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The synthesis of novel photochromic diarylethenes bearing a biphenyl moiety and the effects of substitution on their properties

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ABSTRACT

A new class of diarylethene bearing a biphenyl moiety was synthesized and the effects of substitution on photochromism, fluorescence and electrochemical character, were investigated. Under alternating irradiation with UV and visible light, the compounds exhibited good photochromism and functioned as fluorescent photoswitches both in solution and in PMMA film. Electron-donating substituents shifted the λ_{max} of the diarylethenes to longer wavelengths and decreased their cyclization quantum yield, while electron-withdrawing substituents greatly increased both cyclization and cycloreversion quantum yield. In addition, cyclic voltammetry revealed that the substituents had a significant effect on the electrochemical behaviour of the diarylethene derivatives.

1. Introduction

Photochromic compounds can undergo a light-induced reversible transformation between two forms that differ not only in their absorption characteristics but also in terms of many physical and chemical characteristics, such as geometry (structure), refractive index and oxidation/reduction potential [1–6]. The photoresponsive character associated with this fascinating class of organic molecules offers a wealth of potential application in widely divergent areas, ranging from biomedical research to information technology [2,7,8]. Diarylethene derivatives, especially those with heterocyclic aryl groups, have recently received much attention as they have notable fatigue resistance, high thermal stability, rapid response and high reactivity in the solid state [2,9–11].

Currently, the design and synthesis of new photochromic compounds are an active area of research, with many reports on the synthesis and investigation of the properties of diarylethenes with heterocyclic aryl rings. Among diarylethenes hitherto reported, the majority of the heteroaryl compounds bear thiophene or benzothiophene rings [12–19], with only a few reports concerning other heteroaryl moieties, such as furan [20], thiazole [21,22], indole [23], benzofuran [24], pyrrole [25–27] and pyrazole [28]. A change in aryl group can result in significant modification of the photochromic properties of each type of diarylethene molecule. For example, diarylethenes comprising thiophene or benzothiophene moieties exhibit excellent thermal stability and outstanding fatigue resistance [2,9], whereas symmetrical diarylethenes with two pyrrole rings are thermally unstable and return to the open-ring isomer, even in the dark [26]. Moreover, Kawai et al. [29] reported triangular terthiophene derivatives that displayed reversible photochromic reactions of high cyclization quantum yield. Yamaguchi et al. [30] developed a novel type of 6π conjugated photochromic system that contained a bis(2,3′-benzothienyl) unit, which showed efficient photochromism and high thermal stability in the case of the colored isomers. Yokoyama et al. [31] and Branda et al. [32] synthesized independently a new class of photochromic compound based on a modified hexatriene skeleton. This novel molecular scaffold offers the chance to decorate photoresponsive systems with a wide range of functional groups without sacrificing photochromic behaviour.

Studies on the hexatriene backbone of diarylethenes are mainly confined to the five-membered heteroaryl moieties. In the case of six-membered, aryl ring moieties, only a few symmetrical diarylethene derivatives bearing two phenyl/naphthyl groups have been reported [33–35], the majority of which are thermally reversible with poor photochromism. Previous reports by the present authors have concerned a new class of photochromic diarylethene derivatives bearing both five-membered and six-membered moieties that show some novel characteristics which differ to diarylethenes

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containing five-membered aryl rings [36–38]. The design of a diarylethene molecule bearing both five-membered and six-membered groups prompted the synthesis of unsymmetrical diarylethene derivatives by the introduction of a biphenyl unit as one aryl moiety of the diarylethene skeleton. Compared with reported diarylethene derivatives, diarylethenes bearing a biphenyl unit have two distinct advantages insofar as, the greater the number of benzene rings the molecule contains, the easier it is to modify the molecular structure as the reactive sites of the benzene ring can be easily modified using different electron-donating/withdrawing substituents, thereby influencing the optoelectronic properties of the diarylethene derivatives. In addition, diarylethenes bearing a biphenyl unit also have a unique molecular skeleton compared to those reported bearing five-membered heteroaryl groups. As an aryl moiety, the biphenyl unit connected directly to the central ethene unit can efficiently modulate the extent of π-conjugation in the diarylethene between the open-ring and the closed-ring isomers. It was interesting to discover that in the biphenyl segment, the second phenyl participated in the π-conjugation of the open-ring isomer, but not in the closed-ring. As a result, the π-conjugation is delocalized from the biphenyl moiety to the ethene unit in the open-ring isomer while in the closed-ring isomer, the second phenyl is separated from the first one. This inevitably influences the optical and electrochemical properties of the corresponding diarylethene derivatives.

The purposes of this work were to develop a new class of diarylethenes bearing a biphenyl unit and to investigate substituent effects on optoelectronic properties. Accordingly, five new unsymmetrical diarylethenes with different substituents at the meta-position of the second phenyl ring of the biphenyl were prepared (**1o**–**5o** as shown in Fig. 1). Each of the diarylethenes showed good photochromism both in solution and in amorphous PMMA film; to the best of our knowledge, they are the first examples of this class of photochromic diarylethene derivatives bearing both biphenyl and thiophene moieties.

2. Experimental

2.1. General methods

Solvents were purified by distillation before use. Mass spectra were measured with an Agilent MS Trap VL spectrometer. Elemental analyses were determined with a PE CHN 2400 analyzer. 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 recorded on a Bruker Vertex-70 spectrometer. The absorption spectra were measured using an Agilent 8453 UV/VIS spectrophotometer. Photoirradiation was carried out using SHG-200 UV lamp, CX-21 ultraviolet fluorescence analysis cabinet, and BMH-250 visible lamp. The required wavelength was isolated by the use of the appropriate HB ML UV Narrow Bandpass Filters. The quantum yields were determined by comparing the reaction yields of these diarylethene compounds in hexane against 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene in hexane (with their respective absorption maxima visible light irradiation) [39]. Fluorescence spectra were measured using a Hitachi F-4500 fluorimeter. Electrochemical examinations were performed in a one-compartment cell by using a Model 263 potentiostat–galvanostat (EG&G Princeton Applied Research) under computer control at room temperature. Platinum electrodes (diameter 0.5 mm) served as working electrode and counter electrode. Platinum electrodes served as a quasi reference electrode and was calibrated using the ferrocene (F_c/F_c^+) redox couple which has a formal potential $E_{1/2} = +0.35$ V versus platinum wire. The typical electrolyte was acetonitrile (5 mL) containing 0.1 mol L^{-1} tetrabutylammonium tetrafluoroborate ($(TBA)BF_4$) and 4.0×10^{-3} mol L^{-1} dithienylethene. All solutions were deaerated by a dry argon stream and maintained at a slight argon overpressure during electrochemical experiments.

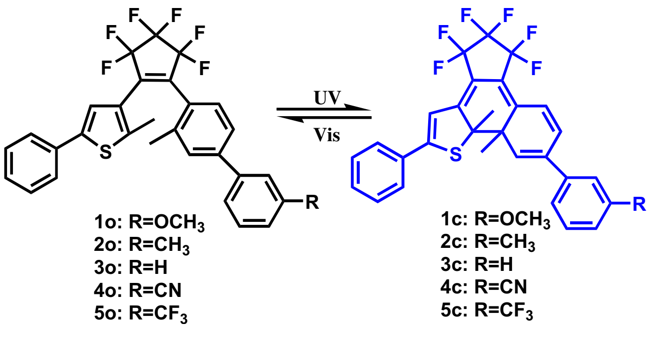

Fig. 1. Photochromism of diarylethenes **1**–**5**.

