Molecular structure, linear optical, second and third-order nonlinear optical properties of two non-centrosymmetric thiophene-chalcone derivatives

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Highlights

- Two NLO active chalcones have been synthesised and optimised by DFT method.
- The molecular structures have been confirmed by experimental and theoretical methods.
- The transparency, energy gap are determined by experimental and calculation methods.
- The thermal stability, FMOs, MEP and NBO of the chalcone are studied.
- The optical limiting, second and third order NLO properties are determined.
- Dipole moment, polarizability and hyperpolarizability are compute theoretically.

Journal

Molecular Structure, Linear Optical, Second and Third-Order Nonlinear Optical Properties of Two Non-centrosymmetric Thiophene-Chalcone Derivatives

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Abstract

Two chalcones, (2E)-1-(5-bromothiophen-2-yl)-3-(3-fluorophenyl) prop-2-en-1-one (**3F5B2SC**) and (2E)-1-(5-bromothiophen-2-yl)-3-(4-methoxyphenyl) prop-2-en-1-one (**4M5B2SC**) were synthesised and crystallized by slow evaporation solution growth technique to investigate their structural, linear, thermal and nonlinear optical properties. Initially, the structures of **3F5B2SC** and **4M5B2SC** were confirmed by FT-IR and NMR (¹H and ¹³C NMR) spectroscopic studies. Detail solid state structures of these grown crystals were determined by single crystal XRD data. Both the chalcones are crystallized in the non-centrosymmetric monoclinic crystal system. The thermal analysis (DSC, TGA, DTA and DTG) revealed that **3F5B2SC** and **4M5B2SC** molecules are thermally stable upto their melting points for solid state studies. The linear optical properties of these chalcones were studied in the UV-Vis-NIR region. The estimated direct energy band gap of the molecules by Tauc's plot (4.7 eV for **3F5B2SC** and **4.2** eV for **4M5B2SC**) are comparable with HOMO-LUMO gaps. The MEP and NBO of both molecules are studied by DFT method. The second harmonic generation (SHG) efficiency of **4M5B2SC** and **3F5B2SC** determined by Kurtz-Perry powder method is found to be 5.3 and 4.2 times that of urea, respectively. Third-order NLO parameters, such as nonlinear absorption coefficient ($\beta = \sim 10^4$ cm/W), nonlinear

refractive index ($n_{2=} \sim 10^{-9} \text{ cm}^2/\text{W}$), susceptibility ($\chi^{(3)} = \sim 10^{-7} \text{ esu}$) and molecular hyperpolarizability ($\gamma_{h=} \sim 10^{-27} \text{ esu}$) were determined unambiguously from Z-scan experimental data analysis. The molecules exhibited optical limiting behaviour for continuous wave (CW) laser operating at 532 nm wavelength. Computationally, the static and dynamic dipole moment, polarizability and hyperpolarizability were determined by TD-DFT and TD-HF method. The obtained results suggest that the studied thiophene-chalcones may be used in optical device as frequency generator, optical limiters and optical switches.

Keywords: Chalcone derivatives; Single crystal XRD; Nonlinear optical materials; Z-scan technique; Optical limiting; Density functional theory.

1. Introduction

Non linear optical (NLO) materials are capturing the attention of material scientists because of their potential applications in optical fields [1, 2]. Over the few decades organic, inorganic, organo metallic and organic-inorganic hybrid materials have been explored for NLO applications [3, 4]. The realization of suitable organic materials as NLO devices, they must constituent molecules with unique properties of spatial arrangement of charge transfer chromophores and also outstanding optical and thermodynamic endurance [5].

Chalcones consist of two aromatic rings, mainly benzene, thiophene, biphenyl and pyridine groups, are linked by α , β unsaturated carbonyl system. Different electron donor/or acceptor substitution groups attached to two aromatic rings at different position leads to change in the properties of these molecules [6-9]. The numerous pharmacological activities of chalcone derivatives with electron rich thiophene heterocyclic system are subjects of great interest for researchers [10-13]. In the last decade many researchers have reported the chalcones, with bromo and sulphur atom especially in the form of thiophene ring, due to its ability to form good quality crystals with moderately higher NLO properties [14-16]. In recent years, chalcones with thiophene moiety have acquired considerable attention because of their immense tendency to crystallise in non-centrosymmetric structures, exceptional second-order (Second Harmonic Generation) and third-order (n₂, β , $\chi^{(3)}$, γ_h) NLO properties [17-20].

The numerous applications of these chalcones in the different fields and change in the properties of these chalcone with different structures inspire us to synthesise two novel chalcones (2E)-1-(5-bromothiophen-2-yl)-3-(3-fluorophenyl)prop-2-en-1-one (**3F5B2SC**) and (2E)-1-(5-bromothiophen-2-yl)-3-(4-methoxy phenyl)prop-2-en-1-one (**4M5B2SC**). We crystallised these two chalcones to find molecular structures with the help of single crystal XRD data. The structure was further confirmed by experimental and computed IR spectrum. The transparency in the visible region was determined using experimental and

calculated UV-Vis-NIR spectrum. The optical energy gap was calculated using Tauc's plot and HOMO-LUMO plots. Thermal stability and melting point were estimated by DSC and DTA/DTG/TGA graphs. The second order nonlinear optical properties were characterised and compared its efficiency with urea. The third-order NLO properties and optical limiting were characterised by Z-scan technique and different parameters were calculated. The NLO parameters dipole moment, polarizability and hyperpolarizability were computed with DFT and TDHF methods.

2. Experimental

2.1. Synthesis and crystal growth of chalcones

The chalcones reported in this research article **3F5B2SC** and **4M5B2SC** were prepared by Claisen -Schmidt condensation method [14, 19]. The given compounds were synthesised by using commercially available AR grade reactants purchased from sigma Aldrich. Solution of 5-Bromo-2-acetylthiophene (0.01 mol) dissolved in methanol (20 ml) was mixed with for **3F5B2SC** 3-fluorobenzaldehyde (0.01 mol) dissolved in methanol (20 ml) and for **4M5B2SC** 4-methoxybenzaldehyde (0.01 mol) dissolved in methanol (20 ml). Dissolved mixture in the conical flask was set for the vigorous stirring using magnetic stirrer and litle quantity of NaOH (5 ml, 20%) was added slowly to the mixture with burette. For the better yield stirring the mixture for 4 hours and the ice-cold water (250 ml) was poured into the conical flask. The conical flask was kept undisturbed for 24 hour. The product formed were filtered, repeatedly washed with distilled water, dried and purified by repeated crystallization. The reaction mechanism is displayed in Fig. 1.





The **3F5B2SC** and **4M5B2SC** samples were dissolved in acetone and a supersaturated solution was obtained at ambient temperature. The prepared solutions were filtered and filtrate was collected in the beaker. The beaker was warmed and kept undisturbed in the dust free laboratory environment. The beaker top was closed with paper to avoid quick evaporation. The defect free and good quality seed crystals were

selected for single crystal XRD analysis. The well known slow evaporation technique was used to grow large size crystals from seed crystals [20]. The grown single crystals of **3F5B2SC** and **4M5B2SC** are shown in Fig. 2.



Fig. 2. Single crystals of (a) 3F5B2SC and (b) 4M5B2SC.

2.2. Characterisation

Crystal structures of **3F5B2SC** and **4M5B2**SC were determined by single crystal X-ray diffraction method at room temperature. Each single crystal was mounted on a glass fiber with epoxy cement. X-ray measurement was carried out using Bruker APEX II DUO CCD area detector diffractometer with graphitemonochromated Mo K_a radiation (0.71073 Å). The sample-to-detector distance is 5 cm. The collected raw data were reduced by using *SAINT* program [21] and empirical absorption correction was applied by using *SADABS* program [21]. Both structures were solved by direct methods and refined by full-matrix leastsquares techniques by using SHELXTL software package [22, 23]. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were positioned geometrically and assigned isotropic displacement coefficients with a riding model, U_{iso} (H) = 1.2 U_{eq} (C) or 1.5 U_{eq} (C). The methyl group of **4M5B2SC** was applied with a rotating group model (AFIX 137). The crystal **3F5B2SC** was refined as a 2-components inversion twin with structure parameter of 0.55 (2). Molecular graphics and publications materials were prepared by *Mercury* [24] and *PLATON* [25]. The intermolecular interaction energies [26] were calculated using *Crystal Explorer* version 17.5 [27] at HF/3-21G level of theory. Crystal data, data collection and structure refinement details are summarized in Table 1.

