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Crystal Growth, Spectral and Optical Properties of Quinolinium Single Crystal: 1-Ethyl-2-[2-(4-Nitro-Phenyl)-Vinyl]-Quinolinium Iodide

S. Karthigha¹, C. Krishnamoorthi^{1,a}

¹ – Department of Physics, School of Advanced Sciences, VIT University, Vellore – 632 014, India

a – krishnamoorthi.c@vit.ac.in



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Keywords: organic crystals, crystal growth, powder XRD, FTIR and photoluminescence.

ABSTRACT. N-Ethyl quinolinium derivative of PNQI has been successfully synthesized by Knoevenagel condensation reaction and purified by repeated recrystallization process. The single crystal of title material was grown by slow evaporation technique using methanol as a solvent. The crystallinity of grown crystal was confirmed by powder X-ray diffraction analysis. Fourier Transform Infrared (FTIR) and Nuclear Magnetic Resonance (NMR) spectroscopic studies were performed for the identification of functional groups present in the grown crystal. The linear optical property of the grown crystal was studied by UV-Vis-NIR spectral analysis. The photoluminescence spectrum of title crystal PNQI exhibits prominent emission peak at 567 nm.

Introduction. Synthesis and design of new organic molecules with high nonlinear optical susceptibilities have been investigated due to their potential applications in telecommunications, optical computing, optical data storage, bioimaging and optical information processing [1]. In order to satisfy the day to day technological requirements, new organic nonlinear materials are mandatory which exhibits large nonlinear response compare to inorganic counterparts due to the presence of large polarisable π -conjugated system. Recently it has been found that the ionic organic stilbazolium family crystals are of considerable attention due to their large second and third order optical nonlinearities. In this series, quinolinium derivatives are one of the stilbazolium family and many researchers made an attempt to grow quinolinium derivative single crystals, because it possesses a large number of conjugated π -electrons exhibits high nonlinear optical properties. Generally, the heteroaromatic salt type electron acceptors show high electron withdrawing strength and lead to large nonlinear optical response [2]. Thus these compounds take quinolinium moiety as an electron acceptor and, their crystal phase exhibits attractive characteristics such as high macroscopic nonlinearity, advantageous spatial arrangements, high environmental stability and optical quality [3]. In the present work, we report the material synthesis, growth, spectral and optical properties of PNQI.

Synthesis and Crystal growth. The quinolinium derivative PNQI was synthesized by taking equimolar ratio of 1-ethyl-2-methyl quinolinium iodide and 4-nitro benzaldehyde in methanol solution and piperidine is added as a catalyst. The solution was refluxed for 35mins using round bottomed flask. Further the solution was cooled to room temperature and the red coloured PNQI product was collected and the salt was dried in hot air oven at 100°C for an hour. The final product was purified by repeated recrystallization process using methanol. In order to grow the PNQI single crystals, a saturated solution was prepared at room temperature. After slow evaporation of solvent over a period of 25 days, the spontaneous nucleation was occurred in the supersaturated solution and the single crystals of PNQI have been harvested. The grown crystal is shown in Fig 1.

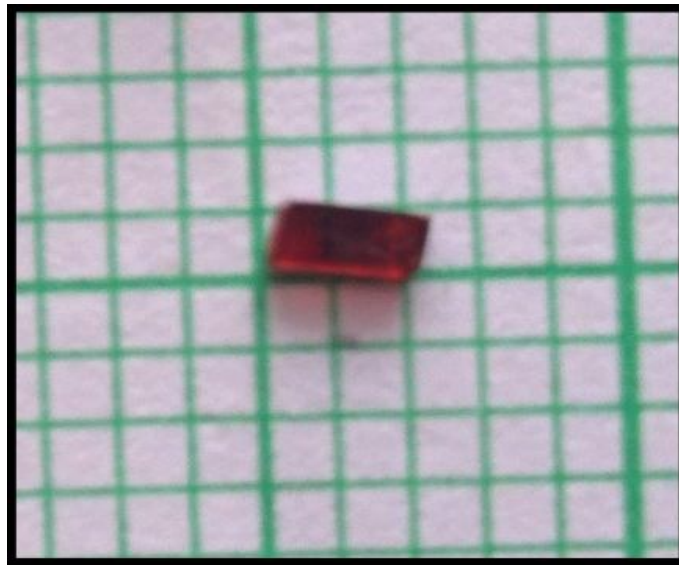


Fig. 1. As grown crystal of PNQI.

