

EXPERIMENTAL AND THEORETICAL PERSPECTIVES ON L-TRYPTOPHAN: AN AMINO ACID SINGLE CRYSTAL FOR NONLINEAR OPTICAL APPLICATIONS

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ABSTRACT

In this investigation, an optically transparent nonlinear optical (NLO) single crystal of L-Tryptophan (LTP) was grown using the solution technique. The crystalline nature and various vibrational numbers are confirmed by powder XRD and FTIR investigation. Photoconductivity performance has been probed for the LTP sample. To study the mechanical strength of single crystal sample, Vickers hardness measurement and void percentage analysis were performed. Second order nonlinear optical (NLO) characteristic was examined using Nd: YAG laser study. In addition to that, density functional theory (DFT) has been used to study the theoretical calculations on LTP by using B3LYP system with 6-311++G (d,p) basis set. The computed first order hyperpolarizability was determined to be two times greater than that of urea. These experimental and computational investigations obviously proposed that LTP can be a striking candidate for optoelectronic applications.

Keywords: Crystal growth, Hardness, Nonlinear, Density functional theory.

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INTRODUCTION

In recent years NLO materials have been a great interest due to their effective applications in the field of optical communication, frequency doubling, electro-optic modulator and optical data storage.¹⁻⁶ NLO materials are also widely exploited in numeral applications in the field of optical and photonic applications.⁷ The potential applications of NLO materials induce researchers to discover a new class of materials with superior characteristics including good optical frequency conversion efficiency, high transparency in the visible region, high laser-induced damage threshold (LDT) and low dielectric constant to full fill the needs of above fields and also expected to substitute the custom made materials.^{8,9} In particular, several organic and inorganic NLO materials have been established by scientists over the past few decades. The inorganic materials showed a lack of π -electron delocalization with moderate optical nonlinearities, difficult to form acentric crystal packing and modest LDT value. But organic materials exhibit very large and fast nonlinear response over inorganic owing to their occurrence of delocalization of π -electron moiety in their organic chromophores. Furthermore, organic chromophores display more structural flexibility thereby facilitates modification of the chemical constituents easily in the desired manner, as a consequence demonstrated acentric crystal packing with large hyperpolarizability and admirable second order NLO activity.^{10,11} In general, amino acid molecules composed of π -electron donor (NH_3^+) and acceptor (COO^-) constituents, results in the intramolecular transfer of charge which indicates the interesting characteristics of noncentrosymmetry (NCS) and enhanced frequency conversion. Accordingly, L-tryptophan ($\text{C}_{11}\text{H}_{12}\text{N}_2\text{O}_2$) occurs naturally and belongs to the classification of essential

amino acids for humans particularly owing to its unavoidable importance in many organisms. Moreover, L-tryptophan plays an important role as building blocks in biosynthesis of proteins and biochemical precursor to the neurotransmitters melatonin and serotonin.¹² LTP existed in zwitterionic system in which the amino group (NH_3^+) is protonated and carboxylic acid group (COO^-) is deprotonated and crystallized in triclinic system with NCS, having space group P1.¹³ Owing to its Zwitterionic and NCS nature, amino acids single crystals have been revealed promising characteristics such as good NLO efficiency and high LDT.¹⁴ L-Tryptophan was complexed with p-nitrophenol previously and showed powder second harmonic conversion efficiency (SHG) of 1.2 times that of reference KDP.¹⁵ In this current era among other theoretical methods, DFT has been emerging, owing to their better accurateness with the experimental values.¹⁶ To probe the relationship between NLO properties and molecular structure, DFT studies provide more accurate results about the microscopic origin of NLO materials. In this work, structural, mechanical, photoconductivity and SHG studies were experimentally done. Furthermore, structural optimization, frontier molecular orbital (FMO) and theoretical NLO analysis were done by the DFT technique.

EXPERIMENTAL

Material and Methods

Spectroscopic grade L-tryptophan was purchased from the Aldrich chemicals (99 %) and used for the growth. The purity of the LTP was done by repeated recrystallization using high pure methanol. Large single crystals of LTP were obtained at room temperature by the slow evaporation method. The saturated solution was taken into the crystallizing vessel and shielded with a perforated lid so that the evaporation of the solvent was reduced significantly. Spontaneously nucleated grown crystals were attained at the size of ($2.3 \times 3 \times 1.5 \text{ mm}^3$) at a time interval of 20 days. Figure-1 depicted the crystal image of LTP.