Compound	3F5B2SC	4M5B2SC
CCDC deposition number	1897984	1897986
Molecular formula	C ₁₃ H ₈ BrFOS	$C_{14}H_{11}BrO_2S$
Molecular weight	311.16	323.20
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁	Pc
<i>a</i> (Å)	3.9815 (6)	4.0500 (4)
<i>b</i> (Å)	10.7217 (15)	16.0451 (15)
<i>c</i> (Å)	14.728 (2)	10.1569 (9)
β (°)	96.286 (2)	96.114 (2)
$V(\text{\AA}^3)$	624.92 (16)	656.27 (11)
Ζ	2	2
D_{calc} (g cm ⁻³)	1.654	1.636
Crystal dimensions (mm)	$0.39 \times 0.37 \times 0.14$	$0.41 \times 0.19 \times 0.16$
Crystal colour, shape	Yellow, plate	Yellow, block
μ (mm ⁻¹)	3.45	3.28
Radiation, λ (Å)	Μο Κα, 0.71073	Mo <i>K</i> α, 0.71073
T_{\min}, T_{\max}	0.129, 0.214	0.228, 0.282
Measured reflections	9732	7775
hkl range	$-5 \le h \le 5$	$-4 \le h \le 4$
	$-14 \le k \le 14$	$-19 \le k \le 19$
	$-19 \le l \le 19$	$-12 \le l \le 12$
θ limit (°)	1.4–28.1	2.4–25.0
Unique reflections	3035	2247
Observed reflections $[I > 2\sigma(I)]$	2273	2150
Parameters	149	164
Goodness of fit on F^2	1.04	1.06
$R[F^2 > 2\sigma(F^2)], wR(F^2)$	0.059, 0.177	0.022, 0.054

Table 1. Crystallographic data and structure refinement for 3F5B2SC and 4M5B2SC.

The IR spectrum of the synthesised **3F5B2SC** and **4M5B2SC** chalcones were obtained from FT-IR spectrometer (Nicolet 5700). The molecular structure was further verified by ¹H and ¹³C NMR spectrum using 400 MHz NMR spectrometer (JNM-ECZ4005, JOEL). Using UV-Vis-NIR spectrophotometer V670

was used to record the absorption spectrum. The melting point and thermal proficiency were analysed using Differential Scanning Calorimeter (DSC Q20) and TGA/DTA analyser (SDT Q600) at a heating rate of 10^oC /min in nitrogen atmosphere. The classical powder technique developed by Kurtz - Perry [28] was used to evaluate SHG conversion efficiency of these samples. The beam energy of the Nd:YAG laser operating at 1064 nm with 3.7 mJ/pulse beam energy, pulse width of 10ns and a repetition frequency of 10Hz was applied to the upgraded microcrystalline powder samples **3F5B2SC** and **4M5B2SC** which were tightly packed in a glass capillary.

The beam energy of the Nd: YAG laser operating at 1064 nm with 3.7 mJ/pulse beam energy, pulse width of 10 ns and a repetition frequency of 10Hz was applied to the upgraded microcrystalline powder samples **3F5B2SC** and **4M5B2SC** which were tightly packed in a glass capillary. The *Z*-scan experiment was performed using a 532 nm and 200 mW continuous wave diode-pumped solid-state laser, which was focused by a 28.6 cm focal length lens. The laser beam waist at the focus was measured to be 0.242 μ m, the Rayleigh length was 3.46 mm and laser beam input intensity at the focus 2.14X10⁸ W/m².

2.3. Computational details

The **3F5B2SC** and **4M5B2SC** are theoretical studied with the help of Gaussian 09 [29] program package and all the images and graphs are viewed by Gauss view 5.0 program [30]. The molecular structures are optimized and further these optimized structures are used to compute FTIR and NMR (¹H and ¹³C) spectrum using B3LYP/6-311+G(d,p) by DFT method. The molecular electrostatic potential (MEP) of both molecules are plotted using the same level of theory. The electronic absorption spectrum, major contribution of electronic orbits in the electron transition, global chemical reactivity descriptor (GCRD), HOMO-LHMO energies and energy gap are calculated with TD-DFT at same level of theory. The NBO analysis is done with the help of NBO 5.0 Program included in the Gaussian 16. The nonlinear optical parameters such as static dipole moment (μ), static and dynamic polarizability (α) and static and dynamic first order hyperpolarizability (β) are calculated by B3LYP/6-311+G(d,p) method with DFT [31]. using Gaussian 09. The static and dynamic second order hyperpolarizability (γ) is calculated by time dependent Hartree Fock theory (TDHF) with 6-31G method using GAMESS program package [32]. The dipole moment, polarizability, first and second hyperpolarizability are computed using x, y and z components are defined by [33, 34].

$$\mu_{total} = \sqrt{(\mu_x^2 + \mu_y^2 + \mu_z^2)}$$
(1)

$$<\alpha>=\frac{1}{3}(a_{xx}+a_{yy}+a_{zz})$$
 (2)

$$\Delta \alpha = \frac{1}{\sqrt{2}} \sqrt{(a_{xx} - a_{yy})^2 + (a_{yy} - a_{zz})^2 + (a_{zz} - a_{xx})^2 + 6a_{xz}^2 + 6a_{xy}^2 + 6a_{yz}^2}$$
(3)

$$<\beta>=\sqrt{(\beta_{xxx}+\beta_{xyy}+\beta_{xzz})^{2}+(\beta_{yyy}+\beta_{yzz}+\beta_{yxx})^{2}+(\beta_{zzz}+\beta_{zxx}+\beta_{zyy})^{2}}$$
(4)

$$<\gamma>=\frac{1}{5}\left[(\gamma_{xxxx}+\gamma_{yyyy}+\gamma_{zzzz})+2(\gamma_{xxyy}+\gamma_{xxzz}+\gamma_{yyzz})\right]$$
(5)

3. Results and discussions

3.1. Single crystal X-ray diffraction

The asymmetric unit of **3F5B2SC** and **4M5B2SC** are shown in Fig. 3. Both compounds are crystallized in the non-centrosymmetric monoclinic crystal system having different space group ($P2_1$ for **3F5B2SC** and Pc for **4M5B2SC**). The structure of both molecules *meta*-substituted fluoro group for **3F5B2SC** and *para*-substituted methoxy group for **4M5B2SC** closely resemble each other with molecule overlay RMSD of 0.0584 Å and maximum deviation of 0.1161 Å. Both molecules exist in an *trans* configuration with reference to their C6=C7 double bond as recorded by the C5—C6=C7—C8 torsion angle of -177.1(8)° and -178.3(4)° for **3F5B2SC** and **4M5B2SC**, respectively. The thiophenyl ring (S1/C1–C4) of **3F5B2SC** and **4M5B2SC** are almost co-planar to their corresponding phenyl ring (C8–C13) with dihedral angles of 4.1(5)° and 3.4(2)°, respectively. The planarity of **4M5B2SC** is marginally greater than **3F5B2SC** as signaled by its smaller RMS deviation of least-squares mean plane (excluding H atoms), i.e. 0.0683 Å for **3F5B2SC** and 0.0452 Å for **4M5B2SC**.

Both compounds show one dimensional structural similarity. The hydrogen bonded chains with $C_2^2(5)$ graph-set motifs are created *via* intermolecular C3—H3A···O1 hydrogen bonds (Table 2) in side by side fashions. However, the C3—H3A···O1 hydrogen bonds in **3F5B2SC** are considered as weak intermolecular interaction due to its longer H···O distance of 2.69 Å. In crystal **3F5B2SC** (Fig. 4a), in addition these chains are connected into two-dimensional corrugated sheet, parallel to (101) plane *via* Br1···F1 short contacts [d = 3.319(7) Å) which is shorter than the sum of *van der Waals* radii of bromine and fluorine (3.32 Å)]. In crystal **4M5B2SC** (Fig. 4b), the bromine atoms form short contact with oxygen atom of methoxy groups [d = 3.219(3) Å, which is shorter than the sum of *van der Waals* radii of Br and O (3.37 Å)], linking these hydrogen-bonded chains into two-dimensional linear sheet, parallel to (10 $\overline{2}$) plane. Both crystal structures are consolidated by weak parallel-displaced $\pi \cdots \pi$ interactions [$Cg1\cdots Cg1 = 3.982(4)$ Å, $Cg2\cdots Cg2 = 3.982(7)$ Å and 3.981(7) Å in **3F5B2SC** (Fig. 5a); $Cg3\cdots Cg3 = 4.050(3)$ Å and $Cg4\cdots Cg4 = 4.050(3)$ Å in **4M5B2SC** (Fig. 5b)] with symmetry code of -1+x, *y*, *z* and 1+x, *y*, *z*. Cg1 and Cg3 are centroid of S1/C1–C4 thiophenyl rings, Cg2 and Cg4 are centroid of C8–C13 phenyl rings.



