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Investigation on growth, structural, dielectric, optical and third-order optical nonlinear properties of 8-hydroxyquinolinium 4-chloro-3-nitrobenzoate 4-chloro-3-nitrobenzoic acid crystal

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Abstract

An organic 8-hydroxyquinolinium 4-chloro-3-nitrobenzoate 4-chloro-3-nitrobenzoic acid (8-HQCN) was synthesized and the crystals were grown by employing solution growth method. Single crystal XRD data revealed crystal system (monoclinic, space group P21/n), and cell dimensions (a = 6.9806(2) Å, b = 11.9919(4) Å, c = 26.8872(8) Å). The FT-IR, FT-Raman and NMR spectral analyses provide the molecular structure. UV–visible spectrum provides a band gap (3.03 eV) and cut off wavelength (404 nm) of the crystal. The broad emission at 580 nm in PL spectrum reveals the suitability of the material yellow light emission. Vicker’s microhardness study gives the mechanical stability of the grown crystal. The nonlinear optical susceptibility (χ(3)) of the molecule was calculated as 16.78 × 10−6 esu from Z-scan technique and from DFT theory it was calculated to be 5.632 × 10−6 esu using cam-b3lyp/6–311G (d, p). Thermo-optic coefficient of 8-HQCN was predicted to be 3.805 × 10−6 K−1 by thermal conductivity studies. This thermally prompted defocusing character can be made useful in optical limiters. The thermal investigation exhibits the bearing proficiency of 8-HQCN to be 127 °C. The orbital energy, band gap and the second hyperpolarizability were also studied by varying the applied field. The dispersion of the dielectric constant illustrates the usual behavior and the enhanced quality of the material gives the low dielectric loss. Antibacterial studies were taken to check the resistance to harmful bacteria of the grown crystal.

1. Introduction

Nonlinear-optics is an enticing domain of research exploration due to their broad range utilization in photonic devices. The quick nonlinear response, less costs, easy way by which the structure is tuned to manipulate either physicochemical properties which in turn enhances the NLO effect make the organic compounds beneficial over the inorganic materials [1, 2]. The presence π-electron delocalization makes importance of many of the organic materials in designing the nonlinear optical devices [3, 4]. The planarity [4, 5], functionalization with proper groups (e.g., π-electron rich) [3] and the di-radical character (DC) may add to large third-order NLO properties. Organic chromophores having a wider band gap are applicable for NIR photodetectors and NLO materials [6, 7]. The 8-hydroxyquinoline (8-HQ) contains a ring of phenol connected with a pyridine. The optical nonlinearity of 8-HQ can be notably refined on raising the accepting tendency of the pyridine and/or raising the donating tendency of the benzene ring. 8-hydroxyquinoline accept proton when reacts with acids and forms charge transfer compounds. In experimental and analytical point of view, the electroluminescent materials are established with 8-hydroxyquinoline. Hence, many researchers concentrate on studying 8-HQ related complex compounds [8–11]. Zidan et al [12] reported the optical nonlinearity of 8-HQ with 2-chloroacetate and (2)–3-carboxyacrylate salts by Z-scan technique but their nonlinear optical susceptibility values are lower compared

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to the present work. Thirumurugan et al. [13] discussed the SHG property of 8-HQ with succinic acid. Similarly, on keeping 8-hydroxyquinoline as a base dibenzoyl (L)-tartaric acid [14], 3, 5-dinitrobenzoic acid [15] and picric acid [16], were reacted to form a pure crystal but its efficiency was discussed only through linear optical absorption but not in its nonlinear optical property. Selvakumar et al. [17] has already reported the characterization of 8-hydroxyquinolinium 4-nitrobenzoate 4-nitrobenzoic acid crystal. Furthermore the optical third order nonlinearity has not been discussed. But the present work has more advantages over the others by exhibiting a higher value of third order nonlinear optical susceptibility and also it exhibits the optical limiting behavior. So far the reported papers mentioned have not reported about the optical limiting nature. In this context, the grown 8-HQCN crystal shines towards using it in applications over effect of lasers, the interaction between laser materials, in the outstanding field of information technology, which is inclusive of sensing, communicating, storing and processing of information. In this treatise, we communicate the structural analysis, optical, thermal and nonlinear activities of 8-hydroxyquinolinium 4-chloro-3-nitrobenzoate 4-chloro-3-nitrobenzoic acid (8-HQCN) single crystal. In addition, the theoretical study was also done to find out the orbital’s energy, band gap and the second hyperpolarizability by varying the applied field and the nonlinear optical susceptibility was also found using DFT.

2. Materials and methods

2.1. Synthesis and crystal growth

The 8-hydroxyquinolinium 4-chloro-3-nitrobenzoate 4-chloro-3-nitrobenzoic acid (8-HQCN) was prepared from 8-hydroxyquinoline (Merck) and 4-chloro-3-nitrobenzoic acid (AR Grade, Sigma Aldrich) in the equimolar ratio. The 8-hydroxyquinoline gently added to the ethanol solution of 4-chloro-3-nitrobenzoic acid it with a continuous stirring. The small amount of double distilled water was poured to reduce the evaporation speed with the aim to yield good quality crystal. The 8-HQCN compound is feebly soluble in water, but highly in ethanol and methanol. However, good yield of crystals is being obtained using ethanol as a solvent. The solubility was tested from 30 °C. The equilibrium state of the solute for every 5 °C was found using gravimetric analysis when the solution attains the saturation. The solubility curve attained for 8-HQCN is visualized in figure 1(a).

The solubility curve shows the fitness of ethanol medium for the growth of 8-HQCN crystal from the slow evaporation method. The saturated solution was maintained at 35 °C without disturbing. In a time of 30 days, a transparent crystal, with dimensions $8 \times 4 \times 1$ mm$^3$ was collected from mother solution and shown in figure 1(b).

2.2. Experimental details

Bruker Kappa APEX II diffractometer with MoKα radiation of wavelength 0.71073 Å was employed to study the crystal structure. The intensities of 4956 distinctive reflections were utilized out of the 18 779 reflections in a limit of 1.52 to 27.16°. The structure was analyzed by direct method using SHELXL97 [18] to refine the structure with refinement value $R = 0.0379$ and $wR(F^2) = 0.0969$ for the intensity $I > 2\sigma(I)$. The FT-IR spectrum was obtained using PERKIN ELMER SPECTRUM one FT-IR spectrometer by employing KBr pellet technique. Mercury lamp was used as the source and the measurements were taken with a resolution of 1.0 cm$^{-1}$. The

![Figure 1. (a). Solubility curve of 8-HQCN in ethanol and (b). As grown crystal of 8-HQCN (inset).](image-url)
The molecular geometry optimization, without symmetry restrictions, was performed using density functional theory (DFT) with the hybrid exchange correlation functional (CAM-B3LYP) and using the 6–311G(d,p) basis set. The Gaussian 09 package [21] was employed for the above calculation and molecule was visualized by Gauss View [22]. The TD-DFT at B3LYP/6–311++G (d, p) level of theory was employed to study the electronic absorption spectrum of the optimized molecule in gas and solvent (DMSO and chloroform) phases. The nature of the excited state, the oscillator strength ($\Omega$) and the difference in dipole moment between ground and excited states ($\Delta \mu_{\text{rup}}$) were also obtained.

