INVESTIGATIONS ON SOME ORGANIC CRYSTALS TOWARDS NONLINEAR OPTICAL APPLICATION

Upgrading technological and industrial applications deposit overloads to the discovery of new materials with multifunctional applications. This leads to escalation of numerous research findings and innovations in the field of crystal growth towards device fabrication. Novel growth of single crystals with potentially fascinating properties is the eventual objective for the researches to impact the scientific expansion. Especially, detection of enhanced optical properties with remarkable characteristics materials is required for the future laser technologies. Progressive inventions in the optoelectronic and photonics zones are due to the efficient growth of nonlinear optical properties of organic crystals. To promote the growth of new organic crystals and to explore the enhanced optical properties of materials with proficient optoelectronic properties for industrialized fabrications is a difficult task. However, the investigation on the organic nonlinear optical materials settles a sturdy basis for the upcoming laser and optical communication systems. With the assistance of theoretical perspectives and computational studies, the interactions between the structures and their related properties can be studied in detail.

This thesis focuses on growth and characterization of organic single crystals towards second order and third order nonlinear optical properties with some quantum chemical calculations. Among the classified materials, organic compounds have large nonlinear response, high second order & third order nonlinear susceptibility, low dielectric constant, high electro-optic coefficient, and high resistant to laser damage. So these organic compounds have been extensively studied for the efficient nonlinear optical phenomena for further

development in photonics, electro-optic modulators, optical switches and large-capacity communications. In this work, growth of new organic single crystals and improved nonlinear properties of well-known organic crystals by suitably designed molecules are discussed.

The grown crystals were subjected to different characterizations such as single crystal X-ray diffraction, FT- Raman, FTIR, UV-Vis spectral analysis, Thermogravimetric and differential thermal analysis, Photoluminescence, micro hardness and dielectric studies. Also the grown crystals were subjected to the application oriented studies such as piezoelectric, ferroelectric and laser damage threshold furthermore the second order and third order nonlinear optical parameters were measured by powder SHG and Z-scan techniques. In order to investigate the intermolecular interactions, structure-property relationship, Mulliken atomic charge distribution, frontier molecular orbital analysis, molecular electrostatic potential map analysis and NLO calculations were carried out for the optimized molecular structure using density functional theory. The outcomes of the research findings were published in international journals and conferences. This thesis consists of seven chapters.

Chapter I

Introduction

Chapter I discussed about the introduction of organic compounds and its classifications, salient features of organic NLO materials, basic requirements and necessity for the enhancement of nonlinear properties of organic materials towards NLO applications. In addition to that the basics of NLO, principles and formulation associated with NLO were conferred. Crystal growth techniques employed and overview about the basis and applications of density functional theory used to explore intermolecular interactions and its properties by utilizing different basis sets were also given.

Chapter II

Growth, characterization and DFT studies on novel organic NLO crystal 3-hydroxy 2-nitro pyridine

In **chapter II,** growth, structure elucidation, various characterization techniques and computational studies were carried out for 3-hydroxy 2-nitropyridine (3H2NP). The title compound has been grown using slow evaporation solution growth technique. 3H2NP was crystallized in monoclinic system with centrosymmetric space group $P2_1/c$. FT-Raman and FTIR spectral studies were carried out to confirm various functional groups and vibrational modes present in 3H2NP compound. UV-Vis transmittance and absorbance studies confirmed good optical property of the grown 3H2NP crystal. Thermal, mechanical, dielectric and photoluminescence studies were effectively performed for 3H2NP crystal.

