

# Synthesis and Application of 1-(3, 5-dimethyl-4-isoxazolyl)-2-{2-methyl-5-[4-(1,3-dioxolane)-phenyl]-3-thienyl} Perfluorocyclopentene

Yinglong Fu, Dandan Xue, Congbin Fan and Shouzhi Pu

Jiangxi Key Laboratory of Organic Chemistry  
Jiangxi Science and Technology Normal University  
Nanchang 330013, P.R.China  
e-mail: congbinfan@163.com

**Abstract**—A new unsymmetrical photochromic diarylethene 1-(3,5-dimethyl-4-isoxazolyl)-2-{2-methyl-5-[4-(1,3-dioxolane)-phenyl]-3-thienyl}perfluorocyclopentene (1o) has been synthesized. Its properties have been discussed systematically, including photochromic, fluorescence switch and kinetics experiments in acetonitrile solution. The result indicated that this diarylethene had good thermal stability and exhibited reversible photochromism, changing the color from colorless to pink in acetonitrile solution upon appropriate irradiation with 297 nm UV light, respectively. What is more, the kinetic experiments illustrated that the cyclization/cycloreversion process of this compound was determined to be the zeroth/first reaction. The fluorescence intensity of diarylethene decreased dramatically along with the photochromism from open-ring isomer to closed-ring isomer upon irradiation with UV light in acetonitrile solution.

**Keywords**-diarylethene; photochromic; fluorescence; kinetics

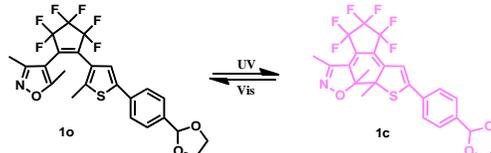
## I. INTRODUCTION

Photochromic materials have attracted considerable attention due to their wide applications in optical memory media and photo-optical switching devices [1]. The two isomers differ from each other not only in their absorption spectras, but in many changes of various physical and chemical properties, such as dielectric constant, refractive index, as well as oxidation/reduction potential, etc [2]. Among the various types of photochromic compounds, diarylethenes are regarded as the most promising candidates, because of diarylethene derivatives have excellent thermal stability of the respective isomers, notable fatigue resistance, and rapid response, and high reactivity in solid state. This characteristic of diarylethene compounds makes them available in the field of photo-mode optical recording.

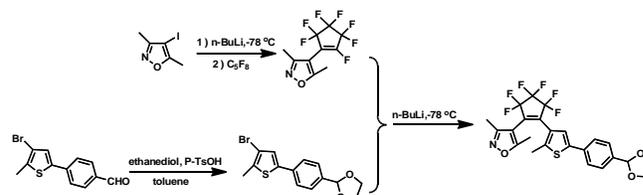
In previous papers, diarylethene with heterocyclic aryl rings are the most promising candidates for photoelectronic applications among various types of photochromic compounds [3-5]. However, there were few publications report photochromic unsymmetrical hybrid diarylethene derivatives with isoxazol moieties [6].

In this paper, we synthesized a new unsymmetrical diarylethene, 1-(3,5-dimethyl-4-isoxazolyl)-2-{2-methyl-5-[4-(1,3-dioxolane)-phenyl]-3-thienyl}perfluorocyclopentene

(1o), which presents photochromism in solution. Its photochromic reaction is shown in Scheme 1.



Scheme 1. Photochromism of diarylethene 1o.



Scheme 2. The synthetic route of diarylethene 1o

## II. EXPERIMENTS

### A. Synthesis of diarylethene

The synthetic route for 1o was described in Scheme 2. It was synthesized according to the similar procedure of [7]. The structure of 1o was confirmed by <sup>1</sup>H NMR spectroscopy. NMR spectra were recorded on Bruker AV400 (400 MHz) spectrometer with CDCl<sub>3</sub> as the solvent and tetramethylsilane as an internal standard. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ (ppm): 2.03 (s, 3H), 2.03 (s, 3H), 2.22 (s, 3H), 4.02-4.07 (m, 2H), 4.09-4.14 (m, 2H), 5.81 (s, 1H), 7.26 (s, 1H), 7.50 (d, 2H, *J* = 8.0 Hz), 7.55 (d, 2H, *J* = 8.0 Hz).

