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### An experimental and theoretical study on a novel donor- $\pi$ -acceptor bridge type 2, 4, 5-

Trimethoxy-4'-chlorochalcone for optoelectronic applications: A dual approach

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#### Abstract

In this article the authors aim is to investigate and analyze the various key parameters of a organic D- $\pi$ -A type novel nonlinear optical material 2, 4, 5-Trimethoxy-4'-chlorochalcone (2,4,5TMCC) through experimental and quantum chemical studies. The Claisen–Schmidt condensation reaction mechanism was applied to synthesize the 2,4,5-TMCC compound and its single crystal was grown by a slow evaporation solution growth (low cost) technique. The crystal structural was confirmed by powder X-ray diffraction analysis. The robust vibrational study has been done using FT-IR and FT-Raman spectra and its NLO activity has been discussed. The factor group analysis was also performed. The optical absorption spectrum was recorded and the band gap was calculated to be 2.8 eV. In Photoluminescence spectrum, an intense emission band at ~540 nm has been observed which shows that the grown crystals can be used in green organic light emitting diodes and laser applications. To achieve the stable ground state molecular geometry of 2,4,5TMCC, the computational techniques were applied at different levels of theory using 6-31G\* basis set. The calculated geometrical parameters and vibrational spectra are found to be in good agreement with the experimental results. To probe the optical properties of the title compound the time dependent density functional theory has been applied. The excitation wavelength was observed at ~398.63 nm calculated at B3LYP/6-31G\* level of theory and found

close to experimental value (i.e. 396 nm). The static first hyperpolarizability value is found to be 136 times higher than prototype urea molecule. Additionally, the molecular level approach was attained as HOMO–LUMO gap and electrostatic potential maps. The DSC study reveals that the titled material is stable up to 149 °C. The photophysical and nonlinear optical properties suggest that the titled material could be a better choice for the fabrication of optoelectronic devices.

Keywords: Chalcones, vibrational spectroscopy, optical properties, nonlinear optical material,

Density functional theory.

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### 1. Introduction

Nonlinear optical (NLO) materials in the form of single crystal or fiber are having enormous applications in photonic devices which are used for carrying the information, data storage, telecommunications, lasers, optical computers, optical sensing, lighting, energy and display, national security and devices and manufacturing the optical systems and components etc. [1-5]. Among the large number of nonlinear optical materials, the single crystals of chalcone (1, 3-diaryl-2-propen-1-ones) derivatives show brilliant stability, relatively short cutoff wavelengths of transmittance, outstanding blue light transmittance [6-11], remarkable NLO or second harmonic generation (SHG) efficiency response due to flexible intermolecular interactions [12-18], and extraordinary optical properties along with high extinction coefficients for ultra-violet absorption [19-22]. These are open chain flavonoids that are broadly biosynthesized in plants and having a variety of applications in medical and biomedical science as anti-cancer, anti-ulcer, anti-mitotic, anti-inflammatory, anti-malarial, anti-fungal, anti - HIV and antioxidants etc. [23-30]. Furthermore, the chalcone molecules with a  $\pi$ -conjugated arrangement provide a large charge

transfer axis in which on two aromatic rings the opposite groups of molecules act as donors and acceptors and use to transfer the charge [31, 32]. Due to such significant importance of chalcones, in recent past the NLO properties of a series of chalcone derivatives have been studied experimentally and shown inspiring result to be applied in the future device like nonlinear frequency conversion and optical limiters [12, 17, 33-36]. Therefore, it is necessary to grow the good quality single crystals of such kind of materials and also to build up such devices for future applications, it is essential to figure out the principal chattels concerning their structural and electronic origin of the optoelectronic properties. The density functional theory (DFT) has been found to be extremely effective and computationally unpretentious for elucidation the above key properties in an enormous class of materials such as from atoms and molecules to crystals and complex lengthened structures including liquids and glasses. Because of such effectiveness of DFT method it has established as common machination in firstprinciples computation aimed at to visualize and illustrate the key functions of molecular and solid state design. The density functional theory offers unique spectra for every definite compound to identify the constituents and given the information about the molecular structure, conformation, functional groups and inter and intra-molecular exchanges. In recent the Hartree-Fock (HF) and density functional theory (DFT) studies has been performed on a variety of organic, semiorganic, inorganic, chalcones, and their complexes and interconnected well with experimental reports [15, 37-56]. Recently, we have studied the experimental and theoretical properties on 1-(4-bromophenyl)-3-(2,4,5-trimethoxyphenyl) prop-2-en-1-one (2,4,5 TMBC) chalcone derivative [15]. Here we have chosen a another relatively new chalcone derivative 2, 4, 5-Trimethoxy-4'-chlorochalcone (2,4,5TMCC) [see chemical structure in Figure 1] of D- $\pi$ -A type structure reported by Patil et al., and shows its importance in optoelectronic devices [57,

58]. In their report they have found that the 2,4,5TMCC molecule possess high second harmonic generation as it is 4.3 times higher than standard urea molecule as well as that many other previously reported chalcone derivatives [15, 59, 60]. Due to such exceptional properties of 2,4,5TMCC molecule it seems to be necessary and justified for further studies from various applications point of view and also to have deep understanding of it.



Figure 1: Chemical structure of 2, 4,5TMCC molecule.

Consequently, as per the current available literature there is no report on its relationship between experimental and theoretical investigations. In the current work, we have performed both experimental and theoretical studies on 2,4,5TMCC in details as these are essential components to have bottomless understanding of it for various photonic device applications. In experimental part, the single crystal were grown by a simplest route and subjected to FT-IR, FT-Raman, ultra violet-visible-near infrared (UV-VIS-NIR), Photoluminescence (PL) and thermal etc. studies. Furthermore, the unique and cost effective computational methods has been applied to evaluate the molecular structure, photophysical and nonlinear optical properties and compared with the experimental findings.

### 2. Experimental details

The synthesis and single crystal growth of 2,4,5-TMCC was attain by taking and mixing the calculated amount of 2,4,5-trimethxybenzaldehyde (0.01 mol) with 4-chloroacetophenone (0.01 mol) each in 50 ml ethanol in the presence of catalytic NaOH solution (5 mL, 20%)as per the previously reported procedure [57, 58].

Further, the grown crystals were subjected to FT-IR spectroscopy measurement in the wavenumber range of 4000–400 cm<sup>-1</sup> using a NICOLET 6700 FT-IR spectrometer with the resolution of 4 cm<sup>-1</sup>at room temperature. The FT-Raman spectroscopy measurement was carried out on grown crystal at THERMO SCIENTIFIC, DXR FT-RAMAN spectrometer in the wavenumber range of 3500-9 cm<sup>-1</sup> using a green laser of wavelength and power of 532 nm and 2 mW, at estimated resolution 5.1 to 8.3 cm<sup>-1</sup> and size of the aperture pinhole was kept 50 µm. The optical absorbance of the grown crystals was recorded using a JASCO V-570 UV-VIS-NIR spectrophotometer in the wavelength range of 190-1300 nm at room temperature and optical parameters such as optical transparency and optical band gap was calculated.

The photoluminescence (PL) spectrum of titled material was documented using a Lumina fluorescence spectrophotometer (Thermo Fisher Scientific) having PMT of voltage 700V, in the wavelength range of 400 - 750 nm at room temperature. The spectral bandwidth was kept 1 nm for emission monochromator.

Thermal analysis was carried out on the titled compound using DSC (SETARAM)measurement in the range of 34 to 300 °C at the heating rate of 10 °C/m.

#### **3.** Computational details

GAUSSIAN 09 program [61] was used for all the theoretical calculations of the titled molecule by taking the initial geometrical data from its crystal structure report (CCDC-624172) [58]. The stable molecular geometry 2,4,5TMCC molecule has been obtained using B3LYP (Becke's three

parameter exchange functional B3 combined with Lee-Yang-Parr correlation functional LYP) [62, 63] with 6-31G\* basis set. The stability of the optimized geometry was further confirmed by evaluating their analytical frequencies using B3LYP as well as Hartree-Fock (HF) at same basis sets. The foremost advantages these methods are to establish and imitate the sensible and precise molecular geometries, vibrational frequencies. For calculating the electronic properties of the titled compound we have applied five different methods such as hybrid functionals B3LYP, PBE0 [64] and MO6 [65], long range corrected functionals CAM-B3LYP [66] and wb97xd [67]. These methods are proficient in computing the electronic properties which are greatly better than the conventional methods [41, 43, 44, 47, 48, 68-72]. Gauss view 5 visualization program [73] was used to visualize all the obtained results. It is well known that the range separated functionals are greatly reliant on the range separation parameters. Therefore there is a way to eliminate these uncertainties is to tune the range separation parameter particularly for donoracceptor complexes [74, 75]. In addition, these techniques may well correlate the theoretical calculations with experiment. The obtained results by all the applied methods were compared and discussed.

The values of total static first hyperpolarizability ( $\beta_{tot}$ ) and its components were calculated using finite field (FF) approach at different levels of theory. This approach has been extensively applied to compute the value of first hyperpolarizability of organic, inorganic as well as semiorganic molecules and offers stable results. In FF approach, usually a static electric field (*F*) is applied and the energy (*E*) of the subjected molecule has been stated as per the following equation:

$$E = E^{(0)} - \mu_1 F_1 - \frac{1}{2} \alpha_{ij} F_i F_j - \frac{1}{6} \beta_{ijk} F_i F_j F_k - \frac{1}{24} \gamma_{ijkl} F_i F_j F_k F_l - \cdots$$
(1)

Here the total energy of molecule in the absence of an electronic field, vector component of the dipole moment, linear polarizability, second and third order polarizability are represented by  $E^{(0)}$ ,  $\mu$ ,  $\alpha$ ,  $\beta$  and  $\gamma$  respectively, while *x*, *y* and *z* label the *i*, *j* and *k* components, respectively. For obtaining the values of  $\mu$ ,  $\alpha$ ,  $\beta$ , and  $\gamma$  it can be seen from Eq.1 that differentiating E with respect to F. In the current work we have determined the values of electronic dipole moment ( $\mu$ ), molecular polarizability ( $\alpha$ ) and first hyperpolarizability ( $\beta$ ).

