Photochromic diarylethene for two-photon 3D optical storage

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Abstract

We had accomplished recording and readout of bit patterns by two-photon 3D optical storage technology using a new photochromic diarylethene, 1,2-bis(2-methyl-5-methylene-n-butylamido-thien-3-yl)perfluorocyclopentene (BMMBTP), as memory medium. The photochromic reaction, both in solution and in poly(methyl methacrylate) (PMMA) amorphous film, and fluorescence property of BMMBTP were investigated. © 2006 Elsevier B.V. All rights reserved.

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1. Introduction

With the increasing demands for higher information storage densities, many researchers are devoting to pursue a number of strategies to develop high-density capabilities for optical data storage in organic-based systems [1]. Various approaches have been proposed to enhance the memory density, such as three-dimensional (3D) recording, magnetically induced super-resolution, and near-field optical recording and multiple-wavelength recording, etc. [2–5]. 3D memory based two-photon absorption is one of the most promising for increasing the capacity of computer data storage as a means of achieving high-density, fast access, volume optical information storage [6]. One advantage of 3D memory based two-photon absorption is that there is less cross talk between neighboring data layers because the probability of two-photon excitation is proportional to the squared intensity of the incident light so that this effect produces excitation only within a small region of the focus spot of the recording objective. Another merit is the use of infrared illumination, which results in the reduction of scattering and permits the recording of layers at a deep depth in thick material [7].

Until now, most photochromic media have been prepared by doping photochromophores in a polymeric media and applied to various optical storage [5–8–10], and there were some publications concerning 3D memory based two-photon absorption [11–13]. As described in the above references, it could be easily concluded that three kinds of photochromic organic compounds, benzopyrylospiran [11], dicyanoethene [12], and spiro-naphthoxazine [13], were used as two-photon 3D optical storage media. So far, to the best our knowledge, there is only one example of using photochromic diarylethene compound for application in two-photon 3D optical storage reported by Zhou et al. [14]. In that paper, they used a hybrid diarylethene substituted by thienyl and benzothienyl groups at 2-position, whose photochromic properties both in solution and in PMMA film are very faint. Compared to these photochromic organic compounds, diarylethene compounds are regarded as the best potential candidates for high-density photon-mode optical storage because of their good thermal stability of two isomers, remarkable fatigue resistance, rapid response, and high reactivity in the solid state [15–17]. In this paper, the photochromic properties of 1,2-bis(2-methyl-5-methylene-n-butylamido-thien-3-yl)perfluorocyclopentene (BMMBTP) both in solution and doped in poly(methyl methacrylate) (PMMA) matrix were investigated and its application for two-photon 3D optical recording medium was presented.

2. Experiment

Mass spectra were measured with a HP5989A mass spectrometer. 1H 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 a PerkinElmer Lambda-900 UV/VIS/NIR 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. Fluorescence spectra were measured using a Hitachi F-4500 spectrophotometer.

The new diarylethene BMMBTP was prepared by the condensation reaction of 1,2-bis(2-methyl-5-formyl-thien-3-yl)perfluorocyclopentene (BMFTP) [18] with butyl amine (Scheme 1). A solution of BMFTP (0.0850 g, 0.2 mmol) and butyl amine (0.1 mL, 1 mmol) in anhydrous ethanol (30 mL) was heated to reflux for 2 h. After the reaction mixture was cooled to room temperature, the solvent was removed under vacuum. Column chromatography (silica gel, ethyl acetate–oil ether 1:10) afforded BMMBTP in 93% yield (0.0995 g). Its structure was confirmed by mass spectrometry and NMR (MS m/z 535(M+1), 534(M), 504(–2CH₃), 474(–4CH₃); ¹H NMR (400 MHz, CDCl₃): δ 0.92–0.96 (m, 6H), 1.36–1.42 (m, 4H), 1.62–1.67 (m, 4H), 2.03 (s, 6H), 3.54–3.58 (m, 4H), 7.22 (s, 2H), 8.25 (s, 2H)).

The photochromic diarylethene-PMMA film was prepared as follows: 10.0 mg BMMBTP was dissolved in a 1.0 mL PMMA-chloroform solution (including 100 mg PMMA). The film was obtained by spin-coating of the diarylethene-PMMA solution on an optical glass (20×20×1 mm), dried in air and kept in darkness at room temperature. The thickness of the film was about 20 μm.

Two-photon 3D optical storage was accomplished by the setup described in Fig. 1 [19]. It could be functionally divided into four parts: (1) femtosecond laser system (a pump Nd:YVO₄ laser (532 nm continuous light) and a Ti: sapphire laser (the pulse width: 80 fs, the central wavelength: 800 nm and the repetition frequency: 80 MHz)); (2) confocal laser scanning microscopy (high NA (1.25) objective lens, the excitation intensity in its focal point > 100 GW/cm²); (3) exposure controlling system and (4) real-time monitor system. A reflection confocal scanning-fluorescence microscope was used as a readout system for digital data stored in a 3D photochromic optical recording.

