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## **Graphical Abstract**

Four novel new halogenated chalcones are successfully synthesized and characterized using IR, <sup>1</sup>H and <sup>13</sup>C NMR and UV-Vis methods. The compounds have been solved and refined using X-ray single crystal diffraction data. The geometrical parameters results are compared with density functional theory (DFT) method with B3LYP/6-311G++ (d,p) level. The energy gaps are obtained for all compounds and the Mulliken analysis was also theoretically computed. The nonlinear optical (NLO) analysis is performed by calculating the third-order nonlinear polarizability.



# New halogenated chalcones: Synthesis, crystal structure, spectroscopic and theoretical analyses for third-order nonlinear optical properties

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**Abstract:** *The halogen chalcones have* been prepared by a simple condensation reaction of 4-bromoacetophenone with different substituted halogen benzaldehydes by presence of catalyst of sodium hydroxide. The proposed structures were solved and refined by single crystal X-ray diffraction analysis and the optimized molecular structure at the ground state were further performed using density functional theory (DFT) method with B3LYP/6-311G++(d,p) basis set level. The supramolecular C—H···O, C—H···Cl and C—H···π hydrogen bonds and halogen···halogen interactions observed stabilize and strengthen the crystal structure of the halogen chalcones. All the newly synthesized compounds were characterized by spectroscopic methods including, FT-IR, <sup>1</sup>H and <sup>13</sup>C NMR and UV-Visible. The experimental geometrical parameters were compared with the calculated TD-DFT, where the values are in good agreement. All compounds exhibiting a good HOMO-LUMO energy gap values in a range of 4.0 and 4.2 eV. Additionally, Hirshfeld surfaces analysis was used to quantify the intermolecular interactions and to analyze intercontacts in the crystal structure. Results revealed mono-substitution molecules with *ortho* position will give a high impact on electronic dipole moment, thus offering a better quality NLO properties of the compounds.

Keywords: Halogen chalcones, Crystal structure, Hirshfeld surface, DFT, Nonlinear optical property

#### 1. Introduction

Chalcones are natural or synthetic compounds belonging to the flavonoid family with widespread distribution in vegetables, fruits and spices and are present in a variety of plant species [1] Chemically, they consist

of open-chain flavonoids in which two aromatic rings are joined by a three carbon  $\alpha,\beta$ -unsaturated carbonyl system. Chalcones have been reported to possess many pharmacological activities [2] including anti-inflammatory [3], *antituberculosis* [4], antifungal [5], anticancer [6, 7], analgesic, antipyretic, antioxidant [8, 9], antibacterial, anti-HIV [10, 11], antimalarial [12, 13], antiprotozoal activities [14], antimutagenic, *antitumorigenic* [15] and antileishmanial [16, 17] properties. Many chalcones have been described for their high anti-malarial activity [18].

Recently, many organic crystals have also been found to be capable of showing strong third-order nonlinear optical (NLO) properties. Chalcone have been subjected to extensive study with regards to their potential applications in optical communications, data processing, optical switching and optical power limiting [19-21]. The essential feature for large NLO responses in organic molecules arises from highly delocalized  $\pi$ -electron systems and the strength of substituent groups in terms of their donor (D) or acceptor (A) nature [22]. Recently, many researchers work on halogens to study the chemical and physical properties of organic materials in accordance to the nonlinear optical characteristics. The introduction of halogen atom can modify physical and optical properties along with chemical reactivity of organic compounds. The high NLO responses can be found mostly in organic molecules possessing an electron donor (D) group and an electron acceptor (A) group which promotes the charge-transfer process [23, 24]. For instance, the chalcone derivatives representing D- $\pi$ -A configuration [25-27], suggest promising candidates for NLO applications due to the existence of intramolecular charge transfer between the electron donor and acceptor groups in the molecule. However, in this research work, we modify the structure design at both ends capped with electron acceptor groups (A- $\pi$ -A).

The density functional theory (DFT) that has been tremendously used is effective in explicating the structural and electronic properties in subclass of materials. Many studies [28, 29] have been performed by DFT on various organic compounds and chalcones correlated with experimental reports showing an outstanding performance in dipole moment, average polarizability, anisotropic polarizability and first hyperpolarizability. The present studies [30, 31] investigates efficient NLO materials, which may induce the interest of scientific community by exploring their potential in utilization for optical device applications.

The crystal structures of closely related chalcones, viz. 1,3-bis(4-bromophenyl)prop-2-en-1-one [32], 1-(4bromophenyl)-3-(4-chlorophenyl)-prop-2-en-1-one [33], (2E)-1-(4-bromophenyl)-3-(4-fluorophenyl)prop-2-en-1one [34], 1-(4-bromophenyl)-3-(2,4-dichlorophenyl)-prop-2-en-1-one [35], 3-(3-bromophenyl)-1-(4-bromophenyl)-1-(4-bromophenyl)-3-(2-chloro-6-fluorophenyl)prop-2-en-1-one prop-2-en-1-one [36]. [37]. (2E)-1-(4bromophenyl)-3-(4-nitrophenyl)-prop-2-en-1-one [38], 1-(4-bromophenyl)-3-(4-methylphenyl)prop-2-en-1-one [39] and (E)-1-(4-bromophenyl)-3-(napthalen-2-yl)prop-2-en-1-one [40] have been reported. In continuation of halogen chalcones research [41-43], we synthesized and report herein the new crystal structure of halogen substituted chalcone analogues with 4-bromoacetophenone moiety using the conventional base-catalyzed Claisen-Schmidt condensation. The molecular structure and spectroscopic properties were investigated by single crystal XRD, infrared (IR), <sup>1</sup>H and <sup>13</sup>C Nuclear Magnetic Resonance (NMR) and UV-Visible analyses. In addition, the density functional theory (DFT) at B3LYP methods in 6-311G++(d,p) basis set were employed to predict the structural parameters of the compound in the gas phase. To confirm the existence of the intermolecular interactions, the Hirshfeld surface analysis was performed and described. Besides, the Mulliken studies are also reported to determine the electronic charge potential and the third-order nonlinear optical susceptibility are discussed to evaluate its optical properties.

#### 2. Methodology

#### 2.1 Synthesis and crystal growth

A mixture of 4-bromoacetophenone (0.01mol) and a halogen-substituted benzaldehyde (0.01mol) was dissolved in methanol (20 mL). Catalytic amount of 20% NaOH (5 ml) was added to the solution dropwise with vigorous stirring. The reaction mixture was stirred for about 5–6 hours at room temperature. The resultant crude products were filtered, washed successively with distilled water and recrystallized from acetone to get the corresponding chalcones (Scheme 1). Crystals suitable for X-ray diffraction studies were obtained by the slow evaporation technique using acetone solvent. The yellow crystals of different shaped for all compounds are shown in Fig. 1.

