Synthesis and application for optical recording of a new diarylethene having a benzene unit

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Abstract. A novel photochromic diarylethene was synthesized and its photochromism, fluorescence properties have been investigated. This compound exhibited good photochromism and functioned as a fluorescence switch upon alternating irradiation with UV and visible light both in solution and in PMMA film. When diarylethene was used as recording medium, the results demonstrated that the diarylethene compound had attractive properties for high density optical storage.

1. Introduction
The demand for higher storage capacity in optical storage is rapidly increasing. So, many research activities have focus on the development of new storage materials [1] and innovative technologies [2] to simultaneously increase the storage density and data-transfer rates. Organic photochromic compounds that undergo reversible color changes upon illumination have long been viewed as potential media for high-density optical memory devices. Upon photolysis, the photochromic compounds reversibly change not only the absorption spectra but also other physicochemical properties, such as refractive index, electrical moment, dielectric constants, chelate formation, ion dissociation, oxidation/reduction potentials and phase transitions during the photochromic reaction [3]. There are some advantages of photochromic materials for optical recording: (1) fast response time, (2) high spatial resolution, (3) re-writability, and (4) without special fixing information. Moreover, to the best of our knowledge, diarylethene is regarded as one of the most promising candidates because of their good thermal stability of two isomers, notable fatigue resistance, high quantum yields, rapid response and high reactivity in solid state [4].

To date, there are many reports on diarylethene derivatives with heteroaromatic rings as both thermally irreversible and reversible photochromic compounds. Among diarylethene derivatives so far synthesized, most of the hetero-aryl moieties have been thiophene or benzothiophene rings, and other hetero-aryl moieties, such as such as furan [5], thiazole [6], indole [7], benzo[8], pyrrole [9], and indene [10], have also been reported partially. Recently, photochromic hybrid diarylethene derivatives bearing both five-membered and six-membered moieties have been reported by Pu et al. [11]. They are the first class example of photochromic diarylethene derivatives bearing both five-membered and six-membered moieties, and all of them showed good reversible photochromism both in solution and in PMMA amorphous film. In this paper, we also have designed and prepared a new photochromic diarylethene derivative bearing benzene and thiophene moieties, i.e., 1-(2-trifluoromethylphenyl)-2-[2-methyl-5-(4-cyanophenyl)-3-thienyl]perfluorocyclopentene (1o). Its photochromic reactivity,
fluorescence switch property and application for optical recording were investigated. The photochromic reaction of diarylethene 1 is shown in Scheme 1.

2. Experiments
The synthetic route for diarylethene 1o is shown in Scheme 2. Firstly, 2-bromobenzotrifluoride (2) was lithiated and then coupled with octafluorocyclopentene to give 2-trifluoromethylphenyl-perfluorocyclopentene (3); Then, Suzuki coupling of 3-bromo-4-cyano-benzene with 3-bromo-2-methyl-5-thienylboronic acid (4) [12] gave 3-bromo-2-methyl-5-(4-cyanophenyl)thiophene (5). Finally, compound 5 was lithiated and then coupled with compound 3 to give the target diarylethene 1o. The structure of diarylethene 1o was confirmed by $^1$H NMR and $^{13}$C NMR spectroscopy.

$^1$H NMR (CDCl$_3$, 400 MHz, TMS): 2.22 (s, 3H, -CH$_3$), 7.07 (s, 1H, thienyl-H), 7.47 (t, 3H, $J$=9.1 Hz, phenyl-H), 7.58 (t, 1H, $J$=7.7 Hz, phenyl-H), 7.64-7.72 (m, 2H, phenyl-H), 7.92 (d, 2H, $J$=8.3 Hz, phenyl-H).

$^{13}$C NMR (CDCl$_3$, 100 MHz, TMS) 13.92, 121.92, 124.64, 124.77, 125.38, 125.59, 125.63, 127.58, 127.63, 127.68, 127.72, 128.89, 128.99, 130.43, 130.99, 131.81, 136.07, 137.47, 140.29, 142.28.

3. Results and Discussion
3.1. Photochromism of diarylethene

Figure 1. Absorption spectral changes of diarylethene 1 both in hexane and in PMMA film at room temperature: (A) in hexane ($c=2.0 \times 10^{-4}$ mol L$^{-1}$); (B) in PMMA film (10%, w/w).

