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Photochromism of new unsymmetrical diarylethene derivatives bearing both benzofuran and thiophene moieties

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ABSTRACT

A new class of unsymmetrical photochromic diarylethenes bearing both benzofuran and thiophene moieties was synthesized and the effects of substitution on their properties were discussed systematically. Two compounds among them show distinctly different conformation in the single crystalline phase: one crystallizes with an *anti*-parallel conformation which exhibit good photochromism, whereas the other crystallizes with a parallel conformation which exhibits no photochromism in the crystalline phase. Each of the compounds exhibited remarkable photochromism and functioned as a fluorescent switch in both solution and PMMA films. The electron-donating groups significantly increased the cyclization quantum yield, depressed the cycloreversion quantum yield, shifted the emission peak to a longer wavelength, and decreased the emission intensity; while the electron-withdrawing groups functioned as an inverse action for these diarylethene derivatives. The cyclic voltammograms results revealed that these diarylethenes exhibited evident electrochromism during electrolysis and the oxidative cyclization is thermodynamically.

1. Introduction

Currently, organic photochromic materials have received considerable attention because of their potential for photonic applications such as optical storage materials, photoswitches, and organic semiconductor devices [1–5]. To date, various types of photochromic compounds such as diarylethenes [6], fulgides [7], and phenoxynaphthacenequinines [8,9], have been developed in an attempt to satisfy the requirements of these optoelectric devices. Among the reported photochromic systems, photochromic diarylethenes are the most promising candidates for such applications because of their good thermal stability, excellent fatigue resistance, rapid response, and high reactivity in the solid state [2,10–15]. Especially, dithienylethenes bearing terminal benzene rings are of considerable interest because the hydrogen atoms of the terminal benzene ring can be replaced by different electron-donating/withdrawing substituents, which efficiently modulate their photochromic characteristics [16].

As we all know, the photochromic reactivity of diarylethene mainly depends on the categories of heteroaryl groups and different electron donor/acceptor substituents. On the one hand, the nature of the heteroaryl moieties greatly influences the photoreactivity and the distinguishable features of diarylethenes. For example, diarylethenes with thiophene/benzothiophene moieties have good thermal stability and remarkable fatigue resistance [6,17–19], whereas diarylethenes bearing two pyrrole groups are thermally unstable and return to the open-ring isomers even in the dark [20]. On the other hand, electron donor/acceptor substituents and their substitution positions also have a significant effect on the photochromic properties of diarylethene derivatives [21–24]. In a typical example, the electron-donating substituents of the bis(3-thienyl)ethene diarylethenes can be effective to increase the absorption coefficients of the closed-ring isomers and decrease the cycloreversion quantum yields [25,26], however, those attached bis(2-thienyl)ethene diarylethenes can increase the absorption maxima of the open-ring isomers and reduce the cyclization quantum yields [27].

Maybe for the above reasons, the design and synthesis of new photochromic diarylethene skeletons with different substituents has become an active area of research at the present stage. Among the reported diarylethenes, most of the heteroaryl diarylethenes bear thiophene or benzothiophene rings which exhibit good thermal stability and outstanding fatigue resistance [2,6], with only a few reports concerning other heteroaryl moieties such as furan [28], thiazole [29–31], pyrrole [32], indene [33], indole [34,35], among others. Benzofuran is an attractive aryl unit with low

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aromatic stabilization energy and its molecular structure is similar to that of benzothiophene, suggesting that introduction of the benzofuran ring into the heteroaryl moieties of diarylethenes can be expected to undergo thermally irreversible photochromic reactions [36]. Up to date, there are a few examples of photochromic diarylethenes bearing two benzofuran rings [36–39]. The diarylethenes bearing benzofuran moieties exhibit good photochromism and outstanding fatigue resistance in solution as well as in the single crystalline phase [36]. The results give us valuable insight and encourage us to develop a new class of hybrid photochromic diarylethene derivatives bearing a benzofuran moiety. To date, most of the reported diarylethenes bearing benzofuran rings are symmetrical compounds, unsymmetrical diarylethenes bearing a benzofuran moiety are very rare [33,39]. As far as our knowledge, no affiliation concerning photochromic hybrid diarylethene bearing both benzofuran and thiophene moieties has been reported so far.

In this work, one of the main purposes was to explore a new class of hybrid photochromic diarylethene derivatives bearing both benzofuran and thiophene moieties and to discuss the effects of substitution on their physicochemical properties. Accordingly, five new hybrid diarylethene derivatives with different substituents at the *para*-position of the terminal benzene ring were synthesized. The synthesized diarylethenes are 1-(2-ethyl-3-benzofuranyl)-2-[2-methyl-5-(4-methoxyphenyl)-3-thienyl]perfluorocyclopentene (**1o**), 1-(2-ethyl-3-benzofuranyl)-2-[2-methyl-5-(4-methylphenyl)-3-thienyl]perfluorocyclopentene (**2o**), 1-(2-ethyl-3-benzofuranyl)-2-(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene (**3o**), 1-(2-ethyl-3-benzofuranyl)-2-[2-methyl-5-(4-fluorophenyl)-3-thienyl]perfluorocyclopentene (**4o**), and 1-(2-ethyl-3-benzofuranyl)-2-[2-methyl-5-(4-cyanophenyl)-3-thienyl]perfluorocyclopentene (**5o**). The photochromic scheme of the diarylethenes is shown in Fig. 1.

2. Experiment

2.1. General

The solvents were purified by distillation before use. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AV400 (400 MHz) spectrometer with $CDCl_3$ as the solvent and tetramethylsilane as an internal standard. IR spectra were performed on a Bruker Vertex-70 spectrometer. Elemental analyses were determined with a PE CHN 2400 analyzer. Melting point was determined by a WRS-1B melting point determination apparatus. The absorption spectra were measured using an Agilent 8453 UV/VIS spectrophotometer. Photoirradiation was carried out using an SHG-200 UV lamp, CX-21 ultraviolet fluorescence analysis cabinet and a BMH-250 visible lamp. Light of appropriate wavelength 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 by using a Model 263 potentiostatgalvanostat (EG&G Princeton Applied Research) under computer control at room temperature. Platinum-electrodes (diameter 0.5 mm) served as working electrode and counter electrode. Platinum wire served as a quasi reference electrode. It was calibrated using the ferrocene (Fc/Fc+) redox couple which has a formal potential $E_{1/2} = +0.35$ V versus platinum wire. The typical electrolyte was acetonitrile (5.0 mL) containing 0.1 mol L^{-1} tetrabutylammonium tetrafuoroborate ($(TBA)BF_4$) and 4.0×10^{-3} mol L^{-1} diarylethene sample. All solutions were deaerated by bubbling with a dry argon stream and maintained at a slight argon overpressure during electrochemical experiments. The PMMA films of diarylethenes **1**–**5** were prepared by dissolving 10 mg of diarylethene sample and 100 mg of polymethylmethacrylate (PMMA) in chloroform (1 mL) with the aid of ultrasound, and the homogeneous solution was spin-coated on a quartz substrate ($20 \times 20 \times 1$ mm^3) with a rotating speed at 1500 rpm. The films dried in air and kept in darkness at room temperature. The thickness of each film was about 3 μm.

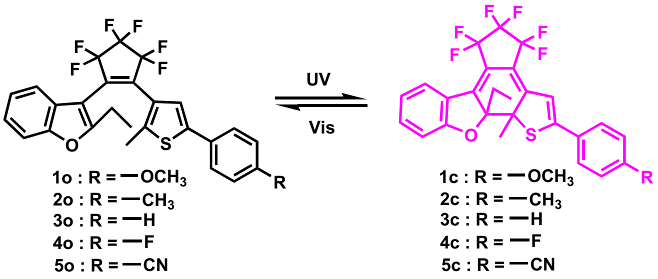

Fig. 1. Photochromism of diarylethenes **1**–**5**.

Suitable crystals of **3o** and **5o** were obtained by slow evaporation of a hexane solution. All the measurements were collected by a Bruker SMART APEX II CCD diffractometer using a MULTI scan technique at room temperature using Mo Kα radiation. The structures were solved by direct methods and refined by full-matrix least-squares procedures on F^2 by full-matrix least-squares techniques using SHELXTL-97 program. Further details on the crystal structure investigation have been deposited with The Cambridge Crystallographic Data Centre as supplementary publication CCDC 823604 for **3o** and 823605 for **5o**. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 0 1223 336033 or e-mail:deposit@ccdc.cam.ac.uk).

2.2. Synthesis of diarylethenes

The synthetic route for diarylethenes **1o**–**5o** is shown in Fig. 2. Suzuki coupling of five bromobenzene derivatives with thiophene boronic acid (**10**) [40,41] gave alkylphenylthiophene derivatives (**11a**–**e**). 1-(2-Ethyl-1-benzofuran-3-yl)perfluorocyclopentene (**9**) was prepared by alkylation, bromination, and lithiation reactions from benzofuran. Finally, compounds **11a**–**e** was separately lithiated and then coupled with the mono-substituted compound **9** to give the unsymmetrical diarylethene derivatives **1o**–**5o**, respectively. The structures of **1o**–**5o** were confirmed by elemental analysis, NMR, and IR.

2.2.1. 2-Ethylbenzofuran (**7**)

To a stirred anhydrous THF solution (100 mL) containing benzofuran (**6**) (6.1 g, 51.64 mmol) was slowly added 20 mL *n*-BuLi/hexane (2.84 mol L^{-1}) at 195 K under nitrogen atmosphere, and the solution was stirred for 45 min. Then the ethyl-bromide (4.63 mL, 62 mmol) was added slowly to the reaction mixture, and the reaction mixture was warmed to room temperature, kept stirring for another 16 h. Then the reaction mixture was poured into concentrated sodium chloride solution and extracted with diethyl ether. The organic layer was dried, filtrated, and concentrated. The residue was purified by column chromatography using petroleum ether as the eluent to give 6.3 g of **7** as a colorless liquid in 84% yield. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.33 (t, 3H, $J = 7.4$ Hz, $-CH_3$), 2.76–2.82 (m, 2H, $-CH_2$), 6.36 (s, 1H, thienyl–H), 7.15–7.23 (m, 2H, phenyl–H), 7.40 (d, 1H, $J = 8.0$ Hz, phenyl–H), 7.47 (d, 1H, $J = 6.8$ Hz, phenyl–H).

