

Synthesis and Properties of 1-(2-methyl-5-(4-tolyl)-3-thienyl)-2-[2-methyl-5-(4-n-pentyl phenyl)-3-thienyl] Perfluorocyclopentene

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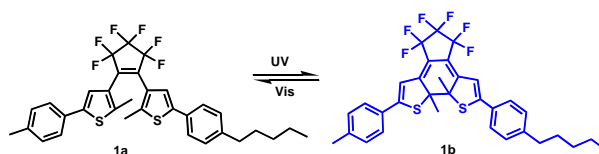
Abstract—An unsymmetrical photochromic diarylethene, 1-(2-methyl-5-(4-tolyl)-3-thienyl)-2-[2-methyl-5-(4-n-pentyl phenyl)-3-thienyl] perfluorocyclopentene was synthesized, and its photochromic properties, kinetics of the photochromic cyclization/cycloreversion and fluorescence were investigated in detail. The fluorescence spectra of the diarylethene were depended on the concentration. Moreover, the diarylethene showed fluorescence switches upon irradiation with UV/Vis light.

Keywords—photochromism; diarylethene; kinetics; fluorescence

I. 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] As one of the most promising photoresponsive materials for applications in photonic devices, [3] diarylethenes have been well recognized for their excellent photochemical reactivity, thermal stability, and fatigue resistance. [4-5] 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. [6-7] Among the reported photochromic systems, diarylethenes are the most promising candidates for optoelectronic devices due to their good thermal stability, excellent fatigue resistance, and high reactivity. In particular, diarylethenes with different substituted ring systems have been of considerable interest which different substituted ring could be resulted in different color change upon UV/Vis light irradiation [8-9].

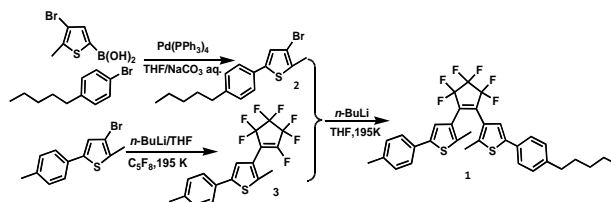
In this work, an unsymmetrical photochromic diarylethene 1-(2-methyl-5-(4-tolyl)-3-thienyl)-2-[2-methyl-5-(4-n-pentylphenyl)-3-thienyl]perfluorocyclopentene has been synthesized. Its photochromic properties, reactive kinetics, fluorescence are investigated in detail. The photochromic reaction of 1o is shown in Scheme 1.



Scheme 1. Photochromism of 1o.

II. EXPERIMENTS

The target diarylethene was synthesized by the method as shown in Scheme 2. Under an argon gas atmosphere, 1 was synthesized by 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. After stirring for 1 h at room temperature. The reaction was quenched by water. The product was extracted with ether. The organic layer was dried over MgSO₄, filtrated and evaporated. The crude product was purified by column chromatography. The structure of 1o was characterized by ¹H NMR spectroscopy. ¹H NMR spectra were recorded on Bruker AV400 (400 MHz) spectrometer with CDCl₃ as the solvent and tetramethylsilane as an internal standard. ¹H NMR (400 MHz, CDCl₃), δ (ppm) 0.90 (s, 3H, J = 8.0 Hz, -CH₃), 1.33-1.35 (m, 4H, J = 8.0 Hz, -CH₂), 1.61-1.64 (m, 2H, J = 8.0 Hz, -CH₂), 1.95 (s, 6H, J = 8.0 Hz, -CH₃), 2.58-2.63 (m, 2H, J = 8.0 Hz, -CH₂), 3.80 (s, 3H, J = 8.0 Hz, -OCH₃), 6.9 (s, 2H, J = 8.0 Hz, thiophene-H), 7.15 (d, 2H, J = 8.0 Hz, benzene-H), 7.23 (d, 2H, J = 8.0 Hz, benzene-H), 7.40 (d, 4H, J = 8.0 Hz, benzene-H).



Scheme 2. The synthesis route of 1o.

III. RESULTS AND DISCUSSION

A. Photochromism of 1o

The changes in the absorption spectra of 1o induced by photo-irradiation at room temperature in hexane solution are shown in Figure 1. Upon irradiation with 297 nm UV light, the colorless solution of 1o turned to blue with a new visible absorption band centered at 580nm attributable to the closed-ring isomer 1c. The blue colored solution reverted to colorless upon irradiation with visible light ($\lambda > 500$ nm), indicating that 1c returned to the initial state 1o, and a clear isosbestic point was observed at 287 nm.

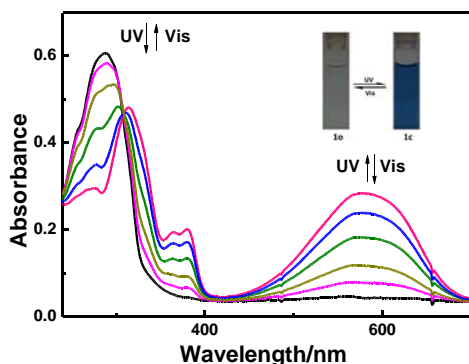


Figure 1. Absorption spectral changes of 1o in hexane

B. Photochromic reaction kinetics in hexane solution.

The photochromic cyclization / cycloreversion kinetics of 1o in hexane solution 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 Figure 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 Figure 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, it is $1.00 \text{ mol L}^{-1} \text{ s}^{-1}$ in hexane solution. As shown in Figure 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. So k of cycloreversion (k_{c-o} , 10^{-3}) process of 1c can be easily obtained, it is 15.7 s^{-1} in hexane.