The dipole moment  $(\mu)$  is defined as follows:

$$\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{\frac{1}{2}}$$
(2)

The average polarizability  $(\alpha_0)$  can be evaluated by:

$$\alpha_0 = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \tag{3}$$

The anisotropy of polarizability ( $\Delta \alpha$ ) can be calculated by:

$$\Delta \alpha = \frac{1}{\sqrt{2}} \sqrt{\left[ \left( \alpha_{xx} - \alpha_{yy} \right)^2 + \left( \alpha_{yy} - \alpha_{zz} \right)^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6\alpha_{xz}^2 \right]}$$
(4)

The resultant of total static first hyperpolarizability ( $\beta_{tot}$ ) value can be calculated by:

$$\beta_{tot} = \sqrt{\left(\beta_x^2 + \beta_y^2 + \beta_z^2\right)} \tag{5}$$

*Where*  $\beta_x$ ,  $\beta_y$  and  $\beta_z$  are:

$$\beta_x = (\beta_{xxx} + \beta_{xxy} + \beta_{xyy})$$
$$\beta_y = (\beta_{yyy} + \beta_{xxz} + \beta_{yyz})$$
$$\beta_z = (\beta_{xzz} + \beta_{yzz} + \beta_{zzz})$$

Hence,

$$\beta_{tot} = \sqrt{\left[\left(\beta_{xxx} + \beta_{xxy} + \beta_{xyy}\right)^2 + \left(\beta_{yyy} + \beta_{xxz} + \beta_{yyz}\right)^2 + \left(\beta_{xzz} + \beta_{yzz} + \beta_{zzz}\right)^2\right]} \quad (6)$$

The static first hyperpolarizability or second-order polarizability ( $\beta$ ) is a third rank tensor which can be illustrates by a 3 × 3 × 3 matrix. As per rule of Kleinman symmetry ( $\beta_{xyy} = \beta_{yxy} = \beta_{yyy}$ ,  $\beta_{yyz} = \beta_{yzy} = \beta_{zyy}$ ,... likewise other permutations also take similar value), the 27 components of the 3D matrix can be reduced to 10 components (the details are presented in Table 4) [76]. In the same way, the time dependent density functional theory (TD-DFT) has been applied to evaluate the values of transition energies of titled molecule using all above explained methods.

#### 4. Results and discussion

#### 4.1. X-ray diffraction analysis

Powder X-ray diffraction pattern of grown crystals was recorded using a Shimadzu X-600 Japan powder X-ray diffractometer (PXRD) at the scan rate of 0.02°/m over the angular range of 5°  $\geq$  $2\theta \geq 70^{\circ}$  at 300K as shown in Figure 2 with hkl indexing. The highly crystalline nature of the grown crystals has been confirmed by sharpness of the peaks and their intensity. The recorded data was further used to calculate the lattice parameters and confirm the crystal system. The crystal system is found to be orthorhombic with space group P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub> and lattice parameters are found to be a= 7.02950 Å, b= 10.51419 Å and c= 22.24292 Å and unit cell volume 1643.96357 Å<sup>3</sup> which are in great agreement with the reported values [58]. The density of the grown crystals was also calculated and found to be 1.344 mg m<sup>-3</sup>.



Figure 2: Powder X-ray diffraction pattern of 2,4,5TMCC crystals

### 4.2. Molecular Geometry analysis

The optimized geometry of 2,4,5TMCC molecule has been shown in Figure 3 (a) obtained at B3LYP/6-31G\* level of theory. Additionally the geometry optimization was also performed at other levels of theory [see supplementary information Figure 1S (a-e)]. The achieved theoretically optimized molecular geometry is found to be in good agreement with the experimentally obtained geometry [Figure 3(b)]. The calculated values of bond lengths and angles of the titled molecule are found to be in very good agreement to the experimentally reported values of current as well as other similar kind of molecules [15, 58, 77].



**Figure 3:** Molecular geometry of 2,4,5TMCC molecule (**a**) Optimized at B3LYP/6-31G\* level of theory and (**b**) experimentally observed (ORTEP diagram)

The 2,4,5TMCC molecule possess two intra-molecular hydrogen bonding between O(2) and H(19) with bond length 2.332 Å and O(1) and H(19) with bond length 2.433 Å calculated by B3LYP, while these values by HF are 2.364 Å and 2.448 Å, by CAM-B3LYP are 2.314 Å and 2.378 Å, LC-BLYP are 2.314 Å and 2.378 Å, by wb97xd are 2.346 Å and 2.436 Å, by MP2 are 2.332 Å and 2.433 Å, by PBE0 and MO6 are 2.332 Å and 2.433 Å,, respectively. All these values are in fine relation with the experimental values. As shown in figure 3(a) that in 2,4,5TMCC molecule two methoxy group are attached at C(24) and C(25) are almost coplanar with attached aryl group of benzene ring C(32)-O(3)-C(24)-C(22) and C(36)-O(4)-C(25)-C(26). The third methoxy group attached at C(21) is twisted away from atom C(20) and C(21) of aryl group of benzene ring. As per the experimental findings reported by Patil et al., [58] the crystal

structure of the titled molecule has been stabilized by C—H··· $\pi$  intermolecular interactions involving the C(12) and C(14) benzene ring centroid Cg1 and Vander wall forces.

#### 4.3. Vibrational (Experimental and theoretical) study

To recognize the existence of various kinds of functional groups, bonding as well as to understand different molecular conformations and reaction mechanism the Infrared (IR) and Raman spectroscopy methods are very helpful through tentatively assigning their critical vibrational modes [78-85]. The variation in the position of vibrational bands is particularly explained in terms of the alteration in crystalline field effect rouse electronic effects, bonding of hydrogen and Fermi resonance Electronic effects occurs due to back donation and induction of bonded groups exists in any molecule. It is well known that when H atom and N, O or F atoms are present within the molecule or between two molecules, the intermolecular and intramolecular hydrogen bonding appears. The modes of vibration in two phenyl rings will vary in wave number and the magnitude of splitting will be dependent on the strength of interaction between different parts of the two rings. This splitting is too small for some that they may be considered as quasidegenerate and a significant splitting is found for the other vibration modes. A comprehensive experimental and theoretical vibrational analysis has been performed on 1-(4-Chlorophenyl)-3-(2,4,5-trimethoxyphenyl)prop-2-en-1-one or 2, 4, 5-Trimethoxy-4'-chlorochalcone (2,4,5 TMCC, molecular formula:  $C_{18}H_{17}ClO_4$ , acquire orthorhombic structure with lattice Parameters: a = 7.0295 (4) Å, b = 10.5127 (6) Å, c = 22.2438 (13) Å, Space group:  $P2_12_12_1$ , Z= 4 number of molecules per unit cell) molecule.

It is well known that for the analysis of spectra of solids the site group and the factor group are key factors in group theoretical methods. Moreover, the factor group analysis method offers a foundation for the prophecy of theoretical lattice vibrations and can be acquired by IR and

Raman spectral analyses. The titled molecule belongs to orthorhombic crystal system with space group  $P2_12_12_1 (D_4^2)$  with four numbers of molecules per unit cell present at  $C_1$  site symmetry and  $C_{2v}$  factor group symmetry. Rousseau et al. [86]factor group analysis method is used for this crystal IR and Raman vibrations analysis. TMCC single molecule consists of 40 atoms and its unit cell contains (40×4) 160 atoms. According to Group theory, it has total 480 vibrational optical modes which can be given:  $\Gamma_{480} = 120A + 119B_1 + 119B_2 + 119B_3$  apart from three acoustic modes  $B_1 + B_2 + B_3$ . The symmetry of the factor group analysis of TMCC is given in Table 1.

Factor	Si	ite Sy	mmetry	С	Н	0	Cl	Optical	Acoustic	Activity		Total
$\begin{array}{c} Group \\ (D_2^{4}) \end{array}$	Exter	rnal	Internal	18	17	4		Modes	Modes	IR	Raman	
А			114	54	51	12	3	120	0		α <sub>xx</sub> ,	120
				K							$\alpha_{yy}, \alpha_{zz}$	
<b>B</b> <sub>1</sub>	3T	4R	114	54	51	12	3	120	1	Ζ	$\alpha_{xy}$	119
<b>B</b> <sub>2</sub>	3T	4R	114	54	51	12	3	120	1	Y	$\alpha_{xz}$	119
<b>B</b> <sub>3</sub>	3T	4R	114	54	51	12	3	120	1	Х	$\alpha_{yz}$	119
Total	9T	12R	456	216	204	48	12	480	3			477

Table 1 Factor group analysis of 2,4,5 TMCC crystal

The basic modes of vibrations of 1-(4-Chlorophenyl)-3-(2,4,5-trimethoxyphenyl)prop-2-en-1one achieved theoretically reveals 456 internal vibrations and 24 external modes. The external modes are categorized into 9 translational and 12 rotational modes apart from 3 acoustic modes. The bands between the wavenumber range of 4000 - 400 cm<sup>-1</sup> region arise from the internal vibrations of the different groups present in TMCC. A( $\alpha_{xx}, \alpha_{yy}, \alpha_{zz}$ ), B<sub>1</sub>( $\alpha_{xy}$ ), B<sub>2</sub>( $\alpha_{xz}$ ) and B<sub>3</sub>( $\alpha_{yz}$ ) symmetry components are Raman active and B<sub>1</sub>(zz), B<sub>2</sub>(yy) and B<sub>3</sub>(xx) are IR active [87], their correlation is shown as follows:



Further the optimized values of lattice parameters were used in the evaluation of vibrational frequencies. No imaginary frequency has been found in the calculated vibrational frequencies, which shows that the optimized molecular geometry of titled molecule is located at the local minimum point of the potential energy surface. The scaling factor was applied for the calculated spectra [for B3LYP it was 0.9613 and for HF it was 0.8929][15] to compare with experimental results. The theoretically calculated (at B3LYP/6-31G\* level of theory) and experimentally recorded FT- IR and FT- Raman spectra are shown in Figure 4 (a1,b1) and (a2,b2) respectively. Here B3LYP and HF both the methods have been applied using same basis set to obtain the infrared (IR) and Raman spectra.The experimental and theoretical IR and Raman spectra examination of 2,4,5-TMCC crystal has done on the basis of the typical vibrations of the various functional groups available in the molecule such as: methoxy, carbonyl, methyl, phenyl ring with ortho- and para-substitution, chloro-phenyl group and prop-2-en-1-one bridge. The entire investigation of obtained vibration peaks pertaining to different functional groups are discussed in the following sections:

### 4.2.1. Phenyl ring vibrations

2.4.5 TMCC molecule contains two phenyl rings bonded at 1 and 3 position of prop-2-en-1-one as 4-Chlorophenyl (ring1) and 2,4,5-trimethoxyphenyl (ring2) groups. It is well known that benzene ring has  $D_{6h}$  symmetry and acquire  $C_{2v}$  site symmetry in crystal lattice which permits activation of its all twenty vibrations in IR and Raman vibrational spectra. The logical Herzberg's numbering scheme has been employed for tentative assignment of phenyl ring modes [84, 85]. The C-H stretching vibrations in 2,4,5 TMCC phenyl ring are observed in 3100-2990  $cm^{-1}$  region. The non-degenerate  $1(a_{1g})$  and  $5(b_{1u})$  vibrations of benzene C-H stretching modes are obtained at [3085 (exp.), 3075 (HF), 3108 (B3LYP) cm<sup>-1</sup>], [2999 (exp.), 3046 (HF), 3047 (B3LYP) cm<sup>-1</sup>] in IR spectra and at [3085 (exp.), 3075 (HF), 3108 (B3LYP) cm<sup>-1</sup>], [3034 (exp.), 3053 (HF), 3047 (B3LYP) cm<sup>-1</sup>] in Raman spectra respectively as very weak bands. The low intensity of these peaks is attributed to stearic hindrance caused by conjugated structure and charge carrier localization in twisted phenyl rings. The C-C asymmetric stretching vibration of  $e_{2g}$  (16) mode of two phenyl rings are observed at [1681, 1654 (ring1), 1512 (ring2) cm<sup>-1</sup>] (exp.), 1532 (ring2) cm<sup>-1</sup> (HF), [1687 (ring1), 1514 (ring2) cm<sup>-1</sup>] (B3LYP) in IR transmission spectra and at [1683, 1650 (ring1), 1510 (ring2) cm<sup>-1</sup>] (exp.), 1532 (ring2) (HF) in Raman spectra. The minor variation in C-H stretching modes peak position for these two rings mode are not substituent dependent as they have different bonding groups and at nearly same frequencies. IR transmission spectra shows C-H ring stretching mode at [1610, 1590, 1577 cm<sup>-1</sup>] (exp.), 1617 cm<sup>-1</sup> (HF), 1576 cm<sup>-1</sup> (B3LYP), while in Raman spectra C-H ring stretching mode is obtained at 1577 (exp.), 1617 (HF), 1576 (B3LYP) cm<sup>-1</sup>. The interaction between C-C stretching and C-H in-plane bending vibrations results in appearance of number of peaks in both IR and Raman experimental and theoretical spectra in the region 1500-1100 cm<sup>-1</sup>. C-C symmetric stretching e<sub>1u</sub> (13) vibration mode expected at ~ 1450 cm<sup>-1</sup> and  $b_{2u}$  (9) vibration mode at ~ 1300 cm<sup>-1</sup> for these

two phenyl rings are observed at [1410, 1398 (ring1), 1326 (ring2)  $\text{cm}^{-1}$ ] (exp.), [1403 (ring1), 1317 (ring2) cm<sup>-1</sup>] (HF), [1398 (ring1) cm<sup>-1</sup> (B3LYP) in IR transmission spectra and at [1408, 1395 (ring1), 1321 (ring2) cm<sup>-1</sup>](exp.), [1403 (ring1), 1317 (sh) (ring2) cm<sup>-1</sup>] (HF) and 1398 (ring1) cm<sup>-1</sup> (B3LYP) in Raman experimental and theoretical spectra. The intensity variation between the two phenyl rings C-C stretching vibrational modes is explained on the electron withdrawing or donating effects arising from three methoxy and one chloro groups bonded to the two phenyl rings present in this crystal structure. The  $b_{2u}$  (9) mode vibration is observed as strong band at 1363 cm<sup>-1</sup> and 1360 cm<sup>-1</sup> in IR and Raman (exp.) spectra respectively. The simultaneous activation of the phenyl ring  $e_{2g}$  (16),  $e_{1u}$  (13) and  $b_{2u}$  (9) IR and Raman vibrational modes confirms the charge transfer from electron donating methoxy group to phenyl ring  $\pi$ system to facilitate easy transfer of electron within crystalline network. In tetra-substituted benzene, the C-C-H in-plane bending modes of  $a_{2g}$  (3),  $e_{2g}$  (17)a,  $e_{1u}$  (14)a and  $e_{1u}$  (14)b vibrations are observed in 1300–1000 cm<sup>-1</sup>[83] region where a and b are assigned for higher and lower wavenumbers respectively doubly degenerate e vibrations. The strong band in IR at 1189  $cm^{-1}$  corresponds to ring vibration of  $e_{1u}$  (14)b mode. While  $e_{2g}$  (17)a vibration mode is observed as a very weak band in Raman (exp.) spectrum at 1187 cm<sup>-1</sup>. The higher intensity in (exp.) spectra as compared to theoretical spectra has been attributed to the presence of strong electron donor substituent (OCH<sub>3</sub> groups) [78, 79, 83] which strongly interact with the phenyl ring. The out-of-plane C-C-H bending vibrational modes are obtained in 1000-675 cm<sup>-1</sup>[79, 83, 88] region. The C-C-H out-of-plane e<sub>2u</sub> (19) bending vibration is obtained as a weak band at 856 cm<sup>-</sup>  $^{1}$  and 855 cm  $^{-1}$  in IR and Raman (exp.) spectra respectively. The e<sub>1g</sub> (11)a vibration modes corresponding to are observed as medium intensity and weak band at 744 cm<sup>-1</sup> and 745 cm<sup>-1</sup> in IR transmittance (Exp.) and Raman spectrum respectively. These results are in agreement with

the theoretical results. As evident from PED, the symmetric and asymmetric, puckering and trigonal deformation modes of phenyl ring 1 and ring 2 are highly coupled modes.

### 4.2.2. Chloro-phenyl vibrations

The stretching mode of chloro phenyl (Cl-C<sub>6</sub>H<sub>4</sub>) group is expected at ~ 1100 cm<sup>-1</sup>, in these spectra as strong peak at 1091 cm<sup>-1</sup> IR (exp.) and as weak peak at 1102 cm<sup>-1</sup> in Raman (exp.) spectra. The asymmetric stretching vibrations C-Cl occur in 900 - 700 cm<sup>-1</sup> region. In IR (exp.) spectrum, the asymmetric stretching peaks on interaction with phenyl ring pertaining to HC=C-Cl, C-Cl and HC-C-C-Cl bonding groups are found at 830 and 813 cm<sup>-1</sup> respectively. The theoretical HF and B3LYP calculated IR peak position for this mode are at [839, 817 cm<sup>-1</sup>] and [821, 805 cm<sup>-1</sup>] respectively. Similarly in Raman (exp.), (HF) and (B3LYP), the symmetric stretching modes of C-Cl bonded groups appear at [832, 817 cm<sup>-1</sup>], [846, 817 cm<sup>-1</sup>] and [851, 828 cm<sup>-1</sup>] respectively. C-Cl vibrational mode at 832 cm<sup>-1</sup> has dominating contribution. Besides C-Cl symmetric stretching modes is observed at 660, 651, 628 cm<sup>-1</sup> in (exp.) IR transmission spectrum. The removal of degeneracy among these components arises from the phenyl ring contribution and low site symmetry in crystal lattice. The C-Cl in-plane and out of plane bending vibrations are predicted in the region 550-250 cm<sup>-1</sup> in both calculated FTIR and FT-Raman spectra. The C-Cl out-of-plane bending vibrations are assigned in FT-Raman spectra as a strong band at 269 and 375  $\text{cm}^{-1}$ .

#### 4.2.3. Hydroxyl group vibrations

The hydroxyl (OH) or hydrogen bonded group vibrations are very sensitive to the environment, which effects its peak position, intensity and shape. The free hydroxyl group absorbs strongly in the region  $3600-3300 \text{ cm}^{-1}$ , while hydrogen bonded O-H stretching vibrations appears in  $3500-3100 \text{ cm}^{-1}$  region as a broad absorption/transmission band pertaining to intermolecular or intra-

molecular hydrogen bonding in molecule. The asymmetric stretching vibration of O-H group is obtained as broad transmission band in 3600 – 3300 cm<sup>-1</sup> region with maximum at 3455 cm<sup>-1</sup>. The presence of this peak confirms the atmospheric moisture. While, hydrogen bonded of ketone and methoxy oxygen group shows peaks at 3297 cm<sup>-1</sup> in IR(exp) transmission spectrum. In Raman (exp.) spectrum this mode appeared at 3157 and 3139 cm<sup>-1</sup>. The O-H bending vibration interacts with phenyl ring C-C stretching and C-H bending vibrations which may result in the shift in peak position. The O-H out-of-plane bending vibrations are obtained in IR spectra at [717, 690 cm<sup>-1</sup>] (exp.), 735 cm<sup>-1</sup> (B3LYP) and at [724, 713 cm<sup>-1</sup>] (exp.), [732, 703 cm<sup>-1</sup>] (HF), [735, 704 cm<sup>-1</sup>] (B3LYP) in Raman spectra. The calculated values for these vibrations are in good agreement with the experimental ones. The C=O..H stretching mode is appeared at [1295, 1278 cm<sup>-1</sup>] and [1287, 1274 cm<sup>-1</sup>] in (exp.) IR transmission and FT Raman spectra respectively. The existence of C=O stretching mode in these spectra confirms of the hydrogen bonded enol form in this crystal.

