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Synthesis and the effects of substitution upon photochromic diarylethenes bearing an isoxazole moiety

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ABSTRACT

A new class of unsymmetrical photochromic diarylethenes bearing an isoxazole moiety was synthesized and the effects of substitution on their optical and electrochemical properties were investigated systematically. Each of the compounds exhibited remarkable photochromism and functioned as a fluorescent photoswitch both in solution and in poly(methyl methacrylate) films. The electron-donating substituents effectively shifted the absorption maximum and the emission peak to a longer wavelength direction, while the electron-withdrawing substituents notably enhanced the fluorescent quantum yields and oxidation onsets of these diarylethene derivatives. As compared to the unsubstituted parent diarylethene, introduction of the electron-donating/withdrawing substituents could efficiently modulate the optical and electrochemical properties of the diarylethenes bearing an isoxazole moiety. All results indicated that the isoxazole moiety and the substitution effects played a very important role during the process of photochromic reaction for these diarylethene derivatives.

1. Introduction

In the past several decades, photochromic compounds have been a growing interest from the viewpoints of fundamental academic research and also of practical applications as photoresponsive materials because of the control of their optoelectronic features using external stimuli, such as light, temperature, electricity, etc.[1] To date, various types of photochromic compounds have thus far been synthesized for possible application in some optoelectronic devices, such as optical memories and photoswitches.[2] Among these compounds, photochromic diarylethenes have attracted much attention as highly promising candidates for these applications because of their excellent thermal stability of the respective isomers, notable fatigue resistance, and high reactivity in the solid state.[2,3] Photochromic diarylethenes can undergo reversible photoisomerization reactions upon photoirradiation both in solution and in the solid state.[2a,4] During the reversible photoisomerization process, photochromic diarylethenes can cause changes of not only their molecular structures but also their physicochemical properties, such as absorption spectra,[2a,b,5] fluorescence,[6] oxidation/reduction potential,[7] reflective index,[8] shape of a single crystal,[9] contact angle,[10] and so on. Such property changes have potential application in optical memories, switching devices, displays, and photo-mechanical actuators.[2,9a,b,11]

Recently, the design and synthesis of new photochromic diarylethene skeletons with different aryl moieties has become an active area of research, with many reports on the synthesis and investigation of the properties of diarylethenes with the heterocyclic aryl rings. Among the diarylethenes hitherto reported, most of the heteroaryl diarylethenes bear thiophene or benzothiophene rings, which exhibit excellent thermal stability and outstanding fatigue resistance,[2] with only a few reports concerning other heteroaryl moieties, such as furan,[12] thiazole,[13] indole,[14] benzofuran,[15] indene,[16] pyrazole,[17] pyrrole,[18] chryso[*b*]thiophene,[19] among others. These heteroaryl groups have a significant effect on the characteristics of diarylethene derivatives. For instance, diarylethenes having thiophene or benzothiophene moieties exhibit good thermal stability and excellent fatigue resistance,[2a,b] whereas symmetrical diarylethenes with two pyrrole rings are thermally unstable and return to the open-ring isomer even in the dark.[20] Diarylethenes with a pyrazole unit have a fairly high cycloreversion quantum yield,[17a] whereas dithienylethenes with bulky alkoxy groups at 2- and 2′-positions of the thiophene rings have a fairly small cycloreversion quantum yield.[21] Up to date, there are a few examples of photochromic diarylethenes bearing oxazole rings.[22] The diarylethene derivatives exhibit good photochromism in hexane and are very useful materials for full-color imaging because they provide one of the three primary colors.[22c] The results give us valuable insight and encourage us to develop a new class of hybrid photochromic diarylethene derivatives bearing an isoxazole moiety. The structure of the heterocyclic isoxazole ring is similar to that of oxazole ring. Therefore, introduction of isoxazole

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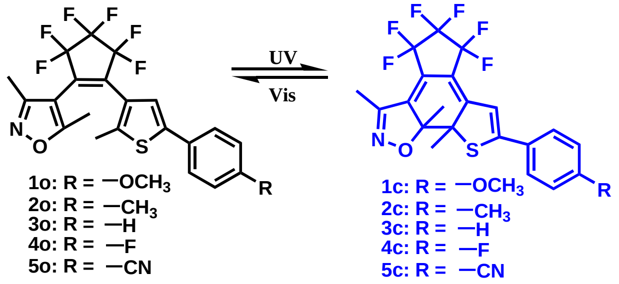
ring into the heteroaryl moieties of diarylethene derivatives can be expected to undergo excellent photochromic reactions. As far as we are aware, photochromic diarylethenes bearing both isoxazole and thiophene moieties have not hitherto been reported.

In this work, one of the main purposes was to explore a new class of hybrid photochromic diarylethene derivatives bearing both isoxazole 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 diarylethene derivatives are 1-(3,5-dimethyl-4-isoxazolyl)-2-[2-methyl-5-(*p*-methoxyphenyl)-3-thienyl]perfluorocyclopentene (**1o**), 1-(3,5-dimethyl-4-isoxazolyl)-2-[2-methyl-5-(*p*-methylphenyl)-3-thienyl]perfluorocyclopentene (**2o**), 1-(3,5-dimethyl-4-isoxazolyl)-2-(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene (**3o**), 1-(3,5-dimethyl-4-isoxazolyl)-2-[2-methyl-5-(*p*-fluorophenyl)-3-thienyl]perfluorocyclopentene (**4o**), and 1-(3,5-dimethyl-4-isoxazolyl)-2-[2-methyl-5-(*p*-cyanophenyl)-3-thienyl] perfluorocyclopentene (**5o**). Each of the diarylethenes showed notable photochromism both in solution and in polymer amorphous films; to the best of our knowledge, they are the first examples of this class of photochromic diarylethene derivatives bearing both isoxazole and thiophene moieties. The photochromic scheme of diarylethenes **1**–**5** by photoirradiation is illustrated as shown in Scheme 1.



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

2. Experimental

2.1. General

Melting point was taken on a WRS-1B melting point apparatus. NMR spectra were recorded on a Bruker AV400 (400 MHz) spectrometer with $CDCl_3$ as the solvent and tetramethylsilane as an internal standard. Infrared spectra (IR) were recorded on a Bruker Vertex-70 spectrometer. Elemental analysis was measured with PE CHN 2400 analyzer. Fluorescent spectra were measured using a Hitachi F-4500 fluorimeter. 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. The required wavelength was isolated by the use of the appropriate filters. The quantum yields of cyclization and cycloreversion were determined by comparing the reaction yield with the known yield of the compound 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene in hexane.[23] 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. Ag/AgCl served as a quasireference electrode. It was calibrated using an internal ferrocene (Fc/Fc^{+}) standard with a formal potential of $E_{1/2}=+0.35$ V versus platinum wire. Solvents used were spectroscopic grade and were purified by distillation.

2.2. Synthesis

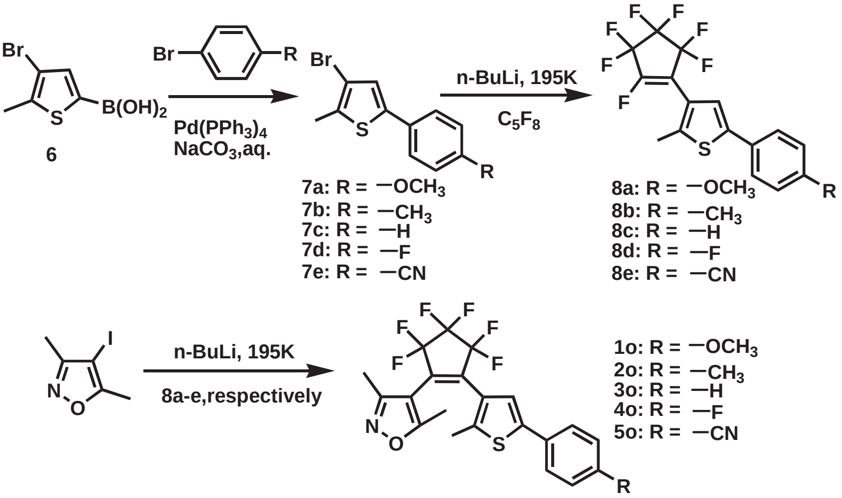
The synthesis route for the diarylethenes **1o**–**5o** is shown in Scheme 2. Suzuki coupling of the five bromobenzene derivatives with a thiophene boronic acid (**6**)[17b,24] gave the compounds **7a**–**e**. Then, compounds **7a**–**e** were separately lithiated and coupled with perfluorocyclopentene to give mono-substituted perfluorocyclopentene derivatives **8a**–**e**, respectively. Finally, 4-iodo-3,5-dimethylisoxazole[25] was lithiated and then separately coupled with compounds **8a**–**e** to give the unsymmetrical diarylethene derivatives **1o**–**5o**, respectively. The structures of diarylethenes **1o**–**5o** were confirmed by elemental analysis, NMR and IR.

