CHAPTER - IV
SYNTHESIS, CRYSTAL GROWTH AND CHARACTERIZATION OF ETHYLENEDIAMINIMUM DI (4-NITROPHENOLATE)

4.1 INTRODUCTION

Search of efficient novel organic materials has always been under focus due to their distinctive properties and potential usage in nonlinear optics (NLO), electronics and photonics [1]. Even though good quantum of research has been conducted on synthesis and characterization of new molecular structures for second-order nonlinear optical applications, the study of third-order nonlinear processes on molecular materials has received relatively limited attention [2]. However, in recent years with intense development in photonics industry, third-order NLO applications like third harmonic generation, four-wave mixing and optical limiting have received great deal of attraction. Especially in this modern world, the usage of continuous wave (cw) lasers at power levels ranging from mW to kW in various applications has become more common. But, it is worthy to note that exposures to laser beam of even a few mW for a short duration of about 0.25 s can cause permanent damage to the human eye [3]. Hence, the need for protecting the human eye and the photosensitive components of sensors used in handling the cw output has become increasingly important. Materials such as liquid crystals, porphyrins, organics such as azobenzene, etc. are known to be optically nonlinear under cw laser illumination [4]. But, the identification of stable and efficient media capable of optical limiting action at lower intensities is still under search.
The microscopic theoretical models predict large non-resonant third-order optical nonlinearity associated with delocalized $\pi$ electron systems. Due to the presence of delocalized electrons, these materials generally have ultra fast response time, photo stability and large first order hyperpolarizability ($\beta$) values. One such class of species is the p-nitrophenolates which serve as push–pull chromophores, since an electron is transferred from the negatively charged phenolate to the nitro group upon photoexcitation, with a significant change in the charge distribution [5]. Literature has plenty of derivatives of p-nitrophenol [6-9] and recently Long Liu et al. [10] explained the synthesis procedure of a series of phenol-ammonium salts and reported the crystal structure of a new centric system ethylenediaminum di (4-nitrophenolate) [EDA4NP]. This chapter makes a detailed study on the synthesis, crystal growth and characterization of EDA4NP. Also as the system belongs to a centric space group, its third order NLO properties and its possible usage as low power optical limiters are discussed in detail.

4.2 EXPERIMENT

4.2.1 Material Synthesis

EDA4NP was synthesized directly from commercially available Ethylenediamine [EDA] and 4-nitro phenol [4NP]. Figure 3.1 briefly illustrates the reaction of Ethylenediamine with 4-nitro phenol along with their molecular structures. The calculated amount of Ethylenediamine (0.18 g) and 4-nitro phenol (1.00 g) was thoroughly dissolved in methanol (5 ml, 50 ml) separately [10]. The above solution was added together and the mixture was stirred for 3 hrs at room temperature (30 °C). The obtained clear solution was kept for evaporation of methanol and after 24 hours a crystalline brownish -yellow salt was collected through filtration. The product was washed and dried at 40 °C for 12 h.
4.2.2. Solubility and Crystal Growth

In solution growth techniques, the size of a crystal depends on the amount of the material available in the solution which in turn is decided by the solubility of the material in the solvent. The solubility of EDA4NP in ethanol was determined as a function of temperature in the temperature range of 25–50 °C. The beaker containing the solution was maintained at a constant temperature and continuously stirred. The amount of EDA4NP required to saturate at this temperature was estimated and this process was repeated for various temperatures. On reaching saturation, the equilibrium concentration of the solute was determined by gravimetric method. The variation of solubility with temperature is shown in Figure 4.2. EDA4NP exhibits good solubility and a positive solubility temperature gradient in ethanol solvent.
Figure 4.2 Solubility curve of EDA4NP

Figure 4.3 Grown crystal of EDA4NP
The saturated solution of EDA4NP was prepared at room temperature from the recrystallized salt. The solution was then filtered twice to remove the suspended impurities by using Whatman filter paper. The clear solution was transferred into another vessel having perforated closure. As the material exhibits positive solubility temperature gradient, slow evaporation method was employed for the growth process. For solvent evaporation, the vessel was then kept in a constant temperature bath (CTB) at 30 °C. Single crystals of dimensions 8 x 3 x 2 mm³ were grown over a period of 21 days. The grown single crystals are shown in Figure 4.3 and they are found to be stable in environment without sacrificing its optical transparency.

The melting point of EDA4NP was measured as 144 °C by using a melting point apparatus (Model: Tempo PT 100–230 V) with the finely powdered sample. The sharp melting point confirms the purity of the sample.

