Studies on Electro Chemical Activity and Third Order Non Linear Optical Properties of Novel (E) -4-Chloro -2-((Phenylimino)Methyl)Phenol, (4C2PMP) Covalent Molecular Coloured Single Crystal : A Potential Organic Crystalline Material for Optical and Electro Chemical Biosensor Applications

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Abstract: In this research, we developed and characterized a novel Schiff base compound, 4-Chloro -2-((Phenylimino)methyl)phenol, (4C2PMP) , focusing on its nonlinear optical and electrochemical properties. Crystals were synthesized using the slow evaporation technique. We employed both powder X-ray diffraction and single-crystal X-ray diffraction to verify the crystal structures. Our optical characterization revealed a lower cut-off wavelength of 563 nm in UV-Visible spectroscopy. The compound exhibited second harmonic generation with emission at 532 nm, while photoluminescence measurements showed a violet shift with a peak at 384 nm and a band gap of 3.21 eV. Laser damage threshold measurements yielded an energy value of 75 mJ, with the crystal demonstrating a power density of 3.98 GW/cm², exceeding the performance of standard reference materials. Infrared spectroscopy confirmed the successful formation of the schiff base ligand, particularly highlighting the -NH_2 nitrogen and -OH oxygen atom bonds. Through Z-scan analysis, we determined the third order non linear optical parameters: nonlinear refractive index (n_2) of 3.84×10^{-8} cm²/W, absorption coefficient (β) of 2.11×10^{-4} cm/W, and third-order susceptibility (χ^3) of 4.07×10^{-6} esu. Electrochemical characterization through impedance spectroscopy revealed reaction kinetics, while cyclic voltametry provided insights into electron transfer mechanisms and redox properties critical for biological signal transduction.

Keywords: Crystal growth; PXRD; SXRD; UV-vis; Z-scan; PL; EIS; CV.

1. Introduction

Nonlinear optical(NLO) materials, particularly organic compounds exhibiting strong nonlinear responses, have emerged as crucial components in various applications including optical frequency conversion, high-speed information processing, photonics, and optoelectronics. The significance of organic materials in these applications stems from their delocalized conjugated π-electron systems, which create efficient pathways between electron donor (D) and acceptor

(A) groups, leading to asymmetric charge transfer processes and resulting in microscopic nonlinearities.Schiff base crystals, characterized by their C=N functionality, represent a particularly interesting class of organic materials for both linear and nonlinear optical applications. Their extended conjugation and mesomeric effects make them promising candidates for second-order and third-order NLO applications. Our research focuses on 4-Chloro -2-((Phenylimino)methyl)phenol, (4C2PMP) , which forms intermolecular hydrogen bonds with CCl_4. This compound's molecular structure and bonding characteristics suggest potential applications in organic chemistry and biological systems.The present study encompasses the synthesis of (4C2PMP) and a comprehensive investigation of its third-order nonlinear optical properties using Z-scan technique, along with electrochemical characterization through electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV). Our work builds upon previous research in organic crystals exhibiting non-centrosymmetric structures with second and third harmonic generation properties. We employed multiple analytical techniques including Single crystal XRD, UV-Vis spectroscopy, IR spectral analysis, SHG measurements, Z-scan analysis, and electrochemical methods to evaluate the material's potential for optical, optoelectronic, and biosensor applications.

2. Materials and Methods

In our synthesis procedure, we combined 5-Chloro salicylaldehyde (99.9%, Sigma Aldrich) and aniline (AR grade) in equimolar ratios (1:1). These reactants were dissolved in 25 ml of CCl_4 solvent. The mixture underwent continuous stirring for 1 hour until achieving a clear saturated solution. We then transferred the solution to a clean beaker covered with perforated silver foil. After maintaining the solution undisturbed for one week, pure orange-colored crystals were obtained.

Crystal Picture

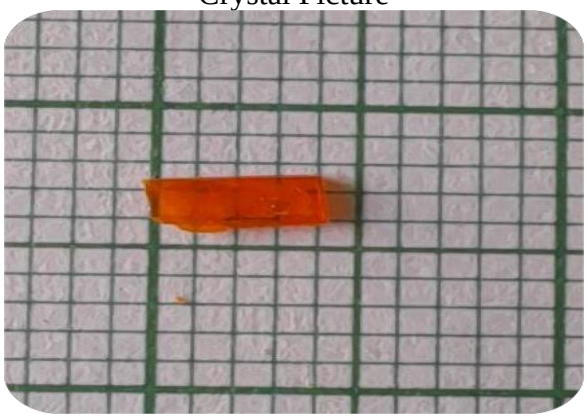

Fig-(1) (4C2PMP) crystal

3. Result and discussion

3.1 Powder XRD analysis

We conducted powder X-ray diffraction analysis using a BRUKER-binary diffractometer with CuKα radiation, scanning through 2θ angles from 5° to 80°. The diffraction pattern revealed distinct peaks, which were indexed using powder X software to determine their (hkl) values. The presence of sharp, well-defined peaks at specific 2θ angles indicated the high crystallinity of our synthesized material.

