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Photochromism of new unsymmetrical diarylethenes based on the hybrid of azaindole and thiophene moieties



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ABSTRACT

A new class of photochromic diarylethenes with both azaindole and thiophene moieties were synthesized to investigate the effects of the substituents on their photochromic behaviors, and their structures were determined by single crystal X-ray diffraction analysis. The azaindole moiety was connected directly to the central cyclopentene ring as a heteroaryl moiety to participate the photoisomerization reaction in solution, solid amorphous films, and the single crystalline phase. Each of the diarylethenes exhibited remarkable fluorescent photo-switches in both solution and solid media. The electrondonating substituents significantly enhanced their cyclization quantum yields, while the electronwithdrawing groups greatly increased the molar absorption coefficient of their closed-ring isomers. Cyclic voltammetry studies indicated that the band-gaps of diarylethenes with an azaindole notably increased when going from electron-donating substituents to electronwithdrawing substituents. The results revealed that the azaindole moiety and substituents played a vital role in the process of photoisomerization reactions for these diarylethenes.

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1. Introduction

Photochromic compounds can experience a reversible photoisomerization reaction between their two isomers with distinguishable absorption spectra upon irradiation with light of appropriate wavelength [1-3]. Among all the reported photochromic compounds, diarylethenes with different heterocyclic aryl rings are the most promising candidates for practical applications to rewritable optical memories and photoswitches due to their excellent photochromic features, such as remarkable fatigue resistance, good thermal stability of both two isomers, high sensitivity, as well as rapid response [3-6].

Among the diarylethenes hitherto reported, most of the heteroaryl moieties have been thiophene or benzothiophene rings [3,7,8], with just a few reports concerning other heteroaryl moieties, including benzofuran [9], isoxazole [10,11], pyrrole [12], thiazole [13], pyrimidine [14], pyridine [15], naphthalene [16]. These different heteroaryl moieties have a vital role to play in modulating the photochromic properties of diarylethenes during the processes of photoisomerization. The reported diarylethenes with indole moieties are well known to exhibit strong fluorescence [17,18]. However, the indole moiety is rarely used in photochromic diarylethene systems because 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 [19–22]. Recently, azaindoles have been caused growing interest of the scientific community and pharmaceuticals firms [23,24]. Specially, 7-azaindole is considered as a bioisostere of indole or purine moiety, and it is found to be integral part of many bioactive molecules [25]. Therefore, the azaindole derivatives have been widely used as anthelmintic agents, optical probes for protein structure and dynamics, as well as coordination reagents [26-30]. Introduction of an azaindole ring into the photochromic diarylethene system can be expected to undergo favorable photochromism with special characteristics. However, to the best of our knowledge, the azaindole-containing diarylethene derivatives have not hitherto been reported.

In this work, a new class of diarylethenes with an azaindole moiety were synthesized and their structures and properties were systematically investigated. The synthesized compounds are 1-(1,2-dimethyl-7-azaindole-3-yl)-2-[2-methyl-5-(4-trifluorophenyl)-3-thienyl]perfluorocyclopentene (**10**), 1-(1,2-dimethyl-7-azaindole-3-yl)-2-[2-methyl-5-(4-fluorophenyl)-3-thienyl]perfluorocyclopentene (**20**), 1-(1,2-dimethyl-7-azaindole-3-yl)-2-(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene (**30**), 1-(1,2-dimethyl-7-azaindole-3-yl)-2-[2-methyl-5-(4-methylphenyl)-3-thienyl]perfluorocyclopentene







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(**4o**), and 1-(1,2-dimethyl-7-azaindole-3-yl)-2-[2-methyl-5-(4-methoxyphenyl)-3-thienyl]perfluorocyclopentene (**5o**). All of these diarylethene derivatives exhibit good thermal irreversible photochromism in solution, in PMMA amorphous films, and even in the single crystalline phase. The photochromic scheme of the diarylethenes **1–5** is shown in Fig. 1.

2. Experimental

2.1. General

All solvents were spectroscopic grade and were purified by distillation before use. NMR spectra were recorded on a Bruker AV400 (400 MHz) spectrometer with CDCl₃ as the solvent and tetramethylsilane as an internal standard. Infrared spectra (IR) were recorded on a Bruker Vertex-70 spectrometer. Melting point was measured on a WRS-1B melting point apparatus. Absorption spectra were measured using an Agilent 8453 UV/VIS spectrophotometer. Photoirradiation was carried out using an SHG-200 UV lamp, a CX-21 ultraviolet fluorescence analysis cabinet, and a BMH-250 visible lamp. The required wavelength was isolated by the use of appropriate filters. Fluorescence spectra were measured using a Hitachi F-4600 spectrophotometer. Electrochemical examinations were performed in a one-compartment cell by using a Model 263 potentiostat-galvanostat (EG&G Princeton Applied Research) under computer control at room temperature. Platinum-electrodes (diameter 0.5 mm) served as working electrode and counter electrode. The PMMA films of **10–50** were prepared by dissolving 5.00 mg of diarylethene sample and 50.00 mg of PMMA in 0.5 mL chloroform, and the homogeneous solution was spin-coated on a quartz substrate $(20 \times 20 \times 1 \text{ mm}^3)$ at a rotating speed of 1500 rpm.

