

Quantum Mechanical Study of Three Aromatic Bioactive Fatty Alcohol Compounds with Nonlinear Optical and Potential Light Harvesting Properties

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ABSTRACT

In the present work, Quantum mechanical properties of three different organic compounds [(2S)-1-(4-nitrophenyl) pyrrolidin-2-yl] methanol (NPPM), 2-(Methyl(4-nitrophenyl) nitro) ethanol (MNAE), and N, N-Bis (2-hydroxyethyl)-4-nitroaniline (HENA) were investigated by computational approach. The geometries were optimized to ground state using the density functional theory (DFT) with level B3LYP/6311-G (++d, p) basis set. The Mulliken charge distribution and molecular electrostatic potential (MEP) map of the title molecules shows the existence of huge charge distribution and the charge transfer within the molecules due to the presence of nucleophilic and electrophilic moieties. The vibrational spectra of the title molecules seem to have high intensity Raman modes. The UV–Vis spectra for the three molecules were found to indicate the presence of π - π^* and n - π^* electronic transitions between wavelength 300–500 nm. The computed value of first-order hyperpolarizability for the molecules were found to be higher than the reference materials. This validates the nonlinear optical responses of the title molecules. The light harvesting efficiency of the molecules were also determined. For the NPPM molecule, light harvesting efficiency of 64% was obtained. This validates the potential applications of NPPM in designing new photosensitizer solar cells.

1. Introduction

From the past few years, considerable attempts had been done for designing nonlinear optical (NLO) materials. NLO materials have been found employed in frequency generations, telecommunications, optoelectronic devices, optical data transmission, and computing, etc [1–4]. The organic NLO materials are reported with faster response time, strong intramolecular charge transfer (ICT) and high thermal stability [5]. Because of being more characteristic than inorganic NLO materials, organic NLO materials had been into lights for the last three decades. However, the researchers are targeting the molecules having conjugated electron donor and acceptor moieties for the development of the novel NLO materials. Due to the presence of donor and acceptor parts, such molecules can be considered chemically reactive and can be preferred for the development of required materials [6]. The fatty alcohol compounds have followed the same criteria and similarly have donor and acceptor parts. The fatty alcohol compounds contain nitro groups that are strongly electron-withdrawing and hydroxyl groups that are strongly

electron-donating [7,8]. Moreover, the fatty alcohol compounds have promising applications in the field of pharmaceutical science, pesticides, dyes, explosives, etc., that give insights to the interdisciplinary works with such type of probe systems [9–11]. The literature survey proclaimed the applications of fatty alcohols in the generation of photoluminescent polymers with potential active sites exhibiting multi-responsive fluorescence sensing [12], catalytic reducers [13], dyes [14], pesticides [15], fungicides [16], and energetic salts [17]. A number of computational and experimental research works have been reported with fatty alcohol compounds [18,19]. In history, many studies of development of spectral properties and optical nonlinearity of the aminopyridines and 4-nitrophenol [20], dimethyl amino pyridinium 4-nitrophenolate 4-nitrophenol (DMPNP) [21], urotropine p-nitrophenol [22], 2-amino-4-picolinium-nitrophenolate-nitrophenol [23], L-tryptophan p-nitrophenol [24], ortho, meta, para-nitro-phenolic isomeric compounds [25] has been seen. However, neither such study of the quantum chemical properties of the title molecules has been reported so far. Motivated by the mentioned studies, three active fatty

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alcohol compounds have been taken for the investigation of NLO activities.

The fatty alcohol compounds considered for this study are [(2S)-1-(4-nitrophenyl) pyrrolidin-2-yl] methanol (NPPM), 2-(Methyl(4-nitrophenyl) nitro) ethanol (MNAE), and N, N-Bis (2-hydroxyethyl)-4-nitro-aniline (HENA) (Fig. 1). Being fatty alcohols, these compounds consist of the electron-withdrawing nitro ($-\text{NO}_2$) and electron-donating hydroxyl group ($-\text{OH}$).

The NPPM and MNAE molecule consist of one nitro and one hydroxyl group and the HENA molecule has one nitro group and two hydroxyl groups. The presence of these functional groups develops the possibility of the existence of ICT within fatty alcohol compounds which will make them more polarizable, hence more NLO active. These compounds also have very similarity in structure and atomic density. This is the main motivation behind the selection of the title molecules. The present study aims to establish the comparison between the geometry and quantum mechanical properties of the molecules.

In the present paper, the theoretical predictions have been

performed for the title molecules including stability and chemical reactivity analysis. The frontier molecular orbitals (FMO) analysis, spectral analysis, and the polarizability and hyperpolarizability analysis were performed for the investigation of NLO behavior of the considered fatty alcohol compounds. The light-harvesting efficiency (LHE) was also computed for the title molecules for the development of the novel organic dye for the development of the dye-sensitized solar cells (DSSCs) to increase the efficiency solar cells [26,27].

2. Computational details

The structure of NPPM, MNAE, and HENA were downloaded from the online database PubChem in SDF format. The files are converted into Gaussian input file from graphic user interface “Open Babel”. The ground state optimization and other spectral calculations of the structures were done with the help of the software “Gaussian 09” [28]. The structure of the title molecules is optimized with the density functional theory with the most general B3LYP/6311-G (+,d, p) basis set. “Gauss View 5.0” was used to analyze all the quantum mechanical properties and spectra analysis [28]. The energies corresponding to the highest occupied molecular orbital and lowest unoccupied molecular orbital (HOMO and LUMO) were also obtained by the optimized structure. These energies were used for calculating the global reactivity parameters like energy gap (ΔE), ionization potential (IP), electron affinity (EA), chemical potential (CP), electronegativity (χ), softness (S), and hardness (η) with the help of Koopman’s equations [29].

$$IP = -E_{HOMO} \quad (1)$$

$$EA = -E_{LUMO} \quad (2)$$

$$CP = \frac{E_{HOMO} + E_{LUMO}}{2} \quad (3)$$

$$\chi = \frac{(IP + EA)}{2}, \quad (4)$$

$$\eta = \frac{E_{LUMO} - E_{HOMO}}{2}, \quad S = \frac{1}{\eta} \quad (5)$$

UV spectra was computed by energy optimization by TD-SCF method. The vibrational analysis was also done by ground state frequency optimization. The Raman intensity was also computed for the high frequency modes by the following expression [30]:

$$I = \frac{f(\nu_o - \nu_i)^4 S_i}{\nu_i \left[1 - \exp\left(-\frac{h\nu_i}{KT}\right) \right]} \quad (6)$$

where the Raman intensity of the considered mode was represented by I , f is a constant with value 10^{-12} , ν_o has value 9398.5 cm^{-1} ν_i and S_i is the vibrational wavenumber and Raman activity of selected mode respectively. h , c , K , and T have their usual meanings. The graphs of Mulliken charge, UV-Vis spectra, and Raman spectra were plotted using software “Origin 2021”. As the present study deals with the computational investigation of the quantum chemical properties of the title molecules, we have also computed the Raman spectra using software Orca (<https://orcaforum.kofo.mpg.de/>) with Avogadro GUI (<https://avogadro.cc/>) [31,32]. The geometry optimization and the other details were performed in Avogadro using Merge molecular force field (MMFF94) with steepest descent algorithm. MMFF94 is known to be the most accurate force field for the quantum chemical calculations of organic molecules. As the UV-Vis spectra had been computed using Gaussian software. Thus, in order to validate the results obtained from the Gaussian, Spartan software packages (<https://store.wavefun>.

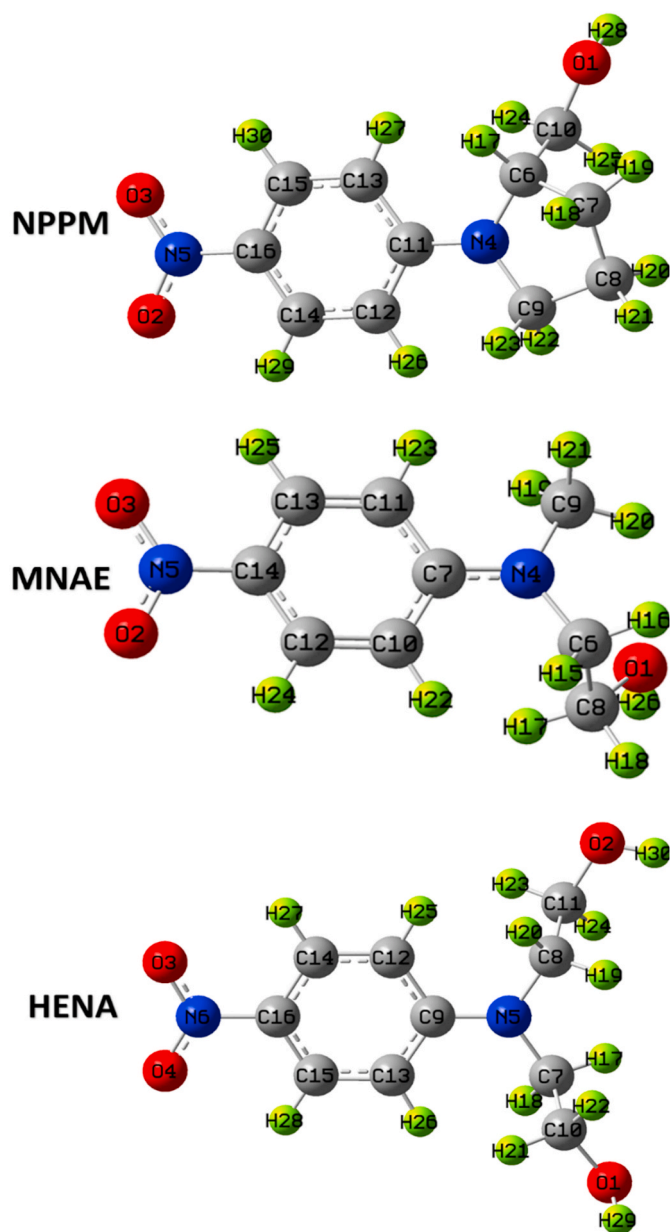


Fig. 1. Optimized structures of NPPM, MNAE and HENA with B3LYP/6311G (+,d, p) basis set.

