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ABSTRACT

Using green chemical method a series of fifteen systematically substituted 3-(9-substituted anthracen-10-yl)-1-(4-phenyl substituted)prop-2-en-1-one derivatives having high nonlinear absorption coefficient have been synthesized. The nonlinear absorption properties of these compounds were studied using nanosecond pulses at 532 nm wavelength. All 15 derivatives are found to show high nonlinear absorption in the range of 35–640 cm/GW. Among these the derivatives with –NO₂ as one of the substitution group show higher nonlinear absorption. The origin of high nonlinear absorption with low linear absorption in the compounds has been attributed to two-step two-photon absorption process. We have shown that the energy bands of these compounds are distributed such that for excitation at 532 nm they have strong nonlinear absorption. These properties of the reported compounds make them a potential candidate for biological imaging and other applications which are based on nonlinear absorption.

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1. Introduction

Nonlinear optical properties of organic molecules including chalcone derivatives are being studied for applications like twophoton fluorescence excitation microscopy, two-photon up-conversion lasing, 3D nano/microfabrication, and photodynamic therapy etc. [1-14]. For such applications, molecules with high nonlinear absorption cross-sections with low linear absorption are required. To design compounds with such optimized properties it is essential to understand the correlation between the energy level structure of the compound and its optical response. In principle it is possible to theoretically calculate the optical response of the designed molecule. However, these calculations are complex and computationally demanding and the calculated results would still have to be verified by experiments [15]. Therefore, preparing a set of compounds with specific systematic changes in the structure and measuring the optical properties is a more direct way to understand the correlation between the structure of a compound and optical response.

In compounds having π -electrons, the primary origin of

nonlinearity is the delocalization of these electrons [15,16]. The nonlinearity of a compound can be directly correlated to the number of π -electrons in it. Due to this scaling with π -electrons, the nonlinear coefficient of these compound is normally divided by the number of π -electrons in order to have an idea of the effect of other factors [15,16]. In principle it is possible to have a large nonlinear optical response by designing the molecule to have a large number of π -electrons. However it is also desirable to minimize the size of the molecule so that it can be densely packed for device applications. Hence it is essential to design and optimize other properties of the compound also in order to maximize the nonlinear response with the smallest possible size.

Attaching a electron donor (D) and/or electron acceptor (A), to a compound is one of the effective ways to improve its nonlinear optical response [17–22]. Different configurations like D- π -A, D- π -A- π -D and D- π -A- π -A are being studied extensively for their contribution to nonlinear optical properties as well as for other applications [17–19,22]. Further, the position of the D and/or A in the compound as well as its donating or accepting strength are known to affect the nonlinear optical response [17,20,21]. Based on the "isolated molecule approach", the electronic effect that a substituent can exert on the compound can be broadly classified into either a resonance or an inductive effect. The resonance effect occurs through π -electrons while the inductive effect occurs through



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σ-electrons. Substituted groups like –OCH₃ and –NO₂ interact with an aromatic compound through a resonance effect by donating an electron or withdrawing an electron respectively. On the other hand, substitution of –CH₃, a electron donating group, leads to interaction via σ-electrons (inductive effect). Halogen substitutions are known to interact with the base compound via both resonance as well as inductive effects [17–22]. However, systematic studies on linear as well as nonlinear properties of chalcones by changing the attached groups R₁ and R₂ (See Fig. 1) of different D or A properties, in an R₁-π-A-π-R₂ configuration are not available.

In this article, we present the synthesis procedure and nonlinear absorption properties of a series of fifteen new anthracene-based chalcone derivatives (labeled S01 to S15). This series of compounds can be further divided into three sub-series according to the group attached in the 9th position of the anthracene skeleton. The general structure of these compounds under study can also be categorized into two basic structural families of D- π -A- π -D and A- π -A- π -D. We have targeted anthracene, as it is one of the most attractive π centers; it is planar as well as an excellent fluorophore [23,24]. Compounds containing the anthracene moiety have ample advantages over many other π -centers and are being widely studied for their nonlinear optical properties [9,25–29]. Moreover, chalcone derivatives have the -C=O group as acceptor and are well known for their NLO properties like second harmonic generation and lasing [20,30]. Our focus is investigate the dependence of the third-order optical nonlinearity, specially the nonlinear absorption coefficient, on substituents like -Cl, -Br, -NO₂, -CH₃, -OCH₃.

2. Synthesis procedure and experimental details

E/Z-3-(9-substitutedanthracen-10-yl)-1-(4-phenylsubstituted) prop-2-en-1-one derivatives have been synthesized by Claisen-Schmidt condensation (process A) as shown in Fig. 1. The intermediate compound S17 was prepared by the Wittig reaction, a one step alkene-forming reaction, on S16 with reasonable yield. This process is shown as B in Fig. 1. The compounds S18 and S21 were prepared by Vilsmeier Haack reaction on S17 and S20 respectively with modest yields which are shown as process C in Fig. 1. Methylation of the compound S19 with dimethyl sulphate, using phase transfer catalyst, furnished S20 (process D). The detailed preparation procedure of these compounds and the structure estimated from ¹H NMR, ¹³C NMR, IR, and ESI-HRMS measurements are given below. The spectra of some of the synthesized chalcones shows presence of both *E* and *Z* forms. Their corresponding ratio has also been mentioned in the corresponding synthesis and characterization portion of the compound.

