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Crucial role of molecular planarity on the second order nonlinear optical property of pyridine based chalcone single crystals

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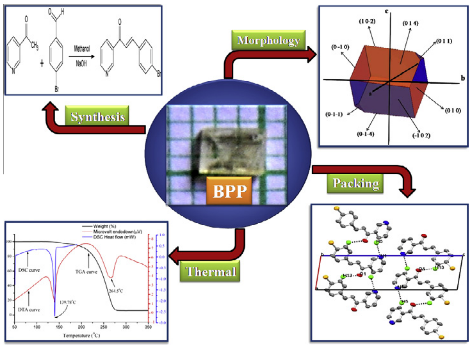
HIGHLIGHTS

- Efficient NLO single crystals are grown by slow evaporation solution growth technique.
- Scanning electron microscope image reveals that the crystal has smooth surface morphology.
- Crystal melts at 139 °C and decomposes at 264 °C.
- Molecular dipoles are stacked in zigzag head–tail fashion in the crystal structure consolidated by hydrogen bonds.
- The pyridine ring plays a significant role in forming enantiomorphic crystal system.

GRAPHICAL ABSTRACT



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ABSTRACT

An efficient nonlinear optical material 2*E*-3-(4-bromophenyl)-1-(pyridin-3-yl) prop-2-en-1-one (BPP) was synthesized and single crystals were grown using slow evaporation solution growth technique at room temperature. Grown crystal had prismatic morphology and its structure was confirmed by various spectroscopic studies, elemental analysis, and single crystal X-ray diffraction (XRD) technique. The single crystal XRD of the crystal showed that BPP crystallizes in monoclinic system with noncentrosymmetric space group $P2_1$ and the cell parameters are $a = 5.6428(7)$ Å, $b = 3.8637(6)$ Å, $c = 26.411(2)$ Å, $\beta = 97.568(11)$ deg and $v = 575.82(12)$ Å^3. The UV–Visible spectrum reveals that the crystal is optically transparent and has high optical energy band gap of 3.1 eV. The powder second harmonic generation efficiency (SHG) of BPP is 6.8 times that of KDP. From thermal analysis it is found that the crystal melts at 139 °C and decomposes at 264 °C. High optical transparency down to blue region, higher powder SHG efficiency and better thermal stability than that of urea makes this chalcone derivative a promising candidate for SHG applications. Furthermore, effect of molecular planarity on SHG efficiency and role of pyridine ring adjacent to carbonyl group in forming noncentrosymmetric crystal systems of chalcone family is also discussed.

Introduction

The demonstration of second harmonics in quartz single crystal by Franken et al. led to the development of an exhilarating field of modern times known as nonlinear optics (NLO) which has plethora of applications in the field of opto-electronics [1–3]. The most desirable properties for a material to be the best NLO material are high power conversion efficiency, large transparency extending down to UV region, high melting point, high mechanical stability, high chemical inertness, high laser damage threshold, phase matching, etc. [4,5]. Among the various classes of materials inves-

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tigated for NLO properties, organic materials received unique consideration. The optical nonlinear behavior in this class of materials is electronic in origin and can be tuned through structural modifications [6]. These are characterized by an extremely extended π-conjugated chain with strong electron acceptor–donor pairs at the ends (D–π–A) [4,7]. Organic NLO materials are very often formed by hydrogen bonds and Van der Waals forces and hence posses high degree of delocalization. Due to the overlap of π orbits, delocalized electronic charge distribution leads to high mobility of the electron density. The optical nonlinearity can be increased by functionalizing the ends of the π bond system with apt electron donor and acceptor groups [8]. Hence, the search for new NLO materials had never ceased.

Chalcone derivatives are an interesting type of organic NLO materials which can be tuned to match the requirements. In these systems, two aromatic rings have to be substituted with suitable electron donor or acceptor groups like —OCH_3, —SCH_3, —Cl, —Br, etc. to increase the asymmetric charge distribution in either or both ground state and excited states, giving rise to an enhanced optical nonlinearity [9,10]. The substitution of electron acceptors/donors on either of the benzene rings of chalcones significantly influences the noncentrosymmetric crystal packing structures requisite for second harmonic generation (SHG) [11]. Thus, chalcones can be considered as cross-conjugated molecules that possess two independent hyperpolarizable parts to have a two-dimensional β character [12]. Recently several chalcone derivatives have been reported where the phenyl moiety adjacent to carbonyl group was replaced with pyridine moiety [13–19]. The results show that these derivatives exhibit good second order NLO response. Among these, the chloro substituted chalcone [17] showed a SHG efficiency of 3.68 times that of urea and methoxy group substituted chalcone MPP [13] showed a SHG efficiency of 4.7 times that of urea. This high SHG response is attributed to the donor group substituted at *para* position of the phenylene moiety and the zigzag head-to-tail alignment of molecular dipoles in the crystal structure. This shows that a *para* substituent on the phenyl ring and the zigzag head-to-tail alignment of molecular dipoles connected through strong intermolecular hydrogen bonds in the crystal structure is necessary for enhancing the SHG activity of organic materials [12,20]. It is well known that for a material to have highly efficient NLO properties, the constituting molecules must exhibit large molecular hyperpolarizabilities (β). Further, β increases with the increase in the electron donating strength of the substituent [21]. The electronegativity of Br group is 2.8 (Pauling value) [22] and hence its electron donating ability is greater than that of chloro and methoxy groups. Also it is reported that the Br substitution in chalcones results in non-centrosymmetric crystal structure, required for a crystal to exhibit second order optical nonlinearity [23]. With the anticipation of an efficient NLO material, a pyridine based bromo substituted donor–π–acceptor (D–π–A) type chalcone derivative was designed. The present article describes the synthesis, crystal growth and characterization of a nonlinear optical material, 2*E*-3-(4-bromophenyl)-1-(pyridin-3-yl) prop-2-en-1-one (BPP).

