J. Indian Chem. Soc.,
Vol. 96, January 2019, pp. 90-92

Synthesis, growth, vibrational, thermal and birefringence property of NLO active organic crystal: Quinolinium fumarate

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Manuscript received online 20 August 2018, accepted 09 October 2018

The slow evaporation method is used to grow quinolinium fumarate (QF) at room temperature. The crystal comes under orthorhombic crystallographic system with $Pca2_1$ space group. The FT-IR study confirmed the vibrational groups in the crystal. The thermal measurement is used to analyze the thermal firmness of the crystalline sample. The birefringence measurement is taken on single crystal (QF) by technique named channeled spectrum.

Keywords: Crystal growth, slow evaporation, FT-IR analysis, thermal study, birefringence.

Introduction

Organic materials having optical property that contains aromatic rings render large class materials with high nonlinearity, fast response and high optical damage threshold. Organic materials have higher optical susceptibilities, large optical threshold in terms of laser power, low frequency dispersion and large optical coefficient resulting in large optical property than inorganic analogues. Materials depicting large optical nonlinearity are of exceptional interest for applications in conversion of frequency, optical computing, telecommunication, optical information processing and large optical disk data storage. Quinolines have the potential to π-stack amid themselves that seeks attention in supramolecular chemistry and in biology. Ning Shan *et al*. reported the structure of quinolinium fumarate[1]. Hereby we report the synthesis, growth, FT-IR spectral analysis and thermal study and birefringence study of QF single crystal.

Material synthesis and single crystal X-ray diffraction:

QF single crystal was synthesized by the reaction between quinoline and fumaric acid taken in equimolar ratio. Fumaric acid was first dissolved in ethanol:water mixed solvent. The calculated amount of quinoline was added slowly to this solution with continuous stirring. The prepared mixture was continuously stirred for about 5 h and clear solution was obtained. The solution was filtered off to remove the insoluble impurities. The evaporation of the solution at room temperature is noted carefully. The mother solution yields good quality single crystals in forty five days and the as-grown crystal is shown in Fig. 1.

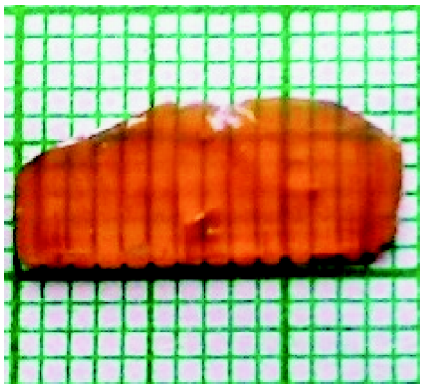

Fig. 1. As-grown QF crystal.

The unit cell parameters of the grown QF crystals were obtained using ENRAF NONIUS CAD4/MAC4 X-ray diffractometer with MoK_α. The cell parameter values are a = 22.58 Å, b = 3.72 Å, c = 13.29 Å, V 1118.81 Å^3 and agrees well with the reported values[1]. QF crystal falls under orthorhombic system with non-centrosymmetric space group $Pca2_1$.

FT-IR spectral analysis:

FT-IR spectrum of the QF crystal was recorded to confirm its composition using Perkin-Elmer FT-IR spectrometer in the range 4000–400 cm^{-1} by the KBr pellet method. The functional group of the synthesized compound is confirmed from FTIR spectroscopy. The recorded FTIR spectrum is shown in Fig. 2. The quinoline and fumaric acid molecules were held together by the intermolecular hydrogen bonding. The broad band at 2797 cm^{-1} in FTIR spectrum was assigned to NH stretching vibrations. The band at 2793 cm^{-1} in FTIR spectrum was assigned to NH stretching vibrations[2]. The protonation of the heterocyclic N atom in quinoline is confirmed from the above said band. The vibration at 988 cm^{-1} in FT-IR spectrum is due to C-H out-of-plane bending. The band at 1230 cm^{-1} in FT-IR spectra is due to in-plane C-H bending. The C-H stretching vibration overlapped with N-H stretching vibration is observed at 2600 cm^{-1}. The OH stretching vibration was observed at 3054 cm^{-1}, 2930 cm^{-1} in FT-IR spectrum. The asymmetric C=O stretching[3] was identified at 1712 cm^{-1} in FT-IR spectrum respectively.

