

# Studies on the Synthesis, Growth and Characterization of ([Paranitrophenyl]Imino)Benzene NLO Crystal by Sankaranarayanan-Ramasamy Method

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## ABSTRACT

The study of imine-bridged organics has been the hot spot synthesis of second order nonlinear optical (SONLO) and photo-responsive materials in recent years. Herein we present a study of synthesis, growth, and characterization of ([paranitrophenyl]imino)benzene (PNPIB) NLO single crystal. The title compound was synthesized in one step by Schiff base formation. <110> PNPIB single crystal of diameter of 40 mm and length 50 mm was successfully grown by SR method using a seed as the nucleus. The growth rate formula is derived for the SR method. PNPIB single crystals of 10 mm diameter and 60 mm height have been grown at an average growth rate of 3 mm per day from the point seed in a glass crystallizer. Almost 100% stable crystal conversion efficiency was achieved. The as grown PNPIB crystals were characterized using single crystal X-ray diffraction (XRD), X-ray powder diffraction (XRPD), Fourier Transform Infrared (FTIR), Ultraviolet-Visible-Near Infrared (UV-Vis-NIR), <sup>1</sup>H & <sup>13</sup>C NMR spectral studies, dielectric measurement and NLO studies. Single crystal XRD analysis confirms that the grown ingot belongs to the space group of *P*<sub>2</sub> of monoclinic system thus exhibiting noncentrosymmetric structure. The crystalline perfection was assessed by XRPD. The powder diffraction pattern of the grown crystal has been indexed. The presence of C=N bond with intramolecular hydrogen bonding and the protonation of ions were confirmed by FTIR analysis. The UV-Vis-NIR spectrum of the crystal shows that the crystal has a cut-off at 298 nm. The <sup>1</sup>H & <sup>13</sup>C NMR spectra confirm the molecular structure. The dielectric behaviour was measured in the frequency range 1 KHz - 10 KHz for the temperature range from 30°C to 170°C. The slight decrease in dielectric constant has been observed as the frequency is increased and the dielectric loss is very low for the entire frequency range. The second harmonic generation (SHG) in the crystal was observed by Kurtz powder technique.

**Keywords:** Single Crystal Growth; S-R Method; Nonlinear Optical Materials

## 1. Introduction

Second order non-linear optical (SONLO) materials have recently attracted much attention because of their potential application in emerging optoelectronic technologies [1,2]. Materials with large second order optical nonlinearities are used in the area of laser technology, laser communication and data storage devices [3,4]. The search for new conversion materials over the past decades lead to the discovery of many organic NLO materials with high nonlinear susceptibilities. Organic materials have been demonstrated in recent years to possess superior second order and third order NLO properties compared

to the more traditional inorganic materials. The structural flexibility of organic compounds is an asset for materials with optimised second order NLO susceptibility, fast response and tailor made flexibility [5]. An innumerable of organic crystals are synthesized and grown in this fashion [6-11]. One of the obvious requirements for nonlinear crystal is that it should have excellent optical quality. For a device to succeed, it is vital that it should meet a number of criteria such as optical nonlinearity, chemical and thermal stability for life time system capability [12]. The above said parameters fit excellently to imine materials. Hence, the imino heterojunction organic materials are used as bio-functional compounds with excellent NLO responses [13-19]. We also know that the

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heterojunction units are the core structures of a number of natural products like imine acids, bioelectric and photovoltaic materials. Here Schiff bases have been produced to be a class of functionally active compounds in these areas. Recently *Unver et al.* have reported the structural and NLO properties for some imine bridged aromatic compounds [13,19,20]. *Volodymr et al.* have designed thermostable acentric nonlinear optical crystalline imine derivatives [21,22]. *Heravic et al.* have reported a theoretical investigation of the structure electronic properties and second harmonic generation of imine ligands [23]. *Oleinik et al.* have performed systematic studies in the field of structural modifications of metal complexes of imine derivatives [24]. It has been produced that the phenoxy imine crystals containing an aldimine group shows higher catalytic and photoresponsive activity than their analysis with ketimine groups [25]. Recently the Hyper-Rayleigh scattering and the electric field induced SHG measurements for two anil systems and in particular their variations upon switching between the enol-imine and keto-amine derivatives were reported by *Plagvet et al.* [26]. A new novel crystalline structure 2-hydroxy-N-[3(5)-pyrazolyl]-1-4-naphthoquinone-4-imine was grown by *Speranedo et al.* and the characterization studies such as DSC, TG/DTA, FTIR, HRXRD were carried out [27]. The intermolecular interaction between the carbonyl and the imine groups in the crystalline compounds containing six member heterocycles were identified by *Golovina et al.* [28]. Based on these results our group has been engaged in the synthesis and growth of organic crystalline materials for NLO applications [29-31]. Motivated by the findings, a novel growth by Sankaranarayanan-Ramasamy (S-R) method [32] has been introduced to grow PNPBI crystals for NLO applications for the first time. The main features of this method over others are microbial growth is naturally avoided, less sophisticated instrument and maximum soluble crystal conversion efficiency is achieved and moreover the growth rate is visualised precisely for individual faces. The as grown crystals were characterized by XRD, XRPD, FTIR, UV-Vis-NIR,  $^1\text{H}$  &  $^{13}\text{C}$  NMR, NLO and dielectric studies.