## III. RESULTS AND DISCUSSION

### A. Photochromism of diarylethene 1o

The photochromic behavior of 1o ( $2.0 \times 10^{-5}$  mol L<sup>-1</sup>) induced by photoirradiation was measured at room temperature are shown in Figure 1. In acetonitrile, 1o exhibited a sharp absorption peak at 283 nm due to a  $\pi-\pi^*$  transition [8]. Upon irradiation with 297 nm light, it turned to pink due to form closed-ring isomer 1c, accompanying a new absorption band centered at 533 nm. When the pink

solution was irradiated with visible light ( $\lambda > 500$  nm), the color could return back to colorless and its spectrum became the same as that of original one, indicating 1o returned to the initial open ring isomer.

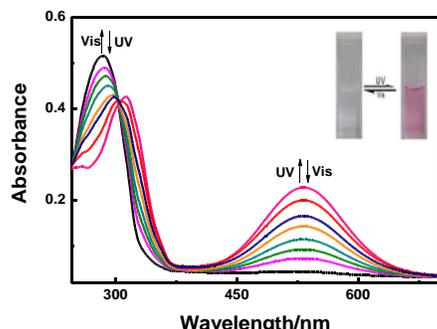


Figure 1. Absorption spectra changes upon alternating irradiation with UV-Vis light of the compound 1o in acetonitrile ( $2.0 \times 10^{-5}$  mol L<sup>-1</sup>)

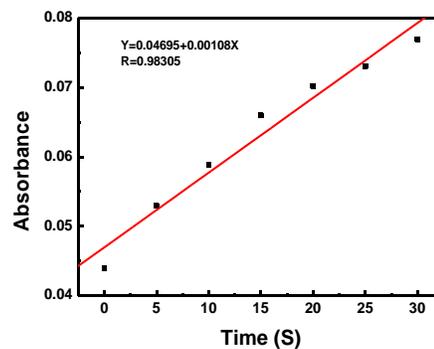
### B. Photochromic reaction kinetics in acetonitrile solution

The photochromic cyclization and cycloreversion kinetics of this diarylethene in acetonitrile were determined by UV-Vis spectra upon alternating irradiation with appropriate wavelength UV and visible light at room temperature. The cyclization and cycloreversion curves of 1o were shown in Figure 2(a) and Figure 2(b), respectively. It can be seen that the relationships between the absorbance and exposal time have good linearity upon irradiation with 297 nm UV light. The slope of line in (a) and (b) represents the reaction rate constant ( $k$ ) of 1o in acetonitrile. It is suggesting that the cyclization processes of compound 1o belong to the zeroth order reaction when open-ring isomers changed to closed-ring isomers. At the same time, during the cycloreversion of 1c, the relationship between  $-\log(\text{Abs.})$  and exposal time also behave perfect linearity, as shown in Figure 2(b), indicating that the cycloreversion process belong to the first order reaction. So all  $k$  of cyclization/cycloreversion process ( $k_{o-c}$ , 10<sup>-3</sup>) of diarylethene 1c can be easily obtained in solution, respectively.

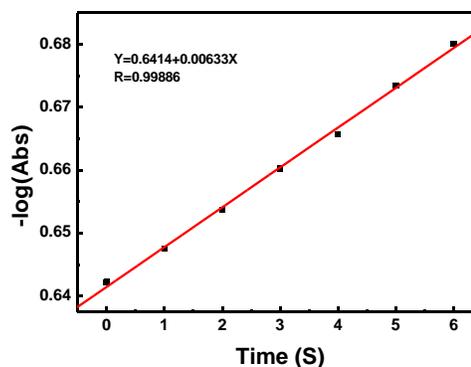
### C. Fluorescence of Diarylethene

The fluorescence emission spectra of diarylethene 1o in acetonitrile ( $2.0 \times 10^{-5}$  mol L<sup>-1</sup>) was evaluated at room temperature, and the result is shown in Figure 3. The emission peak of 1o in acetonitrile was observed at 486 nm when excited at 299 nm. Typically, the fluorescence of diarylethene could be reversibly modulated by photoirradiation during the process of photoisomerization [9]. Upon irradiation with 297 nm light, we could clearly see that the fluorescent emission of 1o was at 486 nm when excited at 300 nm. The fluorescence of 1o effectively decreased along with photocyclization due to the production of the non-fluorescence closed-ring isomer 1c. The emission intensity of diarylethene 1o was quenched to ca. 72% at the photostationary state in acetonitrile solution. This phenomenon indicated that cyclization reaction is

incomplete and the existence of parallel conformation may be the main cause for the change in fluorescence intensity [10]. The reversible changes of the emission intensity of diarylethene 1o are useful for application as the fluorescence switches



