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Photochromism of asymmetrical diarylethenes with a pyrimidine unit: Synthesis and substituent effects

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ABSTRACT

Five photochromic diarylethenes with a six-membered pyrimidine moiety were synthesized to investigate the effects of the substituents on their photochromic behaviors, and the structures of four of the diarylethenes were determined by single-crystal X-ray diffraction analysis. The pyrimidine moiety was connected directly to the central cyclopentene ring as an aryl moiety to participate the photoisomerization reaction in solution, solid amorphous films, and crystalline phase. All of the diarylethene derivatives showed favorable photochromism and functioned as notable fluorescent photo-switches in both solution and solid media. The electron-donating substituents enhanced their cyclization quantum yields, fatigue resistance, and fluorescence quantum yields, whereas the electron-withdrawing groups exerted inversed actions on the diarylethenes. The results revealed that the pyrimidine moiety and substituents played a very important role during the process of photoisomerization reactions.

1. Introduction

Photochromism is a photo-induced reversible transformation of a chemical species between two isomers [1–3]. During the reversible photoisomerization process, some physicochemical properties of photochromic compounds, such as absorption spectra, fluorescence, electrochemical property, magnetic properties, dipole interaction, as well as refractive indice could be tuned by light [4–6]. The instant property changes by photoirradiation lead to their wide applications in optical memory and photo-optical switching devices [5–8]. Among various photochromic materials, the diarylethenes with heteroaryl groups are the most promising candidates for their thermal irreversibility and high photochromic reactivity [9–11].

In the past several decades, numerous studies have focused on molecular design, especially the synthesis of symmetrical and asymmetrical frameworks in diarylethenes with different heteroaryl units such as thiophene, benzothiophene [4–6], furan [12], thiazole [13–15], indole [16,17], benzofuran [18], indene [19], pyrazole [20,21], pyrrole [22], benzene [23,24], chryso[*b*]thiophene [25], etc. It has been revealed that the aryl moieties and functional substituents impose significant influence on their photochromic properties. For example, diarylethenes having two thiophenes, furans, or thiazoles exhibit excellent thermal stability. The ones with two indoles, pyrroles, or benzenes are thermally unstable [4,5,12,26]. In a previous work, we revealed that the thiazole moiety could decrease the absorption maxima of the closed-ring isomers compared with the thiophene or pyrazole moiety [15]. Irie et al. reported that the introduction of alkoxy groups at the reactive carbon sites in diarylethenes remarkably suppressed the cycloreversion quantum yields [27]. Nevertheless, the hexatriene backbones necessary for the versatility of the diarylethenes reported so far have been mostly limited to the five-membered aryl rings. The diarylethenes with six-membered aryl rings were rarely reported due to the poor photochromic activity and thermal stability [28–30]. For a more detailed research on the effects of six-membered aryl rings as the hexatriene backbones, we synthesized a new class of diarylethenes with both five-membered and six-membered moieties, which exhibited favorable photochromism, fluorescence switching properties, and excellent thermal stability [15,23,31,32]. To date, the six-membered aryl rings used in known diarylethenes include benzene, pyridine, and naphthalene. Pyrimidine as a critical intermediates for drugs and pesticides [33], however, has rarely been reported in the synthesis of diarylethenes [34].

In this work, five photochromic diarylethenes with pyrimidine and thiophene moieties were synthesized. In order to discuss the substituent effects on their physicochemical properties, different substituents were introduced into *para*-position of the terminal

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benzene. All of these diarylethenes showed good photochromism in solution, ploy(methylmethacrylate) (PMMA) films, and crystalline phase. The photochromic scheme of diarylethenes **1**–**5** by photoirradiation is illustrated as shown in Fig. 1.

2. Experimental

2.1. General methods

Melting points were measured with 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. Mass spectra were obtained on an Agilent 1100 ion trap MSD spectrometer. Fluorescence spectra were measured on a HITACHI 4500 fluorescence spectrophotometer. Absorption spectra were measured using an Agilent 8453 UV/Vis spectrometer. Photoirradiation was carried out using an SHG-200 UV lamp, a CX-21 ultraviolet fluorescence analysis cabinet and a BMH-250 visible lamp. All solvents were dried and distilled according to standard procedures. Other reagents were used without additional purification.

Suitable crystals of **1o**, **2o**, **3o** and **5o** were obtained by slow evaporation in hexane. All the measurements were collected by a Bruker SMART APEX II CCD diffractometer using a MULTI scan technique at room temperature using Mo Kα radiation. The structures of **1o**, **2o**, **3o** and **5o** were solved by direct methods and refined by full-matrix least-squares procedures on F^2 by full-matrix least-squares techniques using SHELXTL-97 program. Further details on the crystal structure investigation have been deposited with The Cambridge Crystallographic Data Center as supplementary publication CCDC 950116 for **1o**, 950117 for **2o**, 950118 for **3o**, and 950119 for **5o**. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 0 1223 336033 or e-mail:deposit@ccdc.cam.ac.uk).

2.2. Synthesis of diarylethene derivatives

The synthetic route for diarylethenes **1o**–**5o** is shown in Fig. 2. The phenylthiophene derivatives **7a**–**e** were prepared by Suzuki coupling of five bromobenzene derivatives with a thiophene boronic acid **6** [35,36]. Then, compounds **7a**–**e** were lithiated and coupled with perfluorocyclopentene to give monosubstituted perfluorocyclopentene **8a**–**e**, respectively. Finally, 5-bromo-2,4-dimethoxypyrimidine was lithiated and coupled with **8a**–**e** to give the unsymmetrical **1o**–**5o**, respectively. The structures of **1o**–**5o** were confirmed by elemental analysis, NMR, IR, and MS.

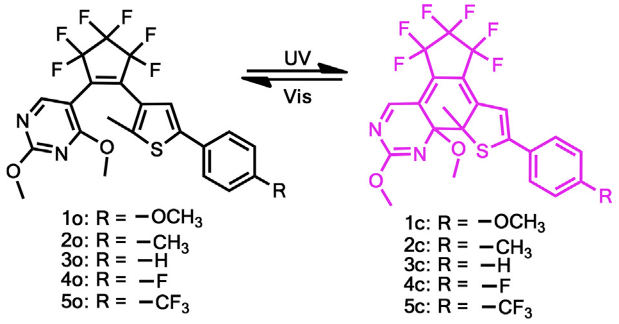

Fig. 1. Photochromism of diarylethenes **1**–**5**.

2.2.1. 3-Bromo-2-methyl-5-(4-methoxyphenyl)thiophene (**7a**)

7a was prepared by reacting compound **6** (4.00 g, 18.1 mmol) with 4-bromoanisole (3.38 g, 18.1 mmol) in the presence of $Pd(PPh_3)_4$ and Na_2CO_3 (6.40 g, 60 mmol) in THF (80 mL containing 10% water). After refluxing for 15 h at 368 K, the product was extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$, filtrated, and evaporated. Column chromatography on SiO_2 with petroleum ether as the eluent afforded 3.99 g of **7a** as a yellowish solid in 78% yield. M.p. 378–379 K; ^1H 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).

