-pyrazol-4-yl]-2-[2-méthyl-5-(3-méthoxyphényl)-1-thién-3-yl]perfluorocyclopentène (2a), le 1-[1,3,5-triméthyl-1-pyrazol-4-yl]-2-[2-méthyl-5-(2-méthoxyphényl)-1-thién-3-yl]perfluorocyclopentène (3a) et le 1-[1,3,5-triméthyl-1-pyrazol-4-yl]-2-[2-méthyl-5-phényl-1-thién-3-yl]perfluorocyclopentène (4a). Les propriétés optiques et électrochimiques, telle la photochromie, la cinétique de la cyclisation/cycloréversion photochromique, la fluorescence et les propriétés électrochimiques ont toutes été étudiées en détail. Les résultats montrent que tous ces composés ont une bonne photochromie, un rendement quantique de cycloréversion élevé et une fluorescence relativement forte. On a déterminé que le processus des réactions cyclisation/cycloréversion est d'ordre zéro/un. Les oxydations des diaryléthènes **1a-4a** sont respectivement initiées à 0,73, 1,11, 0,79 et 1,03 V. De plus, on a observé que l'introduction du groupe méthoxy électrochimiques examinées plus haut.

Mots-clés : photochromie, diaryléthène, groupe électrodonneur, propriétés optiques et électrochimiques.

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## Introduction

Photochromic compounds have attracted considerable attention because of their potential application in photonic devices such as optical memories, photo-switches, and fullcolor displays (1–3). For practical application in optoelec-

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**S. Pu.<sup>1</sup>** Jiangxi Key Lab of Organic Chemistry, Jiangxi Science and Technology Normal University, Nanchang 330013, China; School of Chemistry & Chemical Engineering, Jiangsu Teachers University of Technology, Changzhou 213001, P.R. China.

**T. Yang, B. Chen, and J. Xu.** Jiangxi Key Lab of Organic Chemistry, Jiangxi Science and Technology Normal University, Nanchang 330013, P.R. China.

<sup>1</sup>Corresponding author (e-mail: pushouzhi@tsinghua.org.cn).

tronic devices, photochromic compounds should have good thermal stability at room temperature and high sensitivity. In addition, it is required to further develop thermally irreversible photochromic compounds whose photogenerated colored isomers are very stable and never return to the initial colorless isomers in the dark (4). Recently, several thermally irreversible photochromic compounds, such as furylfulgides, phenoxynaphthacene-quinones, and diarylethenes have been developed (5). Of these compounds, diarylethene derivatives are the most promising candidates for these applications because of their excellent thermal stability in both isomers, fatigue-resistant character, rapid response, and high reactivity in the solid state (6, 7).

To date, a large number of results concerning the synthesis and photochromic properties of diarylethenes with heterocyclic aryl rings have been reported. Among diarylethene derivatives synthesized to date, most are composed of thiophene or benzothiophene hetero-aryl groups (6–13). These compounds are known to exhibit excellent thermal stability of both isomers and fatigue-resistant characteristics (6). In particular, diarylethenes with thiophene ring systems bearing terminal phenyl groups have been of considerable interest because the end group can be substituted by an electron-donating or -withdrawing group. These groups can inevitably influence the optoelectronic properties of corresponding diarylethenes (14). Besides diarylethene derivatives with thiophene or benzothiophene moieties, other hetero-aryl moieties, such as thiazole, (15–17), pyrrole (18), indole (19, 20), indene (21), benzofuran (22), crysothiophene (23) have also been reported. The photochromic performance of each kind of diarylethene derivative is strongly dependent on the aryl moieties. For example, diarylethenes with indole rings exhibit strong fluorescence (19), whereas those with pyrrole rings are thermally unstable and return to open-ring isomers even in the dark (22). When the aryl groups have low aromatic stabilization energy, the derivatives undergo thermally irreversible photochromic reactions (21). Pyrazole is an attractive aryl unit because of its low aromatic stabilization energy and the structure is similar to isothiazole and so is expected to undergo thermally irreversible photochromic reactions. Until now, photochromic hybrid diarylethene derivatives with pyrazole and thiophene moieties have not been reported, with the exception of one letter published by us (24).

For this paper, one of our research goals was to develop a new class of diarylethene derivatives that show good photochromic behavior. We also want to discuss the effect of electron-donating methoxyl group position on the optical and electrochemical properties of diarylethenes. Therefore, we have synthesized four asymmetrical diarylethene derivatives bearing a pyrazole unit and a thiophene moiety with methoxyl group at the para, meta, and ortho positions of terminal phenyl group, i. e. 1-[1,3,5-trimethyl-1-pyrazol-4-yl], 2-[2-methyl-5-(4-methoxylphenyl)-1-thien-3-yl]perfluorocyclopentene (1a), 1-[1,3,5- trimethylpyrazol-4-yl],2-[2-methyl-5-(3-methoxylphenyl)-1-thien-3-yl]perfluorocyclopentene (2a), 1-[1,3,5-trimethyl-pyrazol-4-yl],2-[2-methyl-5-(2-methoxylphenyl)-1-thien-3-yl]perfluorocyclopentene (3a), 1-[1,3,5-trimethyl-pyrazol-4-yl],2-[2-methyl-5-phenyl-1-thien-3-yl] perfluorocyclopentene (4a). The photochromism of diarylethenes 1a-4a, which are discussed in this study, is shown in Scheme 1.