Suitable crystals of **10–50** were obtained by slow evaporation of ethyl acetate mixed with petroleum ether solutions of the five diarylethenes. All the measurements were collected by a Bruker SMART APEX II CCD diffractometer using a MULTI scan technique at room temperature using M_0 K_{α} radiation. The structures were solved by direct methods and refined by full-matrix least-squares procedures on F^2 by full-matrix least-squares techniques using SHELXTL-97 program. Further details on the crystal structure investigation have been deposited with The Cambridge Crystallographic Data Center as supplementary publication CCDC 963071 for **10**, 963070 for **20**, 963067 for **30**, 963068 for **40**, and 963072 for **50**. 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

The synthesis route for diarylethenes **1o**–**5o** is shown in Fig. 2. First, 1,2-dimethyl-3-bromine-7-azaindole (**9**) was derived from 7-azaindole by the procedures of acylation, methylation, and bromination [25]. Compounds **10a**–**e** were synthesized according to the reported method [13]. Finally, the compound **9** was lithiated and then separately mixed with **10a**–**e** afforded the target diarylethenes **1o**–**5o**, respectively. The structures of **1o**–**5o** were confirmed by NMR, IR, mass spectrum, elemental analysis, and single-crystal X-ray diffraction analysis.

2.2.1. 1-Phenylsulfonyl-7-azaindole (6)

Sodium hydroxide (1.25 g) was added to a solution of CH₂Cl₂ containing benzyltriethylammonium chloride (0.07 g, 0.3 mmol) and 7-azaindole (1.18 g, 10.0 mmol). The mixtures reacted 10 min at the 273 K, and then benzenesulfonyl chloride (2.21 g, 12.5 mmol) was slowly added to the solution. After the addition, the solution was stirred for 20 min and then warmed to the room temperature. After 12 h, the suspension was extracted with dichloromethane and the organic layer was collected and washed with NaCl solution and then water. The organic layer was dried over MgSO₄, filtrated, and evaporated. The crude product was purified by column chromatography on silica gel using dichloromethane as eluent to give 6 (2.32 g) as a colorless solid in 90% yield. Mp: 402–403 K. ¹H NMR (400 MHz, CDCl₃): δ 6.51 (d, 1H, J = 4.0 Hz, azaindolyl-H), 7.06–7.10 (m, 1H, azaindolyl-H), 7.38 (t, 2H, *J* = 8.0 Hz, phenyl-H), 7.47 (t, 1H, *I* = 7.2 Hz, phenyl-H), 7.64 (d, 1H, *I* = 4.0 Hz, azaindolyl-H), 7.75 (d, 1H, *J* = 4.0 Hz, azaindolyl-H), 8.10 (s, 1H, phenyl-H), 8.11 (s, 1H, phenyl-H), 8.34 (d, 1H, *J* = 4.8 Hz, azaindolyl-H).

2.2.2. 1-Phenylsulfonyl-2-methyl-7-azaindole (7)

1-Phenylsulfonyl-7-azaindole **6** (2.58 g, 10.0 mmol) in anhydrous THF was added dropwise to a 2.0 mol L^{-1} LDA in hexane/THF solution (10.0 mL) at 248 K under an argon atmosphere. Stirring was continued for 0.5 h. Excess iodomethane (3.0 mL) was added. After 6 h, the mixture was warmed to room temperature and reacted 4 h. The mixture was extracted with dichloromethane and the organic layer was collected washing with NaCl solution and then water. The organic layer was dried over MgSO₄, filtrated, and evaporated. The crude product was purified by column



Fig. 1. Photochromism of diarylethenes 1-5.



Fig. 2. Synthetic route for diarylethenes 10-50.

chromatography on silica gel using petroleum ether: ethyl acetate (3:1) as eluent to give **7** (2.54 g) as a colorless solid in 93% yield. Mp: 369–370 K. ¹H NMR (400 MHz, CDCl₃): δ 2.73 (s, 3H, –CH₃), 6.28 (s, 1H, azaindolyl-H), 7.10–7.13 (m, 1H, azaindolyl-H), 7.46 (t, 2H, *J* = 8.0 Hz, phenyl-H), 7.54 (t, 1H, *J* = 7.6 Hz, phenyl-H), 7.68 (d, 1H, *J* = 7.6 Hz, azaindolyl-H), 8.14 (d, 2H, *J* = 7.2 Hz, phenyl-H), 8.35 (d, 1H, *J* = 4.0 Hz, azaindolyl-H).

2.2.3. 1-Phenylsulfonyl-2-methyl-3-bromo-7-azaindole (8)

At the room temperature, NBS (2.14 g, 12.0 mmol) was slowly added to a stirring solution of CCl₄ containing 1-phenylsulfonyl-2-methyl-7-azaindole **7** (2.72 g, 10.0 mmol). After 12 h, quenched with saturated Na₂S₂O₈ and extracted with dichloromethane. The organic layer was collected washing with NaCl solution and then water. The organic layer was dried over MgSO₄, filtrated, and evaporated. The crude product was purified by column chromatography on silica gel using petroleum ether: ethyl acetate (5:1) as eluent to give **8** (2.90 g) as a colorless solid in 83% yield. Mp: 389–390 K. ¹H NMR (400 MHz, CDCl₃): δ 2.77 (s, 3H, –CH₃), 7.21–7.24 (m, 1H, azaindolyl-H), 7.48 (t, 2H, *J* = 8.0 Hz, phenyl-H), 7.58 (t, 1H, *J* = 7.6 Hz, phenyl-H), 8.42 (d, 1H, *J* = 4.4 Hz, azaindolyl-H).

