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# Structural, third-order optical nonlinearities and figures of merit of (E)-1-(3substituted phenyl)-3-(4-fluorophenyl) prop-2-en-1-one under CW regime: New chalcone derivatives for optical limiting applications

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#### Abstract

In the present work, the crystal structures and third-order nonlinear optical (NLO) properties of two novel chalcone derivatives, (E)-1-(3-bromophenyl)-3-(4-fluorophenyl) prop-2-en-1-one (F3BC) and (E)-1-(3-nitrophenyl)-3-(4-fluorophenyl) prop-2-en-1-one (F3NC) have been experimentally investigated. Both chalcones were synthesized by Claisen-Schmidt condensation reaction. The single-crystals were obtained from slow evaporation solution growth method and were structurally characterized by single-crystal X-ray diffraction. Both studied crystals are crystallized in centrosymmetric space groups. The existence of C—H $\cdots \pi$  interactions in F3BC and C—H…O and C—H…F hydrogen interactions in F3NC play important roles in creating supramolecular structures. The linear optical absorption coefficient ( $\alpha$ ) of F3BC and F3NC were analyzed by UV-Vis-NIR spectral analysis and the optical band gaps  $(E_g)$  were estimated. TG-DTA analysis revealed that the F3NC crystal has higher thermal stability than F3BC crystal. The third-order nonlinear optical properties of these crystals were studied in solution using Z-scan technique with a continuous wave (cw) DPSS laser operating at 532 nm wavelength. The molecules reveal a strong third-order nonlinear absorption (NLA) and negative nonlinear refraction (NLR). The calculated values of nonlinear absorption coefficient  $\beta$ , nonlinear refraction coefficient  $n_2$  and third-order nonlinear susceptibility  $\chi^{(3)}$  were found to be of the order

of  $10^{-5}$  cm/W,  $10^{-8}$  cm<sup>2</sup>/W and  $10^{-6}$  esu, respectively. The value of the two-photon absorption (2PA) cross section at 532 nm for both chalcones is of the order of  $10^{8}$  GM. These crystals also exhibited optical limiting (OL) properties under CW laser excitation.

**Keywords:** Chalcone derivatives; crystal growth; nonlinear optical materials; optical limiting; Z-scan.

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#### **1. Introduction**

Chalcones, belonging to the flavonoid family, are an important class of natural products with widespread distribution in fruits, vegetables, spices and tea [1-2]. Chemically, chalcones are 1,3-diaryl-2-propen-1-ones in which two aromatic rings, mainly benzene groups, are joined by a three-carbon bridge having a carbonyl moiety and  $\alpha$ , $\beta$ -unsaturation [3]. Chalcones are subjects of great interest for their wide range of interesting pharmacological activities, such as potential cytotoxic, antimicrobial, antiviral, anti-inflammatory, antioxidant, antimalarial, anti-HIV, antitumor and anticancer activities [4-13]. Further, many studies have shown that chalcone derivatives optically limit a high power pulsed laser beams through nonlinear absorption (NLA) mechanism, and have also been reported to exhibit negative values of nonlinear refractive index (defocusing nature) [14-16]. Along with the extensive use of continuous wave (CW) lasers at power levels ranging from mW to kW in various applications, the need of protections for the human eye and the sensors used in handling the CW output has become increasingly important [17–19]. In this context, organic molecules such as chalcone derivatives have received special attention as they have absorption bands in the visible region of electromagnetic spectrum (300-500 nm) [20-22].

Our research group was interested in preparing new organic second- and third-order nonlinear optical materials, in particular, donor-acceptor substituted chalcone derivatives with high nonlinear optical susceptibilities, for various potential applications [23-25]. We had reported the synthesis, single-crystal structures, and nonlinear optical properties of novel chalcone derivatives substituted with OCH<sub>3</sub>, N(CH3)<sub>2</sub>, NH<sub>2</sub>, F, Cl, Br, CH<sub>3</sub>, and NO<sub>2</sub>, as electron donor or acceptor [26-30]. These novel chalcone derivatives exhibited good thermal stability, brilliant second harmonic generation efficiency (SHG) and large third-order nonlinearity. The

donor and acceptor strength, nature of the  $\pi$ -conjugated group, and the symmetry have marked effects on the nonlinear properties of these derivatives [27-30].