## Experimental

#### **General methods**

All solvents were purified by distillation before usage. NMR spectra were recorded on a Bruker AV400 (400 MHz) spectrometer using CDCl<sub>3</sub> as solvent and tetramethylsilane as an internal standard. IR spectra were recorded on a Bruker Vertex-70 spectrometer and mass spectra were measured with an Agilent MS Trap VL spectrometer. The absorption spectra were measured using an Agilent 8453 UV–vis spectrometer. Photo-irradiation was carried out using an SHG-200 UV lamp, a CX-21 UV fluorescence analysis cabinet, and a BMH-250 visible lamp. Light of appropriate wavelengths was isolated by different light filters. Fluorescence spectra were measured using a Hitachi F-4500 spectrophotometer. Electrochemical examinations were performed in a one-compartment cell using a Model





263 potentiostat–galvanostat (EG&G Princeton Applied Research) under computer control at RT. Platinum electrodes (diameter 0.5 mm) served as working electrode and counter electrode. Platinum wire was used as a quasireference electrode. It was calibrated using the ferrocene (Fc – Fc+) redox couple that has a formal potential,  $E_{1/2}$ , of +0.35 V vs. platinum wire. The typical electrolyte was acetonitrile (5.0 mL), which contained LiClO<sub>4</sub> (0.10 mol/L) and diarylethene (4.0 × 10<sup>-3</sup> mol/L). All solutions were deaerated by a dry argon stream and maintained at a slight argon overpressure during electrochemical experiments.

## Synthesis

The four diarylethenes **1a–4a** were prepared by the method shown in Scheme 2, and experimental details are given in the following.

#### Synthesis of 3,5-dibromo-2-methylthiophene (5)

To a stirred solution of 2-methylthiophene (24.0 g, 244.8 mmol) in acetic acid (100 mL) at 0 °C was slowly added a Br<sub>2</sub>-acetic acid solution (v/v, 29:40). The reaction mixture was stirred overnight at this temperature. The reaction was stopped by the addition of water. The mixture was neutralized by Na<sub>2</sub>CO<sub>3</sub> and extracted with ether. The ether extract was dried, filtrated, and concentrated. The residue was purified by distillation in vacuo. Compound **2** was obtained as a colorless oil, 50.7 g in 81.2% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta$ : 2.94 (s, 3H), 7.61 (s, 1H).

#### Synthesis of 3-bromo-2-methyl-5-thienylboronic acid (6)

To a stirred solution of **2** (16.3 g, 63.7 mmol) in dry ether (150 mL) was added a 1.6 mol/L *n*-BuLi–hexane solution (40.6 mL, 65.0 mmol) at -78 °C under nitrogen atmosphere. Stirring continued for 30 min, and boric acid tri-butyl ester (18.8 mL) was quickly added to the reaction mixture. After increasing the temperature to RT, the reaction was stopped by the addition of 4% HCl (10 mL). The mixture was extracted with 4% NaOH (100 mL), and the aq. NaOH solution was neutralized by 10% HCl. The residue was washed, filtrated, and dried. The product **3** was obtained as yellowish solid, 12.0 g in 85.5% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS)  $\delta$ : 2.51 (s, 3H), 4.59 (s, 2H), 7.33 (s, 1H).

#### 3-Bromo-2-methyl-5-(4-methoxylphenyl)thiophene (7c)

Compound **7c** was prepared by reacting compound **6** (5.0 g, 22.6 mmol) with 4-bromoanisole (4.23 g, 22.6 mmol) in the presence of Pd(PPh<sub>3</sub>)<sub>4</sub> (0.8 g) and Na<sub>2</sub>CO<sub>3</sub> (6.40 g, 60 mmol) in tetrahydrofuran (THF) (80 mL containing 10% water) for 15 h at 70 °C. Compound **7c** was purified by col-

Scheme 2. Synthetic route for diarylethenes 1a-4a.



umn chromatography on SiO<sub>2</sub> using hexane as the eluent and obtained as baby-yellow solid in 78.3% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 2.40 (s, 3H, -CH<sub>3</sub>), 3.83 (s, 3H, -CH<sub>3</sub>), 6.89–6.91 (d, 2H, J = 8.8 Hz, phenyl-H), 6.99 (s, 1H, thienyl-H), 7.42–7.44 (d, 2H, J = 8.8 Hz, phenyl-H).

#### 3-Bromo-2-methyl-5-(3-methoxylphenyl)thiophene (7d)

Compound **7d** was prepared by a method similar to that used for **7c** and obtained as a buff solid in 75.3% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 2.41 (s, 3H), 3.83 (s, 3H), 6.82– 6.84 (d, 1H, J = 8.0 Hz, phenyl-H), 7.03 (s, 1H, thienyl-H), 7.08–7.10 (t, 2H, J = 4.0 Hz, phenyl-H), 7.25–7.29 (t, 1H, J = 8.0 Hz, phenyl-H).

