Nonlinear optical properties of alkyl phthalocyanines in the femtosecond, nanosecond, and cw excitation regimes

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ABSTRACT

We present our results of nonlinear optical properties of 2(3), 9(10), 16(17), 23(24) tetra tert-butyl phthalocyanine (pc1) and 2(3), 9(10),16(17), 23(24) tetra tert-butyl Zinc phthalocyanine (pc2) studied in solution using Z-scan technique with 800 nm, 100 fsec pulses, 532 nm, 6 nsec pulses and 633 nm continuous wave (cw) laser excitation. Femtosecond open-aperture Z-scan data revealed these molecules exhibited strong 3PA coefficient (α_3). The estimated value of α_3 was ~**9.1 × 10^{-5} and ~9.5 × 10^{-5} cm^3/GW^2** for pc1 and pc2 respectively. Nanosecond open aperture Z-scan studies indicated the presence of strong nonlinear absorption with effective coefficients (α_2) of ~**310 and ~420 cm/GW** for pc1 and pc2 respectively which are at least two orders higher than the recently reported phthalocyanines. These phthalocyanines also exhibited strong optical limiting properties with nsec excitation with recorded limiting thresholds of ~**0.45 J/cm^2**. We observed large nonlinear response in the cw regime at 633 nm. The performance of these alkyl phthalocyanines in various time domains vis-à-vis recently reported phthalocyanines is discussed in detail.
Key words: Nonlinear optical, Z-scan, Three-photon absorption, Two-photon absorption

1. INTRODUCTION

Organic materials such as porphyrins and phthalocyanines along with their metallated derivatives are a class of macromolecules possessing large number of delocalized π electrons resulting in interesting third-order nonlinear optical properties that find extensive applications in optical limiting and all-optical switching.[1-27] The high stability and capability of phthalocyanines, especially, to accommodate different metallic ions in their cavity results in the diverse optical properties. The presence of strong nonlinear absorption enhances the limiting properties whereas the presence of strong nonlinear refraction facilitates all-optical switching. Optical limiting studies domain has been mainly in the nanosecond domain while the switching studies utilized picosecond and femtosecond pulses. Even though nonlinear optical properties of plethora of phthalocyanines and their derivatives have been investigated till date their performance for optical limiting applications, in general, ranged from good to excellent but for applications related to optical switching in particular, there remains scope for investigation of novel structures with superior figures of merit.[16-27] That the best optical limiting performance till date has been achieved using a phthalocyanine in tandem with another nonlinear optical material justifies the potential of these molecules.[27] In this paper we present the results of our studies on the nonlinear optical properties of 2(3), 9(10), 16(17), 23(24) tetra tert-butyl phthalocyanine (referred to as pc1) and 2(3), 9(10),16(17), 23(24) tetra tert-butyl Zinc phthalocyanine (referred to as pc2) in solution obtained using the Z-technique scan with 800 nm, 100 fsec pulse, 532 nm, 6 nsec pulse, 633 nm continuous wave excitation. From the fsec open-aperture (OA) Z-scan data we derived that these molecules exhibit good three-photon absorption (3PA) coefficient/cross-sections even at moderate input intensities. The nanosecond (nsec) OA Z-scan studies revealed strong effective nonlinear coefficients for these molecules at an excitation wavelength of 532 nm. We also estimated the sign and magnitude of the third order nonlinearity by means of the closed aperture scans from cw, nsec, and fsec data. Our study concludes that these alkyl phthalocyanines are prospective candidates for multi-photon applications in the fsec regime, potential candidates for optical limiting applications in the nsec and cw domains.

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2. EXPERIMENTAL DETAILS

Alkyl phthalocyanines were synthesized according to the procedures reported in literature[1] and both pc1 and poc2 were purified before use. Each sample was subjected to a column chromatographic purification process prior to the nonlinear optical measurements. The details of molecular structures are depicted in figure 1. All the experiments were performed with samples dissolved in chloroform and were placed in 1-mm glass/quartz cuvettes. Femtosecond laser pulses were obtained from a conventional chirped pulse amplification system comprising of an oscillator (MaiTai, Spectra-Physics Inc.) that delivered ~80 fsec, 82 MHz at 800 nm and a regenerative amplifier (Spitfire, Spectra Physics Inc.), from which we obtained 1 kHz amplified pulses of ~100 fsec, with output energy of ~1 mJ. A frequency doubled Nd:YAG laser (Spectra-Physics INDI-40) with 6 nsec pulse duration and 10 Hz repetition rate was used for measurements in the nsec regime. Z-scan studies[28] were performed by focusing the input beam using an achromatic doublet (f = 120 mm) for fsec excitation and a convex lens (f = 60 mm) for nsec experiments. The peak intensities used in experiments were in the 200-400 GW/cm^2 and 10-150 MW/cm^2 range for fsec and nsec pulse excitation respectively. All the studies were performed with solution concentrations of 5×10^{-4} M providing ~75% linear transmission for 532 nm and 85% for 800 nm. We maintained similar intensity levels ensuring identical experimental conditions for both the samples. For evaluating the nonlinear optical properties at 633 nm a Helium–Neon laser was the source used for exciting the sample solutions and thin films. Typical values of the parameters used for the experiment were input beam of size (diameter) 0.70 mm focused to a spot size of ~30 μm (~65 μm) using 5 cm (10 cm) lens, with input powers in the 5–14 mW range.

