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Optical characterization and all-optical switching of benzenesulfonamide azo dye

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ABSTRACT

A film of benzenesulfonamide azo dye has been prepared by spray pyrolysis method onto BK7 glass substrate with average thickness of 2.7 μ m. This azo dye was derived from sulfamethoxazole and chromotropic acid by the Fox method. The optical constants (refractive index, *n*, extinction coefficient, *k*, dielectric constant, ε , optical, σ_{opt} , and electrical, σ_e , conductivities) were calculated for azo dye film by using spectrophotometer measurements of the absorption, transmittance and reflectance at normal incidence in the spectral range 300–900 nm. Third order nonlinear properties has been characterized by calculating the effective thermal nonlinear refractive index, *n*₂, and thermo-optic coefficient, *dn/dT*, of the azo dye solution using thermal lens technique. Furthermore, the thermal lens effect was utilized to demonstrate all optical switching for the sample solution.

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1. Introduction

In recent years, the search for novel optical materials has increased owe to their applications in optical devices such as optical modulation, optical information, optical data storage and imaging [1,2]. Detailed investigations of linear and nonlinear optical coefficients enable to fabricate materials, appropriately designed at the molecular level for specific applications such as optoelectronic devices [3,4]. Azo dyes have drawn considerable attention due to their optical characteristics such as optical data storage and nonlinear optics [5]. Although the optical parameters of thin films are of crucial importance, few researches have so far focused on optical parameters of azo dye films [6]. Optical tests giving transmittance and reflectance spectra provide the data to determine optical constants such as refractive index, n, extinction coefficient, k, and dielectric constant, ε [7]. The analysis of optical absorption could provide useful information to the elucidation of electronic structure of material [8]. Other analysis showed that optical absorption spectra could provide the necessary parameters to determine direct and indirect transitions occurring in the band gaps of the materials [9]. High-speed and high-sensitivity optical devices play important roles in optical information processing, optical computation and optical communication. Therefore, the study of all-optical

http://dx.doi.org/10.1016/j.ijleo.2015.08.176 0030-4026/© 2015 Elsevier GmbH. All rights reserved. switching characteristics is of importance. The optical switching property is closely concerned with the material of the device. Many materials for optical switching device have been reported, including Rhodamine-B-doped and Au(111)-doped PMMA film [10], 2-(2'-hydroxy phenyl)benzoxazole [11], hydrogenated amorphous silicon-sulfur alloy [12], Pt:ethynyl complex [13], photochromic dithienylethene derivatives [14], ethyl red doped polymer film [15], bromophenol blue solutions [16], antiferroelectric liquid crystals [17], congo red in solution [18], dye doped liquid crystal gel [19], liquid crystal cells [20], ytterbium doped fiber [21–23], etc. The optical switches based on organic materials are superior to traditional ones based on inorganic materials due to their higher sensitivities and easier fabrication process. Especially, the azo polymer offers great potential applications ranging from optical data storage [24], to optical switching, due to the flexibility [25], the compatibility in fabrication [26] and the reversible trans-cis-trans photoisomerization [27].

Optical switching has been studied extensively in azo materials such as azobenzene containing polymer films [28], in azo-dye doped polymer waveguide [29], azo polymer material [24,27] and azo polymer waveguide [18]. In these studies the switching process is attributed to trans–cis photo isomerization of azo dyes followed by cis–trans thermal or optical relaxation [29].

This work reports the optical properties of azo dye (1,8-Dihydroxynaphthalene-3,6-disulfonic acid-[2-(4-Azo)]-N-(5-methyl-3-isoxazolyl)benzenesulfonamide) film prepared by spray pyrolysis method onto BK7 glass substrate by using







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spectrophotometer measurements of the absorbance, transmittance and reflectance to determine the type of optical transition responsible for optical absorption. Also, we have investigated the nonlinear optical properties of the azo dye solution sample using thermal lens technique and optical switching based on thermal lens (TL).