com/Spartan_Software_s/12.htm) have been also used for computing absorption spectra. The results obtained from the Gaussian software were compared to the results obtained from Avogadro and Spartan to validate the results. The similarity between the graphs shows the high probability of the experimental graphs being quite similar to computational graphs. The optical responses of the title molecules were reported with the help of computing the polarizability parameters like total dipole moment (μ_{total}), total isotropic polarizability (α_{total}), and anisotropic polarizability ($\Delta\alpha$). μ_{total} , α_{total} , $\Delta\alpha$ and β_{total} . The polarizability parameters help in understanding the drifting of the electron cloud within the compound [33]. These parameters are computed by the below given equations.

$$\mu_{tot} = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{\frac{1}{2}} \quad (7)$$

$$\alpha_{tot} = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad (8)$$

$$\Delta\alpha = \frac{1}{\sqrt{2}} \left[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6\alpha_{xz}^2 + 6\alpha_{xy}^2 + 6\alpha_{yz}^2 \right]^{\frac{1}{2}} \quad (9)$$

$$\langle\beta\rangle = \left[(\beta_{xxx} + \beta_{xyz} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yzx} + \beta_{yxx})^2 + (\beta_{zzx} + \beta_{zxx} + \beta_{zyy})^2 \right]^{\frac{1}{2}} \quad (10)$$

where μ_x , μ_y , and μ_z are the tensor components dipole moment, α_{xx} , α_{yy} , and, α_{zz} are the tensor components of polarizability and β_{xxx} , β_{yyy} , and β_{zzz} are the tensor components of hyperpolarizability.

3. Results and discussions

3.1. Structure analysis

The structures of the NPPM, MNAE and HENA were optimized to the ground state and are shown in Fig. 1. The computed dipole moments are reported quite high for NPPM (9.09 Debye), MNAE (8.88 Debye) and HENA (9.24 Debye) molecules. These high values of the dipole moment show the possibility of ICT within the molecules. The bond lengths and the bond angles of the optimized geometries are mentioned in SD 1 and SD 2. The NPPM has the non-planar geometry with dihedral angle 4 N–6C–10C–1O with one nitro group (–NO₂) and one hydroxyl group (–OH). The bond length between the atoms 1O and 28H associated to the electron donating hydroxyl group has bond length 0.97. The bond angle 3O–5 N – 2O associated to nitro group has the maximum bond angle 122.94. More the bond angle, more it will be easier to dissociate the bond and reform the bond with the donated electrons. The total energy of the NPPM molecule is –762.63 a.u. The structure of MNAE molecule is non-planar with dihedral angle N4 – 6C–8C–1O and one nitro group (–NO₂) and one hydroxyl group (–OH) with total energy –685.21 a.u. The bond 1O–26H related to the hydroxyl group has the minimum bond length of 0.97. The 2O–5 N – 3O bond of nitro group of the MNAE molecule has the maximum bond angle of 122.93. This will lead to the easier bond dissociation of the amino group and easy donating of the electron cloud from hydroxyl group towards nitro group. The HENA molecule has non-planar geometry with dihedral angles 5 N–7C–10C–1O and 5 N–8C–11C–2O. Its geometry has two hydroxyl groups (–OH) and one nitro group (–NO₂). The bond 1O–29H associated to the hydroxyl group has the bond length 0.97. The dihedral angle between the 4O, 6 N and 3O atoms of nitro group is 123.04. Due to the high electronegativity of the nitrogen atoms of the nitro group, the bonds associated to the nitro group can easily dissociate. The total energy of HENA molecule is –799.73 a.u.

3.2. Charge analysis

The charge contribution of all the atoms is reported by the Mulliken charge analysis and the graphs of the charge distribution of all the probe systems are shown in Fig. 2. The positive charge contribution of the hydrogen atoms and the negative charge distribution of the oxygen and nitrogen atoms. The variation of the charge of carbon atoms is observed for all the title compounds. The atoms 2O and 3O of the nitro group of NPPM molecule have negative charge –0.29 e and 5 N atom has negative charge –0.001e (Fig. 2(a)) showing negativity of the nitro group. The 28H atom of the hydroxyl group has positive charge of 0.37 e and 1O has charge –0.60 e. Being electron donor, the hydroxyl group releases the electron cloud and it is transported towards the nitro group. For MNAE molecule, the charge associated to the nitro group atoms are –0.29 e, –0.29 e and –0.002e for 2O, 3O and 5 N respectively (Fig. 2 (b)). The atoms of the hydroxyl group have charge 1O (–0.60 e) and 26H (0.37 e). The variation of the charge denotes the ICT property of MNAE molecule. The oxygen atoms 3O and 4O associated to the nitro group have negative charge –0.29 e and the hydrogen atoms 29H and 30H of the hydroxyl groups have positive charge 0.37 e and 0.36 e. Similar to the first two molecules, 1O, 2O, 29H, 30H atoms associated to the two hydroxyl groups have charge –0.60 e, –0.57 e, 0.37 e, and 0.36 e. The atoms 3O, 4O, and 6 N associated to the nitro group of the HENA molecule has charge –0.29 e, –0.29 e, and 0. The nitro groups of the HENA molecule acts as an electron withdrawing groups. The variation in the magnitude of the charge indicates the charge transfer from nitro groups to the hydroxyl groups. Such ICT result in a large transition dipole moment which strongly influence the polarizability of the title molecules.

3.3. Frontier molecular orbital analysis

The FMO energies were used to calculate the global reactivity parameters for the selected probe molecules. The HOMO and LUMO energies play a vital role in evaluating the global reactivity parameters as they correspond to IP and EA of the molecule respectively [34]. The HOMO basically imparts in donating the free electron while the LUMO acts as accepting orbital. These global reactivity parameters are used to account the conjugation and effect of the lone pair electrons [35]. The global reactivity parameters of the title molecules are mentioned in Table 1. The LUMO energy of NPPM, MNAE and HENA is –2.46 eV, –2.44 eV and –2.56 eV and HOMO energy of NPPM, MNAE and HENA is –6.06 eV, –6.02 eV and –6.20 eV respectively. The energy gap of the

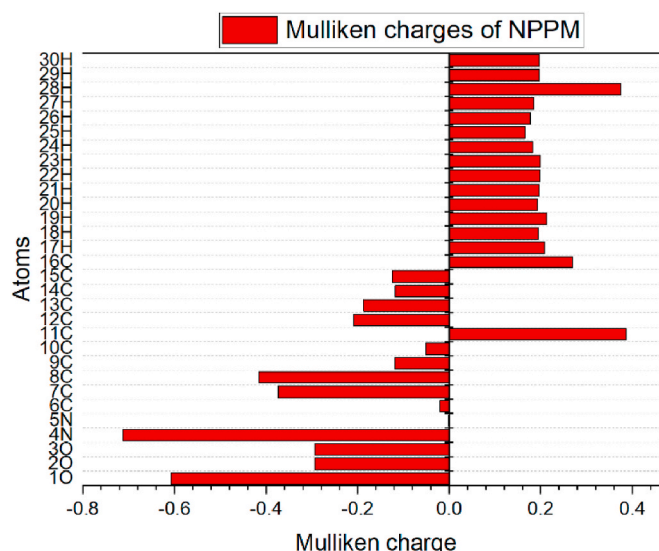


Fig. 2a. Mulliken charge distribution of the NPPM molecule.

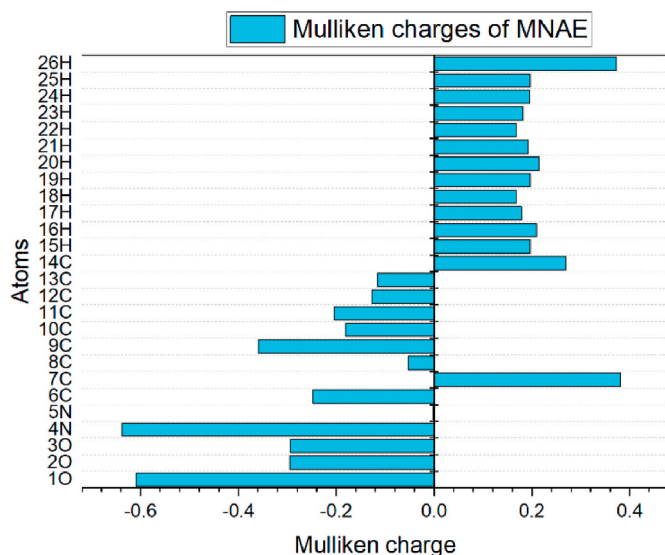


Fig. 2b. Mulliken charge distribution of the MNAE molecule.

