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Photochromism of new 3,5-position hybrid diarylethene derivatives bearing both thiophene and thiazole moieties

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ABSTRACT

Five new diarylethenes based on a hybrid structure of bis(5-thiazolyl)ethene and bis(3-thienyl)ethene were synthesized, and the structures of the four compounds were determined by single-crystal X-ray diffraction analysis. The properties of these diarylethenes, such as photochromism, fluorescence, and electrochemical properties were investigated in detail. All of these compounds showed good photochromism and fluorescence both in solution and in PMMA films. The electron-donating substituents could effectively increase the cyclization and cycloreversion quantum yields, and the fluorescence emission peaks, whereas the electron-withdrawing groups functionalized an inverse action for these diarylethene derivatives. Cyclic voltammetry revealed that great differences existed amongst the electrochemical behaviors of these compounds. The oxidation potentials and the band gaps of these diarylethenes increased remarkably with the increase in electron-withdrawing ability. All results suggested that the effects of substitution have a significant effect on the photochemical and electrochemical behaviors of these diarylethene derivatives.

1. Introduction

Photochromic compounds have attracted much attention because of their potential application to photonic devices, such as high-density optical recording materials and photoswitches.[1] Among various types of photochromic compounds, diarylethene derivatives with heterocyclic aryl rings are the most promising candidates for photoelectronic applications because of the excellent thermal stability of the respective isomers, notable fatigue resistance, and rapid response, and high reactivity in solid state.[2]

Among the diarylethenes hitherto reported, most of them have an absorption peak with the region between 550 and 750 nm wavelengths,[3] with just a few reports concerning photochromic diarylethenes whose absorption peaks beyond this wavelength range. The longest wavelength of diarylethene so far reported was observed at 828 nm,[4] and the shortest one showed its longest absorption bands in the UV light region (260 nm).[5] For the application to optical recording, it is very important to develop photochromic diarylethenes with different absorption wavelengths, which can expect to match perfectly with the wavelength of recording laser. Especially, it is indispensable to prepare diarylethene derivatives with a shorter absorption wavelength because the recording capacity is proportional to the recording laser wavelength.[6] That is to say, the shorter the absorption wavelength of diarylethene contains, the higher recording density is expected to achieve because the light can be focused more sharply. Therefore, developing diarylethene derivatives with an absorption band around 500 nm or even shorter for making use of short-wavelength optical recording materials is very necessary.

Guided by this aim, several approaches to shift the absorption maximum of the closed-ring isomer to a shorter wavelength are to attach the thiophene rings to the ethene moiety at the 2-position.[3,7,2d] As we all known, the absorption spectrum is dependent on the substituent effects[8] and the π-conjugation length in a diarylethene molecule.[9] In bis(2-thienyl)ethene photochromic system, the π-conjugation in closed-ring isomer is only localized in a cyclohexadiene structure, shifting the absorption to shorter wavelength, as compared with the closed-ring isomer of bis(3-thienyl)ethene photochromic system where the π-conjugation extends throughout the whole molecule.[3,7b] For instance, the absorption maximum of the closed-ring diarylethene with a structure of 1,2-bis(2-thienyl)ethene was observed at 425 nm,[10] while that of the reported diarylethene with a structure of 2,3-position hybrid thiophene rings was observed at 469 nm.[11] However, the absorption maximum of the closed-ring isomer with a structure of 1,2-bis(3-thienyl)ethene was observed at 534 nm.[10,12] Compared with the parent analogues, diarylethene derivatives with oxidized thiophene/benzothiophene rings could also significantly shift their absorption band to a shorter

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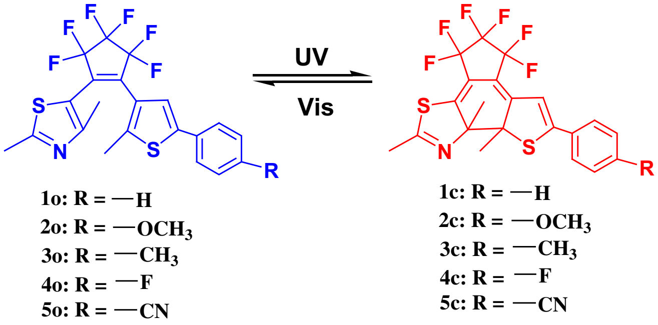
wavelength during the process of photocyclization.[5,13,14] Another attempt is to introduce the thiazole rings into the diarylethene system as the aryl moieties.[15] When the thiophene rings of 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene[16] are replaced with thiazole rings, the absorption maximum of the closed-ring isomer shifts from 575 nm to 525 nm.[15a,d] Similarly, when the thiophene rings of 1,2-bis(3,5-dimethyl-2-thienyl)perfluorocyclopentene[10,17] are replaced with thiazole rings, the absorption maximum shifts from 432 nm to 391 nm.[15a]

From the reports described above, it can be easily concluded that most of diarylethenes with thiazole rings reported to date are symmetrical compounds or the thiazole ring is attached to the ethene moiety at the 4-position. Report concerning diarylethenes with 5-thiazolyl moieties is very rare. To the best of our knowledge, diarylethenes with a hybrid structure of 5-thiazolyl and 3-thienyl moieties have not hitherto been reported. In this study, we have synthesized a new class of photochromic diarylethene derivatives bearing both 5-thiazolyl and 3-thienyl moieties (**1o**–**5o**). All of these diarylethenes showed good photochromism both in solution and in PMMA amorphous films, and most of them also showed good photochromism in the crystalline phase. The photochromic scheme of diarylethenes **1o**–**5o** is shown in Scheme 1.



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

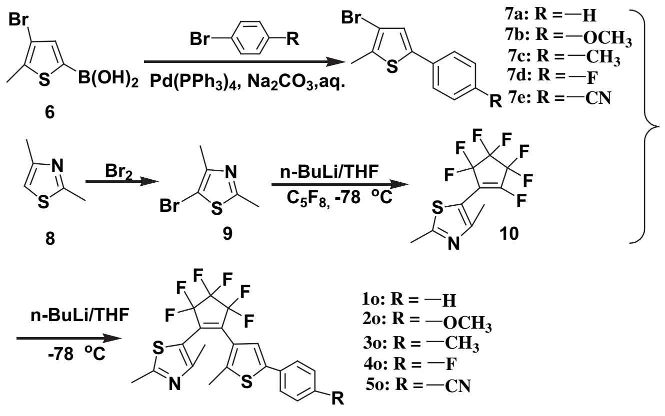
2. Experimental

2.1. General methods

All solvents used were spectroscopic grade and were purified by distillation before use. 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. Melting point was taken on a WRS-1B melting point apparatus. Absorption spectra were measured using an Agilent 8453 UV/vis spectrophotometer. Photoirradiation was carried out using a 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. Fluorescence spectra were measured using a Hitachi F-4500 spectrophotometer. 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 wires (diameter 0.5 mm) served as the working electrode and counter electrode. Platinum wire (diameter 0.5 mm) in the supporting electrolyte solution served as a quasi-reference electrode, which was calibrated using an internal ferrocene (F_c/F_c^+) standard with a formal potential of $E_{1/2}$=+0.35 V versus platinum wire in the same electrolyte. The typical electrolyte was acetonitrile (5 mL) containing 0.1 mol/L tetrabutylammonium tetrafluoroborate ((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.

