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Experimental and computational studies on second-and third-order nonlinear optical properties of a novel D- π -A type chalcone derivative: 3-(4-methoxyphenyl)-1-(4-nitrophenyl) prop-2-en-1-one



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ABSTRACT

The present study reports the theoretical and experimental investigations of linear and nonlinear optical (static and dynamic) properties of 3-(4-methoxyphenyl)-1-(4-nitrophenyl)prop-2-en-1-one (MNC). The crystal structure was confirmed from powder X-ray diffraction (PXRD) analysis and evaluated the crystalline quality using high-resolution X-ray diffraction (HRXRD). Linear absorption and fluorescence spectra were recorded and the optical band gap was determined by Tauc's relation. Third-order nonlinear optical (NLO) characteristics along with optical limiting behavior were explored using the femtosecond (fs) Z-scan technique at 800 and 900 nm wavelengths (Ti: sapphire laser, 150 fs, 80 MHz). The experimental results are supported by theoretical calculations obtained from the density functional theory (DFT). The optimized geometry, linear optical absorption, HOMO-LUMO energy gap, molecular electrostatic potential (MEP), dipole moments and global chemical reactivity descriptors (GCRD) were computed by employing B3LYP/6-311+G(d) level of theory. The static and dynamic linear polarizability (α), first hyperpolarizability (β) and second hyperpolarizability (γ) components were calculated using time-dependent Hartree–Fock (TDHF) method. The computed first hyperpolarizability $\beta(-2\omega;\omega,\omega)$ at 1064 nm wavelength was found to be 55 times greater than that of urea standard. The experimental and calculated dynamic molecular second hyperpolarizabilities $\gamma(-3\omega;\omega,\omega,\omega)$ are in good accordance at 800 and 900 nm wavelengths.

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1. Introduction

The chalcone derivatives have been significantly studied and documented to own varied biological and pharmacological effects, including anti-inflammatory, antimicrobial, antifungal, antioxidant, cytotoxic, antitumor and chemo-preventive activities [1–7]. These are abundant in fruits, vegetables and various edible plants and spices, which are often used in traditional medicine [8–10]. In recent years, among the explored variety of organic nonlinear optical materials, there is colossal attentiveness on development of second and third-order nonlinear optical chalcone derivatives because of their huge structural diversity and larger nonlinear optical (NLO) coefficients for feasible uses in electro-optics [11–15]. The NLO properties of several synthesized chalcones have

* Corresponding author. E-mail addresses: pspatilcrystal@gmail.com, pspatil@kleit.ac.in (P.S. Patil). been studied by theoretical and experimental techniques [16–20]. In previous reports, the use of chalcones was done within a polymeric matrix with enhanced NLO response of the polymer without damaging the chalcones [21–23]. These investigations suggest that the chalcones have been found to exhibit large second-order nonlinear responses and strong optical limiting properties [24–30]. It has been reported that extended conjugation and enhanced electrophilicity may be among the key reasons for the observed high nonlinearities of this class of compounds [31–33].

The computational NLO properties of different materials have been investigated at various DFT methods and compared with the experimental results [34,35]. Interestingly, the frequencydependent nonlinear optical properties predicted at TDHF method have reasonable accuracy in the results [36,37]. From the literature, it has been found that among the reported NLO chalcone derivatives, only a few chalcones have been investigated both experimentally and theoretically [25,38–40]. This motivated us to investigate second and third-order NLO properties of the title chalcone experimentally and theoretically. Previously, a few studies have reported on crystallographic structure and experimental second harmonic generation (SHG) efficiency of the title molecule [41,42]. It crystallizes in the orthorhombic noncentrosymmetric space group $P2_12_12_1$, possesses 5 times higher SHG efficiency than urea molecule and own D– π –A type structure. In the title molecule, 4-methoxy aryl ring acts as a donor and 1-(4-nitrophenyl) ethanone aryl ring acts as an acceptor. Considering this push-pull configuration of **MNC**, it's expected to be a potential NLO material. In the continuation of our recent work, we performed a combined theoretical and experimental studies on static and dynamic second and third-order nonlinear optical properties of **MNC** crystal for possible future NLO device applications.

2. Experimental details

2.1. Material synthesis and crystal growth

The title chalcone is synthesized by Claisen-Schmidt condensation reaction from an equimolar ratio of 4-methoxybeznaldehyde and 4'-nitroacephonone according to literature method [33,41]. The precipitated product was purified by recrystallization with DMF solvent.

Large sized good feature single crystals of **MNC** were grown by slow evaporation solution technique using DMF as a solvent at ambient temperature. Light brownish and transparent thick needles like crystals of maximum dimensions $13 \times 3 \times 2 \text{ mm}^3$ are obtained by solvent evaporation at room temperature (Fig. 1). The grown crystals are non-hygroscopic and stable in nature.

2.2. Characterization techniques

The powder X-ray diffraction (PXRD) studies were carried out using a Bruker D8 Advance powder diffractometer with CuK α radiation as an X-ray source (λ = 1.5418 Å). The sample was scanned in the 2 θ range of 10–75° at a scan speed of 1°/min. The diffraction pattern was indexed by Powder X software. To study the crystalline perfection of the grown **MNC** crystals, a multicrystal X-ray diffractometer (MCD) was used to record high-resolution diffraction curves (DCs) [43,44]. Linear absorption spectrum of MNC crystal of 1.5 mm thickness was recorded using a Perkin-Elmer UV–vis-NIR spectrometer (Lamada-900) in the wavelength range of 300–900 nm. Fluorescence spectrum was acquired using the Edinburgh Analysis Instruments FLS920 spectrophotometer with Xenon lamp as a light source.



Fig. 1. As grown single crystals of MNC.

Third-order NLO studies of MNC in DMF solution were determined using open and closed-aperture Z-scan techniques [45,46]. The experiment was performed in the femtosecond (fs) laser regime using a Ti: sapphire oscillator with 80 MHz repetition rate, 150 fs pulse duration, and ${\sim}50$ nJ pulse energy, which are tunable in the wavelength region of 680-1060 nm. The sample of 0.01 M concentration was scanned along the Z-direction through a 100 mm focal length lens. Input beam was spatially filtered to accomplish a pure Gaussian profile in far field. Since the modelocking technique in the laser optimizes the beam itself, therefore the beam profile was observed to a circular Gaussian one showing an ideal Gaussian TEM₀₀ mode. The sample positioned on a platform of 10 µm resolution and data was recorded manually using a power meter detector (Field-Max) in steps of 1 mm. The beam waist (ω_0) estimated at the focus was $\sim 25 \,\mu m$ with a corresponding Rayleigh range of \sim 2.26 mm. Initially, closed aperture scans were performed at intensities where the contribution from the higher order nonlinear effects are negligible ($\Delta \phi$ value was estimated in all the cases and it was found to be $<\pi$). Further, the open aperture scans were measured by removing the previously placed aperture in front of the detector. The nonlinear refraction and absorption measurements were performed at 800 and 900 nm wavelengths with 80 MHz laser repetition rate. The wavelength dependent nonlinearities were observed in the results. The Zscan data for DMF solvent was also recorded and found that there was no effect of solvent to the obtained nonlinearities, which confirms that the results are purely from MNC molecule.

