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Nonlinear optical and optical limiting studies of alkoxy phthalocyanines in solutions studied at 532 nm with nanosecond pulse excitation

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ABSTRACT We report our results on the nonlinear optical and optical limiting properties of two alkoxy phthalocyanines namely 2,3,9,10,16,17,23,24-octakis-(heptyloxy) phthalocyanine and 2,3,9,10,16,17,23,24-octakis-(heptyloxy) phthalocyanine zinc(II) studied at a wavelength of 532 nm using 6 ns pulses. Using the standard Z-scan technique we observed that both the phthalocyanines exhibited negative nonlinearity as revealed by the signature of closed aperture data. The magnitude of the nonlinear refractive index n_2 evaluated from the closed aperture data was $\sim 1.61 \times 10^{-11} \text{ cm}^2/\text{W}$ for the free-base phthalocyanine and $\sim 1.56 \times 10^{-11} \text{ cm}^2/\text{W}$ for the metallic phthalocyanine. Open aperture Z-scan data indicates strong nonlinear absorption in both the phthalocyanines with measured nonlinear coefficients of $\sim 1650 \text{ cm/GW}$ and $\sim 1850 \text{ cm/GW}$ respectively. We also report optical limiting properties of these phthalocyanines with limiting thresholds ($I_{1/2}$) of $\sim 0.5 \text{ J/cm}^2$. Our studies suggest that these phthalocyanines are one of the best molecules for nonlinear optical applications studied recently.

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1 Introduction

Phthalocyanines and porphyrins along with their metal derivatives are macromolecules with large number of delocalized electrons possessing interesting third-order nonlinear optical properties finding extensive applications in optical limiting and all-optical switching [1–11]. The high stability and capability of phthalocyanines to accommodate different metallic ions in their cavity result in the diverse optical properties [10]. The presence of strong nonlinear absorption enhances the limiting properties while the presence of strong nonlinear refraction facilitates the switching properties of organic molecules in general. Optical limiting studies domain has been mainly in the nanoseconds while the switching studies have used picosecond and femtosecond pulses. Inter-

estingly, molecules with large two-photon cross-sections find potential in fluorescence and imaging applications. Phthalocyanines are versatile enough possessing all the above properties in the visible spectrum. Even though nonlinear optical properties of plethora of phthalocyanines and their derivatives have been investigated till date [11–46], their performance for optical limiting applications, in general, ranged from superior to excellent but for applications related to optical switching in particular, there remains scope for investigation of novel structures with superior figures of merit. That the best optical limiting performance till date has been achieved using a phthalocyanine [47] in tandem with another NLO material vindicates the potential of these molecules and their derivatives. An iterative process of synthesizing new molecules, testing their nonlinear properties, exploring and understanding the structure-property relationship to improve the molecular properties is indispensable for identification of materials with actual device potential. We report here some of our results on the nonlinear optical properties of two phthalocyanines (2,3,9,10,16,17,23,24-octakis-(heptyloxy) phthalocyanine and 2,3,9,10,16,17,23,24-octakis-(heptyloxy) phthalocyanine zinc(II); herewith represented as Pc1 and Pc2 respectively throughout this paper) studied at a wavelength of 532 nm using 6 ns pulses with the standard Z-scan technique. The advantage of these phthalocyanines comprise:

- Planar structure combined with a facile synthesis route,
- Easy dissolution in most of the common solvents implying that it can be easily embedded in majority of the polymers,
- Excellent chemical stability and thermal stability.

The sign and magnitude of nonlinear refractive index was obtained from the closed aperture Z-scan data while an effective nonlinear absorption coefficient was evaluated from the open aperture Z-scan data. Further, we report our results on the nanosecond optical limiting properties of these molecules in solution obtained at 532 nm. We also attempt to contrast the magnitude of the nonlinear optical coefficients with those reported earlier using data analysis similar to ours. Our studies provide evidence that these molecules possess superior figures of merit for applications in broadband optical limiting.

