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Growth and characterization of 2-amino-4-picolinium toluene sulfonate single crystal

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ABSTRACT

2-Amino-4-picolinium toluene sulfonate (2A4PTS), a new organic material, was synthesized and grown as single crystals in room temperature by slow evaporation solution growth technique using water as solvent. The crystal structure of 2A4PTS has been determined using single crystal X-ray diffraction studies. 2A4PTS belongs to monoclinic crystal system. The molecular arrangements in the crystal were studied. The structural perfection of the grown crystals has been analysed by high-resolution X-ray diffraction (HRXRD) rocking curve measurements. Fourier transform infrared (FTIR) spectral studies have been performed to identify the functional groups. The optical transmittance window and the lower cutoff wavelength of the 2A4PTS have been identified by UV–Vis–NIR studies. The nonlinear optical properties have been investigated by Z-scan method. The nonlinear refractive index and linear absorption coefficient of the 2A4PTS are found to be in the order of 10^{-8} cm^2/W and 10^{-4} cm/W, respectively. The laser induced surface damage threshold for the grown crystal was measured using Nd:YAG laser. Thermal analysis carried out on the compound reveals that 2A4PTS is stable up to 133 °C. The microhardness test was carried out and the load dependent hardness was measured.

1. Introduction

The origins of the nonlinear processes are well understood and the progress now depends on the development of materials technology compatible with the various device embodiments [1]. Compared to the extensive amount of research conducted on the synthesis and characterization of new molecular structures for second-order nonlinear optical applications, the study of third-order nonlinear processes on molecular materials has received relatively limited attention. Recently, the scope for the synthesis and characterization of third-order materials has expanded considerably. The impetus for this increased activity has been a quest for fundamental understanding of the structure property relationship and the strong technological interest in all optical signal processing provided by the third-order processes [2]. Development of novel molecular and crystal design techniques for assembling such materials is of great current interest [3,4]. The desirable properties of 2A4PTS which include stable physio-chemical properties and absence of any phase transition highlight this material as a potential candidate for nonlinear optical applications, and thereby attracted our interests towards a thorough investigation of this compound. In this paper, we report on synthesis, crystal growth, single crystal structure determination by single-crystal X-ray diffraction, high resolution X-ray diffraction, optical, thermal, laser-induced surface damage threshold, NLO properties by Z-scan technique and mechanical properties of 2A4PTS presented for the first time.

2. Material synthesis and single crystal growth

The 2A4PTS salt was obtained by dissolving 2 Amino 4-Picoline and p-Toluene sulfonic acid in methanol at room temperature in the molar ratio 1:1. The reaction scheme and the chemical structures are illustrated in Fig. 1. The salt was purified by the recrystallization process. The single crystals were grown from aqueous solution. Single crystal of size $15 \times 8 \times 5$ mm^3 has been obtained after a typical period of 90 days. Grown single crystals of 2A4PTS are shown in Fig. 2. As highlighted by the chemical bonding theory of single crystal growth, the growth shape of 2A4PTS single crystals is closely correlated to their crystallographic characteristics [5–10].

3. Sample characterization

3.1. Single-crystal X-ray diffraction study

The crystal structure was determined from the single crystal X-ray diffraction data obtained with a three-circle Enraf Nonius

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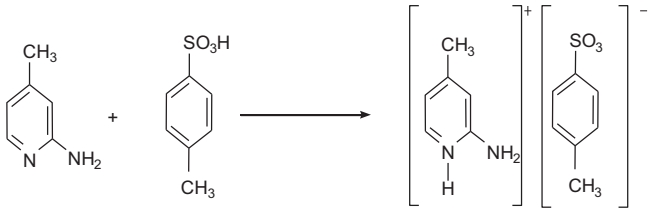

Fig. 1. Reaction of 2 Amino 4-Picoline with p-Toluene sulfonic acid.

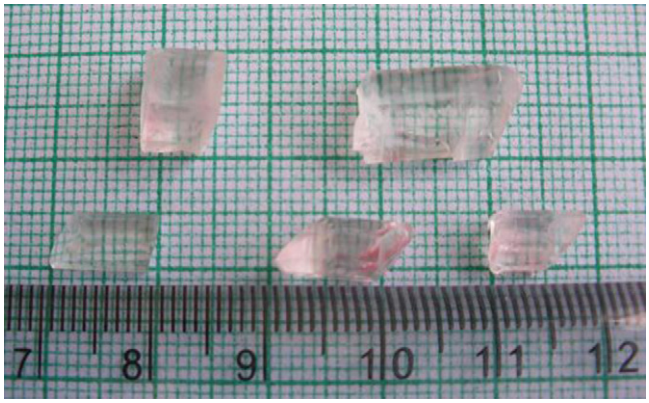

Fig. 2. Grown single crystals of 2A4PTS.