2.2.4. 1,2-Dimethyl-3-bromo-7-azaindole (9)

At 273 K, NaH (8.70 g) was added to a stirring solution of DMF containing 1-phenylsulfonyl-2-methyl-3-bromo-7-azaindole **8** (2.14 g, 12.0 mmol). After reaction 30 min, iodomethane (1.5 mL) was added dropwisely. And then the product was quenched with water after reacted 24 h. The organic layer was extracted with dichloromethane and washed with plenty of water. The organic layer was dried over MgSO₄, filtrated, and evaporated. The crude product was purified by column chromatography on silica gel using petroleum ether: ethyl acetate (5:1) as eluent to give **9** (0.38 g) as a faint yellow liquid in 34% yield. ¹H NMR (400 MHz, CDCl₃): δ 2.46 (s, 3H, -CH₃), 3.81 (s, 3H, -NCH₃), 7.09–7.10 (m, 1H, azaindolyl-H), 7.75 (d, 1H, *J* = 7.6 Hz, azaindolyl-H), 8.27 (d, 1H, *J* = 7.6 Hz, azaindolyl-H).

2.2.5. 1-(1,2-Dimethyl-7-azaindol-3-yl)-2-[2-methyl-5-(4-trifluoromethylphenyl)-3-thienyl] perfluorocyclopentene (10)

Raw material 1,2-dimethyl-3-bromo-7-azaindole 9 (0.45 g, 2.0 mmol) in anhydrous THF was added to a 2.4 mol L^{-1} *n*-BuLi in hexane solution (1.0 mL, 2.4 mmol) at 195 K under an argon atmosphere. Stirring was continued for 0.5 h and 10a (1.13 g, 2.6 mmol) was slowly added to the reaction mixture at 195 K and stirred for 2 h at this temperature. The reaction was quenched with water. The mixture was warmed to room temperature and extracted with CH₂Cl₂. The organic layer was dried over MgSO₄, filtrated, and evaporated. The crude product was purified by column chromatography on SiO₂ using petroleum ether: ethyl acetate (5:1) as eluent to give **10** (0.23 g, 21%) as a yellowish solid. Mp: 457-458 K; Calcd for C₂₆H₁₇F₉N₂S (%): Calcd C, 55.72; H, 3.06; N, 5.00. Found C, 55.73; H, 3.01; N, 5.04; ¹H NMR (400 MHz, CDCl₃): δ 1.79 (s, 3H, -CH₃), 2.06 (s, 3H, -CH₃), 3.77 (s, 3H, -NCH₃), 7.08-7.11 (m, 1H, azaindolyl-H), 7.42 (s, 1H, thienyl-H), 7.63 (s, 4H, phenyl-H), 7.87 (d, 1H, J = 8.0 Hz, azaindolyl-H), 8.31 (d, 1H, I = 4.4 Hz, azaindolyl-H).¹³C NMR (100 MHz, CDCl₃, ppm): δ 11.60, 14.64, 28.50, 99.14, 117.21, 118.34, 124.11, 125.36, 125.62, 125.98, 126.02, 126.84, 127.43, 129.82, 136.73, 138.92, 140.19, 142.12, 143.05, 148.10. MS *m*/*z* (M⁺): 561.1; IR (KBr, *ν*, cm⁻¹): 732, 774, 794, 816, 832, 850, 891, 976, 993, 1014, 1045, 1067, 1111, 1189, 1263, 1325, 1427, 1466, 1532, 1616, 2930.

2.2.6. 1-(1,2-Dimethyl-7-azaindol-3-yl)-2-[2-methyl-5-(4-fluorophenyl)-3-thienyl] perfluorocyclopentene (**20**)

Diarylethene **20** was prepared by an analogous method to that used for compound **10** using **10b** instead of **10a**. The crude product was purified by column chromatography on SiO₂ using petroleum ether: ethyl acetate (5:1) as eluent to give **20** (0.23 g, 23%) as a yellowish solid. Mp: 441–442 K; Calcd for C₂₅H₁₇F₇N₂S (%): Calcd C, 58.82; H, 3.36; N, 5.49. Found C, 58.84; H, 3.35; N, 5.51; ¹H NMR (400 MHz, CDCl₃): δ 1.72 (s, 3H, –CH₃), 2.09 (s, 3H, –CH₃), 3.71 (s, 3H, –NCH₃), 7.10–7.14 (m, 1H, azaindolyl-H), 7.21–7.26 (m, 2H, phenyl-H), 7.54 (s, 1H, thienyl-H), 7.63–7.67 (m, 2H, phenyl-H), 7.79 (d, 1H, *J* = 7.6 Hz, azaindolyl-H), 8.26 (d, 1H, *J* = 3.6 Hz, azaindolyl-H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 11.59, 14.54, 28.48, 99.21,

115.83, 116.05, 117.15, 118.38, 122.59, 126.45, 127.30, 129.68, 138.94, 140.64, 140.89, 142.93, 148.04. MS m/z (M⁺): 511.1; IR (KBr, ν , cm⁻¹): 775, 794, 810, 830, 852, 890, 975, 995, 1047, 1077, 1124, 1158, 1192, 1234, 1271, 1303, 1335, 1429, 1469, 1511, 2926.