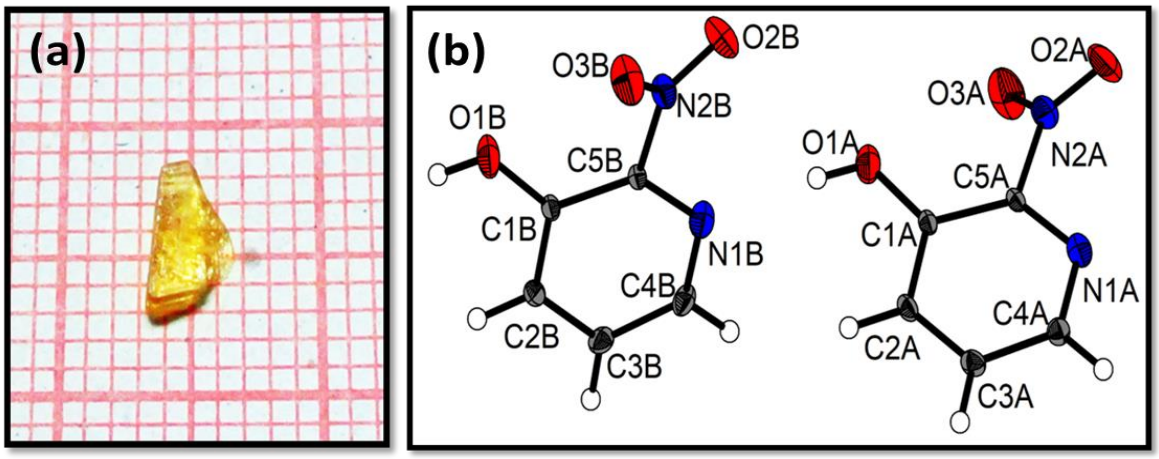

Fig.1 (a) Grown 3H2NP single crystal, (b) Molecular structure of 3H2NP.

In this chapter the third order nonlinear optical susceptibility of 3H2NP crystal was found to be ($\chi 3$) = 4.2483 × 10-5 esu and laser induced damage threshold value of grown crystal was found to be 42.2 mJ. Quantum chemical calculations showed that the hyper polarizability was 4.9 times larger than that of the urea. The intermolecular charge transfer within the molecule

was explained by HOMO-LUMO analysis. This work was published in the journal of optical materials.

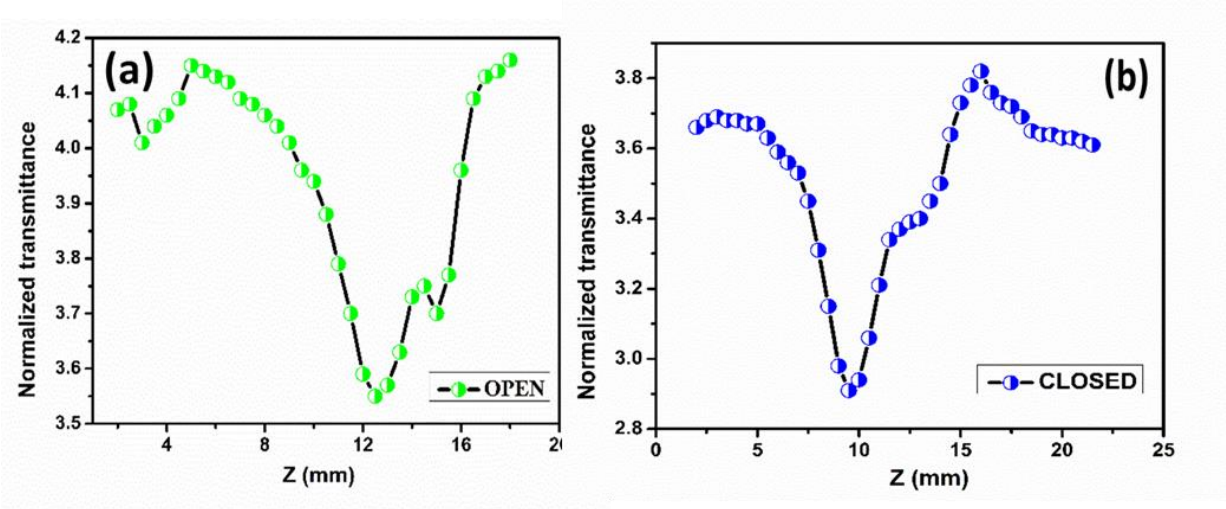

Fig.2 (a) Open aperture z-scan of 3H2NP, (b) closed aperture z-scan of 3H2NP.

