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SYNTHESIS, CHARACTERIZATION AND THIRD-ORDER NONLINEAR OPTICAL PROPERTIES OF SCHIFF BASE DIMER

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ABSTRACT

The Schiff base dimer (SHBD) [2,2'-(4,4'-methylene bis(4,1-phenylene) bis (azan-1-yl-1-ylidene) bis (methane-1-yl-1-ylidene) diphenol] was prepared characterized and studied. Several techniques have been used to characterize the new dimer such as FTIR spectroscopy and CHN analysis. The SHBD polymer film was prepared by the repeat-spray method. The third order nonlinear optical properties were investigated by Z-scan measurements using cw laser. The experimentally determined values of nonlinear absorption β and nonlinear refractive index n_2 are 2.79 $x10^{-2}$ cm/W and 6.12 $x10^{-7}$ cm^2/W respectively. Optical limiting characteristics of the SHBD polymer film was studied. The experimental results indicated that the SHBD polymer film was a promising candidate in the applications of third order nonlinear optical materials.

KEYWORDS: Polymer, Nonlinear Materials, Z-Scan, Optical Limiting

INTRODUCTION

Nonlinear optical materials are attracting much attention because of their potential applications in optical communication, data storage, optical computing, dynamic holography, harmonic generators, frequency mixing, optical switching and optical limiting [1–18]. In order to utilize nonlinear optical (NLO) materials in photonic devices, such materials should possess a high NLO chromophore density so as to display large optical nonlinearity, low optical losses and ultrafast response time. Because there exists no symmetry requirement for third-order nonlinear optical effect this allows studies on a variety of organic molecules and polymers. A large number of organic dyes, fullerenes, charge transfer complexes, p-conjugated polymers, organometallic compounds, nano-composites and liquid crystals have been extensively investigated for third-order nonlinear optics. The third-order optical nonlinearity includes optical bleaching (i.e., saturation) or reverse saturation in the absorption aspect, whereas self-focusing or self-defocusing occurs in the refraction aspect. Of the various techniques available, Z-scan method [19,20] is a simple and effective tool for determining nonlinear properties and is used widely in material characterization because, it provides not only the magnitudes of the real and imaginary parts of the nonlinear susceptibility, but also the sign of the real part. Optical limiting is a nonlinear optical process in which the transmittance of a material decreases with increased incident light intensity. It has been demonstrated that optical limiting can be used for pulse shaping, smoothing and pulse compression [21]. The potential applications of optical limiting devices are sensor and eye protection.

Here, we report on the synthesis of Schiff base dimer (SHBD) [2,2'-(4,4'-methylene bis (4,1-phenylene) bis(azan-1-yl-1-ylidene))bis(methane-1-yl-1-ylidene) diphenol] polymer and investigation of their spectral characteristics. The nonlinear optical properties of Schiff base dimer (SHBD) polymer film were studied using the Z-scan method in order to determine both the nonlinear refractive index n_2 and the nonlinear absorption coefficient β. The experiments was

performed using cw laser of wavelength 532 nm**.** We report what are to our knowledge the first experimental observation of optical limiting response of Schiff base dimer (SHBD) polymer film.

EXPERIMENTAL

Materials and Procedures

Ortho hydroxy benzaldehyde and diphenyl diamine were obtained from Fluka, Methanol and Ethanol solvents were obtained from Merck. The chemical structure of the SHBD is shown in Figure 1.

In round bottle flask (20 m mol) from ortho hydroxy benzaldehyde and the a ppropriate 4,4-Diaminodiphenyl-methane (10m mol) in ethanol (30 ml) are refuxed for 1 hr. The pale yellow precipitate which formed was removed by filtration, washed with methanol and purified by recrystallization and dried in a vacuum oven at 60 °C, their melting point was 190°C.