4.3. ELEMENTAL, STRUCTURAL AND THERMAL ANALYSES

4.3.1 Elemental Analysis

The elemental analysis for the grown sample was carried out by using CHN elemental analyzer to confirm the chemical composition of the synthesized compound. The analysis reveals that EDA4NP contains one water molecule and the percentage of carbon, nitrogen and hydrogen are found to be 47.28[47.19], 15.54[15.72] and 5.68[5.66] respectively. The values given in square bracket are the calculated values from its molecular structure of mono hydrated EDA4NP (C_{14}H_{20}N_{4}O_{7}) and it shows a good agreement with the measured values. Based on the elemental composition identified, neglecting the mono hydrated water molecule, the molecular formula of EDA4NP is found to be C_{14}H_{18}N_{4}O_{6}. Also the molecular weight is estimated to be 338.32 g and it shows good agreement with the value reported in literature [10].
4.3.2 Crystal Structural Analysis

The structure of the grown crystals was confirmed by single crystal X-ray diffraction. It is found that the grown crystals belong to monoclinic system with space group of C2/c and the cell dimensions are determined as \( a = 11.326 \) (8) [11.328 (2)] Å, \( b = 7.264 \) (7) [7.2623 (15)] Å, \( c = 20.036 \) (9) [20.038 (4)] Å, \( \beta = 93.55 \) (2) [93.58 (3)] °, \( V = 1648.4 \) (1) [1645.2 (6)] Å\(^3\). The values given in the square bracket are the corresponding values already reported in the literature [10]. The unit cell is found to be tetramolecular. As the title compound crystallizes in a centrosymmetric space group, this material will be a potential candidate for investigation of third order NLO applications like optical limiting.

![Figure 4.4 Powder X-ray diffraction pattern of EDA4NP](image_url)

Figure 4.4 Powder X-ray diffraction pattern of EDA4NP
The powder sample was subjected to powder XRD analysis. All the peaks were indexed to the monoclinic phase of EDA4NP and the recorded PXRD pattern of the compound is depicted in Figure 3.4. No peaks corresponding to any impurity were detected, indicating the material to be pure and well crystallized. The EDA4NP lattice constants obtained by refinement of the XRD data for the sample were \( a = 11.321 \) (2) Å, \( b = 7.260 \) (1) Å, \( c = 20.031 \) (8) Å and \( \beta = 93.52 \) (5)\(^\circ\) consistent with the standard values obtained from the single crystal XRD.

4.3.3 Molecular Structural Analyses

4.3.3.1 FTIR and Laser Raman Analyses

The various functional groups available in the compound were identified in the wave number range 400-4000 cm\(^{-1}\). A weak absorption band around the region 1579 – 1661 cm\(^{-1}\) in the FTIR spectrum (Figure 4.5) confirms the presence of the phenolic ring. A broad intermolecular hydrogen bonded OH stretching at 3325 cm\(^{-1}\) of p-nitrophenol is shifted to the higher frequency 3403 cm\(^{-1}\) in EDA4NP. This shift increases the polarizable nature of p-nitrophenol to a higher order and it easily forms a new molecular structure with EDA [11]. Also a strong absorption peak at 3403 cm\(^{-1}\) can be assigned to N-H stretching vibration. The strong peak at 1579 cm\(^{-1}\) can be assigned to N=O of the nitro group. The peak at 1454 cm\(^{-1}\) is assigned to CH\(_2\) bending and peaks at 854, 758 cm\(^{-1}\) are all due to C=H vibrations. The presence of C-N bond is confirmed by the presence of peak at 1277 cm\(^{-1}\). The strong peaks at 1171, 1113, 1018 cm\(^{-1}\) are all due to C-H group vibrations. The sharp peak at 642 cm\(^{-1}\) is due to C-C stretching vibrations.
Figure 4.5 FTIR spectrum of EDA4NP

Figure 4.6 Laser Raman spectrum of EDA4NP
From the recorded Raman spectrum (Figure 4.6), the peak at 1563 cm\(^{-1}\) can be assigned to C=O stretching, which confirms the bond between oxygen atom and phenolic group. The strong vibration band at 1263 cm\(^{-1}\) is due to C-N stretching. The peaks at 1159, 1098 and 1027 cm\(^{-1}\) confirms the presence of C-H rocking vibrations. Also the presence of C-H stretching is confirmed by the peak at 858 cm\(^{-1}\). The results obtained from FTIR and Laser Raman spectra are tabulated in Table 4.1

