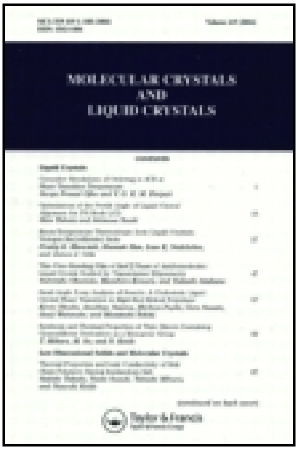
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Optical Properties and Applications of Photochromic Fulgides

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The optical properties and potential applications of four kinds of fulgide and fulgimide were studied. A parallel optical storage apparatus was set up, which could reach the area density of 4.8×10^7 bits/cm^2 on the fulgide/PMMA film. Fourier transform orthogonal circular polarization holographic data storage was performed with high signal-to-noise-ratio reconstruction image, which obtained the storage density of 2×10^8 bits/cm^2 for single hologram. Two-photon induced micro-patterns were recorded on the fulgimide/PMMA film with 800 nm, 100 fs, 1 KHz, 50 mW femtosecond laser. Dual-wavelength (650 nm and 488 nm) optical images storage were tested on a two-color mixing fulgides/PMMA film.

Keywords: fulgide; optical data storage; photochromism; photoinduced anisotropy; polarization holography; two-photon absorption

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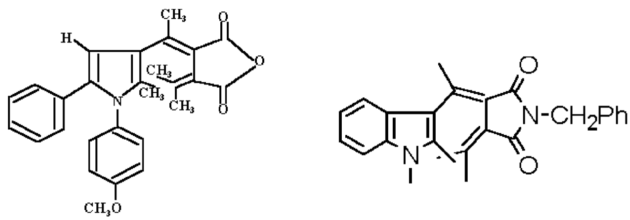
1. INTRODUCTION

The investigation of organic photochromic materials is one of the attractive topics in material chemistry because of their potential applications in optical memories and switches. From the view point of application, an ideal photochromic compound should have the following characteristics: (1) high thermal stability, (2) high fatigue resistance, (3) high quantum yield of photoreactions, (4) high speed of photoreactions, (5) good solubility in polymer matrix for easy optical components preparation and integration; and (6) wavelength match to diode lasers for easy engineering realization. Although many photochromic organic compounds have been synthesized such as spiroheterocyclic compounds (spiropyran, spiro-oxazine), azo compounds (azobenzene), fulgides, diarylethenes, etc., there is not a compound that can meet all of the characteristics. In this paper we focus our research on several kinds of fulgides – concerning their optical properties and potential applications. Yokoyama [1] has given a comprehensive review about the development history and recent research progress of fulgides. In our previous work [2–5], we had synthesized a few types of fulgides, e.g., pyrrylfulgide, 3-indolyfulgimide, bisfurylfulgide, etc., and had studied some of their optical properties, e.g., image storage, holographic recording, fatigue resistance test, etc. In this paper we give some new results of the optical properties and applications of the fulgides, including parallel optical data storage, holographic data storage, femtosecond laser induced two-photon image recording, and dual-wavelength images recording on two-color mixing fulgides/PMMA film.

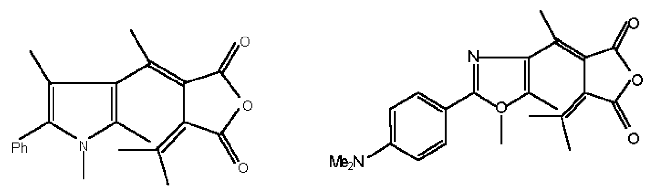
2. MATERIALS

Four kinds of fulgide and fulgimide are used in our experiment. Figure 1 gives the molecular formula of the E-form of the four fulgide and fulgimide. The procedure of their synthesis follows the Stobbe condensation routine. The target compounds ($1\sim3$ mg) are dissolved in 0.1 ml 10% (by weight) PMMA cyclohexanone solution. The polymeric films are obtained by spreading of the target compounds/PMMA solution on a $\phi 25\,\text{mm}\times1.5\,\text{mm}$ optical glass and dried in air. The thickness of the films is about $10\sim30\,\mu\text{m}$. The concentration of the compounds is about $3\sim10\%$ (w/w, target compounds/PMMA). The absorption spectra of the bleached state and the colored state are measured by UV-VIS-IR spectrophotometer (UV-3101PC, Shimadzu Inc., Japan).

