Femtosecond and continuous wave nonlinear optical properties of $(H_2)_2SnPc$, $Sn(OH)_2Pc$, $Sn(Cl)_2Pc$ studied using Z-scan technique

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ABSTRACT

Herein we report our experimental results on nonlinear optical properties of $(H_2)_2SnPc$ (I) , $Sn(OH)_2Pc$ (II), and $Sn(Cl)_2Pc$ (III) studied using Z-scan technique with 800 nm, 100 fsec 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 values of α_3 were **~4.0×10^{-5}, ~2.0×10^{-5} cm^3/GW^2, and ~1.5×10^{-5} cm^3/GW^2** for I, II, and III respectively obtained after deducting the solvent contribution. Closed aperture data recorded with femtosecond pulses revealed positive nonlinearity for all the molecules. We also observed large nonlinear response in the cw regime at 633 nm. Closed aperture scans performed with 633 nm indicated strong negative nonlinearity while open aperture scans depicted mixed response. 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

1. INTRODUCTION

Porphyrins, Phthalocyanines and metallophthalocyanines are macromolecules with huge number of delocalized π electrons resulting in interesting third-order nonlinear optical (NLO) properties leading to extensive applications in optical limiting and all-optical switching.[1-27] The high stability and capability of phthalocyanines, especially, to accommodate different metal ions within their cavity result in diverse optical properties. Even though nonlinear optical properties of surplus of phthalocyanines and their derivatives have been investigated till date to assess their performance for NLO applications there remains further scope for investigation of novel structures with superior figures of merit.[16-27] The best optical limiting performance till date has been achieved using a phthalocyanine in tandem with another nonlinear optical material justifying the potential of these molecules.[28] We have been investigating a number of porphyrins and phthalocyanines for their NLO properties in the cw, nanosecond (nsec), picosecond (psec), and femtosecond (fsec) domains. We reported large nanosecond and picosecond nonlinearities in tetratolyl porphyrins and their metal derivatives with reasonably fast response times.[9-13] Our recent studies focused on alkyl and alkoxy phthalocyanines which also exhibited huge nonlinear coefficients in the cw, nsec, and fsec domains with potential applications in optical limiting, switching, and bio-imaging.[14-21] We have also investigated the NLO properties of these molecules in thin film form and nanoparticles form. These studies suggest that it is possible to achieve large nonlinear coefficients combined with superior figures of merit with a systematic study. However, there is necessity to incorporate these materials in a proper matrix such as polymer or glass, while preserving their NLO properties and response times, for crucial device applications. In this paper we present the results of our studies on nonlinear optical properties of $(H_2)_2SnPc$ (herewith referred to as I) , $Sn(OH)_2Pc$ (herewith referred to as II), and $Sn(Cl)_2Pc$ (herewith referred to as III) studied using the Z-scan technique[29] with 800 nm, 100 fsec pulses, and 633 nm continuous wave (cw) laser excitation. From the fsec open-aperture (OA) Z-scan data we derived that these molecules have strong three-photon absorption (3PA) coefficient/cross-sections at moderate input intensities. We also estimated the sign and magnitude of the real part of third order nonlinearity (n_2) by means of the closed aperture scans from cw and fsec data. We observed reverse saturable absorption type of behavior with cw excitation for I and III. Fsec data suggested positive nonlinearity while the cw study indicated negative nonlinearity for these structures. We attempt to analyze the data obtained and compare the performance of these molecules with some of our earlier reported molecules. Our detailed study concludes that these phthalocyanines are prospective candidates for multi-photon applications in the fsec regime, potential candidates for optical limiting applications in the cw domain.

