International Research Journal of Engineering and Technology (IRJET) e-ISSN: 2395-0056
Volume: 04 Special Issue: 09 | Sep -2017 www.irjet.net p-ISSN: 2395-0072
One Day International Seminar on Materials Science & Technology (ISMST 2017)
4th August 2017
Organized by
Department of Physics, Mother Teresa Women's University, Kodaikanal, Tamilnadu, India

Synthesis, Structural and Optical Properties of an Organic Stilbazolium Single Crystal of 4-(4-Hydroxy Styryl)-1-Methylpyridinium 4-Styrene Sulfonate

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Abstract - *A new organic nonlinear optical crystal from stilbazolium family 4-(4-hydroxy styryl)-1-methylpyridinium 4-styrene sulfonate (HSSS) was grown by slow solvent evaporation method. The grown crystal structure was confirmed by single crystal X-ray diffraction analysis. HSSS was found to crystallize in monoclinic crystal system with centrosymmetric space group $P2_1/n$. The proton NMR spectrum was recorded by dissolving the sample in deuterated methanol to confirm the presence of hydrogen. The presence of various vibration modes of the expected functional groups were identified by FT-IR analysis. The optical properties of the grown crystal were also analyzed by using UV-Vis-NIR spectral analysis.*

Key Words: Ionic organic crystal, Stilbazolium derivative, Single crystal XRD, NLO material, Styrene sulfonate

1. INTRODUCTION

Nonlinear optics (NLO) has been recognized for several decades as a promising field with important applications such as photonics applications, optical information processing, optical memory storage, electro-optic switches, color display and second harmonic generation. In particular, a molecule with an electron donating (D) and accepting groups (A) connected via a π-conjugated system has received far superior nonlinear performance in terms of high hyper polarizability. There has been particular interest in ionic organic nonlinear optical materials because of their chemical, mechanical and thermal properties that could be altered by simply changing the counter-ions, also, the electron donor and electron acceptor moieties at their ends of the π-conjugated systems. Up to now, many kinds of organic materials were reported with the good nonlinear response. Among of them, styryl pyridinium derivatives are considered to be good conjugated π-systems, and that have been put to practical uses for their large NLO efficiencies, high-speed electro-optic applications and THz generation and detection. In continuation of our ongoing research on nonlinear optical materials, the title compound 4-(4-hydroxy styryl)-1-methylpyridinium 4-styrenesulfonate (HSSS) was grown by adopting slow evaporation solution growth technique at room temperature. In this article, the synthesis, growth, structural and optical properties of the title compound are reported for the first time.

2. SYNTHESIS AND CRYSTAL GROWTH

HSSS was prepared by metathesization of the (4-(4-hydroxystyryl)-1-methylstilbazolium iodide (HSMI) salt with sodium 4-styrenesulfonate. HSMI was synthesized by the condensation of 1,4-dimethyl pyridinium iodide (2.35 g,10 mmol), methanol (30 ml) and 4-hydroxy benzaldehyde (1.22 g, 10 mmol) in the presence of piperidine (0.2 ml). The total mixture was taken in a round-bottom flask and refluxed for 8 h and cooled to room temperature. The product was filtered and recrystallized from methanol at least three times. The metathesizaton reaction was carried out as follows: Initially, 0.678 g (2 mmol) of HSMI was dissolved in 70 ml of distilled water by heating and simultaneously 0.412 g (2 mmol) of sodium 4-styrenesulfonate was dissolved in30 ml of water with continued heating. These two hot solutions were mixed and further heated for 30 min at 70 °C and then cooled to room temperature. The reaction resulted in the appearance of a yellowish red precipitate and the left out aqueous sodium iodide was separated from the former by vacuum filtration. The purity of HSSS was further improved by successive recrystallization.

For growing single crystal, the purified salt of HSSS was dissolved in methanol and kept in a 250 ml beaker. After getting the homogeneous solution it was allowed for crystallization by slow evaporation kept it in the room temperature. After a period of 20-25 days, the good quality crystals have a typical size of 3 × 1 × 0.32 mm^3 were harvested and the grown crystals as shown in Figure 1.

