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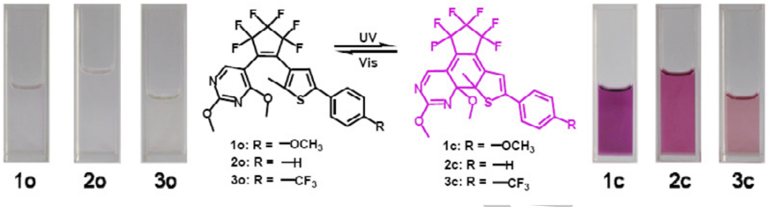

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New photochromic diarylethenes with a pyrimidine moiety

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Abstract—A novel class of photochromic diarylethene derivatives based on the hybrid skeleton of six-membered pyrimidine and five-membered thiophene moieties has been firstly synthesized. The substituent effects on their properties, including photochromism, fatigue resistance, and fluorescence, have been systematically investigated. All these diarylethenes showed significant photochromism and notable fluorescence switching properties in both solution and poly(methylmethacrylate) films. The electron-donating substituent enhanced their cyclization quantum yield, fatigue resistance, and fluorescence quantum yield, whereas electron-withdrawing group exhibited contrary effects.

During the past few decades, various types of photochromic molecules,[1] such as stilbene,[2] azobenzenes,[3] furylfulgides,[4] spirooxazines,[5] and diarylethenes,[6] have been developed. These photochromic compounds have been applied as optical memories and switches.[7] Among them, diarylethene derivatives with heterocyclic aryl rings are one of the most promising candidates for practical applications because of their excellent thermal stability, notable fatigue resistance, and high photo reactivity in solid state.[8]

Generally, the aryl moieties and functional substituents have important effects on the photochromic properties of diarylethenes. For example, diarylethenes with thiophene or benzothiophene moieties show excellent thermal stability and fatigue resistance,[8a,9] and the diarylethenes with indole rings can act like effective fluorescent photoswitches.[10] Yamaguchi and Irie[11] reported that bulky alkyl chains at 2-positions of benzothiophene and benzofuran rings improved the cyclization quantum yield. Morimitsu et al.[12] and Pu et al.[13] revealed that bulky alkoxy substituents at the reactive carbons decreased the thermal stability and fatigue resistance. So far, the hexatriene backbones of the reported diarylethene systems are mainly confined to the five-membered heteroaryl rings.[14] In the cases of six-membered heteroaryl rings, only a few symmetrical diarylethene derivatives with two phenyl/naphthyl groups have been reported.[15] The majority of these derivatives are thermally reversible and have poor photochromic activity. In previous publications,[13,16] we reported a new class of diarylethenes with both five- and six-membered aryl rings, which showed new characteristics different from the ones with five-membered aryl rings. All of these compounds exhibited excellent photochromic and fluorescence switching properties in both solution and poly (methylmethacrylate) (PMMA) films. These diarylethenes with a six-membered aryl moiety are potential candidates for optoelectronic applications.

To date, the six-membered aryl rings used in known diarylethenes were only limited to benzene and pyridine.[13,16] To the best of our knowledge, photochromic diarylethenes based on a hybrid structure of pyrimidine and thiophene have not hitherto been reported. In this Letter, we designed and synthesized a new class of diarylethenes (**1o**–**3o**) with both pyrimidine and thiophene, and systematically investigated their properties. All of these diarylethenes showed good photochromism in solution, PMMA amorphous films, and crystalline phase. The photochromic scheme of diarylethenes **1o**–**3o** is shown in Scheme 1.

Keyword: Diarylethene; Photochromism; Pyrimidine moiety; Optical characteristic.