2.2. Synthesis of diarylethenes

The synthetic route used to obtain **1o**–**5o** is shown in Fig. 2. Five bromobenzene derivatives were firstly coupled with phenyl boronic acid (**6**) [40,41] by means of the Suzuki reaction to yield the biphenyl derivatives (**7a**–**7e**). Separately, 2-methyl-5-phenyl-3-thienyl-perfluorocyclpentene (**9**) was prepared from 2-methylthiophene according to the procedure described previously [32,42] and, finally, compounds **7a**–**7e** were separately lithiated and then coupled with compound **9** to give **1o**–**5o**, respectively.

2.2.1. 1-Bromo-2-methyl-4-(3-methoxylphenyl)benzene (*7a*)

7a was prepared by reacting 1-bromo-2-methyl-4-phenyl boronic acid (**6**) [40,41] (2.50 g; 11.6 mmol) with 3-bromoanisole (2.18 g, 11.6 mmol) in the presence of $Pd(PPh_3)_4$ (0.8 g, 0.53 mmol) and Na_2CO_3 (6.40 g, 60 mmol) in tetrahydrofuran (THF) (80 mL containing 10% water) for 16 h at 90 °C. The product **7a** was purified by column chromatography on SiO_2 using petroleum ether as an eluent and 2.22 g obtained as a colorless oil in 69.1% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.46 (s, 3H, $-CH_3$), 3.86 (s, 3H, $-CH_3$), 6.90 (d, 1H, $J = 8.0$ Hz, phenyl-H), 7.08 (s, 1H, phenyl-H), 7.13 (d, 1H, $J = 7.8$ Hz, phenyl-H), 7.25 (d, 1H, $J = 8.0$ Hz, phenyl-H), 7.35 (t, 1H, $J = 8.0$ Hz, phenyl-H), 7.43 (s, 1H, phenyl-H), 7.57 (d, 1H, $J = 8.0$ Hz, phenyl-H).

2.2.2. 1-Bromo-2-methyl-4-(3-methylphenyl)benzene (*7b*)

7b was prepared by a method similar to that used for **7a**. The crude product was purified by column chromatography on SiO_2 using petroleum ether as an eluent to give **7b** (2.13 g, 70.3%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.44 (s, 3H, $-CH_3$), 2.48 (s, 3H, $-CH_3$), 7.13 (t, 1H, $J = 7.0$ Hz, phenyl-H), 7.20 (d, 1H, $J = 8.0$ Hz, phenyl-H), 7.34–7.38 (m, 3H, phenyl-H), 7.47 (s, 1H, phenyl-H), 7.59 (d, 1H, $J = 8.0$ Hz, phenyl-H).

2.2.3. 1-Bromo-2-methyl-4-phenylbenzene (*7c*)

7c was prepared by a method similar to that used for **7a**. The crude product was purified by column chromatography on SiO_2 using petroleum ether as an eluent to give **7c** (1.96 g, 68.3%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.45 (s, 3H, $-CH_3$), 7.24 (d, 1H, $J = 8.0$ Hz, phenyl-H), 7.34 (t, 1H, $J = 7.2$ Hz, phenyl-H), 7.40–7.44 (m, 3H, phenyl-H), 7.53–7.58 (m, 3H, phenyl-H).

2.2.4. 1-Bromo-2-methyl-4-(3-cyanophenyl)benzene (*7d*)

7d was prepared by a method similar to that used for **7a**. The crude product was purified by column chromatography on SiO_2 using the mixture of petroleum ether and acetic ether ($v/v = 6/1$) as an eluent to give **7d** (2.17 g, 68.7%) as a white solid. M.p. 57–59 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.47 (s, 3H, $-CH_3$), 7.22 (d, 1H,

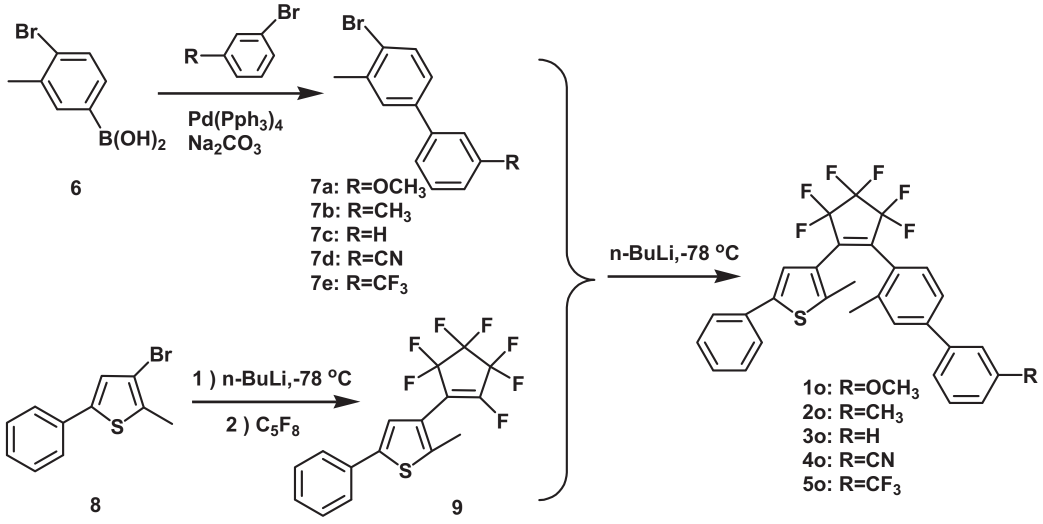

Fig. 2. Synthetic route for diarylethenes **1o**–**5o**.

J = 8.0 Hz, phenyl-H), 7.41 (s, 1H, phenyl-H), 7.54 (t, 1H, *J* = 7.6 Hz, phenyl-H), 7.59–7.64 (m, 2H, phenyl-H), 7.77 (d, 1H, *J* = 8.0 Hz, phenyl-H), 7.82 (s, 1H, phenyl-H).

2.2.5. *1-Bromo-2-methyl-4-(3-trifluoromethylphenyl)benzene (**7e**)*

7e was prepared by a method similar to that used for **7a**. The crude product was purified by column chromatography on SiO_2 using petroleum ether as an eluent to give **7e** (2.39 g, 65.5%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.51 (s, 3H, $-CH_3$), 7.29 (d, 1H, *J* = 8.0 Hz, phenyl-H), 7.47 (s, 1H, phenyl-H), 7.57 (t, 1H, *J* = 7.8 Hz, phenyl-H), 7.64 (d, 2H, *J* = 8.0 Hz, phenyl-H), 7.75 (d, 1H, *J* = 7.6 Hz, phenyl-H), 7.82 (s, 1H, phenyl-H).