Chapter III

Growth, characterization and DFT studies on novel organic NLO crystal 3-hydroxy 6-methyl 2-nitro pyridine

Chapter III discussed the growth of 3-hydroxy 6- methyl 2-nitropyridine (3H6M2NP) and its structural, spectral, NLO, and computational studies. Organic single crystals of nitropyridine derivative, 3-hydroxy 6- methyl 2- nitropyridine was crystallized by controlled slow evaporation solution growth technique at room temperature. 3H6M2NP was crystallized in orthorhombic crystal system with centrosymmetric space group Pbca. The confirmation of functional groups and its vibrational assignments were assigned by Raman and FTIR spectroscopic techniques. UV-Vis studies suggest high optical transmittance in the visible region for the grown crystal.

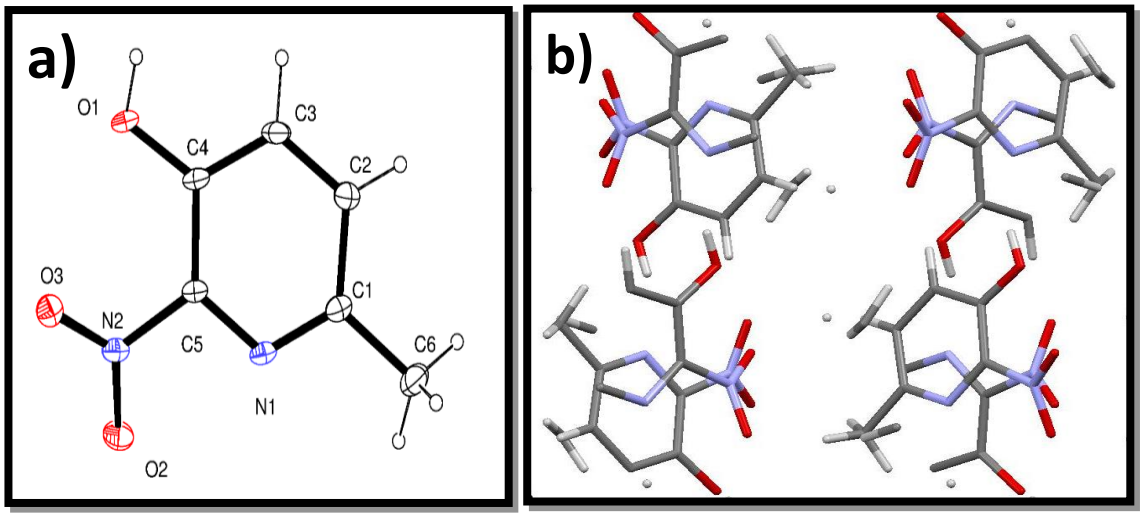

Fig.3 (a) ORTEP of 3H6M2NP, (b) Packing diagram of 3H2NP.

The luminescence properties and thermal stability of 3H6M2NP crystal were exhibited by PL and thermal studies. The third order nonlinear optical properties of 3H6M2NP was investigated using Z-scan technique. This title compound was optimized theoretically using B3LYP/6-311++G(d,p) basis set. All quantum chemical calculations were performed to know the structure property relationship, intermolecular interactions, dipole moment, HOMO-LUMO analysis in order to support the NLO activity. The calculated value of dipole moment and hyperpolarisablity of 3H6M2NP was found to be 7.1250 Debye and 4.6648×10^{-31} esu. All the physical parameters of 3H6M2NP was calculated and discussed effectively.

