Synthesis and Properties of 1-[2-methyl-5-(2-methoxyphenyl)-3-thienyl]-2-[2-methyl-6’-(diethylamino)-2-(4-cyclopent-methylene-amino-2’-hydroxyspiro (isoindoline-1, 9’-xanthen))]-3-thienyl Perfluorocyclopentene

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Abstract. A new unsymmetrical photochromic diarylethene 1-[2-methyl-5-(2-methoxyphenyl)-3-thienyl]-2-[2-methyl-6’-(diethylamino)-2-(4-cyclopent-methylene-amino-2’-hydroxyspiro (isoindoline-1, 9’-xanthen))]-3-thienyl perfluorocyclopentene (1O) has been drafted and constructed triumphantly, and its photochromic properties, fatigue resistance, photochromic cyclization/cycloreversion kinetics and fluorescence were studied at great length. Moreover, the diarylethene showed fluorescence switches upon irradiation with UV/Vis. The present results are useful for the design of efficient and excellent characteristic diarylethene compounds.

Introduction

Photochromic compounds have drawn much consideration due to their latent adhibition in high-density optical documentary materials [1], photoinduced switches [2,3]. These diarylenes derivatives with two thiophene or benzothiophene rings are taken as the befitting candidates for photonics application such as optical memory [4] and switch [5], because of their prominent thermally nonreversibility, great efficiency of photoisomerizations, high fatigue resistance, and rapid response [6]. In particular, diarylenes with individual substituted ring systems have been of crucial interest which different vice ring could be generated by unlike color change on the basis of UV/Vis light irradiation [7-9].

In this research, a new unsymmetrical photochromic diarylethene has been synthesized triumphantly. And its photochromic and fluorescence properties was researched by a series of chemical methods. The photochromic reaction of 1O is demonstrated in Scheme 1.

Experiments

The synthetic route of 1O was displayed in Scheme 2. 2 and 3 were stirred in ethyl alcohol and reflux for 24 h to obtain 1O. 1O was characterized by $^1$H NMR spectroscopy. $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ (ppm): 1.05 (t, 3H), 1.84 (s, 3H), 1.86 (s, 3H), 3.28 (d, 4H, J = 8.0 Hz), 3.77 (s, 3H), 6.0 (d, 1H, J = 8.0 Hz), 6.31-6.34 (m, 1H), 6.38-6.42 (m, 2H), 6.72-6.75 (m, 1H), 6.96 (d, 2H, J = 8.0 Hz), 7.12 (d, 2H, J = 8.0 Hz), 7.29 (s, 1H), 7.42 (s, 1H), 7.52 (d, 2H, J = 8.0 Hz), 7.57-7.64 (m, 2H), 7.91 (d, 1H, J = 8.0 Hz), 9.15, (s, 1H), 9.34 (s, 1H).

![Scheme 1. Photochromism of 1O.](image-url)
Results and Discussion

The photochromism of 1O was researched in acetonitrile \((2.0 \times 10^{-5} \text{ mol L}^{-1})\) at room temperature. And its results were demonstrated in Figure 1. The maximal absorption peak occurred at 275 nm thanks to \(\pi-\pi^*\) transition [10]. An overt absorption peak appeared at 624 nm under the irradiation with 297 nm light. Correspondingly, the color of 1O solution changed from colorless to blue as a result of formation of the closed-ring isomer 1C. Reversely, the solution of 1c could be entirely bleached upon irradiation with visible light \((\lambda > 500 \text{ nm})\).

Fatigue Resistance of 1O

The fatigue resistance of 1O was researched in acetonitrile \((2.0 \times 10^{-5} \text{ mol L}^{-1})\) at room temperature (Figure 2), which revealed that 1O only degraded 9% after 10 cycles with alternate irradiation of ultraviolet light.

Photochromic Reaction Kinetics in Acetonitrile Solution.

The photochromic cyclization/cycloreversion kinetics of 1 in acetonitrile were acquired by UV-Vis spectrometer. There is a good linear relationship between exposure time and absorbance in Figure 3, which demonstrated that the cyclization process of 1a belongs to the zeroth order reaction when open-ring isomer changed to closed-ring isomer.
**Fluorescence of 1O**

The fluorescence spectra of 1O in acetonitrile at room temperature was elucidated in Figure 4. The fluorescence emission peak at 561 nm when excited at 360 nm. The fluorescent intensity of 1O declined gradually along with the photochromism from open-ring isomers to closed-ring isomers upon ultraviolet irradiation of 297 nm.

![Figure 3. Fluorescent intensity changes of 1 in acetonitrile.](image)

![Figure 4. The cyclization/cycloreversion kinetics of 1 in acetonitrile (c = 2.0 × 10-5 mol L-1).](image)

**Summary**

A novel photochromic diarylethene was synthesized and its properties of photochromism, fatigue resistance and kinetics were discussed at great length. It possess remarkable photochromic and fluorescent switching behaviors with apart color changes. These data attest that it has high application value for optoelectronic devices.

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References