## 2. Synthesis and Growth Studies

### 2.1. Synthesis of PNPIB

Most of the chemicals in this work were purchased from E-Merck and used without further purification. The title compound was synthesised by one step condensation method. Equimolar ratio of para-nitrobenzaldehyde and aniline were dissolved. The reaction mixture was stirred for about an hour to give a yellow crystalline salt. The as obtained crystalline salt was used for solubility and growth experiments. The reaction scheme is shown in

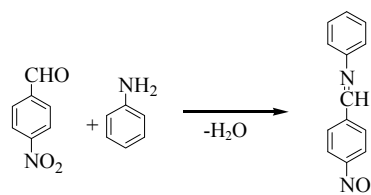
**Figure 1.**

### 2.2. Solubility Studies of PNPIB

The synthesized salt was used to measure the solubility of pure PNPIB crystals in Dimethyl formamide (DMF). A 250 ml borosil glass beaker filled with 100 ml DMF was placed inside a constant temperature bath. An acrylic sheet with a circular hole at the middle was placed over the beaker through which a spindle from an electric motor, placed on the top of the sheet was introduced into the solution. A Teflon paddle was attached at the end of the rod for stirring the solution. The synthesized salt was added in small amounts with DMF solvent and stirring was continued till the formation of precipitate, which confirmed the supersaturation of the solution. A 20 ml of the saturated solution was withdrawn by means of a warmed pipette and the same was poured into a clean, dry and weighed petri dish. The solution was kept in a heating mantle for slow evaporation till the whole of the solution got evaporated and the mass of PNPIB in 20 ml of solution was determined by weighing petri dish with salt and hence the solubility, *i.e.* quantity of PNPIB salt in gram dissolved in 100 ml of the solvent was determined. The solubility of PNPIB crystals in DMF solvent was determined for five different temperatures (30°C, 35°C, 40°C, 45°C and 50°C) by adopting the same procedure. The resulting solubility curve of pure PNPIB is shown in **Figure 2**.

### 2.3. Growth Rate of PNPIB

It is well known that the evaporation rate of the solvent DMF into the atmosphere is a function of temperature, humidity and air velocity. It is evident that the evaporation process in the atmosphere is diffusion of DMF molecules coming out of its surface through the air larger covering its surface. To calculate theoretically the absolute evaporation rate, we must know the diffusion coefficient of DMF vapour in air and the thickness of the boundary layer accurately. Kazuo Histake *et al.* reported a detailed survey on the evaporation rate [33]. A reaction for the growth rate of S-R method is given by  $R_T = 0.318 K (SE)/r^2d$  (cm per day), where  $K$  is the proportionality constant,  $S$  is the solubility of the material (g/ml) of the solvent,  $E$  is the evaporation rate of the solvent (ml per day),  $r$  is the radius of the vessel,  $d$  is the density of the



