

New, High Efficiency Nonlinear Optical Chalcone Co-Crystal and Structure–Property Relationship

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Supporting Information

ABSTRACT:



In our present study, we attempted to grow the single crystals of (2E)-1-(4-chlorophenyl)-3-[4-(methylsulfanyl)phenyl]prop-2-en-1-one by making use of the slow evaporation solution growth technique at room temperature. But the single crystal X-ray diffraction technique revealed that the grown crystal was a co-crystal with molecular formula $C_{16}H_{13}Br_{0.66}Cl_{0.34}OS$ (4Br4MSP/4Cl4MSP). The presence of functional groups in the molecular structure is confirmed by Fourier transform infrared (FT-IR) spectroscopy. The UV-vis-NIR absorption spectrum shows that this co-crystal has a good transparency window for optical application. Second harmonic generation (SHG) analysis was done to explore nonlinear optical (NLO) characteristics of the material, and the co-crystal was found to have the highest SHG efficiency when compared with all the co-crystals reported in the literature.

1. INTRODUCTION

Chalcone molecules with a π -conjugated system provides a large charge transfer axis. The appropriate groups of molecules on two aromatic rings act as donors and acceptors.^{1,2} The charges can transfer from donor to acceptor through the charge transfer axis. Strong intermolecular interactions result due to this, giving rise to second harmonic generation (SHG) efficiency.^{3,4} Chalcone may find industrial, biological, and pharmaceutical applications. 5^{-7} The co-crystal is also equally important in these fields of application and in the field of crystal engineering to study the possible tuning of the structure to enhance the nonlinear optical (NLO) properties.⁸ A co-crystal is defined as a crystal that is built out of two or more organic compounds that are, in their pure forms, solid at ambient conditions.^{9–11} A co-crystallization process is an attempt to bring together different molecular species within one periodic crystalline lattice without making or breaking covalent bonds. The chances of accidentally making a co-crystal and bringing together different molecular species within one periodic crystalline lattice without making or breaking covalent bonds are very small without effective synthetic protocols. Even though there are different methods to synthesize cocrystals such as solution method and solid state grinding, it is

difficult to mention a suitable technique for a particular cocrystal to synthesize, unless it is confirmed by trial and error methods.^{12,13}

In this paper, we deal with the co-crystal of chalcone: its synthesis, growth, characterization, and structure—NLO property relationship. The co-crystal obtained has co-formers, namely, (2*E*)-1-(4-chlorophenyl)-3-[4-(methylsulfanyl) phenyl]prop-2-en-1-one (4Cl4MSP) and (2*E*)-1-(4-bromophenyl)-3-[4-(methylsulfanyl) phenyl]prop-2-en-1-one (4Br4MSP). The molecular structure of the co-crystal is given by C₁₆H₁₃Br_{0.66}OS/C₁₆H₁₃Cl_{0.34}OS (4Br4MSP/4Cl4MSP). The co-crystal is a donor- π -acceptor- π -donor (D- π -A- π -D) type of the molecule, and SHG efficiency is found to be greater than that of any of the co-crystals so far reported to our best knowledge.

2. EXPERIMENTAL PROCEDURES

Synthesis and Growth. The standard technique Clainsen-Schmidt condensation method was used to synthesize the chalcone

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Figure 1. Photograph of the crystal 4Br4MSP/4Cl4MSP.

derivative.¹⁴ Commercially available 4-chloroacetophenone and 4-methylthiobenzaldehyde were used without further purification. A mixture of equimolar quantities (0.01 mol each) of 4-chloroacetophenone and 4-methylthiobenzaldehyde in ethanol (60 mL) were stirred for 2 h. Aqueous solution of sodium hydroxide (5 mL, 10%) was added slowly while stirring. Then the contents of the flask were poured into ice cold water (250 mL) and left for 12 h. The resulting crude solid was collected by filtration, dried, and purified by repeated crystallization.

