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Self-assembled supramolecular structure of 1-methyl piperazinium 4-nitrophenolate 4-nitrophenol monohydrate single crystal: Synthesis, growth, thermal and photo physical properties

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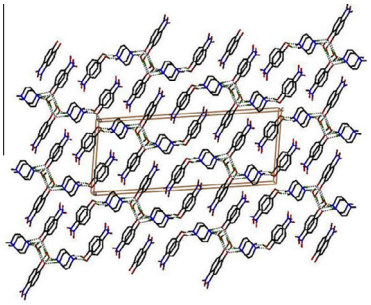
HIGHLIGHTS

- Single crystals of MP4NPM were grown by slow evaporation solution growth technique.
- Self-assembled supramolecular structure of MP4NPM was established from XRD.
- Molecular structure was further confirmed using modern spectroscopic techniques.
- Thermal and photo physical properties were correlated with the structure.

GRAPHICAL ABSTRACT

Molecular packing of MP4NPM view down along *b* axis.



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ABSTRACT

A new photoactive organic crystal, 1-methyl piperazinium 4-nitrophenolate-4-nitrophenol monohydrate (MP4NPM) has been synthesised at 35 °C. Good quality single crystals of MP4NPM have successfully been grown by slow evaporation solution growth technique. Single crystal X-ray diffraction analysis shows that MP4NPM belongs to monoclinic crystal system with space group $P2_1/n$. The molecular structure was further confirmed by modern spectroscopic techniques like FT-NMR (both 1D and 2D), FT-IR, UV–Vis–NIR and fluorescence. The UV–Vis–NIR spectrum was performed to understand the range of optical transparency and the results showed its suitability for nonlinear optical applications. Fluorescence emission revealed that MP4NPM can serve as a photo active material. Thermal properties of MP4NPM were investigated using simultaneous TG–DSC analysis. Frequency and temperature dependent dielectric properties were studied in the frequency range 500 Hz–5 MHz and 40–50 °C, respectively. Vicker's microhardness measurements revealed that MP4NPM belongs to the category of soft material. Kurtz and Perry powder technique shows that MP4NPM has SHG efficiency 0.89 times that of potassium dihydrogen phosphate (KDP).

Introduction

There has been an increasing interest in the recent past to synthesize and grow novel organic crystals with high nonlinear optical efficiency and ultrafast response for nonlinear optical (NLO) and

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optoelectronic applications [1–3]. The absence of centre of inversion symmetry and presence of delocalized electronic cloud are the essential requirements for such systems to exhibit second order nonlinear optical (NLO) properties. However, for exhibiting higher order nonlinear optical properties, the symmetry of the compound does not have any significance, and the contribution from other characteristics play major roles [4,5]. Syntheses of such organic compounds are generally based on their donor–acceptor substituents and π conjugation. Towards attaining this goal, 4-nitrophenol derivatives are potentially promising not only to the presence of their electron donor "–OH" and electron acceptor "$–NO_2$" substituents, but also to their capability to form strong hydrogen bonds with other systems [6,7]. The donor groups are often involved in proton transfer process while reacting with suitable bases which could further increase molecular hyperpolarizability and ultimately leads to the NLO activity. Moreover, the ionic form of 4-nitrophenol has wide band gap which is essential for optical applications. There are several reports on 4-nitrophenol derivatives exhibiting very good second and third order nonlinear optical properties [8–11]. Organizing the molecules in parallel fashion is recognized as an important crystal engineering strategy to enhance the SHG efficiency [12,13]. However, implementation of this strategy is plausible only for certain molecules. This is because of the desired organization of molecules in the crystal requires an additional member besides main members. 4-nitrophenol, a polar molecule that bears hydrogen bonding – OH substituent, plays a pivotal role in the enhancement of SHG by incorporating as a second member which can attract and hold the main members via hydrogen bonding. On the other hand, piperazine and its derivatives have wide range of applications in pharmaceuticals as antifungal, anti-tuberculosis, anti-malarial, anti-tumor, anticancer and antiviral agents. For piperazine derivatives of organic crystals, center of inversion is often noticed [14–17] and hence only scarce investigation on the NLO characteristics of crystals with piperazine and 4-nitrophenol combination exists. In the present study, piperazine is used as a diagnostic probe capable of de-protonating 4-nitrophenol and stabilizing the resultant structure through strong hydrogen bonds. The self assembled supramolecular structure of 1-methyl piperazinium 4-nitrophenolate 4-nitrophenol monohydrate (MP4NPM) crystal is established and the structure–property correlation is also investigated.

