Synthesis and Application of 1-[2-methyl-5-(4-chlorophenyl)-3-thienyl]-2-[2-methyl-5-formyl-3-thieryl]perfluorocyclopentene

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ABSTRACT: A new unsymmetrical photochromic diarylethene 1-[2-methyl-5-(4-chlorophenyl)-3-thienyl]-2-[2-methyl-5-formyl-3-thienyl]perfluorocyclopentene (1o) has been synthesized. In the meantime, its photochromic, kinetics and fluorescence properties were investigated in detail. This diarylethene had good thermal stability and exhibited reversible photochromism. What is more, the kinetic experiments illustrated that the cyclization/cycloreversion process of this compound was determined to be the zeroth/first reaction. The fluorescence intensity of diarylethene decreased dramatically along with the photochromism from open-ring isomer to closed-ring isomer upon irradiation with UV light in acetonitrile solution.

1 INTRODUCTION

Organic photochromic materials have attracted much attention, because of their potential application to optical memory media and optical switches (Irie, 2002, p. 759–760, Berkovic, 2000, p. 1741–1751, and Tian, 2004, p. 85–97). Photochromism is defined as reversible transformation between open-ring and closed-ring states with different absorption spectra. The two isomers differ from each other not only in their absorption spectra, but in many changes of various physical and chemical properties, such as dielectric constant, refractive index, as well as oxidation/reduction potential (Chen, 2004, p.75–77). During the past several decades, there have been important achievements in the synthesis of new families of organic photochromic molecules (Raymo, 2005, p. 327–336, and Matsuda, 2006, p. 1204–1209). There are various types of photochromic compounds that have been reported, such as azobenzenes (Feng, 2005, p. 306), fulgides (Liang, 1998, p. 905–914). Among all photochromic compounds, diarylethenes are one of the most promising candidates for photoelectronic applications owing to their excellent thermal-stability, remarkable fatigue-resistance, rapid response and fairly high photo-cyclization quantum yields (Shiozawa, 2010, p. 4885–4787).

In previous papers, a large number of publications concerning synthesis and investigation of their photochromic properties of diarylethene have been reported (Irie, 1994, p. 9894–9900, and Uchida, 1998, p. 6627–6638). However, there were few publications reported photochromic unsymmetrical hybrid diarylethene derivatives with thiazole moieties.
In this paper, we synthesized a new unsymmetrical diarylethene, 1-[(2-methyl-5-(4-chlorophenyl)-3-thienyl)]-2-[2-methyl-5-formyl-3-thienyl]perfluorocyclopentene(1o), which presents photochromism in solution. Its photochromic reaction is shown in Scheme 1.

Scheme 1. Photochromism of 1o.

2 EXPERIMENTS

Synthesis of 1o. The synthetic route for the 1o was described in according to the method described in Scheme 2. It was synthesized according to the similar procedure of (Irie, 1995, p. 8305–8309). The structure of 1o was confirmed by NMR. $^1$H NMR spectra were recorded on Bruker AV400 (400 MHz) spectrometer with CDCl$_3$ as the solvent and tetramethylsilane as an internal standard. $^1$H NMR (400 MHz, CDCl$_3$, ppm): δ (ppm): 1.92 (s, 3H, –CH$_3$), 2.04 (s, 3H, –CH$_3$), 7.23 (s, 1H, thienyl-H), 7.36 (d, 2H, $J = 8.0$ Hz, phenyl-H), 7.46 (d, 2H, $J = 8.0$ Hz, phenyl-H), 7.7 (s, 1H, thienyl-H), 9.86 (s, 1H, formyl-H).

Scheme 2. Synthetic route for 1o.

