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Design, Synthesis and nonlinear optical properties of
(E)-1-(4-substituted)-3-(4-hydroxy-3-nitrophenyl)
prop-2-en-1-one compounds

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Abstract

A new series of (E)-1-(4-substituted)-3-(4-hydroxy-3-nitrophenyl)prop-2-en-1-one compounds have been synthesized by Claisen-Schmidt condensation reaction. Nonlinear optical characterization were carried out using z-scan technique with nanosecond pulses. These samples are found to exhibit strong nonlinear absorption at 532 nm and the nonlinear absorption coefficient of these samples exponentially increases with the increase of phonon characteristic energy. This relation speaks the role of phonon in the origin of nonlinear absorption in these compounds. The reported dependence of optical nonlinearity of the chalcone derivatives on the phonon characteristic energy will help in designing similar class of new molecules with high nonlinear coefficients.

Keywords: Chalcone, Nonlinear absorption, Phonon Contribution, Two-Photon Absorption.

1. Introduction

Large nonlinear optical coefficient, good transparency, high thermal and chemical stability are some of the most important requirements for a good nonlinear optical (NLO) material [1, 2, 3]. In the field of photonics, the search for advanced nonlinear optical materials possessing all these properties are

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important areas of research. Efforts are being made in recent years to develop such materials for their applications in telecommunication, optical data storage, nonlinear metamaterials and optical information processing [4, 5, 6]. Organic materials have most of the characteristics required for a good NLO material like high optical nonlinearity, ultrafast response and high damage resistance. In the quest for good nonlinear materials it is essential to identify how the nonlinear behaviour of the material scales with its other physical properties. Such scaling functions can be used for designing new materials and the structure can be modified by functional substitution to get desired optical nonlinear response. Conjugated compounds with electron donor and acceptor substituents are extensively studied for such optimizations. These materials generally show high second harmonic generation efficiency due to the presence of delocalized electrons. Chalcone based materials portray properties of a good nonlinear material like higher power conversion efficiency, chemical resistance with high damage threshold and these properties can be further enhanced with a suitable electron donor and acceptor substitution. Due to the conjugation the chalcone derivatives also display excellent blue light transmittance, large non-linear optical coefficients, and relatively short cutoff wavelength in transmission [7, 8, 9, 10, 11, 12, 13, 14, 15].

A series of new chalcones were synthesized with a minor modification in the well known (D- π -A- π -D) or (D- π -A- π -D) motif [16]. Chalcones are cross conjugated system as the carbonyl (C=O) group in the center operates as an electron acceptor. So, charge transfer is assumed to initiate from the ends of the molecule towards its center portion [17]. For each of the four compounds reported in this work, the -OH group acts as a donor group in conjugation with the α , β unsaturated carbonyl group. The motif was further tuned with the introduction of electron withdrawing -NO₂ group in ortho position to the hydroxyl group. In another part of the system, different kinds of substituents were incorporated. In the first sample, the substitution is -H, which has no electron donating or electron withdrawing effect. In the second sample, an electron withdrawing effect was introduced using -Br substituent. An even higher electron withdrawing effect with -Cl substitution was brought about in the third sample. The substituent Methoxy group, -OCH₃, (-OMe) was chosen to insert electron donating effect in the fourth compound. The structure of these compounds were identified using NMR spectrometer. Linear optical properties of the samples were studied using emission and absorption spectra. A comparative study of their nonlinear optical properties was done by z-scan measurements.

2. Experimental

2.1. Chemicals

Para Chloro Acetophenone, (GC 98%), para bromo acetophenone (GC 98%) and Para methoxy acetophenone (GC 99%) were obtained from Sisco Research Laboratories Pvt. Ltd, Para hydroxy benzaldehyde (GC 98%) and benzaldehyde (GC 98%) were obtained from Spectrochem. Chemical reagents were used without any further purification.

