

# Anomalous Nonlinear Absorption Behavior in an Unsymmetrical Phthalocyanine Studied Near 800 nm using Femtosecond and Picosecond Pulses

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The nonlinear optical properties of an unsymmetrical Zinc phthalocyanine were studied using the Z-scan technique in femtosecond and picosecond time domains. Open aperture Z-scan studies with  $\sim 110$  femtosecond pulses revealed an intriguing behavior exhibiting switching phenomena (from saturable absorption to reverse saturable absorption and back to saturable absorption) as a function of concentration and the peak intensities used. Similar behavior was observed with  $\sim 2$  picosecond pulse excitation. The observed results are qualitatively explained using an effective three-level model vis-à-vis a recent report on nonlinear absorption in a chloro-aluminum phthalocyanine where analogous performance was reported due to the solute migration. Such behavior is explicated as due to the consequence of combined effects of solvent contribution, large peak intensities, concentration, etc. The nonlinear absorption coefficients were established from the fits to the data.

*Keywords:* Femtosecond, picosecond, nonlinear absorption, switching, Z-scan, phthalocyanines, two-photon absorption, reverse saturable absorption.

## INTRODUCTION

We have recently been investigating new classes of porphyrins and phthalocyanines measuring their nonlinear optical and optical limiting properties along

with their figures of merit, employing the techniques of Z-scan and DFWM, in the cw, nanosecond (ns), picosecond (ps), and femtosecond (fs) time domains for their potential applications in optical limiting and optical switching. [1–17] Several groups have discussed about the connotation of these materials in extensive range of photonic applications. [18–22] Our comprehensive experiments and detailed modeling, along with the obtained nonlinear coefficients, strongly suggest that these are prospective molecules with large nonlinear coefficients in all the ns, ps, and fs time domains with ultrafast response times. Nonlinear absorption, associated to the imaginary part of the nonlinear susceptibility, is pertinent to optical limiting and biomedical imaging applications. Nonlinear absorption behavior using short pulses (ns, ps, and fs) in most of the organic moieties is characterized either by reverse saturable absorption (RSA) [including two-photon absorption (TPA) and three-photon absorption (3PA)] or saturable absorption. The Z-scan data acquired using nanosecond pulses are, generally, analyzed using an effective nonlinear coefficient,  $\beta$ . This is because the excitation can lead the population from ground state to any of the higher excited singlet or triplet states depending on the wavelength, peak intensities used, and the lifetimes of the excited states. In particular, we have analyzed such data using a rigorous five-level energy model including all nonlinear processes and the lifetimes involved. [23, 24] The data obtained using ps and/or fs pulses are universally analyzed using a three-level model ignoring the contribution of triplet states and sometimes the excited state absorption from the singlet states also. In each case the open aperture Z-scan reveals a peak or valley indicating saturable or reverse saturable absorption. However, there have been few reports in literature which indicate the switching of nonlinear absorption behavior from RSA to SA and vice-versa in these kinds of materials. We have observed such behavior in alkyl phthalocyanines [10] using fs pulses and interpreted in terms of the absorption cross-sections of ground and excited states in combination with the presence of 2PA/3PA. Here, we investigate an unsymmetrical Zinc phthalocyanine [**2-(3-(Butane-1,4-dioic acid)-9(10),16(17),23(24)-tri tert-butyl Phthalocyanine Zinc(II)** and herewith referred to as PCH001] using both fs and ps pulses with the Z-scan technique. We interpret the results taking into deliberation the concentrations used, peak intensities present, the contribution from solvent, and other parameters (e.g. continuum generation or solute migration [25])

## EXPERIMENTAL DETAILS

All the experiments were performed with samples dissolved in ethanol and were placed in 1-mm glass/quartz cuvettes. Nearly transform-limited femtosecond laser pulses were obtained from a conventional chirped pulse amplification system comprising of an oscillator (MaiTai, Spectra-Physics Inc.) that delivered  $\sim 80$  fsec, 82 MHz at 800 nm and a regenerative amplifier

(Spitfire, Spectra Physics Inc.), from which we obtained 1 kHz amplified pulses of  $\sim 100$  fsec duration, with maximum output energy of  $\sim 1$  mJ. The pulses were focused using a 120 mm achromatic doublet. Typical energies used for the experiments were in the 2–10  $\mu\text{J}$  range. For picosecond Z-scan, laser pulses were obtained from a conventional chirped pulse amplification system comprising of an oscillator (MICRA, Coherent Inc.) that delivered  $\sim 15$  fsec, 86 MHz pulses at 800 nm pumping a regenerative amplifier (Legend, Coherent Inc.), from which we obtained 1 kHz amplified pulses of  $\sim 2$  ps duration, with a maximum output energy of  $\sim 2.5$  mJ. The pulses were focused using a 120 mm lens. All the studies were performed with solution concentrations (in ethanol) ranging from  $5 \times 10^{-5}$  M to  $3 \times 10^{-4}$  M providing  $>85\%$  linear transmission near 800 nm. Several calibrated neutral density filters were utilized for attenuating intensity of the laser pulses. Each data point in the fsec data was a result of more than 50 averages. Picosecond data was collected manually which resulted in large scattering in the data.