2.2.2. 3-Bromo-2-ethyl-benzofuran (**8**)

To a stirred THF solution (100 mL) containing compound **7** (3.0 g, 20.53 mmol) was slowly added 4.02 g N-bromosullirimide

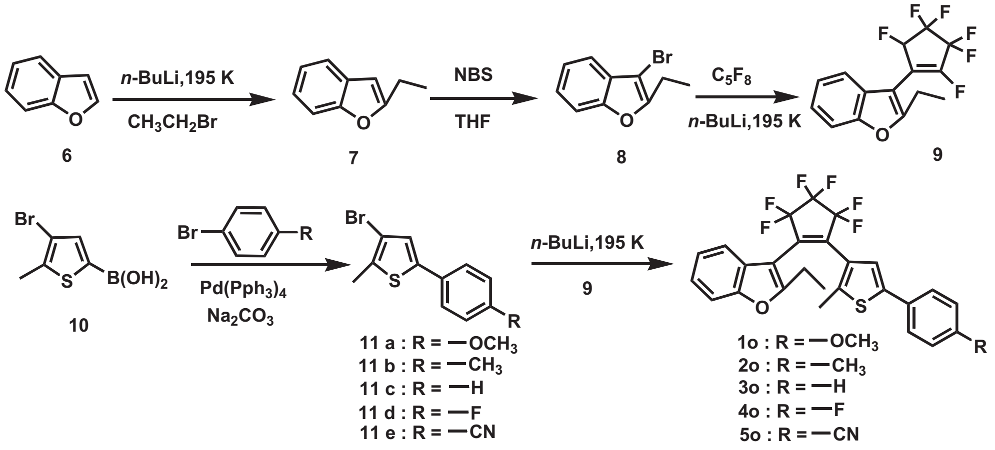

Fig. 2. Synthetic route for diarylethenes **1o**–**5o**.

(22.58 mmol) at 273 K. The reaction mixture was stirred for 24 h, then was poured into sodium thiosulfate solution and extracted with diethyl ether. The organic layer was dried, filtrated, and concentrated. The residue was purified by column chromatography using petroleum ether as the eluent to give 3.62 g of **8** as a pale yellow liquid in 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.32 (t, 3H, $J = 7.6$ Hz, $-CH_3$), 2.82–2.87 (m, 2H, $-CH_2$), 7.24–7.29 (m, 2H, phenyl–H), 7.39–7.45 (m, 2H, phenyl–H).

2.2.3. *(2-Ethyl-1-benzofuran-3-yl) perfluorocyclopentene (**9**)*

To a stirred THF solution (100 mL) containing compound **8** (3.0 g, 13.33 mmol) was slowly added 5.2 mL n-BuLi/hexane (2.84 mol L^{-1}) at 195 K under nitrogen atmosphere. After 40 min, octaperfluoropentene (2.2 mL, 0.136 mL/mol) was added quickly to the reaction mixture, and kept stirring for 2 h at 195 K under nitrogen atmosphere. Then the reaction mixture was extracted with diethyl ether and evaporated in vacuum. The residue was purified by column chromatography using petroleum ether as the eluent to give 2.6 g of **9** as a yellow oil liquid in 61% yield. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.36 (t, 3H, $J = 7.6$ Hz, $-CH_3$), 2.76–2.82 (m, 2H, $-CH_2$), 7.27–7.36 (m, 2H, phenyl–H), 7.49–7.54 (m, 2H, phenyl–H).

2.2.4. *3-Bromo-2-methyl-5-(4-methoxylphenyl)thiophene (**11a**)*

Compound **11a** was prepared by reacting 3-bromo-2-methyl-5-thienylboronic acid (**10**) [40,41] (3.32 g, 15.0 mmol) with 1-bromo-4-methoxylbenzene (2.8 g, 15.0 mmol) in the presence of $Pd(PPh_3)_4$ (0.40 g, 0.35 mmol) and Na_2CO_3 (6.36 g, 60 mmol) in tetrahydrofuran (THF) (80 mL). After refluxing for 16 h at 95 °C, the product was extracted with ether. The organic layer was dried over $MgSO_4$, filtrated, and evaporated. The crude product was purified by column chromatography on SiO_2 using petroleum ether as the eluent and 2.09 g of **11a** obtained as a pale yellow solid in 49% yield. M.p. 106–107 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 2.40 (s, 3H, $-CH_3$), 3.83 (s, 3H, $-OCH_3$), 6.90 (d, 2H, $J = 8.7$ Hz, phenyl–H), 6.98 (s, 1H, thienyl–H), 7.43 (d, 2H, $J = 8.7$ Hz, phenyl–H).

2.2.5. *3-Bromo-2-methyl-5-(4-methylphenyl)thiophene (**11b**)*

Compound **11b** was prepared by a method similar to that used for **11a** and obtained as a colorless solid in 57% yield. M.p. 68–69 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 2.36 (s, 3H, $-CH_3$), 2.41 (s, 3H, $-CH_3$), 7.06 (s, 1H, thienyl–H), 7.17 (d, 2H, $J = 8.0$ Hz, phenyl–H), 7.40 (d, 2H, $J = 8.0$ Hz, phenyl–H).

2.2.6. *3-bromo-2-methyl-5-phenyl-thiophene (**11c**)*

Compound **11c** was prepared by a method similar to that used for **11a** and obtained as a colorless solid in 55% yield. M.p. 66–68 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 2.44 (s, 3H, $-CH_3$), 7.13 (s, 1H, thienyl–H), 7.30 (d, 2H, $J = 8.0$ Hz, phenyl–H), 7.37 (t, 2H, $J = 7.6$ Hz, phenyl–H), 7.53 (d, 2H, $J = 7.6$ Hz, phenyl–H).

2.2.7. *3-bromo-2-methyl-5-(4-fluorophenyl)thiophene (**11d**)*

Compound **11d** was prepared by a method similar to that used for **11a** and obtained as a colorless solid in 33% yield. M.p. 61–63 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 2.41 (s, 3H, $-CH_3$), 7.03 (s, 1H, thienyl–H), 7.06 (d, 2H, $J = 8.0$ Hz, phenyl–H), 7.46 (d, 2H, $J = 8.0$ Hz, phenyl–H).

2.2.8. *3-Bromo-2-methyl-5-(4-cyanophenyl)thiophene (**11e**)*

Compound **11e** was prepared by a method similar to that used for **11a** and obtained as a pale yellow solid in 51% yield. M.p. 79–80 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 2.45 (s, 3H, $-CH_3$), 7.23 (s, 1H, thienyl–H), 7.59 (d, 2H, $J = 8.4$ Hz, phenyl–H), 7.65 (d, 2H, $J = 8.4$ Hz, phenyl–H).

2.2.9. *1-(2-ethyl-3-benzofuranyl)-2-[2-methyl-5-(4-methoxyphenyl)-3-thienyl]perfluorocyclopentene (**1o**)*

To a stirred anhydrous THF (50 ml) containing **11a** (0.57 g, 2.0 mmol) was added dropwise 0.75 mL n-BuLi/hexane solution (2.93 mol L^{-1}) at 195 K under argon atmosphere. After the mixture has been stirred for 35 min, compound **9** (0.71 g, 2.1 mmol) in solvent of anhydrous THF was added. The reaction was further stirred at 195 K for 2 h, and the reaction was allowed to slowly warm to the room temperature. The reaction was quenched with water. The product was extracted with ether, dried with $MgSO_4$, filtered, and evaporated. The crude product was purified by column chromatography (ether/acetyl acetate mixture, v/v = 5:1) to give 0.54 g of **1o** as a colorless solid in 52% yield. M.p. 64–65 °C; Anal. Calcd for $C_{27}H_{20}F_6O_2S$ (%): C, 62.06; H, 3.86. Found C, 62.01; H, 3.73; ^{1}H NMR(400 MHz, $CDCl_3$, TMS): δ 0.98 (t, 3H, $J = 7.5$ Hz, $-CH_3$), 1.87 (s, 3H, $-CH_3$), 2.43–2.48 (m, 2H, $-CH_2$), 3.82 (s, 3H, $-OCH_3$), 6.90 (d, 2H, $J = 8.4$ Hz, phenyl–H) 7.17 (s, 1H, thienyl–H), 7.21 (d, 1H, $J = 8.0$ Hz, phenyl–H), 7.28 (t, 1H, $J = 8.0$ Hz, phenyl–H), 7.44 (t, 3H, $J = 8.4$ Hz, phenyl–H), 7.51 (d, 1H, $J = 7.6$ Hz, phenyl–H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 11.34, 14.64, 20.84, 55.38, 104.35, 111.09, 114.24, 114.42, 120.13, 121.42, 121.84, 123.56, 124.49, 125.33, 126.04, 126.22, 126.48, 126.79, 126.99, 140.36, 142.30, 154.29, 159.58, 160.40; IR (ν, KBr, cm^{-1}): 747, 803, 826, 893, 986, 1107, 1249, 1339, 1452, 1476, 1516, 1555, 1573, 1638, 1657, 2839, 2958.