2.2.2. 3-Bromo-2-methyl-5-(4-methylphenyl)thiophene (**7b**)

7b was prepared by a method similar to that used for **7a**. Column chromatography on SiO_2 with petroleum ether as the eluent afforded 3.86 g of **7b** as a pale yellow solid in 80% yield. M.p. 340–341 K; ^1H 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).

2.2.3. 3-Bromo-2-methyl-5-phenyl-thiophene (**7c**)

7c was prepared by a method similar to that used for **7a**. Column chromatography on SiO_2 with petroleum ether as the eluent afforded 3.52 g of as a pale yellow solid in 77% yield. M.p. 339–340 K; ^1H 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).

2.2.4. 3-Bromo-2-methyl-5-(4-fluorophenyl)thiophene (**7d**)

Compound **7d** was prepared by a method similar to that used for **7a**. Column chromatography on SiO_2 with petroleum ether as the eluent afforded 3.77 g of **7d** as a pale yellow solid in 77% yield. M.p. 334–335 K; ^1H NMR (400 MHz, $CDCl_3$): δ 2.43 (s, 3H), 7.05 (s, 1H), 7.09 (d, 2H, $J = 8.0$ Hz, phenyl-H), 7.46–7.50 (m, 2H, phenyl-H).

2.2.5. 3-Bromo-2-methyl-5-(4-trifluoromethylphenyl)thiophene (**7e**)

Compound **7e** was prepared by a method similar to that used for **7a**. Column chromatography on SiO_2 with petroleum ether as the eluent afforded 3.85 g of **7e** as a pale yellow solid in 79% yield. M.p. 359–360 K; ^1H NMR (400 MHz, $CDCl_3$): δ 2.44 (s, 3H, $-CH_3$), 7.02 (s, 1H, thienyl-H), 7.58–7.64 (m, 4H, phenyl-H).

2.2.6. [2-Methyl-5-(4-methoxyphenyl)-3-thenyl] perfluorocyclopentene (**8a**)

To a stirred anhydrous THF containing 3-bromo-2-methyl-5-(4-methoxyphenyl)thiophene (**7a**) (1.00 g, 3.5 mmol) was added dropwise a 2.5 M *n*-BuLi hexane solution (1.5 mL, 3.9 mmol) at 195 K under an argon atmosphere. Stirring was continued for 30 min. Excess octafluorocyclopentene (0.6 mL, 3.8 mmol) was then added. The reaction was quenched with 20 mL water after 2 h. The mixture was warmed to room temperature and extracted with ether. The organic layer was collected and washed with saturated salt water (30 mL) and then water (50 mL). The organic layer was dried over $MgSO_4$, filtrated, and evaporated. Column chromatography on SiO_2 with petroleum ether as the eluent afforded 0.60 g of **8a** as a colorless solid in 43% yield. ^1H 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).

2.2.7. [2-Methyl-5-(4-methylphenyl)-3-thienyl] perfluorocyclopentene (**8b**)

8b was prepared by a method similar to that used for **8a**. Column chromatography on SiO_2 with petroleum ether as the eluent afforded 0.86 g of **8b** as a yellow solid in 60% yield. ^1H NMR

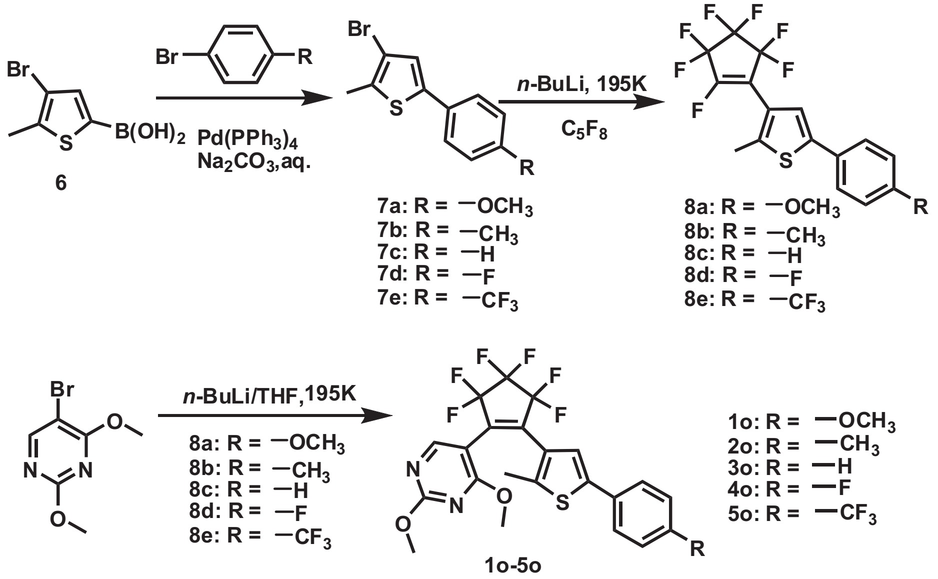

Fig. 2. Synthetic route for diarylethenes **1**–**5**.

(400 MHz, $CDCl_3$): δ 2.37 (s, 3H, $-CH_3$), 2.47 (s, 3H, $-CH_3$), 7.17–7.20 (m, 3H, thienyl and phenyl-H), 7.43 (d, 2H, $J = 8.0$ Hz, phenyl-H).

2.2.8. (2-Methyl-5-phenyl-3-thienyl)perfluorocyclopentene (*8c*)

Compound **8c** was prepared by a method similar to that used for **8a**. Column chromatography on SiO_2 with petroleum ether as the eluent afforded 0.81 g of **8c** as a buff solid in 55% yield. ^1H 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).

2.2.9. [2-Methyl-5-(4-fluorophenyl)-3-thienyl] perfluorocyclopentene (*8d*)

Compound **8d** was prepared by a method similar to that used for **8a**. Column chromatography on SiO_2 with petroleum ether as the eluent afforded 0.72 g of **8d** as a colorless solid in 49% yield. ^1H 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).

2.2.10. [2-Methyl-5-(4-trifluoromethylphenyl)-3-thienyl] perfluorocyclopentene (*8e*)

Compound **8e** was prepared by a method similar to that used for **8a**. Column chromatography on SiO_2 with petroleum ether as the eluent afforded 0.87 g of **8e** as a buff solid in 57% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 2.44 (s, 3H, $-CH_3$), 7.20 (d, 1H, thienyl-H), 7.59–7.61 (m, 4H, phenyl-H).