The selection of the proper solvent is important for the growth of good quality crystals. We found acetone was the best solvent. The solution of the growth material was prepared in acetone. After filtration by using Whatman filter paper, the solution was transferred into a crystal growth vessel. Next, it was kept for crystallization by slow evaporation at room temperature (28 °C). Good quality crystals were obtained within a week. Figure 1 shows the photograph of crystals. The crystals are nonhygroscopic, stable at room temperature, and have a maximum size of $13 \times 2 \times 2$ mm³.

Single Crystal X-ray Diffraction. Crystal was mounted on glass fibers. X-ray data were collected with a Bruker AXS SMART APEX diffractometer, using Mo–K α radiation at 100 K, with the SMART suite of Programs. Data were processed and corrected for Lorentz and polarization effects with SAINT, and for absorption effect with SA-DABS. Structural solution and refinement were carried out with the SHELXTL suite of programs.¹⁵ The structure was solved by direct methods to locate the heavy atoms, followed by difference maps for the light, non-hydrogen atoms. The small organic molecules commonly refine to better than R = 0.05. Final R values of present refinement are $R_1 = 0.0503$ and $wR_2 = 0.1152$ for 2-theta maximum of 55°. It implies that a good agreement exists between observed and calculated intensities.

IR Spectroscopy. The Fourier transform infrared (FT-IR) spectrum of the co-crystal was taken to investigate the presence of functional groups and their vibrational modes. The sample was mixed thoroughly with dried KBr. The spectrum was recorded between 400 to 4000 cm⁻¹ using a Thermo Nicolet Avatar 370 FT-IR spectrometer. The characteristic transmission peaks are consistent with the functional groups present in the molecular structure. The recorded spectrum is shown in Figure S1 in the Supporting Information.

UV—vis—NIR Spectrum. The UV—vis—NIR absorption spectrum¹⁶ of the crystals was recorded using a Cary SE high resolution spectrophotometer in the wavelength range of 200—1100 nm. Crystals with parallel surfaces and thickness of 1 mm were used for this purpose.

Thermal Analysis. To investigate the thermal stability¹⁷ of the cocrystal, thermogravimetric analysis (TGA) was carried out. Powdered sample of the crystal was selected for this purpose, and the analysis was carried out under the nitrogen atmosphere at a heating rate of 10°/min using the Perkin-Elmer simultaneous TGA/DTA analyzer.

Mechanical Stability. The mechanical study of chalcone co-crystal was made by Vickers and Knoop microhardness tests at room temperature.

Crystals, with flat and smooth faces, were chosen for the static indentation tests.¹⁵ The crystal slices are well polished with a thickness variation less than 10 μ m to avoid the surface defects which may influence the hardness value strongly. The crystal 4Br4MSP/4Cl4MSP was mounted properly on the base of the microscope. The indentor orientation was fixed throughout the measurements along a direction with respect to the plane studied. Now the selected faces were indented gently by varying loads for a dwell period of 10 s using both Vicker's and Knoop indenter attached to a research microscope Clemex. For a particular load, at least five well-defined impressions were considered, and the average of all the diagonals (*d*) was considered.

Laser Damage Threshold. The experimental arrangement consisted of a Q-switched Nd:YAG laser, a low power He–Ne laser, a power meter, a beam splitter, and a quartz lens. A suitable beam splitter (50:50) was used to split the laser beam into two parts having equal beam power. One beam was used as a reference beam to monitor the laser power, and other was focused into the sample using a 15 cm lens. A crystal was placed at focus of the lens and the on-axis irradiance was varied in steps of 0.2 GW/cm² and the laser beam passed through the crystal was monitored. Damage was checked for an average of 100 laser pulses for fixed on-axis irradiance. The on-axis irradiance at which the crystal show scattering of laser pulses due to damage produced in the crystal is referred to as the laser damage threshold of the crystal.

Second Harmonic Generation. The experimental setup used in the present investigation of SHG efficiency was similar to the generic one devised by Kurtz.¹⁸ DCR-11-type Nd:YAG laser with a pulse energy of 3 mJ/pulse was used as a source. Microcrystalline powdered sample of 4Cl4MSP/4Br4MSP was tightly packed in a glass capillary and exposed to a fundamental wave with a pulse width of 8 ns, repetition frequency 10 Hz, and a wavelength of 1064 nm. The generated second harmonic wave of 532 nm was detected by a photomultiplier tube (Hamamatsu-R 2059) and converted into electrical signal. The electrical signal was displayed on the oscilloscope (Tektronix-TDS 3000B). The signal amplitudes in volts indicate the SHG efficiency of the sample.