Fig. 3. ORTEP diagram of asymmetric unit of (a) **3F5B2SC** and (b) **4M5B2SC** shown in 50% probability displacement ellipsoids with labels for non-hydrogen atoms.



Fig. 4. Partial crystal packing of (a) **3F5B2SC** and (b) **4M5B2SC** viewed along *a*-axis shows a twodimensional layer with C—H···O hydrogen bonds (cyan lines) and Br···F/O short contacts (magenta lines).



Fig. 5. Partial crystal packing of (a) **3F5B2SC** and (b) **4M5B2SC**, showing three separated layers in contrast colours with intermolecular $\pi \cdots \pi$ interactions (purple dashed lines). Hydrogen atoms not involving in the packing of the molecules have been omitted for clarity.

Compound	D—H···A	<i>D</i> —Н	$H \cdots A$	$D \cdots A$	D—H···A	Symmetry code
3F5B2SC	C3—H3A…O1	0.93	2.69	3.345 (10)	128	-x+2, y-1/2, -z+1
4M5B2SC	C3—H3A…O1	0.93	2.54	3.416 (5)	158	<i>x</i> +1, - <i>y</i> +1, <i>z</i> +1/2

Table 2 Hydrogen-bond geometry (Å)

3.2. Geometry optimization and vibrational analysis

The vibrational analysis of molecules **3F5B2SC** and **4M5B2SC** are done by experimental IR spectrum and computed IR spectrum of optimized structure. The geometry optimization of these molecules are done by DFT. The optimized structures with labelled atomic symbols and numbers are displayed in Fig. 6. The bond lengths, bond angles and dihedral angles of both chalcones calculated by DFT and experimental XRD data are in close agreement.



Fig. 6. Geometry Optimized molecular structure of **3F5B2SC** and **4M5B2SC** using B3LYP/6-311+G (d, p) level theory.

The recorded IR spectrums of the synthesised compounds and computed IR spectrum by DFT method are shown in Fig. 7. The difference between experimental and computed vibrational modes is observed. These small differences due to the experimental vibrations results are in solid phase but theoretical calculations are in the gaseous phase. It is clear that unscaled wave numbers are higher than the experimental wavenumber because of approximate nature of quantum mechanical method. The unscaled wave numbers are scaled down by a uniform scaling factor 0.967 [35] and know the scaled and experimental wave numbers are in close agreement. The comparison of experimental and calculated vibrational assignment of **3F5B2SC** and **4M5B2SC** are shown in Tables 1S and 2S (see supplementary information).

Phenyl ring vibrations

The wavenumber range of 3000-3120 cm⁻¹ were reported for aromatic CH stretching modes [36]. The CH stretching modes of **3F5B2SC** molecule is calculated in the range 3100-3073 cm⁻¹ by DFT method and observed experimental values in the range 3079-3057 cm⁻¹. The CH stretching modes of **4M5B2SC** is computed in the 3105-3043 cm⁻¹ range band observed experimental value in 3084-3057 cm⁻¹ range by IR.

The in-plane and out-of-plane CH bending were reported in the literature at wavenumber range 1300-1000 cm⁻¹ and 1000-700 cm⁻¹ [37]. In this present report CH in-plane bending modes of **3F5B2SC** molecule is calculated in the range 1471-1064 cm⁻¹ (DFT) and 1445-1103 cm⁻¹ (IR spectrum). The assigned wavenumber range for CH in-plane bending modes of **4M5B2SC** molecule is 1492-988 cm⁻¹ and observed IR experimental value 1492-974 cm⁻¹. The **3F5B2SC** molecule CH out-of-plane bending modes calculated by DFT in the range 954-769 cm⁻¹ and experimental IR spectrum avenumber range 941-844 cm⁻¹. The CH out-of-plane bending modes of **3F5B2SC** molecule is calculated in the range 945-414 cm⁻¹ and observed experimental value in the range 817-426 cm⁻¹. The calculated wave numbers range 1595-982 cm⁻¹ and experimental wave numbers range 1617-989 cm⁻¹ assigned to the **3F5B2SC** molecule corresponds to the aromatic CC stretching vibrations. The calculated wave numbers range 1594-1620 cm⁻¹ and experimental wave numbers range 1611-1032 cm⁻¹ assigned to the **4M5B2SC** molecule corresponds to the aromatic CC stretching vibrations. The CCC in-plane bending was reported in the range 1000–600 cm⁻¹ [38]. The CCC out-of-plane bending was repoted at 739 and 571 cm⁻¹. The **3F5B2SC** molecule CCC in-plane bending modes calculated by DFT in the region 982-507 cm⁻¹ and experimental IR spectrum values in the range 941-505cm⁻¹. The computed and observed experimental CCC in-plane bending modes of 4M5B2SC molecule is 988-565 cm⁻¹ and 974-697 cm⁻¹ range respectively. In the present work **3F5B2SC** molecule shows theoretical CCC out-of-plane bending vibrations at wave numbers656, 440 cm⁻¹ and experimental CCC out-of-plane bending vibrations at wave numbers667, 444 cm⁻¹. The **4M5B2SC** contributes calculated CCC out-of-plane bending vibrations at wavenumber range 945-414 cm⁻¹ and is in agreement with experimental values in the wavenumber range 739-426 cm⁻¹. The calculated vibrations by DFT method experimental IR spectrum are in good agreement.

Thiophene ring vibrations

The CH stretching vibrations were reported in the wavenumber region 3133-3076 cm⁻¹ [39]. In this report CH stretching modes of **3F5B2SC** molecule calculated at wavenumber3118, 3105 cm⁻¹ by DFT method and observed experimental value at3105 cm⁻¹ with PED 100%. The CH stretching modes of **4M5B2SC** molecule is calculated at wavenumber 3118, 3104 cm⁻¹ and observed IR value at 3100 cm⁻¹. The CH inplane and out-of-plane bending vibrations were reported earlier in the wavenumber region 1260-960 cm⁻¹ and 990-680 cm⁻¹ [40] respectively. The **3F5B2SC** shows theoretical CH in-plane bending vibrations in the range 1508-1056 cm⁻¹ and experimental vibrations are in the range 1486-1076 cm⁻¹. The **4M5B2SC** contributes calculated CH in-plane bending vibrations at wavenumber range 1510-1055 cm⁻¹ and is in agreement with experimental values in the 1509-1032 cm⁻¹. Here the present work **3F5B2SC** molecule shows theoretical out-of-plane CH bending vibrations at 868,779 and 539 cm⁻¹ and experimental vibrations are observed in the wavenumber 796 cm⁻¹. The **4M5B2SC** contributes calculated out-of-plane CH bending vibrations at 868,779 and 539 cm⁻¹ and experimental values in Page **13** of **42**

