Optoelectronic and photoacoustic studies of an organic dye synthesized through green route

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Abstract. An azo dye was prepared through an environmentally benign and economically feasible synthesis route with cardanol as a starting material. Cardanol is a cost-effective and renewable natural source obtained from Cashew Nut Shell Liquid, a by-product of the cashew industry. The dye was spectrally characterized by IR, UV-Vis, NMR and fluorescence studies. UV-Vis absorption showed a bathochromic shift between solvents of lower and higher polarities. Nonlinear optical and photoacoustic properties were studied using a frequency doubled Nd:YAG laser producing 532 nm laser pulses of 3 ns pulse width. Results show that the nonlinear absorption coefficient decreases with the increase of on-axis intensity, suggesting excited state absorption as the principal mechanism. The observed nonlinearity has applications in optoelectronics.

1. Introduction
The rapid development of photonic technology demands new materials of precisely controlled chemical and structural properties [1]. Organic materials, specifically azobenzene molecules have gained wide interest due to their promising uses in many fields such as optoelectronics, biomedical studies, liquid crystalline displays, and pharmaceutical industry [2]. They absorb light in the visible spectrum (400-700 nm) and exhibit resonance of electrons, which is a stabilizing force in organic compounds. The nonlinearity of these molecules has been found to originate from a strong delocalization of π-electrons along the length of the molecule [3]. Apart from the established applications of azobenzene molecules recently they have recently been considered as an alternative material for use in dye-sensitized solar cells [4]. Also, azobenzene derivatives are effectively used as smart targeted carrier for drug delivery systems [5]. However, when it comes to the choice of sensitizer synthesis, environmental and toxicological concerns, as well as economic feasibility should be taken into consideration. Motivated by these concerns, we synthesized the azobenzene compound cardanol as a starting material. Cardanol, a mixture of meta alkylphenols is obtained from Cashew Nut Shell Liquid (CNSL), a by-product of the cashew industry. Optimization of photophysical and chemical characteristics along with independent measurement of both nonlinear optical and photoacoustic properties is important to identify such materials for practical applications. In this paper we report the spectral, nonlinear optical and photoacoustic properties of an azo dye, 4-(2-carboxyl-phenylazo)-3-[pentadec-8-enyl] phenol synthesized using green-chemistry techniques. The results show that the dye is suitable for optoelectronic applications and its photoacoustic response can be further exploited as a contrast agent in photoacoustic imaging.
2. Methods

The prepared dye was purified by column chromatography [hexane:chloroform(1:1)] and was spectrally characterized by IR, UV-Vis, NMR and fluorescence studies. For nonlinear optical and photoacoustic studies, we used novel photoacoustic z-scan (PAZ-scan) technique [6] which enables concurrent monitoring of both the optical transmission and photoacoustic response of the sample under investigation. A frequency doubled Nd:YAG laser (Minilite II, Continuum) is focused onto the sample with a 20 cm focal length lens. The sample is placed in a 2 mm quartz cuvette and mounted in a custom-made cell that contains water for ultrasound coupling. The sample cell is placed at 45° with respect to the incident laser beam and the effective optical path length equal to 2.83 mm. The whole system is mounted on a XYZ translation stage (Thorlabs NRT 150) and is moved such that the focal point of the beam scans the sample along its length (in the z direction). As the laser pulse is incident on the sample, some of the energy delivered is absorbed and converted into heat. This produces pressure transients and wideband ultrasonic emission which is detected using a 10 MHz focused water immersion transducer (Olympus NDT Inc.).

3. Results

The dye was synthesized in two steps namely diazotization using anthranilic acid followed by coupling with cardanol (figure 1). The pH of the diazonium solution was adjusted to 6.5 by the addition of an appropriate amount of 1M sodium bicarbonate solution. The precooled solution of cardanol in ethanol was injected drop-wise to the above pH monitored solution at 0°C. The reaction mixture was stirred at 0°C for 40 minutes by which time the product was formed as an orange viscous liquid.

The optical absorption and fluorescence emission spectra of the dye is shown in the figure 2. The UV-Vis studies of the dye in different solvents hexane and chloroform indicates that the dye exhibited \( \pi \rightarrow \pi^* \) transition and showed a bathochromic shift when switching over from less polar to more polar solvents. This depends on the nature of the electron donating and accepting groups. In the case of \( \pi \rightarrow \pi^* \) transition, the excited state is more polar than the ground state and the dipole-dipole interaction with solvent molecules lower the energy of the excited state more than that of the ground state. Therefore a polar solvent decreases the energy of \( \pi \rightarrow \pi^* \) transition and absorption maxima appear red shifted from hexane to chloroform solvent. The fluorescence emission spectra of the dye was recorded in chloroform at 293 K excited at 350-400 nm and a high intensity was recorded in the range ~600-700 nm. In accordance with these results the material is suitable for using as a fluorescent marker and light emitter in organic light emitting diodes.