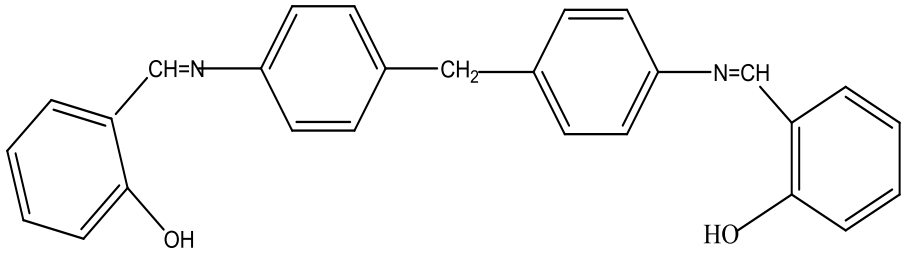

Figure 1: The Chemical Structure of the SHBD

FTIR Spectra

The FTIR spectra were obtained with a FT/IR-model 8400s spectrophotometer by SHIMADZU, under ambient condition. Infrared spectroscopic studies were conducted to investigate the type of chemical bondings which is illustrated in Figure 2. The FTIR spectra of SHBD has fairly strong absorption in the region (1000-1600) cm^{-1} and the bands in this region have contribution mainly from C=N (1569.95) cm^{-1}, C-N(1282.57) cm^{-1}, C-O(1184.21) cm^{-1}stretch, C=C(1618.17) cm^{-1} aromatic and C-H(2920.03) cm^{-1} aromatic bonds. The stretching vibration of the O-H group which appeared at 3382.91 cm^{-1} cancels the absorption peak of (-NH2) group supposed to appear at same region. The band shows broad appearance due to its relatively low frequency. It can be concluded that the (-OH) group may form a hydrogen bonding with nitrogen atom.

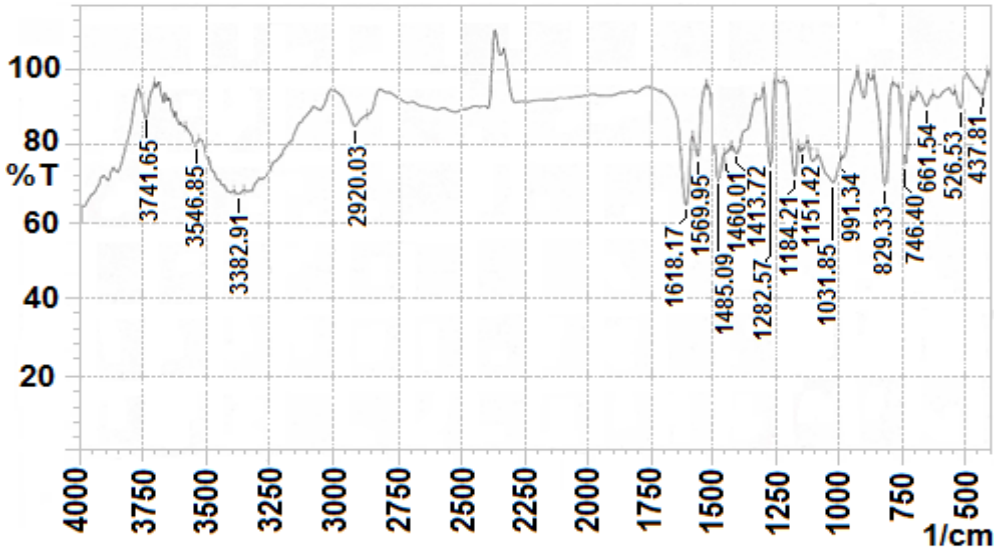

Figure 2: IR Spectrum of SHBD

Elemental Analysis

Elemental analysis of the polymers was carried out using a Euro Vector EA 3000A Italy instrument, and which is shown in table 1.

Table 1: Elemental Analysis of Functionalized Polymers

C%		N%		H%	
Theoretical	**Calculated**	**Theoretical**	**Calculated**	**Theoretical**	**Calculated**
86.63	86.91	7.48	7.13	5.88	5.36

The Preparation of Sample

The SHBD polymer film used in the present study was prepared as follows: 0.2 g of the SHBD powder was dissolved in 10 ml of ethanol, the polymer solution was stirred at room temperature for 45 min and then the solution was filtered through a 0.2 mm syringe filter. The film was prepared by the spin coating method on a clean glass slide substrate of 25 mm x 25 mm x 1 mm which was heated up to 70 ^{o}C. A smooth film without dust and solvent residues were obtained. The thickness of the film was about 35 μm. An accurate knowledge of linear absorption coefficient α is necessary for the use of this technique, an easy way to measure (α =226.85 cm^{-1}) is to use the Bear's low.

