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Synthesis of a new Diarylethene for Optical Recording

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Abstract. A novel photochromic diarylethene bearing five and six-membered aryl units 1-[(2-methyl-5-(3-pyridinyl)-4-thienyl)]-2-[(2-methoxylphenyl)]perfluorocyclopentene was synthesized and its photochromic, fluorescent electrochemical properties were investigated in detail. Using diarylethene (1a) as recording medium, polarization holographic optical recording was carried out successfully.

1. Introduction
With the increasing requirements of the huge information storage, higher density and higher data transfer rate become the trends of optical data storage. Current commercial recordable and rewritable optical storage systems are heat-mode recording systems, which limits the size of recorded pits and writing speed. During the past decades, there have been important achievements in the synthesis of new families of organic photochromic molecules [1,2]. Among the various photochromic molecular systems, diarylethene especially diarylenes with heterocyclic aryl rings, is one of the most promising organic photochromic molecules because of its high fatigue resistance. These molecules can play a key role in materials for photonic switches, memories, sensors, or actuators, and this wide range of applications involve large-size devices (e.g., sunglasses) as well as miniaturized ones (e.g., memory media) [3]. In order to find out diarylenes with excellent characters, a lot of molecules were designed and synthesized [4-6]. Up to date, design and synthesis of new photochromic compounds is an very active area of research, and many publications concerning synthesis and investigation of the properties of diarylenes with the heterocyclic aryl rings have been reported. However, there are few publications that contribute to holographic recording using diarylenes as recording media, except for several papers reported by us [7, 9].

The photochromic reaction of diarylethene 1a is shown in Scheme 1. In this paper, we synthesized a photochromic diraylethene 1-[(2-methyl-5-(4-pyridinyl)-3-thienyl)]-2-[(2-methoxylphenyl)] perfluorocyclopentene. Its recording media properties was also investigated in detail.

Scheme 1. Photochromism of diarylethene 1a. Scheme 2. Synthetic route for the compound 1a
2. Experimental

The synthetic route for diarylethene 1a is shown in Scheme 2. It was synthesized according to the similar procedure of [10]. NMR spectra were recorded on Bruker AV400 (400 MHz) spectrometer with CDCl₃ as the solvent and tetramethylsilane as an internal standard. The absorption spectra were measured using Agilent 8453 UV/Vis spectrometer. Photoirradiation was carried out using SHG-200 UV lamp, CX-21 ultraviolet fluorescence analysis cabinet, and BMH-250 Visible lamp. Light of appropriate wavelengths was isolated by different light filters. The fluorescent property was measured using a Hitachi F-4500 spectrophotometer. Electrochemical examinations were performed in a one-compartment cell with the use of a Model 263 potentiostat–galvanostat (EG&G Princeton Applied Research). The structure of compound 1a was confirmed by 1H NMR. NMR spectra were recorded on Bruker AV400 (400 MHz) spectrometer with CDCl₃ as the solvent. 1H NMR (400 MHz, CDCl₃): δ 1.96 (s, 3H, -CH₃), 3.51 (s, 3H, -OCH₃), 6.84 (d, 1H, J=8.0), 7.00 (t, 1H), 7.38 (t, 3H, J=7.8), 7.52 (s, 1H), 7.21 (d, 1H), 8.58 (d, 2H).

3. Result and discussion

3.1. Photochromism of diarylethene 1a

The photochromic properties of diarylethene 1a irradiation by photoirradiation at room temperature were measured both in hexane and in PMMA amorphous film. As shown in Figure 1A, compound 1a exhibited an absorption peak at 297 nm (ε = 1.7 × 10⁴ L mol⁻¹ cm⁻¹) in hexane, which was arisen from the •* transition [11] Upon irradiation with 313 nm light, a new visible absorption band at 584 nm (ε = 3.51 × 10³ L mol⁻¹ cm⁻¹) appeared while the original peak at 297 nm decreased, indicating the new formation 1b produced. Correspondingly, the colorless solution of 1a turned blue. The blue colored solution turned colorless by irradiation with visible light (λ > 500 nm), indicating that 1b returned to the initial state 1a.

