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Third-order nonlinear optical response of indigo carmine under 633 nm excitation for nonlinear optical applications

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ABSTRACT

We report thermally induced third-order nonlinearity and optical limiting behaviour of Indigo Carmine dye. *z*-Scan technique was used to determine the sign and magnitude of absorptive and refractive nonlinearities. Continuous wave (CW) He–Ne laser operating at 633 nm was used as source of excitation. In open aperture *z*-scan experiments, samples exhibited reverse saturable absorption (RSA) process. For closed aperture *z*-scan experiments, samples revealed self-defocusing property. The presence of donor and acceptor groups in the structure increases the conjugation length and in turn increases the optical nonlinearity. Induced self-diffraction rings pattern was recorded for the samples and it is attributed to refractive index change and thermal lensing. Also, optical limiting and clamping studies were carried out for various input power. Optical clamping of about ~1 mW was observed. This endorses that the dye under investigation is a positive candidate for opto-electronic and photonic applications.

1. Introduction

The present dye applications extend beyond their use for the coloration of bulk materials. As functional dyes these are useful as optical switches, light emitting diodes, photovoltaic devices, dye lasers, photodynamic therapy, etc. [1]. Among the dyes available, amino- and hydroxy-substituted quinones are having immense importance in biology, dye and pharmaceutical chemical industries [2]. Due to the presence of the quinonoid moiety, these dye molecules act as good electron acceptors. Due to good electron accepting properties, a variety of quinones and substituted quinones have also been used in exploring the dynamics and mechanism of electron transfer processes under both intramolecular and intermolecular conditions [3].

In aromatic conjugated compounds, the delocalization behaviour of the π-electrons makes their distribution highly deformable and gives rise to large optical nonlinearities. Nonlinear optical properties of organic dye molecules are important from the point of view of understanding their photo-physics and realizing the potentiality of using these molecules in applications like optical processing, computing, all-optical switching and optical limiting [4–6]. Indigo carmine is one of the indigoid dyestuffs. Indigo dye has a distinctive blue colour and is one of the oldest and important dyes. Indigo carmine is popularly known as Indigo-5,5′-disulfonic acid disodium salt, Indigotine, FD & C Blue #2 or acid blue 74. The dye consists of donor–acceptor–donor electron groups which results in a remarkable third-order nonlinear optical property. These dyes absorb at around 610 nm and their excellent photo-physical properties make them highly suitable for a wide range of applications. These include photodynamic therapy, protein detection, photoconductors in solar cells, nonlinear optics, fluorescence imaging, chemosensor, etc. [7,8].

2. Experimental

2.1. Material

Indigo Carmine dye was purchased from Sigma Aldrich Company and used without further purification. The molecular formula is $C_{16}H_8N_2Na_2O_8S_2$ and molecular weight is 466.35 g/mol. The structure scheme of indigo and indigo carmine is given in Fig. 1. In order to determine the absorptive and refractive nonlinearities, solutions with concentrations 20 μM, 25 μM and 30 μM were prepared using research grade *N*,*N*-dimethyl formamide (DMF) and labelled as a, b and c. For optical limiting measurements and diffraction ring patterns, additional samples with concentrations of 35 μM and 40 μM were prepared and labelled as d and e, respectively.

2.2. z-Scan technique

The sign and magnitude of real and imaginary parts of third-order nonlinear susceptibility of dye was evaluated using *z*-scan technique. *z*-Scan technique developed by Sheik-Bahae et al. [9,10]

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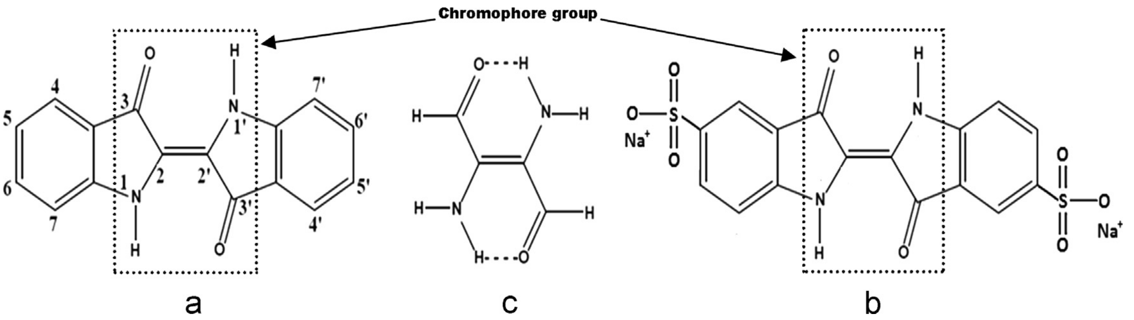

Fig. 1. Structure scheme of (a) indigo, (b) indigo carmine and (c) H-like chromophore.

is a single-beam method using which one can obtain the nonlinear absorption and refraction nonlinearities simultaneously. The experimental setup used is similar to our previous work [11]. *z*-Scan experiments were performed by using Thor labs HRP350-EC-1 CW He–Ne laser at 633 nm wavelength as an excitation source. The laser beam was focussed to a spot size of 36.78 μm and the Rayleigh length Z_R of 6.71 mm using a 5 cm focal length lens with input power 22 mW. The samples were placed in a cuvette of 1 mm thickness. Hence, the thin sample approximation is valid as the sample thickness is less than the Rayleigh length Z_R [9,10].