3. Results and discussion

3.1. Crystal structure analysis

The crystal data of 8-HQCN crystal are represented in table 1. From table 1, one can infer that 8-HQCN belongs to the monoclinic system with space group P2$_1$/n and the computed lattice constants are: $a = 6.9806(2)$ Å, $b = 11.9919(4)$ Å, $c = 26.8872(8)$ Å and $V = 2248.52(12)$ Å$^3$. The ORTEP and packing diagram are represented in figures 2 and 3 while the table 2 gives hydrogen bond geometry. In addition, the bond distances and bond angles are produced in table S1 is available online at stacks.iop.org/MRX/6/125114/mmedia and the values about anisotropic parameters in table S2 and the fractional atomic coordinates along with deracination parameters (Å$^2$) which are equally isotropic in table S3. The 8-HQCN compound ($C_22H_{13}N_2O_6$), consist of a protonated 8-hydroxyquinolinium cation, 4-chloro-3-nitrobenzoe acid and a neutral 4-chloro-3-nitrobenzoic acid molecule being in the structural unsymmetrical unit. The unsymmetrical unit involves two aromatic loops of neutral 4-chloro-3-nitrobenzoic acid molecule which is planar with 3.58$^\circ$ dihedral angle. The networks of O···H–O, N···H–O and C–H···O hydrogen bonds stabilizes the 8-HQCN. The carboxylate (COO–) oxygen atoms act like hydrogen bond acceptors, and 8-hydroxyquinolinium N atoms provide the most extensive part as donors in the network. Hydrogen bonding happens in every 8-hydroxyquinolinium hydrogen atoms as a donor. Furthermore, the carboxyl O5 atom involves one hydrogen bond as an acceptor with H1 atom from the 8-hydroxyquinolinium cation group. The nitro O7 atom of neutral 4-chloro-3-nitrobenzoic acid is connected to the H2 atom via C–H···O hydrogen bond (table S1). The intermolecular C–H···O bonds connect...
the neighbouring cation and anion molecules into infinite one dimensional chains along a \([1 0 0]\) axis. The chains connecting \(O--H...O\) and \(N--H...O\) form a three dimensional grid. Weak intermolecular \(\pi...\pi\) interactions exhibits in the structure. The C16--O3 (1.209(2) Å) and C16--O2H (1.316(2) Å) has typical bond lengths for C=O and C--OH respectively for COOH groups. The COOH group of 4-chloro-3-nitrobenzoic acid gets deprotonated, whereas the 8-hydroxyquinolinium group gets protonated at N2 position. The approximately equal bond lengths C23--O4 (1.239(2) Å) and C23--O5 (1.269(2) Å) are typical for the delocalized

Table 1. Crystal data and structure refinement for 8-HQCN.

| Property                          | Value                                      |
|-----------------------------------|--------------------------------------------|
| Empirical formula                 | C_{23}H_{15}Cl_{2}N_{3}O_{9}              |
| Formula weight                    | 548.28                                     |
| Temperature                       | 295(2) K                                   |
| Wavelength                        | 0.71073 Å                                  |
| Crystal system                    | Monoclinic                                  |
| Space group                       | \(P2_1/n\)                                 |
| Unit cell dimensions              | \(a = 6.9806(2)\) Å \(\alpha = 90^\circ\) |
|                                  | \(b = 11.9919(4)\) Å \(\beta = 92.5470(10)^\circ\) |
|                                  | \(c = 26.8872(8)\) Å \(\gamma = 90^\circ\) |
| Volume                            | 2248.52(12) Å                             |
| Z                                 | 4                                          |
| Density (calculated)              | 1.620 Mg m\(^{-3}\)                      |
| Absorption coefficient            | 0.352 mm\(^{-1}\)                         |
| \(F(000)\)                        | 1120                                       |
| Crystal size                      | 0.30 \(\times\) 0.26 \(\times\) 0.20 mm\(^{3}\) |
| Theta range for data collection   | 1.52 to 27.16\(^\circ\)                   |
| Index ranges                      | \(-8 \leq h \leq 8, -14 \leq k \leq 15, -34 \leq l \leq 34\) |
| Reflections collected             | 18 779                                     |
| Independent reflections           | 4956 \([R(int) = 0.0213]\)                |
| Completeness to theta = 27.16\(^\circ\) | 99.6\%                                  |
| Max. and min. transmission        | 0.9329 and 0.9016                          |
| Refinement method                 | Full-matrix least-squares on \(F^2\)      |
| Data/restraints/parameters        | 4956/2/346                                 |
| Goodness-of-fit on \(F^2\)        | 1.079                                      |
| Final \(R\) indices              | \(R1 = 0.0379, wR2 = 0.0969\)              |
| \([I > 2\sigma(I)]\)              | \(R1 = 0.0475, wR2 = 0.1022\)             |
| R indices (all data)              | 0.0033(5)                                  |
| Extinction coefficient            | 0.309 and \(-0.346\) eÅ\(^{-3}\)          |

Figure 2. Molecular structure of 8-HQCN crystal.
carboxylate COO$^-$ groups. The data related to 8-HQCN have been submitted to the Cambridge Crystallographic Data Centre (CCDC–1405242).