2.2.11. 1-(2,4-Dimethoxy-5-pyrimidinyl)-2-[2-methyl-5-(4-methoxyphenyl)-3-thienyl]perfluorocyclopentene (*1o*)

To a stirred anhydrous THF containing 5-bromo-2,4-dimethoxypyrimidine (0.29 g, 1.3 mmol) was added dropwise a 2.5 M n-BuLi/hexane solution (0.6 mL, 1.4 mmol) at 195 K under argon atmosphere. After 30 min, **8a** (0.52 g, 1.3 mmol) was added and the reaction mixture was stirred for 2 h at this temperature. The reaction was allowed to warm to room temperature and quenched by addition of water. The product was extracted with diethyl ether. Then the combined organic layers were dried over $MgSO_4$, filtered and concentrated. Column chromatography on SiO_2 with petroleum ether and ethyl acetate ($v/v = 6/1$) as the eluent afforded 0.35 g of **1o** as a colorless solid in 52% yield. M.p. 367–368 K; Calcd for $C_{23}H_{18}F_6N_2O_3S$ (%): Calcd C, 53.49; H, 3.51; N, 5.42. Found C, 53.53; H, 3.54; N, 5.47; ^1H NMR (400 MHz, $CDCl_3$): δ 2.01 (s, 3 H, -CH_3), 3.74 (s, 3H, $-OCH_3$), 3.84 (s, 3H, $-OCH_3$), 4.01 (s, 3H, $-OCH_3$), 6.91 (d, 2H, $J = 8.0$ Hz, benzene-H), 7.06 (s, 1H, thiophene-H), 7.45 (d, 2H, $J = 8.0$ Hz, benzene-H), 8.33 (s, 1H, pyrimidine-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.08, 54.16, 55.21, 55.30, 104.13, 114.36, 121.38, 125.91, 126.16, 126.84, 138.58, 142.05, 159.04, 159.47, 166.05, 168.03; IR (KBr, ν, cm^{-1}): 739, 758, 799, 822, 841, 891, 986, 1003, 1034, 1074, 1123, 1198, 1257, 1298, 1337, 1371, 1408, 1476, 1518, 1549, 1595, 1647, 2843, 2941, 2964, 3014, 3412, 3688; LRMS, ESI^+ m/z 517.1 (MH^+, $[C_{23}H_{19}F_6N_2O_3S]^+$ requires 517.1).

2.2.12. 1-(2,4-Dimethoxy-5-pyrimidinyl)-2-[2-methyl-5-(4-methylphenyl)-3-thienyl]perfluorocyclopentene (*2o*)

2o was prepared by a method to that used for **1o** using **8b** instead of **8a**. Column chromatography on SiO_2 with petroleum ether and ethyl acetate ($v/v = 5/1$) as the eluent afforded 0.31 g of **2o** as a colorless solid in 48% yield. M.p. 378–379 K; Calcd for $C_{23}H_{18}F_6N_2O_2S$ (%): Calcd C, 55.20; H, 3.63; N, 5.60. Found C, 55.27; H, 3.65; N,5.64; ^1H NMR (400 MHz, $CDCl_3$): δ 2.03 (s, 3 H, $-CH_3$), 2.37 (s, 3H, $-CH_3$), 3.73 (s, 3H, $-OCH_3$), 4.01 (s, 3H, $-OCH_3$), 7.14 (s, 1H, thiophene-H), 7.19 (d, 2H, $J = 8.0$ Hz, benzene-H), 7.42 (d, 2H, $J = 8.0$ Hz, benzene-H), 8.34 (s, 1H, pyrimidine-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.15, 21.13, 54.19, 55.24, 104.15, 122.00, 125.48, 125.99, 129.66, 120.62, 137.88, 139.04, 142.29, 159.06, 166.09, 168.05; IR (KBr, ν, cm^{-1}): 737, 804, 854, 893, 981, 1015, 1067, 1123, 1196, 1242, 1269, 1292, 1333, 1404, 1476, 1555, 1593, 1647, 2868, 2962, 2993, 3024, 3439; LRMS, ESI^+ m/z 501.1 (MH^+, $[C_{23}H_{19}F_6N_2O_3S]^+$ requires 501.1).

2.2.13. 1-(2,4-Dimethoxy-5-pyrimidinyl)-2-(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene (*3o*)

Diarylethene **3o** was prepared by a method to that used for **1o** using **8c** instead of **8a**. Column chromatography on SiO_2 with petroleum ether and ethyl acetate ($v/v = 5/1$) as the eluent afforded 0.40 g of **3o** as a colorless solid in 56% yield. M.p. 358–359 K; Calcd for $C_{22}H_{16}F_6N_2O_2S$ (%): Calcd C, 54.32; H, 3.32; N, 5.76. Found C, 54.43; H, 3.37; N, 5.81; ^1H NMR (400 MHz, $CDCl_3$): δ 2.04 (s, 3H, $-CH_3$), 3.74 (s, 3H, $-OCH_3$), 4.01 (s, 3H, $-OCH_3$), 7.19 (s, 1H, thiophene-H), 7.29 (t, 1H, $J = 7.6$ Hz, benzene-H), 7.39 (t, 2H,

$J = 7.6$ Hz, benzene-H), 7.53 (d, 2H, $J = 7.6$ Hz, benzene-H), 8.35 (s, 1H, pyrimidine-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.22, 54.23, 55.30, 104.10, 122.47, 125.53, 126.05, 127.88, 129.00, 133.31, 142.09, 146.34, 159.04, 166.04, 167.98; IR (KBr, ν, cm^{-1}): 762, 799, 827, 845, 856, 893, 934, 984, 1003, 1074, 1134, 1194, 1248, 1296, 1335, 1375, 1410, 1479, 1545, 1599, 1649, 1599, 1649, 2868, 2966, 3020, 3306, 3689; LRMS, ESI$^+$ m/z 487.1 (MH^+, $[C_{22}H_{17}F_6N_2O_2S]^+$ requires 487.1).

*2.2.14. 1-(2,4-Dimethoxy-5-pyrimidinyl)-2-[2-methyl-5-(4-fluorophenyl)-3-thienyl]perfluorocyclopentene (**4o**)*

Diarylethene **4o** was prepared by a method similar to that used for **1o** using **8d** instead of **8a**. Column chromatography on SiO_2 with petroleum ether and ethyl acetate ($v/v = 6/1$) as the eluent afforded 0.35 g of **4o** as a colorless solid in 53% yield. M.p. 365–366 K; Calcd for $C_{22}H_{15}F_7N_2O_2S$ (%): Calcd C, 52.38; H, 3.00; N, 5.55. Found C, 52.45; H, 3.03; N, 5.57; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.04 (s, 3H, $-CH_3$), 3.75 (s, 3H, $-OCH_3$), 4.02 (s, 3H, $-OCH_3$), 7.06–7.10 (m, 2H, benzene-H), 7.11 (t, 1H, thiophene-H), 7.43–7.56 (m, 2H, benzene-H), 8.33 (s, 1H, pyrimidine-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.13, 54.20, 55.27, 104.05, 116.00, 122.54, 126.09, 127.29, 129.64, 139.60, 141.05, 159.10, 162.50, 166.12, 168.05; IR (KBr, ν, cm^{-1}): 737, 800, 826, 893, 982, 1005, 1072, 1126, 1194, 1248, 1296, 1333, 1377, 1406, 1477, 1514, 1547, 1599, 1726, 2868, 2963, 3024, 3446; LRMS, ESI$^+$ m/z 505.1 (MH^+, $[C_{22}H_{16}F_7N_2O_2S]^+$ requires 505.1).