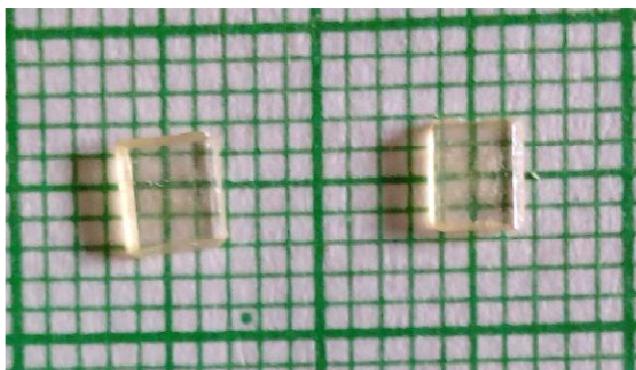


Fig. -1: As Grown Crystals of LTP.

Physicochemical Analysis

The Oxford diffraction Xcalibur Gemini single crystal X-ray diffractometer ($\text{MoK}\alpha, \lambda = 0.71073 \text{ \AA}$) was used to measure the unit cell parameters at room temperature. The FTIR spectrum of the grown crystal was recorded using BRUKER IFS 66V model spectrophotometer. Photoconductivity response of grown LTP crystal was measured by Keithley 6517 B electrometer. Mechanical properties were explored utilizing Vicker's microhardness tester attached with a diamond pyramidal indenter. A Nd:YAG laser with the fundamental wavelength of 1064 nm was used to study the powder second harmonic conversion of powdered LTP.

Quantum Chemical Analysis

Theoretical studies for LTP molecule were done using Gaussian 09 software program and the GaussView visualization software.^{17,18} The optimization of molecular geometry was done using B3LYP (Becke's three-parameter hybrid model using the Lee-Yang-Parr correlation functional) method with 6-311++G (d,p) basis set.^{19,20} The acceptor and donor tenancy together with the stabilization energy for dissimilar overlapping atomic orbitals of LTP molecule was investigated. The frontier molecular orbital analysis (HOMO and LUMO) analysis was performed using B3LYP/6-311++G (d,p) basis set. Theoretical

NLO coefficients such as dipole moment, polarizability and hyperpolarizability were computed. Molecular docking of compounds into the α -amylase enzyme was carried out by the Auto-Dock software (version 4.2). Accelrys discovery studio client 4.1 visualizers were used for visualizing the protein-ligand complex. The crystal structure of the α -amylase enzyme (1HNY) was downloaded from the Protein Data bank. All bound water and ligand were eliminated from the protein and polar hydrogen was added. In addition to this in the docking studies a grid box size of 60 x 60 x 60 points in X,Y and Z direction is exploited with a grid spacing of 0.375 Å.

RESULTS AND DISCUSSION

X-ray diffraction studies

The acquired unit cell values are $a=11.430$ Å, $b=11.464$ Å $c=35.606$ Å, $\alpha=84.421^\circ$, $\beta=87.694^\circ$ and $V=4025$ Å³. The results revealed that the LTP crystal crystallized in the triclinic crystal system with the noncentrosymmetric space group of $P1$. The lattice constants found in the current investigation are in virtuous match with the formerly stated values.¹³

FTIR Analysis

The amine functional group NH stretching is observed at 3404 cm^{-1} . The assigned vibrations for OH stretching are 3076 and 3038 cm^{-1} . The asymmetric and symmetric stretching vibrations occur at 2851 cm^{-1} and 2726 cm^{-1} . The C=C stretching vibrational mode is observed at 2075 cm^{-1} . The NH₂ Scissoring and NH bending modes appear at 1666 cm^{-1} and 1590 cm^{-1} . A peak at 1455 cm^{-1} and 1413 cm^{-1} is attributed to the CC stretching and C-O-H in-plane bending vibrations. The peaks at 1354 and 1316 cm^{-1} are assigned for the CN stretching mode. The vibration at 1231 cm^{-1} is due to the stretching of CO. The peaks at 1007 cm^{-1} , 987 cm^{-1} and 744 cm^{-1} are ascribed to the NH wagging, OH bending and CH rocking vibrations. The vibrations at 1099 cm^{-1} , 1077 cm^{-1} , 526 cm^{-1} and 508 cm^{-1} are due to the CH in the plane and out plane bending. The observed FTIR spectrum is given in Fig.-2.