### 3.2. Functional group analysis

The information associated with the configuration of the molecule structure and nature of chemical bonds was identified by the modes of vibration. The recorded spectra are produced in figures 4 and 5. The spot of the O-H bond relays upon the potency of hydrogen bonds abiding in the material. The broad O-H stretching normally expected between 2700 and 3540 cm$^{-1}$. The broad peak seen in FT-IR at 3433 cm$^{-1}$ is accredited to O-H stretching of 8-hydroxyquinoline [23]. The configuration of proton transfer is strongly evidenced by the N-H stretching vibration at 3091 cm$^{-1}$ in FT-IR and FT-Raman at 3078 cm$^{-1}$ [11]. The 8-HQCN structure comprises of a COOH; COO$^-$ of 4-chloro-3-nitrobenzoic acid where one is ionized and the other is neutral. The COOH stretching vibration of 4-chloro-3-nitrobenzoic acid moiety is observed around 1700 cm$^{-1}$ in both the spectra. The peak occupying at 1595 cm$^{-1}$ corresponds to asymmetric stretching while the one observed at 1400 cm$^{-1}$
Table 2. Hydrogen bond geometry for 8-HQCN [Å and °].

| D-H | Ad(D-H) d(H...A) d(D...A) <(DHA) | D-H | H...A | D...A | D-H...A |
|-----|---------------------------------|-----|------|-------|--------|
| N(1)-H(1)...O(1) | 0.882(9) | 2.37(2) | 2.6908(18) | 101.5(15) |
| C(2)-H(2)...O(7) | 0.93 | 2.44 | 3.338(2) | 161.3 |
| N(1)-H(1)...O(5)i | 0.882(9) | 2.053(15) | 2.8133(19) | 143.8(18) |
| O(1)-H(1A)...O(4)ii | 0.88(3) | 1.73(3) | 2.6137(17) | 174(3) |
| C(7)-H(7)...O(3)iii | 0.93 | 2.48 | 3.348(2) | 154.6 |
| O(2)-H(2A)...O(5)iii | 0.830(10) | 1.722(11) | 2.5451(17) | 171(3) |
| C(1)-H(1B)...O(2)iv | 0.93 | 2.50 | 3.395(2) | 161.4 |
| C(5)-H(5)...O(9)v | 0.93 | 2.58 | 3.489(2) | 166.3 |
| C(11)-H(11)...O(1)vi | 0.93 | 2.53 | 3.291(2) | 139.7 |

Symmetry codes: (i) x+1/2, −y+3/2, z-1/2; (ii) x+3/2, −y+3/2, z-1/2; (iii) x-1/2, y+1/2, −z+1/2; (iv) −x, −y+2, −z; (v) x+1, y, z; (vi) x-1/2, −y+3/2, z+1/2.

Figure 4. FT-IR spectrum of 8-HQCN crystal.

Figure 5. FT-Raman spectrum of 8-HQCN crystal.
attributes the symmetric stretching of COO$^-$ (figure 4). These vibrations in FT-Raman spectrum were found at 1604 and 1432 cm$^{-1}$ in FT-Raman spectrum [11]. The NO$_2$ asymmetric vibrations were present at 1533 cm$^{-1}$ in FT-IR and at 1538 cm$^{-1}$ present in FT-Raman and similarly corresponding symmetrical stretching in FT-IR occupied at 1350 cm$^{-1}$ and in FT-Raman occupied at 1392 cm$^{-1}$ [24]. The peaks detected at 2919 cm$^{-1}$ and 2777 cm$^{-1}$ in FT-IR and 2593 cm$^{-1}$ in FT-Raman was attributed to C–H stretching vibrations. The C–H out of plane bending vibration was observed at 847 cm$^{-1}$ [24]. The peak at 1523 cm$^{-1}$ in FT-Raman is due to C=C bending [25]. The phenolic C-O stretching creates a vibrational peak is recorded at 1267 cm$^{-1}$ in FT-IR spectrum and 1272 cm$^{-1}$ in FT-Raman [17]. The OH in plane distorting vibrations is accredited to the bands at 1306 cm$^{-1}$ both the spectra of FT-IR and FT-Raman. The vibrational stretching is noticed at 1108 and 1041 cm$^{-1}$ in the FT-IR and 1110, 1065 and 1045 cm$^{-1}$ in FT-Raman corresponds to a C–Cl. The C–N deformation observed at 910 cm$^{-1}$ and 912 cm$^{-1}$ in FT-IR and FT-Raman spectrum respectively. The C–N stretching vibration is observed at 882 cm$^{-1}$ in FT-IR and at 880 cm$^{-1}$ in FT-Raman. There are out of plane bending vibrations found at 418 and 220 cm$^{-1}$ in FT-Raman because of C–C–C, but these peaks are not seen in the IR.

| FT-IR (cm$^{-1}$) | FT-Raman (cm$^{-1}$) | Assignments |
|-----------------|---------------------|-------------|
| 3433            | —                   | O–H stretching |
| 3091            | 3078                | N–H stretching |
| 2919            | —                   | C–H stretching |
| 2777            | —                   | C–H stretching |
|                 | 2593                | C–H stretching |
| 2483            | —                   | C–H stretching |
| 1953            | —                   | C–H stretching |
| 1812            | —                   | C–H stretching |
| 1702            | 1700                | COOH stretching |
| 1595            | 1604                | COO– asymmetric stretching |
|                 | 1565                | C–H stretching |
| 1533            | 1538                | NO$_2$ asymmetric stretching |
|                 | 1523                | C = C bending |
|                 | 1475                | C = C stretching |
| 1400            | 1432                | COO– symmetric stretching |
| 1350            | 1392                | NO$_2$ symmetric stretching |
| 1354            | —                   | C–H bending |
| 1306            | 1306                | Inplane O–H deformation vibration |
| 1267            | 1272                | C–O stretching |
| 1234            | —                   | C–N stretching |
| 1108            | 1110                | Ring C–H deformation |
|                 | 1065                | C–Cl stretching |
| 1041            | 1045                | C–Cl stretching |
| 992             | 994                 | C–H in plane bending |
| 910             | 912                 | C–N deformation |
| 882             | 880                 | C–N stretching |
| 847             | —                   | C–H out of plane bending |
|                 | 817                 | Ring C–H stretching |
| 804             | 805                 | C–N stretching |
| 761             | 765                 | C–H bending |
|                 | 711                 | C–H bending |
| 688             | —                   | C–H stretching |
| 661             | 661                 | C = O deformation |
| 597             | 580                 | C–O deformation |
| 539             | 539                 | Rocking N = O |
| 486             | 486                 | O–H inplane bending |
|                 | 418                 | C–C–C out of plane bending |
| 373             | 373                 | C–N inplane bending |
|                 | 328                 | C–N stretching |
|                 | 274                 | C–N deformation |
| 220             | —                   | C–C–C out of plane bending |
|                 | 115                 | Lattice vibrations |
|                 | 103                 | Lattice vibrations |

Table 3. Vibrational frequency assignments of 8-HQCN crystal.
spectra [11]. The vibrations noticed at 115 and 103 cm\(^{-1}\) are the lattice mode vibrations [26]. The vibrational assignments are compiled in table 3.