3. Quantum chemical calculations

The computational studies for **MNC** molecule have been carried out under density functional theory by using Gaussian09 [47], and Gamess [48] programs. Gauss view 5 program was used to visualize and build the molecule [49]. The suitable DFT level of theory B3LYP was chosen for geometrical optimization at 6-311+G(d) basis set. The TD-DFT studies were performed to understand the electronic and linear optical properties at various levels of theory like: B3LYP/6-311+G(d), HF/6-311+G(d), range separated CAM-B3LYP/6-311+G(d), and wb97xd/6-311+G(d). Further, HOMO-LUMO studies, global chemical reactivity descriptors (GCRD), and molecular electrostatic potentials (MEP) were also calculated at the same level of theory. In the computational NLO studies, we calculated both static and dynamic linear polarizabilities (α), first hyperpolarizabilities (β) and second hyperpolarizabilities (γ) using TDHF method developed in the Gamess program [48]. It has been found that the 6-31G (d) polarized basis set was good enough to obtain hyperpolarizability values, and therefore the calculations were performed at TDHF level of theory using 6-31G (d) basis set. The static polarizability, $\alpha(0;0)$, first hyperpolarizability, β (0;0,0), and second hyperpolarizability, $\gamma(0;0,0,0)$ components were obtained at $\omega = 0$. The dynamic polarizability $\alpha(-\omega;\omega)$, first hyperpolarizability $\beta(-2\omega;\omega,\omega)$, and second hyperpolarizability γ $(-3\omega;\omega,\omega,\omega)$ components were calculated at three different frequencies $[\omega = 0.05695 \text{ a.u} (800 \text{ nm}), 0.05062 \text{ a.u} (900 \text{ nm}), \text{ and}$ 0.04282 a.u (1064 nm)] using the TDHF method in the Gamess program. The isotropic polarizability (∞), anisotropic polarizability $(\Delta \alpha)$, beta vector (β -V) of the first hyperpolarizability, and the average (isotropic) second hyperpolarizability (γ) values were calculated using following equations [50],

$$\langle \alpha \rangle = \frac{1}{3} (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \tag{1}$$

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

$$\beta - V = \left(\beta_x^2 + \beta_y^2 + \beta_z^2\right)^{1/2}$$
(3)

$$\beta_i = \frac{1}{3} \sum_{i,j=x,y,z} (\beta_{ijj} + \beta_{jij} + \beta_{jji}) \tag{4}$$

$$\langle \gamma \rangle = \frac{1}{5} [\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2(\gamma_{xxyy} + \gamma_{xxzz} + \gamma_{yyzz})]$$
(5)

The above mentioned tensor components values will be in a.u., and can be converted into esu using the conversion factors (1 a.u. = 0.15×10^{-24} esu for α , 1 a.u. = 8.64×10^{-33} esu for β , and 1 a.u. = 5.04×10^{-40} esu for γ).

4. Results and discussion

4.1. Powder X-ray diffraction

Powder X-ray diffraction pattern of **MNC** is shown in Fig. 2. The analysis of the peaks positions (2θ) revealed that the title crystal crystallizes in the orthorhombic crystal system with space group P2₁2₁2₁. The estimated cell parameters are in good agreement with the reported single crystal XRD values [40]. The presence of well defined reflections (peaks) in the pattern, announces the existence of periodically ordered atomic planes in the **MNC** crystals.

4.2. High-resolution X-ray diffraction

Fig. 3 shows the recorded high-resolution diffraction curve (DC) of a **MNC** single crystal specimen using (004) diffracting planes. As seen in the figure, the solid line (convoluted curve) is well fitted to the experimental points represented by the filled rectangles. On deconvolution of the diffraction curve, it is clear that the curve contains two additional peaks, which are 156 and 306 arc s away from the main peak. These two additional peaks correspond to two internal structural low angle (tilt angle ≥ 1 arc min but less than a degree) boundaries whose tilt angles (misorientation angle between the two crystalline regions on both sides of the structural grain boundary) are 156 and 150 arc s from their adjoining regions. The FWHM (full width at half maximum) of the main peak and the low angle boundaries are respectively 54, 136 and 160 arc s. Though the title crystal contains low angle boundaries, the relatively low angular spread of around 10 arc min of the diffraction curve and the low FWHM values show that the crystalline perfection is reasonably good. The entrapment of impurities or solvent molecules could be responsible for the formation of these grain



Fig. 2. Powder X-ray diffraction pattern of MNC.



Fig. 3. Diffraction curve recorded for MNC single crystal for (004) diffracting planes by employing the multicrystal XRD with MoK α_1 radiation.

boundaries, which may be segregated at the boundaries during the growth process. Such a low angle boundary could be detected with well-resolved peak in the diffraction curve only because of the high-resolution of the multicrystal X-ray diffractometer. The influence of such minute defects on the NLO properties is very insignificant. However, a quantitative analysis of such unavoidable defects is of great importance, particularly in the case of phase matching applications.

4.3. Geometry optimization

The optimized molecular geometry of **MNC** is shown in Fig. 4. The optimized geometrical parameters such as bond length, bond angle, and the positions are in accordance with the experimentally obtained XRD data [40]. We present some of the main parameters for comparison. From the optimized geometry, the bond length of 11C=O24 (carbonyl) is found to be 1.227 Å and from XRD it is 1.230 Å. The bond length of 6C–N30 is measured theoretically as 1.507 Å and experimentally 1.469 Å. The computed bond length of 30N–032 is found to be 1.278 Å, and that of experimental one is 1.229 Å. The inter-atomic distance between 34H and 20H is observed to be 2.361 Å theoretically and 2.328 Å experimentally. The bond angle of 21C-25O-26C is measured at DFT is 114.88°, and that of XRD is 116.34°. The angle between 310-30N-6C is found to be 117.93° theoretically, and 117.60° experimentally. The angle of 310–30N–320 is observed from optimized geometry as 124.14° and 123.56° from experimental one. These calculated geometrical parameters are found to be very close to the experimental one and hence confirms the molecular structure of MNC.

4.4. Linear absorption and fluorescence emission spectra

The normalized UV–visible absorption spectrum of **MNC** crystal is shown in Fig. 5. The spectrum has 2 intense bands with maxima at 334 and 408 nm. The cutoff wavelength ($\lambda_{cut-off}$) of absorption is around 460 nm. Maximum absorption observed at 408 nm is assigned to the $\pi \rightarrow \pi^*$ transition, i.e. the transition of an electron from bonding (π) to anti-bonding (π^*) molecular orbitals and this transition could be attributed to C=O group and aromatic ring excitations in MNC. The other peak appeared at 334 nm, which is originated due to the $n \rightarrow \pi^*$ transitions. As we can see, the sample is transparent at a wavelength of the second harmonic wave (532 nm) of fundamental wavelength 1064 nm and also at laser wavelengths of Z-scan studies (800 and 900 nm).

