Photochromism of a new symmetrical diarylethene with a trimethylsilylacetylene unit

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Abstract. A new symmetrical photochromic diarylethene 1o, 2–bis(2–methyl-5-(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, diarylenes 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 diarylenes 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](image)

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]. 'H NMR (400 MHz, CDCl₃), δ (ppm): 0.27 (s, 18H, –CH₃), 1.90 (s, 6H, –CH₃), 7.22 (s, 2H, thiophene-H).
Results and discussion

Photochromism of 10. The photochromic property of 10 was measured. Fig. 1 shows the absorption spectra and color changes of 10 in hexane solution (2.0 × 10⁻⁵ mol L⁻¹). 10 exhibited a sharp absorption peak at 268 nm (ε = 2.62 × 10⁴ L mol⁻¹ cm⁻¹). Upon irradiation with 297 nm UV light, the color of solution turned from colourless to blue, accompanied with a new broad absorption bands appeared at 583 nm (ε = 6.79 × 10³ L mol⁻¹ cm⁻¹). This can be assigned to form the closed-ring isomer 1c. When 1c was irradiated with visible light (λ > 510 nm), the blue solution turned to colorless. This indicates that photochromism of 10 is reversible.

Fluorescence of 10. The fluorescence properties of 10 in hexane solution were measured. Fig. 3. shows the emission spectral changes of 10 at 459 nm in hexane (2.0 × 10⁻⁵ mol L⁻¹) upon
photoirradiation with 297 nm light when excited at 290 nm. Obviously, the fluorescence of \(I_0\) could be modulated by light, reversibly [12-14]. Once irradiated with 297 nm light, the emission intensity of \(I_0\) 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 \(I_0\) arrived at the photostationary state in hexane. At the same time, the emission intensity of \(I_0\) was quenched to ca. 70%. Relatively, the fluorescence of \(I_0\) could be recovered by irradiation with appropriate visible light (\(\lambda > 510\) nm). Therefore, the fluorescent modulation efficiency of \(I_0\) was 30% in hexane. The result showed that the change of the emission intensity of \(I_0\) is reversible and \(I_0\) is useful for application as the fluorescence switches [14].

![Graph](image-url)

**Fig. 3.** Emission intensity changes of \(I_0\) upon irradiation with 297 nm UV light at room temperature in hexane (2.0 \(\times\) 10\(^{-5}\) mol L\(^{-1}\))

**Summary**

In brief, a novel symmetrical diarylethene containing two 2-menthy l-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 open-ing diraylethene is much more stronger than closed-ring diraylethene. The results suggested that the diarylethene could apply to optical recording on account of their fascinating properties.

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**References**


