Scientific Research

Nonlinear Optical Properties and Optical Limiting Measurements of {(1Z)-[4-(Dimethylamino)Phenyl]Methylene} 4-Nitrobenzocarboxy Hydrazone Monohydrate under CW Laser Regime

Fryad Z. Henari[1*], P. S. Patil[2]

[1]Department of Medical Sciences, Royal College of Surgeons in Ireland, Medical University of Bahrain, Busaiteen, Kingdom of Bahrain
[2]Department of Physics, K. L. E. Institute of Technology, Hubli, India
Email: [*]fzhenar@rsci-mub.com

Abstract

We report results from the investigation of the nonlinear refractive index and nonlinear absorption coefficient of {(1Z)-[4-(Dimethylamino)phenyl]methylene} 4-nitrobenzocarboxy hydrazone mono-hydrate (DMPM4NBCHM) solution using Z-scan technique with a continuous wave (CW) Argon ion laser. The results show that this type of organic material has a large nonlinear absorption and nonlinear refractive index at 488 nm and 514 nm. The origin of the nonlinear effects was discussed. We demonstrate that the light induced nonlinear refractive index variation, leads to limiting effect. The results indicated that DMPM4NBCHM could be promising candidates for application on nonlinear photonic devices and optical limiters.

Keywords

**Nonlinear Absorption, Nonlinear Refractive Index, Z Scan, Optical Limiting,
{(Z)-[4-(Dimethylamino)Phenyl]Methylene} 4-Nitrobenzocarboxy Hydrazone Monohydrate**

1. Introduction

In general, the variation of optical properties of materials induced by high intensity light is divided into light in-

[*]Corresponding author.

duced absorption changes and light induced refractive index changes. The light induced absorption changes are commonly describe by $\alpha = \alpha_o + \beta I$, where α is linear absorption coefficient; I is the intensity of the light and β is a nonlinear absorption coefficient. This coefficient contains interesting nonlinear optical effects such as: Reverse Saturation Absorption (RSA), Two Photon Absorption (TPA), and Saturation Absorption (SA). The light induced refractive index changes are described by the relationship $n = n_o + n_2 I$, where n_o is the linear refractive index; I is the intensity of the light and n_2 is a nonlinear refractive index coefficient. This coefficient is an effective parameter that contains many interesting nonlinear optical effects, such as laser induced grating, soliton pulse propagation in waveguides [1] [2], optical switching [3]-[6] self-focusing, self-defocusing, self-phase modulation, self diffraction, optical bistability and optical limiting [7]-[11].

A large number of materials have been found to exhibit laser induced refractive index changes such as fullerenes, liquid crystals, natural substances such as Henna, Chinese tea and Curcumin and organic materials such as Porphyrin, Phthalocyanine and their derivatives. Among organic materials, hydrazones and their derivatives have recently attracted much attention due to their high tendency to crystallize in asymmetric structure and for their synthetic flexibility that can offer the modification of nonlinear properties. The nonlinear optical response of this type of materials can be enhanced by following suitable synthetic procedures to design molecules with delocalize π electrons, donor-accepter-donor (D-A-D) and acceptor-donor-acceptor (A-D-A) properties [12]-[14]. The nonlinear properties and optical limiting behaviours of these types of materials were investigated using nanosecond and femtosecond laser pulses [12]

In this work, we report the experimental measurements of nonlinear refractive index and the nonlinear absorption of DMPM4NBCHM solution with continuous wave (CW) argon ion laser at 488 nm and 514 nm (power 10 mW) using the Z-scan technique [15]. The optical limiting behaviour based on nonlinear refractive index was also investigated.

2. Synthesis

{(1Z)-[4-(Dimethylamino)phenyl]methylene} 4-nitrobenzocarboxy hydrazone monohydrate (DMPM4NBCHM) was obtained by refluxing 4-nitrophenyl hydrazide (0.01 mol) and 4-(dimethylamino)benzaldehyde (0.01 mol) in ethanol (30 ml) with the addition of 3 drops of concentrated sulfuric acid for 3 hr. Excess ethanol was removed from the reaction mixture under reduced pressure. The solid product obtained was filtered, washed with water and dried [16] (**Figure 1**).

