

## Growth and characterization of an organic stilbazolium family single crystal of DESI

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**Abstract:** Organic stilbazolium family single crystal 4-N, N-diethylamino-4-N-methyl-stilbazolium Iodide (DESI) has been successfully grown from aqueous methanol solution by adopting slow solvent evaporation technique. Single crystal X-ray diffraction analysis was carried out and it shows that DESI crystal belongs to triclinic structure with P-1 space group. The presence of hydrogen in the crystal structure was determined by recording  $H^1$  NMR spectrum. The excitation spectrum of the DESI was recorded by fluorescence analysis. The thermal study confirms the stability of the material.

**Keywords:** Organic compound; X-ray diffraction; Thermal Analysis; Proton NMR

### Introduction

The design and synthesis of organic materials for high second order nonlinear optical effect is become an important research area due to their potential and wide applications in the fields of optical signal processing, integrated photonics, optical switching, optical data storage, bioimaging, electro-optic modulation, spectroscopy and THz wave generation and detection. Hence, efforts have been made to engineer novel  $\pi$ -conjugated organic molecules because of their second and third-order nonlinear optical activities. Ionic organic crystals with high chromophore density are of special interest for high NLO activity [1-3]. The stable packing of chromophores in these crystals results in high thermal, mechanical and photochemical stability. The design of NLO chromophore crystals has an electron withdrawing group that bear an electron donating group interacting through the  $\pi$ -conjugated system with parallel alignment in the crystal structure. The formation of the carbon-carbon bridge (C=C) with  $\pi$ -conjugation chromospheres of an organic molecule can be obtained by Knoevenagel condensation reaction []. This method is most favorable and easy method for to form a carbon-carbon double bond. By successfully engineering the organic chromophore, a novel crystal of 4-N, N-diethylamino-4-N-methyl-stilbazolium iodide (DESI) has been developed in this work. DESI single crystal has been grown by adopting slow evaporation solution growth technique. In this article, the structural, optical and mechanical properties of the title compound are discussed.

### Synthesis and Crystal growth

DESI was synthesized by the Knoevenagel condensation of 1,4-dimethyl pyridinium iodide (2.35 g, 10 mmol), methanol (30 ml) and 4-N, N-diethylamino-benzaldehyde (1.772 g, 10 mmol) in the presence of piperidine (0.2 ml) (Adachi et al 1999). The total mixture was taken in a round-bottom flask (1000 ml capacity) of a Dean-Stark apparatus. The mixture was then refluxed for 12 hours and cooled to room temperature. The product was filtered and recrystallized from methanol at least three times. The synthesis scheme of DESI is presented in Figure. In a 250 ml beaker, 2g of the DESI was dissolved in methanol. After getting the homogeneous solution it was sealed with perforated cover and kept in the temperature bath. The growth temperature was maintained at 35 °C and after a period of 10-15 days the crystals were harvested (Fig 1.)



