Synthesis, Growth, Optical and Dielectric Characterization of 8-Hydroxyquinolinium Hydrogen Fumarate Single Crystal

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Abstract. An organic nonlinear optical single crystal, 8-hydroxyquinolinium hydrogen fumarate (8HQF) was grown from mixed solvent of ethanol and water using slow evaporation solution growth technique. The single crystal XRD studies confirmed that the grown crystal belongs to the triclinic crystal system with the centrosymmetric space group \( P \bar{1} \). FT-IR spectral analysis confirms the various functional groups present in the compound. The optical absorption studies shows that the crystal is transparent with a lower cut-off wavelength of 439 nm and the optical energy band gap \( E_g \) is found to be 2.66 eV. The variation of dielectric properties of the grown crystal with respect to the frequency has been investigated at different temperatures.

Keywords: Solution growth, Optical transmittance, Vibrational analysis.

1. Introduction
The explore of new advanced materials is an essential area of current research in many branch of knowledge in science and the development of new technologies. The inception of nonlinear properties is well grasped phenomenon and the advancement of optical research relies on the development of new materials compatible with various devices [1]. A non linear optical material unveiled a wide range of applications in telecommunication, optical information processing and integrated optics [2]. These materials play a vital role in the development of modern technology and industrial applications [3]. In this context, organic molecules materialize as promising candidates since they have several advantages such as low dielectric constant with electronic polarizability, refractive index, etc., over inorganic nonlinear optical crystals. Organic 8-Hydroxyquinoline is a proton donor which forms variety of charge transfer complexes and their complexes are well known for their anti microbial and antifungal activities. Generally aromatic compounds containing electron releasing substituent group act as donors and those containing highly electron with drawing group act as acceptors [4-6]. Franklin et al. has reported the crystal structure of 8-hydroxyquinolinium hydrogen fumarate (8-HQF) using the compound 8-hydroxyquinoline and fumaric acid as precursors [7]. In this present investigation we report the growth, vibrational, optical and dielectric studies of an organic 8-hydroxyquinolinium hydrogen fumarate single crystal for the first time.
2. Experimental Details
The title compound 8-hydroxyquinolinium hydrogen fumarate was synthesized by the reaction of commercially available 8-hydroxyquinoline (Merck) with that of Fumaric acid (Sigma Alderich, AR Grade) in the stochiometric ratio of 1:1 in a mixed solvent of ethanol and water. It is a proton transfer reaction where a proton is transferred from the electron donor group of fumaric acid to the electron acceptor group of 8-hydroxyquinoline. A yellow precipitate was formed on continuous stirring. The title crystal was obtained by repeated recrystallization of the combined compound. The reaction scheme of the 8HQF is shown in Fig.1. Yellow color crystals of size 5 x 5 x 3 mm$^3$ were harvested in 20 days of evaporation at room temperature from the saturated solution. The as grown crystal is shown in Fig.2.

![Reaction scheme of 8HQF crystal](image1)

![As grown crystal of 8HQF](image2)

**Figure 1.** Reaction scheme of 8HQF crystal

**Figure 2.** As grown crystal of 8HQF
3. Results and Discussion

3.1 Single X-Ray Diffraction Studies

The single crystal diffraction data of 8HQF crystal were collected using Bruker Kappa Apex II CCD diffractometer with Mo–Kα radiation (λ=0.71073 Å: graphite monochromator). It is observed that the crystal belongs to the triclinic system with the centrosymmetric space group P 1. The obtained lattice parameters are presented in Table 1. These values are in good agreement with the literature [7].

| Parameter | Presented study | Reported values [7] |
|-----------|-----------------|---------------------|
| a         | 7.36Å           | 7.3282(3)Å          |
| b         | 7.48Å           | 7.4363 (3)Å         |
| c         | 11.64Å          | 11.5680(5)Å         |
| α         | 79.39°          | 79.349 (2)°         |
| β         | 74.85°          | 74.994 (2)°         |
| γ         | 89.32°          | 89.337 (2)°         |
| V         | 608Å³           | 597.97 (4) Å³       |
| System    | Triclinic       | Triclinic           |
| Space group | P 1            | P 1                 |

3.2 Spectral Analysis

FT-IR spectroscopy is used to identify the functional groups of the synthesized compound and hence to elucidate its molecular structure [8]. The FTIR spectrum of 8-hydroxyquinolininium hydrogen fumarate crystal was recorded using Perkin Elmer FT-IR spectrometer in the range 4000-450 cm⁻¹ by the KBR pellet method. The FT-IR spectrum is depicted in Fig.3. The related assignments of the functional groups are tabulated in Table 2. The 8HQF compound includes weak to strong intermolecular hydrogen bonding. The peak observed at 3419 cm⁻¹ was attributed to O-H stretching vibration attached to quinoline group in FT-IR spectrum [9]. The medium intensity sharp band observed at 2949 cm⁻¹ is due to the N-H stretching vibration. The absorption bands occurred in the regions 2851, 2776 and 2671 cm⁻¹ corresponds to the C-H stretching vibration [10]. The C=O stretching vibrations of 8HQF complex is observed at 1711 and 1387 cm⁻¹. The bands occurred at 1636, 1491 cm⁻¹ in FT-IR corresponds to C-C stretching vibration [11]. The aromatic C=C stretching vibrations are exhibited at 1598 and 1553 cm⁻¹. The C-H in plane bending vibration is observed vat 1096 and 1136 cm⁻¹. The C-O symmetrical stretching vibrational peak is observed at 1302, 1310 and 1065 cm⁻¹. The band at 1265 cm⁻¹ is due to
the phenolic C-O stretching. The C-N deformation is observed at 927 cm\(^{-1}\) \cite{12} and C-H out of plane bending vibration is observed at 794 cm\(^{-1}\) and 753 cm\(^{-1}\). The C-H rocking vibration appears as a weak band in IR at 884 cm\(^{-1}\). The C=O group deformation stretching vibration appears at 824 cm\(^{-1}\). The bands at 641 cm\(^{-1}\) and 578 cm\(^{-1}\) is due to the O-H and C-O deformation vibration respectively.

