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Synthesis, growth, structure, spectral, thermal and first-order molecular hyperpolarizability of benzophenone-2-furoyl hydrazone single crystal

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ABSTRACT

Single crystals of benzophenone-2-furoyl hydrazone are grown by slow evaporation solution growth technique from ethanol at room temperature. It belongs to monoclinic system with the space group $P2_1/c$ and the cell parameters are, $a = 6.1631(3)$ Å, $b = 13.1397(8)$ Å, $c = 18.0030(11)$ Å and $V = 1457.72(14)$ Å^3. NMR spectral studies reveal the structure and powder XRD indicates the crystallinity of the specimen. The characteristic functional groups present in the molecule are confirmed by Fourier transform infrared spectroscopy. The crystals are transparent in the visible region having a lower optical cut-off at ~406 nm and the band gap energies are estimated by the application of Kubelka–Munk algorithm. Thermal analysis by TG/DTA indicates the stability of the material. The scanning electron microscopy studies reveal the surface morphology of the as-grown crystal. Theoretical calculations were performed using Hartree–Fock method with 6-31G(d,p) as the basis set for to derive the optimized geometry, dipole moment and first-order molecular hyperpolarizability (β) values.

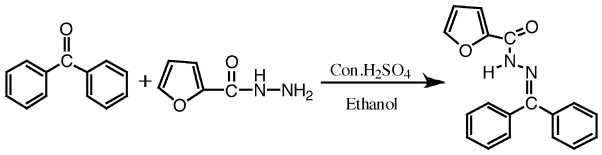
1. Introduction

Hydrazones and their metal compounds are of current interest for their physico-chemical properties and applications in many important chemical processes that include sensors, non-linear optics, medicine and others [1–6]. They are versatile class of compounds with several applications due to their chelating behavior. Used in analytical chemistry as selective metal extracting agents as well as in spectroscopic determination of certain transition metals [7]. Hydrazone derivatives are found to possess antimicrobial [8,9], anti-tubercular [10], anti-convulsant [11] and anti-inflammatory activities [12–14]. The growth, structure and characterization of benzophenone-2-furoyl hydrazone (BPFH) have not been reported so far to the best of our knowledge. In the present study, we report the synthesis, growth, structure, dipole moment, hyperpolarizability and characterization of a new organic crystal BPFH.

2. Experimental

2.1. Synthesis and crystal growth

Benzophenone-2-furoyl hydrazone was synthesized by mixing stoichiometric amounts of benzophenone and furan-2-carbohydrazide in the molar ratio of 1:1. The reactants were dissolved in ethanolic medium with catalytic amount of concentrated sulphuric acid and refluxed for 3–5 h to form aryl acid hydrazone. The completion of the reaction was confirmed by thin layer chromatography. The reaction mixture was then poured in ice cold water and the precipitate obtained was filtered and dried. Purity of the compound was improved by recrystallization process using ethanol as a solvent.



BPFH single crystals were grown using slow evaporation solution growth technique at room temperature. A saturated solution in ethanol was prepared and the solution was stirred for 2–3 h

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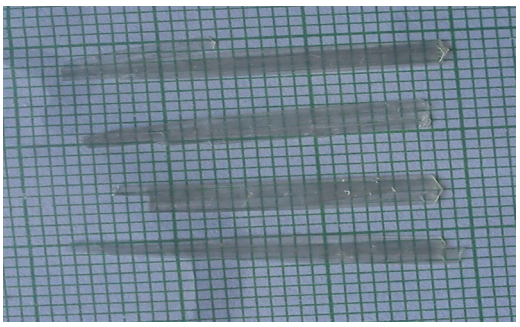

Fig. 1. Photographs of as-grown BPFH crystals.

at room temperature to obtain a homogenous solution. A beaker containing BPFH solution was tightly covered with a thin polythene sheet to control the evaporation rate of the solvent and kept undisturbed in a dust free environment. Numerous tiny crystals were formed at the bottom of the container due to spontaneous nucleation. Needle-like crystals of BPFH were harvested after 7–9 days and the photographs of as-grown crystals are shown in Fig. 1.

3. Results and discussion

3.1. FT-IR

FT-IR spectrum was recorded for BPFH using an AVATAR 330 FT-IR by KBr pellet technique in the spectral range of 400–4000 cm^{-1} (Fig. 2). The absorption band at 1687 cm^{-1} is due to C=O stretching vibration. The absorption bands around 3351 and 3435 cm^{-1} are due to NH stretching frequency. The C=N stretching frequency appeared as sharp intensity band around 1627 cm^{-1}. An absorption band in the region 3000–3100 cm^{-1} is due to C—H stretching frequency of aromatic ring. The band at 1513 cm^{-1} is due to C=C stretching frequency of aromatic region. The absorption band around 1123 cm^{-1} is due to O=C—N stretching vibrations. The peaks around 1119 and 766 cm^{-1} are due to N—N and aromatic C—H out of plane bending vibrations, respectively.