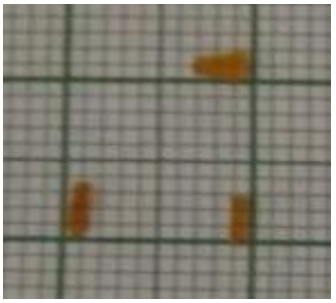

Figure 1: Photograph of HSSS crystal

3. RESULT AND DISCUSSION

3.1 Single crystal X-ray diffraction analysis

The crystallographic structure of HSSS was determined via single X-ray diffraction analysis using a Bruker Kappa APEX II diffractometer. The structure was determined from the single crystal XRD; HSSS crystal belongs to monoclinic aromatic C–H stretching vibrations. The absorption peaks at 2949 and 2803 cm^{-1} are attributed to alkyl C–H stretching. The bands observed at 1624 and 1602 cm^{-1} are assigned to the olefinic C=C stretch and aromatic ring vibrations. The peak at 1477 cm^{-1} is due to CH_2 bending vibration and the C–N stretching vibration is observed at 1289 cm^{-1}. The C–H in-plane and out-plane bending vibrations are observed in the regions of 1200-1100 cm^{-1} and 750-900 cm^{-1}, crystal system, with the space group $P2_1/n$. The unit cell respectively. The sharp peak seen at 921.64 cm^{-1} is due to parameters are a = 8.49 Å, b = 26.39 Å, c = 9.07 Å, α = 90°, β = 104.04°, γ = 90° and volume, V = 1974.07 $Å^3$.

3.2 NMR analysis

The proton NMR spectrum was recorded using a Bruker ADVANCE III 500 MHz FT-NMR spectrometer by dissolving the sample in deuterated methanol is shown in Figure 2. In the proton NMR spectrum of HSSS, the doublets at 8.61 and 8.05 ppm are attributed to the four hydrogens of pyridine ring. The doublet at 7.87 and 7.79 ppm are due to the aromatic C–H hydrogen ortho to $–SO_2$. The doublets at 7.49 and 7.63 ppm are due the two aromatic hydrogens ortho to $–CH_2$ group present in the anion. The multiplets seen at 7.17 and 6.77 ppm are due to the two olefinic hydrogens (HC=CH). The doublets at 6.88 and 6.66 ppm are due to the two hydrogens meta and ortho to C_6H_4–OH respectively. The doublet at 5.87 ppm is due to the CH proton attached to the benzene sulfonate. The doublets at 5.32 and singlet at 4.91 ppm are due the two hydrogens of $–CH_2$ group present in the anion. The singlet observed at 4.63 ppm is due to phenolic –OH. The triplet observed at 4.22 ppm is attributed to the three $N–CH_3$ hydrogens of pyridinium structure.

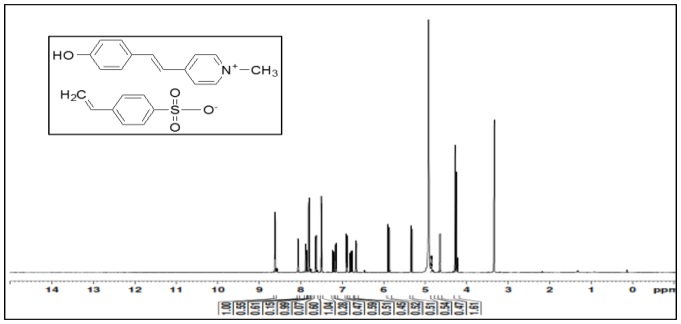

Figure 2: NMR spectrum of HSSS crystal

3.3 FT-IR analysis

The FT-IR spectrum of the HSSS crystal was recorded in the wavenumber range of 400 to 4000 cm^{-1} by KBr pellet technique, and the spectrum is shown in Figure 3. The wavenumber assignments are presented in Table 1. The stretching due to hydroxyl group gives absorption at 3442 cm^{-1}. The band observed at 3053 cm^{-1} is due to vinyl C–H bending vibration and the band at 836 cm^{-1} is ascribed to the 1,4-substituted pyridinium ring vibration.

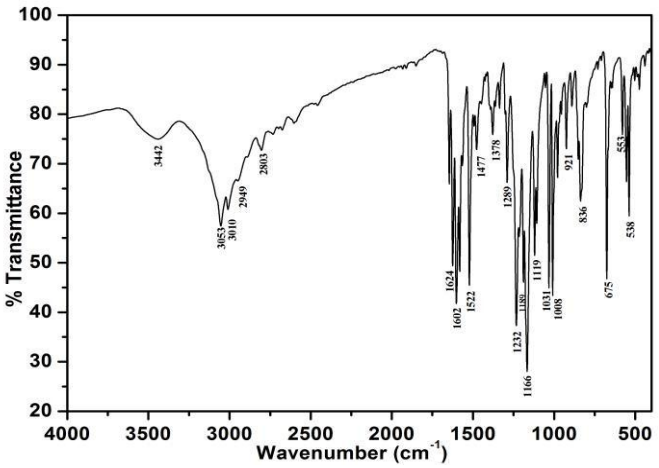

Figure 3: FT-IR spectrum of HSSS crystal

Table 1: FT-IR assignments for HSSS crystal

Wavenumber (cm^{-1})	Assignment
3442	Phenolic O–H stretch
3053	Aromatic C–H stretch
1624,1602	C=C stretch of the olefinic double bond
1522,1477	Aromatic ring vibrations
1378,1119	Asymmetric and symmetric stretching vibrations of $-SO_2$
1289	Phenolic C–O stretch
1031	Olefinic C–H bond
836	C–H bending vibration of the 1,4-disubstituted aromatic rings