<table>
<thead>
<tr>
<th>Experimental wave number</th>
<th>Assignments</th>
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<tbody>
<tr>
<td>FTIR</td>
<td>LASER Raman</td>
</tr>
<tr>
<td>3403</td>
<td>N-H stretching</td>
</tr>
<tr>
<td>3325</td>
<td>OH stretching</td>
</tr>
<tr>
<td>1579</td>
<td>N=O stretching</td>
</tr>
<tr>
<td>1563</td>
<td>C=O stretching</td>
</tr>
<tr>
<td>1454</td>
<td>C-H bending</td>
</tr>
<tr>
<td>1277</td>
<td>1263</td>
</tr>
<tr>
<td>1171</td>
<td>1159</td>
</tr>
<tr>
<td>1113</td>
<td>1098</td>
</tr>
<tr>
<td>1018</td>
<td>C-H rocking, N-H rocking</td>
</tr>
<tr>
<td>854</td>
<td>858</td>
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<tr>
<td>758</td>
<td>C-H rocking</td>
</tr>
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<td>642</td>
<td>635</td>
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4.3.3.2. FT-NMR Analysis

The $^1$H NMR and $^{13}$C NMR spectra provide information about the carbon hydrogen framework in the molecule. In the $^1$H spectrum (Figure 4.7), the signal at $\delta = 2.749$ ppm represent the four protons in aliphatic CH$_2$ group. The doublet at $\delta = 6.572$ and 6.578 ppm represent the four protons in C-H aromatic carbons. The two aromatic group signal is splitted into a multiplet due to hyperfine splitting of neighboring protons, which was confirmed from the signal centered at $\delta = 7.9$ ppm. The doublet at $\delta = 7.968$ and 7.973 ppm represent the four protons in C-H aromatic carbons.

In $^{13}$C spectrum (Figure 4.7), the signal at 38 ppm is attributed to the DMSO solvent and aliphatic C-H groups. The chemically equivalent aromatic carbons (C=C) are confirmed by the absorption peaks found at 117.047 and 126.597 ppm. The signal found at $\delta = 134.975$ ppm represents the C-H environment in aromatic carbons. The signal observed at $\delta = 171.558$ ppm represents the C-O environment in aromatic carbons. All the values correspond to the carbon environment and they agree very well with the expected molecular structure of the compound. In particular, the presence of ring structure (C$_6$H$_6$), alkene (C=C) and alkane (C-H) were confirmed [12].
Figure 4.7 $^1$H NMR spectrum of EDA4NP

Figure 4.8 $^{13}$C NMR spectrum of EDA4NP
4.3.4 Thermal Analysis

EDA4NP sample weighing 2.359 mg was taken for measurement and the obtained TGA curve is illustrated in Figure 4.9. It is observed from the analysis that there is a weight loss of around 7% below 10 °C. Careful examination of this weight loss shows two stages, one occurring at about 70 °C is assigned in the removal of secondary absorbed water or weakly entrapped lattice water. The other occurring at about 104 °C, appears to be small illustrating the removal of water in crystallization. Further, the loss of water molecules in the low temperature region (70-104 °C) evidenced the weak forces acting upon these molecules to connect them with the organic network. In the DTA curve (Figure 4.9), the onset of the first endothermic peak at 104 °C coincides with the initial loss in TGA. This is followed by another endotherm at 143 °C which is due to the melting point of the material.

A sharp endothermic peak in DSC (Figure 4.10) and DTA around 144 °C without any weight loss correspond to the melting point of the material. The final decomposition starts around 150 °C and ends up around 230 °C where the material loses its complete weight due to the dissociation of carbon network [13].
Figure 4.9 TG-DTA curve of EDA4NP

Figure 4.10 DSC curve of EDA4NP
4.4 LINEAR OPTICAL ANALYSIS

The UV-Vis-NIR absorbance on a 2 mm thick crystal has been measured in the range 190-2000 nm with the resolution of 1 nm at 303 K. From the spectrum (Figure 4.11a), it is noted that the UV absorption maxima occurs at 312 nm, and there is no remarkable absorption in the entire visible region of the spectrum. However, it is observed from the absorption spectrum that the material shows a trace of absorption in the 1500 - 2000 nm regions. Hence, the material with low absorbance in the visible region makes them suitable for optoelectronic applications.