(a)   **(b)**
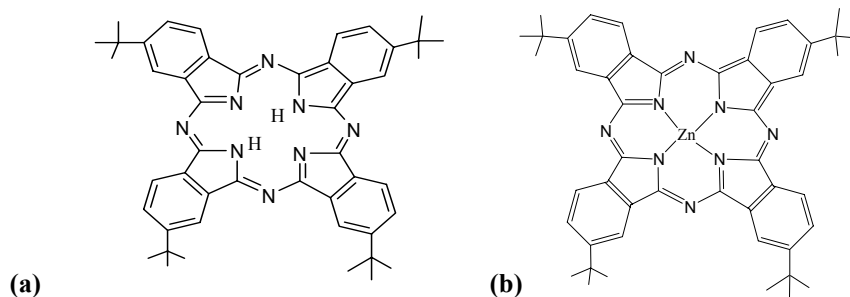
Figure 1 Structures of the phthalocyanines used (a) tetra *tert*-butyl phthalocyanine (pc1) (b) Zinc tetra *tert*-butyl phthalocyanine (pc2)

3. RESULTS AND DISCUSSION

3.1 Spectroscopic characterization:

The absorption spectra were recorded using an UV-visible spectrometer for ~10^{-4} M solutions and are depicted in figure 2(a). These molecules show the characteristic linear absorption features typical of other phthalocyanines, the high energy B (Soret) band and the low energy Q band(s). The compounds remained stable after exposure to laser pulses for a long period of time. Fluorescence spectra of these phthalocyanines, shown in figure 2(b), were recorded using Jobin Yvon Horiba–Fluoromax-3 luminescence spectrometer. Pc1 has a sharp peak at 705 nm with excitation at 350 nm, while pc2 has a broad peak surrounding 475 nm along with a sharp peak at 765 nm. The first excited state lifetimes for these molecules were measured using the fluorescence decay measurements and were 6.31 and 3.18 nsec for pc1 and pc2 respectively. Fluorescence decays shown in fig. 3 were recorded using TCSPC method using the following set up. A diode pumped millennia CW laser (Spectra Physics, 532 nm) was used to pump the Ti–Sapphire rod in Tsunami picosecond mode locked laser system (Spectra Physics). The 750 nm (82 MHz, 2.4 ps FWHM) pulses was taken from the Ti–Sapphire laser and passed through pulse picker (Spectra Physics, 3980 2S) to generate 4 MHz pulses. The second harmonic output (375 nm) was generated by a flexible harmonic generator (Spectra Physics, GWU 23PS). The vertically polarized 375 nm laser was used to excite sample. The incident power at the sample was ~0.3mW. The fluorescence emission at magic angle (54.7^0) was dispersed in a monochromator (*f*/3 aperture), counted by a photomultiplier tube (Hamamatsu R 3809) and processed through multichannel analyzer. The instrument response function for the system was ~52 psec. The fluorescence decay was obtained and was analyzed using IBH software (DAS6).
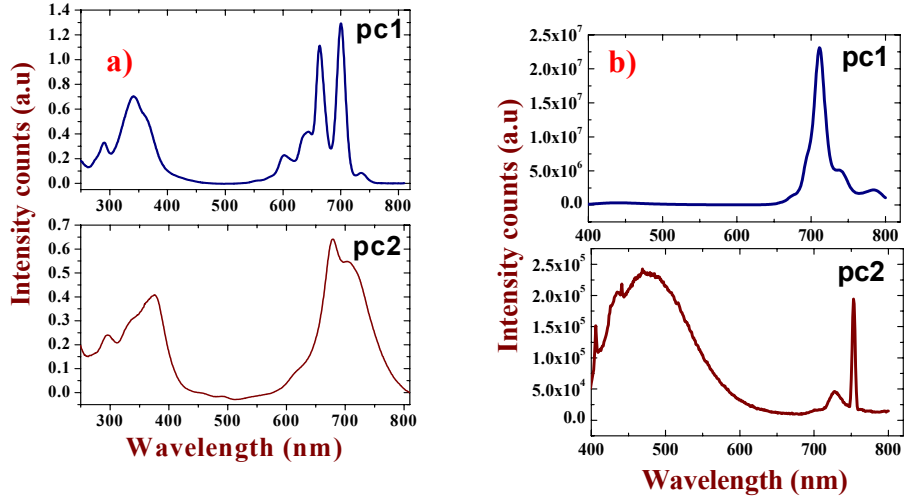
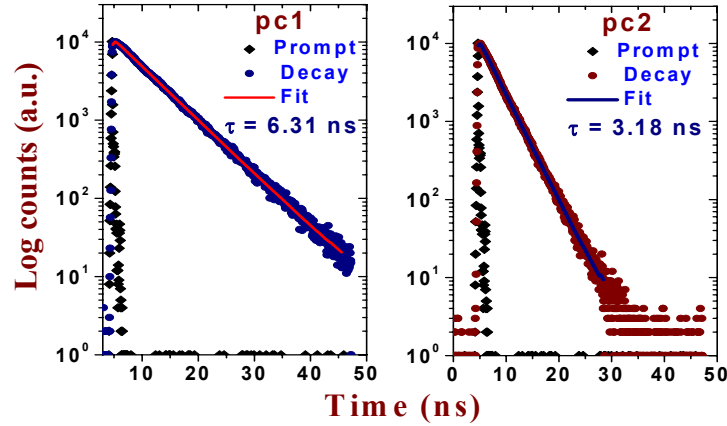Figure 2 (a) Absorption spectra (b) Fluorescence spectra of pc1 and pc2

