

Synthesis and Photochromism Studies of 1-[3,5-dimethyl-4-isoxazolyl]-2-[2-methyl-5-acetynyl-3-thienyl] Perfluorocyclopentene

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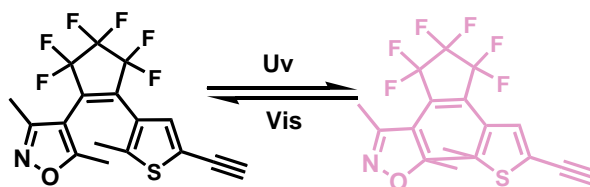
Keywords: Diarylethene, Photochromic, Fluorescence, Isoxazolyl.

Abstract. A new unsymmetrical photochromic diarylethene 1- [3,5-dimethyl-4-isoxazolyl]-2-[2-methyl-5-acetynyl-3-thienyl] perfluorocyclopentene has been synthesized. Its photochromic in hexane solution and kinetics experiment were investigated in detail. The result indicated that this diarylethene had reversible photochromism, changing the color from colorless to purple in hexane solution upon appropriate irradiation with UV, respectively.

Introduction

Photochromic compounds have been extensively investigated due to their potential applications in optical switches and memories [1]. Up to now, various types of photochromic compounds, such as spirobenzopyrans [2], azobenzenes [3], fulgides [4], and diarylethenes [5], Among various organic photochromic compounds, diarylethene derivatives are regarded as the best promising candidates because they have notable thermal irreversible photochromic behaviour [6] and remarkable fatigue resistance [7], which make them promising for the application in optical memory devices, displays, molecular sensors, and photoactuators [8, 9]. It is well known that diarylethenes can reversibly transform from the open-ring isomers to the close-ring isomers upon irradiation with UV light, and their physicochemical properties mainly depend on several factors, such as the categories of heterocyclic moieties, substituents and extension of p- π^* [10,11]. For example, Shoji *et al.* introduced alkyl substituents at the reactive positions of the oxidized dithienyl diarylethenes, which could efficiently accelerate the thermal fading reaction, while introduction of a methyl group at the 4-position of thiophene ring could accelerate the formation of thermal byproducts [12].

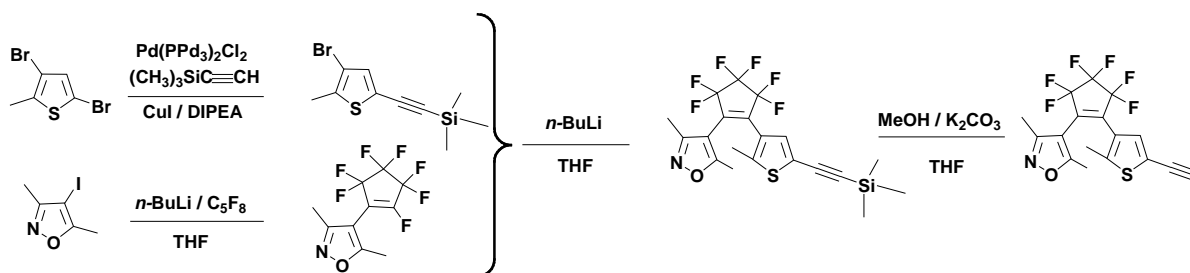
In this work, we synthesized a new unsymmetrical diarylethene 1-[3,5-dimethyl-4-isoxazolyl]-2-[2-methyl-5-acetynyl-3-thienyl] perfluorocyclopentene (**1o**). The synthetic route and the photochromic scheme for **1o** are shown in Scheme 1.



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

Experiments

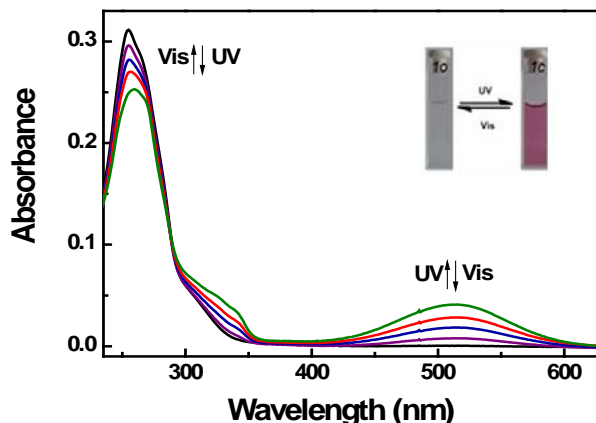
The synthesis route for **1o** was shown in Scheme 2. NMR spectra were recorded on Bruker AV400 (400 MHz) spectrometer with CDCl_3 as the solvent and tetramethylsilane as an internal standard. The structure of **1o** were confirmed by ^1H NMR (400 MHz, CDCl_3 , TMS): 1.95 (d, 6H, $J = 8.0$ Hz, $-\text{CH}_3$), 2.13 (s, 3H, $-\text{CH}_3$), 3.30 (s, 1H, $-\text{C}\equiv\text{CH}$), 7.14 (s, 1H, thienyl-H).