*2.2.15. 1-(2,4-Dimethoxy-5-pyrimidinyl)-2-[2-methyl-5-(4-trifluoromethylphenyl)-3-thienyl]perfluorocyclopentene (**5o**)*

Diarylethene **5o** was prepared by a method similar to that used for **1o** using **8e** instead of **8a**. Column chromatography on SiO_2 with petroleum ether and ethyl acetate ($v/v = 5/1$) as the eluent afforded 0.46 g of **5o** as a colorless solid in 47% yield. M.p. 406–407 K; Calcd for $C_{23}H_{15}F_9N_2O_2S$ (%): Calcd C, 49.83; H, 2.73; N, 5.05. Found C, 49.95; H, 2.77; N, 5.07; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.06 (s, 3H, $-CH_3$), 3.73 (s, 3H, $-OCH_3$), 4.01 (s, 3H, $-OCH_3$), 7.27 (s, 1H, thiophene-H), 7.63 (s, 4H, benzene-H), 8.34 (s, 1H, pyrimidine-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.22, 54.20, 55.29, 103.90, 123.98, 124.0, 126.04, 126.44, 129.70, 136.66, 140.30, 141.04, 159.10, 166.17, 168.00; IR (KBr, ν, cm^{-1}): 737, 797, 826, 854, 893, 984, 1015, 1067, 1128, 1177, 1198, 1242, 1271, 1298, 1323, 1377, 1410, 1476, 1493, 1555, 1591, 1651, 2937, 2963, 2993, 3416, 3470; LRMS, ESI$^+$ m/z 555.1 (MH^+, $[C_{23}H_{16}F_9N_2O_2S]^+$ requires 555.1).

3. Results and discussion

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

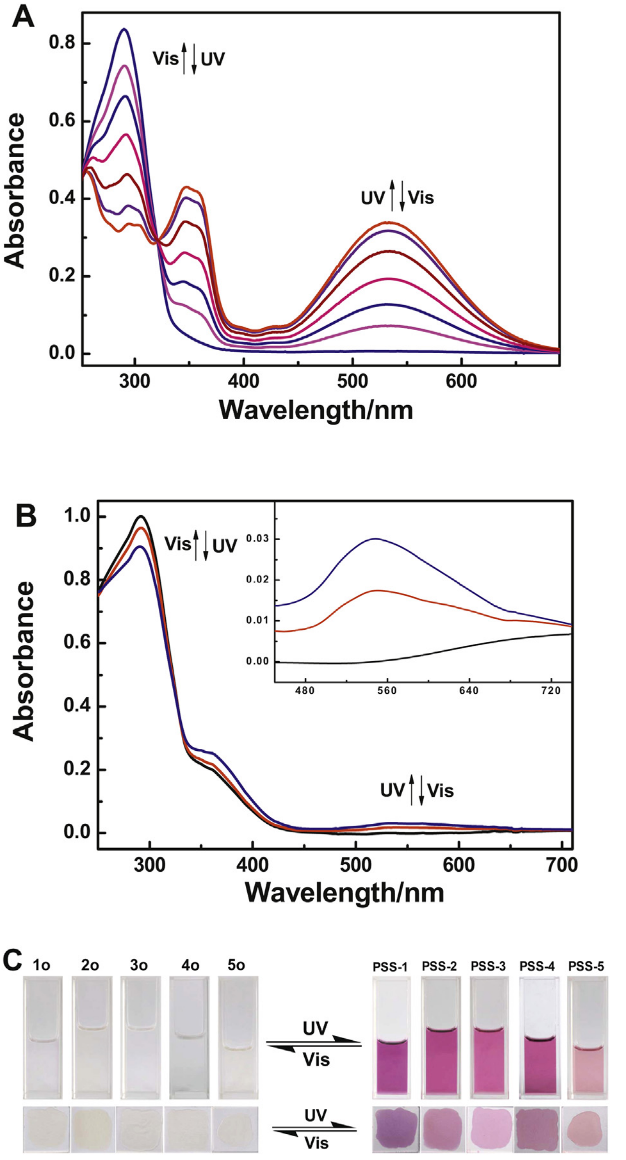

Fig. 3. Absorption spectral changes of diarylethene **1** and color changes of diarylethenes **1**–**5** upon alternating irradiation with UV and visible light at room temperature: (A) spectral changes for **1** in hexane (2.0×10^{-5} mol L^{-1}); (B) spectral changes for **1** in a PMMA film (10%, w/w); (C) color changes for **1**–**5** in both hexane and PMMA films. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The photochromic behaviors of **1**–**5** induced by photoirradiation were measured in both hexane (2.0×10^{-5} mol L^{-1}) and PMMA films (10%, w/w) at room temperature. The absorption spectral change of **1** and color changes of diarylethenes **1**–**5** induced by alternating irradiation with UV and visible light in hexane and PMMA films are shown in Fig. 3. In hexane, **1o** was found to show an intense absorption band at 290 nm (ε, 3.92×10^4 L mol^{-1} cm^{-1}) due to π–π^* transition [37], and give a colorless solution without any absorption bands in the visible range. Upon UV irradiation at 297 nm, the closed-ring isomer **1c** was produced by the typical photocyclization as the colorless solution changed to red, thereby resulting in broad absorption bands centered at 533 nm (ε, 1.95×10^4 L mol^{-1} cm^{-1}). Reversely, the red solution of **1c** could be completely bleached upon irradiation with visible light ($\lambda > 450$ nm). The significant difference in absorption bands of the closed-ring isomers compared to their open-ring isomers is mainly due to the increase in π conjugation, which dramatically changes the electronic structure as a whole in such a way that new electronic transitions are observed in the visible region [38,39]. **2**–**5** exhibited photochromism similar to **1** in hexane. Upon irradiation with 297 nm light, the solutions containing **2o**–**5o** turned red as a result of the cyclization reactions to produce the closed-ring isomers **2o**–**5o**, whose absorption maxima were observed at 526, 522, 517 and 518 nm, respectively. The red colored solutions of **2o**–**5o** could again be bleached by irradiation with visible light because the compounds returned to the open-ring isomers **2o**–**5o** respectively. As shown in Fig. 4, the photoconversion ratios from open-ring to closed-ring isomers of **1**–**5** were analyzed by HPLC in the photostationary state (PSS). The photoconversion ratios of **1**–**5** were 80% for **1**, 63% for **2**, 72% for **3**, 47% for **4**, and 84% for **5**. Compared with diarylethenes with a pyrrole moiety [40], the photoconversion ratios of **1**–**5** were significantly decreased in solution. However, they were approximately equal to those of diarylethenes with pyridine or isoxazole moieties [32,41]. In PMMA