Figure 3 Fluorescence decay curves for pc1 and pc2 with TCSPC measurements

3.2 Theoretical considerations:

Assuming a spatial and temporal Gaussian profile for laser pulses and utilizing the open aperture Z-scan theory for multi-photon absorption (MPA) given by Sutherland et al.[29] we have the general equation for open aperture (OA) normalized energy transmittance given by:

$$T_{OA(nPA)} = \cfrac{1}{\left[1 + (n-1)\alpha_n L \left(I_{00} / \left(1 + \left(z / z_0 \right)^2 \right) \right)^{n-1} \right]^{1/n-1}} \tag{1}$$

where α_n is the effective MPA coefficient (n = 2 for 2PA; n = 3 for 3PA, and so on); and I_{00} is the input irradiance. If we retain only the 2PA term and ignore all other terms, we have an analytical expression for OA Z-scan for merely two-photon absorbers. Similarly retaining the 3PA term and ignoring the other terms provides us an analytical expression for OA scans for only three-photon absorbers.

$$T_{OA(2PA)} = \frac{1}{1 + \alpha_2 L_{eff}\left(I_{00}/\left(1 + (z/z_0)^2\right)\right)} \tag{2}$$

$$T_{OA(3PA)} = \frac{1}{\left[1 + 2\alpha_3 L'_{eff}\left(I_{00}/\left(1 + (z/z_0)^2\right)\right)^2\right]^{\frac{1}{2}}} \tag{3}$$

with **n** being the order or absorption process, I_{00} is the peak intensity, **Z** is the sample position, $z_0 = \pi\omega_0^2/\lambda$ is the Rayleigh range; ω_0 is the beam waist at the focal point (Z = 0), λ is the laser wavelength; effective path lengths in the sample of

length L for 2PA, 3PA is given as $L_{eff} = \dfrac{1 - e^{-\alpha_0 L}}{\alpha_0}$., $L'_{eff} = \dfrac{1 - e^{-2\alpha_0 L}}{2\alpha_0}$.

3.3 Nonlinear absorption studies at different pulse-width regimes:

3.3.1: Open aperture scans with 532nm, 6 nsec pulses

The open aperture Z-scans for both pc1 and pc2 illustrated a distinct reverse saturable absorption (RSA) behavior with 532 nm, 6 nsec laser pulse excitation. The molecules remained stable for input intensities in the range of 1–500 MW/cm². For intensities above 10^8 W/cm² the normalized transmission dropped below 0.3 representing strong nonlinear absorption behavior. It is well established that nonlinear absorption in such materials due to nsec pulses has contributions from both excited singlet and/or triplet states apart from two-photon absorption depending on the excitation wavelength. However, for 532 nm excitation we can approximate the nonlinear absorption to an effective process and evaluate the nonlinear coefficient. The role of instantaneous two-photon absorption in the present case is negligible due to the excitation wavelength of 532 nm, which is far from two-photon resonance. The effective coefficient incorporates the contribution of both singlet and triplet excited state absorption. Since the lifetimes of first excited singlet state are few nanoseconds for both the phthalocyanines the intersystem crossing rate will effectively determine the involvement of either higher singlet excited states or higher triplet excited states in the nonlinear absorption mechanism. A comprehensive five-level modeling [9-11] along with the accurate knowledge of the intersystem crossing times is necessary to pin-point the exact contribution of each of these processes.

