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Fabrication of Fluorescent Holographic Micropatterns Based on Azobenzene-Containing Host–Guest Complexes

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On the basis of photoinduced surface relief gratings (SRGs) with fluorophore/azo-complexes, a novel and facile method for fabricating stable and bright fluorescent two-dimensional micropatterns, whose color could be easily adjusted by changing the corresponding fluorophores, was developed for the first time.

Much effort has been focused on the patterning of organic luminescent molecules with ordered micro/nanoscale features as a result of their applications in photonics, optoelectronics, full-color displays, and other related areas.^{1–3} To achieve these color patterns, many approaches have been proposed, such as dip-pen nanolithography (DPN), inkjet printing, and shadow mask patterning.^{3–7} However, most of the techniques require dedicated equipment and multiple steps are often involved.

Host–guest complexes based on azo-chromophores and polymers have been considered as promising materials for fabrication of surface relief gratings (SRGs), optical information storage, holographic recording and other optoelectronic areas.^{8–10} When

Scheme 1. Schematic of the Design and Fabrication of Fluorescent SRG Patterns

exposed to interferential illumination, these complexes can undergo reversible photoinduced mass migration to form SRGs that are stable over long time periods.^{10,11} These SRGs can be erased by exposing the patterned film under uniform circularly polarized laser light or by heating above the glass transition temperature of the polymer.⁹ The above SRG technique provides new methodology to obtain rewritable micropatterns. Seki et al.^{10b} and Gao et al.^{11c} developed phototriggered SRG patterns in the H-bonded host–guest supramolecular polymer system, and they claimed

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Figure 1. Optical microscope image (A) and AFM image (B) of SRGs formed on PES-azo-RhB film (size $10\ \mu\text{m} \times 10\ \mu\text{m}$).

Scheme 2. Proposed Carboxylic Acid-Containing Polymer (A), azo-Chromophore (B), and Fluorophore (C,D)

that the SRG patterning films demonstrated good thermal stability. Kulikovska et al. also successfully employed ionic interactions to form high stable surface relief patterning structures.^{11a} The formation mechanism of SRGs is very complicated. Several models were suggested by Kumar, Barrett, and Sumaru et al.¹² They also tried to confirm their viewpoints using various techniques. Their results indicated that the SGRs based on azo-polymer/compound were caused by photoirradiation mass-migration resulting from trans-cis-trans photoisomerization cycles of the azobenzene groups.

Most recently, Ishow et al. combined the SRG and fluorescence techniques to fabricate fluorescent micropatterns for the first time.¹³ After construction of uncoupled azobenzene chromophore and fluorophore bilayer materials, they successfully generated stable and rewritable photopatterns under holographic recording and nondestructive near-infrared read-out conditions. These studies open up a new way of recording optical information, and this approach could be applicable to various organic systems. However, the bilayer materials of the fluorescent and photochromic components must comply with stringent material processing and spectral requirements. In this communication, we present a facile method for fabricating fluorescent patterned polymer film by combination of fluorophore/azo-host-guest

complexes and the holography technique. In addition, the color of the fluorescent two-dimensional (2D) photopatterns could be tuned by changing the fluorophores, and the schematic representation is shown in Scheme 1.

Strong molecular interactions between the different molecular components are important for the blending system to maintain good dispersion and stability. It is well-known that polymers containing certain functional groups, such as carboxylic acid and hydroxyl groups, have the ability to form stable and functionalized systems with small molecular compounds containing hydroxyl or pyridine groups through acid-base or hydrogen-bond interactions.^{10,11} In order to increase the molecular interaction between dopants and polymer host, we selected a hydroxyl (–OH)-containing azo-chromophore, a carboxylic acid (–COOH)- and N^+ -containing fluorophore Rhodamine B (RhB), a quinoline-containing fluorophore tris(8-hydroxy-quinoline)aluminum (AlQ_3), and a –COOH-containing aromatic polymer to fabricate the complex films, designated as PES-azo-RhB and PES-azo- AlQ_3 . In our case, different from a simple point-to-point interaction system, many supramolecular interactions exist in our system among functional groups, such as –OH, SO_2 –, –COOH, $\text{N}=\text{N}$ –, and fluorophore. This makes the system rather complex, and the existence of these interactions seems most likely.¹⁴ Scheme 2 shows the chemical structures of polymer (A), azo-chromophore (B), RhB fluorophore (C), and AlQ_3 fluorophore (D) used for materials preparation.