#### 2.2 Spectroscopy analysis

The sample of chalcone was analyzed using Fourier transform infrared (FT-IR) with a PerkinElmer Spectrum GX Frontier Spectrophotometer using KBr pellet and the spectrum was recorded in the frequency range of 4000-400 cm<sup>-1</sup> region. <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were recorded at 500 and 125 MHz, respectively, in DMSO- $d_6$ , on Bruker 500MHz Avance III spectrometer. The chemical shifts are reported in parts per million (ppm) downfield from internal tetramethylsilane (TMS). UV-Visible absorption spectrum was recorded using SHIMADZU UV-1800 Spectrophotometer in the wavelength range of 200-800 nm in acetonitrile (CH<sub>3</sub>CN) solution with quartz cell of 1.0 cm path length.

(*E*)-1-(4-bromophenyl)-3-(2-chloro-4-fluorophenyl)prop-2-en-1-one [1]: Solvent for growing crystals: acetone; Yield: 65%; IR (FT-IR Spectrometer with KBr pellets, cm<sup>-1</sup>): 3072 (Ar-H), 1663 (C=O), 1583 (-CH=CH–), 1214 (C–F), 859 (C–Cl), 548 (C–Br). <sup>1</sup>H NMR [500 MHz, DMSO,  $\delta$ (ppm)]: 8.01 (d, 2H, Ph, *J* = 9.9 Hz), 7.88 (d, 2H, Ph, *J* = 10.2 Hz), 7.74 (s, 1H, Ph), 7.63 (d, 1H, -CH=CH–, *J* = 8.8 Hz), 7.38 (d, 1H, -CH=CH–, *J* = 8.5 Hz), 7.18 (d, 1H, Ph, *J* = 2.6 Hz), 7.06 (d, 1H, Ph, *J* = 2.6 Hz). <sup>13</sup>C NMR [125 MHz, DMSO;  $\delta$ (ppm)]: 187.9 (C=O), 136.4 (HC=CH), 121.6 (HC=CH), 163.9, 161.9, 161.7, 138.8, 137.8, 135.5, 131.7, 130.6, 130.4, 129.9, 129.7, 128.9, 127.4, 124.1, 117.2, 115.2, 114.4 (Ar, CH). CCDC No.: 1013205.

(E)-1-(4-bromophenyl)-3-(4-chloro-3-fluorophenyl)prop-2-en-1-one [2]: Solvent for growing crystals: acetone; Yield: 68%; IR (FT-IR Spectrometer with KBr pellets, cm<sup>-1</sup>): 3081 (Ar-H), 1660 (C=O), 1584 (-CH=CH-), 1212 (C-F), 831 (C-Cl), 528 (C-Br). <sup>1</sup>H NMR [500 MHz, DMSO,  $\delta$ (ppm)]: 8.09 (d, 2H, Ph, J = 1.9 Hz), 7.81 (d, 1H, -CH=CH-, J = 8.6 Hz), 7.77 (d, 2H, Ph, J = 1.9 Hz), 7.73-7.71 (m, 2H, Ph), 7.69 (d, 1H, -CH=CH-, J = 8.2 Hz), 7.56 (s, 1H, Ph). <sup>13</sup>C NMR [125 MHz, DMSO;  $\delta$ (ppm)]: 188.0 (C=O), 141.9 (HC=CH), 121.5 (HC=CH), 158.4, 156.4, 136.2, 135.9, 131.9, 131.7, 131.0, 129.9, 127.5, 126.6, 123.6, 116.2 (Ar, CH). CCDC No.: 1013209.

(*E*)-1-(4-bromophenyl)-3-(3-chlorophenyl)prop-2-en-1-one [**3**]: Solvent for growing crystals: acetone; Yield: 68%; IR (FT-IR Spectrometer with KBr pellets, cm<sup>-1</sup>): 3077 (Ar-H), 1662 (C=O), 1582 (–CH=CH–), 825 (C–Cl), 524 (C–Br). <sup>1</sup>H NMR [500 MHz, DMSO,  $\delta$ (ppm)]: 8.12 (d, 2H, Ph, *J* = 7.7 Hz), 8.06 (d, 2H, Ph, *J* = 11.4 Hz), 7.77 (d, 1H, –CH=CH–, *J* = 8.4 Hz), 7.68 (s, 1H, Ph), 7.48 (d, 1H, –CH=CH–, *J* = 6.7 Hz), 7.47-7.45 (m, 2H, Ph). <sup>13</sup>C NMR [125 MHz, DMSO;  $\delta$  (ppm)]: 188.9 (C=O), 143.5 (HC=CH), 123.9 (HC=CH), 137.6, 137.1, 134.6, 132.6, 131.5, 131.1, 128.8, 128.3 (Ar, CH). CCDC No.: 1013206.

(*E*)-1-(4-bromophenyl)-3-(2-fluorophenyl)prop-2-en-1-one [4]: Solvent for growing crystals: acetone; Yield: 67%; IR (FT-IR Spectrometer with KBr pellets, cm<sup>-1</sup>): 3092 (Ar-H), 1662 (C=O), 1589 (–CH=CH–), 1218 (C–F), 547 (C–Br). <sup>1</sup>H NMR [500 MHz, DMSO,  $\delta$ (ppm)]: 8.08 (d, 2H, Ph, *J* = 8.6 Hz), 7.78 (d, 2H, Ph, *J* = 8.6 Hz), 7.71 (d, 1H, –CH=CH, *J* = 8.6 Hz), 7.54-7.50 (m, 4H, Ph), 7.31 (d, 1H, –CH=CH–, *J* = 7.9 Hz). <sup>13</sup>C NMR [125 MHz, DMSO;  $\delta$  (ppm)]: 188.0 (C=O), 136.2 (HC=CH), 123.6 (HC=CH), 161.9, 159.9, 135.5, 135.4, 132.8, 132.7, 131.8, 131.7, 130.5, 129.9, 129.1, 127.5, 127.3, 124.9, 124.8, 122.2, 122.1, 116.1, 115.9 (Ar, CH). CCDC No.: 1013725.