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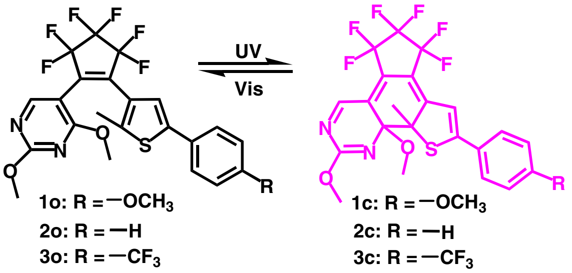
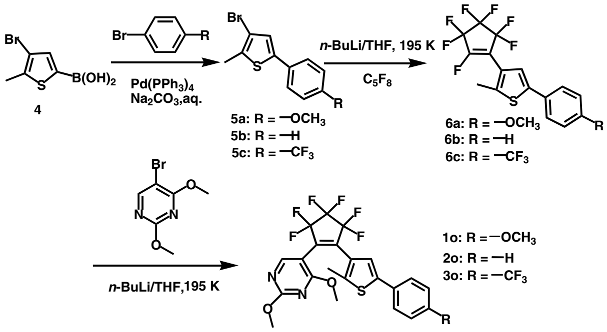


Scheme 1. Photochromism of diarylethenes **1o**–**3o**.



Scheme 2. Synthetic route for diarylethenes **1o**–**3o**.

The synthetic route for **1o**–**3o** is shown in Scheme 2. Suzuki coupling of bromobenzene derivatives with thiophene boronic acid (**4**)[17] afforded compounds **5a**–**c**. Lithiation and coupling with perfluorocyclopentene gave mono-substituted **6a**–**c**. Lithiation of 5-bromo-2,4-dimethoxypyrimidine and coupling with **6a**–**c** afforded the unsymmetrical diarylethenes **1o**–**3o**, respectively. The structures of **1o**–**3o** were confirmed by elemental analysis, NMR, IR, and MS.[18] The PMMA films of **1o**–**3o** were prepared by dissolving 10 mg of diarylethene sample and 100 mg of PMMA in chloroform (1 mL) with the aid of ultrasound, and the homogeneous solution was spin-coated on a quartz substrate (20 × 20 × 1 mm^3) with a rotating speed at 1500 rpm. The films were dried in air and kept in darkness at room temperature.

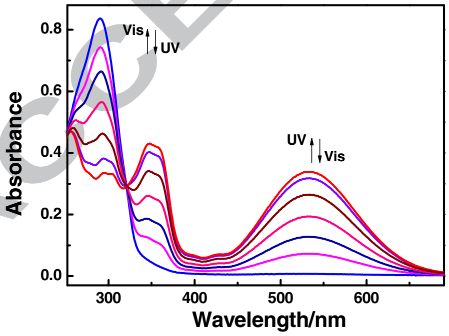


Figure 1. Absorption spectral changes of diarylethene **1** by photoirradiation in hexane (2.0 × 10^{-5} mol L^{-1}) at room temperature.

Diarylethenes **1**–**3** showed evident photochromism and could be toggled between the colorless open-ring isomers (**1o**–**3o**) and the colored closed-ring isomers (**1c**–**3c**) by alternating irradiation with UV light and visible light of appropriate wavelength in both solution and solid media. The absorption spectral changes of diarylethene **1** upon photochromic reactions are shown in Figure 1. In hexane, the absorption maximum of **1o** was observed at 290 nm (ε, 3.92 × 10^4 L mol^{-1} cm^{-1}) due to $\pi \rightarrow \pi^*$ transition.[19] Upon irradiation with 297 nm light, a new visible absorption band centered at 533 nm (ε, 1.95 × 10^4 L mol^{-1} cm^{-1}) emerged, while the original peak at 290 nm decreased with color change from colorless to red (Figure 2A), which could be ascribed to the formation of closed-ring isomer **1c**. Reversely, the red solution of **1c** could be completely bleached upon irradiation with visible light ($\lambda > 450$ nm). In photostationary state, the isosbestic point of **1** was observed at 320 nm, which was in agreement with the reversible two-component photochromic reaction scheme.[20] Similar to **1**, diarylethenes **2** and **3** also exhibited evident photochromism by photoirradiation. The absorption maxima were observed at 522 nm for **2c** and 518 nm for **3c**. The color changes of **2** and **3** by photoirradiation in hexane are also showed in Figure 2A. In photostationary state, the isosbestic points of **2** and **3** were observed at 310 and 318 nm, respectively. In addition, the photoconversion ratios of **1**–**3** were obtained by HPLC analysis in photostationary state, with the value of 80% for **1**, 72% for **2**, and 84% for **3** (Table 1).