### 3.3. NMR spectral analysis

The \(^1\)H NMR and \(^{13}\)C NMR spectrum are presented in figures 6 and 7 with the chemical diagram. A singlet (–CH) proton of 8-hydroxyquinoline appears at \(\delta = 9.828\) ppm. The doublet observed at \(\delta = 8.464\) and 8.461 ppm is due the aromatic protons. Similarly, the para position of 4-chloro 3-nitrobenzoic acid produces a singlet at \(\delta = 8.830\) ppm. The protons aromatic C–H of 8-HQ is noticed as singlet at \(\delta = 7.07\) ppm. The 4-chloro 3-nitrobenzoate acid ring produces a doublet at \(\delta = 7.850\) and 7.870 ppm The N\(^+\)H and OH of 8-hydroxyquinolininium moiety in the complex produces far down field shifted because of the nearby electron withdrawing group and therefore it does not exist in the spectrum [27]. The C=O bond of 8-hydroxyquinoline ring produces a signal at \(\delta = 153.68\) ppm. The C–C atoms linking two rings of 8-hydroxyquinoline (pyridinium and hydroxyl benzene rings) produces a chemical shift in \(\delta = 129.24\) ppm. The carbon atoms detected in the pyridinium ring in 8-hydroxyquinoline appears as individual peaks at \(\delta = 122.27\) and 131.67 ppm. The 8-hydroxyquinoline contains an OH group which produces a peak at \(\delta = 118.16\) ppm. The weak signal produced at \(\delta = 138.80\) ppm is due to the aromatic C–H proton of 8-hydroxyquinoline. Similarly the intense peak produced at \(\delta = 132.71\) ppm belongs to 4-chloro-3-nitrobenzoic acid ring. The –Cl bond and C–N bond of 4-chloro-3-nitrobenzoic acid were identified as shift near \(\delta = 134.44\) and \(\delta = 148.52\) ppm.

### 3.4. Optical studies

#### 3.4.1. UV-visible absorbance spectral analysis

The absorption spectrum was taken between the region 250–450 nm for the donor, acceptor, and finally obtained charge transferred complex keeping ethanol as solvent which is provided in the figure 8(a). A strong colour change is the evidence of charge transfer interactions between the solutions of donor and acceptor when they are mixed together. The spectra obtained for charge transfer complex represent the absorption band at wavelength of 320 nm. This absorption is not due to the precursors and considered to be the results of charge transfer complex formation between the investigated 8-hydroxyquinoline and 4-chloro-3-nitrobenzoic acid [28]. The solvent contains low energy absorptions of donor and an acceptor which can be explained by charge transfer transitions which involves the excitation of an electron on the donor to an empty orbital on the acceptor [29].
3.4.2. UV-visible transmittance analysis

A material used for nonlinear devices needs lower cut off wavelength and large optical transmittance [30]. The crystal shows a cut-off wavelength of 404 nm [31]. The normalized transmittance spectrum is displayed in figure 8(b). The transmission through the crystal occurs since the excitation of electrons when there light source is impended on the crystal. The excitation is observed from the non-bonding to anti bonding \((\pi \rightarrow \pi^*)\). The linear absorption coefficient \((\alpha)\) can be expressed as,

\[
\alpha = \frac{2.3026(1/T)}{t}
\]

(1)

Tauc’s plot [30] provides information about the optical energy band gap of the material which is given by the relation:

\[
\alpha h\nu = A(h\nu - E_g)^m
\]

(2)

where, \(h\) and \(\nu\) represents their usual meanings while \(E_g\) represents the optical band gap respectively. Also, the index \(m\) characterizes the transmission types. In the present case, the transition is a direct allowed transition and hence \(m = 1/2\). The optical band gap was estimated by extrapolating linear part of the curve to \(x\)-axis \((\alpha h\nu)^2 = 0\) in figure 8(c) and the plot gives value as 3.03 eV. This wide band gap endows 8-HQCN suitable for optoelectronic applications [32]. The refractive index is the ultimate property for an optical material. Reflectance \((R)\) and refractive index \((n_o)\) of the crystal in terms of \(\alpha\) and transmittance are expressed as [33],

\[
R = \frac{1 \pm \sqrt{1 - \exp(-\alpha t) + \exp(\alpha t)}}{1 - \exp(-\alpha t)}
\]

(3)

and

\[
n_o = -\frac{(R + 1) \pm \sqrt{-3R^2 + 10R - 3}}{2(R - 1)}
\]

(4)

The refractive index \((n_o = 3.05)\) of 8-HQCN at 532 nm crystal suggests that the material will enhance the performance of optical and photovoltaic devices such as solar cells [34], Bragg gratings [35], photonic crystals [36] and waveguide-based optical circuits [37].

3.5. Photoluminescence spectral analysis

The photoluminescence excitation and emission spectrum was recorded in the range between 200 and 800 nm and it is shown in figure 9. Excitation and emission wavelength were obtained by varying the excitation
wavelength under a fixed emission wavelength and vice versa. However the present spectrum (figure 9) an intense broad emission band around 580 nm which arises due to $\pi^* - n$ transitions of the carbonyl group in 4-chloro-3-nitrobenzoic acid of the 8HQCN crystal. Further the broadening of the emission band is associated with the population of various vibrational levels of the excited states. These broad yellow emission bands suggest

Figure 8. (a). Absorbance spectrum of 8-HQ, 4C3N and 8-HQCN crystal. (b). The transmission spectrum and (c) Tauc’s plot of 8-HQCN crystal along the ($-100$) plane.

Figure 9. Photoluminescence spectrum excited with 430 nm radiation for 8-HQCN.
that the 8HQCN crystal can serve as a potential photoactive material for a new tunable laser system and also to fabricate yellow lasers [38].