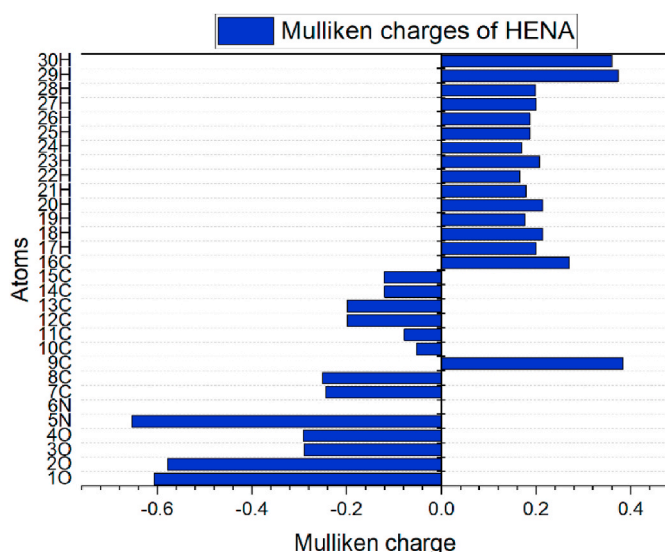


Fig. 2c. Mulliken charge distribution of the HENA molecule.

Table 1

Frontier molecular orbital parameters for the NPPM, MNAE and HENA molecule. All values in eV and value of S is in eV^{-1} .

S No.	Molecular property	NPPM	MNAE	HENA
1.	E_{HOMO}	-6.06	-6.02	-6.20
2.	E_{LUMO}	-2.46	-2.44	-2.56
3.	Energy gap (ΔE)	3.06	3.57	3.63
4.	Ionization potential (IP)	6.06	6.02	6.20
5.	Electron affinity (EA)	2.46	2.44	2.56
6.	Chemical potential (CP)	-4.26	-4.23	-4.38
7.	Electronegativity (χ)	4.26	4.23	4.38
8.	Hardness (η)	1.80	1.78	1.81
9.	Softness (S)	0.55	0.55	0.54

title molecules NPPM, MNAE and HENA is found to be 3.06 eV, 3.57 eV, and 3.63 eV respectively. Less is the difference between the HOMO-LUMO energies, more will be the stability of the molecule [36]. The ΔE for the generally used reference materials Urea is 7.43 eV. The ΔE of the title molecules is observed to be comparatively lower than that of reference material. The low ΔE of the considered molecules shows the

high possibility of electron excitations and hence, high polarizability of the considered compounds. This clearly justifies the chemical reactivity of the molecules. The molecular orbitals with the respective energy gap for the title molecules had been illustrated in Fig. 3. The red and green color surfaces show positive and negative phases in molecular orbital wave function, respectively. Fig. 3 represent that π -antibonding HOMO are distributed throughout the geometry of NPPM molecule while the LUMO are distributed throughout the geometry except for the hydroxyl group. The atoms 2O and 3O associated to nitro groups imparts in the negative phase of the wave function. The positive and negative phases of HOMO-LUMO are same except the 4 N atom that imparts negatively in LUMO but positively in HOMO. The HOMO of MNAE molecule seems to be localized throughout the geometry and the LUMO of MNAE molecule is distributed through the geometry leaving hydroxyl group. The positive and negative phase of the atoms and molecular orbitals of MNAE molecule is similar to that of NPPM. Similar to the former two molecules, the HOMO-LUMO are completely localized throughout the geometry except the absence of LUMO distribution over the hydroxyl group. The 5 N atom of HENA molecule shows the phase change of wave function as it imparts negatively to wave function as LUMO but acts positively as HOMO. The distribution of HOMO-LUMO is however, same for the title molecules. The LUMO in three structures doesn't seem to be localized over the hydroxyl group and the phase change of the wave function is observed due to the nitrogen atom of the title molecules. The value of IP for HENA molecule is 6.20 eV, which is slightly higher than the value for NPPM (6.06 eV) and MNAE (6.02 eV). The high values of IP represent the high ability of the valence electrons of atoms to drift easily from the outermost atomic orbitals to form free electron pairs. The values of EA for the title molecules NPPM, MNAE, and HENA are 2.46 eV, 2.44 eV, and 2.56 eV respectively. These values show that these molecules have the tendency to accept the free electron pairs and bond formation can take place. Among the three molecules, the HENA molecule has the highest value of EA. The energy associated to the molecule during the charge transfer is termed as CP. The lesser the value of CP, more the molecule will be stable. Among the three molecules, the HENA molecule has minimum CP of -4.38 eV. The CP values of molecules of NPPM and MNAE are -4.26 eV and -4.23 eV respectively.

The value of χ for the molecules NPPM, MNAE, and HENA is 4.26 eV, 4.23 eV, and 4.38 eV respectively. The obtained high values for the χ shows the ability of the molecules to attract the free electrons for bond formation. The property of being rigid is accounted by the hardness of the molecule. The value of the η for the molecules NPPM, MNAE, and HENA is evaluated as 1.80 eV, 1.78 eV, and 1.81 eV. The HENA has the highest value of η among the considered molecules. This shows that the HENA molecule has the stiff geometry than the other two molecules. The value of S is smallest for the HENA molecule (0.54 eV^{-1}). This shows that the HENA molecule is less soft than the other two title molecules NPPM (0.55 eV^{-1}) and MNAE (0.55 eV^{-1}). All the above given data validates that the title molecules can be considered chemically reactive and stable molecules. But the HENA molecule has the highest IP, EA, and χ , lowest CP. The values of η and S are respectively higher and lower for the HENA molecule than the other two molecules. Thus, the HENA molecule has comparatively high chemical reactivity than the NPPM and MNAE molecules.

3.4. Molecular electrostatic potential analysis

MEP surface of the probe systems were monitored for the validation of charge transfer and reactive sites observed by the Mulliken charge analysis. The negative, positive and zero potential region indicates the red, blue and green colors in the electrostatic potential surface respectively. The decreasing order of the magnitude of electrostatic potential is blue > green > yellow > orange > red. The color code of shown at the top of the MEP surface indicates the positive and negative electrostatic potential values associated to the molecule. The electrostatic potential for NPPM ranges from $-6.81 \times 10^{-2} \text{ V}$ for nucleophilic to $+6.81 \times 10^{-2}$

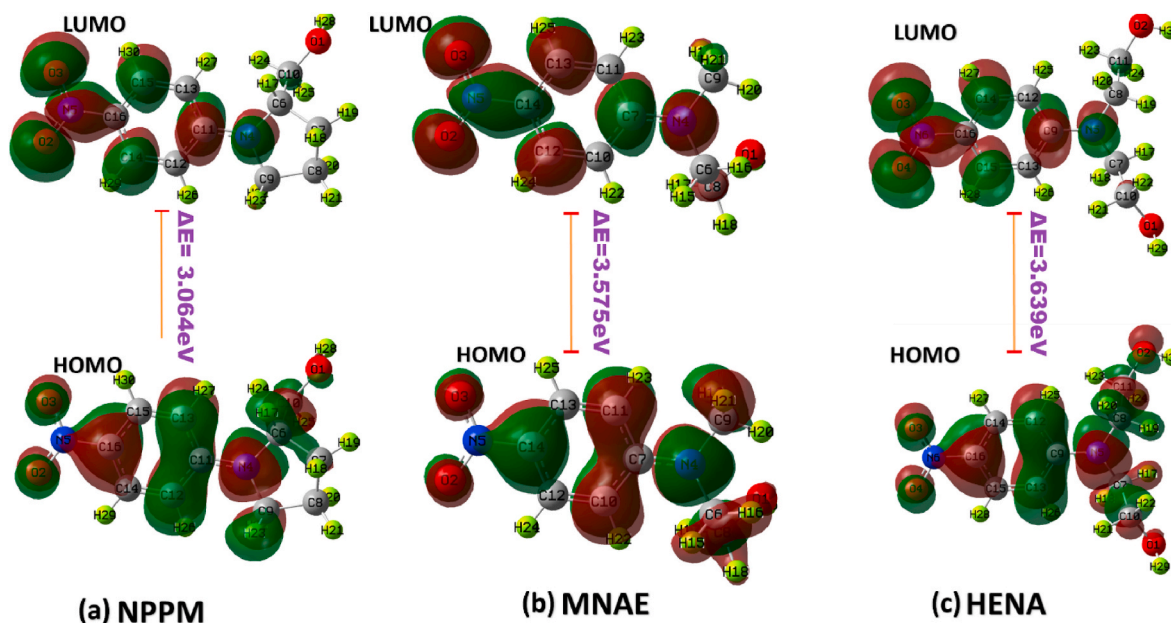


Fig. 3. Molecular orbitals for the (a) NPPM, (b) MNAE and (c) HENA molecules. The lower structure shows HOMO and upper structure shows LUMO of the respective molecules and the band gap is represented by ΔE .