CAD4-MV31 (graphite-monochromated, CuKα = 1.54180 Å). The crystal structure was solved by a direct method with the SIR97 [11] program and refined by full matrix least-squares with SHELX97 [12] program to an *R* value of 0.0544. The structure was solved by direct methods and full-matrix least-squares refinements were performed on F^2 using all unique reflections. All nonhydrogen atoms were refined with anisotropic atomic displacement parameters and the hydrogen atoms were refined with isotropic displacement factors. Drawings of the molecular structure (Fig. 3) and the packing diagram (Fig. 4) were obtained using PLATON. Further crystal data, experimental conditions and structural refinement parameters are presented in Table 1. The crystallographic information file has been deposited by us in the Cambridge structure database (CCDC 781115).

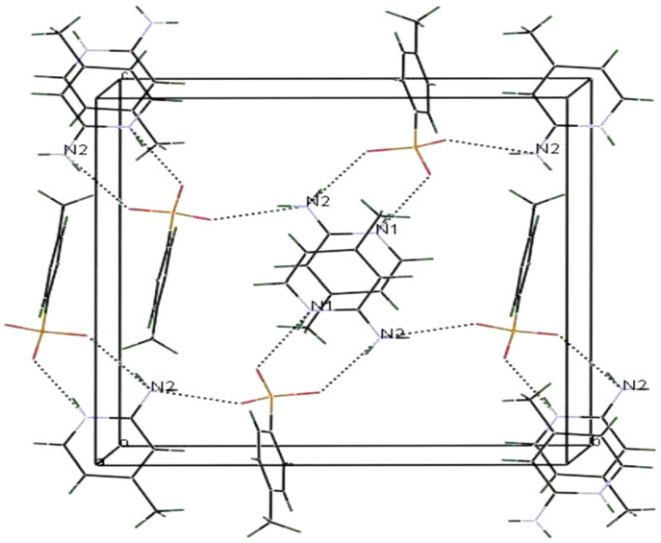

Fig. 4. Packing diagram of 2A4PTS.

2A4PTS crystallizes in the centrosymmetric space group $P2_1/c$ with four formula units of $C_6H_7N_2^+ \cdot C_7H_7SO_3^-$ in the unit cell. A formula unit consists of one 2-amino-4-picolinium cation and one toluene sulfonate anion as shown in Fig. 3.

The protonated N1 atom has lead to a slight increase in the C5–N1–C1 angle to 122.2(2)°. The bond lengths and angles are normal [13]. In the crystal packing (Fig. 4), the protonated N1 atom and 2-amino group (N2) are hydrogen-bonded to the sulfonate oxygen atoms (O2, O3 and O4) via a pair of N–H···O hydrogen bonds and protonated N1 atom is hydrogen bonded sulfonate sulfur atom via a N–H···S hydrogen bond. The crystal structure is stabilized by intramolecular hydrogen bonds to form a three-dimensional network. It should be mentioned that hydrogen bonds are a kind of NLO functional bonds in the crystallographic frame, which was first highlighted by Xue et al. [14–17].

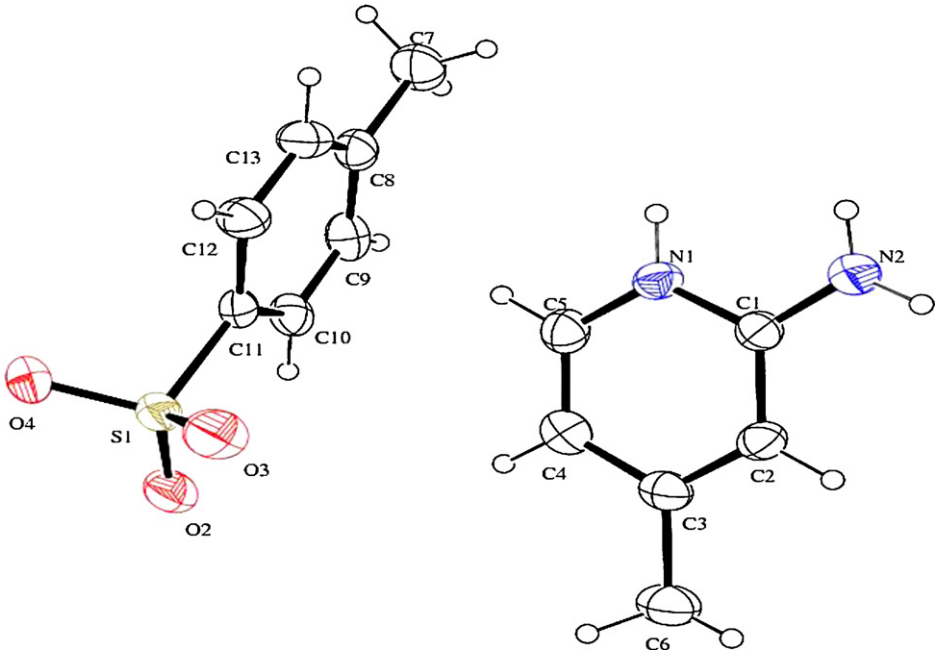

Fig. 3. ORTEP diagram of 2A4PTS.