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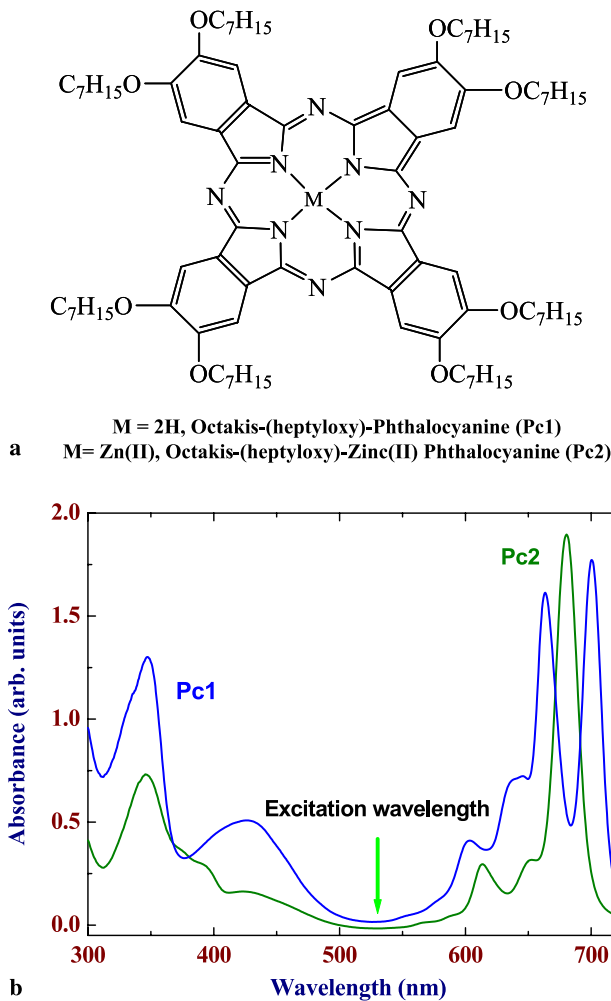


FIGURE 1 (a) Structures of the phthalocyanines (Pc1 and Pc2) used in the present study; (b) absorption spectra of the compounds metal-free Pc1 (blue) and Pc2 (green) dissolved in chloroform. Arrow indicates the excitation wavelength of 532 nm used in this study

2 Experimental details

Figure 1a shows the structure of the phthalocyanines used in this study. The samples were synthesized and purified according to the procedures reported in the literature [10]. Each sample was subjected to a column chromatographic purification process prior to the measurements. All the experiments were performed with sample solutions dissolved in chloroform/DCM and were placed in 1-mm quartz cuvettes. The absorption spectra recorded using an UV-visible spectrometer for $\sim 10^{-4}$ M solutions are depicted in Fig. 1b. 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). Metal-free phthalocyanine had two peaks in the Q-band (blue curve) while the Zn phthalocyanine had one peak (green curve) as depicted in Fig. 1b. The compounds remained stable even after exposure to laser pulses for a long period of time which was confirmed with recording of the absorption spectra before and after the experiments were performed.

A frequency doubled Nd:YAG laser with 6 ns and 10 Hz repetition rate was used for the measurements. Optical limit-

ing and Z-scan [48] studies were performed by focusing the input beam on to the sample using a lens of focal length 60 mm and collecting the output effectively with a large-area fast photodiode (FND100). Typical values of the parameters used for the fits were focal spot size of $\sim 28 \mu\text{m}$ corresponding to Rayleigh range of ~ 0.4 cm. The peak intensities used in the Z-scan experiments were in the range of $1\text{--}150 \text{ MW cm}^{-2}$. The Z-scan and optical limiting studies were performed at similar concentrations of $\sim 10^{-4}$ M (providing at least 70% linear transmission) and at same intensity levels ensuring identical experimental conditions.

3 Results and discussion

Figure 2a and b shows the closed aperture Z-scan curves obtained for Pc1 and Pc2 at peak intensities of $\sim 6.6 \text{ MW cm}^{-2}$. Open circles represent the experimental data while the solid lines are theoretical fits to the closed aperture scans using standard equations [48]. These curves represent the normalized data obtained after division of closed aperture