(E)-3-(anthracen-10-yl)-1-(4-chlorophenyl)prop-2-en-1-one (S01): A solution of 50% NaOH (w/v) was added to a mixture of 4chloroacetophenone (1 mmol, 155 mg) and commercially available 9-anthracenecarboxaldehyde (1 mmol, 206 mg) (S16) in 75 ml of methanol. The mixture was refluxed with continuous stirring for 6 h and then refrigerated overnight. The reaction mixture was neutralized with concentrated HCl. The obtained precipitate was collected by filtration and purified by column chromatography on silica gel (60–120 mesh) using (EtOAc: Hexane = 25:1) as the eluent. Yield: 272 mg (70%). mp 132–134°C. IR (KBr, cm⁻¹): 3048 (Ar-CH), 1655 (C=O). ¹H NMR (400 MHz, CDCl₃): δ 8.84 (d, J = 16 Hz, ¹H), 8.51 (s, 1H), 8.30 (d, J = 8 Hz, 2H), 8.07–8.03 (m, 4H), 7.94 (d, J = 16 Hz, 1H), 7.56–7.50 (m, 5H), 7.44 (d, J = 8 Hz, 1H). ¹³C NMR (CDCl₃): δ 189.09, 142.21, 136.02, 131.11, 130.20, 129.93, 128.91, 128.83, 128.38, 125.30, 125.01. ESI-HRMS [M + H]⁺ calcd for C₂₃H₁₆ClO *m*/*z* 343.0884. found 343.0864.

The ¹H NMR (400 MHz) spectrum of S01 in CDCl₃ solvent is shown in Fig. SI-10 and its structure with the protons designated as Ha and Hb is shown in the inset of Fig. SI-10. A doublet with J = 16 Hz, centered at $\delta = 8.84$ ppm is observed for the Ha proton,



Fig. 1. Scheme: Reagents and conditions: (A) 50% NaOH in Methaol, 60 °C; (B) HOCH₂CH₂OCH₂CH₂OCH₂CH₂OH, NH₂NH₂, aq. KOH, 200 °C, 80%. (C) DMF, C₆H₄Cl₂, POCl₃, 100–110 °C, (18) 52%, (21) 60%; (D) (CH₃)₂SO₄, aq. NaOH, CH₂Cl₂, C₁₃H₂₂ClN, r.t, 85%; The general structure of all the compounds and the groups attached are also shown in the top right corner.

another doublet with J = 16 Hz, centered at 7.94 ppm is observed for the Hb proton. This confirms the trans configuration of the compound. Fig. SI-11 is the ¹³C NMR (100 MHz, CDCl₃) spectrum of S01. $\delta = 189.09$ ppm for the carbonyl carbon. Fig.SI-12 displays the mass spectrum. ESI-HRMS [M + H]⁺ calculated for S01 [C₂₃H₁₆ClO] m/z is 343.0884 from measurement it comes out to 343.0864. The structure of all other compounds were also confirmed by following a similar procedure. The spectra of all these samples are also presented in the Supporting Information (S·I).

(*E*)-3-(*anthracen*-10-yl)-1-(4-*bromophenyl*)*prop*-2-*en*-1-*one* (**S02**): S02 was synthesized from S16 (1 mmol, 206 mg) and 4bromoacetophenone (1 mmol, 199 mg) by the same procedure as described for S01 except that the reaction time was 7 h. The product was purified by column chromatography on silica gel (60–120 mesh) using (EtOAc: Hexane = 25: 1) as the eluent. Yield: 309 mg (80%). mp 149–151°C. IR (KBr, cm⁻¹): 3046 (Ar-CH), 1662 (C=O). ¹H NMR (400 MHz, CDCl₃): δ 8.83 (d, *J* = 16 Hz, 1H), 8.50 (s, 1H), 8.30 (d, *J* = 8 Hz, 2H), 8.05 (d, *J* = 8 Hz, 2H), 7.96 (d, *J* = 8 Hz, 2H), 7.67 (d, *J* = 8 Hz, 2H), 7.58–7.52 (m, 5H). ¹³C NMR (CDCl₃): δ 188.34, 142.30, 136.45, 131.92, 131.13, 130.20, 130.06, 129.50, 128.85, 128.53, 128.42, 126.42, 125.03 ppm. ESI-HRMS [M + H]⁺ calcd for C₂₃H₁₆BrO *m*/*z* 387.0379, found 364.0363.

(*E*)-3-(*anthracen*-10-yl)-1-(4-*nitrophenyl*)*prop*-2-*en*-1-*one* (**S03**): S03 was synthesized from S16 (1 mmol, 206 mg) and 4nitroacetophenone (1 mmol, 165 mg) by the same procedure as described for S01 except that the reaction time was 2 h. The product was purified by column chromatography on silica gel (60–120 mesh) using (EtOAc: Hexane = 25: 1) as the eluent. Yield: 307 mg (87%). mp 142–144°C. IR (KBr, cm⁻¹)): 3041 (Ar-CH), 1657 (C=O). ¹H NMR (400 MHz, CDCl₃): δ 8.90 (d, *J* = 16 Hz, 1H), 8.53 (s, 1H), 8.38 (d, *J* = 8 Hz, 2H), 8.29 (d, *J* = 8 Hz, 2H), 8.23 (d, *J* = 8 Hz, 2H), 8.07 (d, *J* = 8 Hz, 2H), 7.58 (m, 5H). ¹³C NMR (CDCl₃): δ 188.07, 149.65, 143.85, 142.53, 131.24, 129.97, 129.66, 129.13, 129.77, 125.51, 124.51, 124.90, 123.91. ESI-HRMS [M +H]⁺ calcd for C₂₃H₁₆NO₃ *m*/*z* 354.1125, found 354.1124.