In order to understand the third order NLO properties of EDA4NP, it is very essential to know information about the refractive index of the material. Hence the value of refractive index as a function wavelength is calculated from the recorded reflectance data of the sample using the following relation [14]

\[
n = \frac{-(R+1) \pm \sqrt{(-3R^2 + 10R - 3)}}{2(R-1)}
\]

4.1

The energy dependence of linear refractive index is plotted (Figure 4.11b). It is observed from the graph that the refractive index increases with increase in photon energy and the linear refractive index of EDA4NP is estimated to be \( n = 1.38 \) @ 532 nm.
Figure 4.11 (a) UV-Visible absorbance and (b) Refractive index of EDA4NP.
4.5 NONLINEAR OPTICAL ANALYSIS

As EDA4NP crystallizes in a centric system, the third-order NLO properties such as the nonlinear refractive indices, the nonlinear absorption coefficients and the third-order nonlinear susceptibilities of EDA4NP were determined following the theory developed by Sheik Bahae et al. [16]. Figure 4.12 a&b gives the nonlinear pattern obtained for closed and open aperture of Z-scan respectively for EDA4NP dissolved in ethanol at a concentration 1 mM. In the closed aperture pattern (Figure 4.12a), the occurrence of pre-focal peak followed by a post-focal valley-normalized transmittance indicates that the sign of the nonlinear refraction is negative, i.e., occurrence of self-defocusing. The asymmetric nature of the trace along with the source laser is cw and it suggests that the origin of the nonlinear refractive index is thermo-optic. Hence the self-defocusing effect arises due to local variations in the refractive index with temperature. The nonlinear refractive index was estimated to be \( n_2 = -5.46 \times 10^{-8} \text{ cm}^2 \text{ W}^{-1} \). In Figure 4.12b, the pattern from open aperture refers to the saturable absorption. Since the closed aperture transmittance is affected by the nonlinear absorption and refraction, it is necessary to obtain the ratio of the closed aperture transmittance to the corresponding open-aperture scans to obtain pure nonlinear refractive index. The ratio of closed aperture transmittance to the corresponding open aperture scan is shown in Figure 4.12c. From the open aperture, the nonlinear absorption coefficient was estimated to be \( \beta = -0.65 \times 10^{-3} \text{ cm W}^{-1} \). The real and imaginary parts of the third-order nonlinear susceptibilities of EDA4NP were calculated to be \( 2.64 \times 10^{-6} \) and \( 1.33 \times 10^{-6} \) esu respectively. Also the third-order nonlinear susceptibility was estimated to be \( \chi^{(3)} = 2.96 \times 10^{-6} \) esu.
Figure 4.12 (a) Closed aperture pattern, (b) Open aperture pattern, (c) Ratio of closed aperture to open aperture transmittance pattern of Z-Scan and 
(d) Optical limiting pattern of EDA4NP
The experimental setup for the demonstration of optical limiting under cw illumination is reported elsewhere [3]. The optical limiting behavior of the material was tested at 532 nm using diode pumped Nd: YAG laser (1064 nm, 50 mW), in the power range of 0.45-47.1 mW. The sample was placed at the valley position of the Z-scan pattern and the optical limiting curve obtained with EDA4NP is shown in Figure 4.12d.

From the graph it is inferred that the output is found to vary linearly with input intensity only for smaller values of initial intensity thus obeying Beer’s law. And beyond 33 mW, the response becomes nonlinear. The limiting behavior observed in the sample is attributed mainly due to nonlinear refraction. Since the sample was pumped with cw laser beam, the arising nonlinearities are predominantly thermal in nature [17]. The limiting threshold value for saturation was found to be 33 mW and the output is clamped at 8.5 mW (75 %).

Limiters based on nonlinear absorption phenomena have been designed for use with high power pulsed laser sources, but limiters demonstrated based on thermo-optic nonlinearity such as the samples studied here can be used as efficient limiters in the cw regime.

4.6 CONCLUSION

A third order NLO material has been successfully synthesized by proton-base reaction. The title compound exhibits good solubility and a positive solubility temperature gradient in ethanol solvent. A reasonably good quality crystal of EDA4NP has been grown by slow evaporation technique. Single crystal XRD shows that the crystal belongs to centrosymmetric system with space group C2/c. From the molecular structure, one can infer that the main component of the crystal to provide enhanced NLO efficiency is due to p-nitrophenol. The thermal analysis recommends that the material can be placed for any application below 144 °C. UV-Visible studies show that EDA4NP has a wide optical
transmittance window (500 - 1200 nm). The nonlinear optical response of thermo-optic origin, exhibited by EDA4NP at 532 nm low power cw laser, was studied using Z-scan technique. The defocusing effect observed in the sample under cw illumination was utilized to demonstrate their optical limiting action. EDA4NP with large nonlinear response showed a strong limiting (75 %) behavior at 532 nm. Hence, EDA4NP dissolved in ethanol can be used as optical limiter for low-power cw lasers, as liquid media have certain specific advantages over solid media as limiters in terms of dissipation of high incident intensities through solvent heating and bubbling.

REFERENCES


