Growth, Thermal, Optical Limiting and Computational Studies of Organic Single Crystal

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Abstract. 8-hydroxyquinolinium 2-chloro-5-nitrobenzoate dihydrate (8HQ2C5N) single crystal was grown by slow cooling solution growth technique using ethanol: water (1:1) mixed solvent. Powder X-ray diffraction was utilized to compute the unit cell parameters and crystallinity of the crystal. A strong $\pi \rightarrow \pi^*$ absorption was observed at 239 nm, due to protonation of hydrogen from 2-chloro-5-nitrobenzoic acid to 8-hydroxyquinoline. Also, a weak absorption due to $n \rightarrow \pi^*$ located at 282 nm which was due to N=O and C=O of the heteromolecule chromophores of delocalized lone pair electron. The thermal stability was analyzed through the differential scanning calorimetric (DSC) study. Optical limiting property of crystal was studied and the crystal is suitable for optical limiting applications. The electronic properties, such as HOMO and LUMO energies, were calculated by Time-Dependent DFT approach.

INTRODUCTION

The crystallization process of organic and inorganic materials plays an important role in pure and applied science. Organic materials have shown very high nonlinearities, large optical susceptibilities, frequency conversion and ultrafast response times. The basic requirement of π bond system of organic nonlinear optical (NLO) materials is due to the delocalization of electronic charge distribution guidance to a high mobility of the electron density [1]. Functioning of both ends of the π-bond system with suitable electron-donor and -acceptor groups can enrich the asymmetric electronic distribution in either ground or excited states or both ground and excited states, leading to an increased optical nonlinearity [2]. The optical nonlinearity of 8-hydroxyquinoline (8HQ) can be notably refined on raising the accepting tendency of the pyridine and/or raising the donating tendency of the benzene ring. 8HQ accept proton when reacts with acids and forms charge transfer compounds. The crystallographic properties of 8HQ were reported by Roychowdhury et al [3]. The acid base interaction of 8HQ and 2-chloro-5-nitrobenzoic acid resulted a protonated compound of 8HQ2C5N. The crystal structure of the title compound was already reported [4]. In this paper we have report the optical, thermal and optical limiting properties of grown single crystal.