### 2.3 Single crystal X-ray diffraction analysis

X-ray analysis of a suitable single crystal was performed on Bruker SMART Apex II Duo CCD areadetector diffractometers using MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å). Data collection was performed by the APEX2 software [44], whereas the cell refinement and data reduction were performed by the SAINT software [44]. The crystal structures were solved by Direct Method using the program SHELXTL [45] and were refined by full-matrix least squares technique on  $F^2$  using anisotropic displacement parameters by SHELXTL [45]. Absorption correction was applied to the final crystal data using the SADABS software [44]. All geometrical calculations were carried out using the program PLATON [46]. The molecular graphics were drawn using SHELXTL [45] and Mercury program [47]. Anisotropic thermal factors were assigned to all non-hydrogen atoms. In these compounds, all the hydrogen atoms were positioned geometrically and were refined using a riding model, with isotropic displacement parameters set to 1.2 times the equivalent isotropic U values of the parent carbon atoms. In the final refinement, the most disagreeable reflections were omitted [In 1: 2 5 7, 0 1 1, 1 3 5, 1 3 4, 2 5 8, 1 0 11, 2 5 4 and 2 4 10; in 2: 1 3 2, -2 -4 5, 1 0 1, 3 3 2 and 1 -2 2; in 3: -2 1 3 and 0 0 1; in 4: 1 0 0, 1 2 1, 0 0 8, 0 2 0, -3 0 6 and -5 2 4]. Details of the data collections condition and the parameters of refinement process are given in Table 1.

#### 2.4 DFT Calculations

In computational procedures, the starting geometries of the compounds were taken from X-ray refinement data. The optimization of the molecular geometries leading to energy minima was achieved using the DFT [Becke's non-local three parameter exchange and Lee-Yang-Parr's correlation functional (B3LYP)] with the 6-311++G(d,p) basis set as implemented in the GAUSSIAN 09 program package [48]. The time dependent density functional theory (TD-DFT) at 6-311G++(d,p) have been used to determine HOMO-LUMO energies, absorption wavelengths  $\lambda_{max}$  of

the electronic transitions and were compared with the experimental UV absorption spectra. The Mulliken and ground state dipole moment had been computed further with the same level of theory which is B3LYP/6-311G++(d,p) to investigate the strength of push-pull molecules configuration of the compounds.

#### 2.5 Hirshfeld Surface Analysis

The Hirshfeld surface and the related 2-D fingerprint plots for the title compound crystal structures were performed utilizing Crystal Explorer 3.1 [49]. The Hirshfeld surface is given the close interaction in 3-D image in crystal structure which is summarized in a 2-D fingerprint plot. This analysis approaches a graphical tool for visualization and understanding of intermolecular interaction. The distance from hirshfeld surface to the nearest atoms outside and inside the surface are represent as  $d_i$  and  $d_e$  respectively. For the distance from the surface to the nearest atom *interior* to the surface is known as  $d_i$ , while  $d_e$  represents the distance from the surface to the nearest atom *exterior* to the surface [50, 51]. The blue color is referring to the low frequency of occurrence of  $(d_i, d_e)$  pair and the grey color is the outline of the full fingerprint [52].

#### 2.6 Nonlinear optical property (Z-scan)

The refractive index, n of the samples was measured using a digital refractometer (DR201-95, KRUSS). The linear absorption coefficient,  $\alpha$  of all samples were obtained from the absorbance UV-VIS spectra in acetonitrile as the solvent. The Z-scan technique uses computation of intensity-dependent transmission which primarily to investigate the nonlinear optical properties in detecting both nonlinear refraction (NLR) and nonlinear absorption (NLA) simultaneously. The z-scan setup is shown in Fig. 2.

The excitation laser used is a continuous-wave frequency doubled diode pumped solid state (DPSS) laser (Coherent Verdi-V5). The detector used is silicon amplified photodetector PDA55, Thorlabs) with adjustable gain. With a converging lens of f = 20 cm, the radius of the Gaussian beam-spot at focal point was measured via a laser beam profiler (Beam Master) to be 23 µm. The sample was contained in a quartz cuvette with a path length of 1 mm which was mounted into a precision motorized stage (LTS-300, Thorlabs). The sample path length is much smaller than the Rayleigh length at 3.12 mm, which essential prerequisite for z-scan thin sample analysis. The phenomena that contribute to NLR and NLA responses can be studied and further characterized from closed z-scan and open z-scan curves, respectively.

The peak followed by a valley-normalized transmittance obtained from the closed aperture Z-scan is defined as  $\Delta T_{P\cdot V}$  which is given as  $T_P - T_V$ . The variation of this quantity as a function of  $|\Delta \varphi_0|$  is given by  $\Delta T_{P\cdot V} = 0.406(1 - S)^{0.25} |\Delta \varphi_0|$  is on the on-axis phase shift at the focus, S is the aperture linear transmittance with  $r_0$  denoting the aperture radius ( $S = 1 - \exp(-2r_0^2/\omega_0^2)$ ), and  $\omega_0$  denoting the beam radius at the aperture in the linear regime. Then, the nonlinear refractive index,  $n_2$  is given by,

$$n_2 = \frac{\Delta \varphi_0 \lambda}{2\pi I_0 L_{eff}} \tag{1}$$

where  $\lambda$  is the laser wavelength,  $I_0$  is the intensity of the laser beam at focus z = 0,  $L_{eff} = \frac{[1 - \exp(-\alpha L)]}{\alpha}$ ,  $L_{eff}$  is the effective thickness of the sample,  $\alpha$  is the linear absorption coefficient and L is the thickness of the sample. The nonlinear absorption coefficient,  $\beta$  can be estimated from the open aperture Z-scan data. The normalized transmittance for the open aperture condition is given by,

$$T(z, s = 1) = \sum_{m=0}^{\infty} \frac{\left[-q_0(z)\right]^m}{(m+1)^{\frac{3}{2}}}$$

(2)

or  $q_0(z) < 1$ , where  $q_0(z) = \frac{\beta l_0 L_{eff}}{\left(1 + z^2/z_R^2\right)}$ ,  $z_R = \frac{K\omega_0^2}{2}$  is the diffraction length of the beam and  $\omega_0$  is the beam waist radius

at the focal point and  $k = 2\pi/\lambda$  is the wave vector.

#### 3. Results and Discussion

### 3.1 Fourier transform infrared spectroscopy (FTIR) analysis

The IR spectra for all synthesized chalcones obtained from the two reactants; 4-bromoacetophenone and substituted halogen benzaldehydes are clearly observed from the high shifting absorption band of the stretching carbonyl group. The wavenumber of the C=O stretch due to carbonyl group mainly depends of the bond strength, which in turn depends upon inductive, conjugative, steric effects and lone pair of electrons on oxygen [53]. The carbonyl (C=O) stretching vibration is expected in the region of 1680-1750 cm<sup>-1</sup> [53, 54]. In this study, the strong wavenumbers of the stretching carbonyl group (C=O) are found to be in between 1660-1664 cm<sup>-1</sup>. The assignment is also in good agreement with the literature values [55, 56].

The IR band observed at 1581-1589 cm<sup>-1</sup> indicates the presence of the C8=C9 stretching vibration. The IR bands corresponding to asymmetric and symmetric aromatic –CH stretching vibrations are observed at 3072-3092 cm<sup>-1</sup>. The C–H stretching mode occurs above 3000 cm<sup>-1</sup> and is typically exhibited as a multiplicity of weak to moderate bands [57]. From the previous reported C-H stretching frequencies, the wavenumber appears in the range of 3000-3125 cm<sup>-1</sup> [58].

