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Large third-order optical nonlinearity and optical limiting in symmetric and unsymmetrical phthalocyanines studied using *Z*-scan

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Abstract

The third-order nonlinear optical and optical limiting properties of 2,3,9,10,16,17,23,24-octakis-(heptyloxy)-phthalocyanine, 2,3,9,10,16,17,23,24-octakis-(heptyloxy)-phthalocyanine zinc(II) (*symmetric*) and 2(3)-(butane-1,4-dioic acid)-9(10),16(17),23(24)-tri *tert*-butyl phthalocyanine zinc(II) (*unsymmetrical*) have been investigated using a continuous wave laser at 633 nm. We have employed the *Z*-scan technique to evaluate the sign and magnitude of nonlinear refractive index and the nonlinear absorption coefficient. Optical limiting based on nonlinear refraction was performed and limiting thresholds were estimated for all the three samples. The magnitude of the third-order nonlinearities measured were one of the highest reported in the cw regime till date. Unsymmetrical phthalocyanine had better limiting characteristics and its nonlinear coefficients were comparatively high. Results of the nonlinear optical studies performed with these organic dyes doped in Poly(methylmethacrylate) are also presented. Our studies indicate that these phthalocyanines are potential candidates for optical limiting applications in low power cw regime.

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Keywords: Phthalocyanines; *Z*-scan; Optical limiting; Nonlinear optical

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1. Introduction

With the advent of the widespread usage of optical detectors and sensors for scientific and industrial purposes the need has rapidly arisen for optical limiting devices [1] that protect the photosensitive components from intense optical radiation while remaining inactive for low intensity levels. Organic materials [2] characterized with large nonlinear optical (NLO) responses are of major interest in this aspect owing to their fast response time, large nonlinear optical susceptibilities, broadband spectral response combined with low cost and ease of processing. The comparatively large nonlinearity of these materials can also be exploited for all-optical switching applications [3,4], for quantum information processing, and integrated all-optical signal processing due to their instantaneous nonlinear optical response with light interaction. Compared to dynamic devices these NLO materials are passive devices and are referred to as intelligent or smart materials owing to the fact that the sensing, processing, and actuating functions required for optical limiting or switching action are inherent to them which are otherwise separate in dynamic devices. The low threshold of these materials for nonlinear response are of much importance as they could be used for the protection of human eye from

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the enfeebling laser effects as the maximum permissible exposure for human eyes even with a laser pointer is ~2.5 mW/cm^2 in the visible spectral region [5,6]. Optical limiting results from irradiance-dependent NLO properties of materials. The incoming intense light alters the refractive and absorptive properties of the materials resulting in a greatly reduced transmitted intensity and therefore it is important to determine the magnitude of the nonlinearity of materials to select suitable materials as optical limiting media.

After the first reported demonstration of optical limiting using phthalocyanines (Pc) in 1989 [7,8], the material has undergone extensive investigation with regard to its structural and spectroscopic properties, synthesis techniques, and NLO properties [9]. Phthalocyanines and their derivatives [10] among other organic materials like porphyrins [11,12], fullerenes [13,14] and organometallic compounds [15,16] form a class of organic molecules with their extensive two dimensional π-conjugated electron system, which entrust them with high polarizability and fast charge redistribution when they interact with rapidly varying intense electromagnetic fields of laser beams. They exhibit other additional advantages, specifically exceptional stability (thermal and chemical), versatility, and processability features [9,17]. With the additional possibility of axial and peripheral substitution they offer the advantages of the capability to tailor or fine tune the NLO properties. Most of the reported works on nonlinear optical and optical limiting studies of Pcs were based on their absorptive nonlinear properties and it is well established that these materials behave as good reverse saturable absorbers (RSA) with pulsed laser excitation [18,19]. On the contrary optical limiters based on refractive nonlinearity as compared to strictly absorbing devices potentially yield a large dynamic range before the limiter itself gets damaged which is due to the fact that such devices operate by refracting light away from the sensor or the object to be protected, as opposed to simply absorbing the incident radiation. As nonlinear refraction and thermal lensing properties play dominant role in the overall material nonlinearity with continuous wave (cw) pumping [20], we choose a low power cw He–Ne laser at 633 nm for our present studies of nonlinear optical properties of 2,3,9,10,16,17,23,24-octakis-(heptyloxy)-phthalocyanine (referred to as Pc1), 2,3,9,10,16,17,23,24-octakis-(heptyloxy)-phthalocyanine zinc(II) (referred to as Pc2) and 2(3)-(butane-1,4-dioic acid)-9(10),16(17),23(24)-tri *tert*-butyl phthalocyanine zinc(II) (referred to as Pc3) in solution form, which are reported here. These are prone to photo-degradation by continuous exposure to laser light indicating that, with the incorporation of these into appropriate solid matrix the problem could be rectified while retaining their large nonlinear response at the same time. We also report here results of our studies carried out on these phthalocyanines in thin film form by doping them into the polymer Poly(methylmethacrylate) (PMMA).

