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RESEARCH ARTICLE

Polarization holographic optical recording based on a new photochromic diarylethene compound

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A new unsymmetrical photochromic diarylethene, namely1-[2-methyl-5-(p-N,N-dimethylaminophenyl)-3-thienyl]-2-[2-methyl-5-(3-methoxylphenyl)-3-thienyl] perfluorocyclopentene (1a), was synthesized. The compound showed good photochromism, high sensitivity and remarkable fatigue-resistance both in solution and in poly(methyl methacrylate) (PMMA) matrix with UV/Vis light irradiation. The absorption maximum of its closed-ring isomer was observed at 624 nm in PMMA amorphous film. It is a nice match for the wavelength of the recording laser (633 nm). Using this target compound as recording medium, four types of polarization holographic optical recordings were performed successfully using a He-Ne laser. The results showed that only the orthogonal circular polarization recording could obtain a hologram with high diffraction efficiency and high signal-to noise-ratio. With multiplexing recording technology, three types of polarization multiplexing holographic optical recordings, including angular multiplexing, polarization multiplexing, and angular plus polarization multiplexing holographic recording, were also carried out perfectly based on its photo-induced anisotropic phenomenon accompanying the photochromic reaction by photoirradiation. The results demonstrate that the multiplexing recording technology is an effective method to improve recording capacity when using diarylethene 1 as recording medium.

Keywords diarylethene, photochromism, polarization holographic recording, multiplexing recording technology

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1 Introduction

With the increasing requirements of huge information storage, the demand for high speed input and larger memory capacity is becoming mandatory. Holographic recording is thought to be one of the important forms of optical memories because of its advantages of a large capacity and high speed of information input and output [1]. However, materials are always a challenging problem in holographic storage [2–6]. For a holographic recording system, the recording media must satisfy stringent criteria, including high dynamic range, dimensional stability, rapid response time, etc. [7].

Generally, there are two main classes of materials used for holographic recording, photorefractive materials and photosensitive polymerizable acrylic materials [8–10]. Each kind of material has its advantages and disadvantages. For instance, photorefractive materials exhibit high dynamic range, and photopolymer materials are sensitive to light throughout the visible spectral region. However, slow response times for photorefractive materials and special fixing information after recording for photosensitive polymerizable acrylic materials pose major disadvantages [1]. These disadvantages can be overcome by using photochromic compounds as holographic recording media. One of the most promising photochromic candidates is diarylethene.

Upon alternating irradiation with UV and visible light, photochromic diarylethenes reversibly change not only their absorption spectra but also other physicochemical properties, such as oxidation/reduction potentials, dielectric constants, refractive index and so on, during the photochromic reaction [11]. These molecular property changes are of great interest because of their potential applications for designing multi-stable switching materials [12–15]. One the other hand, the advantages of photochromic diarylethenes (for instance, their good thermal stability, remarkable fatigue resistance, high sensitivity and rapid response to different wavelength lasers) all satisfy the requirements of high-density photon-mode optical recording [16]. To date, many researches have been carried out on photochromic diarylethene compounds in various optical recordings, such as multi-wavelength/level optical recording [17–19], near-field optical recording [20,21], and two-photon 3D optical [22,23], etc. However, studies concerning polarization holographic optical recording using diarylethenes as memory media are very rare except for several publications [24–27]. Here in this work, a new photochromic diarylethene, 1-[2-methyl-5-(p-N,N'-dimethylaminophenyl)-3-thienyl]-2-[2-methyl-5-(3-methoxylphenyl)-3-thienyl]perfluorocyclopentene, was synthesized. Mixing this compound into poly(methyl methacrylate) (PMMA) thin film as recording medium, different types of polarization holographic recordings and polarization multiplexing holographic recordings were performed successfully by a He-Ne laser with a 633 nm wavelength. Its photochromic reaction is shown in Scheme 1.