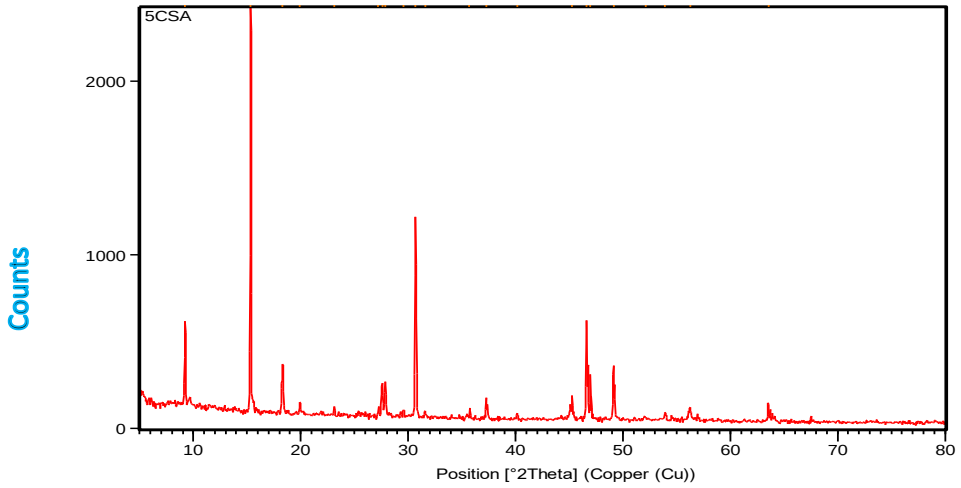

Fig-2 PXRD spectrum of (4C2PMP) crystal

3.2 Single crystal X-Ray diffraction analysis

Our single-crystal XRD analysis revealed that (4C2PMP) crystallizes in the orthorhombic P system with a non-centrosymmetric space group. This structural characteristic is particularly significant as it fulfills a fundamental requirement for NLO activity. The determined lattice parameters are We used (CCDC 119131.cif, Fig. 1), the structure of which has been solved by Keiichiro Ogawa, Yoshiro Kasahara, Yohko Ohtani, and Jun Harada (J. Am. Chem. Soc. 1998, 120, 7107-7108) by a single crystal X-ray method. The input used to the Endeavour software are the unit cell parameters (orthorhombic cell) a = 12.177 Å, b = 4.483 Å, c = 19.271 Å, and α = β = γ = 90°; the space group is P c a 21 (International Tables no. 29) with Z = 4 (chemical formula C13ClH10NO). The diffraction data loaded from the file 119131.dif with a file format (2Theta vs. Intensity), radiation: X-ray-laboratory, wavelength Cu Kα1 (1.540598 Å). After the five calculations using different seed values have finished, Endeavour automatically selects the configuration (solution) with the lowest cost function value. For this structure, the data sheet is displayed. At this stage, the structure solution is complete; all crystal structure data required for the Rietveld refinement (refinement not done for the present case) have been determined (see Fig. 2 and Fig. 3).

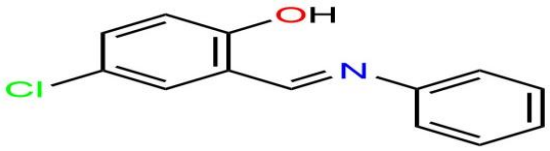

Fig. 1. Constitution of 5CSA.

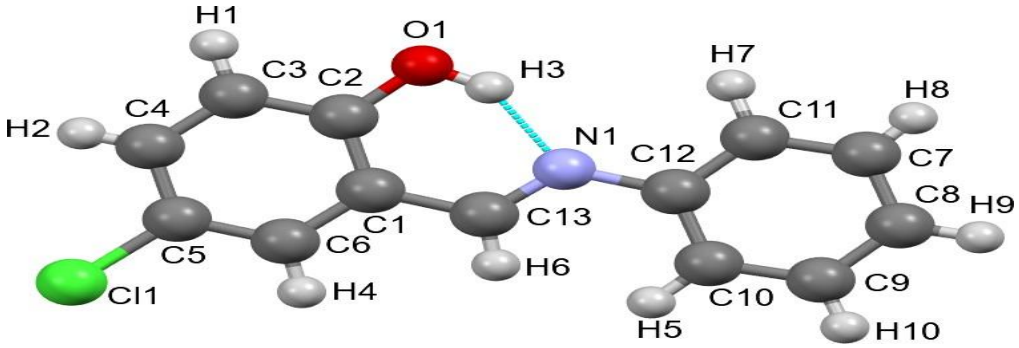

Fig. 2. Perspective view of 5CSA with the atom numbering scheme showing S(6) ring motif involving O1-H3…N1 hydrogen bond.