2.2. Synthesis

Synthesis of 4-hydroxy-3 nitro benzaldehyde was accomplished via nitration of para hydroxy benzaldehyde following the method similar to that reported by P. Ionita [18]. These compounds were synthesized following the conventional method of Claisen-Smith reaction. A solution of acetophenone derivative (3.6 mmol) and 4-hydroxy-3-nitrobenzaldehyde (3.6 mmol) in ethanol (10 ml) was warmed to 30-40° C in water bath. This hot solution was treated with a small portion of NaOH (10 mM). The reaction mixture was stirred for 1-4 hr and then left overnight. Progress of the reaction was monitored by thin layer chromatography using chloroform: methanol (9:1) as developing solvent. The resulting red solution was poured into crushed ice and carefully acidified using concentrated hydrochloric acid. The chalcones, which separated as a yellow solid, were collected by filtration after washing with water. The compounds were further purified by silica gel column (60-120 mesh) chromatography using chloroform as eluent. The general scheme of reaction and the structures of the compounds are given in Fig.1. In this article, the compounds with the substitution -R as Cl, Br, H and OCH₃ were coded as OHNH, OHNBr, OHNCl and OHNMe respectively.

2.3. Instrumentation

¹H (400 MHz spectrometer) and ¹³C (500 MHz spectrometer) Nuclear magnetic resonance spectra were recorded on Bruker DPX and the chemical shifts are expressed in ppm using tetramethylsilane as internal standard. Steady-state absorption spectra were recorded on a Shimadzu UV-1601PC absorption spectrophotometer. Fluorescence spectra of the samples were measured with a PerkinElmer LS 45 spectrofluorometer and the spectra were corrected for the instrument response function. Quartz cuvettes of 10 mm optical path length received from PerkinElmer, USA (part no. B0831009)

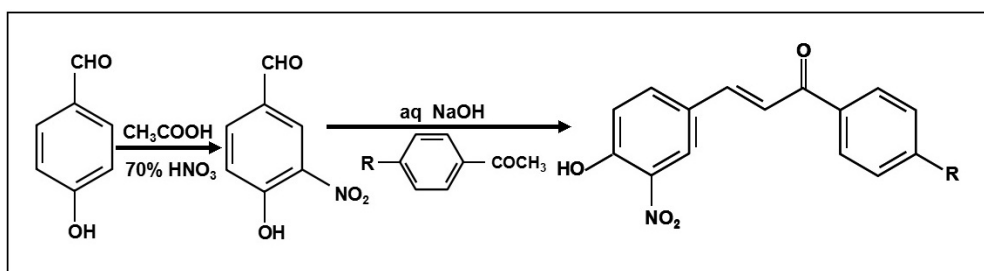


Figure 1: Reaction scheme for the synthesis of 1-(4-substituted)-3-(4-hydroxy-3-nitrophenyl) prop-2-en-1-one compounds. Here R represents any one of -Cl, -Br, -H, or -OCH₃.

and Hellma, Germany (type 111-QS) were used for measuring absorption and fluorescence spectra, respectively.

Z-scan measurements were carried out with the second harmonic of a Q-switched Nd-YAG laser pulses at 532 nm with a pulse duration of 28 ns (FWHM) with 1 Hz repetition rate. The laser beam was focused with a 20 cm focal length lens and the spot size at the focus was $\sim 60 \mu\text{m}$. During Z-scan the sample was kept in 1 mm path-length cell. Concentration of the samples used in the z-scan experiment was 1.3×10^{-8} M. The linear spectrum was found to remain same before and after the Z-scan measurements which ensured the stability of the compounds throughout the measurement.

3. Results and Discussion

3.1. NMR Spectrum

1. (E)-1-(4-bromophenyl) -3- (4-hydroxy-3-nitrophenyl) prop-2-en-1-one (OHNB_r): yellow solid, ¹H NMR (400 MHz, CDCl₃) 10.76 (s, 1H), 8.39(s, 1H), 7.47 (d, 1H, J 15.6 Hz), 7.78(d, 1H, J 15.6 Hz), 7.23(d, 1H, J 8 Hz) 7.87-7.91(m, 4H), 7.89-7.86(dd, 1H, J 2Hz and J 2Hz) ¹³C (500 MHz, CDCl₃) 188.6, 156.4, 142.1, 136.6, 136.5, 132.1, 130.0, 127.5, 121.1, 121.9, 120.9
2. (E)-1-(4-chlorophenyl) -3- (4-hydroxy-3-nitrophenyl) prop-2-en-1-one (OHNC_l) yellow solid, ¹H NMR (400 MHz, CDCl₃) 10.76(s, 1H), 8.39 (s, 1H), 7.47 (d, 1H, J 15.6 Hz), 7.78(d, 1H, J 15.6 Hz), 7.23 (d, 1H, J 8Hz), 7.99-7.95 (m, 4 H), 7.87.89-7.89 (dd, 1H, J 2Hz and J 2Hz) ¹³C (500 MHz, CDCl₃) 188.4, 188.3, 156.3, 142.0, 136.6, 129.9, 129.8, 129.0, 125.1, 121.9, 120.9