The optical band gap (E_g) of the material is a quite essential parameter in optoelectronic applications. To calculate E_g , we have



Fig. 4. The optimized molecular geometry of MNC at B3LYP/6-311+G(d) level.



Fig. 5. Linear absorption and broad fluorescence emission spectra of MNC. The inset contains the plot of $(\alpha hv)^2$ against photon energy (E).

initially determined the optical absorption coefficient (α) using the formula,

$$\alpha = 2.303 \times \frac{A}{t} \tag{6}$$

where, *A* is the absorbance and *t* is the thickness of the crystal. The optical energy band gap (E_g) of title crystal can be calculated by the Tauc's relation,

$$(\alpha h v) = A(h v - E_g)^{1/2}$$
⁽⁷⁾

where, *h* is Planck's constant and *v* is the frequency of incident photons. The energy band gap of **MNC** crystal can be estimated by extrapolating the linear part of the graph of $(\alpha hv)^2$ vs (hv) until it intersects the *hv* axis (see the inset of Fig. 5). The obtained value of direct optical band gap of 2.80 eV proves the suitability of **MNC** crystals for optoelectronic devices.

The fluorescence emission spectrum of MNC with an excitation wavelength of 420 nm is shown in Fig. 5. A pronounced emission maximum appeared at 543 nm. The soaring intensity green emission at 543 nm is credited to the π - π * transitions of the aromatic ring. Broad spectral features observed in **MNC** are due to the intra-molecular interactions [40]. The result indicates that the crystal can be used in the production of green organic LEDs (OLEDs).

4.5. TD-DFT absorption spectrum

To understand the electronic absorption properties of **MNC** molecule, we have applied time-dependent approach at the

B3LYP, HF, range separated CAM-B3LYP, and wb97xd levels of theory with the 6-311+G(d) basis set. The calculations were performed in the solvent phase (N,N-dimethylformamide) with the Polarizable Continuum Model (PCM) using the integral equation formalism variant (IEFPCM). The UV-Vis absorption spectrum of the optimized MNC molecule calculated at different methods is shown in Fig. 6. The vertical transition energies from ground state to each excited states have been computed. Further, the comparison has been made between theoretically calculated and experimentally obtained absorption spectra. The calculated absorption wavelengths at TD-B3LYP/6-311+G(d) method were found to be 396 and 293 nm, which are in close agreement with the experimental values 408 and 334 nm. The TD-DFT calculation shows that the absorption peaks at 396 and 293 nm are due to the transition of electrons from HOMO to LUMO and HOMO to LUMO+1, respectively.

4.6. HOMO-LUMO studies

The HOMO and LUMO acts as an electron donor and acceptor groups, respectively. The HOMO, LUMO and HOMO-1, LUMO+1 orbitals and the energy gaps are shown in the Fig. 7. It is clear from the figure that, the HOMO is localized at 4-methoxybenzaldehyde and C=O group, whereas the HOMO-1 is localized only on the nitro group of the phenyl ring, while LUMO and LUMO+1 are localized on almost all over the molecule indicating the intra-molecular charge transfer (ICT) characteristics. The energy gap between the HOMO and LUMO is found to be 2.68 eV, and that of HOMO-1 and LUMO+1 is found to be 3.91 eV. The small HOMO-LUMO gap



Fig. 6. Computed UV-vis absorption spectrum under TD-DFT method at different levels of theory with 6-311+G(d) basis set.



Fig. 7. HOMO-LUMO orbitals and the band gap of MNC molecule.

means higher polarizability [53] and hence large NLO response could be expected from the title molecule. In view of the chemical hardness and softness rule, if a molecule has a large HOMO-LUMO gap, it can be considered as hard and it is soft if the gap is small. One can relate molecular stability to hardness, which means that the molecule with smaller HOMO-LUMO gap is more reactive. The electronic transitions of MNC molecule, i.e. the transition of an electron from the ground state to first excited state was observed at the excitation energy 3.13 eV, which is corresponding

Table 1

The excitation wavelength, energy, oscillator strengths, major contributions of HOMO-LUMO orbitals and the ground state electric dipole moments of MNC molecule calculated at TD-DFT/B3LYP/6-311+G(d) level of theory.

λ_{ex} (nm)	E(eV)	f_0	Major transitions	Dipole moment (Debye)
396	3.13	0.12	$\mathrm{H} \rightarrow \mathrm{L}(100\%)$	8.05 (µ _x)
363	3.42	0.012	$H-2 \rightarrow L (84\%)$	0.06 (μ _y)
355	3.49	0.01	$H-6 \rightarrow L (94\%)$	0.13 (µ _z)
348	3.56	0.001	$\text{H-1} \rightarrow \text{L} \ (98\%)$	8.05 (µtot)

to the HOMO to LUMO charge transitions (100%). The HOMO-LUMO energy gap (2.68 eV) and the electronic excitation energies (3.13 eV) are in close relation with the experimentally obtained energy band gap (2.8 eV). The excitation wavelengths, energy, oscillator strengths, and the major contribution of the orbitals to the electronic transitions are given in Table 1.

The molecular dipole moment is a basic property of a molecule, which is used to investigate intermolecular interactions. Higher the dipole moment stronger will be the intermolecular interactions. Further, electric responses of a molecule at an applied field can also be understood, which in turn help to figure out optoelectronic chattels. The computed values of electronic dipole moments of MNC molecule at TD-DFT/B3LYP/6-311+G(d) level of theory are tabulated in Table 1. Larger value of dipole moment (8.05 D) and the charge separations are due to the presence of strong electron donor-acceptor configuration in the molecule. The ground state electronic dipole moment is heading from negatively charged part of the molecule to positive part. The major dominant component of the dipole moments is along μ_x which is the main charge transfer axis. The small HOMO-LUMO energy gap and high dipole moments of **MNC** molecule may result to increase NLO activity.

The global chemical reactivity descriptors (GCRD) are the important tools to understand chemical reaction, structure, and stability of the molecule with the help of molecular orbitals. Further, making use of the HOMO and LUMO energy orbitals in the DFT study, we have calculated various global chemical reactivity descriptors such as the global hardness [$\eta = (E_{LUMO} - E_{HOMO})/2$], softness (S = 1/2 η), chemical potential [$\mu = (E_{HOMO} + E_{LUMO})/2$], electronegativity [$\chi = (I + A)/2$], and electrophilic index ($\omega = \mu^2/2 \eta$) by taking the energies of HOMO as ionization potential (I) and LUMO as electron affinity (A) [38]. It is found that the molecule is kinetically stable with the hardness value 1.34 eV, and chemical potential -7.25 eV (Table 2). The rest of the parameters such as softness (0.37 eV⁻¹), electronegativity (7.25 eV), and electrophilic index (19.6 eV) values suggest that the **MNC** molecule possesses excellent chemical strength and stability.