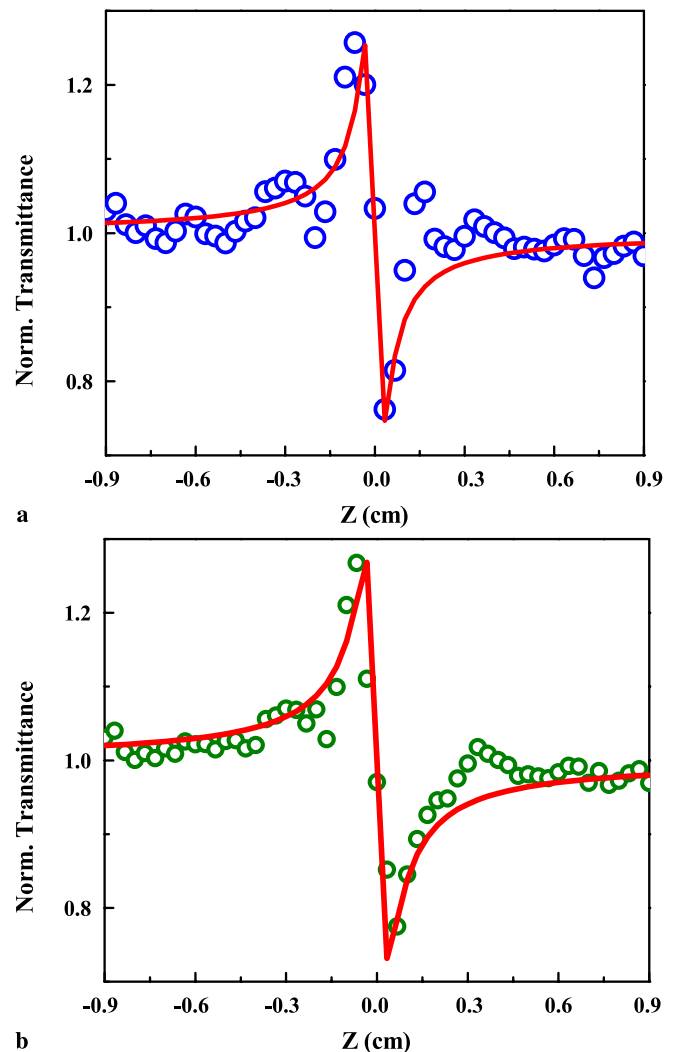


FIGURE 2 Closed aperture Z-scan curves for (a) Pc1 with blue open circles and (b) Pc2 with green open circles obtained at a concentration of 5×10^{-4} M and were recorded with peak intensities of $6.63 \times 10^6 \text{ W cm}^{-2}$. Solid lines are the fits to the standard closed aperture equations

data with the open aperture data to eliminate the contribution of nonlinear absorption. These curves were obtained at low peak intensities to avoid contributions to the nonlinearity that are non-electronic in origin. It is apparent that both of them show negative nonlinearity as indicated by the peak–valley structure. The nonlinear refractive index n_2 was calculated from the difference between normalized peak and valley transmittance (ΔT_{p-v}) in the closed aperture Z-scan.

$$\Delta T_{p-v} = 0.406(1 - S)^{0.25} |\Delta \Phi_0|, \quad (1)$$

$$|\Delta \Phi_0| = \left(\frac{2\pi}{\lambda} \right) \gamma I_0 L_{\text{eff}}, \quad (2)$$

$$L_{\text{eff}} = \frac{1 - \exp(-\alpha L)}{\alpha}, \quad (3)$$

where $I_0(2P/\pi\omega_0^2)$ is the peak intensity within the sample, $|\Delta \Phi_0|$ is the on-axis phase-shift, L is the thickness of the sample, α is the linear absorption coefficient at λ and S is the linear transmittance of the aperture.

$$S = 1 - \exp(-2r_a^2/w_a^2),$$

where, r_a is the radius of the aperture and w_a is the radius of the laser spot before the aperture.

The magnitude of the nonlinear refractive index n_2 evaluated using (1) to (3) was $\sim 1.61 \times 10^{-11} \text{ cm}^2/\text{W}$ for the Pc1 and $\sim 1.56 \times 10^{-11} \text{ cm}^2/\text{W}$ for the Pc2.

The nonlinear refractive index n_2 is expressed in terms of the ordinary linear index n_0 and the real part of third-order

nonlinear susceptibility $\chi^{(3)}$ in Gaussian unit's using the relation [48, 49]

$$\text{Re}[\chi^{(3)}] = 10^{-4} \frac{\epsilon_0 n_0^2 c^2}{\pi} n_2 (\text{cm}^2/\text{W}).$$

For Pc1 and Pc2 we evaluated the $\text{Re}[\chi^{(3)}]$ to be $9.2 \times 10^{-10} \text{ esu}$ and $8.9 \times 10^{-10} \text{ esu}$ respectively.

Figure 3 shows the open aperture Z-scans obtained at various peak intensities for both the phthalocyanines with a concentration achieving 70% linear transmission. For intensities $> 10^8 \text{ W/cm}^2$ the normalized transmission dropped below 0.2 indicating very strong nonlinear absorption behaviour from these molecules. It is well understood that the nonlinear absorption in such materials due to nanosecond pulses has contributions from both excited singlet and/or triplet states apart from two-photon absorption (simultaneous as well as instantaneous), depending on the excitation wavelength. A comprehensive understanding of the population dynamics with ns pulse excitation in typical organic materials can be found elsewhere [50]. A detailed five-level modelling along with the accurate knowledge of the excited state life times is essential to pin-point the exact contribution of each of these processes. However, for 532 nm excitation we can approximate the nonlinear absorption to an effective process and evaluate the nonlinear coefficient approximately [20, 25]. The role of instantaneous two-photon absorption will be negligible and can be ignored due to the nanosecond pulse duration used combined with the excitation wavelength of 532 nm. We have fitted the open aperture data to a more general model and