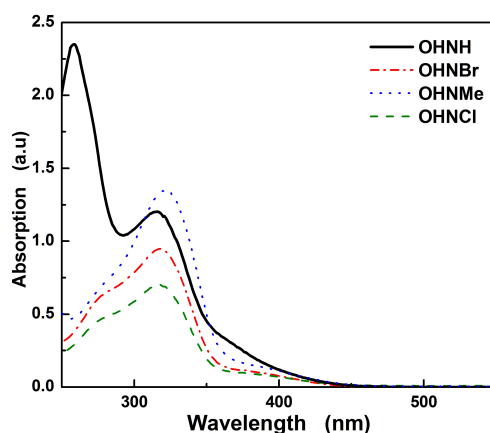


Figure 2: UV-Vis absorption spectra of the four Chalcone derivatives.

3. (E) -3- (4-hydroxy-3-nitrophenyl) -1- (4-methoxyphenyl) prop-2-en-1-one (OHNOMe): yellow shiny solid, $^1\text{H NMR}$ (400 MHz, CDCl_3) 10.74(s, 1H), 8.37(s, 1H), 7.47(d, 1H, J 15.6 Hz), 7.75(d, 1H, J 15.6 Hz), 7.22(d, 1H, J 8 Hz), 6.98-7.01(m, 2H), 7.89-7.86 (dd, 1H, J 2Hz and J 2Hz) 3.09(s, 3H) ^{13}C (500 MHz, CDCl_3) 188.5, 187.9, 156.0, 140.7, 136.6, 130.9, 130.6, 127.9, 122.4, 120.8, 113.9, 55.5
4. (E) -3- (4-hydroxy -3- nitrophenyl) -1- phenylprop -2- en-1-one (OHNH), pale yellow shiny solid, $^1\text{H NMR}$ (400 MHz, CDCl_3) 9.96(s, 1H), 8.39 (s, 1H), 7.28(d, 1H, J 16 Hz), 7.78 (d, 1H, J 16 Hz), 7.33(d,1H, J 8 Hz), 7.51-7.56(m, 1H), 7.61(d, 2H, J 8 Hz), 8.17-8.14 (dd, 1H, J 2Hz and J 2Hz).

3.2. Linear Optical Properties

The linear absorption spectra of the chalcone derivatives are represented in Fig.2. The spectra of all the compounds were recorded at room temperature in chloroform solution with of 0.5×10^{-8} M concentration. Clearly, all of them show two strong peaks in the UV-region, which are due to $\pi-\pi^*$ and $n-\pi^*$ transitions (Table. 1). The $\pi-\pi^*$ and $n-\pi^*$ transitions are attributable to the presence of aromatic ring and $\text{C}=\text{O}$ group respectively. The compounds studied here belong to a group of α , β unsaturated aromatic compounds. The aromatic benzene ring is the source of π electrons. In the present case, the aromatic ring is in conjugation with the carbonyl carbon. Interaction between the benzene ring and the carbonyl carbon induces an opposite polarity and the ring becomes electron deficient. The presence of carbonyl group gives

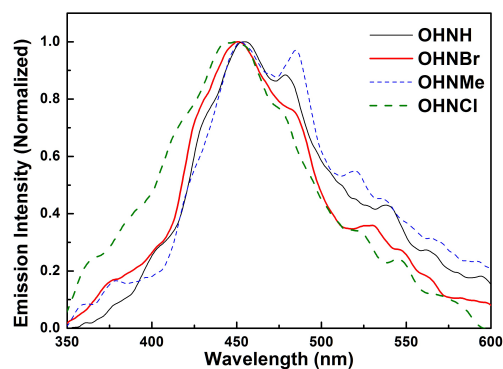


Figure 3: Normalized emission spectra of the four Chalcone derivatives when excited with 320 nm wavelength light.

Table 1: Peak attribution in the absorption and emission spectrum for all the samples.