*2.2.1. 3-Bromo-2-methyl-5-(p-methoxyphenyl)thiophene (**7a**).* This compound was synthesized by the same method as that reported in our previous works.[8b,9a] Compound **7a** was prepared by reacting compound **6** (4.0 g, 18.1 mmol) with 4-bromoanisole (3.4 g, 18.1 mmol) in the presence of $Pd(PPh_3)_4$ and Na_2CO_3 (6.40 g, 60 mmol) in tetrahydrofuran (80 mL containing 10% water) for 15 h at 70 °C. The product **7a** was purified by column chromatography on SiO_2 using hexane as an eluent and 3.8 g obtained as a pale yellow solid in 78% yield. Mp 107–108 °C. Anal. Calcd for $C_{12}H_{11}BrOS$ (%): calcd C, 50.90; H, 3.92. Found C, 50.72; H, 4.04; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.40 (s, 3H, $-CH_3$), 3.83 (s, 3H, $-OCH_3$), 6.90 (d, 2H, J=8.0 Hz, phenyl-H), 6.99 (s, 1H, thienyl-H), 7.43 (d, 2H, J=8.0 Hz, phenyl-H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 14.78, 55.38, 109.63, 114.35, 124.48, 126.04, 126.39, 126.68, 132.57, 136.09, 141.10, 159.41; IR (ν, KBr, cm^{-1}): 797, 818, 946, 1033, 1111, 1161, 1179, 1255, 1288, 1309, 1455, 1541, 1603, 2917.

*2.2.2. 3-Bromo-2-methyl-5-(p-methylphenyl)thiophene (**7b**).* Compound **7b** was prepared by an analogous method to **7a**. The crude product was purified by column chromatography on SiO_2 using petroleum ether as an eluent to give **7b** (3.86 g, 80%) as a pale yellow solid. Mp 67–68 °C. Anal. Calcd for $C_{12}H_{11}BrS$ (%): calcd C, 53.94; H, 4.15. Found C, 54.09; H, 4.03; ^{1}H NMR (400 MHz, $CDCl_3$): 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), 7.39 (d, 2H, J=8.0 Hz, phenyl-H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 14.82, 21.20, 109.71, 125.03, 125.26, 125.46, 129.62, 130.78, 131.15, 132.57,137.52, 141.35; IR (ν, KBr, cm^{-1}): 784, 807, 944, 1007, 1019, 1120, 1162, 1274, 1309, 1327, 1374, 1442, 1511, 2852, 2915.

*2.2.3. 3-Bromo-2-methyl-5-phenylthiophene (**7c**).* Compound **7c** was prepared by an analogous method similar to that used for to **7a**. The crude product was purified by column chromatography on SiO_2 using hexane as an eluent to give **7c** (3.52 g, 77%) as a pale yellow solid. Mp 66–68 °C. Anal. Calcd for $C_{11}H_9BrS$ (%): calcd C, 52.19; H, 3.58. Found C, 52.34; H, 3.43; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.34 (s, 3H, $-CH_3$), 7.02 (s, 1H, thienyl-H), 7.20 (d, 1H, J=8.0 Hz, phenyl-H), 7.29 (t, 2H, J=8.4 Hz, phenyl-H), 7.42 (d, 2H, J=8.0 Hz, phenyl-H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 14.86, 109.85, 125.53, 125.56, 127.77, 127.92, 128.53, 128.96, 133.52, 133.69, 141.15; IR (ν, KBr, cm^{-1}): 754, 792, 827, 904, 946, 1007, 1032, 1072, 1155, 1326, 1443, 1467, 1498, 1537, 2918.

*2.2.4. 3-Bromo-2-methyl-5-(p-fluorophenyl)thiophene (**7d**).* Compound **7d** was prepared by an analogous method similar to that used for to **7a**. The crude product was purified by column chromatography on SiO_2 using petroleum ether as an eluent to give **7d** (3.77 g, 77%) as a pale yellow solid. Mp 61–63 °C. Anal. Calcd for $C_{11}H_8BrFS$ (%): calcd C, 48.73; H, 2.97. Found C, 48.91; H, 2.84; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.43 (s, 3H, $-CH_3$), 7.05 (s, 1H, thienyl-H), 7.09 (d, 2H, J=8.0 Hz, phenyl-H), 7.46–7.50 (m, 2H, phenyl-H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 14.80, 109.40, 115.83, 116.04, 116.31, 125.56, 127.04, 129.83, 133.98, 140.06, 163.68; IR (ν, KBr, cm^{-1}): 789,



Scheme 2. Synthetic route for the target compounds.

818, 837, 945, 1011, 1098, 1158, 1243, 1277, 1303, 1326, 1375, 1469, 1516, 1541, 1602, 1885, 2917.

*2.2.5. 3-Bromo-2-methyl-5-(p-cyanophenyl)thiophene (**7e**).* Compound **7e** was prepared by an analogous method similar to that used for to **7a**. The crude product was purified by column chromatography on SiO_2 using hexane as an eluent to give **7e** (3.96 g, 79%) as a pale yellow solid. Mp 79–80 °C. Anal. Calcd for $C_{12}H_8BrNS$ (%): calcd C, 51.81; H, 2.90; N, 5.04. Found C, 51.99; H, 3.01; N, 4.96; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.44 (s, 3H, $-CH_3$), 7.23 (s, 1H, thienyl-H), 7.58 (d, 2H, J=8.0 Hz, phenyl-H), 7.65 (d, 2H, J=8.0 Hz, phenyl-H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 15.04, 110.70, 110.88, 111.26, 118.06, 118.67, 125.48, 127.65, 128.03, 132.66, 132.81, 133.41; IR (ν, KBr, cm^{-1}): 808, 829, 1013, 1067, 1164, 1329, 1465, 1504, 1604, 2224, 2919.

*2.2.6. [2-Methyl-5-(p-methoxyphenyl)-3-thienyl]perfluorocyclopentene (**8a**).* 3-Bromo-2-methyl-5-(*p*-methoxyphenyl) thiophene (**7a**) (1.00 g, 3.5 mmol) in anhydrous THF was added dropwise to a 2.93 mol/L *n*-BuLi hexane solution (1.31 mL) at −78 °C under an argon atmosphere. Stirring was continued for 30 min. Excess octafluorocyclopentene (0.6 mL, 3.8 mmol) was added. The reaction was quenched with 20 mL water after 1 h. The mixture was warmed to room temperature and extracted with ether. The organic layer was collected and washed with 1 M aq NaCl 30 mL and then water 50 mL. The organic layer was dried over $MgSO_4$, filtrated, and evaporated. The crude product was purified by column chromatography on silica gel using petroleum ether as eluent to give **8a** (0.60 g) as a colorless solid in 43% yield. Mp 59–60 °C. Anal. Calcd for $C_{17}H_{11}F_7OS$ (%): calcd C, 51.52; H, 2.80. Found C, 51.61; H, 2.89; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.46 (s, 3H, $-CH_3$), 3.84 (s, 3H, $-OCH_3$), 6.92 (d, 2H, J=8.0 Hz, phenyl-H), 7.13 (s, 1H, thienyl-H), 7.47 (d, 2H, J=8.0 Hz, phenyl-H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 14.68, 55.39, 114.42, 120.33, 121.14, 121.85, 125.96, 127.08, 131.26, 142.11, 142.49, 159.62; IR (ν, KBr, cm^{-1}): 507, 551, 741, 826, 894, 972, 1031, 1120, 1187, 1203, 1257, 1282, 1331, 1362, 1393, 1443, 1469, 1516, 1608, 1699, 2839, 2904, 2935, 2962.

