

Synthesis and Properties of a Novel Diarylethene 1-(2-cyano-1,5-dimethyl-4-pyrryl)-2-{(2-methyl-4-hydroxymethylphenyl)-3-thienyl} Perfluorocyclopentene

Yaming Xue, Erting Feng, Dandan Xue, Renjie Wang* and Shouzhi Pu

Jiangxi Key Laboratory of Organic Chemistry
Jiangxi Science and Technology Normal University
Nanchang 330013, P.R.China
e-mail : pushouzhi@tsinghua.org.cn

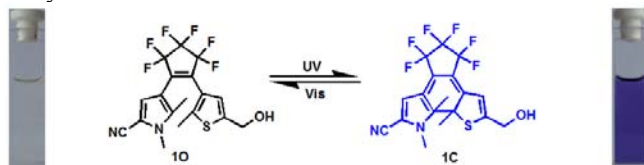
Abstract—An asymmetrical photochromic diarylethene 1-(2-cyano-1,5-dimethyl-4-pyrryl)-2-{(2-methyl-4-hydroxymethylphenyl)-3-thienyl}perfluorocyclopentene (**1o**) was synthesized and its photochromic properties as well as reaction kinetics were investigated in detail. Upon irradiation with 297 nm UV light, diarylethene **1o** exhibited photochromism in solution. Moreover, **1o** also exhibited obviously fluorescence switches along with the photochromism.

Keywords-diarylethene; photochromic; fluorescence; pyrrole

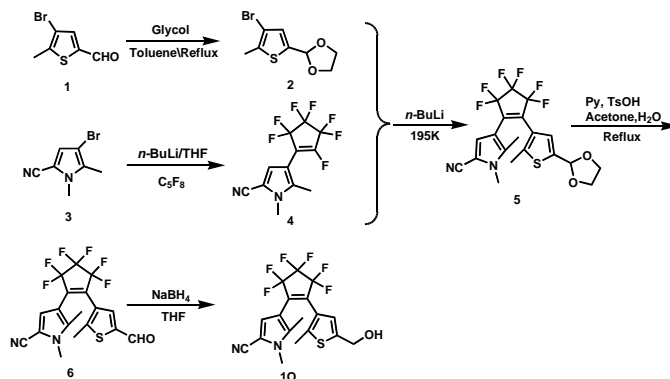
I. INTRODUCTION

Due to the widespread potential application in photonic devices such as recording media and photoswitches, the exploration of photochromic diarylethenes has aroused a surge of interest in materials science [1-5]. In recent decades, various types of photochromic compounds have been synthesized in an attempt to apply them to optoelectronic devices. As one of the most promising photoresponsive materials, diarylethenes have been extensively investigated due to the notable fatigue resistance, high thermal stability, and rapid response [6,7]. In previous literatures, numerous photochromic properties of diarylethene derivatives have been carried out [8,9]. Their photochromic properties depend on several factors, such as conformation of the open-ring isomer [10], nature of heteroarylmoieties [11], and electronic properties of substitutes [12].

In this paper, a novel unsymmetrical diarylethene 1-(2-cyano-1,5-dimethyl-4-pyrryl)-2-{(2-methyl-4-hydroxymethylphenyl)-3-thienyl}perfluorocyclopentene (**1o**) was designed and synthesized. Diarylethene **1o** exhibited excellent photochromism in solution. The photochromism of diarylethene **1o** is shown in Scheme 1.



Scheme 1. Photochromism of diarylethene **1o**.



Scheme 2. The synthetic route of diarylethene **1o**

II. EXPERIMENTS

A. Synthesis of a photochromic diarylethene

The synthesis route for **1o** is shown in Scheme 2. According to the similar procedure [13], diarylethene **1o** was synthesized visible as a light yellow soild with a 57% yield. ¹H NMR (400 MHz, CDCl₃, TMS): δ (ppm) 1.66 (s, 3H, -CH₃), 1.82 (s, 3H, -CH₃), 3.55 (s, 3H, -CH₃), 4.67 (s, 2H, methylene-H), 6.83 (s, 1H, thienyl-H), 6.87 (s, 1H, pyrrolyl-H).