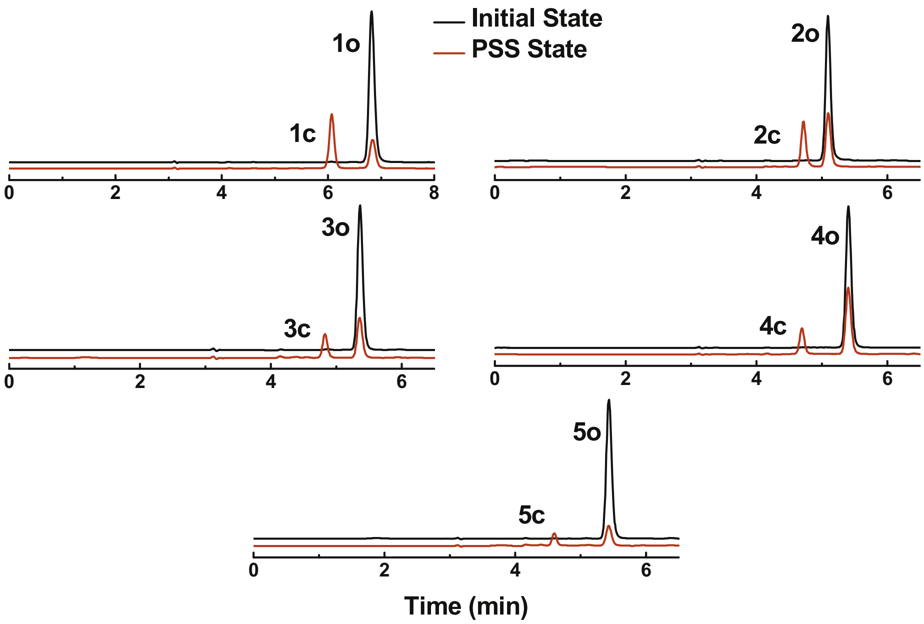

Fig. 4. The photoconversion ratios of diarylethenes **1**–**5** in the photostationary state in hexane by HPLC analysis.

films, **1**–**5** also showed similar phototchromism as observed in hexane (Fig. 3B). Compared to those in hexane, the maximum absorption peaks of **1**–**5** in PMMA films shifted to a longer wavelength. The redshift values of the closed-ring isomers were 3 nm for **1c**, 9 nm for **2c**, 15 nm for **3c**, 9 nm for **4c**, and 10 nm for **5c**. The redshift phenomena were consistent with those of reported diarylethenes [23,42–45], and may be attributed to the polar effect of the polymer matrix in amorphous solid state.

The photochromic features of **1**–**5** in both hexane and PMMA films are summarized in Table 1. As expected, the different substituents at the *para*-position of the benzene ring had remarkable effects on the photochromic properties of these diarylethenes, including the absorption maxima, molar absorption coefficients, and the quantum yields of cyclization and cycloreversion. As shown in Table 1, when an electron-donating substituent (methoxy or methyl group, **1** or **2**) was attached at the *para*-position of the phenyl ring, the molar absorption coefficients of the closed-ring isomers and the cyclization quantum yields rose with the increase of electron-donating ability, but the cycloreversion quantum yields decreased [46]. However, the molar absorption coefficients of the closed-ring isomers and the cyclization quantum yields did not change much when an electron-withdrawing substituent (fluorine or trifluoromethyl group, **4** or **5**) was attached. As a result, **1** had the largest molar absorption coefficient of the closed-ring isomers and the cyclization quantum yield. This indicated that the electron-donating substituent could effectively enhance the molar absorption coefficients of closed-ring isomers and the cyclization quantum yields. The result was well consistent with the

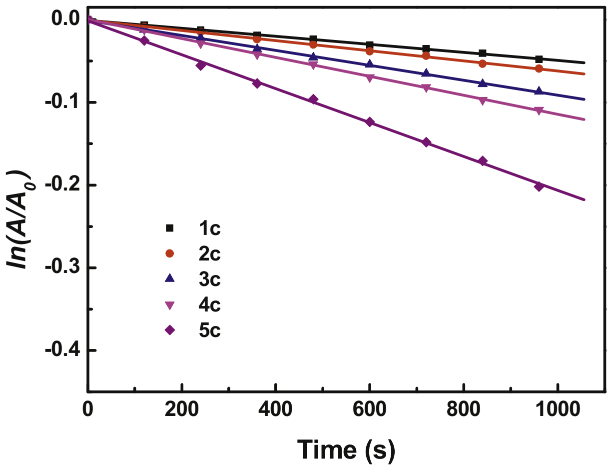

Fig. 5. Thermal fading of **1c**–**5c** at 293 K.

Table 1

Absorption spectral properties and photochromic reactivity of diarylethenes **1**–**5** in hexane (2.0×10^{-5} mol L^{-1}) and in PMMA films (10%, w/w) at room temperature.

Compd	$\lambda_{\text{o,max}}$/nm[a] (ε/L mol^{-1} cm^{-1})		$\lambda_{\text{c,max}}$/nm[b] (ε/L mol^{-1} cm^{-1})		Φ[c]		PR[d] (%)
	Hexane	PMMA film	Hexane	PMMA film	Φ_{o-c}	Φ_{c-o}	
1	290 (3.92×10^4)	291	533 (1.95×10^4)	536	0.51	0.10	80%
2	287 (3.56×10^4)	290	526 (1.47×10^4)	535	0.29	0.19	63%
3	285 (4.02×10^4)	287	522 (1.00×10^4)	537	0.17	0.26	72%
4	284 (3.56×10^4)	285	517 (1.07×10^4)	526	0.14	0.16	47%
5	291 (3.46×10^4)	294	518 (1.01×10^4)	528	0.15	0.29	84%

[a] Absorption maxima of open-ring isomers.
[b] Absorption maxima of closed-ring isomers.
[c] Quantum yields of cyclization reaction (Φ_{o-c}) and cycloreversion reaction (Φ_{c-o}), respectively.
[d] Photoconversion ratio from the open-ring to closed-ring isomers in the photostationary state.

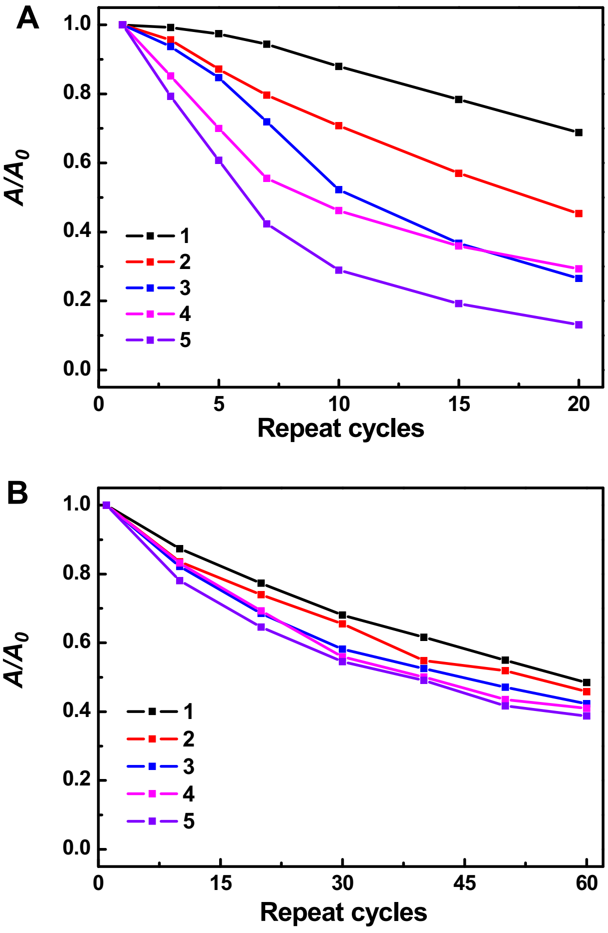

Fig. 6. Fatigue resistance of diarylethenes **1**–**5** in air atmosphere at room temperature: (A) in hexane; (B) in PMMA films. Initial absorbance of the sample was fixed to 1.0.

