

Synthesis and Photochromism Studies of 1-[2-methyl-5-(2-pyridyl)-3-thienyl]-2-[2-methyl-5-(4-bromomethylphenyl)-3-thienyl]perfluorocyclopentene

Xugang Tang, Hongliang Liu*, Shouzhi Pu
 Jiangxi Key Laboratory of Organic Chemistry
 Jiangxi Science and Technology Normal University
 Nanchang 330013, P.R.China
 e-mail: liuhongliang03@163.com

Abstract—A new photochromic diarylethene was synthesized and explored, which is named 1-[2-methyl-5-(2-pyridyl)-3-thienyl]-2-[2-methyl-5-(4-bromomethylphenyl)-3-thienyl]perfluorocyclopentene. The results showed that it have excellent photochromism, accompanied with the color change from colorless to blue, by photoirradiation in acetonitrile. When irradiated with UV light, the absorbance at 298 nm decreased, while the absorption at 598 nm increased significantly in acetonitrile. In acetonitrile, the kinetic experiments showed that the cyclization/cycloreversion process of 10 was determined to be the zeroth/first reaction.

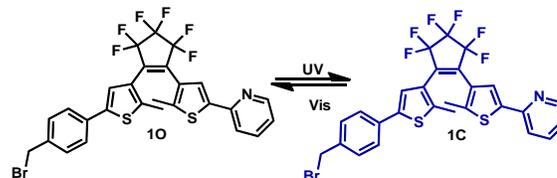
Keywords-diarylethene; photochromism; zeroth/first reaction; concentration

I. INTRODUCTION

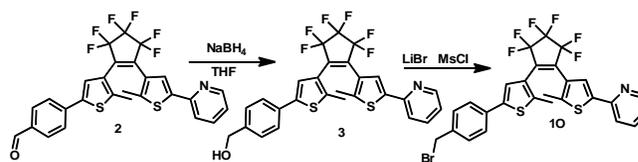
Upon irradiation with UV light, photochromic molecules have proven extremely the fascinating ability to change their structural and electronic properties [1], which can reversibly transform from the colorless ring-open form to the colored ring-closed form. Among all types of photochromic molecules, diarylethenes are one of the most successful superior thermal stability and excellent fatigue resistance, which is crucial for their applications [2, 3]. Besides, the photochemical properties of the diarylethenes can be modified through structural variations influencing the absorption spectra, fluorescence, quantum yields, and fatigue resistance. Diarylethenes have two aryl moieties, which strongly influence the photochromic properties of diarylethene[3, 4]. For example, diarylethenes bearing thiophene moiety and six-membered pyridine unit exhibited good photochromism both in solution and in the crystalline phase by permitting the pyridine unit to participate in the photoinduced cyclization reaction [5-7]. What's more, the bearing of heteroatom of diarylethenes can dramatically change photochromism properties and expand multiple responsive switching systems [8, 9]. Herein, we have designed and synthesized a new diarylethene bearing thiophene moiety and pyridine unit, namely 1-[2-methyl-5-(2-pyridyl-3thienyl)-2-[2-methyl-5-(4-bromomethylphenyl)-3-thienyl]perfluorocyclopentene. Its photochromic and the kinetic experiments were investigated in detail. The photochromic reaction of diarylethene 10 is shown in scheme 1.

II. EXPERIMENTS

The synthetic route for 10 is shown in Scheme 2. The intermediate products 2, 3 were synthesized according to the procedures of similar reported methods [10, 11]. Then, compound 2 was reduced and to give the unsymmetrical diarylethene derivative 3. Finally, a stirred anhydrous CH_2Cl_2 of compound 3 was added methanesulfonyl chloride (MsCl), triethylamine (TEA) with vigorous stirring in the ice-water bath. Stirring was continued for 5 min. at 273 K, 10 mL anhydrous THF containing LiBr was added and the reaction mixture was stirred for 30 min at this temperature. After, the mixture has been stirred for 12 h at room temperature. The crude product was purified by column chromatography on SiO_2 using ethyl acetate as an eluent to give 10 as faint blue solid. 10 was confirmed by ^1H NMR (400 MHz, CDCl_3 , TMS): δ 1.98 (d, 3H, $-\text{CH}_3$), 2.02 (s, 3H, $-\text{CH}_3$), 4.50 (s, 1H, $-\text{CH}-$), 4.64 (s, H, $-\text{CH}-$), 7.10 (s, 1H, thiophene-H), 7.31 (d, 2H, phenyl-H), 7.46(d, 2H, phenyl-H), 7.60 (s, H, thiophene-H), 7.81 (d, H, pyridyl-H), 8.19 (s, 1H, thiophene-H), 8.34 (s, H, pyridyl-H), 8.81(s, H, pyridyl-H),.