3.4 UV-Vis-NIR spectral analysis

The absorption spectrum of HSSS was recorded in the wavelength range 200-1100 nm by dissolving the HSSS in methanol. The spectrum is shown in Figure 4. From the absorption peaks, the optical band gap was calculated and the nature of transitions also identified. The optical absorption spectrum of HSSS in methanol shows two distinct absorption peaks at 255 and 392 nm. The minor peak at 255 nm corresponds to the n-π* transition and the corresponding energy is 7.79×10^{-19} J and the major peak with maximum absorption at around 392 nm represents the π-π* transition with 5.06×10^{-19} J of energy. The material is transparent with very low absorption from 500 to1100 nm. The absence of absorption in this region paves way for NLO applications.

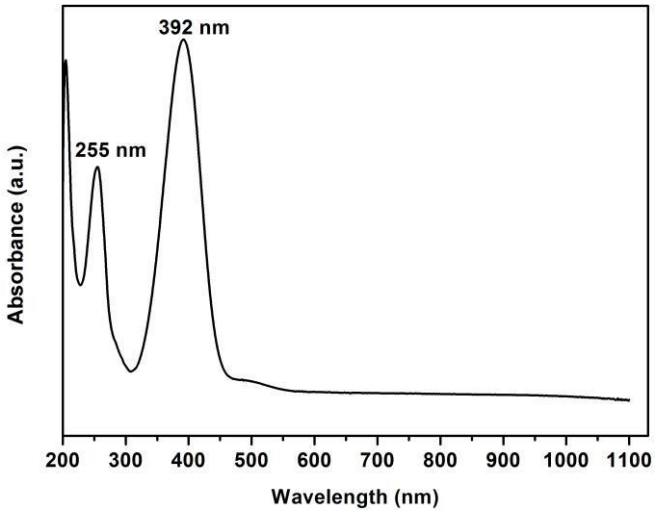

Figure 4: UV-Vis-NIR absorption spectrum of HSSS crystal

4. CONCLUSION

A stilbazolinium derivative salt, 4-(4-hydroxy styryl)-1- methylpyridinium 4-styrenesulfonate (HSSS) was synthesized by metathesization reaction mechanism. Single crystals of HSSS were grown by slow evaporation technique and the crystal structure was confirmed by single crystal XRD analysis. The functional groups identification and the structure of compound were confirmed by FT-IR and NMR spectral analyses. From the absorption spectrum, the nature of transitions was identified.

ACKNOWLEDGEMENT

The authors acknowledge the DST-SERB, India for funding this research work (SR/S2/LOP-29/2013).

REFERENCES

[1] Gunaseelan R. and Sagayaraj P., "Bulk size crystal growth and physicochemical properties of ionic organic NLO crystal of DSMOS: A potential THz emitter", Materials Chemistry and Physics, Vol.136, pp. 379-385,2012.

[2] Jagannathan K., Kalainathan S. and Bhagavannarayana G., "Growth and characterization of organic non-linear optical crystal 4-hydoroxybenzaldehyde-*N*-methyl 4- stilbazolium tosylate (HBST)", Spectrochimica Acta Part A, Vol. 73 pp. 79-83, 2009.

[3] Kumar K., Rai R. N. and Rai S. B., "One and two-photon- pumped luminescence studies on DAST and UDAST organic dye molecules", Applied Physics B: Lasers and Optics, Vol. 96, pp. 85-94, 2009.

[4] Jerald Vijay R., Melikechi N., Tina Thomas., Gunaseelan R., Antony Arockiaraj M. and Sagayaraj P., "Growth, structural, optical and thermal properties of potential THz material: N, N-dimethylamino-N' methylstilbazolium 4-styrenesulphonate", Journal of crystal growth,Vol. 338, pp. 170-176, 2012.

[5] Nivetha K., Madhuri W. and Kalainathan S., "Synthesis, growth, crystal structure and characterization of new stilbazolium derivative single crystal: (E)-4-(3-ethoxy-2- hydroxystyryl)-1-methylpyridiniuiodide (3ETSI)", Journal of Materials Science: Materials in Electronics, Vol. 28, pp. 8937–8949, 2017.

[6] Priya Antony, John Sundaram S., Sagayaraj P., "Growth and characterization of an organic stilbazolium family single crystal of DESI", International Journal of Latest Research in Engineering and Technology, pp.75-77,2016.

[7] John Sundaram S., Dominique, Priya Antony, Antony Raj A., Sagayaraj P., "Growth and characterization of organic stilbazolium single crystal of N,N-dimethylamino-N'- methylstilbazolium p-chlorobenzenesulfonate (DASC) in a mixed solvent system", International Journal for Research in Science Engineering and Technology, Vol. 3, pp. 37-40, 2016.