diarylethenes with a naphthalene, pyridine, isoxazole, or thiazole moiety [31,32,41,47]. In addition, the absorption maxima of **1c**–**5c** were observed between 518 and 533 nm in hexane, which were much shorter than those of the diarylethenes with benzene, pyridine, pyrazole or thiophene moieties [20,23,32,48]. The results suggested that the pyrimidine moiety can effectively shift the absorption maximum of diarylethene to a shorter wavelength.

The thermal stability of the open-ring and closed-ring isomers of **1**–**5** was examined in hexane at both room temperature and 341 K. Storage of the solutions of **1o**–**5o** in the darkness at room temperature and exposure to air for more than 10 days caused no changes in their UV/Vis spectra. But **1c**–**5c** returned to **1o**–**5o** when they were exposed to air in the dark for only 8, 7, 6.5, 5, and 4 h, respectively. At 341 K, the red color of **1c**–**5c** faded completely after 100, 90, 80, 75, and 50 s, respectively. The results revealed that the thermal stability of diarylethenes with a pyrimidine unit is much weaker than that of diarylethenes with five-membered heteroaryl rings due to the higher aromatic stabilization energy of six-membered pyrimidine [4,23,41,47]. The greatly enhanced ground-state energy difference between the open-ring and closed-ring isomers resulted in thermal instability of the closed-ring isomers of **1**–**5** [38,39]. As shown in Fig. 5, the thermal cycloreversion rates of **1c**–**5c** at 293 K accelerated when the electron-donating groups were changed with electron-withdrawing groups. This result indicated that the electron-donating groups could effectively enhance the thermal stability of diarylethenes with a pyrimidine moiety.

As a key factor for practical applications in optical devices [49], the fatigue resistance of **1**–**5** was examined in both hexane and PMMA films by alternative irradiation with UV and visible light in air at room temperature, and the result is shown in Fig. 6. In hexane, the coloration and decoloration cycles of **1**–**5** were repeated 20 times with 31% degradation of **1c**, 55% of **2c**, 74% for **3c**, 71% for **5c**, and 87% of **5c**. The degradation may be ascribed to the formation of an epoxide [50]. The fatigue resistance of **1**–**5** in PMMA films is much stronger than that in solution. After 60 repeat cycles, the degradation percentages of **1**–**5** in PMMA films were 52% for **1c**, 54% for **2c**, 58% for **3c**, 59% for **4c**, and 61% for **5c**. This improvement may result from suppression of oxygen diffusion in solid medium [49]. In addition, the fatigue resistance of the diarylethene with an electron-donating group was better than that of diarylethene with an electron-withdrawing group in both hexane and PMMA films. The result is in accordance with those of reported diarylethenes with a pyridine or thiazole moiety [32,44], but contrary to that of diarylethenes with a naphthalene moiety [31].

The structural conformations of the crystals of **1o**, **2o**, **3o**, and **5o** were provided by X-ray crystallographic analysis. Their ORTEP drawings are shown in Fig. 7, and the X-ray crystallographic analysis data are listed in Tables 2 and 3. In crystalline phase, the four diarylethenes crystallized in photoactive anti-parallel conformations, which can be expected to undergo photocyclization [51]. For the crystal of **3o**, there were two independent molecules in the asymmetric unit and both of them adopted an approximate C_2 symmetry. The two planar aryl moieties exhibited similar geometries in each molecule, with dihedral angles between the cyclopentene ring and the adjacent aryl rings of 48.2° for N1–N2/C17–C20 and 61.8° for S1/C7–C10 in one molecule. In the other molecule, the dihedral angles between the cyclopentene ring and the adjacent aryl rings are 44.5° for N3–N4/C39–C42 and 64.2° for S2/C29–C32. The distances between the photoactive carbons (C10•••C20 and C32•••C42) in each molecule were 3.628 and 3.702 Å, respectively. The distances between the reactive carbons *d* (Å) and dihedral angles *θ* (°) of **1o**, **2o**, and **5o** were shown in Table 3. As expected, the colorless crystal of **1o**, **2o**, **3o**, and **5o** turned red upon irradiation with 297 nm light, and the colored crystals reverted to a colorless state upon irradiation with visible light ($\lambda > 450$ nm). The color changes of the four derivatives in the crystalline phase by photoirradiation are shown in Fig. 8. After 100 repeat cycles, these crystals still exhibited favorable photochromism in the crystalline phase, suggesting that they can be potentially used for the construction of optoelectronic devices [52].

3.2. *Fluorescence of diarylethenes*

The fluorescence of **1o**–**5o** was measured in both hexane (1.0×10^{-4} mol L^{-1}) and PMMA films (10%, w/w) at room temperature, and the result is shown in Fig. 9 and Table 4. The emission peaks of **1o**–**5o** were observed at 449, 439, 427, 426, and 413 nm in hexane, and were observed at 469, 467, 442, 433 and 418 nm in PMMA films. Compared to those in hexane, the emission peaks of **1o**–**5o** in PMMA films showed a bathochromic shift, with the value of 20 nm for **1**, 28 nm for **2**, 15 nm for **3**, 7 nm for **4**, and 5 nm for **5**. When going from electron-donating to electron-withdrawing groups, the emission peaks of **1o**–**5o** gradually shifted to a shorter wavelength in both hexane (from 449 to 413 nm) and PMMA films (from 469 to 418 nm), and their emission intensity also enhanced evidently with the increase in electron-withdrawing ability. The result is consistent with that of diarylethenes with a pyridine, isoxazole or thiazole moiety [32,40,47], but contrary to that of diarylethenes with a biphenyl moiety [24]. The fluorescence quantum yields of **1o**–**5o** were determined to be 0.0179, 0.0075, 0.0065, 0.0056, and 0.0047, respectively, indicating that the

