Synthesis and Properties of 1-(3,5-Dimethyl-4-isoxazolyl) -2-[2-methyl-5-(6-hydroxymethylpyridyl)-3-thienyl] Perfluorocyclopentene

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Abstract. An asymmetrical photochromic diarylethene 1-(3,5-Dimethyl-4-isoxazolyl)-2-[2-methyl-5-(5-hydroxymethylpyridyl)-3-thienyl]perfluorocyclopentene (Io) was synthesized and its photochromic, fluorescent properties were investigated in detail. This compound exhibited remarkable photochromism, upon irradiation with 297 nm UV light, the colorless solution of Io turned to purple with a new visible absorption band centered at 539 nm \((\varepsilon = 9.01 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1})\) attributable to the closed-ring isomer Ic. The kinetic experiments showed that the cyclization and cycloreversion processes were zeroth and first order reaction, respectively. Moreover, diarylethene Io also exhibited obvious fluorescence switch along with the photochromism. The emission intensity of diarylethene Io in a photostationary state was quenched to ca. 38% in acetonitrile.

Introduction

Photochromic materials have been the subject of intense research due to their potential applications in many fields, such as high-density optical data storage,[1,2] molecular switches,[3,4] sensors[5,6] and so on. Diarylenes are one of the representative photochromic molecules because they undergo reversible photoisomerization reactions between two stable forms: the ring open form with the hexatriene backbone and the ring-closed form with the cyclohexadiene backbone.[7–9] Recently, there has been increasing interest in photochromic dithienylethene derivatives due to their remarkable fatigue resistance, excellent thermally irreversible properties, high sensitivity and fluorescence switchable character.[10,11] Therefore, the design, synthesis, and the study of novel photochromic diarylenes are the goal that scientists constantly pursue.

Diarylenes bearing a pyridine group have attracted more and more attention, and these diarylene derivatives exhibited some unusual characteristics.[12,13] Herein, a novel unsymmetrical diarylethene 1-(3,5-Dimethyl-4-isoxazolyl)-2-[2-methyl-5-(5-hydroxymethylpyridyl)-3-thienyl]perfluorocyclopentene (Io) was designed and synthesized. Diarylethene Io exhibited excellent photochromism and obvious fluorescence switch in acetonitrile.

Experiments

Synthesis of the photochromic diarylethene. The synthesis route for diarylethene Io was shown in Scheme 1. According to the similar procedure,[14] diarylethene Io was synthesized visible as a light yellow with a 57% yield. \(^{1}H\) NMR (400 MHz, CDCl\(_3\)): \(\delta\) 1.97 (s, 3H, –CH\(_3\)), 1.99 (s, 3H, –CH\(_3\)), 2.16 (s, 3H, –CH\(_3\)), 3.69 (s, 1H, –OH), 4.70 (s, 2H, –CH\(_2\)), 7.06 (s, 1H, thiophene-H), 7.45 (d, 1H, \(J = 8.0\) Hz, pyridine-H), 7.47 (d, 1H, \(J = 8.0\) Hz, pyridine-H), 7.64 (t, 1H, \(J = 8.0\) Hz, pyridine-H).
Results and Discussion

Photochromism of 1o

The photochromic property of 1o was investigated in acetonitrile (2.0 × 10^{-5} mol L^{-1}) at room temperature, and its absorption spectral and color changes induced by alternating irradiation with UV light (297 nm) and visible light (λ > 500 nm) are shown in Fig.1 and the photochromism of 1o is shown in Scheme 2. The absorption maximum of 1o was observed at 307 nm (ε = 2.15 × 10^{4} L mol^{-1} cm^{-1}) in acetonitrile, as compared to the analogous diarylethene derivative,[15] the molar absorption coefficient increased slightly. Upon irradiation with 297 nm UV light, a new absorption band centered at 539 nm (ε = 9.01 × 10^{3} L mol^{-1} cm^{-1}) emerged with a change in the color of solution from colorless to purple. The change was ascribed to the formation of the closed-ring isomer 1c. For the reverse reaction, the purple solution of 1c faded completely to colorless upon irradiation with visible light (λ > 500 nm). This photoisomerization involved π→π* transition.[16]
Photochromic reaction kinetics in acetonitrile solution

The photochromic cyclization/cycloreversion kinetics of $1o$ in acetonitrile were determined by UV-Vis spectra upon alternating irradiation with UV and appropriate wavelength visible light at room temperature. The cyclization and cycloreversion curves of $1o$ are shown in Fig. 2. It can be seen that the relationships between the absorbance and exposure time have good linearity upon irradiation with 297 nm UV light. It is demonstrating that the cyclization processes of $1o$ belong to the zeroth order reaction when open-ring isomer changed to closed-ring isomer. The slope of every line in Fig. 2(A) and 2(B) represents the reaction rate constant ($k$) of diarylethene $1o$ in acetonitrile. So all $k$ of cyclization ($k_{oc}, 10^{-4}$) / cycloreversion ($k_{co}, 10^{-3}$) process of diarylethene $1o$ can be easily obtained, which are 5.7 mol L$^{-1}$s$^{-1}$ and 4.38 s$^{-1}$ in solution, respectively. As shown in Fig. 2(B), during the cycloreversion of $1c$, the relationship between $-\log$(Abs) and exposure time also behave perfect linearity, indicating that the cycloreversion process belong to the first order reaction.

Fig. 2. The kinetics of diarylethene $1o$ in hexane: (A) cyclization; (B) cycloreversion.

Fluorescence of $1o$

The fluorescence emission spectra of diarylethene $1o$ in acetonitrile ($2.0 \times 10^{-5} \text{ mol L}^{-1}$) were evaluated at room temperature, and the result is shown in Fig. 3. The emission peak of $1o$ in hexane was observed at 461 nm when excited at 288 nm. Typically, the fluorescence of diarylethene could be reversibly modulated by photoirradiation during the process of photoisomerization.[17] Upon irradiation with 297 nm light, the emission intensity of $1o$ was notably decreased in acetonitrile 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. As shown in Fig. 3, the emission intensity of $1o$ was quenched to ca. 38% in acetonitrile in the photostationary state. That is to say, the fluorescent modulation efficiency of $1o$ was 62% in acetonitrile. The fluorescent modulation efficiency of $1o$ was bigger compared to the analogous diarylethene derivative. [15]
Conclusion

In conclusion, a new diarylethene bearing a pyridine group was designed and synthesized. Our experimental results showed that the diarylethene $1o$ had good photochromic behavior in acetonitrile. The cyclization process of $1o$ belongs to the zeroth order reaction and the cycloreversion process belongs to the first order reaction, respectively. Upon irradiation with 297 nm light, diarylethene $1o$ also showed obvious fluorescence switch in solution.

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References


Fig. 3. Emission intensity changes of diarylethene $1o$ upon irradiation with 297 nm UV light at room temperature in acetonitrile (2.0 × 10$^{-5}$ mol L$^{-1}$).