#### 3-Bromo-2-methyl-5-(2-methoxylphenyl)thiophene (7e)

Compound **7e** was prepared by a method similar to that used for **7c** and obtained as a buff solid in 70.2% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 2.41 (s, 3H, -CH<sub>3</sub>), 3.91 (s, 3H, -CH<sub>3</sub>), 6.95–6.99 (m, 2H, J = 7.6 Hz, phenyl-H), 7.27 (s, 1H, thienyl-H), 7.30 (s, 1H, phenyl-H), 7.53–7.55 (d, 1H, J = 8.0 Hz, phenyl-H).

#### 3-Bromo-2-methyl-5-phenylthiophene (7f)

Compound **7f** was prepared by a method similar to that used for **7c** and obtained as a buff solid in 70.0% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 2.28 (s, 3H, -CH<sub>3</sub>), 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).

#### 1-(1,3,5-Trimethylpyrazole)perfluorocyclopentene (9)

To a stirred solution of 4-bromo-1,3,5-trimethylpyrazole (8) (2.84 g, 15 mmol) in 50 mL of THF was added dropwise a 1.6 mol/L *n*-BuLi solution (9.4 mL, 15 mmol) at -78 °C under argon atmosphere. Stirring was continued for 30 min at the low temperature. Perfluorocyclopentene (2.04 mL, 15 mmol) was added to the reaction mixture at -78 °C, the mixture was stirred for another 1 h at this temperature, and then the reaction temperature was increased spontaneously to RT. The reaction was stopped by the addition of water. The mixture was extracted with ether and washed with aq. HCl (1 mol/L) and water, respectively. The organic layer

was dried over MgSO<sub>4</sub>, filtrated, and evaporated. The crude product was purified by column chromatography on SiO<sub>2</sub> using petroleum ether – acetic ether (4:1) as the eluent to give 2.98 g of compound **9** as a yellow oil in 65.8% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) & 2.20 (s, 3H, -CH<sub>3</sub>), 2.22 (s, 3H, -CH<sub>3</sub>), 3.77 (s, 3H, -NCH<sub>3</sub>). <sup>19</sup>F NMR (400 MHz, CDCl<sub>3</sub>) & -107.61 (2F), -118.36 (2F), -129.22 (1F), -130.51 (2F).

#### 1-[1,3,5-Trimethyl-1-pyrazol-4-yl],2-[2-methyl-5-(4methoxylphenyl)-1-thien-3-yl]perfluorocyclopentene (1a)

To stirred anhyd. THF (30 mL) containing 7c (0.568 g, 1.66 mmol) was added dropwise a 1.6 mol/L n-BuLi solution (1.05 mL) at -78 °C under argon atmosphere. After the mixture was stirred for 30 min at -78 °C, compound 9 (0.5 g, 1.66 mmol), dissolved in anhyd. THF solvent, was added quickly. The reaction mixture was continuously stirred at -78 °C for 2 h, and the reaction was allowed to slowly warm to RT. The reaction was quenched by the addition of water. The product was extracted with ether, dried with MgSO<sub>4</sub>, and concentrated in vacuo. The crude product was purified by column chromatography (petroleum ether acetic ether, 4:1) to afford 0.35 g of diarylethene 1a as yellow solid in 45.0% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 1.94 (s, 3H, -CH<sub>3</sub>), 1.97 (s, 3H, -CH<sub>3</sub>), 2.03 (s, 3H, -CH<sub>3</sub>), 3.70 (s, 3H, -OCH<sub>3</sub>), 3.84 (s, 3H, -NCH<sub>3</sub>), 6.90–6.92 (d, 2H, J = 8.4 Hz, phenyl-H), 7.13 (s, 1H, thiophene-H), 7.44–7.47 (d, 2H, J = 8.4 Hz, phenyl-H). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>) δ: 10.54, 12.86, 14.30, 36.27, 55.40, 106.29, 114.38, 121.43, 122.87, 125.72, 126.23, 139.17, 139.63. 141.92, 146.46 159.48. IR (KBr, cm<sup>-1</sup>) v: 800, 821 (benzene 1,4substituted), 1124 (-CF<sub>2</sub>), 1255 (C-N, st), 1341, 1477, 1550 (thiophenene bond), 1611 (benzene skeleton), 2841 (-OCH<sub>3</sub>), 2927, 2960 (-CH<sub>3</sub>). <sup>19</sup>F NMR (400 MHz, CDCl<sub>3</sub>) δ: -109.43 (2F), -110.52 (2F), -132.58 (2F). MS *m*/*z* (M<sup>+</sup>): 487.2 (+H), 509.2 (+Na)