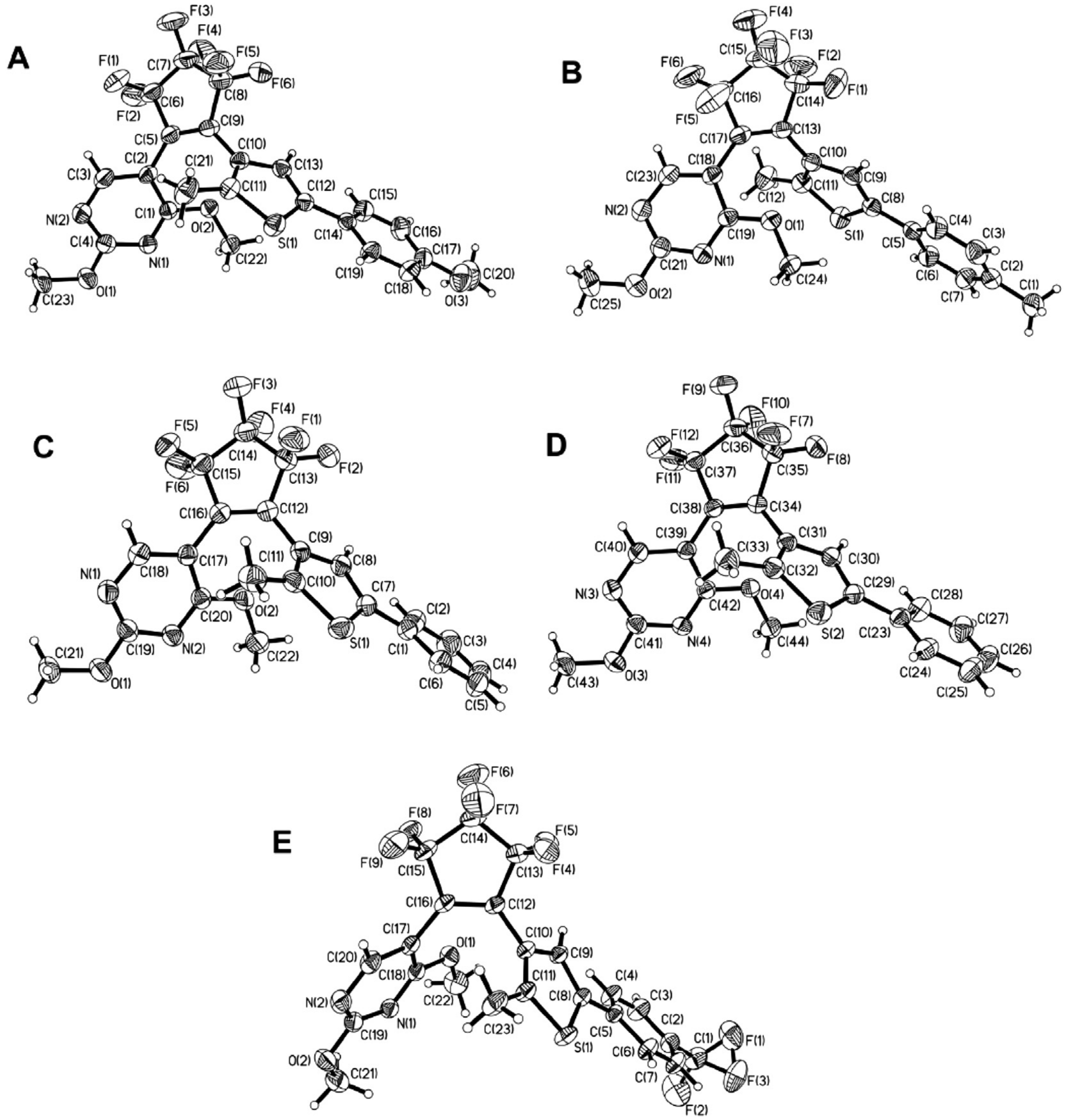

Fig. 7. ORTEP drawings of **1o**, **2o**, **3o**, and **5o**, showing about 30% probability displacement ellipsoids: (A) **1o**, (B) **2o**, (C) **3o**–molecule I, (D) **3o**–molecule II, and (E) **5o**.

Table 2
Crystal data for diarylethenes **1o**, **2o**, **3o**, and **5o**.

	1°	2°	3°	5°
Formula	$C_{23}H_{18}F_6N_2O_3S$	$C_{23}H_{18}F_6N_2O_2S$	$C_{22}H_{16}F_6N_2O_2S$	$C_{23}H_{15}F_9N_2O_2S$
Formula weight	516.45	500.45	486.43	554.43
Temperature (K)	293(2)	296(2)	296(2)	296(2)
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	P2(1)/c	P2(1)/c	P-1	P-1
Unit cell dimensions				
a (Å)	13.0363(7)	13.0447(10)	8.5948(10)	8.1811(17)
b (Å)	8.3736(6)	8.2222(8)	13.1124(15)	9.4444(19)
c (Å)	21.4912(12)	21.6787(15)	19.894(2)	15.778(3)
α (°)	90.00	90.00	80.9400(10)	95.693(2)
β (°)	93.283(5)	91.814(7)	87.6290(10)	100.976(2)
γ (°)	90.00	90.00	76.9200(10)	96.637(2)
Volume (Å^3)	2342.15	2324.0(3)	2156.5(4)	1179.5(4)
Z	4	4	2	2
Density (calcd.) (g/cm^3)	1.469	1.430	1.498	1.561
Goodness-of-fit on F^2	0.999	1.034	0.957	1.063
Final *R* indices [$I/2\sigma(I)$]				
R_1	0.0552	0.0690	0.0453	0.0674
ωR_1	0.1164	0.1910	0.0955	0.2019
R indices (all data)				
R_1	0.1217	0.1182	0.0675	0.0832
ωR_1	0.1538	0.2450	0.1105	0.2207

Table 3
Distances between the reacting carbon atoms *d* (Å) and dihedral angles *θ* (°) of **1o**, **2o**, **3o**, and **5o**.

Compound	*d* (Å)		*θ* (°)[a]		
			θ_1	θ_2	θ_3
1o	C1…C11	3.635	44.7	60.2	13.6
2o	C11…C19	3.595	44.7	60.4	11.0
3o	C10…C20	3.628	48.2	61.8	20.4
	C32…C42	3.702	44.5	64.2	14.4
5o	C11…C18	3.630	51.0	58.8	25.3

[a] θ_1, Dihedral angle between the cyclopentene ring and 2,4-dimethoxypyrimidine ring, θ_2, dihedral angle between the cyclopentene ring and thiophene ring, θ_3, dihedral angel between the thiophene ring and the adjacent benzene ring.

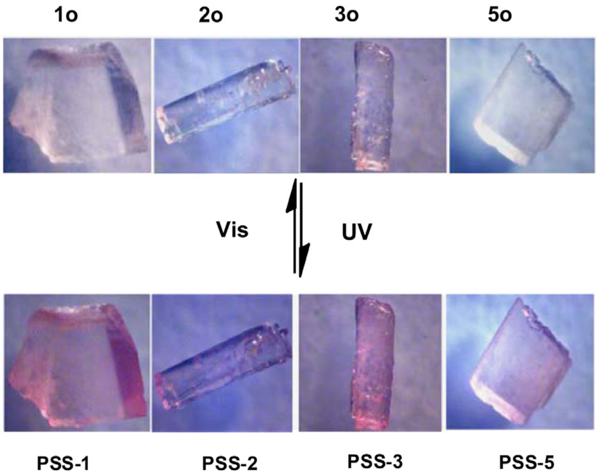

Fig. 8. Photographs demonstrating the photochromic processes of diarylethenes **1**, **2**, **3**, and **5** in the crystalline phase.

