A rapid response photochromic diarylethene material for rewritable holographic data storage

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A novel diarylethene, namely 4,5-(2,5-dimethyl thiophene) phthalimide, was synthesized and successfully introduced to rewritable holographic data storage. Upon the alternative illumination of UV and visible light (λ>400 nm), this compound underwent rapid, reversible inter-conversion between colorless open-ring isomer and yellow-green ring-closed form in both solution and polymethyl methacrylate (PMMA) film. Subsequently, we investigated the characteristics of volume homographic recording of the diarylethene-doped PMMA film (1 μm thick). The maximum refractive index modulation (0.87‰) of the film during recording could be reached within just 120 s which gave the ability of fast recording. The high quality reconstruction after 50 write/erase cycles demonstrated its excellent fatigue-resistance and high resolution. All those results indicated that this molecule was a reliable fast write/erase holographic storage material.

photochromism, diarylethene, rewritable holographic data storage, optical storage

With the development of information science, the demands for large storage systems are increasing daily. Optical data storage was always a very important storage technology for the advantage that the reading and writing of the digital data did not require contact and was therefore wear-free [1]. The optical data-storage formats, currently on the market such as compact disc (CD), digital versatile disc (DVD), Blue-ray disc (BD) and high density DVD (HD DVD), were based on the principles of far-field optics. For those formats, the storage density therefore followed the far-field optics scaling law NA/λ^2, where NA stands for numerical aperture and λ is the wavelength of the recording light. Theoretically, the storage density could be increased by reducing λ and increasing the NA. However, with the advent of BD, the planar data storage has already reached its upper limit [2,3].

Holographic data storage used the entire volume of the storage medium. The data could be arranged in multiple information layers, which made it provide large storage capacity easily. The density potential reaches V/λ^3, where V denotes the recording volume and λ is the wavelength of the recording light source. In addition, holographic memory was a defect-tolerant device since each bit of information was generated from the entirety of a holographic memory. In view of these factors, holographic volume memory was long envisioned as the next generation storage technology [4].

Photochromism was defined as a transformation of a single chemical species between two states that have different geometrical structures, absorption spectra and refractive index, etc. The change was achieved by the illumination of lights with different wavelengths. When using photochromic materials in holographic storage, the refractive index of the photochromic molecules in the film would get changed with the laser irradiation. The holographic diffrac-

tion efficiency mainly came from the refraction index change of the medium. With this feature, it was possible to use the interference field of content light and reference light form the refractive index modulation holographic figure in the photochromic materials film. Some successful applications have been reported [5–10].

Among all kinds of photochromic materials, organic diarylethene derivatives had been extensively studied because of their excellent fatigue resistance and thermal irreversibility [11]. However, most diarylethenes that had been applied in holographic storage suffered from several drawbacks, such as laborious synthesis procedures and rather expensive reagents. Herein, we reported a novel diarylethene, namely 4,5-(2,5-dimethyl thiophene) phthalimide, as a new type of reliable rewritable holographic storage materials. This compound was doped in polymethyl methacrylate (PMMA) thin film using the method of spin coating. The holographic recording characteristics were investigated in detail.

1 Experimental

1.1 Reagents and devices

Reagents were purchased from Beijing Chemical Reagent Company and Alfa Aesar Company. Solvents used in spectroscopy were refined by standard methods, while reagents were used as received in other experiments.

Absorption spectra were measured by using HP8452A Spectrophotometer. IR spectra were performed on a PE 2000 FT-IR Spectrometer. NMR spectra were recorded on JOEL FX-90G Spectrometer with TMS as internal reference. Mass spectroscopy was obtained on Bruker LC-MS/MS (ESQUIRE-LC) 1100 series. A Flash-EA-1112 Element Analyzer was used for elemental analyses. Photo illumination was carried out using a high pressure mercury lamp (Mejiro precision, SHG-200; 1000 W, Japan) with suitable filters.
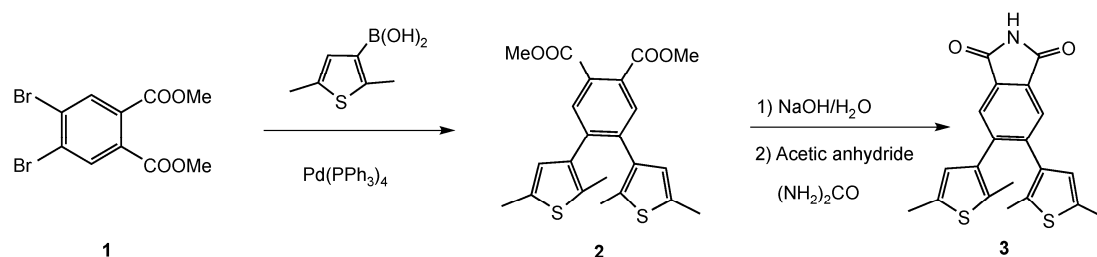
The target molecule 4,5-(2,5-dimethyl thiophene) phthalimide **3** were synthesized according to the literature (Scheme 1) [12]. The products were characterized by NMR, IR, UV-vis, MS and elementary analysis.

