# Key functions analysis of a novel nonlinear optical $D-\pi$-A bridge type (2E)-3-(4-Methylphenyl)-1-(3-nitrophenyl) prop-2-en-1-one chalcone: An experimental and theoretical approach 

Parutagouda Shankaragouda Patil ${ }^{\text {a }}$, Mohd Shkir ${ }^{\text {b, }}{ }^{*}$, Shivaraj R. Maidur ${ }^{\text {a }}$, S. AlFaify ${ }^{\text {b }}$, M. Arora ${ }^{\text {d }}$, S. Venugopal Rao ${ }^{\text {c }}$, Haider Abbas ${ }^{\text {e }}$, V. Ganesh ${ }^{\text {b }}$<br>${ }^{\text {a }}$ Department of Physics, K. L. E. Institute of Technology, Opposite Airport, Gokul, Hubballi, 580030, India<br>${ }^{\mathrm{b}}$ Advanced Functional Materials \& Optoelectronic Laboratory (AFMOL), Department of Physics, Faculty of Science, King Khalid University, P.O. Box 9004, Abha, 61413, Saudi Arabia<br>${ }^{\text {c }}$ Advanced Centre of Research in High Energy Materials (ACRHEM), University of Hyderabad, Hyderabad, 500046, India<br>${ }^{\text {d }}$ CSIR-National Physical Laboratory, New Delhi, 110012, India<br>${ }^{\mathrm{e}}$ Department of Physics, Manav Rachna University, Faridabad, Haryana, 121001, India

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#### Abstract

In the current work a new third-order nonlinear optical organic single crystal of (2E)-3-(4-Methylphenyl)-1-(3-nitrophenyl) prop-2-en-1-one (ML3NC) has been grown with well-defined morphology using the slow evaporation solution growth technique. X-ray diffraction technique was used to confirm the crystal system. The presence of functional groups in the molecular structure was identified by robust FT-IR and FT-Raman spectra by experimental and theoretical analysis. The ultravi-olet-visible-near infrared and photoluminescence studies shows that the grown crystals possess excellent transparency window and green emission band ( $\sim 560 \mathrm{~nm}$ ) confirms their use in green OLEDs. The third-order nonlinear and optical limiting studies have been performed using femtosecond (fs) Z-scan technique. The third-order nonlinear optical susceptibility $\left(\chi^{(3)}\right)$, second-order hyperpolarizability $(\gamma)$, nonlinear refractive index $\left(n_{2}\right)$ and limiting threshold values are found to be $4.03 \times 10^{-12}$ esu, $14.2 \times 10^{-32} \mathrm{esu},-4.33 \times 10^{-14} \mathrm{~cm}^{2} / \mathrm{W}$ and $2.41 \mathrm{~mJ} / \mathrm{cm}^{2}$, respectively. Furthermore, the quantum chemical studies were carried out to achieve the ground state molecular geometry and correlate with experimental results. The experimental value of absorption wavelength ( $\lambda_{\mathrm{abs}}=328 \mathrm{~nm}$ ) is found to be in excellent accord with the theoretical value ( $\lambda_{\mathrm{abs}}=328 \mathrm{~nm}$ ) at TD-DFT/B3LYP/6-31G* level of theory. To understand the static and dynamic NLO behavior, the polarizability ( $\alpha$ ) and second hyperpolarizability $(\gamma)$ values were determined using TD-HF method. The computed second hyperpolarizability $\gamma(-3 \omega$; $\omega, \omega, \omega)$ at 800 nm wavelength was found to be $0.499 \times 10^{-32}$ esu which is in good agreement with experimental value at the same wavelength. These results confirms the applied nature of title molecule in optoelectronic and nonlinear optical devices.


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## 1. Introduction

The use of continuous wave (CW) and pulsed lasers at power levels ranging from mW to kW in various applications, the need for protections of the human eye and solid state optical sensors from powerful lasers has become increasingly important [1,2]. In this context, a lot of attention is being headed for seeking the new and

[^0]low cost optical power limiters. The organic NLO molecules are very attractive due to their high nonlinearities and transparency in the visible region of electromagnetic spectrum [3-5]. Among the organic NLO materials the chalcone derivatives have attracted significant attention mainly because of their availability in natural products, structural flexibility, and high optical nonlinearities that they can exhibit due to the significant delocalization of the electronic clouds [6-8]. In the current work, a relatively new chalcone derivative, (2E)-3-(4-methylphenyl)-1-(3-nitrophenyl) prop-2-en1 -one has been selected on which only crystal structure report is available so far [9].

Due to such excellent applications of organic chalcones it seems to be necessary to perform the synthesis, crystal growth, and linear and nonlinear optical studies. Hence, herein we account the synthesis, single crystal growth, experimental and computational spectral, linear and third order NLO chattels of ML3NC. The grown crystals were subjected to X-ray diffraction (XRD), FT-IR and FTRaman, UV-Vis-NIR, Photoluminescence (PL) spectroscopic studies. The third-order NLO properties were investigated by adopting femtosecond Z -scan technique. The experimental studies are supported with the computational density functional theory (DFT). The DFT/TD-DFT studies are observed to be quite pertinent to experimental results for determining the stable geometry, vibrational and photophysical and NLO characteristics [10-19]. The obtained experimental and computational results are compared and discussed.