2 Experimentals

2.1 Synthesis of recording material

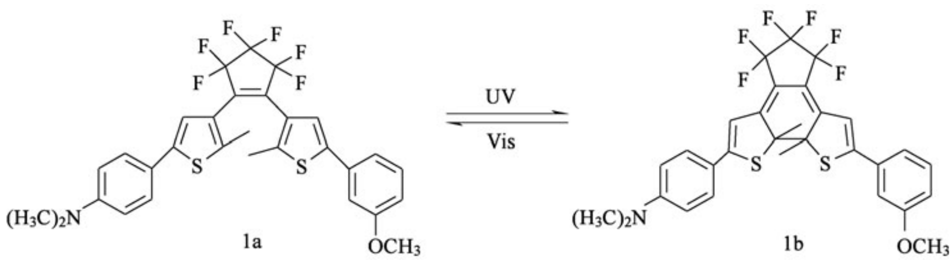
The synthetic route for diarylethene **1a** is shown in Scheme 2. Firstly, Suzuki coupling of 3-bromo-2-methyl-5-thienylboronic acid (**2**) [28–30] with 1-bromo-3-methoxylbenzene yielded 3-bromo-2-methyl-5-(3-methoxylphenyl)thiophene (**4**). It was lithiated and then coupled with octafluorocyclopentene to generate a mono-substituted diarylethene compound (**5**). Finally, 3-bromo-2-methyl-5-[4-(N,N-dimethylammino)phenyl]thiophene (**3**) [31] was lithiated and then coupled with compound **5** to give the target diarylethene compound **1a**. The structure of **1a** was confirmed by NMR spectroscopy, IR, and elemental analysis. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 1.87 (s, 3H,–CH_3), 2.06 (s, 3H, –CH_3), 2.92 (s, 3H, –CH_3), 2.99 (s, 3H, –CH_3), 3.78 (s, 3H, –OCH_3), 6.50 (s, 1H, benzene–H), 6.60 (t, 2H, J = 8.0 Hz, benzene–H), 6.75 (d, 1H, J = 8.0 Hz, benzene–H), 6.98 (s, 1H, thiophene–H), 6.99 (s, 1H, thiophene–H), 7.02-7.37 (m, 4H, benzene–H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 14.42, 40.42, 55.34, 111.28, 112.49, 113.36, 118.202, 119.93, 121.74, 122.77, 125.59, 125.91, 126.56, 130.01, 134.73, 139.13, 141.39, 141.86, 143.09, 150.24, 160.04; IR (KBr,ν, cm^{-1}): 777, 880, 811, 987, 1062, 1115, 1192, 1273, 1341, 1401, 1524, 1611. Anal. Calcd for $C_{30}H_{25}F_6NOS_2$ (%): C, 60.70; H, 4.24; N, 2.36. Found: C, 60.77; H, 4.31, N, 2.35.

2.2 Preparation of recording film

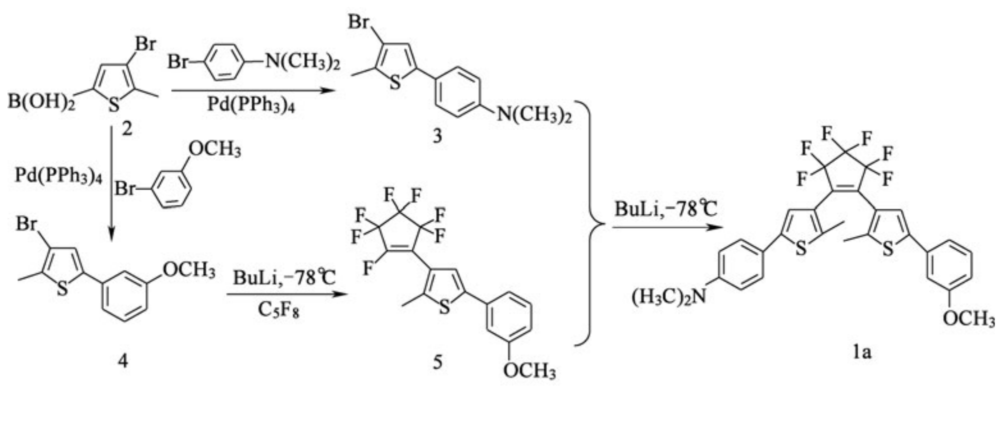
The target compound **1a** (5 mg) was dissolved in PMMA–chloroform solution (10%, w/w, 0.5 mL). The mixture solution was then spin coated on a glass substrate (20 mm × 20 mm × 1 mm) with a spin rotation speed of 1500 rpm. The thickness of the film was about 10 μm. The film was dried in air and kept in darkness at room temperature, and it was colored homogeneously upon irradiation with 313 so that the open-ring isomer **1a** could convert completely to the closed-ring isomer **1b** before being recorded.

2.3 Recording and readout

The experimental setup for polarization holographic recording and readout is presented in Figure 1. A linearly polarized light generated from a He-Ne laser passes through a half-wave plate and a polarized beam splitter after filtering and collimating; the light is divided into two parts as a reference beam and an



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



Scheme 2 Synthes is of diarylethene **1a**.