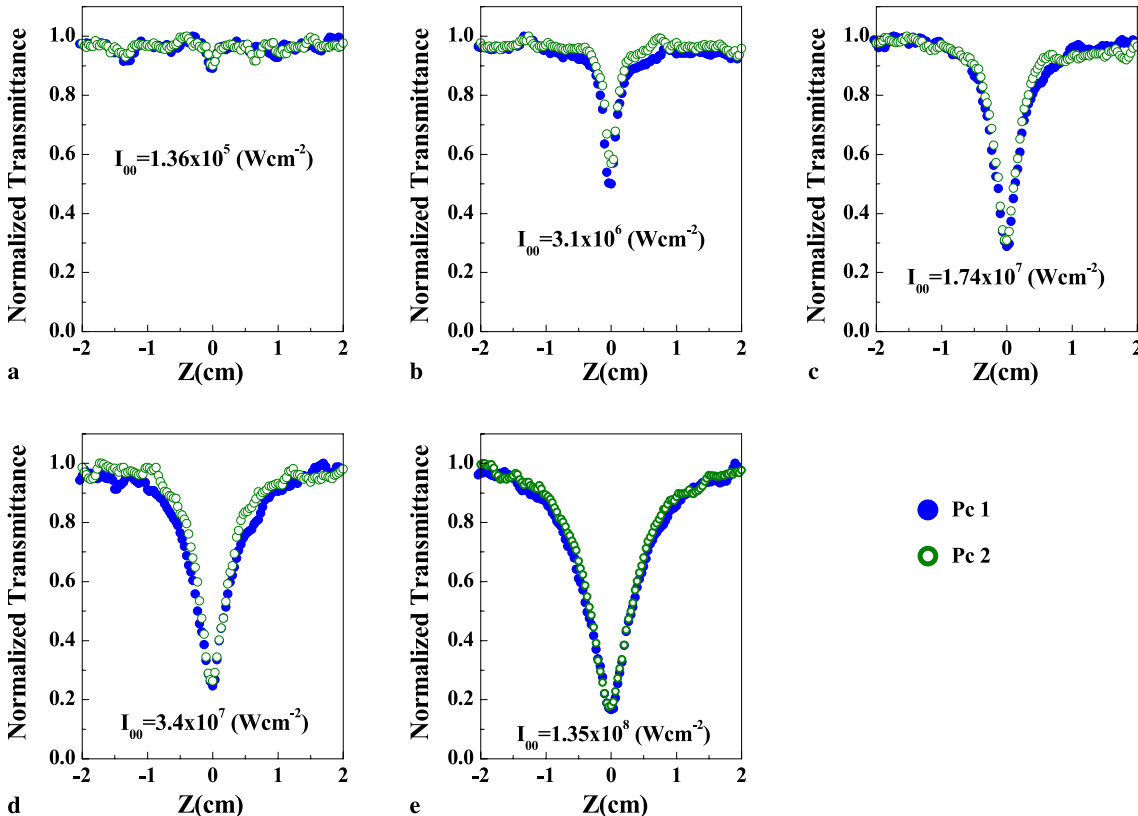


FIGURE 3 Open aperture Z-scan curves (a–e) for Pc1 (blue solid circles) and Pc2 (green open circles) recorded for various intensities at a concentration of $5 \times 10^{-4} \text{ M}$ excited with 532 nm 6 ns pulses

evaluated the nonlinear absorption coefficient (β expressed in cm/GW).

The normalized transmittance for the standard open aperture Z-scan [48] is expressed by the relation:

$$T(z, s = 1) = \sum_{m=0}^{\infty} \frac{[-q_0(z)]^m}{(m+1)^{3/2}}, \quad \text{for } |q_0(0)| < 1, \quad (4)$$

where $q_0(z) = \beta I_0 L_{\text{eff}} / (1 + z^2/z_0^2)$ with z_0 being the Rayleigh range and

$$\text{Im}[\chi^{(3)}] = 10^{-2} \frac{\epsilon_0 n_0^2 c^2 \lambda}{4\pi^2} \beta (\text{cm/W}). \quad (5)$$

The value of the nonlinear absorption coefficient β was evaluated from the fits to the experimental data obtained using (4). Figures 4 and 5 shows the fits to individual curves of