3.6. Mechanical studies
The mechanical stability is more important as concerned with the applications such as for the fabrication of devices. The hardness number (Hv) of the crystal is expressed as:

\[ Hv = \frac{P}{d^2} \text{ (kg mm}^{-2}\text{)} \]  

(5)

In the above equation P represents the load and d represents the diagonal length in μm. From the figure 10(a) it is seen that hardness number (Hv) rises linearly with load (P) and this trend is called as RISE (reverse indentation size effect) [39]. Due to the internal stress there is a crack observed at a load of 100 g [40]. Meyer’s law states that [41],

\[ \log P = \log k + n \log d \]  

(6)

where \(k\) is the material constant. The work hardening coefficient is the slope of the straight line of \(\log d – \log P\) plot (figure 10(b)) and it is \(n = 3.35\). The value of ’\(n\)’ is supposed to lie between 1 and 1.6 for hard materials and the values exceeding more than 1.6 are categorized to be soft materials [42]. The value of \(n (=3.35)\) for the as grown 8HQCN suggests that it is a softer material. The selection of a material for device fabrication depends on fracture toughness (Kc) where the load exceeds the limit or yield point. The Kc (g μm\(^{-3/2}\)) can be computed from the following relation:

Figure 10. (a) Variation of Hv with load of 8-HQCN crystal. (b). Variation of \(\log P\) versus \(\log d\) of 8-HQCN crystal.
Figure 11. (a) The variation of $K_c$ value at each load of 8-HQCN crystal. (b) The variation of brittleness index with load for 8-HQCN crystal.

\[
\frac{P}{l^{3/2}} = \beta_b K_c; \quad l \geq \frac{d}{2}
\]  

(7)

$l$ is half the length of the diagonal indentation mark and $\beta_b = 7$ for diamond indenter. The variation of $K_c$ value at each load is shown in figure 11(a). It gives the knowledge of the depth of penetration of the indenter into the material’s surface [43]. Brittleness is a measure of fracture induced in a material without appreciable deformation. Brittleness index $Bi \left(1 \ \mu m^{-1/2}\right)$ is given by the relation:

\[
Bi = \frac{H_V}{K_c}
\]  

(8)

The variation of brittleness index with load for crystals is shown in figure 11(b). The packing density of bonding between the neighboring atoms can be established by the elastic constant $C_{11}$ was also calculated using Wooster’s empirical formula:

\[
C_{11} = (H_V)^{7/4}
\]  

(9)

The yield strength $\sigma_y$ is given by the relation [44].

\[
\sigma_y = \frac{H_V}{3} (n \geq 2)
\]  

(10)

Table 4 provides various mechanical parameters of 8HQCN and the high value of hardness number shows that the material can withstand while polishing for laser experiments.
3.7. Nonlinear optical study

3.7.1. Z-scan analysis

The Z-scan study \cite{45} proves to be one of the best approaches to gain knowledge of the nonlinear index of refraction ($n_2$) and nonlinear absorption ($\beta$). The Z-scan analysis optimization parameters are given in the table 5. The theoretical and experimental curve for closed aperture, open aperture and the proportion between closed and open aperture are shown in figures 12–14. In the closed aperture figure, it is noticed that the peak pursued by a valley normalized transmittance interpreting the negative sign for nonlinearity refraction which is mentioned to be as self-defocusing effect. $\Delta T^\text{p-v}$, the separation of normalized peak and valley transmittance is given by:

\begin{table}[h]
\centering
\caption{Mechanical properties of 8-HQCN crystal.}
\begin{tabular}{cccccc}
\hline
Load (g) & Hv (kg/mm²) & N & $K_c$ (g/µm²) & $B_l$ (µm⁻¹/²) & $\sigma_r$ (kg/mm²) & $C_{11}$ x 10⁴ (GPa) \\
\hline
10 & 73.2455 & 3.35 & 0.0636 & 1150.538 & 24.4151 & 1.833 \\
25 & 83.2838 & 3.35 & 0.0881 & 944.845 & 27.7612 & 2.296 \\
50 & 129.8107 & 3.35 & 0.1462 & 887.750 & 43.270 & 4.992 \\
100 & 192.5127 & 3.35 & 0.2336 & 823.797 & 64.170 & 9.949 \\
\hline
\end{tabular}
\end{table}

\begin{table}[h]
\centering
\caption{Nonlinear optical parameters obtained from z-scan measurements.}
\begin{tabular}{ll}
\hline
Parameters & Values \\
\hline
Laser beam wavelength & 532 nm \\
Lens focal length ($f$) & 3.5 cm \\
Optical path length & 85 cm \\
Radius of the laser spot before the aperture ($w_0$) & 15.84 µm \\
Aperture radius ($r_a$) & 1 mm \\
Sample thickness ($L$) & 0.5 mm \\
Effective thickness ($L_{eff}$) & 2.040 x 10⁻² m \\
Linear absorption coefficient ($\alpha$) & 5.49 x 10⁻² m⁻¹ \\
Linear refractive index ($n_0$) & 3.05 \\
Nonlinear refractive index ($n_2$) & 9.75 x 10⁻⁶ cm² W⁻¹ \\
Nonlinear absorption coefficient ($\beta$) & 0.10 x 10⁻⁵ cm W⁻¹ \\
Real part of the third-order susceptibility & 16.77 x 10⁻⁶ esu \\
Imaginary part of third order susceptibility & 0.62 x 10⁻⁶ esu \\
Third order nonlinear susceptibility ($\chi^{(3)}$) & 16.78 x 10⁻⁶ esu \\
\hline
\end{tabular}
\end{table}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{12.png}
\caption{Z-scan curve for open aperture of 8-HQCN crystal.}
\end{figure}

3.7. Nonlinear optical study

3.7.1. Z-scan analysis

The Z-scan study \cite{45} proves to be one of the best approaches to gain knowledge of the nonlinear index of refraction ($n_2$) and nonlinear absorption ($\beta$). The Z-scan analysis optimization parameters are given in the table 5. The theoretical and experimental curve for closed aperture, open aperture and the proportion between closed and open aperture are shown in figures 12–14. In the closed aperture figure, it is noticed that the peak pursued by a valley normalized transmittance interpreting the negative sign for nonlinearity refraction which is mentioned to be as self-defocusing effect. $\Delta T^\text{p-v}$, the separation of normalized peak and valley transmittance is given by:
The linear aperture transmittance, 

$$ S = 1 - \exp \left( \frac{-2r_a^2}{\omega_a^2} \right) \quad (12) $$

where $r_a$ denotes the aperture radius while $\omega_a$ radius of laser spot back the aperture. The nonlinear refractive index ($n_2$) [46] is given by:

$$ n_2 = \frac{|\Delta \varphi_0|}{k L_{\text{eff}} l_0} \quad (13) $$

$L_{\text{eff}}$ is given as $L_{\text{eff}} = \left( \frac{1 - e^{-\alpha l}}{\alpha} \right)$ with $L$ denoting the length of the sample, $\alpha$ as the linear absorption coefficient, at the axis of focal point $z = 0$, and the wave vector $k = \frac{2\pi}{\lambda}$.