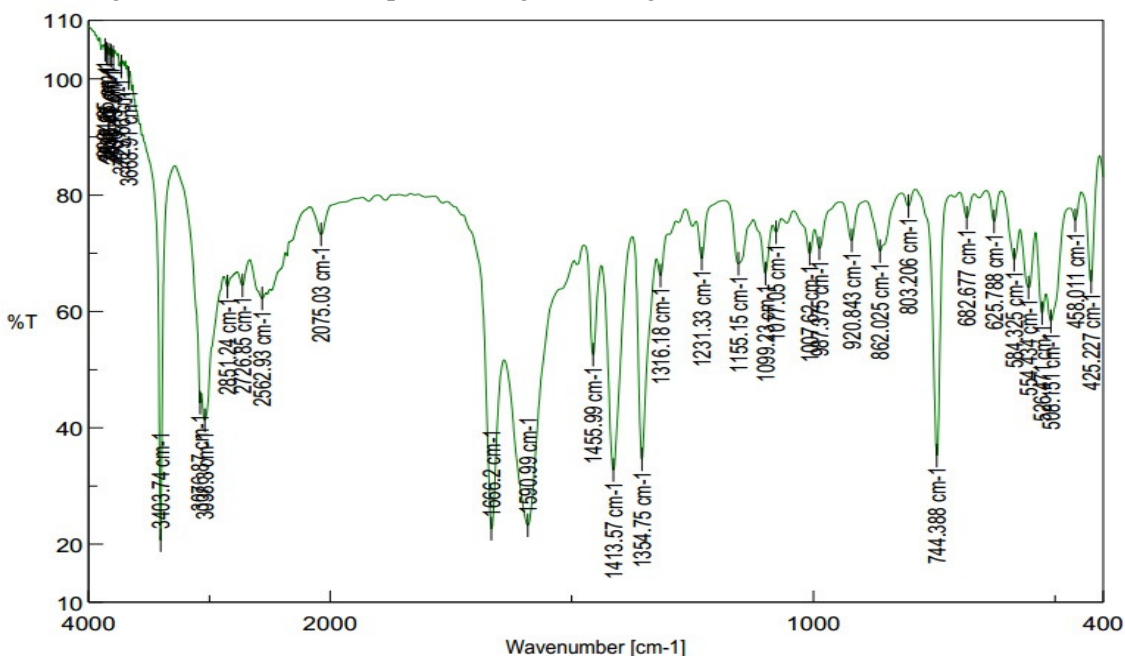


Fig.-2: FTIR Spectrum of LTP.

HOMO LUMO Studies

The HOMO illustrates the capability to contribute an electron. The LUMO demonstrate the capacity to gain an electron. The chemical reactivity, stability and softness of the molecule can be controlled by the HOMO LUMO gap.²¹ Herein these calculations were carried out effectively for probing the expedient

energetic behavior of the LTP molecule. The calculated HOMO and LUMO values are -10.63 eV and -5.54 eV, respectively. The red and green notifies the positive and negative regions (Fig.-3). The energy gap (ΔE) of LTP was estimated as 5.09 eV. This energy gap elucidated the manifestation of subsequent charge transfer interaction inside the LTP molecule.

A molecule with moderately small band gap energy could provide high chemical reactivity and low kinetic stability. The electron affinity (A) and ionization energy (I) of a molecule are of prodigious significance in shaping paths for transfer of electrons. The ionization energy reflects the susceptibility of a molecule during the electrophilic attack. The susceptibility of the molecule was indicated by the electron affinity during the nucleophilic attack. The ionization energy and electron affinity can be articulated over HOMO and LUMO orbital energies by the Koopmans' theorem as $I = -E_{HOMO}$ and $A = -E_{LUMO}$. The electron affinity and ionization energy values are -5.54 eV ($A = -E_{LUMO}$) and -10.63 eV ($I = -E_{HOMO}$).²² An electrophilicity index confirms the ability of charge transfer and stability of the molecule. The values of electronegativity, chemical potential, chemical hardness, softness, and electrophilicity index of LTP molecule were 8.09 eV, -8.09 eV, 2.55 eV, 0.20 eV, and 12.84 eV in the gaseous phase, respectively.²² The high value of chemical potential and chemical hardness evidently proposed that LTP molecule is chemically stable and might offer more mechanical strength and exhibit high surface tolerance to laser power towards device applications.