As an example, Figure 2 shows the photochromic absorption spectra of the fulgide 1/PMMA film. The maximum absorption of the E-form



1a **2a**



3a **4a**

FIGURE 1 Formula of the E-form of the fulgides.

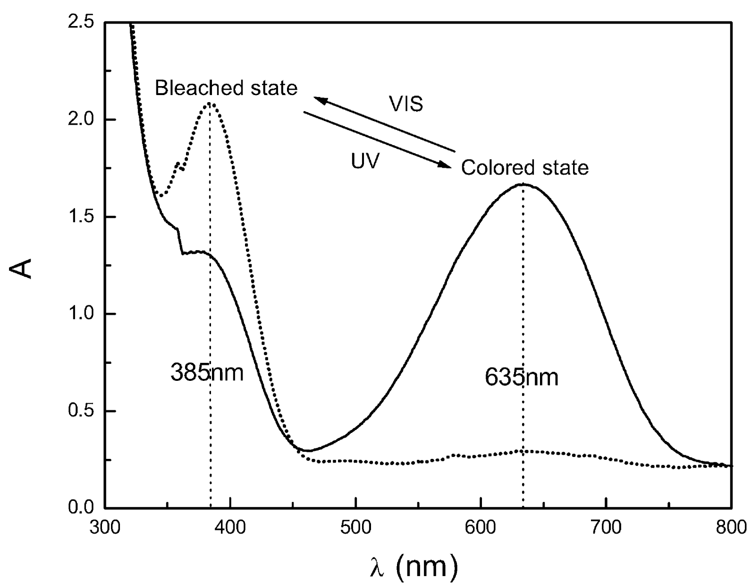


FIGURE 2 Absorption spectra of the bleached state and colored state of fulgide 1/PMMA film.

(1a) and C-form (1b) are respectively at 385 nm and 635 nm. Fulgimide 2/PMMA film has the maximum absorption of the E-form and C-form respectively at 366 nm and 573 nm. Fulgide 3/PMMA film has the maximum absorption of the C-form at 700 nm and fulgide 4/PMMA film has the maximum absorption of the C-form at 500 nm. For dual-wavelength images recording, we make a combined two-color mixing fulgides film with fulgide 3 and fulgide 4.

3. EXPERIMENTAL

3.1. Parallel Optical Data Storage

Compared with the bit-by-bit data storage method, parallel optical data storage method has the advantage of high speed data writing and reading with array detector. The parallel optical data storage system we set up is illustrated in Figure 3. Figure 4 shows an encoded binary data and a micro-image recorded on the fulgide 1/PMMA film. The size of each frame is $182\,\mu m \times 135\,\mu m$. Each frame can holds 128×96 bits data. So the storage density is 4.8×10^7 bit/cm^2.

3.2. Holographic Data Storage

Fulgides and their derivatives have been found having the photoinduced anisotropy (photoinduced dichroism and birefringence) during the photochromic reaction when illuminated by polarization light. This characteristic can be used for polarization hologram recording. Figure 5 is the experimental setup for Fourier transform orthogonal circular polarization holography with the fulgimide 2/PMMA film as recording medium. The recording and reading beam is 3 mW He-Ne 632.8 nm non-polarization laser. It is split into two beams by the

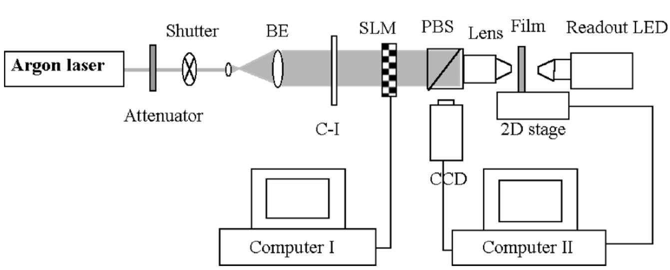


FIGURE 3 Experimental setup for parallel optical data storage. BE: beam expander, C-I: coherent-to-incoherent converter, SLM: spatial light modulator, PBS: polarization beam splitter, Argon laser: 514.5 nm, 100 mW.