*2.2.7. [2-Methyl-5-(p-methylphenyl)-3-thienyl]perfluorocyclopentene (**8b**).* Compound **8b** was prepared by an analogous method similar to that used for **8a**. The crude product was purified by column chromatography on SiO_2 using petroleum ether as eluent to give **8b** as a colorless solid (0.86 g) in 60% yield. Mp 43–44 °C. Anal. Calcd for $C_{17}H_{11}F_7S$ (%): calcd C, 53.69; H, 2.92. Found C, 53.87; H, 2.95; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.37 (s, 3H, $-CH_3$), 2.46 (s, 3H, $-CH_3$), 7.17–7.20 (m, 3H, thienyl and phenyl-H), 7.43 (d, 2H, J=8.0 Hz, phenyl-H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 14.54, 21.13, 120.39, 121.64, 121.98, 125.62, 129.72, 129.97, 130.38, 138.11, 142.59, 142.77; IR (ν, KBr, cm^{-1}): 544, 566, 621, 745, 812, 894, 974, 1029, 1153, 1201, 1280, 1388, 1448, 1514, 1696, 1895, 2861, 2928, 3027.

*2.2.8. (2-Methyl-5-phenyl-3-thienyl)perfluorocyclopentene (**8c**).* Compound **8c** was prepared by an analogous method similar to that used for **8a**. The crude product was purified by column chromatography on SiO_2 using hexane as eluent to give **8c** as a pale yellow liquid (0.81 g) in 55% yield. Anal. Calcd for $C_{16}H_9F_7S$ (%): calcd C, 52.46; H, 2.48. Found C, 52.67; H, 2.52; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.46 (s, 3H, $-CH_3$), 7.25 (d, 1H, thienyl-H), 7.31 (t, 1H, J=8.0 Hz, phenyl-H), 7.39 (t, 2H, J=8.0 Hz, phenyl-H), 7.55 (d, 2H, phenyl-H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 14.75, 120.45, 122.23, 125.15, 125.49, 125.75, 128.11, 129.06, 133.14, 142.56, 143.10; IR (ν, KBr, cm^{-1}): 554, 615, 686, 754, 833, 894, 972, 1029, 1151, 1203, 1278, 1331, 1362, 1447, 1503, 1578, 1699, 2931, 3070.

*2.2.9. [2-Methyl-5-(p-fluorophenyl)-3-thienyl]perfluorocyclopentene (**8d**).* Compound **8d** was prepared by an analogous method similar to that used for **8a**. The crude product was purified by column chromatography on SiO_2 using petroleum ether as eluent to give **8d** as a colorless solid (0.72 g) in 49% yield. Mp 63–64 °C. Anal. Calcd for $C_{16}H_8F_8S$ (%): calcd C, 50.01; H, 2.10. Found C, 50.10; H, 2.14; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.48 (s, 3H, $-CH_3$), 6.71 (s, 3H, thienyl-H), 7.03–7.06 (m, 3H, phenyl-H), 7.48–7.51 (m, 2H, phenyl-H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 15.44, 115.94, 116.16, 120.48, 122.20, 127.45, 127.53, 129.40, 141.45, 143.07, 163.84; IR (ν, KBr, cm^{-1}): 536, 565, 622, 745, 830, 892, 970, 1032, 1143, 1202, 1235, 1279, 1328, 1363, 1386, 1473, 1513, 1603, 1705, 2858, 2925.

*2.2.10. [2-Methyl-5-(p-cyanophenyl)-3-thienyl]perfluorocyclopentene (**8e**).* Compound **8e** was prepared by an analogous method similar to that used for **8a**. The crude product was purified by column chromatography on SiO_2 using petroleum ether as eluent to give **8e** as a yellow solid (0.78 g) in 56% yield. Mp 103–104 °C. Anal. Calcd for $C_{17}H_8F_7NS$ (%): calcd C, 52.18; H, 2.06; N, 3.58. Found C, 52.23; H, 2.13; N, 3.60; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.51 (s, 3H, $-CH_3$), 7.36 (s, 1H, thienyl-H), 7.64–7.68(m, 4H, phenyl-H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 14.63, 111.20, 118.50, 120.96, 124.23, 125.80, 126.86, 132.54, 132.77, 137.18, 140.15, 145.29;

IR (ν, KBr, cm^{-1}): 561, 832, 895, 974, 1031, 1153, 1203, 1280, 1329, 1363, 1387, 1461, 1507, 1604, 1660, 1695, 2227, 2868, 2927, 3072.

*2.2.11. 1-(3,5-Dimethyl-4-isoxazolyl)-2-[2-methyl-5-(p-methoxyphenyl)-3-thienyl]perfluorocyclopentene (**1o**).* Raw material 4-iodo-3,5-dimethylisoxazole[25] (0.28 g, 1.3 mmol) in anhydrous THF was added dropwise to a 2.93 mol/L *n*-BuLi hexane solution (0.47 mL, 1.4 mmol) at −78 °C under an argon atmosphere. Stirring was continued for 30 min and **8a** (0.52 g, 1.3 mmol) was slowly added to the reaction mixture at −78 °C and stirred for 1 h at this temperature. The reaction was quenched with 20 mL water. The mixture was warmed to room temperature and extracted with ether. The organic layer was dried over $MgSO_4$, filtrated, and evaporated. The crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (v/v=6/1) as the eluent resulting in 0.23 g of **1o** being obtained in 38% yield as a pale yellow solid. Mp 73–74 °C. Anal. Calcd for $C_{22}H_{17}F_6NO_2S$ (%): calcd C, 55.81; H, 3.62; N, 2.96. Found C, 55.93; H, 3.69; N, 2.93; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 2.02 (d, 6H, *J*=8.0 Hz, $-CH_3$), 2.23 (s, 3H, $-CH_3$), 3.84 (s, 3H, $-OCH_3$), 6.92 (d, 2H, *J*=8.0 Hz, benzene-H), 7.11 (s, 1H, thiophene-H), 7.45 (d, 2H, *J*=8.0 Hz, benzene-H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 10.70, 12.09, 14.43, 55.40, 105.09, 114.28, 114.48, 120.92, 124.84, 125.85, 127.03, 128.38, 140.15, 142.97, 158.58, 159.76, 169.54; IR (ν, KBr, cm^{-1}): 457, 503, 544, 744, 808, 823, 895, 985, 1036, 1063, 1105, 1136, 1182, 1248, 1277, 1340, 1400, 1512, 1550, 1608, 1658, 2169, 2854, 2930, 3439, 3526.

*2.2.12. 1-(3,5-Dimethyl-4-isoxazolyl)-2-[2-methyl-5-(p-methylphenyl)-3-thienyl]perfluorocyclopentene (**2o**).* Diarylethene **2o** was prepared by an analogous method to that used for compound **1o** using **8b** instead of **8a**. The crude product was purified by column chromatography on SiO_2 using petroleum ether/ethyl acetate (v/v=5/1) as eluent to give **2o** (0.46 g, 47%) as a pale yellow solid. Mp 60–61 °C. Anal. Calcd for $C_{22}H_{17}F_6NOS$ (%): calcd C, 57.76; H, 3.75; N, 3.06. Found C, 57.81; H, 3.79; N, 3.10; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 2.02 (s, 3H, $-CH_3$), 2.07(s, 3H, $-CH_3$), 2.22 (s, 3H, $-CH_3$), 2.36 (d, 3H, $-CH_3$), 7.16(s, 2H, benzene-H), 7.20(s, 1H, thiophene-H), 7.41(d, 2H, *J*=8.0 Hz, benzene-H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 10.72, 12.11, 14.48, 21.16, 105.07, 121.48, 124.86, 125.45, 125.61, 129.71, 130.25, 130.51, 138.22, 142.36, 143.18, 158.58, 169.58; IR (ν, KBr, cm^{-1}): 459, 480, 536, 561, 692, 742, 810, 842, 893, 937, 991, 1064, 1107, 1134, 1193, 1278, 1344, 1400, 1593, 1658, 1699, 3525, 3441.