Figure 4 shows the representative plots of open aperture Z-scans obtained at three different intensities. The data obtained with nsec pulses was fitted using equation 2. The best fit produced an effective nonlinear absorption coefficient (α_2) of 310 cm/GW for pc1 and 420 cm/GW for pc2 measured with a peak intensity of ~6 MW/cm². For higher intensities we expect contribution from higher-order nonlinearities disabling us to judge the exact magnitude of third-order nonlinear coefficient. These values correspond to one of the largest reported till date for any other phthalocyanines. Significantly both pc1 and pc2 possess negligible linear absorption at this wavelength. The values extracted from the fits to the Z-scan data have a maximum error of ±15% owing to the calibration errors of the neutral density filters, errors in the estimation of spot size at focus, and fitting errors. It was observed that α_2 decreased with increasing intensities. At higher intensities there is a possibility of higher order nonlinearities contributing to the observed nonlinear absorption. Hence, the nonlinear coefficient obtained at moderate input peak intensities are considered in the present case. The metallic phthalocyanine has superior nonlinear absorption coefficient compared to free-base pc1 since the spin-orbit coupling could be significantly more efficient with the metal complex species. Table 1 summarizes the recent results reported in literature on the nonlinear absorption properties of different phthalocyanines. Though there are ample results in literature on nonlinear absorption of phthalocyanines obtained with nsec pulses, we have chosen these particular values since they were achieved at 532 nm utilizing analysis similar to the one presented here. The peak intensities also were of similar order of magnitude or higher to those used in our case. There is a clear indication that our samples possess superior nonlinear coefficients and these combined with small linear absorption in the visible range enhances their potential for optical limiting device applications.
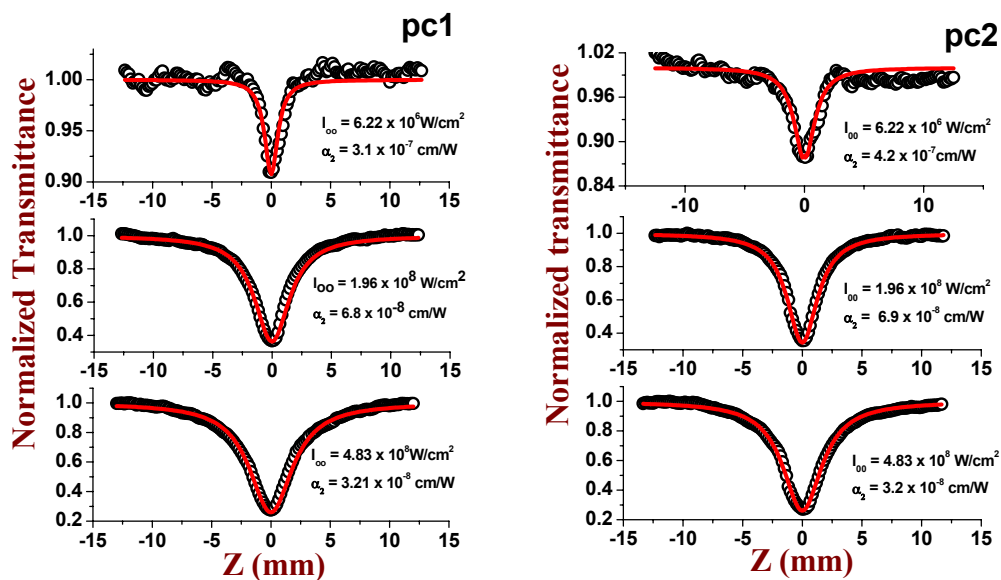
Figure 4 Open aperture z-scan plots of pc1 and pc2 at various input intensities upon excitation with 532nm, 6 nsec laser pulses
The solid line represents the fitting of equation 2 for evaluating the nonlinear absorption coefficient

Sample	Wavelength	α_2 (cm/GW)	Intensity (GW/cm^2)	Reference
Zn Phthalocyanine	532 nm	47.74	-	[30]
Sm(Pc)$_2$ Eu(Pc)$_2$	596 nm 604 nm	31 50	0.143 0.0835	[31]
Alkynyl phthalocyanines	532 nm	12 – 56	0.2 – 2.0	[32]
Nd(Pc)$_2$	532 nm	42	0.09	[33]
GaPc dimers	532 nm	32 - 35	0.5	[34]
Octaalkylphthalocyanines and their 15 metallated derivatives	532 nm	15 - 96	0.5	[35]
Tetra tert-butyl phthalocyanine (Free base and Zn)	*532 nm*	*~310 (pc1) ~420 (pc2)*	*0.006*	*This work*

Table 1: Comparison of two-photon absorption coefficient (α_2) with values reported

The two-photon absorption cross-section (σ_{TPA}) was calculated from the Eqn. (4) given below:

$$\sigma_{TPA} = \frac{h\nu}{N}\beta$$

$$N = N_A D \qquad\qquad (4)$$

where N is the number of molecules per unit volume, D is the molar concentration , N_A is the Avogadro constant, h is the

Planck's constant, ν is the frequency of laser beam used. The two-photon absorption cross-sections (σ_{TPA}) were estimated to be **3.84×10^{-46} and 5.21×10^{-46} cm^{4}s photon^{-1}** for pc1 and pc2 respectively, which is reasonably high value for organic molecules. We are at present analyzing our data in terms of a comprehensive five-level model for exact evaluation of the excited state absorption coefficients (as followed by Venugopal Rao et al.).[10] The knowledge of lifetimes of the excited states then becomes imperative and even in this case we expect significant figures of merit **($\sigma_{ex}/\sigma_{ground}$).** We have, at the moment, limited knowledge about the lifetimes of some excited states of these molecules and we are evaluating the fluorescence lifetime studies to ascertain complete dynamics of the excited states.