To extend our study on nonlinear optical active molecules, two push-pull type chalcone derivatives, (E)-1-(3-bromophenyl)-3-(4-fluorophenyl) prop-2-en-1-one (**F3BC**) and (E)-1-(3-nitrophenyl)-3-(4-fluorophenyl) prop-2-en-1-one (**F3NC**) were synthesized and their molecular structures, thermal stability, linear and third-order nonlinear optical properties were studied. The main goal of this work is to highlight the capability of enhancing or modifying the optical nonlinearity by altering the substituent of these push–pull materials. In this respect, by changing the functional group of the electron accepting end while keeping the electron donating end common, we related the molecular structure with nonlinearity, a property that can be of great importance in terms of their usability in photonic applications. This study demonstrates an efficiently high nonlinear optical response of chalcone derivatives under CW regime.

#### 2. Experimental procedure

#### 2.1. Material synthesis and crystal growth

All solvents and chemicals in spectroscopic grade were obtained from Sigma-Aldrich and used without further purification. The chalcone derivatives, (E)-1-(3-bromophenyl)-3-(4-fluorophenyl) prop-2-en-1-one (**F3BC**) and (E)-1-(3-nitrophenyl)-3-(4-fluorophenyl) prop-2-en-1-one (**F3NC**) were synthesized by Claisen–Schmidt condensation reaction between substituted acetophenones and aryl aldehydes under basic conditions [19]. At room temperature, a clear ethanol solution (30 ml) of 4-fluorobenzaldehyde (0.01 mol) was slowly added into an ethanol solution (30 ml) of 3-substituted acetophenone (0.01 mol) with continuous stirring. Then, a catalytic amount of aqueous NaOH solution (10 ml) was added drop wise into reaction mixture while stirring vigorously. The stirring was continued for about 2-4 hours at room temperature. The precipitated solution was poured into ice cold water and then left overnight. The resulting product was separated and then dried. The scheme of reaction and the chemical structure of the compounds are illustrated in Fig. 1.



**Fig.1.** Schematic representation for the synthesis of (*E*)-1-(3-substituted phenyl)-3-(4-fluorophenyl) prop-2-en-1-one compounds.

The choice of solvent is the key factor to grow good quality crystals. Based on solubility test, a mixed solvent of acetone-dimethylformamide (DMF) (1:1) was used to grow **F3BC** and **F3NC** crystals. Both crystals were grown by the slow evaporation solution growth technique at ambient temperature. **F3BC** and **F3NC** were dissolved separately in a mixed solvent of acetone-DMF (1:1) and stirred well for about few minutes. To remove undissolvable impurities, the prepared solutions were filtered into separate beakers using the Whatman filter paper and covered with a good quality perforated polythene sheet. This solution is slightly warmed and allowed to evaporate at room temperature. At the period of supersaturation, tiny crystals were nucleated. They were allowed to grow into considerable size and then harvested after a period of 12-16 days (Fig. 2). The grown crystals are stable at room temperature and can be stored for indefinite period.



Fig. 2. Photograph of grown single-crystals of F3BC and F3NC.

#### 2.2. Characterization techniques

The crystal structures of the grown crystals were determined by single-crystal X-ray diffraction. Crystal data were collected on Bruker APEX II DUO CCD area-detector diffractometer using graphite monochromated Mo K<sub>a</sub> radiation ( $\lambda = 0.71073$  Å) and sample-to-detector distance of 5 cm. The single crystal ( $0.32 \times 0.21 \times 0.11$  mm<sup>3</sup> of **F3BC** and  $0.54 \times 0.48 \times 0.33$  mm<sup>3</sup> of **F3NC**) was mounted on a glass fibre with epoxy cement and was placed in the cold stream of Oxford Cryosystems Cobra open-flow nitrogen cryostat [31] operating at 100 (1) K. The collected raw data was reduced by using *SAINT* program [32] and empirical absorption correction was applied by using *SADABS* program [32]. The structures were solved by direct methods and refined by full-matrix least-squares techniques by using SHELXTL software package [33-34]. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were positioned geometrically and refined isotropically with a riding model,  $U_{iso}$  (H) = 1.2  $\times U_{eq}$  (C). Two high calculated residual densities (1.96  $e Å^{-3}$  and 2.14  $e Å^{-3}$ ) were observed at distances of 0.87 Å and 0.94 Å from atom Br1 in **F3BC**. Molecular graphics and publication materials were prepared by *Mercury* [35] and *PLATON* [36]. Crystal data and structure refinement information for the title compounds are listed in Table 1.

The UV–Vis–NIR absorption spectra were measured at room temperature with Shimadzu UV-1800 spectrophotometer. The optical energy gap was calculated from the absorption spectrum of each sample by using Tauc's plot [37]. The thermal properties were measured on simultaneous TGA/DSC Q600 thermal analyzer under flowing nitrogen gas with a heating rate of 10  $^{0}$ C min<sup>-1</sup>.

