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Photochromism and holographic recording in polymer film containing chiral azo molecules derived from amino acid

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Abstract

A kind of chiral azo molecule derived from amino acid, *N*-[4-(4-octyloxyphenylazo)benzoyl]-L-glutamic acid (C₈-Azo-L-Glu), was synthesized and the photochromism, photoinduced birefringence, and holographic recording in C₈-Azo-L-Glu doped poly(methyl methacrylate) (PMMA) films were studied. C₈-Azo-L-Glu underwent a reversible *trans*–*cis*–*trans* isomerization in the polymer matrix. The photoinduced birefringence was investigated at various intensities of Ar laser (488 nm) beam. A reversible hologram was recorded in this media and the dependence of the first order diffraction efficiency on the recording beam intensities was also presented.

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1. Introduction

Azobenzene-containing materials have been intensively investigated in the last decade due to their potential applications in optical storage and holographic recording [1–12]. One important property of these materials is the reversible photochromism of azobenzene chromophores be-

tween the more stable *trans*-isomer and its less stable *cis*-isomer upon light irradiation [13,14]. The generally agreed upon the mechanism for optical storage is the following [15]: When irradiated by linearly polarized light the photochromic molecules, considered as anisotropic, undergo the *trans*–*cis*–*trans* photoisomerization cycles and change their orientation. A linearly polarized light beam selectively pumps molecules whose transition dipole moment axis is parallel to its polarization direction. After several *trans*–*cis*–*trans* cycles, the result is an accumulation of molecules in the direction of the smallest probability of pumping, i.e., the direction perpendicular to the

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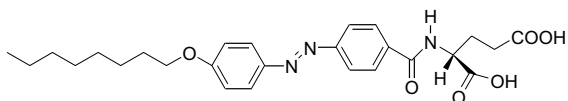
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pump polarization direction. Irradiation of the sample with unpolarized or circularly polarized light at the normal incidence restores isotropic absorption.

Introduction of azobenzene chromophores into biomaterials is of great significance [16,17]. The *cis-trans* isomerization of azobenzene has been applied to the photoswitchable hydrogen-bonding in self-organized cylindrical peptide systems [16] and the photoregulation of the formation and dissociation of a DNA duplex [17]. However, little attention has been drawn on the optical storage of the azo molecules derived from biomaterials. In present work, a kind of chiral azo molecule (C_8 -Azo-L-Glu) was synthesized from L-glutamic acid. The photochromism, photoinduced birefringence, and holographic recording of C_8 -Azo-L-Glu doped PMMA films were studied in detail. This is the first example for the holographic recording of chiral azo molecules derived from amino acids.

2. Materials

The chemical structure of the chiral azo molecule, *N*-[4-(4-octyloxyphenylazo)benzoyl]-L-glutamic acid (C_8 -Azo-L-Glu) was shown in Scheme 1. The synthesis of C_8 -Azo-L-Glu was described as follows. 4-(4-Octyloxyphenylazo)benzoic acid [18] dissolved in $SOCl_2$ and refluxed 8 h to obtain 4-(4-octyloxyphenylazo)benzoyl chloride. L-glutamic acid reacted with 4-(4-octyloxyphenylazo)benzoyl chloride in a mixture of THF and water at basic condition to get C_8 -Azo-L-Glu. The structure of the compound was tested by FT-IR and 1H NMR. FT-IR: 3411 cm^{-1} (N-H), 2922 cm^{-1} and 2853 cm^{-1} ($-CH_3$, $-CH_2-$), 1706 cm^{-1} (carboxyl group), 1643 cm^{-1} (amide I), 1538 cm^{-1} (amide II), 1603 cm^{-1} and 1503 cm^{-1} (benzene rings), 1588 cm^{-1} and 1470 cm^{-1} (N=N). 1H NMR was carried out on Bruker DMX-400 instrument operating at 400



Scheme 1. Chemical structure of C_8 -Azo-L-Glu.

MHz. 1H NMR (CD_3SOCD_3 , δ , ppm) 0.87 (t, 3H, $-CH_3$), 1.35 (m, 8H, $-CH_2-$), 1.43 (t, 2H, $-CH_2-$), 1.75 (m, 2H, $-CH_2-$), 2.09 (2H, $-CH_2-$), 2.23 (m, 2H, $-CH_2-$, link to the carboxyl group), 4.09 (t, 2H, $-CH_2-$, link to oxygen atom), 4.46 (m, $-CH-$, chiral center), 7.15 (2H, CH, benzene ring), 7.92 (4H, CH, benzene ring), 8.06 (2H, CH, benzene ring).

Commercially available PMMA was used without further purification. Both C_8 -Azo-L-Glu and PMMA were dissolved in $CHCl_3$ and then cast on a clean glass substrate. After the solvent evaporated slowly, the composite film was used for the measurements of photoinduced birefringence and holographic recording. The dye concentration was set to be 1.0 wt.% and the thickness of the film was about $10\text{ }\mu\text{m}$.