2.2.6. *2-Methyl-5-phenyl-3-thienyl-perfluorocyclopentene (**9**)*

This compound was synthesized by the same method as that reported in Ref. [32]. To a stirred solution of 3-bromo-2-methyl-5-phenylthiophene (5.06 g, 20 mmol) in THF (80 mL) was added dropwise a 2.5 mol L^{-1} n-BuLi/hexane solution (8.8 mL, 22 mmol) at −78 °C under an argon atmosphere. Stirring was continued for 30 min at this low temperature. Perfluorocyclopentene (3.3 mL, 24 mmol) was then added to the reaction mixture at −78 °C, which was stirred for 2 h at this temperature; the reaction mixture was then warmed to room temperature spontaneously. Reaction was stopped by the addition of methanol (5 mL) and the product was extracted three times with ether (150 ml). The organic layer was washed with 1 M aqueous HCl and water respectively. 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 an eluent to give **9** (5.3 g, 72.6%) as a white solid. M.p. 35–37 °C [32]; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.51 (s, 3H, $-CH_3$), 7.25 (s, 1H, thienyl-H), 7.28 (t, 1H, *J* = 11.4 Hz, phenyl-H), 7.40 (t, 2H, *J* = 7.4 Hz, phenyl-H), 7.55 (d, 2H, *J* = 7.2 Hz, phenyl-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.69, 120.45, 122.28, 125.58, 125.63, 125.78, 128.10, 128.80, 129.05, 133.16, 142.59, 143.05. IR (KBr, ν, cm^{-1}): 689, 758, 835, 855, 894, 972, 1028, 1074, 1120, 1151, 1200, 1278, 1330, 1360, 1386, 1446, 1471, 1502, 1602, 1696, 2929, 3066.

2.2.7. *[1-(2-Methyl-5-phenyl-3-thienyl)-2-(2-methyl-4-(3-methoxylphenyl)-1-phenyl)]perfluorocyclopentene (**1o**)*

To stirred anhydrous THF (50 mL) containing **7a** (0.55 g, 2 mmol) was added, dropwise, a 2.5 mol L^{-1} n-BuLi solution (0.96 mL) at −78 °C under argon atmosphere. After the mixture has been stirred for 30 min at −78 °C, compound **9** (0.73 g, 2 mmol) in anhydrous THF (5 mL) was added. The reaction mixture was further stirred at −78 °C for 1 h and allowed to slowly warm to the room temperature. The reaction was stopped with distilled water. The product was extracted with ether, dried with $MgSO_4$, filtrated and evaporated in vacuo. The crude product was purified by column chromatography using petroleum ether as the eluent to give **1o** (0.34 g, 32%) as a yellow solid. M.p. 116–118 °C; MS m/z (M^+) 545.09; Calcd for $C_{30}H_{22}F_6OS$ (%): Calcd C, 66.17; H, 4.07. Found C, 66.51; H, 4.12; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.99 (s, 3H, $-CH_3$), 2.05 (s, 3H, $-CH_3$), 3.78 (s, 3H, $-OCH_3$), 6.87 (d, 1H, *J* = 8.0 Hz, phenyl-H), 7.09 (s, 1H, thienyl-H), 7.12 (d, 1H, *J* = 7.6 Hz, phenyl-H), 7.21–7.24 (m, 2H, phenyl-H), 7.28–7.32 (m, 3H, phenyl-H), 7.37 (s, 1H, phenyl-H), 7.44–7.49 (m, 4H, phenyl-H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 13.0, 19.0, 54.1, 111.8, 112.2, 118.4, 121.6, 123.8, 124.4, 124.5, 125.7, 126.8, 127.9, 128.5, 128.8, 132.3, 136.4, 140.1, 140.3, 141.0, 141.6, 159.0; IR (KBr, ν, cm^{-1}): 691, 756, 784, 834, 858, 893, 923, 990, 1065, 1164, 1222, 1271, 1401, 1453, 1615, 1667, 2839, 3036.

2.2.8. *[1-(2-Methyl-5-phenyl-3-thienyl)-2-(2-methyl-4-(3-methylphenyl)-1-phenyl)]perfluorocyclopentene (**2o**)*

Compound **2o** was prepared by a method similar to that used for **1o**. The crude product was purified by column chromatography on SiO_2 using petroleum ether as an eluent to give **2o** (0.39 g, 37%) as a yellow solid. M.p. 123–124 °C; MS m/z (M^+) 529.19; Calcd for $C_{30}H_{22}F_6S$ (%): Calcd C, 68.17; H, 4.20. Found C, 68.14; H, 4.22; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.92 (s, 3H, $-CH_3$), 1.96 (s, 3H, $-CH_3$), 2.34 (s, 3H, $-CH_3$), 7.12 (s, 2H, thienyl-H, phenyl-H), 7.23 (t, 1H, *J* = 7.4 Hz, phenyl-H), 7.26–7.29 (m, 4H, phenyl-H), 7.31 (d, 2H, *J* = 7.0 Hz, phenyl-H), 7.37 (d, 1H, *J* = 8.0 Hz, phenyl-H), 7.41–7.45 (m, 3H, phenyl-H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 14.8, 19.9, 21.5, 122.7, 124.2, 124.9, 125.5, 125.6, 126.5, 127.8, 128.6, 128.8, 129.0, 129.5, 129.6, 133.4, 137.4, 138.5, 140.0, 141.1, 142.0, 142.9; IR (KBr, ν, cm^{-1}): 757, 786, 838, 861, 893, 992, 1071, 1166, 1276, 1400, 1455, 1618, 1669, 2839, 3035.

2.2.9. *[1-(2-Methyl-5-phenyl-3-thienyl)-2-(2-methyl-4-phenyl-1-phenyl)]perfluorocyclopentene (**3o**)*

3o was prepared by a method similar to that used for **1o**. The crude product was purified by column chromatography on SiO_2 using petroleum ether as an eluent to give **3o** (0.47 g, 46%) as a yellow solid. M.p. 121–122 °C; MS m/z (M^+) 515.15; Calcd for $C_{29}H_{20}F_6S$ (%): Calcd C, 67.70; H, 3.92. Found C, 67.78; H, 3.98; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.02 (s, 3H, $-CH_3$), 2.05 (s, 3H, $-CH_3$), 7.17

(s, 1H, thienyl-H), 7.28 (d, 1H, $J = 8.0$ Hz, phenyl-H), 7.32–7.38 (m, 3H, phenyl-H), 7.41 (d, 2H, $J = 7.0$ Hz, phenyl-H), 7.44 (s, 1H, phenyl-H), 7.46–7.49 (m, 3H, phenyl-H), 7.53 (t, 1H, $J = 7.8$ Hz, phenyl-H), 7.58 (d, 2H, $J = 7.4$ Hz, phenyl-H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 14.9, 19.9, 122.7, 124.9, 125.5, 125.6, 126.6, 127.1, 127.8, 127.9, 128.9, 129.0, 129.6, 133.4, 137.5, 139.9, 141.2, 142.0, 142.7; IR (KBr, ν, cm^{-1}): 757, 785, 857, 893, 991, 1067, 1164, 1275, 1401, 1453, 1616, 1666, 2622, 2856, 3043.

*2.2.10. [1-(2-Methyl-5-phenyl-3-thienyl)-2-(2-methyl-4-(3-cyanophenyl)-1-phenyl)]perfluorocyclopentene (**4o**)*

4o was prepared by a method similar to that used for **1o**. The crude product was purified by column chromatography on SiO_2 using the mixture of petroleum ether and acetic ether ($v/v = 8/1$) as an eluent to give **4o** (0.44 g, 41%) as a yellow solid. M.p. 151–153 °C; MS m/z (M^+) 540.17; Calcd for $C_{30}H_{19}F_6NS$ (%): Calcd C, 66.78; H, 3.55; N, 2.60. Found C, 66.71; H, 3.59; N, 2.61; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.95 (s, 3H, $-CH_3$), 2.00 (s, 3H, $-CH_3$), 7.11 (s, 1H, thienyl-H), 7.23 (d, 1H, $J = 7.4$ Hz, phenyl-H), 7.30 (t, 3H, $J = 7.4$ Hz, phenyl-H), 7.42 (d, 4H, $J = 7.4$ Hz, phenyl-H), 7.49 (t, 1H, $J = 7.8$ Hz, phenyl-H), 7.59 (d, 1H, $J = 8.0$ Hz, phenyl-H), 7.74 (d, 1H, $J = 8.0$ Hz, phenyl-H), 7.80 (s, 1H, phenyl-H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 13.7, 18.8, 112.2, 117.5, 121.5, 123.7, 124.2, 124.5, 126.9, 128.0, 128.5, 128.7, 128.9, 129.6, 130.2, 130.3, 132.2, 137.0, 139.3, 140.0, 140.2, 141.1; IR (KBr, ν, cm^{-1}): 757, 784, 831, 862, 891, 991, 1068, 1164, 1273, 1401, 1453, 1616, 1667, 2230, 2843, 3039.