4.7. Molecular electrostatic potential (MEP)

MEP map gives the knowledge which is concerning on molecular size, shape, alongside its positive, negative, and neutral electrostatic potential regions in terms of color grading. It can display the regions for an electrophilic attack of charge point like reagents on organic molecules [25]. It is also an important tool to envisage how different types of geometries could interact, and how the charge could transfer. The MEP map of MNC molecule plotted using Gauss view 5 program is shown in Fig. 8. From the plot, the maximum positive region is the preferred site for the nucleophilic attack which is designated by blue color. Likewise, a maximum negative region is a favored spot for an electrophilic attack authorized by red surface. The proton-rich region exhibits the positive potential and the repulsion energy between the protons, which can be seen in the white region. The electron donating group at the negative potential is originated mainly because of the electron rich oxygen atom, the carbonyl group (C=O), a nitro group (O-N-O), and the methoxy group (OCH₃). Further, variance in the MEP surfaces shows an increase in the positive potential due to the proton environment in the molecule.

Table 2

The frontier molecular orbital energies (in eV) and global chemical reactivity descriptors (in eV) such as chemical hardness (η), chemical potential (μ), softness (S), electronegativity (χ), and electrophilic index (ω) of MNC molecule.

НОМО	E _{LUMO}	E _{HOMO-1}	E _{LUMO+1}	ΔE_{H-L}	$\Delta E_{H-1-L+1}$	η	μ	S	χ	ω
-8.59	-5.91	-8.91	-4.99	2.68	3.91	1.34	-7.25	0.37	7.25	19.6



Fig. 8. The molecular electrostatic potential map of MNC molecule.



Fig. 9. Open aperture Z-scan curves of MNC.



Fig. 10. Closed aperture Z-scan curves of MNC.

4.8. Third-order nonlinear optical properties

Table 3

The open aperture Z-scan curves of **MNC** molecule at 800 and 900 nm wavelengths are shown in Fig. 9. Both the curves are symmetric with respect to the focus (*Z*=0). The molecule exhibits reverse saturation absorption (RSA) as the excited state absorption cross section is greater than the ground state absorption cross section at 800 and 900 nm wavelengths (Table 3). From the open aperture curves, nonlinear absorption coefficient (β) can be estimated by fitting the curves using the following equation,

$$T(Z) = 1 - \frac{\beta I_0 L_{eff}}{2\sqrt{2}(1 + Z^2/Z_0^2)}$$
(8)

where, T (z) is the normalized transmittance, I_0 is the intensity at the focus, and L_{eff} is the effective length of the sample. The calculated β values (Table 3) are one order smaller than γ -BBO Nano rods [51], same of the nonlinear absorption measured for DMMC [31]

and two orders higher than 3TM chalcones observed under femtosecond excitation [27].

Fig. 10 shows the normalized transmission for a closed aperture case at 800 and 900 nm wavelengths. The peak-valley configuration indicates a negative nonlinear refractive index n_2 (self-defocusing), i.e., an increase in the transmitted intensity due to refraction as the sample approaches the focal point (Z = 0) followed by a decrease in intensity as it moves away from the focal point and towards the detector. The nonlinear refraction (n_2) can be calculated using the closed aperture curves by fitting them with the relation,

$$T(Z) = 1 - \frac{(4X\Delta\phi_0)}{(X^2 + 1)(X^2 + 9)}$$
(9)

where, $\Delta \phi_0$ is the phase shift, X = Z/Z₀, and n_2 can be calculated by using the $\Delta \phi_0$ value with the relation $\Delta \Phi_0 = kn_2 I_0 L_{eff}$ (Table 3). The calculated values of the nonlinear refractive index are of the order

The third-order nonlinear optical parameters of MNC obtained at 150 fs (80 MHz) laser pulses with 0.01 M concentration.

λ (nm)	$lpha_0 \ (cm^{-1})$	$\begin{array}{c} n_2 (cm^2 W^{-1}) \times \\ 10^{-14} \end{array}$	β (cm $W^{-1}) \times 10^{-9}$	$\begin{array}{l} \text{Re}\chi^{(3)}\left(\text{e.s.u}\right)\times\\ 10^{-12} \end{array}$	${lm \ \chi^{(3)} \ (e.s.u) \times \over 10^{-12}} \\$	$\begin{array}{c} \chi^{(3)} (e.s.u) \times \\ 10^{-12} \end{array}$	$\sigma_{g} \ (10^{-16} cm^{2})$	$\frac{\sigma_{ex}}{(10^{-15}\text{cm}^2)}$	σ _{2PA} (GM)	γ_h (10 ⁻³¹ esu)
800	0.45	-5.45	2.3	-5.64	1.48	5.83	7.44	16.8	928.4	2.93
900	0.63	-9.23	3.5	-9.56	2.59	9.91	2.09	11.2	256.7	5.36

of 10^{-14} cm² W⁻¹. These values are one and two orders higher than the nonlinear refractive index measured for 3TM chalcones, LiNbO3:MgO (LN:Mg), KTiOAsO4, (KTA), KTiOPO4 (KTP), β -BaB2O4 (BBO) and LiB3O5 (LBO) crystals with femtosecond z-scan method [27,52] and in agreement with the results mentioned in Refs. [29,31].

The third-order nonlinear optical susceptibilities, second-order hyperpolarizabilities, and two-photon absorption cross sections were calculated for **MNC** at two different wavelengths by following the procedure explained in our previous article [32] (Table 3).

4.9. Optical limiting studies

The optical limiting threshold (LT) is defined as the input fluence at which transmittance falls to half of the linear transmittance value. From the definition, it follows that lower the LT value, better the optical limiting performance. In the case of open aperture Zscan using a Gaussian beam, input fluence at each z-position is given by,

$$F(z) = 4\sqrt{\ln 2}E_{in}/\pi^{3/2}\omega(z)^2$$
(10)

where, E_{in} is the input laser pulse energy and $\omega(z)$ is the beam radius, which is given by $\omega(z) = \omega(0)[1 + (z/z_0)^2]^{1/2}$, where, $\omega(0)$ is the beam radius at the focus and $z_0 = \frac{\pi \omega(0)^2}{2}$ is the Rayleigh range.

The optical limiting properties of **MNC** were obtained at two laser wavelengths 800 and 900 nm with 80 MHz repetation rate (Fig. 11.). The decreasing transmittance with the increasing incident fluence indicates the optical limiting response of **MNC**. The limiting threshold was observed at 0.75 mJ/cm² for 800 nm, and 1.54 mJ/cm² for 900 nm input laser wavelengths. The obtained threshold values are in accordance with their nonlinear absorptive capacity at experimental wavelengths. The values suggest that the MNC molecule could be a better candidate for the protection of sensitive optical devices.

