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RESEARCH ARTICLE

Two-photon absorption of photochromic diarylethene and its application to rewritable holographic recording

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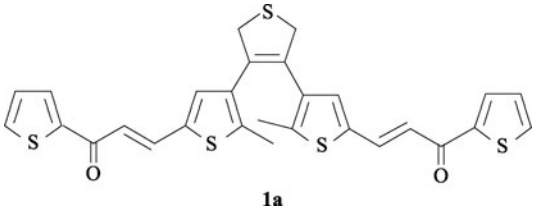
A new photochromic diarylethene (1a) has been prepared. Both its photochromic behavior and nonlinear optical properties are investigated. 1a shows excellent ring-opening (λ_{max} = 386 nm) and ring-closing (λ_{max} = 652 nm) photoisomerization with UV-Vis light irradiation. With 800 nm femtosecond pulsed laser irradiation, 1a shows two-photon-induced photoisomerization, and a two-photon absorption cross-section ($\sigma = 423 \times 10^{50}$ cm^4·s per photon) is obtained by using two-photon induced fluorescence method. The applications of two-photon absorption of 1a to holographic recording has been also investigated. A two-photon induced micro-pattern is recorded on the diarylethene 1a-PMMA film with an femtosecond laser of 800 nm, 100 fs, 1 kHz, 50 mW.

Keywords diarylethene, photoisomerization, two-photon absorption, holographic recording, rewritablity

1 Introduction

Holographic recording has attracted considerable interest in recent years for its advantages of large capacity and high data transfer rate [1,2]. In theory, it is possible to obtain one terabyte on a memory medium of the size of a compact disc by utilizing the entire volume of a medium instead of only its surface. Recent developments in materials and technologies for holographic recording are summarized in some review articles [3,4]. To a great extent, the performance of holographic recording depends on the recording media [5]. Although WORM (write once, read many) memories are close to realization using photopolymer [3,6], the search for rewritable media is still undergoing and challenging because of the high cost or the requirement of very high electric field strength when photorefractive crystals and organic glasses are used [1,4]. Recently, rewritable holographic media using azobenzene-containing polymer has been developed [7–10]. However, low absorption coefficient and small absorption gap between the *cis*-form and *trans*-form of azobenzene are major drawbacks.

Diarylethenes [11,12], as one of the important photochromic molecular systems, have attracted extensive interest because of their fatigue resistance, thermal irreversibility, and potential photoelectronic applications. Photochromic diarylethenes have been widely studied [13–16] for their rewritable optical memory and photoswitching based on the changes in absorbance, fluorescence and chiroptical properties between ring-opening isomers and ring-closing isomers. Although a few examples using photochromic materials as two-photon absorption media for holographic recording have been recently reported [17–21], developments of required materials are still going on and challenging. In this paper, we reported the design and preparation of a new photochromic diarylethene **1a** (as shown in Scheme 1) for two-photon holographic recording media. The diarylethene **1a** used as recording media has several merits: 1) excellent photochromic property and fatigue resistance, which are required for rewritable memory; 2) both ring-open isomer (unrecorded state) and ring-closed isomer (recorded state) are thermally stable; 3) high speed of photoreactions, suitable absorption wavelength, and nonlinear optical property, which are basic elements for two-photon holographic recording; and 4) without special fixing information and negligible shrinkage.



1a

Scheme 1 Chemical structure of photochromic diarylethene **1a**.

2 Experimental

2.1 General

^{1}H NMR spectrum was recorded at 400 MHz with TMS as an internal reference and $CDCl_3$ as solvent. Mass spectrometry (MS) spectra were recorded with GC-MS spectrometer. All chemicals for synthesis were purchased from commercial suppliers, and solvents were purified according to standard

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procedures. Reactions were monitored by thin-layer chromatography (TLC) silica gel plates (60F-254). Column chromatography was performed on silica gel (Merck, 70–230 mesh).