Scheme 1. Photochromism of diarylethene 10.



Scheme 2. Synthetic route of the compound 10.

III. RESULTS AND DISCUSSION

A. Photochromism of Diarylethene in acetonitrile solution.

The photochromic properties of diarylethenes **10** were measured at room temperature in acetonitrile (2.0×10^{-5} mol L⁻¹). Figure 1 shows the changes of absorption spectral and color of **10** in acetonitrile (2.0×10^{-5} mol L⁻¹) under irradiation with 297 nm UV light. The absorption maximum of colorless open-ring isomer was observed at 298 nm ($\epsilon = 2.59 \times 10^4$ mol⁻¹ L cm⁻¹) in acetonitrile, as a result of a $\pi \rightarrow \pi^*$ transition [12]. Upon irradiation with 297 nm UV light, the colorless solution of **10** was converted into a blue solution of the closed-ring isomer **1C** with a new visible absorption band centered at 598 nm ($\epsilon = 1.27 \times 10^4$ mol⁻¹ L cm⁻¹). Alternatively, the blue color of **1C** could be completely bleached upon irradiation with visible light ($\lambda > 500$ nm), indicating **1C** was returning to the initial state **10**.

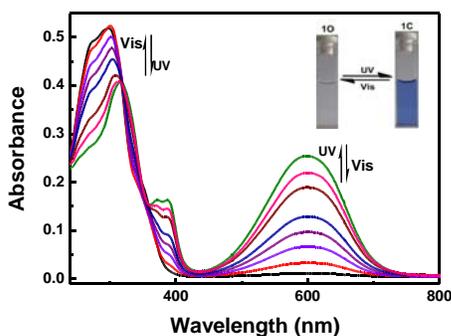


Figure 1. Absorption spectra and color change of diarylethene **10** with stimulation of 297 nm light in acetonitrile (2.0×10^{-5} mol L⁻¹) at room temperature.

B. Photochromic reaction kinetics in acetonitrile solution.

The photochromic cyclization/cycloreversion kinetics of **10** was studied by UV-Vis spectra upon irradiation at 297 nm (open-closed) or visible light (> 500 nm) (closed-open). As shown in Figure 2 and Figure 3, it can be seen clearly that the relationships between absorbance and exposal time have good linearity (linear correction factors > 0.99) upon irradiation with 297 nm UV light, indicating that the cyclization process of the photochromic diarylethene **10** should belong to zeroth order reaction. The slope of line in Figure 2 represents the reaction rate constant k in acetonitrile, and k (1.93×10^{-3} S⁻¹) of cyclization process (k_{o-c} , 10^{-3}) can be easily obtained in figure. At the same time, during the cycloreversion process of **1C** in acetonitrile, the relationships between $-\log A$ and exposal time also show perfect linearity (Figure 3). The values of k (k_{c-o} , 10^{-1}) are 0.72×10^{-3} S⁻¹.

C. Fluorescence intensity of different concentration diarylethene 10.

The concentration depending on the fluorescence

spectrum of diarylethene **10** was measured in acetonitrile at room temperature, as shown in Figure 4. With the concentration increasing of **10** from 1.0×10^{-6} to 5.0×10^{-5} mol L⁻¹, the emission remains at 475 nm when excited at 339 nm and the fluorescence relative intensity increased, but when the concentration increased to 2.0×10^{-4} mol L⁻¹, the fluorescence intensity decreased rapidly. The results show that the fluorescence of **10** is remarkably concentration dependent, and shows a remarkable initial increase with subsequent dramatic decrease with increasing concentration.

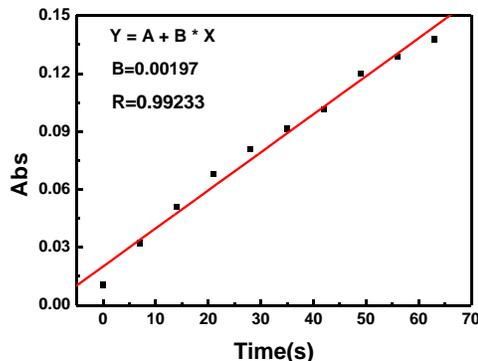


Figure 2. The kinetics of compound **10** in acetonitrile: cyclization.

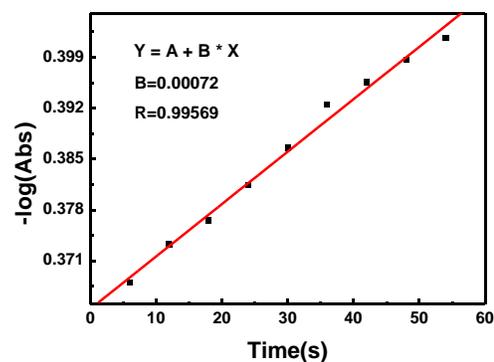


Figure 3. The kinetics of compound **10** in acetonitrile: cycloreversion.