2.2.7. 1-(1,2-Dimethyl-7-azaindol-3-yl)-2-[2-methyl-5-phenyl-3-thienyl]perfluorocyclopentene (**30**)

Diarylethene **30** was prepared by an analogous method to that used for compound **10** using **10c** instead of **10a**. The crude product was purified by column chromatography on SiO₂ using petroleum ether: ethyl acetate (5:1) as eluent to give **30** (0.26 g, 26%) as a yellowish solid. Mp: 413-414 K; Calcd for C₂₅H₁₈F₆N₂S (%): Calcd C, 50.97; H, 3.68; N, 5.69. Found C, 50.99; H, 3.65; N, 5.71; ¹H NMR (400 MHz, CDCl₃): δ 1.76 (s, 3H, -CH₃), 2.05 (s, 3H, -CH₃), 3.76 (s, 3H, -NCH₃), 7.07-7.10 (m, 1H, azaindolyl-H), 7.30 (d, 1H, *J* = 7.6 Hz, phenyl-H), 7.33 (s, 1H, thienyl-H), 7.38 (t, 2H, *J* = 8.0 Hz, phenyl-H), 7.53 (d, 2H, I = 8.0 Hz, phenyl-H), 7.89 (d, 1H, I = 8.0 Hz, azaindolyl-H), 8.30 (d, 1H, J = 4.4 Hz, azaindolyl-H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 11.60, 14.59, 28.49, 99.25, 117.15, 118.41, 122.63, 125.56, 126.43, 127.49, 127.83, 128.99, 133.43, 138.98, 140.67, 142.01, 142.93, 148.08. MS *m*/*z* (M⁺): 493.1; IR (KBr, *v*, cm⁻¹): 691, 734, 752, 776, 796, 817, 852, 891, 975, 994, 1047, 1078, 1124, 1192, 1272, 1301, 1336, 1429, 1467, 1597, 2919.

2.2.8. 1-(1,2-Dimethyl-7-azaindol-3-yl)-2-[2-methyl-5-(4-methylphenyl)-3-thienyl] perfluorocyclopentene (**40**)

Diarylethene **40** was prepared by an analogous method to that used for compound 10 using 10d instead of 10a. The crude product was purified by column chromatography on SiO₂ using petroleum ether: ethyl acetate (5:1) as eluent to give **40** (0.22 g, 22%) as a vellowish solid. Mp: 475–476 K; Calcd for C₂₆H₂₀F₆N₂S (%): Calcd C, 61.65; H, 3.98; N, 5.53. Found C, 61.68; H, 3.94; N, 5.57; ¹H NMR (400 MHz, CDCl₃): δ 1.75 (s, 3H, -CH₃), 2.05 (s, 3H, -CH₃), 2.36 (s, 3H, -CH₃), 3.76 (s, 3H, -NCH₃), 7.07-7.10 (m, 1H, azaindolyl-H), 7.18 (d, 2H, *I* = 8.0 Hz, phenyl-H), 7.28 (s, 1H, thienyl-H), 7.42 (d, 2H, *J* = 8.0 Hz, phenyl-H), 7.89 (d, 1H, *J* = 8.0 Hz, azaindolyl-H), 8.30 (d, 1H, J = 4.4 Hz, azaindolyl-H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 11.61, 14.56, 21.15, 28.49, 117.13, 118.42, 122.08, 125.47, 126.32, 127.49, 129.64, 130.67, 137.81, 138.97, 140.12, 142.13, 142.91, 148.07. MS *m*/*z* (M⁺): 507.1; IR (KBr, *v*, cm⁻¹): 734, 776, 796, 811, 852, 892, 975, 995, 1046, 1123, 1193, 1271, 1302, 1334, 1429, 1467, 1540, 1573, 1648, 2920.

2.2.9. 1-(1,2-Dimethyl-7-azaindol-3-yl)-2-[2-methyl-5-(4-methoxyphenyl)-3-thienyl] perfluorocyclopentene (**50**)

Diarylethene **50** was prepared by an analogous method to that used for compound 10 using 10e instead of 10a. The crude product was purified by column chromatography on silica gel using petroleum ether: ethyl acetate (5:1) as the eluent resulting in 0.27 g of **50** being obtained in 26% yield as a pink solid. Mp: 462–463 K: Calcd for C26H20F6N2OS (%): Calcd C. 59.77: H. 3.86: N. 5.36. Found C, 59.82; H, 3.84; N, 5.38; ¹H NMR (400 MHz, CDCl₃): δ 1.73 (s, 3H, -CH₃), 2.05 (s, 3H, -CH₃), 3.76 (s, 3H, -NCH₃), 3.82 (s, 3H, -OCH₃), 6.90 (d, 2H, *J* = 8.8 Hz, phenyl-H), 7.07–7.10 (m, 1H, azaindolyl-H), 7.21 (s, 1H, thienyl-H), 7.45 (d, 2H, *J* = 8.4 Hz, phenyl-H), 7.89 (d, 1H, J = 8.0 Hz, azaindolyl-H), 8.30 (d, 1H, J = 4.8 Hz, azaindolyl-H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 11.59, 14.52, 28.48, 55.38, 99.29, 114.40, 116.41, 116.61, 117.13, 118.44, 121.50, 126.29, 126.86, 127.49, 135.30, 139.00, 139.68, 141.93, 142.90, 148.08, 159.49. MS m/z (M⁺): 523.1; IR (KBr, v, cm⁻¹): 775, 794, 814, 852, 896, 974, 996, 1041, 1077, 1108, 1176, 1194, 1250, 1270, 1334, 1430, 1470, 1513, 1536, 1610, 2915.