*2.2.10. 1-(2-ethyl-3-benzofuranyl)-2-[2-methyl-5-(4-methylphenyl)-3-thienyl]perfluorocyclopentene (**2o**)*

Diarylethene **2o** was prepared by a method similar to that used for **1o** and 0.38 g of **2o** obtained as a colorless solid in 38% yield. M.p. 95–96 °C; Anal. Calcd for $C_{27}H_{20}F_6OS$ (%): C, 64.03; H, 3.98. Found C, 63.99; H, 3.85; ^{1}H NMR(400 MHz, CDCl$_3$, TMS): δ 0.97 (t, 3H, J = 7.5 Hz, −CH$_3$), 1.87 (s, 3H, −CH$_3$), 2.37 (s, 3H, −CH$_3$), 2.41–2.46 (m, 2H, −CH$_2$), 7.19 (d, 2H, J = 7.8 Hz, phenyl−H), 7.23 (s, 1H, thienyl−H), 7.25 (d, 1H, J = 8.0 Hz, phenyl−H), 7.29 (d, 1H, J = 8.0 Hz, phenyl−H), 7.42 (t, 3H, J = 8.2 Hz, phenyl−H), 7.51 (d, 1H, J = 7.6 Hz, phenyl−H); ^{13}C NMR (100 MHz, CDCl$_3$, TMS): δ 11.34, 14.71, 20.82, 21.18, 104.37, 111.09, 120.12, 121.91, 123.56, 124.48, 125.32, 125.56, 126.39, 129.65, 130.57, 137.92, 140.80, 142.46, 154.24, 160.39; IR (ν, KBr, cm^{-1}): 747, 798, 815, 836, 892, 990, 1043, 1073, 1121, 1143, 1191, 1270, 1345, 1400, 1595, 1639, 3122.

*2.2.11. 1-(2-ethyl-3-benzofuranyl)-2-(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene (**3o**)*

Diarylethene **3o** was prepared by a method similar to that used for **1o** and 0.35 g of **3o** obtained as a colorless solid in 36% yield. M.p. 90–91 °C. Anal. Calcd for $C_{26}H_{18}F_6OS$ (%): C, 63.41; H, 3.68. Found C, 63.37; H, 3.62; ^{1}H NMR(400 MHz, CDCl$_3$, TMS): δ 0.98 (t, 3H, J = 7.4 Hz, −CH$_3$), 1.89 (s, 3H, −CH$_3$), 2.39–2.47 (m, 2H, −CH$_2$), 7.24 (s, 1H, thienyl−H), 7.30 (t, 3H, J = 8.0 Hz, phenyl−H), 7.38 (t, 2H, J = 7.4 Hz, phenyl−H), 7.44 (d, 1H, J = 8.0 Hz, phenyl−H), 7.52 (d, 3H, J = 7.2 Hz, phenyl−H); ^{13}C NMR (100 MHz, CDCl$_3$, TMS): δ 11.35, 14.72, 20.83, 104.35, 111.09, 120.10, 122.49, 123.57, 124.50, 125.66, 126.40, 127.92, 128.99, 133.35, 141.32, 142.33, 154.26, 160.38; IR (ν, KBr, cm^{-1}): 751, 803, 839, 891, 983, 1074, 1126, 1195, 1272, 1337, 1436, 1474, 1552, 1630, 1647, 2932.

*2.2.12. 1-(2-ethyl-3-benzofuranyl)-2-[2-methyl-5-(4-fluorophenyl)-3-thienyl]perfluorocyclopentene (**4o**)*

Diarylethene **4o** was prepared by a method similar to that used for **1o** and 0.65 g of **4o** obtained as a colorless solid in 64% yield. M.p. 102–103 °C; Anal. Calcd for $C_{26}H_{17}F_7OS$ (%): C, 61.18; H, 3.36. Found C, 61.11; H, 3.30; ^{1}H NMR(400 MHz, CDCl$_3$, TMS): δ 0.98 (t, 3H, J = 7.4 Hz, −CH$_3$), 1.88 (s, 3H, −CH$_3$), 2.41–2.47 (m, 2H, −CH$_2$), 7.08 (t, 2H, J = 8.0 Hz, phenyl−H), 7.25 (d, 2H, J = 6.7 Hz, phenyl−H), 7.29 (s, 1H, thienyl−H), 7.44 (d, 1H, J = 8.0 Hz, phenyl−H), 7.45–7.50 (m, 3H, phenyl−H); ^{13}C NMR (100 MHz, CDCl$_3$, TMS): δ 11.37, 14.69, 20.85, 104.35, 111.13, 115.89, 116.11, 116.28, 120.10, 122.52, 123.60, 124.56, 125.50, 126.41, 127.38, 127.46, 129.66, 141.27, 141.33, 154.29, 160.38, 161.33, 163.79; IR (ν, KBr, cm^{-1}): 747, 807, 895, 980, 1066, 1124, 1157, 1190, 1230, 1254, 1275, 1338, 1402, 1468, 1512, 1588, 1629, 1681, 2980.

*2.2.13. 1-(2-ethyl-3-benzofuranyl)-2-[2-methyl-5-(4-cyanophenyl)-3-thienyl]perfluorocyclopentene (**5o**)*

Diarylethene **5o** was prepared by a method similar to that used for **1o** and 0.23 g of **5o** obtained as a colorless solid in 22% yield. M.p. 120–121 °C; Anal. Calcd for $C_{27}H_{17}F_6NOS$ (%): Calcd C, 62.67; H, 3.31; N, 2.71. Found C, 62.62; H, 3.27; N, 2.68; ^{1}H NMR(400 MHz, CDCl$_3$, TMS): δ 1.00 (t, 3H, J = 7.6 Hz, −CH$_3$), 1.94 (s, 3H, −CH$_3$), 2.42–2.48 (m, 2H, −CH$_2$), 7.23 (t, 1H, J = 7.6 Hz, phenyl−H), 7.30 (t, 1H, J = 7.4 Hz, phenyl−H), 7.40 (s, 1H, thienyl−H), 7.44 (d, 1H, J = 8.4 Hz, phenyl−H), 7.48 (d, 1H, J = 7.6 Hz, phenyl−H), 7.59 (d, 2H, J = 8.4 Hz, phenyl−H), 7.65 (d, 2H, J = 8.4 Hz, phenyl−H); ^{13}C NMR (100 MHz, CDCl$_3$, TMS): δ 11.38, 14.82, 20.84, 104.18, 111.18, 118.54, 119.95, 119.99, 120.02, 123.66, 124.63, 124.66, 125.86, 125.99, 126.08, 126.29, 132.83, 137.49, 139.96, 143.55, 154.29, 160.35; IR (ν, KBr, cm^{-1}): 747, 805, 892, 977, 1123, 1194, 1276, 1401, 1567, 1509, 1591, 1629, 1684, 2224.

3. Results and discussion

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

Diarylethenes **1**–**5** exhibited typical absorption changes upon alternating irradiation with UV and visible light in both hexane and polymer matrix at room temperature due to the photochromic reaction. The exposure energy of UV light was determined to *ca.* 29 μw cm^{-2}. Fig. 3 shows the absorption spectral and color changes of diarylethenes **1**−**5** in hexane. For diarylethene **1**, the absorption maximum of the open-ring isomer **1o** was observed at 294 nm. Upon irradiation with 297 nm light, the colorless solution of **1o** turned to be magenta, in which the characteristic absorption maximum was observed at 542 nm arising from the closed-ring isomer **1c**. The photostationary state is achieved upon irradiation with UV light for 600 s. Upon visible light irradiation ($\lambda > 450$ nm) for 100 s, the magenta color was bleached indicating that **1c** returned to the initial state **1o**. Diarylethenes **2**–**5** also exhibited a diarylethenes-specific reversible photoisomerization, generating the closed-ring isomers **2c**–**5c** upon irradiation with UV light, which their absorption maxima were observed at 537, 535, 533, and 541 nm, respectively. In the photostationary state, the isosbestic points for diarylethenes **1**–**5** were observed at 313, 303, 297, 295, and 337 nm in hexane. For diarylethenes **2**-**5**, the irradiation time of achieving the photostationary state is 820 s for **2**, 730 s for **3**, 700 s for **4**, and 610 s for **5**, and the bleaching time is 90 s for **2**, 110 s for **3**, 95 s for **4**, and 85 s for **5**. When arrived at the photostationary state, the photoconversion ratios from the open-ring to the closed-ring isomers of diarylethenes **1**–**5** were analyzed by HPLC method, with the values were 92% for **1**, 88% for **2**, 80% for **3**, 83% for **4**, and 88% for **5**. The photochromic parameters of diarylethenes **1**–**5** are summarized in Table 1. Compared to the unsubstituted parent diarylethene **3**, the absorption maxima of diarylethenes bearing an electron-donating group (such as diarylethenes **1** and **2**) showed a red shift in both hexane and PMMA films. Although the electron-withdrawing fluorine atom (diarylethene **4**) exhibited a shorter wavelength, the strong electron-withdrawing cyano group shifted the absorption maxima of diarylethene **5** to a longer wavelength, compared with diarylethene **3**. As shown in Table 1, the absorption maxima of the closed-ring isomers **1c**–**5c** were appeared at the region 533–542 nm in hexane, which were shorter than that of diarylethenes with the similar molecular skeleton including pyrazole [42], pyrrole [43–45], pyridine [46], or biphenyl moiety [47], but much longer than that of similar skeleton diarylethenes bearing a thiazole or isoxazole moiety [48,49]. This indicated that the benzofuran moiety could be effective to shift the absorption maximum of diarylethene to a shorter wavelength direction, but its action was less than thiazole or isoxazole ring. For the open-ring isomers **1o**–**5o**, the molar absorption coefficients increased notably when going from electron-donating to electron-withdrawing groups, but an inverse trend appeared for the closed-ring isomers **1c**–**5c**. The cyclization and cycloreversion quantum yields of the unsubstituted parent diarylethene **3** are 0.38 and 0.079, respectively. Replacing the hydrogen atom at the *para*-position of the terminal benzene ring with an electron-donating substituent (methoxy or methyl group), the cyclization quantum yields increased and the cycloreversion quantum yields decreased notably with the increase in electron-donating ability; an inverse changing trend appeared when replacing with an electron-withdrawing group (fluorine or cyano group) at the same position. As a result, diarylethene **1** has the biggest cyclization quantum yield and the smallest cycloreversion quantum yield, and