## 2. Experimental

### 2.1. Synthesis and crystal growth

To synthesize (2E)-3-(4-Methylphenyl)-1-(3-nitrophenyl) prop-2-en-1-one (ML3NC), all chemicals of analytical grade were used. The synthesis of ML3NC was achieved by Claisen-Schmidt condensation reaction of 4-methylbenzaldehyde and $3^{\prime}$-nitroacetophenone. A solution of 4-methylbenzaldehyde ( 0.01 mol ) and $3^{\prime}$-nitroacetophenone ( 0.01 mol ) in methanol ( 60 ml ) was stirred well and $10 \% \mathrm{NaOH}$ solution ( 5 ml ) was added. The reaction mixture was stirred for about 2 h . Resulting crude solid was congregate by filtration and dried which was further cleansed by repeated crystallization from acetone. The synthesis process and molecular structure of ML3NC is shown in Fig. 1 (a). A filtered acetone solution of ML3NC was transferred into a beaker and allowed to evaporate slowly under room temperature. Transparent single crystals of considerable size were obtained in a period of about ten days [Fig. 1b].

### 2.2. Characterization techniques

XRD measurement was carried out using a Shimadzu X-600 Japan X-ray diffractometer at the scan rate $2^{\circ} / \mathrm{m}$ over angular range of $5^{\circ} \geq 2 \theta \geq 70^{\circ}$ at 300 K for structural confirmation of the titled crystals. The FT-IR and FT-Raman spectroscopy measurements were carried out in the wavenumber range of $4000-400 \mathrm{~cm}^{-1}$ and 3500 $-20 \mathrm{~cm}^{-1}$ respectively using THERMO SCIENTIFIC, DXR FT-IR and FT-RAMAN spectrometer. JASCO V-570 UV-VIS-NIR spectrophotometer was used to record the optical absorbance spectrum in the wavelength range of $190-1300 \mathrm{~nm}$ at 300 K . The photoluminescence (PL) spectrum was measured using a Lumina fluorescence spectrophotometer (Thermo Fisher Scientific) having PMT of voltage 700 V , in the wavelength range of $200-900 \mathrm{~nm}$ at room temperature. The third-order NLO properties were estimated using the standard well known Z-scan technique which was developed by Sheik-Bahae et al. in 1990 [20]. More detail on the experimental part on Z-scan measurement is provided in Supporting information.

### 2.3. Computational details

For molecular geometry optimization and photophysical properties calculations the GAUSSIAN 09 [21] and Gauss view 5 visualization programs [22] were used. The stable molecular geometry of ML3NC molecule has been obtained using B3LYP [23,24] with 6$31 G^{*}$ basis set. Further the stability of optimized molecular geometry was confirmed by evaluating their analytical frequencies at the
same level of theory. These methods are having the advantage to ascertain the reasonable and exact molecular geometries and vibrational frequencies. For calculating the photophysical properties the five diverse methods like: hybrid functionals B3LYP, PBEO [25] and MO6 [26], long range corrected functionals CAM-B3LYP [27] and wb97xd [28] have been applied. It is well known that these methods are capable of calculating such properties and provides good correlation with conventional methods [13-15,29-36]. The static and dynamic NLO properties of ML3NC were computed using the time-dependent Hartree-Fock (TDHF) method which is developed in the GAMESS program [37]. The calculations were performed with the $6-31 \mathrm{G}(\mathrm{d})$ basis set. The frequency-dependent polarizability $\alpha(-\omega ; \omega)$ and second hyperpolarizabilities $\gamma(-3 \omega$; $\omega, \omega, \omega$ ) were calculated at the input frequency ( $\omega=0.05695$ a.u) same as that of laser wavelength ( 800 nm ) used in experimental Zscan technique. The isotropic average of polarizability $\langle\alpha\rangle$ and second hyperpolarizability $\langle\gamma\rangle$ values are obtained by using the equations [18,38]:
$\langle\alpha\rangle=\frac{1}{3}\left(\alpha_{x x}+\alpha_{y y}+\alpha_{z z}\right)$
$\langle\gamma\rangle=\frac{1}{5}\left[\gamma_{x x x x}+\gamma_{y y y y}+\gamma_{z z z z}+2\left(\gamma_{x x y y}+\gamma_{x x z z}+\gamma_{y y z z}\right)\right]$

## 3. Results and discussions

### 3.1. X-ray diffraction and molecular geometry analyses

The powder X-ray diffraction curve was recorded as shown in Fig. 1S (see supplementary data) for the powdered specimen of the grown crystals. The triclinic crystal system was confirmed with space group P21. The lattice parameters were calculated using POWDERX software and found to be $\mathrm{a}=8.09417 \AA, \mathrm{~b}=11.50771 \AA$, $c=14.69892 \AA, \alpha=80.325^{\circ}, \beta=74.778^{\circ}, \gamma=84.372^{\circ}$ with unit cell volume $1300.21683 \AA^{3}$. These calculated lattice parameters are found to be in first-class harmony with the earlier reported values [9]. It is clear from the diffraction pattern that the grown crystals are highly crystalline in nature. The optimized geometry of ML3NC molecule calculated at B3LYP/6-31G* level of theory along with experimentally obtained geometry is shown in Fig. 2S (a \& b) (see supplementary data). The molecular geometry was also optimized using CAM-B3LYP/6-31G*, and wb97XD/6-31G* levels of theory. The calculated molecular geometry as well as geometrical parameters are in good agreement with experimental values [9]. The bond lengths of O1-C15, O2-N4 and O3-N4 are found to be $1.227 \AA$, $1.228 \AA$ and $1.231 \AA$ respectively which are close to the experimental values [9], similarly the other bond length values are also found to be close to experimental values.

