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Synthesis and photochromism of novel unsymmetrical diarylethenes with an azaindole unit

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ABSTRACT

A new class of unsymmetrical photochromic diarylethenes with an azaindole moiety has been firstly synthesized. Their properties, including photochromism, crystal structure, as well as fluorescence, were investigated systematically. The azaindole was connected directly to the central cyclopentene ring as a heteroaryl moiety and available to participate in the photoisomerization reaction. Each of the diarylethenes exhibited favorable photochromism, good thermal stability, remarkable fatigue resistance, and notable fluorescence switches in both solution and solid media. The substituents at the *para*-position of the terminal benzene ring affected evidently their properties: the electron-donating methoxy could be effective to enhance the cyclization quantum yield, while the electron-withdrawing cyano could shift the absorption maximum to a longer wavelength in both hexane and solid film. The results revealed that the introduction of azaindole moieties and different substituents played an important role in the photoisomerization process of these diarylethenes.

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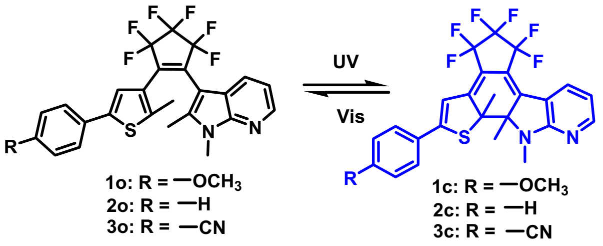
Photochromic compounds have attracted much attention because of their potential applications to photonic devices, such as optical recording and photoswitches.[1] To date, a large amount of photochromic compounds have been explored, including spiropyrans,[2] azobenzenes,[3] fulgides,[4] and diarylethenes.[5] Among all these photochromic compounds, diarylethenes are the best candidates due to their good thermally irreversible stability and remarkable fatigue resistance.[6]

Nowadays, the design of new diarylethene skeletons with different aryl moieties has become an active area of research.[7] Among the diarylethenes hitherto reported, most of the heteroaryl moieties have been thiophene or benzothiophene rings,[8] with just a few reports concerning other heteroaryl moieties, including isoxazole,[9] pyrrole,[10] thiazole,[11] pyrimidine,[12] pyridine,[13] naphthalene,[14] benzofuran,[15] etc. Diarylethenes with indole moiety are well known to exhibit strong fluorescence.[16] However, the indole moiety is rarely used in diarylethenes.[17] The reason is that its bromide can be easily oxidized when exposed to the air and its high aromatic stabilization energy results in low thermal stability of the closed-ring forms.[17b] Azaindole is an attractive aryl unit because of its importance of polyaza tetracyclic compounds as DNA intercalators and possible anticancer agents,[18] wide existence in nature,[19] and its similar structure to that of indole. Consequently, introduction of an azaindole ring into the photochromic diarylethene system can be expected to undergo favorable photochromism with good photochromic properties. However, to the best of our knowledge, photochromic diarylethenes with an azaindole moiety have not hitherto been reported.



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

In this Letter, we explored a new class of diarylethenes with an azaindole moiety (**1o**–**3o**) and systematically investigated their properties. The synthesized compounds are 1-(1,2-dimethyl-7-azaindole-3-yl)-2-[2-methyl-5-(4-methoxyphenyl)-3-thienyl] perfluorocyclopentene (**1o**), 1-(1,2-dimethyl-7-azaindole-3-yl)-2-[2-methyl-5-(4-phenyl)-3-thienyl]perfluorocyclopentene (**2o**), and 1-(1,2-dimethyl-7-azaindole-3-yl)-2-[2-methyl-5-(4-cyanophenyl)-3-thienyl]perfluorocyclopentene (**3o**). All of these diarylethene derivatives exhibit good thermal irreversible photochormism in solution, in PMMA amorphous films, and even in