V for electrophilic region. The electrostatic potential ranges for MNAE and HENA molecules are ± 0.104 , and $\pm 7.18 \times 10^{-2}$ V respectively. These regions show the molecular electrostatic potentials over which the MEP surface lies. MEP map for the title molecules is shown in Fig. 4(A). The probe molecules consist of hydroxyl and nitro groups. The hydroxyl groups have two covalent bonds between C–O bond and the O–H associated to it, which makes it capable for giving up the free charge cloud. However, the N atom of the nitro group has greater electronegativity. Thus, the nitro group behaves as a strong electron withdrawing group. The blue color of the MEP is generally due to the nucleophilic part of the molecule and the electrophilic part imparts the red color in the MEP [37]. In the NPPM molecule, electron donating hydroxyl group shows the blue color near 1O and 28H atoms. The red region near 2O, 3O, and 5 N atoms of nitro group is active region for electrophile attack. Thus, in NPPM molecule, the charge is seen to transfer from hydroxyl group to nitro group. Similarly, in MEP surface of MNAE molecule, the red-color region is due to the 2O, 3O, and 5 N atoms of the nitro group and the blue region of the MEP surface is due to the 26H, and 1O atoms of the hydroxyl group. In MNAE molecule, the charge is transferring from hydroxyl group to nitro group. The 3O, 4O, and 6 N atoms of nitro group in HENA molecule acts as electron donating atoms. There are two hydroxyl groups consisting of atoms 1O, 29H and 2O, 30H and both groups participate in accepting the charge. Thus, similar to the former two molecules, the HENA molecule also possessed the dislocation of the charge cloud from the hydroxyl groups to the nitro group. The counter plot of NPPM, MNAE, and HENA (Fig. 4(B)) molecules seems to be highly accumulated field lines near the functional groups. The magnitudes of the electrostatic potentials indicated on the top of the MEP surface also impacts the counter plots of the title molecules. The field lines are highly accumulated in the regions that is under the influence of higher electrostatic potential. The availability of these lines shows that the bonds near the functional groups are immensely affected by the electrostatic field and hence, they have higher possibility to be unstable and get dissociated. The effect of the field will lead to the generation of the charge cloud for delocalization. Thus, the MEP surfaces and the counter plots of the title molecules validates that the functional groups are most active regions in the molecules and there is a possibility of ICT from hydroxyl group towards nitro groups in the respective title molecules.

3.5. Vibrational analysis

The vibrational analysis was done for the title molecules by frequency optimization using TD-DFT method. The major Raman modes of the NPPM, MNAE, and HENA molecule are shown in Fig. 5. The Raman modes of the NPPM molecule are located between the ranges 44–3693 cm^{-1} . The MNAE molecule has Raman modes in 31–3691 cm^{-1} and HENA molecule has Raman modes falling in range 39–3693 cm^{-1} . For the validation of spectral results, the Raman spectra of the title molecules were also traced using Avogadro and Spartan software packages and the results were found similar as obtained using Gaussian software. The spectra obtained from the Avogadro and Orca for the title molecules were mentioned in SD 6(a), 6(b), and 6(c). The ranges of the Raman intensities for the NPPM, MNAE and HENA molecules by Avogadro software were 41–3850 cm^{-1} , 29–3683 cm^{-1} , 39–3693 cm^{-1} respectively. These ranges are alike the intensity ranges obtained by Gaussian software. High peaks of the Raman vibrations were observed for the NPPM molecule in between 1000 and 1500 cm^{-1} in all the three graphs in 5(a), SD 6(a), and SD 7(a). The calculated Raman intensities for the considered Raman modes for the title molecules are mentioned in SD 3, 4, and 5.

3.5.1. C–C and C=C vibrations

The linear stretching of C–C bonds (ν_{CC}) of the NPPM molecule is computed between the frequency range 1042.33 and 1096.53 cm^{-1} . The C=C bond present in the benzene ring ν_{CC} at 1644.01 cm^{-1} and C–C bonds of the benzene ring shows $\nu_{C=C}$ mode at 604.79 cm^{-1} . The vibration corresponding to C=C bond of the NPPM molecule has Raman intensity of 4982.17 cm^{-1} . The C=C bond of the benzene ring of MNAE molecule is observed at 1645.2 cm^{-1} and ν_{CC} bond of the benzene ring have ν_{CC} mode at frequency 1605.53 cm^{-1} . High value of Raman intensity (3750.07 cm^{-1}) has been recorded for $\nu_{C=C}$ mode of MNAE molecule. The stretched vibrations of the C–C bonds of the HENA molecule falls between frequencies 1010.01–1030.03 cm^{-1} . However, the C=C bond of the benzene ring of the HENA molecule shows the asymmetric stretching (α_{CC}) mode at frequency 1030.03 cm^{-1} and ν_{CC} mode at 1643.43 cm^{-1} . The ν_{CC} mode of HENA molecule has raised value of Raman intensity of 5371.89 cm^{-1} . High values of the Raman intensities are recorded corresponding to C=C vibrations of benzene rings of the title molecules. These values highly impart in the raised

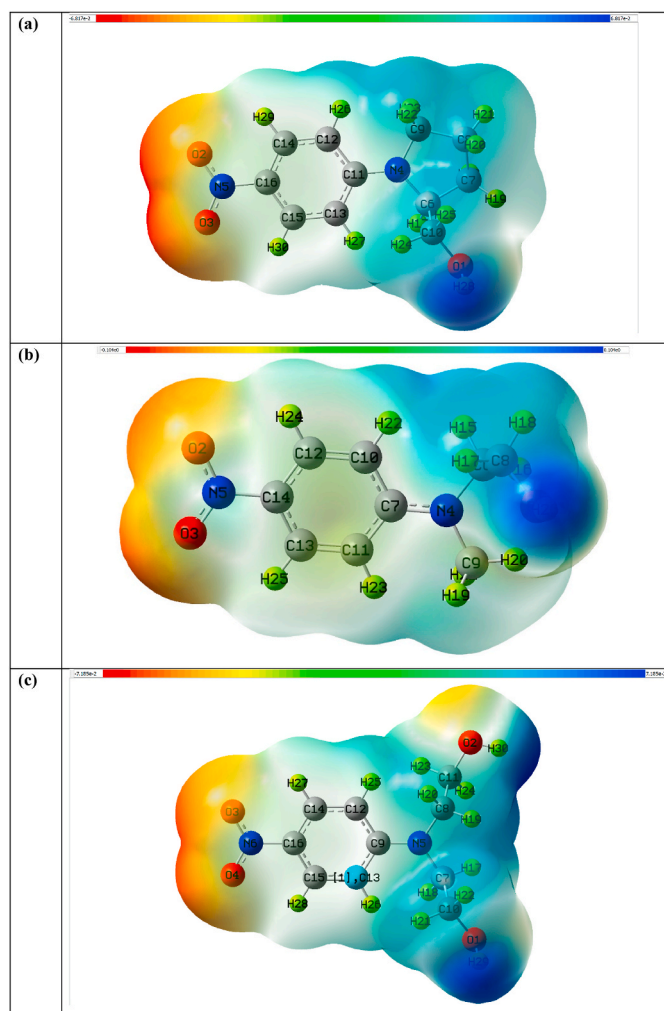


Fig. 4A. The molecular electrostatic potential surfaces of (a) NPPM, (b) MNAE, and (c) HENA molecule (The range of electrostatic potential is shown as a color band on the top of the MEP surface of respective molecules).

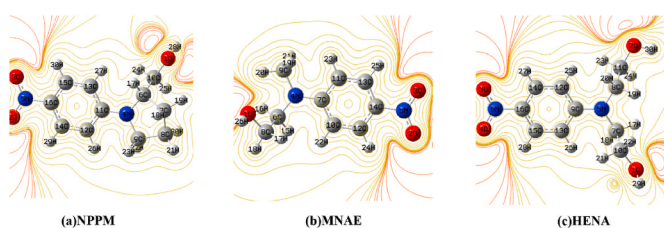


Fig. 4B. Counter maps showing electrostatic field lines of (a) NPPM, (b) MNAE, and (c) HENA molecule.

values of polarizability of the molecules. Thus, the high Raman intensity shares a major reason for the NLO activity of the title molecules.

3.5.2. C–H vibrations

The C–H stretching of the NPPM molecule is observed between 2999 and 3117 cm^{-1} . The H atoms attached to the ortho and meta positions of the benzene ring of the NPPM molecule shows the ν_{CH} mode at frequency 3231.26 cm^{-1} and α_{CH} at frequency 3229.25 cm^{-1} . The torsional bending (δ_{CH}) of the angles between the C and the H atoms is observed between 1457 and 1565 cm^{-1} . For MNAE molecule, the ortho and meta-H atoms of the benzene ring have mode ν_{CH} at 3233 cm^{-1} . The α_{CH} mode of the H atoms of the benzene ring occurred around 3211.03 cm^{-1} .