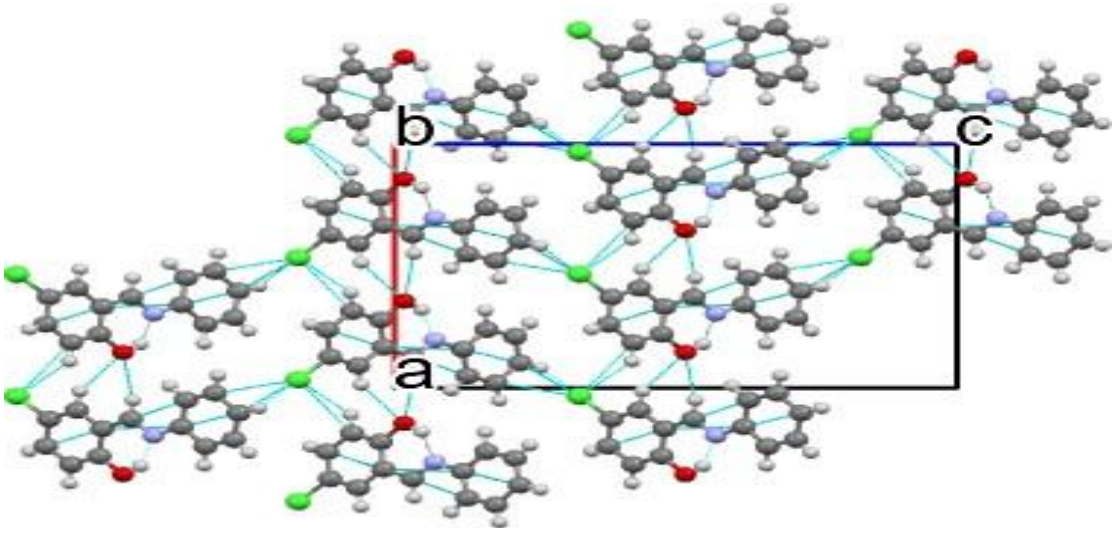

Fig. 3. Unit cell packing of 5CSA viewed along the b-axis.

Table 1: Crystal Structure Parameters

Cell Parameters	Single Crystal XRD
a	4.6 Å
b	12.39 Å
c	19.40 Å
α	90˚
β	90˚
γ	90˚
System	orthorhombic
Lattice, space group	P

3.3 Linear optical property UV- Visible Spectral studies

Optical transparency is an important parameter for any NLO crystal

We investigated the optical properties through UV-Visible spectroscopy over the range of 200-900 nm. The absorption spectrum fig.3(a&b) exhibited a lower cut-off wavelength at 563 nm, with significant absorption between 200-563 nm in the visible region. The crystal (4C2PMP) demonstrated high transparency from 563-900 nm, suggesting its potential applications in optical limiting, optoelectronic devices, and frequency conversion.

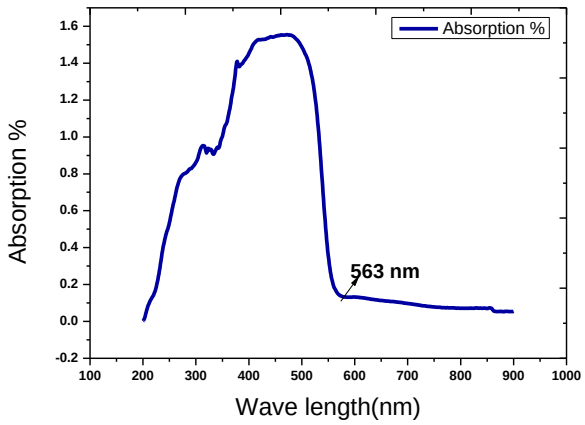

Fig.(3)(a) UV – Vis. Spectrum of (4C2PMP)

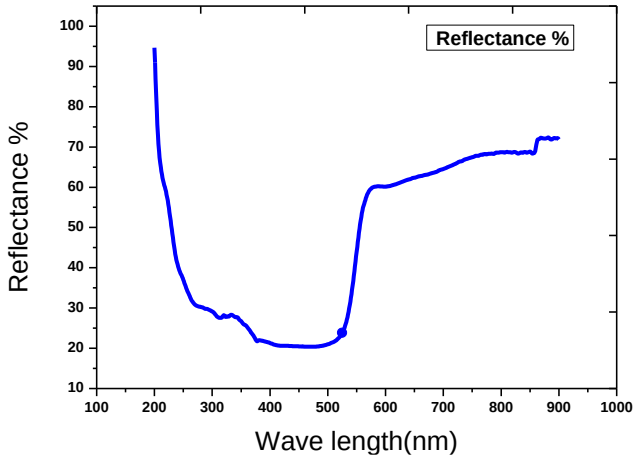

Fig.(3)(b) UV – Vis. Spectrum of (4C2PMP)