UV-Visible Spectroscopic Studies

Optical absorption spectra was recorded at room temperature by using a Cecil Reflected-Scan CE 3055 reflectance spectrometer in the wavelengths range 300-900 nm. The optical absorption for the SHBD polymer film shows absorption peak at λ_{max}=510 nm as can be seen in Figure 3.

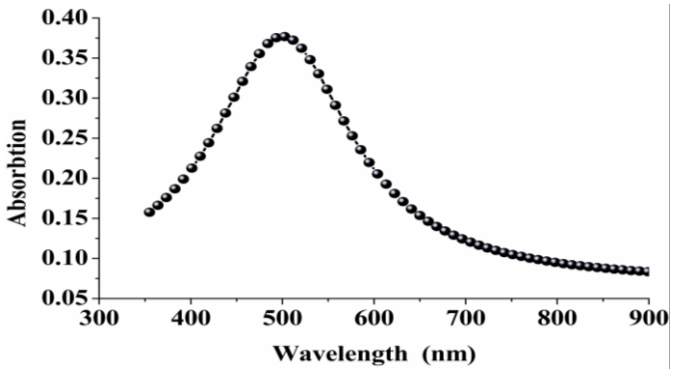

Figure 3: UV-Visible Absorption Spectrum of SHBD Polymer Film

Z-Scan

The Z-scan technique were used to measure the nonlinear refractive index and nonlinear absorption coefficient of the SHBD polymer film. The experiments were performed using a 532 nm laser beam from solid state laser SDL with an average out put power of 50 mW. The beam was focused to a small spot using a convex lens with 5 cm focal length and the sample was moved along the z-axis by a motorized translational stage. The transmission of the beam through an aperture placed in the far field is measured using a photo detector fed to a digital power meter (Field Max II-To+OP-2 Vis Sensor). For an open aperture Z-scan, a lens was used to collect the entire laser beam transmitted through the sample. The laser beam waist ω_o at the focus point was measured to be 21.63 μm and the diffraction length, Z_R was found to be 2.7 mm.

Optical Limiting Technique

The optical limiting response of the SHBD polymer film was performed using a standard experimental

configuration. The experimental set-up for the demonstration of optical limiting is shown in Figure 4. Laser wavelength at 532 nm from a SDL laser was used to excite the sample. The laser beam was focused using a 5 cm focal length convex lens and the sample was placed at the position where the transmitted intensity shows a valley in closed aperture Z-scan curve. An aperture is used to control the cross-section of the beam coming out of the sample. This beam is then made to fall on the Photo detector. The optical limiting response was studied by varying the input power with a laser beam attenuator arrangement and by monitoring the incident and transmitted powers.

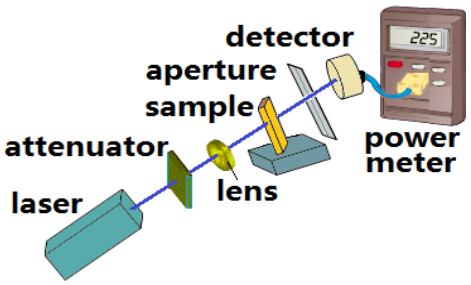

Figure 4: Experimental Set-up for Limiting Effect

RESULTS AND DISCUSSIONS

Nonlinear Optical Properties

The nonlinear refractive index n_2 (cm^2/W) and nonlinear absorption β (cm/W) could be evaluated by the measurements of Z-scan. Figure 5 shows the closed aperture Z-scan experimental data of the SHBD polymer film at I_o =7.48 kW/cm^2 as the incident intensity. The peak followed by a valley-normalized transmittance obtained from the closed aperture curve ($\Delta T_{p-v} = 0.845$) indicates that the sign of nonlinear refractive index is negative, i.e. self defocusing. The physical origin of nonlinear refraction can be electronic, molecular, electrostrictive or thermal in nature. In the present case, the nonlinearity is thermal in nature as a cw laser beam is used. The defocusing effect shown in Figure 5 is attributed to a thermal nonlinearity resulting from absorption of radiation at 532 nm. Localized absorption of a tightly focused beam propagating through an absorbing dye medium produces a spatial distribution of temperature in the dye and consequently, a spatial variation of the refractive index, that acts as a thermal lens resulting in phase distortion of the propagating beam.

