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Third-Order Nonlinear Optical Properties of Phenothiazine-Iodine Charge Transfer Complexes in Different Proportions

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ABSTRACT

The nonlinear optical properties of phenothiazine-iodine (PTZ-I) charge transfer complexes (CTC) in three different proportions were investigated by z-scan set up using Nd: YAG laser at 532 nm wavelength, 7 ns pulse width and 10 Hz repetition rate as excitation source. The interaction between phenothiazine and iodine was analysed using FTIR spectroscopy. The morphological changes after the formation of CTC were observed with the help of scanning electron microscopy and optical microscopy. The CTC system displayed an absorption in the UV-Visible region, which is attributed to the charge transfer between constituents. Optical nonlinearity was observed to be maximum when the molar ratio between phenothiazine and iodine is 1:1, and it strongly depends on the electron donor-acceptor proportion. Optical limiting threshold values of the studied samples are comparable to many reported values. The excellent nonlinear optical properties exhibited by PTZ-I CTC make them promising candidates in nonlinear optical applications.

1. Introduction

Exploring novel materials with enhanced nonlinear optical (NLO) properties is an ever interesting field of researchers, as the materials can be utilized in various photonic applications like optical switches, optical limiters, and signal processing [1–3]. NLO investigations of numerous materials such as organic compounds, inorganic compounds, nanostructures and carbon nanotubes have been conducted and applied in different devices [4–9]. Only a few studies are reported regarding optical nonlinearity of charge transfer complexes (CTC) so far. Both inter molecular and intra molecular charge transfer systems are expected to be with excellent nonlinearity because of the large dipole moment arises by the charge separation [10]. Optical nonlinearity of organic compounds can be tuned by structural alteration, while that of nanostructures by altering their sizes. In the case of an intermolecular CTC, it can be modified by changing the donor-acceptor ratios or by using suitable solvents [1]. Here we report the detailed NLO studies of phenothiazine-iodine charge transfer complex (PTZ-I CTC) in dimethylformamide (DMF). PTZ-I CTC is an organic semiconductor with excellent electronic, magnetic and optical properties which can be proposed for various technological applications [11–14]. Iodine is such an electron acceptor, which interacts with different types of electron donors to form weakest to strongest charge transfer complexes [1]. The charge transfer complex of iodine with a fairly strong electron donor phenothiazine (PTZ) was reported first by Matsunaga [14,15]. PTZ is a heterocyclic compound with sp^3 hybridized nitrogen which blocks the delocalization of electrons in the whole molecule [16] and hence shows poor nonlinear absorption at lower input intensities. Iodine shows saturable absorption (SA) behaviour in inert solvents and in vapour form. Iodine forms complexes with even inert solvents and the optical nonlinearity exhibited by iodine changes from SA to reverse saturable absorption (RSA) for different types of donor solvents like π donors, n donors and inert solvents. Iodine with n donors does not show any nonlinear optical activity [1]. Comparing to other NLO systems, CTC have the benefit of both conjugated electron and the charge transfer, which ensures its good NLO properties.

2. Experimental methods

2.1. Synthesis

Phenothiazine-iodine CTC (1:1) was synthesized by mixing 0.5 g PTZ (>98%, Sigma Aldrich) in 50 ml DMF with the 150 ml solution

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of 0.64 g of iodine in DMF and then stirred continuously for 3 h. PTZ-2I_2 (1:2) and PTZ-3I_2 (1:3) were also synthesized by the same procedure by using 1.28 g and 1.95 g iodine respectively in 150 ml of DMF. Thus three samples were synthesised in three different molar ratios such as PTZ-I_2 (1:1), PTZ-2I_2 (1:2) and PTZ-3I_2 (1:3) and all the three samples appeared to be in dark colour and found to be stable [14,15].

2.2. Characterization

The absorption spectra of PTZ-I with different molar ratios were recorded using a UV-Visible spectrophotometer (Shimadzu-UV 2450). Morphological analysis of the CTCs was carried out using scanning electron microscopy (HITACHI SU6600) and optical microscope (MOTIC BA 300). The interaction among the components was analysed by FT-IR spectrometer (JASCO-FT/IR 4700). The crystalline structure of the CTC was ensured by X ray diffractometer (RIGAKU-MINIFLEX 600) using CuK_α radiation (λ = 1.5418 Å).

Optical nonlinearity of the samples was investigated by simple and sensitive z-scan experimental set up introduced by Sheik Bahae et al. [17]. It has been widely used for measuring the sign and magnitude of both nonlinear absorption coefficient and nonlinear refractive index coefficient separately and finally to evaluate third-order nonlinear optical susceptibility ($\chi^{(3)}$). The nonlinear absorption and refraction properties can be derived separately by open aperture (OA) and closed aperture (CA) z-scan techniques. The schematic diagram of the z-scan experimental set up is given in Fig. 1.