2.2. Synthesis of diarylethenes

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[18] gave the alkylphenylthiophene derivatives (**7a**–**e**). Separately, 1-(2,4-dimethyl-5-thiazolyl)perfluorocyclopentene (**10**) was synthesized by bromination and lithiation reactions from 2,4-dimethylthiazole. Finally, compounds **7a**–**e** were separately lithiated and then coupled with compound **10** to give diarylethenes **1o**–**5o**, respectively. The structures of **1o**–**5o** were confirmed by elemental analysis, NMR, and IR.



Scheme 2. Synthetic route for the target compounds.

*2.2.1. 3-Bromo-2-methyl-5-phenyl-thiophene (**7a**).* This compound was synthesized by the same method as that reported in a reference.[15e] Compound **7a** was prepared by reacting 3-bromo-2-methyl-5-thienylboronic acid[18] (2.90 g, 13.10 mmol) with bromobenzene (2.06 g, 13.10 mmol) in the presence of Pd(PPh$_3$)$_4$ (0.27 g, 0.23 mmol) and Na$_2$CO$_3$ (6.36 g, 60.00 mmol) in tetrahydrofuran (THF) (80 mL containing 10% water). After refluxing for 15 h at 70 °C, the product was allowed to slowly warm to the room temperature and then extracted with ether. The organic layer was collected and dried over MgSO$_4$, filtrated, and evaporated. The crude product was purified by column chromatography on SiO$_2$ using hexane as an eluent resulting in 2.76 g of **7a** being obtained as a buff solid in 83% yield. Mp 66–68 °C; ^{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).

*2.2.2. 3-Bromo-2-methyl-5-(4-methoxyphenyl)thiophene (**7b**).* Compound **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** (2.63 g, 79%) as a buff solid. Mp 106–107 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 2.41 (s, 3H, –CH$_3$), 3.91 (s, 3H, –OCH$_3$), 6.95–6.99 (m, 2H, phenyl-H), 7.27 (s, 1H, thienyl-H), 7.30 (s, 1H, phenyl-H), 7.54 (d, 1H, *J*=8.0 Hz, phenyl-H).

*2.2.3. 3-Bromo-2-methyl-5-(4-methylphenyl)thiophene (**7c**).* Compound **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** (2.66 g, 80%) as a buff solid. Mp 68–69 °C; ^{1}H NMR (400 MHz, CDCl$_3$, TMS): δ 2.37 (s, 3H, –CH$_3$), 2.41 (s, 3H, –CH$_3$), 7.01 (s, 1H, thienyl-H), 7.19 (d, 2H, *J*=8.0 Hz, phenyl-H), 7.38 (d, 2H, *J*=8.0 Hz, phenyl-H).

*2.2.4. 3-Bromo-2-methyl-5-(4-fluorophenyl)thiophene (**7d**).* Compound **7d** 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 **7d** (2.54 g, 77%) as a baby-yellow solid. Mp 61–63 °C; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 2.45 (s, 3H, $-CH_3$), 7.18 (s, 1H, thienyl-H), 7.50 (t, J=7.6 Hz, 1H, phenyl-H), 7.56 (d, 1H, J=8.0 Hz, phenyl-H), 7.73 (d, 1H, J=8.0 Hz, phenyl-H), 7.79 (s, 1H, phenyl-H).

*2.2.5. 3-Bromo-5-(4-cyanophenyl)-2-methylthiophene (**7e**).* Compound **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** (2.33 g, 74%) as a yellow solid. Mp 79–80 °C; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 2.41 (s, 3H, $-CH_3$), 7.03 (s, 1H, thienyl-H), 7.06 (t, 2H, J=8.0 Hz, phenyl-H), 7.44–7.48 (m, 2H, phenyl-H).

*2.2.6. 5-Bromo-2,4-dimethylthiazole (**9**).* Bromine in acetic acid (v/v=29/40) 69 mL was slowly added to a stirred solution of 2,4-dimethylthiazole (3.00 g, 26.50 mmol) in acetic acid (100 mL) at 0 °C. The reaction mixture was stirred overnight at this temperature. The reaction was quenched by the addition of water 20 mL. The mixture was neutralized to pH≥9.0 with Na_2CO_3 solid and extracted with ether. The ether extract was dried, filtrated, and evaporated in vacuo. The residue was purified by column chromatography on SiO_2 using trichloromethane as an eluent to give compound **9** (4.24 g, 83%) as a red solid. Mp 135–136 °C; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 2.46 (s, 3H, $-CH_3$), 2.79 (s, 3H, $-CH_3$).

*2.2.7. 1-(2,4-Dimethyl-5-thiazolyl)perfluorocyclopentene (**10**).* Compound **9** (4.90 g, 25.50 mmol) in anhydrous THF (80 mL) was added dropwise to a 2.5 M *n*-BuLi/hexane solution (10.80 mL) at −78 °C under a nitrogen atmosphere. Stirring was continued for 30 min at this low temperature. Perfluorocyclopentene (C_5F_8, 3.50 mL, 25.50 mmol) was slowly added to the reaction mixture at −78 °C, and the mixture was stirred for another 2 h at this low temperature. The reaction was quenched by the addition of methanol (5 mL). The product was extracted for three times with ether (150 mL). The organic layer was washed with 1 M aqueous NaCl and water, respectively. The organic layer was dried over $MgSO_4$, filtrated, and evaporated. The crude product was purified by column chromatography on silica gel using hexane as an eluent to give **10** (1.11 g, 59%) as a yellow oil. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 2.51 (s, 3H, $-CH_3$), 2.86 (s, 3H, $-CH_3$).

*2.2.8. 1-(2,4-Dimethyl-5-thiazolyl)-2-(2-methyl-5-phenyl-3-thienyl) perfluorocyclopentene (**1o**).* To a stirred anhydrous THF containing **7a** (0.45 g, 1.77 mmol) was added dropwise a 2.5 mol/L *n*-BuLi/hexane solution (0.75 mL, 1.87 mmol) at −78 °C under argon atmosphere. After the mixture has been stirred for 30 min, compound **10** (0.52 g, 1.70 mmol) in solvent of anhydrous THF was added. The reaction was further stirred at −78 °C for 2 h, and the reaction was allowed to slowly warm to the room temperature. The reaction was quenched with distilled water. The product was extracted with ether, dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by column chromatography using petroleum ether as an eluent to afford to 0.38 g in 49% yield of **1o** as white solid. Mp 106–107 °C; calcd for $C_{21}H_{15}F_6NS_2$ (%): calcd C, 54.89; H, 3.29; N, 3.05. Found C, 54.93; H, 3.34; N, 3.08; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 2.01 (s, 6H, $-CH_3$), 2.71 (s, 3H, $-CH_3$), 7.26 (s, 1H, thienyl-H), 7.33 (t, 1H, J=8.0 Hz, phenyl-H), 7.42 (t, 2H, J=8.0 Hz, phenyl-H), 7.57 (d, 2H, J=7.6 Hz, phenyl-H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 14.09, 16.14, 18.72, 116.43, 121.82, 124.90, 125.16, 127.52, 128.52, 132.72, 140.81, 142.26, 154.28, 168.17; IR (ν, KBr, cm^{-1}): 696, 737, 761, 790, 841, 896, 988, 1060, 1106, 1138, 1189, 1273, 1341, 1437, 1471, 1623.

