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Synthesis, growth, structure, mechanical and optical properties of a new semi-organic 2-methyl imidazolium dihydrogen phosphate single crystal

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ABSTRACT

A new semi-organic compound, 2-methyl imidazolium dihydrogen phosphate (2MIDP), was prepared and good quality single crystals of 2MIDP were grown by slow evaporation solution growth technique. Crystal structure elucidated using Single crystal XRD showed that 2MIDP crystallizes in monoclinic system with $P2_1/c$ space group. FT-IR, UV-Vis-NIR, Fluorescence and FT-NMR spectra confirm the molecular structure of 2MIDP. The UV-Vis-NIR spectra established the suitability of the compound for NLO applications. TG-DSC showed that 2MIDP is thermally stable up to 200 °C. Mechanical characteristics like hardness number (H_v), stiffness constant (C_{11}), yield strength (σ_v), fracture toughness (K_c) and brittleness index (B_i) were assessed using Vicker's microhardness tester. Third order nonlinear optical properties determined from Z-scan measurement using femto and picosecond lasers showed two photon reverse saturable absorption. The enhancement of nonlinear optical properties in femto second laser, revealed the suitability of 2MIDP for optical limiting applications.

1. Introduction

Semi-organic nonlinear optical crystals find immense potential in optical switching, optical computing, optical communication, optical limiting, optical signal processing and wave mixing applications [1–3]. Hybrids of organic-inorganic (semi-organic) materials are often employed to elude some of the drawbacks associated with individual organic or inorganic counterparts, getting in an ideal way a synergic effect, which results in the progress of new materials with novel properties [4–6]. The ultimate goal of designing these hybrid materials is to carry over the advantages of the superior properties of both organic and inorganic components concomitantly. The high degree of delocalization and the structural tunability of organic materials should be retained in hybrid compounds, without compromising the advantages of inorganic counterparts (i.e., high melting point, mechanical strength, chemical inertness) [7–10]. Various semi-organic materials have been designed and demonstrated to exhibit good thermal and mechanical properties which ultimately display novel second and third nonlinear optical properties. The successful crystal engineering strategy for designing a molecule to exhibit NLO property is significantly governed by the presence of delocalized electron distributions (π-conjugated systems) with donor-acceptor groups [11–13]. In this perspective, hybrids of dihydrogen phosphates were found to be versatile due to their simplicity of synthesis and ease of single crystal growth [14–16]. Additionally, the phosphate ion plays a dual role in exhibiting nonlinear optical characteristics through its associated delocalized electron cloud, and also to the formation of supramolecular framework via hydrogen bonding [17,18]. In hybrids of dihydrogen phosphates, the phosphate anions often tend to self assemble themselves and generate anionic framework which further act as trapping medium for the assembly of cations [19]. This accounts for their remarkable thermal and mechanical stability [20]. Among the base materials (cationic acceptors), organic cyclic amine derivatives exhibit excellent second and third order nonlinear optical properties [21,22]. The basic nitrogen sites present in these compounds are located as part of an aromatic ring. Once the nitrogen is protonated, the entire positive charge present on it is

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readily available for contributing to the ionic bonding with the phosphate. In the present work, we report the synthesis and growth of a new semi-organic crystal of 2-methyl imidazolium dihydrogen phosphate, by reacting 2-Methyl imidazole base (cyclic amine containing delocalized electrons) with orthophosporic acid. The crystal structure of the new NLO material is determined and its molecular structure is probed by various spectroscopic techniques. The structure-property relationship is also established.

2. Experimental procedure

2.1. Materials

2-Methyl imidazole and phosphoric acid were purchased from Aldrich (with the purity of 98%) and used without further purification.

2.2. Synthesis and crystal growth

The title compound was prepared using the following procedure. Aqueous solutions of ortho phosphoric acid and 2-methyl imidazole were prepared separately (1:1 molar). 2-Methyl imidazole solution was then added drop wise to the aqueous phosphoric acid solution under vigorous stirring. The product formation was occurred in a single step. The preparation route for the formation 2MIDP is depicted in Fig. 1. The compound formation was initially identified from their characteristics peaks of FT-IR spectrum (described vide infra). A saturated solution of 2MIDP was prepared and the solution was stirred well for 5 h to maintain homogeneity. The resultant solution was filtered using Whatmann No. 41 filter paper and then kept in a constant temperature bath for slow evaporation. Single crystals were obtained at 35 °C. The extrinsic impurities were removed and the compound was purified by repeated recrystallization processes and used for further growth. Good quality transparent single crystals of 2MIDP (Fig. 2) were harvested from the mother solution in a period of one month.