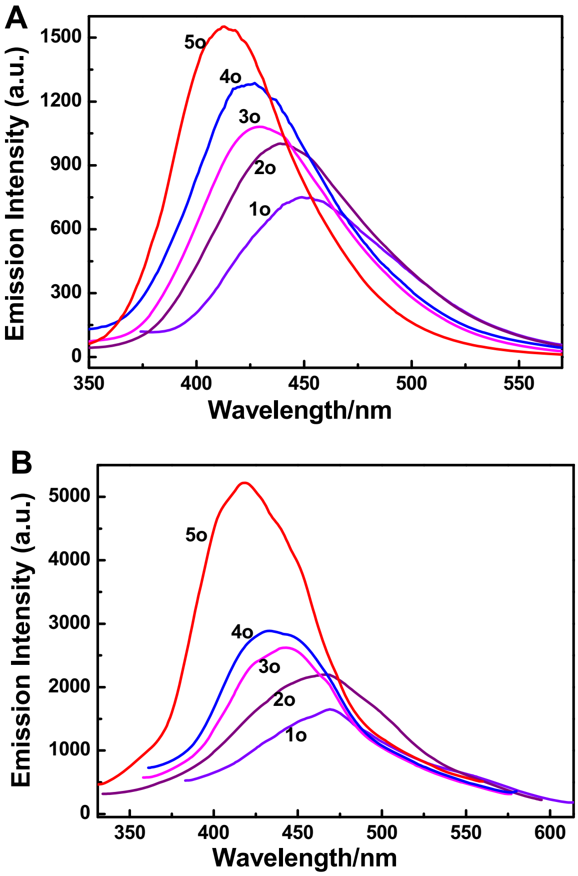

Fig. 9. Emission spectra of diarylethenes **1**–**5** in both hexane solution (1.0×10^{-4} mol L^{-1}) and PMMA films (10%, w/w) at room temperature: (A) in hexane; (B) in PMMA films.

fluorescence quantum yield decreased notably when going from electron-donating to electron-withdrawing groups. The result is different from those of the diarylethenes with a naphthalene or pyridine moiety whose fluorescence quantum yields increased with the increase of electron-withdrawing ability [31,32].

Similar to most reported diarylethenes [53–57], **1**–**5** exhibited notable fluorescent switches by photoirradiation in both hexane and PMMA films, and the result is shown in Fig. 10. Upon irradiation with 297 nm UV light, the fluorescence modulation efficiency of **1** was 83% in hexane and 34% in a PMMA film when arrived at the photostationary state (PSS). Similarly, the fluorescence modulation efficiency of the other four diarylethenes was 70% for **2**, 75% for **3**, 48% for **4**, and 82% for **5** in hexane, and was 34% for **2**, 39% for **3**, 32% for **4**, and 30% for **5** in PMMA films in the photostationary state. Therefore, the fluorescence modulation efficiency of **1**–**5** in hexane was much larger than those in PMMA films. The result is contrary to that of diarylethenes with a naphthalene, pyridine or isoxazole moiety whose fluorescence modulation efficiency in hexane was much lower than that in PMMA films [32,32,41]. In addition, the fluorescent modulation efficiency of **1**–**5** was notably enhanced in hexane as compared with that of all reported diarylethenes with a six-membered aryl rings [15,23,31,32], suggesting that diarylethenes with a six-membered pyrimidine moiety could be potentially applied in certain photoswitchable devices [58,59].

4. Conclusions

A new class of asymmetrical diarylethenes based on the hybrid skeleton of pyrimidine and thiophene moieties was synthesized, and their photochromic and fluorescent properties were investigated systematically. The pyrimidine attached directly to the central cyclopentene ring participated in the photoinduced cyclization reaction in hexane, PMMA films, and crystalline phase. Different substituents at the *para*-position of the terminal benzene ring had significant effects on their properties. The pyrimidine moiety induced some new characteristics which were different from those of reported diarylethenes with other six-membered aryl moieties. The results will be helpful to understand the substituent effects on the properties of diarylethenes with a pyrimidine moiety and synthesize novel diarylethenes with tunable photochromic behaviors.

Table 4
Fluorescence parameters of diarylethenes **1**–**5** in both hexane (1.0×10^{-4} mol L^{-1}) and PMMA films.

	Hexane			PMMA			Φ_f
	λ_{em}/nm[a] (λ_{ex}/nm[b])	I_f[c]	H[d] (%)	λ_{em}/nm (λ_{ex}/nm)	I_f	H (%)	
1o	449 (327)	751	83	469 (319)	1650	34	0.0179
2o	439 (324)	1002	70	467 (311)	2197	34	0.0075
3o	427 (319)	1078	75	442 (300)	2623	39	0.0065
4o	426 (317)	1281	48	433 (300)	2887	32	0.0056
5o	413 (317)	1552	82	418 (291)	5220	30	0.0047

[a] Emission peak.
[b] Excitation wavelength.
[c] Emission intensity.
[d] Fluorescence modulation efficiency in the photostationary state.

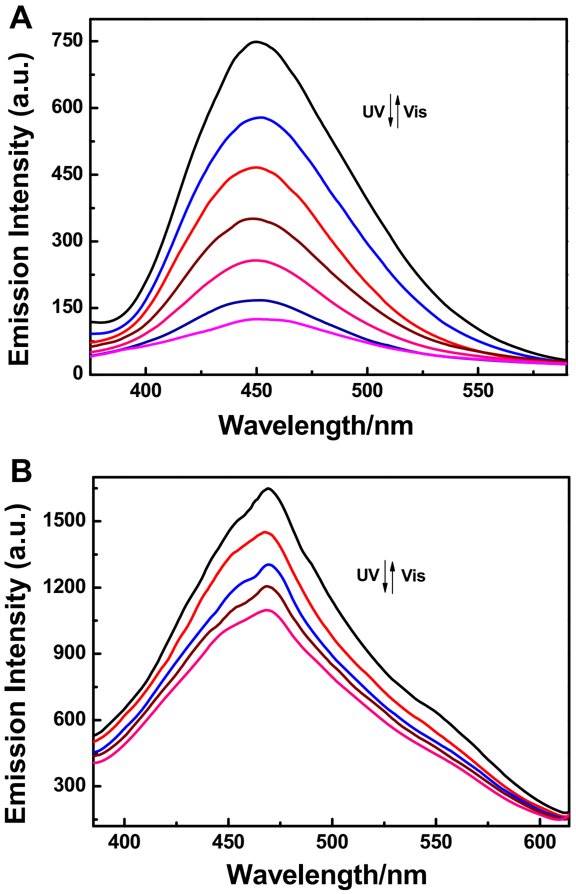

Fig. 10. Emission intensity changes of diarylethene **1** by photoirradiation at room temperature: (A) in hexane (1.0×10^{-4} mol L^{-1}); (B) in a PMMA film (10%, w/w).

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