

Synthesis and Properties of Unsymmetry Diarylethene 1-[2-methyl-5-trimethylsilacetenyl-3-thienyl]-2-[2-Cyanophenyl] Perfluorocyclopentene

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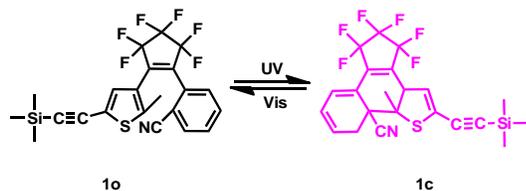
Abstract—A new unsymmetrical photochromic diarylethene 1-[2-methyl-5-trimethylsilacetenyl-3-thienyl]-2-[2-Cyanophenyl] perfluorocyclopentene (**1o**) were synthesized. Under alternating irradiation with UV and visible light, the compounds showed favorable photochromism in hexane. The product changing from colorless to orange after irradiation with 297 nm UV light, and the product has been characterized by UV/Vis spectrophotometry, Fluorescence spectrophotometry. The cyclization processes of compound (**1c**) belong to the zero order reaction.

Keywords-diarylethene; kinetics; photochromic

I. INTRODUCTION

Photochromic compounds have been extensively studied for optoelectronic devices such as for photoswitches, fullcolour displays, and optical data storage [1-3]. Among such compounds, diarylethenes that bear thiophene rings have received the most attention due to the high thermal stability fatigue resistance, notable, and rapid response [4]. Photochromic diarylethenes undergo reversible photoisomerization between two isomers with different absorption spectra upon irradiation with light of appropriate wavelength [5], which makes them good candidates for realizing smart optical modulation.

Up to now, a large number of publications concerning diarylethene derivatives with different aryl moieties, such as benzothiophene [6], thiophene [7], thiazole [8], furan [9], and pyrrole [10], pyrazole [11], have been reported. In this work, a new photochromic diarylethene compound, 1-[2-methyl-5-(4-pentane phenyl)-3-thienyl]-2-[2-phenyl] perfluorocyclopentene (**1o**) was synthesized, which fluorescence, photochromic reactivity were investigated in detail. The photochromic reaction of diarylethene **1o** is shown in Scheme 1.

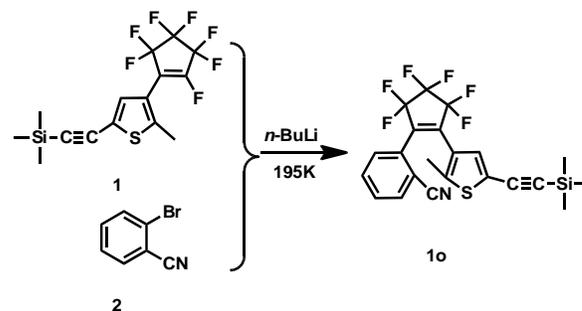


Scheme 1. Photochromism of diarylethene **1o**.

II. EXPERIMENTS

A. 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 [12]. The structure of compound **1o** was confirmed by ¹H NMR (400 MHz, CDCl₃): δ 1.80 (m, 3H, -CH₃), 6.93 (s, 1H, thienyl-H), 7.37 (m, 2H, phenyl-H), 7.49 (m, 2H, phenyl-H).



Scheme 2. Synthetic route for **1o**.

III. RESULTS AND DISCUSSION

A. Photochromism of diarylethene **1o**.

The changes in the absorption spectra of diarylethene **1o**, which were induced by photoirradiation at room temperature in hexane (2.0×10^{-5} mol/L) are shown in Figure 1. After UV irradiation, diarylethene **1o** turned from colorless to orange. Then, the orange colored solution reverted to colorless upon irradiation with visible light ($\lambda > 500$ nm), which indicated that **1c** returned to the initial state **1o**. The maximum absorption of open-ring isomer **1o** was observed at 273 nm and the new absorption band appeared at 545 nm, which can be assignable to the generation of **1c**.

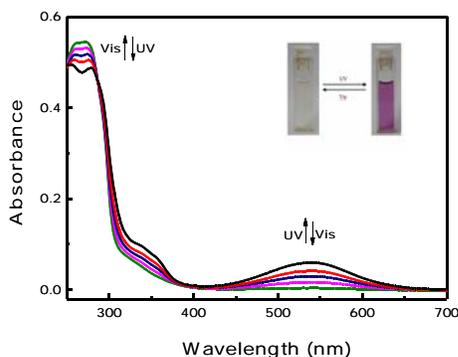


Figure 1. Absorption spectral and color change of compound 1o in hexane.

B. Photochromic reaction kinetics in hexane.

The photochromic cyclization/cycloreversion kinetics of 1o in hexane were determined by UV/Vis spectra upon alternating irradiation with UV and appropriate wavelength visible light at room temperature. The cyclization and cycloreversion curves of compound 1 are shown in Figure 2A. It can be seen that the cyclization processes of compound 1o belong to the zeroth order reaction when opening isomer changed to closed-ring isomer. At the same time, during the cycloreversion of 1c, the relationship between $-\log(\text{Abs})$ and exposal time also behave perfect linearity, as shown in Figure 2B, indicating that the cycloreversion process belong to the first order reaction. So all k of cyclization/cycloreversion process of diarylethene 1c can be easily obtained in solution, respectively.

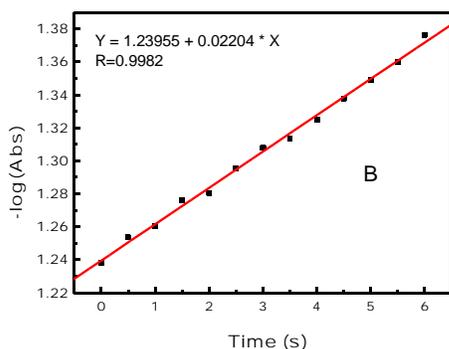
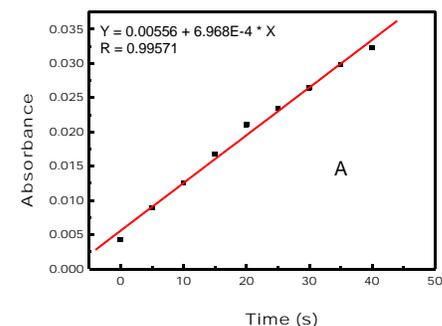


Figure 2. The cyclization/cycloreversion kinetics of compound 1 in hexane.

C. Fluorescence of diarylethene 1o.

Additionally, the fluorescence intensity of diarylethene 1o ($2.0 \times 10^{-5} \text{ mol L}^{-1}$) decreased along with the photochromism because the photocyclization reaction produced the non-fluorescent closed-ring form. The back irradiation by appropriate wavelength visible light regenerated its open-ring isomer and recovered the original emission intensity. The emission intensity of diarylethene 1o was quenched 73% at the photostationary state in dichloromethane 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. The reversible changes of the emission intensity of diarylethene 1o are useful for application as the fluorescence switches [13].

IV. SUMMARY

We synthesize a new unsymmetrical photochromic diarylethene and investigate its photochromic properties. Besides, the cyclization and cycloreversion processes of the compound were determined to be the zeroth and first order reaction by UV/Vis spectra, respectively. All the results will contribute to the further investigation of the diarylethene.

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