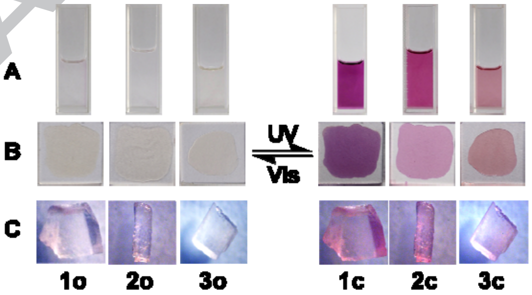


Figure 2. The color changes of diarylethenes **1**–**3** by photoirradiation in different media at room temperature: (A) in hexane, (B) in PMMA films, and (C) in crystalline phase.

In PMMA films, **1**–**3** also showed similar photochromism to those in hexane (Figure 2B). The absorption maxima of the closed-ring isomers **1c**–**3c** in PMMA films are at longer wavelengths than those in hexane. The redshift values of absorption maxima of the closed-ring isomers are 3 nm for **1c**, 15 nm for **2c**, and 10 nm for **3c**, which may be ascribed to the polar effect of polymer matrix and the stabilization of molecular arrangement in solid medium.[21] It was noted that **1o**–**3o** showed obvious photochromism in crystalline phase (Figure 2C), different from the reported diarylethenes with a benzene moiety, which showed no photochromism in crystalline phase.[13a] Compounds **1**–**3** with a pyrimidine were found to be the second class of diarylethenes with a six-membered aryl ring, which exhibited photochromic activity in crystalline phase.[16b]

The cyclization and cycloreversion quantum yields of **1**–**3** were measured in hexane at room temperature. The results listed in Table 1 suggested that altering the substituents at *para*-position of the terminal benzene had significant effects on the photochromic features of **1**–**3**, including the absorption maxima, molar absorption coefficients, and quantum yields. When the hydrogen atom was replaced with a methoxy group at the *para*-position of phenyl ring, the molar absorption coefficients and cyclization quantum yields increased, but the cycloreversion quantum yields decreased. However, the molar absorption coefficients of the closed-ring isomers and the quantum yields did not change much, when the hydrogen atom was replaced with a trifluoromethyl group. Furthermore, no matter replacing the hydrogen atom at the *para*-position of the terminal benzene with an electron-donating methoxy group (**1**) or with an electron-withdrawing trifluoromethyl group (**3**), the molar absorption coefficients of the open-ring isomers clearly decreased. As a result, the unsubstituted parent diarylethene **2** has the largest molar absorption coefficient among the open-ring isomers and the smallest molar absorption coefficient among the closed-ring isomers. The absorption maxima of **1**–**3** in hexane showed remarkable blueshift with increase of electron-withdrawing ability. In addition, all absorption maxima of the closed-ring isomers **1c**–**3c** were observed between 518–533 nm, shorter than the diarylethenes with benzene, pyridine, pyrazole or thiophene moieties.[13a,16b,22] However, their absorption maxima were longer than those of diarylethenes with thiazole or naphthalene moieties.[14c,16a] The results suggested that the pyrimidine can be effective to shift the absorption maximum of diarylethene to a shorter wavelength direction, but its action is slightly less than that of the thiazole or naphthalene.

Table 1. Absorption spectral properties of diarylethenes **1**–**3** in hexane (2.0 × 10^{-5} mol L^{-1}) and in PMMA films (10%, w/w) at room temperature.

Compound	$\lambda_{o,max}$/nm[a] (ε/L mol^{-1} cm^{-1})		$\lambda_{c,max}$/nm[b] (ε/L mol^{-1} cm^{-1})		Φ[c]		PR/%[d]
	Hexane	PMMA	Hexane	PMMA	$\Phi_{o\text{-}c}$	$\Phi_{c\text{-}o}$	
1	290(3.92×10^4)	291	533(1.95×10^4)	536	0.51	0.10	80
2	285(4.02×10^4)	287	522(1.00×10^4)	537	0.17	0.26	72
3	291(3.46×10^4)	294	518(1.01×10^4)	528	0.15	0.29	84

[a] The maximum absorption peak of the open-ring isomers; [b] The maximum absorption peak of the closed-ring isomers; [c] Quantum yields of cyclization ($\Phi_{o–c}$) and cycloreversion ($\Phi_{c–o}$). [d] Photoconversion ratios of **1**–**3** in the photostationary state.