The Z-scan technique developed by Sheik-Bahae *et al.* [38] was used to measure thirdorder nonlinearities of **F3BC** and **F3NC** crystals. It is a simple and sensitive single-beam method for determining both the nonlinear refractive index ( $n_2$ ) and nonlinear absorption coefficient ( $\beta$ ) of a given material, with the advantage of immediate indication of the sign and type of the optical nonlinearity. The experiment was performed in the CW regime consisted of a diodepumped solid state laser (DPSSL) operating at 532 nm wavelength with a maximum power of 200 mW. The concentration of the solution was carefully chosen at 0.01 M before saturation. A quartz cuvette with a 1 mm path length was utilized to contain the sample solutions. This length is considerable thin compared to Rayleigh length ( $Z_R = \pi \omega_o^2/\lambda$ ) [39], *i.e.* 4.15 mm. Hence, the thickness condition could be satisfied as a thin medium for this measurement. The beam was

focused to a beam waist of 26.52  $\mu$ m with a lens of 286 mm in focal length. The sample was moved through the focal point of a laser beam along its optical axis under a computer-controlled translation stage. The reference beam and the on axis transmitted beam energy through a closedaperture (CA) or an open-aperture (OA) were simultaneously measured by a dual-channel energy meter. The distance between the detector and focus of the lens was far enough to satisfy the farfield approximation. Before measuring the samples, the system was calibrated using CS<sub>2</sub> in a cuvette as the reference. Measurements on pure solvent (DMF) in a cuvette were also performed, validating that the measured nonlinearities were originated from chalcone derivatives only.

#### 3. Results and discussion

#### **3.1. Structural description**

#### 3.1.1. Crystal structure of (E)-1-(3-bromophenyl)-3-(4-fluorophenyl) prop-2-en-1-one

The asymmetric unit of **F3BC** consists of a (*E*)-1-(3-bromophenyl)-3-(4-fluorophenyl) prop-2-en-1-one molecule as shown in Fig. 3. The molecule is non-planar and it adopts a *trans* configuration with respect to C8—C9 double bond (C7—C8—C9—C10 = 177.9 (2)°). The phenyl rings are twisted away from each other by a dihedral angle of 47.74 (11)°. In crystal (Fig. 4), type I Br…Br contact (d = 3.6439 (4) Å,  $\angle$ C4—Br1…Br1 = 144.01 (7)°, symmetry operation: -x, -y+2, -z) which is shorter than the sum of *van der Waals* radii (3.70 Å) is observed. The crystal structure is stabilized by weak C—H… $\pi$  interactions (Table 2), involving the centroids of phenyl rings.



**Fig. 3.** ORTEP diagram of asymmetric unit of **F3BC** shown in 50% probability displacement ellipsoids with labels for all non-H atoms.



**Fig. 4.** Partial crystal packing of **F3BC** shows C—H $\cdots \pi$  interactions (cyan dashed lines).

Crystallographic data and structure refinement for F3BC and F3NC crystals

Crystal	F3BC	F3NC
CCDC deposition number	1484019	1484020
Molecular formula	C <sub>15</sub> H <sub>10</sub> BrFO	$C_{15}H_{10}FNO_3$
Molecular weight	305.14	271.24
Crystal system	Triclinic	Monoclinic
Space group	$P\overline{1}$	$P2_{1}/n$
<i>a</i> (Å)	5.8655 (4)	7.1637 (4)
<i>b</i> (Å)	7.4169 (4)	16.0507 (10)
<i>c</i> (Å)	14.0323 (9)	21.2846 (13)
α (°)	90.8150 (18)	90
β (°)	97.0297 (17)	99.4748 (9)
γ (°)	92.5693 (17)	90
$V(\text{\AA}^3)$	605.14 (7)	2414.0 (3)

2	8
1.675	1.493
$0.32 \times 0.21 \times 0.11$	$0.54 \times 0.48 \times 0.33$
Yellow, plate	Orange, block
3.39	0.12
Mo <i>K</i> α, 0.71073	Μο Κα, 0.71073
0.225, 0.329	0.820, 0.907
21041	49976
$-8 \le h \le 8$	$-9 \le h \le 9$
$-10 \le k \le 10$	$-21 \le k \le 21$
$-19 \le l \le 19$	$-28 \le l \le 29$
1.5–29.4	1.6–29.3
3306	6532
3022	5794
163	361
1.06	1.04
0.035, 0.092	0.055, 0.156
	2 1.675 $0.32 \times 0.21 \times 0.11$ Yellow, plate 3.39 Mo Ka, 0.71073 0.225, 0.329 21041 $-8 \le h \le 8$ $-10 \le k \le 10$ $-19 \le l \le 19$ 1.5-29.4 3306 3022 163 1.06 0.035, 0.092