*2.2.9. 1-(2,4-Dimethyl-5-thiazolyl)-2-[2-methyl-5-(4-methoxyphenyl)-3-thienyl]perfluorocyclopentene (**2o**).* Diarylethene **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** (0.16 g, 52%) as a white solid. Mp 71–72 °C; calcd for $C_{22}H_{17}F_6NOS_2$ (%): calcd C, 53.98; H, 3.50; N, 2.86. Found C, 54.04; H, 3.61; N, 2.82; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.89 (s, 3H, $-CH_3$), 1.91 (s, 3H, $-CH_3$), 2.61 (s, 3H, $-CH_3$), 3.77 (s, 3H, $-OCH_3$), 6.84 (d, 2H, J=7.6 Hz, phenyl-H), 7.04 (s, 1H, thienyl-H), 7.40 (d, 2H, J=8.0 Hz, phenyl-H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 14.02, 16.13, 18.71, 54.90, 113.42, 113.92, 116.48, 120.69, 124.78, 125.58, 126.48, 130.88, 139.84, 142.18, 154.26, 159.10, 168.09; IR (ν, KBr, cm^{-1}): 738, 790, 833, 891, 985, 1059, 1106, 1136, 1272, 1338, 1438, 1472, 1514, 1612.

*2.2.10. 1-(2,4-Dimethyl-5-thiazolyl)-2-[2-methyl-5-(4-methylphenyl)-3-thienyl]perfluorocyclopentene (**3o**).* Diarylethene **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** (0.31 g, 54%) as a yellow solid. Mp 87–89 °C; calcd for $C_{22}H_{17}F_6NS_2$ (%): calcd C, 55.81; H, 3.62; N, 2.96. Found C, 55.90; H, 3.78; N, 2.92; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.90 (s, 6H, $-CH_3$), 2.30 (s, 3H, $-CH_3$), 2.61 (s, 3H, $-CH_3$), 7.12 (s, 1H, *thienyl*-H), 7.14 (s, 2H, phenyl-H), 7.37 (d, 2H, J=8.0 Hz, phenyl-H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ13.50, 14.54, 16.61, 19.20, 116.94, 121.77, 125.30, 125.30, 129.66, 130.47, 138.01, 140.76, 142.90, 154.76, 168.59; IR (ν, KBr, cm^{-1}): 740, 815, 841, 893, 987, 1026, 1058, 1105, 1137, 1189, 1290, 1336, 1434, 1476, 1521, 1641, 1807.

*2.2.11. 1-(2,4-Dimethyl-5-thiazolyl)-2-[2-methyl-5-(4-fluorophenyl)-3-thienyl]perfluorocyclopentene (**4o**).* Diarylethene **4o** was prepared by a method similar to that used for **1o**. The crude product was purified by column chromatography on SiO_2 using hexane as an eluent to give **4o** (0.61 g, 57%) as a white solid. Mp 107–109 °C; calcd for $C_{21}H_{14}F_7NS_2$ (%): calcd C, 52.83; H, 2.96; N, 2.93. Found C, 52.89; H, 3.02; N, 2.97; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.91 (s, 6H, $-CH_3$), 2.62 (s, 3H, $-CH_3$), 7.02 (t, 2H, J=8.0 Hz, phenyl-H), 7.09 (s, 1H, thienyl-H), 7.43(t, 2H, J=8.0 Hz, phenyl-H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 14.01, 16.16, 18.74, 115.62, 116.40, 121.80, 124.95, 126.88, 129.02, 140.81, 141.16, 154.28, 160.84, 163.31, 168.22; IR (ν, KBr, cm^{-1}): 738, 820, 846, 897, 948, 987, 1026, 1057, 1106, 1187, 1271, 1335, 1434, 1492, 1551, 2218.

*2.2.12. 1-(2,4-Dimethyl-5-thiazolyl)-2-[2-methyl-5-(4-cyanophenyl)-3-thienyl]perfluorocyclopentene (**5o**).* Diarylethene **5o** was prepared by a method similar to that used for **1o**. The crude product was purified by column chromatography on SiO_2 using hexane as an eluent to give **5o** (0.59 g, 47%) as a white solid. Mp 125–127 °C; calcd for $C_{22}H_{14}F_6N_2S_2$ (%): calcd C, 54.54; H, 2.91; N, 5.78. Found C, 54.64; H, 2.97; N, 5.83; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.92 (s, 3H, $-CH_3$), 1.96 (s, 3H, $-CH_3$), 2.62 (s, 3H, $-CH_3$), 7.27 (s, 1H, thienyl-H), 7.56 (d, 2H, J=8.0 Hz, phenyl-H), 7.61 (d, 2H, J=7.6 Hz, phenyl-H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 14.17, 16.16, 18.71, 112.40, 116.21, 118.01, 124.01, 125.41, 132.34, 136.88, 139.89, 143.01, 154.36, 168.40; IR (ν, KBr, cm^{-1}): 741, 792, 836, 891, 984, 1057, 1104, 1136, 1188, 1272, 1330, 1435, 1470, 1517, 1606, 2231, 2922.

2.3. Determination of crystal structures

Suitable crystals of **1o**, **2o**, **4o**, and **5o** were obtained by slow evaporation of a hexane solution. All the crystal data were made on a Bruker SMART APEX II CCD diffractometer using a MULTI scan technique at room temperature. 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. The linear absorption coefficients, μ, of diarylethenes **1o**, **2o**, **4o**, and **5o** for Mo Kα radiation are 3.22, 3.11, 3.31, and 3.15 cm^{-1}. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were generated geometrically with C–H bond distances of 0.93–0.97 Å according to the criteria described in the SHELXTL manual. They were included in the refinement with Uiso(H)=1.2U_{eq}(C) or 1.5U_{eq}(methyl C). The X-ray crystallographic analysis data are listed in Table 1. Further details on the crystal structures have been deposited in the Cambridge Crystallographic Data Centre as supplemental publication CCDC 774964 for **1o**, CCDC 774967 for **2o**, CCDC 774965 for **4o**, and CCDC 774966 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 1223 336033 or email: deposit@ccdc.cam.ac.uk).

3. Results and discussion

3.1. Photochromic behaviors

The photochromic behaviors of diarylethenes **1**–**5** induced by photoirradiation were measured at room temperature both in hexane (2.0×10^{-5} mol/L) and in PMMA amorphous films (10%, w/w). Fig. 1 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

Table 1
Crystal data for diarylethenes **1o**, **2o**, **4o**, and **5o**

	Compound **1o**	Compound **2o**	Compound **4o**	Compound **5o**
Formula	$C_{21}H_{15}F_6NS_2$	$C_{22}H_{17}F_6NOS_2$	$C_{21}H_{14}F_7NS_2$	$C_{22}H_{14}F_6N_2S_2$
Formula weight	459.46	489.49	477.45	484.47
Temperature	296(2)	296(2)	296(2)	296(2)
Crystal system	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group	*P*2(1)/c	*P*–1	*P*2(1)/c	*P*–1
Unit cell dimensions				
a (Å)	13.622(7)	8.6535(15)	13.588(5)	8.7185(16)
b (Å)	18.270(10)	11.454(2)	18.323(7)	11.360(2)
c (Å)	8.557(5)	12.138(2)	8.589(3)	11.846(2)
α (°)	90.00	110.388(2)	90.00	107.661(2)
β (°)	106.637(6)	103.990(2)	106.594(4)	105.759(2)
γ (°)	90.00	91.912(2)	90.00	93.836(2)
Volume (Å^3)	2040.4(19)	1085.0(3)	2049.5(13)	1061.6(4)
Z	4	2	4	2
Reflections collected	14989	8341	14712	8115
Reflections observed	3803	4011	3725	3926
Number of parameters	274	293	283	292
μ (mm^{-1})	0.322	0.311	0.331	0.315
Density (calcd) (g/cm^3)	1.496	1.498	1.547	1.516
Goodness-of-fit on F^2	1.042	1.017	1.456	1.031
Radiation (Å)	0.71073	0.71073	0.71073	0.71073
Final $R_1[I>2s(I)]$	0.0328	0.0442	0.1731	0.0346
$wR_2[I>2s(I)]$	0.0805	0.1016	0.3899	0.0914
R_1 (all data)	0.0426	0.0794	0.2270	0.0408
wR_2 (all data)	0.0867	0.1213	0.4278	0.0964