the wavenumber 926, 866 and 878 cm⁻¹. The aromatic CC stretching was reported the range between 1650 and 1200 cm⁻¹. The **3F5B2SC** molecule CC stretching modes calculated by DFT in the region1508-1056 cm⁻¹ and experimental values in the range 1486-1076 cm⁻¹. The CC stretching bending modes of 4M5B2SC molecule is calculated in the range 1510-1055 cm⁻¹ and observed experimental value in the range 1509-1198 cm⁻¹. The CCC in-plane bending was observed in the range 1000–600 cm⁻¹. In this present report calculated wave numbers in the range 1219-705cm⁻¹ and experimental wavenumber range 1103-723 cm⁻¹ corresponding to the CCC in-plane bending of **3F5B2SC** molecule. The calculated wave numbers in the range 1177-720cm⁻¹ and experimental wavenumber range 974-697cm⁻¹ corresponding to the CCC in-plane bending of **3F5B2SC** molecule. The calculated wave numbers at 868,539cm⁻¹ and experimental wavenumber range 565cm⁻¹corresponding to the CCC out-of-plane bending of **3F5B2SC** molecule. The calculated wave numbers in the range 866, 540cm⁻¹ and experimental wavenumber range 878cm⁻¹corresponding to the CCC out-of-plane bending of **3F5B2SC** molecule. The CS stretching vibrations were reported at 700 and 622 cm⁻¹ [41]. The molecule **3F5B2SC** shows calculated CS stretching at 965, 934, 718 and 657 cm⁻¹ and **3F5B2SC** molecule shows calculated CS stretching vibration at 931, 717 and 653 cm⁻¹. The CS bending vibration calculated by DFT at 965, 779, 657 and 453 cm⁻¹ for **4M5B2SC** and for **3F5B2SC** at 966, 866, 777, 697 and 653 cm⁻¹. The experimental CS stretching and CS bending vibrations obtained from IR spectrum for **3F5B2SC** molecule in the range 989-444 cm⁻¹ and for 4M5B2SC molecule in the range 974-477cm⁻¹. The calculated values obtained from DFT method and experimental values obtained from FTIR spectrums are compared and indicates the experimental and theoretical values are in close agreement [18, 41-42].

Carbonyl vibrations

The presence of carbonyl group (C=O) confirms the structure of the chalcones. The C=O stretching vibration was reported in the region 1715-1600 cm⁻¹ [43]. In this investigation C=O stretching vibration at1649 cm⁻¹ (DFT) and 1650cm⁻¹(experimental) is assigned to **3F5B2SC** and at 1641 cm⁻¹ (DFT) and 1644cm⁻¹(experimental) is assigned to **4M5B2SC**.

Other vibrations

According to literature C=C stretching mode was at about 1600 cm⁻¹ [37]. Here the C=C stretching vibration in conjugation with C=O shows the vibration at 1582cm⁻¹(calculated) and 1593cm⁻¹(experimental) for **3F5B2SC**. The C=C stretching vibration in conjugation with C=O shows the vibration at 1569 cm⁻¹(calculated) and 1587cm⁻¹(experimental) for **4M5B2SC**. The molecules **3F5B2SC**shows C-Br (thiophene ring) stretching vibration at 934, 464cm⁻¹ (DFT) and 463 cm⁻¹ (experimental). The **3F5B2SC** molecule shows C-Br (thiophene ring) stretchingvibration931, 448cm⁻¹ (DFT) and 926, 460cm⁻¹ (experimental). The molecules **3F5B2SC** shows C-F (benzene ring) stretching vibrations at 1221, 1122, 507

cm⁻¹ (DFT) and 1221, 505cm⁻¹ (experimental). The molecules **3F5B2SC** show C-F (benzene ring) stretching vibrations at 464cm⁻¹ (DFT) and 463 cm⁻¹ (experimental).

Methoxy group vibrations

The methoxy group of **4M5B2SC** has CH symmetric stretching vibrations at higher wavenumber range $3000-2925 \text{ cm}^{-1}$ and CH asymmetric stretching vibration in the lower wavenumber range 2870-2825 cm⁻¹ [44,45]. The experimental band at 3033 cm⁻¹ and theoretical band at 3036 cm⁻¹ alloted to symmetric stretching vibrations whereas the experimental band at 3004, 2933 cm⁻¹ and theoretical band at 2971, 2912 cm⁻¹ alloted to asymmetric stretching vibrations. According to literature [46, 47] the bending vibrations of methyl group are in the range 1465-1440 cm⁻¹ and 1390-1370 cm⁻¹ respectively. The in-plane CH bending vibrations are at wavenumber 1453, 1444, 1427, 1163 cm⁻¹ (theoretical) and 1463 and 1130 cm⁻¹ (experimental). The CH₃ out of plane modes along with inplane bending modes experimentally observed at 1463 and 1130 cm⁻¹ and computed at 1453, 1444, 1163 and 1169 cm⁻¹

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Fig. 7. Comparison between experimental and theoretical (B3LYP/6-311+G(d,p)) IR spectrum.

3.3. Proton and carbon NMR studies

Proton and carbon NMR spectrum of the compounds were taken by dissolving samples in chloroform. The nuclear magnetic resonance (NMR) was calculated using gauge independent atomic orbital (GIAO) at B3LYP/6-311+G (d, p). The standard chemical shift was observed with tetramethylsilane (TMS) as reference material at B3LYP/6-311+G(2d,p) method. The experimental and theoretical (DFT) peaks observed in the spectrum are compared (Figs. 8a and 8b). The protons and carbons present in both structures are identified to confirm the molecular structure formation of both chalcones. The Table 3 shows the co-relation between experimental and DFT chemical shift values, assigned to peak. The interaction between neighboring nuclei and degeneracy from magnetic field applied leads to multiple peaks in the experimental spectrum.



Fig. 8a. Experimental and theoretical ¹H NMR spectra of 3F5B2SC and 4M5B2SC.



Fig. 8b. Experimental and theoretical ¹³C NMR spectra of 3F5B2SC and 4M5B2SC.

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Table 3.

The calculated and experimental chemical shifts of 3F5B2SC and 4M5B2SC.

Proton type		3F5B2SC	Proton type		4M5B2SC
(¹ H)	DFT	Experimental	(¹ H)	DFT	Experimental
5H	7.8997	7.774	19H	8.022	7.807
21H	7.8204	7.736	6H	7.929	7.767
9H	7.512	7.587, 7.578	23H	7.539	7.576
25H	7.473	7.366, 7.357	10H	7.479	7.561, 7.555
22H	7.4187	7.301	4H	7.248	7.248
15H	7.2843	7.263	26H	7.106	7.194, 7.189
18H	7.1549	7.143, 7.131	12H	6.936	7.156, 7.122,
11H	6.9713	6.983	25H	6.643	6.925, 6.904
			21H	4.013	3.836
			29H	3.601	3.71
			22H	3.6	3.71
Carbon		3F5B2SC	Carbon type		4M5B2SC

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type (¹³ C)	DFT	Experimental	(¹³ C)	DFT	Experimental
1C	181.96	180.657	1C	182.48	180.793
16C	172.67	164.34	17C	169.1	161.983
7C	161.5	164.062	8C	162.69	158.313
12C	159.62	161.887	13C	157.81	158.303
4C	147.4	146.911	5C	148.19	147.448
13C	142.82	143.194	15C	140.94	144.65, 144.535
19C	134.54	136.879	11C	133.95	131.744, 131.523
10C	134.11	136.803	14C	132.82	131.389, 131.245
8C	131.74	137.156, 131.552	18C	131.11	130.469, 130.699
14C	125.03	126.412	9C	130.84	129.099, 127.327
20C	124.05	124.759	24C	122.89	122.45
17C	121.93	121.379	3C	115.71	114.554
3C	120.02	121.76	16C	111.83	113.769
			20C	55.19	55.523, 55.235

3.4. Thermal studies

The DSC plot (Fig. 9) displays a sharp peak at 81°C for **3F5B2SC** and 141°C for **4M5B2SC**. These sharp irreversible endothermic transitions produced reveal the melting point of the samples. The curves indicate that both samples are in the same phase before reaching the melting point. The sharpness in the peak produced by both samples indicates better crystalline nature and purity.

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In the plotted TGA/DTG/DTA curves of these samples, peak produced by DTA curve is in good agreement with peak observed by DSC curve confirms the exact melting point of these samples. In the TGA curve, sample **3F5B2SC** is stable upto temperature 240 ^oC and then weight loss is about 81.55% upto the temperature 303 °C (Fig. 10a), **4M5B2SC** is stable up to the temperature 276 °C and the temperature changes in the region 276 to 317 °C, the weight loss observed is 95.42% (Fig. 10b). The weight loss within these temperatures is due to evaporation and does not correspond to self-degradation of the samples. The TGA and DTG curves coincide at 240 ^oC (**3F5B2SC**) and 276 ^oC (**4M5B2SC**) shows stability of these compounds upto this temperature. The DTG curve exothermic peak at 277 ^oC (**3F5B2SC**) and 309 ^oC (**4M5B2SC**) indicates the weight loss due to evaporation and degradation. The peak observed in the DTA curve at 277 ^oC (**3F5B2SC**) and 309 ^oC (**4M5B2SC**) is in agreement with peak observed by DTG curve at the same temperature. These curves indicate that both the compounds

are stable before the melting point and remain in the same phase [10]. The thermal stability of these compounds prompts us that these chalcones can be used as a material for optical applications.