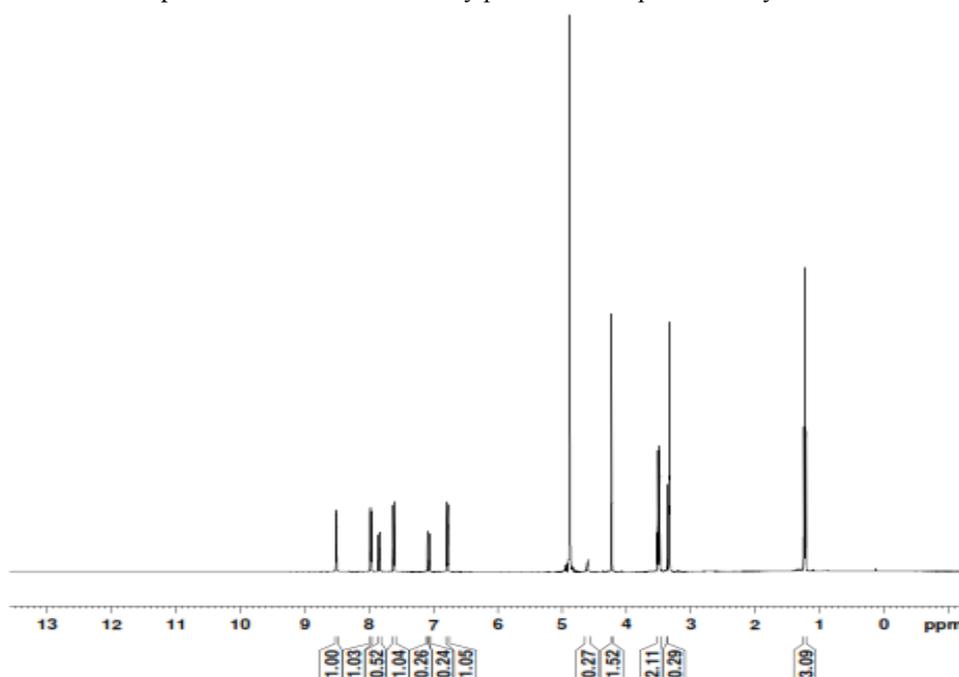
## RESULTS AND DISCUSSION

### Single crystal X-ray Diffraction analysis

The grown crystal was subjected to single crystal X-ray diffraction studies using Bruker Kappa APEXII single crystal X-ray diffractometer with  $MoK_{\alpha}$  radiation ( $\lambda = 0.7170 \text{ \AA}$ ) to solve the structure. The XRD data indicates the *triclinic* structure with centrosymmetric space group P-1. The calculated lattice parameters of DESI crystals are  $a = 7.8203(7) \text{ \AA}$ ,  $b = 15.3176(15) \text{ \AA}$ ,  $c = 17.1742(17) \text{ \AA}$ ,  $\alpha = 75.323(3)^{\circ}$ ,  $\beta = 87.401(3)^{\circ}$ ,  $\gamma = 89.396(3)^{\circ}$  and Volume  $1988.1(3) \text{ \AA}^3$

**NMR analysis**

NMR is used to detect the presence of particular nuclei in a compound, for a given nuclear species. It is also an important tool for the identification of molecule and for the examination of electronic structure. The proton NMR spectrum of DESI was recorded using a Bruker ADVANCE III 500 MHz FT-NMR spectrometer by dissolving the sample in deuterated methanol. In the proton NMR spectrum (Fig. 2), the triplet peak at 1.228 ppm is due to 6H of  $\text{CH}_3$  and the quartet at 3.502 ppm is due to 4H of  $-\text{CH}_2$  of ethyl group attached to nitrogen ( $-\text{N}(\text{CH}_2\text{CH}_3)_2$ ). The dissolving solvent  $\text{CD}_3\text{OD}$  may contain a small quantity of water which is evident from the chemical shift at 3.370 ppm. The singlet observed around 4.228 ppm is attributed for 3H of methyl group attached to pyridinium ring ( $\text{N}-\text{CH}_3$ ). The doublets at 6.777 ppm and 7.073 ppm are due to the two olefinic hydrogens ( $\text{CH}=\text{CH}$ ). The doublets at 7.609 - 7.838 ppm are attributed to the four hydrogens of the benzene ring attached to  $\text{N}(\text{CH}_2\text{CH}_3)_2$ . The doublet at 7.965 ppm is due to the meta hydrogens of the pyridinium ring. The doublet observed at 8.502 ppm is assigned to the ortho H of the pyridinium ring. Thus, the formation the title compound has been confirmed by proton NMR spectral analysis.