2.3. Characterization studies

Bruker AXS Kappa APEX II single crystal X ray diffractometer equipped with graphite-monochromated MoKα radiation (λ = 0.71073 Å) was used for crystal structure determination. Accurate unit cell parameters were determined from the reflections of 36 frames measured in three different crystallographic zones, using the method of difference vectors. The data collection, data reduction and absorption correction were performed by APEX2, SAINT-plus and SADABS programs [23]. The crystal structure was solved by direct methods and the non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least squares on F^2 using SHELXL-97 program [24]. The positions of all the hydrogen atoms were identified from the difference electron density map and they were constrained to ride on the corresponding non-hydrogen atoms. The Cambridge Crystallographic Data Centre (CCDC No.: 1012965) contains the supplementary crystallographic data.

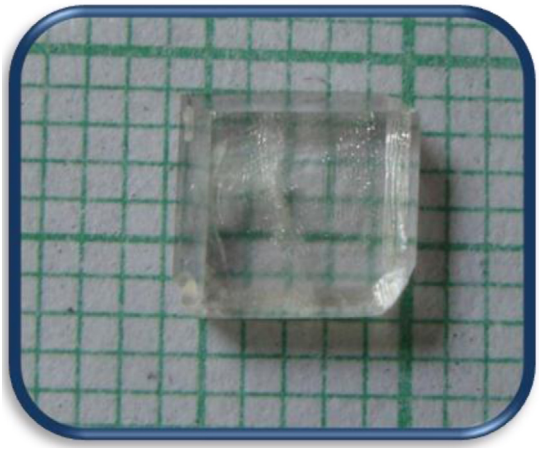

Fig. 2. As grown crystal of 2MIDP.

The FT-IR spectrum was recorded on a Bruker OPTIK 500200 spectrometer in the frequency range of 4000-450 cm^{-1}. KBr pellet method was employed for recording the spectrum. NMR measurements were carried out in deuterated water (D_2O) using a Bruker Avance III 500 MHz instrument with an operating frequency of 500 MHz and equipped with a 5 mm triple resonance broadband probe (90° pulse width: ^1H (10.65 μs), ^{13}C (7.80 μs) and ^{31}P (11.90 μs)). Perkin Elmer Lambda 35 UV-Vis spectrometer was employed to record the UV-Vis-NIR spectra. The fluorescence spectrum was recorded using a JobinYvon Fluorolog-3-11 Spectrofluorimeter. Thermal properties were measured using NETZSCH STA 449 F3 simultaneous thermal analyzer in Nitrogen atmosphere at a heating rate of 10 °C/min.

Hardness measurements of 2MIDP with the crystal dimension $9 \times 6 \times 2\ mm^3$ were performed using MATSUZAWA MMTX Vickers's microhardness tester with diamond pyramid indenter at room temperature. The effects of loads on 2MIDP were studied for the applied load of 1, 3, 5, 10, 25 and 50 g with a constant loading time of 5 s on the surface of the prominent plane (1 0 0). Indentation for each load was repeated five times at different locations (distance between successive indentation was increased 10 times than the previous one for avoiding surface effects on the crystals) on the surface of the crystals.

Open aperture Z-scan experiment was carried out using two lasing conditions. The details of the experimental setup used for

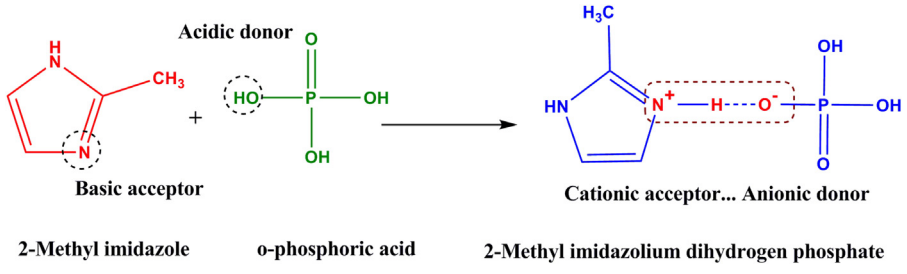

Fig. 1. Schematic sketch for the formation of 2MIDP.