Figure 6 shows typical open aperture Z-scan curve. The *Z*-scan curve exhibits a minimum of transmittance at the focal point z = 0 with a symmetrical shape. The decrease of transmission at the focal point is indicative of the presence of nonlinear absorption. We did not observe any changes in the *Z*-scan trace during the 2 h long experiment. This fact indicates good photochemical stability of SHBD polymer film.

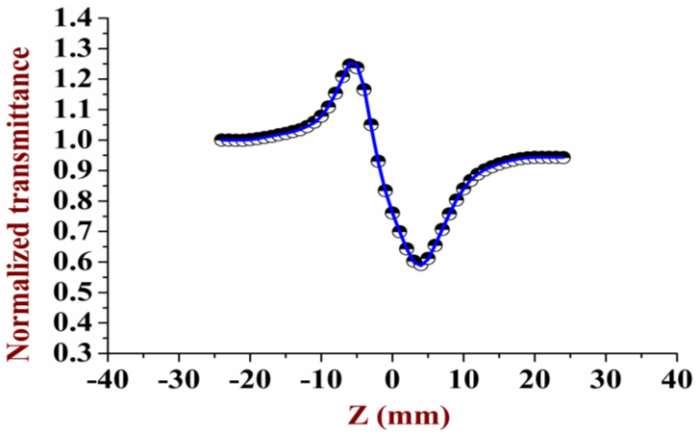

Figure 5: Closed-Aperture Z-Scan Result for SHBD Polymer Film

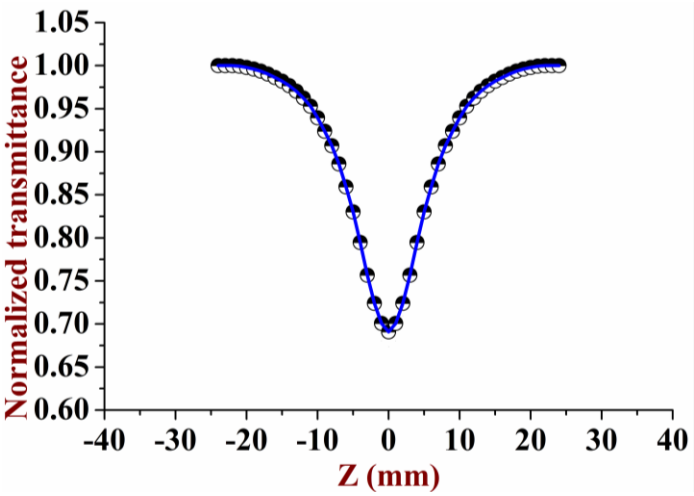

Figure 6: Open-Aperture *Z*-Scan Data for SHBD Polymer Film

Generally, the measurements of the normalized transmittance, allow determination of the nonlinear refractive index n_2 and the nonlinear absorption coefficient β. Here, since the closed aperture transmittance is effected by the nonlinear refraction and absorption, the determination of n_2 is less straight forward from the closed aperture scans. It is necessary to separate the effect of nonlinear refraction from that of the nonlinear absorption. A method [20] to obtain purely effective n_2 is to divide the closed aperture transmittance by the corresponding open aperture scans. The ratio of Figure 5 and Figure 6 scans is shown in Figure 7. The data obtained in this way reflects purely the effect of nonlinear refraction.