3.4 FT-IR and FT-Raman spectral studies

The (4C2PMP) with aniline were qualitatively analyzed to determine the presence of various kinds of functional groups and the formation of the hydrogen bonding in the mentioned crystal have been identified by Bruker optics FT-IR spectrometer in the region 400 cm^{-1} to 4000 cm^{-1}.The stretching vibration peaks occurs at 1605.5cm^{-1} is due to the formation of imine group (C=N) as a result of condensation reaction between aldehyde and amine[12] ,the aromatic stretching vibrations at 3024 cm^{-1},C=O stretching vibrations observed at 1744 cm^{-1},C=C aromatic ring stretch was observed at 1556 cm^{-1},C-N stretching vibrations at1268,1169,1023 cm^{-1},C-H out of plane bend at 915 cm^{-1} and C-Cl stretching of (4C2PMP) crystal occurs 802.66cm^{-1},the OH out of plane bend at 639cm^{-1}.From the FT-Raman spectrum the peak seen at 1616 cm^{-1} due to the C=N stretching vibrations this confirms the presence of imine group ,C=C aromatic ring stretching at 1565 cm^{-1} and C-H stretching vibrations at 1437,923,861 cm^{-1}, C-N stretching vibration occurs at 1314,123,1180,1000.05cm^{-1}.The stretching at 785$cm^{-1}$is due to C-Cl.

