Synthesis and Application of 1,2-bis-[2-methyl-5-(3-pentyl)phenyl-3-thienyl]perfluorocyclopentene

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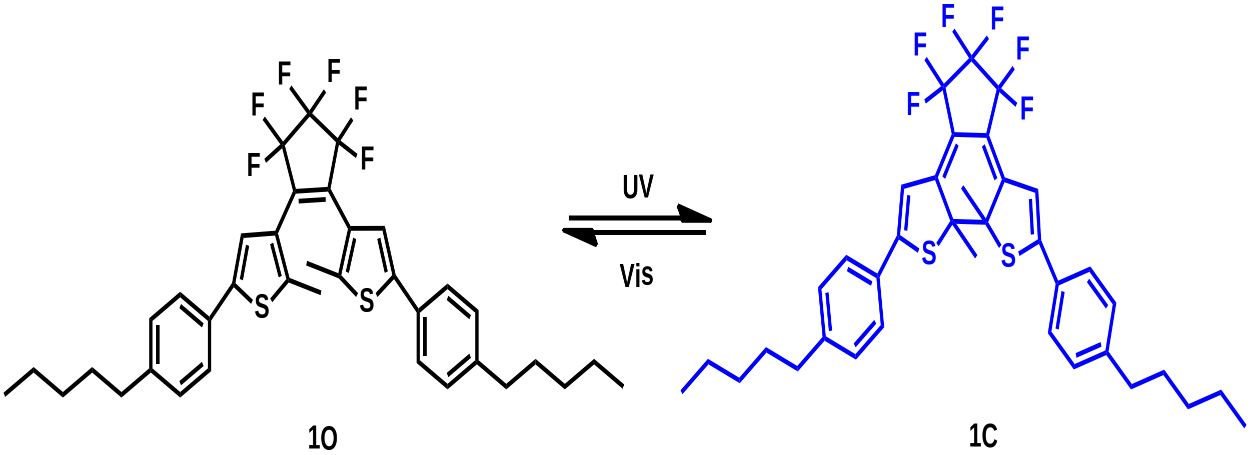
Keywords: Diarylethene, Kinetics, Fluorescence.

Abstract. A photochromic diarylethene 1, 2-bis-[2-methyl-5-(3-pentyl) phenyl-3-thienyl] perfluorocyclopentene was synthesized and characterized. Its properties, such as photochromism and fluorescence were investigated systematically. Upon irradiation with UV light, it underwent a reversible transformation from the open-ring isomer to the closed-ring isomer. The kinetic experiments showed that the cyclization and cycloreversion processes were zeroth and first order reaction. This new photochromic system also exhibited fluorescence switching in hexane solution.

Introduction

Photochromic compounds have been a growing interest in fundamental academic research as well as practical applications such as photo-responsive materials. [1,2] In the past few years, there have been important achievements in the synthesis of new photochromic molecules, [3-5] various types of photochromic compounds have been synthesized in an attempt to apply them to optoelectronic devices. Among all the reported photochromic compounds, [6-8] diarylethenes with aryl are the most promising candidates for practical applications to rewritable optical memories and photoswitches due to their excellent photochromic features, such as remarkable fatigue resistance, good thermal stability, high sensitivity, as well as rapid response. [9] In this study, an unsymmetrical photochromic diarylethene 1,2-bis-[2-methyl-5-(3-pentyl)phenyl-3-thienyl]perfluorocyclopentene (1O) has been synthesized. It's photochromic reactivity, fluorescence were investigated in detail. The photochromic reaction of 1O was shown in Scheme 1.