3. Experimental Procedure

Solutions of different concentrations for the sample were prepared in dimethylformamide (DMF) and placed in 1 mm cuvette. The linear absorption spectra of the sample were recorded with a Shimadzu UV-1800 spectrometer. The linear absorption spectrum for the sample at the concentration 0.25 g/l is shown in **Figure 2**. The spectrum shows absorption peaks at 331 nm and 434 nm.

The Z-scan technique [15] was used to measure the nonlinear refractive index. This technique relies on the fact that the intensity varies along the axis of the convex lens and is maximum at the focus. Hence, by shifting the sample through the focus, the nonlinear refraction can be measured by observing the spot size variation at the plane of finite aperture/detector combination. The experiment was performed with an air-cooled Ar ion laser beam at 488 nm and 514 nm with an average power of 10 mW. The beam was focused to a beam waist of 20 μm with a lens of 5 cm focal length, giving a typical power density range of 1.6×10^7 W/m^2. The transmission for the samples was measured with and without aperture in the far-field of the lens, as the sample moved through the focal point.
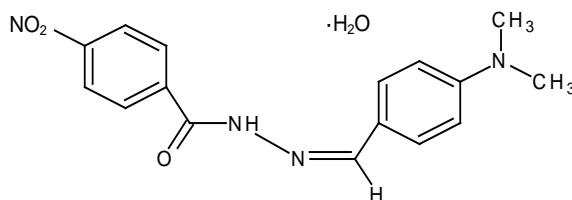

Figure 1. Chemical structure of the DMPM4NBCHM compound.

4. Results and Discussion

Figure 3 shows a typical normalized transmission at wavelengths 514 nm (closed Z-scan) for sample, as a function of the sample position: The normalized transmittance curves for all samples were characterized by a prefocal peak followed by a postfocal valley. This peak valley configuration implies that the nonlinear refractive index of solution is negative ($n_2 < 0$) (self defocusing). Similar characteristics were shown by the sample studied at 488 nm. The observed asymmetric nature of the Z-scan measurements a long with fact that the laser beam used in the experiment is a CW, peak valley configuration suggests that the nonlinear refractive index observed is of thermal-origin [17]. The nonlinear refractive index effect may arise from different physical mechanisms such as electronic (Kerr effect) or thermal effect (focusing and defocusing). The nonlinear refractive index for all samples in this case may be attributed to a thermal nonlinearity resulting from the absorption of incident beam by
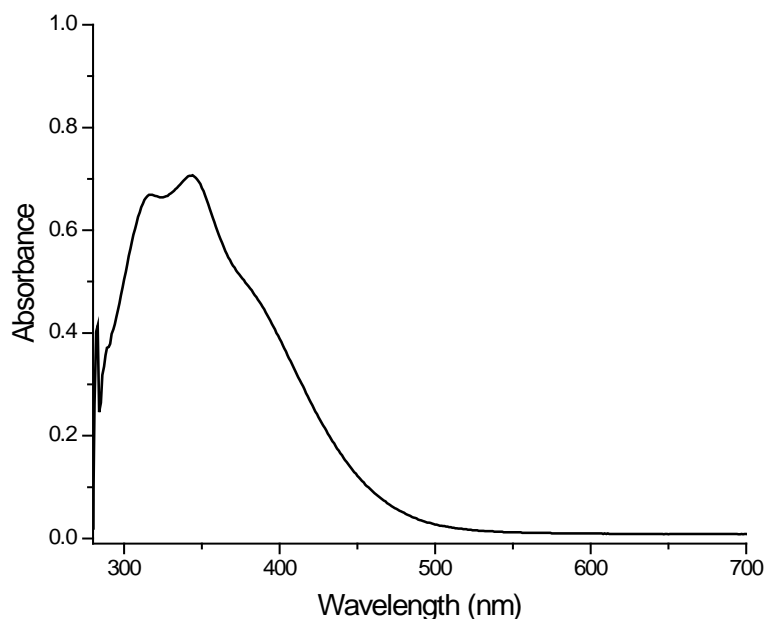