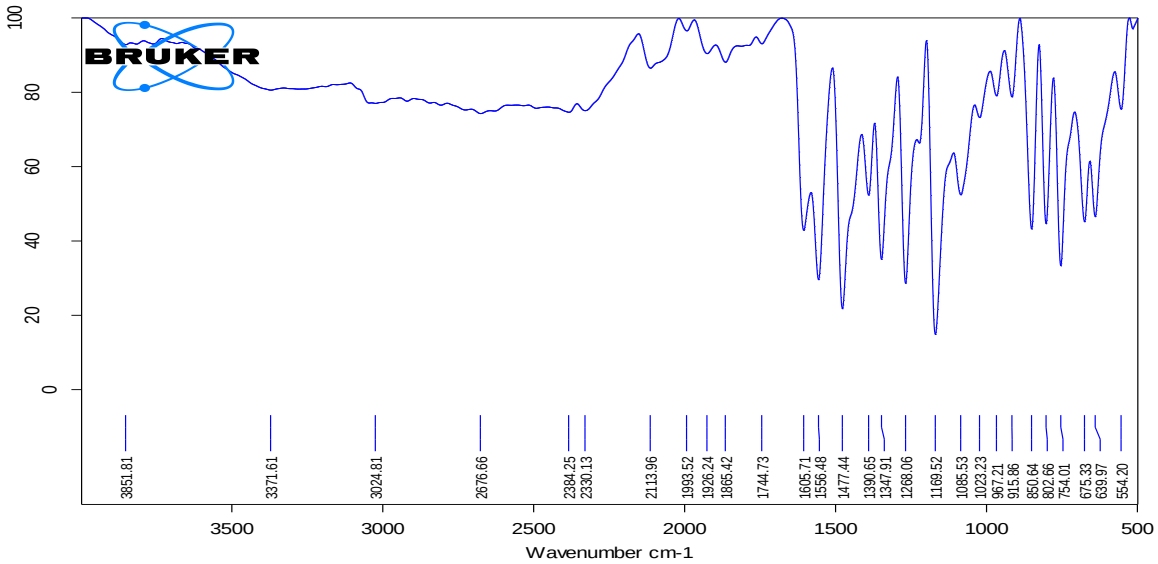

Fig-(4) FT-IR spectrum of (4C2PMP) crystal

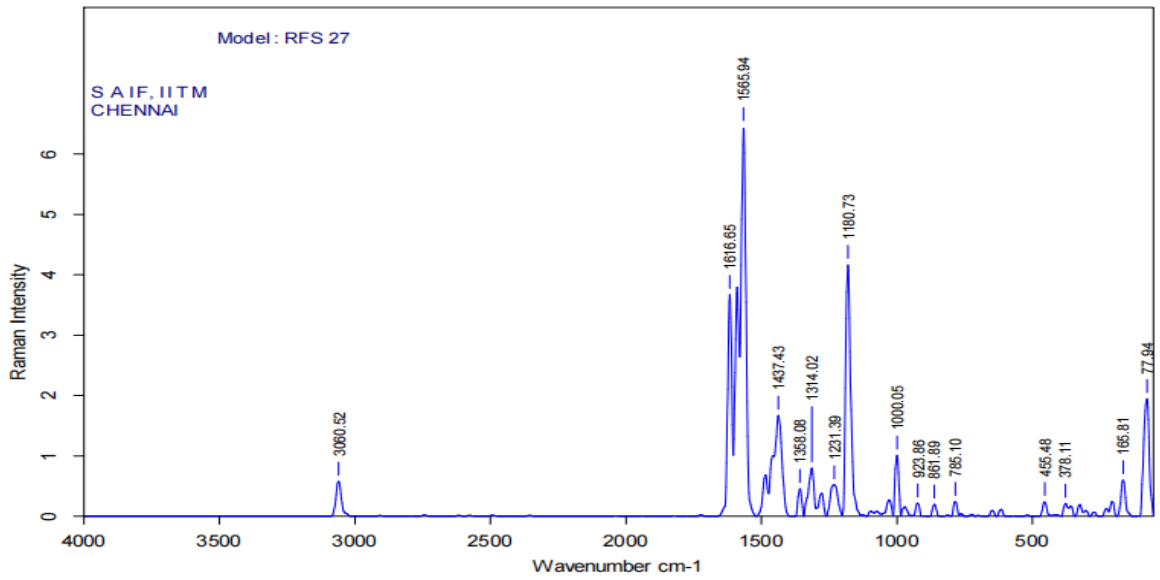

Fig-(5) FT-Raman spectrum of (4C2PMP) crystal

Table - 2 Important spectral assignment of FT-IR and FT-Raman

Modes of vibrations	FT-IR	FT-Raman
OH stretching	3024 cm^{-1}	3060 cm^{-1}
C=N imine group due to aniline	1605 cm^{-1}	1616 cm^{-1}
C=C aromatic ring vibrations	1556 cm^{-1}	1565 cm^{-1}
OH bend	1390 cm^{-1}	1358 cm^{-1}
C-N aromatic secondary amine	1347 cm^{-1}	1314 cm^{-1}
C-Cl stretching of (4C2PMP)	802 cm^{-1}	785 cm^{-1}

3.5 Thermal Studies

DSC curve

Differential scanning Calorimetry was carried out for (4C2PMP) crystals in NETZSH STA 449F3.A powder sample was used for the analysis in the temperature range from 27^0 C to 1400^0C with heating rate of 10^0C /min in the Nitrogen atmosphere.The crucible used was alumina Al_2O_3 which served as a reference for the sample .In DSC curve the sharp exothermic peaks at 77.5^0Cwith area of energy 101.5 J/g and a broad endothermic peak at 266.5^0C with area of energy 396.7 J/g .The exothermic peak caused by crystallization and the endothermic peak refers to the melting.The area of the peak represents the amount of energy involved in transition.DTG curve was used to measure the rate of weight change in a material as a function of time .which gives the decomposition temperature at 295.7^0C