2. Experimental

The measurements of the nonlinear optical properties for our samples were performed using the standard *Z*-scan technique [21]. This technique, known for its simplicity and sensitivity, relies on the distortions induced in the spatial and temporal profile of the input beam on passing through the sample. For the present studies a low power (15 mW) He–Ne laser at 633 nm wavelength was used as the source of excitation. The beam diameter of the Gaussian output from the laser head measured using the knife-edge scan method was found to be ~0.70 mm. The beam was then focussed using a 10 cm (5 cm) lens to a spot size of ~55 μm (~27 μm) with Rayleigh range $z_0 \sim 1.53$ cm (~0.38 cm). The *Z*-scans were performed in the range of $\sim -7z_0$ to $+13z_0$. For closed-aperture scans the distance between the focussing lens and the aperture and the aperture size was adjusted so as to get the optimum value of the linear aperture transmittance $s \sim 0.4$, which averages out possible beam non-uniformities, thus reducing background signals and loss in sensitivity [22]. For open aperture ($s = 1$), all the transmitted power was collected and focussed on to the detector using another lens. The *Z*-scans for solutions were performed by using a standard 1-mm quartz cuvette. For solutions the focussing was done using 10 cm lens ($z_0 \sim 1.53$ cm) and for thin films 5 cm lens ($z_0 \sim 0.38$ cm) was used. We ensured that in either cases the thin sample condition $L < n_0 z_0$ [22] was satisfied in our experiments, where L is the sample thickness (1 mm for solution and ~10 μm for thin films), n_0 is the linear refractive index of the sample and z_0 is the Rayleigh range for the focussed Gaussian beam.

The phthalocyanines were synthesized and purified according to the standard techniques [23] before NLO studies were performed on them. For solution studies chloroform ($CHCl_3$) was used as the solvent in the case of Pc1 and Pc2 and ethanol for Pc3. For thin films, high molecular weight PMMA (350 K) was dissolved in $CHCl_3$ and the Pc's were doped into it by 1% weight. For the case of Pc3 a few drops of ethanol were added to the solution for complete dissolution of sample as it is sparingly soluble in $CHCl_3$. The films were obtained from the solutions by spin coating on to commercially available microscopic slides at different spinning speeds. The thickness of the films determined by the standard m-line technique (Metricon Prism coupler 2010) was found to vary from 9 μm to 15 μm and the uniformity of the films was within ±1 μm range. The spectral response of both solution and thin film samples was recorded using a UV–vis spectrophotometer (Varian Cary 50 Bio UV–vis spectrophotometer). Optical limiting for the phthalocyanines were performed with the same set up as for closed-aperture *Z*-scan since the nonlinear refractive properties were to be exploited in our case. A high power He–Ne laser (25 mW) with similar beam parameters was used for this purpose. The limiting experiments were performed with solution samples by using a lens of focal length

~10 cm and by choosing the optimum concentration of samples for better limiting.