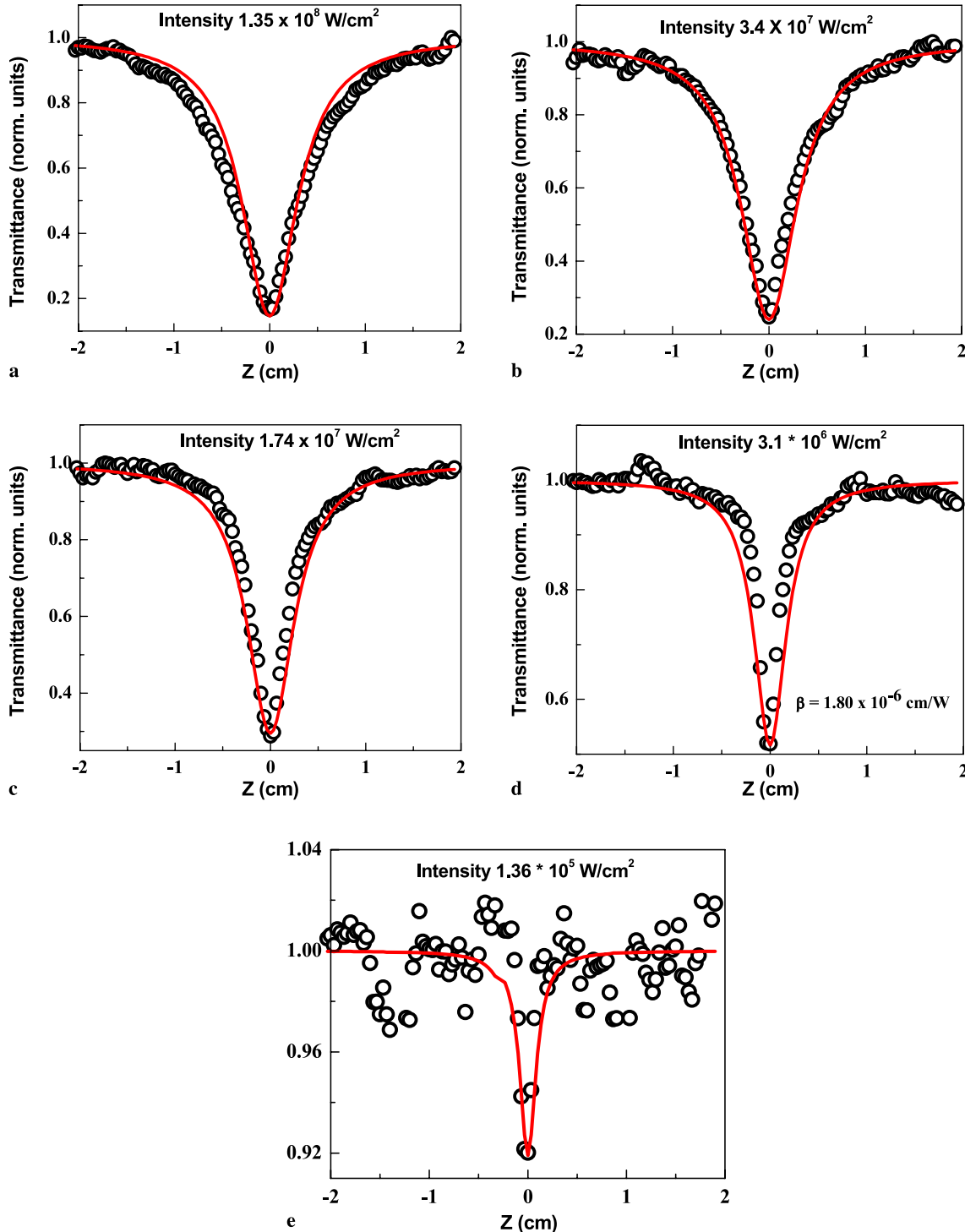


FIGURE 4 Open aperture Z-scan curves (a–e) recorded for Pc1 (open circles). The solid line represents the fitting of (4) for evaluating the nonlinear absorption coefficient β . Linear transmittance was $\sim 70\%$

Pc1 and Pc2 obtained for various peak intensities. The best fit to the data produced a nonlinear absorption coefficient (β) of 1650 cm/GW for Pc1 (Fig. 4d for a peak intensity of 3.1×10^6 W/cm²) and 1850 cm/GW for Pc2 (Fig. 5d for a peak intensity of 3.1×10^6 W/cm²). For higher intensities we expect contribution from higher-order nonlinearities disabling us to judge the exact third-order nonlinear coefficient. These values represent one of the largest for any of the phthalocyanines reported till date. 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 $\pm 20\%$ owing to the calibration errors of neutral density filters, errors in the estimation of spot size at focus, and fitting errors.

Figure 6 shows the plot of nonlinear coefficient magnitude as a function of input peak intensities and trend observed was a decreasing one with increasing intensities. For higher peak intensities we expect contributions to the nonlinear absorption from higher order terms of the nonlinear susceptibility [25, 31, 32]. The values presented here reflect the strong