(*E*)-3-(*anthracen*-10-yl)-1-(4-*methoxyphenyl*)*prop*-2-*en*-1*one* (**S04**): S04 was synthesized from S16 (1 mmol, 206 mg) and 4methoxyacetophenone (1 mmol, 150 mg) by the same procedure as described for S01 except that the reaction time was 3 h. The product was purified by column chromatography on silica gel (60–120 mesh) using (EtOAc: Hexane = 25: 1) as the eluent. Yield: 262 mg (78%). mp 114–116°C. ¹H NMR (400 MHz, CDCl₃): δ 8.79 (d, *J* = 16 Hz, 1H), 8.47 (s, 1H), 8.33 (d, *J* = 8 Hz, 2H), 8.10 (d, *J* = 8 Hz, 2H), 8.04 (d, *J* = 8 Hz, 2H), 7.57 (d, *J* = 16 Hz, 1H), 7.53–7.51 (m, 4H), 7.00 (d, *J* = 8 Hz, 2H), 3.89 (s, 3H). ¹³C NMR (CDCl³): δ 187.56, 163.39, 140.66, 131.04, 130.80, 130.66, 130.17, 129.37, 128.68, 128.02, 126.11, 125.17, 124.84, 113.73, 112.98, 55.21. ESI-HRMS [M + H]⁺ calcd for C²⁴H¹⁹O² *m*/*z* 339.1380, found 339.1381.

(*E*)-3-(*anthracen*-10-yl)-1-*phenylprop*-2-*en*-1-*one* (**S05**): S05 was synthesized from S16 (1 mmol, 206 mg) and acetophenone (1 mmol, 120 mg) by the same procedure as described for S01 except that the reaction time was 4 h. The product was purified by column chromatography on silica gel (60–120 mesh) using (EtOAc: Hexane = 25: 1) as the eluent. Yield: 206 mg (67%). mp 120–122°C. IR (KBr, cm⁻¹): 3049 (Ar-CH), 1655 (C=O). ¹H NMR (400 MHz, CDCl₃): δ 8.82 (d, *J* = 16 Hz, 1H), 8.48 (s, 1H), 8.33 (d, *J* = 8 Hz, 2H), 8.11 (d, *J* = 8 Hz, 2H), 8.05 (d, *J* = 8 Hz, 2H), 7.59 (d, *J* = 16 Hz, 2H), 7.54–7.52 (m, 5H). 7.62 (d, *J* = 8 Hz, 1H). ¹³C NMR (CDCl₃): δ 189.43, 141.67, 132.92, 131.06, 130.76, 129.88, 129.42, 128.55, 128.29, 126.25, 126.22, 125.06. ESI-HRMS [M + H]⁺ calcd for C₂₃H₁₇O *m/z* 309.1274, found 309.1273.

(E)-1-(4-chlorophenyl)-3-(9-methylanthracen-10-yl)prop-2-

en-1-one (**S06**): 9-methylanthracene-10-carbaldehyde (S18) was synthesized in aqueous KOH solution and hydrazine hydrate following the reported procedure from commercially available S16.

A 50% NaOH (w/v) solution was added to a mixture of 4chloroacetophenone (1 mmol, 155 mg) and (S18) (1 mmol, 220 mg) in 25 ml of methanol. The mixture was refluxed with continuous stirring for 6 h and then refrigerated overnight. The reaction mixture was neutralized with concentrated HCl and precipitate obtained was collected by filtration and purified using column chromatography on silica gel (60–120 mesh) using (EtOAc: Hexane = 1: 20), *trans* 20%. Yield: 192 mg (54%). mp 139–141°C. ¹H NMR (400 MHz, CDCl³): δ 8.38 (d, *J* = 12 Hz, 1H), 8.35–8.31 (M, 4H), 8.04 (d, *J* = 8 Hz, 2H), 7.82 (d, *J* = 8 Hz, 2H), 7.57 (d, *J* = 8 Hz, 2H), 7.52 (d, *J* = 8 Hz, 2H), 7.48 (d, *J* = 12 Hz, 1H), 3.17 (s, 3H). ¹³C NMR (CDCl³): δ 188.29, 143.08, 140.37, 139.44, 130.38, 130.03, 129.72, 129.40, 129.25, 129.14, 128.99, 128.61, 128.51, 127.75, 125.86, 125.30, 125.19, 125.07, 124.93, 124.01, 14.42, 14.11. ESI-HRMS [M + H]⁺ calcd for C₂₄H₁₈ClO *m/z* 357.1041, found 357.1049.

(*Z*)-1-(4-bromophenyl)-3-(9-methylanthracen-10-yl)prop-2en-1-one (S07): S07 was synthesized from S18 (1 mmol, 220 mg) and 4-bromoacetophenone (1 mmol, 199 mg) by the same procedure as described for S06. The product was purified by column chromatography on silica gel (60–120 mesh) using (EtOAc: Hexane = 1: 20) as the eluent. Yield: 236 mg (59%). mp 190–192°C. IR (KBr, cm⁻¹): 3026 (Ar-CH), 1666 (C=O). ¹H NMR (400 MHz, CDCl³): δ 8.26 (d, *J* = 8 Hz, 2H), 8.09 (d, *J* = 8 Hz, 2H), 8.00 (d, *J* = 8 Hz, 1H), 7.51–7.44 (m, 5H), 7.29 (d, *J* = 8 Hz, 2H), 7.08 (d, *J* = 8 Hz, 2H), 3.06 (s, 3H). ¹³C NMR (CDCl³): δ 192.14, 140.38, 138.26, 130.73, 130.47, 129.45, 128.71, 129.24, 125.92, 125.44, 125.14, 124.98, 14.19. ESI-HRMS [M + H]⁺calcd for C₂₄H₁₈BrO *m/z* 401.0536, found 401.0538.