Hydrogen-bond geometry (Å, °) in F3BC

D—H···A	<i>d</i> ( <i>D</i> —H)	$d(\mathbf{H}\cdots A)$	$d(D \cdots A)$	$\angle D$ —H···A	Symmetry code
C2—H2 $A$ ···· $Cg2$	0.95	2.85	3.488 (2)	126	- <i>x</i> +2, - <i>y</i> +2, - <i>z</i> +1
C5—H5A…Cg2	0.95	2.87	3.535 (2)	128	- <i>x</i> +1, - <i>y</i> +1, - <i>z</i> +1
C14—H14A····Cg1	0.95	2.81	3.501 (2)	130	- <i>x</i> +2, - <i>y</i> +1, - <i>z</i> +1

Cg1 and Cg2 are the centroids of C1–C6 and C10–C15 phenyl rings, respectively.

#### 3.1.2. Crystal structure of (E)-1-(3-nitrophenyl)-3-(4-fluorophenyl) prop-2-en-1-one

The asymmetric unit of **F3NC** consists of two crystallographically independent molecules (*A* and *B*) as shown in Fig. 5. The molecular conformations of both molecules are highly similar with overlay RMS deviation of 0.2067 Å and maximum deviation of 0.5542 Å. The phenyl rings are nearly co-planar as indicated by dihedral angles of 2.51 (5)° and 10.65 (5)° in molecules *A* and *B*, respectively. In crystal (Fig. 6), molecules *A* and *B* are connected by weak intermolecular C—H…O hydrogen bonds into two-fold (along *b*-axis) related dimers

incorporated with  $R_2^1(6)R_2^2(10)R_2^1(6)$  graph-set motif [40]. Each dimer is surrounded by six adjacent dimers *via* intermolecular C—H···O and C—H···F interactions (Table 3) into two-dimensional supramolecular layers parallel to (101).



**Fig. 5.** ORTEP diagram of asymmetric unit of **F3NC** shown in 50% probability displacement ellipsoids with labels for all non-H atoms.



**Fig.6.** Partial crystal packing of **F3NC** viewed along *a*-axis shows a supramolecular layer constituted by molecules A (green) and B (blue) under hydrogen interactions (cyan lines).

D—H···A	<i>d</i> ( <i>D</i> —H)	$d(\mathbf{H}\cdots A)$	$d(D \cdots A)$	$\angle D$ —H···A	Symmetry code
C9A—H9AA…O1B	0.95	2.55	3.4144 (14)	152	-x+1/2, y+1/2, -z+3/2
C11A—H11A…O1B	0.95	2.39	3.2806 (13)	156	-x+1/2, y+1/2, -z+3/2
C11 <i>B</i> —H11 <i>B</i> ⋯O1 <i>A</i>	0.95	2.37	3.2625 (13)	156	- <i>x</i> +1/2, <i>y</i> -1/2, - <i>z</i> +3/2
C9 <i>B</i> —H9 <i>BA</i> ⋯O1 <i>A</i>	0.95	2.54	3.3956 (13)	149	- <i>x</i> +1/2, <i>y</i> -1/2, - <i>z</i> +3/2
C14A—H14A…F1B	0.95	2.51	3.4532 (12)	173	- <i>x</i> +1/2, <i>y</i> -1/2, - <i>z</i> +3/2
C14 <i>B</i> —H14 <i>B</i> ····F1 <i>A</i>	0.95	2.54	3.4837 (12)	172	-x+1/2, y+1/2, -z+3/2
C15A—H15A…O2B	0.95	2.52	3.4670 (14)	174	- <i>x</i> +1, - <i>y</i> , - <i>z</i> +1
C15 <i>B</i> —H15 <i>B</i> ····O2 <i>A</i>	0.95	2.49	3.4252 (14)	170	- <i>x</i> +1, - <i>y</i> +1, - <i>z</i> +1