Experimental procedure

Material synthesis and single crystal growth

BPP was synthesized by the Claisen–Schmidt condensation reaction [24]. A mixture of Analytical Reagent grade chemicals, 3-acetyl pyridine (0.01 mol) and 4-bromobenzaldehyde (0.01 m ol) in methanol (50 ml) was prepared without further purification. Aqueous solution of sodium hydroxide (5 ml, 20%) was then added drop wise, and the mixture is stirred for 2 h. The temperature of the solution was maintained within the range of 26–30 °C throughout the stirring process. The contents of the flask were poured into a beaker containing ice-cold water and kept aside for 24 h. The crude product was then collected by filtration, washed with excess of water and dried. The crude product was used for the single crystal growth without further purification. The synthetic scheme of the product is shown in Fig. 1.

Single crystals of BPP were grown by slow evaporation solution growth technique using N,N-dimethyl formamide (DMF) as the solvent at room temperature. A saturated growth solution was prepared by dissolving the synthesized compound in DMF in a 100 ml beaker at room temperature; the solution was filtered to remove suspended particles. The solvent was allowed to evaporate slowly by covering the beaker with a polythene sheet with few pin holes in it. Single crystals of BPP were harvested from the growth solution after 45–50 days. Good quality single crystals were selected for further study. A photograph of the grown crystals is shown in Fig. 2a. The morphology of the single crystal of BPP was simulated using the software WinXMorph [25,26]. Data obtained from the single crystal XRD study were used as the input to index the faces in the crystal and is shown in Fig. 2b. The crystal has a higher growth rate along crystallographic b-axis compared to other two axes which results in the elongation of the crystal along this direction. Morphology of BPP may change if it is crystallized by changing the solvent.

Characterization methods

In order to establish that the material (BPP) obtained is certainly that of the desired compound, energy dispersive X-ray analysis (EDAX) was carried out on the sample. The grown crystal was subjected to EDAX analysis using JEOL JSM-6380LA analytical scanning electron microscope (SEM) system. The recorded spectrum of BPP is shown in Fig. 3. The peaks in the EDAX spectrum confirm the presence of C, N, O and Br in the compound. The EDAX elemental analysis confirms the formation of the compound.

The surface morphology of the BPP single crystal was studied by scanning electron microscopy (SEM). A JOEL JSM-6380LA analytical scanning electron microscope was used for the analysis. SEM was operated at 20 kV and probe current was 1 nA and the sample was kept in high vacuum. Due to the non-conducting behavior of the organic materials, gold coating is done by sputtering technique before subjecting the surface of BPP crystal to electron beam.

The FT-Raman and FT-IR spectral analysis of BPP was carried out to identify the presence of functional groups and their vibrational modes. A BRUKER RFS 27, Stand alone FT-Raman Spectrometer, having spectral resolution of 2 cm^{-1} with an exciting wavelength of 1064 nm from an Nd: YAG laser source was used to record the FT-Raman spectrum. The FT-IR spectrum was obtained by mixing the compound with KBr pellets. The spectrum was recorded between 500 cm^{-1} and 3500 cm^{-1} by a Thermo Nicolet, Avatar 370 FTIR spectrometer outfitted with KBr beam splitter and a DTGS detector, with a spectral resolution of 4 cm^{-1}.

A Bruker Avance III FT-NMR spectrometer was used to record the ^1H NMR spectrum of BPP with CDCl3 as the solvent and tetramethylsilane (TMS) as the internal standard. The grown crystal was subjected to single-crystal X-ray diffraction (XRD) studies. A Bruker SMART APEX diffractometer with CCD area detector using graphite monochromated MoKα radiation of wavelength 0.71073 Å was used to solve the three dimensional structure. Crystal data were collected with a scan width of 1°. The crystal structures were solved by direct method and refined by full matrix least squares method using SHELXL-97 [27] in the WinGx package suite [28] with isotropic temperature factors for all the atoms. For molecular graphics X-seed [29] and Mercury [30] software was used. A transmission spectrum is very important for any NLO materials as a non linear material can be used for practical applications such as