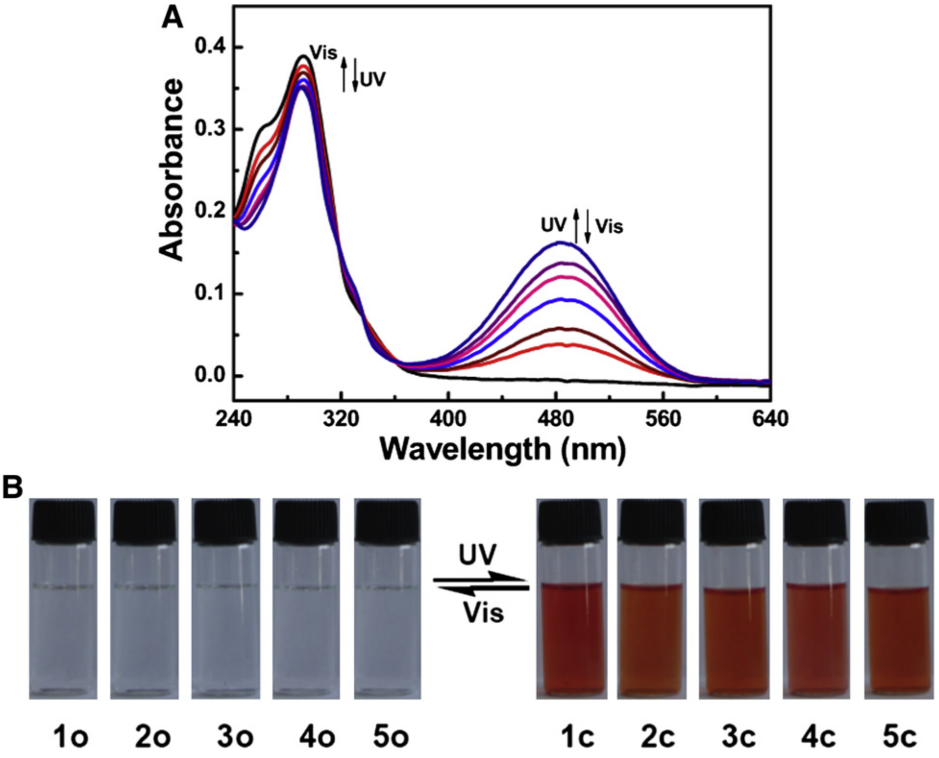


Fig. 1. Absorption spectral change of diarylethene **1** (A) and color changes of diarylethenes **1**–**5** (B) upon alternating irradiation with UV and visible light in hexane (2.0×10^{-5} mol/L) at room temperature.

Fig. 1A, compound **1o** exhibited a sharp absorption peak at 291 nm in hexane, as a result of a $\pi \rightarrow \pi^*$ transition.[11] Upon irradiation with 297 nm light, a new visible absorption band centered at 483 nm emerged while the original peak at 291 nm decreased, indicating the formation of the closed-ring isomer **1c**. This could be seen with the naked eye, as the colorless solution of **1o** turned red. Alternatively, the red colored solution could be bleached completely to colorless upon irradiation with visible light (λ>450 nm), indicating that **1c** returned to the initial state **1o**. As same as diarylethene **1**, diarylethenes **2o**–**5o** also showed photochromism in hexane. Upon irradiation with 297 nm light, absorption bands in visible region appeared and the solutions **2o**–**5o** turned red (Fig. 1B) as a result of the cyclization reactions leading to produce the closed-ring isomers **2c**–**5c**, which their absorption maxima were observed at 491, 489, 485, and 496 nm, respectively. All the solutions of **2c**–**5c** can be decolorized by irradiation with appropriate wavelength visible light, indicating return to the open-ring isomers **2o**–**5o**. The absorption spectral features of these compounds are summarized in Table 2. The results showed that different substituents at the *para*-positions 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 unsubstituted parent compound **1** has the smallest absorption maximum among diarylethenes **1**–**5**, both for its open-ring and closed-ring isomers. No matter replacing the hydrogen atom at the *para*-position of the terminal benzene ring with an electron-donating (methoxy or methyl group, such as in compound **2** or **3**) or with an electron-withdrawing substituent (fluorine or cyano group, such as in compound **4** or **5**), the absorption maxima have notably increased with the increase in both electron-donating and electron-withdrawing ability. That is to say, the stronger the electron-donating/withdrawing ability of the substituent is, the greater the absorption maximum of diarylethene is achieved both in the open-ring and the closed-ring isomers. Therefore, the absorption maximum of **2** is greater than that of diarylethene **3** due to the stronger electron-donating ability of methoxy group as compared to a methyl group, and the similar change occurs in between **5** and **4** because of the stronger electron-withdrawing ability of cyano group as compared to a fluorine group. The result is in agreement with that of diarylethenes bearing a six-membered aryl unit.[19] In addition, all the absorption maxima of the closed-ring isomers **1c**–**5c** were observed at 480–500 nm, which were much shorter than that of diarylethenes with the similar molecular skeleton including thiophene, pyrazole or benzene moiety.[19,20] This indicated that the thiazole moiety could be effective to shift the absorption maximum of diarylethene to a shorter wavelength. As shown in Table 2, the cyclization and cycloreversion quantum yields of the unsubstituted parent compound **1** are 0.39 and 0.11, respectively. When replacing the hydrogen atom at the *para*-position of the terminal benzene ring with an electron-donating substituent (methoxy or methyl group), the cyclization, and cycloreversion quantum yields increase evidently with the increase in electron-donating ability in hexane. When the same position instead contains an electron-withdrawing substituent (fluorine or cyano group), the quantum yields decrease to some extent with the increase in electron-withdrawing ability. As a result, both the cyclization and cycloreversion quantum yields of diarylethenes **2** and **3** bearing electron-donating groups are much higher than those of **4** and **5** bearing electron-withdrawing groups. The result is quite different from those reported for diarylethenes bearing a phenyl moiety, where the cyclization quantum yield significantly increased with the increase of electron-withdrawing ability and cycloreversion quantum yield showed the reverse trend.[19]

Table 2
Absorption spectral properties of diarylethenes **1**–**5** in hexane at 2.0×10^{-5} mol/L

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]	
	Hexane	PMMA film	Hexane	PMMA film	Φ_{o-c}	Φ_{c-o}
1	291 (1.9×10^4)	297	483 (8.1×10^3)	496	0.39	0.11
2	297 (2.3×10^4)	302	491 (1.1×10^4)	499	0.43	0.17
3	293 (1.8×10^4)	297	489 (7.0×10^3)	498	0.41	0.15
4	292 (1.8×10^4)	294	485 (7.3×10^3)	496	0.23	0.11
5	310 (3.2×10^4)	313	496 (1.2×10^4)	505	0.21	0.07

[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.