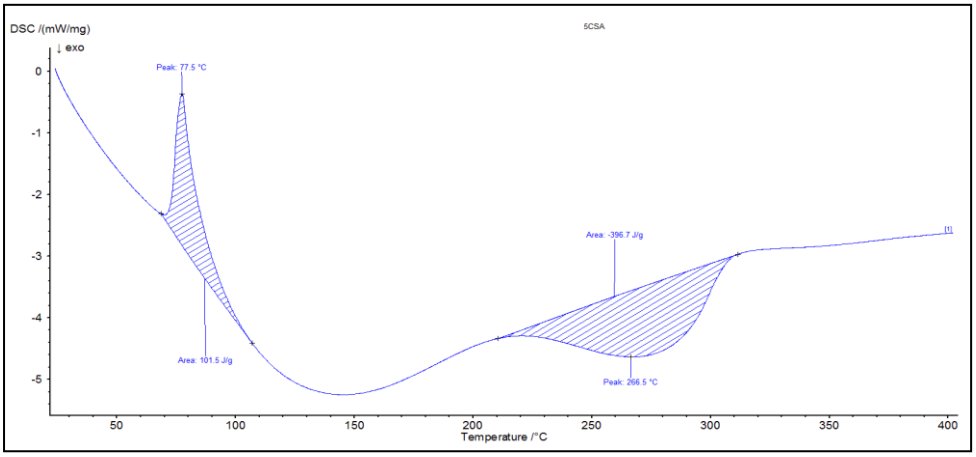

Fig-(6) DSC Curve of (4C2PMP) crystal

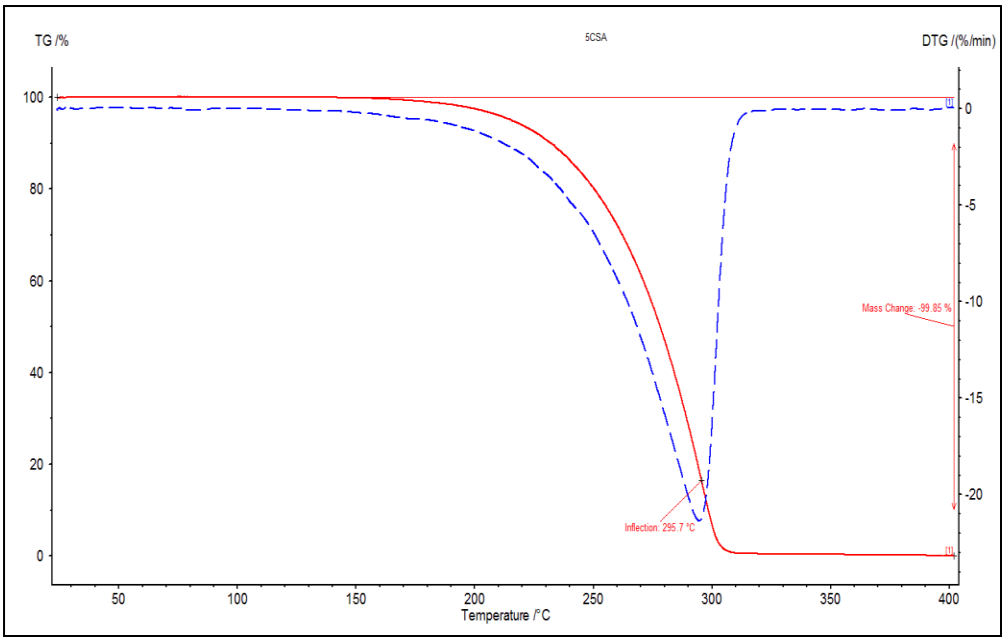

Fig-(7) DTG Curve of (4C2PMP) crystal

3.6 Photoliminesence study (PL)

The PL spectrum of the grown crystal was recorded at room temperature with excitation wavelength at 300 nm the spectrum captured from 300 nm to 500 nm. A high intensity peak centered at 383 nm in a violet shift and an energy band gap of 3.21 eV.

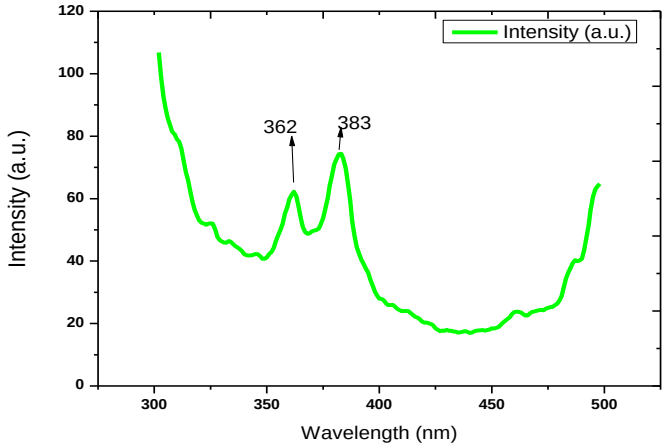

Fig-(8) PL spectrum of (4C2PMP) crystal

3.7 Non linear optical properties Second Harmonic Generation studies

The second harmonic generation (SHG) test on the (4C2PMP) crystal was performed by the Kurtz and Perry powder SHG method (Kurtz and Perry method 1968).A Q switched Nd.YAG Laser with fundamental wave length of 1064nm was used as an optical source energy ranges from 1.5mJ to 3 mJ, repetition rate 10 Hz pulse width 6 ns and the wavelength of the light emitted from (4C2PMP) crystal was 532nm thus doubling of frequency was confirmed by the emission of green radiation of wave length 532 nm[20] indicates NLO behaviour of the (4C2PMP) crystal.

3.8 Z Scan Studies

Our Z-scan measurements shown in fig(9)(a)(b) revealed significant nonlinear optical properties Low linear absorption in the visible range, indicating minimal intensity loss Reverse saturated absorption (RSA) at maximum laser irradiance Nonlinear absorption coefficient (β) 2.11×10^{-4} cm/W Third-order susceptibility (χ^3) 4.07×10^{-6} esu The closed-aperture Z-scan

curves exhibited pre-focal peak followed by post-focal valley, indicating self-defocusing behavior, which is particularly relevant for vision sensor device applications.