3. Results and discussion

3.1. Photochromism in solution and PMMA films

Diarylethenes **10–50** could be toggled between the colorless open-ring isomers (10-50) and the colored closed-ring isomers (1c-5c) in both solution and solid media. The photochromic behaviors of diarylethenes 1-5 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 changes of 1 and color changes of 1–5 by alternating irradiation with UV and visible light in hexane are shown in Fig. 3. In hexane, the maximum absorption of diarylethene **10** was observed at 296 nm (ε , 2.64 × 10⁴ L mol⁻¹ cm⁻¹) due to $\pi \to \pi^*$ transition [31]. Upon irradiation with 297 nm light, a new absorption band observed at 584 nm (ϵ , 1.74 × 10⁴ L mol⁻¹ cm⁻¹) due to the formation of the closed-ring isomer 1c, accompanied with an evident color change from colorless to blue. Reversely, the blue colored solution was entirely bleached upon irradiation with visible light ($\lambda > 450$ nm), indicating that 1c returned to the initial state 1o. Diarylethenes 2-5 also exhibited analogous photochromism as observed for 1 in hexane. Upon irradiation with 297 nm UV light, the solution changed from colorless to blue and new visible absorption bands



Fig. 3. Absorption spectra changes of diarylethene 1 and color changes of 1-5 by photoirradiation in hexane (2.0×10^{-5} mol L^{-1}) at room temperature: (A) absorption spectral changes of 1 and (B) color changes of 1-5. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 4. The photoconversion ratios of $1\!-\!5$ in the photostationary state by HPLC analysis.

centered at 581, 579, 579, and 581 nm emerged, respectively. In the photostationary state, the isosbestic points of **1–5** were observed at 360, 356, 355, 358, and 321 nm, respectively. This indicates that there exists only a two-component photochromic reaction between the open-ring and the closed-ring isomers of these diarylethene derivatives. The photoconversion ratios of **1–5** from open-ring to closed-ring isomers in hexane were measured by HPLC analysis, with the value of 62% for **1**, 51% for **2**, 61% for **3**, 67% for **4**, and 74% for **5** (Fig. 4).

In PMMA films, **1–5** also showed similar photochromism as observed in hexane, and the absorption spectral changes of **1** and color changes of **1–5** are shown in Fig. 5. Upon irradiation with UV light, the colors of diarylethene-containing films **1–5** changed from colorless to blue, and the new absorption bands were observed at 600 nm for **1c**, 593 nm for **2c**, 592 nm for **3c**, 595 nm for **4c**, and 598 nm for **5c**. Compared to those in hexane, the absorption maxima of the closed-ring isomers **1c–5c** in PMMA films are at longer wavelengths, with the redshift value of 16 nm for **1c**, 12 nm for **2c**, 13 nm for **3c**, 16 nm for **4c**, and 17 nm for **5c**. The polar effect of the polymer matrix and the stabilization of molecular

arrangement in solid state may be resulted in this redshift phenomenon [32].

The absorption spectral features of these compounds in both hexane and PMMA films are summarized in Table 1. The results showed that the azaindole moiety and the different substituents linked at the *para*-position of the terminal benzene ring had a significant effect on the photochromic features of diarylethenes 1–5. For both the open-ring and the closed-ring isomers of diarylethenes 1–5, the absorption maxima only changed slightly in both hexane and PMMA films when different substituents were linked at the para-position of the terminal benzene ring. However, their molar absorption coefficients, quantum yields of cyclization and cycloreversion, and photoconversion ratios changed notably when different substituents were introduced into the para-position of the terminal benzene ring. The absorption maxima of the closed-ring isomers **1c–5c** were observed at 579–600 nm, which were much longer than those of analogous diarylethenes with a pyridine [15], benzothiophene [10], or benzofuran [33]. The results revealed that the azaindole moiety could be effective to shift the absorption maxima of these diarylethenes to a longer wavelength. Compared to diarylethenes with an electron-withdrawing group (trifluoromethyl or fluoro group, such as in compound **1** or **2**), the molar absorption coefficients of the closed-ring isomers of diarylethenes with an electron-donating group (methyl or methoxy group, such as in compound **4** or **5**) decreased evidently, but their photoconversion ratios in the photostationary state increased remarkably. As shown in Table 1, the cyclization quantum yields of diarylethenes with an electron-donating group are much bigger than those of diarylethenes with an electron-withdrawing group. Compared with the unsubstituted parent diarylethene 3, the cyclization guantum yields of diarylethenes with a functional group (such as in compounds 1, 2, 4, and 5) enhanced, and their cycloreversion quantum yields decreased evidently. As a result, diarylethene 3 has the smallest cyclization quantum yields ($\Phi_{\text{o-c, 3}} = 0.25$) and the biggest cycloreversion quantum yields ($\Phi_{ ext{c-o, 3}} = 0.28$) among the five derivatives. Compared to the analogous diarylethenes with an isoxazole [10], pyrrole [34], or benzofuran moiety [33], the cycloreversion quantum yields of diarylethenes with an azaindole moiety increased significantly. However, the cyclization quantum yields of diarylethenes with an azaindole moiety are much higher than those of diarylethenes with a naphthalene moiety [35]. The results suggested that the azaindole moiety could significantly influence the photochromic reactivity of these diarylethene derivatives.

The thermal stability of the open-ring and the closed-ring isomers of **1–5** was tested in ethanol at room temperature and 351 K.