3. Results and discussion

The molecular structure and the absorption spectrum of the phthalocyanines in solution (solid line) and in thin film form (dotted line) are depicted in Fig. 1a–c. The spectra are in accordance with their electronic structures, as phthalocyanines usually possess intense π–π bands in the visible (Q band) and UV (B or Soret band) spectral regions that mostly determine the NLO response. For Pc1 the Q band (620–700 nm) is split into two main components, while Pc2 and Pc3 exhibits only a single Q band owing to the axial metal (zinc) substitution. The *Z*-scan curves obtained for Pc solution samples are shown in Fig. 2. The closed-aperture scan for all the phthalocyanines Fig. 2a, c and e show a pre-focal peak followed by a post-focal valley signature indicating negative nonlinear refraction and the open aperture (Fig. 2b, d, and f) shows saturable absorber type behaviour. This suggests that with cw pumping and for these samples only nonlinear refraction could result in optical limiting.

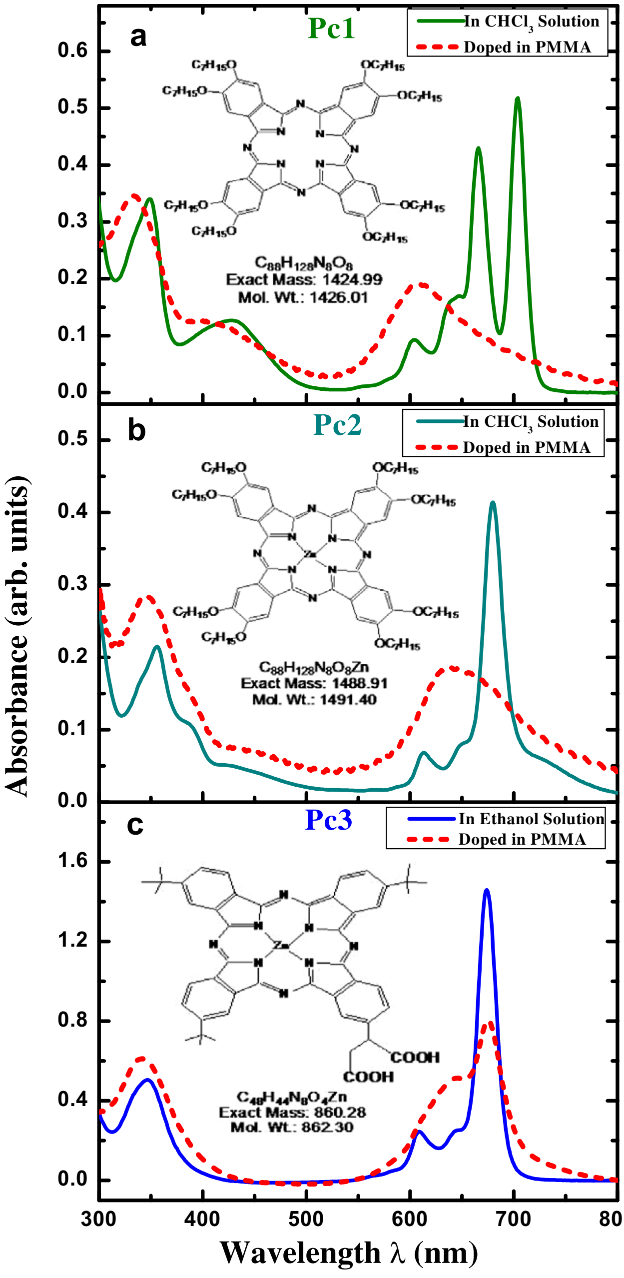

Fig. 1. Absorption spectra of phthalocyanines in solution form (solid line) and thin film form (dotted line) and their corresponding structure. (a) Pc1 in CHCl$_3$ solution and in PMMA (350 K). (b) Pc2 in CHCl$_3$ solution and in PMMA (350 K). (c) Pc3 in ethanol solution and in PMMA (350 K).