Compound	Absorption Band		Emission Band	
	Peak (nm)	Peak Attribution	Peak (nm)	Width (nm)
OHNH	257	$\pi-\pi^*$	454	90
	315	$n-\pi^*$		
OHNBr	318	$\pi-\pi^*$	318	82
	394	$n-\pi^*$		
OHNMe	321	$\pi-\pi^*$	452	105
	400	$n-\pi^*$		
OHNCl	316	$\pi-\pi^*$	446	94
	395	$n-\pi^*$		

the possibility of $n-\pi^*$ and also $\pi-\pi^*$ transitions. Unsaturated molecules that contain oxygen undergo $n-\pi^*$ transitions due to the presence of non-bonding electrons in the oxygen atom [19]. In the spectral region from 420 nm to 800 nm the compounds are nearly transparent. Note that the linear absorption coefficient of the samples is negligible at the wavelength of Z-scan measurements (532 nm). Figure 3 shows the emission spectra of the compounds when excited at 320 nm. All the compounds have an emission maximum near 450 nm and the emission spectra has a full width at half maximum of nearly 100 nm. We attribute the shift between the absorption band edge and the emission peak wavelength to the solvent induced stokes-shift [20, 21].

The optical energy gap was calculated from the absorption spectrum of each sample (Fig.4) [22] using the Tauc's plot. Where α is the linear absorption coefficient, h is the Planck's constant and ν is the optical frequency. In case of indirect bandgap materials, both the bandgap (E_g) and phonon characteristic energy (E_p) defines the variation of linear absorption with incident photon energy. The dual slope behavior of the Tauc plot near the band edge clearly indicates that the compounds have indirect bandgap [23]. By fitting two straight lines to the near band edge data (as presented in Fig.4) and identifying where it intersects the photon energy axis, we estimated the values of $(E_g - E_p)$ and $(E_g + E_p)$ for each of the sample [23]. From these two parameters the E_g and E_p were calculated. The values of the bandgap obtained by this method are 2.9 eV, 2.88 eV, 2.96 eV, and 2.89 eV for OHNH, OHNCl, OHNBr, and OHNMe respectively and their corresponding phonon characteristic energies are 0.25 eV, 0.41 eV, 0.34 eV and 0.37 eV. (Table-2).

3.3. Nonlinear Optical Properties

Figure 5 shows the open aperture data of Z-scan measurements with 532 nm beam for the samples. Single laser pulse energy was $\sim 570 \mu\text{J}$. When the samples are far off the focal point of the beam the transmission (larger z values) is ~ 1.0 , as at 532 nm the samples have negligible absorption at low intensities. On the other hand, near the focal point the transmission reduces and reaches a minimum at $z = 0$. The lowering of transmission at higher intensities refers to nonlinear absorption.

The rate of change in intensity (I) as the beam propagates through a sample which has absorption originating only from third-order susceptibility can be written as