(*E*)-3-(9-*methylanthracen*-10-yl)-1-(4-*nitrophenyl*)*prop*-2-*en*-1-*one* (**S08**): S09 was synthesized from S18 (1 mmol, 220 mg) and 4-nitroacetophenone (1 mmol, 165 mg) by the same procedure as described for S06 except that the reaction time was 1 h. The product was purified by column chromatography on silica gel (60–120 mesh) using (EtOAc: Hexane = 1: 10) as the eluent. Yield: 300 mg. (78%). mp 172–174°C. IR (KBr, cm⁻¹): 3031(Ar-CH), 1658 (C=O). ¹H NMR (400 MHz, CDCl₃): δ 8.91 (d, *J* = 16 Hz, 1H), 8.39–8.36 (m, 4H), 8.32 (d, *J* = 8 Hz, 2H), 8.22 (d, *J* = 8 Hz, 2H), 7.54–7.60 (m, 4H), 7.51 (d, *J* = 16 Hz, 1H), 3.17 (s, 3H). ¹³C NMR (CDCl₃): δ 187.71, 149.78, 144.20, 142.27, 132.76, 129.66, 129.20, 127.60, 125.82, 125.53, 125.33, 125.08, 124.99, 123.54, 14.25. ESI-HRMS [M + H]⁺ calcd for C₂₄H₁₈NO₃ *m*/*z* 368.1281, found 368.1283.

(*E*)-3-(9-methylanthracen-10-yl)-1-(4-methoxyphenyl)prop-2-en-1-one (S09): S09 was synthesized from S18 (1 mmol, 220 mg) and 4-methoxyacetophenone (1 mmol, 150 mg) by the same procedure as described for S06 except that the reaction was refluxed for 7 h and stirred at room temperature for 5 h. The product was purified by column chromatography on silica gel (60–120 mesh) using (EtOAc: Hexane = 40: 1) as the eluent. *trans* 75%. Yield: 235 mg. (67%). mp 159–161°C. ¹H NMR (400 MHz, CDCl₃): δ 8.80 (d, J = 16 Hz, 1H), 8.36 (t, J = 8 Hz, 2H), 8.10 (d, J = 8 Hz, 2H), 7.57–7.50 (m, 5H), 7.00 (d, J = 8 Hz, 2H), 3.90 (s, 3H), 3.17 (s, 3H). ¹³C NMR (CDCl₃): δ 188.23, 163.89, 142.02, 132.25, 131.32, 130.07, 129.58, 126.45, 125.99, 125.60, 125.45, 114.24, 55.79, 14.72. ESI-HRMS [M + H]⁺ calcd for C₂₅H₂₁O₂ m/z 353.1536, found 357.1541.

(*Z*)-3-(9-methylanthracen-10-yl)-1-phenylprop-2-en-1-one (**S10**): S10 was synthesized from S18 (1 mmol, 220 mg) and acetophenone (1 mmol, 120 mg) by the same procedure as described for S06 except that the reaction time was 4 h. The product was purified by column chromatography on silica gel (60–120 mesh) using (EtOAc: Hexane = 1: 10) as the eluent. Yield: 58%. mp 125–127°C. IR (KBr, cm⁻¹): 2932 (Ar-CH), 1660 (C=O). ¹H NMR (400 MHz, CDCl₃): δ 8.36 (d, *J* = 8 Hz, 2H), 8.26 (d, *J* = 8 Hz, 2H), 8.14 (d, *J* = 8 Hz, 2H), 8.11 (d, *J* = 8 Hz, 2H), 7.93 (d, *J* = 12 Hz, 1H), 7.48 (d, *J* = 8 Hz, 2H), 7.45 (d, *J* = 12 Hz, 1H), 7.52–7.56 (m, 3H), 3.05 (s, 3H). E: Z = 47: 53.¹³C NMR (CDCl₃): δ 192.18, 142.59, 140.16, 132.21, 130.34, 129.48, 128.71, 128.02, 127.79, 126.11, 125.79, 125.20, 124.90, 14.43, 14.12. ESI-HRMS $[M + H]^+$ calcd for $C_{25}H_{21}O$ m/z 323.1430, found 323.1438.

(*E*)-1-(4-chlorophenyl)-3-(9-methoxyanthracen-10-yl)prop-2en-1-one (S11): S11 was synthesized from S21 (1 mmol, 236 mg) and 4-bromoacetophenone (1 mmol, 199 mg) by the same procedure as described for S12. The product was purified using column chromatography on silica gel (60–120 mesh) using (EtOAc: Hexane = 1: 4), Yield: 193 mg (52%). mp 138–140°C. IR (KBr, cm⁻¹): 3056 (Ar-CH), 1657 (C=O). ¹H NMR (400 MHz, CDCl³): δ 8.80 (d, J = 16 Hz, 1H), 8.39 (d, J = 8 Hz, 1H), 8.34–8.32 (m, 4H), 8.03 (d, J = 8 Hz, 1H), 7.83–7.80 (m, 3H), 7.56–7.49 (m, 4H), 4.19 (s, 3H). ¹³C NMR (CDCl³): δ 188.30, 153.75, 142.24, 139.45, 136.21, 134.02, 130.59, 130.03, 129.02, 127.13, 126.67, 125.92, 125.50, 125.33, 124.24, 122.79, 63.39. ESI-HRMS [M + H]⁺ calcd for C²⁴ ²⁴H₁₈ClO₂ m/z 373.0990, found 373.0989.