Hydrogen-bond geometry (Å, °) in F3NC

### 3.2. Thermo-gravimetric and differential thermal analysis

The TGA and DTA curves of two chalcone crystals are shown in Figure 7. The TGA traces show the first minor weight loss before the melting temperature illustrates the loss of physically absorbed moisture and volatile solvents during the crystallization. On the other hand, it was observed total sample degradation at temperatures higher than that of the melting point for the chalcones under investigation. In DTA curves, sharp first endothermic peaks at 108.5  $^{\circ}$ C (Fig.7a) and 177.0  $^{\circ}$ C (Fig.7.b) are corresponding to the melting point of **F3BC** and **F3NC**, respectively. The broad endothermic peak of **F3BC** and **F3NC** at 276.0  $^{\circ}$ C and 308.9  $^{\circ}$ C in DTA curves are found to be matching with the corresponding major weight loss of about 82.95% and 98.77% in TGA curves. These major weight losses are due to the decompositions of the materials. No residual product was left after the complete heating process in which the temperature reached 1000  $^{\circ}$ C. The decomposition mechanism clearly indicates that the **F3NC** has higher thermal stability than **F3BC** chalcone. **F3NC** has relatively high melting point, which suggests that it may have high thermal damage threshold and hence is a promising candidate for NLO application.



Fig. 7.TG/DTA curves of F3BC and F3NC crystals.

#### 3.3. Linear absorption and optical energy gap

Optical material can be of practical device use only if it has a lesser absorption of light in the Vis-NIR region. The linear absorption spectra of **F3BC** and **F3NC** are represented in Fig. 8. Clearly, both of them show two strong peaks in the UV-region, which are due to  $\pi$ - $\pi$ \* and n- $\pi$ \* electronic transitions. The  $\pi$ - $\pi$ \* and n- $\pi$ \* transitions are attributable to the presence of aromatic ring and C=O group, respectively. Unsaturated molecules that contain oxygen undergo n- $\pi$ \* transition due to the presence of non-bonding electrons in the oxygen atom [41]. In both chalcones, different substituents (bromo and nitro) are attached at the *meta* position of terminal phenyl ring which is nearer to the carbonyl group. Such varying substitution brings notable changes in the light absorption in these molecules due to their different electron donating and accepting abilities. The chalcones **F3BC** and **F3NC** with electron accepting substituents showed a notable bathochromic shift in the absorption maxima. The chalcone **F3NC**, having the strong electron accepting nitro group, showed a well pronounced absorption band. Note that both chalcones are transparent at the wavelength of Z-scan measurements (532 nm).

The optical energy gap was calculated from the absorption spectrum of each sample (Fig. 8) using Tauc's relationship as follows [42].

$$ahv = a_0 (hv - E_g)^n \tag{1}$$

where  $\alpha_0$  is a band tailing constant parameter and it is an energy independent constant,  $E_g$  is the optical energy gap, and *n* is called the power factor of the transition mode. The value of *n* is dependent upon the nature of the material, whether it is crystalline or amorphous, and the photon transition. The values of *n* for direct allowed, indirect allowed, direct forbidden and indirect forbidden transitions are 1/2, 2, 3/2 and 3, respectively. After the plotting of all power probabilities of 1/2, 2, 3/2 or 3 versus the photon energy (*hv*) for the present crystalline chalcone derivatives, the results showed the most suitable and adequate plot is that when n = 1/2. Therefore, Tauc's relation is in the form of  $(\alpha hv)^2 = \alpha_0 (hv \cdot E_g)$  for direct allowed band gap. To determine the optical energy gap, a graph which illustrates the relationship between  $(\alpha hv)^2$  and photon energy (*E*) was plotted, using the data obtained from the optical absorption spectra (Fig. 8.). In order to obtain the value of the direct allowed optical energy gap (*Eg*), the slanted straight line was extrapolated and intercepted *E*-axis at  $(\alpha hv)^2 = 0$  (insets of Fig. 8). The estimated values of the energy gaps were tabulated in Table 4.



Fig. 8. Normalized electronic absorption spectrum of DMF solutions of (a) F3BC and (b) F3NC at room temperature. Inset contains the plot of  $(\alpha hv)^2$  against photon energy (*E*).

Absorption maximum, band gap  $(E_g)$  and melting point for **F3BC** and **F3NC** crystals.

Compound	Absorption maximum $\lambda_{max}$ (nm)	Band Gap $E_g$ (eV)	Melting Point ( <sup>0</sup> C)	~
F3BC	375	3.03	108.45	
F3NC	396	3.00	177.01	ζ