Figure 2. Linear absorption spectrum of DMPM4NBCHM in DMF.
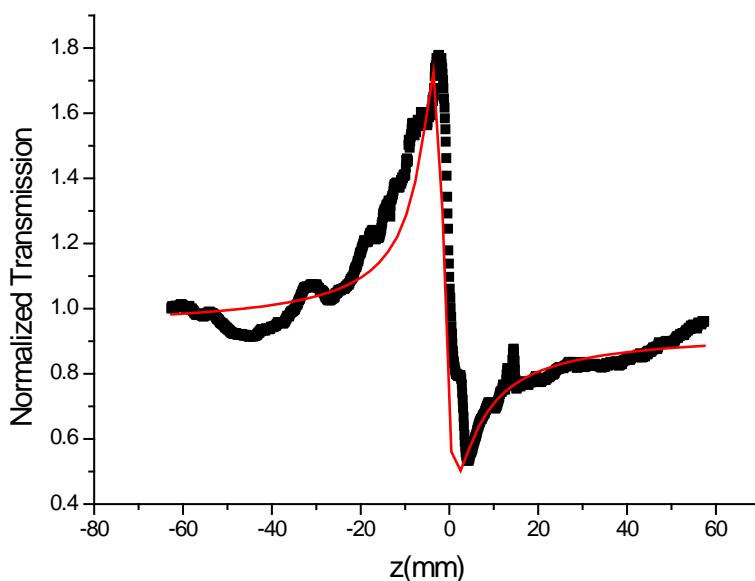

Figure 3. Closed-aperture Z-scan for DMPM4NBCHM in DMF at 488 nm for 10 mW incident power.

the medium which results in deposition of heat via non-radiative decay from excited states where a transverse temperature gradient is established due to the temperature coefficient of the refractive index (dn/dt). The produced refractive index gradient creates a lens like optical element, a thermal lens (thin lens in Z-scan), resulting in the phase distortion of the propagating beam at the farfield.

The normalized transmission of closed aperture Z-scan is given by [17]

$$T = \left(1 + \phi \frac{2x}{1+x^2} + \phi^2 \frac{x}{1+x^2}\right)^{-1} \tag{1}$$

where $x = z/z_o$ (with $z_o = \pi w_o^2 / \lambda$) is the diffraction length of the Gaussian beam, w_o is the beam waist at focus and ϕ is the nonlinear phase change. The normalized closed aperture Z-scan data are fitted with Equation (3) to obtain ϕ values. The nonlinear refractive index n_2 is then related to ϕ by [15]

$$n_2 = \frac{\phi \alpha \lambda}{2\pi I_o \left(1 - e^{-\alpha l}\right)} \tag{2}$$

where α is the linear absorption coefficient at 514 nm ($\alpha = 0.297$/mm) and l is the thickness of the sample. I_o is the peak intensity at the focus, and λ is the wavelength of the laser beam.

A fit of Equation (1) to the experimental data is depicted in **Figure 3**, and yields the value of nonlinear refractive index $n_2 = 3.39 \times 10^{-11}$ m^2/W at 488 nm. A similar fit was performed on the experimental data at 514 nm and yielded the values of nonlinear refractive index $n_2 = 7.82 \times 10^{-12}$ m^2/W. The values reported in this work are in the same order with the values reported for Basic Violet 16 dye, fast green FCF and CIAI-Phthalocyanine [18]-[20] and two orders lower than the reported value for Henna [21]. Hydrazones similar to Phthalocyanine, chalcones and C60 are found to be a promising material for various optical devices. Since hydrazones contain the asymmetric transmitter back bone, the compound can be utilized for designing compounds with large third order nonlinear optical properties [12].