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

Results and Discussion

Photochromism of **1o**

The photochromic behaviors of **1o** ($2.0 \times 10^{-5} \text{ mol L}^{-1}$) induced by photoirradiation were measured in hexane at room temperature. As shown in Fig 1, **1o** exhibited a sharp absorption peak at 255 ($\epsilon = 1.56 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$) nm due to a $\pi\text{-}\pi^*$ transition. Upon irradiation with 297 nm light, a new visible absorption band was observed at 515 ($\epsilon = 2.07 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$) nm with the solution changed from colorless to purple due to the formation of closed-ring isomer **1c**. Reversely, the purple solution could be completely bleached upon illumination with visible light ($\lambda > 500 \text{ nm}$), indicating that **1c** returned to the initial state **1o** and a clear isosbestic point was observed. 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.

Fig. 1. Absorption spectra and color changes of **1o** in hexane

Photochromic Reaction Kinetics

The photochromic cyclization and cycloreversion kinetics of **1o** in hexane were determined by UV-Vis spectra upon alternating irradiation with UV and visible light at room temperature. The cyclization and cycloreversion curves of **1o** were shown in Fig. 2. It can be seen that the relationships between the absorbance and exposal time have good linearity upon irradiation with 297 nm UV light. The results suggesting that the cyclization processes of **1o** belong to the zeroth order reaction when open-ring isomer changed to closed-ring isomer. The slope of every line in Fig. 2 (A) and 2 (B) represents the reaction rate constant (k) of diarylethene **1o** in hexane. So all k of cyclization (k_{o-c} , 10^{-4}) / cycloreversion (k_{c-o} , 10^{-4}) process of diarylethene **1o** can be easily obtained, which are $2.2 \text{ mol L}^{-1} \text{ s}^{-1}$ and $10.1 \text{ mol L}^{-1} \text{ s}^{-1}$ in solution, respectively.

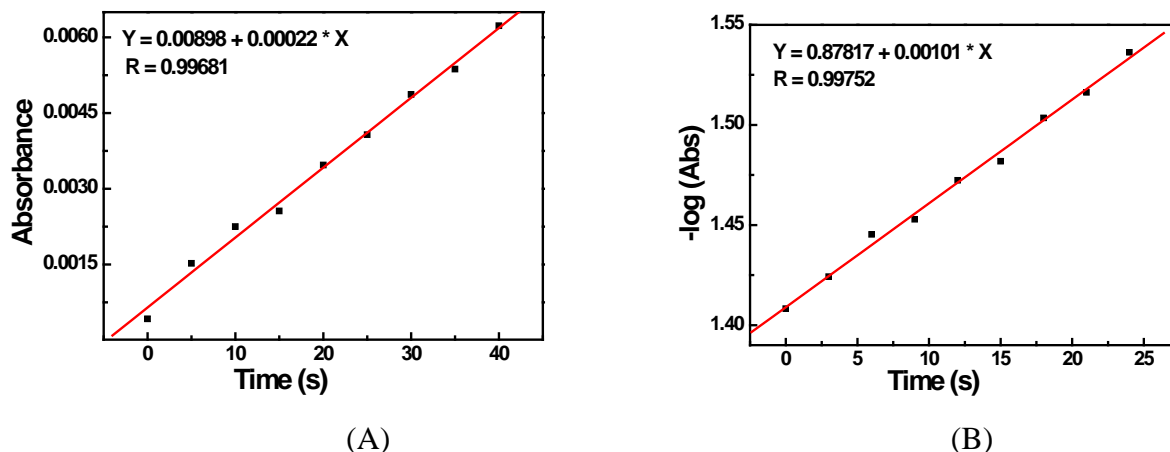


Fig. 2. The cyclization (A) and cycloreversion (B) kinetics of **1o** in hexane.

Fluorescence of **1o**

The fluorescence emission spectra of **1o** in hexane (2.0×10^{-5} mol L⁻¹) were evaluated at room temperature. The emission peak of **1o** in hexane was observed at 441 nm when excited at 285 nm (Fig. 3). Upon irradiation with UV light, the emission intensity of **1o** was decreased notably due to the formation of the weak fluorescent closed-ring isomer **1c**. The back irradiation by visible light regenerated the open-ring isomer **1o** and recovered the original emission spectra.

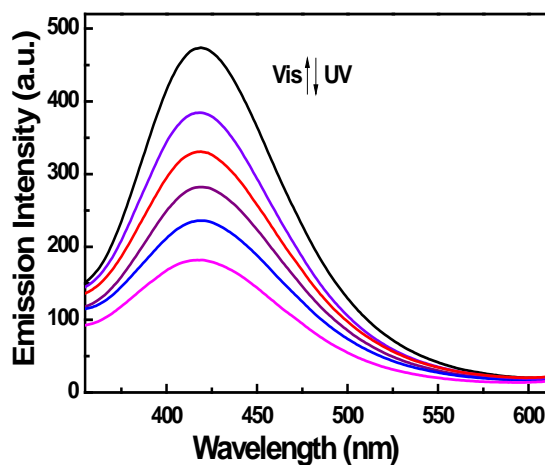


Fig. 3. Emission intensity changes of **1o** upon irradiation UV at room temperature: in hexane

Summary

In summary, a novel photochromic diarylethene was synthesized. **1o** exhibited good photochromism and notable fluorescence switch in hexane solution. The results are useful for the design of diarylethene with efficient and excellent characteristic.

Acknowledgement

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