Theoretically the normalized transmittance can also be obtained for open and closed curvature with the help of following two equations:

$$ T_{OA}(Z, S = 1) = \sum_{m=0}^{\infty} \frac{|q_0(Z, 0)|^m}{(m + 1)^{3/2}}, \quad \text{where } q_0 = \frac{\beta l_0 L_{\text{eff}}}{1 + Z^2/Z_0^2} \quad (14) $$
\[ T_{CA}(Z, \Delta \Phi_0) = 1 - \frac{4\pi \Delta \Phi_0}{(x^2 + 1)(x^2 + 9)} \]  
(15)

where \( Z \) places the sample position and \( Z_0^2 \) is the Rayleigh range of the beam and is given by
\[ Z_0^2 = \frac{2\pi \omega_0^2}{\lambda} \]  
(16)

The nonlinear absorption coefficient \( \beta \) is calculated from the following equation:
\[ \beta = \frac{2\sqrt{T} \Delta T}{I_0 L_{eff}} \]  
(17)

The Rayleigh length, \( Z_R = \frac{k \omega_0^2}{2} \), where \( \omega_0 \) is the beam waist at focal spot. The real part (Re \( \chi^{(3)} \)) and the imaginary part (Im \( \chi^{(3)} \)) bestowing to the subsequent relation:
\[ \text{Re} \chi^{(3)} (\text{esu}) = \frac{10^{-4}(\epsilon_0 C^2 \eta_0^2 \eta_2)}{\pi} (\text{cm}^2 \text{ W}^{-1}) \]  
(18)
\[ \text{Im} \chi^{(3)} (\text{esu}) = \frac{10^{-2}(\epsilon_0 C^2 \eta_0^2 \lambda \beta)}{4\pi^2} (\text{cm}^2 \text{ W}^{-1}) \]  
(19)

where \( \epsilon_0, c \) are the universal constants, \( n_0 \) is the linear index of refraction of the sample and \( \lambda \) is the wavelength of the laser beam. 

From equations (18) and (19), third order nonlinear susceptibility is given by:
\[ |\chi^3| = (|\text{Re} (\chi^3)|^2 + |\text{Im} (\chi^3)|^2)^{1/2} \]  
(20)

The calculated values of \( n_2, \beta, \text{Re} \chi^{(3)} \) and \( \text{Im} \chi^{(3)} \) are compared with the literature values which are specified in table 6 [48–50,48–50]. Finally the effective nonlinear optical susceptibility calculated as \( 16.78 \times 10^{-6} \) esu. One can understand from the table 6 that the effective values of \( (\chi^{(3)}) \) and \( (\gamma) \) can be attributed to the delocalized \( \pi \)-electron configurations, and also the effective protonation process occurred in the crystal structure would enhance the third order optical nonlinearities. The saturation absorption leads to nonlinear absorption and refraction attributing to the self defocusing in 8-HQCN crystal. The optical limiting curve for 8-HQCN crystal is represented in figure 15. When input intensity increases the output intensity also rises linearly up to 27.4 mW and saturation is reached to a certain value. These outcomes are possibly used in nonlinear optical devices equally preventive in optical damage to the sensitive sensors [51].

The \( n_2 \) value acquired has its benefaction of noticeable origins on thermal effects or electronic effect. It is well established that refractive depends on temperature which is origin for nonlinearity and hence thermal origin is taken. CW lasers were used as a source of excitation in the current situation, the source of nonlinearity was solely thermal, and the sample acted as a thermal lens [52]. The laser heating leads to the generation of acoustic wave that changes the medium density followed by a variation of refractive index [53, 54]. The expression connecting thermal nonlinearity and thermo optic coefficient is depicted as below:
\[ \frac{dn}{dT} = \frac{4n_2 K}{\alpha_0 \omega_0^2} \]  
(21)

where \( dn/dT \) is the thermo-optic coefficient which is the differential of temperature dependable refractive index, \( \omega_0 \) owes to the waist of laser beam, \( n_2 \) and \( K \) the thermal conductivity of 8-HQCN respectively. The thermal conductivity \( (\kappa) \) of 8-HQCN was predicted as \( 0.073 \pm 0.0037 \text{ W m}^{-1} \text{ K}^{-1} \) at 50°C. By making use of \( \kappa \), the thermo-optic coefficient was calculated as \( 3.805 \times 10^{-6} \text{ K}^{-1} \). The material’s polarizability and thermal expansion will cause this result. The self-defocusing effect exhibits in 8-HQCN crystal is ascertained to the thermal effect of continuous wave Nd:YAG laser beam of wavelength 532 nm which makes a spatial distribution of temperature in the crystal. The temperature dependent refractive index will cause optical nonlinearity. The fundamental investigation of thermal-induced nonlinearity will be valuable in better understanding the physics inherent of the nonlinear optical properties of materials. Moreover, thermal lens effect has found valuable application in measurement of weak absorption [55]. It is known that the NLO response of 8-HQCN is initiated from a structure factor [56] and the enhanced optical nonlinearities due to their expanded \( \pi \)-electron system [57–59].

3.7.2. Theoretical analysis

DFT is an efficient tool for the prediction of the NLO properties of macroscopic systems at low computational cost with electron-correlation effects [60]. The finite-field (FF) approach employed in first-principle techniques are the effectively applied in the investigation of NLO response since it illustrates the various electronic-structure techniques to estimate the NLO coefficients [61]. The induced molecular polarization can be articulated by a power series:
Table 6. Comparison of nonlinear optical data with some related crystals.

| Compound                                         | $n_0$ | $n_2 \times 10^{-8}$(cm$^2$/W) | $\beta \times 10^{-4}$(cm) | Re$\chi^{(3)} \times 10^{-7}$(esu) | Im$\chi^{(3)} \times 10^{-5}$(esu) | Reference |
|--------------------------------------------------|-------|--------------------------------|---------------------------|-----------------------------------|-----------------------------------|-----------|
| 8-hydroxyquinolinium (Z)-3-carboxyacrylate (II)  | 1.3616| 1.91                           | 6.56                      | 9.02                              | 1.56                              | [12]      |
| 8-hydroxyquinolinium 2-chloroacetate(I)          | 1.3624| 0.41                           | 8.54                      | 1.94                              | 2.03                              | [12]      |
| 1- (carboxymethyl)-8-hydroxyquinolin-1-ium chloride | 1.3621| $-4.66$                        | 8.37                      | 21.9                              | 1.99                              | [48]      |
| Quinolinium 2-carboxy-6-nitrophthalate monohydrate | 1.7923| 1.176                          | $-4.59$                   | 2.08                              | $-4.09$                          | [51]      |
| 8-hydroxyquinolinium 2-chloro-5-nitrobenzoate dihydrate | 2.8100| 7.23                           | 2.04                      | 4.46                              | 2.51                              | [52]      |
| 8-HQCN                                           | 3.05  | 9.75                           | 0.10                      | 16.77                             | 0.62                              | Present work |


where the polarization $P_i$ induced along the $i$th molecular axes due to the electric field, $E_j$ in the $j$th direction, and $\alpha, \beta, \gamma$ are the linear, first and second order polarizability tensors respectively. The average second order hyperpolarizability ($\gamma$) is given by the expression:

$$\gamma_{\text{tot}} = \frac{1}{5} [\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2(\gamma_{xyxy} + \gamma_{xxyz} + \gamma_{yyzz})]$$

