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Growth, spectral, optical, laser damage threshold and DFT investigations on 2-amino 4-methyl pyridinium 4-methoxy benzoate (2A4MP4MB): A potential organic third order nonlinear optical material for optoelectronic applications

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ABSTRACT

In present investigation, single crystals of organic charge transfer complex, 2-amino-4-methyl pyridinium-4-methoxy benzoate (2A4MP4MB) was grown by controlled slow evaporation solution growth technique using methanol as a solvent at room temperature. Single crystal XRD analysis confirmed the crystal system and lattice parameters of 2A4MP4MB. The crystalline nature, presence of various vibrational modes and other chemical bonds in the compound have been recognized and confirmed by powder X-ray diffraction, FT-IR and FT-Raman spectroscopic techniques respectively. The presence of various proton and carbon positions in title compound was confirmed using ^{1}H NMR and ^{13}C NMR spectral studies. The wide optical operating window and cut-off wavelength were identified and band gap value of the title compound was calculated using UV-vis-NIR study. The specific heat capacity (c_p) values of the title compound, 1.712 J $g^{-1}\cdot K^{-1}$ at 300 K and 13.6 J g^{-1} K^{-1} at 433 K (melting point) were measured using Modulated Differential Scanning Calorimetric studies (MDSC). From Z-scan study, nonlinear refractive index (n_2), nonlinear absorption (β) and third order nonlinear susceptibility ($\chi^{(3)}$) values were determined. The self-defocusing effect and saturable absorption behavior of the material were utilized to exhibit the optical limiting action at $\lambda = 532$ nm by employing the same continuous wave (cw) Nd: YAG laser source. The laser damage threshold (LDT) study of title compound was carried out using Nd: YAG laser of 532 nm wavelength. The Vickers' micro hardness test was carried out at room temperature and obtained results were investigated using classical Meyer's law. In addition, DFT calculations were carried out for the first time for this compound. These characterization studies performed on the title compound planned to probe the valuable and safe region of optical, thermal and mechanical properties to improve efficacy of 2A4MP4MB single crystals in optoelectronic device applications.

1. Introduction

In recent past, many new organic crystals have been encountered based on the predictive molecular engineering approach and have been depicted to have potential applications in the fields of science and technology [1]. In recent years, research in the field of NLO single crystal design and development with advanced efficacy has been focused due to extensive range of applications like generation of higher harmonic frequencies, electro optic modulation, self-focusing, frequency mixing, optical limiting, optical rectification, parametric oscillation, optical switching and terahertz wave generation etc [2–4]. The development of highly efficient nonlinear optical materials for opto-electronic applications, such as high speed information processing, optical communication, optical data storage has been the subject to intense research activity throughout the world. Organic nonlinear optical (NLO) single crystals acquire superior second and third order NLO properties compared to inorganic crystals, owing to advantages involve effortless tailoring of molecular arrangements, higher β values, low dielectric constant, multifunctional substitution, higher

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resistance to optical damage and maneuverability for certain device applications [5–9]. Molecular flexibility of organic materials is an added advantage to enhance their nonlinear optical properties in a desired manner [9]. In organic materials, the presence of various organic sub-networks induces noncentrosymmetry in the bulk which enhance thermal and mechanical stabilities through hydrogen bonding interactions [10–12]. An organic molecule with significant nonlinear optical activity generally consists of π electron conjugated moiety substituted by an electron donor group on one end of the conjugated structure and an electron acceptor group on the other end [13]. The conjugated π electron moiety provides a pathway for the entire length of conjugation under the perturbation of an external field. The donor and acceptor groups provide the ground state charge asymmetry of the molecule, which is required for second order and third order nonlinearity [7,8]. In supramolecular architecture, hydrogen bonding arrangements formed between pyridine and carboxylic acid derivatives has been confirmed as an important organizing force [14,15].

2-amino-4-methyl-pyridine (2A4MP) is a pyridine based complex possessed nitrogen (amino group), which readily accepts proton and donating electrons in the direction of assembly of donor-acceptor (D-A) system. Also, previously these effects have been studied in different kinds of organic acids like carboxylic, benzoic and other acid derivatives. In addition, the nitrogen atom attached with pyridine ring of 2A4MP favored reactions with various organic acids during formation of salts. Recently, organic compounds such as 2-amino-4-methyl pyridinium-4-Nitro phenolate 4-Nitrophenol [8], 2-amino-4-picolinium 4-aminobenzoate [16], 4-dimethyl amino–N-methyl-4-stilbazolium tosylate (DAST) [9,12], 4-dimethylaminopyridinium dihydrogen phosphate [17], 2-amino pyridinium trichloro acetate [18], Dimethyl amino pyridinium-4-Nitrophenolate 4-Nitrophenol (DMAPNP) [19] 2,6-Diaminopyridinium-4-Nitrophenolate 4-Nitrophenol (DAPNP) [20], 2-Aminopyridinium-4-Nitrophenolate Nitrophenol (2APNP) [21], 2-amino-5-chloro pyridinium-L-Tartrate [7], 2-amino-5-chloro pyridinium-4-amino benzoate [22] have been reported for their significant NLO properties. However, only a preferred group of compounds listed above acquired large molecular polarizabilities due to their favorable delocalized electron (π–electrons) arrangements with improved second and third order optical nonlinearities, exhibited enhanced physicochemical properties.