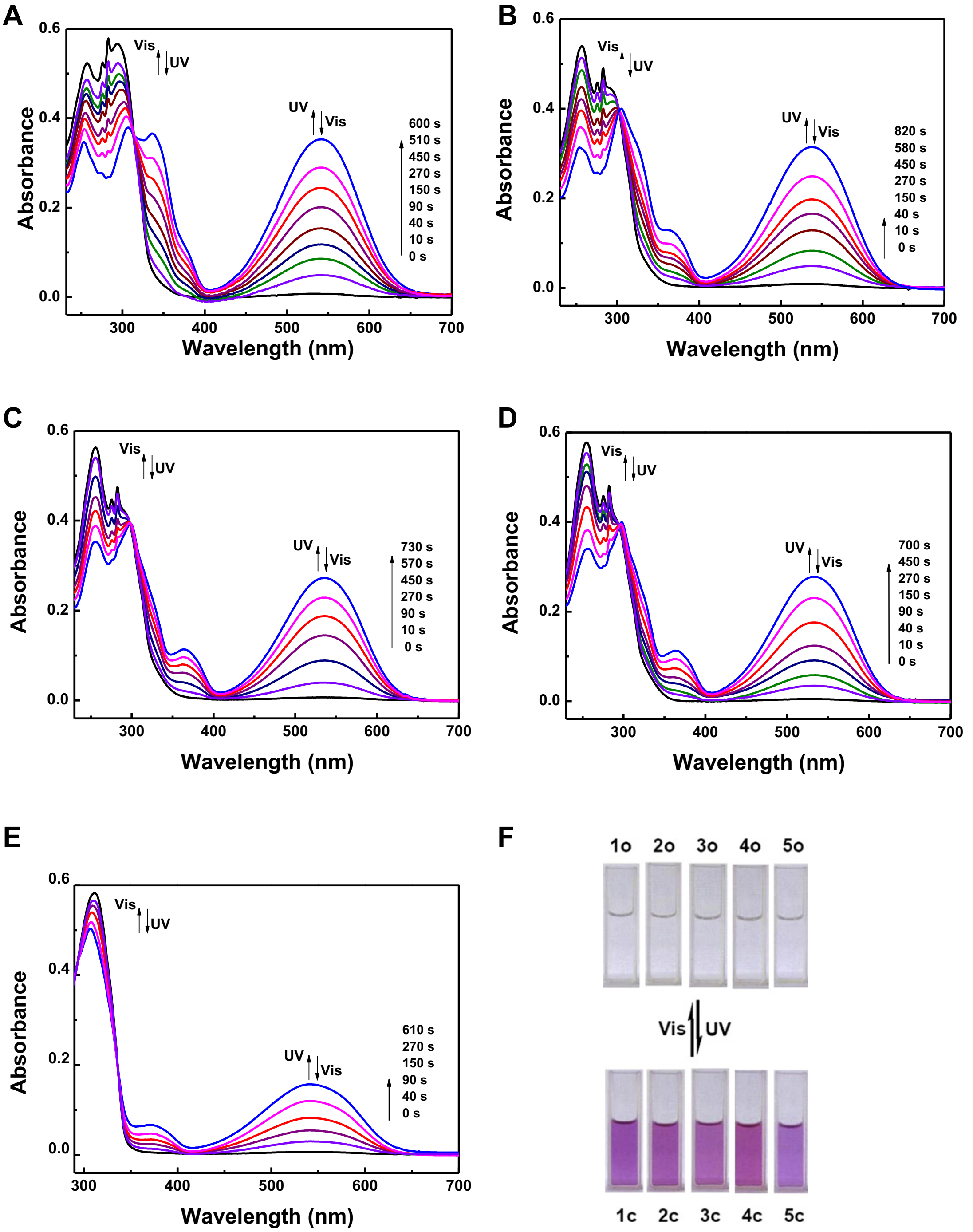

Fig. 3. Absorption spectra and color changes of diarylethenes **1**–**5** by photoirradiation in hexane ($C = 2.0 \times 10^{-5}$ mol L^{-1}) at room temperature: (A) spectral changes for **1**, (B) spectral changes for **2**, (C) spectral changes for **3**, (D) spectral changes for **4**, (E) spectral changes for **5**, (F) color changes for **1**–**5**.

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

Compound	$\lambda_{o,max}$/nm[a] (ε/L mol^{-1} cm^{-1})		$\lambda_{c,max}$/nm[b] (ε/L mol^{-1} cm^{-1})		Φ[c]		Conversion at PSS in hexane
	Hexane	PMMA film	Hexane	PMMA film	Φ_{o-c}	Φ_{c-o}	
1	294 (2.61×10^4)	298	542 (1.91×10^4)	553	0.46	0.053	92%
2	257 (2.70×10^4)	257	537 (1.78×10^4)	547	0.42	0.062	88%
3	256 (2.81×10^4)	257	535 (1.71×10^4)	544	0.38	0.079	80%
4	255 (2.89×10^4)	257	533 (1.69×10^4)	541	0.30	0.089	83%
5	311 (2.91×10^4)	313	541 (1.00×10^4)	552	0.28	0.11	88%

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

diarylethene **5** has the smallest cyclization quantum yield and the biggest cycloreversion quantum yield. The result indicated that the substituent at the *para*-position of the terminal benzene ring plays an important role during the process of the photochromic reaction for these diarylethenes.

Just as in hexane, diarylethenes **1**–**5** also showed photochromism in amorphous PMMA films. Their spectral and color changes are shown in Fig. 4. Upon irradiation 313 nm light, the colors of diarylethenes **1**–**5** in PMMA films changed from colorless to magenta, with the appearance of a new broad absorption band centered at 553, 547, 544, 541 and 552 nm, respectively. This band was assigned to the formation of the closed-ring isomers **1c**–**5c**. In PMMA films, the photostationary equilibriums of diarylethenes **1**–**5** are achieved by irradiation with UV light for 960, 1050, 1000, 940, and 780 s, respectively. All colored diarylethene/PMMA films can revert to colorless upon irradiation with visible light ($\lambda > 450$ nm). The bleaching irradiation time is 120 s for **1**, 135 s for **2**, 125 s for **3**, 115 s for **4**, and 100 s for **5**. As has been observed for most of the reported diarylethenes [16,50,51], the absorption maxima of the closed-ring isomers **1c**–**5c** are found at longer wavelengths in PMMA films than those in hexane solution. The red shift values of the absorption maxima for the closed-ring isomers are 11 nm for **1c**, 10 nm for **2c**, 9 nm for **3c**, 8 nm for **4c** and 11 nm for **5c**, respectively. The red shift phenomena may be ascribed to the polar effect of the polymer matrix in the solid state [52,53].

The thermal stability of diarylethene is an indispensable property for the application to optical memory media [36], and it is mainly dependent on the aromatic stabilization energy of the aryl

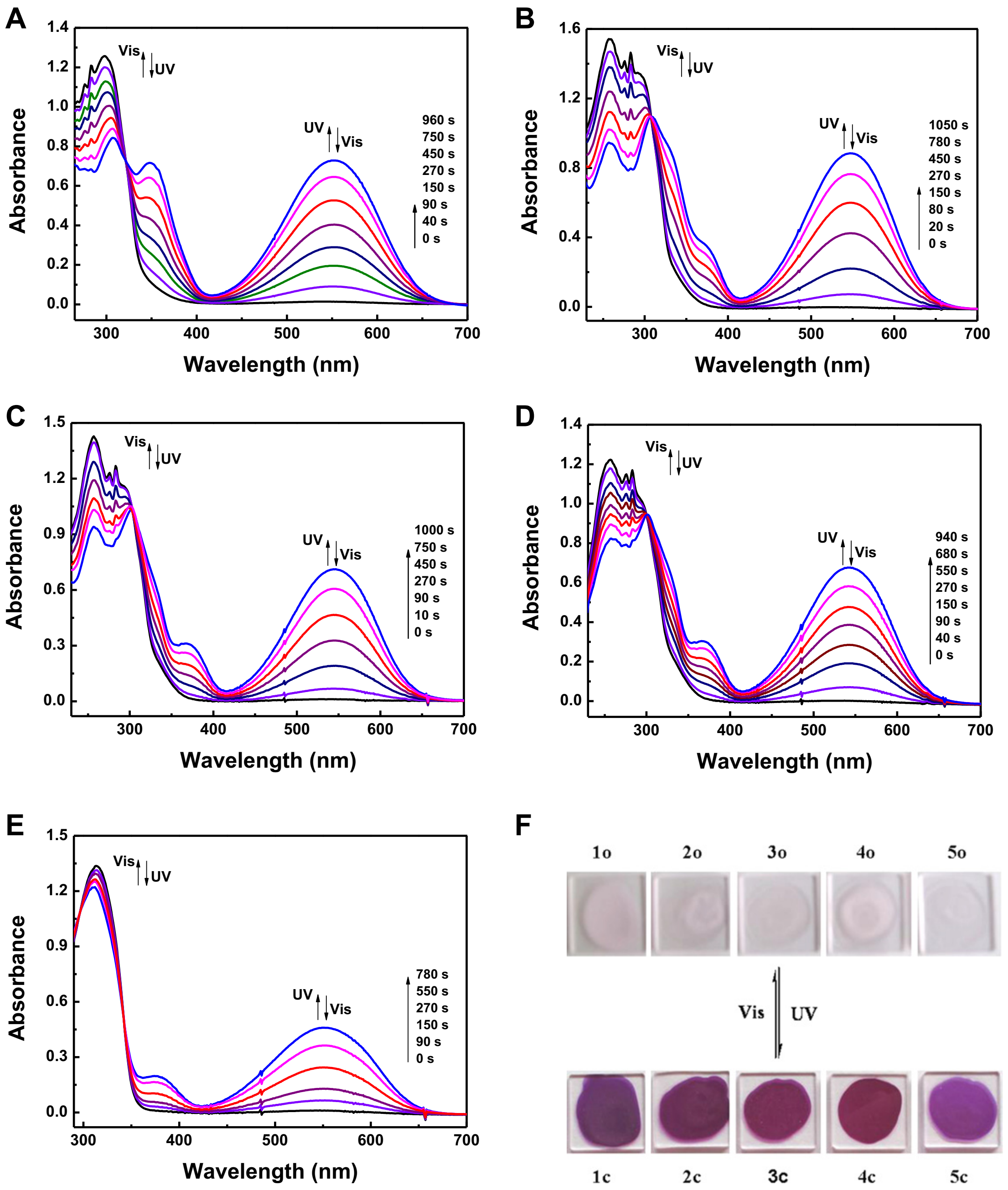

Fig. 4. Absorption spectra and color changes of diarylethenes **1**–**5** by photoirradiation in PMMA films (10%, w/w) at room temperature: (A) spectral changes for **1**, (B) spectral changes for **2**, (C) spectral changes for **3**, (D) spectral changes for **4**, (E) spectral changes for **5**, (F) color changes for **1**–**5**.

