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Investigation of third-order nonlinear optical properties of conjugated benzodioxal derivatives

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ABSTRACT

An investigation of third-order nonlinear optical characterization of newly synthesized conjugated benzodioxal derivatives has been done by using nanosecond Z-scan technique at 532 nm. The molecules demonstrate self-defocusing effect with intensity dependent refractive index (n_2) of the order of 10^{-14} cm^2/W. The measured molecular TPA cross-section is ranging from 2.47 $\times 10^{-47}$ cm^4 s/photon to 6.00 cm^4 s/photon. Their input-output curves indicate that there is a clear optical power limiting behavior with the limiting threshold in the range 125–181 μJ. The main factor to exhibit the observed nonlinearity in these molecules is the presence of charge donor and acceptor groups. The increased conjugation length increases the nonlinear refraction and increased electron density enhances the nonlinear absorption. The molecules exhibit good nonlinear optical properties, comparable to those of regular azoaromatic compounds. Therefore, the molecules investigated here are promising candidates for optical power limiting devices.

1. Introduction

The third-order nonlinear optical (NLO) materials have attracted considerable attention due to their potential applications including optical power limiting, optical switching and 3-D optical memory devices. Thus, the design and synthesis of new molecules with large macroscopic optical nonlinearities is an active research field in material science [1–3]. In recent years, π-conjugated organic compounds have been investigated as a new class of third-order NLO materials due to their high NLO properties and fast response time. The NLO behavior of organic molecules originates mainly from a strong donor–acceptor intermolecular interaction and delocalized π-electron system [4–6].Of the several organic compounds known to exhibit NLO properties, chalcone derivatives are seen to show large nonlinear coefficients on account of the fact that they consist two planar rings connected through a conjugated double bond [7].

In this paper we report the investigation of third-order nonlinear optical parameters of newly synthesized six molecules that belong to the chalcone systems with common benzodioxal group, using the single beam Z-scan technique [8,9]. The aim was to correlate the observed nonlinearity with structure of the compound to tailor the best suitable nonlinear material for optical device applications.

2. Experiment

The molecules considered in this work (Fig. 1) have been designed based on Donor–Acceptor–Donor scheme. The substitution on either side of the phenyl rings greatly influences the non-centrosymmetric crystal packing. The carbonyl group (C=O) at the centre acts as an electron withdrawing group [10]. The synthesis procedure and the characterizing data for these compounds are given below.

2.1. Synthesis and characterization

The chalcones have been synthesized taking 1-(1,3-benzodioxol-5yl) ethanone (0.01 mol) in ethanol mixed with benzaldehyde or substituted benzaldehydes (0.01 mol) in 30 ml of ethanol and the mixture was treated with an aqueous solution of potassium hydroxide (10 ml, 10%). This mixture was stirred well and kept aside for 8–10 h. The resulting solid mass was collected by filtration and recrystallized from toluene by slow

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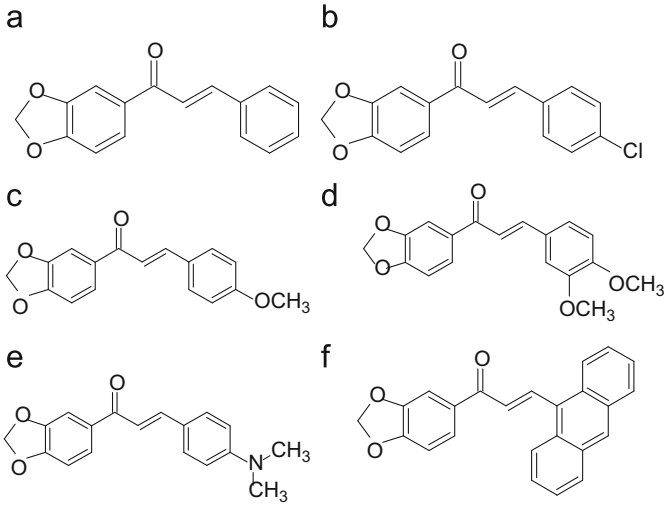
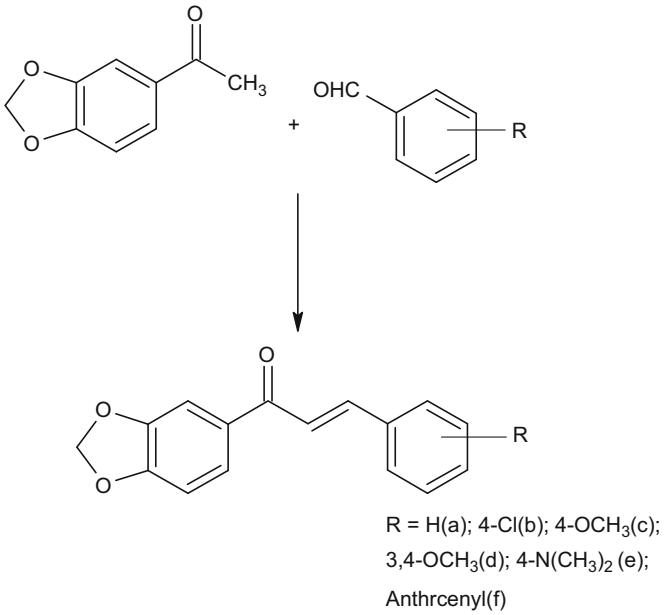