In this direction, an organic nonlinear optical material 2-amino-4-methyl pyridinium-4-methoxy benzoate (2A4MP4MB) has been synthesized incorporating 2-amino-4-methyl pyridine (2A4MP) and 4-methoxy benzoic (4MB) acid. A detailed literature survey showed there were no other studies available in this material. Based on these facts in the present work, 2-amino 4-methyl pyridinium 4-methoxy benzoate (2A4MP4MB) single crystals were grown by slow evaporation solution growth technique and the physiochemical properties such as single crystal XRD, powder XRD, FTIR, FT-Raman, NMR studies have been carried out. Further optical (both linear and nonlinear) studies like UV-vis-NIR, Photoluminescence (PL) spectroscopy, photoconductivity, Laser Damage Threshold (LDT) and Z-scan studies, Optical limiting studies were reported for the first time. In addition, quantum chemical density functional calculations (DFT) including Frontier Molecular Orbital (FMO) analysis, Mulliken atomic charge studies and molecular electrostatic potential have been calculated for the 2A4MP4MB crystal.

2. Experimental details

2.1. Synthesis, microanalysis and growth of 2A4MP4MB

Commercially available 2-amino 4-methyl pyridine ($C_6H_8N_2$) (AR grade) and 4-Methoxy benzoic acid ($C_8H_8O_3$) (AR grade) were purchased from Sigma Aldrich and used without further purification. The title compound salt was obtained by adding one mole of 2-amino 4-methyl pyridine and one mole of 4-methoxy benzoic acid in methanol solvent. To obtain the resultant product, two solutions were mixed together and stirred well for about 2 h to get homogeneous solution using mechanical stirrer and resulting solution was filtered through Whatmann 40 filter paper. The reaction mechanism of 2A4MP4MB is shown in Scheme 1. The Carbon-Hydrogen-Nitrogen (CHN) elemental composition percentage of 2A4MP4MB crystals were determined using Vario EL III Elemental analyzer (Germany) employing helium as a carrier gas. The analyzed results were given in Table 1. From the table, it could be observed that the experimentally obtained and theoretical results closely agreed with each other, also confirmed the presence of the compound.

The crystal growth vessel having filtrate was then covered using very thin polythene sheet to avoid fast evaporation. For controlled growth of 2A4MP4MB single crystal, the crystal growth vessel containing filtrate was placed in a constant temperature bath, whose temperature could be controlled by a programmable temperature controller (Model: 3216; accuracy ±0.01 °C). For the growth of single crystals of the title compound, slow evaporation solution growth method was employed and HPLC grade methanol was used as a solvent. The grown single crystals present inside vessel were taken out cautiously with the help of cleaned forceps. The typical dimension of crystal was about $10 \times 6 \times 4\ mm^3$ collected, dried and then used in X-ray diffraction studies. The Theoretical BFDH morphology of the crystalline compound was resolved with the help of unit cell and positional coordinates. Figs. 1a and 1b showed as grown single crystal and theoretical BFDH morphology of the title compound.

2.2. Solubility studies

The variation in solubility of title compound as a function of temperature is shown in Fig. 2. The information on solubility and Metastable Zone width (MSZW) plot are useful to ascertain optimal growth and perfection in crystallization process. The solubility of a material should be maintained in a controlled level to enhance the growth of superior quality single crystals. Further, it is required that the solute should remain in the solution till higher level of supersaturation has been attained in the solution to promote spontaneous nucleation. The solubility data of 2A4MP4MB was measured using methanol solvent as a function of temperature (from 25 °C to 45 °C) in the interval of 5 °C. Initially, the saturated solution of the compound has been prepared in a well-controlled thermal environment. The solution with excess amount of solute in the beaker was allowed to agitate for nearly 5 h before each sample was taken out. Solubility of the material was then measured gravimetrically. To prepare homogeneous mixture, solution in the vessel was filtered and then it was preheated to 5 °C above its saturated temperature. Then the solution was maintained at same temperature for 2 h before cooling process was initiated. The equilibrium-saturated solution in the growth vessel was then cooled from its overheated temperature (at a cooling rate of 2 °C/h) until a first visible crystal was observed. The saturated and nucleation temperature difference was taken as metastable zone width (MSZW) of the system [23]. The solubility of the material was found to rise almost linearly with the temperature.

2.3. Characterization details

The single crystal sample obtained from spontaneous nucleation process was subjected to single crystal X-ray Diffraction method with the help of Bruker smart Apex CCD diffractometer with graphite monochromated MoKα radiation (λ = 0.71073 Å) in the 2θ range 10–79.96° at a scan rate of 0.05°/sec, at ambient