Fig. 5. Absorption spectra changes of diarylethene **1** and color changes of **1**–**5** by photoirradiation in PMMA films (10%, w/w) at room temperature: (A) absorption spectral changes of **1** and (B) color changes of **1**–**5**. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Compd	$\lambda_{o,max}/nm^a$ ($\epsilon/L mol^{-1} cm^{-1}$)		$\lambda_{c,max}/nm^b (\epsilon/L \text{ mol}^{-1} \text{ cm}^{-1})$		Φ^{c}		Conversion at PSS in hexane (%)
	Hexane	PMMA film	Hexane	PMMA film	Φ_{o-c}	Φ_{c-o}	
1	296 (2.64×10^4)	298	$584~(1.74 imes 10^4)$	600	0.32	0.12	62
2	$290~(2.58 imes 10^4)$	292	581 (1.84 $ imes 10^4$)	593	0.26	0.21	51
3	291 (2.42 $ imes$ 10 ⁴)	293	579 (1.63×10^4)	592	0.25	0.28	61
4	292 (2.61 $ imes$ 10 ⁴)	295	579 (1.60×10^4)	595	0.43	0.26	67
5	296 (2.63 $ imes 10^4$)	296	581 (1.66×10^4)	598	0.45	0.13	74

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

^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.

Storing these solutions in the dark and then exposing them to air for more than 30 days at room temperature, we found that no changes in the UV/Vis spectra of 1-5 were observed. At 351 K, the ethanol solutions of diarylethenes 1-5 still exhibited excellent thermal stability for more than 15 days. Fig. 6 shows the thermal fading of 1c in hexane at various temperatures. The result revealed that the absorbance decay of 1c became fast with the increase of temperature, but the thermal fading change was very slight in the range of 298 – 343 K. As like 1c, the thermal fading change of 2c–5c is very small in the range of 298 - 343 K. The result indicated that diarylethenes with an azaindole moiety possessed very excellent thermally irreversible photochromic behaviors. In addition, the fatigue resistance of diarylethenes 1–5 was tested in both hexane and PMMA films at room temperature, and the result is presented in Fig. 7. In hexane, the coloration and decoloration cycles of 1–5 could repeat more than 100 times with the degradation of 5% for **1c**, 6% for **2c**, 10% for **3c**, 4% for **4c**, and 7% for **5c**. After repeating 200 times in PMMA films, these derivatives still exhibited favorable photochromism with the degradation of 10% for 1c, 7% for 2c, 5% for 3c, 8% for 4c, and 11% for 5c, respectively. Therefore, diarylethenes with an azaindole moiety exhibited very strong fatigue resistance in both hexane and PMMA films.

3.2. Crystal structures and photochromism in the crystalline phase

In general, diarylethene has two conformations with two heterocyclic rings in C_2 symmetry (*anti*-parallel conformation) and in mirror symmetry (parallel conformation) [3,36,37]. In order to know the relation between conformation and photochromic behaviors of diarylethenes in the crystalline phase, the final structural



Fig. 6. Thermal fading of 1c in hexane at various temperature.

conformations of **10–50** were provided by X-ray crystallographic analysis. Their ORTEP drawings and photochromism in the crystalline state are shown in Fig. 8, and X-ray crystallographic analysis data are listed in Table 2. The five azaindole-containing diarylethenes crystallized with photoactive *anti*-parallel conformations in the crystalline phase, and the distances between the two reactive carbon atoms are 3,629 Å for **10** (C11···C19), 4.021 Å for **20**



Fig. 7. Fatigue resistance of diarylethenes **1–5** in air atmosphere at room temperature: (A) in haxane and (B) in PMMA films. Initial absorptance of the sample was fixed to 1.0.



Fig. 8. ORTEP drawings of crystals of 10–50 and their photochromism in the single crystalline phase: (A) 10, (B) 20, (C) 30, (D) 40, (E) 50, and (F) photochromism of 1–5 in the crystalline phase.

Table 2

Crystal data for diarylethenes **10–50**.

	10	20	30	40	50
Formula	C ₂₆ H ₁₇ F ₉ N ₂ S	C ₂₅ H ₁₇ F ₇ N ₂ S	C ₂₅ H ₁₈ F ₆ N ₂ S	C ₂₆ H ₂₀ F ₆ N ₂ S	C ₂₆ H ₂₀ F ₆ N ₂ OS
Formula weight	560.48	510.47	492.45	506.50	522.50
Temperature	296(2)	296(2)	296(2)	296(2)	296(2)
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic
Space group	P-1	P-1	P-1	P-1	P-1
Unit cell dimensions					
a (Å)	9.4766(3)	9.3690(14)	9.3685(9)	9.4712(7)	9.3224(3)
b (Å)	11.933(3)	11.431(15)	11.390(12)	11.378(8)	11.583(3)
<i>c</i> (Å)	11.979(3)	11.794(16)	11.909(12)	11.775(9)	11.610(3)
α (°)	68.5330(10)	85.061(8)	85.357(5)	85.840(4)	85.3150(10)
β(°)	83.125(2)	70.229(8)	69.878(4)	71.517(4)	74.2740(10)
γ (°)	76.820(2)	73.707(8)	72.830(5)	76.946(4)	81.5730(10)
Volume (Å ³)	1226.48(6)	1141.0(3)	1139.8(2)	1172.4(15)	1192.60(6)
Ζ	2	2	2	2	2
Reflections collected	5614	4005	5188	5333	4179
Reflections observed	3933	3016	4259	4477	3674
Number of parameters	392	319	311	339	339
Density (calcd.) (g/cm ³)	1.518	1.486	1.426	1.435	1.455
Goodness-of-fit on F ²	1.062	1.031	1.049	1.055	1.112
Final R_1 [$I > 2s(I)$]	0.0864	0.0930	0.0789	0.0664	0.0710
$wR_2[I > 2s(I)]$	0.2140	0.2230	0.2052	0.1828	0.1859
R ₁ (all data)	0.0641	0.0733	0.0660	0.0562	0.0647
wR ₂ (all data)	0.1911	0.1925	0.1899	0.1684	0.1803