#### 1-[1,3,5-Trimethyl-1-pyrazol-4-yl],2-[2-methyl-5-(3methoxylphenyl)-1-thien-3-yl]perfluorocyclopentene (2a)

Diarylethene **2a** was prepared by a method similar to that



Fig. 1. Absorption spectral changes of diarylethenes 1–4 in hexane solution at RT ( $2.0 \times 10^{-5}$  mol/L): (A) 1, (B) 2, (C) 3, and (D) 4.

used for **1a** and obtained as a solid in 38.0% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 1.96 (s, 3H, -CH<sub>3</sub>), 1.97 (s, 3H, -CH<sub>3</sub>), 2.03 (s, 3H, -CH<sub>3</sub>), 3.70 (s, 3H, -OCH<sub>3</sub>), 3.86 (s, 3H, -NCH<sub>3</sub>), 6.84–6.86 (d, 1H, J = 8.0 Hz, phenyl-H), 7.05 (s, 1H, thiophene-H), 7.11–7.13 (d, 1H, J = 7.6 Hz, phenyl-H), 7.24 (s, 1H, phenyl-H), 7.28–7.32 (t, 1H, J = 8.0 Hz, phenyl-H). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 10.01, 12.33, 13.98, 35.67, 54.85, 105.73, 110.92, 112.71, 117.67, 122.27, 125.29, 129.54, 134.17, 138.10, 138.65, 140.17, 141.32, 145.92, 159.54. IR (KBr, cm<sup>-1</sup>) v: 687, 770, 799, 882 (benzene 1,3-substituted), 1121 (-CF<sub>2</sub>), 1271 (C-N, st), 1336,1434 (thiophenene bond), 1602 (benzene skeleton), 2841 (-OCH<sub>3</sub>), 2948, 2966 (-CH<sub>3</sub>, st). <sup>19</sup>F NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : –109.45 (2F), –110.51 (2F), –132.58 (2F). MS *m/z* (M<sup>+</sup>): 487.2 (+H), 509.1 (+Na).

# 1-[1,3,5-Trimethyl-1-pyrazol-4-yl],2-[2-methyl-5-(2-methoxylphenyl)-1-thien-3-yl]perfluorocyclopentene (3a)

Diarylethene **3a** was prepared by a method similar to that used for **1a** and obtained as solid in 41.2% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 1.96 (s, 3H, -CH<sub>3</sub>), 1.97 (s, 3H, -CH<sub>3</sub>), 2.04 (s, 3H, -CH<sub>3</sub>), 3.69 (s, 3H, -OCH<sub>3</sub>), 3.92 (s, 3H, -NCH<sub>3</sub>), 6.96–7.02 (dd, 2H, J = 8.0 Hz, phenyl-H), 7.27– 7.29 (d, 1H, J = 8.0 Hz, phenyl-H), 7.42 (s, 1H, thiophene-H), 7.57–7.59 (dd, 1H, J = 7.6 Hz, phenyl-H). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 10.49, 12.86, 14.21, 36.25, 55.53, 106.36, 111.69, 113.90, 121.01, 122.36, 124.59, 124.84, 127.86, 128.73, 137.05, 139.19, 140.96, 146.48, 146.95, 155.49. IR (KBr, cm<sup>-1</sup>) v: 751 (benzene 1,2-substituted), 1127 (-CF<sub>2</sub>), 1274 (C-N, st), 1341, 1438 (thiophenene bond), 1635 (benzene skelteton), 2839 (-OCH<sub>3</sub>), 2942 (-CH<sub>3</sub>).



<sup>19</sup>F NMR (400 MHz, CDCl<sub>3</sub>) δ: -109.46 (2F), -110.51 (2F), -132.57 (2F). MS *m*/*z* (M<sup>+</sup>): 487.2 (+H), 509.2 (+Na), 467.2 (-F).

#### 1-[1,3,5-Trimethyl-1-pyrazol-4-yl],2-[2-methyl-5-phenyl-1thien-3-yl]perfluorocyclopentene (4a)

Diarylethene **4a** was prepared by a method similar to that used for **1a** and obtained as solid in 44.1% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 1.96 (s, 3H, -CH<sub>3</sub>), 1.97 (s, 3H, -CH<sub>3</sub>), 2.03 (s, 3H, -CH<sub>3</sub>), 3.84 (s, 3H, -NCH<sub>3</sub>), 7.26 (s, 1H, thiophene-H), 7.30–7.32 (d, 1H, J = 7.6 Hz, phenyl-H), 7.37–7.40 (d, 2H, J = 7.6 Hz, phenyl-H), 7.52–7.54 (d, 2H, J = 7.6 Hz, phenyl-H). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 10.54, 12.87, 14.51, 36.29, 106.25, 122.55, 125.60, 125.85, 127.85, 129.00, 133.37, 139.17, 140.61, 142.00, 146.45. IR (KBr, cm<sup>-1</sup>) v: 689, 756, 894 (benzene 1-substituted), 1124 (-CF<sub>2</sub>), 1277 (C-N, st), 1341, 1443 (thiophenene bond), 1626 (benzene skeleton), 2928, 2960 (-CH<sub>3</sub>). <sup>19</sup>F NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : –109.45 (2F), –110.52 (2F), –132.58 (2F). MS m/z (M<sup>+</sup>): 457.2 (+H), 479.2 (+Na), 437.3 (-F), (M<sup>-</sup>) 413.4 (-3CH<sub>3</sub>).