For the calculation of the nonlinear refractive index (n_2) the following standard relations [21] were utilized,

$$\Delta T_{\text{p-v}} = 0.406(1-s)^{0.25}|\Delta\phi_0| \tag{1}$$

$$n_2 = \frac{\Delta\phi_0\lambda}{2\pi I_0 L_{\text{eff}}} \tag{2}$$

where, $\Delta T_{p\text{–}v}$ is the peak–valley transmittance difference from the closed-aperture scan, $|\Delta\phi_0|$ is the on-axis nonlinear phase-shift and s is the linear aperture transmittance given by $s = 1 - \exp(-2r_a^2/\omega_a^2)$ where r_a is the aperture radius and ω_a is the beam radius at the aperture in linear regime when kept in the far field. Also, λ is the source wavelength (633 nm), $I_0 = 2P/\pi\omega_o^2$ is the peak intensity within the sample and $L_{\text{eff}} = (1 - e^{-\alpha L})/\alpha$ is the effective length of the sample with α as the linear absorption coefficient and L as the sample thickness. From the values of n_2 thus estimated for all the three phthalocyanines, we found that Pc3 had the highest value of $\sim 2.6 \pm 0.52 \times 10^{-6}$ cm^2/W. The values estimated for Pc1 and Pc2 were $\sim 1.6 \pm 0.32 \times 10^{-6}$ cm^2/W and $\sim 0.8 \pm 0.16 \times 10^{-6}$ cm^2/W, respectively.

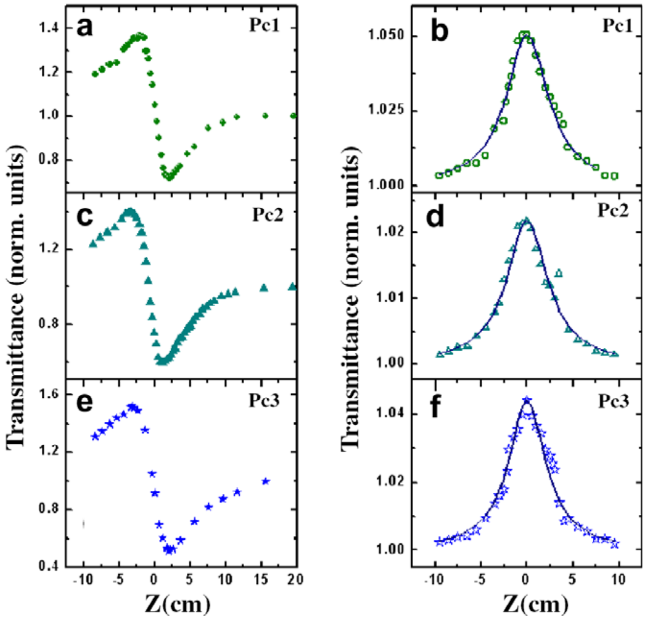

Fig. 2. *Z*-scan curves obtained for solution. (a), (c) and (e) Closed-aperture *Z*-scans of Pc1 and Pc2 in CHCl$_3$ solution and Pc3 in ethanol, indicating negative refractive nonlinearity. (b), (d) and (f) Open-aperture *Z*-scans of Pc1, Pc2 and Pc3, respectively, indicative of saturable absorption type of nonlinearity.

We fitted the open-aperture curves to estimate the value of nonlinear absorption coefficient β as it showed saturable absorption behaviour for all phthalocyanines, with the following relations:

$$T(z, s=1) = \sum_{m=0}^{\infty} \frac{[-q_0(z)]^m}{[m+1]^{3/2}} \quad \text{for } |q_0(0)| < 1, \tag{3}$$

where

$$q_0(z) = \frac{\beta I_0 L_{\text{eff}}}{(1+z^2/z_0^2)} \quad \text{with } z_0 \text{ as the Rayleigh range.} \tag{4}$$