3.3.2: Open aperture scans with 800 nm, 100 fsec pulses

The open aperture scans for pc1 and pc2 recorded at 800 nm using ~100 fsec pulses with an input irradiance of ~387 GW/cm^2 is shown in figure 5. We observed strong reverse saturable absorption (RSA) kind of behavior in the intensity range of 200–400 GW/cm^2 beyond which the sample was damaged (seen through the discoloring of solutions). Open aperture Z-scan with nanosecond laser pulses usually has dominant contribution to the observed RSA behavior from excited state absorption. We cannot expect the same for femtosecond laser pulse excitation since the excited state lifetimes and intersystem crossing rates are much slower. Moreover, owing to large peak intensities at the focal point we can expect either 2PA or 3PA as the possible nonlinear absorption mechanism. Further, due to presence of large number of absorption bands in the excited state there is a possibility of resonance enhancement for these processes. In order to distinguish the multi-photon process contributing to the present data we performed intensity dependent absorption studies in the open aperture configuration. Obtained experimental data was fitted using equations 2 and 3 and we found the best fit was obtained with the transmission equation for three-photon absorption (3PA).
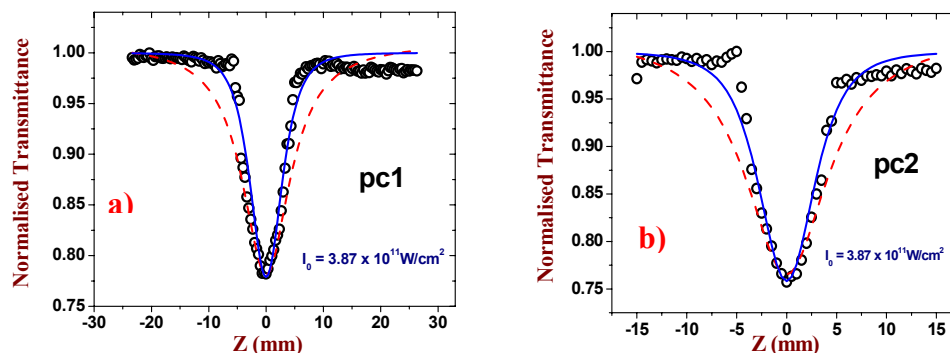
Figure 5 Open aperture z-scan plots of (a) pc1 and (b) pc2 at upon excitation with 800 nm, 100 fsec laser pulses Open circles represents experimental data while the solid line represents theoretical fit with three-photon absorption. Dashed-doted line represents the fit obtained with two-photon absorption.
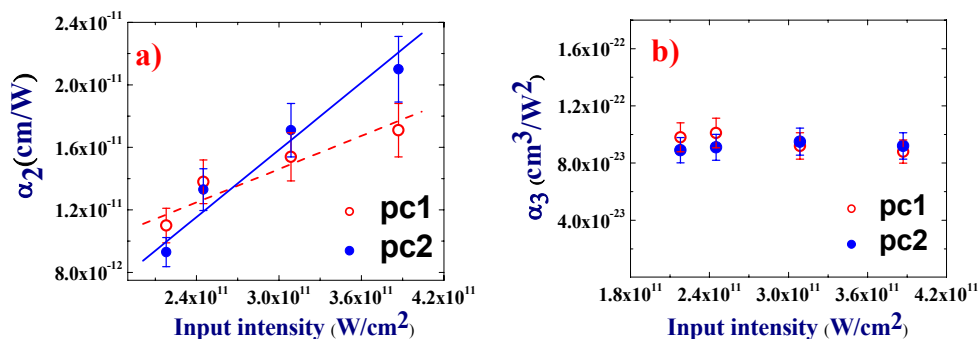
Figure 6 Plots showing the comparison of intensity dependence of (a) α_2 and (b) α_3 for pc1 (open circles) and pc2 (solid circles) obtained with 800 nm pulses

The dashed line in the figures 5(a) and 5(b) represents the theoretical fit with equation 2 and the solid line with equation 3. It is evident that 3PA is the dominant mechanism for the observed RSA kind of behavior. To verify the presence of 3PA in the OA data we carried out the least square fitting test and obtained a value of $\chi^2 \sim 0.0002$ for pc1 and pc2. We obtained values of α_2 and α_3 for both the phthalocyanines with the theoretical fits with equation 1 and equation 2 for four different intensities in the range of 200–400 GW/cm^2. The intensity dependent behavior of α_2 (α_3) is depicted in figure 6 for both the samples pc1 (open circles) and pc2 (solid circles). The error bars in the figure are indicative of maximum experimental error, which was ~20% in our case. We observed that for both phthalocyanines α_2 increases linearly with intensity (lines are linear fits). However, as is evident in figure 5b, we find that α_3 remained constant with increasing intensities. This clearly indicates that the nonlinear absorption process involved is certainly 3PA. Interestingly, within these range of intensities, the samples remained stable after long exposure to the laser irradiation. However, beyond the intensities of 400 GW/cm^2 we noted that the sample started degrading. For evaluating the strength of nonlinear coefficients obtained with our samples we compare them with those reported in literature, which are presented in table 2. We note that our values are one order higher than those reported in organic molecules with fsec excitation.[36, 37] However, the values reported by He et al.[38] are three orders of magnitude higher than ours which is quite sensible since the nonlinear properties will, expectedly, be enhanced due to quantum confinement effects.