#### **Results and discussion**

## Photochromism of diarylethenes 1-4

In hexane solution, the photochromic reactivity of diarylethenes 1–4 was examined. Figure 1 shows their absorption spectral changes induced by UV light at RT (2.0 ×  $10^{-5}$  mol/L). Compounds 1a–4a exhibited good photochromic properties and can be toggled between their colorless openring isomers (1a–4a) and colored closed-ring isomers (1b–

Compound	$\lambda_{o,max} (nm)^a, \ \epsilon \ (L \ mol^{-1} \ cm^{-1})$	$\lambda_{c,max} (nm)^b,$ $\epsilon (L mol^{-1} cm^{-1})$	$\Phi^c$	
			$\Phi_{\text{o-c}}$	$\Phi_{c-0}$
1	291, 2.9 × $10^4$	573, $1.0 \times 10^4$	0.47	0.57
2	284, 2.5 × $10^4$	573, 7.9 $\times$ 10 <sup>3</sup>	0.45	0.53
3	278, 2.7 × $10^4$	573, $1.1 \times 10^4$	0.43	0.46
4	287, $3.2 \times 10^4$	575, $8.8 \times 10^3$	0.27	0.40

**Table 1.** Absorption spectral properties of diarylethenes 1–4 in hexane at  $2.0 \times 10^{-5}$  mol/L.

<sup>a</sup>Absorption maxima of open-ring forms.

<sup>b</sup>Absorption maxima of closed-ring forms.

<sup>c</sup>Quantum yields of cyclization reaction,  $\Phi_{o-c}$ , and cycloreversion reaction,  $\Phi_{c-o}$ , respectively.

**4b**) by alternating irradiation with UV and visible light, as monitored using UV-vis absorption and <sup>1</sup>H NMR spectroscopy. Upon irradiation with 313 nm light, absorption bands in the visible region appear and the solutions turns blue as a result of the cyclization reactions to produce 1b-4b (Fig. 1 and Table 1). In the photostationary state, the content of the closed-ring isomer can be easily analyzed with <sup>1</sup>H NMR spectroscopy by comparing the relative intensities of thiophene proton signals. According to this method, <sup>1</sup>H NMR spectroscopic studies performed on CDCl<sub>3</sub> ( $1.0 \times 10^{-3}$  mol/L) solutions of 1a-4a reveal that the contents of the closed-ring isomers (1b-4b) in photostationary states are 67% for 1b, 69% for 2b, 68% for 3b, and 69% for 4b, respectively. All the solutions of 1b-4b can be decolorized by irradiating them with visible light of wavelengths greater than 500 nm to induce the cycloreversion reactions and reproduce 1a-4a. The coloration-decoloration cycles of the four compounds could be repeated more than 20 times and a clear isosbestic point was observed at 315, 318, 327, and 309 nm for diarylethenes 1, 2, 3, and 4, respectively. The absorption spectral properties of the four compounds are summarized in Table 1. The quantum yields were determined by comparing the reaction yields of diarylethenes 1-4 in hexane against 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene in hexane (25), and the results are also shown in Table 1. These data suggest that the maximum absorption wavelengths of closed-ring forms and the molar absorption coefficients of both open- and closed-ring forms of the four diarylethene compounds are not evidently different. However, the maximum wavelengths of open-ring forms and their cyclization-cycloreversion quantum yields are relatively remarkable. Among diarylethenes 1-4, the quantum yields of cyclization and cycloreversion reactions of the paramethoxyl substituted derivative (1) are the greatest ( $\Phi_{O-C}$  = 0.47,  $\Phi_{C-O} = 0.57$ ), while those of the the non-methoxyl substituent derivative (4) are the smallest ( $\Phi_{O-C} = 0.27, \Phi_{C-O} =$ 0.40). The values of the other two compounds are between those of diarylethenes 1 and 4. As shown in Table 1, all cyclization-cycloreversion quanta of diarylethene derivatives with methoxyl group substituent (1a-3a) are much higher than that of the diarylethene with no methoxyl group (4a). The results indicate that the cyclization-cycloreversion quantum yield could be effectively increased when the electron-donating methoxyl group was introduced into the benzene rings. In addition for diarylethenes 1-4, the values of their cycloreversion quantum yields are much higher than those of cyclization quantum yields (Table 1). This is an interesting characteristic of diarylethene derivatives having a pyrazole unit and is a significant difference between the diarylethenes reported here and other diarylethenes reported to date.

The property of fatigue resistance, i.e., the number of times photocyclization and ring-opening reaction cycles can be repeated without loss of performance, was examined at RT according to ref. 18. The hexane solution of compound **1** was irradiated alternatively with UV light (313 nm) and visible light (510 nm). The irradiation time was long enough for coloration to reach the photostationary state and for the color to be completely bleached. The absorbance of the open-ring form remained almost constant even after 200 coloration–decoloration cycles and a clear isosbestic point was observed at 315 nm after 200 cycles. Compounds **2–4** showed similar properties to that of **1**. The results suggested that the diarylethene derivatives bearing heterocyclic pyrazole ring show excellent fatigue resistance.

