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New photochromic diarylethenes bearing a condensed aromatics moiety

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ABSTRACT

A new class of diarylethenes based on a hybrid structure of naphthalene and thiophene have been developed and their properties including photochromism, fatigue resistance, and fluorescence have been investigated. The condensed aromatic naphthalene was connected directly to the central cyclopentene ring as an aryl moiety and available to participate in the photoinduced cyclization reaction. All of these compounds have exhibited good photochromism, notable fatigue resistance, and obvious fluorescence photo-switches in both solution and polymer matrix. Nevertheless, significantly different properties have been observed among these diarylethenes, which may be attributed to the effect of different substituent groups. Compared with the analogs bearing other six-membered aryl unit, the naphthalene moiety is more conducive, which leads to higher molar absorption coefficient and blue shift of the absorption maximum.

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Organic photochromic materials have attracted much attention due to their potential application in erasable optical memory, photo physical switch components, and display devices.¹ In the past several decades, many new diarylethene systems with different heteroaryl moieties were explored. Among them, most of the central ethene containing bridging units were 3-thienyl,² 3-benzothienyl,³ and 2-thienyl⁴ groups. While others involved heteroaryl moieties, such as 3-pyrolyl,⁵ 4-thiazolyl,⁶ 4-oxazolyl,⁷ 4-pyrazolyl,⁸ 3-indolyl,⁹ and so on. Generally, the aryl moieties of diarylethene can strongly influence their photochromic characteristics. For instance, the diarylethenes having indole rings exhibit excellent fluorescent photoswitches,9 and diarylethenes bearing thiophene/benzothiophene moieties show excellent thermal stability and outstanding fatigue resistance.¹⁰ Nakagawa et al. developed triangular terthiophene derivatives which showed relatively high fluorescence quantum yield.¹¹ Yamaguchi et al. developed a new kind of 6π conjugated photochromic system with a bis(2,3'benzothienyl) unit, which exhibited efficient photochromism and thermal stability for the colored isomers.¹² However, diarylethenes bearing pyrrole rings are thermally unstable even at rt in the dark.^{5a} Apart from the fact that the aryl moieties have critical effects on the photochromic characteristics of diarylethene derivatives, the functional substituent can also notably affect photochromic properties, such as the absorption maxima, the absorption coefficients, and the quantum yields. Representatively, the electrondonating substituents of bis(3-thienyl)ethene diarylethenes can decrease the cycloreversion quantum yields and increase the absorption coefficients of the closed-ring isomers, while electronwithdrawing groups can shift the absorption maxima to longer wavelengths and decrease the cyclization quantum yield.¹³ Previously, we have reported that diarylethenes bearing different substituents can exhibit distinguishable features that resulted from the substituent effects.¹⁴

The hexatriene backbone of photochromic diarylethene systems is mainly confined to the five-membered heteroaryl rings. In the case of six-membered rings as aryl moieties, only a few symmetrical diarylethenes having two phenyl/naphthyl rings have been reported, and most of these derivatives are thermally reversible with poor photochromism.¹⁵ We have reported a new class of diarylethene derivatives bearing both five-membered and six-membered moieties, which have shown new characteristics as compared to the diarylethenes containing only five-membered heteroaryl rings.¹⁶ The condensed aromatics naphthalene is a unique arvl unit because of its strong aromatic stabilization energy. To the best of our knowledge, there has been only one example of a symmetrical photochromic diarylethene bearing two naphthyl rings, as reported by Uchida et al.^{15b} The diarylethene bearing naphthyl rings possesses excellent thermal stability, where the absorption intensity of its closed-ring isomer remains relatively constant for more than 500 h even at 343 K.^{15b} However, photochromic diarylethene derivatives based on a hybrid structure of condensed aromatics and five-membered heteroaryl moieties have not hitherto been reported.

In this Letter, we have investigated a new class of asymmetrical photochromic diarylethene derivatives bearing both naphthalene and thiophene moieties. The synthesized diarylethenes are 1-(2-methylnaphthyl)-2-(methyl-5-phenyl-3-thienyl)perfluorocyclopentene (**1o**), 1-(2-methylnaphthyl)-2-[2-methyl-5-(3-methoxyphenyl)-3-thienyl]perfluorocyclopentene (**2o**), and 1-(2-





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methylnaphthyl)-2-[2-methyl-5-(3-trifluoromethylphenyl)-3-thienyl]perfluorocyclopentene (**30**). All of these diarylethene derivatives showed good photochromism in both solution and poly (methyl methacrylate) (PMMA) amorphous films. The photochromic scheme of **10–30** is shown in Scheme 1.