(a)



(b)

Figure 2. The cyclization/cycloreversion kinetics of compounds 1o in acetonitrile ( $c = 2.0 \times 10^{-5}$  mol L<sup>-1</sup>)

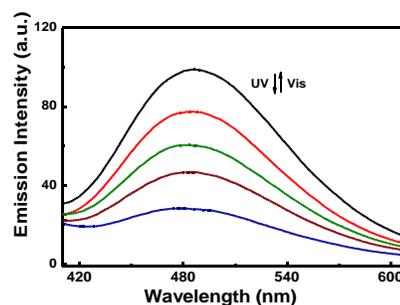


Figure 3. Fluorescence spectra of 1o in acetonitrile with 297 nm UV light

## IV. SUMMARY

A new unsymmetrical photochromic diarylethene was synthesized. 1o changed the color from colorless to pink in

acetonitrile solution upon appropriate irradiation with 297 nm UV light, respectively. What is more, the kinetic experiments illustrated that the cyclization/cycloreversion process of this compound was determined to be the zeroth/first reaction. Fluorescent properties were investigated in detail. Upon excited at 300 nm, the fluorescence intensity decreased along with the photochromism, the open-ring isomer of **1o** exhibited relatively strong fluorescence at 486 nm in acetonitrile solution. The results will be helpful for the synthesis of efficient photoactive diarylethene derivatives with fluorescence switches.

#### ACKNOWLEDGMENT

The authors are grateful for the financial support from the National Natural Science Foundation of China (21363009) and the Masters' Innovative Foundation of Jiangxi Province (YC2014-S433).

#### REFERENCES

- [1] H. Tian and S.J. Yang, "Recent progresses on diarylethene based photochromic switches," *Chem. Soc. Rev.* vol. 33, 2004, pp. 85-97, doi:10.1039/B302356G.
- [2] Y. Chen, C.M. Wang, M.G. Fan, B.L. Yao and N. Menke, "Photochromic fulgide for holographic recording," *Opt. Mater.* vol. 26, 2004, pp. 75-77, doi:10.1016/j.optmat.2004.01.00.
- [3] M. Irie, "Diarylethenes for Memories and Switches," *Chem Rev.* vol. 100, 2000, pp. doi:1685-1716, 10.1021/cr980069d.
- [4] K. Matsuda and M. Irie, "Diarylethene as a photoswitching unit," *J. Photochem. and Photobio. C.* vol. 5, 2004, pp. 169-182, doi:10.1016/j.jphotochemrev.2004.07.003.
- [5] M. Morimoto and M. Irie, "Photochromism of diarylethene single crystals: crystal structures and photochromic performance," *Chem. Commun.* vol. 36, 2005, pp. 3895-3905, doi:10.1039/B505256D.
- [6] S.Z. Pu, Z.P. Tong, G. Liu and R.J. Wang, "Multi-addressable molecular switches based on a new diarylethene salicylal Schiff base derivative," *J. Mater. Chem.* vol. 1, 2013, pp. 4726-4739, doi:10.1039/c3tc30804a.
- [7] S.Z. Pu, G. Liu, L. Shen and J.K. Xu, "Efficient Synthesis and Properties of isomeric Photochromic Diarylethenes Having a Pyrrole Unit," *Org. Lett.* vol. 9, 2007, pp. 2139-2142, doi:10.1021/ol070622q.
- [8] Z. X. Li, L. Y. Liao and W. Sun, "Reconfigurable cascade circuit in a photo-and chemical-switchable fluorescent diarylethene derivative," *J. Phys. Chem. C.* vol. 112, 2008, pp. 5190-5196, doi: 10.1021/jp711613y.
- [9] S.Z. Xiao, T. Yi, Y.F. Zhou, Q. Zhao, F.Y. Li and C.H. Huang, "Multi-state molecular switches based on dithienylperfluorocyclopentene and imidazo [4,5-f] [1,10] phenanthroline," *Tetrahedron.* vol. 62, 2006, pp. 10072-10078, doi:10.1016/j.tet.2006.08.061.
- [10] C.B. Fan, S.Z. Pu, G. Liu and T.S. Yan, "Substituent position effect on the properties of isomeric photochromic diarylethenes bearing chlorine atoms," *J. Photochem. and Photobio A: Chem.* vol. 194, 2008, pp. 415-425, doi:10.1016/j.jphotochem.2008.02.004.