*2.2.13. 1-(3,5-Dimethyl-4-isoxazolyl)-2-(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene (**3o**).* Diarylethene **3o** was prepared by an analogous method to that used for compound **1o** using **8c** instead of **8a**. The crude product was purified by column chromatography on SiO_2 using petroleum ether/ethyl acetate (v/v=6/1) as eluent to give **3o** (0.39 g, 45%) as a pale yellow solid. Mp 67–68 °C. Anal. Calcd for $C_{21}H_{15}F_6NOS$ (%): calcd C, 56.88; H, 3.41; N, 3.16. Found C, 56.97; H, 3.39; N, 3.20; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 2.04 (s, 6H, $-CH_3$), 2.23 (s, 3H, $-CH_3$), 7.25 (d, 1H, *J*=8.0 Hz, thiophene-H), 7.33 (d, 1H, *J*=8.0 Hz, benzene-H), 7.39 (t, 2H, *J*=8.0 Hz, benzene-H), 7.53 (d, 2H, *J*=8.0 Hz, benzene-H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 10.67, 12.09, 14.47, 100.50, 105.03, 122.03, 123.11, 124.90, 125.66, 128.13, 129.02, 132.96, 141.69, 142.99, 158.51, 169.55; IR (ν, KBr, cm^{-1}): 461, 501, 545, 684, 752, 808, 850, 894, 989, 1031, 1062, 1105, 1134, 1193, 1278, 1340, 1398, 1423, 1444, 1500, 1550, 1598, 1659, 2918, 3028, 3439, 3525, 3612.

*2.2.14. 1-(3,5-Dimethyl-4-isoxazolyl)-2-[2-methyl-5-(p-fluorophenyl)-3-thienyl]perfluorocyclopentene (**4o**).* Diarylethene **4o** was prepared by an analogous method to that used for compound **1o** using **8d** instead of **8a**, The crude product was purified by column chromatography on SiO_2 using petroleum ether/ethyl acetate (v/v=6/1) as eluent to give **4o** (0.32 g, 47%) as a pale yellow solid. Mp 85–86 °C. Anal. Calcd for $C_{21}H_{14}F_7NOS$ (%): calcd C, 54.67; H, 3.06; N, 3.04. Found C, 54.85; H, 3.10; N, 3.05; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 2.04 (s, 6H, $-CH_3$), 2.24 (s, 3H, $-CH_3$), 7.10 (t, 2H, *J*=8.0 Hz, benzene-H), 7.17 (s, 1H, thiophene-H), 7.49–7.52 (m, 2H, benzene-H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 10.76, 12.16, 14.51, 37.43, 115.98, 116.20, 121.99, 124.99, 127.44, 127.51, 128.79, 128.82, 129.30, 141.92, 158.56, 169.59; IR (ν, KBr, cm^{-1}): 455, 495, 536, 559, 744, 808, 827, 894, 985, 1062, 1103, 1134, 1161, 1193, 1230, 1278, 1342, 1400, 1471, 1512, 1552, 1598, 1629, 1644, 1735, 2320, 2349, 2378, 3440, 3525, 3612.

*2.2.15. 1-(3,5-Dimethyl-4-isoxazolyl)-2-[2-methyl-5-(p-cyanophenyl)-3-thienyl]perfluorocyclopentene (**5o**).* Diarylethene **5o** was prepared by an analogous method to that used for compound **1o** using **8e** instead of **8a**. The crude product was purified by column chromatography on SiO_2 using petroleum ether/ethyl acetate (v/v=3/1) as eluent to give **5o** (0.38 g, 45%) as a pale yellow solid. Mp 66–67 °C. Anal. Calcd for $C_{22}H_{14}F_6N_2OS$ (%): calcd C, 56.41; H, 3.01; N, 5.98. Found C, 56.53; H, 3.06; N, 6.01; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 2.03 (s, 3H, $-CH_3$), 2.06 (s, 3H, $-CH_3$), 2.23 (s, 3H, $-CH_3$), 7.35 (s, 1H, thiophene-H), 7.61–7.69 (m, 4H, benzene-H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 10.77, 12.18, 14.67, 104.89, 111.54, 118.47, 124.16, 125.58, 125.80, 126.00, 132.92, 137.17, 140.68, 143.32, 158.44, 169.64; IR (ν, KBr, cm^{-1}): 443, 505, 530, 551, 565, 592, 617, 684, 744, 808, 840, 894, 987, 1062, 1112, 1136, 1178, 1195, 1274, 1323, 1342, 1402, 1423, 1506, 1546, 1602, 1629, 1658, 2223, 2925, 2985, 3440, 2525, 3631.

3. Results and discussion

3.1. Photoisomerization of photochromic diarylethenes

The photochromic behaviors of diarylethenes **1**–**5** induced by photoirradiation were measured at room temperature both in hexane and in poly(methyl methacrylate) (PMMA) films. The changes in the absorption spectra and color of diarylethenes **1**–**5** in hexane induced by photoirradiation are shown in Fig. 1. The absorption band of the open-ring isomer **1o** in hexane appeared at 288 nm (ε, 2.28×10^4 L mol^{-1} cm^{-1}). Upon irradiation with 297 nm UV light, the colorless solution of **1o** was converted into a purple solution of the closed-ring isomer **1c** with a new visible absorption band centered at 532 nm. The shoulder at 339 nm is assigned to the $S_0\rightarrow S_2$ transition.[26] Alternatively, the purple-colored solution could be bleached to colorless upon irradiation with visible light (λ>450 nm), indicating that **1c** returned to the initial state **1o**. As with compound **1**, diarylethenes **2**–**5** also exhibited notable photochromism in hexane. Upon irradiation with 297 nm light, absorption bands in the visible region appeared and the colorless solutions **2o**–**5o** turned purple (Fig. 1F) due to cyclization reactions resulting in the formation of the closed-ring isomers **2c**–**5c**, which their absorption maxima were appeared at 530, 526, 523, and 527 nm, respectively. All of the purple-colored solutions **2c**–**5c** can be decolorized by irradiation with visible light of wavelength greater than 450 nm, suggesting return to the open-ring isomers **2o**–**5o**. In the photostationary state, the isosbestic points for diarylethenes **1**–**5** in hexane were observed at 313, 304, 298, 297, and 329 nm, respectively. When arrived at the photostationary state, the photoconversion ratios from open-ring to closed-ring isomers of the five derivatives were analyzed by HPLC in hexane, and the results are shown in Fig. 2. From this figure, it can be easily calculated the photoconversion ratios of diarylethenes **1**–**5** in the photostationary state, which their values are 87% for **1**, 75% for **2**, 64% for **3**, 60% for **4**, and 80% for **5** (Table 1). Compared with diarylethenes bearing a pyrrole moiety,[27] the photoconversion ratios of diarylethenes **1**–**5** were significantly decreased in solution.