Fig. 1. Structure of the compounds: (a) (2*E*)-1-(1,3-Benzodioxol-5-yl)-3-phenylprop-2-en-1-one (SSP1); (b) (2*E*)-1-(1,3-Benzodioxol-5-yl)-3-(4-chlorophenyl)prop-2-en-1-one (SSP2); (c) (2*E*)-1-(1,3-Benzodioxol-5-yl)-3-(4-methoxyphenyl)prop-2-en-1-one(SSP3); (d) (2*E*)-1-(1,3-Benzodioxol-5-yl)-3-(3,4-dimethoxyphenyl)prop-2-en-1-one (SSP4); (e) (2*E*)-1-(1,3-Benzodioxol-5-yl)-3-[4-(dimethylamino)phenyl]prop-2-en-1-one (SSP5); (f) (2*E*)-3-(Anthracen-9-yl)-1-(1,3-benzodioxol-5-yl)prop-2-en-1-one (SSP6).

evaporation (Scheme 1)



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2.2. Elemental analysis

Compound SSP1: (2*E*)-1-(1,3-Benzodioxol-5-yl)-3-phenylprop-2-en-1-one:
C: 76.18% (76.04); H: 4.79% (4.52); mp: 412–414 K,
SSP2: (2*E*)-1-(1,3-Benzodioxol-5-yl)-3-(4-chlorophenyl)prop-2-en-1-one,
C: 67.03% (67.14); H: 3.87% (3.60); mp: 435–439 K,
SSP3: (2*E*)-1-(1,3-Benzodioxol-5-yl)-3-(4-methoxyphenyl)prop-2-en-1-one,
C: 72.33% (72.20); H: 5.00% (4.98); mp: 420–422 K,
SSP4: (2*E*)-1-(1,3-Benzodioxol-5-yl)-3-(4-chlorophenyl)prop-2-en-1-one,
C: 69.22% (69.20); H: 5.16% (5.00); mp: 405–407 K,
SSP5: (2*E*)-1-(1,3-Benzodioxol-5-yl)-3-[4-(dimethylamino)-phenyl]prop-2-en-1-one,
C: 73.20% (73.12); H: 5.80% (5.68); N 4.74% (4.81); mp: 365–367 K,
SSP6: (2*E*)-3-(Anthracen-9-yl)-1-(1,3-benzodioxol-5-yl)prop-2-en-1-one,
C: 81.80% (81.89); H: 4.58% (5.00); mp: 395–397 K.

2.3. Nonlinear measurements

In Z-scan measurement set up[8], a plano-convex lens of 25 cm focal length was used to focus the laser pulses. A quartz cuvette of thickness 1 mm was used to hold the liquid sample. The cuvette was moved along the beam axis using a motorized linear translation stage. The detector was placed at a distance of about 30 cm from the focal spot, $Z=0$. A circular aperture of diameter 5 mm was mounted in front of the detector and the detector output was monitored as the cuvette was translated along the laser beam axis from $Z=-20$ mm to $Z=+20$ mm. The transmission measurement was done using two Pyroelectric detectors with Laser Probe (Rj-7620 energy meter).