The substitution of heavy atoms fluorine and chlorine in the phenyl ring significantly affect the normal vibration modes of the ring. C–X [X=F, Cl and Br] absorption occurs in the broad region between 1234 and 492 cm<sup>-1</sup>, depending on the configuration and conformation of the compound [59]. The position of the bands is influenced by neighboring atoms and groups. The smaller the halide atom, the greater the influence of the neighbor [60]. The C-F stretching vibration of fluoro-substituted aromatic rings are found over a wide frequency range in the vibrational spectra at 1000-1360 cm<sup>-1</sup> due to easy change in the vibrational wavenumbers by adjacent atoms or groups [61, 62]. The C-Cl stretching vibration is observed in the range of 688.14-563.50 cm<sup>-1</sup> in FTIR spectrum being in good agreement with literature [63] where generally the C–Cl wavenumber was obtained in the region 850-550 cm<sup>-1</sup> [64]. In addition, the stretching C–Br frequencies are also found in the IR spectra which are within the range of 524-548 cm<sup>-1</sup>. Xiao *et al.* [65] designated the band at 526 cm<sup>-1</sup> is correspond to the C–Br stretching

mode. The region where the bands appear depending on the type of aromatic rings as well as the substituents present on the ring.

#### 3.2 Nuclear Magnetic Resonance (NMR) spectra analysis

The chemical shift analysis is done using Nuclear Magnetic Resonance (NMR) spectroscopy that helps to determine the content and purity of the compound. The parameters such as chemical shifts, multiplicities and electronic effect of all the chalcones are obtained from high resolution <sup>1</sup>H and <sup>13</sup>C NMR spectra. In chalcones, the H- $\alpha$  and H- $\beta$  protons occur as two doublets in the ranges of 6.7-7.4 ppm (H- $\alpha$ ) and 7.3-7.7 ppm (H- $\beta$ ) in the <sup>1</sup>H NMR spectra [66] which correspond to the *trans* double-bond configuration which is commonly found in naturally occurring chalcones [67]. In this study, the corresponding values are within the range of 7.31-7.69 ppm (H- $\alpha$ ) and 7.63-7.81 ppm (H- $\beta$ ). The  $\delta$  of C<sub> $\alpha$ </sub> and C<sub> $\beta$ </sub> hydrogen atoms are found to be slightly shifted which is due to the conjugation effect with the carbonyl group and aromatic rings [68] where the studied compounds consist of highly electronegativity halogenated substituent elements. Additionally, the presence of weak intramolecular C9–H9A····O1 hydrogen bond in the molecular structure, shifting the  $\delta$ H- $\beta$  values higher than the  $\delta$ H- $\alpha$ . In general, the aromatic protons usually appear in the range of  $\delta = 6.9$ -8.0 ppm, depending on the type of aromatic ring and based on the electronic effects of the substituent present on the ring. Rajesh Kumar *et al.* in their reported structure of chalcone stated that the aromatic proton chemical shifts of all chalcones in this report are found in the range of 8.12-7.43 ppm.

For <sup>13</sup>C NMR, the carbonyl carbon of the chalcones appears at the chemical shift ( $\delta$ ) values ranging from 188.6 to 194.6 ppm [70]. The carbonyl groups are found at the most de-shielded area (188.9-187.9 ppm) compared to other carbon atoms because of the environment factor and the increasing of electronegativity from oxygen atom. The  $\alpha$ - and  $\beta$ -carbon atoms with respect to the carbonyl group (–OC–CH=CH–) give rise to characteristic signals in between  $\delta_{C8} = 121.5$ -123.9 ppm and  $\delta_{C9} = 136.2$ -143.5 ppm, respectively. All other carbon chemical shift ( $\delta$ ) values are in the normal ranges.

#### 3.3 Molecular and optimized structural analysis

The molecular structure and optimized structure of the compounds 1, 2, 3 and 4 with assigned atomnumbering scheme are presented in Fig. 3 (a) and Fig. 3 (b), respectively. All the new halogen chalcones containing similar bromo-substituent unit at *para* position of phenyl ring (R1) and different substituents at the phenyl ring (R2). Two halogen chalcones namely (E)-1-(4-bromophenyl)-3-(2-chloro-4-fluorophenyl)prop-2-en-1-one (1) and (E)-1-(4-bromophenyl)-3-(4-chloro-3-fluorophenyl)prop-2-en-1-one (2) are isomers consisting fluoro and chloro substituent units at *ortho-para* and *para-meta* position, respectively. Meanwhile, another two halogen chalcones (E)-1-(4-bromophenyl)-3-(3-chlorophenyl)prop-2-en-1-one (3) and (E)-1-(4-bromophenyl)-3-(2-fluorophenyl)prop-2en-1-one (4) consist of different substituent units, *meta*-chloro and *ortho*-fluoro, respectively. These compounds correspond to the acceptor-pi-acceptor (A- $\pi$ -A) intermolecular charge transfer system, where all halogen atoms represent electron acceptor. The crystal structure **1** and **4** crystallize in monoclinic system with  $P_{1/n}$  space group and  $P_{2_1/c}$  space group, respectively. On the other hand, both compound **2** and **3** crystallize in triclinic system with P-1 space group. Interestingly, the asymmetric unit of compounds **3** contains two crystallographically independent molecules, A and B while the other compounds comprise one molecule. The optimized structure were performed by DFT at B3LYP/6-311G++(d,p) basis set and the geometrical parameters was listed in Table 2. All bond lengths and angles of the optimized structure are compared to the experimental values and both results are unexceptional and fall within the expected ranges.