(C10...C18), 4.059 Å for **30** (C8...C16), 3.960 Å for **40** (C11...C19), and 3.755 Å for **50** (C7…C13), respectively (Table 3). Based on the empirical rule that the molecule undergoes the photocyclization reaction if the molecule is fixed in an anti-parallel mode and the distance between reacting carbon atoms on the aryl rings is less than 4.2 Å [38,39], all of these crystals should be expected to display favorable photochromism by photoirradiation in the single crystalline phase. As expected, **10–50** exhibit favorable photochromism in the crystalline phase (Fig. 8F). Upon irradiation with UV light, the crystals of 10-50 turned blue. When the colored crystals were dissolved in hexane, intense absorption maxima were observed at the same wavelengths as those of their respective closed-ring isomers in solution. Reversely, the colored crystals were bleached completely and their absorption spectra were returned to their initial states upon irradiation with visible light of the appropriate wavelength. This characteristic could be potentially used for the construction of certain optoelectronic devices [40].

3.3. Fluorescence of diarylethenes

Fluorescent property of diarylethene can be useful in molecularscale optoelectronics and fluorescence photoswitching materials [41–43]. Recently, the fluorescent properties of many diarylethene derivatives have been extensively attracted [44–47]. The fluorescence emission spectra of diarylethenes 10-50 in both hexane $(2.0 \times 10^{-5} \text{ mol L}^{-1})$ and PMMA films (10%, w/w) were investigated at room temperature, and the results are shown in Fig. 9. In hexane, the emission peaks of diarylethenes 10-50 were observed at 426 $(\lambda_{ex}, 294 \text{ nm}), 426 (\lambda_{ex}, 292 \text{ nm}), 428 (\lambda_{ex}, 290 \text{ nm}), 431 (\lambda_{ex}, \lambda_{ex}, \lambda_{ex})$ 287 nm), and 437 nm (λ_{ex} , 289 nm), respectively. In PMMA films, the emission peaks were observed at 445 (λ_{ex} , 350 nm), 447 (λ_{ex} , 345 nm), 445 (λ_{ex} , 340 nm), 448 (λ_{ex} , 337 nm), and 452 nm (λ_{ex} , 342 nm). Compared to those in hexane, the emission peaks in PMMA films exhibited a remarkable redshift with the value of 19 nm for **10**, 21 nm for **20**, 17 nm for **30**, 17 nm for **40**, and 15 nm for **50**. The result is in accordance with that of the analogous diarylethenes with an indole moiety [21]. In addition, the emission intensity of diarylethenes with an electron-withdrawing group (trifluoromethyl or fluorine) was much stronger than that of diarylethenes with an electron-donating group (methyl or methoxy) in hexane. Among the five derivatives, the emission intensity of 10 is the strongest in both hexane and a PMMA film. The results indicated that different substituents attached at the terminal of benzene ring had a significant effect not only on the emission peak but also on the emission intensity. The fluorescence quantum yields of **10–50** in acetonitrile were determined to be 0.073 for **10**, 0.062 for **20**, 0.079 for **30**, 0.066 for **40**, and 0.044 for **50** with anthracene as a reference. The result indicated that either the electronwithdrawing or electron-donating substituents could effectively suppress the fluorescence quantum yield of diarylethene with an azaindole unit, as compared to the unsubstituted parent **30**.

Table 3

Distances between the reacting carbon atoms d (Å) and dihedral angles θ (°) of diarylethenes **10–50**.

Compd	d (Å)		θ (°) ^a	θ (°) ^a			
			θ_1	θ_2	θ_3		
10	C11…C19	3.629	48.1	46.0	14.1		
20	C10…C18	4.021	66.3	58.1	26.3		
30	C8…C16	4.059	68.6	59.5	26.3		
40	C11…C19	3.960	60.8	59.5	17.1		
50	C7…C13	3.755	52.1	50.8	2.9		

^a θ_1 , Dihedral angle between the cyclopentene ring and the azaindole ring; θ_2 , dihedral angle between the cyclopentene ring and the thiophene ring; θ_3 , dihedral angle between the thiophene ring and the adjacent benzene ring.