3. Photochromism

The UV-vis spectra were carried out using a Shimadzu-1600 spectrometer. For the photochromism measurements, the sample was irradiated by a 100 W mercury-arc lamp through a filter in the range of 300–400 nm and a 40 W incandescent lamp.

The UV-vis spectrum of C_8 -Azo-L-Glu doped PMMA film is shown as Fig. 1a. It manifests two characteristic spectral bands: band T at 361 nm corresponds to $\pi-\pi^*$ electronic transition in the

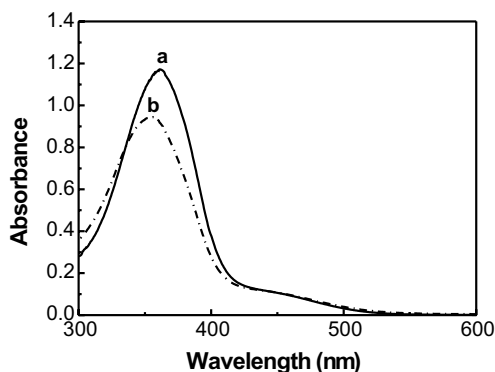


Fig. 1. UV-vis spectra of C_8 -Azo-L-Glu: (a) in dilute chloroform solution with the concentration of $1 \times 10^{-6}\text{ M}$ and (b) doped in PMMA film with the concentration of 1.0 wt.%.

trans-isomer of azo-chromophore and band (shoulder) C at 440–450 nm corresponds to $n-\pi^*$ transition in the *cis*-isomer [12]. There is an equilibrium between *trans*-isomer and *cis*-isomer in the composite film. For comparison, the UV-vis spectrum of C_8 -Azo-L-Glu in dilute solution is also included. The absorption maximum (λ_{\max}) of C_8 -Azo-L-Glu doped PMMA film is red shifted by 5 nm (361 nm) in comparison to that in dilute solution (356 nm), indicating a slight J-aggregation of azobenzene chromophores in polymer film [19].

It is well known that azo-dye molecules exist in two forms, *trans*- and *cis*-isomers. On illuminating the dye, a process of *trans-cis* isomerization followed by a *cis-trans* thermal or optical isomerization takes place. Fig. 2 shows the photochromism of C_8 -Azo-L-Glu doped polymer film. Irradiation with UV-light strongly suppresses the *trans*-band and slightly increases absorption in the range of 400–500 nm, a maximum forms corre-

sponding to the $n-\pi^*$ transition in *cis*-isomer. After the irradiation for 1 min, the *trans*- $n-\pi^*$ band almost disappears and the $n-\pi^*$ band increases. The excess $n-\pi^*$ absorption is due to contribution of *cis*-isomers. UV-light converts almost all the *trans*-isomer into their *cis*-counterparts for 60 s. This is caused by *trans-cis* isomerization until the photostationary state is reached. The photoinduced isomerization can be reversed by thermal relaxation or irradiation by visible light. Thermal relaxation of *cis*-isomer in darkness is rather slow. After 4 h relaxation in darkness the film still contains many *cis*-isomers. Almost all the *cis*-isomer converts to *trans*-form by irradiation with the light of incandescent lamp for 5 min. The experiments indicate that *trans-cis* and *cis-trans* transitions are induced by UV light and visible light, respectively.

4. Photoinduced birefringence

The experimental setup for measuring the photoinduced birefringence is schematically shown in Fig. 3. The major elements of our experimental apparatus are linearly polarized Ar laser (488 nm) as a pumping beam and linearly polarized He-Ne laser (632.8 nm) as a probe beam. The sample is placed between two crossed polarizers in the path of He-Ne laser beam. The film is irradiated by the pumping light with different intensities from 10 to 80 mW. The birefringence is attributed to the sufficient overlapping of the $n-\pi^*$ absorption band of *cis*-AZO with the 488 nm Ar^+ laser beam [20,21]. A result of photoinduced birefringence in the investigated sample with the pumping light of