Third-Order Nonlinearity. The Z-scan experiment¹⁹ was performed with a picosecond (ps) amplifier (COHERENT) [seed pulse was from Micra laser oscillator (COHERENT)] generating 2 ps at a repetition of 1 kHz. The experiment was performed at a wavelength of 800 nm. The average and peak powers were \sim 2 W and \sim 1 GW, respectively. The diameter of the beam from the amplifier was 4 mm. Using ND filters the input energy was reduced so as to avoid higher order nonlinearities and/or damage.

3. RESULTS AND DISCUSSION

Characterization. The grown crystals were subjected to single crystal X-ray diffraction (XRD), and it was confirmed that instead of getting the final product 4Cl4MSP a co-crystal (2E)-1-(4bromophenyl)-3-[4-(methylsulfanyl)phenyl]prop-2-en-1-one/(2E)-1-(4-chlorophenyl)-3-[4-(methylsulfanyl)phenyl]prop-2-en-1-one (4Br4MSP/4Cl4MSP) was obtained. This is due to the presence of the impurity 4-bromoacetophenone in the starting material 4-chloroacetophenone. We synthesized repeatedly with the same initial materials, crystals were grown and characterized by single crystal XRD, and we got the same results. Ravindra et al.²⁰ studied chalcone co-crystal (C₁₈H₁₉NO₄/C₁₇H₁₆NO₃Br, 0.972/0.028), gotten accidentally due to the presence of impurity in the starting material. The co-crystal 4Br4MSP/4Cl4MSP belongs to the monoclinic crystal system having non-centrosymmetric space group Cc. The asymmetric unit contains one molecule of the compound 4Br4MSP/4Cl4MSP. The empirical formula of the compound is given by C₁₆H₁₃Br_{0.66}Cl_{0.34}OS, where Br was partially replaced by Cl. The occupancy ratio of Br and Cl is 66:34. Unit cell consists of four molecules; all the molecules are facing same direction. Along the chain molecules are arranged in a head to tail fashion. Molecules are arranged along the *a*-axis, facing the *bc* plane. The dihedral angle between the two aromatic rings of the molecule is found to be 47.98° . The details of the crystal data and refinement are given in Table 1. The molecular structure with thermal ellipsoids at 50% probability is represented in Figure 2. The hydrogen coordinates and isotropic displacement parameters are given in Table 2. The molecular packing with intermolecular hydrogen bonding is shown in Figure 3.

The UV-vis-NIR spectrum of the crystal is shown in Figure 4. Usually chalcone crystals show wider transparency range extending into the entire visible and IR region. The cutoff wavelength for this crystal is found to be at about 395 nm beyond which (typically from visible to IR region) there are no prominent absorption peaks. The peak absorption of the curve is mainly due to $n \rightarrow \pi$, $\pi - \pi^*$ transition and also due to the excitation of the C=O group of the molecule. The large cutoff wavelength may be attributed to the presence of Cl, Br groups in

Table 1. Crystal Data and Structure Refinement of the Co-Crystal

empirical formula	C ₁₆ H ₁₃ Br _{0.66} Cl _{0.34} OS
formula weight	318.12
temperature (K)	100(2)
wavelength (Å)	0.71073
crystal system	monoclinic
space group	Cc
unit cell dimensions	a = 33.690(5) Å
	b = 6.9613(10) Å
	c = 5.8427(9) Å
	$\beta = 90.577(4)^{\circ}$
volume	1370.2(3) Å ³
Ζ	4
density (calculated)	1.542 Mg/m ³
absorption coefficient	2.460 mm^{-1}
F(000)	654
crystal size	$0.44\times0.40\times~0.04~mm^3$
theta range for data collection	2.99-27.48°
index ranges	$-42 \le h \le 43, -9 \le k \le 8, -7 \le l \le 5$
reflections collected	4640
independent reflection	2571 [R(int) = 0.0398]
final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0503, wR_2 = 0.1152$
R indices (all data)	$R_1 = 0.0535, wR_2 = 0.1181$
refinement method	full-matrix least-squares on F^2

the structure. The molecule can be considered for device application in its region of transmission. It is desirable to have low absorption coefficient for NLO materials. The larger the absorption coefficient, the more is the dissipation of energy in materials. This causes undesirable thermal effects. The dependence of absorption coefficient α in terms of direct and indirect transition is most often performed with the help of formula derived for three-dimensional (3D) crystals. Their simplest form is as follows