The synthetic route for diarylethenes **10–30** is shown in Scheme 2. First, the phenylthiophene derivatives (**5a–c**) were prepared by Suzuki coupling of the three bromobenzene derivatives with a thiophene boronic acid.¹⁷ Then, 2-methyl-1-bromonaphthalene (**6**) was lithated and coupled with octafluorocyclopentene to give 2-methyl-1-naphthyl-perfluorocyclopentene (**7**). Finally, compounds **5a–c** were separately lithiated and then coupled with compound **7** to give diarylethenes **10–30**, respectively. The structures of diarylethenes **10–30** were confirmed by elemental analysis, NMR, and IR.¹⁸

The photochromic behaviors of diarylethenes **1–3** induced by photoirradiation at rt were measured both in hexane $(2.0 \times 10^{-5} \text{ mol L}^{-1})$ and in PMMA films (10%, w/w). In hexane, the absorption spectral change of diarylethene **1** and the color changes of diarylethenes **1–3** are shown in Figure 1. The open-ring isomer **10** exhibited a sharp absorption peak at 261 nm (ε , 2.76 × 10⁴ L mol⁻¹ cm⁻¹) in hexane, which arose from $\pi \rightarrow \pi^*$ transition.¹⁹ Upon irradiation with UV light, the colorless solution of **10** turned red and a new visible absorption band was observed at 508 nm (ε , 1.5 × 10⁴ L mol⁻¹ cm⁻¹), while the intensity of the original peak at 261 nm decreased indicating the formation of the closed-ring isomer **1c**. After irradiation with a visible light (λ >500 nm), the red color was bleached to colorless by virtue of



Scheme 1. Photochromism of diarylethenes 10-30.



Figure 1. Absorption spectral changes of diarylethene 1 (A) and the color changes of diarylethenes 1–3 (B) by photoirradiation in hexane $(2.0 \times 10^{-5} \text{ mol } L^{-1})$ at rt.

the reproduction of the original open-ring isomer **1o**. At the photostationary state, the isosbestic point of diarylethene **1** was observed at 289 nm, which supported the reversible two component photochromic reaction schemes.²⁰ Likewise, the spectra of diarylethenes **2** and **3** demonstrated similar photochromism trend in hexane. Their color changes upon photoirradiation are shown in Figure 1(B). In the photostationary state, the isosbestic points of diarylethenes **2** and **3** were observed at 290 and 277 nm, respectively. In addition, the photoconversion ratios of the three diarylethenes were analyzed by HPLC in the photostationary state, with the value of 63% for **1**, 78% for **2**, and 64% for **3**, respectively (Table 1). In PMMA films, diarylethenes **1–3** also showed similar photochromic property, but the absorption



Scheme 2. Synthetic route for diarylethenes 10-30.

Table 1	
Absorption spectral properties of diarylethenes 1–3 in hexane	$(2.0\times 10^{-5}\mbox{ mol }L^{-1})$ and in PMMA films (10%, w/w) at rt

Compd	$\lambda_{o,max}/nm^a \ (\epsilon/L \ mol^{-1} \ cm^{-1})$		$\lambda_{c,max}/nm^{b} (\epsilon/L mol^{-1} cm^{-1})$		\varPhi^{c}		PR ^d (%)
	Hexane	PMMA	Hexane	PMMA	Φ_{o-c}	\varPhi_{c-o}	
1	$261~(2.76\times 10^4)$	264	$508~(1.5 imes 10^4)$	524	0.31	0.21	63
2	$264~(3.22 imes 10^4)$	265	$514~(2.1 imes 10^4)$	528	0.55	0.13	78
3	$263~(2.46\times 10^4)$	266	$510~(1.3 imes 10^4)$	528	0.32	0.29	64

^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 (Φ_{o-c}) and cycloreversion (Φ_{c-o}), respectively.