For practical applications in optical devices, it is very important that photochromic materials can keep good photochromism in a polymer film, such as PMMA.[1b,21] Dissolved ultrasonically 10 mg diarylethene sample and 100 mg PMMA into 1.0 mL chloroform, the film was prepared by spin-coating on the surface of quartz substrate. In PMMA amorphous film, diarylethenes **1**–**5** also showed good photochromism similar to samples in solution. The absorption spectral change of **1** and color changes of **1**–**5** are shown in Fig. 2, and the data are listed in Table 2. Upon irradiation with 297 nm light, the colors of the diarylethene/PMMA films **1**–**5** changed from colorless to red, with the appearance of a new broad absorption band centered at 496, 499, 498, 496, and 505 nm, respectively, which was assigned

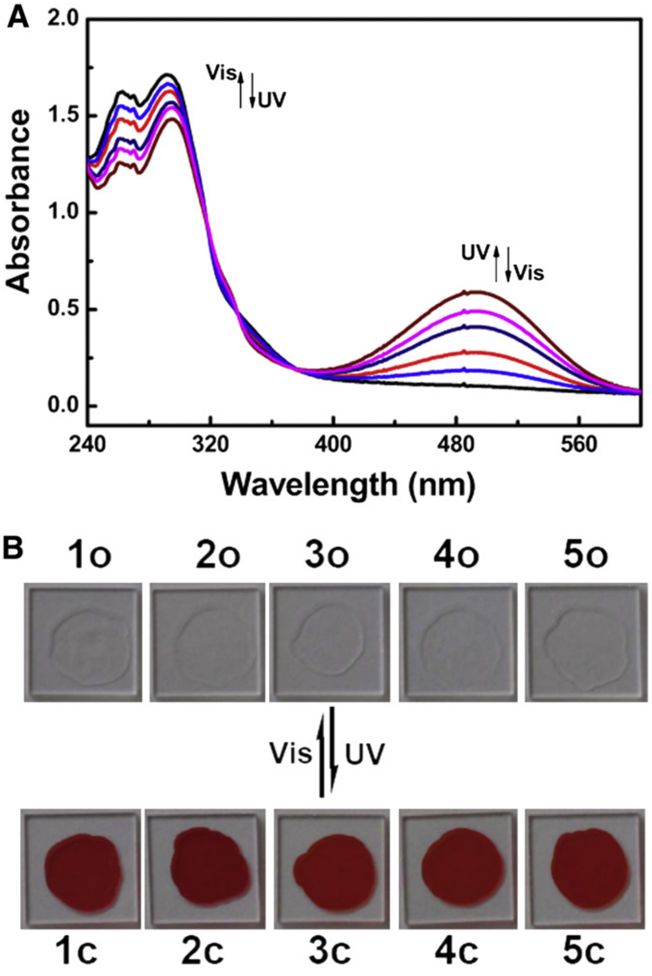


Fig. 2. Absorption spectral change of diarylethene **1** (A) and color changes of diarylethenes **1**–**5** (B) upon alternating irradiation with UV and visible light in PMMA film (10%, w/w) at room temperature.

to the formation of the closed-ring isomers **1c**–**5c**. All colored diarylethene/PMMA films can revert to colorless upon irradiation with visible light ($\lambda > 450$ nm). As has been observed for most of the reported diarylethenes,[22] the maximum absorption peaks of both the open-ring and the closed-ring isomers in PMMA film are longer than those in hexane solution. The red shift values of the absorption maxima for the open-ring isomers are 6 nm for **1o**, 5 nm for **2o**, 4 nm for **3o**, 2 nm for **4o**, and 3 nm for **5o**, and those for the closed-ring isomers are 13 nm for **1c**, 8 nm for **2c**, 9 nm for **3c**, 11 nm for **4c**, and 9 nm for **5c**, respectively. The red shift phenomena may be attributed to the polar effect of the polymer matrix and the stabilization of molecular arrangement in solid state.[23]

Single crystals of diarylethenes **1o**, **2o**, **4o**, and **5o** were obtained by slow evaporation of a hexane solution. To know better the relation between the conformation and the photochromic behaviors of these diarylethene derivatives in the crystalline phase, their final structural confirmations were provided by X-ray crystallographic analysis. The ORTEP drawings of the single crystals are shown in Fig. 3. These molecules crystallize with an appropriate C_2 symmetry with the photoactive anti-parallel conformation in the crystalline phase, which can undergo photocyclization.[24] For diarylethene **1o**, the dihedral angles between the hexafluorocyclopentene ring and the two heteroaryl rings are 46.4(3)° for S1/C7-C10, and 42.0(3)° for S2/C17, C18/N1/C20, and that between the thiophene ring and the linked benzene ring is 36.9(3)°. In hexafluorocyclopentene ring, the distances clearly show that the C12–C16 bond (1.353(2) Å) is a double bond, being significantly shorter than other carbon–carbon single bonds (1.505(3) Å–1.531(3) Å) of the ring. The thiophene and thiazole moieties are linked by the C12=C16 double bond. The two methyl groups are located on opposite sides of the double bond, reflected in the torsion angles C16–C12–C9–C10 [−42.7(3)°] and C12–C16–C17–C18 [−43.7(3)°] and are thus trans with respect to the double bond. This kind conformation is crucial for the compound to exhibit photochromic and photo-induced properties.[25] The intramolecular distance between the two reactive C atoms (C10–C18) is 3.593(4) Å. The corresponding data of compounds **2o**, **4o**, and **5o** are summarized in Table 3. For these compounds, both of them also adopt the anti-parallel conformation in the crystalline phase, and the distance between the two reactive C atoms is 3.589 (2) Å for **2o**, 3.554(7) Å for **4o**, and 3.562 (3) Å for **5o**. As a result, all molecules of crystals **1o**, **2o**, **4o**, and **5o** are fixed in an anti-parallel mode in the crystalline phase and the distances of the two reactive C atoms are less than 4.2 Å, which is close enough for the photocyclization reaction to take place.[24c,25,26] In fact, crystals of **1o**, **2o**, **4o**, and **5o** showed good photochromism, in accordance with the expected ring closure, to form **1c**, **2c**, **4c**, and **5c** upon irradiation with UV light. The color changes of crystals **1o**, **2o**, **4o**, and **5o** upon photoirradiation in the crystalline phase are shown in Fig. 4. The colorless crystals of these compounds turned red upon irradiation with 297 nm UV light. When the red crystals were dissolved in