### 4.2.4. Methoxy group vibrations

In 2,4,5 TMCC molecule, three methoxy groups are bonded at 2, 4 and 5 positions in phenyl ring, the electronic charge is back donated from the oxygen lone pair to the of C-H bonds which weaken C-H bonds due to increase in C-H bond length and the decrease in force constant. The CH<sub>3</sub> asymmetric and symmetric stretching vibrations are observed as strong peak at [2999], [2952, 2929] cm<sup>-1</sup> and [3034], [2934] cm<sup>-1</sup> in IR transmission and Raman (exp.) spectra respectively. In theoretically calculated spectra, these stretching vibrational peaks appeared at [3046], [2925] cm<sup>-1</sup> (HF), [3047], [2916] cm<sup>-1</sup> (B3LPY) IR transmission and [3053], [2925] cm<sup>-1</sup> (HF), [3047], [2916] cm<sup>-1</sup> (B3LYP) Raman spectra. Methyl group bending modes calculated values 1482 cm<sup>-1</sup> (HF), 1475 cm<sup>-1</sup> (B3LYP) for IR transmission spectra and at 1460 cm<sup>-1</sup> (HF), 1475 cm<sup>-1</sup> (B3LYP) respectively in Raman spectra. C=O..H bending vibration appears as a

medium intensity at 1745 cm<sup>-1</sup> and 1744 cm<sup>-1</sup> in (exp.) IR transmission and Raman spectra of this sample. The very strong broad transmittance peaks in 1225 - 1150 cm<sup>-1</sup> region with components at 1216, 1205, 1172 cm<sup>-1</sup> are tentatively assigned to C-H<sub>bend</sub> and CH<sub>3rock</sub> modes as observed (exp.) IR transmission spectrum. The peak components at 1216 and 1205 cm<sup>-1</sup> are attributed to C-H<sub>bend</sub> modes. While the peak component at 1172 cm<sup>-1</sup> is tentatively assigned to CH<sub>3</sub> rocking mode. When the CH<sub>3</sub> group is directly attached to an oxygen atom, the C-H stretching and bending bands peak position shifts due to change in crystalline field effect depending upon the nature of bonded substituting groups present in molecule. This may result in the wide spread of O-CH<sub>3</sub> stretching bands over a larger region than that of C-CH<sub>3</sub> group. In the present case, this spreading is observed between 1100 and 950 cm<sup>-1</sup>. The vibrational peak pertaining to C-O<sub>str.</sub> and O-C<sub>str.</sub> stretching modes are obtained in (exp.) IR transmission spectrum as medium intensity peaks at [1041, 1029] and [1010, 991] cm<sup>-1</sup> respectively. The C-O-CH<sub>3</sub> in plane bending vibration is observed as a greatly mixed mode in the region 600–200 cm<sup>-1</sup>. The O-CH<sub>3</sub> torsion mode has been calculated at 296, 237 cm<sup>-1</sup> and found to be in good match with the peaks observed at 318, 241 cm<sup>-1</sup> in FT-Raman spectra. The current mode is attached with phenyl ring torsion modes and the torsion about C-C bonds bridging the two phenyl rings.

### 4.2.5. Methylene group vibrations

C-H stretching vibration of the methylene group is at low frequencies than those of the aromatic C-H ring stretchings. The asymmetric  $CH_2$  stretching vibrations are generally observed in the region of 3000 of 2900 cm<sup>-1</sup>, while the  $CH_2$  symmetric stretching found in the region of 3000-2900 cm<sup>-1</sup>. In the current study the  $CH_2$  asymmetric and symmetric stretching vibrations are observed at [2975], [2867] cm<sup>-1</sup> and strong peaks observed at [2975], [2867] cm<sup>-1</sup> in FT-IR/FT-Raman spectra by both the computational method. The four bending vibrations of the

methylene group are referred as scissoring, twisting, wagging and rocking. The scissoring mode is distinguished by the strong IR band at 1475 cm<sup>-1</sup> and the FT-Raman band at the same value which is computed at 1436 cm<sup>-1</sup>. The vibrational modes subsequent to the twisting, wagging and rocking of the methylene group emerge in the region 1200–900 cm<sup>-1</sup>. C-H in-plane bending vibrations are identified at 1151 and 1128 cm<sup>-1</sup> and three C-H out-of-plane bending vibrations are found at 950 and 904 cm<sup>-1</sup>. As per the available literature, the in-plane and out-of-plane bending vibrational frequencies are established to be well within their attributed regions.

### 4.2.6. Understanding NLO activity through Vibrational Spectroscopy

The vibrational spectroscopy has been successfully used to reveal Non-Linear Optical (NLO) activity possessing  $\pi$ -conjugated systems present in a single crystal molecule. Such molecules have large second order molecular polarizabilities which activate of some modes in IR as well as Raman spectrum. In 2,4,5 TMCC crystal, 16, 13 and 9 phenyl ring modes are observed in both IR and Raman spectra. They play vital role in NLO activity of the crystal. The C-C asymmetric stretching e2g (16) mode of two phenyl rings are observed at [1681, 1654 (ring1), 1512 (ring2) cm<sup>-1</sup>] and [1683, 1650 (ring1), 1510 (ring2) cm<sup>-1</sup>] (exp.)in IR and Raman (exp.) spectra respectively. While C-C symmetric stretching  $e_{1u}$  (13) and  $b_{2u}$  (9) vibration modes phenyl ring are expected at ~ 1450 cm<sup>-1</sup> and ~ 1300 cm<sup>-1</sup> for these two phenyl rings are observed at [1410, 1398 (ring1), 1326 (ring2) cm<sup>-1</sup>] in IR (exp.) spectrum and at 1408, 1395 (ring1), 1321 (ring2) cm<sup>-1</sup>]in Raman(exp.) spectrum. The  $b_{2u}$  (9) mode vibration is observed as strong band at 1363 cm<sup>-1</sup> and 1360 cm<sup>-1</sup> in IR and Raman (exp.) spectra respectively. The simultaneous activation of the phenyl ring  $e_{2g}$  (16),  $e_{1u}$  (13) and  $b_{2u}$  (9) IR and Raman vibrational modes confirms the charge transfer from electron donating methoxy group to phenyl ring  $\pi$ -system to facilitate easy transfer of electron within crystalline network.



**Figure 4:** Estimated and experimental FT-IR (a1 & b1) and Raman (a2 & b2) spectra of 2, 4, 5-Trimethoxy-4'-chlorochalcone

### 4.3.Opto-electronic properties

### 4.3.1. UV-vis.-NIR spectroscopic study

To know the appropriateness of any materials to be used in optoelectronic device it is essential to examine the optical absorption or transmission phenomenon of light in it. Hence, the UV-vis.-NIR spectrum of 2,4,5TMCC crystals was recorded from which we can get the vital evidence about its structure, as it is know that the absorption of UV-VIS light engaged with the promotion of electrons in  $\sigma$  and  $\pi$  orbitals from the ground to higher energy states. To fabricate the optoelectronic device from any nonlinear optical material it must have wide range of optical

transparency window, thus it seems to be compulsory to study the UV-vis.-NIR spectrum. The recorded UV-vis.-NIR absorbance spectrum of 2,4,5TMCC crystals has been shown in Figure 5(a). From figure it is confirmed that the grown crystal is having very low absorbance in 500-1300 wavelength range. This indicates that the grown crystal is highly transparent which makes it suitable to be used in optical window for SHG laser radiation applications [49, 89, 90]. Three absorption bands are observed in 2,4,5TMCC at 397 nm, 280 nm and 220 nm.



Figure 5: (a) Recorded UV-vis.-NIR optical absorbance spectrum and (b) Plots of

 $(\alpha h v)^2$  vs hv for 2,4,5 TMCC crystals.

#### 4.3.2. Optical band gap analysis

The recorded absorbance data was used to calculate the optical energy band gap of 2,4,5TMCC to have bottomless understanding about its enactment and function in photonic devices. Therefore, the optical energy band gap  $(E_g^{opt})$  was evaluated according to following steps:

The absorption coefficient ( $\alpha$ ) was calculated using the following relation:

$$\alpha = 2.303 \frac{Absorbance}{d} \tag{1}$$

Where, d = 0.12 cm) is the thickness of the crystal.

The  $E_g^{opt}$  was calculated using the following equation [91-93]:

$$(\alpha h\nu)^{\frac{1}{r}} = A(h\nu - E_g)$$
<sup>(2)</sup>

Where, the constants such as *A*, *h*, *v* are having their standard meanings, r is defined as an index value that differentiate the optical absorption process and the value of it for direct allowed transitions, 1/2, for direct forbidden transitions, 3/2, for indirect allowed transitions, 2 and for indirect forbidden transitions, 3 [94-97].  $E_g^{opt}$  of 2,4,5TMCCcrystals was calculated for all the transition values of r. The best fitting curve was noticed for n=1/2 which indicates to direct allowed transition in the titled molecule. The  $(\alpha hv)^2 vs hv$ , plot has been shown in Figure 5(b) and the value of optical energy band gap was obtained from the point of interception on x(hv) axis  $(\alpha hv)^2 = 0$  and found to be 2.8 eV.

### 4.3.3. Photoluminescence (PL) study

The PL is a light emission from any kind of material after the absorption of photons or electromagnetic radiation. The recorded PL excitation and emission spectra of 2,4,5TMCC crystals at room temperature are shown in Figure 6 (a) and (b) respectively. For measuring the emission spectrum the grown crystals were crushed into fine powder and dissolved in DMF solution. In the excitation spectrum, the strong and high intensity absorption at ~415 nm of violet light has been observed. Further to record the emission spectra it was excited at 415 nm and a strong and intense emission band at ~522 nm has been observed which is assigned to green emission of light and shows that the titled compound possess green fluorescence and may used in the fabrication of green light emitting diodes (LEDs).



Figure 6: Photoluminescence (a) excitation and (b) emission spectra of 2,4,5TMCC crystals

#### 4.3.4. TD-DFT study

TD-DFT is established as an excellent tool to calculate the electronic structure in both quantum chemistry and solid state physics. The modern density functional approach shows a gratifying balance between precision and computational cost in comparison to traditional ab initio and semi-empirical approaches.

To explore the nature of electronic transition in 2,4,5-TMCC molecule, the TD-DFT approach has been applied five different levels of theory such as B3LYP, CAM-B3LYP, wb97xd, M06, PBE0 at 6-31G\* basis set in gas phase. It is well know that an accurate absorption wavelength can be easily perceive by such study at reasonably small computing time on the basis of optimized ground state geometry [98-100]. The experimental UV-vis.-NIR spectrum of 2,4,5-TMCC has been shown in Figure 5. The calculated excitation wavelength, energies, oscillator strengths and major contributions and given in Table 2. Figure 7 shows the theoretically obtained UV-vis. spectrum of 2,4,5-TMCC at different levels of theory. It is clear from figure that there is a great variation in the value of absorption wavelengths evaluated at CAM-B3LYP and wb97xd levels of theory while calculated at other methods are moderately varied. The comparison has been made between theoretically calculated and experimentally recorded absorption spectrum.

