

Synthesis and Properties of a New Unsymmetrical Diarylethene 1-{2-methyl-[5-(4-trifluoromethyl)phenyl]-3-thienyl}-2-[[2-methyl-5-(3-chlorine)phenyl]-3-thienyl]perfluorocyclopentene

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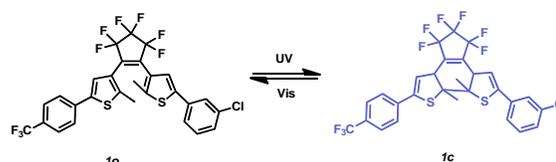
Abstract—A novel unsymmetrical isomeric photochromic diarylethene, 1-{2-methyl-[5-(4-trifluoromethyl)phenyl]-3-thienyl}-2-[[2-methyl-5-(3-chlorine)phenyl]-3-thienyl]perfluorocyclopentene, was designed and synthesized. Its fluorescent and photochromic properties were also investigated in detail. The compound exhibited excellent photochromism, changing from colorless to blue after irradiation with UV light in solution. The results showed that it exhibited excellent photochromism.

Keywords-photochromism; diarylethene; kinetics

I. INTRODUCTION

Photochromic materials are a family of compounds which can undergo reversible photo-switches between two different isomers having remarkably various properties [1]. Photochromic materials have been extensively investigated due to their widely applications in various of optical storages, such as multi wavelength optical storage [2], near-field optical storage [3] and two-photon 3D optical storage [4], etc. Among various types of photochromic compounds, diarylethenes have been investigated due to the good fatigue resistance, fairly high photocyclization quantum yields, high reversibility of the forward and reversed photo processes triggered by irradiation with light of different wavelengths and thermal stability of the products [5,6]. Up to date, the design and synthesis of new photochromic compounds is still an active area of research [7].

In previous papers, numerous studies on the synthesis and investigation of their photochromic properties of diarylethene derivatives have been carried out [8,9]. To the best of our knowledge, Diarylethenes bearing phenyl groups are the most common class of examples because they can be rapidly substituted by different electron-donating/withdrawing substituents at different positions of the benzene ring, which influences the optoelectronic properties of those diarylethenes. In this work, a new unsymmetrical 1o was synthesized. Then, the photochromic properties and fluorescence properties were discussed and investigated in detail. The photochromic reaction of 1o is shown in Scheme 1.

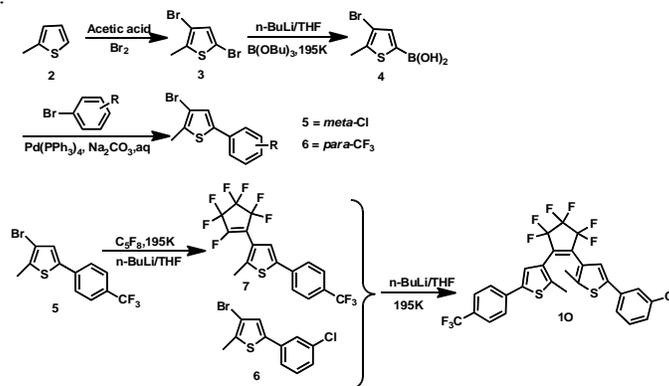


Scheme 1. Photoisomerization of 1o

II. EXPERIMENTS

A. Synthesis of 1o.

The synthetic route for diarylethene 1o was shown in Scheme 2. The structure of compound diarylethene 1o was characterized by ^1H NMR spectroscopy. ^1H NMR (400 MHz, CDCl_3 , TMS): δ 2.42 (s, 3H, $-\text{CH}_3$), 7.49 (s, 1H, phenyl-H), 7.12 (s, 1H, thiophene-H), 7.25-7.30 (m, 3H, phenyl-H).



Scheme 2. Synthesis of 1o

III. RESULTS AND DISCUSSION

A. Photochromism of 1o in acetonitrile solution.

The photochromic behaviours of diarylethene were investigated in acetonitrile solution ($(2.0 \times 10^{-5} \text{ mol L}^{-1})$). Diarylethene showed good photochromic properties and could be toggled between their colourless open-ring isomers

(1o) and coloured closed-ring isomers (1c) by alternating irradiation with UV light and appropriate wavelength visible light, as monitored using UV-Vis absorption. The absorption spectroscopic change of diarylethene 1 induced by photoirradiation at room temperature is shown in Figure 1. The absorption maximum of the colourless open-ring isomer (1o) was observed at 296 nm (ϵ , $5.67 \times 10^4 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$) in acetonitrile solution. Upon irradiation with 254 nm light, the colourless solution turned blue with a new broad absorption band centred at 592 nm. The blue colour is a result of the formation of the closed-ring isomer (1c). The blue coloured solution returned to colourless upon irradiation with visible light ($>450 \text{ nm}$), which indicates that 1c returned to the initial open-ring isomer (1o). From the above description, we can easily get a conclusion that 1o showed excellent photochromic properties.