Fig. 9. DSC curve of 3F5B2SC and 4M5B2SC chalcones





Fig. 10. TGA/DTA/DTG curve of (a) 3F5B2SC and (b) 4M5B2SC chalcones

3.5. Linear Optical properties and optical energy gap

The recorded experimental absorption curve of **3F5B2SC** and **4M5B2SC** are depicted in Fig. 11. The maximum absorption observed at 242 and 329 nm for **3F5B2SC** and 248 and 352 nm for **4M5B2SC** are in the UV region. The absorption peaks observed from the experimental graph is in close agreement with theoretically calculated absorption peaks from DFT method. The calculated absorption peaks in the gaseous phase are at 243 and 346 nm for **3F5B2SC** and 260 and 366 nm for **4M5B2SC**. These observed peaks prove the n- π^* and π - π^* transitions and the existence of carbonyl group. In general transparency in the visible region is a characteristic feature of these chalcones and can be used as a NLO material [11]. It is clear from the figures that given samples have observed and calculated lower optical cut-off at 400 and 430 nm by **3F5B2SC** and 420 and 450 nm by **4M5B2SC** respectively and produces transparency in the remaining region. The experimental and theoretical absorption peak and cut-off wavelength values are very close. The experimental values taken in the liquid medium and computations in the gaseous phase leads to difference in the values. The π - π * transition attributed to HOMO-LUMO transitions.



Fig. 11. Theoretical and experimental UV-Vis-NIR absorption spectra of 3F5B2SC and 4M5B2SC

Table 4.

The excitation wavelength, energies, oscillator strength and major contribution for transition in **3F5B2SC** and **4M5B2SC** molecules.

Samples	The excitation	Electronic		Oscillator strengths	Major contributions of
	wavelength (nm)	transitions	Energy (eV)	\mathbf{f}_{o}	HOMO-LUMO orbital
	374.81	$S_0 \longrightarrow S_1$	3.308	0	H-2→L (97%)
F5B2SC	347.03	$S_0 \longrightarrow S_2$	3.573	0.7547	H → L (99%)
	318.34	$S_0 \longrightarrow S_3$	3.894	0.0552	H-1→L (90%)
	369.091	$S_0 \longrightarrow S_1$	3.359	0	H-2→L (97%)
M5B2SC	367.13	$S_0 \longrightarrow S_2$	3.377	0.8773	H→L (98%)
	317.99	$S_0 \longrightarrow S_3$	3.899	0.1028	H-1→L (93%)

The optical band gap (E_g) of **3F5B2SC** and **4M5B2SC** were estimated by experimental absorption data. The following relation is used to estimate band: $\alpha hv = A (hv - E_g)^{1/2}$

The optical band energy gap (E_g) was estimated by data obtained from experimental absorption spectrum. A graph of $(\alpha hv)^2$ vs hv was plotted to estimate the direct optical band energy gap (E_g) from Tauc's plot [48]. The slated straight line was extrapolated and intercepted hv-axis at $(\alpha hv)^2=0$ and the value thus obtained is $E_g= 4.7$ eV for **3F5B2SC** and 4.2 eV for **4M5B2SC**. The band gap values thus obtained as the intercept of the linear fit of $(\alpha hv)^2$ with the abscissa (Fig. 12).



Fig. 12. Tauc's plot of 3F5B2SC and 4M5B2SC.

3.6. HOMO-LUMO, GCRD and MEP

The FMOs 3D plots of **3F5B2SC** and **3F5B2SC** molecules are as dispalayed in Fig. 13. The HOMO (highest occupied molecular orbital) which can be considered as outer most orbital containing electron and acts as electron donor. The LUMO (lowest unoccupied molwcular orbital) which can be considered as inner most orbital containing free electrors and acts as electron acceptor. The HOMO-LUMO energy difference is called energy gap. The energy gap between HOMO-LUMO ($\Delta E=E_H-E_L$) for **3F5B2SC** is 3.96 eV and **3F5B2SC** is 3.69 eV. The energy gap between HOMO-1 and LUMO+1 ($\Delta E=E_{H-1}-E_{L+1}$) for **3F5B2SC** is 5.44 eV and for **3F5B2SC** is 5.47 eV. The lower value of the energy is responsible for high reactivity, chemical stability and ability of the molecule to transfer large number of electrons through π -conjugation from ground state HOMO to excited state LUMO within the molecule leads to high value of polarizability and hyperpolarizability and molecule acts as NLO active. The small HOMO-LUMO energy gap means molecule is hard. The transition of

electrons from ground state (S₀) to various excitation states (S_n) i.e. electronic excitation energies at various energy levels, oscillator strength and major percentage contributions are calculated and present in the Table 4. The excitation energy (S₀ \rightarrow S₂) for **3F5B2SC** is 3.573 eV and for **3F5B2SC** is 3.377 eV which is in agreement with experimental energy gap. The major contribution of electron transition (99% for **3F5B2SC** and 98% **3F5B2SC**) is from the ground state to first excited sate corresponds to the HOMO to LUMO transition.



Fig. 13. HOMO-LUMO plots of 3F5B2SC and 4M5B2SC

The global chemical reactivity descriptor (GCRD) parameters correlate the chemical stability and structure of the molecule [49, 50]. The HOMO and LUMO energy values of molecules are utilised to compute Ionization potential (I=-E_H) and Electron affinity (A=-E_L). The electro negativity, $\chi = (I+A)/2$ value is opposite to chemical potential, $\mu = -(I+A)/2$. The electronically stable systems have negative chemical potential values. The **3F5B2SC** and **4M5B2SC** have negative chemical potential values -4.86 and -4.395 eV respectively. The negative value of chemical potential indicates that both molecules are stable and does not decompose into its constituent elements. The positive sign of chemical potential indicate the auto-ionisation of the molecule and that leads to lower its energy. The chemical hardness (η) and chemical softness (S) of both molecules are calculated by $\eta = (I-A)/2 = (E_L - E_H)/2$ and S=1/2 η Page **24** of **42**

calculated. The chemical hardness of **3F5B2SC** and **4M5B2SC** are 1.98 and 1.84 eV respectively which are higher and hence both molecules are chemically stable. The higher value of energy gap HOMO-LUMO indicates large value of chemical hardness and small value of energy gap indicates smaller value of chemical hardness. The higher value of chemical hardness indicates that both molecules are hard and chemically stable. The smaller value of chemical hardness indicates molecule is soft and is more polarisable, because small energy required for excitation. The electrophilicity index, $\omega = \mu^2/2\eta$ of **3F5B2SC** and **4M5B2SC** are 5.96 and 5.23 eV respectively and the value is moderate, these values indicate strong energy transformation between HOMO and LUMO. The computed values (Table 5) confirm that both the chalcones shows good chemical stability and chemical strength.

Table 5

C	$E_{\rm H}$	E_{L}	E_{H-1}	E_{L+1}	$\Delta E = E_{H}$ -	Ι	Ā	χ	μ	η	S	ω
Samples	(eV)	(eV)	(eV)	(eV)	$E_L\left(eV ight)$	(eV)	(eV)	(eV)	(eV)	(eV)	(eV^{-1})	(eV)
3F5B2SC	-6.84	-2.88	-7.06	-1.62	-3.96	6.84	2.88	4.86	-4.86	1.98	0.25	5.96
4M5B2SC	-6.24	-2.55	-6.75	-1.28	-3.69	6.24	2.55	4.39	-4.39	1.84	0.27	5.23

Global chemical reactivity descriptor (GCRD) of 3F5B2SC and 4M5B2SC.

Molecular electrostatic potentials (MEP) 3D mapping predict the electrophonic and nucleophilic attack of the molecule. The MEP predicts the molecular size, molecular shape, molecular charge transfer, molecular interaction and large macroscopic properties of the molecules. The electrostatic potential on constant electron density surface is studied by well known MEP plots overlap on the total electron density using DFT method in the gaseous phase. In the plot red colour represents the atoms with negative potential due to high electron density promoting the site for electrophilic attack. The blue colour in the plot corresponds to the atoms with positive potential due to low electron density promoting the site for nucleophilic attack [51,52]. As in Fig. 14. **3F5B2SC** molecule negative electrostatic potential are localized over the proton of the molecule. In the **4M5B2SC** molecule negative electrostatic potential are localized over the carbonyl group. The positive electrostatic potential localized over proton of the molecule.