A frequency doubled Q switched Nd: YAG laser (Quantaray-IND-10–40) operating at 532 nm wavelength, 10 Hz repetition rates and 7 ns pulse width was used as the excitation source of the z-scan experiment. M^2 (laser beam quality factor) value of the laser was estimated as 2. Laser beam waist ω_0 (where intensity fall $1/e^2$ of the maximum value) estimated as 1.5 mm by knife edge experiment [8,18]. The laser beam was split into two using a beam splitter, in which one beam was taken as the reference beam and the other beam was focused using a convex lens of focal length 150 mm and was allowed to transmit through the sample taken in a quartz cuvette having thickness 1 mm. The sample was moved in the propagation direction of the laser beam from −z to +z about the focus of the lens in a step of 1000 microns with the help of a translational stage which was controlled by a computer program. Both the reference beam and the transmitted beam were detected using two identical pyroelectric detectors (RjP-735, laser Probe Inc, USA) and were recorded in the energy meter (Rj-7620, Laser Probe Inc, USA). Thickness of the sample was less than Rayleigh range, z_0 = 1.69 mm, calculated using the formula, $z_0 = \pi\omega_0^2/\lambda$ and hence the thin sample approximation can be applied. The intensity dependent transmittance measured using detector were plotted against the position of the sample. The nonlinear refraction properties were extracted from the transmitted signatures obtained by CA z-scan method in which an aperture of diameter 4 mm was placed in front of the detector while the nonlinear absorption properties were extracted by OA z-scan method without an aperture [19]. The linear transmittance of the all the samples under study were kept around 70% at 532 nm.

3. Results and discussion

3.1. Absorption studies

The linear absorption spectra of PTZ-I in three different proportions are shown in Fig. 2. PTZ- I gave similar absorption spectra of charge transfer band in the UV-Visible region for all three proportions [1,20] and the spectra was devoid of any characteristic peaks of PTZ (266 nm, 318 nm) and that of iodine (520 nm) [21,22]. The charge transfer band is formed by the electron transfer from the nonbonding highest occupied molecular orbital of PTZ to the lowest unoccupied molecular orbital of iodine [22].

3.2. Structural and morphological analysis

SEM images of pure PTZ and that of PTZ-I in three different ratios are given in Fig. 3, to compare the morphological changes occurred during CTC formation. PTZ shows a needle-like morphology and that of the CTC changes to spherical morphology as the concentration of iodine increases. The optical microscope images of PTZ and CTC in three different concentrations at the resolution of 4×/0.10 are given in Fig. 4. XRD spectrum of PTZ-I CTC is given in Fig. 5 which ensures the crystalline nature with major diffraction peaks at 8.26°, 12.52°, 16.75°, 21.03°, 33.53° and 38.46° and XRD data on the crystal structure of PTZ-I CTC is not available for comparison [14]. Singh et al. deduced the crystalline structure of various charge transfer complexes of PTZ as orthorhombic, using Ito's method [23].

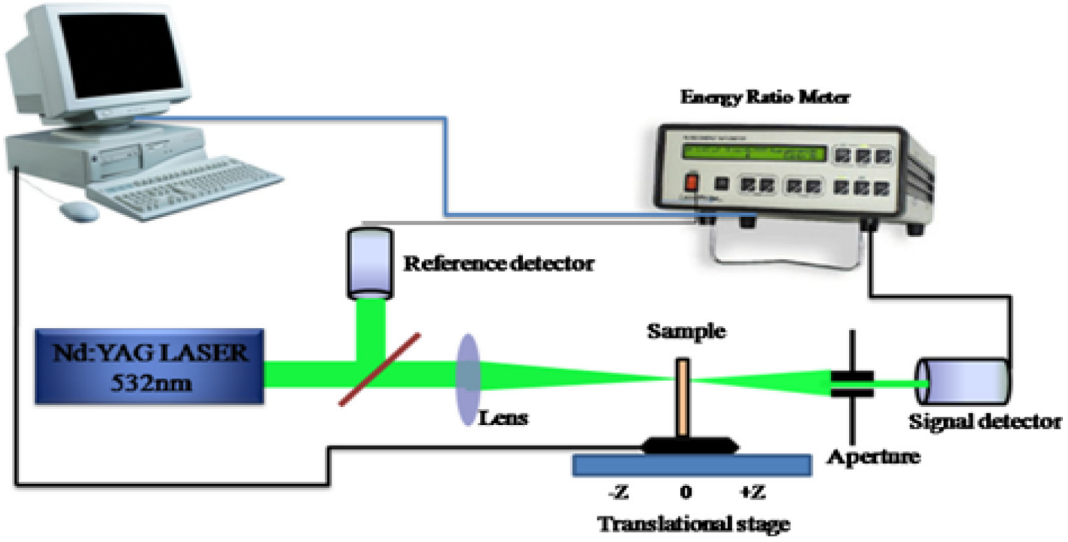

Fig. 1. Schematic diagram of z-scan experimental set up.