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Synthesis, single crystal growth, spectral, optical and luminescence studies of stilbazoliumiodide crystal: EESI

K.Senthil[1], S.Kalainathan[1]*, A.Rubankumar[1],

[1,1]*Centre for Crystal Growth, School of Advanced sciences, VIT University,Vellore - 632 014, Tamilnadu, India.

***Corres.author: kalainathan@yahoo.com**
Phone: +91-416-2202350 Fax: 0416-2243092

Abstract: A new stilbazolium derivative salt 2-[2-(4-Ethoxy-phenyl)-vinyl]-1-ethyl-stilbazolium iodide have been successfully synthesized and purified by repeated recrystallization process. Single crystals of EESI have been grown by the slow evaporation solution growth method at room temperature by using methanol-acetonitrile mixed solvent. The crystal system and cell parameters have been confirmed by single crystal XRD analysis. The crystallinity of grown crystal has been identified by powder X-ray diffraction analysis. The molecular structure of EESI was confirmed by ^{1}H NMR spectral studies. The UV-Vis-NIR optical absorption study reveals that the grown crystals have transmitting ability in the entire visible region. The luminescence property of the EESI was investigated by using spectrophotometer.
Keywords: Organic compounds, crystal growth, slow evaporation method, spectroscopy studies.

1. Introduction and Experimental

Organic crystals with large nonlinear optical (NLO) materials are having attracted for their potential in electronics and photonics applications due to their design, and synthesis to suit the requirements of optoelectronic applications. Organic molecule with preferred orientation of chromophores present in the crystal, which are responsible for the high second order optical nonlinearities [1-2]. Aromatic compounds with delocalized π-electrons system usually have a significant impact to the process of second harmonic generation compared to inorganic material. However, their practical applications are limited by poor chemical stability, mechanical and thermal properties and low laser damage threshold, due to the presence of large organic conjugated system [3-4]. Among many organic NLO materials, stilbazolium and its derivatives materials have been reported in the literature because of their salts exhibit larger NLO response and better photo/thermal stability compared to their neutral analogues [5-6]. In this present work, we report the material synthesis, growth and characterization of stilbazolium iodide EESI.

1.1. Material synthesis

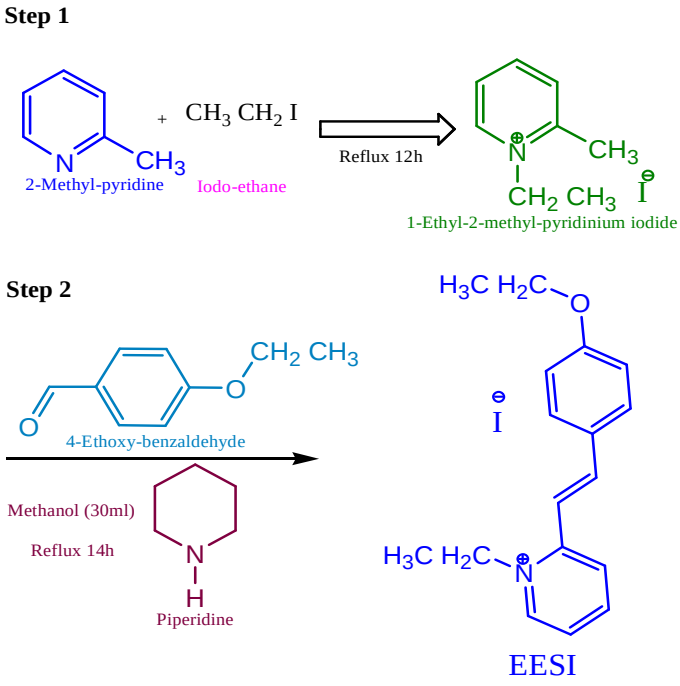
The title material 2-[2-(4-Ethoxy-phenyl)-vinyl]-1-ethyl-stilbazolium iodide (EESI) was synthesized by condensation of 1-ethyl-2- methylpyridinium iodide with 4-ethoxybenzaldehyde in the presence of piperidine as a catalyst. The reaction mechanism of compound and the synthesis process is shown in scheme 1.