Sample	Wavelength, pulse-width	α_3 (cm^3/GW^2) $\times 10^{-5}$	Reference
4,4'-bis(diphenylamino) stilbene (BDPAS) dendrimers	1100 nm, 150 fsec	0.51	[36]
Multi-branched chromophore	1300 nm, 160 fsec	0.385	[37]
ZnS NC's	800 nm, 120 fsec	2400	[38]
Tetra tert-butyl phthalocyanine (Free base and Zn)	*800 nm ~100 fsec*	*9.1 (pc1) 9.5 (pc2)*	*This work*

Table 2: Comparison of three-photon absorption coefficient **(α_3)** with other reported values in literature

We have evaluated the three-photon absorption cross-section (σ_3) using the relation-5:

$$\sigma_3 = \frac{(\hbar\omega)^2}{N}\alpha_3 \qquad (5)$$

where ω is the frequency of the laser radiation. The values for pc1 and pc2 were ~**1.85x 10^{-80}** cm^{6}s^2/photon^2 and ~**1.93x 10^{-80}** cm^{6}s^2/photon^2 respectively. In organic materials 3PA typically occurs at longer wavelengths in the near infrared region (NIR) introducing advantages including minimization of the scattered light losses and reduction of undesirable linear absorption. The ramifications of such properties in biological and medical applications include maximization of the radiation penetration depth through tissue, facilitating tumor imaging, and photo-annihilation in the absence of complicated and risky surgery. Such materials will have a broad impact in biology and medicine through three-photon induced photodynamic therapy (PDT) in cancer treatment. In recent times novel materials including organic fluorophores like halogenated fluorine molecules, polydiaectylenes, semiconductor nanoparticles have been investigated for their 3PA properties using femtosecond and picosecond pulses in the NIR spectral regions.[36-39] However, we discovered that there are sporadic reports on organic molecules exhibiting 3PA in the significant wavelength region of 750–850 nm corresponding to the output of commercially available femtosecond Ti:sapphire source routinely used by the researchers for biological applications. One such report measured two-photon absorption (2PA) spectra of a number of symmetrically substituted polydiaectylenes in the excitation wavelength region from λ_{ex} = 800 to 1600 nm.[39] Thus, considering this scenario, the phthalocyanines under study provides us with an appropriate organic molecule exhibiting good three-photon absorption (3PA) coefficient/cross-sections even at moderate input intensities.

3.3: Nonlinear optical studies with 633 nm, He-Ne laser:

Figures 7(a) and 7(b) shows the closed aperture and open aperture Z-scan curves obtained for pc1 (metal-free phthalocyanine). A signature of peak-valley indicating a negative type of nonlinearity from closed aperture and saturable absorption type behavior from open aperture scan was observed. Figure 7(c) and 7(d) shows the closed aperture and open aperture Z-scan traces for pc2 (metal phthalocyanine) again indicating negative and saturable type of nonlinearities. Using the peak valley distances measured from the closed aperture Z-scans we estimated the values of n_2 as ~20.0 ± 4.0 x 10^{-7} cm^2/W for pc1 and ~2.5 ± 0.5 x 10^{-7} cm^2/W for pc2. Figures 2 (e) and (f) depict the optical limiting curve in chloroform solutions recorded for concentrations of 10^{-5} M and 5 x 10^{-5} M for pc1 and pc2 respectively. We could reproduce this behavior several times within some experimental errors. It is evident from the figure that the limiting threshold was low and was estimated to be ~7 mW.
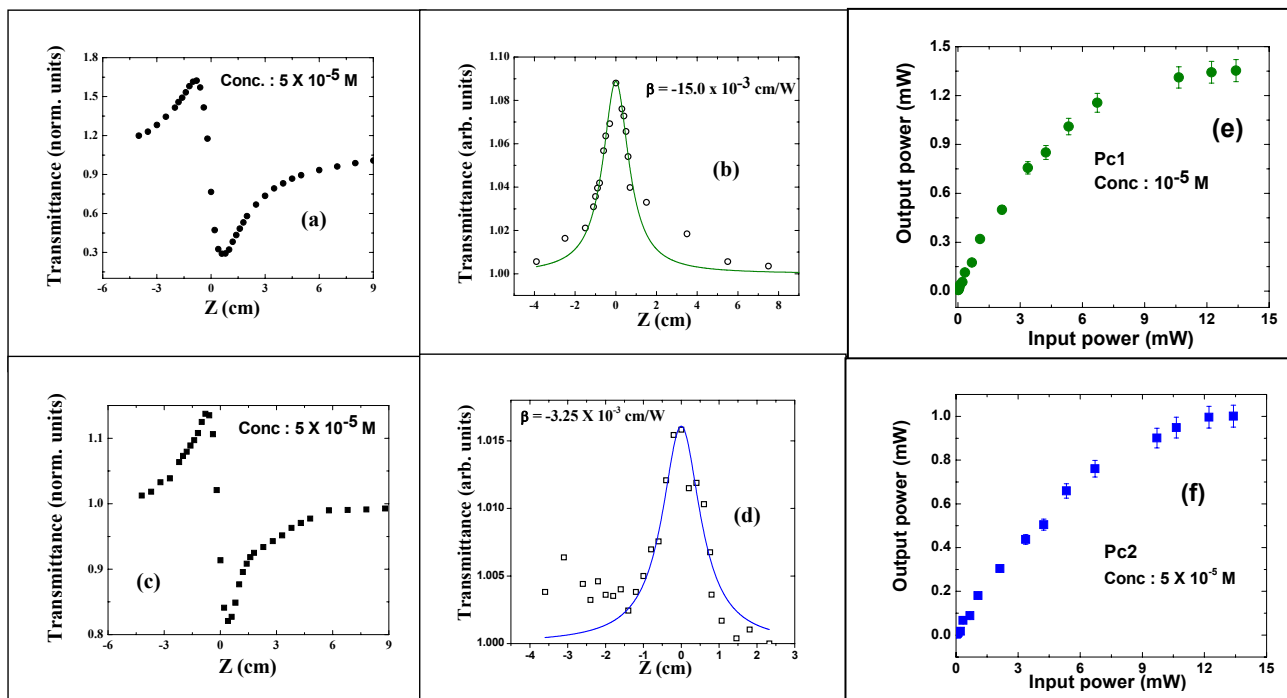
Figure 7 (a) and (c) Closed aperture Z-scans of pc1 and pc2 in chloroform solution indicating a negative type of nonlinearity. (b) and (d) Open aperture Z-scans for pc1 and pc2 indicating a saturable absorption type of nonlinearity. (e) Optical limiting curve recorded for pc1 in chloroform solution for a concentration of 10^{-5} M (f) Optical limiting curve for pc2 in chloroform for a concentration of 5 X 10^{-5} M.