(23)

The molecular geometry optimization is shown in figure 16. The average static second order hyperpolarizability was estimated to be $\gamma_{\text{tot}}(0;0,0,0) = 43.542 \times 10^{-36}$ esu. The $\pi$-conjugation of organic molecules enacts a climactic lead for acquiring third order nonlinearities. The charge transfer is more stabilized on enhancing the $\gamma$ values and raise $\gamma$ values arises from the hydrogen bonds of 8-HQCN and hence gives the NLO property [62, 63]. Normally, the apparent static third order susceptibility $\chi^{(3)}$ can be specified by the ensuing expression, $\chi^{(3)} = M \left[ \frac{n_r + 2}{5} \right]^4 \langle \gamma \rangle$, where $M$ is number density of atoms and $n_r$ be the refractive index.
of the crystal. In the above relation, the local-field alterations in the Lorentz approximation are also taken into account [64] and the calculation gives \( \chi^{(3)} \) as 0.5632 \( \times 10^{-5} \) esu.

Figure 16 shows the dependence of second hyperpolarizability on frequency and is seen that the electro-optical Kerr effect (\( \langle \gamma(-\omega_0,0,0) \rangle \)) and the electric-field-induced second-harmonic generation (\( \langle \gamma(-2\omega_0,0,0) \rangle \)) increase to a different extent with frequency. The energy gap (\( E_{\text{HL}} \)) plays significant role in enhancing the optical properties [65]. The figure 17 clearly shows the influence of external electric field on the energy distribution around the HOMO and LUMO along different directions. The decrease of band gap with the increase of the frequency of the applied field leads to the increase of \( \langle \gamma \rangle \). The value of EHL and \( \langle \gamma \rangle \) are found to be 3.557 eV and 43.542 \( \times 10^{-6} \) esu, respectively. Moving from the field \( F_x = 0 \) to \( F_y = 0.03 \) and 0.06 au, the EHL value reduces by 1.027 and 0.899 eV whereas the \( \langle \gamma \rangle \) value increases by 21.09 \( \times 10^{-6} \) esu and 77.98 \( \times 10^{-6} \) esu, respectively. When moving from the zero-field to \( F_y = 0.03 \) and 0.06 au, the EHL value reduces to 2.687 and 1.475 eV whereas the \( \langle \gamma \rangle \) value increases by 96.5 \( \times 10^{-6} \) esu and 67.74 \( \times 10^{-6} \) esu, respectively. A similar effect was observed when moving from the zero-field to \( F_z = 0.03 \) and 0.06 au, the EHL value reduces to 3.209 and 1.459 eV whereas the \( \langle \gamma \rangle \) value increases by 9.16 \( \times 10^{-6} \) esu and 59.86 \( \times 10^{-6} \) esu, respectively (table 7).

Bai et al [66] established that the external electric field induces the changes in electron-density distribution on the molecules which in turn increases \( \langle \gamma \rangle \). It is also seen from figure 18, there is a reduction and enlargement of lobes in the positive and negative direction of the electric field respectively, in HOMO. However, when \( F_x = 0.06 \) au lobes of the LUMO are pushed strongly along the positive direction of the electric field. This charge transfer enhancement produces a highly polarized electron density distribution responsible for the higher NLO response [67] which proves that external electric field can also tune the NLO properties.

### 3.8. Electronic excitation

Fifty excited states were identified and some of the excited states with k values having significant contributions are listed in table 8. From the table it is noticed that the state 1st, 13th, 14th and 19th have larger k values making dominant contributions to \( \beta \) values. Major contribution is from 13th state which emanate owing to the excitation of charges from HOMO \(-6\) to LUMO \(+1\) which belongs to the transition occurring between the orbital composed of 4-chloro-3-nitrobenzoate group to that of NO2 group. The next major contribution is found in 14th and 19th state where the charges excite from HUMO \(-5\) to LUMO \(+4\) owing to the charge transfer between the 4-chloro-3-nitrobenzoate to the carboxyl group. 1st state contributes to \( \beta \) values between HUMO \(-6\) to LUMO \(+0\) in reasons with the nitrobenzoic group present in the 8-HQCN compound.
Moderate k values of 4th, 5th, 6th and 8th state are due to the transitions occurring in 8-hydroxyquinoline molecule.

3.9. Thermal analysis

The TG-DTA curve shown in figure 19 indicates that the crystal is stable up to 120 °C. A small inflection around 120 °C in TGA matches with a DTA peak 127 °C. TGA curve shows single stage decomposition between 198 °C and 317 °C and this corresponds to the liberation of major organic molecules of the 8-HQCN compound. Thus, 8-HQCN is stable up to 120 °C and the crystal can be implemented for various solid state applications.

3.10. Dielectric studies

The dielectric analysis of a material is an essential characterization to avail the details of the electrical properties of the material. Dielectric constant can be related to dimensions (thickness & area of the sample) and capacitance of the sample (C):

\[ \varepsilon' = \frac{Ct}{\varepsilon_0 A} \]  

\[ \frac{\varepsilon''}{\varepsilon'} = \tan \delta \]

where \( \varepsilon_0 \) is the permittivity of free space. Figure 20(a) shows the normal behavior of the dielectric dispersion and the dispersion was large at lower frequency while being constant at higher frequency. The dielectric permittivity
Table 8. Excited state energy, oscillator strength and major contribution for orbits obtained at td-hf/6-311g(d, p) level.