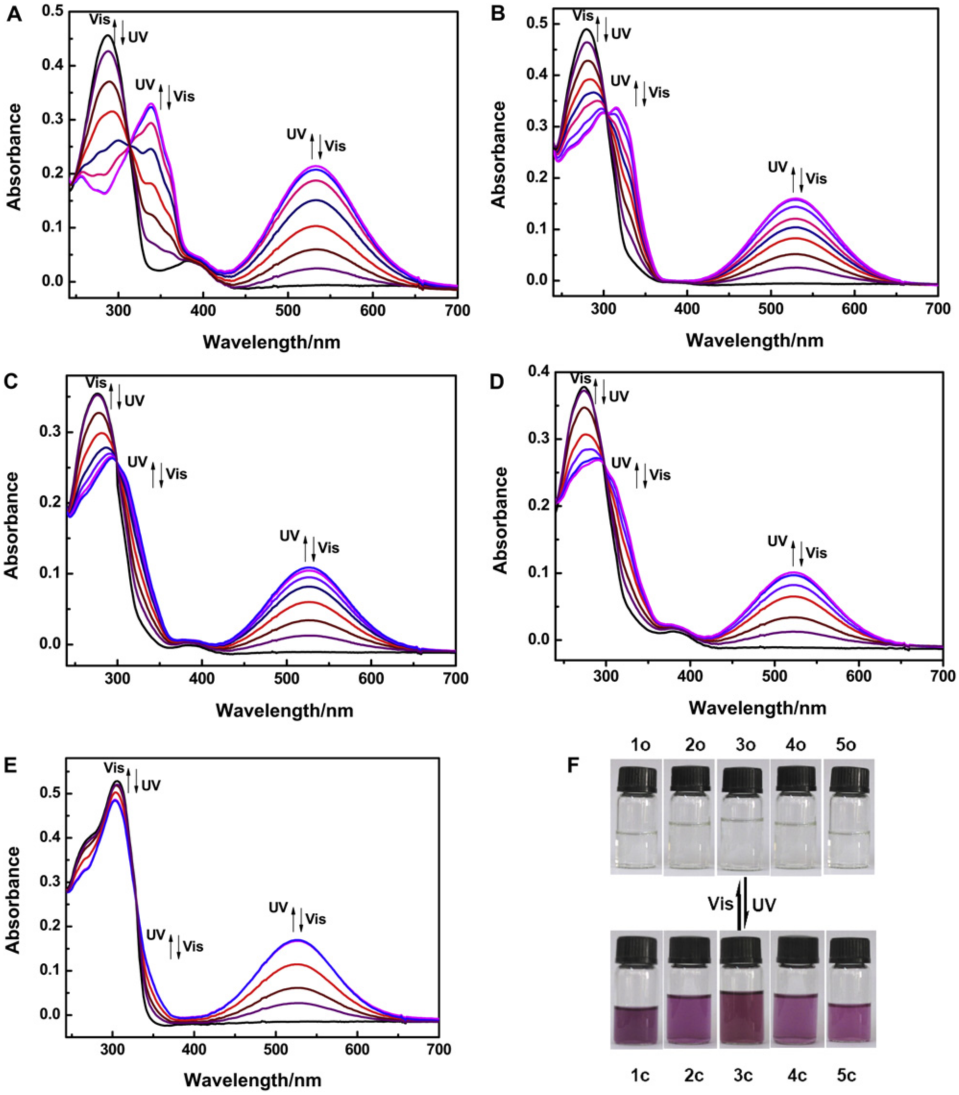


Fig. 1. Absorption spectral and color changes of diarylethenes **1**–**5** upon alternating irradiation with UV and visible light in hexane (2.0×10^{-5} mol L^{-1}) at room temperature: (A) spectral changes for **1**, (B) spectral changes for **2**, (C) spectral changes for **3**, (D) spectral changes for **4**, (E) spectral changes for **5**, (F) color changes for diarylethenes **1**–**5**.

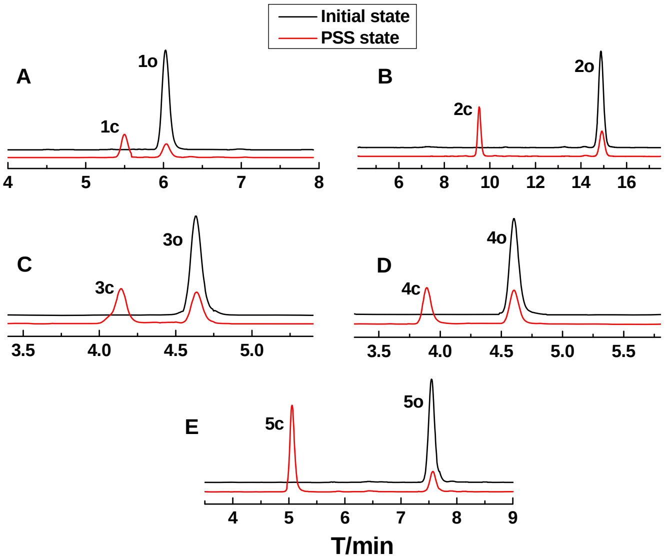


Fig. 2. The photoconversion ratios of diarylethenes **1**–**5** at photostationary state in hexane analysized by HPLC method.

However, they were approximately equal to those of diarylethenes bearing oxazole moieties.[22c,d] In PMMA films, diarylethenes **1**–**5** also showed similar photochromism as in hexane, and their spectral and color changes are shown in Fig. 3. The PMMA films were prepared by dissolving 10 mg of diarylethene sample and 100 mg of poly(methyl methacrylate) in chloroform (1 mL) with the aid of ultrasound, then spin-coating the homogeneous solution on a quartz substrate ($20\times10\times1$ mm^3) at 1500 rpm. Compared to those in hexane, the maximum absorption peaks of both the open-ring and the closed-ring isomers of diarylethenes **1**–**5** in PMMA film are at longer wavelengths than those in hexane. The red shift values of the absorption maxima of the open-ring isomers are 3 nm for **1o**, 4 nm for **2o**, 3 nm for **3o**, 3 nm for **4o**, and 6 nm for **5o**, and those of the closed-ring isomers are 17 nm for **1c**, 13 nm for **2c**, 11 nm for **3c**, 12 nm for **4c** and 10 nm for **5c**, respectively. The red shift phenomena are consistent with those of the majority of the reported diarylethenes,[28,29] which may be attributed to the polar effect of the polymer matrix in amorphous polymer state. In addition, the fatigue resistances of diarylethenes **1**–**5** were examined both in hexane and in PMMA films by alternating irradiation with UV and visible light in air at room temperature. In hexane, the coloration and decoloration cycles of diarylethenes **1**–**5** can be

Table 1
Absorption spectral properties of diarylethenes **1**–**5** in hexane at 2.0×10^{-5} mol/L and in PMMA films

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	288(2.28×10^4)	291	532(1.23×10^4)	549	0.41	0.15	87%
2	280(2.45×10^4)	284	530(1.07×10^4)	543	0.19	0.14	75%
3	276(1.77×10^4)	279	526(8.51×10^3)	537	0.15	0.20	64%
4	274(1.89×10^4)	277	523(8.38×10^3)	535	0.16	0.19	60%
5	306(2.64×10^4)	312	527(1.06×10^4)	537	0.21	0.14	80%

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

repeated more than 50 times with only ca. 7% degradation of each of **1c**, 8% degradation of **2c**, 8% degradation of **3c**, 9% degradation of **4c**, and 6% degradation of **5c**, respectively. The fatigue resistance of diarylethenes **1**–**5** in PMMA films is much stronger than that in solution. After 200 repeated cycles, these diarylethenes still exhibited good photochromism with only ca. 5% degradation of **1c**, 6% degradation of **2c**, 6% degradation of **3c**, 7% degradation of **4c**, and 5% degradation of **5c**, respectively.

