Synthesis, kinetics and application for optical recording of a new asymmetrical photochromic diarylethene

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Abstract. A novel photochromic diarylethene was synthesized and its photochromic, fluorescence and kinetics properties were investigated detail. This compound exhibited remarkable photochromism, changing from colorless to blue after irradiation with UV light both in solution and in PMMA amorphous film. In hexane, the kinetic experiments showed that the cyclization /cycloreversion process of the compound was determined to be the zeroth/first reaction, respectively. Finally, The results demonstrated that the diarylethene compound had attractive properties for high density optical storage.

1. Introduction
Organic photochromic molecules have raised considerable interest because of their potential applications to optical memory and molecular switches [1]. Among the various photochromic molecular systems, diarylethene with derivatives bearing thiophene or benzothiophene ring systems are regarded as the best candidates for applications because of their good thermal stability of both forms, remarkable fatigue resistance, rapid response and high reactivity in the solid state [2-5]. Recently, many investigations have been carried out on photochromic diarylenes in various optical memory media [6], such as switch devices [7], and photomechanical actuators [8, 9], etc. In order to research the diarylethene, which have the excellent properties, a larger number of molecules have been designed and synthesized. In particular, diarylenes with thiophene ring systems bearing terminal phenyl groups have been of considerable interest, because the hydrogen atoms attached to the terminal phenyl groups can be substituted by many other electron-donating groups or electro-withdrawing groups, which inevitably influence the optoelectronic properties of corresponding diarylenes [10].

In this paper, we have designed and synthesized a new unsymmetrical photochromic diarylethene compound 1-[2-methyl-5-(3-methylphenyl)-3-thienyl]-2-[2-methyl-5-(2,4-difluorophenyl)-3-thienyl]perfluorocyclopentene (1a), and its photochromic reactivity, fluorescence, kinetics and application for holographic optical recording medium was investigated in detail. The photochromism of diarylethene 1a is shown in Scheme 1.

2. Experiments
The target diarylenes were synthesized by the method as shown in Scheme 2. Similar detailed synthetic method was described in references [11]. First, 3-bromo-2-methyl-5-methylphenyl-thiophene (3) and 3-bromo-2-methyl-5-(2,4-difluorophenyl)thiophene (5) was prepared by reacting 3-bromo-2-methyl-5-thenylboronic acid (1) with 1-bromo-3-methylbenzene and 1-bromo-2,4-difluorobenzene in the presence of tetrakis(triphenylphosphine)palladium(0) and Na₂CO₃ in THF for 16 h at 378K. Under
an argon gas atmosphere, compound 3 was dissolved in THF and n-butyl lithium hexane was added at 195K. Stirring was continued for 30 min at this low temperature; octafluorocyclopentene was added and the mixture was stirred for 2 h at this temperature. After extracting with diethyl ether and evaporation in vacuum, the residue was purified by column chromatography on silica gel (petroleum ether) to obtain 6. Compound 1a was prepared by reacting compound 5 in dry THF at 195K, then through purified by column chromatography on silica gel (petroleum ether), and 1a was obtained. The structure of compound diarylethene 1a was characterized by $^1$H NMR spectroscopy. $^1$H NMR (400 MHz, CDCl$_3$): $^1$H NMR (400 MHz, CDCl$_3$, ppm): $\delta$ 2.28 (s, 3H, $-\text{CH}_3$), $\delta$ 2.32 (s, 3H, $-\text{CH}_3$), $\delta$ 2.47 (s, 3H, $-\text{CH}_3$), $\delta$ 6.65 (d, 1H, thiophene-H), $\delta$ 6.72 (d, 1H, thiophene-H), $\delta$ 6.75(d, 1H, benzene $-\text{H}$), $\delta$ 7.06(s, 1H, benzene $-\text{H}$), $\delta$ 7.10(m, 2H, benzene $-\text{H}$), $\delta$ 7.19(d, 2H, benzene $-\text{H}$), $\delta$ 7.3(s, 1H, benzene $-\text{H}$).

3. Result and Discussions

3.1. Photochromism of diarylethene 1a

The photochromic behaviors of diarylethene 1a in hexane (2.0 $\times$ 10$^{-5}$ mol/L) and in PMMA film (10% w/w) induced by photo-irradiation at room temperature are shown in Figure 1A and 1B. From Figure 1A, the colorless diarylethene 1a show the sharp absorption peak at 284 nm in hexane solution. The colorless solution 1a turned blue and a new absorption band centered at 575 nm emerged while the original peak at 284 nm decreased when irradiation with 313 nm UV light. The results indicated that the closed-ring isomer 1b was formed. Upon irradiation with visible light of wavelength longer than 500 nm, the blue color turned to colorless and the maximum absorption returned to the initial state, which demonstrated that the closed-ring 1b was returned to open-ring 1a, and a clear isosbestic point was observed at 303 nm.