The calculated value of absorption wavelengths at TD-B3LYP/6-31G\* level of theory was found at ~398 nm, 296 nm and 240 nm which are in close agreement with the experimental values observed at 397nm, 280 nm and 220 nm (see figure 4). The value of maximum absorption wavelength (398nm) obtained from theoretical (at TD-B3LYP/6-31G\* level of theory) and experimental (397nm) results are in good agreement when compared with all other applied methods (Table 2).The optimized molecular geometry indicates that the visible absorption maximum is corresponds to the electron transition from HOMO to LUMO.TD-DFT calculation shows that the absorption bands at 398 nm and 296 nm initiates mainly due to  $H \rightarrow L$  and  $H \rightarrow L + 1$  excitations respectively.

**Table 2** Excitation wavelength ( $\lambda_{exc}$ ), energies E(eV), oscillator strengths ( $f_0$ ), and major contributions for transitions in 2,4,5TMCC calculated at different levels of theory.

-	Method	$\lambda_{\rm exc}$	E(eV)	${f}_0$	Major contributions
_					
	B3LYP	398.63	3.110	0.506	H→L (69.4%)
	CAM-B3LYP	334.704	3.704	0.655	H→L (62%)
	Wb97xd	330.12	3.756	0.663	H→L (61%)
	PBE1	384.71	3.223	0.554	<i>H→L (70%)</i>
	MO6	383.28	3.235	0.592	H→L (70%)



**Figure 7:** UV-vis. spectrum of the 2,4,5TMCC molecule calculated at different levels of theory using 6-31G\* basis set.

### 4.3.5. Frontier molecular orbitals (FMOs) and GCRD parameters analysis

The FMOs play a vital role in understanding the phenomenon of reactivity in any molecule and for the development of any chemical reaction which involves in the formation of complex, the communication of HOMO and LUMO between reacting species is very important amongst other FMOs. These orbitals also play the same role as donor and acceptor respectively and used for predicting the reactive position in  $\pi$ -electron system. The energy values HOMO and LUMO were obtained at five different levels of theory, the values calculated at B3LYP/6-31G<sup>\*</sup> are given in Table 3. The value of energy gap between HOMO and LUMO is found to be 3.402eV with its chemical hardness value of 1.701 eV, these values indicates that the titled molecule possess better kinetic stability. The electronic transition in 2,4,5TMCC molecule has been observed at 3.110 eV predicted by TD-DFT calculations which is corresponding to the transition from

ground state to first excited state and also show charge transfer from HOMO to LUMO. The value of excitation energy obtained at same level of theory from TDDFT is in good relationship with HOMO-LUMO energy gap. Figure 8 shows the 3-D plots of HOMO and LUMO orbitals and the values of their respective energy (in a.u. as well in eV) are presented in Table 3. HOMO shows that the charge density is localized mainly on carbonyl, methylsulfanyl, ethylenic bridge and ring 2 while LUMO is delocalized over the Cl group, ring1, carbonyl and ethylenic bridge. The small value of the energy separation between the HOMO and LUMO and their atomic orbital compositions imply a charge transfer interaction within the molecule, which influence the NLO activity of the molecule. The lowering of the HOMO-LUMO band gap is essentially a consequence of the large stabilization of the LUMO due to the strong electron-acceptor ability of the electron-accepter group. Experimental result shows that the titled compound has an advantage of low value of absorbance and significant optical transparency. Further this was also demonstrated by the theoretically obtained transition energy value which is comparatively higher and belongs to violet region of the spectrum.



**Figure 8:** The 3-D plot of the frontier molecular orbital's of 2, 4, 5-Trimethoxy-4'- chlorochalcone molecule with counter values of  $\pm 0.02$  a.u.

Orbital energy	a.u.	eV.
E <sub>HOMO</sub>	-0.195	-5.306
E <sub>HOMO-1</sub>	-0.234	-6.368
$E_{LUMO}$	-0.070	-1.905
$E_{LUMO+1}$	-0.022	-0.599
$\Delta E_{HOMO-LUMO}$	0.125	3.402
$\Delta E_{HOMO-1-LUMO+1}$	0.212	5.769
Hardness (η)	0.063	1.701
Potential $(\mu)$	-0.133	-3.606
Softness (S)	0.011	0.294
<i>Electronegativity</i> $(\chi)$	0.133	3.606
Electrophilic index ( $\omega$ )	0.141	3.822

Table 3 Calculated energy values and their differences of frontier molecular orbitals (FMOs)

To understand the correlation between structure, stability and global chemical reactivity of molecules the study of GCRD parameters are very important. These are useful in the development of quantitative structure activity, property, and toxicity relationships. DFT gives the explanation of foremost universal insight on stability of the structure of molecule and reactivity [101] and the strength of any material is connected to the aromaticity [102]. Here we have calculated the various global chemical reactivity descriptor such as  $\eta$ ,  $\mu$ ,  $\chi$  and  $\omega$  by taking orbital energies of HOMO and LUMO as ionization energy (I) and electron affinity (A) respectively. The absolute global hardness( $\eta$ ), electronic chemical potential( $\mu$ ), softness(S), electronegativity( $\eta$ ) and electrophilicity( $\omega$ ) parameters were evaluated by using  $\eta = \frac{1}{2}$  (E<sub>LUMO</sub> – E<sub>HOMO</sub>),  $\mu = -\left(\frac{l+A}{2}\right)$ ,  $S = \frac{l}{2\eta}$ ,  $\chi = \left(\frac{l+A}{2}\right)$  and  $\omega = \frac{\mu^2}{2\eta}$ , respectively and presented in Table 3.

The obtained GCRD result reveals that the titled molecule possesses good chemical strength and chemical stability.

### 4.3.6. Second order polarizability analysis

Hyperpolarizability plays a significant role to understand the nonlinear optical process in any molecule to be used for the fabricate the technologically important nonlinear optical devices and justify the increasing applications of it to calculate accurately [103, 104]. It is clear from the currently available literature [105-107] that in addition to a suitable action of electron correlation and a careful selection of the functional and basis set, the insertion of the contributions occurring from the nuclear activity is of basic significance for the estimation of electrical properties such as polarizability and hyperpolarizability at molecular level. Hence, we have calculated such parameters using various schemes like B3LYP, CAM-B3LYP, LC-BLYP, wb97xd and MP2 at 6-31G\* basis set. The values of electronic total dipole moment ( $\mu_{tot}$ ), molecular total and anisotropy of polarizability ( $\alpha_0$  and  $\Delta \alpha$ ), static and total first hyperpolarizability ( $\beta_0$ ,  $\beta_{tot}$ ) along with their components determined at B3LYP/6-31G\* level of theory are given in Table 4. Further the calculated values of all above parameters estimated at HF, CAM-B3LYP, LC-BLYP, wb97xd and MP2 are also provides in Table 1S (1-5) (see supplementary information). The obtained result shows that the values of polarizability and hyperpolarizability are leaded by their diagonal components (i.e. the components along dipole moment axis) of  $\alpha_{xx}$  and  $\beta_{xxx}$ . Figure 2S (supplementary information) shows the variation of total hyperpolarizability values determined at all currently applied levels of theory and concludes that its value is higher at B3LYP levels of theory in comparison to other applied techniques. The value of total dipole moment ( $\mu_{tot}$ ) is found to be 6.043D and the highest value of component of  $\mu_{tot}$  is  $\mu_x$  (=-5.905D) which is a major contributor to it. Also, the value of average polarizability ( $\alpha_0$ ), anisotropy of polarizability ( $\Delta \alpha$ ) and total first hyperpolarizability ( $\beta_{tot}$ ) are  $38 \times 10^{-24}$ ,  $45 \times 10^{-24}$  and  $30 \times 10^{-30}$  esu. respectively. The value of  $\beta_{tot}$  for titled molecule at molecular level is found to be 136 times larger than that of prototype urea molecule as well as comparable to other molecules calculated at same level of

theory recently [15, 108]. The measured experimental second harmonic generation value of the titled molecule at bulk level is observed to be 4.3 times higher than urea [57]. Therefore, the values of calculated hyperpolarizability ( $\beta_{tot}$ ) and measured second harmonic generation are numerous times superior than the other reported organic as well as other materials [52-54, 109-116]. The high value of  $\beta_{tot}$  and SHG makes the titled molecule a unique candidate for nonlinear optical applications.

Polarizabi	lity and dipe	ole moment	7		
Components	а. и.	$esu (\times 10^{-24})$	Components	а. и.	esu (×10 <sup>-30</sup> )
$\alpha_{xx}$	443	65.653	$\beta_{xxx}$	4781	41.256
$\alpha_{xy}$	4	0.593	$\beta_{xxy}$	-1940	-16.74
$lpha_{yy}$	237	35.123	$eta_{xyy}$	43	0.371
$\alpha_{xz}$	6	0.889	$eta_{_{yyy}}$	-18	-0.155
$lpha_{yz}$	-8	-1.186	$eta_{xxz}$	94	0.811
$\alpha_{zz}$	94	13.931	$\beta_{xyz}$	-16	-0.138
$lpha_0$	258	38	$eta_{yyz}$	1	0.009
Δα	304	45	$\beta_{xzz}$	-46	-0.397
$\mu_x$	-2.323	-5.905D	$eta_{yzz}$	-13	-0.112
$\mu_y$	0.505	1.283D	$oldsymbol{eta}_{zzz}$	-5	-0.043
$\mu_z$	-0.076	-0.194D	$eta_0$	2078	18
$\mu_{tot}$	2.378	6.043D	$eta_{tot}$	3463	30
$\mu_{tot}(urea)$	1.66	4.24D	$\beta_{tot}(urea)$	26	0.22[108]

**Table 4** Calculated values of polarizability, hyperpolarizability and dipole moment along their individual tensor components of titled molecule at B3LYP/6-31G\* level of theory.

For  $\alpha$ , 1 a. u. = 0.1482×10<sup>-24</sup> esu, for  $\beta$ , 1 a. u. = 0.008629×10<sup>-30</sup> esu,  $\mu_{\text{Urea}}$  = 1.3732 D and  $\beta_{\text{Urea}}$  =

0.3728×10<sup>-30</sup>esu[109]

### 4.4. Molecular Electrostatic Potential (MEP)

Figure 9 shows the theoretically obtained 3-D plot of molecular electrostatic potential (MEP) for the titled compound to have healthier idea at molecular level. It is well know that it is a study of electrostatic potential on constant electron density surface. Figure shows that the MEP plots overlap on the top of total energy density surface. It helps us to inspect the reactivity of molecular species by predicting their nucleophile and electrophile parts whether the nucleophile is approaching to positive region and electrophile is approaching to negatively charged surface of the molecule respectively. It can be seen in figure that the blue color represents the maximum positive potential and red color represents the maximum negative potential which are preferred sites for nucleophilic and electrophilic attacks, respectively [55, 117, 118]. The MEP plot also provides the information concerning the molecular size, shape along with its positive, negative and neutral electrostatic potential sections in terms of color grading.



