Synthesis and Properties of 1-(3,5-Dimethyl-4-isoxazolyl)-2-[2-methyl-5-(3-fluoro-4-chloro)phenyl-3-thienyl]perfluorocyclopentene


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ABSTRACT: An asymmetrical photochromic diarylethene 1-(3,5-Dimethyl-4-isoxazolyl)-2-[2-methyl-5-(3-fluoro-4-chloro)phenyl-3-thienyl]perfluorocyclopentene (1o) was synthesized and its photochromic properties were investigated. Upon irradiation with 297 nm UV light, diarylethene 1o exhibited photochromism in solution and in PMMA film. Moreover, 1o also exhibited obviously fluorescence switches along with the photochromism.

1 INTRODUCTION

Photochromic compounds have attracted much attention due to their potential application in high-density optical recording materials (Niu, 2009, p. 6024–6046) photoinduced switches (Whalley, 2007, p. 12590–12591, and Tian, 2008, p. 1617–1622). As one of the most promising photoresponsive materials, diarylethenes have been extensively investigated (Poon, 2010, p. 13992–13993) due to the notable fatigue resistance, high thermal stability, and rapid response (Wang, 2012, p. 320–324). In the past several decades, significant advancement has been made in the synthesis of novel photochromic diarylethene systems (Tan, 2011, p. 1263–1268, and Kutsunugi, 2012, 838–846). Perfluorodiarylethenes are well known as one of the most popular class of photochromic diarylethenes (Irie, 2000, p. 1685–1716). Their photochromic properties depend on several factors, such as conformation of the open-ring isomer (Irie, 1994, p. 9894–9900), nature of heteroarylmoieties (Irie, 2000), and electronic properties of substitutes (Pu, 2008, p. 2576–2585). Particularly, the nature of heteroaryl moieties mainly dictates the properties of photochromic systems. Upon recent reports (Liu, 2012, p. 2265–2267, and Pu, 2011, p. 1438–1447 & 2013, p. 4726–4739), the isoxazole moiety induced some new features differing from diarylethenes with other heteroaryl moieties reported. The substituent effects of fluorine and chlorine atoms can also affect the photochromic properties (Liao, 2015, p. 98–101).

In this work, a novel unsymmetrical diarylethene 1-(3,5-Dimethyl-4-isoxazolyl)-2-[2-methyl-5-(3-fluoro-4-chloro)phenyl-3-thienyl]perfluorocyclopentene was designed and synthesized. Diarylethene 1o exhibited excellent photochromism in both solution and PMMA amorphous film. The photochromism of diarylethene 1o is shown in Scheme 1.
Scheme 1. Photochromism of 1o.

2 EXPERIMENTS

Synthesis of a photochromic diarylethene. The synthesis route for 1o is shown in Scheme 2. According to the similar procedure (Pu, 2007, p. 2139–2142), diarylethene 1o was synthesized visible as a light yellow solid with a 54% yield. $^1$H NMR (400 MHz, CDCl$_3$, TMS): δ (ppm) 2.04 (s, 3H, –CH$_3$), 2.05 (s, 3H, –CH$_3$), 2.22 (s, 3H, –CH$_3$), 7.22 (s, 1H, thiophene-H), 7.30 (s, 1H, benzene-H), 7.40 (d, 1H, $J$ = 8.0 Hz, benzene-H), 7.42 (d, 1H, $J$ = 8.0 Hz, benzene-H).

Scheme 2. Synthetic route for 1o.