^d Photoconversion ratios of diarylethenes **1–3** (PR%) in the photostationary state.



Figure 2. Fatigue resistance of diarylethenes 1-3 in hexane (A) and in PMMA films (B) in air atmosphere at rt. Initial absorbance of the sample was fixed to 1.0.

maxima of the closed-ring isomers of diarylethenes **1–3** in PMMA films are at longer wavelengths than those in hexane.^{13b,16,21} The red shift values of the absorption maxima of the closed-ring isomers are 16 nm for **1c**, 14 nm for **2c**, and 18 nm for **3c**, respectively. The red shift phenomenon may be attributed to the polar effect of the polymer matrix in solid medium.²²

The photochromic features of diarylethenes 1-3 are summarized in Table 1. The absorption maximum of the unsubstituted parent diarylethene 1 was at the shortest wavelength both in hexane and in a PMMA film. Replacing the hydrogen atom at the meta-position of the terminal benzene ring with either an electron-donating substituent (methoxy, such as in compound 2) or with an electron-withdrawing substituents (trifluoromethyl, such as in compound **3**) resulted in a minor red shift. When substituting with the electron-donating methoxy group in the same diarylethene system, the molar absorption coefficients of the two isomers increased notably, compared with the unsubstituted parent diarylethene 1. However, the replacement with the strong electron-withdrawing trifluoromethyl group decreased significantly the molar absorption coefficients of the two isomers of diarylethene 3. The result is consistent with that of diarylethenes bearing a pyrrole unit.²³

The quantum yields of unsubstituted parent diarylethene **1** were 0.31 for the cyclization reaction and 0.21 for the cycloreversion reaction. The quantum yield in cyclization increased significantly when the electron-donating group was substituted at the *meta*-position of the terminal benzene ring, and the quantum yield in cycloreversion improved notably when the electron-withdrawing group was substituted at the same position, compared with the parent diarylethene **1**. Therefore, diarylethene **2** has the highest cycloreversion quantum yield and the lowest cycloreversion quantum yield and the lowest cycloreversion quantum yield among the three-diarylethene derivatives. The result indicated that the electron-donating substituent could notably enhance the cyclization quantum yield and suppress the cycloreversion quantum yield, but the electron-withdrawing substituents could increase the cycloreversion quantum yield. Our findings are

quite different from those reported on diarylethenes bearing a phenyl moiety, in which the cyclization quantum yield significantly increased with the increase of electron-withdrawing ability, and the cycloreversion quantum yield showed the reverse trend.^{16a} Furthermore, the naphthalene moiety has also a significant effect on the photochromic features of diarylethenes **1–3**. When replacing the naphthalene moiety with a pyridine unit in the same molecular skeleton of diarylethene, the absorption maximum markedly shifted to a longer wavelength and the cycloreversion quantum yield notably decreased.^{16c}

The thermal stabilities of open-ring and closed-ring isomers of diarylethenes **1–3** were tested in ethanol both at rt and at 351 K. We stored these solutions in ethanol at rt in the dark and then exposed them to air for more than 10 days, and no changes have been observed in the UV/Vis spectra of diarylethenes **1–3**. At 351 K, diarylethenes **1–3** still showed excellent thermal stabilities for more than 8 h.

Fatigue resistance is a critical factor for the practical applications in optical devices.^{10a,24} The fatigue resistances of diarylethenes **1–3**



Figure 3. Emission spectra of diarylethenes 1–3 in hexane $(2.0\times 10^{-5}\,mol\;L^{-1})$ at rt when excited at 298 nm.



Figure 4. Emission intensity changes of diarylethenes 1 both in hexane $(2.0 \times 10^{-5} \text{ mol L}^{-1})$ and in PMMA film (10%, w/w) by photoirradiation at rt: (A) in hexane $(\lambda_{ex} = 298 \text{ nm})$, (B) in PMMA films ($\lambda_{ex} = 300 \text{ nm}$).