Results and Discussion

Powder X-ray diffraction analysis. The fine powder of grown crystals has been characterized by using Bruker X-ray diffractometer with $\text{CuK}\alpha$ radiation (1.5405 \AA) to identify the crystalline nature and reflection planes. The sample was recorded in the range of $10\text{-}50^\circ$ at a scanning rate of 0.02°S^{-1} . Powder XRD pattern was investigated by using powder X software program. Fig 2 shows that the well defined Bragg's peaks at specific 2θ angles confirm good crystalline property of the grown PNQI crystal. The single crystal XRD analysis has carried out using Bruker Kappa APEX II diffractometer with $\text{MoK}\alpha$ radiation of wavelength $\lambda=0.71073 \text{ \AA}$ at room temperature. The title material crystallized in triclinic crystal system with space group P-1 and the lattice parameters were determined to be $a=8.66423(8) \text{ \AA}$, $b=9.9639(10) \text{ \AA}$, $c=10.1012(9) \text{ \AA}$, $\alpha=85.648(5)^\circ$, $\beta=83.440(5)^\circ$, $\gamma=87.782(5)^\circ$.

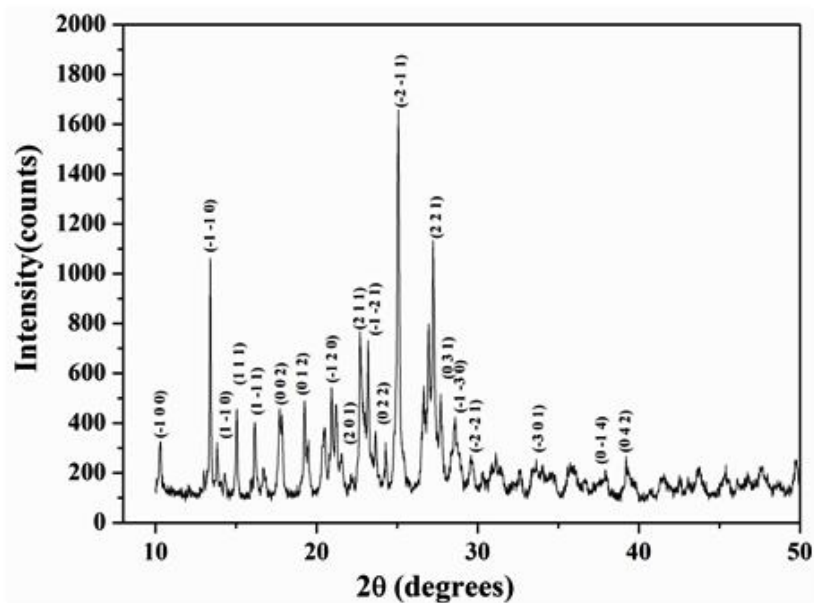


Fig. 2. Indexed powder XRD pattern of PNQI.

Proton NMR. ^1H NMR (400 MHz, DMSO- d_6): δ = 8.063-8.236 (d, H-1'), 8.277-8.319 (d, H-2'), 8.002-8.039 (t, H-6), 8.236-8.255 (t, H-7), 8.443-8.446 (d, H-5), 8.626-8.641 (d, H-8), 8.648-8.664 (d, H-3), 9.200-9.222 (d, H-4), 8.381-8.403 (d, H-2'', 6''), 8.423-8.426 (d, H-3'', 5''), 1.581-1.616 (t, NC_2H_5), 5.207-5.260 (m, NC_2H_5)

Carbon NMR. ^{13}C NMR (400 MHz, DMSO- d_6): δ = 14.82, 39.38, 39.59, 39.80, 40.00, 40.21, 40.42, 40.36, 47.81, 119.67, 122.37, 123.32, 124.62, 129.26, 130, 130.61, 131.03, 136.11, 138.63, 141.40, 144.69, 145.76, 148.86, 155.25.