4.10. Static and frequency-dependent NLO-DFT studies

In the theoretical study, we have used time-dependent Hartree-Fock (TDHF) method to investigate NLO properties of **MNC** molecule. In order to understand both static and dynamic hyperpolarizabilities of organic molecules, TDHF procedure is generally used to predict the approximate values of NLO properties [54]. The static dipole polarizability $\alpha(0;0)$, first hyperpolar-



Fig. 11. Optical limiting curves of MNC.

izability $\beta(0;0,0)$, and second hyperpolarizability $\gamma(0;0,0,0)$ components were computed (at $\omega = 0.0$), and some of the tensor components and their isotropic average values are tabulated in Table 4. By observing, all of the tensor components found to have non-zero values and are in particular direction as indicated. The axial x-component of dipole polarizability (α_{xx}), first hyperpolarizability (β_{xxx}), and second hyperpolarizability (γ_{xxxx}) have been taken as the longitudinal components, which are the dominant components along with the corresponding mean values. Since the major contribution to the average values is from xcomponent, it is the evidence for the charge transfer interaction along the X-axis in the MNC molecule [55]. The static <\appa\ (isotropic), $\Delta \alpha$ (anisotropic), β -Vector, and γ_{γ} (isotropic) values are found to be 28.7×10^{-24} esu, 32.0×10^{-24} esu, 53.8×10^{-30} esu, and 33.6×10^{-36} esu, respectively. The magnitude of the values obtained in this case is comparatively larger and suggests that the **MNC** molecule has good NLO properties.

The dynamic NLO properties such as polarizability $\alpha(-\omega;\omega)$, first hyperpolarizability $\beta(-2\omega;\omega,\omega)$, and second hyperpolarizability $\gamma(-3\omega;\omega,\omega,\omega)$ tensor components of **MNC** were predicted at three different frequencies ($\omega = 0.05695$, 0.05062 and 0.04282 a. u). The response of a molecule with respect to an applied external electric field can be understood by determining the response of tensor components of dynamic hyperpolarizabilities at the molecular level. The dynamic polarizability components $\alpha(-\omega;\omega)$ values are shown in Table 5. The orientationally averaged isotropic and anisotropic values and the response of all the tensor components increases as the input frequency increases. It is observed that the static polarizability values are lower compared to the dynamic ones. Hence, the polarizability of a molecule is dependent on the applied field. Here, the polarizability values are larger at ω = 0.05695 ($\lambda = 800 \text{ nm}$) i.e. $\alpha = 29.67 \times 10^{-24} \text{ esu}$, $\Delta \alpha = 34.1 \times 10^{-24} \text{ esu}$ 10^{-24} esu, and comparatively decreases as the frequency decreases. The α_{xx} component is considered as the axial or a longitudinal component since it has the largest contribution $(50.4 \times 10^{-24} \text{ esu})$ to the mean polarizability vector.

To understand the second-and third-order nonlinear optical properties of **MNC** at a molecular level, we computed dynamic hyperpolarizabilities at three frequencies ($\omega = 0.04282, 0.5062,$ and 0.05695 a.u.) using TDHF method with respect to their experimental laser wavelengths to compare the results. The computed dynamic first hyperpolarizability (β) tensor components and β -V (beta vector) values of MNC molecule and a reference molecule urea are given in Table 6. The β -V value of the **MNC** molecule at ω = 0.04282 a.u. is found to be 55 times higher than the urea standard (β -V_{MNC} = 73.3 × 10⁻³⁰ esu and β -V_{urea} = 1.3 × 10⁻³⁰ esu). The computed and experimental SHG efficiency of MNC is 55 and 5 times higher than that of urea standard, respectively, which suggests that the title molecule can be an efficient NLO candidate. The deviation in the results could be raised due to the fact that the experiment was carried out with the solid crystalline phase, whereas the theoretical predictions were made with the gas phase. Further, the computational β-V values are also obtained at ω = 0.05695 and 0.05062 a.u. frequencies and these values are found to be slightly higher than that of the static and computed β -V at ω = 0.04282 a.u., and SHG efficiency is measured to be 75 and 64 times larger than the urea standard, respectively. It is observed that, with an increase in the frequency of the electric field, the hyperpolarizability components interaction within the molecule also increases and hence resulting in the larger values of the NLO coefficients.

The dynamic second-order hyperpolarizability $\gamma(-3\omega;\omega,\omega,\omega)$ tensor components of **MNC** molecule are computed at $\omega = 0.05695$, 0.05062, and 0.04282 frequencies (Table 7). The molecular second hyperpolarizability values depend on the number of factors such as the extent of π -electron conjugation, the

Table 4

The static dipole polarizability $\alpha(0;0)$, first hyperpolarizability $\beta(0;0,0)$, and second hyperpolarizability $\gamma(0;0,0,0)$ components and their isotropic values of **MNC** calculated at $\omega = 0.0$ using the TDHF method.

Components	(esu) 10 ⁻²⁴	Components	(esu) 10 ⁻³⁰	Components	(esu) 10 ⁻³⁶
α_{xx}	47.9	β _{xxx}	17.34	γ _{xxxx}	145.3
α_{xv}	-0.33	βγγγ	-0.47	γννν	1.27
α _{yy}	26.6	βzzz	-0.13	Ŷzzzz	0.16
α_{xz}	1.74	β_x	51.9	γxxyy	10.3
α_{yz}	-0.64	β _y	-14.0	γxxzz	0.18
α _{zz}	11.4	βz	-2.3	γyyzz	0.13
⊲o⊳ (iso)	28.7	β-V	53.7	$\langle \gamma \rangle$ (iso)	33.6
$\Delta \alpha$ (aniso)	32.0	β-V _{urea}	1.3		

Table 5

The frequency-dependent dipole polarizability $\alpha(-\omega;\omega)$ components and their average values of **MNC** at three different frequencies.

Components	ω = 0.05695 a.u. esu (10 ⁻²⁴)	ω = 0.05062 a.u. esu (10 ⁻²⁴)	ω = 0.04282 a.u. esu (10 ⁻²⁴)
$\alpha_{\rm xx}$	50.38	49.83	49.26
α_{xy}	-0.43	-0.40	-0.38
α_{vv}	27.16	27.04	26.92
α_{xz}	1.79	1.786	1.77
α_{vz}	-0.67	-0.66	-0.65
α _{zz}	11.48	11.47	11.45
⊲o⊳ (iso)	29.67	29.45	29.21
$\Delta \alpha$ (aniso)	34.06	33.58	33.09

Table 6

The frequency-dependent first-order hyperpolarizability $\beta(-2\omega;\omega,\omega)$ components and their β -vector values of **MNC** and urea molecule at three different frequencies.

Components	ω = 0.05695 a.u.	ω = 0.05062 a.u.	ω = 0.04282 a.u.
	esu (10 ⁻³⁰)	esu (10 ⁻³⁰)	esu (10 ⁻³⁰)
β _{xxx}	35.62	29.69	24.91
β _{yyy}	-4.78	-3.61	-2.68
βzzz	-0.17	-0.16	-0.15
β _x	98.25	82.73	70.11
β _y	-29.91	-25.13	-21.27
βz	-3.89	-3.41	-3.01
β-V	102.77	86.53	73.33
β-V _{urea}	1.38	1.36	1.33

Table 7

The frequency-dependent some of the second hyperpolarizability $\gamma(-3\omega;\omega,\omega,\omega)$ components and their isotropic average values of **MNC** molecule at three different frequencies.

