

## Photochromism of a new symmetrical diarylethene with a trimethylsilylacetylene unit

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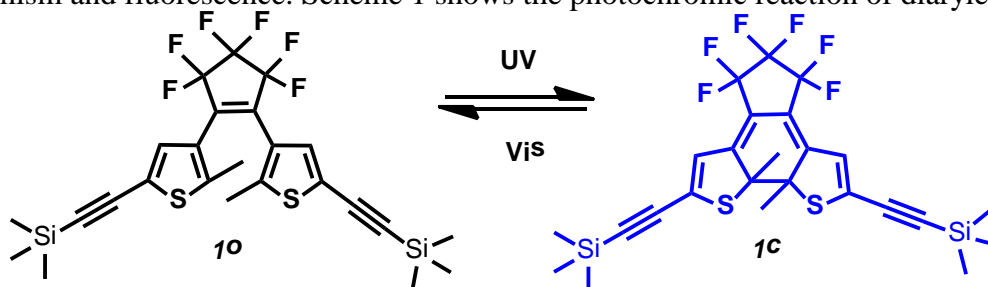
**Keywords:** Photochromism, Diarylethene, Fluorescence switching, Trimethylsilylacetylene

**Abstract.** A new symmetrical photochromic diarylethene **1**, 2-bis(2-(trimethylsilylacetylene)-3-thienyl)perfluorocyclopentene (**1o**) based on a dithiophene structure has been constructed, and the photochromic and fluorescent properties of **1** were investigated. The results indicated diarylethene **1o** showed good photochromism and notable fluorescence switching, which make it possible potential application in optical recording.

### Introduction

During the past decade, a number of works were focused on the photochromic compounds due to their potential applications in optical switches and memories [1-4]. Since the development of the photochromic compounds, diarylethenes have drawn greater attention on photocontrollable elements in molecular devices and switches [5-6]. Because of their distinguished thermal stability [7] and remarkable fatigue [8] resistance of the cyclization and cycloreversion reactions, Photochromic materials can reversibly interconvert between open ring and closed ring conformations [9]. Up to now, some researches about photochromic diarylethenes containing heteroaryl moieties including benzothiophene, benzofuran, thiophene, thiazole, pyrrole, benzene, pyridine, and indole [10] have been put into effect. Moreover, diarylethene derivatives bearing a dithiophene skeleton is the most promising because either the open ring or the closed ring isomer exhibits excellent properties about thermal stability, fatigue resistance, response and reactivity in solution [11]. However, the study about diarylethene bearing a dithiophene skeleton is extremely rare reported.

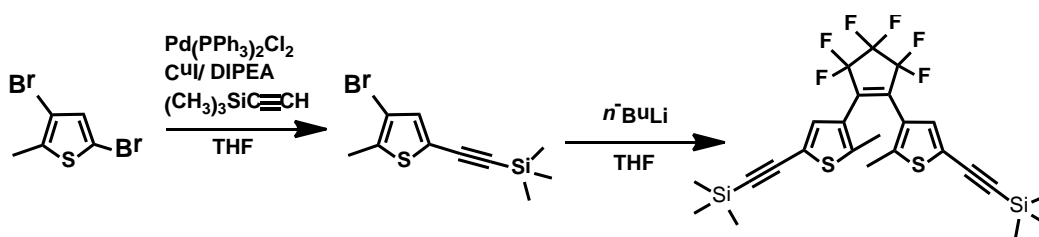
In the present report, we synthesized a photochromic symmetrical diarylethene **1o** with good photochromism and fluorescence. Scheme 1 shows the photochromic reaction of diarylethene **1o**.



Scheme 1. Photochromism of **1o**

### Experiment

The synthetic route used to obtain **1o** is shown in Scheme 2. **1o** was facilely synthesized as a canary solid with a 52% yield by the method in some literatures [2, 11]. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 0.27 (s, 18H, -CH<sub>3</sub>), 1.90 (s, 6H, -CH<sub>3</sub>), 7.22 (s, 2H, thiophene-H).



Scheme 2. The synthetic route of *1o*

## Results and discussion

**Photochromism of *1o*.** The photochromic properties of *1o* were measured. Fig. 1 shows the absorption spectra and color changes of *1o* in hexane solution ( $2.0 \times 10^{-5} \text{ mol L}^{-1}$ ). *1o* exhibited a sharp absorption peak at 268 nm ( $\epsilon = 2.62 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ ). Upon irradiation with 297 nm UV light, the color of the solution turned from colorless to blue, accompanied by new broad absorption bands appearing at 583 nm ( $\epsilon = 6.79 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$ ). This can be assigned to the formation of the closed-ring isomer *1c*. When *1c* was irradiated with visible light ( $\lambda > 510 \text{ nm}$ ), the blue solution turned colorless. This indicates that the photochromism of *1o* is reversible.