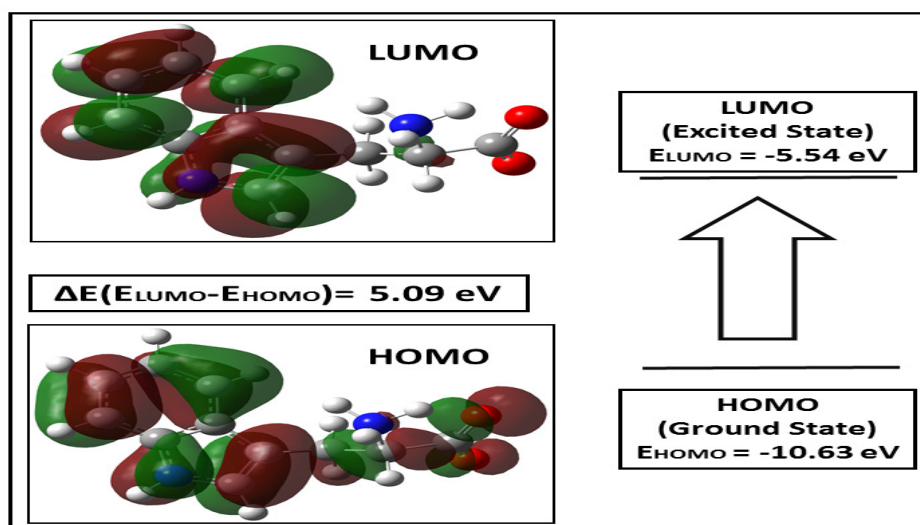


Fig.-3:HOMO LUMO Analysis of LTP.

Photoconductivity

The photoconducting materials can produce electric pulses by conversion of low energy sub picosecond laser pulses. This frames the photoresistors and other sensor devices.²² Herein, Dark current and photocurrent were measured by a two-probe method at ambient temperature. As grown LTP crystal was polished and using the silver paste two copper wires were attached the surface of the crystal. A series connection was made with crystal, a Keithley electrometer, and DC power supply. For dark current studies, the crystal was shielded from all type of radiation. For photocurrent measurements, 100 W halogen lamp containing iodine vapor and tungsten filament was used as an optical source. The applied voltage was increased from 10V to 100 V in steps of 10V. Both the dark and photocurrent were recorded. Figure-4 illustrated the dark current and photocurrent trace of grown LTP crystal. It was obviously concluded from the figure that both currents are in linear increment with respect to the applied input voltage. But the photocurrent was found to be superior. It also confirmed the positive photoconductivity nature of the LTP crystal which accredited to the creation of mobile charge carriers instigated by the absorption of photons. When the crystal was irradiated with photons of energy greater than the band gap,

electron-hole pairs were produced which spontaneously increased the conductivity. The high value of photocurrent has been measured for LTP crystal due to the direct excitation of charge carriers and nonexistence of traps.

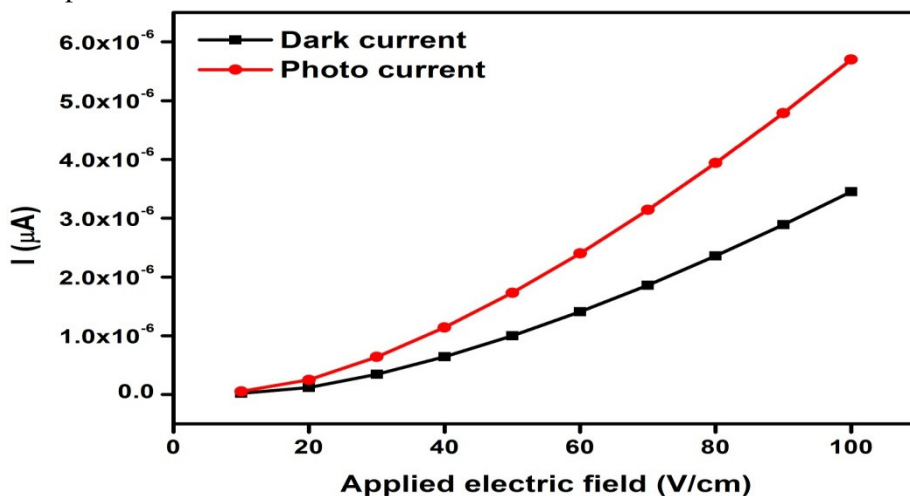


Fig.-4: Photoconductivity Response of LTP Crystal with Applied Voltage.

Measurement of Microhardness

Hardness study plays a significant role in NLO device applications. A crack-free LTP crystal was subjected to microhardness measurements. Figure-5a revealed the variation of hardness with the load. It was obvious that an increase of hardness value with load is endorsed to the reverse indentation size effect. The slope of Fig.-5b provides the value of Meyer's index "n" as 2.593. If the 'n' lies between 1 to 1.6 then it is considered as hard materials if the value is greater than 1.6 endorsed to the soft materials.^{23,24} Therefore the grown LTP belongs to the soft material category. Void surface analysis was performed in order to achieve strong evidence about the mechanical strength of LTP crystal²⁵ using crystal structure and it was shown in Fig.-5c. The surface area and volume occupied by the void within the unit cell of LTP crystal has been calculated as 1567.18 Å² and 479.38 Å³, respectively. The void occupied only 8.4 % of volume inside the unit cell and it was determined to be similar with the creatininium L-tartrate monohydrate NLO single crystal.²⁵ The void space within the unit cell could provide appropriate flexibility towards device fabrication applications.