The thermal stability of the open-ring and closed-ring isomers of **1**–**3** was tested in hexane at both room temperature and 341 K. After the solutions of **1o**–**3o** were stored in the dark at room temperature and exposed to air for more than 10 days, no changes in the UV/Vis spectra were observed. But **1c**–**3c** returned to **1o**–**3o**, when exposed to air in the dark for only 8 h, 6.5 h and 4 h, respectively. At 341 K, the red color of diarylethenes **1c**–**3c** faded completely after 100 s, 80 s and 50 s, respectively. These results suggested that the thermal stability of diarylethenes with a pyrimidine are different from that of diarylethenes with five-membered rings.[14c,d] The weak thermal stability of **1c**–**3c** was expected due to the higher aromaticity of six-membered pyrimidine, compared to five-membered heteroaryl rings. The greatly enhanced ground-state energy difference between the open-ring and closed-ring forms ultimately results in the thermal instability of the closed-ring forms of **1–3**.[23]

The fatigue resistance of **1**–**3** was tested in both hexane and PMMA films by alternative irradiation with UV and visible light in air at room temperature (Figure 3). In hexane, the coloration and decoloration cycles of **1**–**3** were repeated 20 times with 21% degradation of **1c**, 74% of **2c**, and 87% of **3c**, which may result from the formation of epoxides.[24] Their fatigue resistance in PMMA films is much better. After 50 repeated cycles, the degradation percentages of **1**–**3** in PMMA films were 45% for **1c**, 53% for **2c**, and 59% for **3c**. This improvement may result from suppression of O_2 diffusion in solid medium.[8g] The fatigue resistance of the diarylethene with an electron-donating methoxy group (**1**) was better than that of diarylethene with an electron-withdrawing trifluoromethyl group (**3**) in both hexane and a PMMA film, which is in accordance with the results reported for diarylethenes with a pyridine,[16b] but contrary to the results reported for diarylethenes with a naphthalene.[16a] Compared to the diarylethenes with a naphthalene or pyridine moiety,[16] **1**–**3** showed weaker fatigue resistance. But its fatigue resistance was stronger than that of the diarylethenes with a benzene moiety.[13b]

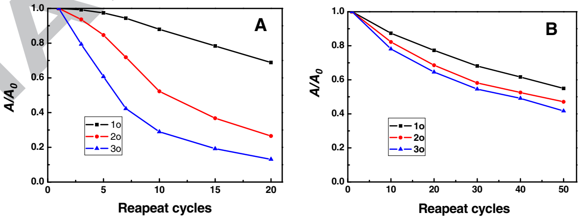


Figure 3. Fatigue resistance of **1**–**3** in hexane and PMMA films in air atmosphere at room temperature: (A) in hexane, (B) in PMMA films. Initial absorbance of the sample was fixed at 1.0.

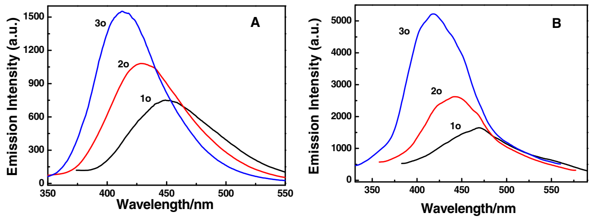


Figure 4. Emission spectra of **1o**–**3o** in hexane (1.0 × 10^{-4} mol L^{-1}) and in PMMA films (10%, w/w) at room temperature: (A) in hexane and (B) in PMMA films.