The photochromic parameters of diarylethenes **1**–**5** are summarized in Table 1. It can be easily seen from this table that the different substituent at the *para*-position of the benzene ring has a remarkable effect on the photochromic properties of these diarylethenes derivatives, including the absorption maxima, molar absorption coefficients, and the quantum yields of cyclization and cycloreversion. As shown in Table 1, the stronger the electron-donating/withdrawing ability of the substituent is, the greater the

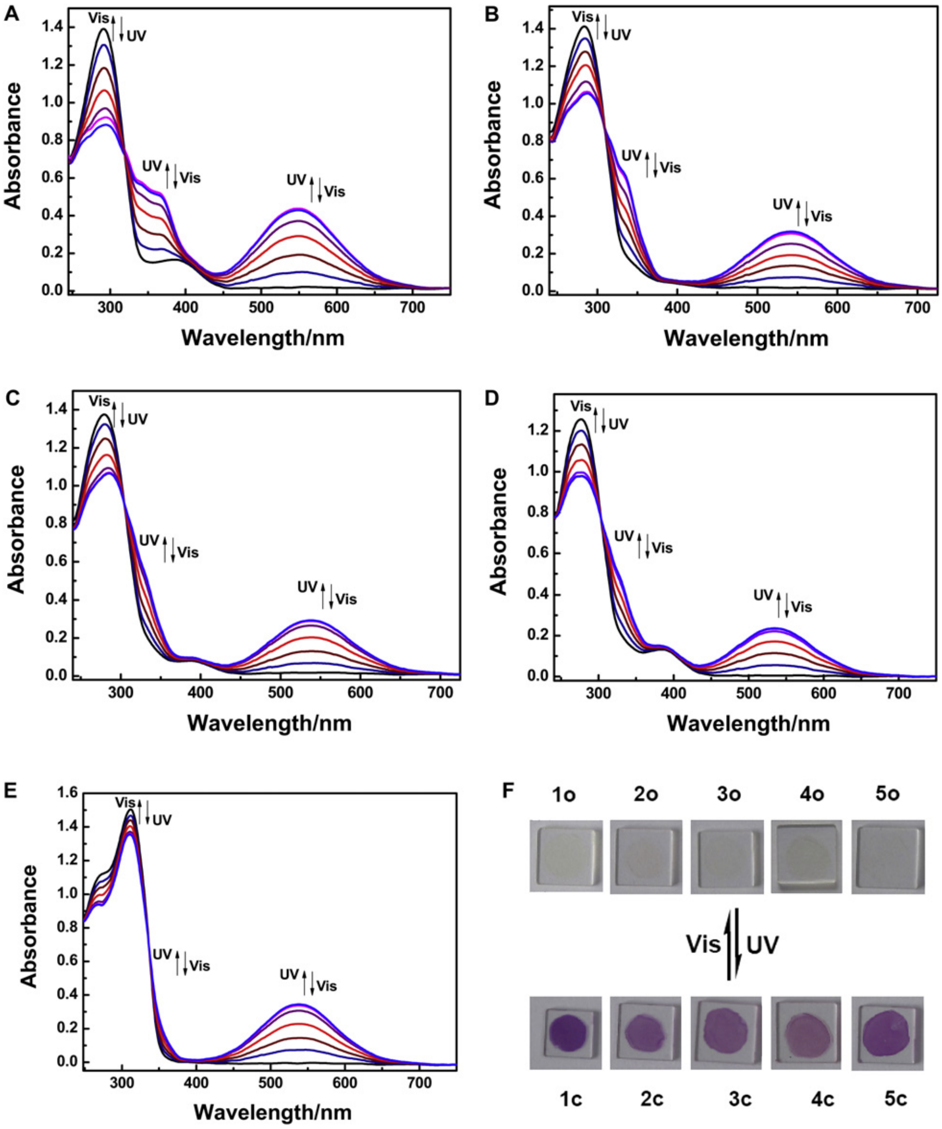


Fig. 3. Absorption spectral and color changes of diarylethenes **1**–**5** upon alternating irradiation with UV and visible light in PMMA films (10%, w/w) at room temperature: (A) spectral changes for **1**, (B) spectral changes for **2**, (C) spectral changes for **3**, (D) spectral changes for **4**, (E) spectral changes for **5**, (F) color changes of diarylethenes **1**–**5**.

absorption maximum and the molar absorption coefficient of diarylethene are achieved both in the open-ring and the closed-ring isomers with the exception of diarylethene **2o**. As a result, the absorption maximum and the molar absorption coefficient of diarylethene **1b** are greater than those of diarylethene **2b** because of the stronger electron-donating ability of methoxy group as compared to a methyl group,[30,31] and the similar change occurs in between **5** and **4** due to the stronger electron-withdrawing ability of cyano group as compared to a fluorine atom.[32] Compared to the unsubstituted parent diarylethene **3**, the absorption maxima exhibited a clear red shift both in the open-ring and the closed-ring isomers when replacing the hydrogen atom at the *para*-position of the terminal benzene ring with an electron-donating substituent (methoxy or methyl group, such as in diarylethene **1** or **2**). For diarylethenes **1**–**5**, the absorption maxima of their closed-ring isomers were observed at 523–532 nm in hexane, which were much shorter than that of diarylethenes with the similar molecular skeleton including pyrazole, benzene, or thiophene.[17a,30,33,34] However, their absorption maxima were much longer than that of similar skeleton diarylethene bearing a thiazole moiety.[32] The result suggested that the isoxazole moiety can be effective to shift the absorption maximum of diarylethene to a shorter wavelength direction, but its action is slightly less than thiazole ring. The cyclization and cycloreversion quantum yields of the unsubstituted parent compound **3** are 0.15 and 0.20, respectively. No matter replacing the hydrogen atom at the *para*-position of the terminal benzene ring with an electron-donating (methoxy or methyl group) or with an electron-withdrawing substituent (fluorine or cyano group), the cyclization quantum yields have clearly increased with the increase in both electron-donating and electron-withdrawing ability and the cycloreversion quantum yields showed a reverse trend. As a result, the unsubstituted parent diarylethene **3** has the smallest cyclization quantum yield and the biggest cycloreversion quantum yield. Furthermore, the cyclization quantum yield of **1** (Φ_{o-c}=0.41) is twofold larger than that of **2** (Φ_{o-c}=0.19) and its cycloreversion quantum yield (Φ_{c-o}=0.15) is almost equal to that of **2** (Φ_{c-o}=0.14). This indicated that the ability of the electron-donating substituent can influence significantly the cyclization quantum yield but not notably for the cycloreversion quantum yield. However, the cyclization quantum yield of **4** is much smaller than that of **5** and its cycloreversion quantum yield is larger than that of **5**, suggesting that the electron-withdrawing substituent plays an important role during the process of the photochromic reaction for the diarylethenes bearing an isoxazole moiety. The result is quite different from those reported for diarylethenes bearing a phenyl moiety, where both the electron-donating groups and the electron-withdrawing groups can notably influence the quantum yields of photochromic reactions.[13c,28,29] In addition, the cycloreversion quantum yields of diarylethenes **3** and **4** are greater than their cyclization quantum yields, which is the same as that of diarylethenes bearing a pyrazole unit.[17a]

3.2. Fluorescence of diarylethenes

The fluorescence properties of diarylethenes **1o**–**5o** both in solution (2.0×10^{-5} mol/L) and in amorphous PMMA films (10%, w/w) were measured at room temperature. In hexane, the emission peaks of diarylethenes **1o**–**5o** were observed at 436 nm, 420 nm, 412 nm, 411 nm, and 396 nm, respectively, when excited at 290 nm (Fig. 4). The result showed that the emission peaks of diarylethenes **1o**–**5o** gradually shifted to a shorter wavelength in hexane (from 436 to 396 nm) when going from electron-donating to electron-withdrawing groups, and their emission intensity increased evidently with the increase in electron-withdrawing ability. In PMMA films, the emission peaks of diarylethenes **1o**–**5o** were observed at 498 nm, 490 nm, 496 nm, 497 nm, and 488 nm when excited at 390 nm. Compared to those in hexane, the emission peaks of diarylethenes **1o**–**5o** showed a remarkable bathochromic shift in PMMA film consistently across their maxima absorption wavelengths with values of 62 nm for **1**, 70 nm for **2**, 84 nm for **3**, 85 nm for **4**, and 92 nm for **5**, respectively. By using anthracene as the reference, the fluorescence quantum yields of diarylethenes **1**–**5** were determined to be 0.0062, 0.0071, 0.0094, 0.0091, and 0.0172, respectively. The results indicated that the fluorescence quantum yield increased notably when going from electron-donating to electron-withdrawing groups. This is completely contrary to that of diarylethenes bearing a biphenyl moiety, where the fluorescence quantum yield increased with the increase in the electron-donating ability.[28,30]