The solid lines in Fig. 2b, d and f are the theoretical fittings for the open-aperture scans using the above relations. The real and imaginary part of third-order nonlinear optical susceptibility $|\chi^{(3)}|$ was calculated from the estimated values of n_2 (closed-aperture scans) and β (open-aperture scans) using the following relations:

$$\text{Re}[\chi^{(3)}] = 10^{-4} \frac{\varepsilon_0 n_0^2 c^2}{\pi} n_2 \tag{5}$$

$$\text{Im}[\chi^{(3)}] = 10^{-2} \frac{\varepsilon_0 n_0^2 c^2 \lambda}{4\pi^2} \beta \tag{6}$$

where, ε_0 is the permittivity of free space, c is the speed of light in vacuum and n_0 is the linear refractive index of the sample. The third-order nonlinear susceptibility calculated for Pc1, Pc2 and Pc3 in solution form using the above relations (5) and (6) were $\sim 9.0 \pm 1.8 \times 10^{-5}$ esu, $\sim 4.6 \pm 0.9 \times 10^{-5}$ esu and $\sim 14.8 \pm 3.0 \times 10^{-5}$ esu, again a comparatively and markedly higher value of $|\chi^{(3)}|$ was noted for Pc3.

A similar behaviour for the open and closed aperture was observed in the case of thin films. The closed-aperture scans depicted in Fig. 3a, c and e and the open-aperture scans depicted in Fig. 3b, d and f for the thin films verify that they are characterized by negative nonlinear refraction (peak–valley signature) and saturable absorber type behaviour. This also confirms that incorporation of these phthalocyanines into the PMMA matrix does not hamper or alter their nonlinearity but provides more stability and carefree handling in comparison with solutions. The n_2 and $|\chi^{(3)}|$ values evaluated for thin films follow a similar pattern as in the case of solutions with higher values being measured for Pc3. For Pc1, Pc2 and Pc3 the estimated n_2 values were $\sim 7.1 \pm 1.4 \times 10^{-6}$ cm^2/W, $\sim 6.4 \pm 1.2 \times 10^{-6}$ cm^2/W and $\sim 16.0 \pm 3.2 \times 10^{-6}$ cm^2/W and the $|\chi^{(3)}|$ values were $\sim 4.0 \pm 0.8 \times 10^{-4}$ esu, $\sim 3.6 \pm 0.7 \times 10^{-4}$ esu and $\sim 10.0 \pm 2.0 \times 10^{-4}$ esu, respectively. The values reported here represent an average of two independent set of measurements. The error involved in the estimation of these values arise from the errors in the measurement of beam waist, peak intensities, absorbance from UV–vis spectrum and the thickness measurement in the case of thin films. We expect the maximum error in such measurements to be ~20%. These values are approximately an order of magnitude higher than that obtained for solutions. The reason for this could be possibly explained from the local heating of the Pc doped PMMA film by strong light absorption since the linear absorption is enhanced for thin film samples at 633 nm (Fig. 1).

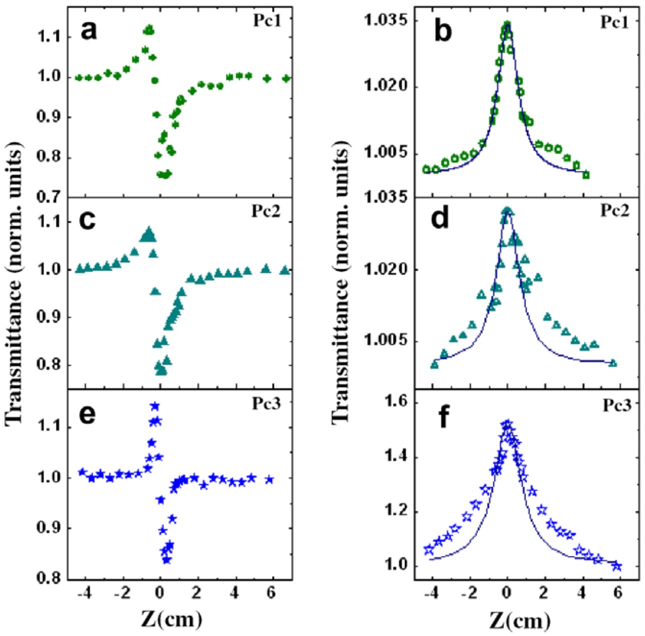

Fig. 3. Z-scan curves obtained for phthalocyanines doped PMMA (350 K) thin films (a), (c) and (e) Closed-aperture Z-scans of Pc1, Pc2 and Pc3 thin films, respectively, indicating negative refractive nonlinearity. (b), (d) and (f) Open-aperture Z-scans of Pc1, Pc2 and Pc3 thin films, indicative of saturable absorption type of nonlinearity.

