CHAPTER 8

SUMMARY AND SUGGESTIONS FOR FUTURE WORK

8.1 SUMMARY

Crystal Engineering of organic solids, especially with respect to understanding the nature of various intermolecular interactions, has influenced the concepts of supramolecular chemistry. Supramolecular chemistry is the chemistry of molecular aggregates assembled via non-covalent interactions. The main objective of the present thesis is to grow melamine based compounds (3-NPM, MAC, MTFA, MPH & MOX) and to characterize them by single crystal XRD, powder XRD, FT-IR, FT-Raman, FT-NMR, thermal, mechanical, dielectric studies. DFT calculations were performed using the B3LYP method for all the compounds and thermal decomposition behaviour of MPH, MOX was also carried out. The results are summarized as below.

Growth of cocrystal 3-nitrophenol-1,3,5-triazine-2,4,6-triamine (2/1) (3-NPM) was carried out in aqueous solution using the slow solvent evaporation technique at room temperature. Single crystal X-ray diffraction analysis reveals that 3-NPM crystallizes in the orthorhombic system with centrosymmetric space group Pbca. The geometry, fundamental vibrational frequencies were analysed with the aid of structure optimization and normal coordinate force field calculations based on density functional theory (DFT) B3LYP/6-311G (d, p) method. FT-IR and FT-Raman spectra of 3-NPM have been recorded and analysed. The electric dipole moment, polarizability and
the first order hyperpolarizability values of the 3-NPM were calculated. Thermal studies reveal that melting point of 3-NPM is 168.26°C. The presence of various functional groups present in the structure of the compound is further confirmed by $^1$H and $^{13}$C NMR chemical shift values. Moreover, molecular electrostatic potential (MEP) reveals that negative potential sites are on electronegative atoms and positive potential sites are around the hydrogen atoms of 3-NPM. HOMO-LUMO energy gap was calculated by the TD - DFT method and it was found to be 2.365 eV. Mulliken and Natural charges of the title molecule were also calculated and interpreted. The dielectric studies of 3-NPM reveal that dielectric constant and dielectric loss decreases with increase in frequency.

New organic crystals of 2, 4, 6-triamino-1, 3, 5-triazin-1-ium 3-(prop-2-enoyloxy) propanoate acrylic acid monosolvate monohydrate (MAC) was grown by the slow solvent evaporation method at room temperature. The structure of the crystal was solved by direct methods. Single crystal X-ray diffraction analysis reveals that the compound crystallises in the triclinic system with centrosymmetric space group P-1. FT-IR and FT-Raman spectra of MAC were recorded and analysed. Structure optimization of MAC based on density functional theory (DFT) B3LYP method with 6-31G (d, p) basis set was done and the molecular geometry and vibrational frequencies and intensity of the vibrational bands were interpreted. The calculated vibrational frequency values show good agreement with experimental values. The calculated Mulliken charges and NBO charges of the title molecule show that Mulliken charges are less compared with natural charges. A study of the electronic properties, such as HOMO and LUMO energies and Molecular
electrostatic potential (MEP) were performed. The HOMO-LUMO energy gap was found to be 9.6886 eV. Thermogravimetric analyses of MAC reveal that it has thermal stability up to 77°C. The MEP map of MAC indicates that the entire molecule is associated with negative potential and it shows the region of strongest repulsion. The $^{13}$C and $^1$H NMR of the compound show multiple peaks and the observed values agree well with the calculated chemical shift values. The dielectric behaviour of the MAC shows that dielectric properties vary with frequency.

Single crystals of melaminium bis (trifluoroacetate) trihydrate (MTFA) of dimensions $(8 \times 8 \times 4 \text{ mm}^3)$ were grown successfully by slow evaporation technique. The unit cell dimensions and morphology were identified from the single crystal XRD analysis. Further, MTFA has been characterized by FT-IR, FT-Raman spectroscopy and their thermal stability was investigated by TG/DTA techniques and various kinetic parameters were calculated from the TG data. DFT calculations were performed by the B3LYP method with 6-311G (d, p) basis set. The theoretical results show that the crystal structure can be reproduced by optimised geometry and the vibrational frequencies show good agreement with experimental values. The $^{13}$C and $^1$H NMR chemical shifts were compared with measured experimental values. The melting point of the crystal was found to be 82.85°C from TG-DTA studies. The activation energies for the decomposition of melaminium ion and trifluoroacetate ion were found to be 145.38 and 156 kJ respectively. HOMO – LUMO, and other related molecular and electronic properties were also calculated by DFT method. The Mulliken charge distribution shows that the protonated nitrogen atom has a less negative charge than other nitrogen atoms.
of the molecule. The hardness data of MTFA confirm that it is a soft material and the value of the work hardening coefficient was found to be 2.28. The UV absorption edge was found to 345 nm with a wide optical transmittance window covering the visible region and the optical band gap of the compound was found to be 4.571 eV. Dielectric studies of the sample showed that dielectric constant decreases with increase in frequency. The laser damage threshold value for the grown MTFA crystal was calculated to be 8.6 GW/cm².