Components	ω = 0.05695 a.u esu (10 ⁻³⁶)	ω = 0.05062 a.u esu (10 ⁻³⁶)	ω = 0.04282 a.u esu (10 ⁻³⁶)
γ _{xxxx}	3233	837	412
γ_{yyyy}	5.9	4.65	3.22
Yzzzz	0.23	0.19	0.19
γ_{xxyy}	139.8	41.96	23.53
γ_{xxzz}	1.08	0.83	0.53
γ _{vvzz}	0.23	0.2	0.17
«γ»(iso)	704.3	185.6	92.8

dimensionality of the molecule, and the nature of the substituents. Since **MNC** has the donor-acceptor π -conjugated bridge system, the charge could transfer through the phenyl rings from the substituent groups, which is responsible for determining NLO properties. The phenyl rings mainly act as a bridge in presence of strong donor-acceptor substituents and this is a reason for obtaining the nonzero values of static and dynamic hyperpolarizabilities as microscopic NLO responses. As we see from the Table 7, the magnitude of the dynamic hyperpolarizability increases with increase in the frequency. The orientationally averaged γ value is larger $(7.0 \times 10^{-34} \text{ esu})$ for $\omega = 0.05695$ ($\lambda = 800 \text{ nm}$), and is $1.85 \times$

 10^{-34} esu for $\omega = 0.05062$ ($\lambda = 900$ nm), and is lower (0.93 $\times 10^{-34}$ esu) for $\omega = 0.04282$ ($\lambda = 1064$ nm).

The experimentally and theoretically obtained second hyperpolarizabilities are found to be 2.9×10^{-31} esu & 0.7×10^{-33} esu, respectively at $\omega = 0.05695$ ($\lambda = 800$ nm), and 5.4×10^{-31} esu & 0.19×10^{-33} esu, respectively at $\omega = 0.05062$ ($\lambda = 900$ nm). The obtained results are comparatively good and agreed well. The slight deviation in few orders of magnitude between the results is because the experiment was carried out in the liquid phase using the DMF solvent while the computational studies were performed in the gaseous phase. Further, the experimental results not only depend on the input laser frequency, but also depend on the concentration of the solution [23], the laser repetition rate, pulse width [56], and the intensity of the beam used during the experiment [57], whereas the computational NLO results are only dependent on the given input frequency.

5. Conclusions

In summary, a combined experimental and theoretical linear and frequency-dependent nonlinear optical properties of MNC was studied. Nonlinear optical properties of MNC were investigated by the determination of static and dynamic electric dipole moments, polarizabilities, first and second-order hyperpolarizabilities. The theoretical results of dynamic second hyperpolarizabilities $\gamma(-3\omega;\omega,\omega,\omega)$ are significantly comparable with the experimental molecular second hyperpolarizabilities (γ) at two laser frequencies ($\omega = 0.05695$ a.u. and $\omega = 0.05062$ a.u.). The observed small HOMO-LUMO gaps revealed that MNC can be easily polarized and exhibits considerable NLO properties. The title chalcone display good optical limiting properties with femtosecond laser pulses at 800 and 900 nm wavelengths and the limiting threshold values were found to be 0.75 and 1.54 mJ/cm^2 , respectively. The magnitudes of the NLO coefficients obtained in the present work highlight the potential advantage of the title chalcone in NLO applications.

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References

^[1] L. Feng, M.M. Maddox, M.Z. Alam, L.S. Tsutsumi, G. Narula, D.F. Bruhn, X. Wu, S. Sandhaus, R.B. Lee, C.J. Simmons, Y.-C. Tse-Dinh, J.G. Hurdle, R.E. Lee, D. Sun, Synthesis, structure-activity relationship studies, and antibacterial evaluation of 4-chromanones and chalcones, as well as olympicin a and derivatives, J. Med. Chem. 57 (2014) 8398–8420.