2.2 Material

Preparation of photochromic diarylethene 1a. Diarylethene **1a** was prepared according to the synthetic route illustrated in Scheme 2. The details are described as follows: NaOH (120 mg) was added into a solution of 2-acetylthiophene (378 mg, 3.0 mmol) in EtOH (10 mL). The mixture was stirred for 1 h at room temperature. A solution of 3,4-Bis (5-formyl-2-methylthien-3-yl)-2,5-dihydorthiophene [22] (500 mg, 1.5 mmol) in THF (60 mL) was added slowly into the solution. The mixture was stirred at room temperature and the reaction was detected using TLC plate. When starting material was no longer detected by TLC plate, the mixture was poured into water (50 mL). The product was extracted with dichloromethane methylene chloride (DCM), and combined organic phase was dried with anhydrous Na_2SO_4. After evaporation of the solvent, the crude product was purified by flash column chromatography with petroleum/ethyl acetate (2∶1) as eluent to afford target compound **1a** (610 mg, 70% yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.80 – 7.66 (m, 6H), 7.16 – 7.02 (m, 6H), 4.14 (s, 4H), 2.03 (s, 6H). MS (CI, *m/z*) [M^+]: 550 (100%).

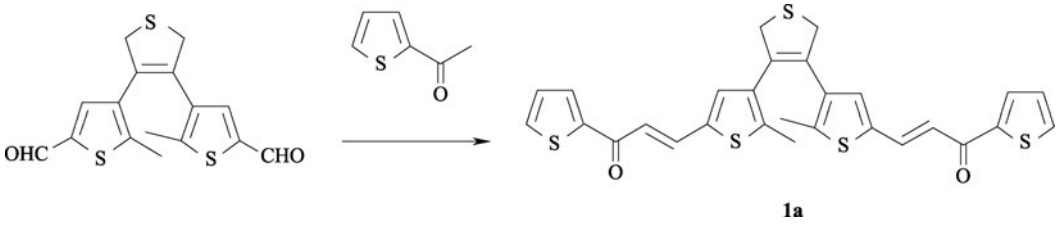
Preparation of diarylethene 1a – PMMA thin film. Diarylethene **1a** (5.0 mg) was dissolved in a 1.0 mL of PMMA-cyclohexanone solution (10%, *w*/*w*). The film was obtained by spin coating on an optical glass (25 mm × 25 mm × 1.5 mm) with a gradient of 700 rpm (10 s) followed by 1200 rpm (30 s) (25°C) and dried in air and kept in the darkness at room temperature. The thickness of the film was about 10 μm.

2.3 Instrumentation

Absorption spectra were measured using an absorption spectrophotometer (Hitachi U-3010). A 360 nm lamp (6 W) and a Xeon light (500 W), with different wavelength filters, were used as light sources for photocoloration and photobleaching, respectively. Two-photon absorption cross sections (TPACS) were measured on Ti:Sapphire femtosecond laser (Tsunami, Spectra-physics, USA) with oscillating wavelength, pulse energy, and repetition rate are of 800 nm, 700 mW, and 1 kHz, respectively. Two-photon image recording was carried out on a Ti:Sapphire self ode-locking oscillator and a Ti:Sapphire regeneration amplifier. The output wavelength is 800 nm, pulse width of 100 fs, repetitive rate of 1 kHz, average power of 50 mW.

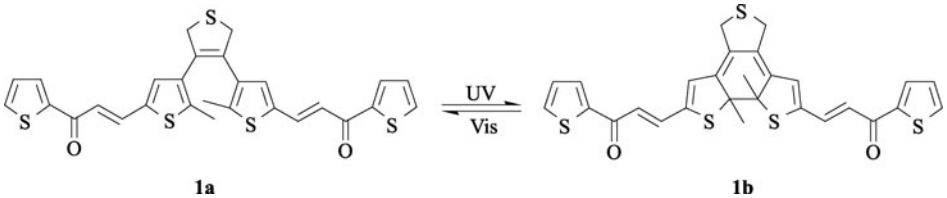
3 Results and discussion

The ring-opening and ring-closing photoisomerization of diarylethene **1a** with UV-Vis irradiation is illustrated in Scheme 3. Upon the irradiation with light of 365 nm, the absorption band of 376 nm ($\varepsilon = 2.7 \times 10^4$, dichloromethane) that is attributed to the ring-open isomer **1a** decreased along with the increase of new band at 642 nm, which corresponds to the ring-closed isomer **1b** (Figure 1). Accompanying the photocyclization, the colorless solution was converted into a green solution. **1b** could be bleached completely back to **1a** with visible light ($\lambda \geqslant 480$ nm), resulting in the color change



1a

Scheme 2 Preparation of diarylethene **1a**.