Fourier Transform Infrared Spectral analysis. The characteristics vibrational modes and functional groups present in PNQI were analysed by FTIR spectroscopic technique. The spectrum was recorded in the range of 400-4000 cm^{-1} using an SHIMADZU IRAFFINITY spectrometer. From Fig. 3 it was observed that the peak appears at 3057.16 and 3016.67 cm^{-1} are ascribed to aromatic C-H stretching vibrations. The alkyl C-H stretching mode is observed at 2939.52 cm^{-1} . The absorption peak at 1570.16 cm^{-1} is assigned to olefinic C=C stretching vibration and the peaks that were observed at 1734.01 and 1598.99 cm^{-1} are due to the aromatic C=C stretching vibrations. The peak observed at 1078 cm^{-1} is corresponds to the olefinic =C-H bond. Absorption peaks observed around 1440.83 and 1516.06 cm^{-1} corresponds to the symmetric and asymmetric stretching of nitro (NO_2) group, which confirms the formation of the title material. Thus all the functional groups present in the crystal structure of PNQI has been confirmed.

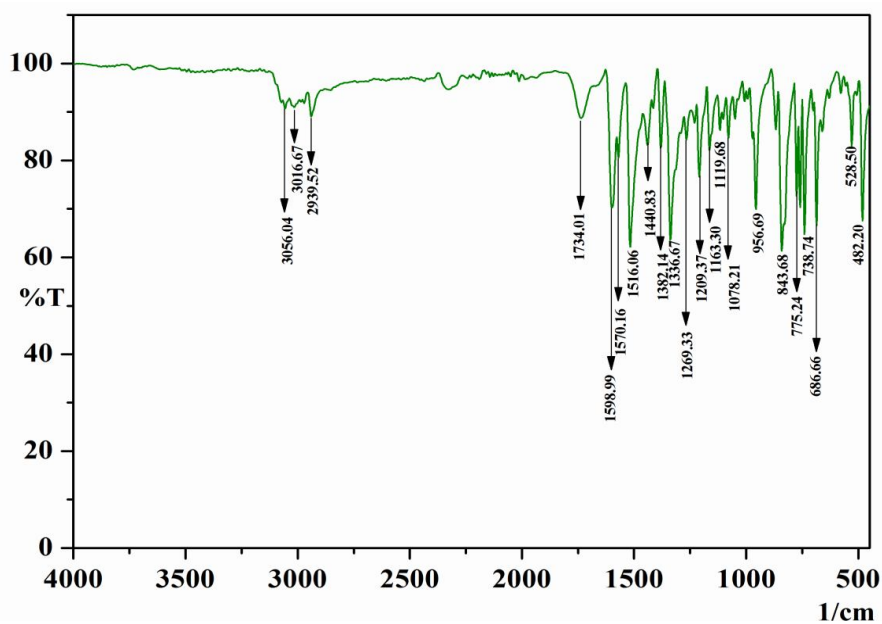


Fig. 3. FTIR spectrum of PNQI.

UV-Vis-NIR spectral analysis. The absorption spectrum of PNQI was recorded for the wavelength range of 200- 1100 nm. The recorded spectrum is shown in Fig. 4. The optical transparency is high in near IR region of the spectrum and there is no significant absorption between 506-1100 nm. The cut-off wavelength of grown crystal is 506 nm, which is assigned to π - π^* transition contributed by extended conjugation in the stilbazolium chromophore.