We could not verify the performance (damage or breakdown threshold) above 14 mW due to limitations with our laser source power. We observed a low limiting threshold of ~**8 mW** for pc2 also. The limiting behavior observed in both the samples is attributed mainly to nonlinear refraction. Since the samples were pumped with cw laser beam the arising nonlinearities are predominantly thermal in nature.

3.4: Optical limiting properties with nsec pulses:

The optical limiting data obtained for pc1 and pc2 at 532 nm using 6 nsec pulses are shown in figure 8 with both the samples exhibiting limiting thresholds ($I_{1/2}$) of ~0.45 J/cm2. The mechanism for optical limiting could be predominantly excited state absorption since with nsec pumping though there is possibility of contribution from two photon absorption (two-step) also. Our studies suggest that the effect of the metal ion on the nonlinear optical properties is not significant for alkyl phthalocyanines. The advantages of these molecules stem from the fact that they have

insignificant linear absorption especially in the 450-600 nm spectral range indicating prospective applications in broadband optical limiting. A detailed five-level modeling is in progress for estimating the contributions of different nonlinear absorption processes and will be reported elsewhere.
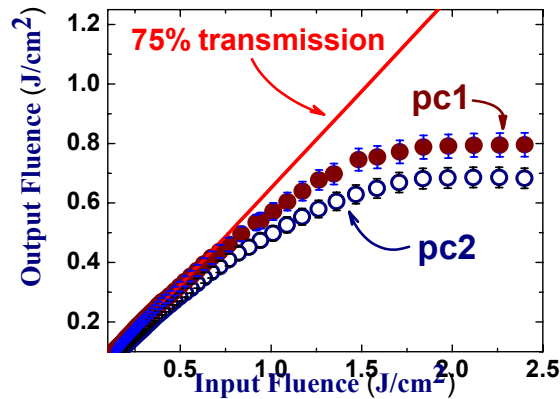

Figure 8: Plots showing the optical limiting curves obtained for pc1 and pc2 for nsec pumping

3.5: Nonlinear refraction properties with closed aperture Z- scans:

Both pc1 and pc2 exhibited negative nonlinearity (clearly indicated by the peak-valley structure in closed aperture Z-scans) in all pumping regimes. Figure 9(a) depicts the closed aperture curves obtained for both pc1 and pc2 with fsec pulses while the figure 9(b) illustrates the closed aperture curves obtained with nsec pulses. The magnitude of the nonlinear refractive index n_2 was ~0.56×10^{-15} cm^2/W for pc1 and ~1.14×10^{-15} cm^2/W for pc2 with fsec pulse excitation. With nsec excitation the magnitude of nonlinear refractive index n_2 evaluated was ~1.13×10^{-11} cm^2/W for pc1 and ~0.86×10^{-11} cm^2/W for pc2. With cw excitation n_2 evaluated was ~12×10^{-6} cm^2/W for pc1 and ~14.2×10^{-6} cm^2/W for pc2. These results suggest that the metal phthalocyanine has better nonlinear coefficients compared to the free-base phthalocyanine in both fsec and cw domains. The trend reversed in the nanosecond domain and the reason for this is being investigated at present. Our immediate analysis on this discrepancy showed that the scattering of the data in the closed aperture Z-scans of pc2 with nsec laser pulse excitation was very high, possibly owing to the laser energy fluctuation, leading to larger error in the evaluation of the coefficients. However, a detailed investigation would shed more light on this issue and the work in this regard is in progress.
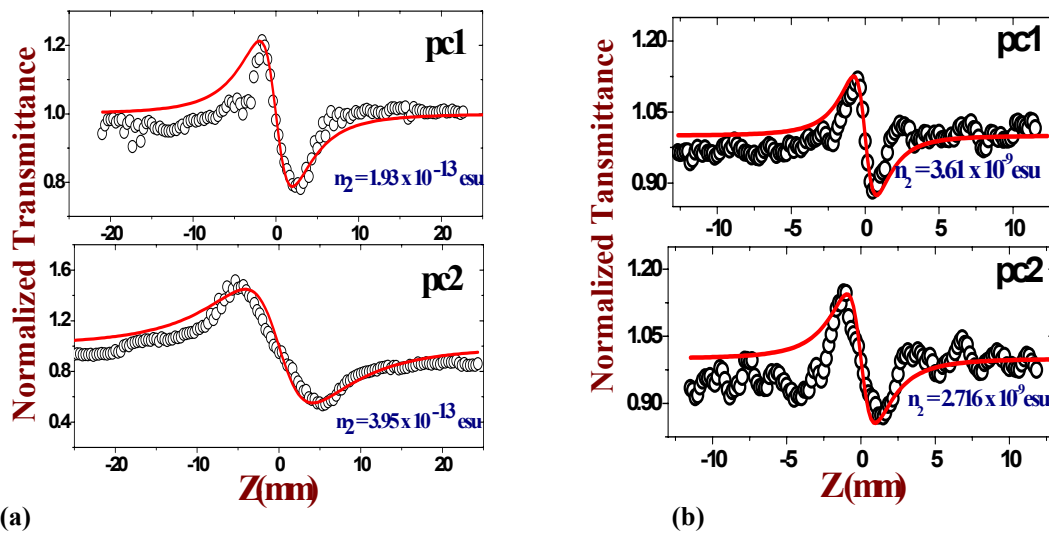