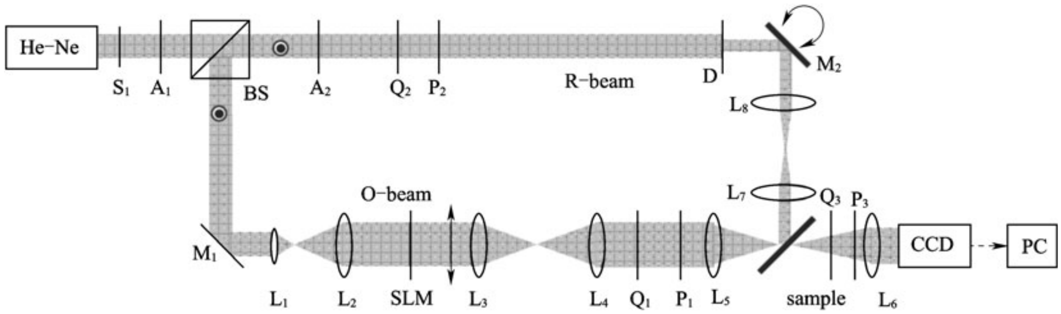


Figure 1 Schematic diagram of the holographic storage setup: BS = beam splitter; M = mirror.

object beam. The hologram was recorded by the intersecting of the object beam containing the information and a reference beam in the sample film, and the hologram images on the sample film were readout by the attenuated reference beam with different angles; the reconstructed hologram images were recorded on a charge-coupled device (CCD) camera.

3 Results and discussion

3.1 Photochromism of diarylethene

The photochromic property of diarylethene **1a** was investigated both in hexane (c, 3×10^{-5} mol·L^{-1}) and in PMMA amorphous film (10%, w/w). Its absorption spectral changes induced by photoirradiation at room temperature are shown in Figure 2. In hexane, the maximum absorption peak of the open-ring isomer **1a** was observed at 315 nm (ϵ, 3×10^{4} L·mol^{-1}·cm^{-1}). Upon irradiation with a light at 254 nm, the colorless solution turned blue due to the appearance of a new visible absorption band at 603 nm attributable to the formation of the closed-ring isomer **1b** (ε, 1.9×10^{4} L·mol^{-1}·cm^{-1}). The solution reverted from blue to colorless upon irradiation with the appropriate wavelength visible light ($\lambda > 450$ nm), indicating that **1b** returned to the initial state **1a**, and a clear isosbestic point was observed at 350 nm (Figure 2(a)). The cyclization and cycloreversion quantum yields of diarylethene **1** were 0.42 and 0.0017, respectively, using 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene as a reference [32]. Similarly, diarylethene **1a** also underwent reversible photochromic reaction in PMMA film, as shown in Figure 2(b). In PMMA amorphous film, the open-ring isomer **1a** has maximum absorption at 318 nm. Upon irradiation with 313 nm UV light, the colorless **1a** turned blue with the appearance of a new broad absorption band centered at 624 nm, which was assigned to the formation of the closed-ring isomer **1b**. The colored **1b**/PMMA film can revert to colorless upon irradiation with visible light ($\lambda > 500$ nm). Compared to that in hexane, the maximum absorption peak of the closed-ring isomer **1b** shows a clear bathochromic shift (21 nm) in PMMA film, which may be attributed to the polar effect of the polymer matrix and the stabilization of molecular arrangement in solid state [33]. In

