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Photochromism of new 3,5-position hybrid diarylethene derivatives bearing both thiophene and thiazole moieties

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ABSTRACT

Five new diarylethenes based on a hybrid structure of bis(5-thiazolyl)ethene and bis(3-thienyl)ethene were synthesized, and the structures of the four compounds were determined by single-crystal X-ray diffraction analysis. The properties of these diarylethenes, such as photochromism, fluorescence, and electrochemical properties were investigated in detail. All of these compounds showed good photochromism and fluorescence both in solution and in PMMA films. The electron-donating substituents could effectively increase the cyclization and cycloreversion quantum yields, and the fluorescence emission peaks, whereas the electron-withdrawing groups functionalized an inverse action for these diarylethene derivatives. Cyclic voltammetry revealed that great differences existed amongst the electrochemical behaviors of these compounds. The oxidation potentials and the band gaps of these diarylethenes increased remarkably with the increase in electron-withdrawing ability. All results suggested that the effects of substitution have a significant effect on the photochemical and electrochemical behaviors of these diarylethene derivatives.

1. Introduction

Photochromic compounds have attracted much attention because of their potential application to photonic devices, such as high-density optical recording materials and photoswitches.[1] Among various types of photochromic compounds, diarylethene derivatives with heterocyclic aryl rings are the most promising candidates for photoelectronic applications because of the excellent thermal stability of the respective isomers, notable fatigue resistance, and rapid response, and high reactivity in solid state.[2]

Among the diarylethenes hitherto reported, most of them have an absorption peak with the region between 550 and 750 nm wavelengths,[3] with just a few reports concerning photochromic diarylethenes whose absorption peaks beyond this wavelength range. The longest wavelength of diarylethene so far reported was observed at 828 nm,[4] and the shortest one showed its longest absorption bands in the UV light region (260 nm).[5] For the application to optical recording, it is very important to develop photochromic diarylethenes with different absorption wavelengths, which can expect to match perfectly with the wavelength of recording laser. Especially, it is indispensable to prepare diarylethene derivatives with a shorter absorption wavelength because the recording capacity is proportional to the recording laser wavelength.[6] That is to say, the shorter the absorption wavelength of diarylethene contains, the higher recording density is expected to achieve because the light can be focused more sharply. Therefore, developing diarylethene derivatives with an absorption band around 500 nm or even shorter for making use of short-wavelength optical recording materials is very necessary.

Guided by this aim, several approaches to shift the absorption maximum of the closed-ring isomer to a shorter wavelength are to attach the thiophene rings to the ethene moiety at the 2-position.[3,7,2d] As we all known, the absorption spectrum is dependent on the substituent effects[8] and the π-conjugation length in a diarylethene molecule.[9] In bis(2-thienyl)ethene photochromic system, the π-conjugation in closed-ring isomer is only localized in a cyclohexadiene structure, shifting the absorption to shorter wavelength, as compared with the closed-ring isomer of bis(3-thienyl)ethene photochromic system where the π-conjugation extends throughout the whole molecule.[3,7b] For instance, the absorption maximum of the closed-ring diarylethene with a structure of 1,2-bis(2-thienyl) ethene was observed at 425 nm,[10] while that of the reported diarylethene with a structure of 2,3-position hybrid thiophene rings was observed at 469 nm.[11] However, the absorption maximum of the closed-ring isomer with a structure of 1,2-bis(3-thienyl)ethene was observed at 534 nm.[10,12] Compared with the parent analogues, diarylethene derivatives with oxidized thiophene/benzothiophene rings could also significantly shift their absorption band to a shorter

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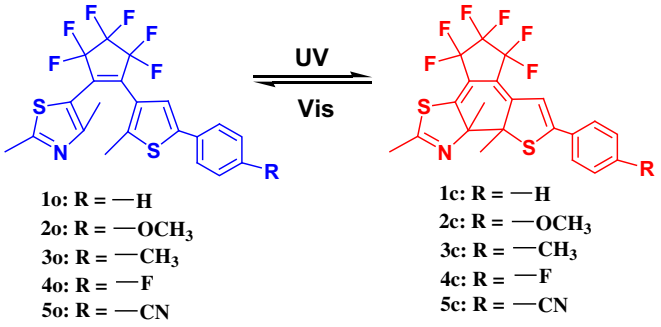
wavelength during the process of photocyclization.[5,13,14] Another attempt is to introduce the thiazole rings into the diarylethene system as the aryl moieties.[15] When the thiophene rings of 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene[16] are replaced with thiazole rings, the absorption maximum of the closed-ring isomer shifts from 575 nm to 525 nm.[15a,d] Similarly, when the thiophene rings of 1,2-bis(3,5-dimethyl-2-thienyl)perfluorocyclopentene[10,17] are replaced with thiazole rings, the absorption maximum shifts from 432 nm to 391 nm.[15a]

From the reports described above, it can be easily concluded that most of diarylethenes with thiazole rings reported to date are symmetrical compounds or the thiazole ring is attached to the ethene moiety at the 4-position. Report concerning diarylethenes with 5-thiazolyl moieties is very rare. To the best of our knowledge, diarylethenes with a hybrid structure of 5-thiazolyl and 3-thienyl moieties have not hitherto been reported. In this study, we have synthesized a new class of photochromic diarylethene derivatives bearing both 5-thiazolyl and 3-thienyl moieties (**1o**–**5o**). All of these diarylethenes showed good photochromism both in solution and in PMMA amorphous films, and most of them also showed good photochromism in the crystalline phase. The photochromic scheme of diarylethenes **1o**–**5o** is shown in Scheme 1.