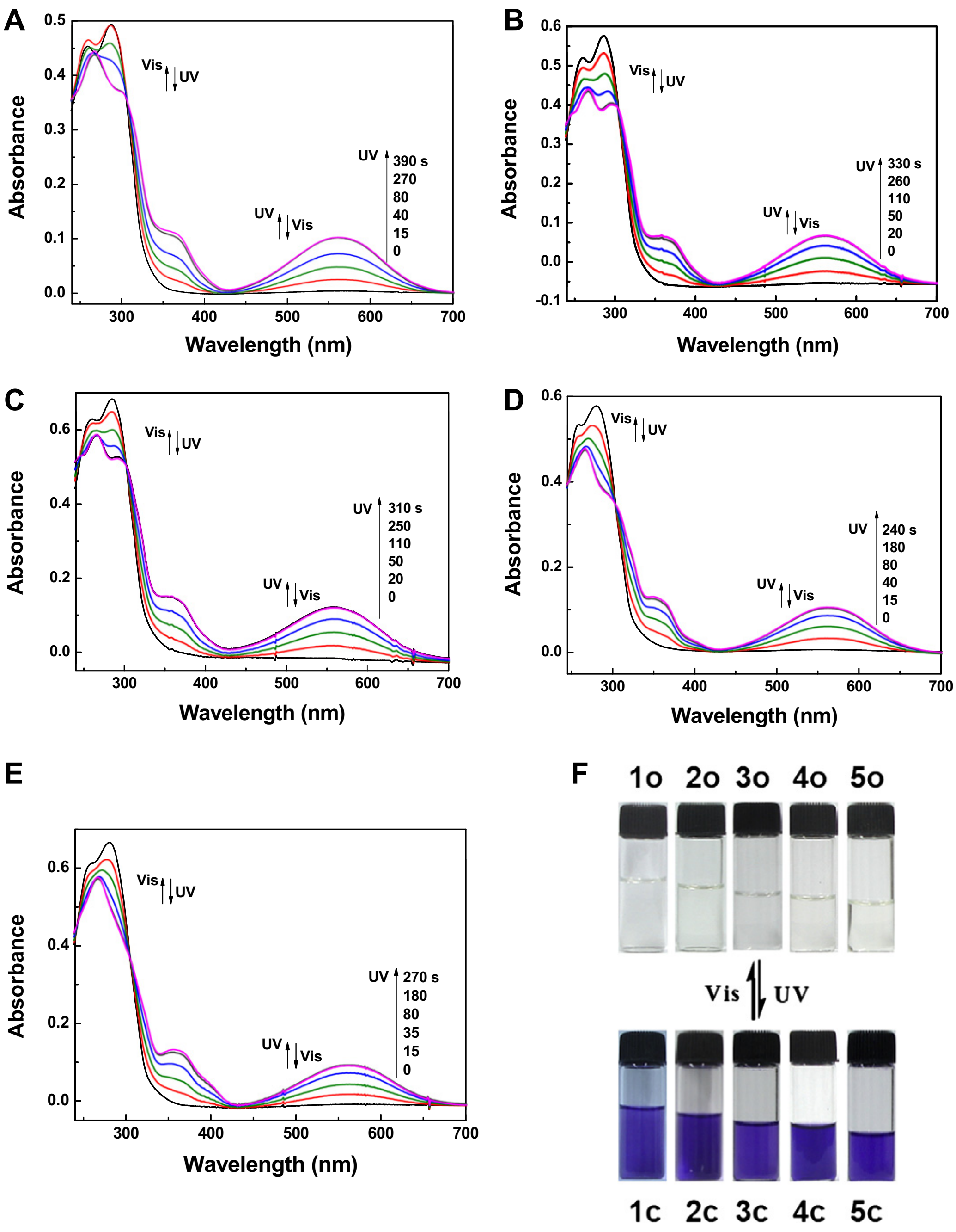

Fig. 3. Absorption spectra and color changes of diarylethenes **1**–**5** by photoirradiation in hexane (2.0×10^{-5} mol L^{-1}) at room temperature: (A) spectral changes for **1**; (B) spectral changes for **2**; (C) spectral changes for **3**; (D) spectral changes for **4**; (E) spectral changes for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

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

Compound	$\lambda_{0,\max}$ (nm)[a] (ε/L mol^{-1} cm^{-1})	$\lambda_{c,\max}$ (nm)[b] (ε/L mol^{-1} cm^{-1})		Φ[c]	
	Hexane	Hexane	PMMA film	Φ_{o-c}	Φ_{c-o}
1	288 (2.47×10^4)	563 (5.16×10^3)	581	0.29	0.14
2	286 (2.88×10^4)	559 (3.44×10^3)	575	0.32	0.13
3	285 (3.42×10^4)	556 (6.11×10^3)	573	0.37	0.11
4	280 (2.89×10^4)	560 (5.32×10^3)	573	0.40	0.26
5	281 (3.33×10^4)	560 (4.65×10^3)	577	0.39	0.30

[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.

*2.2.11. [1-(2-Methyl-5-phenyl-3-thienyl)-2-(2-methyl-4-(3-trifluoromethylphenyl)-1-phenyl)]perfluorocyclopentene (**5o**)*

5o was prepared by a method similar to that used for **1o**. The crude product was purified by column chromatography on SiO_2 using petroleum ether as an eluent to give **5o** (0.49 g, 42%) as an yellow oil. MS m/z (M^+) 583.18; Calcd for $C_{30}H_{19}F_9S$ (%): Calcd C, 61.86; H, 3.29. Found C, 61.93; H, 3.35; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.96 (s, 3H, $-CH_3$), 2.00 (s, 3H, $-CH_3$), 7.10 (s, 1H, thienyl-H), 7.21 (d, 1H, $J = 8.0$ Hz, phenyl-H), 7.28 (t, 2H, $J = 7.6$ Hz, phenyl-H), 7.33 (s, 1H, phenyl-H), 7.39–7.41 (m, 3H, phenyl-H), 7.48 (t, 2H, $J = 7.8$ Hz, phenyl-H), 7.55 (d, 1H, $J = 8.0$ Hz, phenyl-H), 7.68 (d, 1H, $J = 7.8$ Hz, phenyl-H), 7.74 (s, 1H, phenyl-H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 14.8, 19.9, 122.6, 123.9, 124.5, 124.9, 125.3, 125.6, 127.5, 127.9, 129.0, 129.3, 129.6, 129.8, 130.4, 131.2, 131.5, 133.3, 137.9, 140.8, 141.1, 141.2, 142.1; IR (KBr, ν, cm^{-1}): 752, 785, 829, 860, 889, 992, 1071, 1165, 1401, 1451, 1617, 1668, 2850, 3035.

