

Synthesis and Properties of 1-(3, 5-dimethyl-4-isoxazolyl)-2-[2-methyl-3-benzothiophenyl] Perfluorocyclopentene

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Abstract—A novel asymmetrical photochromic diarylethene compound 1-(3,5-dimethyl-4-isoxazolyl)-2-[2-methyl-3-benzothiophenyl]perfluorocyclopentene (1o) has been synthesized, its photochromic properties and fluorescent properties were investigated in detail, such as photochromic, fluorescence switch and kinetics experiments, and its optoelectronic properties. The maxima absorption of compound closed-ring isomer 1c is 536 nm. Its fluorescence intensity decreased along with the photochromism from opening isomers to closed-ring isomers upon irradiation with 297 nm UV light. The kinetic experiments showed that the cyclization and cycloreversion processes were zeroth and first order reaction, respectively.

Keywords—photochromism; fluorescence switch; diarylethene

I. INTRODUCTION

Recently, photochromic compounds have been a growing interest from the viewpoints of fundamental academic research and also of practical applications as photoresponsive materials [1-3]. Photochromic compounds have attracted more and more attention due to their unique characteristics in simulating functional electronic components. Among all the photochromic compounds, diarylethene derivatives are one of the most attractive families because of their excellent thermal stability [4], remarkable fatigue resistance [5], and non-destructive [6,7]. Upon irradiation with different wavelength lights, photochromic compounds are capable of undergoing clean interconversions between two perceptibly different states. Diarylethene derivatives are the most promising candidates for such applications because of their excellent photochromic characteristics [8-10].

Photochromic diarylethenes undergo reversible photoinduced cyclization/cycloreversion reactions between two isomers upon irradiation with UV and visible light. To date, some investigations have been carried out on photochromic diarylethenes in various optical storage, such as multiwavelength optical storage, near field optical storage and two photon 3D optical storage [11]. The results are very interesting and important, and they contribute to a broad understanding of the photochromism of diarylethene derivatives with various aryl groups. At the same time, the results have also given us some good suggestions to design some new photochromic diarylethene systems.

In this paper, we designed a purple photochromic diarylethene compound, 1-(3,5-dimethyl-4-isoxazolyl)-2-[2-methyl-5-bromomethyl-3-thienyl]perfluorocyclopentene(1o). The photochromic reaction of 1o is shown in Figure 1.

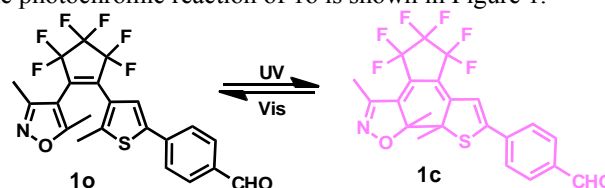


Figure 1. Photochromism of 1o

II. EXPERIMENTS

A. Synthesis of 1o.

The synthetic route for 1o was shown in Figure 2. The structure of 1o was confirmed by NMR. 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): 2.05 (s, 3H), 3.13 (s, 3H), 3.02 (s, 3H), 7.39 (s, 1H), 7.69 (d, 2H, J = 8.0 Hz), 7.91 (d, 2H, J = 8.0 Hz), 10.02 (s, 1H).

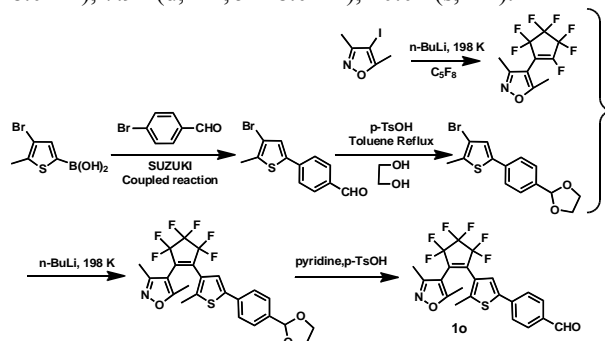


Figure 2. Synthetic route to 1o

III. RESULT AND DISCUSSION

A. Photochromism in solution

Figure 3 showed the changes of 1o in the absorption spectral and color of 1o in methanol (2×10^{-5} mol L⁻¹) by photoirradiation at room temperature. The symmetrical diarylethene 1o exhibits good photochromic properties, it

can change from colorless ring-open form to colored ring-closed forms by alternate irradiation with appropriate wavelengths of light. Upon irradiation with 297 nm UV light, the colorless solution of 1o turned purple and absorption maxima of 1c were observed at 536 nm. The purple turned colorless, upon irradiation with visible light ($\lambda > 500$ nm). It indicating that 1c returned to the initial state 1o and a clear isosbestic point was observed at 357 nm. For practical applications in optical devices, it is very important that photochromic materials can keep good photochromism in the methanol solution. The results indicated that the closed-ring isomer 1o was formed when irradiated with 297 nm UV light, and the maximum absorption was easily reversed back to the initial state. So it is also demonstrated that the closed-ring 1c can return to its open-ring 1o.

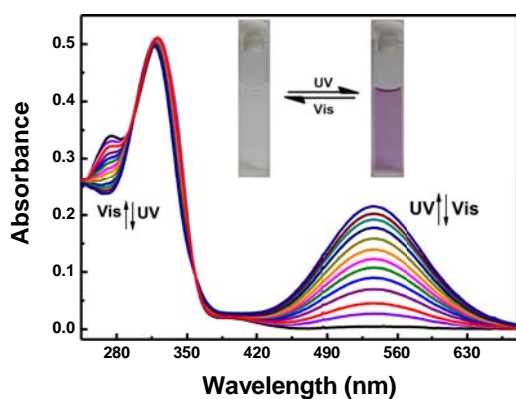


Figure 3. Absorption spectral and color change of 1o by photoirradiation in methanol (2.0×10^{-5} mol L⁻¹).