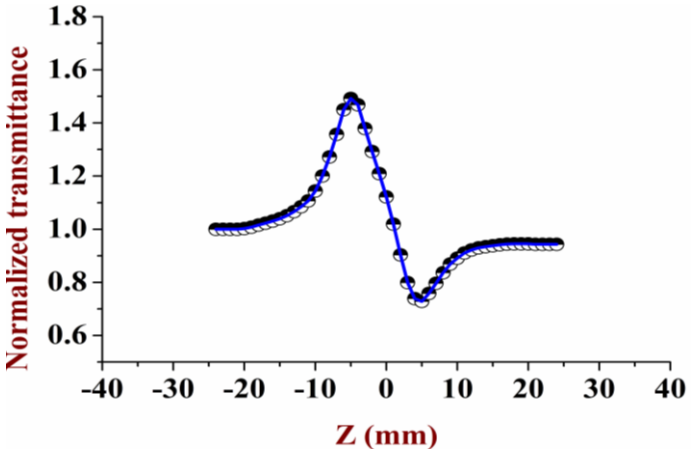

Figure 7: Pure Nonlinear Refraction Z-Scan Data for SHBD Polymer Film

The calculation of the values of the nonlinear absorption coefficient β and nonlinear refractive index n_2 have been discussed in detail elsewhere [20]. From Figures 6 and 7, the calculated β and n_2 values were 2.79 $x10^{-2}$ cm/W and $6.12x10^{-7}$ cm^2/W respectively. The high nonlinear refractive index compares favorably with the nonlinearities of other representative third-order nonlinear optical materials, such as the poly (phenylacetylene) and poly (p-methoxyphenylacetylene) which they have $n_2 = 6x10^{-18}cm^2/W$ and $n_2 = 1.1x10^{-17}$ cm^2/W, respectively [22] and for eosin doped in a polymer film, $n_2 = 5.58x10^{-16}$ cm^2/W [23]**.** These results suggest that the SHBD polymer films have potential applications in nonlinear optics.

Optical Limiting Studies

Figure 8 shows the variation of the output power as a function of the input power, which points out the optical

limiting behavior of SHBD polymer film. It can be seen from the curve that the sample show obvious optical limiting behaviors. The transmitted output intensity was found to vary linearly with the incident input intensities at low input intensities but starts to deviate at high incident intensities. With further increment increase of the input power, the transmitted intensity reaches a plateau and is saturated at a point defined as the limiting amplitude: i.e. the maximum output power, showing obvious limiting property.

Figure 9 shows the normalized transmission curve as a function of incident input power for sample. The optical limiting threshold value (defined as the incident input power where the transmission reduces by 50%) at which the limiting occurs is found to be 9.5 mW. The SHBD polymer film investigated here exhibits good optical power limiting for low cw laser. Thus, SHBD polymer film would be a promising material for making optical power limiting devices.

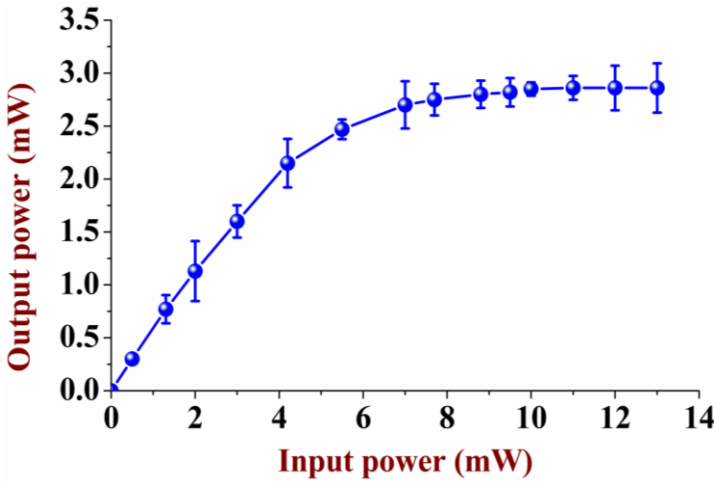

Figure 8: Optical Limiting Behavior of SHBD Polymer Film

Optical limiting can be achieved by means of various nonlinear optical mechanisms, including self-focusing, self-defocusing, induced scattering, induced-refraction, induced aberration, excited state absorption, two-photon absorption, photo-refraction and free-carrier absorption in nonlinear optical media [24-28]. In our case the optical limiter behavior appears to arise from the nonlinear refraction. Since the samples were pumped with cw laser beam the arising nonlinearities are predominantly thermal in nature. Due to change in refractive index of the material self-focusing and self-defocusing can be observed in the material, leading to reduction of transmittance at far field (due to distortion of spatial profile of Gaussian beam). Reduced transmittance in the far field gives better optical limiting performance.