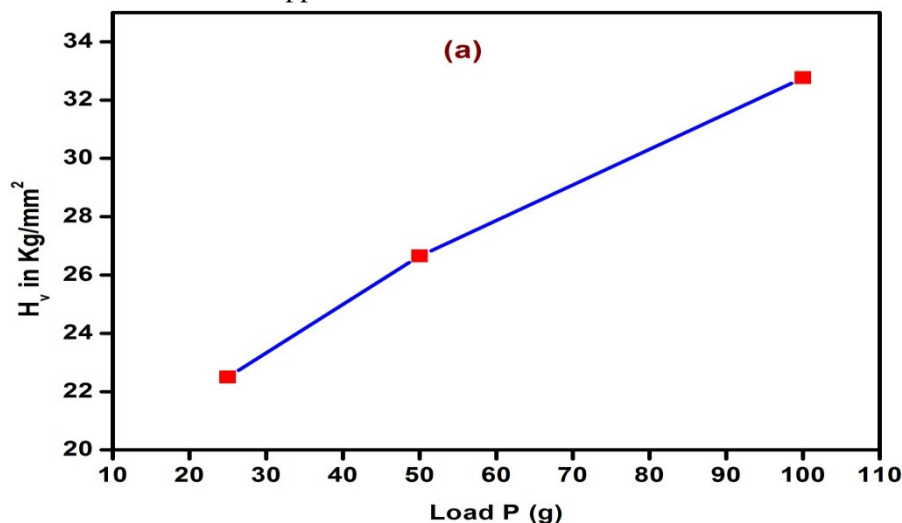


Fig.-5a: Hardness with respect to load for LTP

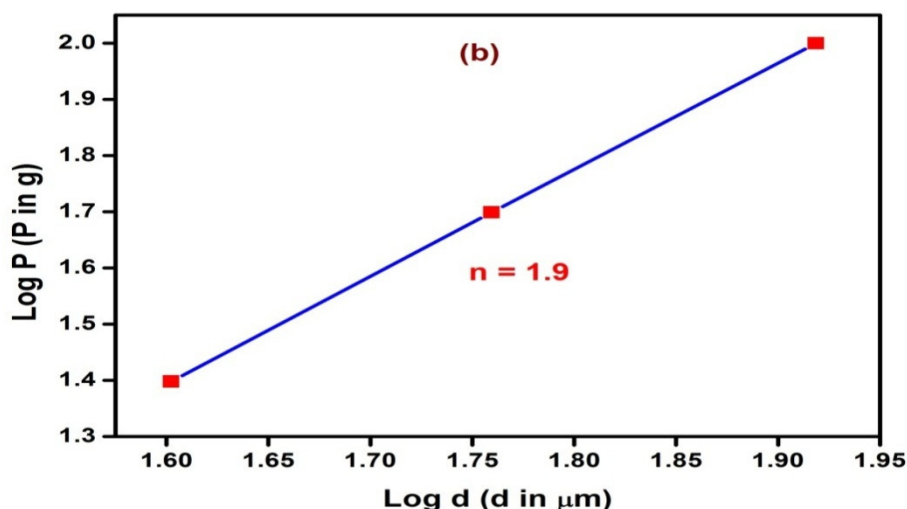


Fig.-5b: Mayer index evaluation of LTP.