Chapter IV

Growth, characterization and DFT studies on Nitrobenzimidazolium pthalate single crystal

In **chapter IV,** Structural investigation, spectral characterization, NLO studies and DFT calculation were carried out for nitrobenzimadazolium phthalate (NBIPTH). The present compound NBIPTH has been synthesized and crystallized by slow evaporation solution growth technique. The crystal belongs to monoclinic crystal system with centrosymmetric space group $P2_1/c$. The asymmetric unit of NBIPTH contains nitrobenzimidazolium cation, pthalate anion which are held together by N-H..O hydrogen bonding interactions. NBIPTH complex were formed through proton transfer from pthalic acid to nitrobenzimidazole in which the imine site is protonated and it is revealed by ORTEP. The physico- chemical properties of NBIPTH were extensively studied by quantum chemical density functional theory (DFT) calculations and experimental techniques. The present work deals with structural, optical, vibrational studies of NBIPTH based on FT-IR and Raman spectroscopy, thermal and third order NLO property by Z-scan technique. The molecular structure features, structure property relationship, intermolecular interactions, and NLO properties were elucidated by DFT theoretical support.

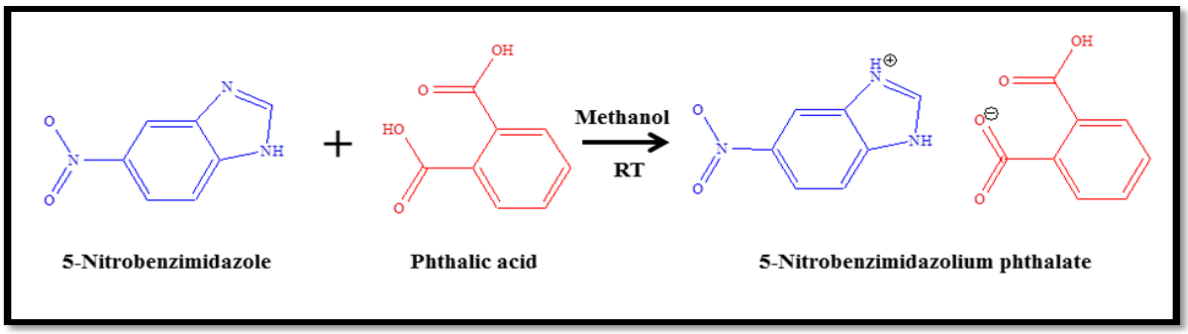

Fig.4. Reaction Scheme of Nitrobenzimidazolium phthalate (NBIPTH).