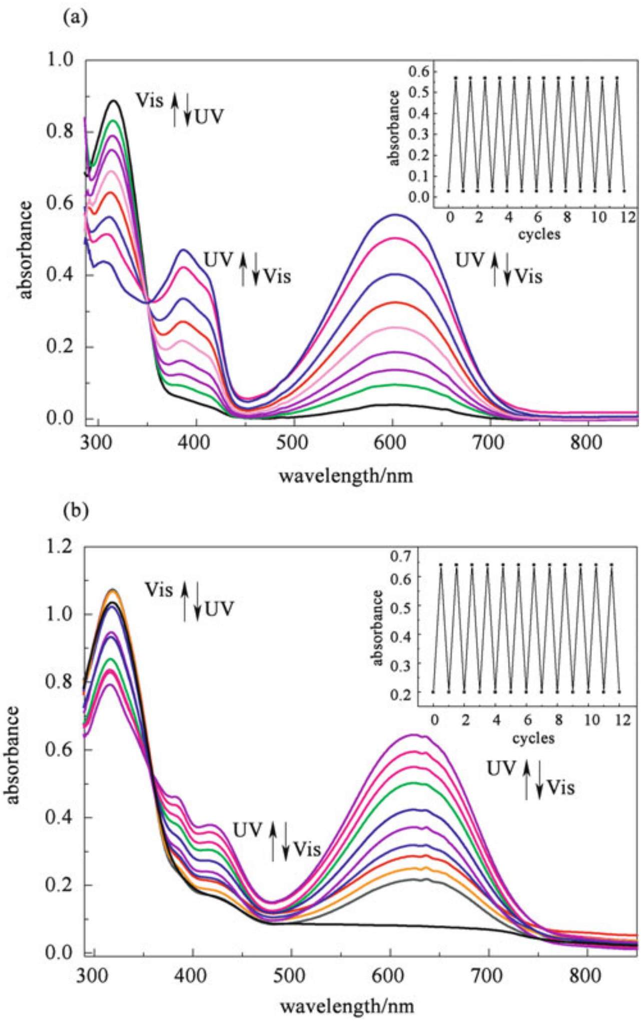


Figure 2 Absorption spectral changes of diarylethene **1** (a) in hexane (3.0×10^{-5} mol dm^{-3}) and (b) in PMMA film (10%, w/w). The insert graph shows the photoswitching repeated cycles of diarylethene **1**.

addition, both in hexane and in PMMA film, the two isomers of diarylethene **1** were stable for more than 3 months at room temperature in darkness. The insert graphs in Figure 2 showed that no degradation was detected by UV-Vis absorption after 12 cycles of photocoloration and photobleaching, indicating that diarylethene **1** had relatively remarkable fatigue resistance. Therefore, the thermal stability and fatigue-resistance of diarylethene **1** were satisfied with the requirement of optical recording media.

3.2 Polarization holographic recording

With the experimental setup shown in Figure 1, we have evaluated the potential application of photochromic diarylethene as an erasable polarization holographic optical recording medium by recording, reading and erasing the holograms in a real-time operation. For the sake of obtaining high quality and large area solid films, we doped diarylethene **1** into a polymer matrix (PMMA) and prepared some solid films on glass substrates by the spin-coating method. The hologram was recorded by the intersecting of the object beam containing the information and a reference beam in the photochromic diarylethene sample [27]. Using diarylethene **1b**/PMMA film as recording medium, we accomplished some different types of polarization holographic optical recordings and polarization multiplexing holographic optical recordings.

3.2.1 Four types of polarization holographic optical recording

In diarylethene **1b**/PMMA film, four types of polarization holographic optical recordings, including parallel linear polarization recording, parallel circular polarization recording, orthogonal linear polarization recording and orthogonal circular polarization recording, were tested. The retrieved diffracted images obtained by the four types of polarization holographic recordings are shown in Figure 3. The experimental conditions of each type of polarization holographic recording were illustrated in detail in a previous paper [24]. As shown in Figure 3, we can see that both the parallel linear polarization recording (Figure 3(a)) and the orthogonal linear polarization recording (Figure 3(c)) obtain low diffraction efficiency as well as low scattering noise when the intensities of the recording wave and the readout wave are fixed at 393 $mW \cdot cm^{-2}$; meanwhile, the orthogonal circular polarization recording (Figure 3(d)) gets both high diffraction efficiency and high signal-to noise-ratio (SNR), which are both very important in holographic optical recording. The orthogonal linear polarization recording (Figure 3(b)) has not only the highest diffraction efficiency but also the highest scattering noise. Therefore, a conclusion can be drawn that the orthogonal circular polarization holographic optical recording is the best method for diarylethene **1** among the four types of polarization recording methods. The reason is that a polarization modulation grating is mainly recorded there rather than an absorption modulation grating, as is the case for parallel polarization recording [34].