![Figure 1](image)

Figure 1. Absorption spectral changes of compound 1a in hexane (A) (2.0 × 10⁻⁵ mol/L) and in PMMA film (B) (10%, w/w)

For practical applications in optical devices, it is very important that photochromic materials can keep good photochromism in a polymer film, such as the PMMA film [12-14]. In PMMA amorphous film, diarylethene 1a also showed good photochromism as similar to that in solution. In PMMA amorphous film, diarylethene 1a also showed good photochromism (Figure 1B) as similar to that in solution. The colorless diarylethene 1a/PMMA film turned blue for which the maximal absorption were observed at 585 nm, as the closed-ring isomer 1b was generated. Upon irradiation with 313 nm light. The colored diarylethene/PMMA films can return to colorless upon irradiation with visible light (λ > 500 nm). Figure 1 show the color changes of diarylethene upon photoirradiation in hexane and in PMMA respectively. The quantum yields of cyclization and cycloreversion reaction of diarylethene in hexane solution were 0.36 and 0.07 at room temperature, respectively.

3.2. Fluorescence of diarylethene 1a

The fluorescence intensity of diarylethene 1a decreased along with the photochromism from open-ring isomer to closed-ring isomer upon irradiation with 265 nm light in hexane(5.0 × 10⁻⁵ mol/L). As shown in Figure 2, the photocyclization reaction was carried out and the fluorescent closed-ring form of the compound was produced. The irradiation by appropriate wavelength visible light regenerated the
open-ring forms of diarylethene and return the original emission spectra. The phenomena are useful for application as the fluorescence switches [15].

The concentration dependence on the fluorescence spectrum of diarylethenes 1a was measured in hexane at room temperature, as shown in Figure 3.

**Figure 2.** Fluorescence spectral changes (A) of spectra(B) of diarylethene 1a in hexane (5.0×10⁻⁵ mol/L).

When the solutions at 2.0 × 10⁻⁶, 5.0 × 10⁻⁶, 1.0 × 10⁻⁵, 2.0 × 10⁻⁵, 5.0 × 10⁻⁵, and 2 × 10⁻⁴ mol/L were excited at 305 nm, the relative fluorescence intensity decreased the increase in the concentration. when the concentration decreased to 2.0 × 10⁻⁵ mol/L, the fluorescence intensity remarkably.

### 3.3. Electrochemical properties of diarylethenes 1a

Reversible modulation of electrochemical properties by photoirradiation is of basic importance for the development of molecular electronic devices. To date, many diarylethene derivatives and their electrochemical properties have been reported [16-18].

In this work, the electrochemical properties of 1a was investigated. The typical electrolyte was acetonitrile (5 mL) containing 0.10 mol/L tetrabutylammonium tetrafluoroborate ((TBA)BF₄) and 2.0×10⁻⁵ mol/L diarylethenes 1a. Figure 4 shows the CV curves of diarylethene 1a with the scanning rate of 50 mV/s.

With regard to the energy level of the ferrocene reference (4.8 eV below the vacuum level), the HOMO and LUMO energy levels can also be estimated. As shown in Figure 5, it can be clearly seen that the onset potentials of oxidation and reduction for 1a were observed at +1.44V and -0.68V, and those for 1b were observed at +1.57 V and -0.79V, respectively. Therefore, the values of IP and EA were calculated to be +6.24 and 5.56 eV. Based on the HOMO and LUMO energy levels, the band gap (Eg, Eg = LUMO-HOMO) of 1a can be calculated as 2.12 eV, and that of 1b is 2.36 eV.

**Figure 3.** Fluorescence emission spectra of diarylethene 1a in various concentrations in hexane.

### 3.4. Polarization multiplexing holographic recording

With a He-Ne laser (wavelength: 650 nm, 105mW) in the experimental setup, the evaluation of potential of photochromic diarylethene as a polarization medium by recording and reading in a real-time operation was investigated. Using diarylethene 1b/PMMA film as recording medium. The polarizations of the patterns recorded on the film are shown in Figure 5. The exposure time for each pattern was 0.04 s and the wide of each pattern was about 20 µm. The result indicated that the new photochromic diarylethene can be applied in high capacity optical storage.

**Figure 4.** CV of 1a in 0.1 mol/L ((TBA)BF₄)

**Figure 5.** Readout patterns from 1b/PMMA film
In conclusion, an unsymmetrical dithienylethene was synthesized to investigate its photochromism, fluorescence and electrochemical properties. Dithienylethene 1a showed good photochromism both in solution and in PMMA amorphous film. The diarylethene exhibited a relatively strong fluorescence switches along with the photochromism from open-ring isomers to closed-ring isomers in hexane. The oxidation potential differences of the open-ring and closed-ring forms of compound 1 were 0.24 V, because the $\pi$-conjugation length of 1b was get longer. The present results are useful for the designation of efficient photactive and excellent characteristic diarylethene compounds.

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