The diarylethene 1o exhibits good photochromism both in hexane solution and in PMMA amorphous film at room temperature. This diarylethene could be toggled between its colorless open-ring isomers (1o) and colored closed-ring isomers (1c) by alternating irradiation with UV light and appropriate wavelength visible light, and its absorption spectral changes in hexane upon photoirradiation were shown in Figure 1A. As shown in Figure 1A, the absorption maximum of colorless open-ring isomer 1o was observed at 315 nm ($\varepsilon = 3.1 \times 10^4$ L mol$^{-1}$ cm$^{-1}$) in hexane. Upon irradiation with UV light ($\lambda = 297$ nm), the colorless solution turned purple with a new visible absorption band centered at 551 nm ($\varepsilon = 4.6 \times 10^3$ L mol$^{-1}$ cm$^{-1}$) emerging, while the original peak at 315 nm decreased, indicating the formation of the closed-ring isomer 1c. Correspondingly, The purple colored solution returned to colorless upon irradiation with visible light ($\lambda > 500$ nm), indicating that 1c returned to the initial open-ring isomer 1o. Similarly, as shown in Figure 1B, upon irradiation 297 nm light, the color of dithienylethene 1o /PMMA film ($\lambda_{max} = 320$ nm) changed from colorless to purple with the appearance
of a new broad absorption band at $\lambda_{\text{max}} = 561$ nm, which was assigned to the formation of the closed form $1c$. The colored PMMA film can invert to colorless, on irradiation of appropriate visible light ($\lambda > 500$ nm). As has been observed for most of the reported diarylethenes [13,14], the maximum absorption peaks of both the open-ring and the closed-ring isomers in PMMA film are longer than those in hexane solution. The red shift phenomena may be ascribed to the stabilization of molecular arrangement in solid state.

![Figure 2. Fatigue resistance of diarylethene 1 in hexane and in PMMA film in air atmosphere at room temperature. Initial absorbance of the sample was fixed to 1.0; (A) in hexane; (B) in PMMA film](image)

Fatigue-resistant property, i.e., how many times photocyclization and cycloreversion reaction cycles can be repeated without loss of performance, is an very important factor for practical applications in optical devices. The fatigue resistances of diarylethene 1 were examined both in hexane and in PMMA amorphous film at room temperature, as shown in Figure 2. In hexane, diarylethene 1 were irradiated alternatively with 297 nm and visible light ($\lambda > 500$ nm), respectively. The irradiation time was long enough for coloration to reach the photostationary state and for the color to be completely bleached. As shown in Figure 2A, the fatigue-resistant characteristic of 1 in solution indicated that ~85% of $1c$ was destroyed after 10 repeat cycles. This may be ascribed to degradation resulting from the formation of an epoxide.[15] Similarly, the fatigue resistances of diarylethene 1 were tested in PMMA film by alternatively irradiating with 313 nm and visible light, respectively. As shown in Figure 2B, the fatigue resistance of diarylethene 1 in the solid state (PMMA amorphous film) are much stronger than those in solution. After 40 repeated cycles, this compound still showed good photochromism with ~58% degradation of $1c$. This remarkable improvement may result from effectively suppressing the oxygen diffusion.[16] As described above, it can be easily concluded that the fatigue resistance of diarylethene 1 is weakness than those of report by Pu et al. [11].

3.2. Fluorescence switch properties

![Figure 3. Fluorescent intensity changes of diarylethene 1 in hexane($c=2.0\times10^{-7}$ mol L$^{-1}$).](image)

The fluorescence properties in hexane solution of the compound $1o$ were measured using a Hitachi F-4500 spectrophotometer, and the breadths of excitation and emission slit were selected 10.0 nm. Figure. 3 shows the emission intensity changes of diarylethene 1 during the process of
photoisomerization in hexane. Upon irradiation with 313 nm light at room temperature, the emission intensity of compound 1 decreased remarkably along with the photoisomerization from open-ring isomers to closed-ring isomers when excited at 318 nm. When arrived at the photostationary state, the emission intensity was quenched to ca. 18%. The incomplete cyclization reaction and the existence of parallel conformations may be the main cause for the moderate change in fluorescence induced by photoirradiation in hexane. The back irradiation by appropriate wavelength visible light regenerated its open-ring isomer and recovered the original emission intensity. The reversible changes of the emission intensity of diarylethene 1 are useful for application as optical memory with fluorescence readout method and photo-modulation switches.

3.3. Optical recording
The evaluation of potential of photochromic material as an erasable storage medium by recording, reading and erasing the optical image in a real-time operation was investigated. For the sake of long-term stability and environmental durability of storage devices, photoresponsive materials must be processed into large-area, high quality solid films. Usually, photochromic materials are doped into a polymer matrix for investigation of applications, and PMMA was chosen in this paper to be used as polymer matrix for optical recording. When this diarylethene was used as recording medium, optical storage was performed by a 650 nm He-Ne laser. With a He-Ne laser in the experimental setup, the exposure time for each spot was 0.08 s and the patterns were about 20 µm. The polarizations of the patterns recorded on dithienylethene 1c/PMMA film is shown in Figure 4. The result indicated that the new photochromic diarylethene can be applied in high capacity optical storage. As shown in Figure 4, the quality of optical recorded in 1c/PMMA film is also fairly good.

In conclusion, a novel photochromic diarylethene 1o was synthesized and its photochromic and fluorescent properties were also investigated. The results showed that this compound exhibited good reversible photochromism both in solution and in PMMA amorphous film. It also exhibited remarkable fluorescence switching in hexane solution. When this diarylethene was used as recording medium, the results demonstrated that the diarylethene compound had attractive properties for high capacity optical storage.

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