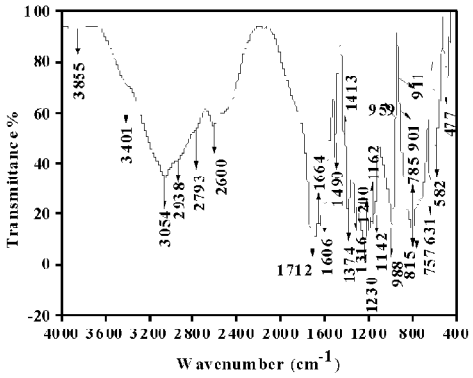

Fig. 2. FT-IR spectrum of QF crystal.

Thermal analysis:

The firmness of the crystalline sample is examined by thermo gravimetric/differential thermal analysis (TG-DTA). The TG-DTA of QF crystal was carried out between 30–500°C in the nitrogen atmosphere. A sample of weight 2.128 mg is kept in an alumina pan. The heating rate was maintained at 20°C/min. The TG-DTA thermo gram is shown in the Fig. 3. In TG analysis, the exact weight loss starts at 104°C. A 42% weight loss is achieved between 104°C and 172.4°C in the first stage of decomposition. A 55% weight loss is achieved between 179°C and 266°C. The DTA curve clearly shows two significant endothermic peaks. The melting point of the crystalline sample corresponds to the endothermic peak at 155°C. This is followed by another endothermic peak at 245°C which matches with the decomposition stages obtained in TGA. Thus the TGA spectrum indicates the crystal is stable up to 104°C without any decomposition of molecules and hence the title compound QF is useful for optical device fabrication

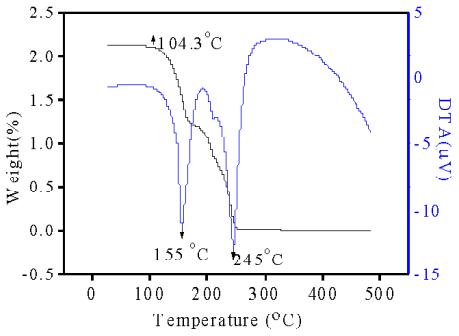

Fig. 3. TG-DTA trace of QF crystal.

Birefringence studies:

The birefringence measurement is taken on QF single crystal using spectral dependence of the visibility of interference fringes with halogen lamp as a source. The birefringence is calculated by the relation: $\Delta n = k\lambda/t$. The graph showing dispersion of birefringence (∇n) versus wavelength (λ) is represented in Fig. 4. The birefringence value of the conventional grown crystals was found to be 0.039741 at the wavelength 650 nm for the thickness of 0.0.902 mm. The obtained birefringence value decreases with wavelength, which explains that the grown QF crystal possesses nega-

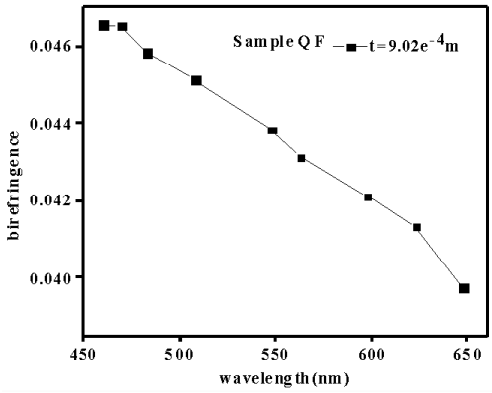

Fig. 4. Birefringence plot of QF crystal.

tive dispersion of birefringence and was optically positive at room temperature[4].

Conclusions

The slow evaporation method is used to grow QF crystal and single crystal XRD data provides the unit cell parameters. The functional groups were confirmed by FT-IR analysis. The title compound QF is useful for optical device fabrication and is stable up to the temperature 104°C. The decrease in birefringence value with wavelength shows negative dispersion of birefringence.

References

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