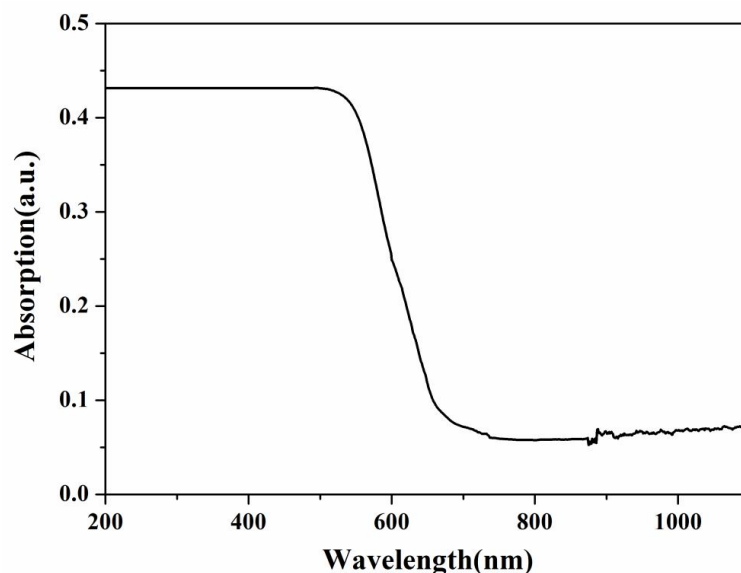


Fig. 4. Absorption spectrum of PNQI.

Photoluminescence Analysis. Photoluminescence studies are highly preferred to detect the lower concentrations of defects. Since the impurity on absorption of light gives rise to the bound excited state, which it returns to its ground state abiding in the analysis of colour centre creation mechanism [5]. The emission spectrum of PNQI was recorded using Jobin-Yvon spectrophotometer at room temperature and 450 W high pressure xenon lamp was used as an excitation source. The photoluminescence spectrum was measured in the range of 550- 580 nm and the sample was excited at 480 nm. The recorded luminescence spectrum of PNQI was shown in Fig. 5. From the emission spectrum, the broad emission peak observed at 567 nm which corresponds to the mobility of π electrons between p-nitro anion and the quinolinium cation through stilbazolium chromophore. Thus, this indicates the band appeared at 567 nm owing to the emission of green radiation and is high importance for opto electronic and solid state lighting applications [4]. The band gap of energy was calculated using the formula, $E_g = hc/\lambda_e$. The band gap energy calculated is about 2.18 eV for PNQI crystal.

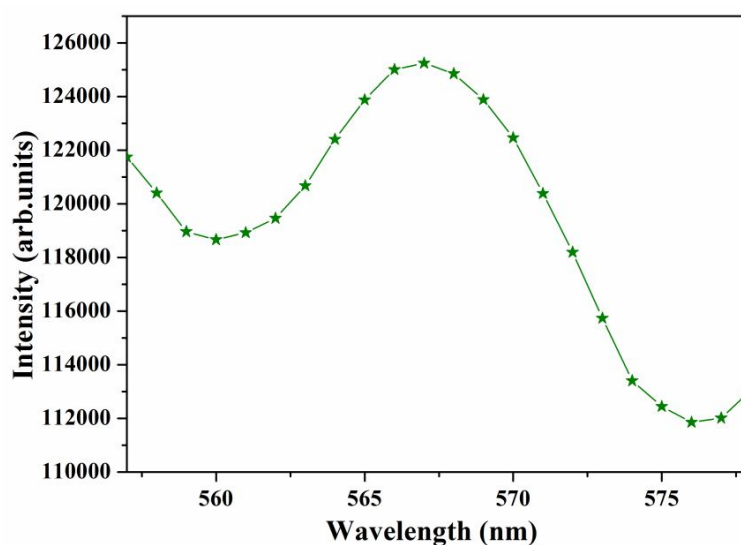


Fig.5. Emission spectrum of PNQI.

Summary. An organic single crystal of PNQI was grown by slow evaporation method. Powder XRD reveals the crystalline nature of grown crystal and Single crystal X-ray diffraction study confirms that the PNQI crystal belongs to triclinic crystal system. The molecular formation of title material was confirmed by using FTIR and NMR spectroscopic studies. The UV-Vis spectroscopy study shows that the crystal cut-off wavelength at 506 nm and the emission behaviour of PNQI was confirmed by Photoluminescence analysis.

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