$$\frac{dI}{dz} = -\beta I^2, \quad (1)$$

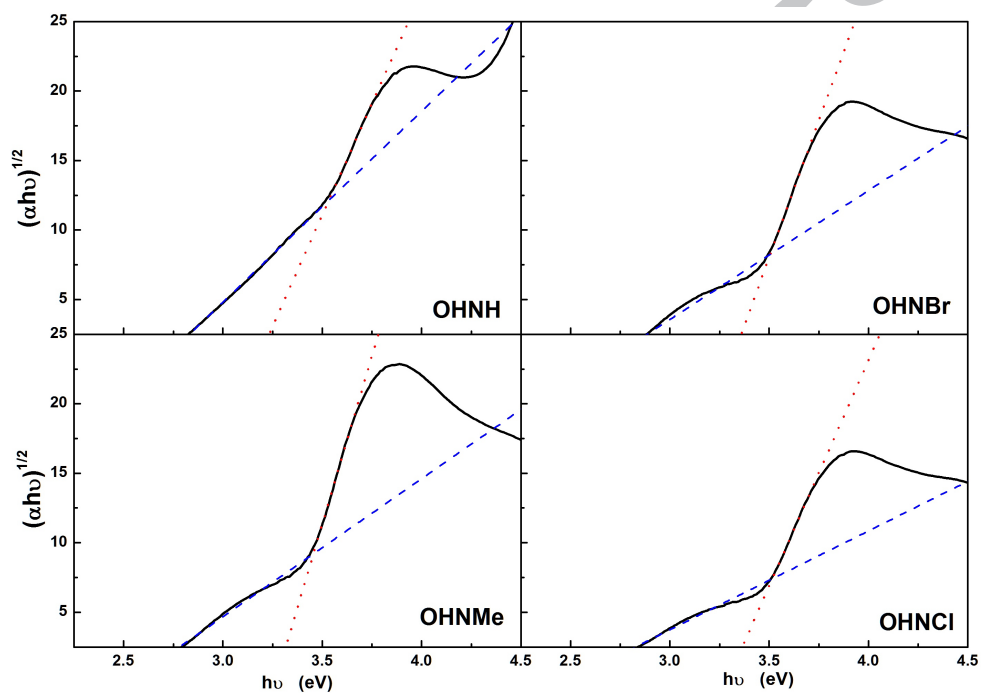


Figure 4: Tauc plot of the compounds for estimation of the bandgap. Solid curve is the experimental data. Blue dashed lines and red dotted lines are the linear fit to a part of the data to calculate the values of $(E_g - E_p)$ and $(E_g + E_p)$ respectively.

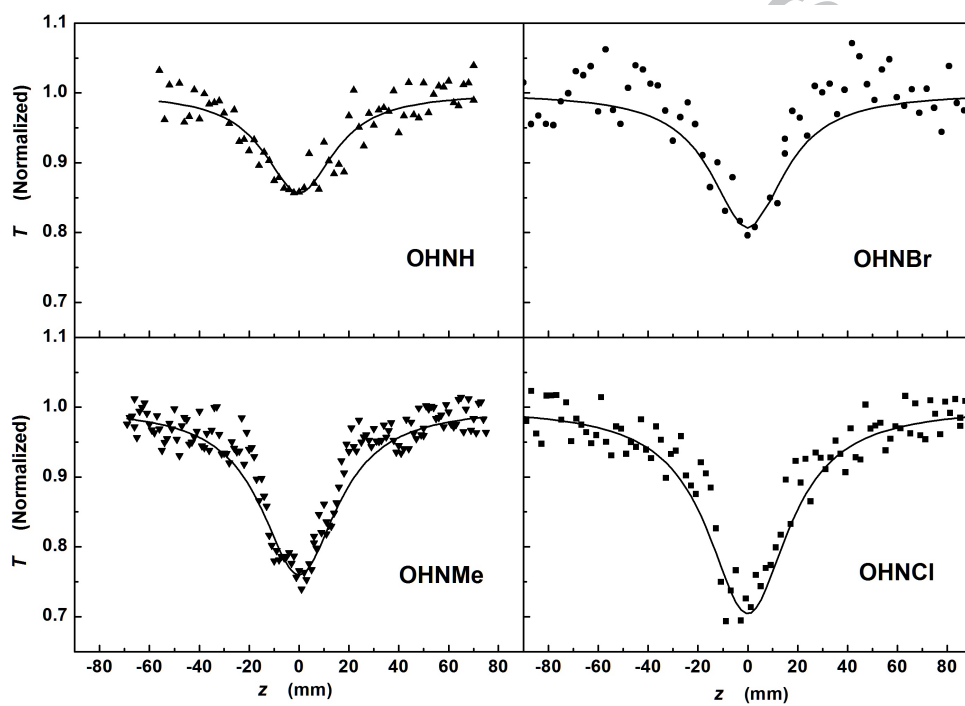


Figure 5: Open aperture z-scan data of the chalcone derivatives measured with pulse energy $\sim 570 \mu\text{J}$. Solid lines are the best fit to the data using Eq.3.

where β is the nonlinear absorption coefficient related to the imaginary part of third-order nonlinearity of the sample. For a Gaussian intensity distribution (in space and time), when the sample is kept at z , the intensity distribution at the entrance segment of the sample is given by,

$$I(r, t, z) = \frac{I_0}{1 + (z/z_0)^2} \exp \left[-2 \left(\frac{r}{\omega_0} \right)^2 - \left(\frac{t}{t_0} \right)^2 \right], \quad (2)$$

where ω_0 is the beam radius, I_0 is the peak intensity and t_0 is the pulse width. z_0 is the Rayleigh range given by $z_0 = \pi\omega_0^2/\lambda$, where λ is the wavelength of light used. Using Eq.1 and Eq.2 the energy of the pulse transmitted through the sample kept at z (T) can be obtained by integration over space and time and is given by [24],