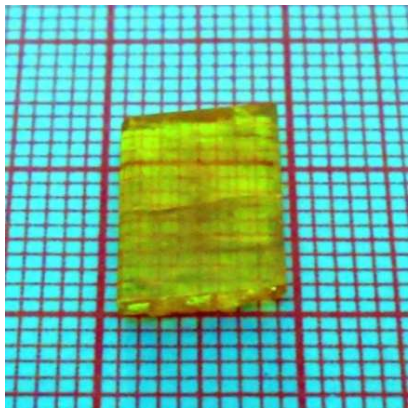
1-ethyl-2- methylpyridinium iodide (A)

The compound A was prepared from 2-picoline (20mmol) and iodoethane (20mmol) were taken in 100ml RB flask and refluxed with continuous stirring for 12 h at 60°C, which yielded pale yellow product of A. The obtained salt was washed with acetone to remove the starting material and dried.

2-[2-(4-Ethoxy-phenyl)-vinyl]-1-ethyl-stilbazolium iodide(EESI)

Stoichiometric (1:1) ratio of compound A, 4-ethoxybenzaldehyde and piperidine (0.2ml) were mixed in hot methanol.The resulting mixture was refluxed for 14h until crystallize as yellow salt. The resultant salt was separated, and purified by successively recrystallized from methanol. The single crystal of EESI has been grown from the saturated solution of EESI in methanol: acetonitrile mixed solvent over a period of 25 days by slow evaporation method. The grown EESI crystal is shown in Fig. 1.





Scheme.1. Synthesis process of EESIFig.1.As-grown single crystal of EESI.

2. Results and discussion

2.1. Powder X-ray diffraction analysis

The crystallinity of the grown crystals has been characterized by X-ray powder diffraction analysis using BRUKER X-ray diffractometer with a scan speed of 0.02° S^{-1} (2θ).The obtained Bragg's peaks at specific 2θ angles show a high degree of crystallinity of the title compound. From the single crystal XRD studies, the lattice parameter values were calculated, and the grown EESI crystal belongs to the triclinic crystal system and the lattice parameters were determined to be a= 7.612(18) Å, b=10.354(18) Å, c=11.214(7) Å and angles α=97.72(8) °, β=102.47(9)°, γ=97.59(16) ° and V=843.1(2) $Å^3$.

2.2. ^{1}H NMR spectral studies

The molecular structure of the EESI was confirmed through BRUKER instrument operating with 400MHz model FT-NMR spectrometer. Fig.2 shows the ^{1}H-NMR spectra of EESI.The triplet peak at δ = 1.132 ppm was due to the presence of -CH_2 in ethoxy group.Similarly,the quartet peak was observed at δ =1.461ppm due to the CH_3 group protons in the ethoxy group.The ethyl group was attached in the pyridinium ring, since this group gives one triplet peak at δ =4.115 ppm, and another one quartet was seen at δ=4.779 ppm. The doublet peak at δ=7.440 and δ=7.839 ppm are due to the presence of two olefinic hydrogens (-CH=CH-).The two doublet signal was observed at δ=7.034 and δ=7.896ppm are ascribed to the aromatic ring protons. The pyridinium ring produces two doublet peaksand one triplet peaks were identified at δ=8.445, δ=8.9 and δ=7.920 ppm.

2.3. UV–Visible spectral analysis

The optical absorption spectrum of EESI as recorded for the wavelength range of 190–1100 nm using a ELICO SL 218 double beam UV-Vis-NIR spectrometer. The recorded spectrum is depicted in Fig. 3. The crystal is observed to be transparent and the absorbance is less in the entire visible region is a significant factor for NLO device applications [4]. It is observed that the maximum absorption peak at 373nm, which is assigned to π–π* transition and may attribute to the extended conjugated system in the stilbazolium ring.

