

# Synthesis and Properties of 1-[2-methyl-5-(9-anthracyl)-3-thienyl]-2-[2-methyl-5-(4-n-pentyl phenyl)-3-thienyl]perfluorocyclopentene

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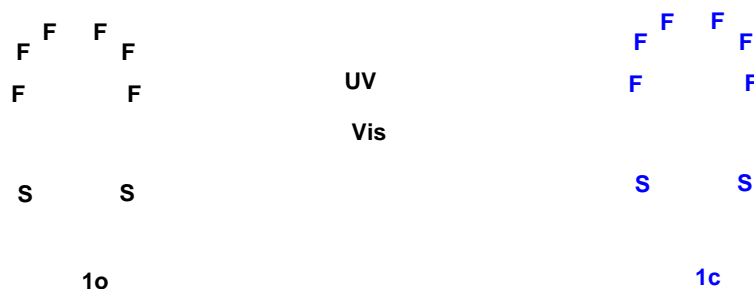
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**Abstract.** An unsymmetrical photochromic diarylethene, 1-(2-methyl-5-(9-anthracyl)-3-thienyl)-2-[2-methyl-5-(4-n-pentylphenyl)-3-thienyl] perfluorocyclopentene was synthesized at first. Its photochromic and fluorescence properties were investigated in detail. This compound exhibited reversible photochromism, changing from colorless to blue after irradiation with UV light in solution. Moreover, the diarylethene showed fluorescence switches upon irradiation with UV/Vis light.

## Introduction

Photochromism is the term used for a reversible photo-induced transformation of a molecule between two isomers whose absorption spectra are of distinguishable difference [1,2]. During the reversible photoisomerization, the physical properties of photochromic compounds, such as absorption spectra and fluorescence, can be tuned by light. These reversible changes can be potentially used for optical data storage, photoswitching devices [3,4]. Over the past several decades, an increasing number of photochromic compounds have been synthesized because of their potential applications in optoelectronic devices, such as photochemical reactivity, thermal stability, and fatigue resistance [5,6]. In particular, diarylethenes with different substituted aryl group can be readily modulated to influence the optoelectronic properties of corresponding diarylethenes. An unsymmetrical photochromic diarylethene 1-(2-methyl-5-(9-anthracyl)-3-thienyl)-2-[2-methyl-5-(4-n-pentylphenyl)-3-thienyl] perfluorocyclopentene has been synthesized. The photochromic reaction of 1o is shown in Scheme 1.

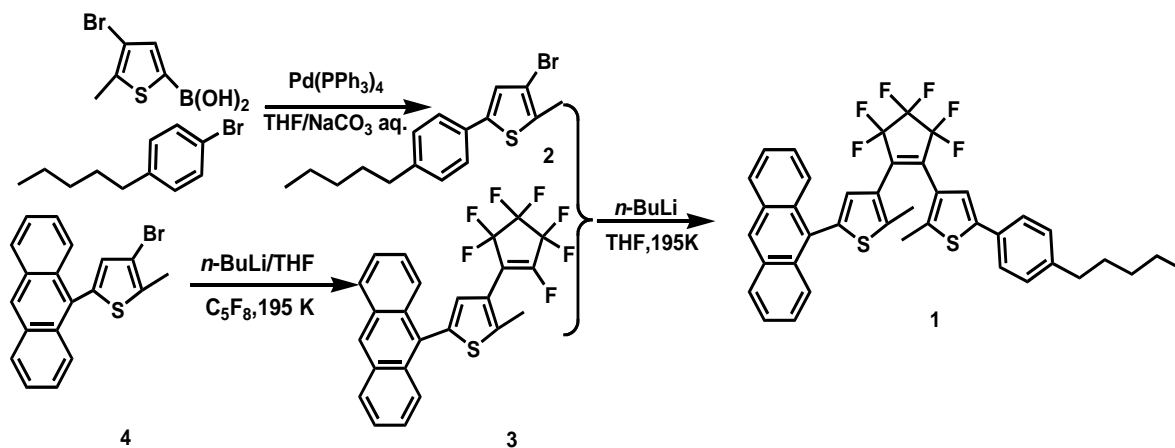


Scheme 1. Photochromism of 1o

## Experiments

1o was synthesized by the method as shown in Scheme 2. It was synthesized according to the similar procedure Pu et al [6]. Under an argon gas atmosphere, dissolving compound 2 in dry THF and then n-butyllithium was added at 195 K. Stirring was continued for 0.5 h, then compound 3 was added and the mixture was stirred for 1 h at this low temperature. The crude product was purified by column chromatography. The structure of 1o was characterized by NMR spectroscopy. <sup>1</sup>H NMR spectra were recorded on Bruker AV400 (400 MHz) spectrometer with CDCl<sub>3</sub> as the solvent and