### 3.2. Vibrational study

The experimental (Exp.) and theoretically (Theo.) derived IR transmittance and Raman spectra of ML3NC $\left(\mathrm{C}_{16} \mathrm{H}_{13} \mathrm{NO}_{3}\right)$ chalcone crystal are presented in Fig. 2 (a1, b1) and 4 (a2, b2) respectively to tentatively assign the vibrational peaks of phenyl rings and functional groups [39-42] in 4000-400 $\mathrm{cm}^{-1}$. The broad IR transmittance band of water ( $\mathrm{H}-\mathrm{O}-\mathrm{H}$ ) stretching vibrations at $3433 \mathrm{~cm}^{-1}$ with weak superimposed components at 3312 and $3236 \mathrm{~cm}^{-1}$ are observed in Fig. 2 (a1) IR (Exp.) spectrum. Phenyl ring, olefin and methyl C-H stretching modes were observed in $3150-3050 \mathrm{~cm}^{-1}$, 3035-2980 $\mathrm{cm}^{-1}$ and $2925-2830 \mathrm{~cm}^{-1}$. In ML3NC crystal, ketone $\mathrm{C}=\mathrm{O}$ functional group is bonded in conjugation to nitrophenyl at C3
(a)

(b)


Fig. 1. (a) Synthesis scheme, chemical structure and (b) as grown single crystals of ML3NC.
and 2-propene at C 1 positions observed at $1665 \mathrm{~cm}^{-1}$ as very strong and medium intensity peak at $1680 \mathrm{~cm}^{-1}$ in IR (Exp.) and (Theo.) spectra, respectively and a very weak peak at $1662 \mathrm{~cm}^{-1}$ in Raman (Exp. and Theo.) spectra. The medium intensity IR transmittance $C=C$ stretching peak of $\alpha, \beta$-unsaturated prop-2-en-1-one ketone present in this chalcone merged with strong $-\mathrm{NO}_{2}$ group stretching vibration appears at 1622 and $1618 \mathrm{~cm}^{-1}$ in IR (Exp.) and (Theo.) spectra, respectively but not observed in Raman (Exp. and Theo.) spectra. The asymmetric stretching and symmetric stretching modes of nitro $\left(-\mathrm{NO}_{2}\right)$ functional group of 3-Nitrophenyl ring are observed as strong peaks at [1589, $1356 \mathrm{~cm}^{-1}$ (Exp.), 1584, $1342 \mathrm{~cm}^{-1}$ (Theo.) and [1594, $1350 \mathrm{~cm}^{-1}$ (Exp.), 1586, $1348 \mathrm{~cm}^{-1}$
(Theo.)] in IR transmittance and Raman spectra respectively. The three C-C stretching vibrations due to charge transfer interaction between donor and acceptor groups through $\pi$-system are observed in $\left[1530-1500 \mathrm{~cm}^{-1}, 1460-1410 \mathrm{~cm}^{-1}\right.$ and $1330-1270 \mathrm{~cm}^{-1}$ ] regions in IR and Raman (Exp. and Theo.) spectra. The scissoring, wagging, twisting and rocking vibrations of $\mathrm{CH}_{2}$ group were observed in $1410-1370 \mathrm{~cm}^{-1}, 1280-1200 \mathrm{~cm}^{-1}, 1190-$ $1170 \mathrm{~cm}^{-1}$ and $1055-1030 \mathrm{~cm}^{-1}$ regions in IR transmission and Raman (Exp. and Theo.) spectra. C-N stretching mode of $\left(\mathrm{PhNO}_{2}\right)$ is observed as medium and weak intensity peaks at [867 $\mathrm{cm}^{-1}$ (Exp.), $850 \mathrm{~cm}^{-1}$ (Theo.)] and [ $876 \mathrm{~cm}^{-1}$ (Exp.), $851 \mathrm{~cm}^{-1}$ (Theo.)] in IR transmittance and Raman spectra respectively. C-C stretching