The enone moiety (O1/C7-C9) of all compounds exist in s-cis configurations with respect to their C7=O1 and C8=C9 [bond distances of 1.214 (10) Å in 1; 1.228 (2) Å in 2; 1.223 (4) Å in 3 (A), 1.204 (5) Å in 3 (B); 1.210 (5) Å in 4 and 1.302 (12) Å in 1; 1.335 (3) Å in 2; 1.315 (5) Å in 3 (A), 1.323 (5) Å in 3 (B); 1.319 (6) Å in 4] double bonds (Table 2). The 4-bromophenyl moiety (Br1/C1-C6) of compound 1 deviates slightly from the (E)-4-(2chloro-4-fluorophenyl)but-3-en-2-one planarity [Cl1/F1/O1/C10-C15; maximum deviation: 0.086 (8) Å at O1] at the C6-C7 bond with the C1-C6-C7-C8 torsion angle being 172.7 (9)°. Meanwhile, for the compound 4, the bromo-substituent benzene ring (Br1/C1-C6) is slightly twisted at the C6-C7 bond from the mean plane of the (E)-4-(2-fluorophenyl)but-3-en-2-one [O1/F1/C7-C15; maximum deviations: 0.171 (4) Å at atom O1] with the C1-C6-C7-C8 torsion angle value of 17.2 (7)°. The corresponding torsion angles for DFT are -165.51° (1) and  $16.64^{\circ}$  (4). Furthermore, the compound 2 is almost planar where the least-square plane through the enone group [O1/C7-C9; maximum deviation: 0.0233 (16) Å at atom C7] makes dihedral angles of 8.55 (11)° and 8.04 (10)° with the C1—C6 and C10—C15 benzene rings, respectively. Compound 3 is also found to be almost planar where the dihedral angles between the mean plane through the enone group [O1/C7-C9; maximum deviations: 0.040 (4) Å at C7A and 0.018 (4) Å at C7B] with the terminal benzene rings C1—C6 and C10—C15 are 9.5 (3) and 6.2 (3)°, respectively in molecule A and 2.7 (3) and 3.1 (3)°, respectively in molecule B. The dihedral angle between two C1-C6 (R1) and C10-C15 (R2) phenyl rings for compound 1-4 is portrayed in Fig. 3 (c). The dihedral angles formed being 15.36° (1), 8.89° (2), 6.30° (3) (molecule A); 7.98° (3) (molecule B), and 25.85° (4). It is found that, compound 1 and 4 exhibit a large dihedral angle as compared to the compound 2 and 3. The large dihedral angle would be diminishing the electronic effect between two phenyl rings through the enone moiety.

In the crystal packing of **1**, the intermolecular C5—H5A····O1 hydrogen bonds (Table 3) link the molecules into chains along the *b*-axis as shown in Fig. 4 (a). In addition, the halogen···halogen interactions (Table 4) between the bromine and fluorine atoms of C—Br···F (-3/2+*x*,3/2-*y*,-1/2+*z*) [Br···F = 3.215 (6) Å] and C—F···Br (3/2+x,3/2-y,1/2+z) [F···Br = 3.215 (6) Å] are also observed in the crystal packing where the Van der Walls radii of F and Br atoms are 1.47 and 1.86 Å, respectively [71]. These interactions further bridge the chains into a two-dimensional sheet parallel to *bc*-plane. In compound **2**, the molecules are linked by intermolecular C11—H11A···O1 (-*x*+1, -*y*+1, -*z*) hydrogen bond (Fig. 4 (b); Table 3) into cyclic centrosymmetric  $R_2^2(14)$  dimers [72]. In the crystal structure of **3**, molecules A and B are interlinked *via* three C—H···O hydrogen bonds (Table 3) to form two dimensional layers parallel to the *ac*-plane (Fig. 4 (c)). These layers are further inter-connected into a three-dimensional network *via* C1A—H1AA···Cl1A (-*x*+1, -*y*+2, -*z*) hydrogen bonds. The crystal packing of compound **4** is stabilized by intermolecular C1—H1A···O1 (*x*, -*y*+3/2, *z*+1/2) hydrogen bonds (Table 3), forming one-

dimensional chain running along the *c*-axis (Fig. 4 (d)). The short  $Br1\cdots Br1(-x,1/2+y,3/2-z)$  (Table 4) contacts [contact distance: 3.6196 (9) Å] less than the sum of Van der Walls radii of Br (1.86 Å) which is 3.72 Å [73]are also observed, forming a one-dimensional zig-zag chain along the *b*-axis (Fig. 4 (d)). The formation of chains *via* C— H···O and Br···Br interactions connect the molecules into a two-dimensional layer parallel to the *bc*-plane and further stabilize the crystal structure. Furthermore, the presence of this Br···Br contacts is due to the greater polarizability and high electronegativity of Br atoms.

#### 3.4 UV-Vis spectral and frontier molecular orbitals (FMO) analysis

The UV-vis absorption spectra of compounds **1-4** was recorded using 1800 Shimadzu UV-vis spectrophotometer in acetonitrile (CH<sub>3</sub>CN) solution. The spectra and their respective frontier molecular orbital are presented in Fig. 5. The corresponding data are summarized in Table 5. The most part of the absorption spectroscopy of organic are based on the transitions of *n* or  $\pi$  electrons to the  $\pi^*$  excited state which happens in the range of 200-700 nm [74]. As can be seen from the UV-Vis spectra (Fig. 5), all compounds indicate comparable spectra with the strong absorption maximum ( $\lambda_{max}$ ) at 300-320 nm are correspond to the  $n-\pi^*$  transition which attribute to the excitation in the aromatic ring and C=O group [75]. All compounds have a lower optical cut-off at 340-350 nm which are transparent in the entire visible region and the absorption takes place in the UV range. The absence of the absorptions in the visible region shows the potential of all compounds to act as nonlinear optical materials [76]. The UV spectra showed similar patterns, but different intensity of the peaks depending on the substituents of the halogens group [77]. From the UV spectra, the maximum absorption wavelength is implied in the mathematical equation  $E_g = hc \lambda_{max}^{-1}$  where *h* is the Planck constant and *c* is the speed of light to calculate the energy gap for each compounds. The experimental energy gap calculated from the UV spectra are found in the range of 3.9 to 4.1 eV as presented in Table 5.

HOMO and LUMO energies are important parameters for quantum chemistry. The electronic transition between frontier molecular orbitals HOMO LUMO are usually corresponds to the maximum absorption wavelength. The conjugated molecules are characterized by a highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO-LUMO) separation, which is the result of a significant degree of ICT (Intramolecular Charge Transfer) from the end-capping electron-donor groups to the efficient electron-acceptor groups through  $\pi$ -conjugated path [24]. The difference in energy between these two frontier orbitals known as HOMO LUMO gap is associated to the electronic charge transfer interaction which occurred within the molecule. Results from the TD-DFT at B3LYP 6-311 basis set level showing the energy gap of all compounds **1-4** are found in the range of 4.0 eV to 4.1 eV. These values are in close agreement with the  $E_g$  value calculated using the mathematical expression. At HOMO state, the orbitals are localized mainly over the phenyl ring R2 and enone chain, while LUMO orbitals localized over the entire molecules, illustrated in the inset of Fig. 5.