tetramethylsilane as an internal standard.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ),  $\delta$  (ppm) 0.83 (t, 3H,  $J=8.0$  Hz,  $-\text{CH}_3$ ), 1.27-1.28 (m, 4H,  $-\text{CH}_2$ ), 1.54-1.56 (m, 2H,  $-\text{CH}_2$ ), 2.04 (s, 6H,  $-\text{CH}_3$ ), 2.55 (t, 2H,  $J=8.0$  Hz,  $-\text{CH}_2$ ), 7.14 (s, 1H, phenyl-H), 7.15 (d, 2H,  $J=8.0$  Hz, thienyl-H), 7.41 (d, 3H,  $J=8.0$  Hz, phenyl-H), 7.50-7.55 (m, 3H), 7.61 (t, 2H,  $J=8.0$  Hz, phenyl-H), 7.69 (s, 1H, phenyl-H), 7.82 (d, 1H,  $J=8.0$  Hz, phenyl-H), 8.06 (d, 1H,  $J=8.0$  Hz, phenyl-H), 8.63 (d, 1H,  $J=8.0$  Hz, phenyl-H), 8.69 (d, 1H,  $J=8.0$  Hz, phenyl-H).



Scheme 2. The synthesis route of 1o

## Results and Discussion

### Photochromism of 1o

The photochromic behaviors of diarylethene 1o induced by photoirradiation at room temperature were measured in hexane solution ( $2.0 \times 10^{-5} \text{ mol L}^{-1}$ ). As shown in Fig.1, compound 1o exhibited an absorption peak at 288 nm ( $\epsilon = 3.03 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ ) in hexane solution. Upon irradiation with 297 nm UV light, the colorless solution of 1o turned to blue with a new visible absorption band centered at 580 nm ( $\epsilon = 1.42 \times 10^4 \text{ mol}^{-1} \text{ L cm}^{-1}$ ) attributed to the closed-ring isomer 1c. The blue colored solution reverted to colorless upon irradiation with visible light ( $\lambda > 450 \text{ nm}$ ), indicating that 1c returned to the initial state 1o, and a clear isosbestic point was observed at 309 nm.

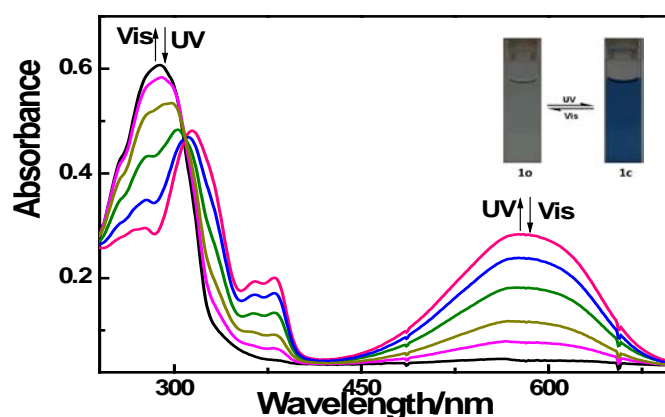


Fig. 1 Absorption spectral changes of 1o in hexane.

### Photochromic Reaction Kinetics in Hexane Solution.

The photochromic cyclization/cycloreversion kinetics of 1o in hexane solution ( $2.0 \times 10^{-5} \text{ mol L}^{-1}$ ) was determined by irradiation with UV light and appropriate wavelength 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 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 line in Fig. 2A represents the reaction rate constant ( $k$ ) of 1o in hexane solution. So  $k$  of cyclization process ( $k_{o-c}$ ,  $10^{-3}$ ) of 1o can be easily obtained. As shown in Fig. 2B, during the cycloreversion of 1c, the relationship between  $-\log(\text{Abs.})$  and exposal time also behave perfect linearity, indicating that the cycloreversion process belong to the first order reaction.