$$T(z) = \frac{1}{\sqrt{\pi}q(0, 0, z)} \int_{-\infty}^{\infty} \ln [1 + q(0, 0, z) \exp(-\tau^2)] d\tau \quad (3)$$

where, $q(r, t, z) = \beta I(r, t, z)L$ and L is the thickness of the sample. The experimental z-scan data was fit to Eq.3 by solving it numerically with β as the fitting parameter. The best fit values of β are given in the Table.2. Among the four samples, OHNCl showed the maximum nonlinear absorption which is nearly 3 times than that of the OHNH. Note that the samples show some emission at 532 nm. This implies that there are some states which can absorb the wavelength at which the z-scan experiment was performed. At higher intensities these carriers which are excited by a single 532 nm photon may farther get excited to higher energy states at 266 nm where the sample has strong absorption (Fig. 2). Hence, we attribute the measured nonlinear absorption to the two-step two-photon absorption involving vibrational states [25].

As discussed earlier, the substituents in the compounds have different electron donating or withdrawing effects. Methoxy group (-OMe) has electron donating capacity, -Br and -Cl has electron withdrawing effect while H has no electron donating or electron withdrawing effect. However, the nonlinear absorption did not show any correlation with electron donating or withdrawing effects. On an average, the nonlinear absorption coefficient of the samples reported here is much higher as compared to other compounds of similar genre [26, 27, 28]. Thus, the (E)-1-(4-substituted)-3-(4-hydroxy-3-nitrophenyl) prop-2-en-1-one derivatives are strong nonlinear absorption materials for operation at 532 nm.

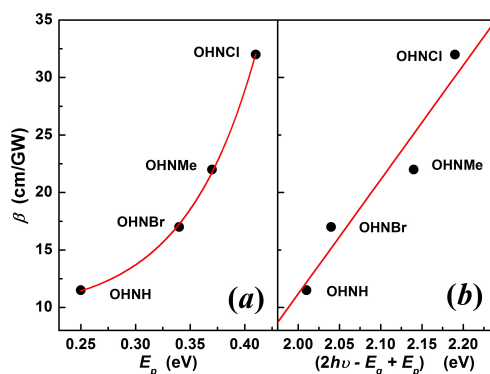


Figure 6: Variation of nonlinear absorption coefficient of the four samples (a) with the phonon characteristic energies, E_p , and (b) with the $(2h\nu - E_g + E_p)$. The red line is the best fit to the data with an exponential growth and linear functions for the above two cases respectively.

We found that the nonlinear absorption of (E)-1-(4-substituted)-3-(4-hydroxy-3-nitrophenyl)prop-2-en-1-one derivatives do not reveal any consistent variation with the bandgap of the material (See Table.2) but manifested intriguing relation with the phonon characteristic energy. Figure 6(a) shows the variation of nonlinear absorption of the four compounds with the phonon characteristic energies. The nonlinear absorption increases exponentially with the increase in photon characteristic energies. Studies depicted that phonons can play a strong role in the nonlinear absorption properties of different kinds of materials [25, 29, 30, 31, 32]. Hence, the phonons and the vibrational states must be playing a strong role in the nonlinear absorption observed in the present samples in nanosecond time scale [25].

A. R. Hassan has theoretically studied the dependence of two-photon absorption on the indirect bandgap of bulk semiconductors and semiconductors confined in one or two dimensions [33]. They have affirmed that the two-photon absorption coefficient scales with $(2h\nu - E_g + E_p)^\sigma$ where ν is the frequency at which β was measured. The value of σ depends on the dimensions of the semiconductor [33]. Although chalcones are very different from semiconductors, it would be interesting to see how the measured nonlinear absorption scales with $(2h\nu - E_g + E_p)$. In this present report, we explored that the nonlinear absorption coefficients of the samples increase nearly linearly with $(2h\nu - E_g + E_p)$ (Fig.6(b)).