were examined both in hexane and in PMMA films by alternating irradiating with UV and visible light in air at rt, as shown in Figure 2. In hexane, the coloration and decoloration cycles of diarylethenes **1**–**3** can be repeated at least 100 times with 14% degradation of **1c**, 12% of **2c**, and 8% of **3c**, respectively, which may result from the formation of an epoxide.²⁵ In PMMA films, diarylethenes **1**–**3** exhibited excellent photochromism after 200 cycles with only 28% degradation of **1c**, 21% degradation of **2c**, and 8% of **3c**, respectively. Overall, the fatigue resistance of diarylethene bearing an electron-withdrawing group was much better than that of diarylethene bearing an electron-donating group both in hexane and in PMMA films. The result is in good agreement with that reported for diarylethenes bearing both thiophene and benzene moieties,^{16a} but is completely contrary to that reported for analogs bearing a pyridine moiety.^{16c}

The fluorescence spectra of diarylethenes **10–30** both in hexane $(2.0 \times 10^{-5} \text{ mol } \text{L}^{-1})$ and in PMMA films (10%, w/w) were measured at rt. In hexane, the emission peaks of **10–30** were observed at 420, 415, and 424 nm when excited at 298 nm (Fig. 3), and 428, 425, and 421 nm in PMMA films when excited at 300 nm. Compared to those in hexane, the emission peaks of diarylethenes **10** and **20** show a bathochromic shift in PMMA films, which is well consistent with those of their maxima absorption wavelengths. However, the emission peak of **30** shows a minor hypsochromic shift in PMMA film. Among the three compounds, the emission intensity of **30** is the strongest and that of **10** is the smallest both in hexane solution and in PMMA films. The result suggested that different substituents attached at the meta-position of the benzene ring had a significant effect not only on the emission peak but also on the emission intensity. The fluorescence quantum yields of diarylethenes 10-30 were determined to be 0.011, 0.012, and 0.018, respectively, and anthracene was used as reference. The results demonstrated that the electron-withdrawing substituent could effectively enhance the fluorescence quantum yield of diarylethene bearing a naphthalene unit. This observation is opposite to those of the diarylethenes bearing a biphenyl unit whose fluorescence quantum yields increased with the electron-donating ability.26

Just like most of the diarylethenes,²⁷ the fluorescence of closedring isomers of diarylethenes is inactive. When the pohoisomerization reaction of diarylethens **1–3** occurs, the notable fluorescent switches were observed both in hexane and in PMMA films. Upon irradiation with UV light, the photocylization reaction induced the closed-ring isomers and the emission intensity of diarylethenes **1– 3** decreased gradually. The reverse irradiation by appropriate wavelength visible light regenerated their open-ring isomers and the original emission intensity. During the process of photoisomerization, diarylethene **1** exhibited changes in its fluorescence both in hexane and in a PMMA film as shown in Figure 4. Upon irradiation with UV light, the sample reached the photostationary state, in which its emission intensity was quenched to ca. 43% in hexane and 47% in PMMA film, respectively. As with diarylethene **1**, the diarylethenes **2** and **3** also functioned as a notable fluorescent switch upon photoirradiation both in hexane and in PMMA films. In the photostationary state, their emission intensities were quenched ca. 24% for **2** and 32% for **3** in solution and ca. 39% for **2** and 34% for **3** in PMMA films. The result showed that the fluorescent modulation efficiencies of diarylethenes **1–3** in hexane were higher than those in PMMA film. This result is in stark contrast to the diarylethenes bearing both thiophene and benzene moieties, where the fluorescent modulation efficiencies in hexane were much lower than those in PMMA film.^{16a} The excellent fluorescent modulation efficiency found in diarylethenes **2** and **3** could find promising application in photoswitchable devices, such as optical memory and fluorescent modulation switches.^{27a,28}

In conclusion, three new photochromic diarylethenes based on a condensed aromatic naphthalene skeleton have been explored for the first time and their properties have been investigated. This new photochromic system showed good photochromism, strong fatigue resistance, and obvious fluorescent switch behavior both in hexane solution and in PMMA films. Our results indicate that the substituents at the *meta*-position of the terminal benzene ring had a significant effect on the properties of these diarylethene derivatives. In addition, the condensed aromatics aryl moiety induced dramatic properties differing from other diarylethenes with five and six-membered aryl moieties reported so far. The present work provides a useful design strategy in tuning the photochromic properties of diarylethenes and seeking for their potential applications.