![Scheme 1](image1.png)

**Scheme 1.** Photochromism of diarylethene 1a. 1a.

![Scheme 2](image2.png)

**Scheme 2.** Synthetic route for the compound

**Figure 1.** Absorption spectral changes of compound 1 in hexane (A) and in PMMA film (B).

In PMMA amorphous film, diarylethene 1a has also shown good photochromism. Upon irradiation with 313 nm UV light, the colorless PMMA film changed to blue, and a new absorption band appeared at 587 nm, which was assigned to the formation of the closed-ring isomer 1b, the colored PMMA film can invert to colorless on irradiation of appropriate wavelength visible light ( $>500$ nm). The red shift of the maximum absorption of 1b in PMMA film in comparison with those in hexane.
solution could be mainly ascribed to the molecular arrangement in solid state is more stable than in solution [12]. The quantum yields of cyclization and cycloreversion reaction of diarylethene 1 in hexane solution were 0.27 and 0.20 at room temperature, respectively. In addition, it was also found that both open-ring isomer and closed-ring isomer of diarylethene 1 were stable at room temperature in darkness.

3.2. Photochromic reaction kinetics in hexane solution
The photochromic cyclization/cycloreversion kinetics of 1a in hexane 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 1a were shown in Figure 3. It can be seen that the relationships between the absorbance and exposal time have good linearity upon irradiation with 298 nm UV light suggesting that the cyclization processes of 1a belong to the zeroth order reaction when open-ring isomer changed to closed-ring isomer. The slope of every line in Figure 3(A) and 3(B) represents the reaction rate constant (k) of diarylethene 1a in hexane. So all k of cyclization/cycloreversion process (k_o-c / k_c-o, 10^{-3}) of diarylethene 1a can be easily obtained, which are 1.07 s^{-1} and 7.02 s^{-1} in solution, respectively. As shown in Figure 3(B), during the cycloreversion of 1b, the relationship between –log(Abs) and exposal time also behave perfect linearity, indicating that the cycloreversion process belong to the first order reaction.

![Graph A and B](image)

**Figure 3.** The cyclization/cycloreversion kinetics of compounds 1a in hexane

3.3. Fluorescence of diarylethene
The fluorescence properties in the hexane solution of the compound were measured using a Hitachi F-4500 spectrophotometer, and the breadths of excitation and emission slit were selected 10.0 nm. From Figure 4, it could be clearly seen that the solution of 1a exhibited relatively strong fluorescence at 388nm when excited at 328 nm. In order to investigate the relationship between fluorescence and concentration, we measured the fluorescence in different concentration of hexane solution at room temperature. As shown in Figure 4, when the concentration of diarylethene 1a in hexane increased from 2 × 10^{-6} mol/L to 1 × 10^{-4} mol/L the emission intensity is significantly increased, and the fluorescence peak gave a minor red shift from 366 nm to 388 nm when irradiated by light of 328 nm. However, when the concentration increased 2 × 10^{-4} mol/L the fluorescence intensity decreased, and the fluorescence appeared self-quench when the concentration at 1 × 10^{-3} mol/L. This self-quench phenomenon maybe resulted from the formation of excimers and or exciplexes in high concentration solutions so that deactivation effect can occur during the excited-state lifetime [13].

3.4. Optical storage properties
With a He-Ne laser (wavelength: 650nm, 105mW) in the experimental setup. The experimental system for recording was described and shown in [14]. Using diarylethene 1b as the recording medium, polarization recording was performed. The images recorded on diarylethene 1b/PMMA film is shown in Figure 5. The size of recording marks was about 20µm, the interval distance between two spots was 80µm. As shown in Figure 5, the quality of images recorded in 1b/PMMA film showed a clear contrast and without cross talk, which are important in rewritable data storage. The recorded images can be
erased completely along with irradiated with UV light. The result demonstrated that the photochromic diarylethene can be used in high capacity optical storage.

Figure 4. Fluorescence spectra of diarylethene 1a in various concentrations in hexane excited at 328 nm.

In conclusion, a new unsymmetrical photochromic diarylethene was synthesized and its photochromic, fluorescence and kinetics properties were investigated. The results indicated that the compound exhibited good reversible photochromic behavior both in solution and in PMMA film. In hexane solution, the fluorescence spectra of diarylethene 1a depended on the concentration, when the concentration at $1 \times 10^{-3}$ mol/L the fluorescence self-quench was observed. The kinetics properties indicated that the cyclization/cycloreversion processes belong to zeroth/first order reaction in hexane. Rewritable holographic recording experiments were carried out on 1b/PMMA film successfully. The results demonstrated that the diarylethene compound had attractive properties for polarization holographic optical recording.

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