For NLO and PA studies the dye is dissolved in chloroform with a concentration of \( 1 \times 10^{-4} \text{mol/mL} \). The normalized open aperture (OA), closed aperture (CA) Z-scan curves and PA curve at on-axis peak intensity \( 1.16 \times 10^{13} \text{W/m}^2 \) is shown in figure 3. As the intensity of the incident light changes, the optical transmittance varied in a way which depends on the nonlinear absorption properties of the sample. When an aperture is inserted prior to the output detector, the phase variation will induce a change in energy transmittance through the aperture. The CA Z-scan curve shows this variation and the dye exhibits a self-defocussing effect which leads to negative nonlinear refractive index.
For a temporally Gaussian pulse, when all the transmitted energy is collected, the OA normalized transmittance is given by,

\[ T(Z) = \sum_{m=0}^{\infty} \left( \frac{\beta I(Z) L_{\text{eff}}}{(m+1)^{3/2}} \right)^m, \quad L_{\text{eff}} = \frac{1 - e^{-dL}}{\alpha} \]

where \( \beta \) is the nonlinear absorption coefficient, \( I(Z) \) is the incident laser intensity, \( L \) is the sample length and \( \alpha \) is the linear absorption coefficient. Fitting the OA data with equation (1) gives a \( \beta \) value which in the present study is found to be \( 5.80 \times 10^{-10} \text{ m/W} \). Again, when light energy is absorbed by the sample and converted in to heat, thermal expansion of the media arises and acoustic waves (PA signal) are formed. The generated acoustic waves can be given as [6],

\[ p = \Gamma \mu_a I(Z) \]

where \( \mu_a \) is the optical absorption coefficient of the sample and \( \Gamma \) is the Gruneisen parameter. Fitting the PA experimental data with equation (2), also measured the nonlinear absorption properties of the sample. The obtained value of \( \beta \) in this case is \( 5.23 \times 10^{-10} \text{ m/W} \) in agreement with the NLO measurement. Comparison of the reported studies of the nonlinear optical properties of novel azo benzenes [7], suggests that the dyes possess large third order nonlinear optical properties. In addition, the dye shows good photoacoustic response which suggests their applicability as contrast agents in PA imaging.

To understand the mechanism behind the observed nonlinear absorption, the excited state absorption cross-section (\( \sigma_{eS} \)) of the sample was measured from the open-aperture Z-scan data [8]. For this OA data is fitted to the transmittance equation,

\[ T = \ln \left( \frac{1 + \frac{q_0}{1 + x^2}}{1 + \frac{q_0}{1 + x^2}} \right), \quad q_0 = \frac{\sigma_{eS} \alpha F_0 I_{\text{eff}}}{2h\omega} \]

\( F_0 \) is the fluence of the laser at the focus, \( h \) is the Planck’s constant, \( \omega \) is the angular frequency of the laser, \( x=Z/Z_R \) where \( Z \) is distance of the sample from the focus with a positive value between focus and detector and \( Z_R \) is the Rayleigh length. The ground state absorption cross-section, \( \sigma_{gS} \) is calculated from the equation, \( \sigma_e = \sigma_{gS} N_C \) where \( N_a \) is the Avogadro’s number and \( C \) is the concentration in moles/cm\(^3\). The measured value of \( \sigma_{gS} \) is \( 1.55 \times 10^{-18} \text{ cm}^2 \) which is found to be larger than the value of \( \sigma_{gS} \), \( 1.32 \times 10^{-19} \text{ cm}^2 \). This is a favourable condition for reverse saturation absorption to occur. To confirm this, the value of \( \beta \) was evaluated with different on-axis peak intensities (\( I_0 \)) ranging from \( 1.16 \times 10^3 \text{ W/m}^2 \) to \( 1.70 \times 10^3 \text{ W/m}^2 \) and found to decrease in value from \( 5.8 \times 10^{-10} \text{ m/W} \) to \( 3.21 \times 10^{-10} \text{ m/W} \) (figure 4). This result along with positive value of \( \beta \)
suggests that excited state absorption be the principal mechanism for nonlinear absorption [9], which finds applications in optoelectronics.

4. Conclusion

An azo dye namely 4-(2-carboxyl-phenylazo)-3-[pentadec-8-enyl] phenol was prepared through green synthesis methods using cardanol as a starting material. Nonlinear optical, and photoacoustic studies were carried out at 532 nm with 3ns laser pulses using a photoacoustic Z-scan experiment. The material shows a self-defocussing nature and excited state absorption at 532 nm. The nonlinear absorption coefficient was estimated and found to be on the order of $10^{-10}$m/W.

Acknowledgments

S Vijayakumar acknowledges the University Grants Commission, New Delhi, India for RAMAN Fellowship for Post Doctoral Research in USA.

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