#### 3.4. Nonlinear absorption and refraction

Fig. 9 shows the normalized OA and CA Z-scan curves obtained from DMF solutions of F3BC and F3NC chalcones with CW DPSS laser as a source. The OA curves of both chalcones (Fig.9 a &b) indicate strong nonlinear absorption of the incident laser beam, which is attributed to strong reverse saturation absorption (RSA) as the excited state absorption cross sections are higher than the ground state absorption cross sections (Table 5). The CA curves for both the chalcones exhibited a pre-focal peak followed by a post-focal valley configuration. This peakvalley configuration indicates that the nonlinear refractive index is negative ( $n_2 < 0$ ) which gives rise to the self-defocusing property possessed by these chalcones. The self-defocusing effect is due to local variation of refractive index with temperature. The possible mechanism can be explained as follows. Beginning as far from the focus (Z < 0), the beam irradiance is low and nonlinear refraction is negligible, which makes the measured transmittance to remain constant (*i.e.*, Z-independent). As the sample tends towards Z = 0, irradiance increases, leading to selflensing in the sample. A negative self-lens due to the nature of the material before the focal plane tend to collimate the beam on the aperture and thereby increases the measured transmittance. After the focal plane, the self-defocusing increases the beam divergence, leading to widening of the beam at the iris and thus reducing the measured transmittance. Far from focus (Z > 0), again the nonlinear refraction is low, resulting in a transmittance Z-independent. Thus, a pre-focal transmittance maximum (peak), followed by a post-focal transmittance minimum (valley) is a Zscan signature of a negative nonlinearity of the materials. The large value of the phase shift (2.8) along with the fact that the source laser is CW suggests that the origin of the nonlinear refractive index is thermo-optic.

The laser beam induced absorption and refraction changes are given by the relationships,  $\alpha(I) = \alpha_0 + \beta I$  and  $n(I) = n_0 + n_2 I$ , respectively. The magnitudes of  $n_2$ ,  $\beta$ , and real and

imaginary parts of third-order nonlinear optical susceptibility  $\chi^{(3)}$  can be calculated from the standard Z-scan relations as follows. The difference between peak and valley transmittances,  $\Delta T_{p-\nu}$ , is given by [38]

$$\Delta T_{p-\nu} = 0.406(1-S)^{0.25} |\Delta \phi_0| \qquad (2)$$

where  $|\Delta \phi_0|$  is the on-axis phase shift at the focus and *S* is the linear transmittance of the aperture in the absence of a sample which is obtained using the following relationship

$$S = 1 - exp\left(\frac{-2r_a^2}{\omega_a^2}\right) \tag{3}$$

Where,  $r_a$  is the radius of the aperture and  $\omega_a$  is the laser beam radius at the entrance of the aperture.

The third-order nonlinear refractive index  $(n_2)$  of the chalcones were calculated using closed aperture data, and it is given by

$$n_2 = \frac{\Delta \phi_0}{K I_0 L_{eff}} \tag{4}$$

Where  $K (= 2\pi/\lambda)$  is the wave vector,  $I_0 (= 2P/\pi w_0^2)$  is the intensity of the laser beam at the focal point (Z = 0). The L<sub>eff</sub> is the effective length of the sample and is given by

$$L_{eff} = 1 - \exp(-\alpha L)/\alpha \tag{5}$$

Where, *L* is the sample length.

The third-order nonlinear absorption coefficient ( $\beta$ ) can be determined using OA Z-scan data by the following relation

$$T(Z) = 1 - \frac{\beta I_0 L_{eff}}{2\sqrt{2} \left(1 + \frac{Z^2}{Z_0^2}\right)}$$
(6)

Where, T(Z) is the normalized transmittance and  $Z_0$  is the Rayleigh range.

The real and imaginary parts of the third-order nonlinear optical susceptibilities of chalcones can be obtained by the following equations

$$\chi_{\rm R}^{(3)}(\rm esu) = \frac{cn_0^2}{120\pi^2}n_2 \quad (m^2/W) \quad (7)$$
  
$$\chi_{\rm I}^{(3)}(\rm esu) = \frac{c^2n_0^2}{240\pi^2\omega}\beta \quad (m/W) \quad (8)$$

The measured values of  $\chi_{\rm R}^{(3)}$  and  $\chi_{\rm I}^{(3)}$  for both chalcones are of the order of 10<sup>-6</sup> and 10<sup>-8</sup> esu, respectively, which are comparable to other organic materials [43]. The absolute value of the third-order nonlinear optical susceptibility  $\chi^{(3)}$  can be calculated by the equation  $|\chi^{(3)}| =$ 

 $\sqrt{\chi_R^{(3)^2} + \chi_I^{(3)^2}}$ . The obtained values are of the order 10<sup>-6</sup> esu, indicating the large third-order nonlinear optical properties in **F3BC** and **F3NC**, using CW laser excitation.

The molecular second-order hyperpolarizability  $\gamma$  can be calculated by the equation

$$\gamma_h = \frac{\chi^{(3)}}{[(1/3)(n_0^2 + 2)]^4 N} \tag{9}$$

where,  $N = N_A C \times 10^{-3}$ , is the number density of molecules in unit volume,  $N_A$  is the Avogadro's number and *C* is the concentration of the solution in moles. The calculated second-order hyperpolarizabilities are tabulated in Table 5.