Fig. 2. Experimental and calculated (a1, b1) IR and (a2,b2) Raman spectra of ML3NC.
modes of Prop-2-en-1-one coupled with substituted phenyl rings are observed at $826,809 \mathrm{~cm}^{-1}$ (Exp.) in the IR spectrum. In ML3NC, the medium intensity wagging modes of nitro group are obtained at [751, $718 \mathrm{~cm}^{-1}$ ] (Exp.) and [748, $714 \mathrm{~cm}^{-1}$ ] (Theo.) IR transmittance spectra and at [764, $722 \mathrm{~cm}^{-1}$ ] (Exp.) and [789, $743 \mathrm{~cm}^{-1}$ ] (Theo.) in Raman spectra. $\mathrm{C}=\mathrm{O}$ in-plane and out-of-plane bending modes are observed as very strong peaks at [ $693 \mathrm{~cm}^{-1}$ (Exp.) and $681 \mathrm{~cm}^{-1}$ (Theo.)] and [535, $503 \mathrm{~cm}^{-1}$ (Exp.) and 535, 498 (Theo.)] in IR transmittance and Raman (Exp.) spectra as very-very weak bands. The olefine C-H out-of-plane modes are obtained at [651, $643 \mathrm{~cm}^{-1}$ (Exp.), $635 \mathrm{~cm}^{-1}$ (Theo.)] and [ $647 \mathrm{~cm}^{-1}$ (Exp.), $634 \mathrm{~cm}^{-1}$ (Theo.)] in IR transmittance and Raman spectra, respectively. The rocking mode of $-\mathrm{NO}_{2}$ group in aromatic nitro compound appears as weak band components at [535, $552 \mathrm{~cm}^{-1}$ (Exp.) and $534 \mathrm{~cm}^{-1}$ (Theo.)] and at [549, $535 \mathrm{~cm}^{-1}$ (Exp.) and $530 \mathrm{~cm}^{-1}$ (Theo.)] in IR transmittance and Raman spectra, respectively. Phenyl ring torsional deformation mode is obtained at $452 \mathrm{~cm}^{-1}$ and $457 \mathrm{~cm}^{-1}$ in IR (Exp. and Theo.) spectra and at $427 \mathrm{~cm}^{-1}$ in Raman (Exp.) spectrum, respectively. The skeletal lattice vibration modes were observed below $400 \mathrm{~cm}^{-1}$ in both IR and Raman spectra.

### 3.3. Linear optical analysis

Fig. 3 (a) shows the recorded UV-Vis-NIR spectrum of ML3NC crystal. The grown crystals possess very low absorbance in $400-900 \mathrm{~nm}$ wavelength range. The optical transparency was reckon from absorbance which indicates high optical transparency of the crystals in above region makes it appropriate for optical window for nonlinear applications $[16,43,44]$. In the recorded spectrum, two absorption bands at 328 nm and 228 nm are observed, which are corresponding to the $\pi \rightarrow \pi^{*}$ and $\mathrm{n} \rightarrow \pi^{*}$ transitions, respectively. The optical direct band gap of title crystal was calculated using Tauc's relation and found to be 3.34 eV [see inset of Fig. 3 (a)].

Time-Dependent Density Functional Theory (TD-DFT) is applied at various levels of theory like: B3LYP, CAM-B3LYP, wb97xd, M06, PBEO using $6-31 \mathrm{G}^{*}$ basis set to understand the character of electronic transition in ML3NC. It is well documented that TD-DFT study can predict the absorption wavelength with high accuracy at small computing time on the basis of optimized geometry [45-47]. The theoretically calculated absorption spectrum has been shown in Fig. 3b. From figure it is clear that the value of absorption wavelength ( $\sim 328 \mathrm{~nm}$ ) calculated at B3LYP $/ 6-31 \mathrm{G}^{*}$ level of theory is in great correlation with the experimental value viz. also $\sim 328 \mathrm{~nm}$
see Fig. 5a. The calculated values of absorption wavelength $\lambda_{\text {abs }}$ ( nm ), energy $\mathrm{E}(\mathrm{eV})$, oscillator strength (f) and major contributions are presented in Table 1. The absorption bands observed at 328 nm and 250 nm has been created principally due to $H \rightarrow L(61 \%)$ and $H-$ $4 \rightarrow L$ (50\%) transitions respectively.

### 3.4. HOMO-LUMO, GCRD and MEP analyses

HOMO and LUMO play a very important role to get the idea of reactivity and process of chemical reaction in any material or complex. Their energy values are calculated at different levels of theory and Table 1S (see supplementary data) presents these values obtained at B3LYP/6-31G* level of theory. The energy gap is computed to be 3.946 eV and its chemical hardness value is 1.973 eV , this signify the ML3NC molecule has good kinetic stability. The electronic transition energy in ML3NC molecule was found to be 3.779 eV calculated at TD-DFT/B3LYP, which is related to the switch from ground state to first excited state and also show charge transfer from HOMO to LUMO in ML3NC. There is a strong agreement between the values obtained experimentally and theoretically as these values are 3.782 eV (Exp.), 3.946 eV (HOMO-LUMO gap) and 3.779 eV (TD-DFT) respectively. The 3-D plots of HOMO, HOMO-1 and LUMO and LUMO+1orbitals are shown in Fig. 4. The energy values of above orbitals are given in Table 1S (see supplementary data). The positions of HOMO and LUMO are very obvious. The title molecule contains one terminal nitro group which is strongly electron-withdrawing by both inductive effect and resonance effect. It also deactivates the benzene ring. That is why LUMO

Table 1
Excitation wavelength ( $\lambda_{\text {exc }}$ ), energies $\mathrm{E}(\mathrm{eV})$, oscillator strengths ( $f_{0}$ ), and major contributions for transitions in ML3NC calculated at different levels of theory.