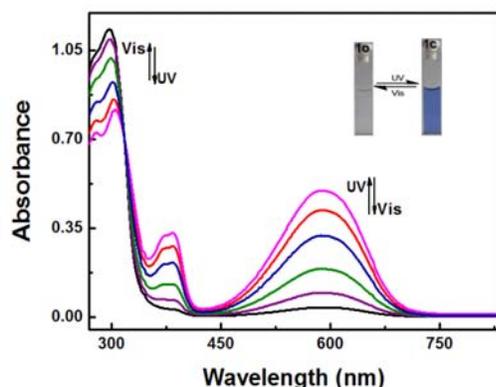


Figure 1. Absorption spectra upon alternating irradiation with UV-Vis light of 1o in acetonitrile ($2.0 \times 10^{-5} \text{ mol L}^{-1}$).

B. 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 exposal 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 opening isomers changed to closed-ring isomers. 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 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

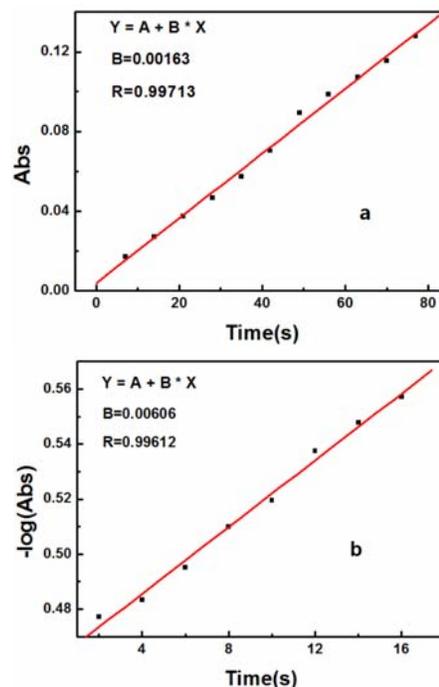


Figure 2. The cyclization (a) and cycloreversion (b) kinetics of 1o in acetonitrile ($2.0 \times 10^{-5} \text{ mol L}^{-1}$).

C. Fluorescence of diarylethenes.

The fluorescence modulation is becoming an intriguing approach, which can be widely applied to molecular-scale optoelectronics, ion-sensors, and digital photoswitches [10,11]. As most reported diarylethenes [12], 1 exhibited fluorescence in acetonitrile. Its fluorescence spectra were measured at room temperature using a Hitachi F-4600 spectrophotometer, and the result is shown in Figure 3. As shown in Figure 3, when irradiated by light of 297 nm, the photocyclization reaction was carried out and the lower-fluorescent closed-ring form of the compound was produced. The back irradiation by appropriate wavelength visible light ($\lambda > 500 \text{ nm}$) regenerated the open-ring forms of diarylethene 1o and recovered the original emission spectra.

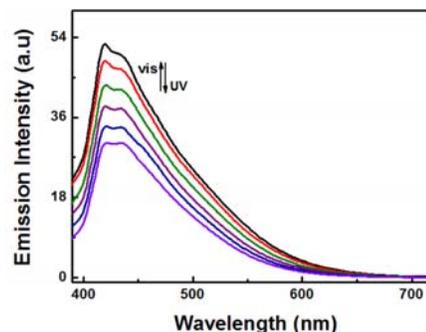


Figure 3. Fluorescence spectral changes of 1 in acetonitrile upon irradiation with 297 nm UV light

IV. SUMMARY

A new unsymmetrical photochromic diarylethene was synthesized. Its photochromic property and the kinetic reactions were investigated by UV-Vis spectra both in acetonitrile solution. The present results indicated that the diarylethene has reversible photochromism. Furthermore, the compound also functioned as a fluorescence switch.

ACKNOWLEDGMENT

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