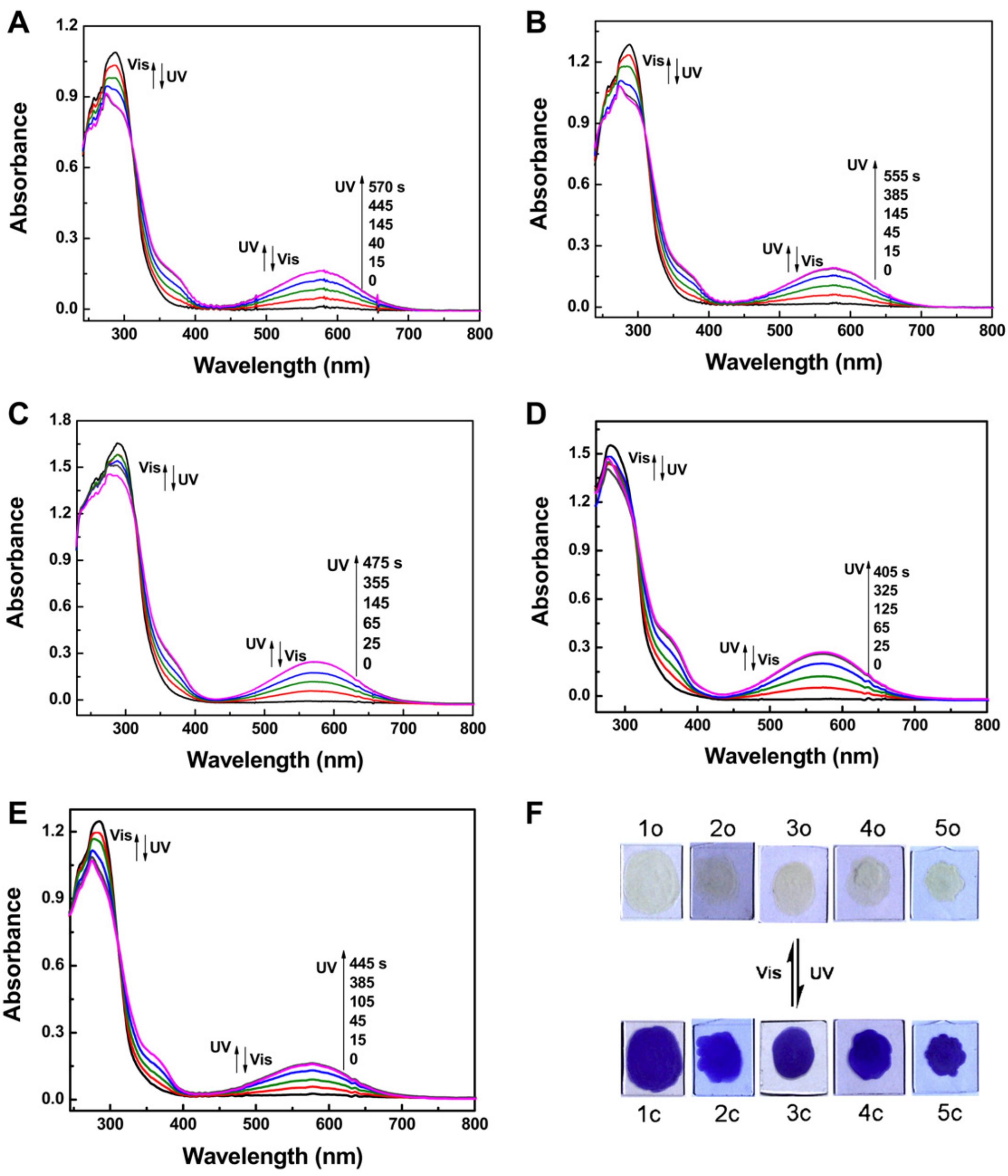

Fig. 4. Absorption spectra and color changes of diarylethenes **1**–**5** by photoirradiation in PMMA film (10%, w/w) at room temperature: (A) spectral changes for **1**; (B) spectral changes for **2**; (C) spectral changes for **3**; (D) spectral changes for **4**; (E) spectral changes for **5**; (F)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

3. Results and discussion

3.1. Photochromism of diarylethenes

The photochromic properties of diarylethenes **1**–**5** were measured at room temperature both in hexane (2.0×10^{-5} mol L^{-1}) and in PMMA medium (10%, w/w). Fig. 3 shows the changes in the absorption spectra and color of diarylethenes **1**–**5** in hexane, induced by alternating irradiation with UV and visible light of appropriate wavelength. As shown in Fig. 3A, compound **1o** exhibited a sharp absorption peak at 288 nm in hexane, as a result of a $\pi - \pi^*$ transition [43]. Upon irradiation with 297 nm light, a new visible absorption band centered at 563 nm emerged while the original peak at 288 nm decreased, indicating the formation of the closed-ring isomer **1c**; this change in absorption was manifest in the colorless solution becoming violet. The photostationary state is achieved upon irradiation with light of wavelength 297 nm for 390 s. Alternatively, the violet solution could be bleached completely to colorless upon irradiation with visible light ($\lambda > 450$ nm) for 110 s, indicating that **1c** was returning to the initial state **1o**. As with diarylethene **1**, compounds **2**–**5** also show good photochromism in hexane (Fig. 3B–E). Upon irradiation with 297 nm light, absorption bands in the visible region appeared and the solutions **2o**–**5o** turned violet due to cyclization reactions leading to the formation of the closed-ring isomers **2c**–**5c**. The photostationary state is achieved by irradiation 330 s for **2**, 310 s for **3**, 240 s for **4**, and 270 s for **5**, respectively. These compounds had the maxima absorption wavelengths in the visible region at 559, 556, 560, and 560 nm, respectively. All of the violet-colored solutions **2c**–**5c** can be decolorized by irradiating with visible light of wavelengths greater than 450 nm, indicating return to the open-ring isomers **2o**–**5o**. The bleaching irradiation time is 125 s for **2**, 150 s for **3**, 80 s for **4**, and 65 s for **5**, respectively. In the photostationary state, the isosbestic points for diarylethenes **1**–**5** were observed at 308, 304, 302, 303, and 305 nm, respectively. The absorption spectral features of these compounds are summarized in Table 1. The quantum yields were determined by comparing the reaction yields of diarylethenes **1**–**5** in hexane against 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene in hexane at room temperature [39], and the results are also in Table 1. The results showed that altering the substituent at 3-position of the benzene ring had a significant effect on the photochromic features of diarylethenes **1**–**5**, including the absorption maxima, molar absorption coefficients and quantum yields. In hexane, the absorption maxima of diarylethenes **1o**–**5o** decreased slightly with the increasing electron-withdrawing ability. Among diarylethenes **1**–**5**, the unsubstituted parent compound **3** has the greatest molar absorption coefficient, both for its open-ring and closed-ring isomers, but the lowest cycloreversion quantum yield. When replacing the hydrogen atom at the *meta*-position of the terminal phenyl ring in the biphenyl moiety with an electron-donating substituent (methoxy or methyl group, such as in compound **1** or **2**), the absorption maxima and the cycloreversion quantum yields increase to some extent, but the molar absorption coefficients and the cyclization quantum yields show a clear reduction. When the same position instead contains an electron-withdrawing substituent (cyano or trifluoromethyl group, such as in compound **4** or **5**), the molar absorption coefficients are still significantly below that of compound **3**, but their absorption maxima, cyclization and cycloreversion quantum yields have notably increased. The absorption maximum and molar absorption coefficient of diarylethene **1c** are much larger than those of diarylethene **2c**, due to the greater electron-donating ability of methoxy group as compared to a methyl group [44], but the cyclization quantum yield of **1c** is smaller than that of **2c**. Although the molar absorption coefficient of diarylethene **4c** is much larger than that of diarylethene **5c**, the cycloreversion quantum yield of **4c** is smaller than that of **5c**. The absorption maxima and cyclization quantum yields of diarylethenes **4** and **5** are almost equal. Moreover, both the cyclization and cycloreversion quantum yields of diarylethenes **4** and **5** bearing electron-withdrawing groups are much higher than those of diarylethenes **1** and **2** bearing electron-donating groups. These results are quite different from those reported for diarylethenes bearing a phenyl moiety, where absorption maxima markedly decreased with the increase of electron-withdrawing ability, and cycloreversion quantum yields showed the reverse trend [36].