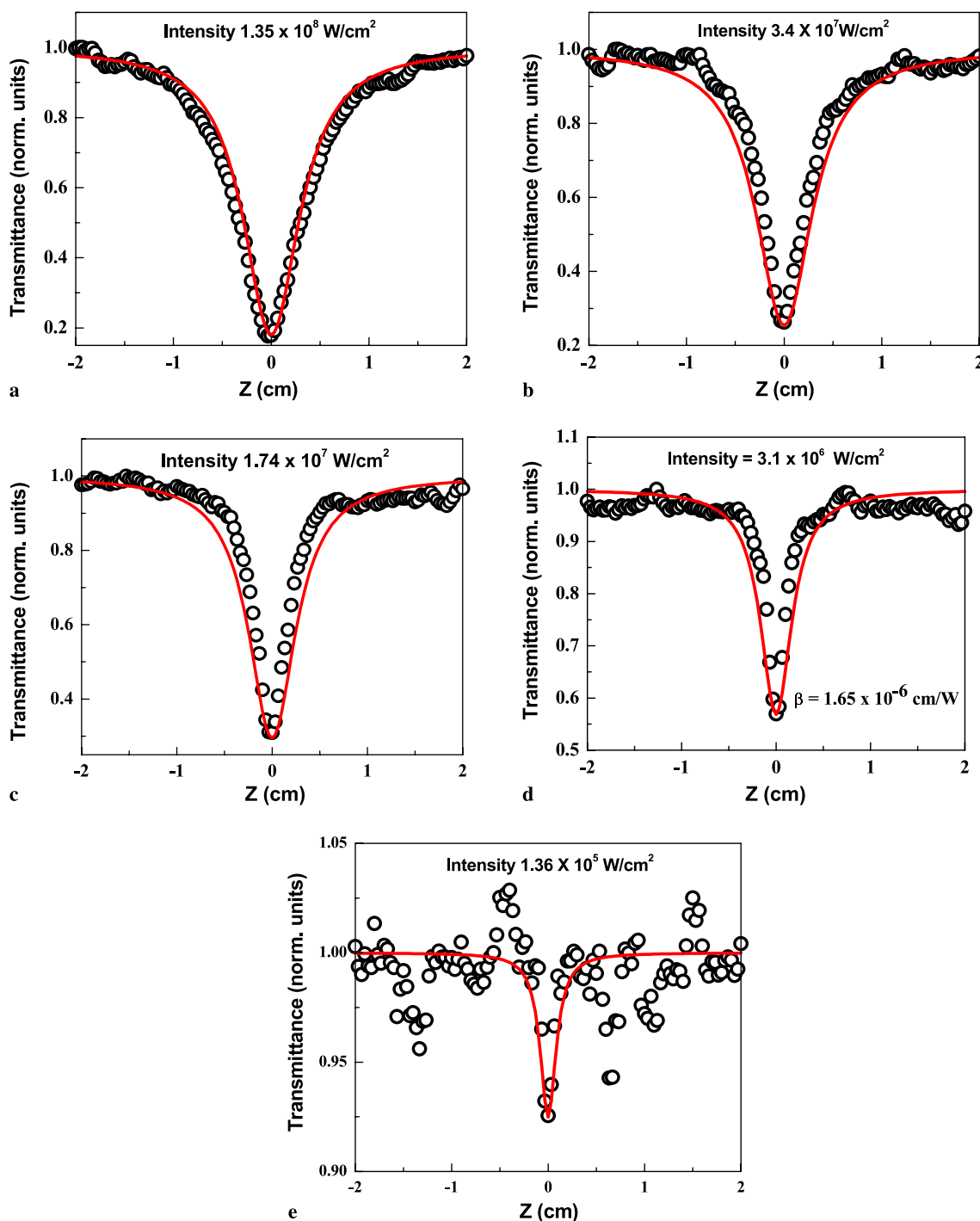


FIGURE 5 Open aperture Z-scan curves (a–e) recorded for Pc2 (open circles). The solid line represents the best fit. Linear transmittance was $\sim 70\%$

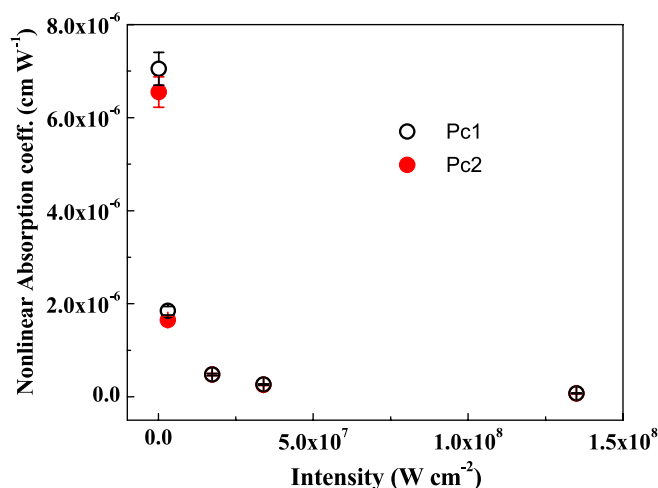


FIGURE 6 Variation of the nonlinear absorption coefficient β with input peak intensity

nonlinear optical properties of our molecules. We had earlier studied a large number of porphyrins and their derivatives using similar experimental conditions and an immediate qualitative assessment revealed the nonlinear absorption was stronger in the phthalocyanines case. Even for moderate peak intensities of 34 MW/cm^2 (where the transmission dipped below 0.3) we obtained the coefficient values of 480 cm/GW and 260 cm/GW respectively for Pc1 and Pc2. For peak intensities lower than 100 MW/cm^2 Pc1 had superior value of β compared to Pc2. The values of $\text{Im}[\chi^{(3)}]$ for Pc1 and Pc2 were found to be $3.98 \times 10^{-10} \text{ esu}$ and $4.46 \times 10^{-10} \text{ esu}$ respectively. Interestingly, Pc2 has smaller n_2 and higher β compared to Pc1. The magnitude of $\chi^{(3)}$ estimated from the real and an imaginary part was $\sim 1.0 \times 10^{-9} \text{ esu}$ for both the samples. It is evident that the total nonlinearity has significant contributions from real and the imaginary parts. We expect the large nonlinearity observed could be due to the contributions from the population in the excited states [51] as well as the

electronic response to the applied field. Z-scan studies using femtosecond pulses along with degenerate four wave mixing studies will resolve the above issues and further studies to this extent are in progress.