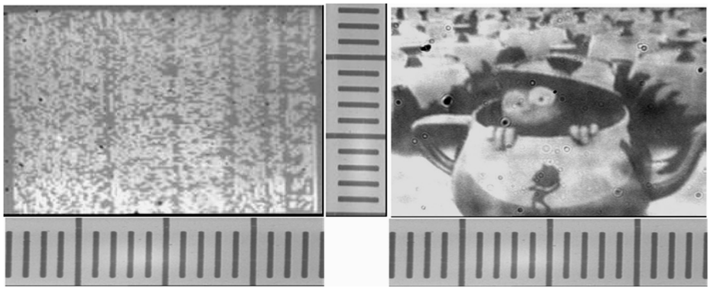


FIGURE 4 Encoded binary data and micro-image recorded on the fulgide 1/PMMA film. The calibration scale beside the images is 10 μm/div.

polarization beam splitter (PBS). The object beam with horizontal polarization state is expanded and collimated by the beam expander (BE) and then illuminates the spatial light modulator (SLM), which is loaded the encoded binary data or images by the computer 1. The Fourier transform spectrum of the modulated beam is generated by the lens L1. The aperture D1 placed at the plan of Fourier transform spectrum is used to select the zero order beam as object beam. This beam is inversely Fourier transformed by lens L2 and passes through a $\lambda/4$ waveplate to become a right-hand circular polarization beam. Then the beam is Fourier transformed again by the lens L3. The recording film is place at the plan of the Fourier transform spectrum

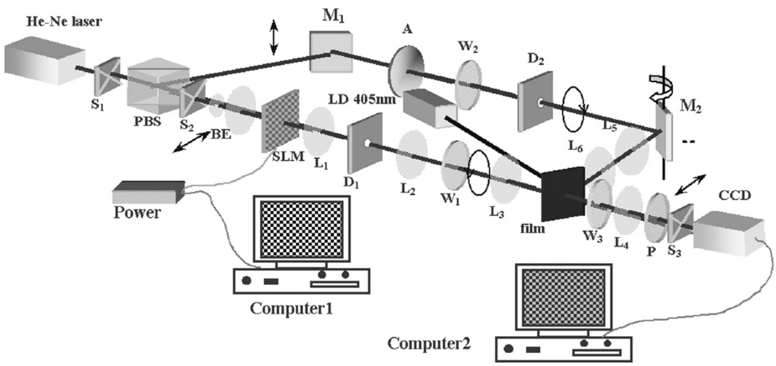


FIGURE 5 Experimental setup for Fourier transform orthogonal circular polarization holographic data storage on the fulgimide 2/PMMA film. $S_1 \sim S_3$: shutters, PBS: polarization beam splitter, BE: beam expander, SLM: spatial light modulator, $L_1 \sim L_6$: lens, $D_1 \sim D_2$: apertures, $W_1 \sim W_2$: $\lambda/4$ waveplates, A: attenuator, P: polarizer, $M_1 \sim M_2$: reflection mirrors.

of the lens L3 with a cline angle of 45° between the normal of the film and the object beam axis. Lens L4 is used to inversely Fourier transform the object beam. The CCD camera is placed at the focal plan of the lens L4 to capture the object image and the reconstruction image. The reference beam with vertical polarization state is reflected by the mirror M1 and becomes a left-hand circular polarization beam by the $\lambda/4$ waveplate W2. The rotation mirror M2 is used to direct the reference beam onto the film with a cline angle of 45° between the normal of the film and the reference beam axis. M2 is also used for angular multiplexing. Lens L5 and L6 consists of a 4 F configuration used for angular multiplexing. The $\lambda/4$ waveplate W3 is used to transform the circular polarization beam into linear polarization beam (object beam becomes horizontal polarization, reference beam becomes vertical polarization). The polarizer P is place with its polarization axis horizontal so that only the object beam can enter into the CCD camera. A 405 nm laser diode is used to erase the hologram.