**Table 2. Vibrational frequency assignments of 8-HQF crystal**

| FT-IR (cm\(^{-1}\)) | Assignments                        |
|---------------------|------------------------------------|
| 3419                | O-H stretching vibration           |
| 2949                | C-H stretching vibration           |
| 2851, 2776, 2671    | N-H stretching vibration           |
| 1711, 1387          | C=O stretching vibration           |
| 1636, 1491          | C-C stretching vibration           |
| 1598, 1553          | C=C stretching vibration           |
| 1302, 1310, 1065, 1265 | C-O symmetric stretching vibration |
| 1096, 1136          | aromatic C-H in plane bending      |
| 927                 | C-N deformation                    |
| 884                 | C-H rocking vibration              |
| 824                 | C=O deformation                    |
| 794, 753            | C-H out of plane bending           |
| 578                 | C-O deformation                    |
3.3 Uv-Vis Studies

The optical transmission spectrum of 8HQF single crystal was recorded in the wavelength region from 190nm to 900nm as shown in Fig.4 (a). The Uv absorption edge of the 8HQF crystal was observed to be around 442nm. The co-relation of optical absorption coefficient with the photon energy helps to study the band structure and the electron transitions [13].

Using the transmittance \( T \) and the thickness of the crystal \( t \), the optical absorption coefficient \( \alpha \) is calculated using the following relation:

\[
\alpha = \frac{1}{t} \log \left[ \frac{1}{T} \right]
\]

For high photon energies the crystal under study obeys the following relation:

\[
\alpha = \frac{A(h\nu - E_g)^{1/2}}{h\nu}
\]

where \( E_g \) is the optical band gap of the crystal and \( A \) is constant. The \( E_g \) is evaluated by extrapolation of the linear portion of the curve to x-axis [14] in the plot of variation of \((\alpha h\nu)^{2}\) vs. \( h\nu \) as depicted in Fig.4 (b) and the band gap is found to be 2.66eV. As a
consequence of wide bandgap, the 8HQF has large transmittance in visible region and therefore it proves to be a suitable candidate for optoelectronic applications[15].

Figure 4. (a) Uv-Vis spectrum of 8HQF crystal and (b) Tauc’s plot for 8HQF crystal

3.4 Dielectric studies
The dielectric analysis is measured to avail the details about the electrical properties of the material at different frequencies. The dielectric studies were carried out using LCR meter in a frequency range 50Hz-5MHz. Silver paste was applied over the cut and polished 8HQF sample and placed in the cell which is connected with a thermocouple. A thermocouple attached to the electrode is used to measure the temperature. Local displacement of electrons in the direction of the applied field takes place due to the electronic exchange of number of ions in the crystals. Fig.5 shows the plot between dielectric constant and log frequency. The dielectric permittivity occurs because of the four polarization mechanisms of materials such as electronic polarization, ionic polarization, orientation polarization, and space polarization. At very low frequencies the dielectric characteristics are affected by interfacial polarization or at the microscopic level by space charge polarization [16]. Thus, the high value of permittivity at low frequency is mainly due to space charge polarization,[17] hence this type of dielectric constant values are good candidates for heating devices [18]. The value of dielectric constant can be calculated using the formula:

$$\varepsilon_r = \frac{Ct}{\varepsilon_0 A}$$

where ‘C’ is the capacitance, ‘t’ is the thickness of the crystal, ‘\(\varepsilon_0\)’is the permittivity of free space and ‘A’ is the area of the crystal. Fig.6 shows the plot between the dielectric loss and log frequency. It is observed that the dielectric loss decreases with the increase in frequency at
different temperatures. The low value of dielectric loss at high frequency of 8HQF crystal sample shows that the grown crystal possesses enhanced optical quality with lesser defects [19]. Thus the good quality crystals are used for extending the applications towards, photonic, electro-optic and NLO devices [20].

![Figure 5](image1.png)

**Figure 5.** Plot between dielectric constant and log frequency of 8HQF

![Figure 6](image2.png)

**Figure 6.** Plot between the dielectric loss and log frequency of 8HQF
4. Conclusion
A new organic material 8HQF was synthesized from solution using ethanol as solvent. The structure of the grown crystal were proved by the powder XRD data and compared with the literature data. Various functional groups present in the grown crystal confirmed from the FTIR spectrum. The UV cut off wavelength was found to 442 nm and the UV–Vis spectrum showed good transparency (43%) in the Uv -Vis region showing that 8HQF is a good candidate for NLO applications. The dielectric studies revealed that the grown crystal has low dielectric constant with less power dissipation and hence this crystal can be used for electro-optic applications.

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