moiety [19]. The thermal stabilities of the open- and closed-ring isomers of diarylethenes **1**–**5** were examined in hexane both at room temperature and at 341 K. Storing these solutions in the dark and then exposing them to air for more than 30 days at room temperature, no changes in the UV/Vis spectra of diarylethenes **1**–**5** were observed. Moreover, no decomposition was detected when the five compounds were exposed to air for more than a half year. At 341 K, diarylethenes **1**–**5** still showed good thermal stabilities for more than 50 h. The result suggests that these diarylethene derivatives have notable thermally irreversible photochromic behaviors, which is similar the bis(3-benzothienyl)perfluorocyclopentene derivatives that undergo thermally irreversible photochromic reactions [18]. The fatigue resistances of diarylethenes **1**–**5** were examined both in hexane and in PMMA films in air at room temperature, as shown in Fig. 5. In hexane, the coloration and decoloration cycles of diarylethenes **1**–**5** can be repeated at least 20 times with almost no photo-degradation. After 50 repeat cycles, only 2% of **1c**, 2% of **2c**, 5% of **3c**, 8% of **4c**, and 2% of **5c** were destroyed at the same condition. Similarly, diarylethenes **1**–**5** showed remarkable fatigue resistance in PMMA films. After 200 repeated cycles, they still showed notable photochromism with only *ca.* 19% degradation of **1c**, 14% of **2c**, 16% of **3c**, 14% of **4c**, and 14% of **5c**.

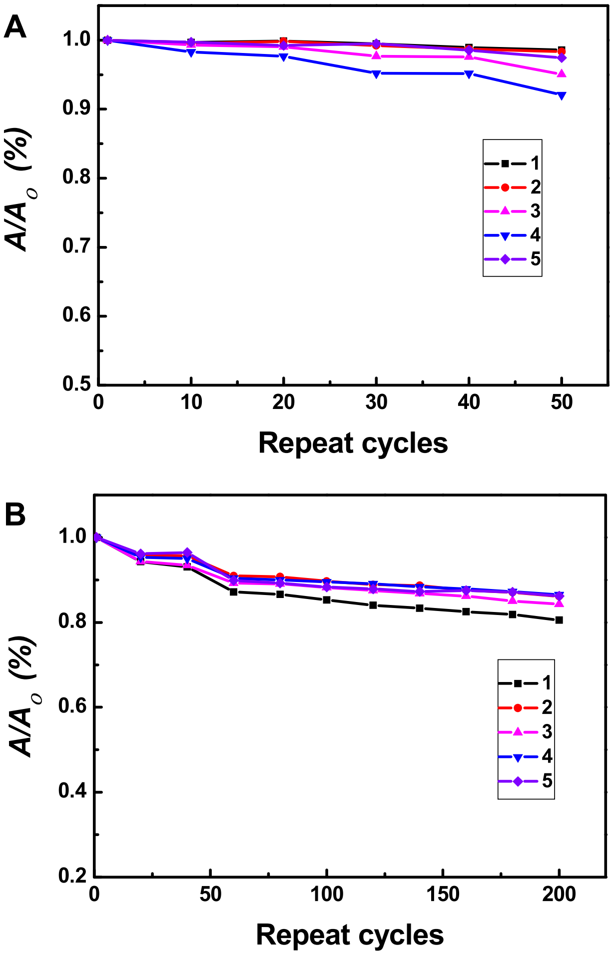

Fig. 5. Fatigue resistance of diarylethenes **1**–**5** in hexane and in PMMA films in air atmosphere at room temperature: (A) in hexane, (B) in PMMA films. Initial absorbance of the sample was fixed to 1.0.

3.2. *Photochromic reactions in the crystalline phase*

It is well known that a diarylethene has two conformations with the two heterocyclic rings in C_2 symmetry (*anti*-parallel conformation) and in mirror symmetry (parallel conformation). Only *anti*-parallel conformation can undergo effective photocyclization reaction by a conrotatory mechanism, while the parallel conformation is photochemically inactive [6]. Although many diarylethene crystals with *anti*-parallel conformation have been so far reported, diarylethene crystals with parallel conformation are very rare [11,54,55]. To know better the relation between the conformation and the photochromic behaviors of photochromic diarylethenes in the crystalline phase, gaining diarylethene crystals with the two structural conformations is very necessary. Fortunately, two single crystals of diarylethenes **3o** and **5o** with different conformation were obtained by slow evaporation of a hexane solution and their final structural confirmations were provided by X-ray crystallographic analysis in this work. The ORTEP drawings of the single crystals are shown in Fig. 6 and the X-ray crystallographic analysis data are listed in Table 2. For diarylethene **3o**, the molecule crystallizes with an *anti*-parallel conformation in the crystalline phase, which can be expected to undergo photocyclization reaction. The dihedral angles between the hexafluorocyclopentene ring and the two heteroaryl rings are 62.9(5)° for O1/C17-C24 and 44.8(5)° for S1/C6-C9, and that between the thiophene ring and the linked benzene ring is 12.1(5)°. The distance between the two reactive C atoms (C6 and C17) is 3.775 Å. For diarylethene **5o**, the molecule crystallizes with a parallel conformation in the crystalline phase, which cannot possibly undergo photocyclization reaction. The dihedral angles between the hexafluorocyclopentene ring and the two heteroaryl rings are 58.3(4)° for O1/C18–C25 and 50.5(4)° for S1/C6–C9, and that between the thiophene ring and the linked benzene ring is 27.0(4)°. The distance between the two reactive C atoms (C9 and C18) is 4.200 Å. 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 [56–58], the two crystals should exhibit different photochemical activity by photoirradiation in the single crystalline phase. In fact, crystal **3o** showed good photochromism, in accordance with the expected ring closure, to form **3c** upon irradiation with UV light, but crystal **5o** didn't show any photochromism upon irradiation with UV light in the crystalline phase. The color changes of diarylethenes **3o** and **5o** upon photoirradiation are shown in Fig. 6C. Upon irradiation with 254 nm light, the colorless crystal of **3o** turned magenta quickly. When the colored crystal was dissolved in hexane, an intense absorption maximum was observed at the same wavelength as that of its ring-closed isomer **3c** in solution. Alternatively, the magenta crystal returned to colorless upon irradiation with the appropriate visible light ($\lambda > 450$ nm). However, crystal **5o** didn't undergo photochromic reaction in the single crystalline phase, which was verified by the fact that irradiating crystal **5o** with UV light for 2 h resulted in no observable color change. When the crystal was dissolved in hexane, the solution remained colorless and the absorption spectrum was the same as that of diarylethene **5o** in solution. Furthermore, diarylethene crystal **3o** exhibited excellent fatigue resistance greater than 100 cyclization/cycloreversion repeated cycles and its closed-ring isomer remained stable for more than 90 days in the dark at room temperature. So, it will be good candidates for the construction of certain optoelectronic devices [59].

3.3. *Fluorescence of diarylethenes **1**–**5***

The fluorescence spectra of diarylethenes **1**–**5** in both hexane and PMMA amorphous films at room temperature are illustrated in

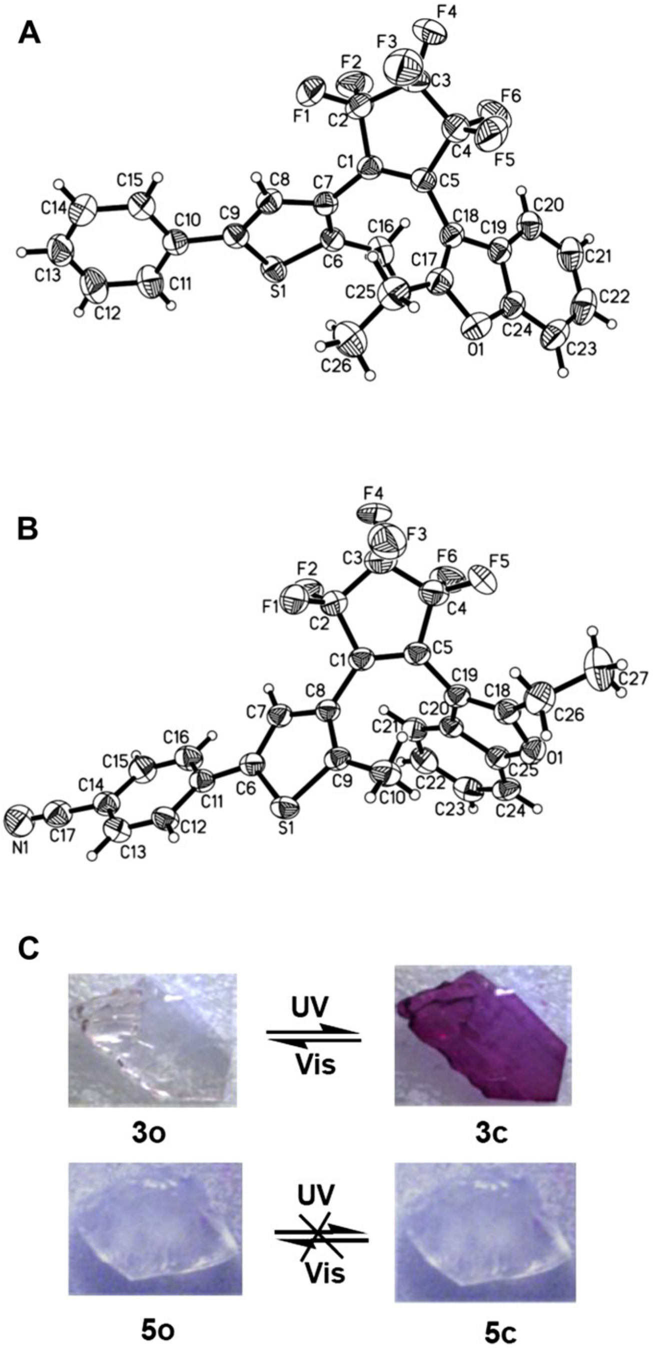

Fig. 6. ORTEP drawings of crystals **3o** and **5o** and their color changes by photoirradiation in the single crystalline phase: (A) ORTEP drawing of **3o**, (B) ORTEP drawing of **5o**, (C) color changes for crystals **3** and **5**.