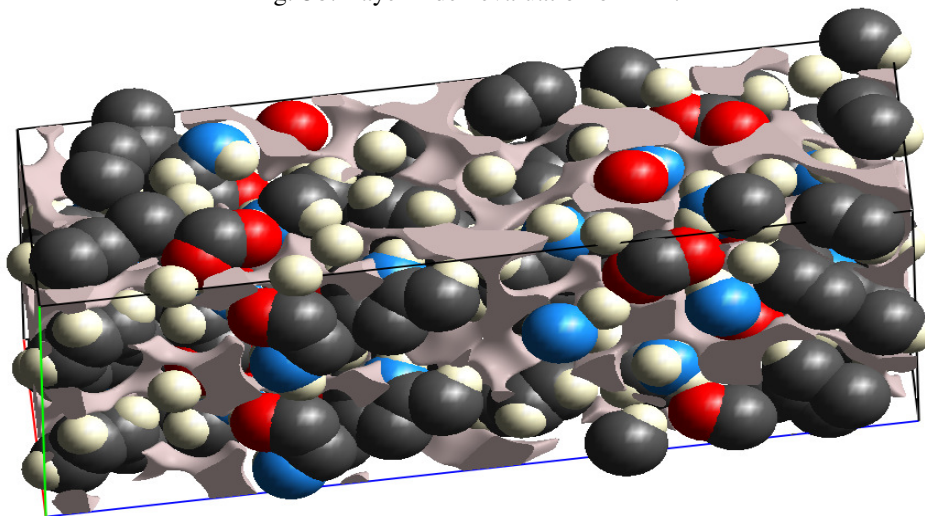


Fig.-5c: The Void Surface of LTP in the Unit Cell Packing.

Powder SHG Measurements

The powder SHG efficient of LTP and potassium dihydrogen phosphate (KDP) were deliberated via Kurtz and Perry technique.²⁶ It enables to find the SHG value comparative to reference KDP. A pulsed 1064 nm wavelength Q-Switched Nd:YAG laser with the input energy of 1.9 mJ/pulse was used (Repetition rate 10Hz). The produced second harmonic sign emerged in the crystalline specimen was inveterate from the emission of green radiation. The SHG signal of 120 mV was noted for LTP crystal however powdered potassium dihydrogen phosphate provides a SHG signal of 49 mV for the same input pulse. The comparative SHG ability of LTP is 2.44 times higher than KDP. It undoubtedly ascertains that LTP convincingly validates exceedingly high competence to KDP. The above reports efficiently acclaim the title amalgam is a potential contender for SHG uses.

Phase Matching Analysis

The strength of second harmonic conversion increases with particle size attain the maximum limit, where SHG of the specimen saturates which confirmed the type I phase matching behavior of the material.²⁷ The habit of particle size dependence of SHG intensity was considered to validate the phase matching chattels. Selected single crystals of LTP was grounded into different particle sizes ranges from 53, 53-105, 105-149 and above 150 μm . The dependence of particle size with respect to SHG intensity of depicted in figure 6. The SHG intensity increases almost linearly with the increase in the particle size up to 150 μm and becomes saturated above 150 μm . This type of behavior was observed in the type I phase matched

materials.²⁸ Therefore, grown LTP can be an excellent candidate for the future frequency doubling and optical parametric oscillator applications.

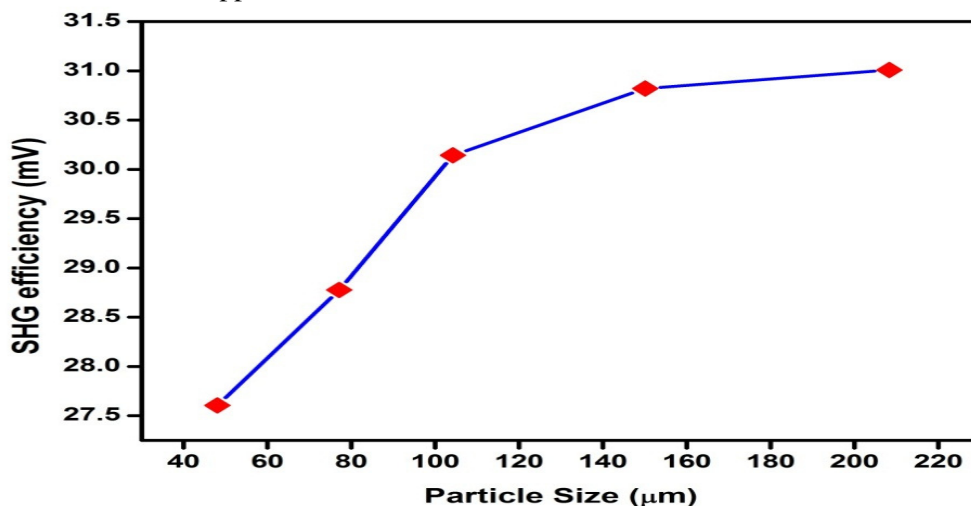


Fig.-6: Powder SHG efficiency with respect to particle size.