Usually, for optical limiting experiments based on nonlinear refractive properties (self-defocusing), the sample is kept at the Z-position where the valley falls in the closed aperture (usually just after focus) as it is at this position the beam is maximum defocused by the sample. In our case for Z-positions very close to focus and at high peak intensities we could observe slow and gradual formation of diffraction ring pattern as shown in Fig. 4 for all the samples. The formation of the spatial ring pattern is attributed to induced spatial self-phase modulation arising from laser

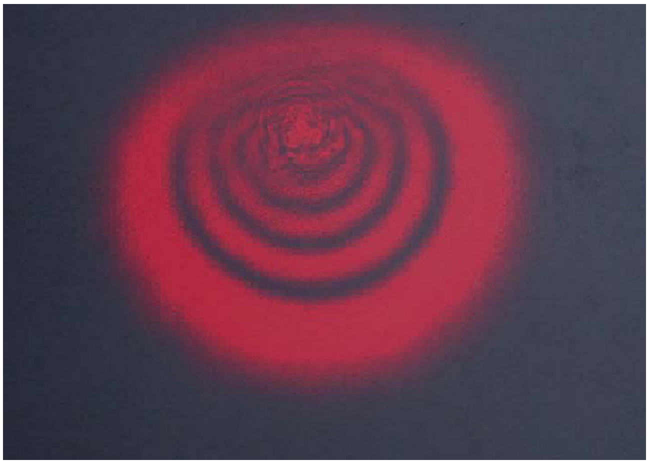

Fig. 4. Spatial rings observed on a screen placed in far field for Pc2 at high powers due to thermal lensing effect.

induced refractive index change and thermal lensing [24]. In particular, with the use of low power cw excitation, slow and gradual formation of ring pattern suggests the domination of thermal effects which are known to have slow response times than other mechanisms like molecular orientation. This produced high irregularities in the limiting curve and therefore we placed the sample away from focus but still in the nonlinear regime to avoid the ring pattern formation. The distance of the aperture–detector combination from the sample along with the aperture size was optimized for better limiting performance and it was observed that the overall output transmittance could be controlled to a greater extent which is otherwise difficult with limiters strictly based on absorptive nonlinearity. The limiting curves obtained for Pc1 and Pc2 in $CHCl_3$ and Pc3 in ethanol solution are depicted in Fig. 5. Low threshold for limiting can be observed for all the three samples. The limiting threshold which is defined as the incident power at which the sample transmittance falls to 50% of the linear transmittance was found to be the least, ~1.8 mW for Pc3 while for Pc1 and Pc2 the thresholds were estimated to be ~3.5 mW and ~3.13 mW, respectively. Despite the high power (25 mW) of the laser used we could not estimate the dynamic range or damage thresholds which were certainly beyond the maximum range of the input powers achievable with our laser. The results are comparable with our previously reported values for 2(3),9(10),16(17),23(24)-tetra-(*tert*-butyl)-phthalocyanine (referred to as Pc4) and 2(3),9(10),16(17),23(24)-tetra-(*tert*-butyl)-phthalocyanine zinc (II) (referred to as Pc5) [20]. For the present three samples (Pc1, Pc2 and Pc3) and for the previous two samples (Pc4 and Pc5) it has been observed that with cw pumping the limiting is due to nonlinear refraction which are predominantly thermal in nature. We have tried to achieve optical limiting from the thin films but were not successful possibly due to lower degree of defocusing as compared to solutions and scattering from the films obtained using a home-made spin coater. Tighter focusing for achieving stronger defocusing from the films resulted in damage. We are in the process of obtaining thicker films with a commercial spin coater and optical limiting studies in those superior quality films will be undertaken.