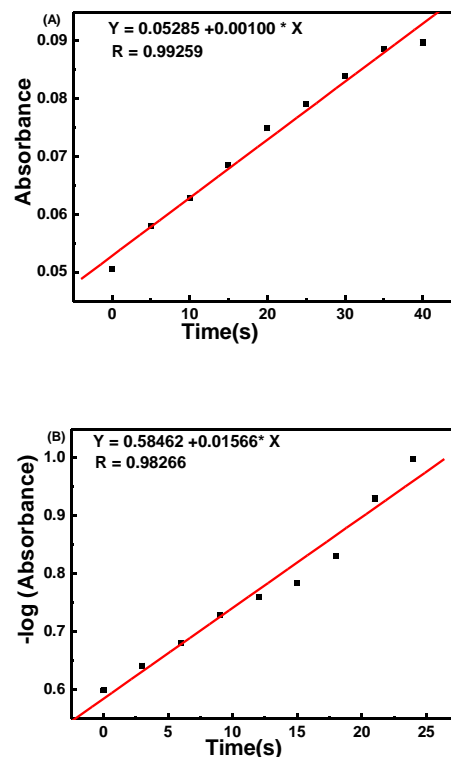


Figure 2. The cyclization kinetics (A) and cycloreversion kinetics (B) of 1o in hexane.

C. Fluorescence of 1o

Fluorescent properties can be useful not only in molecularscale optoelectronics, but for digital photoswitching of fluorescence [10]. In this work, the fluorescent properties of the diarylethene in hexane 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. What's more, it exhibited fluorescence switch on changing from open-ring isomer to closed-ring isomer in hexane ($2.0 \times 10^{-5} \text{ mol L}^{-1}$) as shown in Fig 3. The reversible changes of the emission intensity of 1o are useful for application as the fluorescence switches.

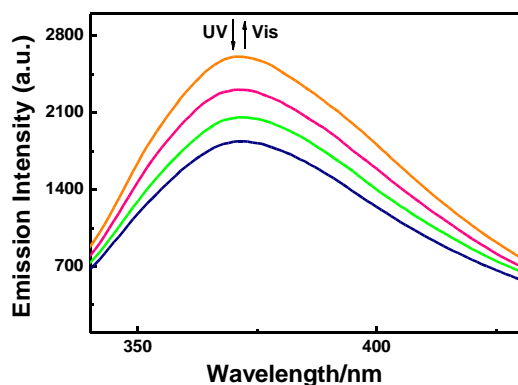


Figure 3. Fluorescent intensity changes of 1o in hexane solution.

IV. SUMMARY

A new unsymmetrical photochromic diarylethene was synthesized. Its photochromic property and the kinetic reactions were investigated by UV/Vis spectra in hexane solution. The present results indicated that the diarylethene has good photochromic properties. Furthermore, the diarylethene also functioned as a fluorescence switch. What's more, the results demonstrated that the 1o had attractive properties as optical recording medium.

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REFERENCES

- [1] H. Tian and J.Y. Song, "Recent progresses on diarylethene based photochromic switches," *Chemical Society Reviews*. vol.33.2,2004, pp. 85-97, doi: [10.1039/B302356G](https://doi.org/10.1039/B302356G)
- [2] J.J. Zhang, Z. Qi, and H. Tian, "Photochromic materials: more than meets the eye," *Advanced Materials*. vol. 25.3,2013, pp. 378-399, doi: 10.1002/adma.201201521
- [3] S. Kawata, and K. Yoshimasa, "Three-dimensional optical data storage using photochromic materials," *Chemical Reviews*. vol. 100.5 ,2000, pp. 1777-1788, doi:10.1021/cr980073p
- [4] M. Irie, "Diarylethenes for memories and switches," *Chemical Reviews*. vol.100.5,2000, pp.1685-1716,doi: 10.1021/cr980069d
- [5] H. Tian, and J.Y. Song, "Recent progresses on diarylethene based photochromic switches," *Chemical Society Reviews*. vol.33.2,2004, pp. 85-97, doi: [10.1039/B302356G](https://doi.org/10.1039/B302356G)
- [6] L. Giordano, "Diheteroarylethenes as thermally stable photoswitchable acceptors in photochromic fluorescence resonance energy transfer (pcFRET)," *Journal of the American Chemical Society*. vol.124.25, 2002, pp. 7481-7489, doi 10.1021/ja016969k
- [7] M. Irie, "Organic chemistry: a digital fluorescent molecular photoswitch," *Nature*. vol.420.6917, 2002, pp.759-760, doi:10.1038/420759a
- [8] T. Nakagawa, "Reversible luminescence modulation in photochromic europium (III) complex having triangle terthiazole ligands," *Chemistry Letters*, vol.36.3,2007, pp. 372-373, doi:10.1246/cl.2007.372
- [9] Q.F. Luo, H. Cheng, and H. Tian, "Recent progress on photochromic diarylethene polymers," *Polymer Chemistry*. vol.2.11 ,2011,pp. 2435-2443,doi: [10.1039/C1PY00167A](https://doi.org/10.1039/C1PY00167A)
- [10] C.B. Fan, "Substituent position effect on the properties of isomeric photochromic diarylethenes bearing chlorine atoms," *Journal of Photochemistry and Photobiology A: Chemistry* vol. 194.2, 2008, pp. 333-343, doi:10.1016/j.jphotochem.2007.08.032