2. EXPERIMENTAL DETAILS

Tin phthalocyanines studied were synthesized according to the procedures reported in literature[1] and 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. 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 ~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 duration, with output energy of ~1 mJ. The peak intensities used in experiments were in the 200-800 GW/cm^2 for fsec pulse excitation. All the studies were performed with solution concentrations of 5×10^{-5} M providing >90% linear transmission near 800 nm. Several calibrated neutral density filters were utilized for attenuating the intensity of the laser pulses. Each data point in all the fsec data was a result of more than 50 averages. For evaluating the nonlinear optical properties at 633 nm a Helium–Neon laser was the source used for exciting the samples. Typical values of the parameters used for the experiment were input beam of size (diameter) 0.75 mm focused to a spot size of ~100 μm using 15 cm lens, with input powers in the 5–14 mW range. A power meter was used for the closed and open aperture measurements in the cw case. Sufficient care was taken to ensure the samples were not damaged due to continuous exposure to the lasers.
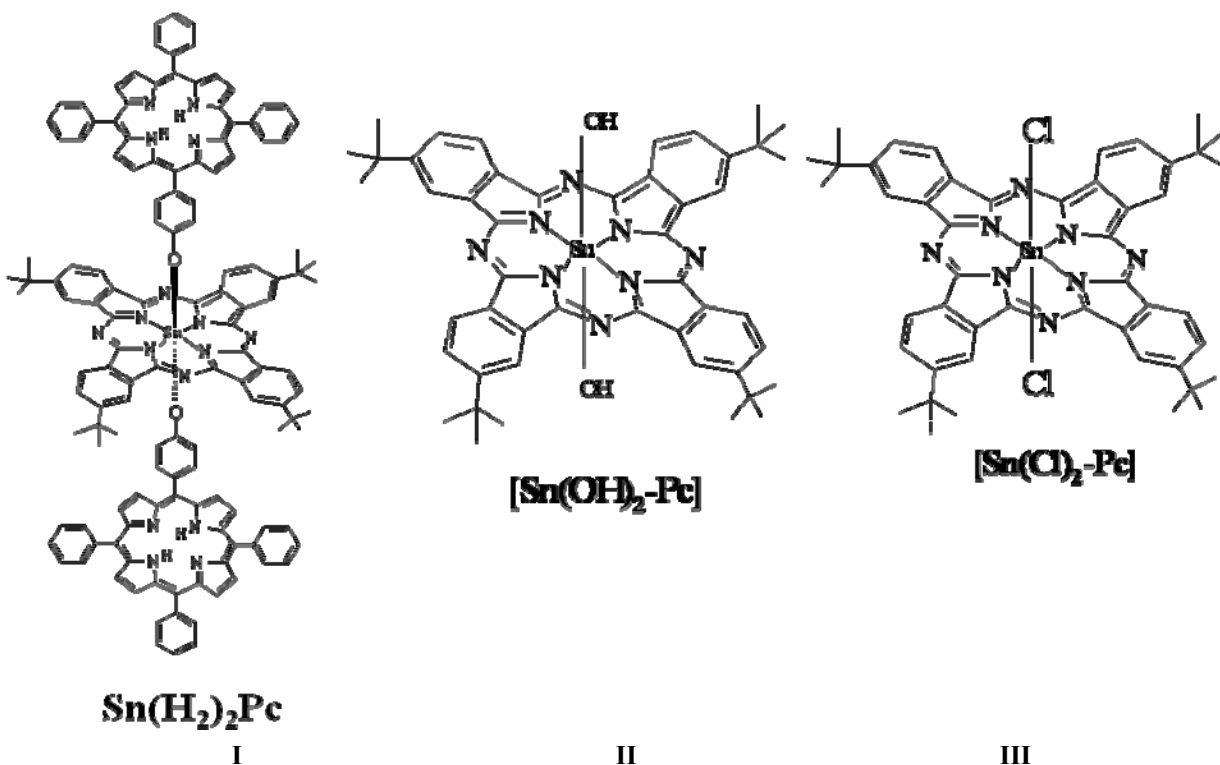

I   II   III

Figure 1 Structures of the phthalocyanines studied using femtosecond pulses.