The observed nonlinear response (Table 5) can be explained based on the electron accepting ability of the groups present in the molecule [44]. In the molecular structures of both chalcones, para-position of phenylene ring is substituted by fluoro group as electron donor followed by a  $\pi$ -bond and carbonyl group as an acceptor and *meta*-position of benzoyl ring with -Br and -NO<sub>2</sub> substituents at the other end as donor and acceptor, respectively. Hence, the synthesized molecules possess a D- $\pi$ -A- $\pi$ -D (F3BC) and D- $\pi$ -A- $\pi$ -A (F3NC) type of arrangement, where charge transfer takes place from the donor ends to the acceptor ends of the molecules, leading to nonlinearity. As given in Table 5, it is found that F3NC show larger optical nonlinearity than F3BC, as expected, due to the higher acceptor strength of F3NC. In D-A compounds, nonlinearity is mainly due to the charge transfer from the donor to the acceptor unit, *i.e.* the strong delocalization of  $\pi$ -electrons. Effective charge transfer depends on the molecular planarity and the twist in molecular conformation may result in an ineffective charge transfer leading to decrease in NLO response [29]. The planarity of the molecule increases the delocalization of electrons and therefore enhances hyperpolarizability. It is clear that the charge transfer is more effective in F3NC with higher molecular planarity. The nonlinear optical parameters of present chalcones are comparable with the recently reported results under CW regime (Table 6).

The excited state absorption cross section ( $\sigma_{ex}$ ) and the ground state absorption cross section ( $\sigma_g$ ) determine whether the absorption is saturable or reverse saturable. If the excited state cross section is greater than the ground state cross section, then the absorption is reverse saturable, otherwise, it is saturable absorption. Using the open aperture Z-scan data, the excited state absorption cross section  $\sigma_{ex}$  can be estimated by the relation,

$$T = \ln[1 + \frac{q_0}{1+x^2}] / (\frac{q_0}{1+x^2})$$
(10)

where,  $x = Z/Z_0$ ,  $q_0 = \alpha_0 \sigma_{ex} F_0 L_{eff}/2hv$ ,  $F_0 = 2E/\pi \omega_0^2$  is the laser fluence at focus point and hv is the incident photon energy. The ground state absorption cross section which is proportional to the linear absorption coefficient and concentration of the solution can be calculated by the relation  $\sigma_g = \alpha_0/N_AC$ . The calculated ground-state absorption cross section and the excited-state absorption cross section of **F3BC** and **F3NC** are in agreement with the conditions for observing RSA and indicates that the nonlinearity here is associated with RSA ( $\sigma_{ex} > \sigma_g$ ) (Table 5).

For a molecular system, the two-photon absorption cross section,  $\sigma_{2PA} = hv\beta/NC \times 10^{-3}$  (cm<sup>4</sup> s photon<sup>-1</sup> molecule<sup>-1</sup>), describes the efficiency of a particular molecule in the ground state to reach the excited state *via* a two-photon absorption process. It can be expressed in the SI unit (GM) and defined as 1 GM = 10<sup>-50</sup> cm<sup>4</sup> s photon<sup>-1</sup> molecule<sup>-1</sup>. The calculated values of 2PA cross-section of **F3BC** and **F3NC** are 3.41 x 10<sup>8</sup> and 0.74 x 10<sup>8</sup> GM, respectively.



**Fig.9.** Normalized OA (a & b) and CA (c & d) Z-scan curves of DMF solution of **F3BC** (left column) and **F3NC** (right column) at 0.01 M concentration.

Sample	α0	β	$n_2$	Re $\chi^{(3)}$	Im χ <sup>(3)</sup>	χ <sup>(3)</sup>	γh	$\sigma_{g}$	$\sigma_{ex}$	<b>σ</b> <sub>2PA</sub>	1P	2P
	( <b>cm</b> <sup>-1</sup> )	(cmW <sup>-1</sup> )	(cm <sup>2</sup> W <sup>-1</sup> )	(e.s.u)	(e.s.u)	(e.s.u)	(esu)	( <b>cm</b> <sup>2</sup> )	( <b>cm</b> <sup>2</sup> )	(GM)	(W)	<b>(T</b> )
		x 10 <sup>-5</sup>	x 10 <sup>-8</sup>	x 10 <sup>-6</sup>	x 10 <sup>-8</sup>	x 10 <sup>-6</sup>	x 10 <sup>-26</sup>	x 10 <sup>-24</sup>	x 10 <sup>-23</sup>	x 10 <sup>8</sup>		
F3BC	0.035	5.5	-0.45	-0.38	1.99	0.38	1.57	0.58	88	3.41	43.3	0.66
F3NC	0.082	1.2	-1.31	-1.13	0.44	1.13	4.64	1.36	7.8	0.74	54.6	0.05

Third-order nonlinear optical parameters and figures of merit (?? and ??) for **F3BC** and **F3NC** in DMF with a concentration of 0.01 M at 532 nm laser excitation.