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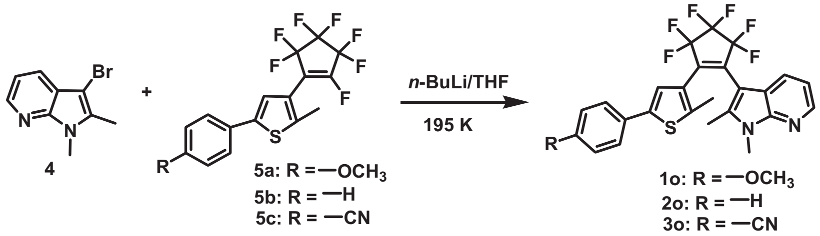

Scheme 2. Synthetic route for diarylethenes **1o**–**3o**.

the single crystalline phase. The photochromic scheme of diarylethenes **1o**–**3o** is illustrated in Scheme 1.

The synthetic route for diarylethenes **1o**–**3o** is shown in Scheme 2. First, 1,2-dimethyl-3-bromine-7-azaindole (**4**) was derived from 7-azaindole by the procedures of acylation, methylation, and bromination.[20] Compounds **5a**–**c** were synthesized by the reported method.[12] Compound **4** was lithiated and then separately coupled with **5a**–**c** to afford the target diarylethenes **1o**–**3o**, respectively. The structures of **1o**–**3o** were confirmed by elemental analysis, NMR, IR, and mass spectrum. The detailed experimental procedures and data are summarized in the Supplementary Information (SI).

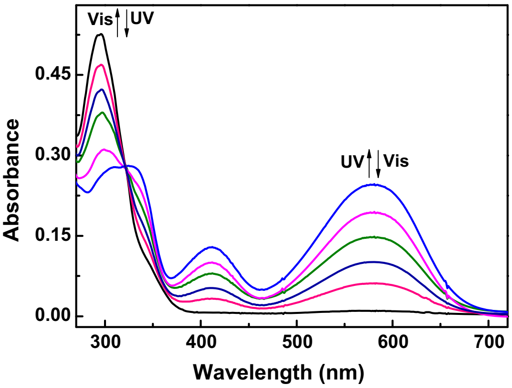

Figure 1. Absorption spectral changes of **1** upon alternating irradiation with UV and visible light in hexane (2.0×10^{-5} mol L^{-1}) at room temperature.

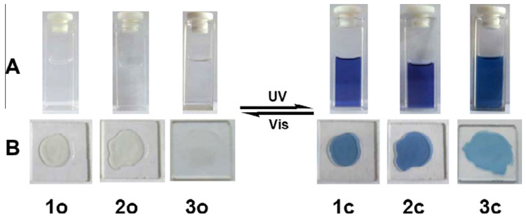

Figure 2. The color changes of diarylethenes **1**–**3** by photoirradiation in both hexane (A) and PMMA amorphous films (B) at room temperature.

Diarylethenes **1o**–**3o** showed excellent 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 appropriate wavelength visible light (Fig. S1). The absorption spectral changes of diarylethene **1** in hexane are shown in Figure 1. The maximum absorption of **1o** was observed at 296 nm (ε, 2.63×10^4 L mol^{-1} cm^{-1}) due to $\pi \rightarrow \pi^*$ transition.[21] Upon irradiation with 297 nm light, a new visible absorption band centered at 581 nm (ε, 1.95×10^4 L mol^{-1} cm^{-1}) emerged and the original peak decreased due to the formation of the closed-ring isomer **1c**. This could be seen with the naked eye, as the colorless solution of **1o** turned blue (Fig. 2). Reversely, the blue solution turned colorless upon irradiation with visible light of appropriate wavelength (λ >450 nm). Diarylethenes **2** and **3** exhibited similar photochromism as observed for **1** in hexane, and their absorption maxima were observed at 579 nm for **2c** and 587 nm for **3c**. Their color changes by photoirradiation are also shown in Figure 2. In the photostationary state, the isosbestic points were observed at 321 nm for **1**, 355 nm for **2**, and 360 nm for **3**, respectively. Moreover, the photoconversion ratios of **1**–**3** were measured by HPLC analysis in the photostationary state, with the value of 74% for **1**, 61% for **2**, and 68% for **3** (Fig. S2). In PMMA films, **1**–**3** also showed similar photochromism as observed in hexane (Fig. S3). Upon irradiation with UV light, the colors of the diarylethene/PMMA films **1**–**3** changed from colorless to blue (Fig. 2), with the appearance of a new broad absorption band centered at 598 nm, 592 nm, and 605 nm, respectively. Upon irradiation with visible light, these colored diarylethene/PMMA films reverted to colorless. Compared to those in hexane, the absorption maxima of the closed-ring isomers **1c**–**3c** in PMMA films are found at longer wavelengths, with the redshift value of 17 nm for **1c**, 13 nm for **2c**, and 18 nm for **3c**. The polar effect of the polymer matrix and the stabilization of molecular arrangement in solid state may be resulted in this redshift phenomenon.[22]