3. Results and discussion

3.1. Photochromism of diarylethene

3.1.1. Photochromism of diarylethene BMMBTP in solution and PMMA film

Photoisomerization of diarylethene BMMBTP was illustrated by Scheme 2. Its absorption spectra changes in chloroform solution...
(3.0 × 10^{-5} \text{ mol/L}) and PMMA film (10\% w/w) before and after irradiation were shown in Fig. 2(a) and (b), respectively. As shown in Fig. 2(a), the absorption of BMMBTP-O was observed at 266 nm ($\varepsilon = 4.09 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$) in chloroform. Upon irradiation with 254 nm light, the chloroform solution turned blue, in which the absorption maximum was observed at 596 nm ($\varepsilon = 9.80 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$). The blue solution returned to a colorless one on irradiation with visible light ($\lambda > 500$ nm). In the PMMA amorphous film, diarylethene BMMBTP-O also showed good photochromic property, as shown in Fig. 2(b). Upon irradiation with 313 nm light, the colorless BMMBTP-O PMMA film ($\lambda_{\text{max}} = 326$ nm) turned blue with a new broad absorption band at $\lambda_{\text{max}} = 610$ nm appeared, which was assigned to the formation of the closed isomer BMMBTP-C. The colored PMMA film can convert to colorless on irradiation of appropriate wavelength visible light ($\lambda > 500$ nm). The red shift of the maximum absorption of BMMBTP-C in PMMA film in comparison with those in hexane solution can be ascribed to the stabilization of molecular arrangement in solid state [20]. It was also found that both open-ring isomer and closed-ring isomer of BMMBTP were stable at room temperature in darkness.

3.1.2. Single-photon fluorescence property of BMMBTP in PMMA film

The fluorescence properties of the above BMMBTP–PMMA film were measured using a Hitachi F-4500 spectrophotometer. Both the breadth of excitation slit and that of emission slit were 2.5 nm. The excitation and fluorescence spectra of BMMBTP in PMMA film at room temperature was illustrated in Fig. 3. In this figure, curve A and C represented the excitation spectra of BMMBTP-O and the

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Fig. 2. Absorption spectra of diarylethene BMMBTP. (a) In chloroform ($C=5.0 \times 10^{-7} \text{ mol/L}$); (b) in PMMA amorphous film (10\% w/w). Open-ring isomer (BMMBTP-O, solid-line), closed-ring isomer (BMMBTP-C, dashed-line), and in the photostationary state under irradiation with 254 nm UV light (dash dotted-line).

Fig. 3. Fluorescence and excitation spectra of BMMBTP in PMMA film. A and C — excitation spectra of BMMBTP-O and PSS, respectively, monitored at 650 nm; B and D — fluorescence emission spectra of BMMBTP-O and PSS, respectively, excited at 610 nm.
photostationary state (PSS) under irradiation with 313 nm light, respectively. Curve B and D represented the fluorescence (emission) spectra of BMMBTP-O and the photostationary state (PSS), respectively. As shown in Fig. 3, it could be clearly seen that the open-ring isomers of BMMBTP–PMMA film showed relatively strong fluorescence at 650 nm when excited at 610 nm. The fluorescence intensity decreased along with the photochromism from open-ring isomers to closed-ring isomers upon irradiation with 313 nm UV light and BMMBTP-C showed almost no fluorescence [21]. When UV irradiation was arrived at the photostationary state, the fluorescence intensity decreased remarkably and its value became very small. The 650 nm band shown in the D line of Fig. 3 was attributed to residual BMMBTP-O.

Because only 532 nm light can be used in our two-photon 3D optical storage system to read out the recorded information, it is needed that the recording materials had clear difference of fluorescence intensity excited at 532 nm light besides two-photon exciting characteristics. Therefore, we also investigated the fluorescence property of BMMBTP–PMMA film excited at 532 nm. As illustrated in Fig. 4, the significant difference between the fluorescence intensity of BMMBTP-O and that of the photostationary state when exciting at 532 nm can be clearly observed. This made the two-photon 3D optical storage using this material possible.

3.1.3. Two-photon 3D optical storage

Two-photon 3D optical storage of a BMMBTP–PMMA film (thickness ≈ 20 μm) was investigated, and the readout images of written bits in two consecutive layers were shown in Fig. 5. The 3D data were written with a Ti: sapphire laser at 800 nm in mode-locked pulse laser operation and with an objective lens with a NA of 1.25 so that two-photon absorption processes induced photoconversion of the chromophore (written bit) at only the focus position. In illuminated areas in which the two-photon absorption did not take place the materials remains transparent. Data were recorded in two layers with bit by bit forming the Chinese word “Jiangxi”. The bit interval was 4 × 4 μm per layer, and the separation distance between layers was ∼ 15 μm. The written data can be clearly read through the significant difference between the fluorescence intensity of the open-ring isomer and that of closed-ring isomer without cross talk with a reflection confocal scanning-fluorescence microscope by 532 nm consecutive light.

4. Conclusion

The new diarylethene BMMBTP was synthesized and its photochromism, fluorescence and two-photon 3D optical recording were investigated in detail. This compound showed good photochromic reactions both in solution and in PMMA amorphous film by photoirradiation. In PMMA film, the closed-ring isomer of BMMBTP presented absorption band at 606 nm upon irradiation at 313 nm, and the open-ring isomer of BMMBTP showed relatively strong fluorescence at 650 nm when excited at 610 nm. Finally, we had accomplished experimentally two-photon 3D optical storage on BMMBTP–PMMA film, and optical bit patterns in a 20 μm thickness film could be efficiently written and read out when a femtosecond laser and a reflection confocal scanning-fluorescence microscope were utilized.

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