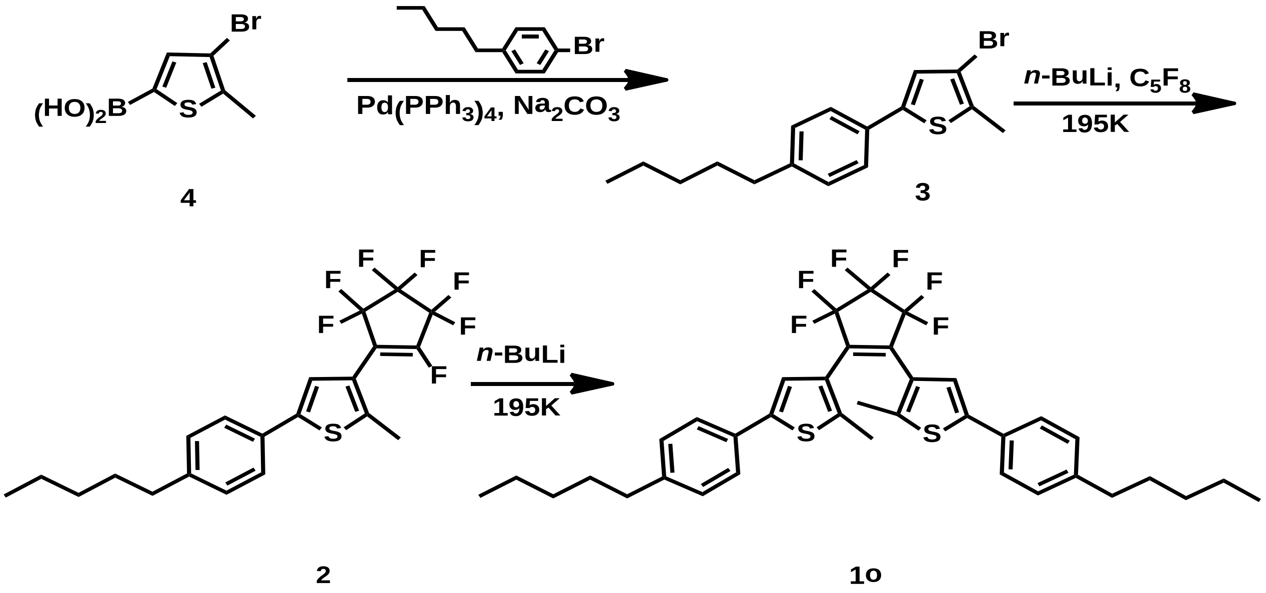


Scheme 1. Photochromism of 1O.

Experiments

Synthesis of 1O.

As shown in Scheme 2, compound 1O was synthesized according to the similar procedure, [10] the structure of 1O was confirmed by NMR. ^{1}H NMR spectra were recorded on Bruker AV400 (400 MHz) spectrometer with $CDCl_3$ as the solvent and tetramethylsilane as an internal standard. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 0.82 (t, 6H, $J = 8$ Hz, -CH_3). 1.18 - 1.27 (m, 8H, -CH_2), 1.49 - 1.57 (m, 4H, -CH_2), 1.87 (s, 6H, -CH_3), 2.54 (t, 4H, $J = 8$ Hz, -CH_2), 7.13 (s, 2H, thienyl-H), 7.17 (d, 2H, $J = 8$ Hz, phenyl-H), 7.38 (d, 2H, $J = 8$ Hz, phenyl-H).



Scheme 2. Synthetic route to 1O.

Results and Discussion

Photochromism of Diarylethene in Hexane.

The photochromic behaviors of diarylethene 1O were measured in hexane (2.0×10^{-5} mol L^{-1}). As shown in Figure 1, compound 1O exhibited an absorption peak at 267 nm (ε, 2.7×10^4 L mol^{-1} cm^{-1}) in hexane. Upon irradiation with UV light, absorption maxima of 1C were observed at 583 nm (ε, 5.1×10^3 L mol^{-1} cm^{-1}), and the colorless solution of 1O turned blue. The blue color is due to the formation of the closed ring isomer.

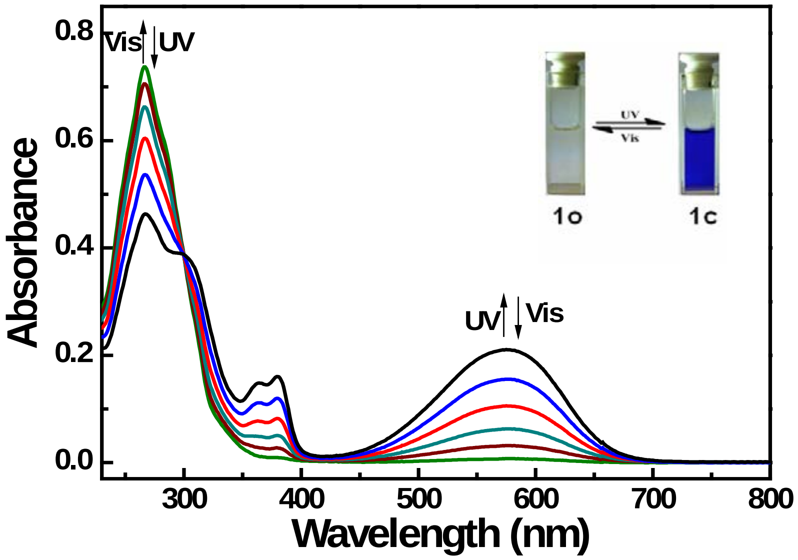
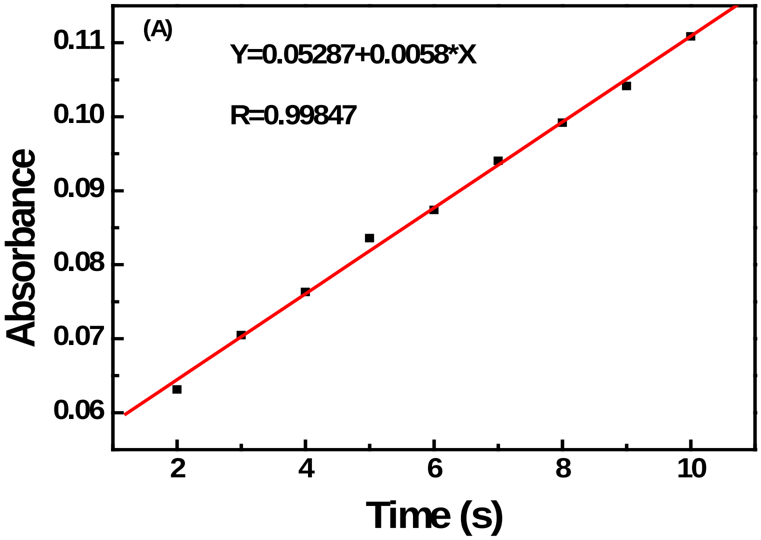


Figure 1. Absorption spectral and color change of 1O by photoirradiation in hexane.

