Synthesis, photochromism and holographic optical recording of a novel diarylethene bearing a pyrrole unit

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Abstract. A unsymmetrical photochromic diarylethene, 1-[2-methyl-5-(3-fluorophenyl)-3-thienyl]-2-(2-cyano-1,5-dimethyl-4-pyrryl)hexafluorocyclopentene (1o), was synthesized. The photoconversion ratios from open-ring to closed-ring isomers at photostationary state under UV irradiation in hexane solution was measured by HPLC, and the properties, including photochromism and fluorescence properties were also investigated systematically. The results showed that this compound had good thermal stability and exhibited reversible photochromism, changing from colorless to blue after irradiation with UV light both in solution and in PMMA amorphous film. The open-ring isomer of the diarylethene 1 exhibited relatively strong fluorescence at 427 nm in hexane solution (5×10⁻⁵ mol/L) when excited at 340 nm. The fluorescence intensity decreased along with the photochromism upon irradiation with 297 nm light and its closed-ring isomer showed almost no fluorescence. Using diarylethene 1 as recording medium, polarization holographic optical recording was carried out successfully.

1. Introduction
Photochromic molecules attract much attention from fundamental as well as practical points of view because of their potential for applications to optical devices, such as optical memories and switches [1,2]. During the past decades, there have been important achievements in the synthesis of new families of organic photochromic molecules [2-4]. Among the photochromic compounds, Diarylethenes are regarded as the best candidates for such devices, owing to its excellent thermal stability, fatigue resistance, and easy monitoring using UV-vis spectroscopy [5,6]. As components of molecular electronics, it is desirable to develop various types of molecular switch devices with diarylethene compounds.

Photochromism is a light-triggered reversible reaction between two isomers. Most diarylethene derivatives show very large spectral shifts upon photoisomerization from the open-ring to closed-ring isomers [1]. The open-ring isomer is colorless in most cases, while closed-ring isomer shows some color, such as yellow, red, or blue. The open and closed isomers differ from each other not only in their absorption but also in various physical and chemical properties, such as π-conjugation length [7], refractive indices [8,9], geometrical structures [10,11], and chiral properties [12,13]. The property changes and the photochromic reactivity strongly depend on the kind of the heteroaryl moieties and the electron donor/acceptor substituents. Formerly, most of the heteroaryl moieties have been thiophene or benzothiophene rings, with just a few reports on other heteroaryl moieties such as thiazole [14], oxazole [15], and so on. Pyrrole is an attractive aryl unit due to its biological characteristics and has been applied in biosensors widely. However, diarylethene derivatives with a
pyrrole unit hitherto reported is very rare. In this study, a photochromic diarylethene compound, 1-[2-methyl-5-(3-fluorophenyl)-3-thienyl]-2-(2-cyano-1,5-dimethyl-4-pyrryl)hexafluorocyclopentene (1o), was synthesized. Its photochromic reactivity, fluorescence property and application for polarization holographic optical recording were investigated in detail. The photochromic reaction of diarylethene 1a is shown in Scheme 1.

\[ \text{Scheme 1. Photochromism of diarylethene 1o.} \]

2. Experiments

The synthetic route for diarylethene 1o is shown in Scheme 2. It was synthesized according to the similar procedure of Pu et al. [16]. The structure of compound 1o was confirmed by IR, \(^1\)H NMR and \(^{13}\)C NMR spectroscopy: Anal. Calcd for C_{23}H_{15}F_7N_2S (%): C, 57.02; H, 3.12; N, 5.78. Found C, 57.09; H, 3.07; N, 5.85; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 1.77 (s, 3H, \(-CH_3\)), 1.97 (s, 3H, \(-CH_3\)), 3.60 (s, 3H, \(-CH_3\)), 6.85 (d, 1H, \(J = 7.6\) Hz, phenyl-H), 6.92 (s, 1H, pyrrole-H), 7.05 (s, 1H, thiophene-H), 7.12 (d, 1H, \(J = 7.6\) Hz, phenyl-H), 7.21 (s, 1H, phenyl-H), 7.28 (t, 1H, \(J = 8.4\) Hz, phenyl-H); 13C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 11.3, 14.5, 33.1, 55.4, 105.5, 109.9, 111.4, 113.3, 118.1, 118.7, 122.8, 125.9, 130.1, 134.6, 135.9, 140.4, 142.3; IR (\(\nu\), KBr, cm\(^{-1}\)): 442, 525, 682, 740, 777, 900, 983, 1032, 1056, 1114, 1137, 1185, 1274, 1335, 1384, 1441, 1488, 1561, 1585, 1612, 2222, 2345, 2370, 2852, 2921.

\[ \text{Scheme 2. Synthetic route for the compound 1o.} \]