## RESULTS AND DISCUSSION

Figure 1 depicts the absorption spectra of PCH001 dissolved in ethanol. Two strong absorption bands, centered near 350 nm and 675 nm, were observed for all the concentrations measured. At higher concentration both the bands

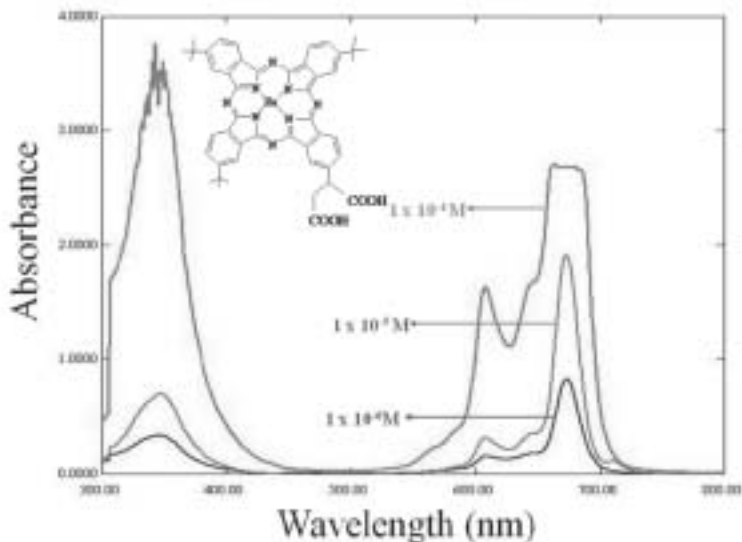


FIGURE 1  
Absorption spectrum of PCH001 in ethanol for different concentrations. Inset shows the compound structure.

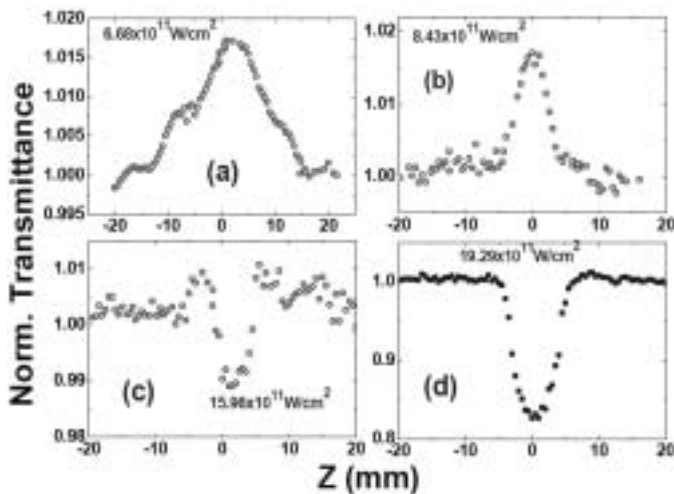


FIGURE 2

Femtosecond (110 fs) open aperture Z-scan data for PCH001 with a concentration of  $5 \times 10^{-5}$  M as a function of increasing intensity from (a) to (d).

broadened appreciably. Figure 2 (a)–(d) shows the open aperture Z-scan data for a  $5 \times 10^{-5}$  M solution recorded at increasing intensities. It is apparent that at lower intensities the behavior was SA type and switched completely to RSA type at higher intensities. For intensities above  $5.0 \times 10^{12}$  W/cm<sup>2</sup> we observed continuum generation and the transmittance dropped drastically. There are two possible explanations for this observation. In the first scenario we presume the material has saturable type of nonlinearity and switches to RSA type at higher intensities due to excited states absorption dominance at higher intensities. In the second situation we may argue that the solvent contribution, which comes in through three-photon absorption (3PA) for intensities  $> 1 \times 10^{12}$  W/cm<sup>2</sup>, is noteworthy and hence the RSA behavior was observed.