**Figure 1. Reaction scheme of PNPIB single crystal.**

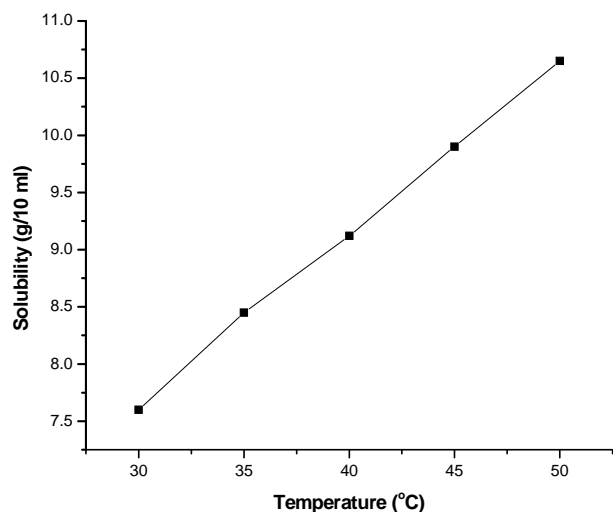


Figure 2. Solubility curve of PNPIB single crystal.

material ( $\text{g}/\text{cm}^3$ ) and  $T$  is the temperature ( $K$ ). By using the above parameters, the growth rate of the crystal is calculated. The evaporation rate of the solvent in an ampoule was also measured by observing the lowering rate of the top surface of the solution level.

### 3. Experimental Set-Up S-R Method

The experimental set-up for the grown PNPIB single crystal by S-R method is shown in **Figure 3**. It consists of a growth ampoule made out of glass. An outer glass shield tube protects and holds the inner growth ampoule. Ring heaters were positioned at the top and the bottom of the ampoule which was connected to a temperature controller. The temperature controller provided the necessary temperature for solvent evaporation. The PNPIB solution of optimized saturation was prepared using DMF solvent. The as grown PNPIB single crystal by slow evaporation technique and  $\langle 010 \rangle$  crystals of PNPIB grown by S-R method are shown in **Figures 4** and **5** respectively.

## 4. Characterization Studies

### 4.1. Single Crystal XRD

The single crystal X-ray diffraction was recorded with Bruker Kappa APEXII diffractometer and the wavelength of X-ray used was  $0.7093 \text{ \AA}$  (Target-Molybdenum). From the single crystal XRD, the lattice parameters were calculated and the crystal belongs to monoclinic system with a space group of  $P_2$ . The lattice parameters are  $a = 14.48 \text{ \AA}$ ,  $b = 10.72 \text{ \AA}$ ,  $c = 14.58 \text{ \AA}$ ,  $\alpha = 90^\circ$ ,  $\beta = 101.95^\circ$  and  $\gamma = 90^\circ$  and  $v = 2214 \text{ \AA}^3$ . The lattice parameters were calculated using SHELXL programme.

### 4.2. XRPD Analysis

Powder XRD analysis was carried out using XPERT



Figure 3. Sankaranarayanan-ramasamy method.



Figure 4. Photograph of as grown crystal of PNPIB by slow evaporation method.



Figure 5. Photograph of as grown PNPIB single crystal by S-R method.

Powder diffractometer with  $\text{CuK}\alpha$  ( $\lambda = 1.541 \text{ \AA}$ ) radiation to confirm the structure of the as grown PNPIB crystals. The sample was scanned over the range  $10^\circ - 60^\circ$  at a rate of  $1^\circ \text{ nm}^{-1}$ . The XRPD and peak indexing are shown in **Figure 6**. The peaks were indexed using X'Pert software. The recorded spectrum confirms the

growth orientation to be  $\langle 110 \rangle$  plane. The XRPD pattern reflects the good crystallinity of the grown crystal.