III. RESULTS AND DISCUSSION

A. Photochromism of diarylethene **1o**

Figure 1 shows the absorption spectral and color changes of **1** in acetonitrile (2.0×10^{-5} mol L⁻¹) induced by alternating irradiation with UV and visible light. The unsymmetrical diarylethene **1o** exhibits photochromic properties and can switch between its colorless ring-open and deep purple ring-closed forms with appropriate wavelengths of light in hexane. The absorption maximum of **1o** was observed at about 360 nm (Figure 1A). Upon irradiation with 297 nm light, the colorless solution of **1o** turned deep purple (Figure 1B) and a new visible absorption band centered at 573 nm emerged due to the formation of closed-ring isomer **1c**. Reversely, the Pink solution of **1c** could be completely bleached upon irradiation with visible light ($\lambda > 450$ nm) and the original absorption spectrum was recovered quantitatively.

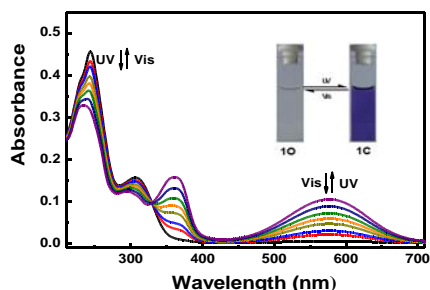


Figure 1. Absorption spectra changes upon alternating irradiation with UV-Vis light of the compound 1o in acetonitrile ($2.0 \times 10^{-5} \text{ mol L}^{-1}$)

B. Fluorescence of diarylethene 1o

The fluorescence properties of the diarylethene 1o in acetonitrile were measured. Figure 2 showed the fluorescence spectral changes of 1 in acetonitrile solution upon irradiation with 297 nm light at room temperature. Figure 2 showed the fluorescence emission peak at 441 nm upon irradiation with 297 nm UV light. The fluorescence intensity decreased along with the photochromism from open-ring isomers to closed-ring isomers upon irradiation with 297 nm UV light.

C. Photochromic reaction kinetics in acetonitrile solution

The photochromic cyclization / cycloreversion kinetics of 1o in acetonitrile 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 3. It can be seen that the relationships between the absorbance and exposal time have good linearity upon irradiation with 297 nm UV light demonstrating that the cyclization process of 1o belongs to the zeroth order reaction when open-ring isomer changed to closed-ring isomer. The slope of the line in Figure 3A represents the reaction rate constant (k) of diarylethene 1o in acetonitrile. So the k of cyclization process (k_{c-o} , 10^{-3}) of diarylethenes 1o can be easily obtained. As shown Figure 3B, during the cycloreversion of 1c, the relationship between $-\log(\text{Abs})$ and exposal time also behave perfect linearity, indicating that the cycloreversion

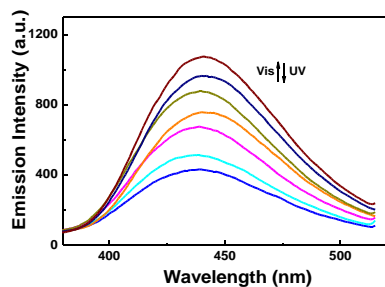
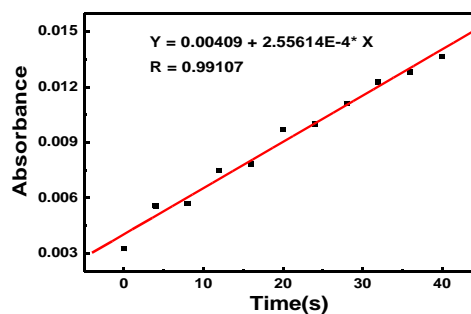
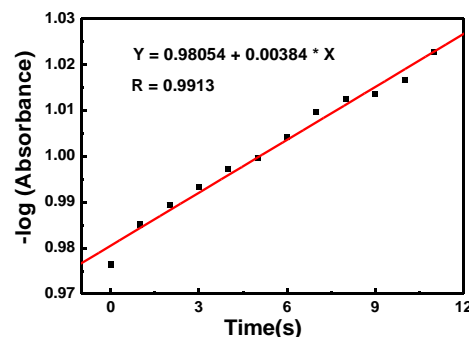


Figure 2. Fluorescent intensity changes of diarylethene 1o in acetonitrile.