Figure 3 (a)–(d) shows the data recorded for a  $5 \times 10^{-4}$  M solution recorded at increasing intensities. At lower intensities we observed SA kind of behavior and immediately switched to RSA for little higher intensities. For much higher intensities the behavior switched (double switching) back to SA. This kind of behavior is intriguing and has not been reported earlier. Several factors again account for this kind of performance (a) Solvent effect: Pure ethanol shows RSA for intensities  $> 10^{12}$  W/cm<sup>2</sup>, though the contribution is negligible at lower intensities. (b) Intensity effect: At higher intensities we expect the saturation of the excited singlet states, including the  $S_n$  states. 2PA, 3PA, and ESA are all intensity dependent processes and it is also well established that there could other complicated nonlinear absorption processes as suggested by Gu *et al.* [26,27] such as two step four-photon absorption (c) Concentration effect: At higher concentrations there is a possibility of aggregation

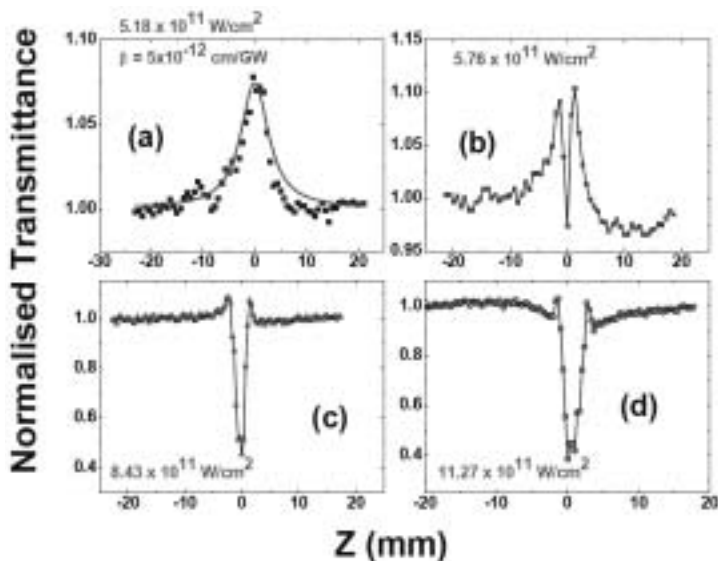


FIGURE 3

Femtosecond (110 fs) open aperture Z-scan data for PCH001 with a concentration of  $5 \times 10^{-4}$  M and as a function of increasing intensity from (a) to (d). Solid (Red) line is the fit in (a) while the solid lines in (b) to (d) are guide to the eye.

thereby modifying the lifetimes of the excited states influencing the nonlinear absorption behavior. The absorption properties of the molecule are itself altered at higher concentrations, as evident from the absorption spectra, again affecting the nonlinear absorption (d) Continuum generation at higher intensities has been identified to reduce the transmission (e) Sample damage: The sample could be completely damaged (irreversibly) at very high intensities thereby affecting the nonlinear transmission. In our case we ensured that factors (d) and (e) are ruled out by recording the spectra several times and achieving reproducible results.

Using the Z-scan technique, Chang *et al.* [25] found that migration of a chloroaluminum phthalocyanine in liquid ethanol can be induced by the absorption of a 19 ps laser pulse with energy exceeding a threshold but not by that of a 2.8 ns pulse depositing more energy at the solute molecules. They considered each solute molecule as an oscillator confined within a potential well and explained that solute molecules excited by a 19 ps pulse retains more translational excess energy to overcome the potential well barrier compared with those excited by a 2.8 ns pulse of equal energy. Therefore, they are more likely to migrate out of the laser beam center, weakening the solution's absorption that we detect in the Z-scan measurements. The possibility of such effects in our case cannot be ruled out. However, we expect the presence of such effects (migration of solute) to be insignificant in our case due to the