3 RESULTS AND DISCUSSION

3.1 Photochromism in solution.

The photochromic behavior of 1o (C = 2 × 10$^{-5}$ mol/L) induced by photoirradiation was measured at room temperature are shown in Figure 1. In acetonitrile, 1o exhibited a sharp absorption peak at 278 nm due to a π–π* transition (Li, 2008, p. 5190–5196). Upon irradiation with 297 nm light, it turned to blue due to form closed-ring isomer 1c, accompanying a new absorption band centered at 610 nm. When the blue solution was irradiated with visible light (λ > 500 nm), the
color could return back to colorless and its spectrum became the same as that of original one, indicating compound 1o returned to the initial open ring isomer.

![Absorption spectra changes of the compound 1o in acetonitrile.](image)

Figure 1. Absorption spectra changes of the compound 1o in acetonitrile.

### 3.2 Photochromic Reaction Kinetics in acetonitrile Solution.

The photochromic cyclization and cycloreversion kinetics of this diarylethene in acetonitrile were determined by UV-Vis spectra upon alternating irradiation with appropriate wavelength UV and visible light at room temperature. The cyclization and cycloreversion curves of 1o were shown in Figure 2(A) and Figure 2(B), respectively. It can be seen that the relationships between the absorbance and exposure time have good linearity upon irradiation with 297 nm UV light. The slope of line in Figure 2(A) and Figure 2(B) represents the reaction rate constant (k) of 1o in acetonitrile. It is suggesting that the cyclization processes of compound 1o belong to the zeroth order reaction when open-ring isomers changed to closed-ring isomers. At the same time, during the cycloreversion of 1c, the relationship between –log(Abs) and exposure time also behave perfect linearity, as shown in Figure 2(B), indicating that the cycloreversion process belong to the first order reaction. So all k of cyclization/cycloreversion process (k_{o-c}, 10^3) of diarylethene 1c can be easily obtained in solution, respectively.

![Cyclization and cycloreversion kinetics of 1o in acetonitrile.](image)

(A) (B)

Figure 2. The cyclization (A) and cycloreversion (B) kinetics of 1o in acetonitrile.
3.3 Fluorescence of diarylethene.

The fluorescence emission spectra of 1o in acetonitrile (2 × 10^{-5} mol/L) and were the fluorescence properties of the 1 in acetonitrile solution were measured using a Hitachi F-4500 spectrophotometer, and the breadths of excitation slit were selected 5.0 nm and emission slit were selected 10.0 nm. Figure 3 shows the fluorescence spectral changes of 1o in acetonitrile (2 × 10^{-5} mol/L) upon irradiation with 297 nm UV light at room temperature. We could clearly see that the fluorescent emission of 1o was at 496 nm when excited at 300 nm. Upon irradiation with UV light, the fluorescence of 1o effectively decreased along with photocyclization due to the production of the non-fluorescence closed-ring isomer 1c. The emission intensity of diarylethene 1o was quenched 60% at the photostationary state in acetonitrile solution. This phenomenon indicated that cyclization reaction is incomplete and the existence of parallel conformation may be the main cause for the change in fluorescence intensity (Tian, 2008, P. 1617–1622). The reversible changes of the emission intensity of diarylethene 1o are useful for application as the fluorescence switches.

![Fluorescence spectra of 1o in acetonitrile with 297 nm UV light.](image)

Figure 3. Fluorescence spectra of 1o in acetonitrile with 297 nm UV light.

4 SUMMARY

In summary, a novel diarylethene with a isoxazole moiety has been synthesized. The results showed that this compound exhibited reversible photochromism in solution. 1o changed the color from colorless to blue in acetonitrile solution upon appropriate irradiation with 297 nm UV light. When the blue solution was irradiated with visible light (λ > 500 nm), the color could return back to colorless. What is more, the kinetic experiments illustrated that the cyclization/cycloreversion process of this compound was determined to be the zeroth/first reaction. Fluorescent properties were investigated in detail and the results indicated that 1o has excellent photochromic property. Upon excited at 300 nm, the fluorescence intensity decreased along
with the photochromism, the open-ring isomer of 1o exhibited relatively strong fluorescence at 496 nm in acetonitrile solution. The reversible changes of the emission intensity of diarylethene 1o are useful for application as the fluorescence switches.

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REFERENCES