Figure 6 shows two reconstruction images of the polarization holograms recorded on the fulgimide 2/PMMA film. For the encoded binary data storage, each page contains 81×61 bits. The hologram size is measured with microscope to be $60 \times 42\,\mu m^2$. So the storage density is calculated to be 2×10^8 bits/cm^2. We tested angular multiplexing scheme by changing the incident angle of the reference beam. The step angle for each hologram is 1°. We multiplexed five holograms on the fulgimide 2/PMMA film without crosstalk each other.

3.3. Femtosecond Laser Induced Two-photon Image Recording

Two-photon absorption belongs to a nonlinear optical phenomenon. It needs a high laser intensity to reach a threshold, where the molecule can absorb two photons simultaneously to transit into a high energy

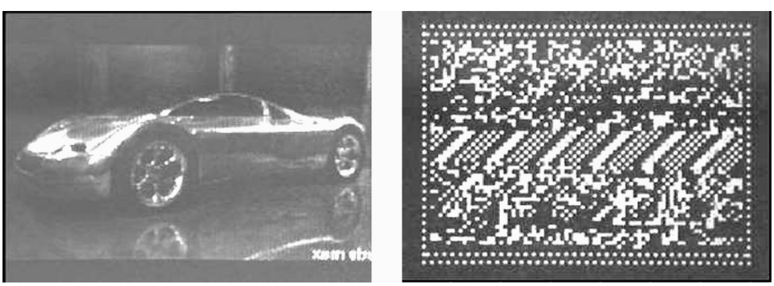


FIGURE 6 Reconstruction images of polarization holograms recorded on the fulgimide 2/PMMA film.

level, which cannot be reached by one photon absorption transition. For two-photon photochromism, the coloration process from E-form to C-form does not use UV light but use red or infrared light. At low intensity, the red or infrared laser cannot be absorbed by the E-form molecule. But at high intensity, the molecule can simultaneously absorb two photons to reach the energy level of UV photon transition, therefore the E-form can transfer into the C-form. Here we prove that the fulgimide 2 we synthesized has a large two-photon absorption coefficient, which can be efficiently used for two-photon images recording by using our microscope with diffractive element.

The experiment for femtosecond laser induced two-photon image recording uses a Ti:Sapphire self mode-locking oscillator and a Ti: Sapphire regeneration amplifier. The output wavelength is 800 nm, pulse width 100 fs, repetitive rate 1 KHz, average power 50 mW. The femtosecond laser is coupled into the microscope via a beam splitter and focused on the fulgimide 2/PMMA film by a 10× objective. A diffractive element with designed pattern is placed on the laser beam pathway, behind which a lens is used to adjust the pattern exactly imaged on the sample. Figure 7 shows some micro-patterns recorded on the fulgimide 2/PMMA film. The size of the micro-pattern is smaller than 200 μm × 200 μm. The recording exposure time is 1 second.

3.4. Dual-wavelength Images Recording on Two-color Fulgides Film

The area storage density of two-dimension plane is mainly limited by the laser wavelength and the numeric aperture of the lens. Adding

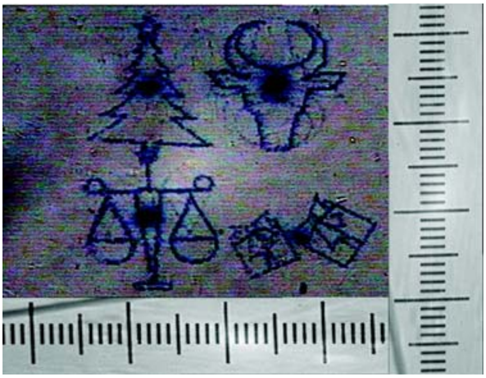


FIGURE 7 Femtosecond laser induced two-photon micro-patterns recorded on the fulgimide 2/PMMA film. The calibration scale beside the images is 10 μm/div.