The fluorescence spectra of **1o**–**3o** in both hexane (1.0 × 10^{-4} mol L^{-1}) and PMMA films (10%, w/w) were measured at room temperature. As shown in Figure 4, the emission peaks were observed at 449 nm (λ_{ex}, 327 nm) for **1o**, 427 nm (λ_{ex}, 319 nm) for **2o**, and 413 nm(λ_{ex}, 317 nm) for **3o** in hexane, and were observed at 469 nm (λ_{ex}, 319 nm) for **1o**, 442 nm (λ_{ex}, 300 nm) for **2o**, and 418 nm (λ_{ex}, 291 nm) for **3o** in PMMA films. Compared to those in hexane, the emission peaks of **1o**–**3o** showed a bathochromic shift in PMMA films, with the value of 20 nm for **1**, 15 nm for **2**, and 5 nm for **3**. Compared to the unsubstituted **2o**, the electron-donating methoxy group of **1o** shifted the emission peak to a longer wavelength and notably decreased the emission intensity. However, the trifluoromethyl group of **3o** shifted the emission peak to a shorter wavelength and greatly increased the emission intensity. The result suggested that different substituents attached at the *para*-position of the terminal benzene ring had significant effects on both wavelength and intensity of the emission peaks. This result is consistent with that of diarylethenes with a pyridine.[16b] The fluorescence quantum yields of **1o–3o** were determined to be 0.018, 0.0065, and 0.0047, using anthracene as reference. The electron-donating methoxy substituent of **1o** effectively enhanced the fluorescence quantum yield. This result is different from those of the diarylethenes with a naphthalene or pyridine moiety, whose fluorescence quantum yields improved with the increase of electron-withdrawing ability of the substituents.[16]

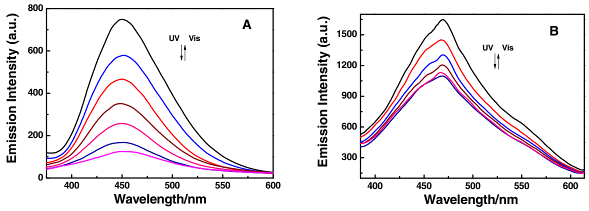


Figure 5. Emission intensity changes of diarylethenes **1** in hexane (1.0 × 10^{-4} mol L^{-1}) and in a PMMA film (10%, w/w) by photoirradiation at room temperature: (A) in hexane (λ_{ex} = 327 nm) and (B) in a PMMA film (λ_{ex} = 319 nm).

For most of the reported diarylethenes,[17b,22c,25] their open-ring isomers exhibit fluorescence, while their closed-ring isomers are non-fluorescent. Consequently, they can act like a fluorescent switch upon changing from open-ring isomers to closed-ring isomers by photoirradiation. Similarly, **1–3** exhibited notable fluorescence switching properties during photoisomerization. The changes in fluorescence of **1** in both hexane and a PMMA film are shown in Figure 5. Upon irradiation with 297 nm UV light, the sample reached the photostationary state, in which its emission intensity was quenched to ca. 17% in hexane and 66% in a PMMA film. Back irradiation with visible light regenerated the open-ring isomer **1o** and restored the original emission spectra. In the photostationary state, the emission intensity was quenched to *ca.* 25% for **2** and 18% for **3** in solution, and *ca.* 61% for **2** and 70% for **3** in PMMA films. As a result, modulation of the fluorescence of **1–3** in hexane was much bigger than that in PMMA films. This result is contrary to that of the diarylethenes with a pyridine moiety,[16b] whose fluorescence modulation efficiency in hexane was much lower than that in PMMA films. Among all known diarylethenes with a six-membered aryl rings,[13b,16] **1–3** showed the biggest fluorescence modulation efficiency in solution, suggesting that this class of diarylethenes may have potential applications in photoswitchable device materials.[27]

In conclusion, three new unsymmetrical diarylethenes with a six-membered pyrimidine moiety have been synthesized for the first time. The pyrimidine attached directly to the central cyclopentene ring participated in the photoinduced cyclization reaction in solution, PMMA films, and even crystalline phase. In addition, different substituents at the *para*-position of the terminal benzene ring showed significant effects on the optical properties and fatigue resistance of the diarylethenes. The pyrimidine moiety rendered this new type of diarylethenes distinctive photochromic features. The results are valuable for design and synthesis of novel photoactive diarylethene derivatives for practical applications in optoelectronic devices.

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18. Data for **1o**: Mp 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; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 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, $CDCl_3$, ppm): 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}): 507, 544, 650, 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$^+$, $[C_{23}H1_9F_6N_2O_3S]^+$ requires 517.1); Data for **2o**: Mp 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; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 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, $CDCl_3$, ppm): 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}): 469, 544, 567, 596, 654, 692, 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); Data for **3o**: Mp 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, $CDCl_3$, ppm): 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}CNMR (100 MHz, $CDCl_3$, TMS): 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}): 519, 561, 600, 640, 704, 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).
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