3. RESULTS AND DISCUSSION

Spectroscopic characterization:

The absorption spectra were recorded using an UV-visible spectrometer for ~10^{-5} M solutions and are depicted in figure 2. 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 and other spectral data of these phthalocyanines have been reported elsewhere.[30]
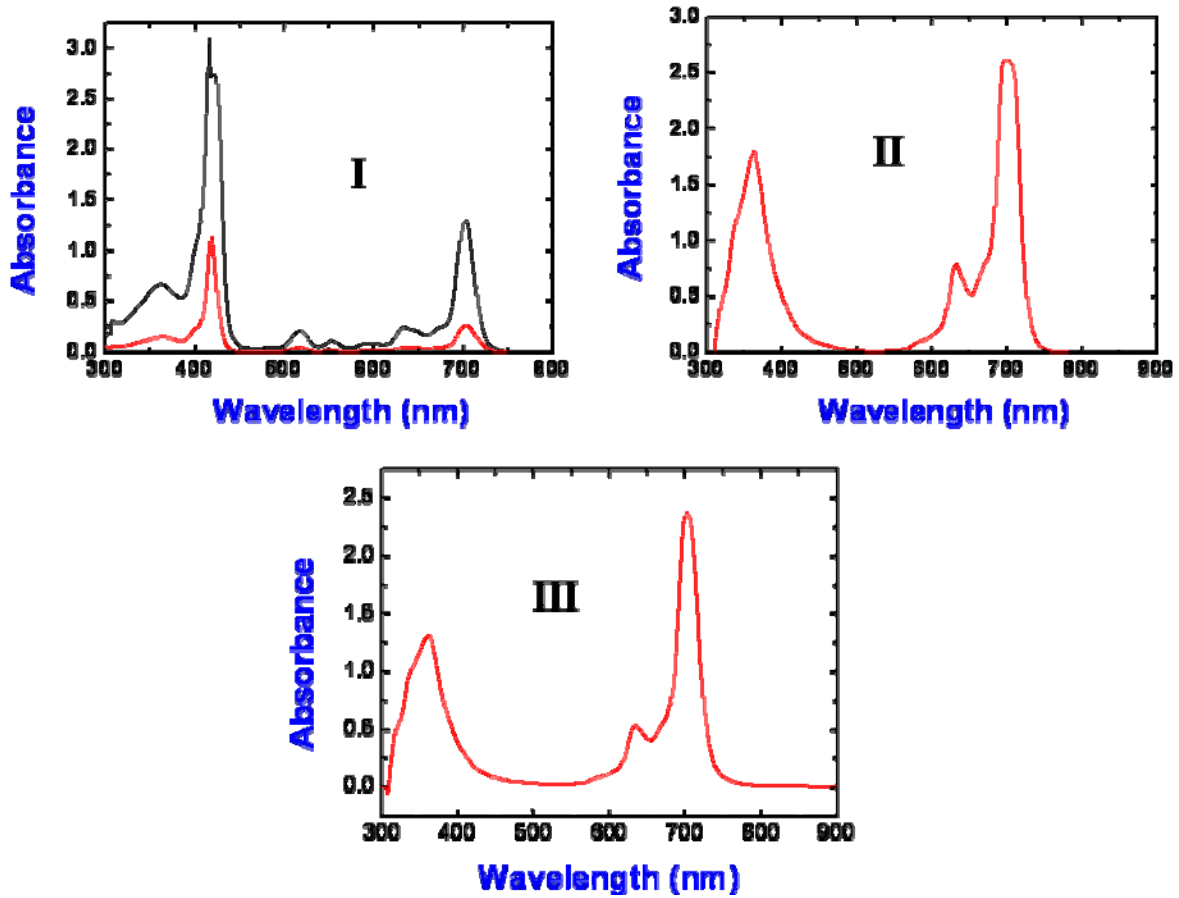
Figure 2 Absorption spectra of I, II, and III dissolved in chloroform

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.[31] we have the general equation for open aperture (OA) normalized energy transmittance given by:

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

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.

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

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

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 $L_{eff} = \dfrac{1 - e^{-\alpha_0 L}}{\alpha_0}$., $L'_{eff} = \dfrac{1 - e^{-2\alpha_0 L}}{2\alpha_0}$.

