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Synthesis, structure, growth and physical properties of a novel organic NLO crystal: 1,3-Dimethylurea dimethylammonium picrate

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ABSTRACT

A novel noncentrosymmetric crystal was prepared from 1,3-dimethylurea dimethylammonium picrate, $C_{11}H_{18}N_6O_8$ (DMUP), which was designed for second harmonic generation. DMUP crystals exist in noncentro symmetric space group $Cmc2_1$ with unit cell dimensions $a = 14.288(4)$ Å, $b = 17.023(5)$ Å, $c = 6.8268(13)$ Å, $\alpha = \beta = \gamma = 90^\circ$ and volume = 1660.5(8) Å^3. The crystal structure of DMUP has been determined using single crystal X-ray diffraction studies. The single crystals of DMUP were successfully grown by the slow evaporation method with dimensions 10 mm × 4 mm × 3 mm using dimethylformamide as solvent. The structural perfection of the grown crystals has been analysed by High-resolution X-ray diffraction (HRXRD) rocking curve measurements. Powder test with Neodymium-doped Yttrium aluminum garnet (Nd:YAG) laser radiation shows a high second harmonic generation (SHG). The laser induced surface damage threshold for the grown crystal was measured using Nd:YAG laser.

1. Introduction

Organic materials with high second harmonic generation have attracted a lot of attention because of their potential applications in electro-optic modulation, frequency conversion and optical parametric oscillations [1–4]. In order to improve the second-order nonlinear optical (NLO) response at the macroscopic level, the NLO response at the molecular level should be first improved. The intellectual construction of structurally controlled supramolecular assemblies (e.g., acentric and chiral solids) remains a great challenge even though the art of chemical synthesis of discrete molecules has significantly advanced in recent decades. According to previous investigations on the structure-property relationship of NLO crystals [5–8], the structure of organic materials can be modified by functional substitution and hence it is possible to fine tune their optical properties. By improving the NLO response at the molecular level, it is possible to achieve better macroscopic second order NLO properties and proper molecular engineering can lead to head to tail alignment of molecules in the solid state structure that results in large SHG efficiencies. Donor/acceptor benzene derivatives are sure to produce high molecular nonlinearity. An organic molecule should have large second-order hyperpolarizability (β) to exhibit good nonlinear optical properties. Extension of benzene derivatives has permitted an increase in the number of π electrons as well as their delocalization length, so as to lead to prodigious enhancement in β. Picric acid forms crystalline picrates of various organic molecules through ionic and hydrogen bonding and π–π interactions [9]. It is known that picric acid acts not only as an acceptor to form various π stacking complexes with other aromatic molecules but also as an acidic ligand to form salts through specific electrostatic or hydrogen bond interactions. Bonding of electron donor/acceptor picric acid molecules strongly depends on the nature of the partners. The linkage could involve not only electrostatic interactions but also the formation of molecular complexes. Previous studies show that hydrogen bonds play a dramatic role in governing NLO property and growth of various single crystals [10–13]. In this article, we report for the first time bulk growth, nuclear magnetic resonance (NMR) studies, single-crystal X-ray diffraction (XRD) studies, HRXRD studies,

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Fourier transform infrared (FTIR) spectroscopy, ultraviolet–visible–near infrared (UV–Vis–NIR) studies, thermogravimetric analysis (TGA), differential thermal analysis (DTA), SHG efficiency test and laser damage threshold studies of the title compound DMUP.

2. Experimental procedures

2.1. Material synthesis

The title compound was synthesized by reacting equimolar quantities of 1,3-dimethylurea and picric acid in dimethylformamide (DMF). DMF absorbs water molecule from the moisture. Aqueous solutions of DMF have tendency to hydrolyze. However the addition of acids or bases accelerates hydrolysis to formic acid and dimethylamine. In this reaction the picric acid OH group necessarily protonates the nitrogen of the dimethylamine and netural dimethyl urea stands as a third partner resulting in the formation of the title compound.

2.2. Solubility, crystal growth and characterization

The solubility of DMUP in DMF was assessed as a function of temperature in the range 25–40 °C. The DMUP exhibits good solubility and a positive solubility–temperature gradient in DMF. Fig. 1 shows the solubility curve for DMUP. Single crystal of size 10 mm × 4 mm × 3 mm has been obtained after a typical period of 90 days. Grown single crystal of DMUP is shown in Fig. 2.

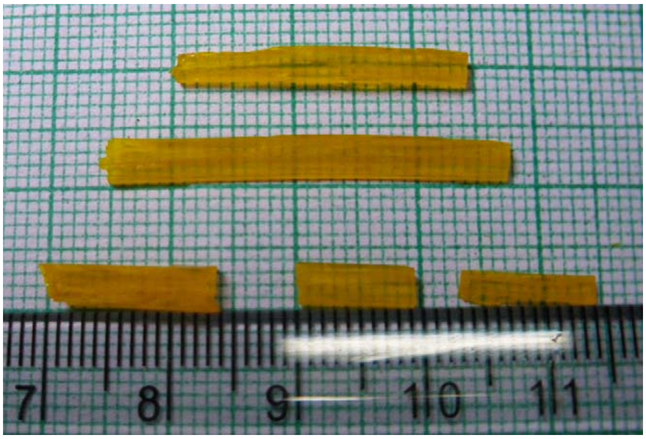

Fig. 2. Grown single crystals of DMUP.