For practical applications in optical devices, it is very important that photochromic materials maintain good photochromism in a polymer film, such as PMMA [36,45]. Films were prepared by dissolving 10 mg diarylethene sample and 100 mg PMMA in 1.0 mL chloroform by ultrasonication, followed by spin-coating on the surface of quartz substrate. In PMMA amorphous film, diarylethenes **1**–**5** also showed good photochromism (Fig. 4) similar to samples in solution. The photochromic properties of diarylethenes **1**–**5** in PMMA film are also summarized in Table 1. Upon irradiation with 313 nm light, the colors of the diarylethene/PMMA films **1**–**5** changed from colorless to blue, with the appearance of a new broad absorption band centered at 581, 575, 573, 573 and 577 nm, respectively. This band was assigned to the formation of the closed-ring isomers **1c**–**5c**. In PMMA solid media, the photostationary equilibriums of diarylethenes **1**–**5** are achieved by irradiation with light of wavelength 313 nm for 570, 555, 475, 405, and 445 s, respectively. All colored diarylethene/PMMA films can revert to colorless upon irradiation with visible light ($\lambda > 450$ nm). The bleaching irradiation time is 125 s for **1**, 130 s for **2**, 160 s for **3**, 108 s for **4**, and 90 s for **5**, respectively. As has been observed for most of the reported diarylethenes [46–49], the maximum absorption peaks of the closed-ring isomers **1c**–**5c** are found at longer wavelengths in PMMA film than those in hexane solution. The red shift of the absorption maxima for the closed-ring isomers are 18 nm for **1c**, 16 nm for **2c**, 17 nm for **3c**, 13 nm for **4c**, and 17 nm for **5c**. This red shift phenomena may be attributed to the polar effect of the polymer matrix and the stabilization of molecular arrangement in solid state [50,51].

3.2. Fluorescence of diarylethenes

Fluorescent properties can be useful in molecular scale optoelectronics [52], digital fluorescence photoswitches [53,54] and ion-sensors [55–58]. In our present work, the fluorescence properties of diarylethenes **1**–**5**, both in solution and in PMMA film, were

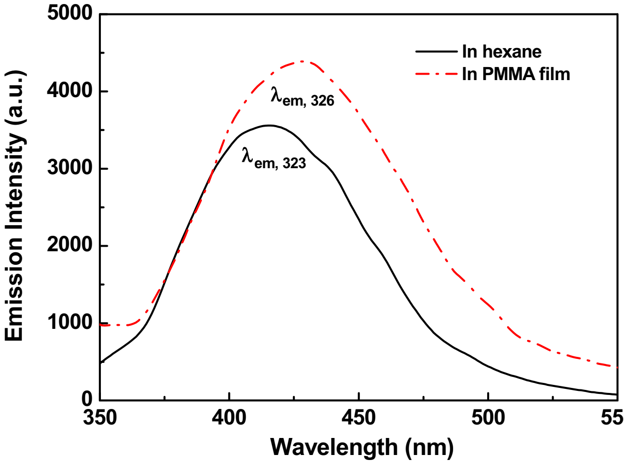

Fig. 5. Emission spectra of diarylethene **1o** both in hexane (1.0×10^{-4} mol L^{-1}, excited at 323 nm) and in PMMA film (10%, w/w, excited at 326 nm) at room temperature.

Table 2
The fluorescence emission features of diarylethenes **1o**–**5o** both in hexane (1.0×10^{-4} mol $L^{-1)}$ and in PMMA film (10%, w/w) at room temperature.

	$\lambda_{em,\ max}$ (Relative intensity)				
	1o	**2o**	**3o**	**4o**	**5o**
Hexane	415 (3558)	420 (3329)	422 (3204)	432 (2228)	431 (2380)
PMMA film	429 (4386)	434 (3738)	436 (3467)	441 (2597)	439 (2753)

measured at room temperature using a Hitachi F-4500 fluorimeter. The fluorescence emission spectra of diarylethene **1o** both in hexane (1.0×10^{-4} mol L^{-1}) and in PMMA film (10%, w/w) are illustrated in Fig. 5. The emission features of diarylethenes **2o**–**5o** are summarized in Table 2. When dissolved in hexane, diarylethenes **1o**–**5o**, excited at 323 nm, exhibited emission peaks at 415, 420, 422, 432, and 431 nm, respectively. When excited at 326 nm, emission peaks of **1o**–**5o** in PMMA were observed at 429, 434, 436, 441, and 439 nm, respectively. The Stokes shift of the fluorescence was relatively large and red shifted, in comparison with the absorption edge. This type of large Stokes shift has been discussed in detail by Sekiya and coworkers [59]. When comparing samples in hexane to those in a PMMA film, the emission peaks of diarylethenes **1o**–**5o** consistently exhibit a bathochromic shift across their maxima absorption wavelengths with values of 14 nm for **1o**, 14 nm for **2o**, 14 nm for **3o**, 9 nm for **4o**, and 8 nm for **5o**. When going from electron-donating to electron-withdrawing substituents, the emission peaks of **1o**–**5o** gradually increased both in hexane (from 415 to 432 nm) and in PMMA film (from 429 to 441 nm); but their emission intensity decreased significantly when the electron-donating groups were replaced with electron-withdrawing groups. The emission intensity of **1o** is the strongest and that of **4o** is the weakest, however, the emission peak of **1o** is at highest energy while **4o** is the lowest both in hexane solution and in PMMA film. By using anthracene (0.27 in acetonitrile) as the reference, the fluorescence quantum yields of