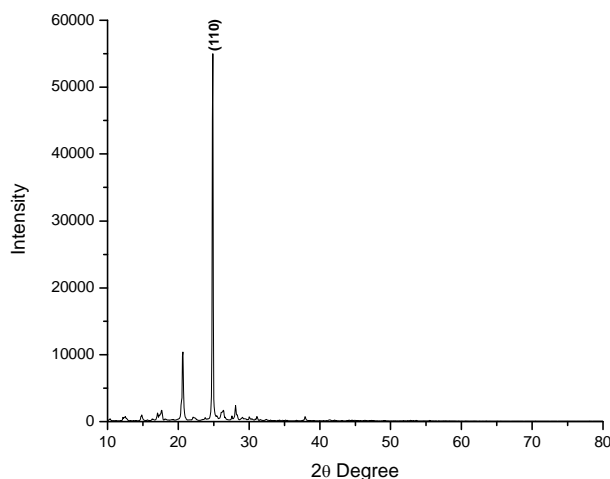
### 4.3. FTIR Spectral Studies

FTIR spectrum is important evidence that provides more information about the structure of a compound. In this technique, almost all functional groups in a molecule absorb characteristically within a definite range of frequency. The absorption of IR radiation causes the various bonds in the molecule to stretch and bend with respect to one another. The most important range ( $4000 - 400 \text{ cm}^{-1}$ ) is of prime importance for the study of an organic compound by spectral analysis [34]. In the present study FTIR spectrum was recorded using Perkin-Elmer spectrometer with KBr pellet technique. The spectrum is shown in **Figure 7**. The vibrational bands for the PNPIB crystal were observed in the  $4000 - 400 \text{ cm}^{-1}$ . Absorption bands at  $3075, 3094, 3003$  ( $\nu_{\text{C-H}}, \nu_{\text{Ar-H}}$ ),  $1452 - 1626$  ( $\nu_{\text{C=C}}$ ),  $2848 - 2916$  ( $\nu \text{ CH}_3$ ),  $744$  ( $\nu_{\text{C-C}}$ )  $\text{cm}^{-1}$  were observed. The absorption band assignable to the stretching of C=N bond was observed at frequency of  $1626 \text{ cm}^{-1}$ . A peak at  $1953 \text{ cm}^{-1}$  is due to C=C stretching. The peak at  $1490 \text{ cm}^{-1}$  is due to N-H in plane bending. A peak at  $1513 \text{ cm}^{-1}$  is attributed to  $\text{NO}_2$  asymmetric stretching. A peak at  $1094 \text{ cm}^{-1}$  is due to C-N stretching. A peak at  $851 \text{ cm}^{-1}$  is due to C-H bending. A peak at  $955 \text{ cm}^{-1}$  is attributed to N-O stretching. A peak centred at  $744 \text{ cm}^{-1}$  is due to C-H out of plane bending. A peak at  $851 \text{ cm}^{-1}$  is attributed to C-H bending. A peak at  $697 \text{ cm}^{-1}$  is due to C-C out of plane bending due to the mono substitutional benzene ring. Thus the FTIR spectral confirms the presence of the functional groups and their mode of vibrations.

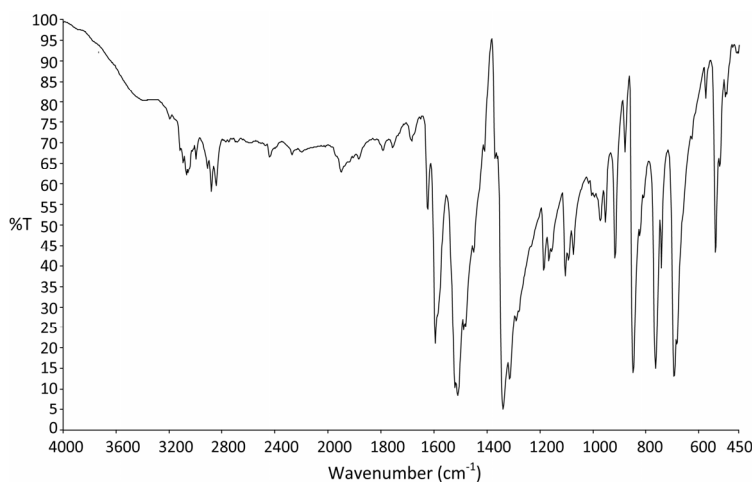
### 4.4. UV-Vis-NIR Study

It is very helpful in the investigation of the NLO materi-

als also making it possible to check, apart from NLO responses and also spectroscopic absorbance in the appropriate wavelength. Therefore the wavelength obtained by UV visible spectral analysis can be helpful in the synthesis of promising NLO materials [35]. Zhou has calculated that the estimated electronic transition wavelengths obtained by UV-Visible spectral analysis for chain compounds are about 10 nm shorter than that of the cycles and the wavelength for both groups should have been found to be shorter than 400 nm implying good thermo parameters and NLO property [36]. Albert et al have reached the conclusion that with the correct substitution in the ring, characterized by strong intramolecular  $\pi \rightarrow \pi^*$  charge transfer transitions found through UV-Visible spectral analysis, some specific electronic and structural properties of this system could produce high NLO responses [37]. The absorption spectrum of PNPIB was recorded using Varian Carry 5E model UV-Vis-NIR spectrometer in the wavelength range 1000 nm - 200 nm by dissolving the PNPIB in DMF. The spectrum is