Fig. 7. When monitored at 297 nm, the fluorescent emission peaks of **1o**, **2o**, **3o**, **4o**, and **5o** were observed at 438, 423, 413, 417 and 401 nm in hexane. Their emission peaks in PMMA films were observed at 423, 425, 419, 420 and 382 nm when monitored at 332 nm. Compared with those in hexane, the emission peaks of diarylethenes **2o, 3o,** and **4o** showed a minor bathochromic shift in PMMA film, which is well consistent with those of their maxima absorption wavelengths. The red shift values of their emission peaks are 2 nm for **2**, 6 nm for **3**, and 3 nm for **4**, respectively. But for diarylethenes **1o** and **5o**, their emission peaks showed a remarkable hypochromic shift in PMMA films with values of 15 nm for **1** and 20 nm for **5**, respectively. Among compounds **1o**–**5o,** the emission peak of **1o** is the longest and that of **5o** is shortest; while the emission intensity of **1o** is the smallest and that of **5o** is the biggest in both hexane and a PMMA film. This indicated that the

Table 2
Crystal data for diarylethenes **3o** and **5o**.

	Compound	
	3o	5o
Formula	$C_{26} H_{18} F_6 O S$	$C_{27} H_{17} F_6 N O S$
Formula weight	492.46	517.48
Temperature	296(2)	296(2)
Crystal system	Orthorhombic	Monoclinic
Space group	Pbca	P2(1)/c
Unit cell dimensions*a* (Å)	10.3270(14)	10.806(5)
b (Å)	19.115(3)	21.700(10)
c (Å)	23.068(3)	10.203(5)
α (o)	90.00	90.00
β (o)	90.00	96.485(6)
γ (o)	90.00	90.00
Volume (Å^3)	4553.4(11)	2377.2(18)
Z	8	4
Density (calcd.) (g/cm^3)	1.437	1.446
Goodness-of-fit on F^2	1.016	1.017
Final R_1[I > 2s(I)]	0.0514	0.0634
wR_2[I > 2s(I)]	0.1130	0.1549
R_1 (all data)	0.0924	0.1345
wR_2 (all data)	0.1354	0.1988

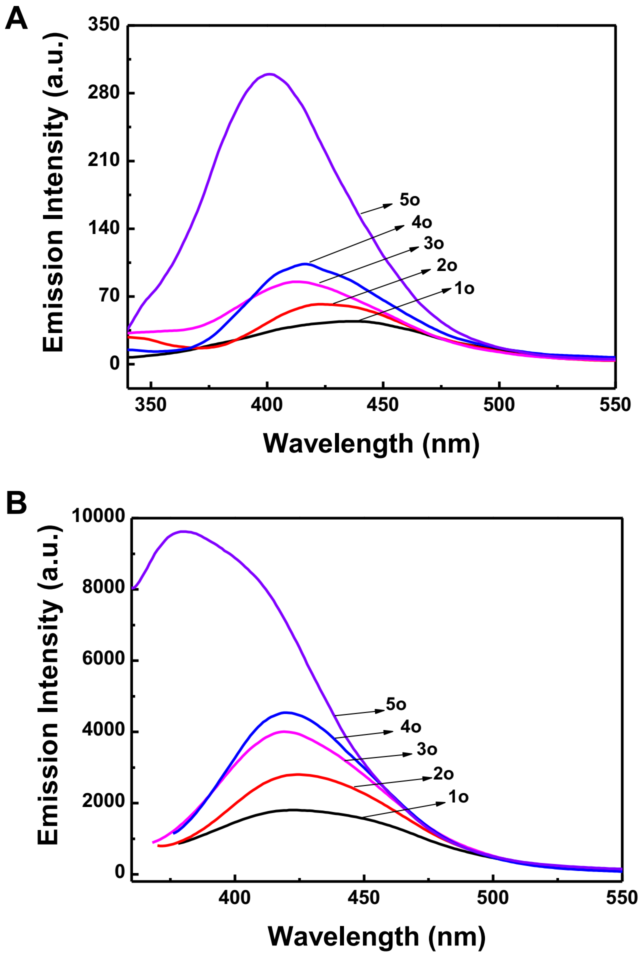

Fig. 7. Fluorescence emission spectra of diarylethenes **1**–**5** both in hexane solution ($C = 2.0 \times 10^{-5}$ mol L^{-1}) and in PMMA films (10%, w/w) at room temperature; (A) emission spectra in hexane, excited at 297 nm; (B) emission spectra in PMMA films, excited at 332 nm.

electron-donating group could be effective to shift the emission peak to a longer wavelength and to decrease the emission intensity of diarylethenes bearing a benzofuran moiety, but the electron-withdrawing group functioned as an inverse action. The result is quite different from that of diarylethenes bearing a pyrrole or thiazole moiety [43,48].

As has been observed for most of the reported diarylethenes [60–63], diarylethenes **1**–**5** exhibited an evident fluorescent switch along with the photochromism from open-ring isomers to closed-ring isomers by photoirradiation in both solution and PMMA films. When irradiated by UV light with the irradiating time of several hundred seconds, the photocyclization reaction was carried out and the non-fluorescent closed-ring isomers of these compounds were produced leading to the decrease of their emission intensity. The back irradiation by appropriate wavelength visible light regenerated their open-ring isomers **1o**–**5o** and recovered the original emission intensity. During the process of photoisomerization, diarylethene **1** exhibited changes in its fluorescence in hexane and in a PMMA film as shown in Fig. 8. Upon irradiation with UV light, the emission intensity of diarylethene **1** decreased because of the formation of its non-fluorescent closed-ring isomer **1c** by photocyclization. When arrived at the photostationary state, its emission intensity quenched to ca. 39% in hexane and 20% in a PMMA film, respectively. Back irradiation of the appropriate visible light regenerated the open-ring isomer **1o** and duplicated its original emission spectrum. The periodic cycles can be repeated greater than 50 times with almost no attenuation of fluorescent intensity. Similarly, diarylethenes **2**–**5** also functioned as a notable fluorescent switch upon photoirradiation both in hexane and in PMMA films. In the photostationary state, their emission intensities quenched to *ca.* 24% for **2**, 36% for **3**, 23% for **4,** and 24% for **5** in solution and *ca.* 20% for **2**, 15% for **3**, 13% for **4**, and 57% for **5**, respectively. Except for diarylethene **5**, the fluorescent modulation efficiencies of diarylethenes **1**–**4** in PMMA films were much bigger than those in hexane. For example, the fluorescent modulation efficiency of diarylethene **1** in a PMMA film was increased about 19% more than that in hexane. Among the five diarylethene derivatives, diarylethene **4** exhibited the biggest fluorescent modulation efficiency both in solution and in a PMMA film, suggesting that it is the most promising candidate for application to the fluorescent switchable devices [64–66].

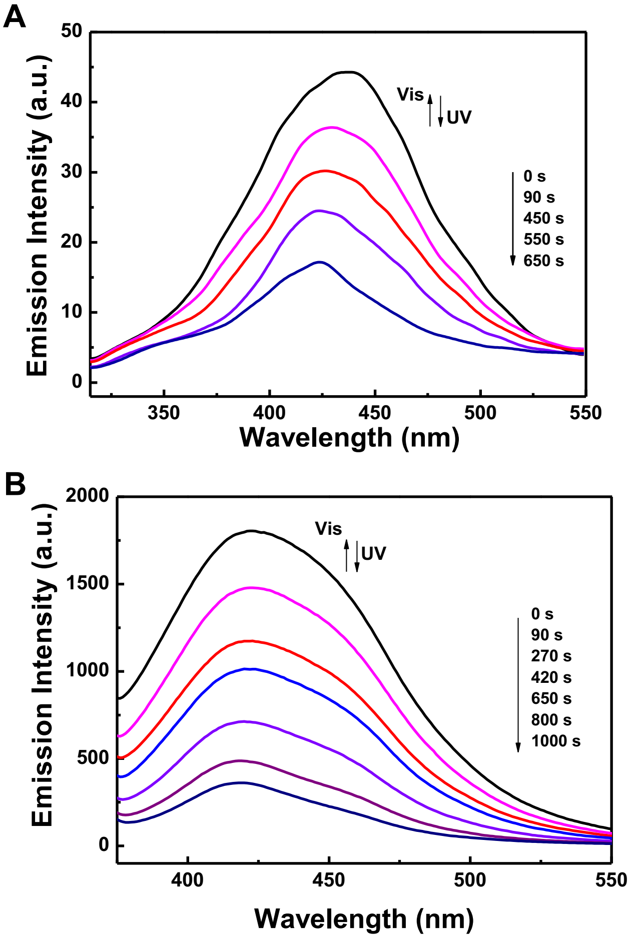

Fig. 8. Emission intensity changes of diarylethene **1** in hexane ($C = 2.0 \times 10^{-5}$ mol L^{-1}) and in a PMMA film (10%, w/w) upon irradiation with UV light at room temperature: (A) in hexane (excited at 297 nm), (B) in a PMMA film (excited at 332 nm).