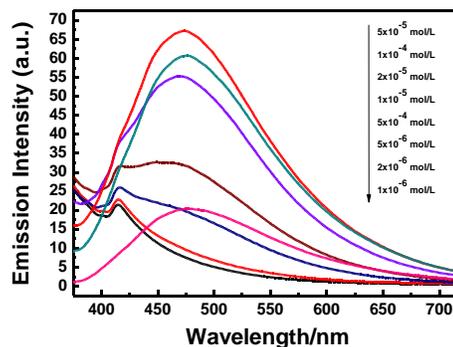


Figure 4. Fluorescence spectra of diarylethene **10** in various concentrations in acetonitrile excited at 339 nm at room temperature.

IV. SUMMARY

An unsymmetrical diarylethene was synthesized to investigate its photochromic and fluorescent properties. The cyclization/cycloreversion process of the photochromic diarylethene 1O should belong to zeroth/first order reaction. Diarylethene 1O showed the fluorescence of 1O is remarkably concentration dependent, and shows a remarkable initial increase with subsequent dramatic decrease with increasing concentration.

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 Science & Technology Normal University (YC2014-X05).

REFERENCES

- [1] F. M. Raymo and M. Tomasulo, "Electron and energy transfer modulation with photochromic switches," *Chem. Soc. Rev.* vol. 34, 2005, pp. 327-336, doi: 10.1039/B400387J.
- [2] M. Irie, "Diarylethenes for memories and switches," *Chem. Rev.* vol. 100, 2000, pp. 1685-1716, doi:10.1021/cr980069d.
- [3] S. Pu, G. Liu, L. Shen and J. Xu, "Efficient synthesis and properties of isomeric photochromic diarylethenes having a pyrrole unit," *Org. Lett.* vol. 9, 2007, pp. 2139-42. doi:10.1021/ol070622q.
- [4] H. Tian and S. Yang, "Recent progresses on diarylethene based photochromic switches," *Chem. Soc. Rev.* vol. 33, 2004, pp. 85-97, doi:10.1039/B302356G.
- [5] G. Liu, S. Pu, X. Wang, W. Liu and C. Fan, "The effect of the cyano group position upon unsymmetrical isomeric diarylethenes bearing a pyrrole unit," *Dyes Pigm.* vol. 90, 2011, pp. 89-99. doi:10.1016/j.dyepig.2010.12.007.
- [6] S. Pu, H. Li, G. Liu, W. Liu, S. Cui and C. Fan, "Synthesis and the effects of substitution upon photochromic diarylethenes bearing an isoxazole moiety," *Tetrahedron.* vol. 67, 2011, pp. 1438-47. doi:10.1016/j.tet.2010.12.041.
- [7] S. Pu, R. Wang, Liu, G. Liu, W. S. Cui, and P. Yan, "Photochromism of new unsymmetrical diarylethene derivatives bearing both benzofuran and thiophene moieties," *Dyes Pigm.* vol. 94, 2012, pp. 195-206, doi:10.1016/j.dyepig.2012.01.003
- [8] M. Milek, FW. Heinemann, and MM. Khusniyarov, "Spin crossover meets diarylethenes: efficient photoswitching of magnetic properties in solution at room temperature," *Inorg Chem* 2013; 52:11585-92. doi: 10.1021/ic401960x
- [9] H. Wong, W. Wong, and V. Yam, "Photochromic thienylpyridinebis(alkynyl)borane complexes: toward readily tunable fluorescence dyes and photoswitchable materials," *Org Lett* 2012; 14:1862-5. doi: 10.1021/ol3004595.
- [10] F. Sun, S. Cui, G Liu, C Zheng, and S Pu, "Photochromism of isomeric diarylethenes with a methylpyridine substituent," *Journal Mole Stru* 2015, 1086 131-137. doi: 10.1016/j.molstruc.2015.01.015.
- [11] S. Pu, L. Ma, G. Liu, H. Ding, and B. Chen, "A multiple switching diarylethene with a phenyl-linked rhodamine B unit and its application as chemosensor for Cu²⁺," *Dyes Pigm.* vol. 113, 2015, pp. 70-77, doi: 10.1016/j.dyepig.2014.07.030.
- [12] Z. Li, L. Liao, W. Sun, C. Xu, C. Zhang, and C. Fang, et al. "Reconfigurable cascade circuit in a photo- and chemical-switchable fluorescent diarylethene derivative," *Journal of Physical Chemistry C.* vol. 112, 2008, pp. 5190-6, doi:10.1021/jp711613y.