 $\alpha h \nu = A (h \nu - E_g)^r$, for direct band gap

$$ahv = \sum_{j} A(hv - E'_{g} \pm E_{pj})^{r}$$
, for indirect band gap

Here, α is the absorption coefficient, calculated as a function of photon energy was derived from optical absorption spectrum. $E_{\rm g}$ is the energy gap for direct transition, $E_{\rm g}'$ is the energy gap for indirect transition, and $E_{\rm pj}$ is the energy of the phonons assisting the direct transition. *A* and *B* are parameters depending in more complicated ways on temperature, photon energy, and phonon energy $E_{\rm p}$. The value of *r* can be given by $^{1}/_{2}$ and 2, respectively, for direct and indirect band gap structure. The direct band gap can be obtained by plotting $(\alpha h \gamma)^{1/2}$ versus energy (ev), and indirect band gap can be determined from extrapolating the linear part of the curve to the energy axis (Figures 5 and 6). The direct and indirect band gap values thus obtained were found to be 2.7 and 2.8 ev, respectively. The energy gap values of the

Table 2. Hydrogen Coordinates (\times 10⁴) and Isotropic Displacement Parameters (Å² × 10³) for 4Br4MSP/4Cl4MSP

		,		
	x	у	z	U(eq)
H(2)	2490	8567	8752	20
H(3)	1846	8757	10200	19
H(5)	1408	6480	4277	19
H(6)	2055	6169	2926	21
H(8)	839	7997	5248	20
H(9)	451	6851	9173	22
H(11)	-246	6125	8959	18
H(12)	-874	6408	7298	21
H(14)	-373	8831	1708	17
H(15)	258	8541	3388	19
H(16A)	-1452	5890	5351	43
H(16B)	-1766	7422	4383	43
H(16C)	-1463	8016	6390	43



Figure 2. Molecular structure of co-crystal, drawn with 50% probability displacement ellipsoids and showing the atom labeling scheme.



Figure 3. Crystal packing when viewed down the *c*-axis.



Figure 4. UV-vis-NIR spectrum of the 4Br4MSP/4Cl4MSP crystal.



Figure 5. Plot of $(\alpha h \gamma)^{1/2}$ vs *E* (ev).

crystals determined at room temperature are within the energy gap range of semiconducting materials and therefore exhibit a semiconducting nature.²¹

The results of the TG/DTA analysis are shown in the Figure 7. The DTA curve implies that the material undergoes an irreversible endothermic transition where melting begins. The peak of the endothermic represents the temperature 143.99 °C at which melting terminates corresponds to its melting point. And it is clear that there is no phase transition before melting. The sharpness of the peak shows good crystallinity and purity of



Figure 6. Plot of $(\alpha h \gamma)^2$ vs *E* (ev).

the sample. The TG curve of this sample indicates that the sample is stable up to 300 °C. The endothermic peak of the DTA at 363.90 °C corresponds to the first phase of the weight loss in the TG curve, indicating decomposition of the sample. This endothermic peak is followed by an exothermic peak at 386.51 °C, indicating evaporation of decomposed compound.