Fig. 14. MEP plots of 3F5B2SC and 4M5B2SC

3.7. Nonlinear Optical Studies

3.7.1. Second order nonlinear optical properties

The **3F5B2SC** and **4M5B2SC** crystallizes in non-centrosymmetric space group and therefore both must produce SHG. The second harmonic wave (532 nm) generated from the samples and urea were detected by photomultiplier tube and converted into electrical signal. The converted electrical signal was displayed on the oscilloscope as output signal (amplitude in volts). The output signal voltage displayed on the oscilloscope by **3F5B2SC** (275.6 mV) and **4M5B2SC** (218.4 mV) as well as reference urea (52 mV) were note down. The SHG potency of **4M5B2SC** and **3F5B2SC** are 5.3 and 4.2 times the urea respectively. The SHG efficiency of **4M5B2SC** is higher than some of the reported NLO molecules [17, 19, 53]. In general, a material with high SHG efficiency should have extensive π conjugation chain with noncentro symmetric nature. Both electron donating and accepting groups, play a major factor in increasing this type of conjugation and leads to delocalization of electrons and increases the first order hyperpolarizability.

3.7.2. Third order nonlinear optical properties

The sample dissolved in DMF solvent (0.01 M) translate along the Z-axis which is the direction of laser beam. The transmitted laser beam was collected by photo detector with aperture (closed aperture) to prove the self-defocusing [54] and without aperture (open aperture) to measure the saturable absorption. Fig. 15 gives the closed and open experimental normalized curves of **3F5B2SC** and **4M5B2SC**. The value of nonlinear phase shift $\Delta \phi$ is calculated by fitting the closed aperture experimental curve with theoretical curve obtained from the equation $T(Z) = 1 - (4X \Delta \phi)/[(X^2 + 1)(X^2 + 9)]$, here $X = Z/Z_0$, Z_0 and Z are the Rayleigh length and distance of the sample from the focus respectively. The nonlinear refractive index [55]

can be calculated by substituting this obtained value of $\Delta \phi$ in the equation $n_2 = \Delta \phi / kL_{eff} I_o$ here, L_{eff} is effective thickness, Io is intensity of the beam at the focus and k is wave vector. The nonlinear absorption coefficient β is computed by fitting the experimental open aperture using the formula $\beta = (2\sqrt{2}.\Delta T) / (I_o.L_{eff})$, here ΔT is the peak value of open aperture.

Graphically determined n_2 and β are substituted in the corresponding equations to enumerate the real, imaginary and absolute value of the third-order nonlinear optical susceptibility (χ^3) and also second order hyperpolarizability (γ_h) [56] according to the following relations.



Where, N is the density of molecules in cm⁻³. The term f is the local field factor. The ground state absorption cross section (σ_g) and excited state absorption cross section (σ_{ex}) in cm² are also calculated as suggested in the literature [57] tabulated in Table 6 along with other nonlinear parameters. The studies show that in both samples excited state absorption cross section is greater than ground state absorption cross section ($\sigma_{ex} > \sigma_g$) and it proves the reverse saturable absorption (RSA).





Fig. 25. Open aperture (a & c) and closed aperture (b & d) Z-scan curve of 3F5B2SC and 4M5B2SC chalcones.

Table 6

Third-order nonlinear parameters of 3F5B2SC and 4M5B2SC chalcones

	n ₂	β	Reχ ⁽³⁾	Imχ ⁽³⁾	$\chi^{(3)}$	γ_h	σ_{g}	σ_{ex}
Chalcone	$(cm^2 W^{-1})$	$(\mathrm{cm}\mathrm{W}^{-1})$	(esu)	(esu)	(esu)	(esu)	(cm^2)	(cm^2)
	x10 ⁻⁹	x10 ⁻⁴	x10 ⁻⁷	x10 ⁻⁷	x10 ⁻⁷	x10 ⁻²⁷	x10 ⁻²³	x10 ⁻²⁰
3F5B2SC	2.07	0.94	1.43	0.26	1.46	3.91	1.21	0.76
4M5B2SC	1.42	2.2	0.98	0.64	1.17	3.18	1.18	2.13

3.7.3. Computational Nonlinear optical studies

The microscopic origin of static and dynamic nonlinear behaviour at the molecular are studied theoretically. The DFT and TD-HF theory is used to calculate tensor components of static dipole moment (μ_{total}); static and dynamic polarizability (α); and static and dynamic hyperpolarizability (β and γ) at different frequencies. The strong donor-acceptor configuration of the molecule results in large separation between the charges and ground state dipole moment. The tensor components and total static dipole moment is displayed in Table 7. The static dipole moment of the molecules **3F5B2SC** and **4M5B2SC** is 4.75 D and 5.35 D respectively. The static dipole moment of the molecules **3F5B2SC** and **4M5B2SC** is 3.5 and 3.9 times the urea respectively [18, 58].

Table 7

Mologulog				Static dipole	Static dipole
Molecules	μ _x	μ_y	μ_z	moment (μ_{total}) a.u	moment (μ_{total}) Debye
3F5B2SC	0.184007	1.85825	0.000118	1.867338	4.75
4M5B2SC	1.826343	-1.047744	0.000157	2.105539	5.35

The electric dipole moment (μ) of $\mbox{3F5B2SC}$ and $\mbox{4M5B2SC}$ by DFT method .

The tensor x, y and z components of **3F5B2SC** and **4M5B2SC** molecules are used to obtain static polarizability $\alpha(0; 0)$ at $\omega=0$ and dynamic polarizability $\alpha(-\omega; \omega)$ at two different wavelengths are computed $\omega=0.083790$ ($\lambda=544.16$ nm), $\omega=0.042820$ ($\lambda=1064.8$ nm) and are shown in the Table 8. The static isotropic polarizability (α_0) of **3F5B2SC** and **4M5B2SC** are $3.34X10^{-23}$ and $3.8X10^{-23}$ esu and static anisotropic polarizability value of **4M5B2SC** and **4M5B2SC** are $3.81X10^{-23}$ and $4.65X10^{-23}$ esu respectively. The static polarizability value of **4M5B2SC** molecule is higher than **3F5B2SC**. The dynamic polarizability x, y and z components and also isotropic and anisotropic polarizability values. Therefore polarizability depends on the incident frequencies. The dynamic polarizability values decreases with increase in wavelength. The polarizability value is higher for **4M5B2SC** compared to **3F5B2SC**.

Table 8

Molecules	3F5B2SC			4M5B2SC		
Componento	ω=0	ω=0.08379	ω=0.04282	ω=0	ω=0.08379	ω=0.04282
Components		544.16 nm	1064.8 nm		544.16 nm	1064.8 nm
α _{xx}	389.501	503.312	410.446	460.086	630.812	489.342
α_{xy}	2.77261	4.93096	3.19298	2.0367	0.861167	1.92562
α_{yy}	186.303	198.564	189.091	196.903	209.259	199.725
α_{xz}	0.02253	0.029174	0.023749	0.003689	0.005349	0.003983
α_{yz}	- 0.004989	-0.005839	-0.005167	0.003508	0.003418	0.003504
α_{zz}	100.131	102.925	100.834	113.033	116.259	113.842
α ₀ a.u.	225.3117	268.267	233.457	256.674	318.77667	267.636
$\alpha_0 \times 10^{\text{-}23} esu$	3.34	3.98	3.46	3.80	4.72	3.97
$\Delta \alpha$ a.u.	257.387	362.2663	276.3224	313.6639	474.934296	340.790548
$\Delta \alpha \times 10^{-1}$	3.81	5.37	4.10	4.65	7.04	5.05
α_0 - Isotropicpo	olarizability,	$\Delta \alpha$ - Aniso	tropic of the pol	larizability		

The static and dynamic polarizability (α) by DFT method.