3.5 Mulliken and ground state molecular dipole moment

The electronic molecular dipole moment signifies the electron movement in a molecule sometimes called as push-pull polarization system. The total dipole moment along with their individual components for four compounds have been summarized in Table 6. The dipole moment magnitude depends on the orientation and position of halogen substituent units. Previous study reported that when both substituents are electron pushing, the para product has the least dipole moment and ortho products has the highest dipole moment [24]. The representation of electronic dipole moment based on charge population analysis for all compound is illustrated in Fig. 6. It is found that, the compound **4** with *o*-F at the phenyl ring showed the greatest dipole moment of 4.61D identified by the longest vector arrow while the compound **2** with *m*,*p*-F,Cl substitution showing the lowest dipole magnitude of 0.68D as represented by the shortest vector. In addition, compound **3** with *m*-Cl substitution signifies the second highest dipole moment with magnitude vector of 3.47D and followed by the compound **1** with 2.98D. This trend of dipole moment magnitude is clearly due to the orientation of halogen substitution at different position and the influence of the number of halogen substituent unit. Single substitution indicates a higher total dipole moment compared to multi-substitution. Even though the UV spectral and FMO analysis of compound **2** exhibit more active NLO, the orientation of the *o* and *m* substitutions result in the higher dipole moment as seen in compound **4** and **3**, respectively. Therefore, the large dipole moment leads to a better nonlinear response of the organic compound.

#### 3.6 Hirshfeld surface analysis

The Hirshfeld surface has proven in discerning the differences of intermolecular interactions and obtaining the quantitatively of 2-D fingerprint plot percentage on intermolecular interactions [50, 78]. Each molecule in the asymmetric unit of a crystal structure gives the unique Hirshfeld surface and hence made percentage contributions of intermolecular contacts. The Hirshfeld surface of the title chalcones was analyzed to clarify the nature of the intermolecular interactions which is illustrated in Fig. 7 showing the surfaces that have been mapped over  $d_{norm}$ . The surfaces are shown as transparent to allow visualization of the chalcones moiety with neighbouring molecules. As expected, the  $d_{norm}$  surfaces of Fig. 7 reveal the close contacts of hydrogen bond donors and acceptor with the large circular depression (red bright) and as evident for other close contacts such as halogen…halogen interactions (compound 1). The dominant C—H…O interactions in the chalcones are evident in the Hirshfeld surface plots by the bright red area (Fig. 7).

2-D fingerprint plots from Hirshfeld surface analysis of these four chalcones have been calculated to gain the quantitative data on the percentage contributions of  $C\cdots H/H\cdots C$  and  $O\cdots H/H\cdots O$  intermolecular contacts on the molecules. For each chalcones, the fingerprint corresponds to its classical hydrogen bond behavior. The overall 2-D fingerprint plot delineated into  $C\cdots H/H\cdots C$  and  $O\cdots H/H\cdots O$  intermolecular contacts are illustrated in Fig. 8. Fingerprint plots can emphasize atom pair close contacts. It enables separation of contributions from different interaction types, which overlap in the full fingerprint (Fig. 8 *left*). The  $C\cdots H/H\cdots C$  close contacts are observed at 11.9% in compound **1**, 20.1% in compound **2**, 23.1% in compound **3** and 17.6% in compound **4**. The  $O\cdots H/H\cdots O$ intermolecular interactions for compounds **1–4** appear as spikes in the 2-D fingerprint plots (Fig. 8 *right*). The  $O \cdots H/H \cdots O$  intermolecular interactions showing two narrow spikes provide the evidence for C—H···O nonclassical hydrogen [52].

#### 3.7 Nonlinear optics (NLO) property

The z-scan measurements were performed using the reported method [24] to study the third-order nonlinear response of the compounds. The close-aperture z-scan profiles of the compounds are shown in Fig. 9. In close-aperture z-scan, the sample which has been contained in a 1 mm quartz cuvette is moved through the tightly focused along the z-axis of the beam. The scan was carried out at 4.1, 8.3, 12.4 and 16.5 kW/cm<sup>2</sup>. All the samples show a transmittance profile with a peak followed by valley which suggest the self-defocusing effect (negative nonlinear refractive index,  $n_2$ ). Considering that in the case of CW laser, the major sources of NLR was originated from nonlocal excitation region due to the thermal nonlinearity effects. The spatial variations were induced because of the non-uniform temperature distribution within the instantaneous beam waist. Consequently, severe phase distortion of the propagating beam occurs, which act as a thermal lensing. This is supported by the peak to valley z separation calculated to be higher than 1.7 zR.

The normalized transmittance in Fig. 9 is fitted using equation from z-scan theory to obtain the sign and the magnitude of  $n_2$  [24]. The values of  $n_2$  of the compounds at different excitation intensity are given in Table 7 which is in the order of 10<sup>-9</sup> cm<sup>2</sup>/W. The intensity-dependent  $n_2$  in Table 7 shows that the absolute value of  $n_2$  generally enhances with the increase in the excitation intensity. These different NLR behavior of such compounds can be attributed to the intrinsic properties at the molecular level. The nature of the  $\pi$ -bonding tail and the donor to acceptor (D-A) translate into the occurrence of intramolecular charge transfer (ICT).

#### Conclusions

The third order nonlinear optical properties of all the halogen-substituted chalcone derivatives were successfully investigated by Z-scan technique. All compounds were synthesized in good yield and characterized by IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, UV-Visible and single crystal X-ray diffraction analyses. The theoretical and experimental geometrical parameter results show a good agreement. All the presented crystal structures show that the intermolecular forces play a major role in the supramolecular arrangement of the crystal structure. The presence of intramolecular C—H···O hydrogen bonds in all the chalcone derivatives stabilizes the individual molecular structure. Intermolecular C—H···O (in 1-4) and C—H···Cl (in 3) hydrogen bonds observed formed a supramolecular assembly of molecular structures. Additionally, in compound 1 and 4, the crystal packing is further stabilized by halogen···halogen [Br...F & Br...Br] contacts. These supramolecular arrangements transform the halogen substituted chalcones into a 1-D and 2-D supramolecular network. Furthermore, the Hirshfeld surface analysis with fingerprint plots reveals the relatively weak intermolecular interactions of these chalcone compounds which are dominated by C...H and O...H interactions dominate the fingerprint plots. The energy gap values

obtained from the experimental and theoretical calculations are in close range (~4.0 eV) and shows the good electronic charge transfer within the molecules. The large dipole moment indicates that the organic compounds possess a good NLO response. However, the orientation of the substitution's unit at ortho position triggered an excellent static dipole magnitude as compared to the meta and para position. It was observed from the closed aperture z-scan that the samples exhibit good transmittance profile and self-defocusing effect where the excitation intensity is in order of  $10^{-9}$  cm<sup>2</sup>/W. This NLR behavior could contribute to intrinsic properties thus exploiting the development of photonics devices.

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#### **Supplementary materials**

This data CCDC: 1013205, 1013209, 1013206 and 1013725 can be obtained free of charge at www.ccdc.cam.ac.uk.conts/retrieving.html/ or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 IEZ, UK; fax: +44(0) 1223-336033; e-mail: deposit@ccdc.cam.ac.uk.

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Fig. 1. The single crystals of compound (a) 1, (b) 2, (c) 3 and (d) 4.



Fig. 2. Z-scan technique.