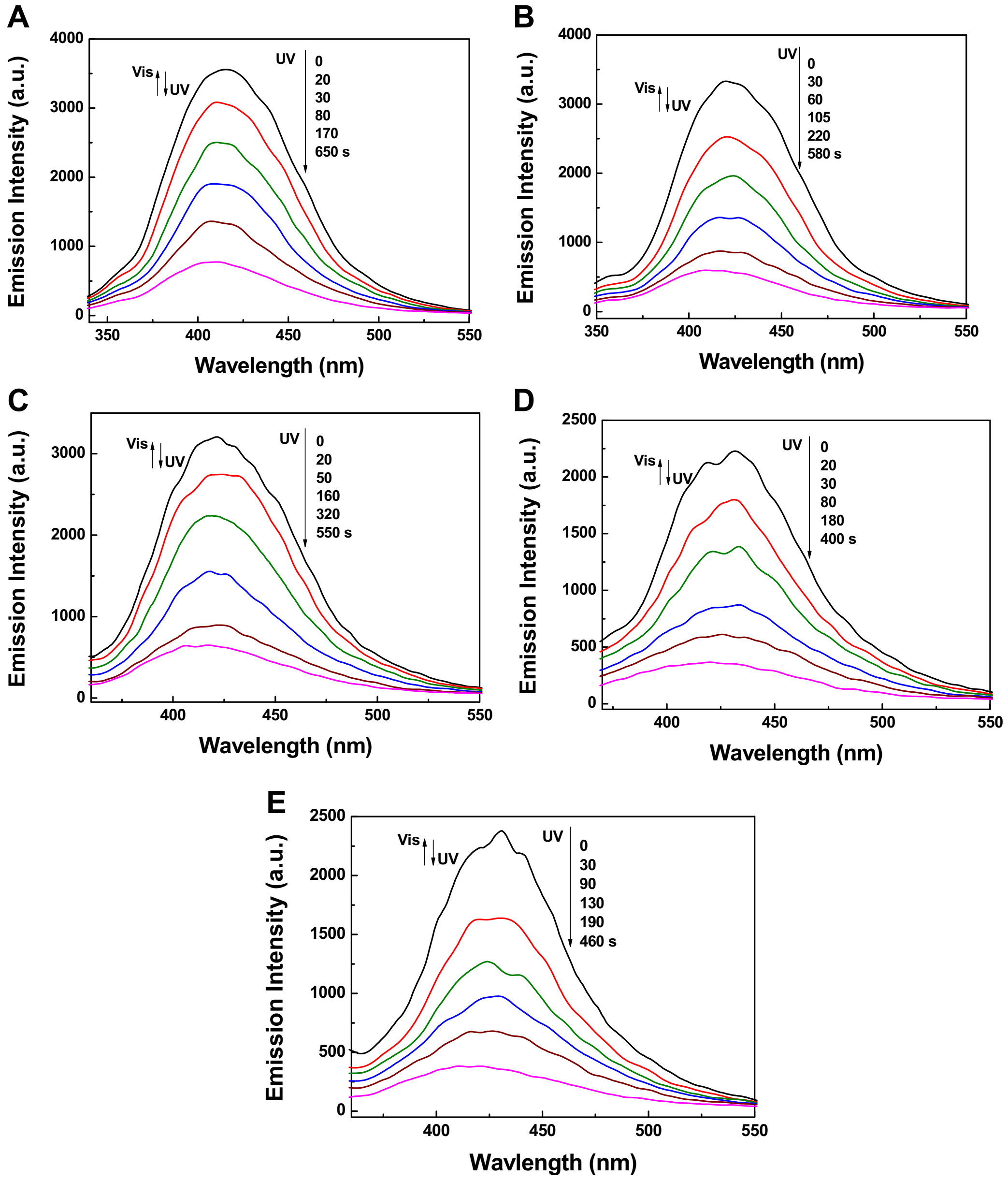

Fig. 6. Emission intensity changes of diarylethenes **1**–**5** in hexane (1.0×10^{-4} mol L^{-1}) upon irradiation with 313 nm UV light at room temperature, excited at 323 nm: (A) **1**; (B) **2**; (C) **3**; (D) **4**; (E) **5**.

1o–**5o** were determined to be 0.0221, 0.0214, 0.0205, 0.0201 and 0.0203, respectively. The results showed that the electron-donating substituent could be effective to increase the efficiency of the fluorescence and decrease the emission peak of diarylethenes bearing a biphenyl unit.

As has been observed for most of the reported diarylethenes [25,60–65], diarylethenes **1**–**5** exhibited a very good fluorescent switch on changing from the open-ring isomers to closed-ring isomers by photoirradiation both in hexane and in PMMA film. Upon irradiation with UV light, the photocyclization reaction was carried out and the non-fluorescent closed-ring isomers **1c**–**5c** were produced. Back irradiation of the appropriate wavelength of visible light regenerated the open-ring isomers **1o**–**5o** and duplicated the original emission spectra. During the process of photoisomerization, the five compounds exhibited changes in their fluorescence in hexane as shown in Fig. 6. Upon irradiation with 297 nm UV light for several hundred seconds varying from 400 to 650 s, the samples arrived at the photostationary state, resulting in emission intensities of diarylethenes **1**–**5** quenched to *ca.* 22%, 18%, 20%, 16%, and 16%, respectively. The back irradiation with visible light ($\lambda > 450$ nm) regenerated the open-ring isomers and reproduced the original emission spectra. When their emission intensities reverted to those of original values, the irradiation times were 200 s for **1**, 225 s for **2**, 240 s for **3**, 160 s for **4**, and 150 s for **5**, respectively. The similar emission intensity changes of diarylethenes **1**–**5** in PMMA film during the process of photoisomerization are shown in Fig. 7. Upon irradiation with 313 nm UV light, emission intensities decreased remarkably along with the photoisomerization from the open-ring isomers to the closed-ring isomers when excited at 326 nm. When the samples arrived at the photostationary state by irradiation with UV light for several hundreds seconds varying from 408 to 568 s, the emission intensities of diarylethenes **1**–**5** were quenched to *ca.* 28%,