The set up was calibrated with carbon disulphide (CS_2) solution, which is reported to be the best nonlinear material.

About 30 mg of each molecule was dissolved in research grade N,N-Dimethyl Formamide (DMF) and a solution of concentration 4.3×10^{-2} mol/l was prepared. This sample was taken in a quartz cuvette of thickness 1 mm for the Z-Scan measurements. A frequency doubled Q-switched Nd:YAG laser (Model: GCR 170, Spectra-Physics) producing 7 ns pulses at wavelength 532 nm was used as the light source. The input intensity used was 2.39 GW/cm^2. To obtain open aperture data, the intensity transmitted by the liquid sample was measured as a function of sample position along the *Z*-axis. Closed aperture data was obtained using an aperture ($S=0.5$) in front of the detector. Optical power limiting experiment was also carried out on these moieties to asses them as possible photonic material for optical power limiting applications. The linear absorption spectrum of the samples was recorded using fiber optic spectrometer (model SD 2000, Ocean Optics Inc) in the wavelength region 200–800 nm at room temperature using DMF solvent as the reference. The UV–visible absorption spectra of the conjugated molecules are shown in Fig. 2.

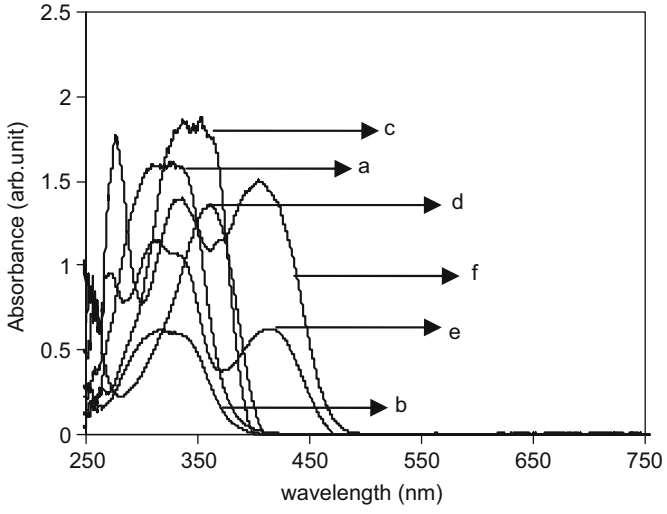

Fig. 2. UV–visible absorption spectra of Chalcones: (a) SSP1; (b) SSP2; (c) SSP3; (d) SSP4; (e) SSP5; (f) SSP6.

Linear refractive index values of the samples used for the experiment have been obtained using Mettler Toledo Refractometer at the experimental wavelength.

3. Results and discussion

The UV absorption spectra show that there is negligible single photon absorption at 532 nm wavelength indicating that our measurements fall into the category of nonresonant interactions. In order to determine the sign of third-order susceptibility ($\chi^{(3)}$) and to investigate the relative contributions from its real and imaginary parts, Z-scan studies were conducted. Fig. 3 shows the experimental open aperture (OA) Z-scan data and the Fig. 4 exhibits pure nonlinear refraction curve for the conjugated chalcone sample SSP1. To study the variation in nonlinear optical parameters with substituent group, Z-scan experiments have also been conducted on other samples of this series and similar curves have been obtained. As seen from Fig. 4, pure nonlinear refraction curve shows the prefocal transmittance peak followed by the postfocal valley, which is the signature of negative nonlinearity. From the Z-scan data, the real and imaginary parts of the $\chi^{(3)}$ have been calculated to be