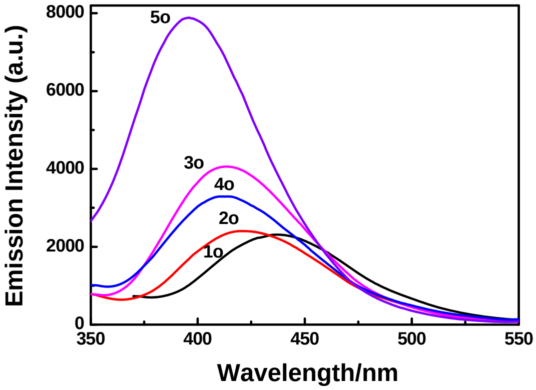


Fig. 4. Fluorescence emission spectra of diarylethenes **1**–**5** in hexane at room temperature when excited at 290 nm.

Just like most of the reported diarylethenes,[27,29a,c,34] diarylethenes **1**–**5** exhibited a notably fluorescent switch on changing from the open-ring isomers to the closed-ring isomers by photoirradiation both in hexane and in PMMA film. When irradiated with UV light, the emission intensity of diarylethene **1o**–**5o** decreased evidently because of the formation of the non-fluorescence closed-ring isomers **1c**–**5c**. The back irradiation by appropriate wavelength visible light regenerated the open-ring isomer and recovered the original emission intensity. During the process of photoisomerization, the fluorescent spectral changes of diarylethene **1**–**5** in hexane and in PMMA films are shown in Figs. 5 and 6, respectively. In hexane, the samples arrived at the photostationary state upon irradiation with 297 nm UV light, resulting in the emission intensities of diarylethenes **1**–**5** being quenched to ca. 16%, 35%, 36%, 46% and 46%, respectively. Similarly, upon irradiation with 297 nm light, the emission intensities at the photostationary state were quenched to ca. 2% for **1**, 8% for **2**, 9% for **3**, 5% for **4**, and 13% for **5**. That is to say, the fluorescent modulation efficiencies of the five diarylethenes in hexane are 84% for **1**, 65% for **2**, 64% for **3**, 54% for **4**, and 54% for **5**, and those in PMMA films are 98% for **1**, 92% for **2**, 91% for **3**, 95% for **4**, and 87% for **5** when arrived at the photostationary state. The result illustrated that the fluorescent modulation efficiencies of **1**–**5** in PMMA films were much greater than those in hexane. This is completely contrary to those of diarylethenes bearing a pyrrole or thiazole moiety whose fluorescent modulation efficiencies in PMMA films were much lower than those in hexane.[27,28,31,32] For practical applications in optoelectronic devices, it is very important that photochromic diarylethenes can function as an effective fluorescent photoswitch in a solid state, such as PMMA film. Therefore, these diarylethene compounds could be potentially suitable for using as optical memory with fluorescence readout method or a fluorescent photoswitch.[6b,35,36] The incomplete cyclization reaction and the existence of parallel conformations of diarylethenes **1**–**5** may be the cause for the smaller change in fluorescent intensity induced by

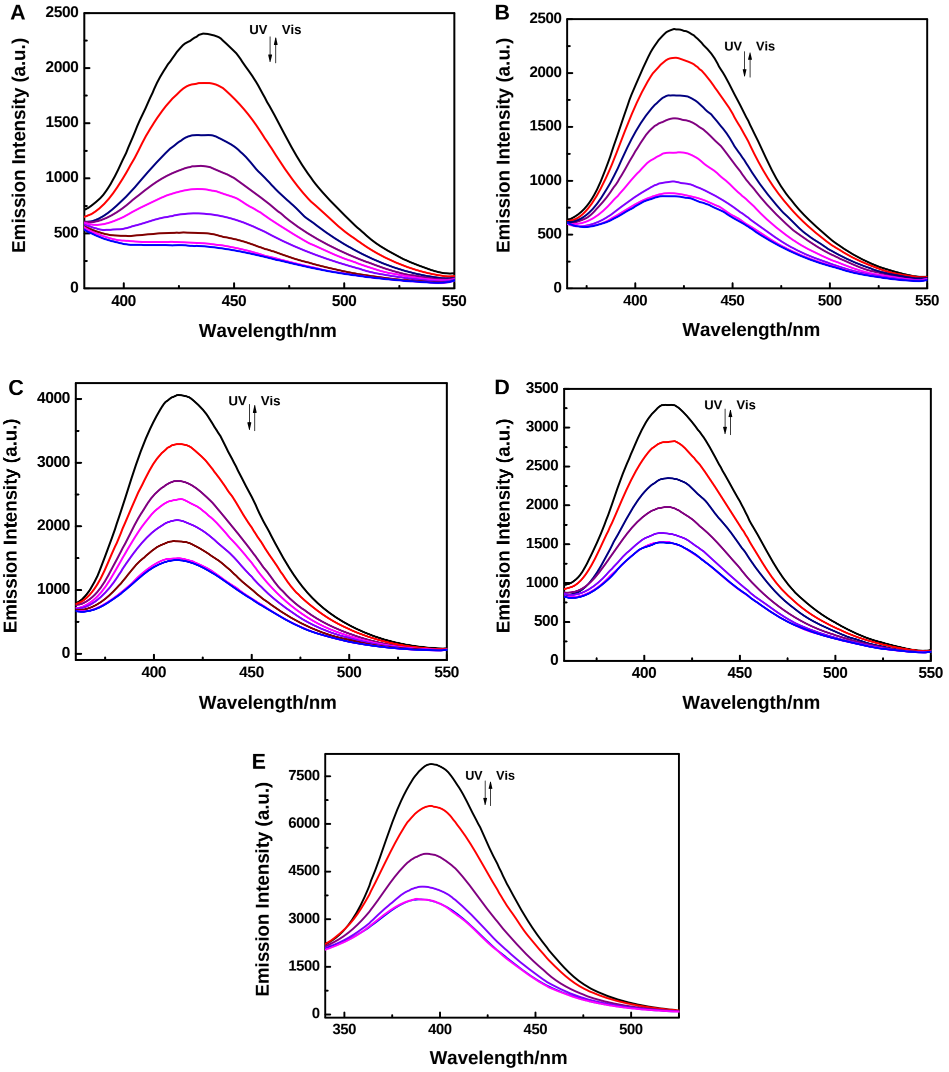


Fig. 5. Emission intensity changes of diarylethenes **1**–**5** in hexane (2.0×10^{-5} mol L^{-1}) upon irradiation with 297 nm UV light at room temperature, excited at 290 nm: (A) **1**, (B) **2**, (C) **3**, (D) **4**, and (E) **5**.

photoirradiation in hexane.[29a,b] Among the five diarylethenes, the fluorescent modulation efficiency of diarylethene **1** was the biggest and that of diarylethene **5** was the smallest both in hexane and in a PMMA film, suggesting that the diarylethene **1** is the best candidate for the fluorescent photoswitching material. In addition, the fluorescent modulation efficiencies of diarylethenes **1**–**5** were significantly enhanced both in hexane and in PMMA films as compared to some reported dithienylethenes derivatives.[29a,b]