1a **1b**

Scheme 3 Photoisomerization of diarylethene **1a.**

of the solution from green to colorless. Both ring-opening isomer **1a** and ring-closing isomer **1b** are stable in the dark. The typical absorption spectra changes of diarylethene derivatives [23–27] in solutions are shown in Figure 1. It can also be clearly seen that an isosbestic point appeared in the absorption spectra changes of photocyclization, indicating that only two isomers existed when **2a** underwent the photoisomerization reaction. The photostationary state (PSS) was achieved quickly (1 min) and the conversion yield of 82% was obtained in photostationary state. The fatigue resistance experiments showed that **1a** performed well: there was only about a 5% decrease in absorption (optical density) detected after 50 cycles of coloration/decoloration.

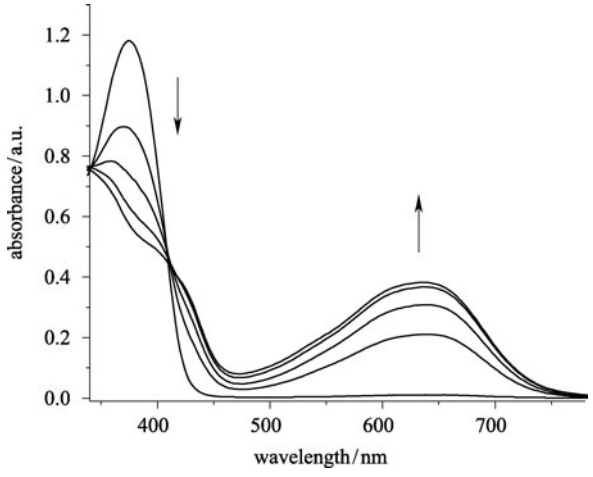


Figure 1 Absorption changes of diarylethene **1a** (2.5×10^{-5} mol·L^{-1}, in CH_2Cl_2) with light irradiation at 365 nm (irradiation period: 0, 15, 30, 45, 60 s).

The nonlinear absorption behavior of diarylethene **1a** was studied by measuring the transmission changes with the incident laser intensity. This measurement was achieved by focusing the excitation beam in the sample cell using a ~20 cm focal length lens. Then the sample cell position was smoothly varied along the laser beam direction so that the local incident intensity could be changed under a fixed incident pulse energy level. The transmitted light changes were monitored using a large area photoelectric detector placed at the far-field region. The measured transmission changes were hence ensured not due to nonlinear refraction contributions. The obtained results are shown in Figure 2. The TPA cross section value of a sample solution can be experimentally determined for a given excitation wavelength by measuring its nonlinear transmissivity as a function of the input light intensity. The TPA cross section value (σ) in DCM is 423×10^{50} cm^4·s per photon by using ~800 nm and ~140 fs Ti:Sapphire laser pulses, respectively.

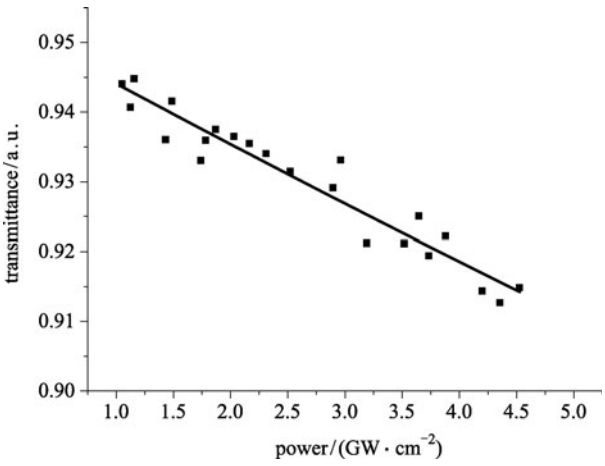


Figure 2 Transmission as a function of the input light intensity, calculated from the experiment (output wavelength 800 nm, pulse width 100 fs, repetitive rate 1 kHz).