1.2 Synthesis of compound 2

A mixture of 4,5-dibromophthalic acid dimethyl ester (3.91 g), 2,5-dimethyl-thien-3-ylboronic acid (2.96 g) and finely grounded dry potassium carbonate powder (9.17 g) was added into dioxane (30 mL) under argon flux. After being stirred for 15 min at room temperature, $Pd(PPh_3)_4$ (0.45 g) was added into the argon flow. The mixture was then heated to 90°C for 9 h with TLC monitoring. After being cooled to room temperature, H_2O (50 mL) and Et_2O (50 mL) were added, and the organic and aqueous phases were separated. The aqueous layer was then extracted twice with Et_2O. The combined organic phase was washed with NaOH solution (2 mol/L) and pure water in turn, dried over anhydride Na_2SO_4 and concentrated. Purification by column chromatography on silica gel gave the product 4,5-bis(2,5-dimethyl thiophen-3-yl) phthalate (compound **2**) (2.94 g). The total yield was 86.7%.

1.3 Synthesis of compound 3

The compound **2** obtained from the Suzuki cross-coupling reaction (2.8 g) was dissolved in THF (10 mL) and slowly added to a NaOH saturated mixed solution with water (10 mL) and methanol (50 mL). This was followed by stirring for 5 h at 40°C. The white precipitate which formed was filtered off and washed with methanol. Then, it was dissolved in water and slowly acidified by dilute HCl (4 mol/L) at 0°C. The yellow precipitate (2.78 g) was collected and dried in vacuum. The crude product obtained in the above steps was added to Ac_2O (12 mL) and the mixture was stirred at 80°C for 2.5 h. AcOH generated in the reaction and excess Ac_2O were removed by azeotropic evaporation with toluene several times, and then dried in vacuum. The product obtained above was placed in a round-bottomed flask containing 16 g urea under argon flow. The solid mixture was then heated to 140°C, forming a clear, yellow melt. It was stirred for 15 min until bubbles ceased and then was allowed to cool to room temperature. Subsequently, water (100 mL) was added and the solid mixture was ultrasonically dispersed. The precipitate was collected and dried in vacuum. Purification by column chromatography on silicagel gave the target molecule 4,5-(2,5-dimethyl thiophene)


Scheme 1 The synthetic of target molecules 4,5-(2,5-dimethyl thiophene) phthalimide.

phthalimide (compoud **3**) 2.11 g. The total yield was 85.3%. ^{1}H NMR (300 MHz, CDCl$_3$) δ: 2.05 (s, 6H, –OCH$_3$), 2.44 (s, 6H, –OCH$_3$), 6.27 (s, 2H), 7.80 (s, 2H), 7.85 (s, 1H). ^{13}C NMR: 13.81, 15.14, 126.00, 127.06, 130.90, 134.27, 135.90, 136.12, 167.98. IR (cm^{-1}): 3215.99, 3069.83, 2953.26, 2917.24, 2853.91, 1774.34, 1715.16, 1614.44, 1494.44, 1438.60, 1372.95, 1327.43, 834.53, 749.49. ESI-MS: 366.17 [M+H]$^+$. Anal. Calcd. for C$_{20}$H$_{17}$NO$_2$S$_2$ (%): C, 65.37; H, 4.66; N, 3.81; Found (%): C, 65.34; H, 4.62; N, 3.82. mp: 180–182°C.