## Photochromic cyclization–cycloreversion kinetics of diarylethenes 1–4

The photochromic cyclization and cycloreversion kinetics of diarylethenes 1-4 in hexane were investigated by irradiation by UV-vis (313 nm, from open to closed form) or visible light ( $\lambda > 500$  nm, closed to open form), as shown in Fig. 2. The concentration of all solutions was  $2.0 \times 10^{-5}$  mol/L. All absorption data were collected at the maximum wavelength of every solution, i.e., at the maximum optical density. As shown in Fig. 2a, the cyclization kinetics of diarylethenes 1-4 in hexane show that the photochromic cyclization reaction follows zeroth-order kinetics; the relationships between absorbance and exposure time (A vs. t) show good linearity (linear correction factors >0.99) upon irradiation with UV light (313 nm) in all solutions. The slopes of the A vs. t lines gave the zeroth order rate constant,  $k_{0-c}$ . According to this method, all the k values for the cyclization process  $(k_{0-c})$  of diarylethes 1–4 can be readily obtained in hexane and are  $2.18 \times 10^{-3}$ ,  $1.25 \times 10^{-3}$ ,  $1.89 \times 10^{-3}$ , and  $0.89 \times 10^{-3}$  mol/L s<sup>-1</sup>, respectively. Similarly, the cycloreversion kinetic curves shown in Fig. 2b can be plotted according to eq. [1] (26),

[1] 
$$kt = \ln\left[\frac{A_{\infty} - A_0}{A_{\infty} - A_t}\right]$$

where k is the first-order rate constant,  $A_0$ ,  $A_{\infty}$ , and  $A_t$  are the observed absorption data measured at the beginning, at the end, and at time t of the reaction, respectively. The data in Fig. 2b represent a perfect linear fit, indicating that the

**Fig. 2.** The cyclization–cycloreversion kinetics of diarylethenes **1–4** in hexane (2.0 × 10<sup>-5</sup> mol/L): (*A*) Cyclization kinetics upon irradiation with light ( $\lambda = 254$  nm), (*B*) Cycloreversion kinetics, upon irradiation with visible light ( $\lambda > 510$  nm).



photochromic cycloreversion process follows first-order reaction kinetics. From Fig. 2b, the rate constant k of the cycloreversion process ( $k_{c-0}$ ) of diarylethenes **1–4** in hexane were calculated to be  $6.25 \times 10^{-2}$ ,  $4.17 \times 10^{-2}$ ,  $5.44 \times 10^{-2}$ , and  $6.55 \times 10^{-2}$  mol/L s<sup>-1</sup>, respectively. Of the four compounds, the  $k_{o-c}$  of diarylethene **4** in hexane is the smallest, while its  $k_{c-0}$  is the greatest in hexane. The result showed that the methoxyl group can effectively accelerate the photochromic cyclization reaction and suppress the cycloreversion reaction.

#### Fluorescence of diarylethenes 1-4

The fluorescence spectra of diarylethenes 1a-4a (5.0 ×  $10^{-5}$  mol/L) in hexane at RT are illustrated in Fig. 3*a*. All exhibited good fluorescence at different wavelengths in hexane solution, when excited by their respective excitation wavelength. From Fig. 3*a*, we can clearly see that the hexane solutions containing diarylethenes 1a-4a showed relatively strong fluorescence at 416, 438, 441, and 439 nm when excited at 280, 317, 315, and 320 nm, respectively.

**Fig. 3.** (*a*) Fluorescence spectra of diarylethenes **1a–4a** in hexane solution  $(5.0 \times 10^{-5} \text{ mol/L})$  at RT, excited at 280, 317, 315, and 320 nm, respectively. (*b*) Fluorescence spectra of diarylethene **1a** in various concentrations in hexane at RT, monitored at 280 nm (*c*) Fluorescence spectra of diarylethene **1a** in different solutions at RT, monitored at 320 nm.



Concn. (mol/L)	$\lambda_{em, max}$ (nm), (fluorescence intensity)				
	<b>1</b> a	2a	3a	<b>4</b> a	
$2 \times 10^{-6}$	414 (102)	438 (219)	440 (699)	422 (273)	
$5 \times 10^{-6}$	418 (193)	438 (484)	441 (1529)	420 (519)	
$1 \times 10^{-5}$	412 (320)	436 (816)	441 (2573)	423 (791)	
$2 \times 10^{-5}$	420 (394)	440 (1323)	441 (3394)	423 (1172)	
$5 \times 10^{-5}$	416 (514)	438 (2180)	441 (4366)	422 (1064)	
$1 \times 10^{-4}$	421 (228)	439 (2005)	442 (2637)	421 (573)	
$2 \times 10^{-4}$	421 (48)	443 (1084)	442 (641)	<i>a</i>	
$1 \times 10^{-3}$	442 (7)	445 (24)	446 (29)	425 (10)	

Table 2. Fluorescence spectral properties of diarylethenes 1a-4a at various concentrations in hexane at RT.