| Method | $\lambda_{\text {exc }}$ | $\mathrm{E}(\mathrm{eV})$ | $f_{0}$ | Major contributions |
| :--- | :--- | :--- | :--- | :--- |
| Experimental | 328 | 3.782 | - | - |
|  | 228 | 5.441 | - | - |
| B3LYP | 328.09 | 3.779 | 0.697 | $\mathrm{H} \rightarrow \mathrm{L}+1(61 \%)$ |
|  | 250.56 | 4.948 | 0.265 | $\mathrm{H}-4 \rightarrow \mathrm{~L}(50 \%)$ |
| CAM-B3LYP | 291.20 | 4.258 | 0.921 | $\mathrm{H} \rightarrow \mathrm{L}(62 \%)$ |
|  | 223.70 | 5.543 | 0.456 | $\mathrm{H}-4 \rightarrow \mathrm{~L}+1(45 \%)$ |
| wb97xd | 288.81 | 4.293 | 0.948 | $\mathrm{H} \rightarrow \mathrm{L}(61.5 \%)$ |
|  | 221.51 | 5.597 | 0.187 | $\mathrm{H} \rightarrow \mathrm{L}+1(35 \%)$ |
| PBE1 | 314.18 | 3.946 | 0.478 | $\mathrm{H} \rightarrow \mathrm{L}+1(69 \%)$ |
|  | 242.55 | 5.112 | 0.321 | $\mathrm{H}-4 \rightarrow \mathrm{~L}+1(51 \%)$ |
| MO6 | 319.41 | 3.882 | 0.478 | $\mathrm{H} \rightarrow \mathrm{L}+1(68 \%)$ |
|  | 250.14 | 4.957 | 0.315 | $\mathrm{H}-4 \rightarrow \mathrm{~L}(51 \%)$ |



Fig. 3. (a) Experimental and (b) calculated UV-Vis spectra of ML3NC molecule.


Fig. 4. HOMO-LUMO plots of ML3NC molecule.
is mainly located on the nitro group and its adjacent ring. Position of HOMO is also self-explanatory. Homo is entirely situated on the other parts of the molecule. Positions of HOMO-1 and LUMO +1 orbitals clearly explain how the charge is transferred from one part of the molecule to the other, where nitro group is dominating. The study of GCRD parameters are very informative to recognize the correlation connecting chemical stability and structure of the molecules. They are particularly useful to know about the quantitative structure activity, property, and toxicity relationships. DFT gives fair prediction about the correlation between the structure and stability of a molecule [48,49]. Here we have calculated the various GCRDs such as absolute global hardness $(\eta)$, electronic chemical potential ( $\mu$ ), softness ( $s$ ), electronegativity ( $\chi$ ), electrophilicity ( $\omega$ ), Ionization energy (I) and electron affinity (A) and were computed by using, $\eta=\frac{1}{2}\left(\mathrm{E}_{\text {LUMO }}-\mathrm{E}_{\text {Номо }}\right)$, $\mu=-\left(\frac{I+A}{2}\right), \quad S=\frac{I}{2 \eta}, \quad \chi=\left(\frac{I+A}{2}\right)$ and $\omega=\frac{\mu^{2}}{2 \eta}$, respectively, and are presented in Table 1S (see supplementary data). The obtained GCRD result reveals that the titled molecule possesses good chemical strength and chemical stability. To get a better insight at molecular level the molecular electrostatic potential (MEP) of ML3NC molecule has been calculated and its 3D plot has been shown in Fig. 3S (see supplementary data). It is a study of electrostatic potential on constant electron density surface. It evident from figure that the MEP overlaps on the top of total energy density surface. MEP provides important information about the molecular species reactivity in forming the complex by predicting the positive and negative charge regions in terms of nucleophile and electrophile respectively. The blue and red regions in MEP plot of ML3NC molecule
which are corresponding to maximum positive and negative potential sites are favored to nucleophilic and electrophilic attacks, respectively [38,50-53]. MEP plot will also provide the concurrent knowledge regarding the molecular size, molecular shape, positive, negative and neutral charges.

### 3.5. Photoluminescence (PL) analysis

Fig. 5 (a) and (b) demonstrates the room temperature recorded PL excitation and emission spectra, respectively. In excitation spectrum [Fig. 5 (a)] a strong and high intensity excitation band at $\sim 465 \mathrm{~nm}\left(\lambda_{\mathrm{em}}=560 \mathrm{~nm}\right)$ of blue light with a shoulder at 430 nm has been observed. In the emission spectra [Fig. 5 (b)] a strong emission band at $560 \mathrm{~nm}\left(\lambda_{\text {exc }}=465 \mathrm{~nm}\right)$ is observed which is assigned to green emission of light with high optical density. The PL study confirms the application of the grown crystals in the fabrication of blue and green LEDs.