First Hyperpolarizability

Understanding of structure-property relationship using computational investigation helped in numerous ways in the design and synthesis of novel NLO materials with enhanced characteristics.²⁹ In order to achieve more accurate results reliable with experimental investigations, a suitable basis set has to be chosen. According to these facts, B3LYP/6-311G++ (d,p) method was employed for the LTP molecule from the literature background. The mathematical values of the NLO factors were acquired by replacing the Gaussian 03 output data appropriately by the equations used in the literature. The polarizabilities (α) and first hyperpolarizability (β) of Gaussian output were obtained in terms of atomic units and converted into the electrostatic unit (For α 1 a.u. = 0.1482×10^{-24} esu and β 1 a.u. = 8.6393×10^{-33} cm⁵/esu). By using the above equations, the values of dipole moment (μ), mean polarizability (α) and anisotropy of polarizability ($\Delta\alpha$) have been calculated as 6.849 Debye, 2.843 Å esu and 1.84 Å esu respectively. The first order hyperpolarizability value (β) which is one of the main aspects for NLO materials of a molecular system and has been calculated for LTP molecule as 0.947×10^{-31} cm⁵ esu⁻¹. Typically, urea is used as a reference to determine the relative NLO efficiency of a material. Accordingly, μ , α , $\Delta\alpha$ and β values have been calculated for urea as 4.303 Debye, 0.139 Å esu, 0.934 Å esu and 0.563×10^{-31} cm⁵ esu⁻¹. The value of the first hyperpolarizability of LTP molecule was found to be two times higher than urea. A large first hyperpolarizability value has been achieved which suggested that LTP molecule might be a favorable NLO material. The prime value was noted to be in the β_{yzz} direction which indicated the consequential delocalization of the electron cloud arisen additional in this specific path.

Molecular Docking Studies

The crystallized compound was docked with the α -amylase enzyme (1HNY) using Autodock tool (1.5.6). The active site of 1HNY was selected Asp167, Asn100, Asp197, Arg195, Arg158, His201, Glu233, Asp300, Asn298, Arg 337 as per the reported literature.³⁰

The binding energy and inhibition constant is calculated as -4.86 kcal/mol and 628.05 μM respectively. The hydrogen bond interaction is formed between the CH of Ile235 and carboxylic acid of ligand (CH---O=C-OH). The bond distance is measured as 2.76 Å correspondingly. The interaction of hydrogen bond is formed among the NH₂ of Lys200 and carboxylic acid of succinate unit (NH---O=C-OH). The measured value of the bond distance is 2.65 Å. The docking interaction image is represented in Fig.-7a. The crystallized compound was docked with the α -amylase enzyme (1HNY) using Autodock tool (1.5.6). The active site of 1HNY was selected Asp167, Asn100, Asp197, Arg195, Arg158, His201, Glu233, Asp300, Asn298, Arg337 as per the reported literature.³⁰

The binding energy and inhibition constant is calculated as -7.28 kcal/mol and 4.59 μM respectively. The hydrogen bond interactions have occurred with amino acids like Asp300 and Asp195. The hydrogen bond interaction is formed between NH of Asp195 and NH_3^+ of ligand ($\text{NH} \cdots \text{O}=\text{C}-\text{OH}$). The bond distance measured as 3.28 Å correspondingly. Another hydrogen bond interaction is generated with a carboxylic acid of Asp300 and NH_3^+ of ligand ($\text{NH} \cdots \text{O}=\text{C}-\text{OH}$). The distance of the bond is measured as 3.24 Å. The docking interaction image is represented in Fig.-7b.

The active site of 1HNY was selected Asp167, Asn100, Asp197, Arg195, Arg158, His201, Glu233, Asp300, Asn298, Arg337 as per the reported literature.³⁰ The binding energy and inhibition constant is calculated as -5.56 kcal/mol and 83.4 μM respectively. The binding complex hydrogen bonded with the amino acid Gln63. The hydrogen bond interaction is formed between carboxamide NH of Gln63 and carboxylic acid of tryptophan (ligand) ($\text{O}=\text{C}-\text{NH} \cdots \text{O}=\text{C}-\text{OH}$). The bond distance is measured as 2.81 Å correspondingly. The docking interaction image is represented in Fig.-7c.

The crystalized compound was docked with the α -amylase enzyme (1HNY) using Autodock tool (1.5.6). The active site of 1HNY was selected Asp167, Asn100, Asp197, Arg195, Arg158, His201, Glu233, Asp300, Asn298, Arg337 as per the reported literature.³⁰ A modest inhibition constant and binding energy was observed in the study. The binding energy and inhibition constant are calculated as -4.86 kcal/mol and 1.63 mM respectively. The hydrogen bond interaction occurs between two Gly306 and Lys200 amino acids. The hydrogen bond interaction is formed between the carbonyl of Gly306 and NH_3^+ of ligand ($\text{NH} \cdots \text{O}=\text{C}$). The distance of the measured bond is 3.32 Å correspondingly. Additional hydrogen bond interaction is formed between the NH_2 of LYS200 and NO_2 of picrate anion (ligand) ($\text{NH} \cdots \text{O}=\text{N}=\text{O}$). The measured bond distance is 2.59 Å. The docking interaction image is represented in Fig.-7d.