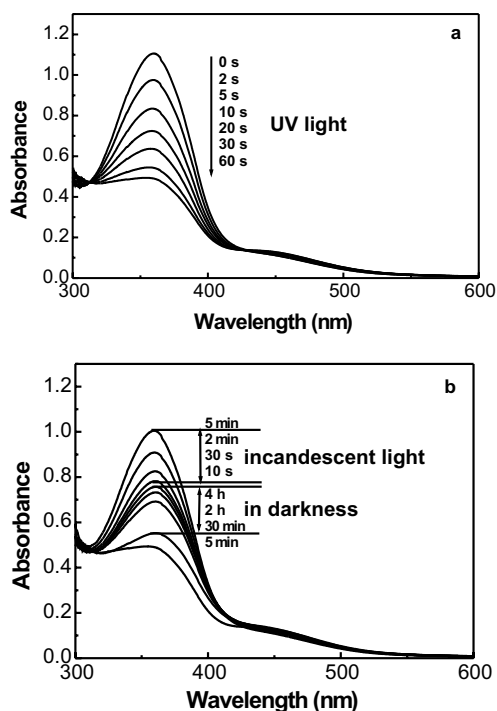


Fig. 2. Photochromism of C_8 -Azo-L-Glu doped PMMA film. Exposure times are shown at the curves: (a) UV light irradiation in the range of 300–400 nm and (b) relaxation in darkness and irradiation by incandescent light.

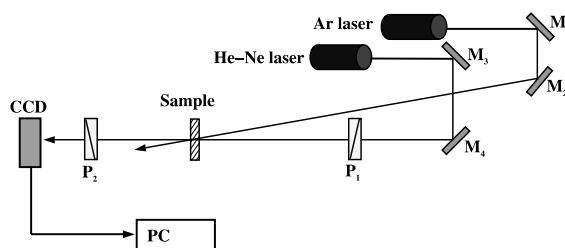


Fig. 3. The experimental setup for measurements of photoinduced birefringence, where M denotes a mirror, P a polarizer, CCD a charge coupled device (sensitive region from 350 to 900 nm), PC a personal computer.

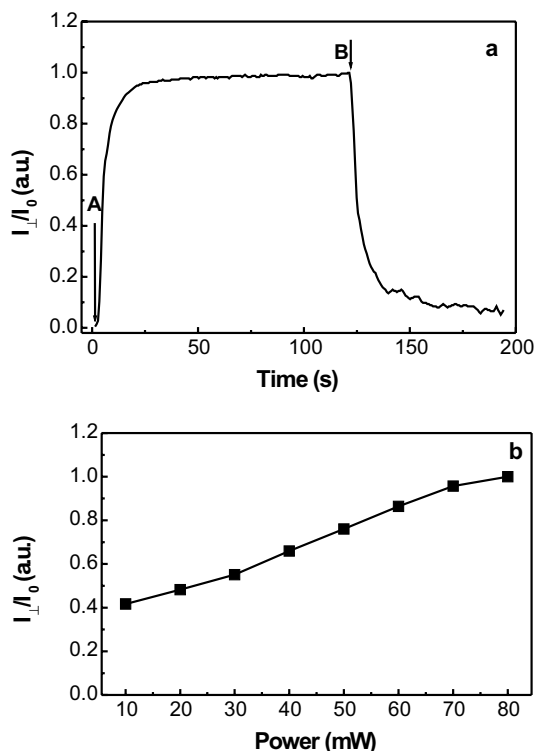


Fig. 4. (a) The rise and decay curve of photoinduced birefringence of the C_{12} -Azo-L-Glu doped PMMA film. The concentration of C_8 -Azo-L-Glu is 1.0 wt.% and pumping light intensity 60 mW. (b) Dependence of laser intensity for the amplitude of the photoinduced birefringence.

60 mW is shown in Fig. 4. No transmission signal is detected before the pumping beam is switched on, indicating the random orientation of the chromophores. When the pump beam is switched on at point A, the transmission increases and reaches 80% of the saturated value in about 7 s. The increase of transmission is directly related to the photoinduced birefringence in the film. On irradiating with Ar^+ laser beam of 488 nm, the *cis*-isomers in the composite film undergo a transition to *trans*-isomers. At the same time, some *trans*-isomers return to *cis*-isomers to keep the equilibrium between them. After several *cis*–*trans*–*cis* cycles, the molecules have a tendency to orient in the direction perpendicular to the pump polarization direction and the birefringence is generated. When the pump beam is switched off at point B, the photoinduced birefringence decreases sharply

and reaches a steady value. The overall change in the photoinduced birefringence is normalized between 0 and 1 for the sake of clarity of presentation, as shown in Fig. 4.

At $\lambda = 632.8$ nm, the transmission is due to the photoinduced birefringence which is given by $I_{\perp} = I_0 \sin^2(\pi \Delta n d / \lambda)$, where I_{\perp} is the intensity of the transmitted light through the crossed polarizers, I_0 is the intensity of the light passing through the pair of parallel polarizers before the irradiation of pumping light, d is the thickness of the film and Δn is the birefringence [10]. The value of Δn depends on the intensity of pumping light, dye concentration and the performance of the investigated material. The influence of the intensity of the pumping light on the photoinduced birefringence has been studied as in Fig. 4b. The birefringence of C_8 -Azo-L-Glu doped polymer film increases with the laser intensity up to 80 mW. This is resulted from the increase of the proportion of the molecules that undergo the *cis*–*trans*–*cis* isomerization cycle. The photoinduced birefringence can be optically erased by overwriting the test spot with a circularly polarized laser light that randomize the chromophores orientation and can be rewritten after erasure. The sample has no apparent fatigue after multiple cycles of write, read and erase.