Figure 4 shows the normalizing transmission for the open aperture case. The transmission is symmetric with respect to the focus ($Z = 0$), where it has minimum transmission. This is an indicative that the sample exhibits reverse saturation absorption, RSA. Similar characteristics were shown by the sample studied at 514 nm. The conditions required for RSA are as follows: 1) Incident photons with the same wavelength can be absorbed by molecules in the ground state and also by excited states; 2) The absorption of the excited states must be larger than that of the ground state. For most organic molecules excited by a laser wavelength of weak ground state absorption, these conditions are often being met. In fact, the ground state absorption cross section σ_g and excited
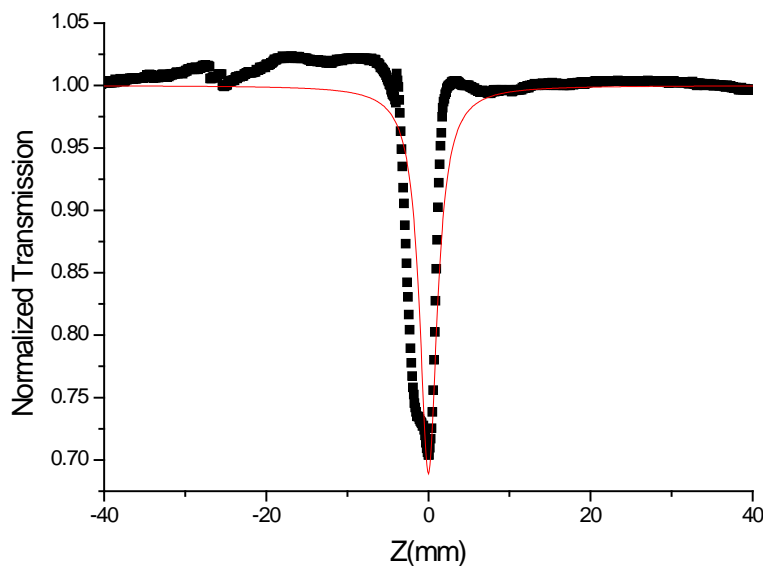

Figure 4. Open-aperture Z-scan for DMPM4NBCHM in DMF at 514 nm for 10 mW incident power.

state absorption cross section were calculated and found that $\sigma_{ex} > \sigma_g$ (see below).

Open aperture Z-scan was performed also with a pure solvent. In this case, no nonlinear absorption was observed within the limit of the intensity used in the experiment. We conclude that the effect seen is due solute rather than solvent.

The normalize transmittance for the open aperture is given by [15].

$$T(z) = 1 - \frac{\Delta\varphi}{\left(1 + x^2\right)} \tag{3}$$

where $x = z/z_o$ (with $z_o = \pi w_o^2 / \lambda$) is the diffraction length of the Gaussian beam, w_o is the beam waist and $\Delta\varphi$ is the nonlinear phase change. The nonlinear absorption β is then related to $\Delta\varphi$ by [15]

$$\beta = \frac{2\sqrt{2}\Delta\varphi\alpha}{I_o\left(1 - e^{-\alpha l}\right)} \tag{4}$$

where α is the linear absorption coefficient at $\lambda = 488$ nm ($\alpha = 0.41$/mm), l is the thickness of the sample and I_o is the peak intensity at the focus. A fit of Equation (4) to the experimental data is depicted in the **Figure 4**, and yields the value of nonlinear absorption $\beta = 9.53 \times 10^{-5}$ m/W at 488 nm. A similar fit was performed on the experimental data for 514 nm which yielded the value of nonlinear absorption $\beta = 8.62 \times 10^{-6}$ m/W. These values are two orders smaller than the values reported for zinc porphyrin polymer measured with Z-scan method [22] in the same order of the value reported fast green FCF and Safranin O Dye [19] [23].

The nonlinear absorption coefficient β is related to the excited-state absorption given by [24]