Photochromic Reaction Kinetics in Hexane Solution.

As shown in Figure 2, the photochromic cyclization and cycloreversion kinetics of this diarylethene in hexane were determined by UV-Vis spectra upon alternating irradiation with UV and visible light (λ > 500 nm) at room temperature. As shown in Figure 2(A), the relationships between the absorbance and exposal time have good linearity upon irradiation with UV light demonstrating that the cyclization process of 1O belongs to the zeroth order reaction when open-ring isomer changed to closed-ring isomer, Figure 2(B) classified that the relationship between –log(Abs.) and exposal time also behave perfect linearity, indicating that the cycloreversion process belong to the first order reaction.



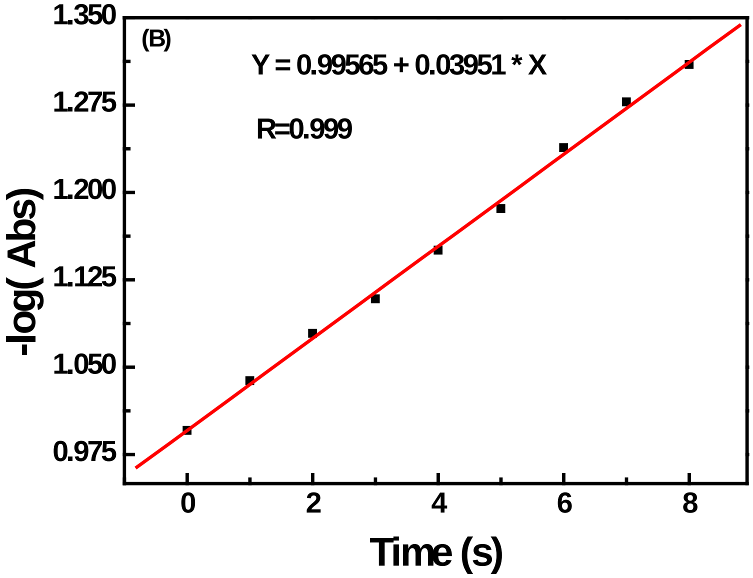


Figure 2. The cyclization (A) and cycloreversion (B) kinetics of 1O in hexane.

Fluorescence of 1O.

Fluorescent properties can be useful not only in molecular optoelectronics, [11,12] but also for digital photoswitch of fluorescence. The fluorescence spectra of 1O in hexane at room temperature were illustrated in Figure 3. It can be seen that the fluorescent emissions of 1O was at 377 nm when excited at 286 nm. The fluorescence intensity of 1O decreased dramatically upon irradiation with 297 nm light. The back irradiation with visible light regenerated the open-ring forms and recovered the original emission spectra. The average times of “on” and “off” state shortened in proportion to the reciprocal power of radiated light by changing the power of the UV-Vis light, indicating that the switching effect is perfect in hexane solution.

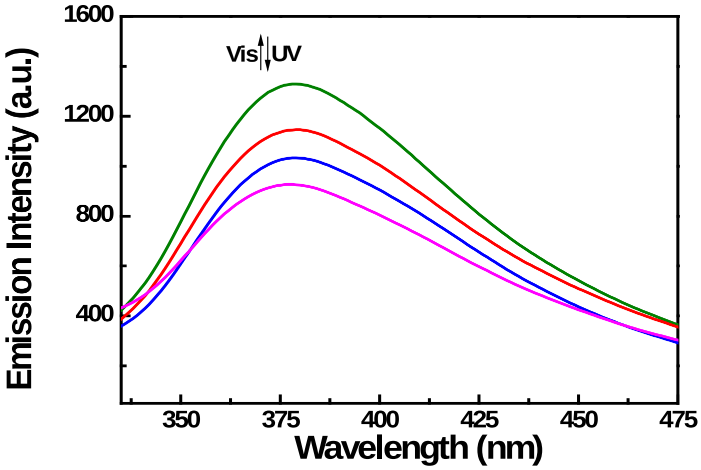


Figure 3. Fluorescence spectral changes of 1O in hexane.

Summary

In conclusion, a novel photochromic diarylethene was synthesized and its photochromic and kinetics properties was investigated. Experimental results showed that the cyclization process of 1O belongs to the zeroth order reaction and the cycloreversion process belongs to the first order reaction. The fluorescence of the compound could also be reversibly modulated by photoirradiation. The present work provides a useful design strategy for effectively tuning the photochromic properties of diarylethenes and seeking for their further applications in different optoelectronic devices.

Acknowledgement

This work was supported by the National Natural Science Foundation of China (51373072).

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