Optical Materials 47 (2015) 398–405

Contents lists available at ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat

Synthesis, growth, structure and nonlinear optical properties of a semiorganic 2-carboxy pyridinium dihydrogen phosphate single crystal

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ARTICLE INFO

Article history:
Received 10 May 2015
Received in revised form 29 May 2015
Accepted 6 June 2015
Available online 15 June 2015

Keywords:
Semiorganic compound
Growth from solution
Single crystal XRD
Thermogravimetric analysis
Optical properties

ABSTRACT

A new semiorganic compound namely, 2-carboxy pyridinium dihydrogen phosphate (2CPDP) was synthesised and grown as single crystals by slow evaporation solution growth technique. Single crystal XRD showed that 2CPDP belongs to monoclinic crystal system with space group $P2_1/n$. The molecular structure was further confirmed by modern spectroscopic techniques like FT-NMR (^{1}H, ^{13}C & ^{31}P), FT-IR, UV–Vis-NIR and Fluorescence. The UV–Vis-NIR analysis revealed suitability of the crystal for nonlinear optical applications. The photo active nature of the material is established from fluorescence studies. TG-DSC analysis showed that 2CPDP was thermally stable up to 170 °C. The dependence of dielectric properties on frequency and temperature were also studied. Nonlinear optical absorption determined from open aperture Z-Scan analysis by employing picosecond Nd-YAG laser, revealed that 2CPDP can serve as a promising candidate for optical limiting applications.

1. Introduction

Design and preparation of new nonlinear optical materials have been the subject of immense importance in recent years due to their potential applications in ultrafast signal processing, optical computing, telecommunications, optical limiting, optical data storage devices, optical communications and harmonic generation [1–4]. The essential characteristics of a compound to exhibit nonlinear optical (NLO) properties are the presence of high nonlinear susceptibility, delocalized electronic cloud with adequate thermal and mechanical stability. In addition to these properties, the absence of center of symmetry is an essential requirement for second order NLO applications while such a constraint is not applicable for third order NLO applications [5,6]. Even though both inorganic and organic materials have been examined for optical non-linearities, the former take precedence over the latter, as they can be easily constructed with extended electron cloud delocalization [7,8]. However, organic compounds suffer from poor thermal and chemical stability. These drawbacks can often be trounced by developing hybrids with inorganic compounds. The resulting semi-organic nonlinear optical (NLO) materials possess the advantages of high optical nonlinearity and chemical flexibility of organic materials as well as the physical ruggedness of inorganic counterparts [9–12].

Among semi-organic compounds, phosphate based salts are unique for nonlinear optical applications due to their intrinsic ionic nature imparted by the free OH and O^- groups, spherical shape with delocalized electron cloud and the capability to form supra molecular architecture [13,14]. Even though several phosphate based materials have been reported for NLO applications, their optical non-linearities have subtle changes depending on the cations to which they are bonded [15–17]. With this view, 2-picolinic acid in which the basic nitrogen can hold a proton abstracted from the phosphate and the positive charge developed can contribute to the coulombic force of the crystal, is chosen as a convenient base to react with phosphoric acid. Additionally it's carboxyl group can freely involve in hydrogen bonding interaction with the phosphate. The resulting crystal is expected to have high lattice energy, thermal stability and negligible light absorption in the entire visible region. In the present investigation, the growth of 2-carboxy pyridinium dihydrogen phosphate and the supramolecular crystal structure is reported. The photo physical properties and the structure -property correlation are also discussed.

2. Experimental procedure

2.1. Synthesis and crystal growth

All chemicals used for the synthesis are AR grade which were procured from commercial sources and used as received. Initially,

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http://dx.doi.org/10.1016/j.optmat.2015.06.012
0925-3467/

one mole of ortho phosphoric acid and 2-picolinic acid solutions were prepared separately in de-ionized water of conductivity 0.05 μS at room temperature. The phosphoric acid solution was then added drop wise to the solution of 2-picolinic acid. Immediate salt formation occurred as per the reaction scheme depicted in Fig. 1. The resultant salt was dissolved with excess de-ionized water. The solution was then stirred well for 5 h to attain homogeneity and filtered using Whatman No. 45 filter paper. The filtrate was collected in a beaker and optimally closed by using a thin perforated plastic paper to control the evaporation of solvent. Then the beaker containing mother solution was housed in a constant temperature bath at 40 °C. The nucleation and growth process of 2CPDP was monitored frequently. Colorless single crystals of 2CPDP were found to be grown in a period of one month. The compound was purified by repeated recrystallisation processes. The purified compound was utilized for further growth of the crystal. Good quality bulk single crystals were harvested from the mother solution. The as-grown crystals of 2CPDP are shown in Fig. 2.