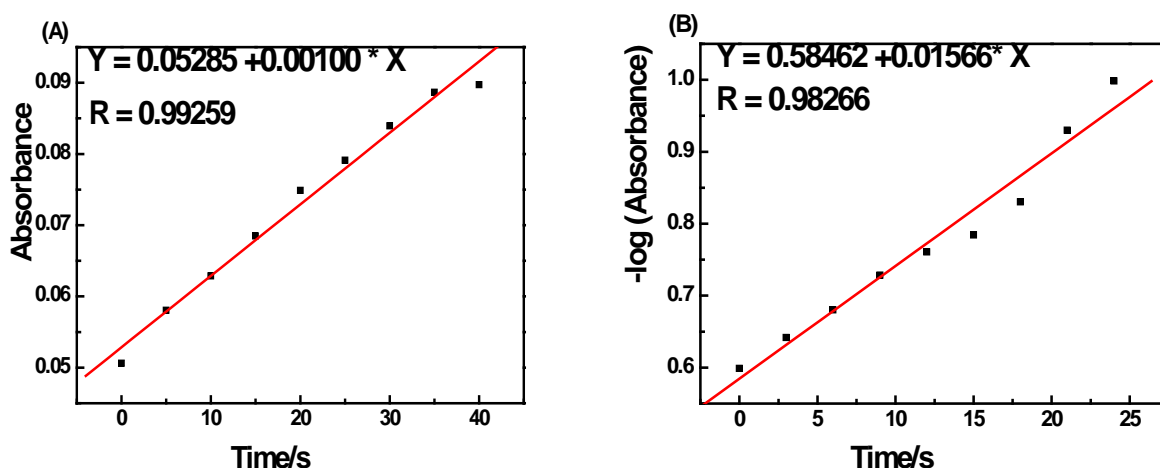


Fig. 2 The cyclization kinetics (A) and cycloreversion kinetics (B) of 1o in hexane.

### Fluorescence of 1o

Fluorescent properties can be useful not only in molecularscale optoelectronics, but for digital photoswitching of fluorescence. In this work, the fluorescent properties of the diarylethene in hexane ( $2.0 \times 10^{-5} \text{ mol L}^{-1}$ ) were measured using a Hitachi F-4600 spectrophotometer, and it could be clearly seen that the hexane solution of 1o exhibited relatively strong fluorescence at 371 nm when excited at 297 nm. The fluorescence intensity decreased along with the photochromism from open-ring isomers to closed-ring isomers upon irradiation with 297 nm UV light, due to producing the weak fluorescence closed-ring isomer. The back irradiation by appropriate wavelength visible light regenerated its open-ring isomer and recovered the original emission intensity. It exhibited that diarylethene 1o could show good fluorescence switches between the open-ring isomer and closed-ring isomer in hexane as shown in Fig 3.

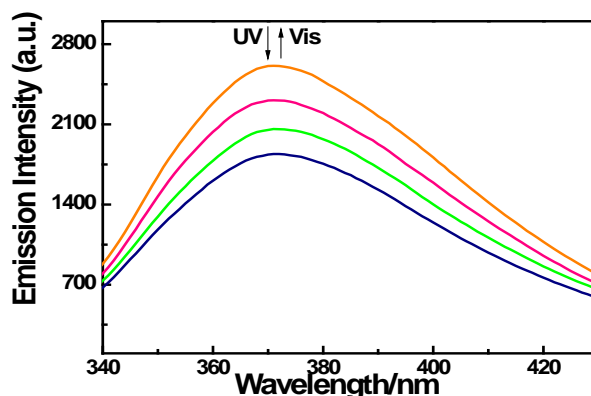


Fig. 3 Fluorescent intensity changes of 1o in hexane solution.

## Summary

A new unsymmetrical photochromic diarylethene was synthesized. Its photochromic property and the kinetic reactions were investigated by UV/Vis spectra in hexane solution. Furthermore, the diarylethene also functioned as a fluorescence switch. What is more, the kinetic experiments illustrated that the cyclization/cycloreversion process of this compound was determined to be the zeroth/first reaction.

## Acknowledgment

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