(E)-1-(4-bromophenyl)-3-(9-methoxyanthracen-10-yl)prop-2en-1-one (S12): 10-methoxy 9-anthraldehyde (S21) was prepared according to the known procedure. Anthrone (S19) on methylation with dimethyl sulphate provides 9-methoxyanthracene (S20). S20 on Vilsmeier reaction with dimethyl formamide and phosphorus oxychloride yields S21. A 50% NaOH (w/v) solution was added to a mixture of 4-chloroacetophenone (1 mmol, 155 mg) and (S21) (1 mmol, 236 mg) in 125 ml of methanol. The mixture was refluxed with continuous stirring for 3 h and then refrigerated overnight. The reaction mixture was neutralized with concentrated HCl. The product was purified by column chromatography on silica gel (60-120 mesh) using (EtOAc: Hexane = 1: 4) as the eluent. Yield: 308 mg (74%), mp 155–157°C, ¹H NMR (400 MHz, CDCl₃); δ 8.81 (d. I = 16 Hz, 1H), 8.40–8.37 (m, 1H), 8.33 (m, 4H), 7.96 (d, I = 8 Hz, 2H), 7.82 (d, J = 8 Hz, 2H), 7.67 (d, J = 8 Hz, 1H), 7.57–7.54 (m, 2H), 7.51 (d, J = 16 Hz, 1H), 4.19 (s, 3H). ¹³C NMR (CDCl₃): δ 188.56, 153.78, 134.22, 134.12, 133.48, 132.15, 132.05, 130.62, 130.29, 130.17, 130.04, 127.22, 126.83, 126.72, 125.63, 125.53, 124.27, 122.93, 122.82. ESI-HRMS $[M + H]^+$ calcd for C₂₄H₁₈BrO₂ m/z 417.0485, found 417.0490.

(*E*)-3-(9-methoxyanthracen-10-yl)-1-(4-nitrophenyl)prop-2en-1-one (S13): S13 was synthesized from S21 (1 mmol, 236 mg) and 4-nitroacetophenone (1 mmol, 165 mg) by the same procedure as described for S12 except that the reaction time was 2 h. The product was purified by column chromatography on silica gel (60–120 mesh) using (EtOAc: Hexane = 25: 1) as the eluent. Yield: 325 mg (85%). mp 195–197°C. IR (KBr, cm⁻¹): 3071 (Ar-CH), 1664 (C=O). ¹H NMR (400 MHz, CDCl₃): δ 8.88 (d, *J* = 16 Hz, 1H), 8.38 (d, *J* = 8.0 Hz, 2H), 8.34–8.31 (m, 2H), 8.23 (d, *J* = 12.0 Hz, 2H), 7.54 (d, *J* = 16 Hz, 1H), 7.58 (d, *J* = 8 Hz, 4H), 4.20 (s, 3H). ¹³C NMR (CDCl₃): δ 188.11, 156.17, 154.25, 143.72, 142.68, 130.74, 129.56, 126.98, 125.44, 125.30, 124.31, 123.93, 122.94, 63.50. ESI-HRMS [M + H]⁺ calcd for C₂₄H₁₈NO₄ *m*/*z* 384.1230, found 384.1233.

(*E*)-3-(9-*methoxyanthracen*-10-yl)-1-(4-*methoxyphenyl*)*prop*-2-*en*-1-*one* (S14): S14 was synthesized from S21 (1 mmol, 236 mg) and 4-methoxyacetophenone (1 mmol, 150 mg) by the same procedure as described for S12 except that the reaction was refluxed for 7 h and stirred at rt for 5 h. The product was purified by column chromatography on silica gel (60–120 mesh) using (EtOAc: Hexane = 40: 1) as the eluent. Yield: 257 mg (70%). mp 170–172°C. E: Z = 66: 34 ¹H NMR (400 MHz, CDCl₃): δ 8.77 (d, *J* = 16 Hz, 1H), 8.36 (t, *J* = 8 Hz, 4H), 8.10 (d, *J* = 8 Hz, 2H), 7.57–7.53 (m, 4H), 7.45 (m, 2H), 7.00 (d, *J* = 8 Hz, 1H), 4.19 (s, 3H), 3.90 (s, 3H). ¹³C NMR (CDCl₃): δ 187.90, 163.55, 153.35, 140.85, 130.96, 130.61, 130.49, 1126.44, 125.69, 125.27, 124.19, 122.66, 113.90, 63.33, 55.44. ESI-HRMS [M + H]⁺ calcd for C₂₅H₂₁O₃ *m/z* 369.1485, found 369.1507.