### 3.6. Experimental and theoretical third-order NLO studies

### 3.6.1. Experimental NLO studies

Fig. 6 (a) and (b) shows a typical normalized transmission as a function of the sample position for open aperture and closed aperture $z$-scans. From the open aperture data, we find two photon absorption coefficients ( $\beta$ ), and from closed aperture data we find nonlinear refractive index $\left(\mathrm{n}_{2}\right)$. The $\mathrm{n}_{2}$ value can be calculated from the peak to valley variation of the measured transmittance [54]. The disparity among normalized peak-valley transmittance $\Delta \mathrm{T}_{\mathrm{pv}}$ is given by,
$\Delta T_{p v}=0.406(1-S)^{0.25}\left|\Delta \Phi_{0}\right|$
where, $\Delta \Phi_{0}$ is the on-axis nonlinear phase shift at focus and $S$ is the linear transmittance of the aperture and is given by,
$S=1-\exp \left(-\frac{2 r_{a}^{2}}{w_{a}^{2}}\right)$
where, $r_{a}$ is the radius of the aperture and $w_{a}$ is the transmittance beam radius at the aperture. The nonlinear phase shift $\Delta \Phi_{0}$ can be estimated by fitting the closed aperture data using the equation [55],
$T(Z)=1-\left(4 X \Delta \Phi_{0}\right) /\left[\left(X^{2}+1\right)\left(X^{2}+9\right)\right]$
where, $\mathrm{X}=\mathrm{Z} / \mathrm{Z}_{0}, \mathrm{Z}$ is position of the sample and $\mathrm{Z}_{0}$ is the Rayleigh range. Once we get the $\Delta \phi_{0}$ value, one can easily calculate thirdorder nonlinear refractive index coefficient for ML3NC compound using the relation,
$n_{2}=\Delta \Phi_{0} / k I_{0} L_{e f f}$
where, $\mathrm{I}_{0}$ is laser beam input intensity at the focus $(\mathrm{Z}=0)$, $L_{e f f}\left[=\left(1-\exp ^{-\alpha L}\right) / \alpha\right]$ is the effective thickness of the sample, $\alpha$ is the linear absorption coefficient, L denotes its sample thickness, and $\mathrm{k}=2 \pi / \lambda$ is the wave vector at given wavelength. The calculated negative nonlinear refractive index coefficient (self-defocusing effect) is found to be $-4.33 \times 10^{-14} \mathrm{~cm}^{2} / \mathrm{W}$. The nonlinear absorption coefficient ( $\beta$ ) value can be obtained from open aperture curve by fitting the experimental data from: $\mathrm{T}(\mathrm{Z})=1-\frac{\beta I_{0} \mathrm{Leff}}{2 \sqrt{2}\left(1+Z^{2} / Z_{0}^{2}\right)}$, and found to be $2.9 \mathrm{~cm} / \mathrm{GW}$. The results of $\mathrm{n}_{2}$ and $\beta$ will help to find out the real, imaginary and magnitude of third-order NLO susceptibilities from following relations [56]:


Fig. 5. Photoluminescence (a) excitation and (b) emission spectra of ML3NL crystals.


Fig. 6. (a) Nonlinear absorption, (b) nonlinear refraction and (c) optical limiting curves of ML3NC.
$\operatorname{Re} \chi^{(3)}(e s u)=\frac{10^{-4}\left(\varepsilon_{0} C^{2} n_{0}^{2} n_{2}\right)}{\pi}\left(\frac{c m^{2}}{W}\right)$
$\operatorname{Im} \chi^{(3)}(e s u)=10^{-2}\left(\varepsilon_{0} C^{2} n_{0} \beta \lambda\right) / 4 \pi^{2}\left(\frac{\left.{c m^{2}}_{W}^{W}\right)}{}\right.$
$\left|\chi^{(3)}\right|=\left[\left(\operatorname{Re} \chi_{\cdot}^{(3)}\right)^{2}+\left(\operatorname{Im} \chi_{\cdot}^{(3)}\right)^{2}\right]^{1 / 2}$

Moreover, third-order NLO susceptibility can be linked to the second-order hyperpolarizability $(\gamma)$ as:

$$
\begin{equation*}
\gamma_{h}=\frac{\chi^{(3)}}{\left[(1 / 3)\left(n_{0}^{2}+2\right)\right]^{4} N} \tag{10}
\end{equation*}
$$

where, N is the molecular density of the sample at given concentration $C$, and is given by the relation, $N=N_{A} C \times 10^{-3} / \mathrm{cm}^{3}, N_{A}$ is the Avogadro's number. All these NLO parameters were calculated
and tabulated in Table 2.
The conversion rate for two photon absorption (TPA) was estimated from equation, $\sigma_{2}=\frac{h \nu \beta}{N C \times 10^{-3}}$, and expressed in units of $\mathrm{cm}^{4} \mathrm{~s} /$ photon [57]. Excited state cross section ( $\sigma_{\mathrm{ex}}$ ) for the sample ML3NC can be determined by fitting the equation to the open aperture data as,
$T=\frac{\ln \left[1+\frac{q_{0}}{1+x^{2}}\right]}{\left(\frac{q_{0}}{1+x^{2}}\right)}$
where, $x=z / z_{0}, \mathrm{q}_{0}=\alpha_{0} \sigma_{e x} \mathrm{~F}_{0} \mathrm{~L}_{\text {eff }} / 2 \mathrm{hv}, \mathrm{F}_{0}=2 \mathrm{E} / \pi \omega_{0}^{2}$ is the laser fluence at the focus point, hv is the incident photon energy. The ground state absorption cross section ( $\sigma_{\mathrm{g}}$ ) can be evaluated from, $\sigma_{g}=\alpha_{0} / N_{A} C$, where $\alpha_{0}$ is the linear absorption coefficient. The $\sigma_{\mathrm{ex}}$ is found to be larger than $\sigma_{\mathrm{g}}$ value, which is related to reverse saturable absorption.
3.6.1.1. Optical limiting studies. Optical limiting (OL) studies were carried out by using an open aperture Z-scan data. The normalized transmittance can be plotted against the input fluence to check the optical limiting behavior of the materials [58].The optical limiting curve for ML3NC compound is shown in the Fig. 6 (c). The input fluence is the energy radiated by the laser pulses per unit area and is given by, $F=2 E / \pi \omega_{0}^{2}$. Where, $\omega_{0}$ is the beam waist radius at the focus, it is found that the beam radius at different positions ( $Z$ ) can be calculated for a Gaussian beam by using the equation, $\omega(z)=\omega_{0} \sqrt{\left[1+\left(Z / Z_{0}\right)^{2}\right]}$. Hence, the input fluence can be obtained easily at any position on the translational stage with the constant incident energy [59]. Optical limiting behavior can be decided with the limiting threshold value; lower the threshold value better will be the performance of the optical limiter. Optical limiting threshold is the input fluence at which the transmittance falls by $50 \%$ of the linear transmittance $[1,2,60]$. The limiting threshold obtained for the sample ML3NC is found to be $2.41 \mathrm{~mJ} / \mathrm{cm}^{2}$, and the value was compared with the reported literature as shown in Table 3. It is confirmed that the ML3NC compound has future applications in optical devices.