Fig. 3. (a) The crystal structure in ORTEP diagram with atom numbering schemes where the displacement ellipsoids are drawn at the 50% probability level and (b) the optimized structure of respective compound (c) the dihedral angles between two main planes.





Fig. 4. (a)(b) Crystal packing showing the infinite C—H…O interactions forming a chain running along the *b*-axis in compound 1 and 2, respectively. The hydrogen bonded R<sub>2</sub><sup>2</sup>(14) ring motif is observed in the compound 2. (c) supramolecular two-dimensional *ac* plane formed *via* C—H…O interaction and connected into a 3-D network *via* C—H…Cl interaction in 3. (d) C—H…O hydrogen bonding patterns extending along *b*-axis in 4. H atoms not involved in the crystal structure have been omitted for clarity.



Fig. 5. UV-Vis absorption spectra of chalcones and their respective frontier molecular orbitals.



Fig. 6. Hirshfeld surfaces mapped over  $d_{norm}$  showing hydrogen-bonding interactions (green dashline) with their neighbouring molecules



**Fig. 7.** 2-D fingerprint plots of the compounds 1-4: full (*left*) and relative contribution of atom pairs to the Hirshfeld surface (C...H %) (*middle*) and (O...H %) (*right*).



Fig. 8. The representation of relative orientation of electronic dipole moment vector (blue arrow) based on Mulliken population analysis with color scheme for partial charges of all atoms in molecule.



Fig. 9. Close-aperture z-scan profile of the compound (a) 1, (b) 2, (c) 3, and (d) 4. The theoretical fit lines are shown in red.

Compounds	1	2	3	4
CCDC deposition numbers	1013205	1013209	1013206	1013725
Molecular formula	C15H9BrClFO	C15H9BrClFO	C <sub>15</sub> H <sub>10</sub> BrClO	C <sub>15</sub> H <sub>10</sub> BrFO
Molecular weight	339.58	339.58	321.59	305.14
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	$P2_{1}/n$	<i>P</i> -1	<i>P</i> -1	$P2_{1}/c$
a/Å	3.9598 (10)	5.4032 (3)	5.7725 (5)	21.287 (3)
b/Å	11.705 (3)	7.7034 (4)	11.5622 (10)	5.0068 (8)
c/Å	29.831 (7)	15.6459 (8)	20.9401 (18)	12.3150 (18)
α /°	90.00	89.4510 (9)	102.8460 (18)	90.00
<b>β/</b> °	90.582 (5)	89.511 (1)	96.4660 (19)	96.536 (4)
γ/°	90.00	87.930(1)	97.8840 (18)	90.00
$V/ \text{\AA}^3$	1382.5 (6)	650.75 (6)	1334.8 (2)	1304.0 (3)
Ζ	4	2	4	4
$D_{\rm calc}/{\rm g~cm^{-3}}$	1.631	1.733	1.600	1.554
Crystal Dimensions /mm	0.20×0.20×0.10	0.82×0.30×0.23	0.34×0.33×0.25	0.60×0.14×0.05
$\mu/\mathrm{mm}^{-1}$	3.17	3.36	3.26	3.15
Radiation λ/Å	0.71073	0.71073	0.71073	0.71073
<b>F(000)</b>	672	336	640	608
$T_{\rm min}/T_{\rm max}$	0.566/0.743	0.170/ 0.513	0.408/0.500	0.256/0.851
<b>Reflections measured</b>	9246	11458	27753	17997
Ranges/indices (h, k, l)	$h = -4 \rightarrow 4$	$h = -6 \rightarrow 7$	$h = -8 \rightarrow 8$	$h = -27 \rightarrow 27$
	$k = -13 \rightarrow 13$	$k = -9 \rightarrow 10$	$k = -16 \rightarrow 16$	$k = -6 \rightarrow 6$
	$l = -35 \rightarrow 35$	$l = -20 \rightarrow 20$	$l = -28 \rightarrow 29$	$l = -16 \rightarrow 16$
θ limit /°	2.2-25.0	2.6-27.5	1.8-30.2	1.9-27.5
Unique reflections	2373	2951	7830	2996
Observed reflections $(I > 2\sigma(I))$	1377	2842	4256	1678
Parameters	172	172	325	163
Goodness of fit on <i>F</i> <sup>2</sup>	1.07	1.09	1.06	1.03
$R_1, wR_2 [I \ge 2\sigma(I)]$	0.081, 0.218	0.026, 0.077	0.059/0.210	0.051/0.154
R <sub>int</sub>	0.063	0.024	0.028	0.071
Largest diff. peak and hole, e/Å <sup>-3</sup>	0.61 and -0.37	1.63 and -0.43	1.16 and -1.05	0.77 and -0.38

Table 1 Crystal data and structure refinement parameters.

For **1**,  $w = 1/[\sigma^2(F_o^2) + (0.0735P)^2 + 5.9781P]$ , For **2**,  $w = 1/[\sigma^2(F_o^2) + (0.0435P)^2 + 0.4652P]$ , For **3**,  $w = 1/[\sigma^2(F_o^2) + (0.1042P)^2 + 0.6416P]$ , For **4**,  $w = 1/[\sigma^2(F_o^2) + (0.0717P)^2 + 0.6719P$ , where  $P = (F_o^2 + 2F_c^2)/3$ ; [a]  $R = \Sigma ||F_o| - |F_c||/\Sigma |F_o|$ , [b]  $R_w = \{w\Sigma(|F_o| - |F_c|)^2/\Sigma w |F_o|^2\}[7, 13]\}^{1/2}$ , [c]  $GOF = \{\Sigma w (|F_o| - |F_c|)^2/(n-p)\}^{1/2}$ , where *n* is the number of reflections and *p* the total number of parameters refined.