The absorption spectral features of **1**–**3** in both hexane and PMMA films are summarized in Table 1. Among **1**–**3**, the absorption maximum of the unsubstituted parent diarylthene **2** was at

Table 1
Absorption characteristics and photochromic reactivity of diarylethenes **1**–**3** in hexane (2.0×10^{-5} mol L^{-1}) and in PMMA films (10%, w/w)

Compd	$\lambda_{o,max}$/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 film	Hexane	PMMA film	Φ_{o-c}	Φ_{c-o}	
1	296 (2.63×10^4)	296	581 (1.66×10^4)	598	0.45	0.13	74
2	291 (2.42×10^4)	293	579 (1.63×10^4)	592	0.25	0.28	61
3	316 (2.86×10^4)	321	587 (1.53×10^4)	605	0.39	0.15	68

[a] Absorption maxima of open-ring isomers.

[b] Absorption maxima of closed-ring isomers.

[c] Quantum yields of open-ring (Φ_{o-c}) and closed-ring isomers (Φ_{c-o}), respectively.

[d] Photoconversion ratios in the photostationary state.

the shortest wavelength in both solution and a PMMA film. Replacing the hydrogen atom at the *para*-position of the terminal benzene ring with either an electron-donating substituent (methoxy, such as in compound **1**) or with an electron-withdrawing substituents (cyano, such as in compound **3**) resulted in a minor redshift wavelength. Compared with the unsubstituted parent diarylethene **2**, the molar absorption coefficients of diarylethene **1** with a methoxy group increased notably for its open-ring and closed-ring isomers. As shown in Table 1, the cyclization quantum yield increased and the cycloreversion quantum yield decreased significantly when the methoxy or cyano group was substituted at the *para*-position of the terminal benzene moiety. As a result, the unsubstituted parent **2** has the smallest cyclization quantum yields ($\Phi_{\text{o-c},\ 2} = 0.25$) and the largest cycloreversion quantum yields ($\Phi_{\text{c-o},\ 2} = 0.28$). This is in good agreement with that of diarylethenes with a pyridine moiety.[13] In addition, the absorption maxima of the closed-ring isomers **1c**–**3c** were observed at 579–605 nm, which were much longer than those of analogous diarylethenes with a pyridine,[13] benzothiophene,[8a] benzofuran,[15b] or naphthalene moiety.[14] This indicated that the azaindole moiety could be effective to shift the absorption maximum of diarylethene to a longer wavelength.

Single crystals of **1o**–**3o** were obtained via slow evaporation of their solutions and subjected to X-ray diffraction analysis. Their ORTEP drawings and photochromic processes in the crystalline phase are shown in Figure 3. The three azaindole-containing diarylethenes crystallized with photoactive *anti*-parallel conformations in crystalline phase, and the distances between the two reactive carbons were shorter than 4.2 Å (3.755 Å for **1o** (C7…C13), 4.059 Å for **2o** (C8…C16), and 3.682 Å for **3o** (C11…C19)) (Tables S1 and S2). As expected, the crystals of **1o**–**3o** exhibited a notable photochromism upon irradiation with UV and visible light.[23] In fact, the three crystals showed favorable photochromism in accordance with the expected analysis in the crystalline phase. The colorless crystals of **1o**–**3o** turned blue quickly upon irradiation with 365 nm light. When the colored crystals were dissolved in hexane, intense absorption maxima were observed at the same wavelength as those of their respective closed-ring isomers in solution. In contrast, exposure to visible light entirely bleached the colors of **1c**–**3c**. The result is consistent with that of the pyridine-containing diarylethenes,[13] but is contrary to that of benzene-containing diarylethenes.[24]