Single crystals of melaminium phthalate (MPH) were grown from aqueous solution by the slow solvent evaporation method at room temperature. Powder X-ray diffraction analysis was carried out and the lattice parameters are calculated. The vibrational frequencies of various functional groups in the crystals were confirmed from FI-IR and FT-Raman analyses. The chemical structure of MPH was established by proton NMR and carbon NMR spectrum. The thermal decomposition behaviour of the crystal was studied by means of thermogravimetric analysis at three different heating rates 10, 15, and 20 °C min⁻¹. The values of effective activation energy (Ea), pre exponential factor (ln A) of each stage were calculated by model free methods: Arrhenius, Kissinger, Kim-Park and Flynn-Wall method. The activation energies obtained from Kim-Park method for stage I and II were found to be 139.29 kJ and 113.72 kJ respectively, higher than those obtained from other methods. A significant variation of effective activation energy (Ea) with conversion (α) indicates that the process is kinetically complex. The linear relationship between the ln A and Ea values was well established (compensation effect). It was also found that the most probable kinetic model
for thermal decomposition of MPH is Avrami Erofeev’s model (A2) for the stage I and Avrami Erofeev’s model (A4) for stage II. From the dielectric studies it is seen that dielectric constant and dielectric loss varies with frequency.

Single crystals of melaminium bis (hydrogen oxalate) (MOX) were grown from aqueous solution by the slow evaporation method at room temperature. X-ray powder diffraction results show that MOX belongs to the monoclinic (C2/c) system. The potential energy curve shows that MOX molecule has two stable structures. The computational results diagnose the most stable conformer of the MOX as the Rot I conformer. The vibrational wavenumbers of MOX in the ground state have been calculated by using B3LYP method employing the 6-311++G (d, p) basis set. The various functional groups were identified by the vibrational spectral analysis of both experimental and calculated FT-IR and FT-Raman studies. Mulliken and natural atomic charges of MOX reveal that the nitrogen atom involved in protonation and hydrogen bond formation has higher value of negative charge. Molecular electrostatic potential (MEP) indicates that the positive potential is on the ring protons and negative potential are on the carboxyl oxygen. The charge transfer interaction taking place in the molecule is understood by NBO analysis. The chemical structure of the compound was established by proton and carbon NMR spectrum. Thermogravimetric analysis at three different heating rates 10, 15 and 20°C min\(^{-1}\) was done to study the thermal decomposition behaviour of the crystal. Non-isothermal studies of MOX reveal that the decomposition occurs in two stages. Kinetic parameters (effective activation energy \(E_a\), pre-exponential factor \((\ln A)\) of
each stage were calculated by model free method: Kissinger, Kim-Park and Flynn-Wall methods. The activation energy calculated by Kissinger and Kim-Park methods were found to be more or less similar. Further the most probable kinetic model for the thermal decomposition of MOX was found to be a power law model P2 for stage I and P4 for stage II. The dielectric studies reveal the low dielectric constant and dielectric loss of the crystal at high frequency region.

8.2 SUGGESTIONS FOR FUTURE WORK

Melamine is extensively studied chemical in terms of its growth, vibrational and thermal properties. Some of the melaminium salts exhibit NLO property. Single crystals of 3-NPM, MAC, MTFA, MPH and MOX having good dimension and optical quality can be grown by carefully adopting modified sophisticated apparatus designed for crystal growth. Attempts can be made to investigate the nucleation parameters such as metastable zone width, induction period, interfacial tension etc., to improve and investigate the optimized growth parameters. A systematic study of pH of the solution will throw more light on the morphology and the growth rate of the crystals. There is very little information available in the literature about melamine forming organo metallic compound. So, attempts can be made to prepare such organo-metallic compound and study its properties and stability as a means of understanding the role of the metal ions in industrial processes. It is well known that by bringing out changes such as deuteration and compositional variation the physical and chemical properties of the compounds can be improved. Efforts can be made to identify suitable metal