<sup>a</sup>No fluorescence peak.

The fluorescence maxima of the four compounds were observed to be between 416 and 441 nm, indicating that the effect on the fluorescence peak of the electron-donating methoxyl group and its position was relatively significant. On the other hand, the fluorescence intensities of diarylethenes **1a–4a** changed dramatically with the substituent position. The fluorescence intensities increased rapidly from the *para*-substituted **1a** to the *ortho*-substituted 3a derivatives. The value of non-methoxyl-substituted diarylethene 4a is located between those of the paramethoxyl-substituted 1a and the meta-methoxly-substituted 2a derivatives. Among the four compounds, the relative fluorescence intensity of the *ortho*-substituted derivative is the strongest, and that of the *para*-substituted derivative is the weakest. The result is exactly contrary to that reported in our previous paper (27). In that paper, the electro-withdrawing fluorine substituent position did not significantly affect the fluorescence peak of dithienylethene, but had a remarkable effect on the fluorescence intensity; the fluorescence intensity of the ortho-substituted derivative was the weakest, and that of the para-substituted derivative was the strongest. The possible reasons are due to the electro-donating nature of the methoxyl substituent of the terminal phenyl group and that the pyrazole ring can also possibly affect the fluorescence properties of the three diarylethenes. Upon irradiation with 313 nm light, their fluorescence intensity decreased, along with the photochromism, from open-ring form to closed-ring form, suggesting that all of the closed-ring forms of these four diarylethenes showed no fluorescence or that their fluorescence was very weak. These results are consistent with those of most reported diarylethenes (28–31).

The concentration dependence of fluorescence spectra of **1a** was measured in hexane solution at RT, shown in Fig. 3*b*. With the concentration increased from  $2.0 \times 10^{-6}$  to  $5.0 \times 10^{-5}$  mol/L, the maximum emission occurred almost at 416 nm when excited at 280 nm, and the relative fluorescence intensity increased further from  $5.0 \times 10^{-5}$  to  $1.0 \times 10^{-3}$  mol/L, the maximum emission appeared redshifted from 416 to 442 nm, and the relative fluorescence intensity decreased remarkably. The hexane solution showed very weak fluorescence when the concentration was increased to  $1.0 \times 10^{-3}$  mol/L. This self-quench phenomenon perhaps resulted from the formation of excimers and (or) exciplexes in high concentration solutions so that a deactivation effect

could occur during the excited state lifetime (32). Moreover, the concentration effect on the fluorescence spectra of diarylethenes 2a–4a were also measured, and the results are summarized in Table 2. As shown in Table 2, compounds 2a-4a showed similar fluorescent properties as 1a, depending on the concentration employed. At high concentration, e.g.,  $1.0 \times 10^{-3}$  mol/L, the fluorescence peak of each diarylethene was obviously redshifted comparing to other concentrations. For all four compounds, the relative fluorescence intensity showed a remarkable initial increase with subsequent dramatic decrease with increasing concentration. The greatest and the smallest values were obtained at  $5.0 \times$  $10^{-5}$  and  $1.0 \times 10^{-3}$  mol/L, respectively. The systematic redshift at high concentrations and the relatively remarkable fluorescence intensity decrease with increased concentration demonstrated that molecular aggregation and fluorescence quench may occur at higher concentration (31, 33).

The effects of the solvent on the fluorescence spectra of diarylethenes **1a–4a** were also investigated. Figure 3*c* shows the fluorescence spectra of **1a** ( $5.0 \times 10^{-5}$  mol/L) in different solvents at RT. As shown in Fig. 3*c*, when excited at 320 nm, the fluorescence peaks of diarylethene **1a** were observed at 418, 440, 443, 456, 470, and 426 nm in hexane, dichloromethane, ethyl acetate, DMF, acetonitrile, and ethanol, respectively. The solvent effect on the fluorescence of diarylethenes **2a–4a** was also measured, and the fluorescence properties of these four diarylethenes in various solvents at RT are summarized in Table 3.

From these data, one can readily see that the fluorescence spectra depended remarkably on the polarity of solvent. The maximum fluorescence peaks of the four compounds appeared to be redshifted as the polarity of the solvent increased, except for ethanol for which the contrary occurred. The reason may be possibly attributed to its specific solvent-solute interaction such as hydrogen bonding with the fluorine atoms of the diarylethenes. In addition, the solvent effect on the relative fluorescence intensity showed relatively complex and irregular changes (Table 3). Under the same experimental conditions, the fluorescence intensities in ethanol are the strongest, except for diarylethene **1a**, for which the strongest intensity appeared in dichloromethane.