The thermal stability and fatigue resistance of diarylethene are crucial factors for practical applications in optical devices,[25] and they are mainly dependent on the aromatic stabilization energy of the aryl group.[10b] Thus, we examined the thermal stability of the closed-ring isomers **1**–**3** in ethanol at room temperature and 351 K. Storing these solutions in the dark and then exposing them to air for more than 30 days, we did not observe decoloration of these diarylethenes. At 351 K, diarylethenes **1**–**3** still showed excellent thermal stability for more than 15 days. The result suggested that these diarylethene derivatives had very excellent thermally irreversible photochromic behaviors. The fatigue resistances of **1**–**3** were measured 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 Figure 4. In hexane, the coloration and decoloration cycles of **1**–**3** could be repeated 100 cycles with only 7% degradation of **1c**, 10% degradation of **2c**, and 12% degradation of **3c**. The degradation may be ascribed to the formation of epoxide.[26] In PMMA films, they could be repeated 200 cycles with only 11% degradation of **1c**, 5% degradation of **2c**, and 9% degradation of **3c**. This improvement may be resulted from suppression of O_2 diffusion in solid medium.[17c] Compared to diarylethenes with an indole moiety,[17d] the fatigue resistance of diarylethenes with an azaindole moiety was enhanced remarkably in both solution and PMMA films, indicating that the azaindole moiety could effectively enhance the fatigue resistance of diarylethenes.

The fluorescence modulation is widely applied to molecular-scale optoelectronics, ion-sensors, and digital photoswitches.[27] The fluorescence spectra of **1o**–**3o** were measured in both hexane (2.0×10^{-5} mol L^{-1}) and PMMA films (10%, w/w) at room temperature. As shown in Figure 5, the emission peaks of **1o**–**3o** in hexane were observed at 437 nm for **1o** (λ_{ex}, 289 nm), 428 nm for **2o** (λ_{ex}, 290 nm), 431 nm for **3o** (λ_{ex}, 328 nm), and were observed at 452 nm for **1o** (λ_{ex}, 342 nm), 445 nm for **2o** (λ_{ex}, 340 nm), and 443 nm for **3o** (λ_{ex}, 351 nm) in PMMA films. The result revealed that the emission peaks in PMMA films were much longer than those in hexane, and the redshift values were 15 nm for **1**, 17 nm for **2**, and 12 nm for **3**. Compared to the unsubstituted parent **2**, both the electron-donating methoxy group and the electron-withdrawing cyano group decreased remarkably the emission intensity in both solution and PMMA films. The results indicated that different substituents attached at the terminal of benzene ring