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

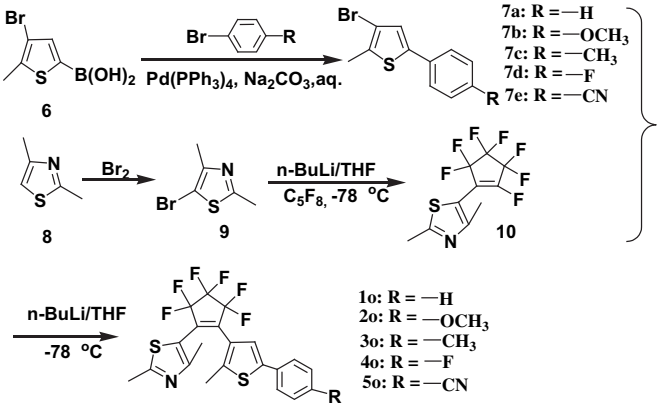
2. Experimental

2.1. General methods

All solvents used 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 Bruker Vertex-70 spectrometer. Elemental analysis was measured with PE CHN 2400 analyzer. Melting point was taken on a WRS-1B melting point apparatus. Absorption spectra were measured using an Agilent 8453 UV/vis spectrophotometer. Photoirradiation was carried out using a SHG-200 UV lamp, CX-21 ultraviolet fluorescence analysis cabinet and a BMH-250 visible lamp. The required wavelength was isolated by the use of the appropriate filters. Fluorescence spectra were measured using a Hitachi F-4500 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 wires (diameter 0.5 mm) served as the working electrode and counter electrode. Platinum wire (diameter 0.5 mm) in the supporting electrolyte solution served as a quasi-reference electrode, which was calibrated using an internal ferrocene (F_c/F_c^+) standard with a formal potential of $E_{1/2}$=+0.35 V versus platinum wire in the same electrolyte. The typical electrolyte was acetonitrile (5 mL) containing 0.1 mol/L tetrabutylammonium tetrafluoroborate ((TBA)BF_4) and 1.0×10^{-3} mol/L diarylethene sample. All solutions were deaerated by bubbling with a dry argon stream and maintained at a slight argon overpressure during electrochemical experiments.

2.2. Synthesis of diarylethenes

The synthesis route for the diarylethenes **1o**–**5o** is shown in Scheme 2. Suzuki coupling of the five bromobenzene derivatives with a thiophene boronic acid[18] gave the alkylphenylthiophene derivatives (**7a**–**e**). Separately, 1-(2,4-dimethyl-5-thiazolyl)perfluorocyclopentene (**10**) was synthesized by bromination and lithiation reactions from 2,4-dimethylthiazole. Finally, compounds **7a**–**e** were separately lithiated and then coupled with compound **10** to give diarylethenes **1o**–**5o**, respectively. The structures of **1o**–**5o** were confirmed by elemental analysis, NMR, and IR.



Scheme 2. Synthetic route for the target compounds.

*2.2.1. 3-Bromo-2-methyl-5-phenyl-thiophene (**7a**).* This compound was synthesized by the same method as that reported in a reference.[15e] Compound **7a** was prepared by reacting 3-bromo-2-methyl-5-thienylboronic acid[18] (2.90 g, 13.10 mmol) with bromobenzene (2.06 g, 13.10 mmol) in the presence of $Pd(PPh_3)_4$ (0.27 g, 0.23 mmol) and Na_2CO_3 (6.36 g, 60.00 mmol) in tetrahydrofuran (THF) (80 mL containing 10% water). After refluxing for 15 h at 70 °C, the product was allowed to slowly warm to the room temperature and then extracted with ether. The organic layer was collected and dried over $MgSO_4$, filtrated, and evaporated. The crude product was purified by column chromatography on SiO_2 using hexane as an eluent resulting in 2.76 g of **7a** being obtained as a buff solid in 83% yield. Mp 66–68 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.34 (s, 3H, $-CH_3$), 7.02 (s, 1H, thienyl-H), 7.20 (d, 1H, J=8.0 Hz, phenyl-H), 7.29 (t, 2H, J=8.4 Hz, phenyl-H), 7.42 (d, 2H, J=8.0 Hz, phenyl-H).

*2.2.2. 3-Bromo-2-methyl-5-(4-methoxyphenyl)thiophene (**7b**).* Compound **7b** was prepared by a method similar to that used for **7a**. The crude product was purified by column chromatography on SiO_2 using petroleum ether as an eluent to give **7b** (2.63 g, 79%) as a buff solid. Mp 106–107 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.41 (s, 3H, $-CH_3$), 3.91 (s, 3H, $-OCH_3$), 6.95–6.99 (m, 2H, phenyl-H), 7.27 (s, 1H, thienyl-H), 7.30 (s, 1H, phenyl-H), 7.54 (d, 1H, J=8.0 Hz, phenyl-H).

*2.2.3. 3-Bromo-2-methyl-5-(4-methylphenyl)thiophene (**7c**).* Compound **7c** was prepared by a method similar to that used for **7a**. The crude product was purified by column chromatography on SiO_2 using petroleum ether as an eluent to give **7c** (2.66 g, 80%) as a buff solid. Mp 68–69 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 2.37 (s, 3H, $-CH_3$), 2.41 (s, 3H, $-CH_3$), 7.01 (s, 1H, thienyl-H), 7.19 (d, 2H, J=8.0 Hz, phenyl-H), 7.38 (d, 2H, J=8.0 Hz, phenyl-H).

*2.2.4. 3-Bromo-2-methyl-5-(4-fluorophenyl)thiophene (**7d**).* Compound **7d** was prepared by a method similar to that used