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Effect of conjugation length on nonlinear optical parameters of anthraquinone dyes investigated using He–Ne laser operating in CW mode

S. Pramodini, P. Poornesh *

Nonlinear Optics Research Laboratory, Department of Physics, Manipal Institute of Technology, Manipal University, Manipal, Karnataka 576104, India

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ABSTRACT

We report the studies on third-order optical nonlinearity and optical limiting of anthraquinone dyes. *Z*-scan technique was employed to evaluate the nonlinear parameters such as nonlinear absorption coefficient β_{eff} and nonlinear index of refraction n_2. Continuous wave He–Ne laser was used as the source of excitation. The estimated values of β_{eff}, n_2 and $\chi^{(3)}$ are of the order of 10^{-3} cm/W, 10^{-5} esu and 10^{-7} esu respectively. The presence of donor and acceptor groups in the structure results in increase in conjugation length. This resulted in the enhancement of nonlinear optical parameters values of the dye. Multiple diffraction rings were observed when the samples were exposed to laser beam due to thermal lensing. Dyes exhibited good optical limiting behavior under the experimental conditions. The results indicate that the dyes investigated here are materialise as candidates for photonics device applications such as optical power limiters.

1. Introduction

The nonlinear optical (NLO) properties of materials are used to control the phase, change the frequency of incident light, polarization, etc. [1]. In the last decade, NLO properties of π-conjugated organic materials have been attracting considerable attention because of their possible applications in a variety of opto-electronic and photonic applications such as optical switching, optical telecommunications devices, optical disks, dye lasers, etc., [2]. Conjugated organic materials possessing electron donors and attractors have been reported to exhibit NLO properties [3]. The strong π-electrons delocalization in the organic materials causes a high molecular polarizability and thus results in a remarkable third-order nonlinear optical property [4]. Continuous wave (CW) lasers ranging from μW to kW are widely used in various applications [5]. This necessitates the need for protection of optical sensors and human eyes, which are vulnerable to damage when exposed for a small duration of 0.25 s with a radiation of ~2.5 mW/cm^2 [6,7]. Also, there is a lack of sufficient information of low threshold nonlinear materials investigated using CW lasers. Various organic and inorganic materials were studied in order to determine the optical nonlinearities under CW lasers [7–17].

The dyes under investigation belong to the class of anthraquinone. Anthraquinone dyes have gained considerable attention in NLO and its applications due to the large delocalized two-dimensional π-electron system, good optical properties and high thermal stability [18,19]. They possess a highly delocalized π-conjugated electron system not only in its nucleus, but also in the substituent's [18]. They are derived from the aromatic compounds by exchanging an even number of groups with proper arrangement of double bonds, thus leading to conjugation with the aromatic structure [20]. These dyes have immense applications in optical switches, light emitting diodes, photovoltaic devices, organic semiconductors, reprographics, thermal printing, in biology, pharmaceutical chemistry and industries, in medical purposes like wound healing and photodynamic therapy, etc. [21–25].

The present dyes studies are of interest because they have π-conjugated planar structural system and also its structure contains electron donating groups and electron accepting groups and hence are suitable for the study of NLO properties. Due to the presence of quinone moiety, these molecules are good electron acceptors. The structure flexibility aids in increasing the optical nonlinearity of the dyes. With this view, we have studied the third-order nonlinear optical properties and optical limiting and clamping behavior of anthraquinone dyes using the *Z*-scan technique. A CW He–Ne laser of wavelength 633 nm was used as the excitation source. Further the induced self-diffraction ring patterns and laser spot size variation were also studied.

* Corresponding author. Tel.: +91 820 2925621; fax: +91 820 2571071.
E-mail address: poorneshp@gmail.com (P. Poornesh).

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2. Experimental

2.1. Materials and methods

The amino substituted quinonoid structured Acid blue 129 (Atanyl Blue PRL) and Remazol Brilliant Blue R (Reactive Blue 19) dyes were purchased from Sigma-Aldrich and used as received. The molecular formulas of dyes are $C_{23}H_{21}N_2NaO_5S$ and $C_{22}H_{16}N_2Na_2O_{11}S_3$ correspondingly. The molecular structures of dyes are shown in Fig. 1. The optical characterization of dyes under investigation was studied by recording the electronic spectra in the wavelength range 300–800 nm using a UV-1601PC Shimadzu spectrophotometer and is shown in Fig. 2. For determining the absorptive and refractive nonlinearities 20, 25, 30 and 35 μM concentrations were prepared by dissolving them in research grade N,N-Dimethyl Formamide (DMF) separately and labeled as (a), (b), (c) and (d) respectively. For optical limiting studies, we prepared an additional concentration of 40 μM and labeled as (e).

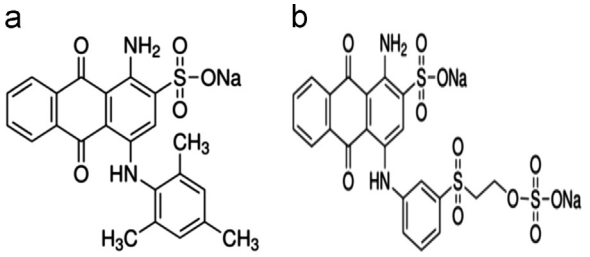

Fig. 1. Molecular structure of (a) AB 129 and (b) RBBR dye.