- [2] M.J. Matos, S. Vazquez-Rodriguez, E. Uriarte, L. Santana, Potential pharmacological uses of chalcones: a patent review, from June 2011–2014, Expert Opin. Ther. Pat. 25 (2015) 351–366.
- [3] F. Pérez-Cruz, S. Vazquez-Rodriguez, M.J. Matos, A. Herrera-Morales, F.A. Villamena, A. Das, B. Gopalakrishnan, C. Olea-Azar, L. Santana, E. Uriarte, Synthesis and electrochemical and biological studies of novel coumarin-chalcone hybrid compounds, J. Med. Chem. 56 (2013) 6136–6145.
- [4] S. Vazquez-Rodriguez, R. Lama López, M.J. Matos, G. Armesto-Quintas, S. Serra, E. Uriarte, L. Santana, F. Borges, A. Muñoz Crego, Y. Santos, Design, synthesis and antibacterial study of new potent and selective coumarin-chalcone derivatives for the treatment of tenacibaculosis, Bioorg. Med. Chem. 23 (2015) 7045–7052.
- [5] H. Wei, J. Ruan, X. Zhang, Coumarin–chalcone hybrids: promising agents with diverse pharmacological properties, RSC Adv. 6 (2016) 10846–10860.
- [6] H.-L. Qin, Z.-P. Shang, I. Jantan, O.U. Tan, M.A. Hussain, M. Sher, S.N.A. Bukhari, Molecular docking studies and biological evaluation of chalcone based pyrazolines as tyrosinase inhibitors and potential anticancer agents, RSC Adv. 5 (2015) 46330–46338.
- [7] E. Winter, P. Devantier Neuenfeldt, L.D. Chiaradia-Delatorre, C. Gauthier, R.A. Yunes, R.J. Nunes, T.B. Creczynski-Pasa, A. Di Pietro, Symmetric bis-chalcones as a new type of breast cancer resistance protein inhibitors with a mechanism different from that of chromones, J. Med. Chem. 57 (2014) 2930–2941.
- [8] Z. Rozmer, P. Perjési, Naturally occurring chalcones and their biological activities, Phytochem. Rev. 15 (2014) 87–120.
- [9] R.S. Varma, Dietary bioflavonoids, chalcones, and related alkenones in prevention and treatment of cancer, Nutrition 12 (1996) 643–645.
- [10] G. Di Carlo, N. Mascolo, A.A. Izzo, F. Capasso, Flavonoids: old and new aspects of a class of natural therapeutic drugs, Life Sci. 65 (1999) 337–353.
- [11] B. Zhao, W.Q. Lu, Z.H. Zhou, Y. Wu, The important role of the bromo group in improving the properties of organic nonlinear optical materials, J. Mater. Chem. 10 (2000) 1513–1517.
- [12] E.D. D'silva, G.K. Podagatlapalli, S.V. Rao, D.N. Rao, S.M. Dharmaprakash, new, high efficiency nonlinear optical chalcone co-crystal and structure–property relationship, Cryst. Growth Des., 11 (2011) 5362–5369.
- [13] P.C. Rajesh Kumar, V. Ravindrachary, K. Janardhana, H.R. Manjunath, P. Karegouda, V. Crasta, M.A. Sridhar, Optical and structural properties of chalcone NLO single crystals, J. Mol. Struct. 1005 (2011) 1–7.
- [14] A. Saha, V. Shukla, S. Choudhury, J. Jayabalan, Design, synthesis and nonlinear optical properties of (E)-1-(4-substituted)-3-(4-hydroxy-3-nitrophenyl) prop-2-en-1-one compounds, Chem. Phys. Lett. 653 (2016) 184–189.
- [15] P.J. Tejkiran, M.S. Brahma Teja, P. Sai Siva Kumar, P. Sankar, R. Philip, S. Naveen, N.K. Lokanath, G. Nageswara Rao, D-A-π-D synthetic approach for thienyl chalcones – NLO – a structure activity study, J. Photochem. Photobiol., A 324 (2016) 33–39.
- [16] H. Pir Gümüş, Ö. Tamer, D. Avcı, Y. Atalay, Density functional theory calculations on conformational, spectroscopic and electrical properties of 3-(2,3-dimethoxyphenyl)-1-(pyridin-2-yl)prop-2-en-1-one: a potential nonlinear optical material, Indian J. Phys. 90 (2015) 79–89.
- [17] O.M. Sayed, H. Moustafa, A.E.M. Mekky, A.M. Farag, A.H.M. Elwahy, Synthesis, reactions and DFT calculations of novel bis(chalcones) linked to a thienothiophene core through an oxyphenyl bridge, RSC Adv. 6 (2016) 10949–10961.
- [18] M.-Y. Teng, J. Zhang, G.-L. Huang, B. Liu, X.-M. Li, M.-Z. Rong, T.-H. Shen, Q.-B. Song, Synthesis and nonlinear optical properties of novel chalcone analogues of ferrocenyl biaryl derivatives, J. Organomet. Chem. 791 (2015) 298–302.
- [19] A. Aditya Prasad, K. Muthu, V. Meenatchi, M. Rajasekar, R. Agilandeshwari, K. Meena, J. Vijila Manonmoni, S.P. Meenakshisundaram, Optical, vibrational, NBO, first-order molecular hyperpolarizability and Hirshfeld surface analysis of a nonlinear optical chalcone, Spectrochim Acta Part A Mol. Biomol. Spectrosc. 140 (2015) 311–327.
- M. Shkir, P.S. Patil, M. Arora, S. AlFaify, H. Algarni, An experimental and theoretical study on a novel donor-*π*-acceptor bridge type 2, 4, 5-trimethoxy-4'-chlorochalcone for optoelectronic applications: a dual approach, Spectrochim Acta Part A Mol. Biomol. Spectrosc. 173 (2017) 445–456.
 S. Shettigar, G. Umesh, K. Chandrasekharan, B.K. Sarojini, B. Narayana, Studies
- [21] S. Shettigar, G. Umesh, K. Chandrasekharan, B.K. Sarojini, B. Narayana, Studies on third-order nonlinear optical properties of chalcone derivatives in polymer host, Opt. Mater. 30 (2008) 1297–1303.
- [22] P. Poornesh, S. Shettigar, G. Umesh, K.B. Manjunatha, K. Prakash Kamath, B.K. Sarojini, B. Narayana, Nonlinear optical studies on 1,3-disubstituent chalcones doped polymer films, Opt. Mater. 31 (2009) 854–859.
- [23] J. Chen, X. Wang, Q. Ren, P.S. Patil, T. Li, H. Yang, J. Zhang, G. Li, L. Zhu, Investigation of third-order nonlinear optical properties of NNDC-doped PMMA thin films by Z-scan technique, Appl. Phys. A 105 (2011) 723–731.
- [24] E.D. D'Silva, G.K. Podagatlapalli, S. Venugopal Rao, S.M. Dharmaprakash, Study on third-order nonlinear optical properties of 4-methylsulfanyl chalcone derivatives using picosecond pulses, Mater. Res. Bull. 47 (2012) 3552–3557.
- [25] A.K. Singh, G. Saxena, R. Prasad, A. Kumar, Synthesis, characterization and calculated non-linear optical properties of two new chalcones, J. Mol. Struct. 1017 (2012) 26–31.
- [26] V. Ramkumar, S. Anandhi, P. Kannan, R. Gopalakrishnan, Synthesis, single crystal growth, characterization and comparison of two new enone shifted chalcones and their NLO behaviour, Cryst. Eng. Commun. 15 (2013) 2438.
- [27] B. Gu, W. Ji, P.S. Patil, S.M. Dharmaprakash, Ultrafast optical nonlinearities and figures of merit in acceptor-substituted 3,4,5-trimethoxy chalcone derivatives: Structure-property relationships, J. Appl. Phys. 103 (2008) 103511.