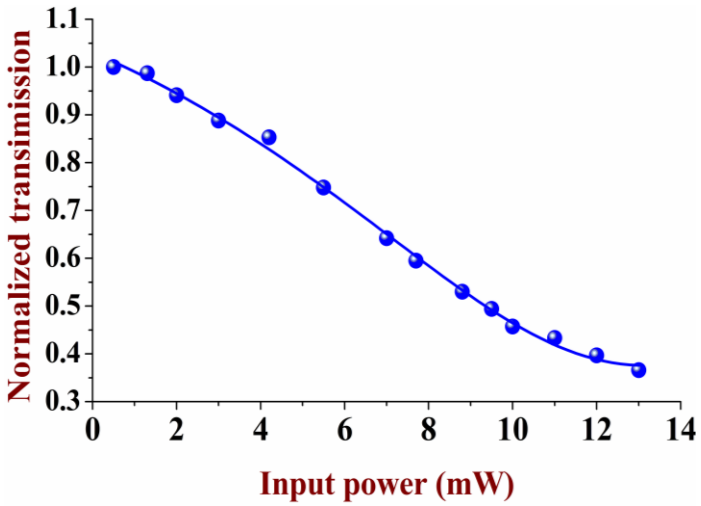

Figure 9: Normalized Transmission Curves of Optical Limiting for SHBD Polymer Film

CONCLUSIONS

The nonlinear absorption and refraction of a newly synthesized Schiff base dimer (SHBD) [2,2'-(4,4'-methylene bis (4,1-phenylene) bis (azan-1-yl-1-ylidene)) bis (methane-1-yl-1-ylidene) diphenol] polymer film have been studied by using a single-beam Z-scan technique under cw laser excitation at 532 nm. Z-scan curve indicated that the sample show negative nonlinear refraction which is regarded as self-defocusing effect. The origin of optical nonlinearity observed in the cw regime is attributed to the thermal variation of refractive index in the medium. The optical limiting behavior of sample has been investigated. The SHBD polymer film exhibits good optical limiting properties at 532 nm, and is a potential candidate for optical limiting applications ranging from human eye protection to sensor protection in optical systems.

REFERENCES

1. Nalwa, H.S. (1993).Organic Materials for Third-Order Nonlinear Optics, Advanced Materials. 5, 341-358.
2. Norwood R. A. & Sounik J. R. (1992). Third order nonlinear optical response in polymer thin films incorporating porphyrin derivatives, Applied Physics Letters, 60, 295-297.
3. Blau W., Byrne H., Dennis W. M. & Kelly J. M. (1985). Reverse saturable absorption in tetraphenyl-porphyrins. Optics Communication, 56, 25-29.
4. Chunfei L., Lei Z., Miao Y., Hui W. & Yuxiao W. (1994). Dynamic and steady-state behaviors of reverse saturable absorption in metallophthalocyanine. Physics Review, A 49, 1149-1157
5. Joel M. Hales, Shijun Z., Stephen B., Seth R. M. & Joseph W. P. (2006). Bisdioxaborine Polymethines with Large Third-Order Nonlinearities for All-Optical Signal Processing. America Chemical Society, 128, 11362-11363.
6. Unnikrishnan K.,Thomas J.,Nampoori V.P.N. &Vallabham C.P.G. (2002).Degenerate four wave mixing in some metal phthalocyanines and naphthalocyanines. Chemical Physics, 279, 209-213**.**
7. Manjunatha K. B., Dileep R., Umesh G. & Ramachandra B. B. (2013). Nonlinear optical and all-optical switching studies of palladium(II) complex. Materials Letters**,** 105, 173-176**.**
8. Manjunatha K. B., Dileep R., Umesh G. & Ramachandra B. B. (2013). Nonlinear optical and all-optical switching studies of novel ruthenium complex. Optics & Laser Technology, 52, 103-108**.**
9. Manjunatha K. B., Dileep R., Umesh G. & Ramachandra B. B. (2013). Study of third-order nonlinear optical and all-optical switching properties of palladium metal–organic complex. Optical Materials, 35, 1366-1372.
10. Manickasundaram S., Kannan P., Hassan Q. M. A. & Palanisamy P. K. (2008). Azo dye based poly (alkyloxymethacrylate)s and their spacer effect on optical data storage. Materials Science: Materials in Electronics, 19, 1045-1053.
11. Manickasundaram S.,Kannan P., Kumaran R.,Velu R.,Ramamurthy P.,Hassan Q. M. A., Palanisamy P. K., Senthil S. & Narayanan S. S. (2011). Holographic grating studies in pendant xanthene dyes containing poly (alkyloxymethacrylate)s. Materials Science: Materials in Electronics, 22, 25-34.
12. Chuanlang Z., Dehua L.,Deqing Z., Wei X.,Yuxin N & Daoben Z. (2004).The excited-state absorption and third-order optical nonlinearity from 1-dodecanethiol protected gold nanoparticles: Application for optical limiting. Optical Materials, 26, 11-15.