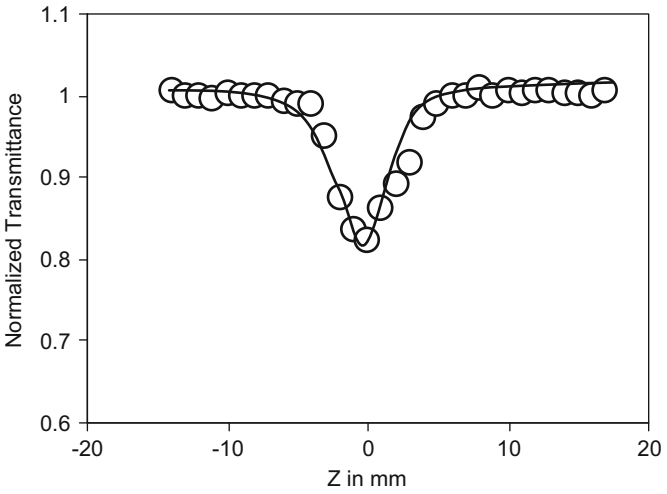

Fig. 3. Normalized transmittance of SSP1 sample using the open-aperture Z-scan scheme.

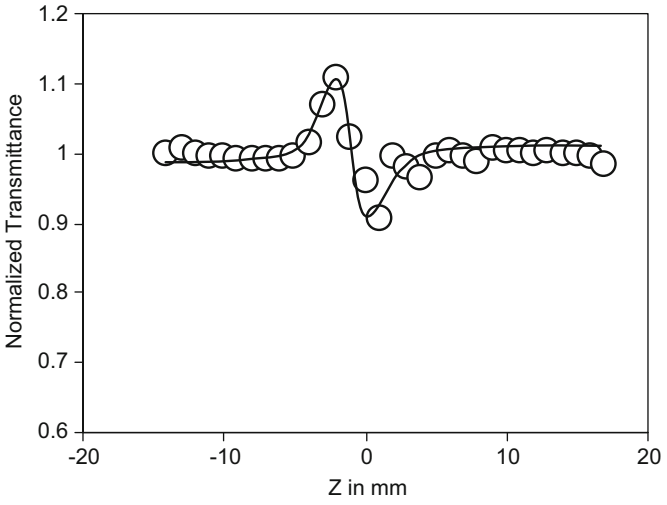

Fig. 4. Normalized transmittance of SSP1 sample using the closed-aperture Z-scan scheme.

-0.81×10^{-13} and 0.37×10^{-13} esu, respectively, for SSP1 molecules with phenyl-substituted donor group.

It is known that nonlinear absorption coefficient β, depends on the number of absorptive centers in a unit volume. Assuming this number is N_0, in units of cm^{-3}, we have [11,12],

$$\beta = \sigma_2 N_0 = \sigma_2 N_A d \times 10^{-3}$$

Here, N_0 is the molecular density of the sample (in units of $1/cm^3$), σ_2 the molecular TPA coefficient (or cross-section) (in units of cm^4/Gw), d the concentration of the molecule and N_A the Avogadro number. For known β and d, the value of σ_2 can be obtained. In the literature [12,13], molecular TPA cross-section (is in units of cm^4 s/photon) is also defined as

$$\sigma\prime_2 = \sigma_2 h\upsilon$$

where σ_2 is in units of cm^4 s and $h\upsilon$ is the energy (in joules) of an incident photon.

For SSP1 molecules, nonlinear absorption coefficient is found to be 2.39 cm/GW and effective two-photon absorption cross-section is 2.47×10^{-47} cm^4 s/photon. The large third-order nonlinear optical properties arise in a material due to the strong delocalization of π-electrons. The chalcone molecules investigated here are designed based on the scheme Donor–Acceptor–Donor group [14]. The dioxol group attached to phenyl ring on one side of the carbonyl group is less electron withdrawing compared to phenyl. Therefore, the phenyl with the dioxol group attached, acts as a donor. On the other side of the carbonyl group, the phenyl ring also acts as donor due to resonance effect. At the centre, the presence of oxygen in the carbonyl group (C=O) is more electronegative. Hence it acts as an acceptor. Thus, charge transfer takes place from the ends to the center of the molecule, leading to the large nonlinearity. When the molecules of SSP1 are substituted with chlorophenyl 3-position (sample SSP2), the real and imaginary parts of $\chi^{(3)}$ changed to -1.31×10^{-13} and 0.4×10^{-13} esu, respectively, and the effective two-photon absorption cross-section increased to 3.10×10^{-47} cm^4 s/photon. The enhancement is due to an increase in electron density by the chlorine, due to the positive inductive effect.