#### **Electrochemistry of diarylethenes 1–4**

It is reported that the ring-opening and -closing transformation of some diarylethenes can be initiated not only by

	$\lambda_{\rm em, \ max}$ (nm), (fluorescence intensity) <sup><i>a</i></sup>				
Solvent	1a	2a	3a	4a	
Hexane	416 (514)	438 (2180)	441 (4366)	439 (1630)	
Dichloromethane	440 (549)	450 (2739)	452 (6354)	451 (2003)	
Ethyl acetate	443 (433)	452 (2196)	452 (5560)	b	
DMF	456 (376)	460 (2225)	460 (5376)	461 (1531)	
Acetonitrile	470 (330)	460 (2130)	463 (5629)	462 (1601)	
Ethanol	426 (415)	449 (2833)	451 (7032)	448 (2176)	

**Table 3.** Fluorescence properties of diarylethenes **1a–4a** in different solvents at  $5.0 \times 10^{-5}$  mol/L.

<sup>*a*</sup>Fluorescent maxima monitored at 320, 330, 333, and 320 nm for **1a**, **2a**, **3a**, and **4a**, respectively. <sup>*b*</sup>No spectrum peaks.

UV or visible light irradiation but also by electrochemical or chemical, i.e., electrochromic, oxidation (34-36). The electrochemical properties of diarylethenes can be potentially applied to molecular scale electronic switches. Electrochemical examinations by the linear sweep method under the same experimental conditions using diarylethenes 1-4 were performed, and the results are shown in Fig. 4. As shown in Fig. 4, para-methoxyl and ortho-methoxyl substituted diarylethenes (1 and 3) showed similar electrochemical behavior. The oxidation onsets of 1a, 1b, 3a, and 3b initiated at 0.79, 1.00, 0.73, and 0.78 V, respectively. Both of the oxidation onsets of the open-ring forms of compounds 1 and 3 are lower than those of the corresponding closed-ring forms. This indicates that the electron-donating effect of the methoxyl group is more significant in the open-ring form. However, the oxidation onsets of compounds 2 and 4 were opposite to those of compounds 1 and 3; the oxidation onsets of 2a, 2b, 4a, and 4b were 1.11, 0.87, 1.03, and 0.94 V, respectively. The oxidation onsets of the open-ring forms are higher than those of the closed-ring forms. This implies that the electron-donating effect of the methoxyl group or hydrogen atom is more significant in the closed-ring form of compounds 2 or 4, respectively. Moreover, the differences between the open- and closed-ring forms of diarylethenes 1-**4** ( $\Delta V_{a-b}$ ) were 0.21 for **1**, 0.24 for **2**, 0.05 for **3**, and 0.09 for 4, respectively. At the same applied potential, the current density of **2b** was higher than that of **2a**, which is exactly opposite to the characterisitcs of 1a and 1b. The electronic current of compounds 3 and 4 at the same applied potential intersected. From the previous description together with Fig. 4, a reasonable conclusion can be drawn that the substitution of the electron-donating methoxyl group has a great effect on 1-3. For ortho or meta position substitution of the methoxyl group, the oxidation potential onset showed a remarkable difference with  $\Delta V_{a-b}$  greater than 0.2 V for 1 and 2. On the other hand, when substituted at the ortho position, the electron-donating effect together with its steric effect plays a main role, which made the oxidation potential onsets of **3a** and **3b** similar to each other ( $\Delta V_{a-b} = 0.05$  V). A similar result was observed when the ortho-methoxyl group was substituted by a hydrogen atom (4a and 4b,  $\Delta V_{a-b} = 0.09$  V). In addition, three oxidation processes can be readily observed during the anodic oxidation of 2a and 2b, while only two oxidation processes can be observed during anodic oxidation of the other three compounds. The three oxidation processes may involve the oxidation of a pyrazole ring, a thiophene ring, together with the benzene ring of compound

Fig. 4. The anodic polarization curves of diarylethenes 1-4.



2. However, the substitution of the methoxyl group, or hydrogen atom, at the para and ortho position made the oxidation process of benzene unclear for 1a, 1b, 3a, 3b, 4a, and 4b. All these electrochemical results indicated that the substitution of the methoxyl group on the benzene and pyrazole units had great effect on both the open- and closed-ring forms of the three diarylethene derivatives. A detailed explanation requires further investigation.

#### Conclusions

Four new asymmetrical diarylethenes bearing a pyrazole unit were synthesized for the investigation of their optical and electrochemical properties. The effect of different substitution positions on the optical and electrochemical performances of diarylethenes was investigated. The results suggested that the optical and electrochemical properties of these diarylethene derivatives, such as photochromic properties, fluorescence, and their electrochemical characteristics, were significantly dependent on the effect of the electrondonating methoxyl substituent position and the pyrazole unit. The reason may be attributed to the different electrondonating effects when the methoxyl group was substituted on the different positions of the terminal benzene ring and the different aromatic stabilization energy of pyrazole unit from that of thiophene unit. All the diarylethenes reported in this study exhibited good photochromism and strong fluorescence. Significantly, their cycloreversion quantum yields are much higher than those of their cyclization quantum yields.

The results are very useful for the design of efficient photoactive and diarylethene compounds with excellent characteristics.

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