Comparing the nonlinear coefficients of our alkoxy phthalocyanines with some of the values reported in literature for other phthalocyanines Unnikrishnan et al. [23] report a maximum β_{eff} value of $\sim 50 \text{ cm/GW}$ for $\text{Eu}(\text{Pc})_2$ at 604 nm and $\sim 31 \text{ cm/GW}$ for $\text{Sm}(\text{Pc})_2$ at 596 nm . Unnikrishnan et al. [24] again report maximum β value of $\sim 3246 \text{ cm/GW}$ at 632 nm , which is a strongly absorbing region for their bis-phthalocyanines. However, for a wavelength of 532 nm they observe a β value of only 42 cm/GW . Unnikrishnan et al. [21] again report the β_{eff} values of $95\text{--}44 \text{ cm/GW}$ for LmPc, $\text{Eu}(\text{Pc})_2$, and $\text{Sm}(\text{Pc})_2$ for intensities in the $0.8\text{--}1.0 \text{ GW/cm}^2$ range. Santhi et al. [20] report their results on the spectral dependence of third order susceptibility of a zinc phthalocyanine. They measure an effective nonlinear absorption coefficient using similar analysis presented above and achieve values of $9\text{--}40 \text{ cm/GW}$ for the $616\text{--}527 \text{ nm}$ spectral region. Auger et al. [32] report nonlinear absorption properties of some 1,4,8,11,15,18,22,25-octaalkylphthalocyanines and their 15 metallated derivatives at 532 nm . They observe a maximum β_I (Intensity dependent nonlinear absorption coefficient) of 96 cm/GW for phthalocyanine with Pd as the metal ion. They calculate these values for an intensity of 0.5 GW/cm^2 (arbitrarily chosen). They argue that beyond these intensities the β_I value decreases. For peak intensities lower than 0.5 GW/cm^2 they do observe an increase in the nonlinear coefficient value. The average values of β_I obtained for different metal phthalocyanines ranged from 15 to 96 cm/GW . Garcia-Furtos et al. [25] report similar measurements for alkynyl substituted phthalocyanines in the range of 12 to 56 cm/GW for peak intensities ranging from 0.5 to 2.0 GW/cm^2 . Bertagnolli et al. [31] obtained β_I values of $32\text{--}35 \text{ cm/GW}$ for their gallium phthalocyanine dimers at 532 nm again studied using ns pulses. Interestingly, we had recently reported femtosecond and nanosecond nonlinear op-

Sample	Wavelength	β_{eff} or β_I (cm/GW)	Intensity (GW/cm ²)	Reference
Zn phthalocyanine	532 nm	47.74	–	Santhi et al. [20]
	596 nm	18.27		
LaPc	532 nm	95.46	0.82	Unnikrishnan et al. [21]
Eu(Pc) ₂		85.2	0.99	
Sm(Pc) ₂		44.1	0.84	
Sm(Pc) ₂	596 nm	31	0.143	Unnikrishnan et al. [23]
Eu(Pc) ₂	604 nm	50	0.0835	
Bis-phthalocyanine	632 nm	3246	0.00064	Unnikrishnan et al. [24]
	Nd(Pc) ₂	532 nm	42	
Alkynyl phthalocyanines	532 nm	12–56	0.2–2.0	Garcia-Furtos et al. [25]
GaPc dimers	532 nm	32–35	0.5	Bertagnolli et al. [31]
1,4,8,11,15,18,22,25-Octaalkyl-phthalocyanines and their 15 metallated derivatives	532 nm	15–96	0.5	Auger et al. [32]
Alkyl phthalocyanines	532 nm	~ 310 (pc-1) ~ 420 (pc-2)	6.0 MW/cm^2	Kumar et al. [52]
Alkoxy phthalocyanines (free base and Zn)	532 nm	~ 1600 (pc1) ~ 1800 (pc2)	3.1 MW/cm^2	This work