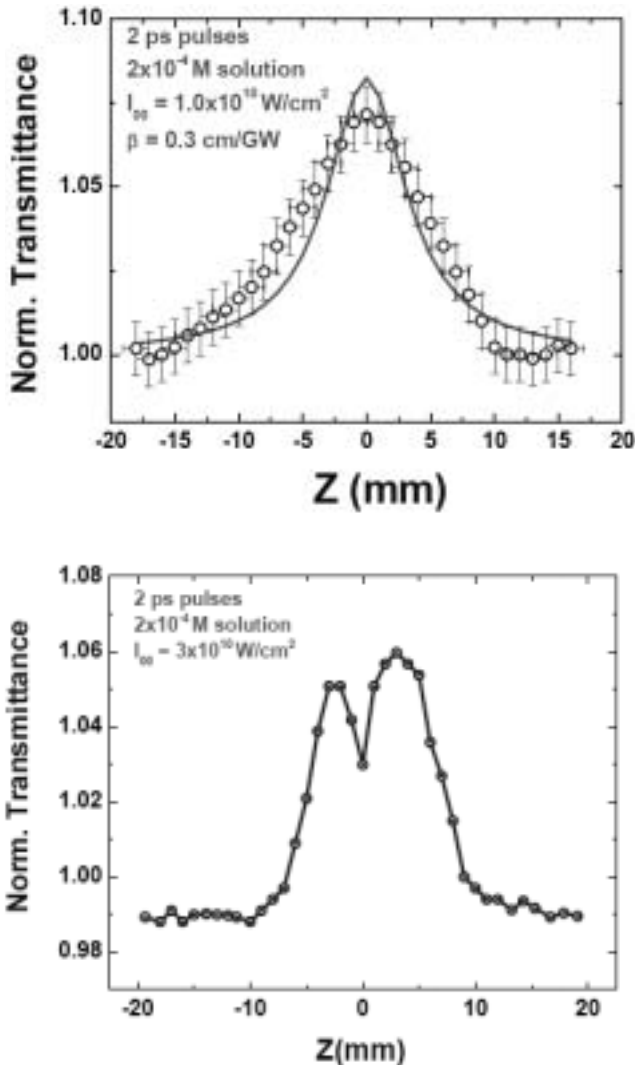


FIGURE 4

Picosecond open aperture data of PCH001 for a concentration of  $2 \times 10^{-4}$  M at different input intensities. Solid (red) line in (a) is the fit while in (b) the solid line is a guide to the eye.

short time sales of excitation (100 fs and 2 ps). There are not many noteworthy reports on the femtosecond nonlinear absorption studies of phthalocyanines. Li *et al.* [28] reported fs nonlinear absorption studies of a CuPc doped in PMMA. They observed switching of the SA behavior to RSA kind with increasing intensities as observed and reported by our group [10]. The transition from SA to RSA was ascribed to the fifth-order effect of excited-state absorption

(ESA) induced by two-photon absorption (TPA) process at higher intensities. Since they performed the experiments in a PMMA matrix the solvent effect will be eliminated. Notwithstanding the absence of solvent effect they observed complicated nonlinear absorption switching behavior which could be perceived at careful inspection of the experimental data.

Rao et al. [9] reported femtosecond NLO properties of several phthalocyanines studied using Z-scan technique. They argue that the solvent contribution is significant at intensities closer to the focus and hence the fit was not ideal. They accounted for the solvent contribution while calculating the nonlinear coefficients. The peak intensities used were  $>4 \times 10^{11}$  W/cm<sup>2</sup> where one can expect the solvent (chloroform) contribution to be important. The intriguing behavior observed at high intensities and concentration could be attributed to the collective effects of solvent contribution, intensities, and concentration. Our initial studies on pure solvent (ethanol) alone indicated the presence of nonlinear absorption for intensities  $>1 \times 10^{12}$  W/cm<sup>2</sup>. In our case, we realized that at these high intensities ethanol contribution (through 3PA) is significant. We attempted to evaluate the nonlinear coefficients at peak low intensities to avoid complications from other contributions. The values of nonlinear coefficient ( $\beta$ ) extracted from the fits were 0.3 cm/GW in the ps case and 0.005 cm/GW in the fs case. However, further detailed studies along with modeling efforts are indispensable to identify the exact magnitude of solvent contribution in these experiments.

Closed aperture studies with fs pulses demonstrated these molecules possessed positive nonlinearity at higher concentration. At lower concentrations the solvent contribution (also positive) dominated to the overall nonlinearity. The presence of excited state absorption [29] can induce thermal refraction in phthalocyanines thereby affecting the shape of the closed aperture Z-scan curves. With ps pulse excitation these clearly exhibited negative nonlinearity while solvent had positive nonlinearity. The value of  $n_2$  calculated from the ps data was  $-2.95 \times 10^{-15}$  cm<sup>2</sup>/W. Doping such molecules into an inert matrix (e.g. preparing thin films [30]) will assist us to diminish the ambiguity in such measurements to a certain extent. Our future endeavors consist of (a) Measurement of the precise magnitude of solvent contribution (b) Doping these molecules into suitable polymer matrix for device applications (c) Evaluate figures of merit and the time response.

## CONCLUSIONS

In conclusion we have studied the nonlinear properties of an unsymmetrical phthalocyanine using Z-scan technique with both fs and ps pulses at 800 nm. A very complicated nonlinear absorption behavior was observed with fs pulses at concentration of  $5 \times 10^{-4}$  M solution. The observed behavior was qualitatively understood as due to the consequences of intensity, concentration,

solvent contribution, and possibly solute migration. The evaluated nonlinear coefficients were found to be strong indicating their potential in several applications.

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