5. Holographic recording

Measurements of diffraction efficiency of transmission holograms are carried out using the system described in Fig. 5. The holographic recording is accomplished by two linearly polarized

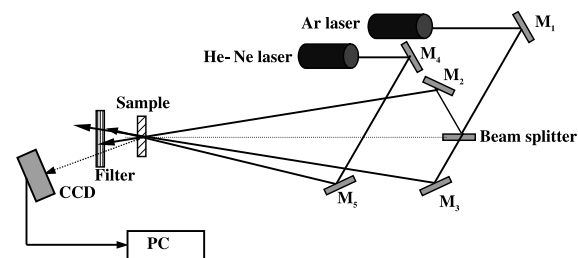


Fig. 5. The experimental setup for creating holographic grating, where M denotes a mirror, CCD a charge coupled device (sensitive region from 350 to 900 nm), PC a personal computer.

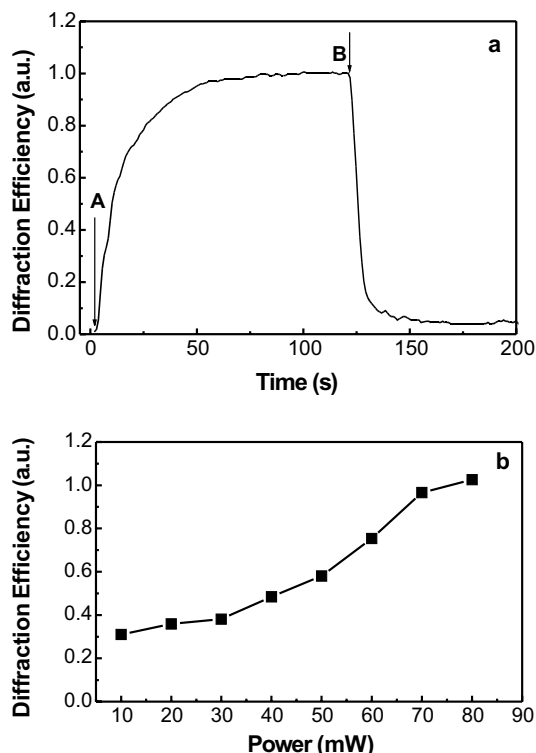


Fig. 6. (a) Rise and decay curves of diffraction efficiencies. The intensity of one recording beam is 60 mW and the concentration of C_8 -Azo-L-Glu is 1.0 wt.%. (b) Dependence of laser intensity for the amplitude of diffraction efficiencies.

488 nm beams of an Ar laser of with the same polarization and the beam ratio of 1/1, and monitored by He-Ne laser of 632.8 nm. The intensity of Ar laser is set in the range between 10 and 80 mW. Fig. 6a shows the generation and annihilation of the holographic grating with the intensity of the Ar laser to be set at 60 mW. The diffraction signal from the photoinduced grating is resulted in sum of phase change through the dye-doped polymer film. The total diffraction efficiency can be ascribed to two kinds of grating, i.e. refractive index grating induced by spatially selective *cis/trans* photoisomerization and birefringence grating induced by orientational changes of AZO chromophores. The moments of turning on and off the recording light are marked as A and B in Fig. 6a. The intensity of diffractive signal versus time increases rapidly and eventually reaches a steady value after turning on the recording light. When

the recording light is turned off, the intensity of the signal falls rapidly at the beginning, then falls gradually, and reaches a steady value.

The saturated value of the diffraction efficiency depends on the intensity of the recording light. This can be anticipated from the relationship between the photoinduced birefringence and the intensity of pumping light. The influence of the intensity of recording light on the diffraction efficiency is shown in Fig. 6b. The diffraction efficiency increases with the recording intensities up to 80 mW. When the hologram is erased by thermal or optical method, it can be rewritten and the same value of diffraction efficiency can be achieved after multiple uses.

6. Summary

A kind of azo molecule derived from amino acid was prepared. The photochromism studies of C_8 -Azo-L-Glu doped in PMMA film have shown a reversible *trans-cis-trans* isomerization induced by the irradiation of UV or visible light. The photo-induced birefringence of C_8 -Azo-L-Glu doped PMMA increases with the intensity of pumping light up to 80 mW. C_8 -Azo-L-Glu is a kind of ideal material for holographic recording. A reversible hologram was recorded on C_8 -Azo-L-Glu doped PMMA using two linearly polarized Ar laser beam of various intensity. It allowed multiple uses without apparent fatigue.

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