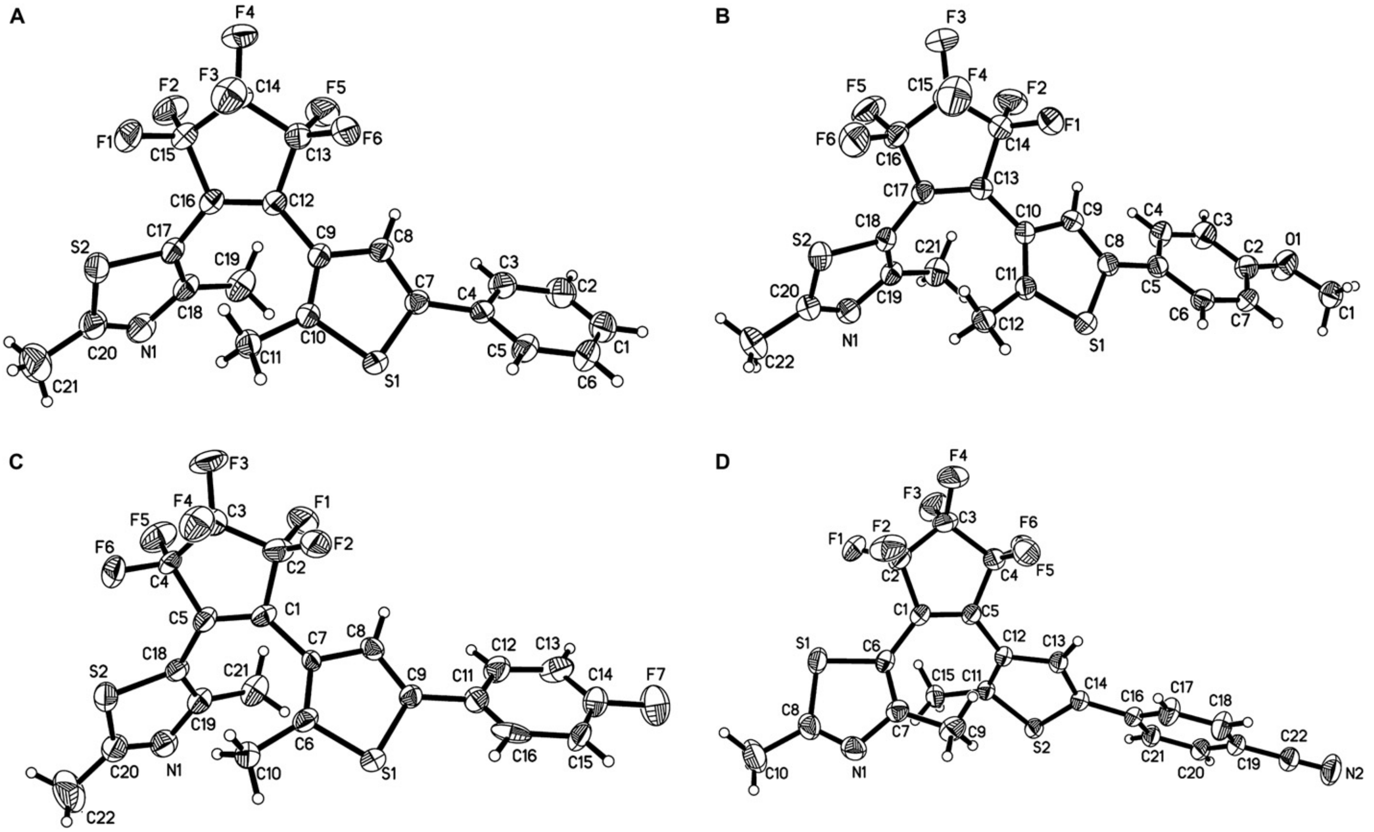


Fig. 3. **ORTEP** drawings of crystals **1o**, **2o**, **4o**, and **5o**, showing about 30% probability displacement ellipsoids: (A) **1o**, (B) **2o**, (C) **4o**, (D) **5o**.

Table 3

Distances between the reacting carbon atoms (d, Å) and dihedral angles (θ, °) of **1o**, **2o**, **4o**, and **5o**

Compound	d (Å)	θ (°)[a]			
		θ_1	θ_2	θ_3	
1o	C10···C18	3.593(4)	42.0(3)	46.4(3)	36.9(3)
2o	C11···C19	3.589(2)	36.5(2)	46.4(2)	28.8(2)
4o	C6···C19	3.554(7)	41.2(5)	46.4(5)	35.9(5)
5o	C7···C11	3.562(3)	37.8(6)	47.0(6)	28.4(6)

[a] θ_1, Dihedral angle between the hexafluorocyclopentene ring and 2,4-dimethylthiazole ring; θ_2, dihedral angle between the hexafluorocyclopentene ring and the thiophene ring attached a benzene ring; θ_3, dihedral angel between the thiophene ring and the adjacent benzene ring.

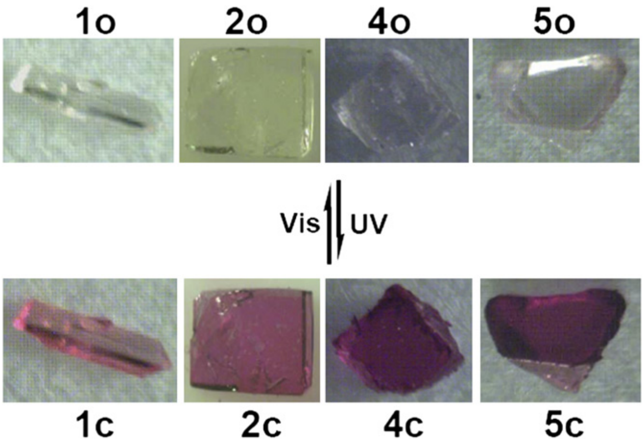


Fig. 4. Photographs of photochromic processes of diarylethenes **1**, **2**, **4**, and **5** in the crystalline phase.

hexane, an intense absorption maximum was observed at the same wavelength as that of their respective ring-closed isomer in solution. Alternatively, the red-colored crystals returned to colorless upon irradiation with the appropriate visible light (λ>450 nm). Furthermore, these diarylethene crystals exhibited remarkable fatigue-resistance greater than 200 cyclization/cycloreversion repeated cycles and their ring-closed isomers remained stable for more than 1000 h in the dark at room temperature. So, they will be good candidates for the construction of certain optoelectronic devices.[27]

The thermal stabilities of the open-ring and closed-ring isomers of diarylethenes **1**–**5** were examined in hexane both at room temperature and at 80 °C. Stored these solutions in the dark and then exposing them to air for more than 1000 h at room temperature, no changes in the UV/vis spectra of diarylethenes **1**–**5** were observed and indeed, no decomposition was detected when the five compounds were exposed to air for more than a year. At 80 °C, diarylethenes **1**–**5** still showed good thermal stabilities for more than 100 h. Fatigue-resistant property, i.e., how many times photocyclization and cycloreversion reaction cycles can be repeated without loss of performance, is a very important factor for practical applications in optical devices.[2g,28] The fatigue resistances of diarylethenes **1**–**5** were examined both in hexane and in PMMA films at room temperature, as shown in Fig. 5. Diarylethenes **1**–**5** were irradiated alternatively by 297 nm UV and visible light (λ>450 nm), respectively. The irradiation time was long enough for coloration to reach the photostationary state and for the color to be completely bleached. In hexane, 27% of **1c** was destroyed after 20 repeat cycles, which may be attributed to degradation resulting from the formation of an epoxide.[29] However, its fatigue resistance in PMMA film is much stronger than that in hexane. After 200 repeat cycles, diarylethene **1** still showed good photochromism with only ca. 6% degradation of **1c** in PMMA film. Similarly, the fatigue resistances of diarylethenes **2**–**5** in PMMA films are also much stronger than those in solution. After 200 repeat cycles, they showed good photochromism with only ca. 10% degradation of **2c**, 13% of **3c**, 19% of **4c**, and 22% of **5c**, respectively. But, the degradation percents of diarylethenes **2**–**5** in hexane are 23% of **2c**, 18% of **3c**, 32% of **4c**, and 39% of **5c**, respectively. This remarkable improvement may result from effectively suppressing the oxygen diffusion in the solid medium.[2g] The result indicated that the fatigue resistances of diarylethenes with an electron-donating group (such as in **2** and **3**) are much better than those of diarylethenes with an electron-withdrawing group (such as in **4** and **5**) both in hexane and in PMMA films. The result is contrary to that of diarylethenes bearing both thiazole and benzene moieties whose fatigue resistance markedly increased with the increase in electron-withdrawing ability.[30]