(*E*)-3-(9-*methoxyanthracen*-10-yl)-1-*phenylprop*-2-*en*-1-*one* (**S15**): S15 was synthesized from S21 (1 mmol, 236 mg) and acetophenone (1 mmol, 120 mg) by the same procedure as described for S12 except that the reaction time was 7 h. The product was purified by column chromatography on silica gel (60–120 mesh) using (EtOAc: Hexane = 1: 4) as the eluent. Yield: 250 mg (74%). mp 120–122°C. IR (KBr, cm⁻¹): 3069 (Ar-CH), 1663 (C=O). ¹H NMR (400 MHz, CDCl₃): δ 8.80 (d, *J* = 16 Hz, 1H), 8.40–8.34 (m, 4H), 8.39 (d, *J* = 8 Hz, 2H), 8.35 (d, *J* = 8 Hz, 2H), 8.10 (d, *J* = 8 Hz, 1H), 7.62 (d, *J* = 8 Hz, 1H), 7.59–7.53 (m, 5H), 4.19 (s, 3H). ¹³C NMR (CDCl₃): δ 191.87, 189.68, 183.07, 159.14, 153.58, 141.73, 137.92, 134.05, 133.83, 133.43, 133.02, 130.69, 130.56, 129.29, 128.72, 127.16, 126.57, 125.62, 123.90, 122.75, 63.39. ESI-HRMS [M + H]⁺ calcd for C₂₄H₁₉O₂ *m/z* 339.1380, found 339.1404.

2.1. Measurement of nonlinear absorption

Z-scan measurements were carried out with linearly polarized Q-switched Nd-YAG laser of pulse width 28 ns (full width at half maximum). The fundamental of the laser beam 1.064 μ m or the second harmonic of the laser beam at 532 nm was used for the zscan measurements. The laser pulse energy was adjusted in the range of 30 μ J-400 μ J by using neutral density filters. The pulse energy for a given sample was chosen such that the lowest transmission in z-scan remains near 0.5. This is because if the overall change in transmission is too high, pump-depletion effects and contributions of higher-order nonlinear effects might also become significant, complicating the analysis of the results [31]. The laser was operated at 1 Hz repetition rate to avoid thermal effects. For the z-scan measurements these compounds were dissolved in chloroform and kept in a 1 mm path-length flow quartz cell (concentration: 1.3×10^{-8} M). The sample was circulated in the cell to avoid any thermal induced damage to it. Further, the stability of the compounds throughout the measurement was ensured by checking that the linear absorption spectra before and after the z-scan measurements remain the same.

3. Results and discussions

In Fig. 2 we show the linear absorption spectra of all the compounds. In the absorption spectra there are two well distinguishable peaks, one in the wavelength range 250-265 nm and another weak peak in the wavelength range 390-425 nm. In table-1 the peak wavelengths in absorption spectra, λ_{abs} , of the compounds in these two wavelength range are tabulated. The origin of these two peaks in compounds containing carbonyl group can be attributed to the well known $\pi - \pi^*$ (stronger) and $n - \pi^*$ (weaker) transitions respectively [32]. Although the nitro derivatives $(R_1 = -NO_2)$ also have these two peaks, the peak in the longer wavelength regime is clearly red-shifted to the 437-454 nm regime when compared to the other compounds. Such red-shift can be attributed to the strong electron withdrawing nature of the –NO₂ group [33,34]. Among the compounds having -NO₂ group the compound S08 has the highest red-shift of $n - \pi^*$ transition. Some of the compounds also show several small peaks in the wavelength range 300-400 nm; these are due to the vibrational fine structure [35,36]. Note that all the compounds are nearly transparent for wavelengths longer than 520 nm. There may be a very small linear absorption present in some of the samples, still the transmission loss through the sample was less than 1%, the detection limit of our spectrograph.

The emission spectra of the compounds were measured by exciting at wavelengths near their absorption peaks. Fig. 3 shows the emission spectra of some of the compounds, S03, S08 and S13. The emission spectra for the rest of the compounds and the emission spectra when excited at different absorption peaks are in SI (Fig.SI-1 to Fig.SI-3). The excitation wavelengths and the corresponding peak wavelength of the emission for all the compounds are tabulated in table- 1. Note that the emission spectra for all the



Fig. 2. Linear absorption spectra of all the compounds in the three different series: (a) S01 to S05, (b) S06 to S10 and (c) S11 to S15. Inset shows the same in expanded scale. The general structure of the compound is also shown in the inset.

1

Table 1

Linear optical properties of the chalcone derivatives (S01–S15). λ_{abs} : main absorption peak wavelengths; λ_{em} : Peak emission wavelength along with the excitation (Ex) wavelength; λ_{st} : Amount of Stokes shift between absorption and emission peaks.

Compound	λ_{abs} (nm)	λ_{em} (nm)	λ_{st} (nm)
S01 (R ₁ = -Cl)	260, 415	302 (Ex 258)	42
S02 ($R_1 = -Br$)	253, 418	532 (Ex 416)	114
$SO3 (R_1 = -NO_2)$	257, 437	567 (Ex 437)	130
$S04 (R_1 = -OCH_3)$	257, 390	523 (Ex 390)	133
S05 ($R_1 = -H$)	NA, 415	528 (Ex 414)	113
S06 ($R_1 = -Cl$)	255, 399	430 (Ex 399)	31
S07 ($R_1 = -Br$)	261, 399	436 (Ex 392)	37
$SO8 (R_1 = -NO_2)$	261, 454	525 (Ex 455)	71
$S09 (R_1 = -OCH_3)$	NA, 400	399 (Ex 258)	-
S10 ($R_1 = -H$)	261, 399	531 (Ex 391)	132
S11 ($R_1 = -Cl$)	251, 421	547 (Ex 327)	126
S12 ($R_1 = -Br$)	259, 421	535 (Ex 424)	114
S13 ($R_1 = -NO_2$)	258, 451	543 (Ex 449)	92
$S14 (R_1 = -OCH_3)$	258, 433	538 (Ex 432)	105
S15 ($R_1 = -H$)	256, 419	296 (Ex 258)	40

compounds are Stokes shifted with respect to the absorption peak and are also listed in table- 1. Apart from the basic structure of the compound, the magnitude of Stokes shift depends on factors such as electron donating or withdrawing property of the substituent group, properties of the solvent and whether the excited state can undergo any specific interactions such as charge transfer or energy transfer [37–41]. A large Stokes shift observed for most of the present compounds indicates that the environment is not rigid and rearrangement is possible.