Figure 9: Molecular electrostatic potential plot of 2,4,5TMCC molecule with iso value of  $\pm 0.02a.u.$ 

### 4.5. Thermal analysis

The thermal stability is a key parameter of any materials before exploit it for device fabrication. Hence to identify the thermal parameters of the grown crystals of 2,4,5TMCC the differential scanning calorimetry (DSC) technique was applied. The fine powder of the grown crystals was

subjected to thermal analysis to get the key information about the accurate melting point with respect to the temperature. The recorded DSC curve has been shown in Figure 10 which indicates that there is no phase transition before melting. The endothermic peak at 149 °C represents its melting point and sharpness indicates high purity and crystallinity of the compound.



**Figure 10:** Differential scanning calorimetry curve for 2,4,5TMCC crystals.

### 5. Conclusion

Single crystals of 1-(4-chlorophenyl)-3-(2,4,5-trimethoxyphenyl) prop-2-en-1-one (2,4,5TMCC) have been grown successfully and used to study the structural (X-ray diffractions), vibrational (FT-IR and FT-Raman) and optical (UV-VIS-NIR and Photoluminescence spectroscopy) properties. Further, the successful optimization of molecular geometry of 2,4,5TMCC molecule was achieved by applying different levels of theory at 6-31G\* basis set. The theoretically obtained geometrical parameters are found to be in good agreement with experimental. The detailed investigations of vibrational spectra have been carried out theoretically and

experimentally for nonlinear optical application of 2,4,5 TMCC crystal. These investigations reveal the existence of hydrogen bond interaction between prop-2-en-1-one carbonyl oxygen with hydrogen and methoxy carbonyl (ring 2) with prop-2-en-1-one hydrogen. Such conjugation results in lowering of carbonyl stretching mode. The electronic effects of hyper-conjugation and back-donation are also observed. The simultaneous IR and Raman activation of the phenyl ring modes of 16, 13 and 9 also provides evidence for the charge transfer interaction. Hydrogen bonding causes appearance of peaks at low frequency. The intermolecular hydrogen bonding in this crystal gives broad bands, while intra-molecular hydrogen bonds induced sharp and strong peaks. The factor group analysis is also discussed. TDDFT has been used at different levels of theory such as at B3LYP, CAM-B3LYP, LC-BLYP, wb97xd, PBE0 and MO6 levels of theory using 6-31G\* basis set to investigate the electronic properties. The excitation wavelengths was found at 398.63 nm with oscillator strength of 0.506 calculated by B3LYP/6-31G\* level of theory which is in good agreement with the experimental result i.e. at 397 nm. The PL study suggests that the titled molecule can be used for green LED fabrication. The highest occupied and lowest unoccupied molecular energy gaps were determined to envisage the prospects of intramolecular charge transfer in the molecule. The calculated first hyperpolarizability value of 2,4,5TMCC molecule is found to be 136 times higher than urea calculated at B3LYP/6-31G\* level of theory. The chemical strength of the titled molecule is found to be good as studied by global chemical reactivity descriptors. MEP plot of the titled molecule confirms the negative potential sites by red color (viz. favorable for electrophilic attack) while the positive potential sites with blue color (viz. favorable for nucleophilic attack). The DSC thermal analysis reveals that the melting point of the titled material is 149 °C. All the obtained results shows that the titled

molecule is possess excellent optoelectronic properties and may be used for photonic device fabrications.

### **Conflict of interest:**

### The authors confirms that there is no conflict of interest exists in the current work.

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### References

[1] S.D. Smith, Lasers, nonlinear optics and optical computers, Nature, 316 (1985) 319-324.

[2] P. Huber, High power in the near ultraviolet using efficient SHG, Optics Communications, 15 (1975) 196-200.

[3] P. Franken, J. Ward, Optical harmonics and nonlinear phenomena, Reviews of Modern Physics, 35 (1963) 23.

[4] I. Ledoux, J. Badan, J. Zyss, A. Migus, D. Hulin, J. Etchepare, G. Grillon, A. Antonetti, Generation of high-peak-power tunable infrared femtosecond pulses in an organic crystal: application to time resolution of weak infrared signals, JOSA B, 4 (1987) 987-997.

[5] M. Iwai, T. Kobayashi, H. Furuya, Y. Mori, T. Sasaki, Crystal Growth and Optical Characterization of Rare-Earth (Re) Calcium Oxyborate ReCa 40 (BO 3) 3 (Re= Y or Gd) as New Nonlinear Optical Material, Japanese journal of applied physics, 36 (1997) L276.

[6] Y. Goto, A. Hayashi, Y. Kimura, M. Nakayama, Second harmonic generation and crystal growth of substituted thienyl chalcone, Journal of crystal growth, 108 (1991) 688-698.

[7] W.T. Harrison, H. Yathirajan, B. Sarojini, B. Narayana, H. Anilkumar, Do C—H… O and C—H…  $\pi$  interactions help to stabilize a non-centrosymmetric structure for racemic 2, 3-dibromo-1, 3-diphenylpropan-1-one?, Acta Crystallographica Section C: Crystal Structure Communications, 61 (2005) 728-730.

[8] W.T.A. Harrison, H.S. Yathirajan, B.K. Sarojini, B. Narayana, J. Indira, 1-(4-Chlorophenyl)-3-(4-methoxyphenyl)prop-2-en-1-one, Acta Crystallographica Section E, 62 (2006) 01647-01649.

[9] P. Patil, J.-J. Teh, H.-K. Fun, I.A. Razak, S. Dharmaprakash, 3-(2, 4-Dichlorophenyl)-1-(4-methylphenyl) prop-2-en-1-one, Acta Crystallographica Section E: Structure Reports Online, 62 (2006) 03096-03098.

[10] T. Uchida, K. Kozawa, T. Sakai, M. Aoki, H. Yoguchi, A. Abdureyim, Y. Watanabe, Novel organic SHG materials, Molecular Crystals and Liquid Crystals, 315 (1998) 135-140.

[11] G. Zhang, T. Kinoshita, K. Sasaki, Y. Goto, M. Nakayama, Crystal growth of 4-Br-4'-methoxychalcone and its characterization, Journal of crystal growth, 100 (1990) 411-416.

[12] B. Gu, W. Ji, P. Patil, S. Dharmaprakash, Ultrafast optical nonlinearities and figures of merit in acceptor-substituted 3, 4, 5-trimethoxy chalcone derivatives: Structure-property relationships, Journal of Applied Physics, 103 (2008) 103511-1035116.

[13] H. Ravindra, A.J. Kiran, S. Dharmaprakash, N.S. Rai, K. Chandrasekharan, B. Kalluraya, F. Rotermund, Growth and characterization of an efficient nonlinear optical  $D-\pi-A-\pi-D$  type chalcone single crystal, Journal of crystal growth, 310 (2008) 4169-4176.

[14] P. Patil, M. Bannur, D. Badigannavar, S. Dharmaprakash, Study on nonlinear optical properties of 2, 4, 5-trimethoxy-4' -bromochalcone single crystal, Optics & Laser Technology, 55 (2014) 37-41.

[15] 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-[small pi]-A type novel chalcone derivative for opto-electronic applications, RSC Advances, 5 (2015) 87320-87332.

[16] B.K. Sarojini, B. Narayana, B.V. Ashalatha, J. Indira, K.G. Lobo, Synthesis, crystal growth and studies on non-linear optical property of new chalcones, Journal of crystal growth, 295 (2006) 54-59.

[17] A.J. Kiran, H. Lee, H. Ravindra, S. Dharmaprakash, K. Kim, H. Lim, F. Rotermund, Designing novel chalcone single crystals with ultrafast nonlinear optical responses and large multi-photon absorption coefficients, Current Applied Physics, 10 (2010) 1290-1296.

[18] 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, Crystal growth & design, 11 (2011) 5362-5369.

[19] M. Cockerham, C. Frazier, S. Guha, E. Chauchard, Second-harmonic generation in derivatives and analogs of benzophenone and chalcone, Applied Physics B, 53 (1991) 275-278.

[20] P. Patil, V. Bhumannavar, M. Bannur, H.N. Kulkarni, G. Bhagavannarayana, Second Harmonic Generation in Some Donor-Acceptor Substituted Chalcone Derivatives, (2013).

[21] R. Nithya, N. Santhanamoorthi, P. Kolandaivel, K. Senthilkumar, Structural and spectral properties of 4-bromo-1-naphthyl chalcones: a quantum chemical study, The Journal of Physical Chemistry A, 115 (2011) 6594-6602.

[22] T. Chandra Shekhara Shetty, S. Raghavendra, C.S. Chidan Kumar, S.M. Dharmaprakash, Nonlinear absorption, optical limiting behavior and structural study of a new chalcone derivative-1-(3, 4-dimethylphenyl)-3-[4(methylsulfanyl) phenyl] prop-2-en-1-one, Optics & Laser Technology, 77 (2016) 23-30.

[23] M. Shigeru, M. Makoto, A. Hironaka, O. Susumu, Inhibition of gastric H+, K+-ATPase by the antiulcer agent, sofalcone, Biochemical pharmacology, 42 (1991) 1447-1451.

[24] R.J. Anto, K. Sukumaran, G. Kuttan, M. Rao, V. Subbaraju, R. Kuttan, Anticancer and antioxidant activity of synthetic chalcones and related compounds, Cancer letters, 97 (1995) 33-37.

[25] S. Ducki, R. Forrest, J.A. Hadfield, A. Kendall, N.J. Lawrence, A.T. McGown, D. Rennison, Potent antimitotic and cell growth inhibitory properties of substituted chalcones, Bioorganic & medicinal chemistry letters, 8 (1998) 1051-1056.

[26] F. Herencia, M.L. Ferrandiz, A. Ubeda, J. Domínguez, J.E. Charris, G.M. Lobo, M.J. Alcaraz, Synthesis and anti-inflammatory activity of chalcone derivatives, Bioorganic & medicinal chemistry letters, 8 (1998) 1169-1174.