Similarly, when chlorine is replaced by methoxy group (SSP3), there is a tendency to release electrons due to two lone pairs of electrons of oxygen. Due to the increased electron density, the coefficient of nonlinear absorption is more than the molecules attached with either only Phenyl (SSP1) or chlorophenyl (SSP2) group.

Similar investigations have made with molecules attached with dimethoxyphenyl (SSP4), dimethylamino (SSP5) and Anthracene (SSP6) to one side of the carbonyl group and the values have been given in Table 1. The coupling factor given in Table 1 is seen to be comparable with the values given in [15] and the observed nonlinearity is mainly electronic in origin [2]. Since the measurements have been done with low-intensity pulses, the influence of thermal effect on the observed nonlinearity is negligible [16]. It is also confirmed through the analysis of pulse waveform variations when the sample is moved from the valley to the peak position during closed aperture Z-scan.

Of all the conjugated systems, the chalcone (2*E*)-1-(1,3-Benzodioxol-5-yl)-3-[4-(dimethyl amino)phenyl] prop-2-en-1-one (SSP5) shows better nonlinear properties due to increased conjugation length because of the presence of dimethylamino group.

Optical power limiting is an area of growing interest due to applications such as eye and sensor protection against intense light [17]. An ideal optical limiter is one which is perfectly transparent at low light intensities until pre-determined intensity level and above which, the transmitted intensity remains clamped at a constant value [1]. The nonlinear mechanisms leading to optical power limiting includes two photon absorption, free carrier absorption, reverse saturable absorption and nonlinear

Table 1
Third-order nonlinear coefficients of conjugated systems at 532 nm. Solvent used is DMF. Concentration of the solution 4.3×10^{-2} mol/l

Sample	$n_2(10^{-14}$ cm^2/W)	Re$\chi^{(3)}10^{-13}$ esu	Im$\chi^{(3)}10^{-13}$ esu	σ_2 10^{-47} s/photon	Coupling factor (ρ)
SSP1	−2.20	−0.81	0.37	2.47	0.43
SSP2	−3.58	−1.31	0.40	3.04	0.31
SSP3	−3.61	−1.32	0.75	5.61	0.57
SSP4	−3.40	−1.25	0.70	6.00	0.61
SSP5	−4.83	−1.77	0.56	4.37	0.32
SSP6	−4.42	−1.62	0.27	2.51	0.17