Fig. 4 shows the open aperture z-scan curves for three compounds S03, S08 and S13. The other compounds also shows similar z-scan curves which are given in SI (Fig.SI-4 and Fig.SI-5). When the sample is kept well away from focus where the intensity is low, the transmission through all the samples is ~ 1.0. This is due to the fact that at 532 nm all the samples have negligible linear absorption. However, as the sample is moved closer to the focus (z = 0) the transmission through the sample reduces, indicating that the absorption in the sample increases with intensity. The incremental change in the intensity (dI) after propagating a small distance dz in the sample having linear and third-order nonlinear absorption is given by [42].

$$\frac{dI}{dz} = -\alpha_0 I - \beta I^2, \tag{1}$$

where α_0 is the linear absorption coefficient and β is the nonlinear absorption coefficient related to the imaginary part of third-order susceptibility of the sample. At a location of the sample *z*, the intensity distribution (*I*), having Gaussian nature in space (*r*) and time (*t*) at the entrance of the cell can be expressed as,

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

 z_0 is the Rayleigh range given by $z_0 = \pi \omega_0^2 / \lambda$, λ is the wavelength of light used, ω_0 is the beam waist and t_0 is the pulse width. Using Eq. (1) and Eq.3 the energy of the pulse transmitted through the sample can be obtained by integration over space and time and is given by Ref. [43],

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

Here $q(r, t, z) = \beta I(r, t, z)L$ and *L* is the thickness of the sample. Fig. 4 also shows the best fit curve obtained for these three samples (see Fig.SI-4 and Fig.SI-5 for other samples). The obtained best fit values of β for all the samples are tabulated in table- 2. In comparison with the reported nonlinear absorption for various molecules in the literature (including most of the references presented here) the present set of compounds can be clearly classified among those having a large nonlinear absorption coefficient.

In the set of 15 compounds studied here, the base structure remains same and the substitutions R_1 and R_2 are changed in each sample. As mentioned before, they can be classified into three subseries of compounds (S01–S05, S06–S10, and S11–S15) based on the group attached in the anthracenyl 9-position (R_2). These groups have an increasing electron donor strength in the order $-H \rightarrow -CH_3 \rightarrow -OCH_3$. The substitutions used at the other end of the compound (R_1) are electron withdrawing functional groups -Cl, -Br,

Table 2

Nonlinear absorption coefficient values for samples S01 – S15. The nonlinear absorption coefficient (β) is specified in the unit of cm/GW.

Compound	Structure	β	Compound	Structure	β	Compound	Structure	β
S01		70	S06	H ₃ C CI	330	S11	CI C	52
S02	CCC L L Br	90	S07	H ₃ C C O C Br	360	S12	Br C CH3	38
S03		550	S08	O_2N CH_3	640	S13	O2N CH3	350
S04	Meo L	180	S09	Meo CH ₃	55	S14	Meo CH3	120
S05		300	S10	H CH ₅	34	S15	H C C H3	35



Fig. 3. Normalized one photon emission spectra for S03, S08 and S13 in chloroform when excited at 437, 455 and 499 nm respectively.





Fig. 4. Open aperture z-scan data of samples S03, S08 and S13 at 532 nm. Scatters are the experimental data and lines are the best fit curves with Eq. (2).

the compound.

From Fig. 5 we see that among the compounds studied here the ones having $-NO_2$ as the substitution R_1 show a large nonlinear absorption coefficient irrespective of the substitution at R_2 . Further, for compounds having an electron withdrawing nature at R_1 , the -Cl, -Br and $-NO_2$, an increased nonlinear absorption is observed when R_2 is $-CH_3$. The nonlinear response of a compound has been shown to increase with donor/acceptor strength in D-A-D and D-A-A type molecules [20,21]. In the present case attaching an even stronger electron donor $-OCH_3$ at R_2 seems to reduce the nonlinear absorption for electron withdrawing attachment at R_1 . This



Fig. 5. The estimated nonlinear absorption coefficient, β , is plotted as a function of substitution in the chalcone derivatives.

reduction tells that A- π -A- π -D is more effective in increasing the nonlinear absorption coefficient than the corresponding D- π -A- π -D motif. However, there is a trade off between A- π -A- π -D and the electron donor moiety and the terminal acceptor group. The unsubstituted 9-position of the anthracene derivatives with the methoxy substituted one was a much more proficient absorber. Probably the extensive conjugation of the methoxy group with the anthracene π -system exceeds the "conjugation signature" and in turn decreases the β value [47].

Now we look at the possible reasons for the higher nonlinear absorption observed in the compounds under study. In nanosecond time scales, multiple processes can contribute to the nonlinear absorption [31]. These include direct two-photon absorption (which is instantaneous) and two-step two-photon absorption involving two successive one-photon transitions. The latter can entail some delay between the two one-photon transitions. It is to be noted that for a sufficiently long laser pulse all these nonlinear absorption processes will have intensity dependence of similar



Fig. 6. (*a*) Schematic of the energy levels in the present set of compounds near the HOMO-LUMO gap E_1 . E_2 is the second lower energy transition. The vertical upward green arrows represent a single photon with energy 2.33 eV (532 nm). The numbers shown are in eV. See the text for the details of δ and Δ . (*b*) the proposed three different processes which can contribute to the measured nonlinear absorption in the compounds.

form and can be clubbed together to give an effective nonlinear absorption coefficient, β . Thus Eqn. (1) would be still applicable.