2   Results and discussion

Generally, the diarylethene had two isomers, one with a less extended π-electron conjugation (open-ring isomer) and the other with a more π-electron conjugation (closed-ring isomer), and they showed distinct colors. The reversible photoisomerization of compound **3** upon the alternative illumination of UV and visible light was depicted in Scheme 2, and such process was demonstrated by UV-vis spectroscopy.

As shown in Figure 1, the solution of the open-ring isomer (**3o**) of compound **3** in chloroform is colorless (2×10^{-5} mol/L), with a strong absorption at about 365 nm. Upon the illumination of 365 nm light, the color of the solution turned to yellow-green. Meanwhile, two new absorption peaks at
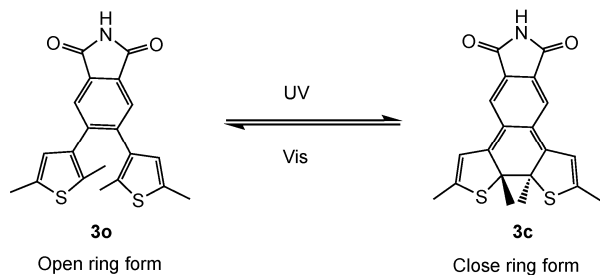
about 420 and 710 nm, appeared. The photostationary state (PSS) was reached after 50 s and at that time, the absorbance at 420 and 710 nm increased to 0.55 and 0.10 respectively. The molar extinction coefficients of initial state and PSS were calculated and displayed in Table 1.

Irradiation of the PSS solution of compound **3** at the wavelength greater than 400 nm resulted in an immediate photo-induced ring-opening reaction which converted **3c** to **3o**. As shown in Figure 2, the original absorption spectrum was regenerated after 120 s and the color of the solution returned to colorless. When doped in PMMA thin film for holographic storage test, the molecule showed good fatigue-resistance. The switching process can be repeated at least 50 times and no obvious degradation was observed in the holographic storage test.

The kinetics of the photoisomerization was also studied in detail [13]. Accurate calculation in Figure 3(a) showed that ln(0.55–Abs) (0.55 is the absorbance of PPS at 420 nm and Abs means the absorbance at 420 nm in the time of t) had a linear relationship with time which proved that this was a first order chemical reaction, the reaction rate constant k_1 is 0.025 s^{-1}. However, in the process from PSS to **3o**, the Abs just had a linear relationship with time. That meant it was a zero-order chemical reaction, and the reaction rate constant k_2 was 1.45×10^{-7} mol/(L s).

Subsequently, we explored the potential application of compound **3** in holographic storage. The novel diarylethene

Scheme 2   Photoisomerization of the compound **3** upon the irradiation of different wavelength lights.

Table 1   Molar extinction coefficient of **3** in chloroform (c=2.0×10^{-5} mol/L)

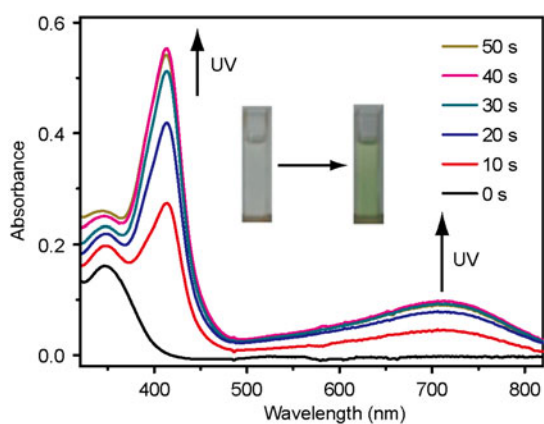| Compound	ε (L/(mol cm))	
	420 nm	710 nm
3o	46.5	97.5
PSS	2.75×10^4	0.50×10^4