- [28] L.M. Saleh, H.A. Hassan, F.Z. Henari, P.S. Patil, M.S. Bannur, Nonlinear refractive and optical limiting measurements of 2-thienylchalcone derivatives under cw laser regime, Appl. Phys. A 116 (2013) 805–810.
- [29] P.S. Patil, P.A. Kumar, S. Venugopal Rao, G. Bhagavannarayana, Growth and characterization of a new organic nonlinear optical crystal: 1-(3-Nitrophenyl)-5-phenylpenta-2,4-dien-1-one, Opt. Laser Technol. 71 (2015) 108–113.
- [30] M. Shkir, S. Muhammad, S. AlFaify, A. Irfan, P.S. Patil, M. Arora, H. Algarni, Z. Jingping, An investigation on the key features of a D-π-A type novel chalcone derivative for opto-electronic applications, RSC Adv. 5 (2015) 87320–87332.
- [31] P.S. Patil, S.R. Maidur, S.V. Rao, S.M. Dharmaprakash, Crystalline perfection, third-order nonlinear optical properties and optical limiting studies of 3, 4dimethoxy -4'-methoxychalcone single crystal, Opt. Laser Technol. 81 (2016) 70–76.
- [32] A. Ekbote, P.S. Patil, S.R. Maidur, T.S. Chia, C.K. Quah, Structure and nonlinear optical properties of (E)-1-(4-aminophenyl)-3-(3-chlorophenyl) prop-2-en-1one: a promising new D-π-A-π-D type chalcone derivative crystal for nonlinear optical devices, J. Mol. Struct. 1129 (2017) 239–247.
- [33] A. Ekbote, P.S. Patil, S.R. Maidur, T.S. Chia, C.K. Quah, Structural, third-order optical nonlinearities and figures of merit of (E)-1-(3-substituted phenyl)-3-(4-fluorophenyl) prop-2-en-1-one under CW regime: new chalcone derivatives for optical limiting applications, Dyes Pigm. 139 (2017) 720–729.
- [34] P.S.P. Silva, H. El Ouazzani, M. Pranaitis, M.R. Silva, C.T. Arranja, A.J.F.N. Sobral, B. Sahraoui, J.A. Paixão, Experimental and theoretical studies of the secondand third-order NLO properties of a semi-organic compound: 6-Aminoquinolinium iodide monohydrate, Chem. Phys. 428 (2014) 67–74.
- [35] S. Narayanan, S.P. Raghunathan, A.C. Poulose, S. Mathew, K. Sreekumar, C. Sudha Kartha, R. Joseph, Third-order nonlinear optical properties of 3,4ethylenedioxythiophene copolymers with chalcogenadiazole acceptors, New J. Chem. 39 (2015) 2795–2806.
- [36] A. Zawadzka, A. Karakas, P. Płóciennik, J. Szatkowski, Z. Łukasiak, A. Kapceoglu, Y. Ceylan, B. Sahraoui, Optical and structural characterization of thin films containing metallophthalocyanine chlorides, Dyes Pigm. 112 (2015) 116–126.
- [37] I. Guezguez, A. Karakas, K. Iliopoulos, B. Derkowska-Zielinska, A. El-Ghayoury, A. Ranganathan, P. Batail, A. Migalska-Zalas, B. Sahraoui, M. Karakaya, Theoretical and experimental investigations on the nonlinear optical properties of gold(III) dithiolene complexes, Opt. Mater. 36 (2013) 106–111.
- [38] A. Kumar, V. Deval, P. Tandon, A. Gupta, E. Deepak, D'silva, Experimental and theoretical (FT-IR, FT-Raman, UV-vis, NMR) spectroscopic analysis and first order hyperpolarizability studies of non-linear optical material: (2E)-3-[4-(methylsulfanyl) phenyl]-1-(4-nitrophenyl) prop-2-en-1-one using density functional theory, Spectrochim. Acta Part A Mol. Biomol. Spectrosc. 130 (2014) 41–53.
- [39] C.S. Chidan Kumar, V. Balachandran, H.-K. Fun, S. Chandraju, C.K. Quah, Synthesis, crystal growth, single crystal X-ray analysis and vibrational spectral studies of (2E)-3-(2-chloro-4-fluorophenyl)-1-(3,4-dimethoxyphenyl)prop-2en-1-one: a combined DFT study, J. Mol. Struct. 1100 (2015) 299–310.
- [40] P. Krawczyk, M. Pietrzak, T. Janek, B. Jędrzejewska, P. Cysewski, Spectroscopic and nonlinear optical properties of new chalcone fluorescent probes for bioimaging applications: a theoretical and experimental study, J. Mol. Model. 22 (2016).
- [41] P.S. Patil, S.M. Dharmaprakash, H.-K. Fun, M.S. Karthikeyan, Synthesis, growth, and characterization of 4-OCH3-4'-nitrochalcone single crystal: a potential NLO material, J. Cryst. Growth 297 (2006) 111–116.
- [42] P.S. Patil, J.B.-J. Teh, H.-K. Fun, I.A. Razak, S.M. Dharmaprakash, 3-(4-Methoxyphenyl)-1-(4-nitrophenyl)prop-2-en-1-one, Acta Crystallogr. Sect. E: Struct. Rep. Online 62 (2006) 0896–0898.
- [43] K. Lal, G. Bhagavannarayana, A high-resolution diffuse X-ray scattering study of defects in dislocation-free silicon crystals grown by the float-zone method and comparison with Czochralski-grown crystals, J. Appl. Crystallogr. 22 (1989) 209–215.
- [44] G. Bhagavannarayana, S. Parthiban, S. Meenakshisundaram, Enhancement of crystalline perfection by organic dopants in ZTS, ADP and KHP crystals as investigated by high-resolution XRD and SEM, J. Appl. Crystallogr. 39 (2006) 784–790.
- [45] M. Sheik-Bahae, A.A. Said, T.H. Wei, D.J. Hagan, E.W. Van Stryland, Sensitive measurement of optical nonlinearities using a single beam, IEEE J. Quantum Electron 26 (1990) 760–769.
- [46] D. Swain, P.T. Anusha, T. Shuvan Prashant, S.P. Tewari, T. Sarma, P.K. Panda, S. Venugopal Rao, Ultrafast excited state dynamics and dispersion studies of nonlinear optical properties in dinaphthoporphycenes, Appl. Phys. Lett. 100 (2012) 141109.
- [47] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery, Jr., J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, O. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, D.J. Fox, Gaussian-09, Revision B.01, Gaussian, Inc., Wallingford CT, 2010.
- [48] M.W. Schmidt, K.K. Baldridge, J.A. Boatz, S.T. Elbert, M.S. Gordon, J.H. Jensen, S. Koseki, N. Matsunaga, K.A. Nguyen, S. Su, T.L. Windus, M. Dupuis, J.A.

Montgomery, General atomic and molecular electronic structure system, J. Comput. Chem. 14 (1993) 1347–1363.

- [49] R. Dennington, T. Keith, J. Millam, GaussView, version 5, Semichem Inc., Shawnee Mission, KS, 2009.
- [50] H.A. Kurtz, J.J.P. Stewart, K.M. Dieter, Calculation of the nonlinear optical properties of molecules, J. Comput. Chem. 11 (1990) 82–87.
- [51] T.C.S. Girisun, R.M. Somayaji, N. Priyadarshani, S.V. Rao, Femtosecond third order optical nonlinearity and optical limiting studies of (γ and β)—barium borate nanostructures, Mater. Res. Bull. 87 (2017) 102–108.
- [52] H.P. Li, C.H. Kam, Y.L. Lam, W. Ji, Femtosecond Z-scan measurements of nonlinear refraction in nonlinear optical crystals, Opt. Mater. 15 (2001) 237– 242.
- [53] A. Aditya Prasad, S. Kalainathan, S.P. Meenakshisundaram, Supramolecular architecture of third-order nonlinear optical ammonium picrate: crystal

growth and DFT approach, Optik – Int. J. Light Electron Opt. 127 (2016) 6134–6149.

- [54] A. Karakas, A. Migalska-Zalas, Y. El Kouari, A. Gozutok, M. Karakaya, S. Touhtouh, Quantum chemical calculations and experimental studies of thirdorder nonlinear optical properties of conjugated TTF-quinones, Opt. Mater. 36 (2013) 22–26.
- [55] K. Hatua, P.K. Nandi, Static second hyperpolarizability of Λ shaped alkaline earth metal complexes, J. Theor. Comput. Chem. 13 (2014) 1450039.
- [56] M.-S. Kim, C.S. Yoon, Intrinsic pulse-width dependence of third-order nonlinear optical susceptibility in the femtosecond regime, Phys. Rev. Lett. 93 (2004).
- [57] L. Polavarapu, N. Venkatram, W. Ji, Q.-H. Xu, Optical-limiting properties of oleylamine-capped gold nanoparticles for both femtosecond and nanosecond laser pulses, ACS Appl. Mater. Interfaces 1 (2009) 2298–2303.