**Figure 6.** XRPD spectrum of PNPIB single crystal.



**Figure 7.** FTIR Spectrum of PNPIB single crystal.

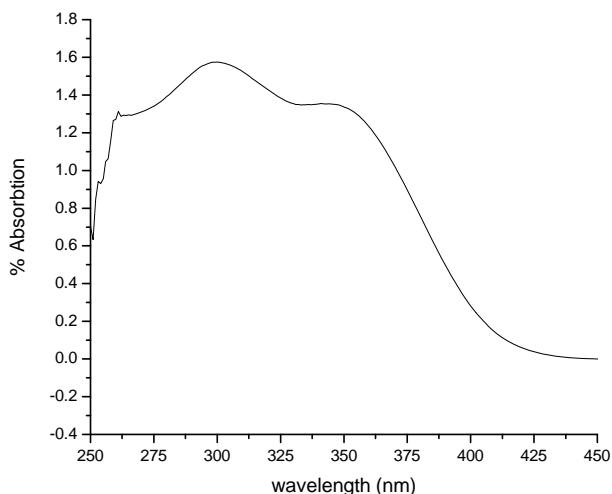
shown in **Figure 8**. It is clear from the spectrum that PNPIB exhibits solvatochromism *i.e.*, its maximum absorption peak show bathochromic behaviour with band shift centred at 275 nm and all the transitions are  $\pi \rightarrow \pi^*$ , generally considered as indicative of molecular first hyperpolarizabilities with non-zero value [36,37]. It is found from the spectrum that the maximum absorption values of  $\pi \rightarrow \pi^*$  transition for PNPIB is all most within 200 - 300 nm.

#### 4.5. $^1\text{H}$ and $^{13}\text{C}$ NMR Spectral Analyses

In order to analyze carbon-hydrogen bonded network,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded using Bruker ARX 300 spectrometer in  $\text{CDCl}_3$  at 300 K.  $^1\text{H}$  and  $^{13}\text{C}$  spectrum of PNPIB single crystals are shown in **Figures 9** and **10** respectively. Signals between 7.2 ppm to 7.5 ppm correspond to aromatic protons attached to imino group. Peak signals between 8 ppm to 8.4 ppm correspond to aromatic protons attached to nitro group. A singlet at 8.6 ppm is attributed to proton attached to nitrogen of imino group. Absence of peak around 3.5 ppm suggests the complete removal of aniline the starting compound. The signals between 148 ppm and 152 ppm are assigned to carbons attached to nitro group and imino group. The absence of signal beyond 160 ppm suggests the complete removal of the starting material benzaldehyde in the crystal. The signals between 120 ppm to 130 ppm correspond to the aromatic carbons.

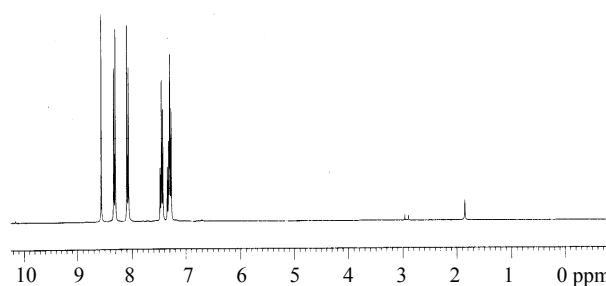
#### 4.6. Dielectric Studies

The dielectric study on PNPIB single crystal was carried out <010> face of PNPIB crystal using the instrument HIOKI 3532-5 LCR HITESTER. A sample of dimension  $2 \times 6 \times 2 \text{ mm}^3$  having silver coating on the opposite faces was placed between the two copper electrodes and thus a

