

A new unsymmetrical dithienylethene contains a protecting aldehyde group

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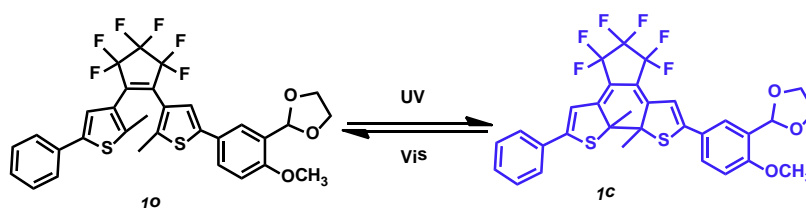
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Abstract. A novel unsymmetrical isomeric photochromic dithienylethene, 1 - (2-methyl- 5- phenyl -3- thienyl)-2- {[2-methyl-5-(3-1,3-dioxolane-4-methoxyl)phenyl]-3-thienyl}perfluorocyclopentene (**1o**), was designed and synthesized. The photochromic and fluorescent properties of **1o** were also studied. It is demonstrated that **1o** exhibited excellent photochromism in acetonitrile solution accompanied with colorless solution changed to blue when irradiation with UV light

Introduction

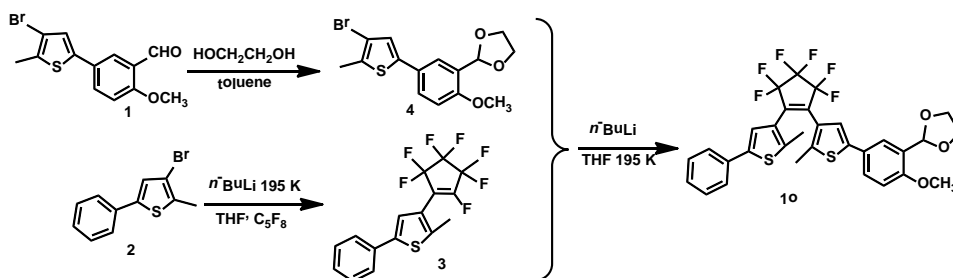
In the past decade, various photochromic materials, such as diarylethenes [1], azobenzenes[2] and spirobenzopyrans[3], have been receiving much attentions. Between most photochromic compounds, diarylethene derivatives become outstanding representatives because they offer enhanced thermal stability of the two interconverting conformations [4], heightened fatigue resistance [5], and remarkable fatigue resistance. Therefore they can be potentially used in photochromic molecules in optical memories, switches, and actuators (or molecular machines) and so on [4-6]. Meanwhile, diarylethenes based on phenyl groups have aroused wide concern because they can increase the conversion efficiency and the absorbance of photochromic molecule at the photostationary state (PSS) [7]. Herein, we report a new unsymmetrical **1o** with phenyl group and a protecting aldehyde group which could achieve deprotection and then extend the molecular for other applications. The photochromic and fluorescent properties of **1o** in solution were presented here.



Scheme 1. Photoisomerization of **1o**

Experiments

Synthesis of 1o. As shown in Scheme 2, 3- Bromo- 2- methyl- 5-(3-formyl -4 - methoxyl-phenyl) thiophene (**1**) and 3-Bromo-2-methyl-5-phenyl-3-thiophene (**2**) were obtained through Suzuki coupling reaction [8], (1-Fluorine-2-methyl-5-phenyl-3-thiophene)perfluorocyclopentene (**3**) was synthesized from **2** consistent with the previous literature [9]. then the formyl was protected with glycol to generate compound **4**. Finally, compound **1o** was obtained by addition with **3** to the lithiation of **4** in THF at 195K [10]. The compound **1o** was characterized by ¹H NMR spectroscopy. ¹H NMR (400 MHz, CDCl₃, TMS): δ 1.94 (s, 6H), 3.86(s, 3H), 4.02 (t, 2H, *J* = 6Hz), 4.13 (t, 2H, *J* = 6Hz), 6.13(s, 1H), 6.88 (d, 1H, *J* = 4Hz), 7.19 (s, 1H), 7.28 (d, 2H, *J* = 12Hz), 7.36 (t, 2H, *J* = 8Hz), 7.46-7.49 (m, 1H), 7.52 (s, 1H), 7.54 (s, 1H), 7.71 (d, 1H, *J* = 4Hz).



Scheme 2. Synthesis of 1o

Results and discussion

Photochromic studies. The absorption band centered at 289 nm (ϵ , $3.00 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$) of 1o was ascribed to $\pi \rightarrow \pi^*$ transition. Upon irradiation with 297 nm light, the band centered at 289 nm gradually decreased, and a new absorption band centered 592 nm (ϵ , $1 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$) progressively increased due to the cyclization of 1o to produce ring-closed isomer 1c. Meanwhile, the colorless solution of 1o turned to blue. On the other hand, the blue solution of 1c turned to colorless and the UV-vis absorption spectra of 1c displayed reversed changes to 1o upon irradiation with visible light ($\lambda > 500 \text{ nm}$) of 1c solution.