$$\beta = \frac{\lambda N_o \Delta\sigma}{4\pi I_s} \tag{5}$$

where $\Delta\sigma = \sigma_{ex} - \sigma_g$ is the difference between the excited-state absorption cross section σ_{ex} and the ground-state absorption cross section σ_g, N_0 is the total concentration ($N_0 = 2.14 \times 10^{17}$ cm^{-3}), and $I_s = hc/\lambda\sigma_g\tau$, where hc/λ is the pump-photon energy, τ is the excited lifetime and taken to be 1 ms (triplet state decay time). The ground-state absorption cross section was calculated from $\sigma_g = \alpha_0/N_0$ and found to be 1.5×10^{-18} cm^2. Using Equation (5), the excited-state absorption cross section was calculated for 488 nm and found to be $\sigma_{ex} = 2.23 \times 10^{-12}$ cm^2. This value is nearly six orders of magnitude higher than the ground-state absorption cross section, which is in agreement with the conditions for observing RSA and indicates that the nonlinearity here is associated with RSA. A similar calculation were performed for 514 nm and found that the σ_{ex} six orders higher than σ_g this because of weaker ground state absorption at this wavelength.

One interesting applications of these materials is optical limiting at low intensity for CW lasers. It has been shown that the optical limiting can be used for the protection of eyes and sensors from high intensity laser beams. Optical limiting is a nonlinear optical process in which the transmitted intensity of the material increases at low incident intensities and at the certain threshold intensity value the transmission remains constant. Optical limiting could arise from thermal defocusing, self diffraction and reveres saturation absorption. In this work the optical limiting experiment based on aperture limited geometry was performed by placing the sample at post focus position and measuring the transmitted power through the aperture for different incident laser powers. **Figure 5** shows the optical limiting curve where the transmission is plotted as a function of input power for 0.25 g/l solution for all samples. As can be seen from **Figure 5**, at low power region the output power increases with an increase in input power. At a certain threshold value the defocusing effect occurs, which results in a greater cross section area and reduces the proportional intensity of the beam passing the aperture. Thus the transmittance recorded by the detector reduced considerably. The limiting effect of the sample occurred at a threshold power value of 6 mW for 488 nm and 9 mW for 514 nm and measured from deviation of linearity. The values obtained here depend on experimental setup parameters such as the focusing lens and the distance between the sample and the detector and the absorption at the probe wavelength.

5. Conclusion

In conclusion, the nonlinear refractive index and nonlinear absorption coefficient has been measured for
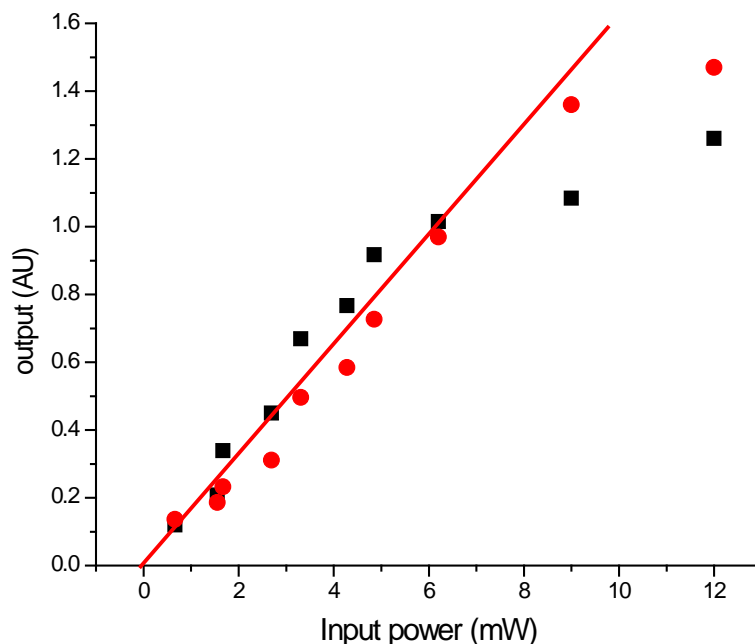
Figure 5. Optical limiting response of DMPM4NBCHM at 488 nm (black squares) and at 514 nm (red circles).