[27] M. Liu, P. Wilairat, M.-L. Go, Antimalarial alkoxylated and hydroxylated chalones: structure-activity relationship analysis, Journal of Medicinal Chemistry, 44 (2001) 4443-4452.

[28] S.N. López, M.V. Castelli, S.A. Zacchino, J.N. Domínguez, G. Lobo, J. Charris-Charris, J.C. Cortés, J.C. Ribas, C. Devia, A.M. Rodríguez, In vitro antifungal evaluation and structure–activity relationships of a new series of chalcone derivatives and synthetic analogues, with inhibitory properties against polymers of the fungal cell wall, Bioorganic & medicinal chemistry, 9 (2001) 1999-2013.

[29] J.-H. Wu, X.-H. Wang, Y.-H. Yi, K.-H. Lee, Anti-AIDS agents 54. A potent anti-HIV chalcone and flavonoids from genus Desmos, Bioorganic & medicinal chemistry letters, 13 (2003) 1813-1815.

[30] L. Mathiesen, K.E. Malterud, R.B. Sund, Antioxidant activity of fruit exudate and C-methylated dihydrochalcones from Myrica gale, Planta medica, 61 (1995) 515-518.

[31] 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, Journal of Materials Chemistry, 10 (2000) 1513-1517.

[32] X. Tao, T. Watanabe, K. Kono, T. Deguchi, M. Nakayama, S. Miyata, Synthesis and characterization of poly (aryl ether chalcone) s for second harmonic generation, Chemistry of materials, 8 (1996) 1326-1332.

[33] P. Patil, S. Dharmaprakash, K. Ramakrishna, H.-K. Fun, R.S.S. Kumar, D.N. Rao, Second harmonic generation and crystal growth of new chalcone derivatives, Journal of crystal growth, 303 (2007) 520-524.

[34] B. Gu, W. Ji, X.-Q. Huang, P. Patil, S. Dharmaprakash, Nonlinear optical properties of 2, 4, 5-Trimethoxy-4'-nitrochalcone: observation of two-photon-induced excited-state nonlinearities, Optics express, 17 (2009) 1126-1135.

[35] L.M. Saleh, H.A. Hassan, F.Z. Henari, P. Patil, M. Bannur, Nonlinear refractive and optical limiting measurements of 2-thienylchalcone derivatives under cw laser regime, Applied Physics A, 116 (2014) 805-810.

[36] J. Chen, X. Wang, Q. Ren, P. 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, Applied Physics A, 105 (2011) 723-731.

[37] T. Vijayakumar, I.H. Joe, C.R. Nair, V. Jayakumar, Efficient  $\pi$  electrons delocalization in prospective push–pull non-linear optical chromophore 4-[N, N-dimethylamino]-4'-nitro stilbene (DANS): A vibrational spectroscopic study, Chemical Physics, 343 (2008) 83-99.

[38] D. Sajan, J. Binoy, I. Hubert Joe, V. Jayakumar, J. Zaleski, Vibrational spectral studies of methyl 3-(4-methoxyphenyl) prop-2-enoate, a new organic non-linear optic crystal, Journal of Raman Spectroscopy, 36 (2005) 221-236.

[39] J. Binoy, I.H. Joe, V. Jayakumar, Changes in the vibrational spectral modes by the nonbonded interactions in the NLO crystal vanillin, Journal of Raman Spectroscopy, 36 (2005) 1091-1100.

[40] D. Sajan, I.H. Joe, V. Jayakumar, NIR-FT Raman, FT-IR and surface-enhanced Raman scattering spectra of organic nonlinear optic material: p-hydroxy acetophenone, Journal of Raman Spectroscopy, 37 (2006) 508-519.

[41] S. Guidara, H. Feki, Y. Abid, Vibrational spectral studies and non-linear optical properties of Lleucine L-leucinium picrate: a density functional theory approach, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 115 (2013) 437-444.

[42] N. Elleuch, W. Amamou, A.B. Ahmed, Y. Abid, H. Feki, Vibrational spectroscopic study, charge transfer interaction and nonlinear optical properties of L-asparaginium picrate: A density functional theoretical approach, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 128 (2014) 781-789.

[43] B.G. Johnson, P.M. Gill, J.A. Pople, The performance of a family of density functional methods, The Journal of chemical physics, 98 (1993) 5612-5626.

[44] S. Elleuch, H. Feki, Y. Abid, HF, MP2 and DFT calculations and spectroscopic study of the vibrational and conformational properties of N-diethylendiamine, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 68 (2007) 942-947.

[45] M. Shkir, H. Abbas, On the ground and excited state of glycine–glutaric acid: A new organic material, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 125 (2014) 453-457.

[46] N. Sudharsana, S. Muthunatesan, G.J. Priya, V. Krishnakumar, R. Nagalakshmi, Experimental and theoretical studies of 2, 5-dichloroanilinium picrate, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 121 (2014) 53-62.

[47] A. Reshak, W. Khan, The density functional study of electronic structure, electronic charge density, linear and nonlinear optical properties of single crystal alpha-LiAITe 2, Journal of Alloys and Compounds, 592 (2014) 92-99.

[48] S. Azhagiri, S. Jayakumar, S. Gunasekaran, S. Srinivasan, Molecular structure, Mulliken charge, frontier molecular orbital and first hyperpolarizability analysis on 2-nitroaniline and 4-methoxy-2nitroaniline using density functional theory, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 124 (2014) 199-202.

[49] M. Shkir, H. Abbas, Physico chemical properties of I-asparagine I-tartaric acid single crystals: A new nonlinear optical material, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 118 (2014) 172-176.

[50] M. Shkir, S. Muhammad, S. AlFaify, A. Irfan, I. Yahia, A dual approach to study the electro-optical properties of a noncentrosymmetric l-asparagine monohydrate, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 137 (2015) 432-441.

[51] A. Kumar, V. Deval, P. Tandon, A. Gupta, E.D. 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, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 130 (2014) 41-53.

[52] M. Shkir, H. Abbas, S. Kumar, G. Bhagavannarayana, S. AlFaify, Experimental and theoretical studies on bis (glycine) lithium nitrate (BGLiN): A physico-chemical approach, Journal of Physics and Chemistry of Solids, 75 (2014) 959-965.

[53] M. Shkir, S. AlFaify, H. Abbas, G. Bhagavannarayana, A physico-chemical approach to study the experimental and theoretical properties of I-ornithine monohydrochloride: An organic nonlinear optical material, Materials Chemistry and Physics, (2015).

[54] H. Abbas, M. Shkir, S. AlFaify, Density functional study of spectroscopy (IR), electronic structure, linear and nonlinear optical properties of L-proline lithium chloride and L-proline lithium bromide monohydrate: For laser applications, Arabian Journal of Chemistry.

[55] M. Shkir, S. Muhammad, S. AlFaify, Experimental and density functional theory (DFT): A dual approach to study the various important properties of monohydrated l-proline cadmium chloride for nonlinear optical applications, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 143 (2015) 128-135.

[56] M. Shkir, Investigation on the key features of L-Histidinium 2-nitrobenzoate (LH2NB) for optoelectronic applications: A comparative study, Journal of King Saud University - Science.

[57] P. Patil, S. Dharmaprakash, Crystal growth of 2, 4, 5-Trimethoxy-4'-chlorochalcone and its characterization, Materials Letters, 62 (2008) 451-453.

[58] P. Patil, S.-L. Ng, I.A. Razak, H.-K. Fun, S. Dharmaprakash, 1-(4-Chlorophenyl)-3-(2, 4, 5-trimethoxyphenyl) prop-2-en-1-one, Acta Crystallographica Section E: Structure Reports Online, 62 (2006) 04448-04449.

[59] P.S. Patil, S.M. Dharmaprakash, K. Ramakrishna, H.-K. Fun, R. Sai Santosh Kumar, D. Narayana Rao, Second harmonic generation and crystal growth of new chalcone derivatives, Journal of crystal growth, 303 (2007) 520-524.

[60] E. D'silva, G.K. Podagatlapalli, S.V. Rao, S. Dharmaprakash, Structural, optical and electrical characteristics of a new NLO crystal, Optics & Laser Technology, 44 (2012) 1689-1697.

[61] 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, J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, 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, Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, D.J. Fox, Gaussian 09, Revision B.01, in, Wallingford CT, 2009.

[62] C. Lee, W. Yang, R.G. Parr, Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density, Physical review B, 37 (1988) 785.

[63] A.D. Becke, Density-functional thermochemistry. III. The role of exact exchange, The Journal of Chemical Physics, 98 (1993) 5648-5652.

[64] C. Adamo, V. Barone, Toward reliable density functional methods without adjustable parameters: The PBE0 model, The Journal of chemical physics, 110 (1999) 6158-6170.

[65] Y. Zhao, D.G. Truhlar, The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals, Theoretical Chemistry Accounts, 120 (2008) 215-241.

[66] T. Yanai, D.P. Tew, N.C. Handy, A new hybrid exchange–correlation functional using the Coulombattenuating method (CAM-B3LYP), Chemical Physics Letters, 393 (2004) 51-57.

[67] J.-D. Chai, M. Head-Gordon, Long-range corrected hybrid density functionals with damped atom– atom dispersion corrections, Physical Chemistry Chemical Physics, 10 (2008) 6615-6620.

[68] N. Sudharsana, S. Muthunatesan, G. Jasmine Priya, V. Krishnakumar, R. Nagalakshmi, Experimental and theoretical studies of 2,5-dichloroanilinium picrate, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 121 (2014) 53-62.

[69] M.E. Foster, B.M. Wong, Nonempirically tuned range-separated DFT accurately predicts both fundamental and excitation gaps in DNA and RNA nucleobases, Journal of chemical theory and computation, 8 (2012) 2682-2687.

[70] B.M. Wong, M. Piacenza, F. Della Sala, Absorption and fluorescence properties of oligothiophene biomarkers from long-range-corrected time-dependent density functional theory, Physical Chemistry Chemical Physics, 11 (2009) 4498-4508.

[71] D. Jacquemin, E.A. Perpète, G. Scalmani, M.J. Frisch, R. Kobayashi, C. Adamo, Assessment of the efficiency of long-range corrected functionals for some properties of large compounds, The Journal of chemical physics, 126 (2007) 144105.