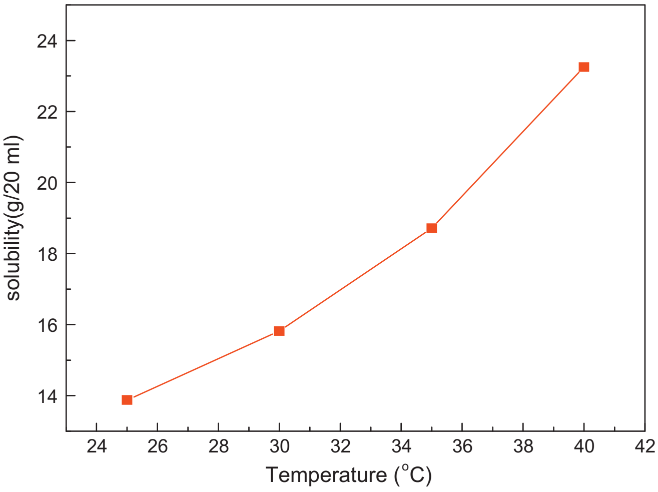

Fig. 1. Solubility curve of DMUP in DMF.

The ^{1}H NMR spectrum of the sample was recorded using an AMX 400 MHz spectrometer in DMSO-d_6 solvent using tetramethyl silane as the internal reference standard. The grown crystals were subjected to X-ray diffraction studies using ENRAF Nonius CAD4 single crystal X-ray difffractometer, using graphite monochromated CuK$_\alpha$ (λ = 1.54180 Å) radiation. The recorded data were corrected for polarization and Lorentz and absorption effects. The crystal diffraction data are shown in Table 1. The crystal structure was solved by a direct method with the SIR97 [14] program and refined by full matrix least-squares with SHELX97 [15] program to an R value of 0.0544. The ORTEP drawing was performed with ORTEP3 program [16]. The crystalline perfection of the DMUP single crystals grown by slow evaporation solution growth technique (SEST) was characterized by HRXRD by employing a multicrystal X-ray diffractometer developed at National Physical Laboratory, New Delhi. The well-collimated and monochromated MoKα_1 beam obtained from the three monochromator Si crystals set in dispersive (+, −, −) configuration has been used as the exploring X-ray beam. The specimen crystal is aligned in the (+, −, −, +) configuration. Due to dispersive configuration, though the lattice constants of the monochromator crystal(s) and the specimen are different, the unwanted dispersion broadening in the diffraction curve (DC) of the specimen crystal is insignificant. The specimen can be rotated about the vertical axis, which is perpendicular to the plane of diffraction, with minimum angular interval of 0.4 arc s. The DC was recorded by the so-called ω scan wherein the detector was kept at the same angular position $2\theta_B$ with wide opening for its slit. Before recording the diffraction curve to remove the non-crystallized solute atoms which remained on the surface of the crystal and also to ensure the surface planarity, the specimen was first lapped and chemically etched in a non preferential etchant of water and acetone mixture in 1:2 volume ratio. FTIR spectrum was recorded from potassium bromide pellets on a Perkin Elmer FTIR spectrometer in the range 4000–450 cm^{-1}. The transmission spectrum of the DMAP solution was studied in the range 200–1100 nm by Perkin Elmer spectrometer. The TGA and DTA experiments were carried out on a NETZSCH STA 409 instrument with a heating rate of 5 °C/min from 30 to 700 °C. Samples were weighed in a platinum crucible. Quantitative

Table 1
Crystal data and structure refinement of DMUP.

Empirical formula	$C_{11}H_{18}N_6O_8$
Formula weight	362.31
Temperature	293(2) K
Wavelength	1.54180 Å
Crystal system, space group	Orthorhombic, $Cmc2_1$
Unit cell dimensions	a = 14.288(4) Å, α = 90°
	b = 17.023(5) Å, β = 90°
	c = 6.8268(13) Å, γ = 90°
Volume	1660.5(8) Å^3
Z, Calculated density	4, 1.449 mg/m^3
Absorption coefficient	1.077 mm^{-1}
F(0 0 0)	760
Crystal size	0.30 × 0.20 × 0.20 mm^3
Theta range for data collection	4.04–64.98°
Limiting indices	$-16 \le h \le 12$, $-12 \le k \le 20$, $-8 \le l \le 0$
Reflections collected/unique	1519/805 [R(int) = 0.0266]
Completeness to theta	64.98, 99.9%
Absorption correction	Psi-scan
Max. and min. transmission	0.8134 and 0.7282
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	805/2/134
Goodness-of-fit on F^2	1.080
Final R indices [$I > 2$sigma(I)]	$R1 = 0.0544$, $wR2 = 0.1426$
R indices (all data)	$R1 = 0.0585$, $wR2 = 0.1476$
Absolute structure parameter	−0.4(7)
Extinction coefficient	0.032(3)
Largest diff. peak and hole	0.709 and −0.284 e A^{-3}