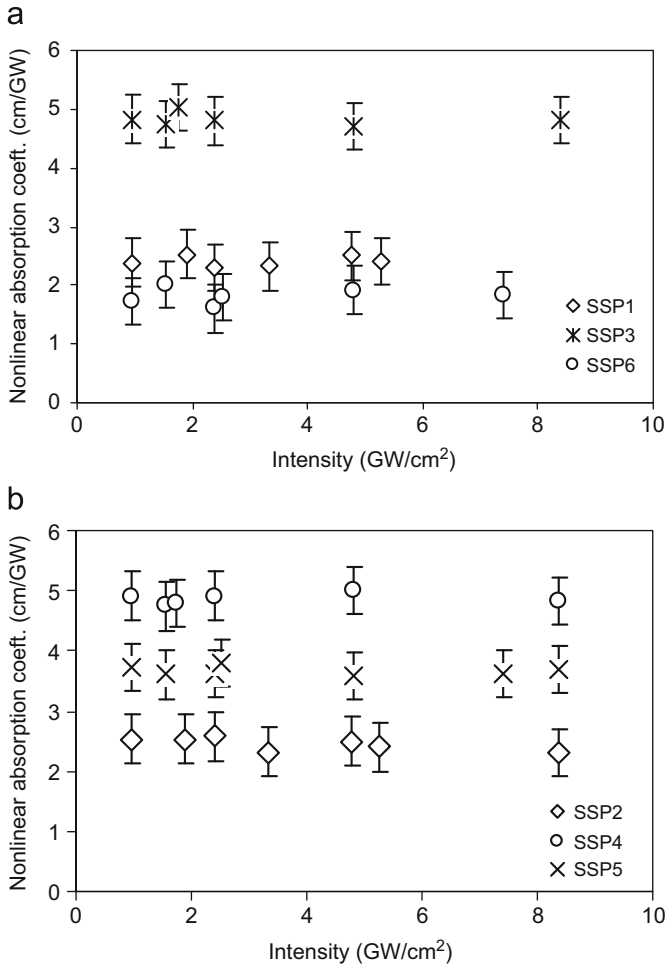

Fig. 5. (a) Measured values of nonlinear absorption coefficient (β) of SSP1, SSP3 and SSP6 molecules at various input intensities. (b) Measured values of nonlinear absorption coefficient (β) of SSP2, SSP4 and SSP5 molecules at various input intensities.

scattering. Advantages of using the materials exhibiting pure TPA process is that, they have very high initial transmission for weak optical signals, very fast response to a change in the intensity of the input optical signals, retention of the optical quality of the input beam after passing through the nonlinear medium [18].

If the nonlinear transmissivity change is due to the pure TPA process, then the nonlinear absorption coefficient β should be independent of the input intensity I_0 [18,19]. One can see from Fig. 5a and b that the measured β values of the molecules are independent of the input intensity I_0. Therefore, the major contribution to the observed nonlinear absorption is due to TPA process. However, if there are additional nonlinear absorption mechanisms such as excited state absorption, three photon or multi-photon absorption, the apparently measured values of nonlinear absorption coefficient β will not remain constant.

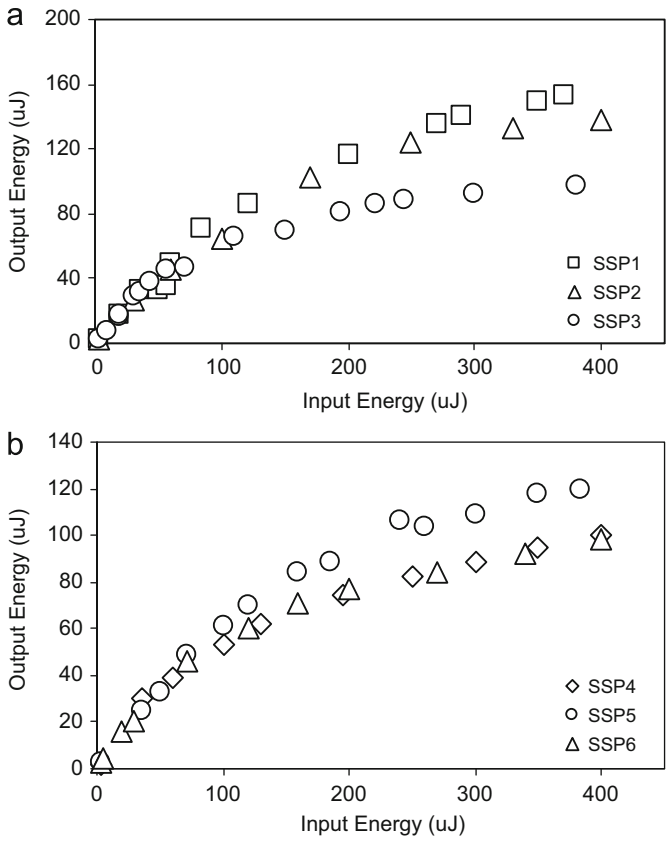

Fig. 6. (a) Optical power limiting behavior of SSP1, SSP2 and SSP3 chalcones. (b) Optical power limiting behavior of SSP4, SSP5 and SSP6 chalcones.

Therefore, we expect these materials to exhibit good optical power limiting properties based on TPA.

Fig. 6a and b show the optical power limiting behavior of the compounds. The limiting threshold of SSP1 was 181 μJ and for SSP2 and SSP3, the clamping levels are 137.5 and 106 μJ, respectively. Similarly, for SSP4, the limiting threshold is 100 μJ and for SSP5 and SSP6 the limiting values are 125 and 175 μJ, respectively. Among the six molecules investigated here, SSP4 shows good optical limiting property, which is due to the strong electron donating ability of dimethoxy group. Thus, the investigated molecules are promising candidates for optical power limiting devices.

