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Elucidation of two photon absorption of ethylenediaminium (2,4-dinitrophenolate) crystals

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ABSTRACT

Optical quality single crystals of ethylenediaminium (2,4-dinitrophenolate) [EDA(2,4)DNP] were grown by solvent evaporation method for optical limiting applications against intense ultrashot pulse lasers. Single crystal XRD showed that the material crystallizes in monoclinic system with centric space group $P2_1/C$. The crystal packing diagram was elucidated for the first time in literature and it revealed six hydrogen bonds played a very important role in stabilizing the structure. A bifurcated hydrogen bond was also observed between ethylenediamminium and dinitrophenolate ions. The formation of charge transfer complex during the reaction of ethylenediamine and 2,4-dinitrophenol was strongly evident through the vibrational spectroscopic studies. TG–DTA and DSC curves indicate that the material exhibited strong decomposition at 224 °C. Ground state absorption analysis showed that the grown crystals possess absorption maxima in UV region (270 nm, 346 nm) and wide optical transmittance window (480–1200 nm) in the entire visible and NIR region. Measurement of two photon absorption (2PA) and optical limiting response by Z-scan technique under nanosecond pulse excitation was reported. Hence EDA(2,4)DNP with high 2PA coefficient ($0.79 \pm 0.04 \times 10^{-10}$ m/W) and low limiting threshold ($2.40 \pm 0.05 \times 10^{12}$ W/m^2) will be a potential candidate for optical limiting applications like eye and sensor protection against short pulse lasers that are well spread in human interactive sectors.

1. Introduction

In both civilian and military applications, due to the strong development of laser technology the photosensitive components have received urgent attention because of the necessity for protection from laser damage [1]. These photosensitive components possess limiting threshold intensity and exposing them above these values can lead to temporary or permanent destruction [2]. Smart materials called as passive optical limiter can extend the dynamical range of the sensor to work optimally at higher input intensities. Materials with weak ground-state absorption and strong excited-state absorption are ideal systems for a good optical limiter. For the moment, single crystals with large transparency range and suffer very low optical losses are critically required for the realization of optical limiting devices [3]. In this search organic nonlinear optical (NLO) materials are exhaustively investigated due to their excellent properties like high synthetic flexibility, molecular engineering to tailor their properties, large hyperpolarizability (β) values and rapid response to electro-optic effect [4–6]. Among the organic systems, donor-acceptor charge transfer based hyperpolarizable materials possesses excellent third-order NLO properties compared to the known traditional inorganic materials [7,8]. Especially organic compounds possessing π-conjugated chains provide the additional contribution to the optical limiting processes through electron–vibration interactions [9]. With the aid of novel synthetic chemistry, ordered aggregate structure with superior NLO characteristics can be generated by molecular designing of organic molecules by substituting with strong electron donating and withdrawing entities [10]. However, appropriate design of organic systems at the molecular level to attain enhanced NLO properties ultimately requires the estimation of linear and nonlinear optical coefficients [11]. In this search, nitro aromatics and their derivatives constitute an important class of industrial chemicals and are already widely used as intermediates in the

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synthesis of products, ranging from drugs, pigments, pesticides and importantly NLO devices [12–14]. Among them, nitrophenolate derivatives are interesting NLO candidates, as they have a typical one-dimensional (1D) donor-acceptor π system and the presence of phenolic OH favours the formation of salts with large hyperpolarizability [15,16]. Recently Liu et al. [17], has proposed a synthetic route using phenol-ammonium salts to attain a new series of ethylenediaminium nitrophenolate. Based on this, ethylenediaminium di(2-nitrophenolate) and ethylenediaminium di(4-nitrophenolate) was identified as a new NLO system and their frequency doubling, and optical limiting capability was recently reported [18,19]. In this continuation, this article attempts on the elucidation of crystal packing, molecular arrangement, thermal, optical and NLO properties of ethylenediaminium (2,4 dinitrophenolate) [EDA(2,4)DNP]. As short-pulse visible (green, most sensitive spectral region of the human eye) lasers are well spread in human interactive sectors, the limiting action of the material under nanosecond-pulse excitation is reported in detail.

2. Material preparation and physical measurement

The title compound was synthesized from ethylenediamine and 2,4-dinitrophenol by a typical acid-base reaction using methanol as solvent. The stoichiometric proportions of the reactants [17] were thoroughly stirred for 3 h and a yellow precipitate of EDA(2,4)DNP microcrystalline substance was obtained with a yield of 91%. The product was filtered, washed and dried at room temperature (32 °C). The synthesized salt was subjected to successive recrystallization process to increase its purity. The purity test and chemical composition determination of the synthesized compound were carried out by the estimation of carbon, hydrogen and nitrogen present in them. The elemental analysis revealed that the percentage composition of the elements present in the compound were found as C = 35.17% (36.21%), H = 4.17% (4.34%) and N = 18.48% (18.10%). Based on the elemental composition, the molecular formula of EDA(2,4)DNP was estimated to be $C_7H_{10}N_3O_6$ and found to be different from the formula proposed by Long Liu et al., [17]. The experimental values were in good agreement with the computed values given in parentheses. The difference is that the material formed in the present case contains one ethylenediamine and one (2,4)-dintrophenol, while two molecules of (2,4)-dintrophenol were present in the previous case [17]. The selection of the solvent for crystal growth was assessed through solubility test to grow good quality single crystals of considerable size. The solubility estimation was carried out by dissolving EDA(2,4)DNP in methanol at the temperature range of 20–45 °C with the interval of 5 °C. Fig. 1 shows that EDA(2,4)DNP exhibits high positive solubility temperature gradient in methanol. Hence single crystals were grown by solvent evaporation technique with methanol as solvent. Transparent yellow coloured good quality single crystals with dimension 10 × 5 × 3 mm^3 were harvested after a period of 15 days. The as-grown crystal of EDA(2,4)DNP is as shown in Fig. 1.