The mechanical property plays a vital role in device fabrication. The hardness of a material depends on its plastic and elastic properties. Microhardness measurement is a general microprobe technique for assessing the bond strength, apart from being a measure of bulk strength. Hardness of a material is the measure of resistance it offers to local deformation. In the case of crystals, it can be understood in terms of resistance offered to dislocation motion. In general, it comes from the intrinsic resistance of crystals and the resistance caused by imperfection in the crystals. Usually the mechanical strength of organic materials is much lower than inorganic materials.^{22,23} Bending of organic crystals is shown to be a widespread phenomenon. It occurs when the packing is anisotropic in such a way that strong and weak interaction patterns are present in nearly perpendicular directions. Bending can be understood on the basis of a structural model that takes into account the highly anisotropic nature of the packing. When a crystal bends, two parallel opposite faces become nonplanar, that is, curved. Mechanical experiments on various types of crystals have established that bending depends completely on the nature of intermolecular interactions and the crystal packing.²⁴ The idea of the homologous temperature and the nature and type of chemical bonding present in the crystal are important. Crystals with comparable intermolecular interactions



Figure 7. TGA/DTA curve of the sample.



Figure 8. Variation of H_v and H_k with load.

in all three directions (when packing is isotropic) do not show bending and will be hard and brittle, whether the interactions in themselves are strong (hydrogen bonds) or weak (vander Waals). 25,26 Hardness testing is helpful in calculations of mechanical properties such as elastic constant, yield strength, etc. The most common method of hardness measurements is indentation type. The hardness is estimated from the ratio of the load applied on indenter to the area of the impression left on the specimen. From this, we are expected to get a constant value for hardness at any load. But in practice, load dependence is observed showing higher hardness values at low loads, and it decreases as the load is increased and finally becomes load independent. In some cases, though few, a different trend of an initial increase of hardness with an increase in load then followed by a decrease and finally hardness becoming load independent at higher loads was also observed.¹⁵ The Vickers hardness number (H_v) was calculated using the standard formula $H_v = 1.8544 P/d^2$, where *P* is the applied load in kg, *d* is in mm, and H_v is in kg/mm².

The Knoop indented impressions were approximately rhombohedral in shape. The average diagonal length (*d*) was considered for the calculation of the Knoop hardness number (H_k) using the relation, $H_k = 14.229 P/d^2$, where *P* is the applied load in kg, *d* in mm, and H_k is in kg/mm². Crack initiation and materials chipping become significant beyond 25 g of the applied load. The hardness test was carried out for the loads 3, 5, and 10 g. Figure 8 indicates the variation of H_v and H_k as a function of applied load. It can be observed that both values H_v and H_k decreases with increasing load, and for further higher loads hardness becomes independent of load. This type of behavior wherein the hardness number decreases with increasing applied load is called normal indentation size effect (ISE).

The ability of a crystal to withstand high power laser radiation is one of the important characteristics that any NLO material should possess for high power laser applications. The laser damage threshold of NLO components (Pockel's cells, frequency doublers, parametric oscillators, etc.) depends on physical and chemical imperfections, specific heat and thermal conductivity, optical absorption, growth imperfections (dislocations, growth ghosts) and impurities concentration and segregation. Usually, organic crystals show a very high damage threshold value compared to inorganic counterparts. The laser damage threshold of an optical crystal is an important factor affecting its applications. If the material has a low laser damage threshold it severely limits its applications, even though it has many excellent properties such as high optical transmittance and high SHG efficiency. The laser damage threshold studies were carried out on solution grown 4Br/ 4Cl4MSP single crystals using a Q-switched Nd:YAG laser of pulse width 6 ns at a wavelength of 1064 nm, and 10 Hz repetition rate, operating in TEM₀₀ mode, was used as the source. It was observed that co-crystal has a laser damage threshold value of 0.6038 GW/ cm^2 , and this value is found to be comparable with other chalcone crystals such as MNC and DMMC.¹⁵

Second- and Third-Order NLO Properties. In order to measure SHG efficiency of the co-crystal, urea crystals grounded into an identical size as that of sample were used as the reference



Figure 9. Open aperture Z-scan curve of the 4Br4MSP/4Cl4MSP compound. The solid line is a theoretical fit of the experimental data.



Figure 10. Pure NLR curve of chalcone cocrystal compound. The solid line is a theoretical fit of experimental data.

material. The SHG efficiency of the compound was found to be 16 times that of urea crystals with an identical particle size. This value is the highest SHG value for the co-crystals so far reported.