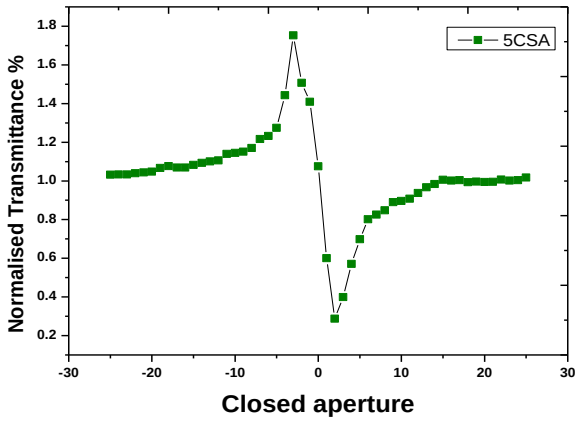

Fig-(9)(a) Z Scan closed aperture

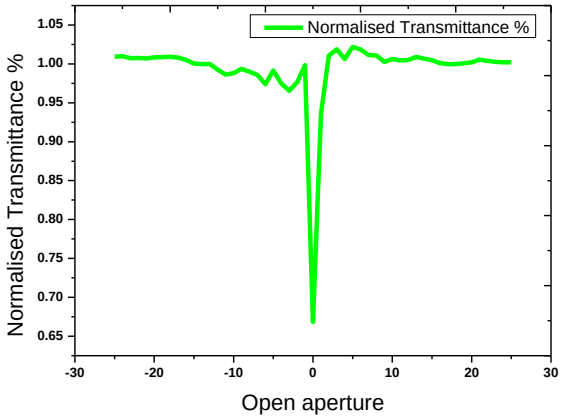

Fig-(9)(b). Z Scan open aperture

Crystals	Third order nonlinear susceptibility $X^{(3)}$(esu)	References
5CSA	$4.07309x10^{-06}$	Present work
Benzimidazolium maleate	$5.5378x10^{-07}$	Shakthipriya et..al (2021)
L-arginine maleate dihydrate	$1.011x10^{-07}$	Shakthipriya et..al (2017)
Pottasium 3,5 -dinitro benzoate	$3.027x10^{-08}$	Karuppasamy et al.(2016)
2-amino-5-nitropyridinium bromide	$6.76x10^{-09}$	Vediyappan et.al(2017)
KBe2BO3F2	$0.99x10^{-13}$	Li et al. (2012)

Table- 3

3.9 Laser Damage Threshold

The laser damage resistance is one of the essential criteria for the NLO crystal to perform as a laser optical device because the high optical intensity are involved in nonlinear phenomenon.The LDT analysis of (4C2PMP) gives the observed energy value of E=75mJ and the power density is around 3.98 GW/cm^2 which is higher than urea ,L arginine phosphate and barium borate.The obtained LDT values confirms (4C2PMP) crystal has high laser damage resistance and it is suitable for fabricating laser based optical devices.

3.10 Cyclic Voltametry analysis

The cyclic voltagram of (4C2PMP) the base line corrected peak analysis shows anodic current and potential. The peak I measures 5.054 µA and the peak V measures 1.433 V From this volta gram the intensity of the current increased with increasing number of cycles. The forward peak represents the oxidation process and the reverse peak represents the deoxidation process.This redox property appears in the crystal due the addition of aniline.The stability and reversibility are studied through redox property,the redox properties of the organic crystals can be tuned by modifying the molecular structure of the organic crystals allows for the design of materials with specific redox potentials and properties tailored for particular applications.

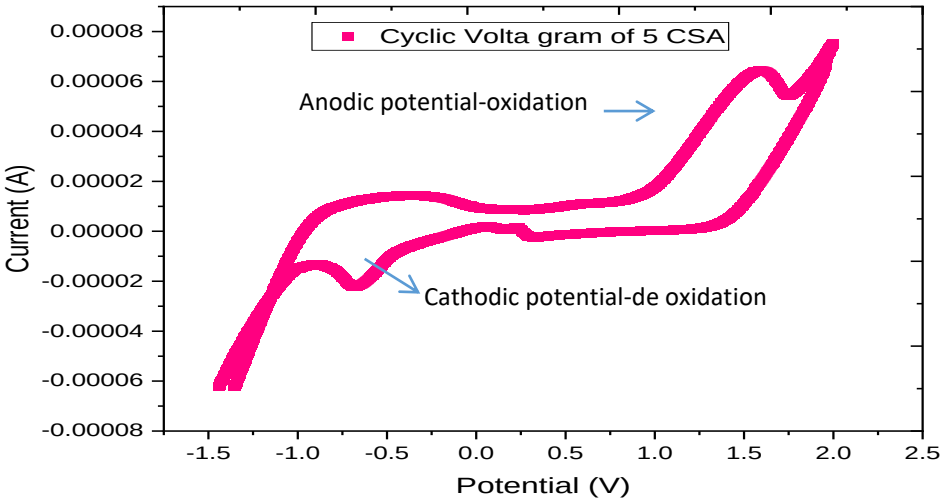

Fig.(11) Cyclic Voltagram of (4C2PMP)

3.11 Electrochemical impedance spectroscopy (EIS)

In order to find the electro chemical parameter,the (4C2PMP) crystal is subjected to electro chemical spectroscopy and plotted in Nyquist fig.12 shows centre point at X axis is 3554.5 ohms ,centre point at Y axis is 2101.2 ohms ,diameter of the semicircle is 6077.6 ohms. Sample deviation is 20.434 and depression value 43.746^0 . Form the Nyquist plot high frequency intercept near the plot origin of the real X axis value gives the solution resistance value Rs. The low frequency intercept of the real axis provides the summation of the polarization resistance and the solution resistance Rp + Rs. Therefore, the semi circle diameter will equal to the polarization resistance.These measured parameters are useful in fabricating equivalent electronic circuits applicable for biosensors and also the polarization resistance is the transition resistance between the electrode and the electrolyte. The electron transfer characteristic of the grown (4C2PMP) crystal has exhibit electro chemical properties and dielectric property which tends to the applicability of the crystal as transducer in electro chemical biosensor to detect biological materials.