3. Results and Discussions

3.1. Photochromism of diarylethene 1o

The unsymmetric diarylethene 1o exhibits good thermal stability and photochromic properties and can be toggled between its colorless ring-open and colored ring-closed forms by alternate irradiation with appropriate wavelengths of light. Figure 1 shows the absorption spectral changes of 1o in hexane (2.0\(\times\)10\(^4\) mol/L) and in PMMA film by photoirradiation, respectively. In hexane solution, the absorption maximum of compound 1o was observed at 253 nm (\(\varepsilon = 3.56 \times 10^4\) L·mol\(^{-1}\)·cm\(^{-1}\)). Upon irradiation with 297 nm light, the color of the hexane solution turned blue, in which the absorption maximum was observed at 589 nm (\(\varepsilon = 1.08 \times 10^5\) L·mol\(^{-1}\)·cm\(^{-1}\)). The blue solution turned colorless, upon irradiation with visible light (\(\lambda > 500\) nm). In the PMMA amorphous film, diarylethene 1o also showed good photochromic property. Upon irradiation 297 nm light, the color of 1o/PMMA film (\(\lambda_{\text{max}} = 255\) nm) changed from colorless to blue with the appearance of a new broad absorption band at 614 nm, which was assigned to the formation of the closed form 1c. The colored 1c/PMMA film can invert to colorless, on irradiation of appropriate visible light (\(\lambda > 500\) nm). The red shift of the ring-closed form of diarylethene 1 in PMMA film in comparison with that in hexane solution can be ascribed to the polar effect of the polymer matrix and the stabilization of molecular arrangement in solid state [17]. In addition, the photoconversion ratio from open-ring to closed-ring isomer of
compound 1 at photostationary state was analyzed under UV irradiation in hexane solution by HPLC, which is shown in Figure 2. The values is 94%.

![Figure 1](image1.png)

**Figure 1.** Absorption spectral changes of compound 1 at room temperature (A) in hexane (2.0×10^{-5} mol/L) and (B) in PMMA film.

![Figure 2](image2.png)

**Figure 2.** the photoconversion ratios of diarylethenes 1 at photostationary state under UV irradiation in hexane solution by HPLC.

3.2. Fluorescence switch properties

![Figure 3](image3.png)

**Figure 3.** Fluorescence spectral changes of 1o upon irradiation in hexane (5×10^{-5} mol/L).

Fluorescent properties can be useful not only in molecularscale optoelectronics, but for digital photoswitching of fluorescence [18]. In this work, the fluorescence properties of the diarylethene 1 in solution was measured using a Hitachi F-4500 spectrophotometer. The result showed that 1o exhibited good fluorescence in hexane solution. By using anthracene (0.27 in acetonitrile) as the reference, the fluorescence quantum yields of 1o was determined to be 0.035. The fluorescence intensity of diarylethene 1 decreased dramatically along with the photochromism from open-ring isomer to closed-ring isomer upon irradiation with 297 nm light. As shown in Figure 3, when irradiated by light of 297 nm, the photocyclization reaction was carried out and the non-fluorescent closed-ring form of the compound were produced. The back irradiation by appropriate wavelength visible light regenerated the open-ring forms of diarylethene 1o and recovered the original emission spectra. The emission
The intensity of diarylethene 1 in a photostationary state was quenched to ca. 12% in hexane. The incomplete cyclization reaction and the existence of parallel conformations may be the main cause for the moderate change in fluorescence induced by photoirradiation. The reversible changes of the emission intensity of diarylethene 1 are useful for application as the fluorescence switches [19].

3.3. Holographic optical recording

Based on the photochromic and photo-induced anisotropic properties of diarylethene 1, we proposed an application as polarization pattern display. We have accomplished three different types of polarization holographic optical recording using diarylethene 1c/PMMA film as recording medium, i.e., copolarization, cross-polarization and 45°-polarization holographic recording. The exposure time for holograms recording was 6 seconds. Readout patterns with the three types of polarization holographic optical recording are shown in Figure 4. As shown in Figure 4(a), we can see that the copolarization holographic recording obtains high diffraction efficiency as well as high scattering noise when the intensities of the recording wave and the readout wave are fixed. Figure 4(b) shows the observed pattern by just using cross-polarization light for readout. The result indicated that cross-polarization holographic recording obtains low diffraction efficiency as well as low scattering noise when the intensities of the recording wave and the readout wave are fixed. If the polarization of P is 45°, from the horizontal direction, only the vertical polarization light patterns can pass through the A-diarylethene-P system. Thus, the readout pattern is like Figure 4(c). By this way, two polarization patterns can be hidden in the pattern and recorded in the diarylethene 1c/PMMA film based on its photochromic and photoinduced anisotropic properties, and only readout with two orthogonal polarizers at certain polarization angles can pick up the patterns separately [20].

In conclusion, A symmetrical photochromic diarylethene was synthesized and its photochromic and fluorescent properties were also investigated. The results showed that this compound exhibited reversible photochromism both in solution and in PMMA amorphous film. The photoconversion ratio from open-ring to closed-ring isomer at photostationary state was analyzed under UV irradiation in hexane solution by HPLC, and the values is 94%. In hexane solution, the open-ring isomer of diarylethene 1 exhibited relatively strong fluorescence at 426 nm when excited at 340 nm. The fluorescence intensity decreased along with the photochromism upon irradiation with 297 nm light and its closed-ring isomer showed almost no fluorescence. Using diarylethene 1 as recording medium, polarization holographic optical recording was carried out successfully. The results demonstrated that the compound had attractive properties for polarization holographic optical recording.

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