3.3. Electrochemistry of diarylethenes

Because of the differences in the π-conjugation of the two isomers of diarylethenes, photochromic diarylethene derivatives possibly allow for changes in the electrochemical property. To date, the oxidative cyclization and cycloreversion of diarylethene derivatives have been attracted much attention due to their potentially important applications in photoelectronic devices.[7,37] Herein, the electrochemical examinations of the diarylethenes **1**–**5** were performed by linear sweep method under the same experimental conditions at a scanning rate of 50 mV/s. The typical electrolyte was acetonitrile (5 mL) containing 0.1 mol/L tetrabutylammonium tetrafuoroborate ($(TBA)BF_4$) and 1.0×10^{-3} mol/L diarylethene sample. All solutions were deaerated by bubbling with a dry argon stream and maintained at a slight argon overpressure during electrochemical experiments. Fig. 7 shows the anodic polarization curves of diarylethenes **1**–**5**. The oxidation onsets of the open-ring isomers **1o**–**5o** were initiated at 1.29 V, 1.47 V, 1.52 V, 1.54 V, and 1.67 V, and those of the closed-ring isomers **1c**–**5c** were initiated at 1.23 V, 1.35 V, 1.44 V, 1.47 V, and 1.57 V, respectively. Therefore, the difference of oxidation onset between the open-ring and closed-ring isomers of diarylethenes **1**–**5** (ΔV_{o-c}) was 0.06 V for **1**, 0.12 V for **2**, 0.08 V for **3**, 0.07 V for **4**, and 0.10 V for **5**. The result shows 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 in accordance with the theory that the longer conjugation length of the closed-ring isomer generally leads to a less positive potentials.[32,38] For the closed-ring isomers, the π-electrons delocalize throughout the two condensed aryl moieties and extend to the substituents causing a lower oxidation onset. Compared to the unsubstituted parent diarylethene **3**, the oxidation onsets decreased clearly when replacing the hydrogen atom at the *para*-position of the terminal benzene ring with an electron-donating substituent (methoxy or methyl group, such as in diarylethene **1** or **2**), and the reverse case occurred when the same position instead contained an electron-withdrawing substituent (fluorine or cyano group, such as in diarylethene **4** or **5**). The results indicated that the

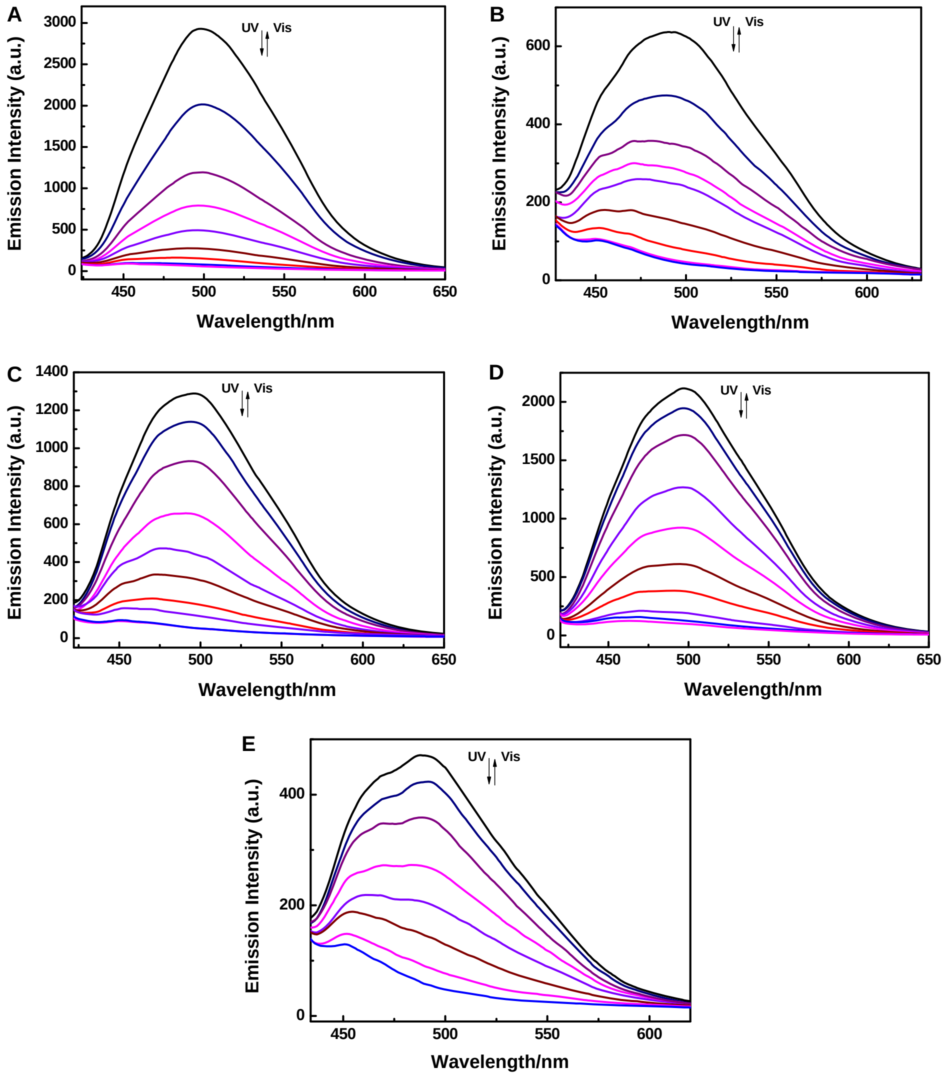


Fig. 6. Emission intensity changes of diarylethenes **1**–**5** in PMMA films (10%, w/w) upon irradiation with 297 nm UV light at room temperature, excited at 390 nm: (A) **1**, (B) **2**, (C) **3**, (D) **4**, and (E) **5**.

oxidation onsets increased evidently when going from electron-donating to electron-withdrawing groups both in the open-ring and the closed-ring isomers. This is distinguishable from other diarylethenes bearing other aryl moiety reported so far, such as pyrrole, biphenyl, thiazole, and so forth.[17a,30,32] In addition, only one oxidation processes can be easily observed during anodic oxidation of **5o** and **5c**, while two oxidation processes can be observed during anodic oxidation of the other four diarylethene derivatives. This phenomenon may be attributed to the different electron mobility resulted from the different substituents at *para*-position of the terminal benzene ring but further explanation is required to quantify the effects.

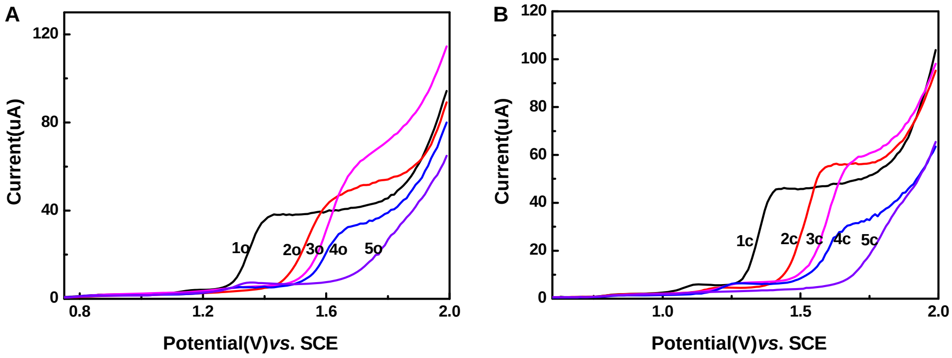


Fig. 7. The anodic polarization curves of diarylethenes **1**–**5** in acetonitrile at a scanning rate of 50 mV/s: (A) the curves of the open-ring isomers **1o**–**5o**, (B) the curves of the closed-ring isomers **1c**–**5c**.

4. Conclusions

Five new unsymmetrical diarylethenes possessing an isoxazole moiety were synthesized to investigate substituent effects on their photochemical and electrochemical properties. The new photochromic systems exhibited remarkable photochromism and acted as a notable fluorescent switch both in solution and in amorphous polymer films. The different substituents at the *p*-position of the terminal benzene ring have a significant effect on the properties of these diarylethene derivatives. The isoxazole moiety induced some new features differing from other diarylethenes with other heteroaryl moieties reported so far. The results will be helpful in designing new diarylethenes for further potential applications.

Acknowledgements

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