The possible nonlinear absorption processes for the present set of compounds can be understood with the help of Fig. 6(a), which shows the lowest energy levels of S01 and S03. Other compounds have a similar energy level structure. Based on the energy bands of the compounds and the photon energy used in the nonlinearity measurements (532 nm), we propose three major contributions to the optical nonlinearity of the present compounds. The schematic of these three processes is given in Fig. 6(b) as P1, P2 and P3. The first process, P1, is the intrinsic two-photon absorption process. As can be seen from Fig. 6(*b*), the π - π^* transition wavelength lies close to 266 nm. The presence of a real energy band at the twophoton energy will lead to a finite contribution to the twophoton absorption at 532 nm [48,49]. The strength of the twophoton absorption will depend on the detuning, δ , between the energy of the π - π^* transition and the total energy of two photons, 4.66 eV. The second process P2 is the two-step two-photon absorption. Due to the large spectral width of the long wavelength absorption band (Fig. 2) a negligibly small linear absorption may occur at the input wavelength 532 nm. The strength of this absorption depends on the detuning, Δ between n- π^* transition and the excitation wavelength, the strength of the transition and its spectral width. This minuscule absorption will excite carriers from *n* to π^* . These carriers can get accumulated in the level π^* and can get further excited to even higher energy levels (like σ^*) by absorption of another photon at 532 nm. We also propose a thirdprocess (P3). The small absorption from *n* to π^* will create empty states in an otherwise filled *n* band. Now absorption from a filled π band to the vacancies created in the *n* band can also contribute to nonlinear absorption process. In addition to the energy of the transitions, their width and transition strength would all contribute in defining the final nonlinear absorption coefficient of a compound.

Electron donating substituents, like –CH₃ are known to increase the π -electron conjugation and can also reduce the energy gap [50]. In the present case, compounds with $-NO_2$ substitution have the lowest energy gap ($n - \pi^*$ transition) reducing the energy difference Δ . Such reduction in Δ can increase the nonlinear absorption through all the processes P1, P2 and P3. Even among these compounds having $-NO_2$ substitution the SO8 has the smallest Δ which also shows the highest nonlinear absorption. We have also performed z-scan measurements at 1064 nm. the fundamental laser wavelength, and found no measurable nonlinear absorption. When measured at 1064 nm processes similar to P2 and P3 would not contribute to the nonlinear absorption. Further the contribution from P1 will also be weak since there is no energy band near singlephoton (linear) absorption. This observation also confirms the presented model of nonlinear absorption at 532 nm. Note that for measurements at 532 nm the compound with the strongest nonlinear absorption, S03, has a very small linear absorption. However, any attempt to increase the nonlinear absorption by further reduction of Δ would result in increasing the linear absorption. Samples having linear absorption loss are in general not good for nonlinear optical applications.

Densely packing the molecules in crystal form can increase the overall nonlinear absorption coefficient of the sample. Further, solid state materials are more suitable for most device applications. We find that it is possible to prepare single crystals of these compounds (preparation method and crystal details of two of the compounds are given section-IV of SI). The formation of single crystals indicates the possibility of using these compounds in solid state form. Many of the applications, for example two-photon fluorescence excitation microscopy, two-photon up-conversion lasing, 3D nano/microfabrications and photodynamic therapy require molecules with high nonlinear absorption cross-sections. Many of the chalcone derivatives reported here have these necessary properties making them suitable candidates for such nonlinear optical applications.

4. Conclusions

A systematic study of nonlinear absorption properties of a set of chalcones has been presented to understand the effect of attached groups of different D or A properties on both sides of R_1 - π -A- π - R_2 configuration. To carryout such studies a new series of E/Z-3-(9substituted anthracen-10-yl)-1-(4-phenyl substituted) prop-2-en-1one derivatives have been synthesized. The energy levels of these compounds are positioned such that for measurements with nanosecond laser pulses at 532 nm a strong nonlinear absorption occur. With experimental results and an energy level model we have shown that a near resonance enhancement of the two-step two-photon absorption due to linear absorption at 532 nm contributes to the enhancement of nonlinear absorption in these compounds. Compounds having an electron withdrawing substituent at one end $(\hat{a} \in NO_2)$ with 9-methyl anthracene on the other, shows an increased nonlinear absorption. These sample also shows the smallest energy gap between 532 nm photon energy and its first excited state. In the present case attaching an even stronger electron donor –OCH₃ with anthracene moeity seems to reduce the nonlinear absorption with the same electron withdrawing attachments in the system. This reduction tells that A- π -A- π -D is more effective in increasing the nonlinear absorption coefficient than the corresponding D- π -A- π -D motif. Compounds showing high nonlinear optical cross-sections find applications in two-photon fluorescence excitation microscopy and photodynamic therapy. The present set of compounds could be successfully used in applications where high nonlinear optical cross-sections are essential.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Amrita Saha: Methodology, Formal analysis, Validation, Investigation, Visualization, Writing – original draft, Writing – review & editing. **Asha Singh:** Formal analysis, Writing – review & editing. **Rama Chari:** Resources, Writing – review & editing. **J. Jayabalan:** Conceptualization, Methodology, Software, Formal analysis, Visualization, Investigation, Writing – original draft, Writing – review & editing.

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Appendix A. Supplementary data

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