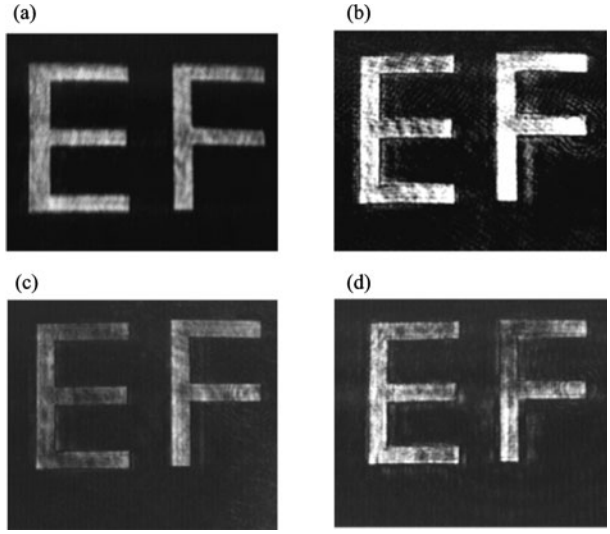


Figure 3 Comparison of retrieved diffracted images with different types of polarization holographic recording in diarylethene **1b**/PMMA film. (a) Parallel linear polarization recording; (b) Parallel circular polarization recording; (c) Orthogonal linear polarization recording; (d) Orthogonal circular polarization recording.

3.2.2 Polarization multiplexing holographic optical recording

The polarization multiplexing scheme is based on the multiple polarization hologram optical recording in polarization-sensitive materials, done by alternating the object and reference beams with parallel and orthogonal polarization, either in linear or in circular polarization [25]. Photochromic diarylethene materials can be potentially used as polarization holographic recording candidates because there is a photo-induced anisotropic phenomenon accompanying the photochromic reaction by photoirradiation [26]. Based on polarization modulation technology, we performed, perfectly, three types of polarization multiplexing holographic optical recordings such as angular multiplexing, polarization multiplexing, and angular multiplexing scheme combined with polarization multiplexing scheme holographic optical recording.

At first, two different images were recorded in the same place with the dimension of 0.78 μm^2 on diarylethene **1b**/

PMMA film with angular multiplexing technology, as shown in Figure 4. Each hologram was recorded by the intersecting of the object beam containing the information and a reference beam in diarylethene **1b**/PMMA film. The intensities of the object beam and the reference beam were fixed at 393 mW·cm^{-2}. The stored information was readout by the attenuated reference beam with an intensity of 80 mW·cm^{-2}, and the reconstructed hologram image was recorded on CCD camera. With 4 deg angular separation, two reference beam angles were used in this experiment and two holograms were recorded in the same region of the sample film. The exposure time for each hologram recording was 5 s. The results showed that the two retrieved images had very good contrast and high SNR. Above all, they could be separated completely from each other without any cross talk, which is very important for successful realization of multiplexing holographic recording [25].

Furthermore, polarization multiplexing holographic optical recordings were carried out successfully using diarylethene **1b**/PMMA film. The retrieved holograms recorded by polarization multiplexing holographic recording method are shown in Figure 5. The hologram recording and reconstruction were in the same optical setup, and the readout of the two object images was controlled by selectively setting the polarization angle of the polarizer P3. In Figure 5, three retrieved holograms were recorded by the circular polarization multiplexing holographic recording method in the same region of the diarylethene **1b**/PMMA medium. When the angle between the polarization direction of P3 and the horizontal direction was 90 deg, namely, the reference beam was kept in left-hand circular polarization and the object beam was set to be right-hand circular polarization during recording, the first hologram was recorded as shown in Figure 5(a). When both the reference beam and the object beam were kept in left-hand circular polarization during recording (the angle is 0 deg), the second hologram was recorded in the same place of diarylethene **1b**/PMMA sample, as shown in Figure 5(b). During the retrieval process, a single left-hand circularly polarization beam is used to reconstruct the two orthogonally circularly polarization images simultaneously. By rotating the polarization angle of the polarizer P3, different images can be selectively read out. When the readout linear polarization angle is 45°, an overlapping image appears as shown in Figure 5(c). In this way, the two polarization holograms can be hidden in the pattern and recorded in the diarylethene **1b**/PMMA film based on its photochromic and photoinduced anisotropic properties, and they can be picked up separately only when the polarizer P3 is located on a certain polarization angle. This phenomenon may be potentially applied in camouflage technology [35].