3 RESULTS AND DISCUSSION

3.1 Photochromism of 1o

The photochromic behaviors of 1o induced by photoirradiation was measured in both acetonitrile (2.0 × 10$^{-5}$ mol/L) and PMMA film (10%, w/w) at room temperature. The absorption spectra change of 1o and color change of 1o are shown in Figure 1. In acetonitrile, the absorption maximum of 1o was observed at 290 nm. Upon irradiation with 297 nm UV light, a new absorption band centered at 530 nm ($\varepsilon$ = 9.31 × 10$^3$ L/mol/cm) emerged due to the formation of the closed-ring isomer 1c, accompanied with a color change from colorless to violet. The orange color faded completely upon irradiation with visible light ($\lambda$ > 510 nm), and the absorption spectrum returned to the initial state of 1o.
In PMMA film, 1o showed similar photochromism as observed in acetonitrile. As shown in Figure 1B, the colorless 1o/PMMA turned violet upon irradiation with 297 nm light, and a new absorption band corresponding to the closed-ring isomer 1c/PMMA was observed at 532 nm. Compared to that in acetonitrile, the maximum absorption peak of 1c in PMMA film was red shifted by 2 nm. The red shift phenomena may be attributed to the polar effect of the polymer matrix and the stabilization of molecular arrangement in the solid state (Kasatani, 1999, p. 11–15.).

3.2 Photochromic reaction kinetics in acetonitrile solution

The photochromic cyclization and cycloreversion kinetics of 1o in acetonitrile were measured by UV-Vis spectra. The cyclization and cycloreversion curves of 1o were shown in Figures 2(A) and 2(B), respectively. It can be seen that the absorbance and exposal time have good linearity upon irradiation with 297 nm UV light, which implying that the cyclization process of 1o
is the zeroth order reaction. As shown in Figure 2(B), during the cycloreversion process of 1c, \( -\log(\text{Abs}) \) and exposure time also behave perfect linearity, which indicating that the cycloreversion process belongs to the first order reaction. In addition, the slope of the line in Figures 2(A) and 2(B) represent the reaction rate constant \( (k_{c\rightarrow o}=0.89 \text{ mol/L/s} \) and \( k_{o\rightarrow c}=9.35/s) \) of diarylethene 1o in acetonitrile.

3.3 Fluorescence of 1o

The fluorescence emission spectra of 1o in both acetonitrile \((2.0 \times 10^{-5} \text{ mol/L})\) and PMMA film \((10\%, \text{ w/w})\) were evaluated at room temperature, and the results are shown in Figure 3. The emission peak of 1o in acetonitrile was observed at 480 nm when excited at 309 nm, and that in PMMA film was observed at 422 nm when monitored at 312 nm. Compared to that in acetonitrile, the emission peak of 1o in PMMA film showed a hypsochromic shift with value of 58 nm. Typically, the fluorescence of diarylethene could be reversibly modulated by photoirradiation during the process of photoisomerization (Xiao, 2006, p. 10072-10078). Upon irradiation with 297 nm light, the emission intensity of 1o was notably decreased in both acetonitrile and PMMA film due to the formation of the weak fluorescent closed-ring isomer 1c. The back irradiation by appropriate visible light regenerated the open-ring isomer 1o and recovered the original emission intensity.

![Emission spectra](image)

Figure 3. Emission intensity changes of 1o upon irradiation with 297 nm UV light at room temperature: (A) in acetonitrile \((2.0 \times 10^{-5} \text{ mol/L})\); (B) in PMMA films \((10\%, \text{ w/w})\).

As shown in Figure 3, the emission intensity of 1o was quenched to ca. 39% in acetonitrile and 45% in PMMA film in the photostationary state. That is to say, the fluorescent modulation efficiency of 1o was 61% in acetonitrile, and that in PMMA films was 55%. The results showed that the fluorescent modulation efficiency in PMMA film was much higher than that in acetonitrile solution.
4 SUMMARY

In summary, a novel diarylethene with a isoxazole moiety has been synthesized. It showed good photochromic behavior in acetonitrile solution and in PMMA film. In both solution and in PMMA film, the diarylethene also showed fluorescence switch upon irradiation with 297 nm light. The results have contributed to a broad understanding of the effects of substituents on the photochromism of diarylenes.

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REFERENCES