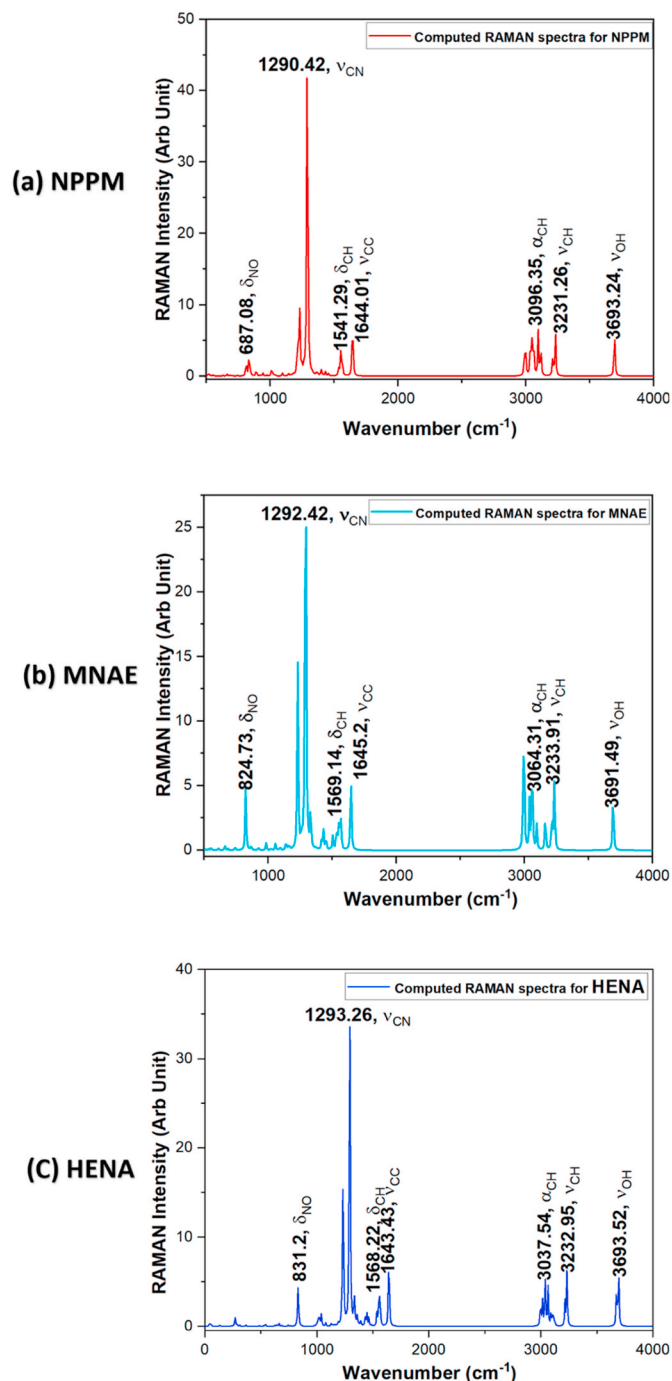


Fig. 5. Computed Raman spectra of (a) NPPM, (b) MNAE, and (c) HENA molecule computed by frequency optimization with B3LYP/6311G (+,d, p) basis set. (Vibrational modes: ν -symmetric stretching, α -asymmetric stretching, δ -torsional bending).

Other than the C–H bonds of the benzene ring, the C–H bonds attached to the 4 N atom and the 1O shows the ν_{CH} mode at 2990.29 and 2997.52 cm^{-1} . The α_{CH} vibrations of MNAE is observed in the range of 3039.05–3163.13 cm^{-1} . The C–H bonds attached to the 4 N atom give δ_{CH} mode between 1505 and 1555.44 cm^{-1} . For HENA molecule, the δ_{CH} mode associated to the alkyl part range between 1536.05 and 1568.22 cm^{-1} and C–H bonds shows α_{CH} modes in frequency between 3037.54 and 3123.16 cm^{-1} . The C–H bonds of the benzene ring show α_{CH} mode at frequency 3214.39 cm^{-1} .

3.5.3. C–N vibrations

The C–N vibrations are generally observed around 1200 cm^{-1} . For NPPM molecule, the $16\text{C}-5\text{ N}$ bond stretches linearly at frequency 1290.42 cm^{-1} . However, this vibration disturbs the whole geometry of the molecule. The computed value of Raman intensity for this mode is observed very high i.e., 49445.34 cm^{-1} . The C–N bond of the MNAE molecule shows the ν_{CH} mode at frequency 1292.42 cm^{-1} . The Raman intensity for this mode is computed as 40438.15 cm^{-1} . The $16\text{C}-6\text{ N}$ bond of the HENA molecule stretches at frequency 1293.26 cm^{-1} and disturb the whole geometry of the HENA molecule. The Raman intensity of this mode 44227.41 cm^{-1} . The raised values of Raman intensities of C–N vibrations leads to the high polarizability of the molecule. When computed using Avogadro, the peak for ν_{CN} for NPPM molecule was found to have intensity 1275.54 cm^{-1} that is very close to 1290.42 cm^{-1} . For same mode, the highest peak for MNAE and HENA molecules had intensities 1288.1 cm^{-1} and 1293.26 cm^{-1} .

3.5.4. N–O vibrations

The 5 N atom attached to the 3O and 2O atoms of the nitro group of the NPPM molecule vibrates linearly with both the bonds at frequency 1432 cm^{-1} . The high value of the frequency for the stretching can be considered as the reason for the high vibrational shift of the nitro functional group. The 5 N atom of the nitro group also shows the δ_{NO} mode at frequency 687.08 cm^{-1} . The δ_{NO} mode of N–O bond of MNAE is observed at 824.73 cm^{-1} . The nitro group of the MNAE molecule shows the ν_{NO} stretching at 1431.42 cm^{-1} . The nitro group of the HENA molecule conducts the α_{NO} at frequency 1434.55 cm^{-1} and δ_{NO} at 831.2 cm^{-1} . The high Raman intensity for the vibrations corresponding to the nitro group atoms of the title molecules leads to the high values of polarizability of the molecules.

3.5.5. O–H vibrations

The δ_{OH} mode of the O–H bond of the hydroxyl group of the NPPM molecule is observed at frequency 269.63 cm^{-1} . The ν_{OH} mode of the $10-28\text{H}$ bond of the NPPM molecule is observed at frequency 3693.24 cm^{-1} . The ν_{OH} mode of the $10-26\text{H}$ bond of the MNAE molecule occurs at frequency 3691.49 cm^{-1} . This vibration has reported to occur at the highest frequency for the MNAE molecule. The δ_{OH} of the O–H bond is observed at 267.13 cm^{-1} . The HENA molecule has two hydroxyl groups. The $10-29\text{H}$ bond of the hydroxyl group of the HENA molecule has the ν_{OH} at frequency 3693.52 cm^{-1} and $20-30\text{H}$ bond vibrates linearly at 3674.78 cm^{-1} . The δ_{OH} of the O–H bonds of the HENA molecule falls in between frequency $267.18-287.81\text{ cm}^{-1}$. For the O–H bonds of the title molecules high frequency for the ν_{OH} mode is observed. The reported high frequency for the O–H linear vibrations results in the high value of the polarizability of the title molecules. When computed from Avogadro, the peaks for ν_{OH} mode for NPPM, MNAE and HENA molecule were observed at 3850.19 , 3683.92 and 3693.52 cm^{-1} respectively.

The obtained Raman modes with high intensity for NPPM, MNAE, and HENA molecule are probably the result of the availability of the conjugated- π electrons in the nitro group and the lone pairs of electrons in hydroxyl groups. The availability of free charges and variation of electron density of donor hydroxyl and acceptor nitro groups results in inducing the ICT. Moreover, the ICT results in the raised values of Raman intensity, dipole moment, and molecular polarizability. Thus, the high intensity Raman modes contributes in the application of title molecules as NLO active molecules.

3.6. UV–Vis analysis

The electronic absorption spectra of the title molecules were calculated using TD-DFT method. The obtained UV–Vis spectra for the title molecules are shown in Fig. 6. The UV–Vis spectra account the vertical excitation energy (E), oscillator strength (f), and the wavelength (λ) at which the transitions occur. The UV–Vis spectra was mainly reported to study about the transactions for high wavelengths and are represented

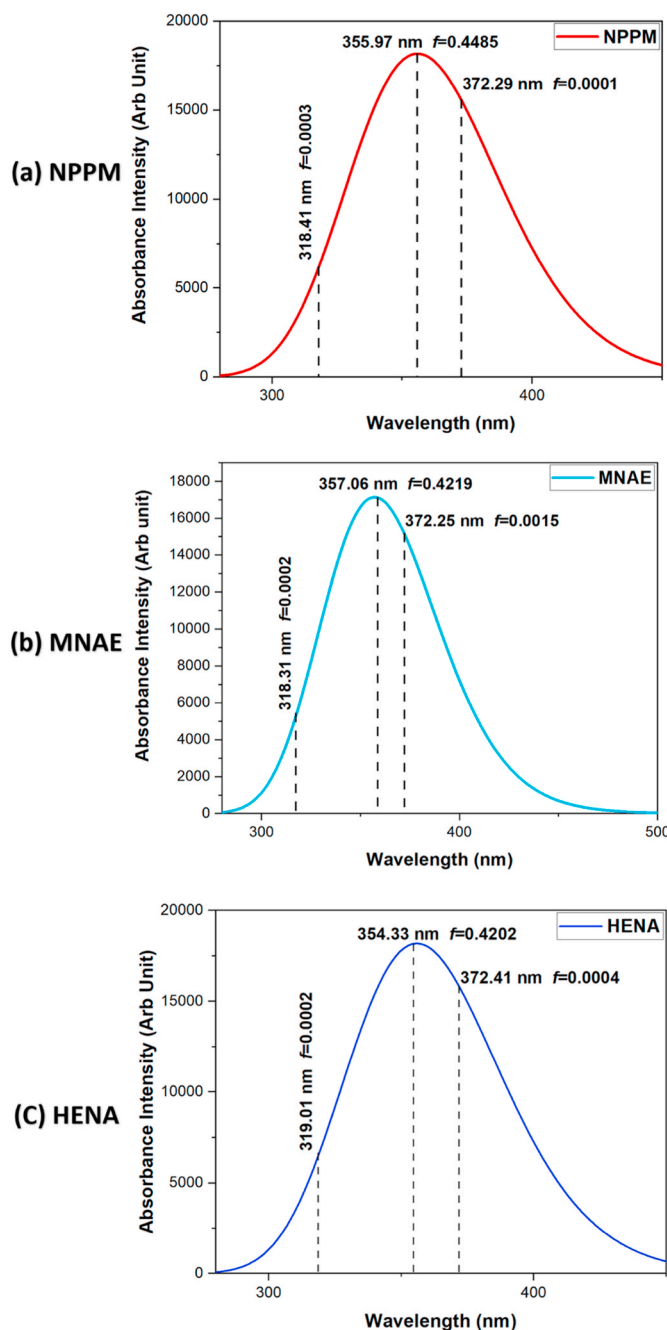


Fig. 6. UV–Vis spectra for the (a) NPPM, (b) MNAE, and (c) HENA molecule obtained by TD-DFT energy optimization method.