[72] G.V. Gibbs, T.D. Crawford, A.F. Wallace, D.F. Cox, R.M. Parrish, E.G. Hohenstein, C.D. Sherrill, Role of Long-Range Intermolecular Forces in the Formation of Inorganic Nanoparticle Clusters, The Journal of Physical Chemistry A, 115 (2011) 12933-12940.

[73] R. Dennington, T. Keith, J. Millam, GaussView, version 5, Semichem Inc., Shawnee Mission, KS, (2009).

[74] T. Stein, L. Kronik, R. Baer, Prediction of charge-transfer excitations in coumarin-based dyes using a range-separated functional tuned from first principles, The Journal of chemical physics, 131 (2009) 244119.

[75] B.M. Wong, J.G. Cordaro, Coumarin dyes for dye-sensitized solar cells: A long-range-corrected density functional study, J. Chem. Phys., 129 (2008) 214703.

[76] D. Kleinman, Nonlinear dielectric polarization in optical media, Physical Review, 126 (1962) 1977.

[77] S.-L. Ng, I.A. Razak, H.-K. Fun, P. Patil, S. Dharmaprakash, V. Shettigar, A cocrystal of 1-(4-chlorophenyl)-3-(3, 4, 5-trimethoxyphenyl) prop-2-en-1-one and 3-(3-chloro-4, 5-dimethoxyphenyl)-1-(4-chlorophenyl) prop-2-en-1-one (0.95: 0.05), Acta Crystallographica Section E: Structure Reports Online, 62 (2006) o2611-o2613.

[78] L.H.D. N.B. Colthup, S.E. Wiberley Introduction to Infrared and Raman Spectroscopy, in, Academic Press, New York, 1990.

[79] G. Socrates, Infrared Characteristic Group Frequencies, in, Wiley, New York, 1980.

[80] W.G.F. F.R. Dollish, F.F. Bentley, , Characteristic Raman Frequencies of Organic Compounds, in, Wiley, New York, 1997.

[81] B.C. Smith, Infrared spectral interpretation: a systematic approach, CRC press, 1998.

[82] N.P. Roeges, A guide to the complete interpretation of infrared spectra of organic structures, Wiley, 1994.

[83] G. Varsanyi, Vibrational Spectra of Benzene Derivatives, in, Academic Press, New York, 1969.

[84] G. Varsányi, Assignments for vibrational spectra of seven hundred benzene derivatives, Halsted Press, 1974.

[85] F.A. Miller, Misassignment of the strong Raman band near 1000 cm-1 in some substituted benzenes, and the Herzberg versus Wilson convention for numbering the vibrations of benzene, Journal of Raman Spectroscopy, 19 (1988) 219-221.

[86] D. Rousseau, R.P. Bauman, S. Porto, Normal mode determination in crystals, Journal of Raman Spectroscopy, 10 (1981) 253-290.

[87] W.G. Fateley, F.R. Dollish, N.T. McDevitt, F.F. Bentley, Infrared and Raman Selection Rules for Molecular and Lattice Vibrations, The Correlation Method, (1972).

[88] G. Socrates, Infrared and Raman characteristic group frequencies: tables and charts, John Wiley & Sons, 2004.

[89] C.N.R. Rao, Ultra-violet and Visible Spectroscopy : Chemical Applications, (1974).

[90] M. Shakir, B. Riscob, K. Maurya, V. Ganesh, M. Wahab, G. Bhagavannarayana, Unidirectional growth of I-asparagine monohydrate single crystal: First time observation of NLO nature and other studies of crystalline perfection, optical, mechanical and dielectric properties, Journal of Crystal Growth, 312 (2010) 3171-3177.

[91] J. Tauc, R. Grigorovici, A. Vancu, Optical Properties and Electronic Structure of Amorphous Germanium, physica status solidi (b), 15 (1966) 627-637.

[92] J. Tauc, Optical properties and electronic structure of amorphous Ge and Si, Mater. Res. Bull., 3 (1968) 37-46.

[93] M. Shkir, H. Abbas, Z.R. Khan, Effect of thickness on the structural, optical and electrical properties of thermally evaporated PbI< sub> 2</sub> thin films, Journal of Physics and Chemistry of Solids, 73 (2012) 1309-1313.

[94] F. Urbach, The long-wavelength edge of photographic sensitivity and of the electronic absorption of solids, Physical Review, 92 (1953) 1324.

[95] M. Shakir, S. Kushwaha, K. Maurya, G. Bhagavannarayana, M. Wahab, Characterization of ZnSe nanoparticles synthesized by microwave heating process, Solid State Communications, 149 (2009) 2047-2049.

[96] M. Shakir, B. Singh, R. Gaur, B. Kumar, G. Bhagavannarayana, M. Wahab, Dielectric behaviour and ac electrical conductivity analysis of ZnSe chalcogenide nanoparticles, Chalcogenide Letters, 6 (2009) 655-660.

[97] M. Shkir, S. Aarya, R. Singh, M. Arora, G. Bhagavannarayana, T. Senguttuvan, Synthesis of ZnTe Nanoparticles by Microwave Irradiation Technique, and Their Characterization, Nanoscience and Nanotechnology Letters, 4 (2012) 405-408.

[98] D. Jacquemin, J. Preat, E.A. Perpète, A TD-DFT study of the absorption spectra of fast dye salts, Chem. Phys. Lett., 410 (2005) 254-259.

[99] D. Jacquemin, J. Preat, M. Charlot, V. Wathelet, J.-M. André, E.A. Perpète, Theoretical investigation of substituted anthraquinone dyes, The Journal of chemical physics, 121 (2004) 1736-1743.

[100] M. Cossi, V. Barone, Time-dependent density functional theory for molecules in liquid solutions, The Journal of Chemical Physics, 115 (2001) 4708-4717.

[101] R.G. Pearson, Recent advances in the concept of hard and soft acids and bases, Journal of Chemical Education, 64 (1987) 561.

[102] A. Vektariene, G. Vektaris, J. Svoboda, A theoretical approach to the nucleophilic behavior of benzofused thieno [3, 2-b] furans using DFT and HF based reactivity descriptors, Arkivoc, 7 (2009) 311-329.

[103] D.M. Bishop, Aspects of non-linear-optical calculations, Advances in Quantum Chemistry, 25 (1994) 1-45.

[104] P.N. Prasad, D.J. Williams, Introduction to nonlinear optical effects in molecules and polymers, Wiley New York etc., 1991.

[105] V.E. Ingamells, M.G. Papadopoulos, N.C. Handy, A. Willetts, The electronic, vibrational and rotational contributions to the dipole moment, polarizability, and first and second hyperpolarizabilities of the BH molecule, The Journal of chemical physics, 109 (1998) 1845-1859.

[106] S. Raptis, M.G. Papadopoulos, A. Sadlej, The correlation, relativistic, and vibrational contributions to the dipole moments, polarizabilities, and first and second hyperpolarizabilities of ZnS, CdS, and HgS, The Journal of chemical physics, 111 (1999) 7904-7915.

[107] U. Eckart, V.E. Ingamells, M.G. Papadopoulos, A.J. Sadlej, Vibrational effects on electric properties of cyclopropenone and cyclopropenethione, The Journal of chemical physics, 114 (2001) 735-745.

[108] S. Muhammad, M. Shkir, S. AlFaify, A. Irfan, A.G. Al-Sehemi, Combined experimental and computational insights into the key features of I-alanine I-alaninium picrate monohydrate: growth, structural, electronic and nonlinear optical properties, RSC Advances, 5 (2015) 53988-54002.

[109] K. Govindarasu, E. Kavitha, Vibrational spectra, molecular structure, NBO, UV, NMR, first order hyperpolarizability, analysis of 4-Methoxy-4' -Nitrobiphenyl by density functional theory, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 122 (2014) 130-141.

[110] C. Adant, M. Dupuis, J. Bredas, Ab initio study of the nonlinear optical properties of urea: Electron correlation and dispersion effects, International Journal of Quantum Chemistry, 56 (1995) 497-507.

[111] M. Karabacak, M. Cinar, FT-IR, FT-Raman, UV spectra and DFT calculations on monomeric and dimeric structure of 2-amino-5-bromobenzoic acid, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 86 (2012) 590-599.

[112] R. Raju, C.Y. Panicker, P.S. Nayak, B. Narayana, B. Sarojini, C. Van Alsenoy, A.A. Al-Saadi, FT-IR, molecular structure, first order hyperpolarizability, MEP, HOMO and LUMO analysis and NBO analysis of 4-[(3-acetylphenyl) amino]-2-methylidene-4-oxobutanoic acid, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 134 (2015) 63-72.

[113] R.N. Singh, A. Kumar, R.K. Tiwari, P. Rawat, V. Baboo, D. Verma, Molecular structure, heteronuclear resonance assisted hydrogen bond analysis, chemical reactivity and first hyperpolarizability of a novel ethyl-4-{[(2,4-dinitrophenyl)-hydrazono]-ethyl}-3,5-dimethyl-1H-pyrrole-2-carboxylate: A combined DFT and AIM approach, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 92 (2012) 295-304.

[114] K. Govindarasu, E. Kavitha, Molecular structure, vibrational spectra, NBO, UV and first order hyperpolarizability, analysis of 4-Chloro-dl-phenylalanine by density functional theory, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 133 (2014) 799-810.

[115] K. Govindarasu, E. Kavitha, N. Sundaraganesan, Synthesis, structural, spectral (FTIR, FT-Raman, UV, NMR), NBO and first order hyperpolarizability analysis of N-phenylbenzenesulfonamide by density functional theory, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 133 (2014) 417-431.

[116] G.A. Babu, P. Ramasamy, Crystal structure, crystal growth and characterization of novel organic
NLO material: 2, 4, 4' -Trimethoxybenzophenone, Materials Chemistry and Physics, 119 (2010) 533-538.
[117] J.S. Murray, K. Sen, Molecular electrostatic potentials: concepts and applications, Elsevier, 1996.

[118] E. Scrocco, J. Tomasi, Advances in Quantum Chemistry, Vol. 2, P. Lowdin, ed, in, Academic Press, New York, 1978.

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Highlights

- 1) First time, a molecular level understanding of 2,4,5TMCC has been presented.
- 2) Transparent single crystals were grown and subjected to experimental measurements.
- 3) Photophysical properties has been studied using TD-DFT approach.
- 4) First hyperpolarizability value is found to be 136 times larger than urea molecule.
- 5) Additionally, several electro-optical and thermal properties have been analyzed.