The second order nonlinearity depends on the value of first order hyperpolarizability (β). The samples second order nonlinearity can be increased by increasing the first order hyperpolarizability by substituting suitable strong electron donor-acceptor pair by increasing the intermolecular charge transfer through delocalization of electrons. The Table 9 shows static first order hyperpolarizability for **3F5B2SC** is 1.07X10⁻²⁹ esu and for **4M5B2SC** is 3.73X10⁻²⁹ esu. The static first order hyperpolarizability value of **3F5B2SC** is 28 times the urea and of **4M5B2SC** is 100 times the urea [58]. The first order hyperpolarizability values are higher than the dynamic first order hyperpolarizability due to the dependence of hyperpolarizability on the incident frequencies. Due to the strong donor OCH₃ group compared to F atom **4M5B2SC** shows higher first order hyperpolarizability value compared to **3F5B2SC**.

Table 9

Molecules	3F5B2SC			4M5B2SC		
Componente	ω=0	ω=0.08379	ω=0.04282	ω=0	ω=0.08379	ω=0.04282
components		(544.16 nm) (1064.8 nm)			(544.16 nm)	(1064.8 nm)
β_{xxx}	-703.716	-19839.4	-1607.92	3959.35	-99853.2	11105
β_{xxy}	1201.47	-21166.3	2387.7	-2018.56	60578.5	-3756.39
β_{xyy}	73.8177	-247.024	115.181	-129.736	-875.571	-210.669
β_{yyy}	-71.0135	-485.318	-60.5883	41.3197	450.59	24.433
β_{xxz}	-0.341786	0.197167	-0.704381	0.147214	-0.12151	0.345006
β_{xyz}	0.080839	-0.885549	0.151125	-0.008135	-0.428774	-0.008078
β_{yyz}	0.018246	0.030994	0.014324	0.01409	0.178192	0.021028
β_{xzz}	16.3697	103.348	19.22	5.20692	444.489	15.6934
β_{yzz}	-57.247	-159.791	-71.6372	-10.5992	-217.773	-12.048
β_{zzz}	0.000425	0.061274	0.006493	-0.017225	-0.037491	-0.022818
β_x	-613.5286	-20535.8859	-1474.9632	3834.82092	-10059.2063	10878.62662
β_y	1073.2095	-11855.853	2377.2111	-1987.8395	26555.51427	-4105.05147
β_z	-0.32311	1.42985	-0.65792	0.14408	-2.39074	0.34563
β a.u.	1236.20228	23712.52573	2797.614964	4319.416325	103523.1381	11627.37996
$\beta \times 10^{-29}$ esu	1.07	20.5	2.42	3.73	89.4	10.0

The static and dynamic first hyperpolarizability by DFT method.

The x, y and z components and second hyperpolarizability values are shown in Table 10. The calculated value of static second hyperpolarizability for **3F5B2SC** is 29.95X10⁻³⁶ esu and for **4M5B2SC** 44.1 X10⁻³⁵ esu. The static second hyperpolarizability of **4M5B2SC** is 1.4 times the **3F5B2SC**. The frequency dependent second order hyperpolarizability at ω =0.08564 a.u. (532 nm), ω =0.05695 a.u. (800 nm) and ω =0.04282 (1064 nm) are 394.35×10⁻³⁶, 1846.87×10⁻³⁶ and 81.28×10⁻³⁶ esu respectively for **3F5B2SC** and the dynamic second order hyperpolarizability γ (-3 ω ; ω , ω , ω) at ω =0.08564 a.u. (532 nm), ω =0.05695 a.u. (800 nm) and ω =0.04282 (1064 nm) are 2777.49×10⁻³⁶, 1717.29×10⁻³⁶ and 138.47X10⁻³⁶ esu respectively for **4M5B2SC**. The difference in results obtained from calculated and experimental values are due to the fact that experimental values are taken in the liquid phase whereas computations are purely electronic and carried out in gaseous phase. The second hyperpolarizability value depends on the frequency and therefore dynamic second hyperpolarizability values are higher than static. The calculated values confirm that second-order hyperpolarizability value is highest for 800 nm and for other wavelengths as the

wavelength increase hyperpolarizability decreases. The substitution of strong electron donor OCH_3 group static and hyperpolarizability values of **4M5B2SC** are greater than the **3F5B2SC**.

Table 10

Molecule	3F5B2SC				4M5B2SC			
Compone nts	ω=0	ω=0.08564 a.u. (532 nm)	ω=0.05695 a.u. (800 nm)	ω=0.04282 a.u. (1064.1 nm)	ω=0	ω=0.08564 a.u. (532 nm)	ω=0.05695 a.u. (800 nm)	ω=0.04282 a.u. (1064.1 nm)
γ_{xxxx}	271136.1	-3361923.95	17101906.3	746891.2	411497.7	18453381.5	-16641989.92	1316158.4
γ_{yyyy}	1624.42	21987.3617	-625.004	1402.37	2136.09	2349840.034	2196.6641	2415.91
γ_{zzzz}	233.58	409.0586	285.48	261.52	403.38	1001.4391	511.9005	460.07
γ_{xxyy}	11747.5	-275729.49	608474.99	28487.43	11109.02	3363490.74	-200747.38	26645.24
γ_{xxzz}	271.21	-11821.81	7490.61	507.19	527.008	-10665.22	-3809.43	885.68
γ_{yyzz}	131.51	-58.4933	338.02	178.86	194.33	31347.79	294.44	241.34
$\gamma_{total}a.u.$	59458.9	-782949.42	3666834.8	161380.4	87539.59	5514513.91	-3409561.22	274915.78
γ _{total} 10 ⁻³⁶ esu	29.95	-394.35	1846.87	81.28	44.1	2777.49	-1717.29	138.47

The static and frequency dependent second hyperpolarizability by TD-HF.

3.8. Optical limiting

The optical power limiting behaviours of the molecules are obtained from the open aperture Z-scan curve. The optical power limiting behaviour is represented by the change of normalized transmittance with respect to input fluence (J/cm^2) and is depicted in Fig. 16. At lower input power output transmittance power varies linearly and hence obeys Beer's law. At higher input value, output reaches the saturation point (limiting amplitude) called optical limiting. The optical limiting threshold values are seen at about 3.5 kJ/cm² for **3F5B2SC** and 9.5 kJ/cm² for **4M5B2SC**.



Fig. 16. Optical limiting curves of 3F5B2SC and 4M5B2SC

3.9. Natural Bond Orbital Analysis

Natural bond orbital (NBO) analysis interprets the electronic wave functions in terms of a set Lewis and a set of non-Lewis localized orbital [59]. Second order Perturbation molecular orbital (PMO) theory Fock matrix 'F(i, j)' in MBO basis indicates intra- molecular hyper- conjugative interaction of electrons as shown in Table 3S and 4S (see supplementary information). The intermolecular hyper-conjugative interactions are initiated by the orbital overlap between $\pi \to \pi^*$ orbital and this causes intra-molecular charge transfer (ITC) resulting in stabilization of the molecule. The **3F5B2SC** molecule shows hyperconjugative interactions of π (C1-O2) $\to \pi^*$ (C3-C4), π^* (C7-C8) is causing conjugation of π bonds of bromothiophene ring. The electron density (ED) at the conjugation of π bonds1.96554e of bromothiophene ring and π^* bonds (0.10291-0.34641e), shows strong π delocalization within the ring and with conjugated C1 = O2 bond stabilizing the molecule in range of 3.75-5.51 kcal/mol. In this report **4M5B2SC** molecule shows hyper-conjugative interactions of π (C1-O2) $\to \pi^*$ (C3-C5), π^* (C8-C9) is causing conjugation of π bonds of bromothiophene ring. The electron density (ED) at the conjugation of π bonds 1.96647e of bonds of bromothiophene ring. The electron density (ED) at the conjugation of π bonds 1.96647e of bromothiophene ring and π^* bonds (0.12846-0.34191e), shows strong π delocalization within the ring and with conjugated C1=O2 bond stabilizing the molecule in range of 3.63-5.51 kcal/mol. In this report **3F5B2SC** shows the hyper-conjugative interaction π (C3-C4) $\to \pi^*$ (C1-O2), π^* (C13-C14) is causing

