

# Synthesis and Properties Study of 1-(2,4-dimethoxyl-5-pyrimidinyl)-2-[2-methyl-5-(3-methyl)-phenyl-3-thienyl] Perfluorocyclopentene

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**Abstract**—A novel photochromic diarylethene bearing a pyrimidine moiety, 1-(2,4-dimethoxyl-5-pyrimidinyl)-2-[2-methyl-5-(3-methyl)-3-thienyl]perfluorocyclopentene has been synthesized. Its properties, including photochromic and fluorescent behaviors, have been investigated. The compound exhibited remarkable photochromism, changing from colorless to red after irradiation with UV light in solution. The cyclization/cycloreversion process of the compound was determined to be the zeroth/first order reaction. The results indicated that the pyrimidine moiety played a very important role during the process of photoisomerization reactions.

**Keywords**-diarylethene; photochromism; pyrimidine; fluorescence

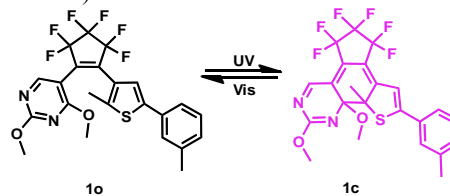
## I. INTRODUCTION

Photochromic molecules attract much attention from fundamental as well as practical points of view because of their potential for applications to optical devices, such as optical memories and switches [1-3]. Among the photochromic compounds, diarylethenes are regarded as the best candidates for such devices, owing to their excellent thermal stability, fatigue resistance, and easy monitoring using UV/vis spectroscopy [4,5].

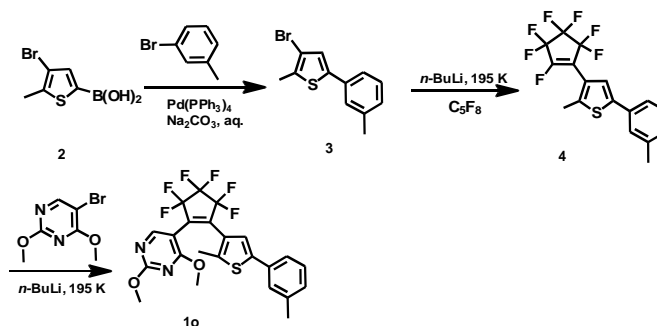
As components of molecular electronics, it is desirable to develop various types of molecular switch devices with diarylethene compounds. During the past decades, there have been important achievements in the synthesis of new families of organic photochromic molecules [3,6,7]. For example, the diarylethenes having two thiophenes [8], furans [9] and thiazoles [10-12] exhibit excellent thermal stability, and the ones with two indoles, pyrroles, and benzenes are thermally unstable [12,13]. Nevertheless, the hexatriene backbones necessary for the versatility of the diarylethenes reported so far have been mostly limited to the five-membered aryl rings. Up to date, the reports about diarylethenes with six-membered pyrimidine rings are still very rare. In this work, we synthesized a new diarylethene bearing a pyrimidine moiety, namely 1-(2,4-dimethoxyl-5-pyrimidinyl)-2-[2-methyl-5-(3-methyl)-3-thienyl]perfluorocyclopentene (1o). Its photochromic reactivity and fluorescence were investigated in detail. The photochromic reaction of diarylethene 1 is shown in Scheme 1.

## II. EXPERIMENTS

The synthetic route for the diarylethene 1 is shown in Scheme 2. Suzuki coupling of the 9-bromophenanthrene with a thiophene boronic acid 2 gave the compound 3. Then, compound 3 was lithiated and coupled with perfluorocyclopentene to give mono-substituted perfluorocyclopentene derivative 4. Finally, 5-bromo-2,4-dimethoxypyrimidine was lithiated and then coupled with compound 4 to give the unsymmetrical diarylethene derivative 1o. The structure of diarylethene 1o was confirmed by <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS): δ 2.03 (s, 3H, -CH<sub>3</sub>), 2.39 (s, 3H, -CH<sub>3</sub>), 3.73 (s, 3H, -OCH<sub>3</sub>), 4.01 (s, 3H, -OCH<sub>3</sub>), 7.11 (d, 1H, *J* = 8.0 Hz, benzene-H), 7.18 (s, 1H, thiophene-H), 7.26-7.45 (m, 3H, benzene-H), 8.35 (s, 1H, pyrimidine-H).



Scheme 1. Photochromism of diarylethene 1.



Scheme 2. Synthetic route for the compound 1o.

## III. RESULTS AND DISCUSSION

### A. Photochromism of Diarylethene

The changes in the absorption spectra of diarylethene 1o induced by photoirradiation at room temperature in hexane

were shown in Figure 1. Upon irradiation with 297 nm UV light, the colorless solution of 1o turned to red with a new visible absorption band centered at 524 nm ( $\epsilon = 2.68 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$ ) attributable to the closed-ring isomer 1c. The red 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 307 nm.