3.2. Optical studies

The optical transmission spectrum of BPFH was recorded using 5E UV–vis spectrophotometer. The optical transmission spectrum shows that the absorption is minimum in the visible region and cut-off wavelength is ~406 nm. The band gap energy E_g is determined using the measurement of $[F(R)h\nu]$ as a function of $h\nu$ where $F(R)$ is Kubelka–Munk function [15]. The indirect band gap energy can be obtained from the intercept of the resulting straight lines with the energy axis at $[F(R)h\nu]^{1/2} = 0$ and the band gap energy of the specimen is deduced as 3.30 eV is shown in Fig. 3.

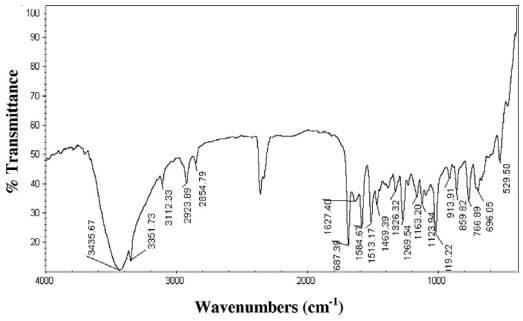

Fig. 2. FT-IR spectrum of BPFH.

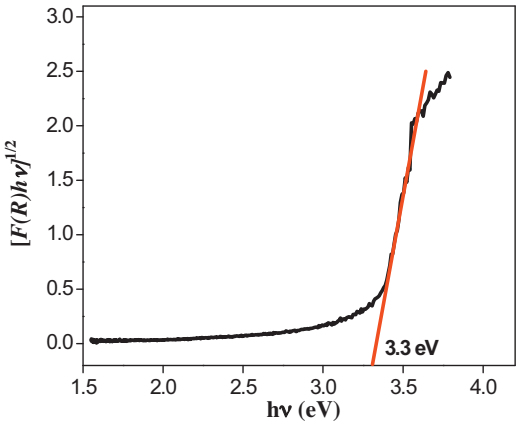

Fig. 3. Tauc plot of BPFH.

3.3. Thermal analysis

TG/DTA analysis of BPFH was carried out using NETZSCH STA 449F3 thermal analyzer in nitrogen atmosphere (Fig. 4). In the TG curve trace there is a single major weight loss starting at ~300 °C. The decomposition is completed at ~370 °C, leaving no residue and it could be due to decomposition of BPFH. A sharp endothermic peak at ~185 °C in DTA is due to the melting point of the material and confirmed by using Sigma instrument melting point apparatus (181–183 °C). The sharpness of the peak shows good degree of crystallinity.

3.4. Powder XRD

As-grown BPFH crystal was finely powdered and subjected to powder XRD analysis using a Philips X'pert pro Triple-axis X-ray diffractometer at room temperature using a wavelength of 1.540 Å and a step size of 0.008°. The samples were examined with Cu K_α radiation in 2θ range of 10–40°. Fig. 5 shows the indexed powder XRD pattern and the XRD profiles show that the sample is of single phase without detectable impurity. The well defined Bragg's peaks at specific 2θ angles show high crystallinity of the material.

3.5. SEM

The surface morphology of the as-grown crystal was observed by using a JEOL JSM 5610 LV scanning electron microscope with a resolution of 3.0 nm and accelerating voltage 15 kV. The SEM micrographs with different magnifications of the as-grown BPFH are shown in Fig. 6. Leaf surface morphology is observed on the surface with imperfections.

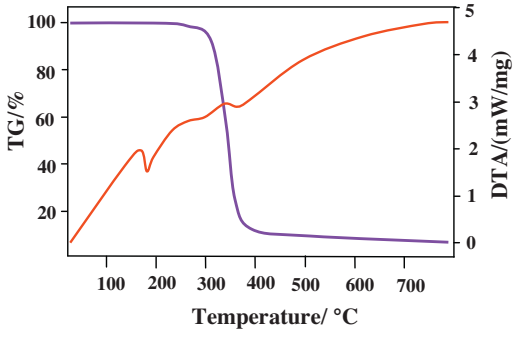

Fig. 4. TG/DTA curve of BPFH.