conjugation of π bonds of fluoro-phenyl ring stabilizing the ring by 15.19- 20.15kcal/mol. The hyperconjugative interactions of π (C13-C14) $\rightarrow \pi^*(C3-C4) / \pi^*(C16-C17) / \pi^*(C19-C20), \pi$ (C16-C17) $\rightarrow \pi^*(C13-C14) / \pi^*(C19-C20), \pi$ (C19-C20)) $\pi^*(C13-C14) / \pi^*(C16-C17)$ are lead for conjugation of respective π bonds of fluoro phenyl ring. The electron density (ED) at the conjugation of π bonds (1.63489 - 1.68173e) of fluoro phenyl ring and π^* bonds (0.10291- 0.36355 e), shows strong π delocalization within the ring and with conjugated C3=C4 bond stabilizing of molecule in range of 23.26-16.11 kcal/mol. In this report **4M5B2SC** shows the hyper-conjugative interaction π (C3-C5) $\rightarrow \pi^*(C1-O2), \pi^*(C14-C15)$ is causing conjugation of π bonds of methoxy-phenyl ring stabilizing the ring by 11.42- 22.03kcal/mol. The hyper-conjugative interactions of $\pi(C8-C9) \rightarrow \pi^*(C1-O2) / \pi^*(C11-C13), \pi(C11-C13) \rightarrow \pi^*(C8-C9), \pi(C14-C15) \rightarrow \pi^*(C18-C24), \pi(C16-C17) / \pi^*(C18-C24), \pi(C18-C24), \pi(C18-C24), \pi^*(C14-C15) / \pi^*(C18-C24), \pi(C16-C17) / \sigma^*(C20-H29) / \sigma^*(C24-H26) are lead for$ $conjugation of respective <math>\pi$ bonds of methoxy phenyl ring and π^* bonds (0.01295- 0.38489e), shows strong π delocalization within the ring and with conjugated C3 = C5 bond stabilizing of molecule in range of 23.13-14.99 kcal/mol.

The interactions LP O2 $\rightarrow \sigma^*(C1-C3) / \sigma^*(C1-C7)$ are stabilizing the **3F5B2SC** molecule in the range of 18.22 -19.11 kcal/mol. LP (Br23) $\rightarrow \pi^*$ (C10-C12) stabilizes the thiophene ring with 18.14 kcal/mol through a charge transfer of 1.92681- 0.36355e. The interactions LP S6 $\rightarrow \pi^*(C7-C8) / \pi^*(C10-C7) / \pi^*($ C12) are stabilizing the thiophene ring in the range of 21.34 -25.79 kcal/mol. $\pi^*(C1-O2) \rightarrow \pi^*(C3-C4)$, $\pi^{*}(C7-C8) \rightarrow \pi^{*}(C1-O2-), \pi^{*}(C10-C12) \rightarrow \pi^{*}(C7-C8)$ and $\pi^{*}(C13-C14) \rightarrow \pi^{*}(C3-C4)$ anti-bonding interactions stabilizes the phenyl and thiophene rings with huge energies 55.65, 197.72, 156.94 and 78.23 kcal/mol through ICT causing enhanced resonance in the molecule. The interactions LPO2 $\rightarrow \sigma^*(C1-C3)$ / $\sigma^*(C1-C8)$ are stabilizing the **4M5B2SC** molecule in the range of 18.16 -18.19 kcal/mol. LP (Br28) \rightarrow $\pi^*(C11-C13)$ stabilizes the thiophene ring with 11.66kcal/mol through a charge transfer of 1.92493-0.36587e. The interactions LP S7 $\rightarrow \pi^*(C8-C89) / \pi^*(C11-C13)$ are stabilizing the thiophene ring in the range of 21.31-25.67 kcal/mol. LP (O27) $\rightarrow \pi^*(C16-C17) / \sigma^*(C20-H22) / \sigma^*(C20-H29)$ stabilizes the phenyl ring by 4.81-31.53 kcal/mol. The $\pi^*(C1-O2) \rightarrow \pi^*(C3-C5), \pi^*(C8-C9) \rightarrow \pi^*(C1-O2-), \pi^*(C11-O2-), \pi^*(C11$ C13) $\rightarrow \pi^*(C8-C9), \pi^*(C14-C15) \rightarrow \pi^*(C3-C5) \text{ and } \pi^*(C16-C17) \rightarrow \pi^*(C14-C15) / \pi^*(C18-C24)$ interactions stabilizes the phenyl and thiophene rings with huge energies 61.19, 182.46, 144.52, 108.56 and 211.39- 262.24 kcal/mol through ICT causing enhanced resonance in the molecule. The secondary hyperconjugative interactions ($\sigma \rightarrow \sigma^*$) are also stabilizes the molecule.

3.10. Structure property relationship

The molecular planarity arising potent nonlinear optical property in both compounds [60-62]. The bromine atom substituted to thiophenyl ring in both molecules and the fluorine atom substituted at *meta* position of benzene ring in **3F5B2SC** serves as weak electron acceptor. The C=O form the bridge between thiophenyl and phenyl ring encompasses a strong electron-withdrawing ability. Hence, **3F5B2SC** possess A- π -A- π -A configuration. However, a high donor methoxy group is present at the *para* position of phenyl ring in **4M5B2SC**, results A- π -A- π -D configuration. A better nonlinear absorption coefficient is found in **4M5B2SC**, which may be attributed to strong delocalization of π electrons from donor ends to acceptor ends, facilitates the charge transfer within the molecule [13, 57, 63]. The molecular structure and crystal structures accountable for optical nonlinearity. The calculated ground state cross-section is less than excited state cross-section, which meet the requirement for reverse saturable which enhance the optical limiting property.

4. Conclusions

The nonlinear optical active, promising novel chalcone derivatives 3F5B2SC and 4M5B2SC were synthesised and crystals were grown. The single crystal XRD data of structures confirm that both crystalised in non-centrosymmetric crystal system. The vibrational analysis confirms the structure formation, by experimental and computed IR spectrum. The structures of both chalcones are further verified by experimental and theoretical ¹H and ¹³C NMR spectra. The DSC studies reveal that the melting point of the given chalcones is 81°C for 3F5B2SC and 141°C for 4M5B2SC and TGA/DTA/DTG studies prove that both compounds are stable before the melting point. UV-Vis-NIR spectrum indicate the good transparency range with lower optical cut-off at 400 nm for 3F5B2SC and 420 nm for 4M5B2SC and are transparent in the entire visible region. From Tauc's plot, shows the optical band gap at 4.7 eV for 3F5B2SC and 4.2 eV for 4M5B2SC. The 4M5B2SC and 3F5B2SC have SHG efficiency value 5.3 and 4.2 times the urea. The third order nonlinear refractive index (n₂), nonlinear susceptibility ($\chi^{(3)}$) and non linear absorption coefficient (β) are of the order 10⁻⁹ cm²/W, 10⁻⁷ esu and 10⁻⁴ cm/W respectively for both chalcones. The relation $\sigma_{ex} > \sigma_g$ for both chalcones proves the reverse saturable absorption cross section. The compound exhibited good optical limiting at about 3.5 Kj/cm² for 3F5B2SC and 9.5 Kj/cm² for 4M5B2SC. The charge distribution, stability and hyper conjugation interactions are studied by MEP and NBO. The good transparency, thermal stability, optical limiting, SHG and THG efficiency of these chalcones can be used for frequency doubling, optical limiters, optical switching and other NLO applications.

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Supplementary information

Crystallographic information files of **3F5B2SC** and **4M5B2SC** were deposited at the Cambridge Crystallographic Data Centre with CCDC deposition number 1897984 and 1897986, respectively. The data can be obtained free of charge *via* http://www.ccdc. Cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033; E-mail: <u>deposit@ccdc.cam.ac.uk</u>).

Conflict of Interest

There are no conflicts to declare.

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Declaration of Interest Statement

The authors whose names are listed immediately below certify that they have NO affiliations with or involvement in any organization or entity with any financial interest (such as honoraria; educational grants; participation in speakers' bureaus; membership, employment, consultancies, stock ownership, or other equity interest; and expert testimony or patent-licensing arrangements), or non-financial interest (such as personal or professional relationships, affiliations, knowledge or beliefs) in the subject matter or materials discussed in this manuscript.

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Vasant S. Naik and Parutagouda Shankaragouda Patil conceived the manuscript, performed the data analysis, Gaussian calculations and drafted the manuscript. Qin Ai Wong and Ching Kheng Quah solved the single crystal structures and drafted the manuscript. Neelamma B. Gummagol performed the Z-scan experiment and data analysis. H. S. Jayanna supervised the findings of this work. All authors discussed the results and contributed to the final manuscript.