



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 electron-donating substituents significantly enhanced their cyclization quantum yields, while the electron-withdrawing 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 electron-withdrawing 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 (**1o**), 1-(1,2-dimethyl-7-azaindole-3-yl)-2-[2-methyl-5-(4-fluorophenyl)-3-thienyl]perfluorocyclopentene (**2o**), 1-(1,2-dimethyl-7-azaindole-3-yl)-2-(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene (**3o**), 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 CDCl_3 as the solvent and tetramethylsilane as an internal standard. Infrared spectra (IR) were recorded 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 **1o–5o** 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 **1o–5o** 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 Mo 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 **1o**, 963070 for **2o**, 963067 for **3o**, 963068 for **4o**, and 963072 for **5o**. Copies of the data can be obtained, free of charge, on application to

CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 0 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

2.2. Synthesis

The synthesis route for diarylethenes **1o–5o** is shown in Fig. 2.

First, 1,2-dimethyl-3-bromo-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 CH_2Cl_2 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 MgSO_4 , 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, CDCl_3): δ 6.51 (d, 1H, $J = 4.0$ Hz, azaindoly-H), 7.06–7.10 (m, 1H, azaindoly-H), 7.38 (t, 2H, $J = 8.0$ Hz, phenyl-H), 7.47 (t, 1H, $J = 7.2$ Hz, phenyl-H), 7.64 (d, 1H, $J = 4.0$ Hz, azaindoly-H), 7.75 (d, 1H, $J = 4.0$ Hz, azaindoly-H), 8.10 (s, 1H, phenyl-H), 8.11 (s, 1H, phenyl-H), 8.34 (d, 1H, $J = 4.8$ Hz, azaindoly-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 MgSO_4 , filtrated, and evaporated. The crude product was purified by column

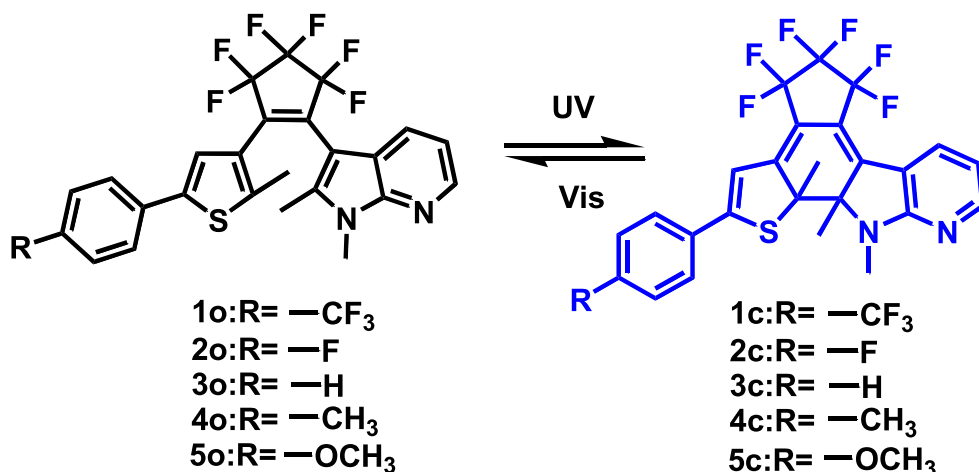


Fig. 1. Photochromism of diarylethenes **1–5**.

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