Figure 1   Absorption spectral changes of compound **3o** in chloroform (2.03×10^{-5} mol/L) with increasing UV irradiation time. Inset: the color changes of compound **3** upon UV irradiation.
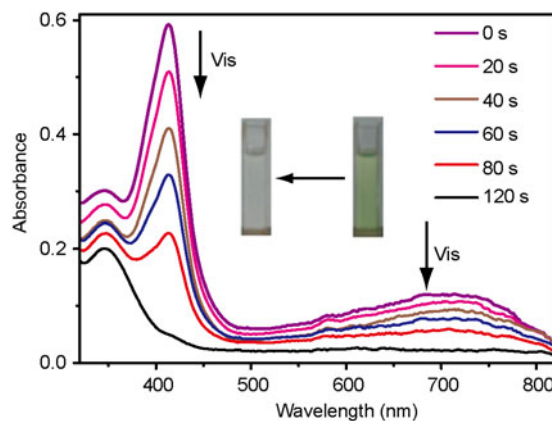
Figure 2   Absorption spectral changes of the photostationary state of compound **3** in chloroform (2.15×10^{-5} mol/L) with increasing visible light irradiation time. Inset: the color changes of compound **3** upon visible light irradiation.
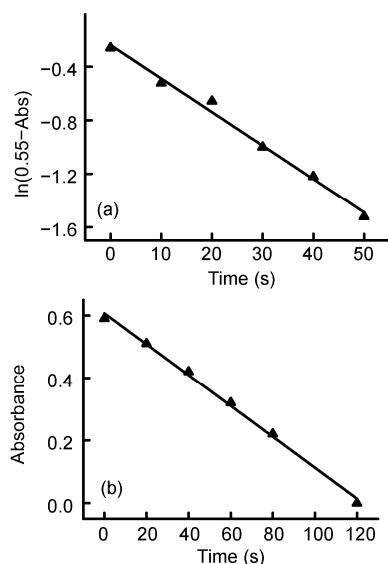
Figure 3   Kinetics of the photoisomerization. (a) From **3o** to PSS upon the illumination of 365 nm light, first-order reaction with k_1=0.025 s^{-1}; (b) from PSS to **3o** upon the illumination of light (λ>400 nm), zero-order reaction with k_2=1.45×10^{-7} mol/(L s).

was doped in PMMA thin film using the method of spin coating [14]. The mass ratio of **3c** : PMMA is 1 : 4 and the thickness was about 1 μm. The film was irradiated for sufficient time to ensure that **3o** translate into **3c** as much as possible before being used.

Figure 4 showed the optical path used to measure the diffraction efficiency and refractive index modulation of the material. A laser (532 nm) was extended, filtered collimated with a collimator filter and diaphragm. When passing through a polarized beam-splitting prism (PBS), the light

was divided into two beams, a reference beam and an object beam. Two half-wave plates HP1 and HP2 were used to adjust the two beams to coherent light. Three computer operating switches were used to control the optical path and the two detectors were used to recorded the light intensity. The diarylethene-doped PMMA film was irradiated sufficient time to achieve closed-ring form. The method we used was recording for 10 s and measuring 10 times in a second and then take the average of 10 data. Repeat this operation to get a time-related data. When recording, the shutter 1, 2 was open, the diarylethene underwent photochemical reaction within the interference fringes of reference light and object light to form the grating. When measuring, the shutter 1, 3 was open. Only the reference beam passed through the film, the detector 1, 2 separately record the diffraction intensity I_d and the transmitted light intensity I_t when the reference beam passed through the newly formed grating. Using the formula diffraction efficiency:

$$\eta = \frac{I_d}{I_d + I_t}. \tag{1}$$

According to Kogelnik's two-wave coupled wave theory [15], the refractive index modulation can be expressed as