Figure 9 Closed aperture Z-scans for (a) fsec pulse excitation (b) nsec pulse excitation. Solid lines are the theoretical fits

The real and imaginary parts of third order nonlinearity for pc1 and pc2 were also evaluated. Re [$\chi^{(3)}$] was estimated to be ~**5.93 × 10^{-10} esu** and ~**4.59 × 10^{-10} esu** and Im [$\chi^{(3)}$] to be ~**0.97 × 10^{-10} esu** and ~**0.71 × 10^{-10} esu** for pc1 and pc2 respectively with nsec pulse excitation. The third order nonlinear susceptibilities for pc1 and pc2 in the cw regime were **10.0 × 10^{-5} esu** and **1.4 × 10^{-5} esu,** respectively. The $\chi^{(3)}$ values measured for pc1 and pc2 in the nsec regime were **6.02 × 10^{-10} esu** and **4.64 × 10^{-10} esu,** respectively.

4.   CONCLUSIONS

We presented our results on the nonlinear optical properties of 2(3), 9(10), 16(17), 23(24) tetra tert-butyl phthalocyanine (pc1) and 2(3), 9(10),16(17), 23(24) tetra tert-butyl Zinc phthalocyanine (pc2) studied in solution using Z-scan technique with 800 nm, 100 fsec and 532 nm, 6 nsec, in addition to 633 nm, cw laser pulse excitation. From the fsec open-aperture Z-scan data we derived that these molecules exhibited strong 3PA coefficient (α_3) / cross-sections (σ_3) at moderate input intensities. We estimated the value of $\boldsymbol{\alpha_3}$ to be ~ **9.1 × 10^{-5} and 9.5 × 10^{-5} cm^3/GW^2** for pc1 and pc2 respectively. This is, to best of our knowledge, first report on the 3PA behavior of phthalocyanines. Such molecules find interesting applications in bio-imaging and optical signal processing. The nanosecond open aperture Z-scan studies revealed strong effective nonlinear absorption coefficient (α_2) of ~**310 and 420 cm/GW** for pc1 and pc2 respectively which is at least two orders higher than the some of the recently reported phthalocyanines. These phthalocyanines exhibited strong optical limiting properties in solutions with nsec excitation with recorded limiting thresholds of ~0.45 J/cm^2. Depending on the spectral response of the nonlinearity such molecules again find tremendous applications in optical limiting devices. The nonlinear optical properties of two phthalocyanines (metal and metal-free) obtained using cw excitation at 633 nm. For samples Pc1 and Pc2, in solution form, the nonlinear refractive indices obtained from the Z-scan data were $< 2.0 \times 10^{-6}$ cm^2/W and $< 2.5 \times 10^{-7}$ cm^2/W. The reported nonlinearities are primarily thermal in nature owing to the cw excitation. Based on nonlinear refraction both the samples behaved as good optical limiters even at low powers with thresholds of ~7 mW and ~8 mW indicating these samples find potential applications in optical limiting and signal processing applications. The observed nonlinearities were large and negative in nature.

Synthesizing phthalocyanines in the nano-domain is an exciting and vigorous area of research with few succeeding in synthesizing phthalocyanine nanoparticles.[40] It is also well established that nonlinear properties are enhanced in nanoparticles due to quantum confinement related effects. [39, 41] Recently we could extend our studies further to the synthesis of nanoparticles of these alkyl phthalocyanines. Our initial studies of these nanoparticles in the fsec domain promise enhanced performance possessing superior nonlinear optical properties in the solution form.

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