### B. Photochromic reaction kinetics in hexane solution.

The photochromic cyclization/cycloreversion kinetics of 1o in hexane were determined by UV-Vis spectra upon alternating irradiation with UV and appropriate wavelength visible light at room temperature. The cyclization and cycloreversion curves of 1o were shown in Figure 2 and Figure 3. It can be seen that the relationships between the absorbance and exposal time have good linearity upon irradiation with 297 nm UV light. It is demonstrating that the cyclization processes of 1o belong to the zeroth order reaction when open-ring isomer changed to closed-ring isomer. The slope of every line in Figure 2 and Figure 3 represents the reaction rate constant ( $k$ ) of diarylethene 1o in hexane. So all  $k$  of cyclization ( $k_{o-c}$ ,  $10^{-3}$ ) / cycloreversion ( $k_{c-o}$ ,  $10^{-1}$ ) process of diarylethene 1o can be easily obtained, which are  $1.50 \text{ mol L}^{-1} \text{ s}^{-1}$  and  $1.09 \text{ s}^{-1}$  in solution, respectively. As shown in Figure 3, 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.

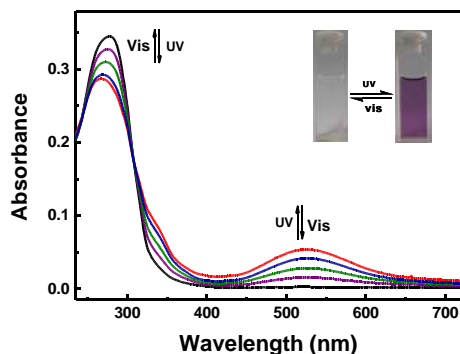


Figure 1. Absorption spectra and color change of diarylethene 1o with stimulation of 297 nm light in hexane ( $2.0 \times 10^{-5} \text{ mol L}^{-1}$ ) at room temperature.

### C. Fluorescence of Diarylethene.

The concentration dependence on the fluorescence spectrum of diarylethene 1o was measured in hexane at room temperature, as shown in Figure 4. When the concentration of diarylethene 1o in hexane was increased from  $1.0 \times 10^{-6} \text{ mol L}^{-1}$  to  $1.0 \times 10^{-4} \text{ mol L}^{-1}$ , the maximum emission almost arose at 438 nm when excited at 330 nm, and the relative fluorescence intensity increased dramatically. However, when the concentration increased from  $2.0 \times 10^{-4}$  to  $5.0 \times 10^{-4} \text{ mol L}^{-1}$ , the relative fluorescence intensity decreased remarkably. The results showed that the fluorescence of the

compound is remarkably concentration dependent. They showed a remarkable initial increase with subsequent dramatic decrease with increasing concentration. The results also demonstrated that molecular aggregation and the fluorescence quenching may occur when the concentration increased [14].

## IV. SUMMARY

An unsymmetrical diarylethene with a pyrimidine unit was synthesized to investigate its photochromism and fluorescence properties. The results showed that diarylethene 1o showed excellent photochromism and its fluorescence had a remarkable initial increase with subsequent dramatic decrease with increasing concentration in solution. In addition, the photochromic reaction kinetics demonstrated that the cyclization processes of 1o belong to the zeroth order reaction and the cycloreversion process belong to the first order reaction.

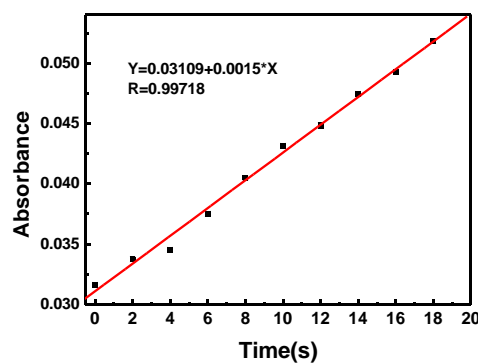


Figure 2. The kinetics of compound 1o in hexane: cyclization.

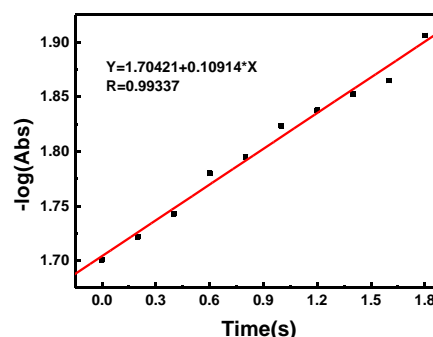


Figure 3. The kinetics of compound 1o in hexane: cycloreversion.

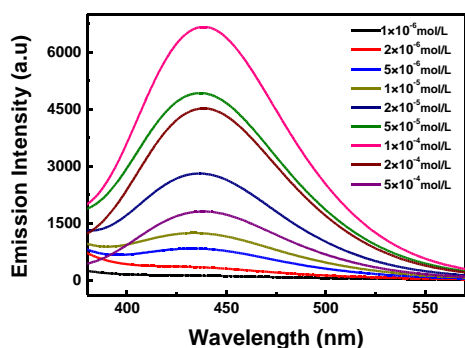


Figure 4. Fluorescence of diarylethene 1o in various concentrations in hexane excited at 330 nm.

#### ACKNOWLEDGMENT

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