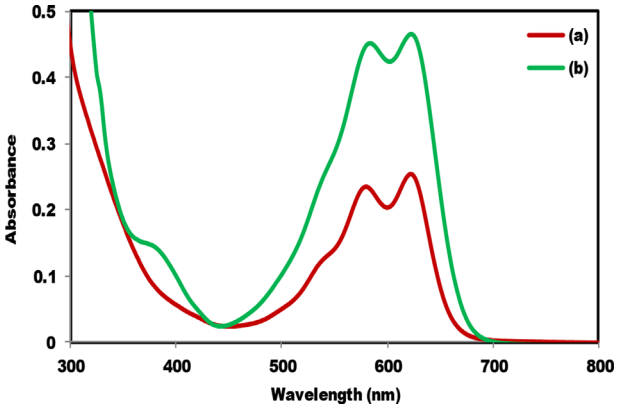

Fig. 2. Absorbance spectra of (a) AB 129 and (b) RBBR dye in DMF.

2.2. Z-scan experimental technique

To determine the sign and magnitude of third-order nonlinear susceptibility of dyes we employed the *Z*-scan technique developed by Sheik Bahae et al. [26,27]. The *Z*-scan technique is an effective tool for determining the third-order nonlinear optical properties of materials, as it provides the sign and magnitude of real and imaginary parts of $\chi^{(3)}$. Nonlinear refractive index n_2 is proportional to the real part of $\chi^{(3)}$ and the nonlinear absorption coefficient β relates to the imaginary part of $\chi^{(3)}$. The experimental setup used in the present method is similar to that reported in our previous work [19]. *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 focused to a spot size of 36.78 μm and the Rayleigh length Z_R of 6.71 mm. A 5 cm focal length lens was used with input power 23 mW and the resultant output power through the samples was recorded using a photodetector fed to a Thor labs PM320E dual channel optical power and energy meter. The samples were placed in a cuvette of 1 mm thickness. Hence, the thin sample approximation is valid [26,27] as the sample thickness is less than the Rayleigh length Z_R.

3. Results and discussions

3.1. UV–vis absorption

The absorption spectra of dyes are shown in Fig. 2. The peaks are broad and continuous in the entire visible region which is suitable for photovoltaic applications. These peaks indicate high degree of conjugation and high intra-chain order in dyes. In the spectra, the absorption maximum at around 300 to 600 nm is due to the π–π* transition. The anthraquinone dyes contains 2 amino groups at 1-, and 4- positions. Hence the main band has a double peak head at 580 nm and 629 nm for dye AB 129 and 590 nm and 630 nm for RBBR dye. The laser wavelength 633 nm is in the resonant absorption region of the dyes. Anthraquinone dyes show intense absorption peaks due to the N–H bonds. Also, the presence of N–H group in the 1-position causes bathochromic shift. This shift is due to the charge transfer from the lone pair of amino group to the oxygen atom of the carbonyl group. By increasing the electron donating ability of substituents, the bathochromic shift enhances. The presence of electron withdrawing group has little effect on the absorption maxima.

3.2. Open aperture and closed aperture measurements

Open aperture experiments were performed in order to determine the nonlinear absorption coefficient β of the dyes. The nonlinear absorption curves obtained for the dyes are shown in Fig. 3. The samples were placed in a cuvette kept on a translation

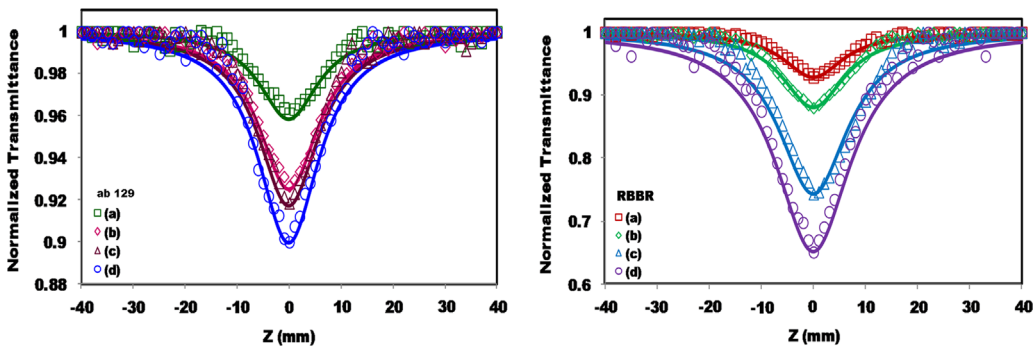

Fig. 3. Open aperture *Z*-scan traces of (a) 20 μM, (b) 25 μM, (c) 30 μM and (d) 35 μM concentrations of dyes. Solid line depicts theoretical fit.