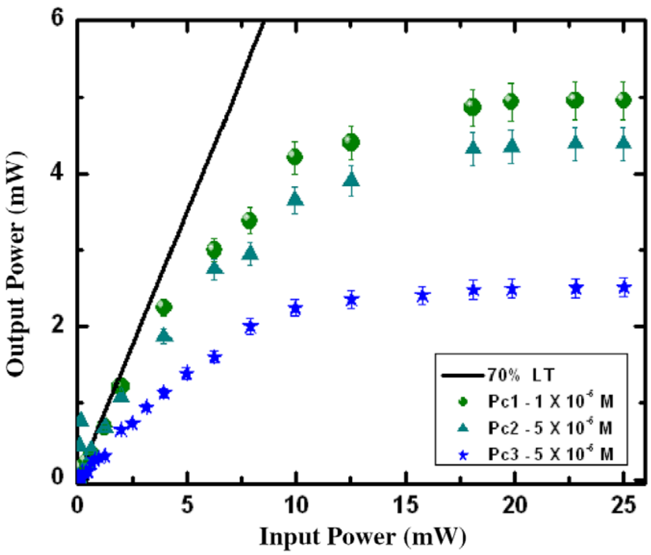

Fig. 5. Optical limiting curves obtained for Pc1 (1×10^{-5} M) and Pc2 (5×10^{-5} M) in $CHCl_3$ solution and for Pc3 (5×10^{-5} M) in ethanol plotted along with 70% linear transmittance (Solid straight line).

The estimated values of nonlinear refractive indices (n_2), nonlinear absorption coefficients (β) and third-order susceptibilities ($|\chi^{(3)}|$) of the three present Pc samples together with the some of the recently reported values of third-order NLO coefficients of different materials with cw illumination are listed in Table 1. To the best of our knowledge, the values reported here are among the highest reported in the literature for nonlinear materials with cw excitation [25–35]. Some of the recently reported materials with high nonlinearity [$\chi^{(3)}$ values] using cw pumping were for Acid blue 7 [26] and Basic green 1 dye [30] and the magnitude of the nonlinearity they observed were 0.0835×10^{-4} esu and 0.0724×10^{-4} esu, respectively at 633 nm. It is evident that the values obtained for our samples are at least one order of magnitude higher than these. The n_2 values reported previously for different materials [25–30,32–35] with cw pumping were also found to be one order of magnitude lower than the n_2 values currently obtained for our samples of Pc1, Pc2 and Pc3 during the present studies and Pc4 and Pc5 previously studied [20]. This clearly suggests that these robust phthalocyanines are characterized by high nonlinearity in the cw regime. Liang et al. [31] reported very high values (three orders of magnitude higher than ours) of n_2 for dispersed Red 13 doped PMMA films. However, the refractive index change in their case was based on the phenomenon of photoisomerization and the thermal contributions were considered to be negligible.

We expect the comparatively higher values of the NLO coefficients for Pc3 due to the lack of symmetry in its structure, resulting from the uneven peripheral substitution. The lack of symmetry generally, increases the magnitude of third-order susceptibility. It has been suggested that they could posses high negative third-order susceptibility if the transition moment between all the excited state are small and asymmetry is small, or, when the transition moment between excited states are large [36]. Also, by maximising the asymmetry large third-order susceptibilities can be obtained. This could be the plausible explanation for the higher values of the NLO parameters of Pc3. The closed-aperture scans for all the phthalocyanines show a peak–valley separation of ~$4.5z_0$ for solutions and ~$3z_0$ for thin films. A peak–valley separation of more than 1.7 times the Rayleigh range (z_0) is clear indication of thermal nonlinearity [37]. The overall high nonlinearity of these molecules probably results due to the strong linear absorption at 633 nm combined with a high thermo-optic coefficient. These molecules could also be used for optical switching applications due to their ultrafast relaxation times with nanosecond excitation. The switching action could be

Table 1
Table depicting the measured values of nonlinear refractive index (n_2), nonlinear absorption coefficient (β) and third-order susceptibility ($|\chi^{(3)}|$) of Pc1, Pc2 and Pc3 from *Z*-scans, along with the recently reported values of third-order NLO parameters of different materials with cw excitation