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

The electrochemical properties of diarylethenes can be used for molecular switching and also can be potentially applied to molecular-scale electronic switches [67]. The electrochemical property of diarylethenes has attracted much attention [68–71]. Herein, the electrochemical properties of **1**–**5** were tested by cyclic voltammetry (CV) methods under the same experimental conditions. The CV curves of diarylethenes **1**–**5** are shown in Fig. 9. The onset potentials (E_{onset}) of oxidation and reduction for **1o** were initiated at +1.09 and −0.83 V, and those of **1c** were at +0.97 and −0.73 V, respectively. According to the reported method [72,73], the ionization potential and electron affinity of **1o** were calculated to be −5.89 and −3.97 eV, and those of **1c** were −5.77 and −4.07 eV, respectively. Based on the highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbital (LUMO) energy level, the band gap E_g (E_g = LUMO-HOMO) of **1o** and **1c** can be determined as 1.92 eV and 1.70 eV, respectively. Just as for diarylethene **1**, the corresponding data for diarylethenes **2**–**5** are summarized in Table 3. The oxidation of **2o**–**5o** is initiated at 1.46, 1.54, 1.34, and 1.77 V, and that of **2c**–**5c** is initiated at 1.05, 1.09, 1.11, and 1.18 V, respectively. The result indicates that the oxidation process for the open-ring isomers **1o**–**5o** occurs at higher potentials than in the corresponding closed-ring isomers **1c**–**5c**. This is because the longer conjugation length of the closed-ring isomers generally leads to a lower positive potential [16,74]. As shown in Table 3, all E_gs of the open-ring isomers **1o**–**5o** were higher than those of the closed-ring isomers **1c**–**5c**. Among these compounds, the E_g of **1c** was the smallest, which implies that the charge transfer of **1c** must be faster compared to that in others [75]. There are great differences amongst the electronic current and polarization curve shapes between the open-ring and closed-ring isomers of diarylethenes **1**–**5** at the scanned voltage region. The results suggest that different substituents have a significant effect on the electrochemical behaviors of these diarylethenes. It should be noted here that the absolute HOMO and LUMO levels in combination with the energy gap calculated by electrochemical data is still require further discussion [73].

Furthermore, electrochromism was observed with the closed-ring isomers **1c**–**5c** when the CV measurement was carried out. During the cyclic voltammetry experiments, the colorless solutions containing diarylethenes **1o**–**5o** around the platinum electrode changed to magenta. This indicates that the open-ring isomers **1o**–**5o** underwent oxidative cyclization to produce the closed-ring isomers **1c**–**5c**, respectively, although no marked changes in the absorption spectra were detected because of the too small amount of the closed-ring isomers **1c**–**5c** in solution. The colored solutions of these diarylethenes in photostationary state were obtained from the conversion of their respective open-ring isomers upon

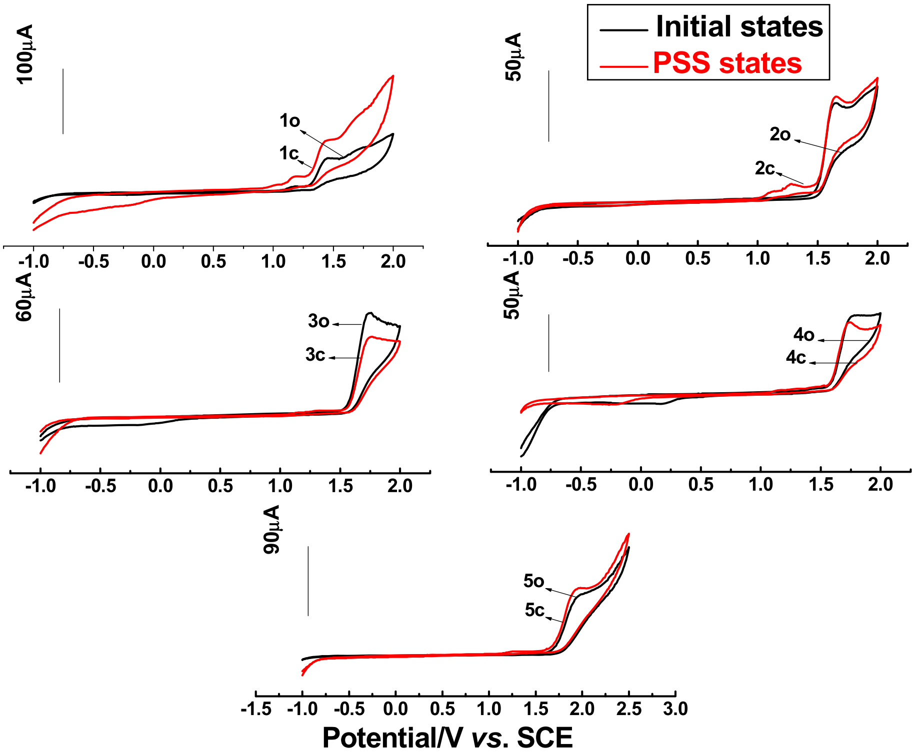

Fig. 9. Cyclic voltammetry of diarylethenes **1**–**5** in 0.1 mol/L ((TBA)BF_4) with a scan rate of 50 mV/s: (A) **1**, (B) **2**, (C) **3**, (D) **4**, (E) **5**.

Table 3
Electrochemical properties of diarylethenes **1**–**5**.

Compound	Oxidation		Reduction		Band gap
	E_{onset} (V)	IP (eV)	E_{onset} (V)	EA (eV)	E_g
1o	+1.09	−5.89	−0.83	−3.97	1.92
1c	+0.97	−5.77	−0.73	−4.07	1.70
2o	+1.46	−6.26	−0.73	−4.07	2.19
2c	+1.05	−5.85	−0.84	−3.96	1.89
3o	+1.54	−6.34	−0.87	−3.93	2.41
3c	+1.09	−5.89	−0.89	−3.91	1.98
4o	+1.34	−6.14	−0.72	−4.08	2.06
4c	+1.11	−5.91	−0.92	−3.88	2.03
5o	+1.77	−6.57	−0.93	−3.87	2.70
5c	+1.18	−5.98	−0.86	−3.94	2.04

irradiation with UV light, but they cannot be bleached during the electrolysis indicating that the closed-ring isomers **1c**–**5c** cannot undergo oxidative cycloreversion. The result suggests that the cation radicals of the closed-ring isomers **1c**–**5c** are more stable than those of the open-ring isomers **1o**–**5o** and the oxidative cyclization is thermodynamically allowed [76,77].

4. Conclusion

Five new unsymmetrical diarylethenes bearing a benzofuran moiety were synthesized and the substituent effects on their optical and electrochemical properties were studied. All of them exhibited remarkable photochromism and good fatigue resistance both in solution and in PMMA films. The results showed that the substituent at the *para*-position of the terminal benzene ring has a significant effect on the properties of these diarylethene derivatives, including photochromic characteristics, fluorescence and electrochemical properties. This work is useful for understanding the substituent effects on the optoelectronic properties of diarylethenes bearing a benzofuran moiety, which may shed some lights on the further application of photochromic diarylethene derivatives.

Acknowledgements

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References

[1] Kawata S, Kawata Y. Three-dimensional optical data storage using photochromic materials. Chemical Reviews 2000;100:1777–88.

[2] Tian H, Yang SJ. Recent progresses on diarylethene based photochromic switches. Chemical Reviews 2004;33:85–97.

[3] Matsuda K, Irie M. Diarylethene as a photo switching unit. Journal of Photochemistry and Photobiology C 2004;5:169–82.

[4] Yun C, You J, Kim J, Huh J, Kim E. Photochromic fluorescence switching from diarylethenes and its applications. Journal of Photochemistry and Photobiology C 2009;10:111–29.

[5] Tsujioka T, Irie M. Electrical functions of photochromic molecules. Journal of Photochemistry and Photobiology C 2010;11:1–14.

[6] Irie M. Diarylethenes for memories and switches. Chemical Reviews 2000; 100:1685–716.

[7] Yokoyama Y. Fulgides for memories and switches. Chemical Reviews 2000; 100:1717–39.

[8] Buchholtz F, Zelichenok A, Krongauz V. Synthesis of new photochromic polymers based on phenoxynaphthacenequinone. Macromolecules 1993;26: 906–10.

[9] Myles AJ, Branda NR. Controlling photoinduced electron transfer within a hydrogen-bonded porphyrin-phenoxynaphthacenequinone photochromic system. Journal of the American Chemical Society 2001;123:177–8.

[10] Li XC, Tian H. One-step synthesis and photochromic properties of a stable triangle terthiophene. Tetrahedron Letters 2005;46:5409–12.

[11] Morimoto M, Irie M. Photochromism of diarylethene single crystals: crystal structures and photochromic performance. Chemical Communications; 2005:3895–905.

[12] Giordano L, Jovin TM, Irie M, Jares-Erijman EA. Diheteroarylethenes as thermally stable photo-switchable acceptors in photochromic fluorescence resonance energy transfer (pcFRET). Journal of the American Chemical Society 2002;124:7481–9.

[13] Kaieda T, Kobatake S, Miyasaka H, Murakami M, Iwai N, Nagata Y, et al. Efficient photocyclization of dithienylethene dimer, trimer, and tetramer: quantum yield and reaction dynamics. Journal of the American Chemical Society 2002;124:2015–24.

[14] Miyasaka H, Murakami M, Itaya A, Guillaumont D, Nakamura S, Irie M. Multiphoton gated photochromic reaction in a diarylethene derivative. Journal of the American Chemical Society 2001;123:753–4.

[15] Morimitsu K, Shibata K, Kobatake S, Irie M. Dithienylethenes with a novel photochromic performance. The Journal of Organic Chemistry 2002;67:4574–8.

[16] Pu SZ, Yang TS, Xu JK, Shen L, Li GZ, Xiao Q, et al. Syntheses and optoelectronic properties of four photochromic dithienylethenes. Tetrahedron 2005;61:6623–9.

[17] Kobatake S, Shibata K, Uchida K, Irie M. Photochromism of 1,2-bis(2-ethyl-5-phenyl-3-thienyl)perfluoro- cyclopentene. Conrotatory thermal cycloreversion of the closed-ring isomer. Journal of the American Chemical Society 2000;122:12135–41.

[18] Kobatake S, Yamada M, Yamada T, Irie M. Photochromism of 1,2-Bis(2-methyl-6-nitro-1-benzothiophen-3-yl)perfluorocyclopentene in a single-crystalline phase: dichroism of the closed-ring form isomer. Journal of the American Chemical Society 1999;121:8450–6.