3. Results and discussions

3.1. Structure scheme and UV–vis measurements

The most fascinating characteristics of indigo carmine is its blue colour. Its first excitation energy is small of order of about 2 eV in polar solvent [12]. As the coloured compounds observed in the range 400 to 700 nm possess excitation energy between 1.77 eV and 3.10 eV. Where as in non-polar solvents indigo is present mainly as a monomer. The origin of blue colour is due to the conjugated system of indigo without benzene ring. The appearance of this blue colour is due to the strong internal hydrogen bonds between both oxygen of the carbonyls and nitrogen that favour a $C^{+}–O^{-}$ resonating structure and thus lowers the gap between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) [12]. The presence of 5,5′-position of di-sulfonic acid disodium salt does not affect the colour. Indigo carmine has its absorption maximum ($\lambda_{\max}$) at 610 nm just like its parent compound indigo.

The optical characterization for the various sample concentrations were studied by recording the electronic spectra in the wavelength range 250 to 800 nm using UV-1601PC Shimadzu spectrophotometer and is depicted in Fig. 2. The absorption maximum is found to be at 610 nm. This peak is responsible for the blue colour of the solution and it is attributed to the $n–\pi^*$ transition of the non-bonding electrons to the anti-bonding π^* group. In the part of UV region, there is a second group of bonds with increasing absorbance towards lower wavelengths, due to the aromatic rings [13].

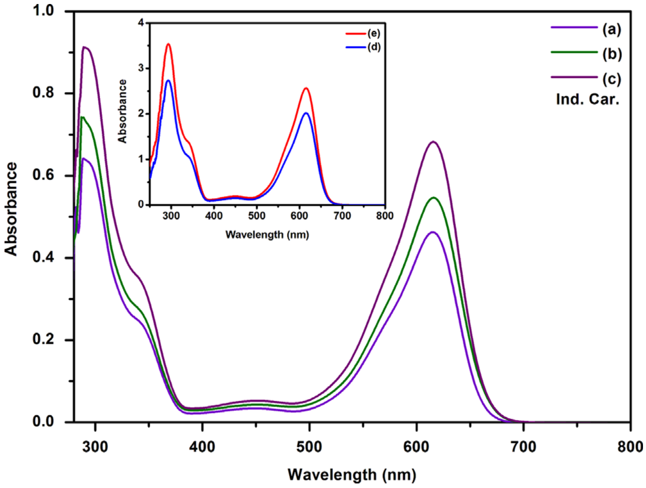

Fig. 2. Absorbance spectra of indigo carmine in DMF at various concentrations.

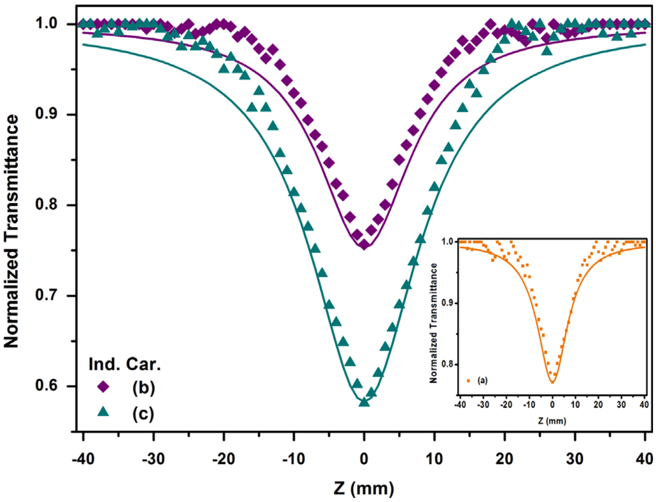

Fig. 3. Open aperture *z*-scan traces of (a) 20 μM, (b) 25 μM and (c) 30 μM concentrations of indigo carmine. Solid line depicts theoretical fit.

3.2. Nonlinear absorption and refraction studies

We performed open aperture and closed aperture *z*-scan experiments in order to determine the nonlinear absorption coefficient β and nonlinear refractive index n_2. The linear absorption coefficient α and refractive index n are determined and found to be 78.337/m and 1.42, respectively.

Fig. 3 shows the open aperture *z*-scan traces for various concentrations of dye. At the far field the laser intensity is less. As the sample translates towards focus from $-z$ to $+z$, the normalized transmittance decreases, forming a valley at the focus. This type of process is known as reverse saturable absorption (RSA). The nonlinear absorption mechanism of a material involves two types of behaviour. One is saturable absorption (SA) and other is reverse saturable absorption (RSA). In the former case, as the sample translates towards focus, the normalized transmittance increases forming a peak at the focus. SA and RSA are also known as negative and positive type of absorptive nonlinearities. Depending on the behaviour of material result as SA or RSA, they are used in different applications. There are several mechanism which