**Photoluminescence (PL) studies**

Photoluminescence spectroscopy is a non destructive method of probing the electronic structure of materials. The photoluminescence spectrum of DESI crystal was recorded in liquid phase using a Jobin Yvon Fluorolog-3-11 spectrofluorimeter with Xenon Lamp 450 W as the excitation source. The experiments were carried out at room temperature with an excitation wavelength of 474 nm. Figure 3 shows the PL spectra of DESI in liquid phase. In the excitation plot, a very strong intense emission peak is observed at 600 nm (2.07eV), which could be attributed the stilbazolium chromophores present in the material. The PL spectra clearly reveal emission from free and bound molecular excitons as well as radiative recombination from free carriers (delocalised  $\pi$ -electron) in stilbazolium chromophores. It is well known that organic molecules with strong donor- $\pi$ -acceptor system exhibit high photoluminescence properties. Especially, organic stilbazolium salts are potentially used as fluorescence probe monitor in the active area of biomedical research (Bajorek et al. 2011). Moreover, the presence of a strong electron acceptor and a strong electron donor is indispensable to the proper red aromaticity and saturated red emission (Danel et al. 2002). The highly intense and broad emissions in the red phase PL regions suggest that DESI could be potentially used in the organic solid state laser device fabrication.

**Thermal Analysis**

The thermal behaviour of DESI was investigated by Thermo gravimetric analysis using Perkin Elmer STA 6000 thermal analyser. The TGA traces were recorded from room temperature to 600 °C, under nitrogen atmosphere at a scanning rate of 20 °C per minute. It is noted from Fig. 4 that DESI undergoes two weight losses. The first stage is attributed to the dehydration that would have occurred between 50-120°C. The 12 % weight loss occurred below 100 °C is due to the contaminated water molecule associated with the compound. During the second stage, it is observed that nearly 75% of the compound is decomposed between 252 and 400

°C, which could be attributed to the removal of stilbazolium cation moieties from benzene ring, leaving the remaining as the residue at 600 °C. From the TG curve, it may be concluded that DESI is stable upto 252 °C, this stability could be useful for the practical applications.

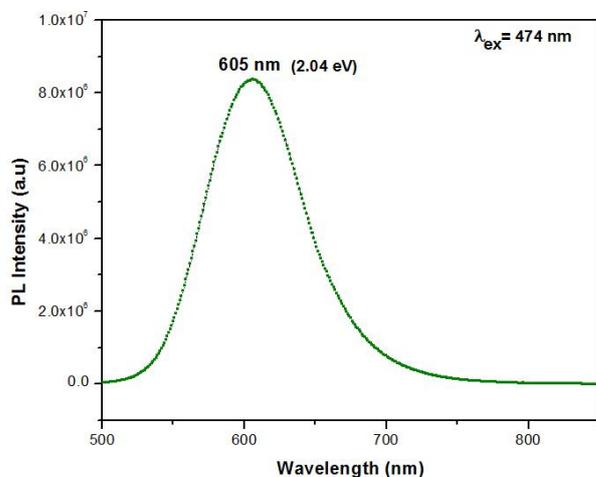


Figure 3 Emission Peak of DESI crystal

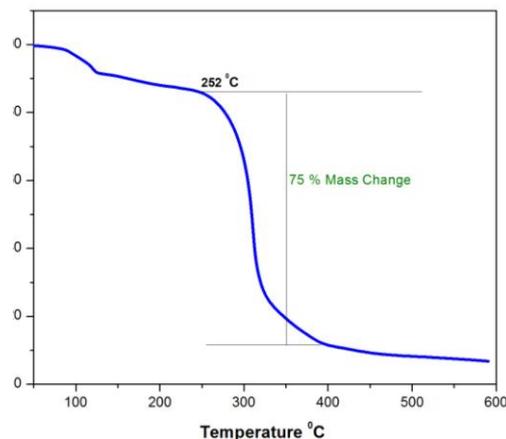


Figure 4 TG trace of DESI crystal

### Conclusion

Single crystal of DESI was successfully synthesized by Knoevenagel condensation method. Single crystal XRD study confirms that DESI belongs to the *triclinic* crystal system with *P-1* space group. The  $H^1$  NMR analysis confirms the presence and positions of hydrogen in the crystal structure. The thermal study reveals the stability of the DESI crystal. The excitation spectrum of the DESI was recorded by fluorescence analysis; it shows a very strong intense emission peak at 605 nm.

### Acknowledgement

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