### 3.6.2. Computational NLO studies

The molecular properties such as dipole moments, polarizability and hyperpolarizabilities are very important parameters to understand the nonlinear optical behavior of any materials. In this case, quantum chemical computations are very much helpful to describe the electronic structure and to correlate them with nonlinear optical responses. Here, we present the static dipole moments ( $\mu$ ), static and frequency-dependent dipole polarizability $\alpha(0 ; 0), \alpha(-\omega ; \omega)$, and second hyperpolarizabilities $\gamma(0 ; 0,0,0), \gamma(-$ $3 \omega ; \omega, \omega, \omega)$ which were computed at the input frequency $\omega=0.05695$ a.u. and are given in Tables 4 and 5. The total electric dipole moment was found to be 9.15 Debye, the low energy gap of the molecule could have more interaction and hence increases the molecular polarizability. Further, the electric dipole moments of the molecule would contribute to enhance the microscopic polarizabilities and hyperpolarizabilities with respect to the applied field strength. The static and frequency-dependent isotropic average
polarizability and second hyperpolarizabilities were obtained to be $28.2 \& 29.3 \times 10^{-24}$ esu and $3.006 \& 499.85 \times 10^{-35}$ esu, respectively. It has been observed from the table that the maximum contribution to the total dipole moment, and average (hyper) polarizability is from x -component, it means that the orientation of the molecule with the applied frequency is in $x$-direction also meant to be the charge transfer (CT) axis.

The second hyperpolarizability in the THG process is also regarded as the efficiency of the third harmonic generation which is obtained both experimentally and theoretically at 800 nm . The computational second hyperpolarizability $\gamma(-3 \omega ; \omega, \omega, \omega)$ was found to be $0.499 \times 10^{-32}$ esu and that of experimental is $14.2 \times 10^{-32}$ esu. The obtained values are reasonably in accordance with each other and the deviation is observed due the different phases, experimental data collected in the liquid phase with DMF solvent whereas the theoretical one computed in the gaseous phase. The larger value of the NLO parameters are attributed due to the donor- $\pi$-acceptor bridge in the molecular system.

## 4. Conclusions

The single crystals of (2E)-3-(4-Methylphenyl)-1-(3nitrophenyl) prop-2-en-1-one with well-faceted morphology were grown for the first time by slow evaporation technique. The crystal structure was confirmed by X-ray diffraction analysis. The robust vibrational study (both experimental and theoretical) was performed. The optical and photoluminescence studies confirm that the grown crystals possess excellent transparency window in the visible region and green emission band at $\sim 560 \mathrm{~nm}$. The nonlinear optical properties of the ML3NC compound were studied by using standard Z-scan technique. From the open aperture Z-scan it is found that the sample exhibits two-photon absorption, and has the value of $2.9 \mathrm{~cm} / \mathrm{GW}$. Closed aperture z-scan suggests that the peak-valley variation is due to the self-defocusing effect by the sample, which indicates the negative nonlinear refraction and the value obtained is $-4.33 \times 10^{-14} \mathrm{~cm}^{2} / \mathrm{W}$. The third-order nonlinear optical susceptibility and second order hyperpolarizability were found to be $4.03 \times 10^{-12}$ esu and $14.2 \times 10^{-32}$ esu, respectively. The computationally obtained second order hyperpolarizability $\gamma(-3 \omega$; $\omega, \omega, \omega)$ at 800 nm wavelength was found to be $0.499 \times 10^{-32}$ esu which is in good agreement with experimental value. From the open aperture data, the optical limiting behavior for the ML3NC compound was studied, and the limiting threshold was found to be $2.41 \mathrm{~mJ} / \mathrm{cm}^{2}$. Due to the low limiting threshold and the significant nonlinear optical properties, ML3NC compound has the better applications in the sensor and photonic devices. The optimized ground state molecular geometry is found to be comparable with experimental one. The value of experimental absorption wavelength ( $\lambda_{\text {abs }}=328 \mathrm{~nm}$ ) is found to be in close agreement with theoretical value ( $\lambda_{\mathrm{abs}}=328 \mathrm{~nm}$ ) obtained at TD-DFT-B3LYP/6-31G* level of theory. The HOMO and LUMO energy gaps were calculated and the prospects of intermolecular charge transfer have been analyzed and good chemical stability was confirmed from GCRD parameters. MEP analysis confirms favorable electrophilic and nucleophilic attacks respectively.