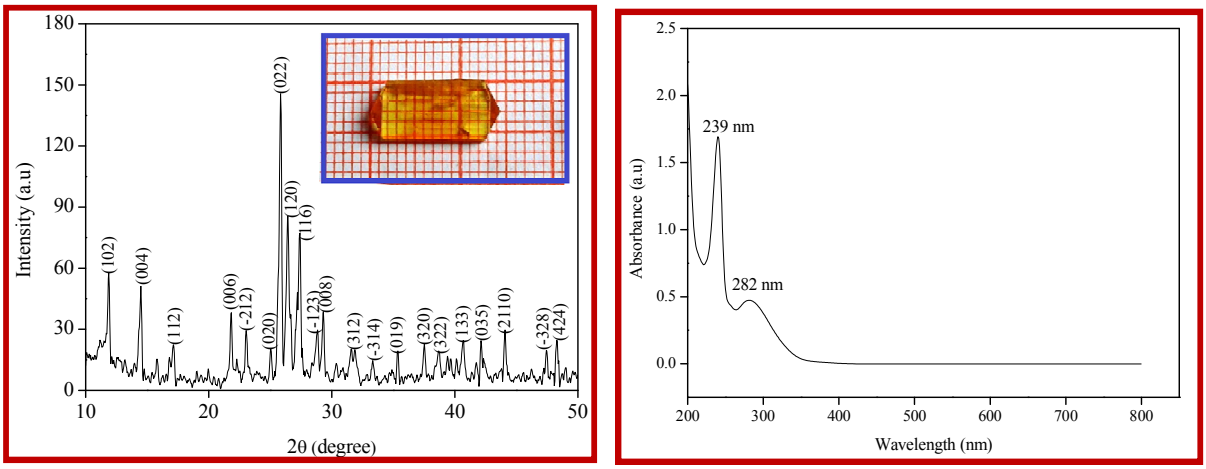
MATERIAL SYNTHESIS

8HQ2C5N was synthesized by taking 8-hydroxyquinoline and 2-chloro-5-nitrobenzoic acid in the equimolar ratio. The calculated amount of 2-chloro-5-nitrobenzoic acid was dissolved in ethanol-water, and the appropriate amount of 8HQ was gradually added into the solution while adding this into the solution yellow precipitate was obtained. Using the recrystallized salt of 8HQ2C5N and ethanol-water (1:1) solvent, the saturated solution was prepared and stirred continuously about 6 h to ensure homogeneous mixture throughout the volume of the solution. Then the solution was filtered by using an A1 filter paper to remove the impurities. The tightly sealed beaker was kept in a constant temperature bath, which was maintained at 45ºC with an accuracy of ±0.01ºC. Then, the solution was allowed for slow cooling by following a cooling rate of 0.5ºC per day. The solution yielded good quality crystals with a size of about $14 \times 7 \times 5$ mm^3 during the growth period of 30 days and the photograph of the as-grown crystal is shown in Fig.1 (a) (inset).

RESULT AND DISCUSSION

Powder X-ray Diffraction Analysis

The SEIFERT X-ray diffractometer with Cu $K\alpha_1$ radiation (λ = 1.5406 Å) with 45 kW power and 20 mA current was used to find the crystallinity of the compound. The powder X-ray diffraction pattern is illustrated in Fig.1 (a). It exhibits sharp and well resolved peaks which indicate the quality and crystalline nature of the crystal. The 8HQ2C5N crystal belongs to the monoclinic crystal system with the space group $P2_1/c$. The lattice parameters values are calculated from XRDA software. The calculated values are, a = 9.6546 ± 0.016 Å, b = 7.16373 ± 0.016 Å, c = 24.3606 ± 0.038 Å and are in good agreement with that obtained from single crystal data [4].



(a) (b)

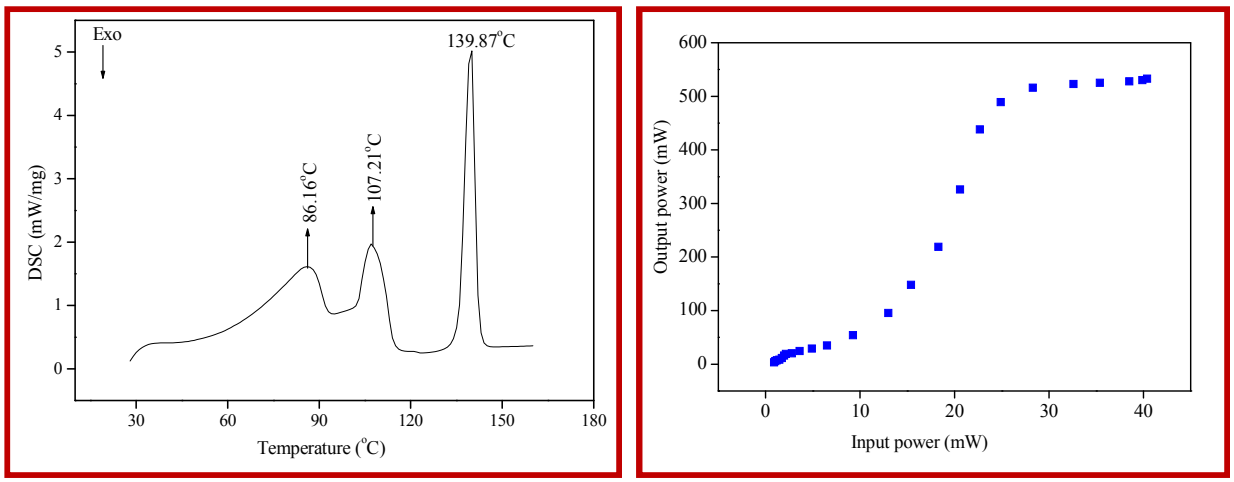
FIGURE 1. (a) Powder X-ray diffraction pattern (b) Optical absorption spectrum of 8HQ2C5N crystal.