Experimental procedure

Materials and methods

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

Synthesis and growth

2 mol of 4-nitrophehol and 1 mol of 1-methyl piperazine were taken in two separate beakers containing 50 ml of acetone and stirred well using motorized magnetic stirrer until clear solutions are obtained. Clear colourless solution of 1-methyl piperazine was added dropwise to the light yellow coloured 4-nitrophenol solution at room temperature. The light yellow colour of the solution is progressively changed to dark yellow indicating the product formation and is further confirmed by thin layer chromatography. After preparing a saturated solution of MP4NPM, the solution was filtered in a beaker using Whattman No. 45 filter paper. The beaker was then kept at 35 °C for slow evaporation. The brownish colour of the solution slowly turned into dark brown due to the photo induced reaction of the compound. Finally, yellow coloured plate like crystals were collected from the mother solution within a period of 20 days. These crystals were recrystallized five times and utilized for further growth. Good quality yellow color single crystal of size $9 \times 6 \times 5$ mm^3 was harvested in a month under optimized conditions. The formation of MP4NPM is depicted in Supplementary Fig. S1. As grown crystal of MP4NPM is shown in the Fig. S2.

Measurements

Single crystal X-ray diffraction analysis

Structure of the title compound 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 MoKα radiation (λ = 0.71073 Å) at room temperature. 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 [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 = 0.93 Å and 0.97 Å with $U_{iso}(H) = 1.2U_{eq}(C)$ and $1.5U_{eq}(C)$ for the methylene and aromatic carbon atoms respectively. Crystallographic data for MP4NPM crystal are presented in Table 1. The Cambridge Crystallographic Data Centre (CCDC No.: 998755) contains the supplementary crystallographic data for MP4NPM.

Perkin Elmer spectrophotometer in the range of 450–4000 cm^{-1} was employed for the Fourier Transform Infrared spectral analysis. NMR measurements were carried out on a Bruker Avance III 500 MHz instrument with an operating frequency of 500 MHz for ^{1}H and 125 MHz for ^{13}C and equipped with a 5 mm triple resonance broadband probe (90° ^{1}H pulse width 10.65 μs and ^{13}C pulse width 7.80 μs). The chemical shifts are reported in ppm relative to tetramethylsilane (TMS) in deuterated Chloroform ($CDCl_3$) solution. The DEPT135 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 analyzer in Nitrogen atmosphere at a heating rate of 10 °C/min. Dielectric properties were studied in the frequency using a HIOKI 3532-50 LCR HITESTER. The precisely cut and polished crystal was mounted in the sample holder. Measurements were carried out in the frequency range of 100 Hz–5 MHz at two different temperatures. The temperature used for the study was below the melting point of the crystal. The absorption spectrum of MP4NPM was recorded in the range 200–1100 nm by subjecting the crystal of thickness of 2 mm into a PERKIN ELMER LAMBDA 35 spectrophotometer. The fluorescence measurements of MP4NPM single crystals were carried out using a Jobin Yvon-Spex Spectrofluorometer (Fluorolog version – 3; Model FL3-11) in the range 200–900 nm. Hardness number of the crystal was measured using MATSUZAWA MMTX Vickers's microhardness tester with a diamond pyramidal indenter attached to an optical microscope. Transparent, free from visible inclusion and the prominent plane (100) of the grown crystal was selected and exposed to static indentations. Loads 1, 3, 5, 10, 25 and 50 g were applied on the