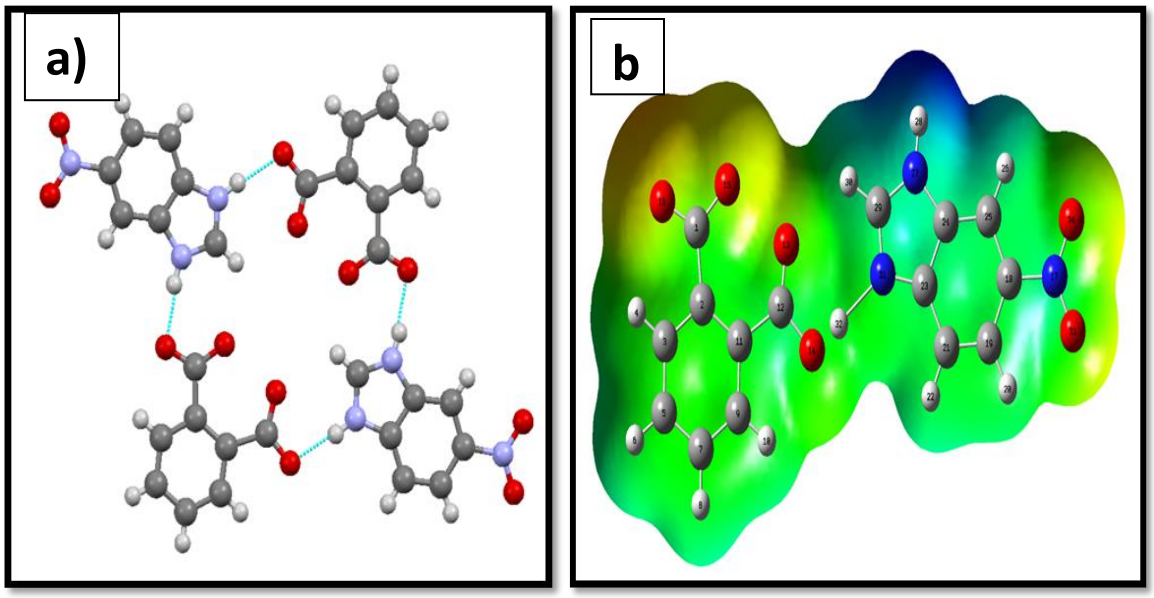

Fig.5 (a) R_4^4(22) ring motif in NBIPTH, (b) Molecular electrostatic potential of NBIPTH.

Chapter V

Growth and characterization of gamma glycine single crystal using formic acid

Chapter V discussed the remarkable influence of formic acid on various properties of glycine single crystals. The structural transformation from centrosymmetric (α-glycine) to non-centrosymmetric (γ-glycine) using additives yields astonishing enhancement in nonlinearities and physical properties. The polymorphism was achieved using formic acid for the growth of γ-glycine crystal. The formic acid added glycine crystals were grown by slow evaporation solution growth technique. The structural parameters of α and γ-glycine crystals were determined using single crystal x-ray diffraction technique. The presence of functional groups and the red shift caused by formic acid were confirmed by FT-IR and Raman spectroscopy. The UV–visible studies confirmed the good optical transparency, wide optical band gap

(6.32 eV) and lower cutoff wavelength in γ-glycine crystal. Dielectric studies explored low dielectric constant and dielectric loss for γ-glycine crystal. The Second Harmonic Generation measurement exhibited high SHG efficiency in γ-glycine crystal compared with other γ-glycine crystals. Enhanced Remnant polarization (95.71 μC cm^{-2}) and coercive field (583.71 kV cm^{-1}) was observed for the γ-glycine crystal through ferroelectric measurement. This work was published in the journal of material research express.

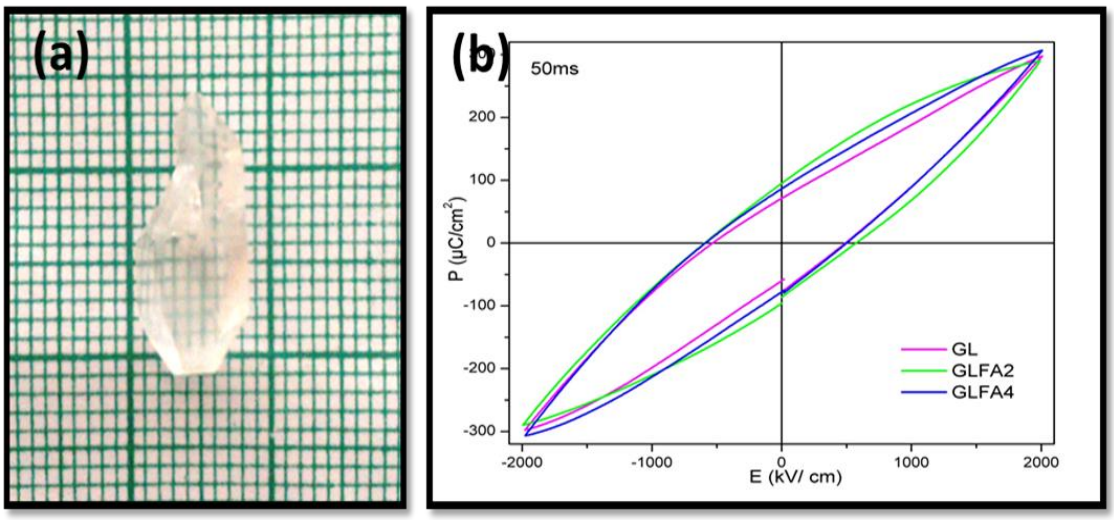

Fig.6 (a) Grown glycine single crystal, (b) P-E loop of glycine single crystals.