Table 2
Shows the obtained nonlinear optical parameters for the ML3NC compound at 800 nm and 80 MHz laser repetition rate.

| $\begin{aligned} & \alpha_{0} \\ & \left(\mathrm{~cm}^{-1}\right) \end{aligned}$ | $\begin{aligned} & \mathrm{n}_{2} \\ & \left(\mathrm{~cm}^{2} \mathrm{~W}^{-1}\right) \times 10^{-14} \end{aligned}$ | $\begin{aligned} & \beta \\ & \left(\mathrm{cmW}^{-1}\right) \times 10^{-9} \end{aligned}$ | $\begin{aligned} & \operatorname{Re} \chi(3)(\text { e.s.u }) \mathrm{x} \\ & 10^{-12} \end{aligned}$ | $\begin{aligned} & \operatorname{Im} \chi(3) \\ & (\text { e.s.u }) \times 10^{-12} \end{aligned}$ | $\begin{aligned} & \chi(3) \\ & (\text { e.s.u }) \times 10^{-12} \end{aligned}$ | $\begin{aligned} & \begin{array}{l} \sigma_{\mathrm{g}}\left(10^{-20}\right. \\ \left.\mathrm{cm}^{2}\right) \end{array} \end{aligned}$ | $\begin{aligned} & \sigma_{\mathrm{ex}}\left(10^{-17}\right. \\ & \left.\mathrm{cm}^{2}\right) \end{aligned}$ | $\begin{aligned} & \sigma_{2}(\mathrm{GM})\left(10^{-50} \mathrm{~cm}^{4} \mathrm{~s}\right. \\ & \text { photon } \left.{ }^{-1}\right) \end{aligned}$ | $\begin{aligned} & \gamma_{\mathrm{h}} \\ & \left(10^{-32} \mathrm{esu}\right) \end{aligned}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 0.47 | -4.33 | 2.9 | -3.7 | 1.58 | 4.03 | 7.8 | 14.5 | 11960 | 14.2 |

Table 3
Optical limiting threshold values comparison for various types of molecules.

| Name of the molecule | Laser parameters | Limiting threshold $\left(\mathrm{J} / \mathrm{cm}^{2}\right)$ | References |
| :--- | :--- | :--- | :--- |
| DMMC | $800 \mathrm{~nm}: 150 \mathrm{fs}: 80 \mathrm{MHz}$ | $5.6 \times 10^{-3}$ | P.S. Patil et al. [55] |
| CNTs (Ink Composites) | $780 \mathrm{~nm}: 100 \mathrm{fs}: 76 \mathrm{MHz}$ | $1.15 \times 10^{-4}$ | $3.7 \times 10^{-1}$ |
| f-MWCNT | $532 \mathrm{~nm}: 5 \mathrm{~ns}$ | $3.8 \times 10^{-2}$ | B. Anand et al. [59] |
| Ag PNC Films | $355 \mathrm{~nm}: 25 \mathrm{~ns}$ | $2.41 \times 10^{-3}$ | N. Misra et al. [60] |
| ML3NC | $800 \mathrm{~nm}: 150 \mathrm{fs}: 80 \mathrm{MHz}$ | Current work. |  |

Table 4
Main components of Static dipole moment, static $\alpha(0 ; 0)$ and dynamic $\alpha(-\omega ; \omega)$ polarizabilities and their average values of ML3NC at $\omega=0.05695$ a.u.

| Dipole moment (D) <br> Static | Polarizability $\left(10^{-24} \mathrm{esu}\right)$ |  |  |  |
| :--- | :--- | :--- | :--- | :--- |
|  |  | Components | Static | Dynamic |
| $\mu_{\mathrm{x}}$ | 7.46 | $\alpha_{\mathrm{xx}}$ | 47.4 | 50.1 |
| $\mu_{\mathrm{y}}$ | 5.28 | $\alpha_{\mathrm{yy}}$ | 27.1 | 27.6 |
| $\mu_{\mathrm{z}}$ | -0.35 | $\alpha_{\mathrm{zz}}$ | 10.2 | 10.2 |
| $\mu_{\text {tot }}$ | 9.15 | $\langle\alpha\rangle$ | 28.2 | 29.3 |

Table 5
Main components of static $\gamma(0 ; 0,0,0)$ and dynamic $\gamma(-3 \omega ; \omega, \omega, \omega)$ second hyperpolarizabilities of ML3NC at $\omega=0.05695$ a.u. $\left(10^{-35} \mathrm{esu}\right)$.

| Components | $\gamma_{\mathrm{xxxx}}$ | $\gamma_{\mathrm{yyyy}}$ | $\gamma_{\mathrm{zzzz}}$ | $\gamma_{\mathrm{xxyy}}$ | $\gamma_{\mathrm{xxzz}}$ | $\gamma_{\mathrm{yyzz}}$ | $\langle\gamma\rangle$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| $\omega=0.0$ | 13.76 | 0.138 | 0.011 | 0.495 | 0.051 | 0.014 | 3.006 |
| $\omega=0.05695$ | 2483.76 | 0.052 | 0.012 | 4.035 | 3.661 | 0.0176 | 499.85 |

## Conflict of interest

Authors declares that there is no conflict of interest in the current article.

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## Appendix A. Supplementary data

Supplementary data related to this article can be found at http:// dx.doi.org/10.1016/j.optmat.2017.06.038.

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[^0]:    * Corresponding author.

    E-mail addresses: shkirphysics@gmail.com, shkirphysics@kku.edu.sa (M. Shkir).