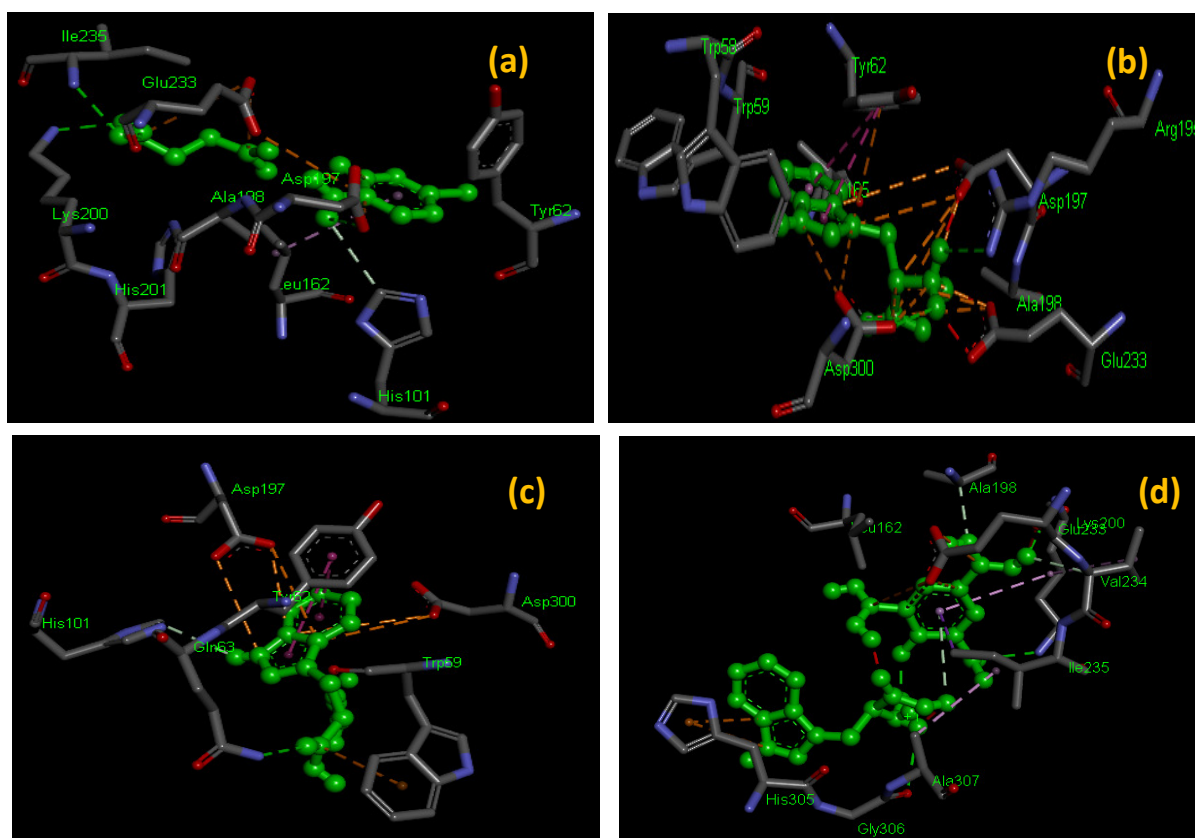


Fig.-7:(a) Docking interaction 2BB with IHNY (b) Docking interaction Trp opt1 with IHNY (c) Docking interaction Trp opt1 with IHNY (d) Docking interaction Trp opt1 with IHNY

CONCLUSION

L-Tryptophan, an organic NLO material has been grown with optical quality using the conventional slow evaporation method. An X-ray diffraction study confirmed the formation of monoclinic crystal system of the crystal with the *P1* space group. Powder SHG conversion efficiency of LTP was found to be 2.44 times higher than that of KDP crystal. The positive photoconducting nature was observed for grown LTP crystal. The void percentage and Vickers microhardness analysis suggested the soft mechanical behavior with enhanced flexibility of LTP crystal. The optimization of molecular geometry was done by DFT-B3LYP method using 6-311++G level set. Frontier molecular orbital analysis clearly proposed high chemical stability of the LTP molecule. First order hyperpolarizability ($\beta_{\text{total}} = 9.47 \times 10^{-33}$ esu) of LTP was determined to be two times greater than that of characteristic urea molecule. All the above physicochemical and theoretical outputs strongly confirmed that LTP is a possible candidate and can be exploited in future optical and photonic technologies.

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