2. Experimental

2.1. Preparation of the azo dye

The azo dve (1.8-Dihvdroxvnaphthalene-3.6-disulfonic acid-[2-(4-Azo)]-N-(5-methyl-3-isoxazolyl)benzenesulfonamide) was prepared by a method similar to that described by Fox [30]. 6 mM (1.5197 g) of the sulfamethoxazole $(C_{10}H_{11}N_3O_3S)$ was dissolved in 2 ml of concentrated HCl then, 10 ml of distilled water was added. 0.456 g of NaNO₂ was dissolved in about 5 ml of distilled water. Diazonium salt was prepared by adding sodium nitrite solution previously prepared to cold solution of amine. 6 mM (2.4017 g) of chromotropic acid disodium salt dehydrate was dissolved in distilled water with the addition of a solution of 8 g of sodium hydroxide of 100 ml of distilled water. The dye was kept in a refrigerator for 24 h, then the prepared dye was neutralized by the addition of dilute hydrochloric acid to convert the azo dye from the sodium salt formula to the hydrogenic one. The product was recrystallized, yield is blood red azo dye was 94%. The melting point of the dye was below 300 °C. The azo dye has been characterized by the elemental analysis, the IR and UV spectra, with spectral resolution of the order of 0.1 nm.

The IR spectrum of the prepared dye is shown in Fig. 1(b). As could be seen from Fig. 1 the spectrum is characterized by a broad and strong band at 3450 cm⁻¹ which could be attributed to the hydrogen bonded hydroxy1 group. These bands obscures relatively weaker bands that are expected for the NH bands which are ordinarily occurs within the same region. The elemental analysis of $C_{20}H_{16}N_4O_{11}S_3$ calculated: C 41.09, H 2.76, N 9.58; found: C 41.75, H 2.25, N 10.15. The chemical structure and molecular formula of the azo dye are shown in Fig. 1(a).

The stretching vibration of the O=H groups appeared in the region of 3448.49 cm⁻¹ while the one belonging to the N=H group supposed to overlapped with H–O bond at 3448.49 cm⁻¹. The stretching vibration band of C=N appeared at 1616.24 cm⁻¹ while the one belonging to the C=C bond of the aromatic structure appeared at 1496.66 cm⁻¹. The azo group band (N=N) appeared at 1461.94 cm⁻¹. At last the bending vibration of the O=H bonding appeared at 829.33 cm⁻¹.

2.2. Film preparation

CodH1eN4O11S

The spray pyrolysis method used here is basically a chemical deposition method in which fine droplets of the desired material



1%

Fig. 1. (a) The chemical structure and molecular formula and (b) IR-spectrum of azo dye.



Fig. 2. Three-dimensional microscopic image surface profile scan of azo dye film.



Fig. 3. One-dimensional microscopic image surface profile scan of azo dye film. Inset is the histogram curve of the azo dye film surface.

are sprayed onto a heated substrate. Continuous films are formed on the hot substrate by thermal decomposition of the material droplets.

The azo films were deposited onto BK7 glass slides, chemically cleaned, using the spray pyrolysis method at 170 °C substrate temperature. Concentration of 0.2 mM of azo dye in dimethylsulfoxide (DMSO) solvent was used for all the films. The nozzle to substrate distance was 30 cm and during deposition, solution flow rate was held constant at 2 ml/min. The substrate temperature was measured using an iron–constantan thermocouple. The thickness of the azo dye film was measured by weight difference method using a sensitive microbalance is found to be 2.7 μ m.

The optical measurements of azo dye film were carried out at room temperature using Cecil ReflectaScan Reflectance Spectrophotometer CE 3055 in the wavelength range 300–900 nm. The substrate absorption is corrected by introducing an uncoated cleaned BK7 glass substrate in the reference beam.

2.3. Surface analysis

Characterization of surface topography is important in optical devices. In general, it has been found that diffusion transmission increases with average roughness. Roughness parameters have important applications in linear and nonlinear optics such as linear electro-optical effect, optical filters and optical storage devices. The surface morphology of the azo dye film is characterized by image processing using Origin Lab program. It is employed to simulate an optical procedure to measure surface roughness. The surface profile of the azo dye film is displayed in Figs. 2 and 3. As can be seen, two typical morphological features are recognized readily by visual

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