A



B

Figure 3. The cyclization/cycloreversion kinetics of compounds 1 in acetonitrile ($c = 2.0 \times 10^{-5} \text{ mol L}^{-1}$)

process belong to the first order reaction. The k of cycloreversion (k_{c-o} , 10^{-3}) process of diarylethene 1 can be easily obtained.

IV. SUMMARY

A new unsymmetrical diarylethene 1o were synthesized and its photochromic were also investigated. The results showed that this compound exhibited reversible photochromism in solution. The photochromic reaction kinetics in solution were studied too. Their cyclization / cycloreversion processes belong to zeroth / first order reaction in acetonitrile.

ACKNOWLEDGMENT

The authors are grateful for the financial support from the National Natural Science Foundation of China (21362013, 51373072), and the Masters' Innovative Foundation of Jiangxi Province (YC2014-S433).

REFERENCES

- [1] T.B. Norsten, A. Peters, and R. McDons, "Reversible [7]-thiahelix formation using a 1, 2-dithienylcyclopentene photochrome," *J. Am. Chem. Soc.*, vol. 123, 2001, pp. 7447-7448, doi:10.1021/ja015988r.
- [2] Y. Yokoyama, "Fulgides for memories and switches," *Chem. Rev.*, vol. 100, 2000, pp. 1717-1740, doi:10.1021/cr980070c.

- [3] M. Irie, T. Fukaminato, and T. Sasaki, "Organic chemistry: A digital fluorescent molecular photoswitch," *Nature*, vol. 420, 2002, pp. 759-760, doi:10.1038/420759a.
- [4] M. Irie, S. Kobatake, and M. Horichi, "Reversible surface morphology changes of a photochromic diarylethene single crystal by photoirradiation," *Science*, vol. 291, 2001, pp. 1769-1772, doi:10.1126/science.291.5509.1769.
- [5] K. Uchida, M. Saito, and A. Murakami, "Three bits eight states photochromic recording and nondestructive readout by using IR light," *Chem. Eur. J.*, vol. 11, 2005, pp. 534-542, doi:10.1002/chem.200400575.
- [6] S.Z. Pu, Q. Xiao, J.K. Xu, L. Shen, G.Z. Li, and B. Chen, "Synthesis, Photochromic Kinetics, Fluorescence and Structure of a New 1, 2 - Diarylcyclopentene," *Chin. J., Chem.*, vol. 24, 2006, pp. 463-467, doi:10.1002/cjoc.200690089.
- [7] S.Z. Pu, G. Liu, 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] C.T. Poon, W.H. Lam, H.L. Wong, and V.W.W. Yam, "A versatile photochromic dithienylethene-containing β -diketonate ligand: near-infrared photochromic behavior and photoswitchable luminescence properties upon incorporation of a boron (III) center," *J. Am. Chem. Soc.*, vol. 132, 2010, pp. 13992-13993, doi:10.1021/ja105537j.
- [9] K. Yumoto, M. Irie, and K. Matsuda, "Control of the photoreactivity of diarylethene derivatives by quaternarization of the pyridylethynyl group," *Org. Lett.*, vol. 10, 2008, pp. 2051-2054, doi:10.1021/ol8005216.
- [10] M. Irie, "Diarylethenes for memories and switches," *Chem. Rev.* vol. 100, 2000, pp. 1685-1716, doi:10.1021/cr980069d.
- [11] M. Irie, O. Miyatake, K. Uchida, and T. Eriguchi, "Photochromic diarylethenes with intralocking arms," *J. Am. Chem. Soc.*, vol. 116, 1994, pp. 9894-9900, doi:10.1021/ja00101a010.
- [12] S.Z. Pu, T.S. Yang, and B.L. Yao, "Photochromic diarylethene for polarization holographic optical recording," *Mater. Lett.*, vol. 61, 2007, pp. 855-859, doi:10.1016/j.matlet.2006.06.084.
- [13] S.Z. Pu, G. Liu, 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.