{(1Z)-[4-(Dimethylamino)phenyl]methylene} 4-nitrobenzocarboxy hydrazone monohydrate in solution using the Z-scan technique. The origin of the nonlinear refractive index observed in the CW illumination is attributed to the process of thermally induced refractive index change. The nonlinear absorption may be explained by reversing saturation effects. The defocusing effect was used to demonstrate the optical limiting. The values obtained in this work can be improved creating (D-A-D) design and (A-D-A) design in the molecules. Low power pumping is important for device manufacturing with respect to cost, compactness and threshold damage. The {(1Z)-[4-(Dimethylamino)phenyl]methylene} 4-nitrobenzocarboxy hydrazone monohydrate investigated in this work seems to be promising candidates for future photonic and optoelectronic devices

Acknowledgements

References

[1]   Nalwa, H.S. and Miyata, S. (1997) Nonlinear Optics of Organic Molecules and Polymers. Chemical Rubber Company, Boca Raton.

[2]   Eichler, H.J., Gunter, P. and Pohl, D.W. (1986) Laser-Induced Dynamic Gratings, Vol. 50 of Springer Series in Optical Sciences. Springer-Verlag, Berlin.

[3]   Henari, F.Z. (2001) Optical Switching in Organometallic Phythalocyanine. *Journal of Optics A*: *Pure and Applied Optics*, **3**, 188-190. http://dx.doi.org/10.1088/1464-4258/3/3/306

[4]   Marder, S.R., Torruellas, W.E., Blanchard-Desce, M., Ricci, V., Stegeman, G.I., Gilmour, S., Brèdas Li, J., Bublitz, G.U. and Boxer, S.G. (1997) Large Molecular Third-Order Optical Nonlinearities in Polarized Carotenoids. *Science*, **276**, 1233-1236. http://dx.doi.org/10.1126/science.276.5316.1233

[5]   Hache, A. and Bougeois, M. (2000) Ultrafast All-Optical Switching in a Silicon-Based Photonic Crystal. *Applied Physics Letters*, **25**, 4089-4092. http://dx.doi.org/10.1063/1.1332823

[6]   Balamurugaraj, P., Suresh, S., Koteeswari, P. and Mani, P. (2013) Growth, Optical, Mechanical, Dielectric and Photoconductivity Properties of L-Proline Succinate NLO Single Crystal. *Journal of Materials Physics and Chemistry*, **1**, 4-8.

[7]   Shen, Y.R. (1984) The Principle of Nonlinear Optics. Wiley, New York.

[8]   Sun, X., Yu, G.R.Q., Xu, Q., Hor, T.S. and Jia, A.W. (1998) Broadband Optical Limiting with Multiwalled Carbon

Nanotubes. *Applied Physics Letters*, **739**, 3632-3634. http://dx.doi.org/10.1063/1.122845

[9]   Dabby, F.W., Gustafson, T.K., Whinnery, J.R., Kohanzadeh, Y. and Kelley, P.L. (1970) Thermally Self-Induced Phase Modulation of Laser Beam. *Applied Physics Letters*, **16**, 362-366. http://dx.doi.org/10.1063/1.1653226

[10] Brugioni, S. and Meucci, R. (2002) Self-Phase Modulation in a Nematic Liquid Crystal Film Induced by a Low-Power CO_2 Laser. *Optics Communications*, **206**, 445-451. http://dx.doi.org/10.1016/S0030-4018(02)01486-4

[11] Talebian, E. and Talebian, M. (2012) Accommodation of Theoretical—Experimental Results of Verdet Constant in First Six Groups of Alcohols. *Optik*, **123**, 1807-1809. http://dx.doi.org/10.1016/j.ijleo.2011.10.041

[12] Vijayakumar, S., Babu, M., Balakrishna, K. and Chandrasekharan, K. (2011) Third-Order Nonlinear Optical Response of Newly Synthesized Accepter/Donor Substituted Propylidene Aryloxy Acet Hydrazide. *Optik*, **123**, 21-25. http://dx.doi.org/10.1016/j.ijleo.2010.09.051

[13] Serbutoviez, C., Bosshard, C., Knopfle, G., Wyss, P., Pretre, P., Gunter, P., Schenk, K., Solari, E. and Chapuis, G. (1995) Hydrazone Derivatives: An Efficient Class of Crystalline Materials for Nonlinear Optics. *Chemistry of Materials*, **7**, 1198-1206. http://dx.doi.org/10.1021/cm00054a020