[19] Nakamura S, Irie M. Thermally irreversible photochromic systems. A theoretical study. The Journal of Organic Chemistry 1988;53:6136–8.

[20] Uchida K, Matsuoka T, Sayo K, Iwamoto M, Hayashi S, Irie M. Thermally reversible photochromic systems. photochromism of a dipyrrolylperfluorocyclopentene. Chemistry Letters 1999;8:835–6.

[21] Yumoto K, Irie M, Matsuda K. Control of the photoreactivity of diarylethene derivatives by quaternarization of the pyridylethynyl group. Organic Letters 2008;10:2051–4.

[22] Bertarelli C, Bianco A, Amore FD, Gallazzi MC, Zerbi G. Effect of substitution on the change of refractive index in dithienylethenes: an ellipsometric study. Advanced Functional Materials 2004;14:357–63.

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

[24] Fan CB, Pu SZ, Liu G, Yang TS. Substituent position effect on the properties of isomeric photochromic diarylethenes bearing chlorine atoms. Journal of Photochemistry and Photobiology A: Chemistry 2008;194:333–43.

[25] Irie M, Sakemura K, Okinaka M, Uchida K. Photochromism of dithienylethenes with electron-donating substituents. The Journal of Organic Chemistry 1995;60:8305–9.

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

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

[28] Deng XD, Liebeskind LS. A contribution to the design of molecular switches: novel acid-mediated ring-closing–photochemical ring-opening of 2,3-bis(heteroaryl)quinones (heteroaryl = thienyl, furanyl, pyrrolyl). Journal of the American Chemical Society 2001;123:7703–4.

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

[31] Pu SZ, Li H, Liu G, Liu WJ. Synthesis and the effects of substitution upon photochromic diarylethenes bearing an isoxazole moiety. Tetrahedron Letters 2010;51:3575–9.

[32] Pu SZ, Liu G, Shen L, Xu JK. Efficient synthesis and properties of isomeric photochromic diarylethenes having a pyrrole unit. Organic Letters 2007;9:2139–44.

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

[34] Yagi K, Irie M. Fluorescence property of photochromic diarylethenes with indole groups. Bulletin of the Chemical Society of Japan 2003;76:1625–8.

[35] Yagi K, Soong CF, Irie M. Synthesis of fluorescentdiar- ylethenes having a 2, 4, 5-triphenylimidazole chromophore. The Journal of Organic Chemistry 2001;66:5419–23.

[36] Yamaguchi T, Irie M. Photochromism of bis(2-alkyl-1-benzofuran-3-yl)perfluorocyclopentene derivatives. The Journal of Organic Chemistry 2005;70:10323–8.

[37] Yamaguchi T, Nanba K, Ozeki T, Irie S, Irie M. Morphology change of diarylethene derivatives having benzofuran derivatives—photoinduced crystallization. Journal of Photochemistry and Photobiology A: Chemistry 2010;213:141–6.

[38] Yamaguchi T, Taniguchi W, Ozeki T, Irie S, Irie M. Photochromism of diarylethene oxazole derivatives in a single-crystalline phase. Journal of Photochemistry and Photobiology A: Chemistry 2009;207:282–7.

[39] Yamaguchi T, Takami S, Irie M. Photochromic properties of 1,2-bis(6-substitute-2-methyl-1-benzofuran-3-yl)ethene derivatives. Journal of Photochemistry and Photobiology A: Chemistry 2008;193:146–52.

[40] Yang TS, Pu SZ, Chen B, Xu JK. Electron-donating methoxyl group position effect on properties of diarylethene derivatives having a pyrazole unit. Canadian Journal of Chemistry 2007;85:12–20.

[41] Pu SZ, Liu G, Li GZ, Wang RJ, Yang TS. Synthesis, crystal structure and its optical and electrochemical properties of a new unsymmetrical diarylethene. Journal of Molecular Structure 2007;833:23–9.

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

[43] Liu G, Pu SZ, Wang XM, Liu WJ, Yang TS. Effects of substitution on the optoelectronic properties of photochromic diarylethenes bearing a pyrrole moiety. Dyes and Pigments 2011;90:71–81.

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

[45] Liu G, Pu SZ, Wang XM. Synthesis and the effect of substituent position upon unsymmetrical isomeric diarylethenes bearing a pyrrole unit. Journal of Photochemistry and Photobiology A: Chemistry 2010;214:230–40.

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

[47] Pu SZ, Miao WJ, Cui SQ, Liu G, Liu WJ. The synthesis of novel photochromic diarylethenes bearing a biphenyl moiety and the effects of substitution on their properties. Dyes and Pigments 2010;87:257–67.

[48] 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.

[49] Pu SZ, Li H, Liu G, Liu WJ, Cui SQ, Fan CB. Synthesis and the effects of substitution upon photochromic diarylethenes bearing an isoxazole moiety. Tetrahedron 2011;67:1438–47.

[50] Tsujioka T, Kume M, Irie M. Photochromic reactions of a diarylethene derivative in polymer matrices. Journal of Photochemistry and Photobiology A: Chemistry 1997;104:203–6.

[51] Fan CB, Pu SZ, Liu G, Yang TS. Substituent position effect on the properties of new unsymmetrical isomeric diarylethenes having a chlorine atom. Journal of Photochemistry and Photobiology A: Chemistry 2008;197:415–25.

[52] Kasatani K, Kambe S, Irie M. Photochromic reaction and fluorescence of dithienylethenes in the solid state. Journal of Photochemistry and Photobiology A: Chemistry 1999;122:11–5.

[53] Hoshino M, Ebisawa F, Yoshida T, Sukegawa K. Refractive index change in photochromic diarylethene derivatives and its application to optical switching devices. Journal of Photochemistry and Photobiology A: Chemistry 1997;105:75–81.

[54] Pu SZ, Zhang FS, Sun F, Wang RJ, Zhou XH, Chan SK. The allomorphism of a photochromic diarylethene. Tetrahedron Letters 2003;44:1011–4.

[55] Kobatake S, Irie M. Single-crystalline photochromism of a diarylethene dimer. Bulletin of the Chemical Society of Japan 2004;77:195–210.

[56] Kobatake S, Uchida K, Tsuchida E, Irie M. Single-crystalline photochromism of diarylethenes: reactivity–structure relationship. Chemical Communications; 2002:2804–5.

[57] Morimoto M, Irie M. Photochromic reactions of diarylethenes in single crystals with intermolecular O-H center dot center dot center dot N hydrogen-bonding networks. Chemistry -A European Journal 2006;12:4275–82.

[58] Ramamurthy V, Venkatesan K. Photochemical reactions of organic crystals. Chemical Reviews 1987;8:433–81.

[59] Morimoto M, Kobatake S, Irie M. Crystal engineering of photochromic diarylethene single. Chemical Recoveries 2004;4:23–38.

[60] Irie M, Fukaminato T, Sasaki T, Tamai N. A digital fluorecent molecular photoswitch. T. Nature 2002;420:759–60.

[61] Li YC, Tian H. High-content pendant photochromic copolymer with dithienylethene/fluorene 2:1 mole ratio. Chemical Physics 2005;206:1769–77.

[62] Tian H, Chen BZ, Tu HY, Müllen K. Novel bisthienylethene-based photochromic tetraazaporphyrin with photoregulating luminescence. Advanced Materials 2002;14:918–23.

[63] Xiao SZ, Yi T, Zhou YF, Zhao Q, Li FY, Huang CH. Multi-state molecular switches based on dithienylperfluorocyclopentene and imidazo [4,5-f] [1,10] phenanthroline. Tetrahedron 2006;62:10072–8.

[64] Tian H, Feng YL. Next step of photochromic switches? Journal of Materials Chemistry 2008;18:1617–22.

[65] Corredor CC, Huang ZL, Belfield KD. Two-photon 3D optical data storage via fluorescence modulation of an efficient fluorene dye by a photochromic diarylethene. Advanced Materials 2006;18:2910–4.

[66] Frigoli M, Mehl GH. Modulation of the absorption, fluorescence, and liquid-crystal properties of functionalised diarylethene derivatives. Chemistry -A European Journal 2004;10:5243–50.

[67] Bonifazi D, Scholl M, Song F, Echegoyen L, Accorsi G, Armaroli N, et al. Exceptional redox and photophysical properties of a triply fused diporphyrin–C_{60} conjugate: novel scaffolds for multicharge storage in molecular scale electronics. Angewandte Chemie 2003;42:4966–70.

[68] Browne WR, Jong JJD, Kuderna T, Walko M. Oxidative electrochemical switching in dithienylcyclopentenes, part 1: effect of electronic perturbation on the efficiency and direction of molecular switching. Chemistry -A European Journal 2005;11:6414–29.

[69] Browne WR, Jong JJD, Kudernac T, Walko M, Lucas LN. Oxidative electrochemical switching in dithienylcyclopentenes. part 2: effect of substitution and asymmetry on the efficiency and direction of molecular switching and redox stability. Chemistry -A European Journal 2005;11:6430–41.

[70] 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.

[71] Peters A, Branda NR. Electrochromism in photochromic dithienylcyclopentenes. Journal of Photochemistry and Photobiology A: Chemistry 2003; 125:3404–5.

[72] Tsai FC, Chang CC, Liu CL, Chen WC, Jenekhe SA. New thiophene-linked conjugated poly(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.

[74] Perrier A, Maurel F, Aubard J. Theoretical investigation of the substituent effect on the electronic and optical properties of photochromic dithienylethene derivatives. Journal of Photochemistry and Photobiology A: Chemistry 2007;189:167–76.

[75] Kim E, Kim M, Kim K. Diarylethenes with intramolecular donor–acceptor structures for photo-induced electrochemical change. Tetrahedron 2006;62: 6814–21.

[76] Moriyama Y, Matsuda K, Tanifuji N, Irie S, Irie M. Electrochemical cyclization/cycloreversion reactions of diarylethenes. Organic Letters 2005;7:3315–8.

[77] Xie N, Chen Y. Combination of fluorescent switch and electrochemical switch based on a photochromic diarylethene. New Journal of Chemistry 2006;30: 1595–8.