by transitions $S_0 \rightarrow S_1$, $S_0 \rightarrow S_2$, $S_0 \rightarrow S_3$. These transitions are majorly occurred due to the presence of the $\pi-\pi^*$ and $n-\pi^*$ electronic transitions occurring at highest wavelengths. For all the title molecules, absorption band is observed between 300 and 500 nm wavelengths. The transitions $S_0 \rightarrow S_1$, S_2 , S_3 are observed at wavelengths 372.29 nm, 355.97 nm, and 318.41 nm respectively for NPPM molecule. The transition $S_0 \rightarrow S_2$ has highest oscillator strength of 0.4485. The MNAE molecule has transitions $S_0 \rightarrow S_1$, S_2 , S_3 at wavelength 372.25 nm, 357.06 nm, and 318.31 nm respectively. The value of oscillator strength for MNAE molecule is highest for the $S_0 \rightarrow S_2$ (0.4219). For HENA molecule, the oscillator strength has the highest value of 0.4244 for $S_0 \rightarrow S_2$ transition at 354.33 nm wavelength. The transitions $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_3$ are observed at wavelength 372.41 nm and 319.01 nm wavelength respectively. These transitions validate the occurrence of the ICT in between the lone pair

(n) electrons and the π electrons and also lead to the unsaturation of the molecule. The peaks of the UV-Vis spectra of the NPPM, MNAE, HENA are at the wavelength 355.97, 357.06, and 354.33 nm respectively. The energies corresponding to these transitions are computed as 3.33 eV, 3.33 eV and 3.32 eV respectively for NPPM, MNAE and HENA molecules. These values are nearly equal to the values obtained from the band gap of NPPM, MNAE, and HENA molecule in HOMO-LUMO analysis respectively. This fact is fair enough to validate the stability of the title molecules. The UV-Vis spectra obtained from the Spartan software for the title compounds are illustrated in the SD 7(a), 7(b) and 7(c). The high peak of the absorption spectra for the NPPM molecule was observed at wavelength 324.27 nm. This value is quite similar to the wavelength of the absorption peak observed in Fig. 6(a). However, the transitions $S_0 \rightarrow S_2$, S_3 have wavelengths 311.82 and 283.01 nm. The absorption spectra obtained for MNAE from Spartan (SD 7(b)) have wavelengths 364.95, 327.06 and 288.06 nm respectively. These values are very near to wavelengths corresponding to $S_0 \rightarrow S_1$, S_2 , S_3 transitions in Fig. 6(b). The absorption spectra obtained from spartan for HENA lies between 200 and 400 nm with wavelengths 324.88, 315.09 and 283.03 nm for transitions $S_0 \rightarrow S_1$, S_2 , S_3 respectively. These values are also very near to that obtained in Fig. 6(c). Thus, the similarity in the obtained spectra from both the software shows enhances the validity of the computed spectra and also shows the probability of the experimental values being nearly equal to the computed values. Also, the presence of such transitions leads to the resemblance of the title molecules as the NLO materials.

3.7. Nonlinear optical analysis

The polarizability parameters are the valid parameters used to explain the NLO behavior of any molecule. For the present study, the values of μ_{total} , α_{total} , $\Delta\alpha$, and β_{total} are computed. The values of all these parameters for title molecules are mentioned in Table 2. The values of μ_{total} is obtained using the tensor components of the dipole moment. The values of the μ_{total} for NPPM, MNAE, and HENA molecules are 3.57 Debye, 3.48 Debye, and 3.63 Debye. These values are higher than the μ_{total} value of commonly used NLO material Urea (1.52 Debye). The material is said to be polarizable when its electron cloud is displaced due to the application of any external electric field [38]. Same effect is observed in the NLO materials when they are kept in non-linear medium. Thus, the NLO materials must have high values of polarizability [39]. The value of α_{total} for NPPM, MNAE, and HENA molecule are 23.52×10^{-24} esu, 20.51×10^{-24} esu, 22.61×10^{-24} esu respectively. These values are compared to the α_{total} value of Urea (5.66×10^{-24} esu) and it was seen that the NPPM has α_{total} approximately four times higher than the Urea. Similarly, the MNAE and HENA molecules has α_{total} value

three times higher than Urea. The values of $\Delta\alpha$ for NPPM, MNAE, and HENA molecules are reported as 67.04×10^{-24} esu, 59.60×10^{-24} esu, and 63.57×10^{-24} esu. The value of $\Delta\alpha$ for NPPM molecule is about ten times higher than the $\Delta\alpha$ value of Urea (6.30×10^{-24} esu). Similarly, the $\Delta\alpha$ of MNAE and HENA are respectively nine and ten times higher than Urea. These values of $\Delta\alpha$ of the title molecules are much higher than $\Delta\alpha$ values of the reference material. The dipole moment is induced within the molecule in the presence of the external electric field [40]. This property is measured by β_{total} . For the molecules NPPM, MNAE, and HENA, the value of β_{total} is 28.2×10^{-30} esu, 25.07×10^{-30} esu, and 33.61×10^{-30} esu respectively. These values are extremely higher than β_{total} of Urea (0.78×10^{-30} esu). For NPPM molecule, β_{total} is about thirty six times that of Urea. The MNAE molecule has β_{total} about thirty two times higher than Urea. The β_{total} of the HENA molecule is the highest among the other title molecules. It is about forty three times higher than Urea. The comparison of the β_{total} was also done with L-leucine nitrate (LLN) (6.13×10^{-30} esu), and L-methionine L-methioninium hydrogen maleate (LMLMHM) (29.1×10^{-30} esu) [41,42]. The value of β_{total} for NPPM was four times higher than LLN and very near to LMLMHM. For MNAE, the value of β_{total} was four times higher than LLN. HENA has the highest value of β_{total} among the three title compounds and three reference compounds. The value of β_{total} for HENA was five times higher than that LLN, and approximately one time higher than that of LMLMHM. The comparison between the NLO parameters of the title molecules and Urea was shown in Fig. 7. The lone pair of electrons associated with the hydroxyl group leads to the high value of β_{total} . The O atoms of the hydroxyl group conjugate with the N atoms of the nitro group and an enhanced variation of the charge density is observed in the charge of the functional groups. The charge is transported from the hydroxyl group towards the nitro groups. The movement of the charge cloud leads to the increased ICT. This results in the high value of β_{total} and this phenomenon give rise to the optical non-linearity of the title molecules.

3.8. Light harvesting properties

The organic dyes are used for increasing the efficiency of photo-sensitizer solar cells [43]. The organic dyes developed by NLO materials have been widely used for increasing the efficiency of DSSCs [40]. These materials are high in demand for the manufacturing of photosensitizer dyes which are highly preferred in DSSC's [44]. LHE of the compounds can be determined with the help of the computed electronic spectra and oscillator strength by using the below mentioned formula:

$$LHE = 1 - 10^{-f} \quad (11)$$

Where f is the oscillator strength of the molecule obtained from the UV

Table 2

Computed values of dipole moment, polarizability and first order hyperpolarizability of NPPM, MNAE, and HENA molecules (dipole moment in Debye and all tensor components are in a.u. and μ_{total} , α_{total} , $\Delta\alpha$ and β_{total} in esu).

Dipole moment					Polarizability					First order hyperpolarizability				
Comp	NPPM	MNAE	HENA	Urea	Comp	NPPM	MNAE	HENA	Urea	Comp	NPPM	MNAE	HENA	Urea
μ_x	3.49	-3.48	3.52	1.28	α_{xx}	247.7	219.51	235.26	39.26	β_{xxx}	-3508.09	3155.04	3640.31	24.72
μ_y	-0.50	-0.20	-0.72	0.00004	α_{xy}	-9.49	-7.87	-0.35	0.29	β_{xxy}	493.2	-523.10	-59.62	-0.49
μ_z	-0.57	0.0046	0.52	-0.83	α_{yy}	144.7	126.2	140.91	24.69	β_{xyy}	198.47	-224.33	160.91	31.81
μ_{total}	3.57	3.48	3.63	1.52	α_{xz}	2.89	10.89	1.05	-1.15	β_{yyy}	142.83	49.67	-74.26	0.006
					α_{yz}	9.28	6.57	15.19	0.45	β_{xxz}	-4.72	258.73	19.45	-61.44
					α_{zz}	83.89	69.59	81.68	38.219	β_{xyz}	8.63	-60.09	38.36	0.22
					α_{total}	23.52×10^{-24}	20.51×10^{-24}	22.61×10^{-24}	5.664×10^{-24}	β_{yyz}	-18.43	-53.62	26.82	-20.59
					$\Delta\alpha$	67.04×10^{-24}	59.60×10^{-24}	63.57×10^{-24}	6.304×10^{-24}	β_{zzz}	101.26	-73.78	87.06	19.37
										β_{yyz}	-34.41	-0.62	-8.22	-20.59
										β_{zzz}	-4.82	-17.07	13.27	32.89
										β_{total}	28.2×10^{-30}	25.07×10^{-30}	33.61×10^{-30}	0.781×10^{-30}