**Z-scan studies with 800 nm, 100 fsec pulses**

The open aperture scans for the samples I, II, and III were recorded at 800 nm using fsec pulses for various input irradiances and the resulting data is shown in figure 3 (a) – (d). All the samples had a concentration of 5×10^{-5} M. For sample I we observed strong reverse saturable absorption (RSA) kind of behavior in the intensity range of 100–200 GW/cm^2. At lower peak intensities noise dominated the signal while at higher peak intensities a smooth reverse saturable absorption (RSA) kind of behavior was observed. Owing to fsec excitation the obtained experimental data was fitted using equations 2 and 3 and we found the best fit was achieved with the transmission equation for three-photon absorption (3PA). However, the fit was not perfect with deviations for the data away from focus. Since the concentrations used were low we expect contribution from the solvent at these peak intensities. We suppose this contribution from solvent to be from four-photon absorption (4PA) or even higher NLO process. Further experiments are necessary to ascertain this which is in progress. We had fitted the data for 3PA coefficient [blue line in figure 3(d)] assuming solute contribution only. We tried to fit 2PA to the data and it is apparent from the fits (red line) that it fails by a large margin. We later estimated the solvent contribution, which was found to be <50% of the fit value. The solvent contribution is over-estimated at this moment and an exact value is being ascertained with a separate study. For molecule I we obtained a fit value of **8.0×10^{-5} cm^3/GW^2** and the final value obtained, minus the solvent part, was **~4.0×10^{-5} cm^3/GW^2,** which is of the order obtained for alkly and alkoxy phthalocyanines reported recently by our group (maximum of ~9.1×10^{-5} cm^3/GW^2 for alkyl phthalocyanines and 3.6×10^{-5} cm^3/GW^2 for alkoxy phthalocyanines). Errors in the values presented here arise from the estimation of peak intensities, fittings, incorrect concentration calculations and we estimate the overall error bar in our fitted data to be less than 20%.

Figures 4 and 5 depict the open aperture data recorded for II and III, respectively. Similar estimates as in the case of sample I were obtained for II and II and the magnitudes of 3PA coefficients acquired from the corrections to the fits were **~2.0×10^{-5} cm^3/GW^2** (for a peak intensity of 600 GW/cm^2) and **~1.5×10^{-5} cm^3/GW^2** (for a peak intensity of 750 GW/cm^2). It is evident that sample I has superior value of 3PA coefficient and can be attributed to the presence of porphyrin molecules in the axial regions of the phthalocyanine thereby providing more number of delocalized π-electrons for participating in the nonlinearity.