Two-photon holographic recording was explored using diarylethene **1a** – PMMA thin film as recording media. The experiment for femtosecond laser induced two-photon holographic imaging was carried out in a laser system of a Ti: Sapphire self mode-locking oscillator and a Ti:Sapphire regeneration amplifier. The output wavelength, pulse width, and repetitive rate are 800 nm, 100 fs, and 1 kHz, respectively. The femtosecond laser was coupled into a microscope via a beam splitter and focused on the diarylethene **1a** – PMMA film by a 10× objective. A diffractive element with designed pattern was placed on the laser beam pathway, behind which a lens was used to adjust the pattern exactly imaged on the sample. Figure 3 shows the micro-pattern recorded on the diarylethene **1a** – PMMA film. The size of the micro-pattern is about 200 μm × 200 μm and the recording exposure time is 3 s.

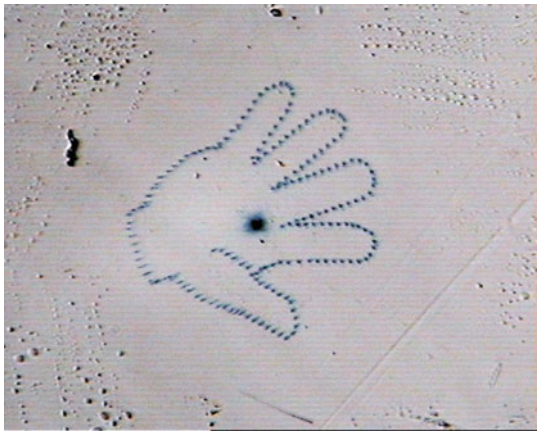


Figure 3 Femtosecond laser induced two-photon micro-pattern recorded on the diarylethene **1a** – PMMA film.

To investigate the lifetime of the diarylethene **1a** in PMMA film and the rewritable property of the material, the following control experiments were performed. First, a sample was kept for six months in darkness at room temperature and then was used to verify its characteristic of two-photon absorption holographic recording. The reconstructed hologram indicated no degradation. In fact, the stability of photochromic diarylethenes with thiophenes was demonstrated. Both isomers were thermally stable even at 80°C [13]. The characteristic of diarylethene allows a wide range of operating temperatures and long lifetime in darkness. Second, the sample that was reconstructed the holographic image was bleached with visible light irradiation ($\geqslant$ 480 nm) for 10 min. When the bleaching was completed, the pattern was recorded on the same place by two-photon absorption hologram. After 10 cycles of recording/bleaching, no significant change was observed (Figure 4) by comparison to the reconstructed image with the original one (Figure 3).

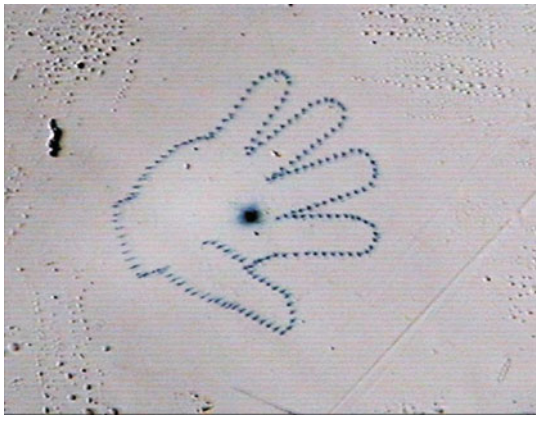


Figure 4 The reconstructed image recorded on the diarylethene **1a** – PMMA film using femtosecond laser induced two-photon holographic recording after 10 write/erase cycles.

4 Conclusion

In summary, a photochromic diarylethene for two-photon absorption holographic recording memory has been demonstrated. With an femtosecond laser of 800 nm, a micro-pattern of 200 μm × 200 μm was recorded on photochromic diarylethene thin film. This material has some good characteristics, such as high resolution, negligible shrinkage, and rewritability. The design and preparation of a material with large two-photon absorption cross-section may be the next goal in this work.

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