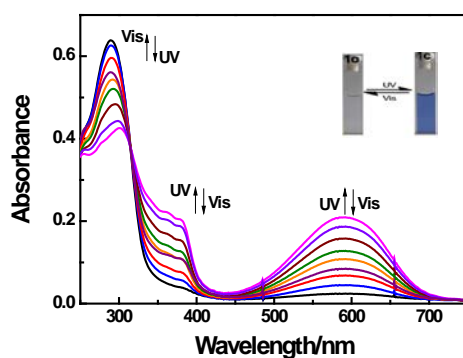


Fig. 1 UV-vis absorption spectral changes of 1o in acetonitrile ($2.0 \times 10^{-5} \text{ mol L}^{-1}$) upon alternating irradiation with UV and Vis light.

Photochromic reaction kinetics studies In order to investigate the relationships between the absorbance and exposure time, we studied the cyclization/cycloreversion kinetics of 1o in acetonitrile solution by UV-vis spectra (Fig. 2). As shown in Fig. 2, for both cyclization and cycloreversion reactions of 1o, the absorbance and exposure time formed good linear dependence. It is well known that the gradient of the line can reflect the reaction rate constant (k). As a result, the cyclization process of 1o in acetonitrile is a zeroth-order reaction and the cycloreversion reaction belongs to the first-order reaction during the cycloreversion of 1c in acetonitrile.

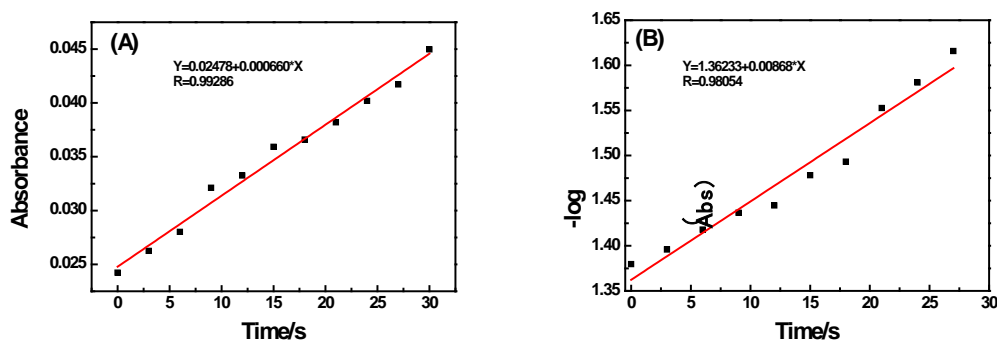


Fig. 2 The cyclization (A) and cycloreversion (B) kinetics of 1o in acetonitrile ($2.0 \times 10^{-5} \text{ mol L}^{-1}$).

Fluorescent studies Fluorescence switching of diarylethene can be used in molecular-scale optoelectronics, and the application of many diarylethenes has been reported [11-15]. Fluorescence

spectra of **1o** were measured at room temperature using a Hitachi F-4600 spectrophotometer in acetonitrile solution. From Fig. 3, the lower-fluorescent ring-closed species **1c** was produced upon irradiated by 297 nm light, and the band centered at 483 nm continually decreased in emission intensity due to the photocyclization reaction $1o \rightarrow 1c$. Instead, if irradiation by visible light ($\lambda > 500$ nm), **1c** changed into **1o** accompanied with the original fluorescence spectrum recovered.

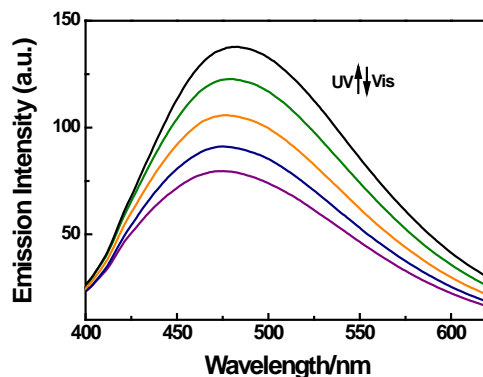


Fig. 3 Fluorescence spectral changes of **1o** in acetonitrile upon irradiation with UV and Vis light

Conclusion

A new unsymmetrical photochromic diarylethene **1o** was synthesized. It is a reversible transformation of a compound between two isomers owning different absorption spectrum induced by UV-Vis light. The studies of photochromic properties and the kinetic reactions in acetonitrile solution illustrated that **1o** exhibited predominantly reversible photochromism. At the same time, the diarylethene can be used as a fluorescent switchable molecule.

Acknowledgment

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