[14] Albota, M., Beljonne, D., Bredas, J.L., Ehrlich, J.E., Fu, J.Y., Heikal, A.A., Hess, S.E., Kogej, T., Levin, M.D., Marder, S.R., McCord-Maughon, D., Perry, J.W., Rochel, H., Rumi, M., Subramaniam, G., Webb, W.W., Wu, X.L. and Xu. C. (1998) Design of Organic Molecules with Large Two-Photon Absorption Cross Sections. *Science*, **281**, 1653-1656. http://dx.doi.org/10.1126/science.281.5383.1653

[15] Sheik-Bahae, M., Said, A.A., Wei, T.H., Hagan, D.J. and Van Stryland, E.W. (1990) Sensitive. Measurement of Optical Nonlinearities Using Single Beam. *IEEE.J.of Quan. Elec. JQE QE*, **26**, 760-769.

[16] Hoong-Kun, F., Jebas, S.R., Sujith, K.V., Patil, P.S. and Kalluraya, B. (2008) {(1Z)-[4(Dimethylamino) Phenyl]Methylene} 4-Nitrobenzocarboxyhydrazone Monohydrate. *Acta Crystallographica*, **E64**, o1907-o1908.

[17] Cuppo, F.L.S., Neto, A.M.F., Gömeze, S.L. and Muhoray, P.P. (2002) Thermal-Lens Model Compared with the Sheik-Bahae Formalism in Interpreting Z-Scan Experiments on Lyotropic Liquid Crystals. *Journal of the Optical Society of America B*, **19**, 1342-1348. http://dx.doi.org/10.1364/JOSAB.19.001342

[18] Rashidian, M.D., Dorranian, S.A., Darani, S. and Saghafi, M.G. (2009) Nonlinear Responses and Optical Limiting Behavior of Basic Violet 16 Dye under CW Laser Illumination. *Optik*, **120**, 1000-1006. http://dx.doi.org/10.1016/j.ijleo.2008.05.001

[19] Ghaleh, K.J., Salmani, S., Hossai, M. and Ara, M. (2007) Nonlinear Responses and Optical Limiting of Fast Green FCF Dye under a Low Power CW He-Ne Laser Irradiation. *Optics Communications*, **27**, 551-554. http://dx.doi.org/10.1016/j.optcom.2006.10.037

[20] Sathiyamoorthy, K., Vijayan, C. and Kothiyal, M.P. (2008) Low Power Optical Limiting in ClAl-Phthalocyanine Due to Self Defocusing and Self Phase Modulation Effects. *Optical Materials*, **31**, 79-86. http://dx.doi.org/10.1016/j.optmat.2008.01.013

[21] Henari, F.Z. (2012) Optical Nonlinear Properties and Optical Switching of Henna (Lawson) Films. *International Journal of Thin Films Science and Technology*, **1**, 255-260.

[22] Qureshi, F.M., Martin, S.J., Long, X., Bradley, D.D.C., Henari, F.Z., Blau, W.J., Smith, E.C., Wang, C.H., Kar, A.K. and Anderson, H.L. (1998) Optical Limiting Properties of a Zinc Porphyrin Polymer and Its Dimer and Monomer Model Compounds. *Chemical Physical*, **231**, 87-94. http://dx.doi.org/10.1016/S0301-0104(98)00081-0

[23] Balaji, G., Rekha, R.K. and Ramalingam, A. (2011) Nonlinear Charactrization of Safranin O Dye for Application in the Optical Limiting. *Acta Physica Polonica A*, **119**, 359-363.

[24] Oliveira, L.C. and Zilio, S.C. (1994) Single Beam Time Resolved z Scan Measurements of Slow Absorbers. *Applied Physics Letters*, **65**, 2121. http://dx.doi.org/10.1063/1.112809

Scientific Research Publishing (SCIRP) is one of the largest Open Access journal publishers. It is currently publishing more than 200 open access, online, peer-reviewed journals covering a wide range of academic disciplines. SCIRP serves the worldwide academic communities and contributes to the progress and application of science with its publication.

Other selected journals from SCIRP are listed as below. Submit your manuscript to us via either submit@scirp.org or Online Submission Portal.