$$\Delta n = \frac{\lambda \cos\theta \arcsin\sqrt{\eta}}{\pi d}, \tag{2}$$

where d is the grating thickness, which was also the thickness of thin film, θ and λ are the Bragg angle and wavelength. Using the date, the refractive index modulation during the grating recording at different times was obtained, which was shown in Figure 5. It showed us that the maximum refractive index modulation (0.87‰) could be reached
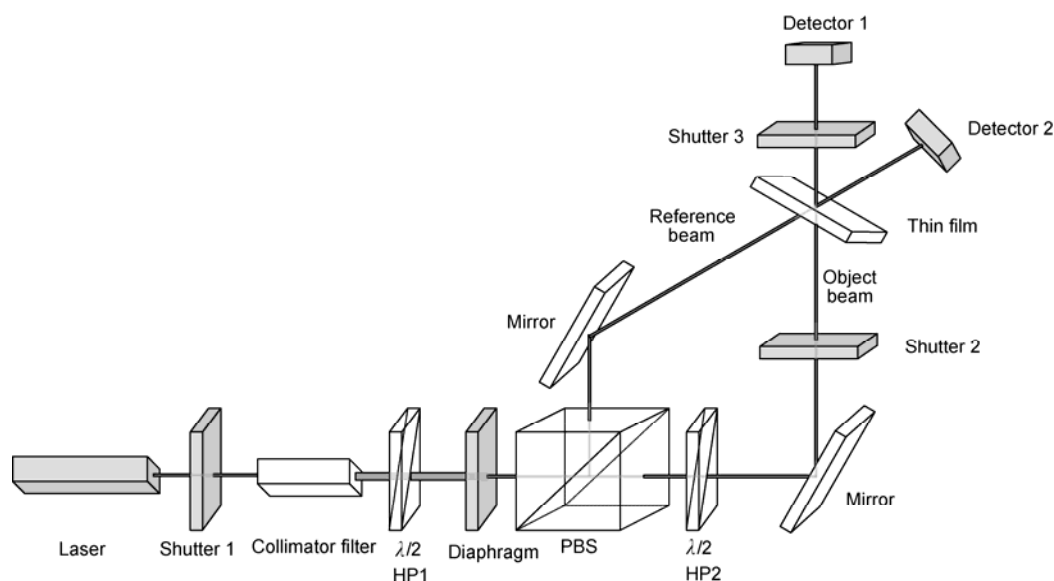

Figure 4   Experimental setup for holographic recording and readout, Grating was formed in the thin film and with the control of shutter, diffraction intensity and transmitted light intensity can be recorded by the two detectors when the reference beam passed through the film.
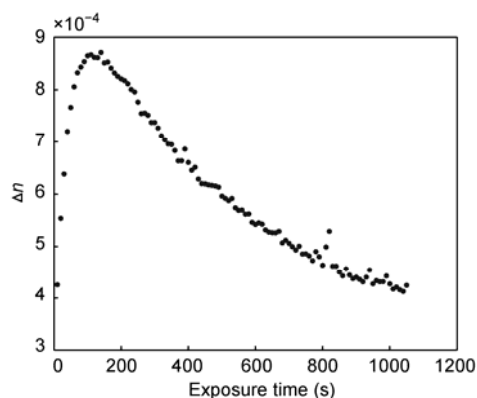
Figure 5 Refractive index modulation during holographic recording. The maximum (0.87‰) can be reached within just 120 s.

quickly within about 120 s. This performance rendered the capability of fast recording of the diarylethene materials. Combined with its rapid cyclization under UV, this molecule showed its potential in fast write/erase volume holographic storage field.

When the resolution chart information was added to the object light, it would be stored on the film in the form of a grating. When the reference beam passed through the film, the resolution chart would be reconstructed. To investigate the reversible holographic storage ability of the diarylethene-PMMA film, we made a comparison between the reconstruction after first recording and the reconstruction after 50 write/erase cycles. As shown in Figure 6, there was no obvious difference between the reconstruction qualities, which indicated that this molecule was reliable rewritable holographic storage material.
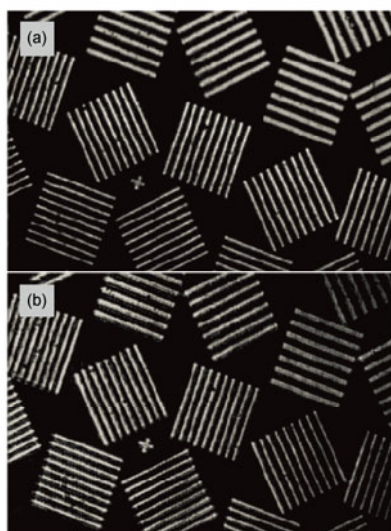

Figure 6 Resolution chart reconstructed with the reference beam (a) after first recording and (b) after 50 write/erase cycles with a negligible decline in resolution.

3 Conclusion

A novel diarylethene was synthesized, and its good reversible photochromic behavior had been demonstrated. The absorption spectral changes and kinetics study of the molecule during the photoisomerization showed its rapid response to light. When the molecule was successfully introduced to the field of holographic storage, the maximum refractive index modulation (0.87‰) could be reached quickly within just 120 s, which gave the ability of fast recording. The reversible holographic storage ability was also confirmed by the high quality reconstruction after 50 write/erase cycles. All those results indicated that this molecule was a reliable fast write/erase holographic storage material. Besides rewritable holographic recording, this molecule may also be useful in other fields based on its good switching property. Future work will focus on higher resolution storage, super fatigue resistance and higher storage density.

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