3.2. Fluorescence of diarylethenes

Fluorescent properties can be useful not only in molecular-scale optoelectronics, but for digital photoswitching of fluorescence.[31] The fluorescence modulation is a particularly intriguing approach due to the stabilization of diarylethene and versatility in materials selection.[32] Until now, many diarylethene derivatives and their fluorescent properties have been reported.[33] In this work, the fluorescence properties of the five diarylethenes both in solution and in PMMA film were measured using a Hitachi F-4500 fluorimeter. The fluorescence emission spectra of **1o**–**5o** at room temperature are illustrated in Fig. 6. When exited at 330 nm, the emission peaks of diarylethenes **1o**–**5o** were observed at 429, 448, 434, 424, and 411 nm in hexane, and were observed at 435, 458, 437, 426, and 419 nm in PMMA films. 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 6 nm for **1**, 10 nm for **2**, 3 nm for **3**, 2 nm for **4**, and 8 nm for **5**, respectively. When going from electron-donating to electron-withdrawing groups, the emission peaks of diarylethenes **1o**–**5o** gradually decreased both in hexane (from 448 to 411 nm) and in PMMA films (from 458 to 419 nm), and their emission intensity also decreased evidently with the increase in electron-withdrawing ability. Therefore, the emission peak and the emission intensity of **2o** are both the biggest and those of **5o** are the smallest in hexane and in PMMA film. The result is completely contrary to that of diarylethenes bearing a biphenyl moiety.[34]

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. When irradiated by UV light, the photocyclization reaction was occurred and the emission intensity of diarylethenes **1o**–**5o** decreased

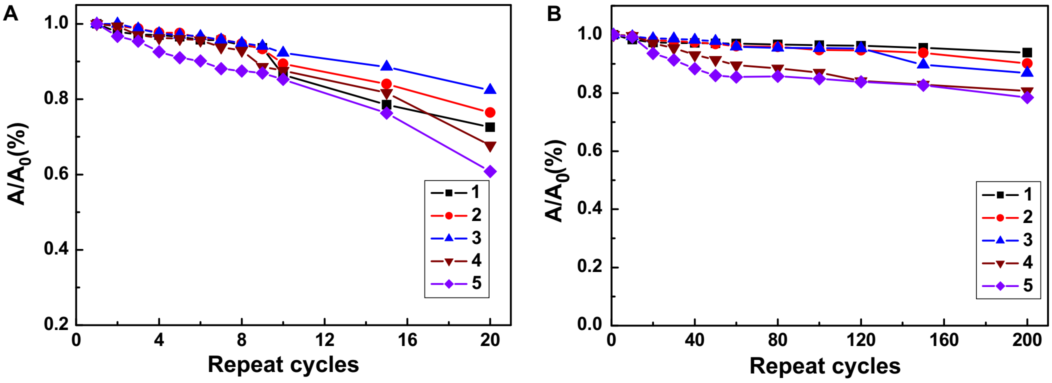


Fig. 5. Fatigue resistance of diarylethenes **1**–**5** in hexane (A) and in PMMA film (B) in air atmosphere at room temperature. Initial absorbance of the sample was fixed to 1.0.

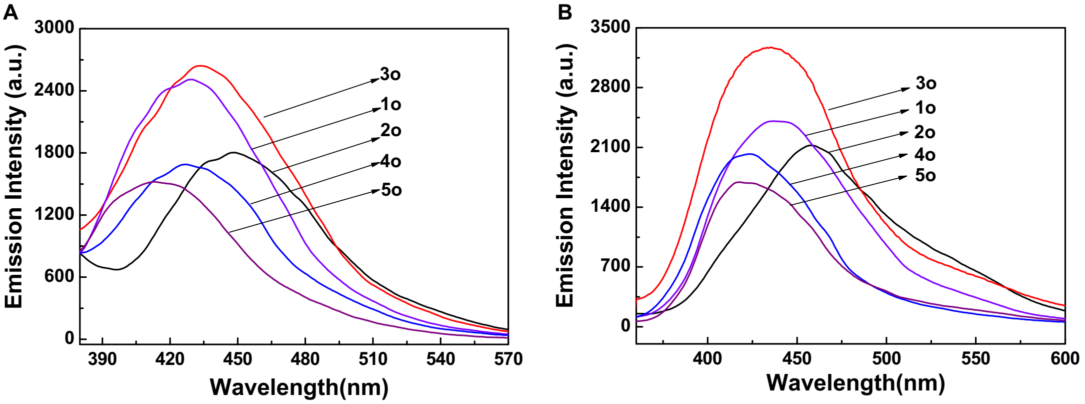


Fig. 6. Fluorescence emission spectra of diarylethenes **1**–**5** both in hexane solution (1.0×10^{-4} mol/L) (A) and in PMMA film (10%, w/w) (B) at room temperature, excited at 330 nm.

significantly due to producing the non-fluorescence closed-ring isomers **1c**–**5c**. The back irradiation by appropriate wavelength visible light regenerated their open-ring isomers **1o**–**5o** and recovered the original emission intensity. Fig. 7 shows the fluorescence changes of diarylethene **1** by photoirradiation in hexane (1.0×10^{-4} mol/L) and in PMMA film (10%, w/w). As shown in Fig. 7, the emission intensity of **1o** was quenched to ca. 17% in hexane and 18% in PMMA film when arrived at the photostationary state. That is to say, its fluorescent modulation efficiency at photostationary state was 83% in hexane and 82% in PMMA film. Just as diarylethene **1**, the fluorescent modulation efficiencies of other four diarylethenes in hexane were 82% for **2**, 81% for **3**, 85% for **4**, and 89% for **5**, and those in PMMA films were 79% for **2**, 69% for **3**, 67% for **4**, and 79% for **5** when arrived at the photostationary state. Therefore, the fluorescent modulation efficiencies of diarylethenes **1**–**5** in hexane were much higher than those in PMMA film. For example, the fluorescent modulation efficiency of diarylethene **4** in PMMA film was reduced about 18% more than that in hexane, and those of other four compounds decreased partly in PMMA films. The result is completely contrary to those of the unsymmetrical dithienylethene derivatives whose fluorescent modulation efficiencies in hexane are much lower than those in PMMA film.[18a,20b] Compared with diarylethenes bearing two thiophene moieties,[22] the fluorescent modulation efficiencies of diarylethenes **1**–**5** were significantly enhanced both in the liquid and solid states. This indicated that diarylethenes bearing a thiazole unit have the potential use as fluorescent modulation switches.[35]