Bonds	1		2		3			4	
					Exp (Å, °)				
	Exp (Å, °)	DFT	Exp (Å, °)	DFT	(A)	(B)	DFT	Exp (Å, °)	DFT
Br1—C3	1.894 (9)	1.914	1.8935 (19)	1.913	1.893 (4)	1.892 (4)	1.914	1.890 (4)	1.914
O1—C7	1.214 (10)	1.223	1.228 (2)	1.223	1.223 (4)	1.204 (5)	1.223	1.210 (5)	1.223
C6—C7	1.469 (12)	1.501	1.498 (2)	1.501	1.487 (6)	1.493 (5)	1.502	1.483 (6)	1.503
C7—C8	1.472 (13)	1.486	1.480 (2)	1.485	1.477 (5)	1.483 (6)	1.485	1.467 (6)	1.484
C8—C9	1.302 (12)	1.345	1.335 (3)	1.345	1.315 (5)	1.323 (5)	1.345	1.319 (6)	1.345
С9—С10	1.457 (13)	1.462	1.464 (2)	1.461	1.462 (5)	1.461 (6)	1.463	1.450 (6)	1.460
01—C7—C6	120.6 (8)	119.920	119.55 (16)	119.887	119.9 (3)	119.6 (4)	119.803	120.1 (4)	119.768
01—C7—C8	118.1 (9)	121.304	120.82 (16)	121.222	120.3 (4)	119.4 (4)	121.340	120.9 (4)	121.488
C6—C7—C8	121.2 (8)	118.772	119.62 (15)	118.885	119.8 (3)	120.9 (3)	118.851	119.0 (3)	118.738
C9—C8—C7	124.4 (9)	120.320	119.54 (16)	120.279	121.6 (3)	122.0 (4)	120.270	122.0 (4)	120.351
C8—C9—C10	129.5 (9)	126.328	126.91 (16)	127.776	127.8 (3)	126.8 (4)	127.707	127.1 (4)	126.888
C1—C6—C7—O1	10.9 (13)	13.743	174.22 (19)	166.152	179.4 (4)	-176.1 (5)	-165.267	-163.7 (5)	-164.290
C5—C6—C7—O1	-165.7 (9)	-164.794	-6.8 (3)	-12.531	0.1 (5)	3.7 (6)	13.413	12.3 (7)	14.314
01-C7-C8-C9	-3.5 (15)	8.069	5.6 (3)	-4.854	-10.0 (6)	2.6 (7)	4.988	7.2 (8)	5.757
C6—C7—C8—C9	180.0 (9)	-172.683	-173.93 (17)	175.972	167.4 (4)	179.0 (4)	-175.898	-173.7 (4)	-175.187
С7—С8—С9—С10	-177.4 (9)	-177.997	-178.70 (16)	179.009	-178.7 (3)	178.1 (4)	-178.920	-178.6 (4)	-178.686
C8—C9—C10—C11	-179.1 (10)	-160.041	-177.01 (18)	177.848	-175.2 (4)	1.6 (7)	1.814	-177.0 (5)	-175.554
C8—C9—C10—C15	4.1 (16)	20.966	4.1 (3)	-2.261	3.9 (6)	-177.3 (5)	-178.342	4.4 (8)	4.766

### Table 2 Selected bond lengths, bond angles and torsion angles for compounds 1-4.

-1/5... 4.1 (16) 20.5v.

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Bond	Bond leng	th, (Å)		Angle
D—H····A	D—H	H···A	D····A	D—H····A, (°)
Compound 1				
C5—H5A····O1 <sup>i</sup>	0.93	2.58	3.251 (10)	129
Compound 2				
C11—H11A…O1 <sup>ii</sup>	0.93	2.39	3.263 (2)	156
Compound 3				
C1A—H1AA…Cl1A <sup>iii</sup>	0.93	2.77	3.648 (5)	157
C11A—H11A…O1A <sup>iv</sup>	0.93	2.40	3.294 (5)	162
$C13B$ — $H13B$ ···· $O1A^{v}$	0.93	2.55	3.449 (5)	163
$C15B$ — $H15B$ ···· $O1B^{vi}$	0.93	2.42	3.295 (5)	157
Compound 4				
C1—H1A…O1 <sup>vii</sup>	0.93	2.50	3.204 (5)	132
Symmetry code (i) $-x+3/2$ , $y+1$	/2, -z+1/2; (ii) -	-x+1, -y+1, -z;	(iii) − <i>x</i> +1, − <i>y</i> +2, −	-z; (iv) $-x+2, -y+1, -z;$ (

 Table 3 Hydrogen bond metrics for compounds 1-4.

x-1, y, z; (vi) -x, -y+1, -z+1; (vii) x, -y+3/2, z+1/2.

**Table 4** Halogen...halogen [I...J = F or Br] interactions.

	X—I…J	Bond length, I—J, (Å)	Angle, X—I…J, (°)
1	C3—Br1…F1 <sup>i</sup>	3.215(6)	173.1(3)
	C13—F1···Br1 <sup>ii</sup>	3.215(6)	152.8(7)
4	C3—Br1···Br1 <sup>iii</sup>	3.6196(9)	163.47(12)

Symmetry code (i) -3/2+x,3/2-y,-1/2+z; (ii) 3/2+x,3/2-y,1/2+z; (iii) -x,1/2+y,3/2-z. Van de Waals radii (Å) : F=1.47 ; Cl=1.76; Br=1.86.

 Table 5 Spectral absorption and their respective molecular orbital of chalcones 1-4.

	$\lambda_{cw} (nm)$	$\lambda_{max}\left(nm\right)$	State transition	HOMO (eV)	LUMO (eV)	H-L gap (eV)	$E_g = hc \lambda_{\max}^{-1}$ (eV)
1	349	313	n-π <sup>*</sup>	-6.975	-2.861	4.114	3.962
2	340	314	n-π <sup>*</sup>	-6.966	-2.961	4.005	3.949
3	342	302	n-π <sup>*</sup>	-6.966	-2.859	4.107	4.106
4	345	304	n-π <sup>*</sup>	-6.907	-2.795	4.111	4.079
	- Y						

	$\mu_x$	$\mu_y$	μ <sub>z</sub>	μ <sub>tot</sub> (D)	
1	-0.37	-2.96	0.03	2.98	
2	-0.63	-0.19	0.20	0.68	
3	-0.38	-3.44	0.23	3.47	
4	2.04	-4.13	-0.24	4.61	

Table 6 The calculated dipole moments (Debye) of compounds 1-4 at B3LYP/6-3111G++(d,p) level of theory.

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Table 7 Nonlinear refractive index of 1-4

	1	2	3	4
Intensity (kW/cm <sup>2</sup> )		$n^2$ (x 10	$0^{-9} \mathrm{cm}^2/\mathrm{W})$	
4.1	$-6.724 \pm 0.494$	$-3.338\pm0.462$	$-2.690 \pm 0.339$	$-7.376 \pm 0.433$
8.3	$-7.472 \pm 0.276$	$-5.080\pm0.325$	$-2.719 \pm 0.189$	$-8.202 \pm 0.256$
12.4	$-8.532 \pm 0.241$	$-4.652\pm0.155$	$-3.176 \pm 0.142$	$-8.373 \pm 0.300$
16.5	$-8.238 \pm 2.104$	$-4.873 \pm 0.220$		$-8.307 \pm 0.253$



Scheme 1. Synthesis of halogen chalcone analogues.







# Highlights

- > Four new halogenated chalcones have been synthesized with A- $\pi$ -A configuration.
- The computational results performed by DFT at B3LYP 6-311G ++ (d,p) are comparable with experimental studies.
- The intermolecular C–H…O, C–H…Cl and halogen…halogen interactions presence in the crystal structures.
- The relatively small HOMO–LUMO energy gap and high dipole moments contribute to high nonlinear responses.