B. Photochromic Reaction Kinetics in Methanol Solution.

The photochromic cyclization and cycloreversion kinetics of this diarylethene in methanol 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. It is demonstrating 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^{-3}) of diarylethene 1c can be easily obtained, which are $2.1 \text{ mol L}^{-1} \text{ s}^{-1}$ and 5.1 s^{-1} in solution, respectively.

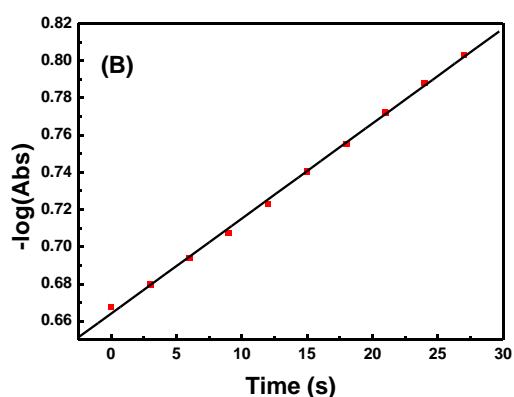
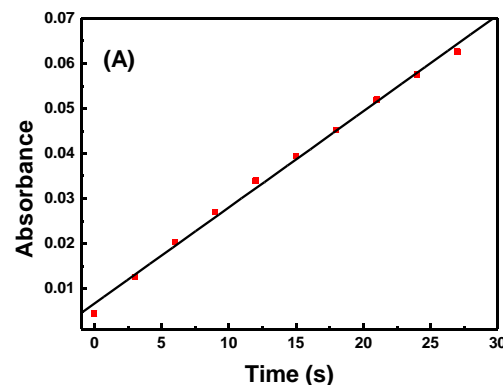


Figure 4. The cyclization (A) and cycloreversion (B) kinetics of 1o in methanol.

C. Fluorescence of diarylethene.

Fluorescent properties can be useful not only in molecularscale optoelectronics, but for digital photoswitching of fluorescence. In this work, the fluorescence properties of the 1o in methanol (2×10^{-5} mol L⁻¹) were measured using a Hitachi F-4600 spectrophotometer, the breadths of excitation and emission were selected 5.0 nm and 10.0 nm. Figure 3 shows the fluorescence spectral changes of 1o upon irradiation with 297 nm UV light at room temperature. We could clearly see that the fluorescent emission of 1o was at 446 nm when excited at 285 nm. Upon irradiation with UV light, the fluorescence of 1 effectively decreased along with photocyclization due to the production of the non-fluorescence closed-ring isomer.

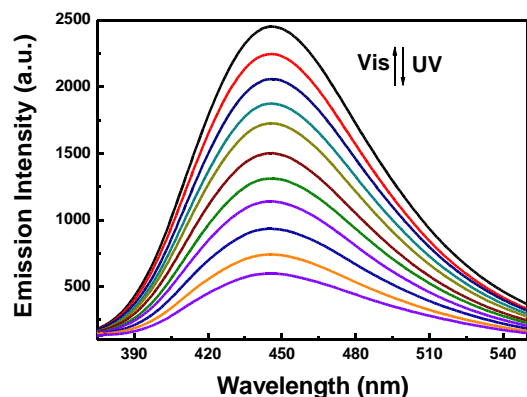


Figure 5. Fluorescence spectral changes of 1o in methanol ($2.0 \times 10^{-5} \text{ mol L}^{-1}$)

The concentration dependence on the fluorescence spectrum of diarylethene 1o was measured in methanol at room temperature, as shown in Figure 4. When the concentration of diarylethene 1o in methanol 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 446 nm when excited at 285 nm, and the relative fluorescence intensity increased dramatically. However, when the concentration increased from 1.0×10^{-4} to $5.0 \times 10^{-4} \text{ mol L}^{-1}$, the relative fluorescence intensity decreased remarkably. The methanol solution showed very weak fluorescence when the concentration was increased to $5.0 \times 10^{-4} \text{ mol L}^{-1}$. The results showed that the fluorescence of the compound was remarkably concentration dependent. The results also demonstrated that molecular aggregation and the fluorescence quenching may occur when the concentration increases.

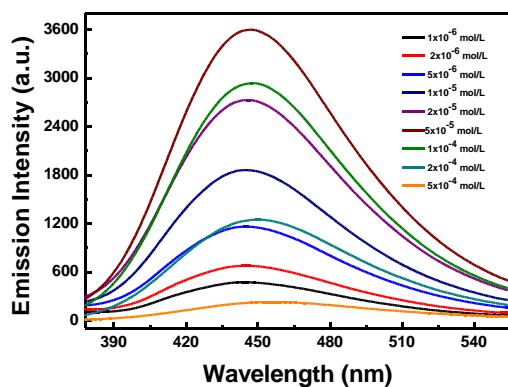


Figure 6. Emission spectral change of 1 in different concentrations in methanol at room temperature excited at 285 nm.

IV. SUMMARY

In summary, a novel diarylethene with a benzothiophene moiety has been synthesized to investigate its photochromism and fluorescence properties. The results showed that this compound exhibited reversible photochromism in solution. The results showed the diarylethene has excellent photochromism and fluorescence properties upon irradiation with 297 nm UV light in methanol solvent. The cyclization processes of 1o belong to the zeroth order reaction and the cycloreversion process belong to the first order reaction.

ACKNOWLEDGMENT

The authors are grateful for the financial support from the National Natural Science Foundation of China (21262015) and the Science Funds of Jiangxi Science & Technology Normal University (YC2014-S430)

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