Chapter VI

Growth and characterization of gamma glycine single crystal using creatinine

Gamma glycine crystals were crystallized using slow evaporation solution growth technique using creatinine and its various essential properties were discussed in this chapter. The polymorphism of glycine and its lattice parameters were confirmed by single crystal x-ray diffraction technique. The intensity enhancement and peak shifting were identified by Raman spectroscopic analysis. Good optical quality was observed and enhanced SHG efficiency was

revealed by Second Harmonic Generation and optical studies. High laser stability (136 mJ) and mechanically harder γ-glycine crystal was exposed from mechanical and LDT studies. Low dielectric constant and loss were observed from dielectric studies. Grown γ-glycine crystal exhibited piezoelectric property with high piezoelectric coefficient (d_{33}) of 8 pC /N. This work was published in the journal of materials science: materials in electronics.

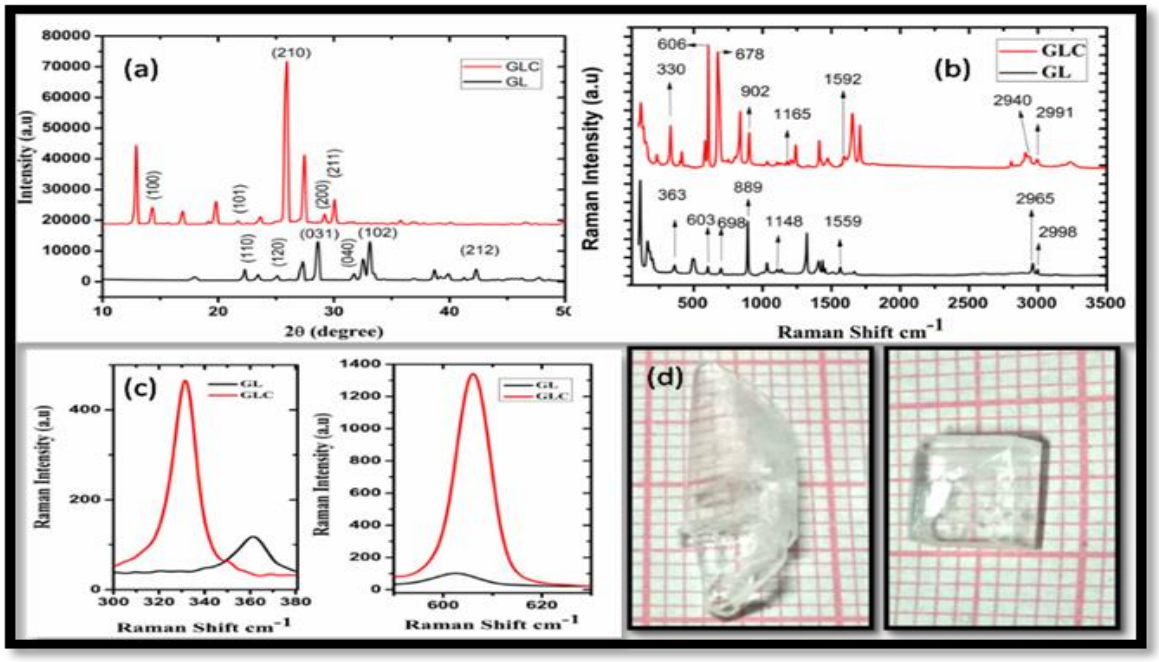

Fig.7 (a) PXRD, (b) Raman spectrum, (c) Raman shift, (d) Grown glycine single crystals.

Chapter VII

Summary

Chapter VII contains summary of all the results and findings of the present work and possible future works are also given.