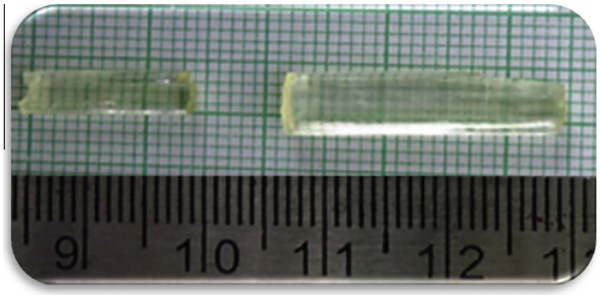

Fig. 2. As grown crystals of 2CPDP.

2.2. Characterisation techniques

Crystal structure of the 2CPDP was analyzed using single crystal X-ray diffraction studies. Intensity data were collected using Bruker AXS Kappa APEX II single crystal X-ray diffractometer, equipped with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at room temperature. The unit cell parameters were determined accurately from the reflections of 36 frames 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 [18]. The 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 [19]. The positions of all the hydrogen atoms were identified from difference electron density map and they were constrained to ride on the corresponding non-hydrogen atoms. The hydrogen atoms bound to carbon atoms were constrained to a distance in the range of C—H = 0.93Å and 0.97 Å with $U_{iso}(H) = 1.2U_{eq}(C)$ and $1.5U_{eq}(C)$ for aromatic carbon atoms. Crystallographic data for 2CPDP are presented in Table 1. The Cambridge Crystallographic Data Centre (CCDC No.: 1012993) contains the supplementary crystallographic data for 2CPDP.

Table 1
Crystallographic data of 2CPDP.

Identification code	2CPDP
Empirical formula	C6 H8 N O6 P
Formula weight	221.10
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, $P2_1/n$
Unit cell dimensions	a = 4.758(5) Å α = 90.000(5)°
	b = 9.460(5) Å β = 95.830(5)°
	c = 19.222(5) Å λ = 90.000(5)°
Volume	860.7(10) Å^3
Z, Calculated density	4, 1.706 mg/m^3
Absorption coefficient	0.325 mm^{-1}
F(000)	456
Crystal size	0.30 × 0.25 × 0.20 mm^3
Theta range for data collection	2.13–28.37°
Limiting indices	−5<=h<=6, −12<=k<=11, −23<=l<=25
Reflections collected/unique	7537/2140 [R(int) = 0.0234]
Completeness to theta	28.37–99.2%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9379 and 0.8789
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2140/0/130
Goodness-of-fit on F^2	1.190
Final R indices [I > 2sigma(I)]	R1 = 0.0425, wR2 = 0.1052
R indices (all data)	R1 = 0.0460, wR2 = 0.1069
Largest diff. peak and hole	0.421 and −0.424 e Å^{-3}

- Perkin Elmer FTIR spectrophotometer in the range of 450–4000 cm^{-1} was employed for functional group identification of the title compound. The spectral resolution of 2 cm^{-1} was used for recording the spectrum. FT-NMR measurements were carried out in D_2O solution on a Bruker Avance III 500 MHz instrument with an operating frequency of 500 MHz for ^{1}H, 202 MHz for ^{31}P and 125 MHz for ^{13}C, and equipped with a 5 mm triple resonance broadband probe (90° pulse width: ^{1}H (10.65 μs), ^{13}C (7.80 μs) and ^{31}P (11.90 μs)). The DEPT135 (Distortionless Enhancement by Polarization Transfer) spectrum was recorded on standard manner θ = 135 pulse program. Gradient enhanced two dimensional NMR spectra were obtained with quadrature detection in both dimensions, using the standard pulse programs from Bruker. A relaxation delay of 2 s was used for all 2D experiments. Thermal properties were studied using NETZSCH STA 449 F3 simultaneous thermal

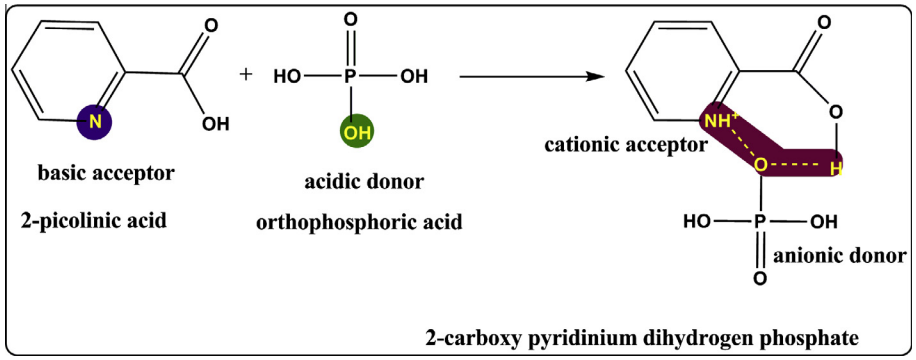

Fig. 1. Schematic drawing of the formation of 2CPDP.