Form of sample	Sample	n_2 (cm^2/W)	β (cm/W)	$\|\chi^{(3)}\|$(esu)
Solution conc.: 5×10^{-5} M solvent: $CHCl_3$ *Ethanol	Pc1	-1.6×10^{-6}	−0.004	$0.9 \pm 0.18 \times 10^{-4}$
	Pc2	-0.8×10^{-6}	−0.0029	$0.46 \pm 0.09 \times 10^{-4}$
	Pc3*	-2.6×10^{-6}	−0.009	$1.48 \pm 0.3 \times 10^{-4}$
	Pc4 [20]	-2.0×10^{-6}	−0.015	$1.0 \pm 0.2 \times 10^{-4}$
	Pc5 [20]	-0.25×10^{-6}	−0.00325	$0.14 \pm 0.03 \times 10^{-4}$
Thin film 1% by wt. (doped in PMMA) solvent: $CHCl_3$	Pc1	-7.1×10^{-6}	−0.061	$4.0 \pm 0.8 \times 10^{-4}$
	Pc2	-6.4×10^{-6}	−0.068	$3.6 \pm 0.7 \times 10^{-4}$
	Pc3	-16.0×10^{-6}	−0.91	$10.0 \pm 2.0 \times 10^{-4}$
	Pc4 [20]	-12.0×10^{-6}	−0.49	$7.0 \pm 1.4 \times 10^{-4}$
	Pc5 [20]	-14.2×10^{-6}	−1.1	$8.6 \pm 1.7 \times 10^{-4}$
Fast green FCF dye (Acid blue 3) @ 632.8 nm [25]		-0.032×10^{-6}	−0.000065	–
Triphenylmethane dye (Acid blue 7) @ 632.8 nm [26]		-0.188×10^{-6}	−0.00308	0.0835×10^{-4}
Castor oil @ 514 nm [27]		-0.032×10^{-6}	–	–
Zinc tetraphenyl porphyrin @ 632.8 nm [28]		-0.14×10^{-6}	–	–
Night blue dye doped PMMA films @ 632.8 nm [29]		-0.1474×10^{-6}	–	–
Basic green 1 dye @ 632.8 nm [30]		-0.16×10^{-6}	−0.0017	0.0724×10^{-4}
Dispersed red 13 doped PMMA films @ 633 nm [31]		-1856.0×10^{-6}	–	–
CdS nanocrystals silica matrix @ 514.5 nm [32]		-1.85×10^{-6}	−0.087	–
Poly(3-dodecylthiophene) @ 633 nm [33]		–	–	$\mathrm{Im}\|\chi^{(3)}\| = -2.0 \times 10^{-4}$
PbS nanoparticle @ 632.8 nm [34]		-0.434×10^{-6}	–	–
In_2O_3 nanoparticle @ 632.8 nm [35]		-0.389×10^{-6}	–	–

achieved even with low power cw lasers by striking a suitable balance between the nonlinear refraction properties and nonlinear absorption properties of these molecules. Studies to this extent are in progress and will be a subject of our future publication.

4. Conclusion

We have evaluated the high nonlinear optical parameters of three phthalocyanine derivatives *(two symmetric and one unsymmetric)* by employing the *Z*-scan technique using cw excitation at 633 nm. The three phthalocyanines studied were characterized with negative nonlinear refraction and saturable absorption behaviour. They possessed high nonlinearities which are primarily thermal in nature. The Pc3 (*unsymmetrical zinc phthalocyanine*) was found to have a higher value of nonlinear parameters due to the unsymmetrical structure. In solution form, its nonlinear refractive index and third-order nonlinear optical susceptibility were recorded as $\sim 2.6 \pm 0.52 \times 10^{-6}$ cm^2/W and $\sim 1.48 \pm 0.3 \times 10^{-5}$ esu, respectively. We have also demonstrated that these phthalocyanines possess low optical limiting thresholds in the range of ~1.8–3.5 mW. These could be efficiently used as optical limiters by utilizing their high refractive nonlinearity and judicious aperture based design in low power cw regime.

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