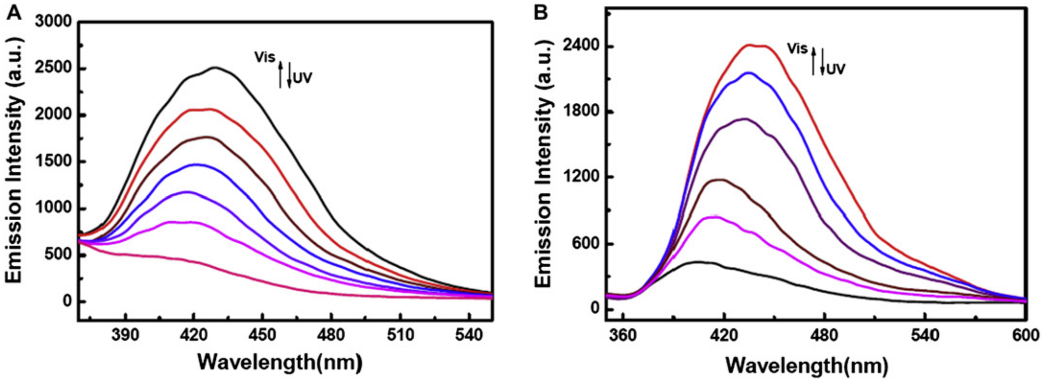


Fig. 7. Emission intensity changes of diarylethene **1** upon irradiation with 297 nm UV light at room temperature, excited at 330 nm: (A) in hexane (1.0×10^{-4} mol/L); (B) in PMMA film (10%, w/w).

In addition, the 'on' and 'off' state of the fluorescence was measured by changing the power of the UV and visible light. The average 'on' and 'off' times shortened with the increase in light power, indicating that the switching effect is indeed photochemical.[2b,15e] Therefore, these diarylethene compounds could be potentially applied to optical memory with fluorescence readout method and fluorescence modulation switches.[36]

3.3. Electrochemistry of diarylethenes

The electrochemical properties of diarylethene can be potentially applied to molecular-scale electronic switches.[37] The electrochemical behavior of diarylethene derivatives has attracted much attention.[38] Herein, cyclic voltammograms (CV) were performed on the diarylethenes **1**–**5** under identical experimental conditions at a scanning rate of 50 mV/s. The CV curves of diarylethenes **1**–**5** are shown in Fig. 8. The oxidation onsets of the open-ring isomers **1o**–**5o** were initiated at 1.39, 0.95, 1.15, 1.31, and 1.39 V, and their closed-ring isomers **1c**–**5c** were initiated at 0.74, 0.60, 0.66, 0.66, and 0.67 V, respectively. The difference of oxidation onset between the open-ring and closed-ring isomers of diarylethenes **1**–**5** ($\Delta V_{\text{o-c}}$) was 0.65 V for **1**, 0.35 V for **2**, 0.49 V for **3**, 0.65 V for **4**, and 0.72 V for **5**. 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 less positive potential.[39] After the cyclization reaction, the π-conjugation of the closed-ring isomers extends across the perfluorocyclopentene ring causing a lower oxidation onset.

For the reduction process, the values of reduction onsets are not very clear from the CV tests. In order to confirm the reduction onsets of CV results, differential pulse voltammetry (DPV) was performed on the diarylethenes **1**–**5** under identical experimental conditions at

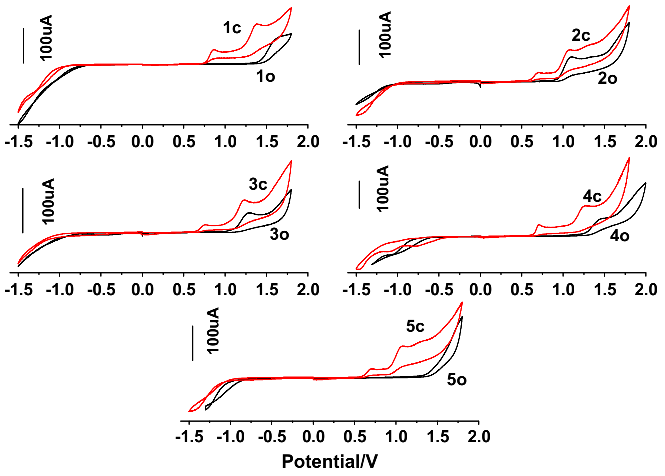


Fig. 8. Cyclic voltammetry (second scan) of **1**–**5** in acetonitrile with the scanning rate of 50 mV s^{-1}.

a scanning rate of 50 mV/s according to the reported method.[40] The results showed that the reduction onsets of the open-ring isomers **1o**–**5o** were initiated at −0.84, −1.07, −0.97, −0.99, and −1.04 V, and their closed-ring isomers **1c**–**5c** were initiated at −0.98, −1.18, −1.08, −1.16, and −1.18 V, respectively. The results indicated that the values of the DPV tests are almost the same as those of the CV tests. So, the band gaps (E_g,) of diarylethenes **1**–**5** can be estimated by using the energy of ferrocene as reference,[41] and the corresponding values are summarized in Table 4. The data showed that the band-gaps of the closed-ring isomers were much lower than those of their corresponding open-ring isomers. Among these compounds, the E_g was the smallest in **1c**, implying that the charge transfer must be faster in **1c** compared to that in others.[42] Furthermore, the oxidation onsets and the E_gs of diarylethenes **1**–**5** increased remarkably with the increase in electron-withdrawing ability. Both the oxidation onsets and the band-gaps of diarylethenes **2** and **3** bearing electron-donating groups are much lower than those of diarylethenes **4** and **5** bearing electron-withdrawing groups. 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 calculation absolute HOMO and LUMO levels from electrochemical data in combination with the energy gap is still in debate.[43]

Table 4
Electrochemical properties of diarylethenes **1**–**5** in acetonitrile

Compound	Oxidation		Reduction		Band gap
	E_{onset} (V)	IP (eV)	E_{onset} (V)	EA (eV)	E_g
1o	1.39	−6.19	−0.84	−3.96	2.23
1c	0.74	−5.54	−0.98	−3.82	1.72
2o	0.95	−5.75	−1.07	−3.73	2.02
2c	0.60	−5.40	−1.18	−3.62	1.78
3o	1.15	−5.95	−0.97	−3.83	2.12
3c	0.66	−5.46	−1.08	−3.72	1.74
4o	1.31	−6.11	−0.99	−3.81	2.30
4c	0.66	−5.46	−1.16	−3.54	1.82
5o	1.39	−6.19	−1.04	−3.76	2.43
5c	0.67	−5.47	−1.18	−3.62	1.85

4.. Conclusions

In conclusion, five new unsymmetrical diarylethenes based on the hybrid skeleton of thiophene and thiazole moieties were synthesized, and their photochemical and electrochemical properties were investigated in detail. All of these compounds showed good photochromism and acted as a remarkable fluorescent switch both in solution and in PMMA film. It has been demonstrated that the thiazole moiety can decrease significantly the absorption maxima of the closed-ring isomers compared with thiophene or pyrazole moiety in the similar photochromic molecular skeleton. These diarylethene derivatives show distinguishable optical and electrochemical characteristics, which may be attributed to the different substituent effects. The results will contribute to understanding of the substituent effects and tuning the optoelectronic properties of photochromic diarylethenes bearing both thiophene and thiazole moieties for further potential applications.

Acknowledgements

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