To study the third-order NLO properties, the single beam Z-scan technique was employed, which readily gives the magnitude and sign of the nonlinearity. The laser beam was focused into a 1 mm quartz cuvette that contained sample solution (dissolved in DMF solvent having 10^{-2} mole concentration) by using a 20 cm biconvex lens. The resulting beam waist radius at the focus was 25.44 μ m, corresponding to a Rayleigh length of 2.54 mm. For measuring the refractive nonlinear property, an aperture was placed in front of the detector and the transmittance was recorded as a function of the sample position on the Z-axis (closed aperture Z-scan). For measuring the nonlinear absorption, the sample transmittance was measured without the aperture as a function of sample position (open aperture Z-scan).

For a temporal Gaussian pulse with an incident Gaussian spatial profile, the on-axis transmission has been shown as a function of sample position relative to the lens focal point and the normalized transmittance for the open aperture Z-scan is given by^{27}

$$T(Z) = 1 - \frac{\beta I_0 L_{\text{eff}}}{2\sqrt{2}} \frac{1}{(1 + z^2/z_0^2)}$$
(1)

where I_0 is the peak irradiance at the focus, β is the nonlinear absorption coefficient, z_0 is the Rayleigh length given by the formula $z_0 = kw_0^2/2$ with k being the wave vector, ω_0 the beam waist radius at the focus, and L_{eff} the effective sample length. The open aperture Z-scan data (at 1 mW of input power) of the



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Figure 12. Plot of dynamic transmission vs I_0 .

80

100

Input intensity (GW/cm²)

120

140

160

60

0.025

0.020

0.015

0.010

40

sample is shown in Figure 9. The nonlinear refraction data obtained by dividing the closed aperture Z-scan data by the open aperture data is given in Figure 10. The nonlinear absorption coefficient was determined by fitting the experimental open aperture Z-scan data with (1). Similarly, the nonlinear refractive index was obtained by fitting the closed aperture Z-scan experimental data with the equation given in ref 28. The n_2 , β_{eff} Im $\chi^{(3)}$, and Re $\chi^{(3)}$ at 1 mW were found to be 3.257 × 10⁻¹⁴ esu, 5× 10⁻¹² cm W⁻¹, 0.98 × 10⁻²² m²/V² and 0.315 × 10⁻²² m²/V², respectively. The molecular hyperpolarizability of this chalcone calculated using the formula $\gamma_{\rm h} = \chi(3)R/L^4N$, where L is the local field factor and N is the number of molecules per cubic centimeter, was 0.045×10^{-32} esu. The observed third-order nonlinear parameters possess less magnitude than the reported values of chalcone samples studied with nanosecond pulse duration and the chalcone co-crystal studied using femtosecond pulse duration by Ravindra et al.^{29,20} It is observed that β_{eff} increases with an increase in I_0 (Figure 11), and the intercept on the vertical axis is nonzero suggesting that a higher order effect,



Figure 13. Crystal packing showing a parallel head-to-tail arrangement of the molecules with inter- and intramolecular bonding.

such as excited state absorption (ESA) via two photon absorption, contributed to nonlinear absorption (NLA).

Optical limiting is a phenomena observed when the transmission of a medium decreases with increasing input laser intensity (or fluence). The optical limiting behavior of this compound solution is shown in Figure 12. Materials that exhibit RSA usually show good optical limiting characteristics of the high intensity laser pulses. In order to observe RSA, the exited state absorption cross-section should be higher than that of the ground state absorption cross-section and is consistent with the present result. The excited state and ground state absorption cross-section determined using the equation present in the literature²⁹ are found to be 8.89×10^{-19} cm² and 2.3×10^{-19} cm², respectively. Therefore, in this chalcone, the two-photon assisted exited state absorption leading to RSA may be responsible for the optical limiting action.³⁰

