Synthesis and Photochromic Properties of Diarylethene 1-[2-methyl-5-phenyl-3-thienyl]-2-[2-methyl-5-(3-fluoro-4-chloro)phenyl-3-thienyl]perfluorocyclopentene


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ABSTRACT: A novel unsymmetrical photochromic diarylethene, 1-[2-methyl-5-phenyl-3-thienyl]-2-[2-methyl-5-(3-fluoro-4-chloro)phenyl-3-thienyl]perfluorocyclopentene, was designed and constructed successfully. Its photochemical properties, including photochromic, fluorescence behavior and kinetics, have been investigated systematically. The results indicated that its photochromic behavior could be modulated by UV/V is light, changing from colorless to blue in hexane. What is more, the kinetic experiments illustrated that the cyclization/cycloreversion process of this diarylethene were determined to be the zeroth/first reaction.

1 INTRODUCTION

Photochromism, a photoinduced reversible reaction between two isomers, is one of the essential photochemical reactions to facilitate the reversible fluorescence switching process in synthetic molecules (Russew, 2010, p. 3348–3360, Wei, 2011, p. 1080–1091, Irie, 2002, p. 759–760, and Bianco, 2011, p. 711–736). Photochromic diarylenes are considered to be among the most promising systems for applications in optical memory media and switching devices due to their excellent photochromic properties coupled with thermal stability, fatigue resistance, and sensitivity (Irie, 2000, p. 1685–1716, Kobatake, 2011, p. 1905–1908, and Tian, 2008, p. 1617–1622). To the best of our knowledge, only a few publications concerning the substituent position effect on the optoelectronic properties of diarylenes have been published (Bianco, 2005, p. 869–874, and Pu, 2006, p. 3167–3171). Previously, the focus has been on the effect of electron-withdrawing groups, such as fluorine or chlorine atoms, and it has been found that these halide substituents and their positions have a significant effect on the properties of the diarylethene compounds (Fan, 2008, p. 415–425).

In this work, an unsymmetrical photochromic diarylethene, 1-[2-methyl-5-phenyl-3-thienyl]-2-[2-methyl-5-(3-fluoro-4-chloro)phenyl-3-thienyl]perfluorocyclopentene (1o) was synthesized and its photochemical properties were investigated in detail. 1o exhibited good photochromism
and fluorescence in hexane. The photochromic reaction of diarylethene 1o is shown in Scheme 1.

![Scheme 1. Photochromism of diarylethene 1o.](image)

2 EXPERIMENTS

Synthesis of diarylethene 1o. The synthetic route of this photochromic compound was shown in Scheme 2. It was synthesized according to the similar procedure of (Pu, 2008, p. 84–93). The structure of compound 1o was confirmed by 1H NMR (400 MHz, CDCl3): δ 1.97 (s, 3H, –CH3), 1.99 (s, 3H, –CH3), 7.24 (s, 1H, thiophene–H), 7.30 (s, 1H, benzene–H), 7.33 (s, 1H, benzene–H), 7.40 (d, 2H, J = 8 Hz, benzene–H), 7.62–7.68 (m, 5H, benzene–H).

![Scheme 2. Synthetic route for 1o.](image)

3 RESULTS AND DISCUSSION

3.1 Photochromism of diarylethene 1o in hexane

The 1o exhibited excellent photochromic properties and could be toggled between its colorless ring-open and colored ring-closed forms by alternate irradiation with appropriate wavelengths of light. The absorption spectral change in hexane is shown in Figure 1. Upon irradiation with 297 nm light, the colorless solution of 1o turned to blue due to the appearance of a new broad absorption band at λ = 587 nm defined as the formation of the closed-ring isomer 1c. Then, the blue colored solution reverted to colorless upon irradiation with visible light (λ > 510 nm), indicating that 1c returned to the initial state 1o, and a clear isosbestic point was observed at 328.
nm. From the above description, we can easily get a conclusion that both open-ring isomer and closed-ring isomer of this diarylethene were stable in solution at room temperature.

![Absorption spectral and color change of 1o in hexane.](image)

**Figure 1.** Absorption spectral and color change of 1o in hexane.

3.2 Photochromic reaction kinetics in hexane

The photochromic cyclization and cycloreversion kinetics of this diarylethene in hexane 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 compound 1 are shown in Figure 2, respectively. It can be seen that the relationships between the absorbance and exposure time have good linearity upon irradiation with 297 nm light (Figure 2A). It is suggesting that the cyclization process of 1o belong to the zeroth order reaction and also interpreted that the $k$ of cyclization ($10^{-3}$) is 2.12 (L/mol/s). At the same time, during the cycloreversion of 1c,

![The cyclization/cycloreversion kinetics of compound 1 in hexane.](image)

**Figure 2.** The cyclization/cycloreversion kinetics of compound 1 in hexane.
the relationship between \(-\log(\text{Abs})\) and exposure time also behave perfect linearity, as shown in Figure 2B, indicating that the cycloreversion process belong to the first order reaction and the \(k\) of cycloreversion \((k, 10^{-2})\) process of \(1c\) can be easily obtained, which is 2.48/s in hexane.

3.3 Fluorescence of diarylethene \(1o\)

The fluorescence property of \(1o\) in hexane was measured by the Hitachi F-4600 spectrophotometer. As shown in Figure 3, \(1o\) exhibited relatively stronger fluorescence at 445 nm, when excited at 297 nm. And the photocyclization reaction was carried out and the weaker fluorescent closed-ring form of the compound was produced upon irradiation with 297 nm UV light. The irradiation by appropriate wavelength visible light regenerated the open-ring forms of diarylethene and return the original emission spectra. The phenomena are useful for application such as the fluorescence switches. The emission intensity of diarylethene \(1o\) in photostationary state was quenched to ca. 87% in hexane. The incomplete cyclization reaction and the existence of parallel conformations may be the main cause for the moderate change in fluorescence induced by photo-irradiation (Liu, 2006, p. 2877–2879).

![Figure 3. Fluorescence spectral of \(1o\) upon irradiation with 297 nm UV light in hexane.](image-url)

4 SUMMARY

A novel diarylethene \(1o\) was synthesized to investigate its photochromism, kinetic and fluorescence. The title compound showed good photochromism and fluorescence upon alternating irradiation with UV light and visible light. The photochromic reaction kinetics were also studied and the results demonstrated that the cyclization processes of \(1\) belong to the zeroth order reaction and the cycloreversion process belong to the first order reaction and indicated that the diarylethene has excellent photochromic properties.
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REFERENCES