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Figure 2. Photoluminescence spectra of PES-azo-RhB (A) and PES-azo-AlQ₃ (C) films. Fluorescence microscopy images of SRG patterns on PES-azo-RhB (B) and PES-azo-AlQ₃ (D) films. The observed emission-intensity pattern of SRGs on PES-azo-RhB film is shown in the inset of B.

A uniform and transparent film, PES-azo-RhB, was prepared by spin-casting from a homogeneous and clear cyclohexanone solution of A, B, and C (the weight ratio of A/B/C is 88:10:2). PES-azo-RhB film shows ultraviolet–visible (UV–vis) absorption bands at 372 and 562 nm corresponding to the characteristic absorption of the azo-chromophore and the RhB fluorophore, respectively (see Figure S1). Under an excitation wavelength of 527 nm, PES-azo-RhB film shows the characteristic fluorescence emission of RhB in the red region at about 588 nm (see Figure S2).

The experimental setup used for micropattern fabrication was similar to that reported previously.¹⁵ A Nd:YAG laser beam of 355 nm wavelength with a moderate intensity of 60 mW/cm² was used as the light source. SRGs were optically inscribed on the PES-azo-RhB film by exposing the complex film to two p-polarized interfering laser beams. Figure 1 shows the optical microscope image and the typical atomic force microscope (AFM) plane image of the surface structures after irradiation for 30 s at room temperature. AFM observation indicated that sinusoidal surface relief patterns at regularly spaced intervals were fabricated on the surfaces of PES-azo-RhB film. From the AFM section analysis, the surface modulation depth is about 130 nm, and the spatial period is about 1.4 μm. The modulation depth depends on the irradiation time, and the spatial period can be adjusted by the angle between the two interfering beams and the wavelength of the writing beams.^{9,13} We found that the azo-component was the resource of the SRGs formation because pure polymer and polymer/RhB films could not be used to fabricate SRG patterns under the same conditions.

Figure 2A,B presents the photoluminescence spectrum and fluorescence microscopy image of SRGs on PES-azo-RhB film, respectively. Under the excitation wavelength of 527 nm, high resolution red fluorescent patterns were successfully fabricated. The measurement of confocal fluorescence microscopy shows the emission-intensity pattern of fluorescent SRGs on PES-azo-RhB film, as shown in the inset of Figure 2B. The fluorescent emission

light intensity is regularly distributed with a spatial period of 1.4 μm, which is in good agreement with the SRGs' shape and the spatial period detected by AFM.

Interestingly, the fluorescent color of the micropatterns could be tuned by changing the corresponding fluorophores. A green light emission patterned PES-azo-AlQ₃ film was obtained when the fluorophore AlQ₃ (D) was used as an alternative to RhB (the weight ratio of A/B/D is 88:10:2). SRGs were also efficiently formed by exposing the PES-azo-AlQ₃ film to two p-polarized interfering 355 nm laser beams for 30 s at room temperature. Figure 2C shows the photoluminescence spectrum of AlQ₃, whose maximum emission wavelength is in the green region at 521 nm. Under the excitation, bright and regular green patterning was obtained on PES-azo-AlQ₃ film (Figure 2D).

Both of the SRGs patterns on PES-azo-RhB and PES-azo-AlQ₃ films have demonstrated good thermal stability, even though they are formed on the basis of host–guest complexes. After 6 months storage under ambient light exposure or 48 h at 100 °C in a constant temperature box, the fluorescent grating patterns showed no change in the emission signal and appeared to be perfectly stable.

In summary, a facile method for fabricating stable fluorescent patterns by combination of the fluorescent host–guest complex materials and holographic technique was demonstrated. It is notable that the color of patterns could be tailored easily by tuning the fluorophores. These studies provide a fascinating and viable strategy to design and fabricate patterned organic light-emitting devices, provide a convenient method to detect the SRGs on the surface of the polymer film, and also open up a new way of recording and detecting optical information.

Supporting Information Available: Detailed materials, measurements, preparation of polymer films, UV–vis absorption spectrum of PES-azo-RhB film, and normalized excitation and emission spectra of PES-azo-RhB film. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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