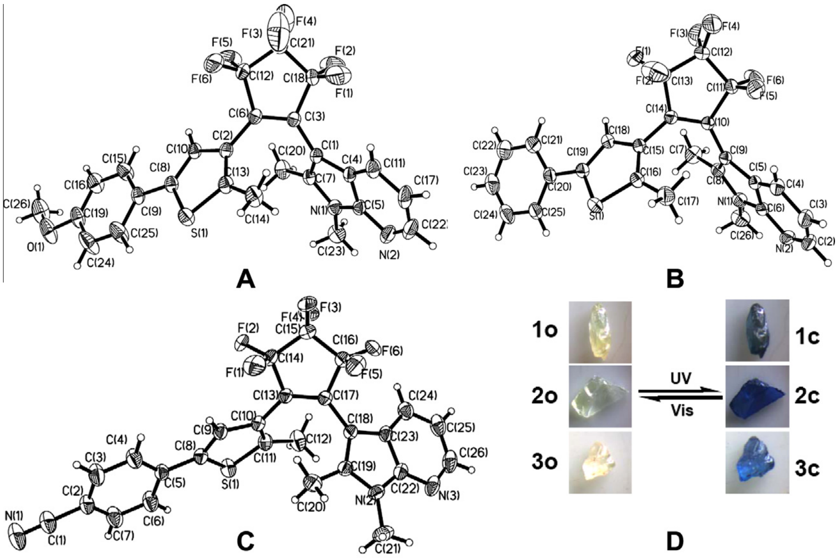

Figure 3. ORTEP drawings of crystals and color changes of **1o**, **2o**, and **3o**: (A) **1o**, (B) **2o**, (C) **3o**, (D) photographs demonstrating their photochromic processes in the crystalline phase.

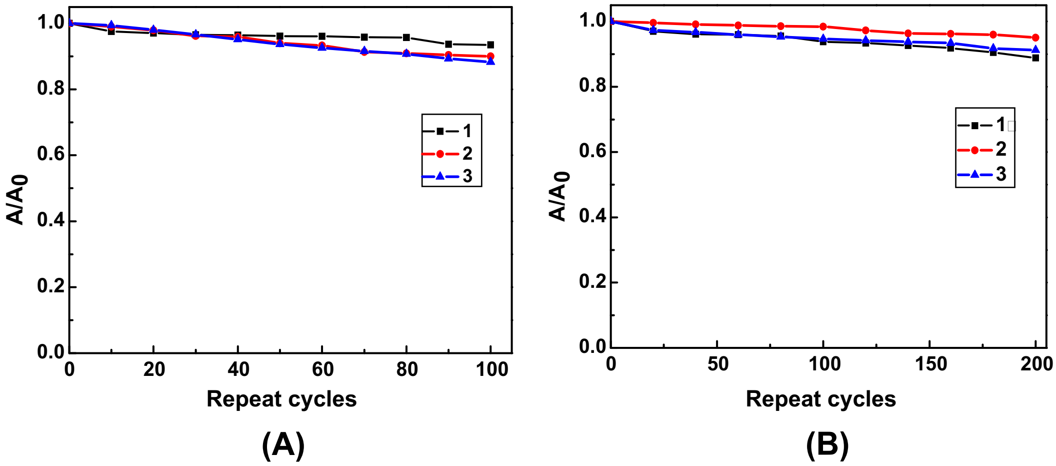

Figure 4. Fatigue resistance of diarylethenes **1**–**3** in hexane (A) and in PMMA films (B) in air atmosphere at room temperature. Initial absorptance of the sample was fixed to 1.0.

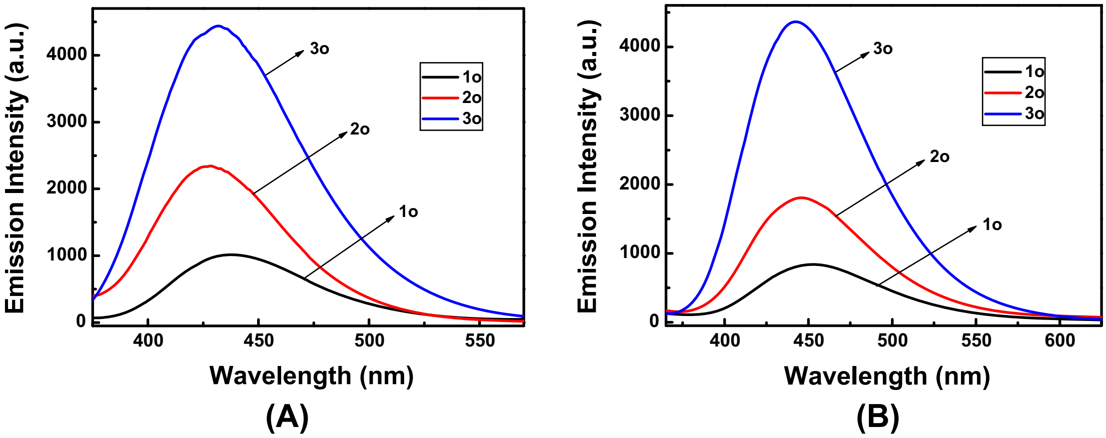

Figure 5. Emission spectra of diarylethenes **1**–**3** at room temperature: (A) in hexane (2.0×10^{-5} mol L^{-1}), (B) in PMMA films (10%, w/w).

had a significant effect not only on the emission peak but also on the emission intensity.