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- 18. Data for **1o**: Calcd for $C_{27}H_{18}F_6S$ (%): calcd C, 66.39; H, 3.71. Found: C, 66.46; H, 3.79; ¹H NMR (400 MHz, CDCl₃, ppm): δ 2.13 (s, 3H, $-CH_3$), 2.30 (s, 3H, $-CH_3$), 6.81 (s, 1H, thiophene-H), 7.20 (d, 2H, benzene-H, J = 8.0 Hz), 7.33 (t, 2H, benzene-H, J = 8.0 Hz), 7.42 (d, 1H, naphthalene-H), 7.42 (m, 3H, naphthalene-H), 7.64 (d, 1H, benzene-H), 7.76 (t, 2H, naphthalene-H, J = 8.0 Hz); ¹³C NMR (100 MHz, CDCl₃, TMS): δ = 14.85, 20.44, 123.38, 123.73, 124.97, 125.37, 125.52, 125.64, 126.96, 127.63, 128.31, 128.55, 128.85, 130.04, 130.47, 131.91, 133.31, 135.54, 140.88, 141.23; IR (KBr, v, cm⁻¹): 690, 756, 774, 815, 871, 891, 984, 1031, 1134, 1191, 1272, 1339, 1445, 1470, 1505, 1554, 1599, 1739, 1944, 2862, 2926, 3062. Data for **20** mp 89–90 °C; calcd for $C_{28}H_{20}F_6OS$ (%): calcd C, 64.86; H, 3.89. Found: C, 64.97; H, 3.95; ¹H NMR (400 MHz, CDCl₃, ppm): δ 2.22

(s, 3H, -CH₃), 2.34 (s, 3H, -CH₃), 3.71 (s, 3H, -CH₃), 6.61 (s, 1H, thiophene-H), 6.74 (d, 1H, benzene-H, J = 8.0 Hz), 6.79 (d, 2H, benzene-H, J = 8.0 Hz), 7.15 (t, 1H, benzene–H, J = 8.0 Hz), 7.33 (d, 1H, naphthalene–H, J = 8.0 Hz), 7.47 (t, 1H, naphthalene–H, *J* = 8.0 Hz), 7.52 (d, 1H, naphthalene–H, *J* = 8.0 Hz), 7.79 (d, 1H, naphthalene–H), 7.81 (m, 2H, naphthalene–H); ¹³C NMR (100 MHz, CDCl₃, TMS): *δ* = 14.91, 20.42, 55.18, 110.48, 113.54, 117.89, 123.66, 125.00, 125.63, 126.99, 128.30, 128.59, 129.87, 130.04, 130.00, 131.67, 133.26, 135.68, 140.96, 141.46; IR (KBr, ν, cm⁻¹): 678, 742, 767, 810, 872, 894, 982, 1046, 1101, 1132, 1190, 1257, 1342, 1437, 1468, 1503, 1582, 1608, 1904, 3300, 3628. Data for **30**: mp 131–132 °C; calcd for C₂₈H₁₇F₉S (%): calcd C, 60.43; H, 3.08. Found: C, 60.51; H, 3.17; ¹H NMR (400 MHz, CDCl₃, ppm): δ 2.25 (s, 3H, –CH₃), 2.35 (s, 3H, -CH₃), 6.84 (s, 1H, thiophene-H), 7.27 (s, 1H, benzene-H), 7.34 (m, 3H, benzene-H, J = 8.0 Hz), 7.50 (m, 3H, naphthalene-H, J = 8.0 Hz), 7.69 (d, 1H, naphthalene–H, J = 8.0 Hz), 7.82 (t, 2H, naphthalene–H, J = 8.0 Hz); ¹³C NMR (100 MHz, CDCl₃, TMS): δ = 14.90, 20.43, 122.03, 123.36, 124.12, 124.70, 124.86, 125.18, 125.74, 125.92, 127.11, 128.41, 128.55, 128.90, 129.36, 130.14, 130.57, 131.22, 131.54, 131.91, 134.06, 135.45, 139.47, 142.00; IR (KBr, v, cm⁻¹): 664, 691, 744, 774, 795, 811, 894, 979, 1049, 1131, 1168, 1195, 1276, 1328, 1443, 1509, 2384, 3300, 3675.

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