The single crystal X-ray diffraction data of the compound were collected using Enraf-Nonius CAD-4 diffractometer with MoKα radiation. A suitable sample of size 0.30 mm × 0.25 mm × 0.19 mm was chosen and mounted on the goniometer. The structure was solved using direct methods with SHELXS-97 and refined using a full matrix least squares method with SHLXL-97 [20]. JASCO 460 Plus FTIR spectrometer was employed to record the infrared spectrum by KBR pellet technique in the region 4000–400 cm^{-1}. Proton NMR (^1H) and carbon NMR (^{13}C) spectra were recorded using DMSO and D_2O as the solvent on a Joel GSX400 MHz FT-NMR spectrometer to confirm the molecular structure of the grown crystal. TG and DTA analysis was carried out using STA 1500 thermal analyser by heating the sample of about 15.969 mg in a crucible between 35 and 700° C at a rate of 20 °C/min in the nitrogen atmosphere. The DSC analysis was carried out in nitrogen atmosphere between 35 and 300° C at heating rate of 10 °C/min using STA 1500 thermal analyser. The ground state absorption of the grown EDA(2,4)DNP crystal was carried out using Perkin Elmer Lambda 35 spectrophotometer, covering the entire near ultra violet, visible and near-infrared regions. By multi-shot method, the laser induced surface damage threshold of EDA(2,4)DNP crystals was found visually using a Nd:YAG laser (532 nm, 5 ns, 10 Hz). The Z-scan technique was employed to measure the nonlinear absorption and optical limiting action under short-pulse excitations. In the experiment, the Gaussian beam from a Q-switched Nd: YAG (532 nm, 5 ns, 10 Hz, 100 μJ) laser was used for molecular excitation. The low repetition rate of 10 Hz was chosen for avoiding thermal accumulation in the crystal during measurement. The beam was focused by a planoconvex lens of 20 cm focal length on the sample to observe the variations in the beam profile. Here the sample was the thin slice (1 mm thick) of cut and polished optical quality crystals of EDA(2,4)DNP with the linear transmission of 70% at 532 nm. Initially several trails were performed on various crystals to ensure the optical quality of the crystals, so as to possess negligible scattering and defect free nature. By moving the sample through the focus of the beam, the intensity dependent absorption as a change of the transmittance in the far-field using detector without aperture (Open mode) was measured. The incident and transmitted pulse energies were simultaneously measured using two pyroelectric energy probes (RjP 735, Laser Probe Inc.,). From the transmission values corresponding to the various position of the sample, the nonlinear absorption coefficient of the sample was calculated. Also, the optical limiting properties were investigated from the open aperture Z-scan experimental data. As the experiment in the present case was done in the single-shot mode with low pulse repetition rate, the measurements were almost independent of beam sequence.

3. Results and discussion

Single crystal XRD analysis shows that ethylenediamminium (2, 4 dinitrophenolate) crystal crystallizes in monoclinic system with space group $P2_1/C$ having lattice parameters of a = 5.880(5) Å, b = 23.408(5) Å, c = 7.063(5) Å, α = 90.000(5)°, β = 96.645(5)° and γ = 90.000(5)°. The evaluated crystal data and refinement details are given in Table 1. The experimental values were found to be in good agreement with the structure which was already reported by Marcio Lazzarotto et al., [21]. In the crystal structure, the asymmetric unit has one half ethylene diaminium cation, one dinitrophenolate anion and one water molecule with the cation lying on the crystallographic centre. Molecular arrangement and thermal ellipsoid plot with 50% probability are given in Fig. 2. Both the ions were inclined at an angle 45.33° while the nitro groups slightly deviated from the plane of the phenolate ring. The deviation of O3 atom was 0.298 Å. A short intermolecular contact between phenolate oxygen and the adjacent nitro group was observed as like trinitrophenolate derivatives [17]. Although the crystal structure of the title compound was reported in literature [21], the crystal packing remained unexplored. Hence attempts were made to elucidate the crystal packing diagram for the first time, and the obtained hydrogen bonding network is given in Fig. 3. Atomic coordinates and anisotropic displacement parameters derived from the crystal structure are given in Tables 2 and 3. The crystal structural details such as bond lengths, hydrogen bonds, bond and torsion angles are given in the Supplementary data. The six hydrogen bonds play a very important role in stabilizing the structure. In the present structure, a bifurcated hydrogen bond was also observed between ethylenediamminium and dinitrophenolate ions.