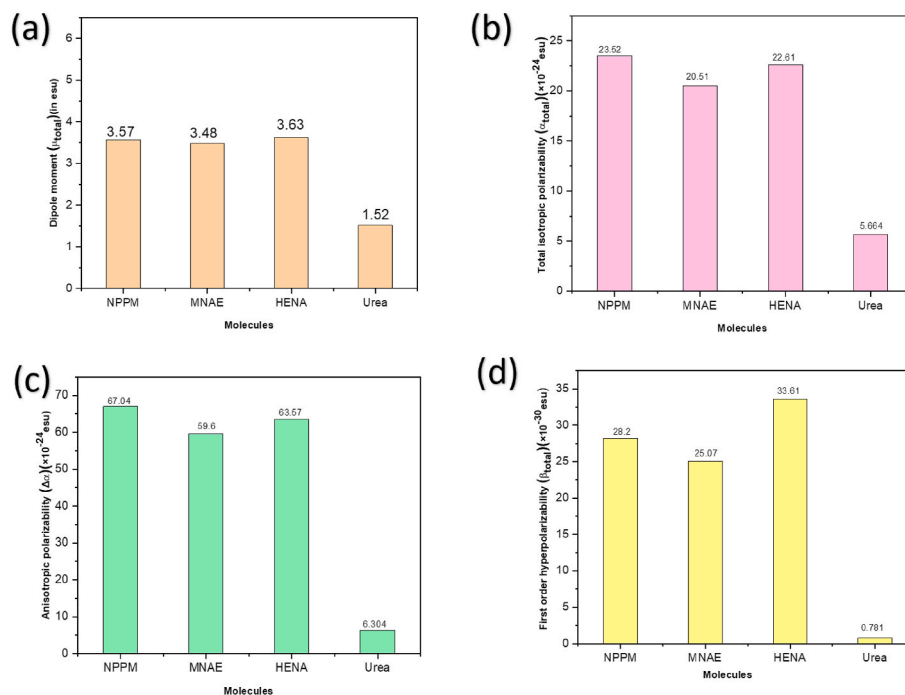


Fig. 7. Comparison of NLO parameters (a) μ_{total} , (b) α_{total} , (c) $\Delta\alpha$ and (d) β_{total} values of the title molecules with reference material Urea.

spectra. The NPPM molecule has highest value of f 0.4485 for the preferred transition $S_0 \rightarrow S_2$. The LHE for the NPPM molecule is 64.39%. For MNAE molecule, the value of f is 0.4219 for transition $S_0 \rightarrow S_2$. The LHE for the MNAE molecule 62.14%. The HENA molecule has f computed as 0.4202 and LHE equal to 61.99%. Among the three title molecules, the NPPM molecule has the highest LHE i.e., it can convert 64.39% of the light energy into electrical energy.

4. Conclusion

Investigation of NLO properties and DSSC characteristics for NPPM, MNAE, and HENA are carried out using DFT calculation. The occurrence of charge distribution between hydroxyl and nitro group was established from MEP surface, molecular orbital parameters and Mulliken charge distribution. Conjugated- π electrons in the nitro group and the lone pairs of electrons in hydroxyl groups leads to the formation of Raman modes with high intensity. The simulated UV-Vis spectra correlated well with the band gap between the HOMO-LUMO. The values of hyperpolarizability of the title molecules were immensely higher than the reference materials. High values of hyperpolarizability showed the title molecules are highly NLO active and well suit in the designing and development of NLO materials. As the oscillator strengths were obtained for the electronic transitions, the LHE was also computed for these molecules using oscillator strength. LHE of the NPPM molecule was highest among the three considered fatty alcohol compounds. The dye made from this compound will convert nearly 64% of the light incident on it into electrical energy. Thus, the NPPM molecule can be used as an organic photosensitizer along with other dyes which are presently used in DSSC's.

CRediT authorship contribution statement

Shradha Lakhera: Data curation, Writing – original draft, preparation, Visualization, Investigation, Software, Validation. **Kamal Devlal:** Conceptualization, Writing – review & editing. **Meenakshi Rana:** Conceptualization, Methodology, Writing – review & editing, Supervision. **Vivek Dhuliya:** Visualization, Investigation, Software, Validation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.optmat.2022.112476>.

References

- [1] M. Rana, N. Singla, A. Chatterjee, A. Shukla, P. Chowdhury, Investigation of nonlinear optical (NLO) properties by charge transfer contributions of amine functionalized tetraphenylethylene, *Opt. Mater.* 62 (2016) 80–89, <https://doi.org/10.1016/j.optmat.2016.09.043>.
- [2] H. Bhatt, T. Pant, C.C. Dhoundiyal, M. Rana, P. Chowdhury, G.C. Joshi, P. Arya, H. Tiwari, Computational study of the intermolecular interactions and their effect on the UV-visible spectra of the ternary liquid mixture of benzene, ethanol and propylene glycol, *J. Mol. Model.* 26 (2020) 268, <https://doi.org/10.1007/s00894-020-04533-y>.
- [3] S. Fantacci, F. De Angelis, A computational approach to the electronic and optical properties of Ru (II) and Ir(III) polypyridyl complexes: applications to DSC, OLED and NLO, *Coord. Chem. Rev.* 255 (2011) 2704–2726, <https://doi.org/10.1016/j.ccr.2011.03.008>.
- [4] F. Ullah, N. Kosar, A. Ali, Maria, T. Mahmood, K. Ayub, Alkaline earth metal decorated phosphide nanoclusters for potential applications as high performance NLO materials; A first principle study, *Physica E Low Dimens. Syst. Nanostruct.* 118 (2020), 113906, <https://doi.org/10.1016/j.physe.2019.113906>.
- [5] M. Rana, N. Singla, A. Pathak, R. Dhanya, C. Narayana, P. Chowdhury, Vibrational-electronic properties of intra/inter molecular hydrogen bonded heterocyclic dimer: an experimental and theoretical study of pyrrole-2-carboxaldehyde, *Vib. Spectrosc.* 89 (2017) 16–25, <https://doi.org/10.1016/j.vibspec.2016.12.003>.
- [6] G. Undavalli, M. Joseph, K. K. Arjun, R. Philip, B. Anand, G.N. Rao, Tuning the nonlinear optical properties by engineering donor-acceptor configurations in nitrochalcone derivatives, *Opt. Mater.* 115 (2021), 111024, <https://doi.org/10.1016/j.optmat.2021.111024>.
- [7] P. Karuppasamy, T. Kamalesh, V. Mohankumar, S.A. Kalam, M.S. Pandian, P. Ramasamy, S. Verma, S.V. Rao, Synthesis, growth, structural, optical, thermal, laser damage threshold and computational perspectives of 4-nitrophenol 4-aminobenzoic acid monohydrate (4NPABA) single crystal, *J. Mol. Struct.* 1176 (2018), <https://doi.org/10.1016/j.molstruc.2018.08.074>.
- [8] C. Vesta, R. Uthrakumar, B. Varghese, S. Mary, P. Navis, S.J. Das, Growth, structural investigation and characterization on novel organic NLO single crystal:

- tri-nitrophenol para hydroxyacetophenone, *J. Cryst. Growth* 311 (2009) 1516–1520, <https://doi.org/10.1016/j.jcrysgro.2008.10.115>.
- [9] S. Selvakumar, M.S. Boobalan, S.A. Babu, S. Ramalingam, A.L. Rajesh, Crystal growth and DFT insight on sodium para-nitrophenolate para-nitrophenol dihydrate single crystal for NLO applications, *J. Mol. Struct.* 1125 (2016) 1e11, <https://doi.org/10.1016/j.molstruc.2016.05.104>.
- [10] O. Tamer, N. Dege, G. Demirtas, D. Avci, Y. Atalay, M. Macit, S. Sahin, Crystal structure and spectroscopic characterization of (E)-2-((4-bromo-2-(trifluoromethoxy) phenyl) imino) methyl)- 4-nitrophenol: a combined experimental and computational study, *J. Mol. Struct.* 1063 (2014) 295–306, <https://doi.org/10.1016/j.molstruc.2014.01.079> 0022-2860.
- [11] K. Thirupugalmani, S. Karthick, G. Shanmugam, V. Kannan, B. Sridhar, K. Nehru, S. Brahadeeswaran, Second- and third-order nonlinear optical and quantum chemical studies on 2-amino-4-picolinium-nitrophenolate-nitrophenol: a phasematchable organic single crystal, *Opt. Mater.* 49 (2015) 158–170, <https://doi.org/10.1016/j.optmat.2015.09.014>.
- [12] A. Otto, M. Schmidt, Towards a universal numerical simulation model for laser material processing, *Phys. Procedia* 5 (A) (2010) 35–46, <https://doi.org/10.1016/j.phpro.2010.08.120>.
- [13] M. Aazza, H. Ahlafi, H. Moussout, C. Mounir, A. Fadel, A. Addad, Catalytic reduction of nitro-phenolic compounds over Ag, Ni and Co nanoparticles catalysts supported on $\text{Fe-Al}_2\text{O}_3$, *J. Environ. Chem. Eng.* 8 (2) (2020), 103707, <https://doi.org/10.1016/j.jece.2020.103707>.
- [14] A. Das, A. Dey, P-Nitrophenol -Bioremediation using potent *Pseudomonas* strain from the textile dye industry effluent, *J. Environ. Chem. Eng.* 8 (4) (2020), 103830, <https://doi.org/10.1016/j.jece.2020.103830>.
- [15] V. Pandiyaraj, A. Murmu, S. K. Pandey, M. Sevanan, S. Arjunan, Metal nanoparticles and its application on phenolic and heavy metal pollutants *Phys. Sci. Rev.* <https://doi.org/10.1515/psr-2021-0058>.
- [16] S.V. Ponikvar, J. Liebman, Interplay of thermochemistry and Structural Chemistry, the journal (volume 17, 2006) and the discipline, *Struct. Chem.* 20 (2009) 1019–1037, <https://doi.org/10.1007/s11224-009-9506-0>.
- [17] Z.B. Zhang, J. Qin, X. Yin, J.G. Zhang, 642, in: Preparation, Crystal Structure, and Thermal Analysis of Two Energetic Salts Based on Nitro Phenolic Compounds with Diamino-Glyoxine, vol. 15, 2016, pp. 840–846, <https://doi.org/10.1002/zaac.201600189>.
- [18] D. Mahadevan, S. Periandy, M. Karabacak, S. Ramalingam, N. Puvirasan, Spectroscopic (FT-IR, FT-Raman and UV-vis) investigation and frontier molecular orbitals analysis on 3-methyl-2-nitrophenol using hybrid computational calculations, *Spectrochim. Acta A Mol. Biomol. Spectrosc. SPECTROCHIM ACTA A* 86 (2012) 139–151, <https://doi.org/10.1016/j.saa.2011.10.020>.
- [19] K.M.A. Ahmady, S.M. Soliman, M.M. Habeeb, A.H.A. Obidan, Spectral analysis and DFT computations of the hydrogen bonded complex between 2,6-diaminopyridine with 2,6-dichloro-4-nitrophenol in different solvents, *J. Mol. Struct.* 1143 (2017) 31–41, <https://doi.org/10.1016/j.molstruc.2017.04.077>.
- [20] I.M. Pavlovic, S. Draguta, M.I. Fokina, T.V. Timofeeva, I.Y. Denisov, Synthesis, crystal growth, thermal and spectroscopic studies of acentric materials constructed from aminopyridines and 4-nitrophenol, *Opt Commun.* 362 (2016) 64–68, <https://doi.org/10.1016/j.optcom.2015.05.034>.
- [21] P. Srinivasan, T. Kanagasekaran, N. Vijayan, G. Bhagavannarayana, R. Gopalakrishnan, P. Ramasamy, Studies on the growth, optical, thermal and dielectric aspects of a proton transfer complex Dimethyl amino pyridinium 4-nitrophenolate 4-nitrophenol (DMAPNP) crystals for non-linear optical applications, *Opt. Mater.* 30 (4) (2007) 553–564, <https://doi.org/10.1016/j.optmat.2007.01.014>.
- [22] R. Durgadevi, A. Steephen, T. Arumanayagam, Growth, thermal, linear and nonlinear optical properties of a novel second-order nonlinear optical crystal: urotropine p-nitrophenol, *J. Mater. Sci. Mater. Electron.* 31 (2020) 18683–18691, <https://doi.org/10.1007/s10854-020-04410-7>.
- [23] K. Thirupugalmani, S. Karthick, G. Shanmugam, V. Kannan, B. Sridhar, K. Nehru, S. Brahadeeswaran, Second- and third-order nonlinear optical and quantum chemical studies on 2-amino-4-picolinium-nitrophenolate-nitrophenol: a phasematchable organic single crystal, *Opt. Mater.* 49 (2015) 158–170, <https://doi.org/10.1016/j.optmat.2015.09.014>.
- [24] N. Sivakumar, S. Srividya, J. Mohana, G. Anbalagan, Growth, crystalline perfection, spectral and optical characterization of a novel optical material: l-tryptophan p-nitrophenol trisolvate single crystal, *Spectrochim. Acta A Mol. Biomol. Spectrosc. SPECTROCHIM ACTA A* 139 (2015) 156–164, <https://doi.org/10.1016/j.saa.2014.12.044>.
- [25] J. Urdaneta, Y. Bermúdez, F. Arrieta, Theoretical study in gas phase of linear and nonlinear optical properties of the ortho-, meta- and para-nitrophenol isomers, *Theor. Chem. Acc.* 126 (2010) 27–37, <https://doi.org/10.1007/s00214-009-0668-z>.
- [26] Y.S. Mary, T.E. Bolelli, R. Thomas, A.R. Krishnan, K. Bolelli, E.N. Kasap, T. Onkol, I. Yildiz, Quantum mechanical studies of three aromatic halogen-substituted bioactive sulfonamidobenzoxazole compounds with potential light harvesting properties, *Polycycl. Aromat. Comp.* 41 (2019), <https://doi.org/10.1080/10406638.2019.1689405>.
- [27] S. Moustafa, M. Abusaif, M.A. Fathy, A. Ahmed, A.B. Elhenawy, Kashyout, M. R. Selim, Y.A. Ammar, New carbazole-based organic dyes with different acceptors for dye-sensitized solar cells: synthesis, characterization, dssc fabrications and density functional theory studies, *J. Mol. Struct.* 1225 (2021), 129297, <https://doi.org/10.1016/j.molstruc.2020.129297>.
- [28] M.J. Frisch, Gaussian 09, Revision B.01, Gaussian Inc., Wallingford CT, 2010.
- [29] O. Gritsenko, E.J. Baerends, The analog of Koopmans' theorem for virtual Kohn–Sham orbital energies, *Can. J. Chem.* 87 (2009), <https://doi.org/10.1139/V09-088>.
- [30] M. Rana, N. Singla, A. Pathak, R. Dhanya, C. Narayana, P. Chowdhury, Vibrational-electronic properties of intra/inter molecular hydrogen bonded heterocyclic dimer: an experimental and theoretical study of pyrrole-2-carboxaldehyde, *Vib. Spectrosc.* 89 (2017) 16–25, <https://doi.org/10.1016/j.vibspec.2016.12.003>.
- [31] F. Neese, The ORCA Program System, Wiley Interdiscip, 2012.
- [32] M.D. Hanwell, D.E. Curtis, D. C. Loni, T. Vandermeersch, E. Zurek, G.R. Hutchison, Avogadro: an advanced semantic chemical editor, visualization, and analysis platform, *J. Cheminf.* 4 (17) (2012).
- [33] A. Ozarslan, D. Çakmaz, F. Erol, H. Şenöz, N. Seferoğlu, A. Barsella, Z. Seferoğlu, Synthesis and Investigation of Photophysical, NLO and Thermal Properties of D- π -A- π -D Dyes, 2020, 129583, <https://doi.org/10.1016/j.molstruc.2020.129583>.
- [34] K.C. Avhad, D.S. Patil, S. Chitrabalam, M.C. Sreenath, I.H. Joe, N. Sekar, Viscosity induced emission of red-emitting NLOphoric coumarin morpholine-thiazole hybrid styryl dyes as FMRs: consolidated experimental and theoretical approach, *Opt. Mater.* 79 (2018) 90–107, <https://doi.org/10.1016/j.optmat.2018.03.024>.
- [35] M. Rana, P. Chowdhury, Nonlinear optical responses of organic based indole derivative: an experimental and computational study, *Mater. Today Proc.* 28 (1) (2020) 241–245, <https://doi.org/10.1016/j.matpr.2020.01.598>.
- [36] N.D. Ojo, R.W. Krause, N.O.O. Egbedi, Electronic and nonlinear optical properties of 3-((2-substituted-4-nitrophenyl)imino)methylphenol, *Comput. Theor. Chem.* 1192 (2020), 113050, <https://doi.org/10.1016/j.comptc.2020.113050>.
- [37] M. Rana, Pooja, P. Chowdhury, Investigation on Nonlinear Optical Responses of Different Pyrrole Derivatives: A Computational Study AIP Conference Proceedings, vol. 2136, 2019, 040005, <https://doi.org/10.1063/1.5120919>.
- [38] M. Iyanar, M. Kolanjinathan, K. SenthilKannan, P. Baskaran, P. Periasamy, Electronic, NLO, computational and interaction analyses of DAPVMPFB crystals for electro-optic and electronic industrial utilities, *Inorg. Chem. Commun.* 133 (2021), 108972, <https://doi.org/10.1016/j.inoche.2021.108972>.
- [39] V. Mohanraj, P. Sakthivel, S. Ponnuswamy, P. Muthuraja, M. Dhandapani, Growth, spectral, thermal, NLO studies and computational studies on novel NLO organic crystals of N-Nitroso-r-2,c-6-bis(4-methoxyphenyl)-t-3-ethyl-piperidin-4-one, *Mater. Today Proc.* 8 (1) (2019) 1–10, <https://doi.org/10.1016/j.matpr.2019.02.074>.
- [40] J.S. John, D. Sajan, Computational analysis of vibrational spectroscopic properties and hyperpolarizability of silver adsorbed organic molecule, N,N Dimethyl Urea Ninhydrin, *Spectrochim. Acta A Mol. Biomol. Spectrosc. SPECTROCHIM ACTA A* 228 (2020), 117698, <https://doi.org/10.1016/j.saa.2019.117698>.
- [41] A. Unal, M. Okur, Y. Atalay, Structural, spectroscopic, electronic analysis with nonlinear optical activity of L-methionine L-methioninium hydrogen maleate: a DFT study, *Opt Spectrosc.* 128 (2020) 582–589, <https://doi.org/10.1134/S0030400X20050173>.
- [42] S. Adhikari, T. Kar, Experimental and theoretical studies on physicochemical properties of l-leucine nitrate—a probable nonlinear optical material, *J. Cryst. Growth* 356 (2012) 4–9, <https://doi.org/10.1016/j.jcrysgro.2012.07.008>.
- [43] J. Sarrato, A.L. Pinto, G. Malta, E.G. Röck, J. Pina, J.C. Lima, A.J. Parola, P. S. Branco, New 3-ethynylaryl coumarin-based dyes for DSSC applications: synthesis, spectroscopic properties, and theoretical calculations, *Molecules* 26 (10) (2021) 2934, <https://doi.org/10.3390/molecules26102934>.
- [44] N. Duvva, L. Giribabu, Hexyl Dithiafulvalene (HDT)-substituted Carbazole (CBZ) D- π -A Based Sensitizers for Dye-Sensitized Solar Cells, *New J Chem.* 2020, <https://doi.org/10.1039/D0NJ04147E>.