Recently reported  $\beta$  and  $n_2$  values of different materials with CW laser excitation.

Sl.No.	Materials	β (cmW <sup>-1</sup> )	$n_2 ({\rm cm}^2 {\rm W}^{-1})$	References
1	Fast green FCF dye	6.5 x 10 <sup>-5</sup>	$3.2 \times 10^{-8}$	[45]
2	Organic dye Nile blue	1.35 x 10 <sup>-5</sup>	$0.42 \text{ x} 10^{-8}$	[46]
3	Basic violet 16 dye	-1.38 x 10 <sup>-3</sup>	2.81 x10 <sup>-8</sup>	[47]
4	Semiconductor ZnS	$-3.2 \times 10^{-3}$	1.38 x10 <sup>-8</sup>	[48]
	nanoparticles			
5	DMPM4NBCHM	$8.62  imes 10^{-4}$	$-7.82  imes 10^{-8}$	[49]
	(Hydrazone)	(514 nm)	(514 nm)	
		$9.53\times10^{-3}$	$-3.39 \times 10^{-7}$	
		(488 nm)	(488 nm)	

## 3.5. One-photon (W) and two-photon (T) figures of merit

Two figures of merit were used to estimate whether the materials can be used as alloptical switching. They are one-photon ( $W=n_2I/\alpha_0\lambda$ ) and two-photon ( $T=\beta\lambda/n_2$ ) figures of merit [50]. According to the requirements, it is necessary to achieve W > 1 and T < 1. The determined W and T values satisfy the requirements for the application of all-optical switching devices (Table 5) [51].

#### 3.6. Optical Limiting (OL)

Optical limiters are devices which are transparent at low input intensities, but become opaque at high inputs, used for the protection of eyes and sensitive optical devices from laser induced damage. The OL property of the chalcones was investigated by using the OA Z-scan data. Fig. 10 shows the transmitted energy of chalcones as a function of input intensity. **F3BC** and **F3NC** show strong optical limiting behavior as the samples transmittance decreases with increase in the pump intensity (Fig. 10). The optical limiting threshold is determined to be 7.41 kW/cm<sup>2</sup> and 1.92 kW/cm<sup>2</sup> for **F3BC** and **F3NC**, respectively. **F3NC** showed better OL response than **F3BC** since the lower OL threshold means the better OL performance of a material. Optical limiting was proved to be varied according to the extent of acceptor strength. This is consistent with the physical origin of nonlinear absorption in the compounds.



Fig.10. Optical limiting behavior of (a) F3BC and (b) F3NC.

#### 4. Conclusions

In summary, third-order nonlinear optical properties of two donor-acceptor chalcone derivatives in DMF solution were investigated using the Z-scan technique under the CW laser. The study of third-order NLO properties reveals that the two chalcones exhibit similar nonlinear

absorption and self-defocusing behaviors in DMF solution. The three-dimensional crystal structures of newly grown chalcones were confirmed by single-crystal XRD analysis. Through chemical substitution, we were able to systematically discern the effects of structural units on the NLO properties. The TGA/DTA study shows that the grown crystals are thermally stable up to their melting point. The ideal one- and two-photon figures of merit suggest that these chalcones should be desirable for potential applications in photonic devices. The molecules exhibit good optical limiting properties at 532 nm. All the above results suggest that the grown crystals can be utilized for NLO applications ranging from UV to near-IR.

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#### Appendix A. Supplementary information

Crystallographic information file of **F3BC and F3NC** was deposited at the Cambridge Crystallographic Data Centre with CCDC deposition number 1484019 and 1484020, respectively. These 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>).

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## Highlights

► Donor-Acceptor substituted two chalcone derivatives were prepared and were structurally characterized by single crystal XRD. ► They exhibited enhanced nonlinear absorption, refraction and optical limiting (OL) action under continuous wave (532 nm) laser illumination. ► The molecules possess optical limiting properties. ►  $\chi^{(3)}$  is of the order of 10<sup>-6</sup> esu in the CW regime.