4. Conclusion

The third-order nonlinear optical parameters of conjugated chalcone molecules in pure form have been investigated by Z-Scan technique using 7 ns laser pulses at 532 nm. The results demonstrate that the molecules possess negative nonlinearity. Of all the conjugated systems, the benzodioxal molecule with dimethylamino group shows better nonlinear properties due to

increased conjugation length. Two photon absorption mechanism plays a major role in the observed nonlinearity and the absorption parameters depend on the strength of the donor group. It is found that the molecule substituted with dimethoxy group found to exhibit good optical power limiting property due to the increased electron density. Thus, increased conjugation length increases the nonlinear refraction part and increased electron density enhances nonlinear absorption. The nonlinear parameters investigated here are comparable with those of azoaromatic compounds such as Disperse Orange 3, Disperse Red 13, Disperse Red 19, Azobenzene, etc., because, they are also conjugated molecules with donor/acceptor groups and commercially available for optical device applications [20].Our investigations on the optical power limiting capability of the compounds indicate that they are very promising nonlinear optical materials for power limiting applications.

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References

[1] Prasad PN, Williams David J. Introduction to nonlinear optical effects in molecules and polymers. New York: Wiley; 1992.
[2] Aggarwal MD, Wang WS, Bhat K, Penn BG, Frazeir DO. In: Nalwa HS, editor. Handbook of advanced electronic and photonic materials and devices. Vol. 9. USA Academic Press 2001 p. 193.
[3] Rath H, Sankar J, Raja VP, Chandrashekar TK, Nag A, Goswami D. J. Am. Chem. Soc. 2005;27:11608.
[4] Kandasamy, Rao KD, Deshpande R, Puntambekar PN, Singh BP, Shetty SJ, Srivastava TS. Appl. Phys. B. Lasers Opt. 1997;64:479.
[5] Falconieri M, Amato RD, Furlani A, Russo MV. Synth. Met. 2001;124:217.
[6] Sun XB, Wang XQ, Ren Q, Zang GH, Yang HL, Feng L. Mater. Res. Bull. 2006;41:177.
[7] Indira J, Karat PP, Sarojini BK. J. Cryst. Growth 2002;242(209).
[8] Sheik-Bahae, Said AA, Wei TH, Hagan DJ, Van Stryland EW. IEEE J. Quantum Electron. 1990;26:760.
[9] Samoc M, Samoc A, Luther-Davies B. J. Opt. .Soc. Am. B 1998;15:817.
[10] Poornesh P, Shettigar, Umesh Seetharam G, Manjunatha KB, Prakash Kamath K, Sarojinid BK, Narayana B. Opt. Mater. 2009;31:854.
[11] He GS, Gvishi R, Prasad PN, Reinhardt BA. Opt. Commun. 1995;117:133.
[12] He GS, Xu GC, Prasad PN, Reinhardt BA, Bhatt JC, Dillard AG. Opt. Lett. 1995;20:35.
[13] He GS, Weder C, Smith P, Prasad. PN. IEEE J. Quantum Electron. 1998;34:2279.
[14] Fitilis I, Fakis M, Polyzos I, Giannetas V, Persephonis P, Vellis P, Mikroyannidis J. Chem. Phys. Lett. 2007;447:300.
[15] Shettigar S, Chandrasekharan K, Umesh G, Sarojini BK, Narayana B. Polymer 2006;47:3565.
[16] Ganeev RA, Baba M, Morita M, Ryasnayansky AI, Suzuki M, Kuroda H. J. Opt. A: Pure Appl. Opt. 2004;6:1076.
[17] Perry JW, Mansour K, Lee I-YS, Wu X-L, Bedworth PV, Chen C-T, Ng D, Marder SR, Miles P, Wada T, Tian M, Sasabe H. Science 1996;273:1533.
[18] Cherukulappurath S, Godet JL, Boudebs G. J. Nonlinear Opt. Phys. Mater. 2005;14:49.
[19] Cronstrand P, Luo Y, Agren H. J. Chem. Phys. Lett. 2002;352:262.
[20] Andrade AA, Yamaki SB, Misoguti L, Zilio SC, Teresa, Atvars DZ, Oliveira Jr. ON, Mendonca CR. Opt. Mater. 2004;27:441.