Finally, we proposed to combine the angular multiplexing scheme with the polarization multiplexing scheme based on the multi-recording ability of diarylethene **1** described above. The retrieved holograms of the combined multiplexing

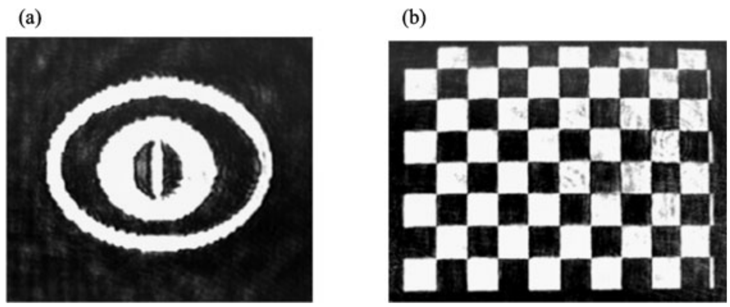


Figure 4 Readout holograms for angular multiplexing holographic optical recording in diarylethene **1b**/PMMA film.

Figure 5 Readout holograms for polarization multiplexing holographic optical recording in diarylethene **1b**/PMMA film. (a) the polarization of P is 90°; (b) the polarization of P is 0° ; (c) the polarization of P is 45°.

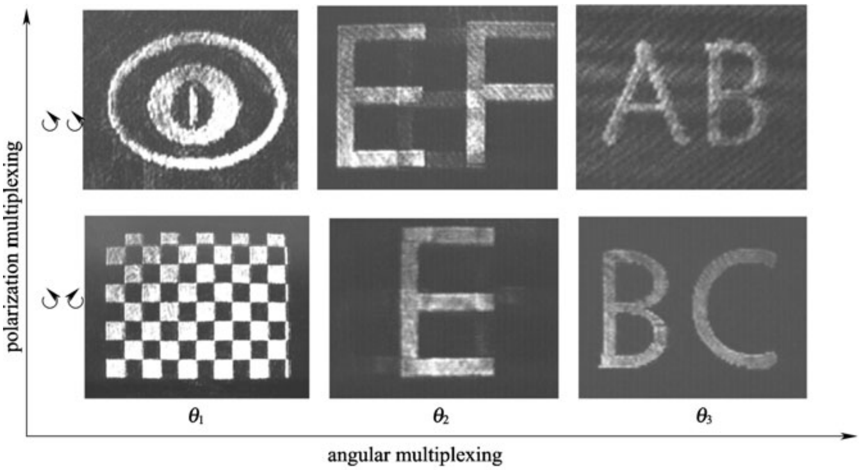


Figure 6 Readout holograms for angular multiplexing scheme combined with polarization multiplexing scheme in diarylethene **1b**/PMMA film.

scheme are shown in Figure 6. In the combined multiplexing scheme, the principal multiplexing scheme is angular multiplexing and the secondary scheme is polarization multiplexing. For each angle of the reference beam, two polarization holograms, i.e. parallel circular polarization hologram and orthogonal circular polarization hologram, were recorded on diarylethene **1b**/PMMA film. During the recording process, the intensities of the object beam and the reference beam were both fixed at 393 $mW \cdot cm^{-2}$. The object beam size on the sample plane was about 100 μm in diameter. With 4 deg angular separation, three angles of reference beam were used in this experiment. Thus, six holograms were recorded in the same place of the diarylethene **1b**/PMMA film, and the exposure time for each hologram recording was 6, 5, 4, 4, 3, and 3 s, respectively. The recorded information was readout by the attenuated reference beam with an intensity of 80 $mW \cdot cm^{-2}$, and the retrieved holograms were recorded on CCD camera. As shown in Figure 6, it can be seen that the six retrieved holograms showed good contrast and no crosstalk with each other. Compared with the single angular multiplexing scheme, the holographic recording density can be increased doubly when using this combined multiplexing technology, which will lead to a higher data capacity of holographic recording than the single angular multiplexing method. In addition, experimental tests showed that the hologram recorded in the diarylethene **1b**/PMMA film is stable at room temperature in darkness and no significant degradation is detected for retrieving of recorded holograms after being stored for more than 2 months. The recorded holograms can be erased entirely upon irradiation with UV light, and no remarkable degradation in resolution of reconstructed image after 12 write/erase cycles was found.

4 Conclusion

In summary, a new unsymmetrical photochromic diarylethene was synthesized and its photochromic properties were investigated both in hexane and in PMMA film. Using this diarylethene compound as recording medium, different types of polarization holographic optical recordings were performed successfully. The results demonstrated that high photosensitivity and easy information processing of photochromic diarylethene materials provide a substantial advantage for polarization holographic recording. The combined multiplexing technique can effectively improve the recording capacity. It will be helpful in accumulating evidence to realize high-density optical recording using photochromic diarylethene materials as recording media.

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