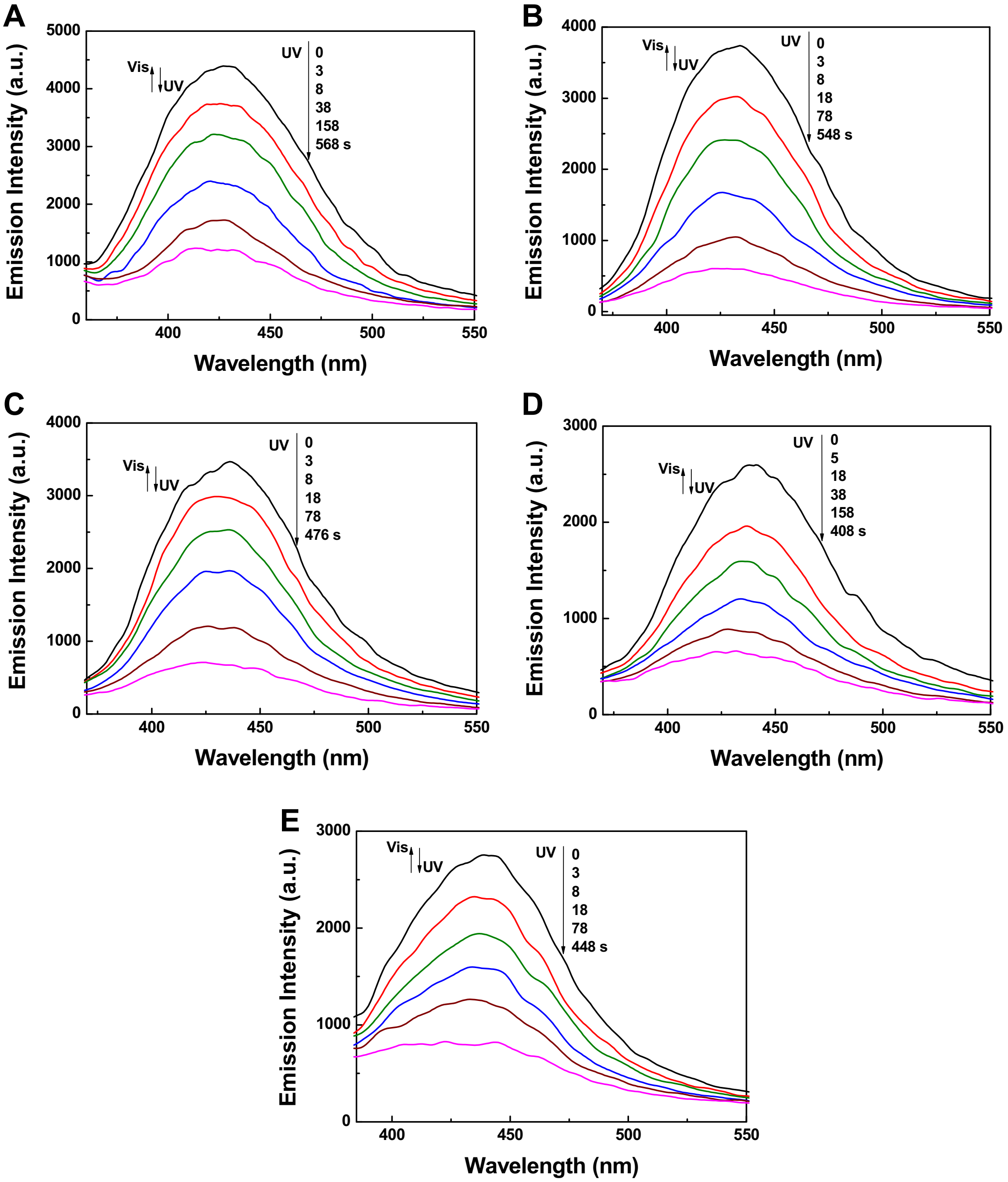

Fig. 7. Emission intensity changes of diarylethenes **1**–5 in PMMA film (10%, w/w) upon irradiation with 313 nm UV light at room temperature, excited at 326 nm: (A) **1**; (B) **2**; (C) **3**; (D) **4**; (E) **5**.

16%, 20%, 25%, and 30%, respectively. In PMMA film, the recovering emission intensities of diarylethenes **1**–**5** are obtained by irradiation with visible light for 130, 145, 150, 110, and 100 s, respectively. After 20 repeat cycles, no obvious changes in the fluorescent modulation efficiency of these diarylethenes were observed, both in hexane and in PMMA films. Compared with those reported diarylethenes [36,47,48], the fluorescent modulation efficiencies of diarylethenes **1**–**5** were significantly enhanced both in the liquid and solid states. This indicated that diarylethenes bearing a biphenyl unit have the potential use as fluorescent modulation switches [66,67]. The residues of fluorescent modulation efficiencies of diarylethenes **1o**–**5o** may be attributed to the incomplete cyclization reaction and the existence of parallel conformations [28,47,48,68,69]. In addition, the average time to switch from an "on" and "off" state shortened in proportion to the reciprocal power of radiated light as the power of the UV and visible light was changed, indicating that the switching effect is indeed photochemical [61].

3.3. *Electrochemistry of diarylethenes*

It is well known that the ring opening and closing transformation of some diarylethenes can be initiated not only by UV or visible light irradiation, but also by an electrochemical redox process [70]. The electrochromic behaviour of diarylethenes have attracted much attention [1,5,18,71].

Cyclic voltammetry (CV) was performed on the diarylethenes **1**–**5** under identical experimental conditions at a scanning rate of 100 mV/s. The CV curves of diarylethenes **1**–**5** are shown in Fig. 8.

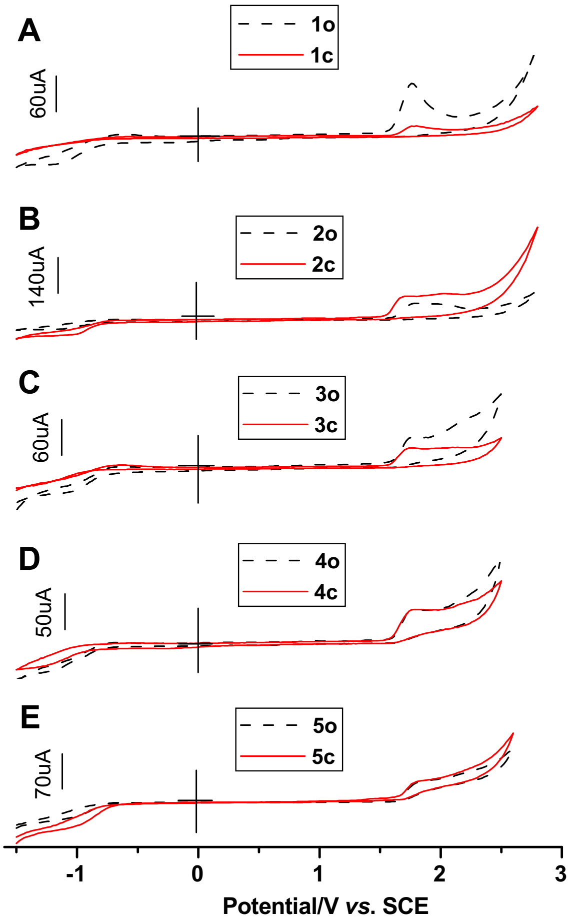

Fig. 8. Cyclic voltammetry (second scan) of diarylethene **1**–**5** in acetonitrile at a scan rate of 100 mV/s: (A) **1**; (B) **2**; (C) **3**; (D) **4**; (E) **5**.

The oxidation onsets of **1o**–**5o** were at +1.65, 1.68, 1.65, 1.64, and 1.67 V, respectively. The CV curves for **1c**–**5c** were at +1.70, 1.55, 1.63, 1.62, and 1.69 V, respectively. The differences of oxidation onset between the open-ring and closed-ring isomers of diarylethenes **1**–**5** were −0.05 V for **1**, 0.13 V for **2**, 0.02 V for **3**, 0.02 V for **4**, and −0.02 V for **5**. This shows that the oxidation process for the open-ring isomers **2o**–**4o** occurs at higher potentials than in the corresponding closed-ring isomers **2c**–**4c** whereas the reverse occurs for diarylethenes **1** and **5**. The reason for the anomalous high oxidation potentials of **1c** and **5c** is currently not clear and further work is in progress. To the best of our knowledge, this is the first diarylethene example for which oxidation onset of the open-ring isomers is lower than that of their closed-ring isomers. Moreover, there are great differences amongst the electronic current and polarization curve shapes between the open-ring and closed-ring isomers of diarylethenes **1**–**3**, but not for diarylethenes **4** and **5** at the scanned voltage region. These results suggest that the different electron-donating/withdrawing substituents have a significant effect on the electrochemical properties of these diarylethene derivatives bearing a biphenyl moiety but further work is required to quantify these effects.

4. Conclusion

In summary, five new photochromic diarylethenes possessing a biphenyl moiety were synthesized to investigate substituent effects upon their properties. These new photochromic systems showed good photochromism and acted as a remarkable fluorescent switch both in solution and in PMMA film. Their distinguishable optical and electrochemical characteristics may be attributed to the different substituent effects. The biphenyl aryl moiety induced some new dramatic properties differing from other diarylethenes with five-membered aryl moieties reported so far. The results will be helpful for the synthesis of efficient photoactive diarylethene derivatives with new molecular skeletons and to understand the substitution effects in diarylethenes bearing a biphenyl unit to aid the rational design of novel diarylethenes for potential application in optoelectronics and other fields.

Acknowledgements

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