Optical Studies

UV-visible techniques are helpful in the investigation of NLO materials making it possible to ensure both NLO responses and spectroscopic absorption in the appropriate wavelength. The absorption spectrum of 8HQ2C5N using ethanol-water as a solvent it was recorded by Specord 210 plus UV-visible Spectrophotometer in the wavelength region of 190-900 nm and is shown in Fig. 1(b). The 8HQ2C5N functional groups influence the conjugated π electron systems, causing the absorption peaks to appear at longer wavelengths. With larger conjugated π electron systems, the absorption peak wavelengths tend to be shifted toward the long wavelength region. A strong $\pi \rightarrow \pi^*$ absorption observed at 239 nm, due to protonation of hydrogen from 2-chloro-5-nitrobenzoic acid to 8-hydroxyquinoline. Then $n \rightarrow \pi^*$ absorption located at 282 nm is weak, due to N=O and C=O of the heteromolecule chromophores of delocalized lone pair electron. The colour of organic compounds, then, is turned more strongly by the size of the conjugated system. The absence of absorption in the region between 364 and 900 nm declared that the crystal could be exploited for optical applications.

DSC Analysis

The NETZSCH DSC 204 instrument was used to record DSC of the 8HQ2C5N powder compound in nitrogen atmosphere at the heating rate of 20ºC/min. It is quite useful, since they provide reliable information on the physio-chemical parameters, characterizing the processes of transformation of solids or participation of solid in process of isothermal or non-isothermal heating. The DSC trace of 8HQ2C5N crystalline powder is shown in Fig.2 (a). There are three endothermic peaks observed at 86.16, 107.21 and 139.87ºC. The first two peaks are attributed to the melting point and the removal of water. The third peak indicates the decomposition of 8HQ2C5N compound. The sharp peak indicates the crystalline nature of the sample and the crystal is stable up to 86.16ºC. Hence the grown crystal can be used for NLO applications.



(a) (b)

FIGURE 2. (a) DSC trace and (b) Optical limiting curve of 8HQ2C5N single crystal.

Optical Limiting Studies

Optical limiting is a NLO process in which the transmitted intensity is raises in lower intensities and it remains constant in higher intensity which can be utilized to shield eyes from the intensity of laser beams which is very high. This measurement is executed by placing the crystal at post focus position and measuring the transmitted power over the aperture for different incident laser powers and it is based on aperture limited geometry. Optical limiting plot of title crystal is represented in Fig. 2(b). The defocusing effect appears at a certain threshold value, which results in a more cross section area and reduces the relative intensity of the beam passing the aperture. Optical limiting study reveals at low power region output power increases with an increase in input power and saturates from the threshold of 28.1 mW.

DFT Analysis

The structure is optimized using IEFPCM SCRF and TD-DFT (Time dependent-Density Functional Theory) calculations were made for the same optimized structure. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are named as frontier molecular orbital. The energies of frontier orbitals were calculated using B3YLP/6-311G (d,p) level. HOMO is an electron donor while LUMO is an acceptor that represents the ability to obtain an electron. The HOMO and LUMO orbital of 8HQ2C5N molecule is shown in Fig.3 The calculated energy values of the HOMO and LUMO are -0.33808 and -0.23857 eV respectively. The energy gap between HOMO and LUMO indicates the molecular chemical stability. The energy of the HOMO is directly related to the ionization potential, LUMO energy is directly related to electron affinity. HOMO-LUMO energy gap = 0.09951 eV. This energy gap characterizes the molecular stability. This results shows that the title molecule have small HOMO-LUMO energy gap. The smaller value of HOMO-LUMO energy gap which explains the fact that eventual charge transfer interaction is taking place within the molecule [5]. Electronic excitation energies and oscillator strength were calculated by time-dependent density functional theory calculation method. The electron transition from the ground state to these states makes a small contribution to hyperpolarizability. In 1st state: It mainly arises from the excitation from HOMO+0 → LUMO+1. Charge transfer happens from the HOMO orbital composed 8HQ cation and carboxyl part to 2C5N anion. The oscillator strength of this transition is 0.0753 and can be described as $\pi \rightarrow \pi^*$ state [6]. In 2nd state: Excitation of charges happens between frontier molecular orbital (HOMO-8 → LUMO+0) is due to the N=O in the 2-chloro-5-nitrobenzoic acid. The oscillator strength of this transition is 0.0001 and can be explained as $n \rightarrow \pi^*$ state.