| n   | Energy (eV) | Wavelength (nm) | Oscillator strength \((k \times 10^3)\) | Symmetry | Major contributions                                      |
|-----|-------------|-----------------|-----------------------------------------|----------|---------------------------------------------------------|
| 1   | 4.8093      | 257.80          | 127.5                                   | Singlet-A | H-6->LUMO (82%) (Nitrobenzoic)                         |
| 4   | 5.1562      | 240.45          | 40.9                                    | Singlet-A | H-8->LUMO (61%) 8-hydroxyquinoline H-6->L + 1 (31%)    |
| 5   | 5.2538      | 235.98          | 91.7                                    | Singlet-A | HOMO->L + 3 (70%) 8-hydroxyquinoline                   |
| 6   | 5.5369      | 223.92          | 54.2                                    | Singlet-A | H-5->L + 2 (59%) quinoline                             |
| 8   | 5.6341      | 220.06          | 34.5                                    | Singlet-A | H-7->L + 2 (35%) quinoline                             |
| 9   | 5.8995      | 210.16          | 6.5                                     | Singlet-A | H-21->L + 2 (30%)                                    |
| 12  | 6.3066      | 196.59          | 0.3                                     | Singlet-A | H-9->L + 4 (45%), H-9->L + 23 (30%) NO2               |
| 13  | 6.3298      | 195.87          | 1028                                    | Singlet-A | H-6->L + 1 (54%) NO2                                  |
| 14  | 6.7053      | 184.90          | 423.3                                   | Singlet-A | HOMO->L + 8 (42%) (C = O)                              |
| 17  | 6.8022      | 182.27          | 8.5                                     | Singlet-A | HOMO->LUMO (71%) (C = O)                               |
| 19  | 6.9426      | 178.58          | 936.7                                   | Singlet-A | H-5->L + 4 (47%) (C = O)                              |
| 23  | 7.2279      | 171.53          | 0.9                                     | Singlet-A | H-1->LUMO (86%)                                       |
| 24  | 7.3020      | 169.79          | 24.5                                    | Singlet-A | H-1->L + 3 (51%)                                      |
| 28  | 7.4960      | 165.40          | 0.2                                     | Singlet-A | H-2->LUMO (86%)                                       |
| 29  | 7.5406      | 164.42          | 0.3                                     | Singlet-A | H-4->LUMO (77%)                                       |
| 31  | 7.7103      | 160.80          | 11.4                                    | Singlet-A | H-3->LUMO (88%) (C = O)                               |
| 32  | 7.7788      | 159.38          | 0.2                                     | Singlet-A | H-3->LUMO (79%) (C = O)                               |
| 33  | 7.8122      | 158.70          | 5.5                                     | Singlet-A | H-3->L + 3 (47%) (C = O)                              |
| 34  | 7.8254      | 158.43          | 5.2                                     | Singlet-A | H-1->L + 8 (42%) (C = O)                              |
| 36  | 8.0284      | 154.43          | 5.1                                     | Singlet-A | H-6->L + 6 (71%) (C = O)                              |
| 38  | 8.1450      | 152.22          | 5.3                                     | Singlet-A | H-7->LUMO (71%) (C = O)                               |
| 41  | 8.2799      | 149.74          | 0.0                                     | Singlet-A | HOMO->L + 1 (96%)                                     |
| 43  | 8.3375      | 148.70          | 30.6                                    | Singlet-A | H-1->L + 2 (62%)                                      |
| 44  | 8.4194      | 147.26          | 3.9                                     | Singlet-A | H-6->L + 7 (47%)                                      |
| 45  | 8.4634      | 146.49          | 3.0                                     | Singlet-A | HOMO->L + 2 (93%)                                     |

Figure 19. TG-DTA thermogram of 8-HQCN crystal.

will be originated from electronic, ionic, orientation and space polarization mechanisms within the material. The high \(\varepsilon'\) at low frequencies originate from the accumulation of charges and theses charges will follow the applied electric field while the lagging of dipoles with electrical field tends decrease \(\varepsilon'\) with frequency. Moreover, dielectric constant almost constant in the region 1 kHz to 2 MHz due to the disappearance of space charge polarization in this frequency region. The observed low value of dielectric constant establishes that the as-grown crystal has potential for microwave applications. Similarly, the dielectric loss (\(\varepsilon''\)) is higher at low frequency (figure 20(b)) attributes the oscillation of dipoles. The low value of (\(\varepsilon''\)) proves the quality of the crystal [68]. Thus the material satisfies one of basic needs of photonic, electro-optic and NLO devices [69].
3.11. Antibacterial activity
The 8-hydroxyquinoline complexes are well entrenched for its antibacterial activity. The 8-HQCN was proved to be antibacterial resistant on testing for the species *E. coli* NCIM 2931 and *S. aureus*. This antibacterial resistant activity of 8-HQCN is depicted in figure 21 and also noted that the measured diameter of the zone after inhibition endured to be same after 24 h and 48 h of incubation. The measurement table of diameter of zone of inhibition coursed 8-HQCN against bacteria is given in table 9. The higher concentration has a larger diameter of zone of inhibition than the lower concentration. Therefore, antibacterial analysis proves that 8-HQCN exhibits good resistance towards the harmful bacteria and hence applicable for medical and bio-medical applications.
4. Conclusion

The structure, lattice constants and the crystal system were obtained from the single crystal XRD analysis. The cut-off wavelength and band gap of the crystal was found by using transmittance spectrum and the absorption spectrum shows the charge transfer of 8HQCN. The molecular structure was well established by the spectral analyses. The photoluminescence of the crystal revealed yellow emission. Mechanical strength of the crystal is revealed from mechanical studies. Z-scan technique was exploited to study nonlinear parameters of the crystal. The thermo–optic effect causes the nonlinearity which helps to implement it to the optical application oriented devices. It is to be noted that reverse saturable absorption establishes the optical limiting effect and hence this material is useful for optical limiting applications. DFT was applied to estimate the theoretical third order nonlinear optical parameters. Also, the theoretical powers and experimental powers of $\chi^{(3)}$ were compared and were affirmed to be in good agreement. The 8-HQCN exhibits high withstanding thermal capacity up to 127 °C. The charge relegation inside the molecule is shown on lowering HOMO-LUMO gap. The applied electric field strongly affects the band gap and hence second order hyperpolarizability. The low dielectric permittivity and the low dielectric loss enhance the optical quality of the material with lesser imperfections. Antibacterial study for the powdered sample was executed and was found that 8-HQCN exhibit good resistance towards the harmful bacteria.

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Table 9. Diameter of zone of inhibition coursed HQCN against bacteria.

| Bacterial species | Concentration (mM) | Diameter of zone of inhibition (mm) | Average diameter of zone of inhibition (mm) |
|-------------------|-------------------|-----------------------------------|------------------------------------------|
| E. coli NCIM 2931 | 0.1               | 0 0 0 0                          | 0 ± 0                                    |
|                   | 0.5               | 8 8.5 7.5                        | 8 ± 0.5                                  |
|                   | 1 10.5 10.5 10.5  | 8.3 ± 0.28                      |                                          |
| S. aureus         | 0.1               | 0 0 0 0                          | 0 ± 0                                    |
|                   | 0.5               | 7.5 8 8                          | 7.83 ± 28                                |
|                   | 1 10 10 10        | 10 ± 0                           |                                          |
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