13. Preeti G. (2009). On the optical limiting and Z-scan of hexamethylin-dotricarbocyanine perchlorate dye. Optical Materials, 31, 1559-1563.

14. Sathiyamoorthy K., Vijayan C. & Kothiyal M. P. (2008). Low power optical limiting in ClAl-Phthalo- cyanine due to self defocusing and self phase modulation effects. Optical Materials, 31, 79-86.

15. Kiran P.P., Raghunath D.R., Bhaskar G.,Maiya & Rao D. N.(2003).Third-order nonlinearity and optical limiting studies in phosphorus (V) porphyrins with charge transfer states. Optical Materials, 21, 565-568.

16. Sheng L. G.Tie P. L., Tie B. W., Zhao S. L. & Tian D. C. (2007). Third-order nonlinearities and optical limiting properties of complex Co_2L_3. Optical Materials, 29, 494-498.

17. Xinyan S., Hongyao X. Junyi Y., Naibo L. & Yinglin S. (2008). Soluble functional polyacetylenes for optical limiting: Relationship between optical limiting properties and molecular structure. Polymer, 49, 3722-3730.

18. Jun W., Daniel F. & Werner J. B. (2010). The importance of solvent properties for optical limiting of carbon nanotube dispersions, Optics Communications, 283, 464-468.

19. Sheik-Bahae M., Said A.A. &Van Stryland E.W.(1989) High-sensitivity, single-beam n_2 measurements. Optics Letters, 14, 955-960.

20. Sheik-Bahae M., Said A. A., Wei T., Hagan D. J. &Van Stryland E. W.(1990). Sensitive measurement of optical nonlinearities using a single beam. IEEE J. Quantum Electron, QE-26**,** 760-766

21. Shiliang Q., Chongjun Z., Xiongwei J., Guangyu F., Yachen G., Huidan Z., Yinglin S., Jianrong Q., Congshan Z. & Hirao K. (2003). Optical nonlinearities of space selectively precipitated Au nanoparticles inside glasses. Chemical Physics Letters368, 352-358.

22. Falconieri M, Amato RD, Furlani A, Russo M V (2001). Z-scan measurements of third-order optical non-linearities in poly(phenylacetylenes). Synthetic Metals, 124, 217-219.

23. Li H. P., Kan C. H, Lam Y.L. & Ji W.(2001). Femtosecond Z-scan measurements of nonlinear refraction in nonlinear optical crystals. Optical Material, 15, 237-242.

24. Said A. A., Sheik-Bahae M., Hagan D.J., Wei T.H., Wang J. &Van Stryland E.W.(1992). Determination of bound-electronic and free-carrier nonlinearities in ZnSe, GaAs, CdTe, and ZnTe. Optical Society of America, B **9,** 405-414.

25. Justus B. L., Huston A. L. & Campillo A. J. (1993). Broadband thermal optical limiter, Applied Physics Letters 63, 1483-1485.

26. Nashold K. M. & Powell W. D. (1995). Investigations of optical limiting mechanisms in carbon particle suspensions and fullerene solutions. Optical Society of America B,12, 1228-1237.

27. Mansour K., Soileau M. J. & Van Stryland E.W. (1992). Nonlinear optical properties of carbon black suspensions (ink). Optical Society of America B, 9**,** 1100-1109.

28. Joudrier V., Bourdon P., HacheF & Flytzanis C. (2000). Characterization of nonlinear scattering in colloidal suspensions of silica particles. Applied Physics B, 70, 105-109.