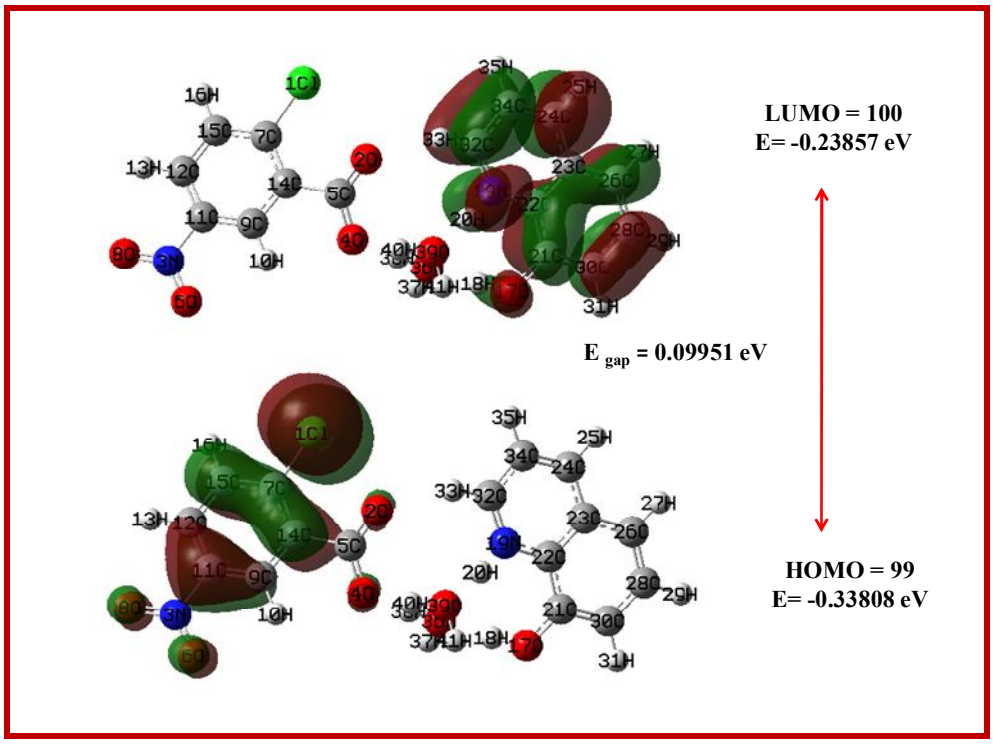


FIGURE 3. HOMO and LUMO diagram for 8HQ2C5N crystal

CONCLUSIONS

The 8HQ2C5N single crystal was grown by the slow cooling method. The unit cell parameter and crystalline nature of the crystal were determined by powder X-ray diffraction analysis. The UV-visible absorption study suggests the suitability of crystal for various optical applications. The differential scanning calorimeteric anlalysis reveals that the 8HQ2C5N crystal is stable upto 86.16ºC. Optical limiting study shows the crystal is desirable for optoelectronic and device applications. HOMO-LUMO analysis has been computed using Time-Dependent model and the energy gap is calculated as 0.09951 eV.

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