As has been observed for most of the reported diarylethenes,[28] **1**–**3** exhibited notable fluorescent switches by photoirradiation in both hexane and PMMA films (Figs. S5 and S6). Figure 6 shows the fluorescence spectral changes of **1** by photoirradiation in hexane and a PMMA film (10%, w/w) at room temperature. Upon irradiation with 297 nm UV light, the fluorescence modulation efficiency of **1** was 76% in hexane and 88% in a PMMA film when arrived at the photostationary state. Similarly, the fluorescence modulation efficiency of the other two diarylethenes was 72% for **2** and 70% for **3**, and was 94% for **2** and 96% for **3** in PMMA films

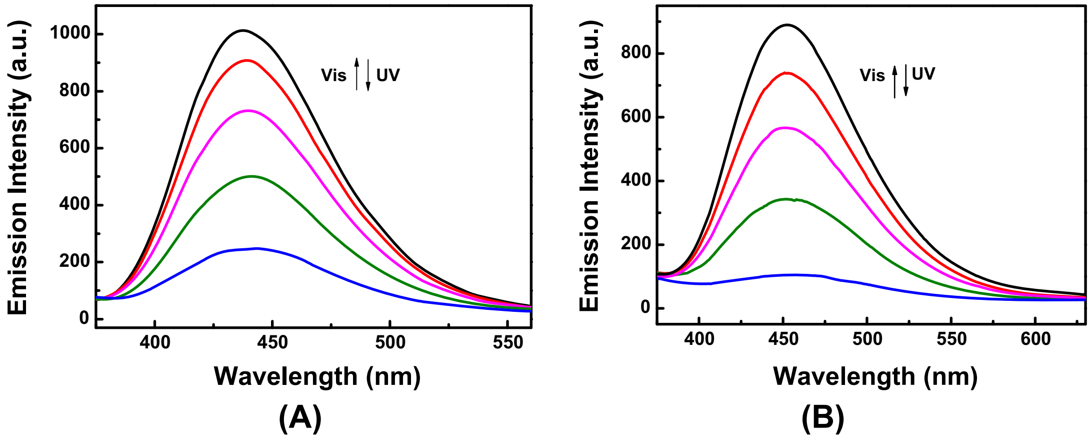

Figure 6. Emission intensity changes of **1** by photoirradiation at room temperature: (A) in hexane (2.0×10^{-5} mol L^{-1}), excited at 289 nm, (B) in PMMA films (10%, w/w), excited at 342 nm.

in the photostationary state. The result indicated that the fluorescence modulation efficiency of **1**–**3** in PMMA films was much larger than that in hexane. The result is in good agreement with that of diarylethenes with an isoxazole, naphthalene, or pyridine moiety.[9a,13,14b] Compared to the pyridine/naphthalene-containing diarylethenes with the similar molecular skeleton,[13,14b] the fluorescent modulation efficiency of **1**–**3** enhanced notably during the process of photoisomerization. Therefore, these diarylethenes can be potentially used for optical memories with fluorescence readout method or fluorescent photoswitches.[29]

In summary, three new unsymmetrical diarylethenes based on the hybrid of azaindole and thiophene moieties were synthesized and their structures were determined by single-crystal X-ray diffraction analysis. All these diarylethenes exhibited favorable photochromism and functioned as notable fluorescence photoswitches in solution, PMMA films, and even in the crystalline phase. The behaviors of the three azaindole-containing diarylethenes were significantly different from each other, which might be attributed to the effects of different substituents in the terminal phenyl group. The results of this study may be useful for a new strategy in developing photoactive diarylethenes based on azaindole and other aryl units.

Acknowledgments

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2014.03.004.

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