TABLE 1 Summary of the nonlinear absorption coefficients of various phthalocyanines reported at 532 nm using nanosecond pulses

tical properties of alkyl phthalocyanines and observed that for similar peak intensities the nonlinear coefficient was estimated to be ~ 400 cm/GW; lower than those reported here. The femtosecond properties of alkyl phthalocyanines suggested presence of higher order nonlinear absorption process and we expect the dynamics of both alkyl and alkoxy phthalocyanines to be in the femtosecond time domain. Table 1 summarizes the nonlinear coefficients obtained by different groups for various phthalocyanines. We have chosen these values from literature since these were performed with ns pulses at 532 nm and analysis similar to the one used here was carried out. The peak intensities also were similar or higher to those used in our case. There is a clear indication that our samples possess superior nonlinear coefficients. 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. [50]). The knowledge of lifetimes of the excited states then becomes imperative and even in this case we expect significant figures of merit ($\sigma_{\text{ex}}/\sigma_{\text{ground}}$). We have, at the moment, limited knowledge about the lifetimes of some excited states of these molecules and we are carrying out fluores-

cence lifetime studies to ascertain the complete dynamics of the excited states.

The optical limiting data obtained for Pc1 and Pc2 at 532 nm using 6 ns pulses are shown in Fig. 7a and b with both the samples exhibiting limiting thresholds ($I_{1/2}$) of ~ 0.5 J/cm². The mechanism for optical limiting could be predominantly excited state absorption since with ns pumping there is possibility of contribution from two photon absorption also. The above studies suggest that the effect of the metal ion on the nonlinear optical properties is negligible for alkoxy 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 [51] is in progress for estimating the contributions of different nonlinear absorption processes and will be reported elsewhere. We are also investigating the femtosecond nonlinear properties of these molecules to establish the electronic part magnitude of nonlinearity useful for ultrafast switching applications.

4 Conclusions

We have investigated the nonlinear optical and optical limiting properties of two alkoxy phthalocyanines at 532 nm. Both these phthalocyanines possess strong nonlinear absorption coefficients and low limiting thresholds. The values of the nonlinear refractive indices for Pc1 and Pc2 were estimated to be $\sim 3.0 \times 10^{-9}$ cm²/W for the free-base phthalocyanine and $\sim 2.94 \times 10^{-9}$ cm²/W for the metallic phthalocyanine. The nonlinear absorption coefficients evaluated were 1650 cm/GW and 1850 cm/GW for Pc1 and Pc2 respectively. The third order nonlinearity was of similar magnitude for Pc1 and Pc2 and was evaluated to be $\sim 10^{-9}$ esu. Our studies reveal that these phthalocyanines have superior nonlinear properties compared to some of the recently reported molecules with potential in broadband optical limiting in the visible region.

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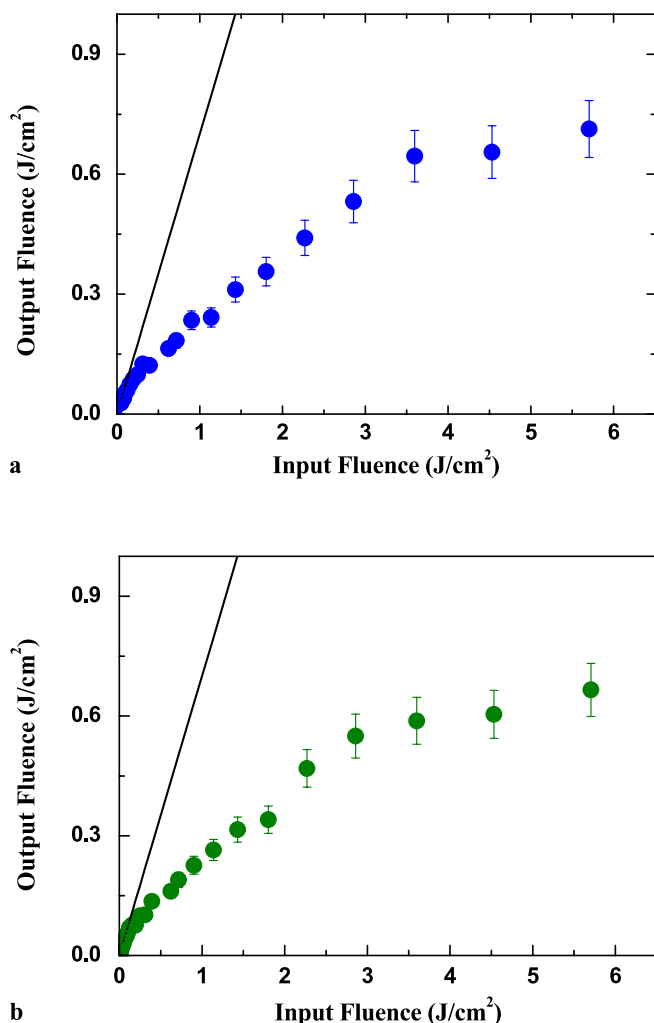


FIGURE 7 Optical limiting curves obtained for (a) Pc1 and (b) Pc2. The solid line represents 70% linear absorption in both the cases

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