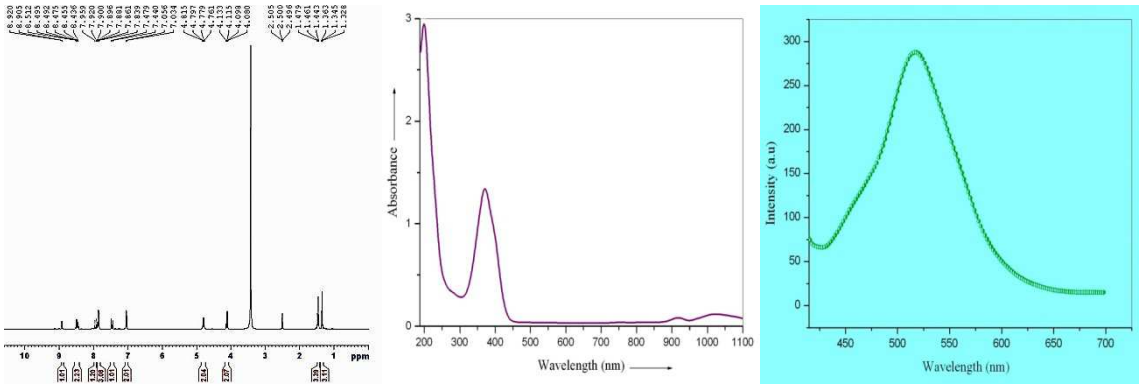


Fig.2. ^{1}H NMR spectra of EESI, Fig.3. UV-Vis-NIR spectra of EESI and Fig.4.Emission spectra of EESI.

2.4. Photoluminescence studies

Photoluminescence spectrum (PL) was recorded between 415 and 700 nm using the instrument F-7000 FL Spectrophotometer.The recorded PL spectrum of EESI crystal is shown in Fig.4. From the PL spectrum, a strong and broad emission peak was identified at about 532nm with excited with 373nm and illustrate that the EESI has an emission of green radiations and which may be due to the mobility of π- electrons through donor to acceptor groups present in EESI crystal.The band gap energy was calculated for the EESI crystal is about 2.33 eV. Thus, the title crystal can be used in laser applications.

Conclusion

Single crystals of EESI have been grown by slow evaporation method. The single crystal XRD diffraction analysis reveals that the crystal belongs to triclinic system. The formation of the EESI was qualitatively confirmed by ^{1}H NMR technique. The optical transparency and emission behaviour of the title crystal was confirmed by UV-Vis-NIR and photoluminescence spectral analysis.

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3. References

1. Thakur.M, Xu.J, Bhowmilk.A, Zhou.L, Single-pass thin-film electro-optic modulator based on an organic molecular salt, Appl. Phys. Lett., 1999, 74, 635.
2. Chemla.D.S, Zyss.J, NonLinear Optical Properties of Molecules and Crystals,Academic Press, New York, 1987, 2.
3. Jiang Min-hua, Fang Qi. Organic and Semiorganic Nonlinear Optical Materials, AdvancedMaterials. 1999, 11, 1147.
4. Crasta. V, Ravindrachary.V, Bhajantri.R.F, Gonsalves.R,Growth and characterization of an organic NLO crystal: 1-(4-methylphenyl)-3-(4-methoxyphenyl)-2-propen-1-one, J. Crystal Growth., 2004,267, 129.
5. Marder.S.R,Perry.J.W, Yakymyshyn.C.P,Organic Salts with Large Second-Order Optical Nonlinearitiesl, Chem. Mater., 1994, 6, 1137.
6. Adachi.H, Takahashi.Y, Yabuzaki.J, Mori.Y, Sasaki.T,Growth of high quality nonlinear optical crystal 4-dimethylamino-N-methyl-4-stilbazolium tosylate (DAST)J. Cryst. Growth. 1999, 568,198-199.

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