As observed for most of the reported diarylethenes [48–50], diarylethenes 1–5 exhibited notable fluorescent switches by photoirradiation in both hexane and PMMA films. The fluorescence changes of **1** by photoirradiation in hexane $(2.0 \times 10^{-5} \text{ mol } \text{L}^{-1})$ and in a PMMA film (10%, w/w) are shown in Fig. 10. Upon irradiation with 297 nm UV light, the emission intensity of diarylethene 10 decreased significantly due to the producing of its closed-ring isomer **1c**. The back irradiation by appropriate visible light regenerated its open-ring isomer **10** and recovered the original emission intensity. When arrived at the photostationary state, the emission intensity of 10 was quenched to ca. 22% in hexane and 6% in a PMMA film. Therefore, its fluorescent modulation efficiency in the photostationary state was 78% in hexane and 94% in a PMMA film. Just like 1, 2–5 also showed remarkable fluorescent switches in both hexane and PMMA films upon alternating irradiation with UV and visible light. In the photostationary state, the fluorescent modulation efficiency of 2-5 in hexane was 68% for 2, 72% for 3, 69% for 4, and 76% for 5, and that in PMMA films was 91% for 2, 94% for 3, 92% for 4, and 88% for 5. The result indicated that the fluorescent modulation efficiency of diarylethenes 1-5 in PMMA films was much higher than that in their respective solutions. This is in accordance with that of diarylethenes with an isoxazole,



Fig. 9. Emission spectra of diarylethenes **1–5** at room temperature: (A) in hexane $(2.0 \times 10^{-5} \text{ mol } L^{-1})$ and (B) in PMMA films (10%, w/w).

naphthalene, or pyridine moiety [10,15,16]. Compared to the pyridine- or naphthalene-containing diarylethenes with the similar molecular skeleton [15,16], the fluorescent modulation efficiency of diarylethenes with an azaindole moiety enhanced notably during the process of photoisomerization. This characteristic is ideal for practical applications in certain optical devices [51,52].

3.4. Electrochemistry of diarylethenes

So far, the electrochemical properties of photochromic diarylethenes have been widely reported [53–56]. In order to investigate the electrochemical properties of **1–5**, the cyclic voltammetry tests were performed under the same experimental conditions at a scanning rate of 50 mV s⁻¹. The electrolyte was acetonitrile (5.0 mL) containing 0.5 mmol tetrabutylammonium tetrafuoroborate ((TBA) BF₄) and 0.2 mmol diarylethene sample. Fig. 11 shows the cyclic voltammetry curves of diarylethenes **1–5**. The oxidation onsets (E_{onset}) of **1–5** were initiated at 1.32 and 0.85 V for **10** and **1c**, 1.29 and 0.81 V for **20** and **2c**, 1.28 and 0.77 V for **30** and **3c**, 1.25 and 0.73 V for **40** and **4c**, and 1.11 and 0.72 V for **50** and **5c**, respectively. The difference of oxidation onset between the open-ring and closed-ring isomers of **1–5** (ΔV_{0-c}) was 0.47 V for **1**, 0.48 V for **2**, 0.51 V for **3**, 0.52 V for **4**, and 0.39 V for **5**. The result indicated that







Fig. 11. Cyclic voltammetry curve of diarylethenes 1-5 in 0.1 mol L⁻¹ ((TBA)BF₄) with a scan rate of 50 mV s⁻¹.

the oxidation process for the open-ring isomers **10–50** occurred at higher potentials than in the corresponding closed-ring isomers **1c–5c**, indicating that shorter conjugation length leads to larger positive potentials [41]. Furthermore, the oxidation potentials of diarylethenes with an electron-donating group (such as in **4** or **5**) were much lower than those of diarylethenes with an electron-withdrawing group (such as in **1** or **2**).

According to the reported method [57,58], the Highest Occupied Molecular Orbitals (HOMO) and the Lowest Unoccupied Molecular Orbitals (LUMO) energy levels could be estimated by using the energy level of ferrocene as a reference. Based on the HOMO and LUMO energy level, the band-gap (E_g) of each compound could be calculated approximately. Their electrochemical characteristics are summarized in Table 4. When replacing the hydrogen atom at the para-position of the terminal benzene ring with an electronwithdrawing substituent (trifluoromethyl or fluorine group, such as in 1 or 2), the band-gaps enhanced significantly. Reversely, the band-gaps decreased notably when replacing the hydrogen atom with an electron-donating group (methyl or methoxy group, such as in 4 or 5). As a result, the band-gaps of 1–5 decreased in order of 1 > 2 > 3 > 4 > 5. The result revealed that different substituents linked at the terminal of benzene ring had a significant effect on the electrochemical properties of these diarylethenes with an azaindole, but further work is required to quantify the effects.

4. Conclusion

Five unsymmetrical photochromic diarylethenes based on the hybrid of azaindole and thiophene moieties have been synthesized

Table 4		
Electrochemical properties of c	liarylethenes 1–5 in aceton	itrile.

Compd	Oxidation		Reduction	Band gap	
	Eonset (V)	IP (eV)	Eonset (V)	EA (eV)	Eg
10	+1.32	-6.12	-0.75	-4.05	2.07
1c	+0.85	-5.65	-0.71	-4.09	1.56
20	+1.29	-6.09	-0.76	-4.04	2.05
2c	+0.81	-5.61	-0.73	-4.07	1.54
30	+1.28	-6.08	-0.76	-4.04	2.04
3c	+0.77	-5.57	-0.67	-4.13	1.44
40	+1.25	-6.05	-0.77	-4.03	2.02
4c	+0.73	-5.53	-0.68	-4.12	1.41
50	+1.11	-5.91	-0.79	-4.01	1.90
5c	+0.72	-5.52	-0.69	-4.11	1.41

to investigate the substituent effects linked at the *para*-position of the terminal benzene ring. The different substituents had a significant effect on the properties of these diarylethene derivatives, including photochromic features, fluorescence, and electrochemistry. The azaindole moiety induced some new characteristics which were different from those of reported diarylethenes with other aryl moieties. The results will be helpful for understanding the substituent effects on the properties of diarylethene with an azaindole moiety and exploring novel diarylethenes with tunable photochromic behaviors.

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