Table 2: The measured nonlinear absorption coefficient of the samples along with their corresponding bandgap (E_g) and phonons characteristic energies (E_p)

Compound	E_g (eV)	E_p (eV)	β (cm/GW)
OHNH	2.9	0.25	11.5
OHNBr	2.96	0.34	17
OHNMe	2.89	0.37	22
OHNCl	2.88	0.41	32

4. Conclusions

Four new chalcone derivatives, abbreviated as OHNH, OHNBr, OHNMe and OHNCl were synthesized using a green and cheap synthetic method. Among them, OHNCl showed the maximum and OHNH had the least nonlinear absorption coefficient. We have shown that the measured nonlinear absorption coefficient of these samples increases exponentially with the increase in phonon characteristic energy and the nonlinear absorption coefficient scales linearly with $(2h\nu - E_g + E_p)$. The origin of nonlinear absorption in nanosecond time scale must be strongly mediated by phonon contributions. The compounds presented here exhibits satisfactory nonlinear optical responses and thus can be considered for designing suitable optical devices for optoelectronic applications.

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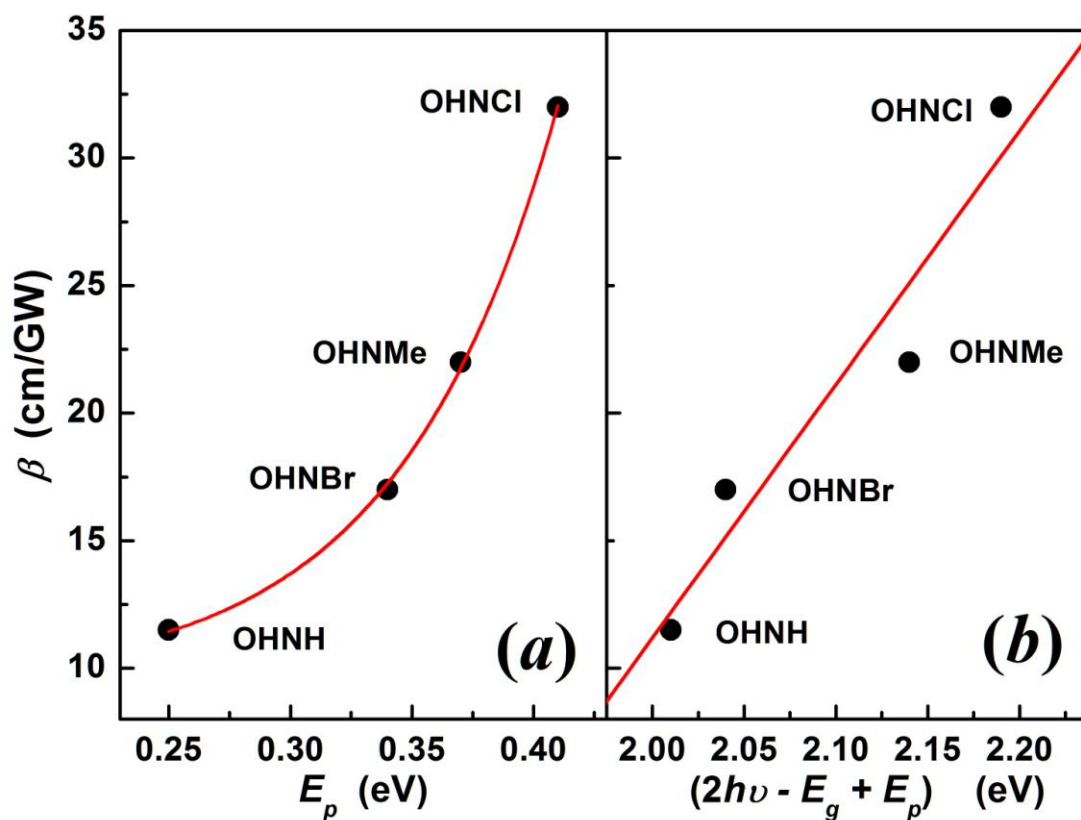
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Synthetic method of a new series of (E)-1-(4-substituted)-3-(4-hydroxy-3-nitrophenyl)prop-2-en-1-one nonlinear optical compounds is reported.

It has been shown that the measured nonlinear absorption coefficient of these materials depend on the phonon characteristic energies, indicating the role of phonon in the origin of nonlinear absorption.

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The variation of nonlinear absorption coefficient of the (E)-1-(4-substituted)-3-(4-hydroxy-3-nitrophenyl) prop-2-en-1-one compounds (a) with the phonon characteristic energies, E_p and (b) with the $(2h\nu - E_g + E_p)$. The red line is the best fit to the data with an exponential growth function and linear function for the above two cases respectively.