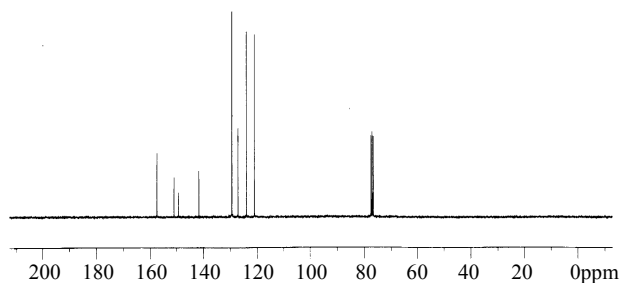


**Figure 8.** UV-Vis-NIR spectrum of PNPIB single crystal.

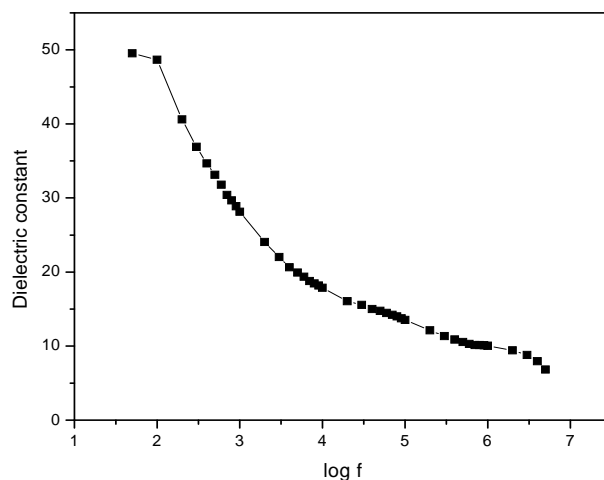
parallel plate capacitor was formed. The capacitance of the sample was measured by varying the frequency from 500 Hz to 5 MHz. **Figure 11** shows the plot of dielectric constant versus applied frequency. The very high values of  $\epsilon_r$  at low frequencies may be due to the presence of space, charge, orientational, electronic and ionic polarization. The low value of  $\epsilon_r$  at higher frequencies may be due to the loss of significance of these polarizations gradually. In accordance with Miller rule, the lower value of dielectric constant is a suitable parameter for the enhancement of NLO applications [38]. The variation of dielectric loss with frequency is shown in **Figure 12**. The characteristic of low dielectric loss at high frequencies for a given sample suggests that the sample possesses an enhanced optical quality with lesser defects [39].



**Figure 9.**  $^1\text{H}$  NMR of PNPIB single crystal.



**Figure 10.**  $^{13}\text{C}$  NMR spectrum of PNPIB single crystal.



**Figure 11.** Dielectric constant of PNPIB single crystal.

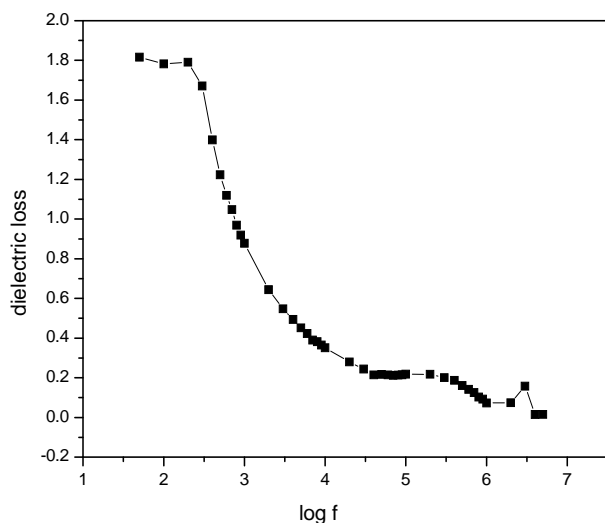


Figure 12. Dielectric loss of PNPIB single crystal.

#### 4.7. NLO Test

A preliminary study on the SHG efficiency of the grown PNPIB crystal was measured by Powder Kurtz method. The measured SHG efficiency was compared with KDP and found that the grown PNPIB crystal has nearly 1.5 times higher NLO efficiency than KDP, which is familiar inorganic NLO material.

#### 5. Conclusion

PNPIB single crystal was synthesized through solvent-free reaction mechanism and grown by both slow solvent evaporation technique and S-R method. The lattice parameters and the noncentrosymmetric space group were confirmed by Single crystal XRD analysis. XRPD analysis ascertained the perfect crystalline arrangement in PNPIB structure. FTIR spectral analysis confirms the presence of functional groups and their mode of vibrations in PNPIB crystal. UV-Vis-NIR spectral analysis has reached the conclusion that PNPIB exhibits solvatochromism and intramolecular  $\pi \rightarrow \pi^*$  charge transfer transition which proves that PNPIB has a good NLO property.  $H^1$  &  $C^{13}$  NMR spectral analysis strongly confirm the carbon-hydrogen network among imino and nitro functional groups. Dielectric measurements were carried over the range 500 Hz - 5 MHz which shows that the dielectric constant decreases slowly with increase in frequency thus PNPIB crystal exhibiting good optical quality.

#### 6. Acknowledgements

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