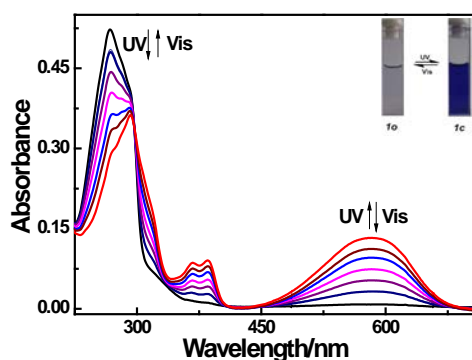


Fig. 1. Absorption spectra and color changes of *1o*

**Photochromic reaction kinetics in hexane solution.** Fig. 2. (A) / Fig. 2. (B) shows the photochromic cyclization / cycloreversion kinetics of *1o* in hexane, respectively. The photochromic kinetics were obtained by the photochromism of *1o* upon irradiation with UV/Vis. It can be seen from Fig. 2. that the absorbance /  $-\log(\text{Abs})$  and exposure time have good linearity and the cyclization / cycloreversion processes of *1o* belong to the zeroth / first order reaction. The reaction rate constant ( $k$ ) of *1o* could be determined from the slope of every line in Fig. 2. (A) and Fig. 2. (B). Hence, the  $k$  of cyclization ( $k_{o-c}$ ,  $10^{-3}$ )/cycloreversion ( $k_{c-o}$ ,  $10^{-2}$ ) kinetics of *1o* are  $0.22 \text{ mol L}^{-1} \text{ s}^{-1}$  and  $0.10 \text{ s}^{-1}$ , respectively.

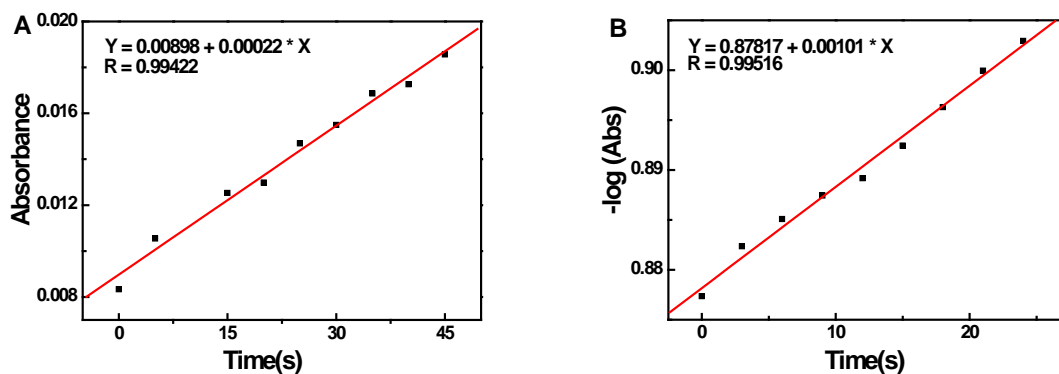


Fig. 2. The cyclization (A) and cycloreversion (B) kinetics of *1o*

**Fluorescence of *1o*.** The fluorescence properties of *1o* in hexane solution were measured. Fig. 3. shows the emission spectral changes of *1o* at 459 nm in hexane ( $2.0 \times 10^{-5} \text{ mol L}^{-1}$ ) upon

photoirradiation with 297 nm light when excited at 290 nm. Obviously, the fluorescence of *Io* could be modulated by light, reversibly [12-14]. Once irradiated with 297 nm light, the emission intensity of *Io* would decrease slowly along with the forming of closed-ring isomer [13]. When further irradiated with 297 nm light for 2 min, the solution of *Io* arrived at the photostationary state in hexane. At the same time, the emission intensity of *Io* was quenched to ca. 70%. Relatively, the fluorescence of *Io* could be recovered by irradiation with appropriate visible light ( $\lambda > 510$  nm). Therefore, the fluorescent modulation efficiency of *Io* was 30% in hexane. The result showed that the change of the emission intensity of *Io* is reversible and *Io* is useful for application as the fluorescence switches [14].

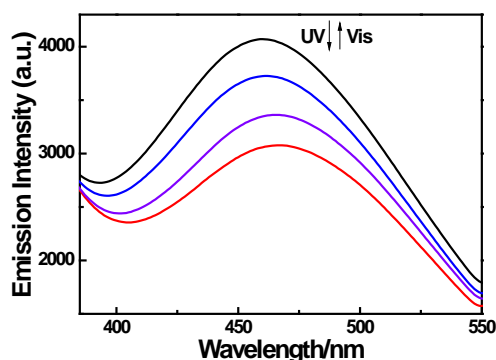


Fig. 3. Emission intensity changes of *Io* upon irradiation with 297 nm UV light at room temperature in hexane ( $2.0 \times 10^{-5}$  mol L<sup>-1</sup>)

## Summary

In brief, a novel symmetrical diarylethene containing two 2-menthyl-5-(trimethylsilylacetylene)-3-thienyl units has been successfully synthesized and fully characterized for the first time. The diarylethene exhibited excellent photochromism in solution. Meanwhile, the fluorescence of the opening diarylethene is much more stronger than closed-ring diarylethene. The results suggested that the diarylethene could apply to optical recording on account of their fascinating properties.

## Acknowledgement

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