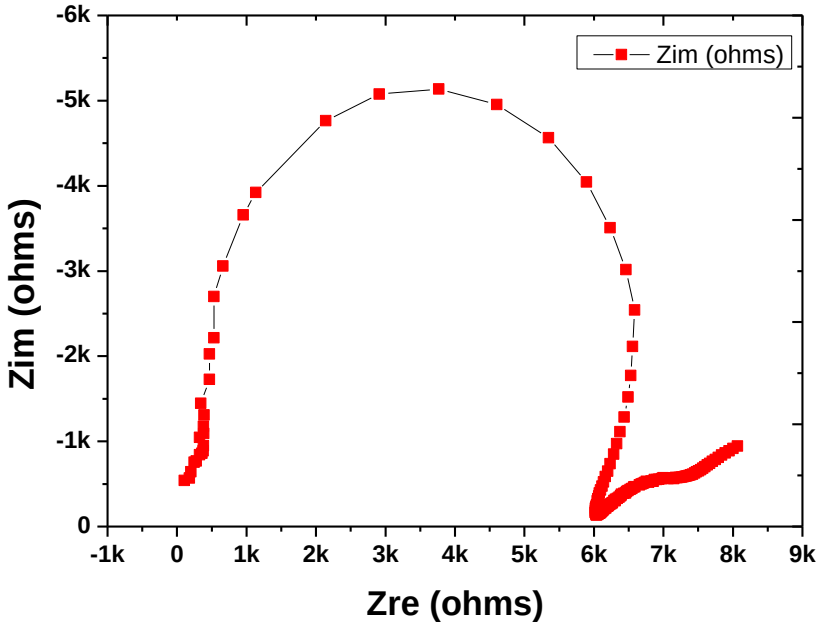

Fig-(12) Electro chemical impedance spectrum

4. Research Implication

The fig.13 shows a schematic diagram of an impedance biosensor (Jordan et al., 2019). The research findings suggest that the grown (4C2PMP) crystal exhibits excellent electrochemical response, implying its suitability as a working electrode for an impedance biosensor (Ghita et al., 2020).

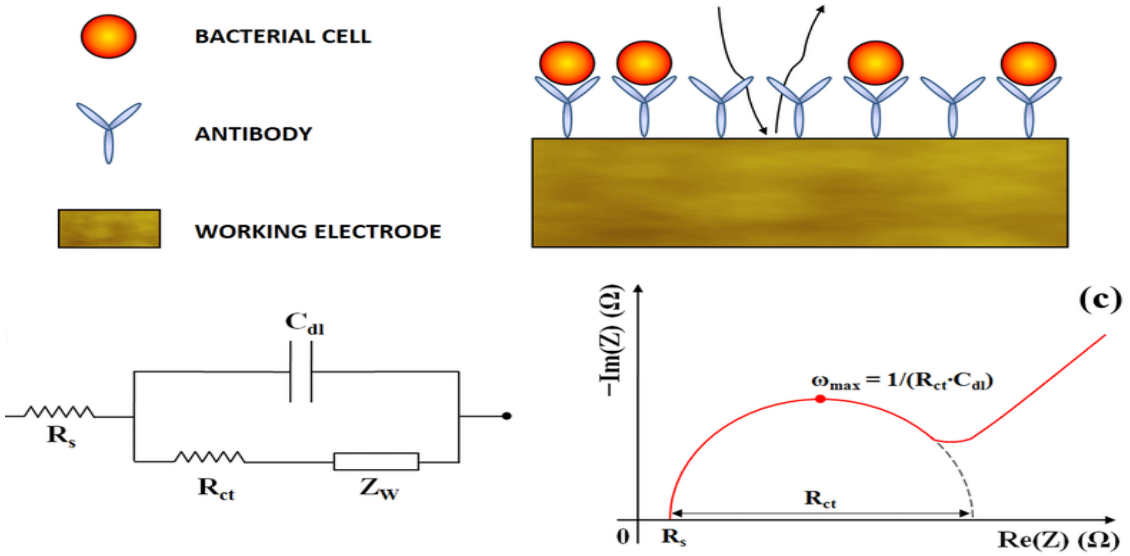

Fig.13 Working principle of impedance biosensor

5. Conclusion

Our comprehensive study of (4C2PMP) crystals demonstrates their multifunctional capabilities: Successful synthesis via slow evaporation technique Strong third - order nonlinear optical response with high susceptibility confirmed electrochemical activity through CV and EIS analyses Direct correlation between impedance data and inter facial electrochemical reaction kinetics. These findings establish (4C2PMP) as a promising candidate for diverse applications including photonics, optoelectronics, and both optical and electrochemical biosensor devices. The combination of NLO and electrochemical properties in a single material makes it particularly valuable for multifunctional applications.

Acknowledgements

One of the authors (BDS) express his sincere thanks to SAIF IITM for providing testing facilities, The authors acknowledge Dr.Vijayaragavan Department of Physics,B.S.Abdur Rehman University,Vandalur for SHG and LDT and a special thanks to Dr.G.Vinitha, Department of Physics,VIT University,Chennai-600127,towards Z-scan studies.

Funding Information

This research did not receive any specific grant from funding agencies in the public , commercial, or not- for -profit sector.

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