Structure and Nonlinear Property Relationship. Chalcones are cross-conjugated molecules, and the carbonyl group in these systems breaks the conjugation system into two independent parts to have a 2D β character. In the molecular structure of chalcone co-crystal, the para position of benzoyl ring consists of a Br atom which is partially replaced by a Cl atom. Both Br and Cl are electron donating groups (the electron donating strength of chlorine is greater than bromine, Cl > Br). The SCH₃ group is also a donor group. The electron donating strength of the SCH₃ group is greater than Cl and Br. The co-crystal containing Br/Cl and SCH₃ at the ends and an electron acceptor carbonyl (C=O) group at the middle forms a donor- π -acceptor- π -donor (D- π -A- π -D) system, where charge transfer takes place from the donor ends to the acceptor at the middle of the molecule. The charge transfer to the carbonyl group is more effective from the donor attached to the phenylene group, rather than the benzoyl group. The shape of the chalcone derivatives can be considered as lambda shape (λ -shape), which helps to align the molecule in a parallel head-to-tail alignment in the crystal packing. Such molecular alignment usually exhibits high SHG efficiency.¹⁵ The presence of strong electron donating groups, the parallel head-to-tail alignment, and inter- and intramolecular hydrogen bonds are the reasons for the high SHG efficiency.

The crystal structure of co-crystal can be explained on the basis of two other crystal structures, namely, (2*E*)-1-(4-chlorophenyl)-3-[4-(methylsulfanyl)phenyl]prop-2-en-1-one (4Cl4MSP) and (2*E*)-1-(4-bromophenyl)-3-[4(methylsulfanyl)phenyl]prop-2-en-1-one

Table 3.	Inter- and Intramolecular Bonds and Bond Length		
in the Crystal Packing of Co-Crystal			

intramolecular bonding	bond length (Å)
Cl/Br···H2	2.932
$Cl/Br \cdots C2$	2.736
Cl/Br···C6	2.825
Cl/Br···H6	2.932
intermolecular bonding	bond length (Å)
Cl/Br···C16	3.603
$Cl-Br\cdots H16(c)$	3.09
С6Н3	2.881
C5H5···O1	2.573
С6Н6С6	2.881
C11H11C11	2.845
C11H11C12	2.894
C14H14C14	2.871

(4Br4MSP),^{31,32} since it contains both Br/Cl substituents. The crystal packing of the co-crystal is similar compared with other two crystals, with molecules aligned in a parallel head-to-tail fashion (Figure 13). The dihedral angles between the aromatic rings are 48.16° and 47.82°, respectively, for 4Cl4MSP and 4Br4MSP and can be comparable with the co-crystal. All the three crystals crystallize in the monoclinic system with Cc space group, and not only that crystallographic data representing the cell parameters are almost similar. The crystal packing of the cocrystal consists of a large number of inter- and intramolecular bonds shown in Table 3. But the crystal packing of 4ClMSP and 4BrMSP have only one intermolecular C-H···O bond. The measured value of the SHG efficiency of 4Br4MSP is 3.92 times that of urea and 4Cl4MSP is 8 times that of urea. The SHG efficiency of 4Cl4MSP is exactly half that of co-crystal. By considering all these facts, it clearly indicates that the presence of inter- and intramolecular bonds plays a significant role in enhancing SHG efficiency.

4. CONCLUSIONS

The co-crystal 4Cl4MSP/4Br4MSP was synthesized, and crystals were grown by the slow evaporation method at room temperature. FT-IR spectrum confirmed the presence of functional

groups in the molecular structure. It has a high melting point when compared to other reported chalcone molecules. The crystal structure was solved by the single crystal X-ray diffraction method and the lattice parameters were obtained. UV-vis-NIR spectra elucidated that the crystal may find useful optical applications in the transparent wavelength window region 400-1100 nm. The energy gap calculations reveal that the cocrystal is semiconductor in nature at room temperature. The SHG efficiency of the material was 16 times than that of urea. This is the highest reported value of SHG efficiency for the chalcone co-crystals. The laser damage threshold was found to be \sim 0.60 GW/cm² at a wavelength of 1064 nm. This co-crystal shows less efficient third-order nonlinear properties when compared with reported chalcone crystals and co-crystal. The present sample exhibited optical limiting behavior for picosecond laser pulses at 800 nm, which helps in designing the material for suitable photonic device applications.

ASSOCIATED CONTENT

Supporting Information. FT-IR spectrum of co-crystal 4Br4MSP/4Cl4MSP. This information is available free of charge via the Internet at http://pubs.acs.org/.

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