another dimension (or physical parameter) to enlarge the density and capacity is an inevitable research direction. Three dimensional volume storage, holographic storage and spectral burning storage are some examples. Among them, using multi-wavelength is an efficient method. A simple and efficient method is to prepare a composite film containing several photosensitive materials, each material has different wavelength response character. To avoid information crosstalk among different wavelengths, it needs that each material should have different absorption peak and also these peaks are separated without overlap. Such photochromic materials are not easy to find and synthesize, because most compounds have broad absorption band at room temperature. Refs. [6,7] reported two wavelengths bit data storage on a two-color film prepared by using two kinds of diarylethene photochromic compounds. Here, we realized two wavelengths images storage on the two-color mixing fulgides (3+4)/PMMA film and obtained a high contrast and little crosstalk of readout images.

To record images on the two-color mixing fulgides (3+4)/PMMA film, a laser diode with 650 nm, 40 mW is used firstly. The beam is expanded and shines a "cross" target. A lens is used to image the target on the sample film. The exposure time is 90 seconds. Then an Argon laser with 488 nm, 100 mW is used to illuminate another target

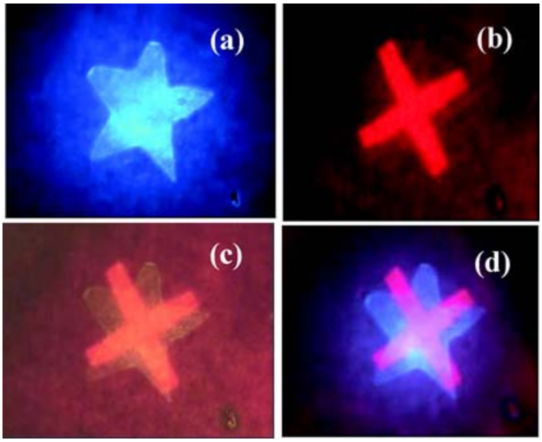


FIGURE 8 Readout images recorded on the two-color mixing fulgides $(3+4)$/PMMA film with different wavelengths. (a) readout with blue light (only the "star" can be seen, no crosstalk); (b) readout with red light (the "cross" is clear, the "star" is dim, weak crosstalk); (c) readout with white light (both can be seen, strong crosstalk); (d) readout with blue light and red light simultaneously (both can be clearly seen).

"star" to image on the sample film at the same area from the other direction. The exposure time is 10 seconds. The beam diameter of the two lasers on the sample is 4 mm. The images recorded on the sample film are read by blue, red and white light LEDs, respectively, which are captured by a digital camera. The results are shown in Figure 8. It can be seen that the red light has little influence on the image recorded on fulgide 4, but the blue light has more influence on the image recorded on fulgide 3. So, when reading by blue light, only "star" can be seen, "cross" can't be seen. But when reading by red light, "cross" can be seen, "star" also can be dimly seen. However, because the recording exposures of the 650 nm and 488 nm lasers are controlled properly, the crosstalk is very small. Both "star" and "cross" can be seen when read by white light or blue light and red light simultaneously.

4. CONCLUSION

Fulgides and fulgimides have good thermal irreversibility. The absorption peak of the colored state can be modified by molecular structure design so that it can match to the conventional lasers. Besides the change of absorption during the photochromic reaction, the refractive index, electric dipole moment, dielectric constant also change simultaneously. These characteristics can be explored in applications. The combination of various fulgides may have more interesting characteristics and find more useful applications. Our studies show that fulgides and fulgimides can be used in parallel optical data storage, holographic data storage, femtosecond laser induced two-photon image recording, and dual-wavelength images recording on two-color mixing fulgides film.

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