Our earlier studies undoubtedly point out that concentration of the sample(s) used and the peak intensities play a significant role in determining the type of nonlinear absorption with a possibility of switching over from SA to RSA and much more complex behavior of SA in RSA and vice-versa. At higher concentrations there is a possibility of aggregation affects which in turn influences the linear and nonlinear absorption properties. At very high peak intensities prospects of higher order nonlinearities and/or Supercontinuum generation are higher in these complex organic molecules. An optimum concentration and peak intensity are therefore essential to identify the nonlinear mechanism(s) without ambiguity. The high nonlinear coefficients obtained with these molecules are important for applications in femtosecond optical limiting and bio-medical imaging applications. Such materials will have special impact in biology and medicine through three-photon induced photodynamic therapy (PDT) in cancer treatment. Table 1 presents a comparison of the nonlinear coefficients of our molecules with those reported recently[37-40] in literature and except for the nanomaterials[39] our materials exhibit superior performance. A thorough analysis[41] based on three level modeling is also required for estimating the presence of other nonlinear processes at different concentrations and peak intensities enabling us to tap the potential of these molecules.
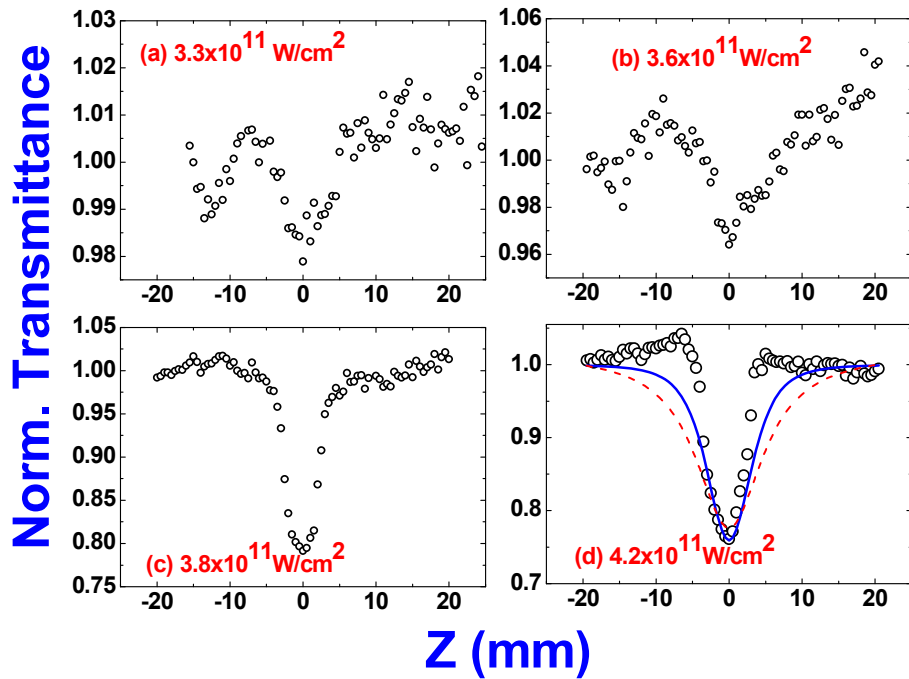
Figure 3 Open aperture Z-scan data for phthalocyanine I obtained at various input intensities. The data was fitted for 2PA and 3PA (fourth figure). 3PA (solid) fit was better compared to 2PA (dashed).
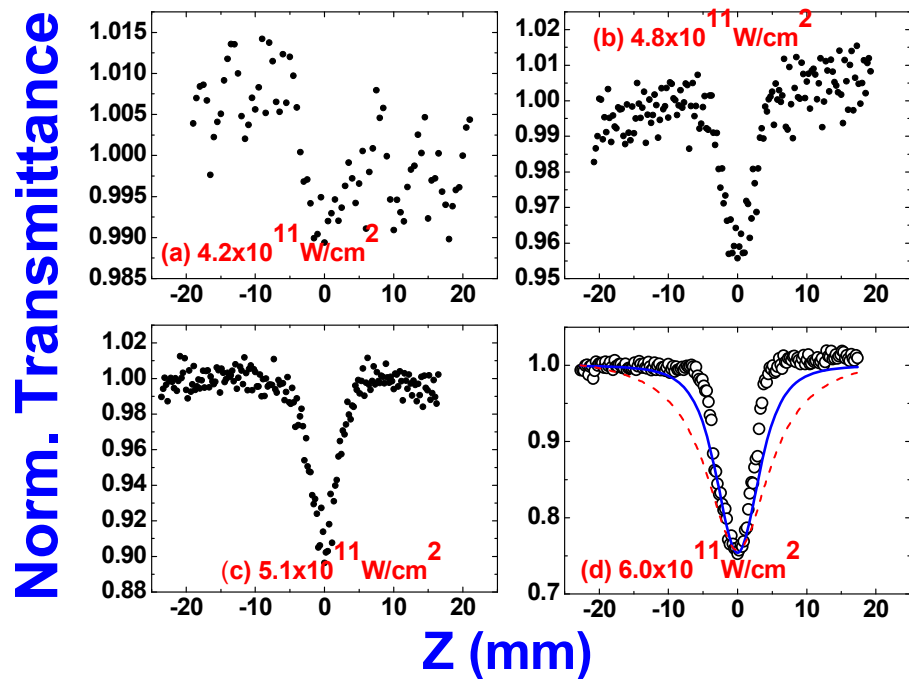

Figure 4 Open aperture Z-scan data for phthalocyanine II obtained at various input intensities. Solid line is the 3PA fit while the dashed line is obtained with 2PA fitting in (d).
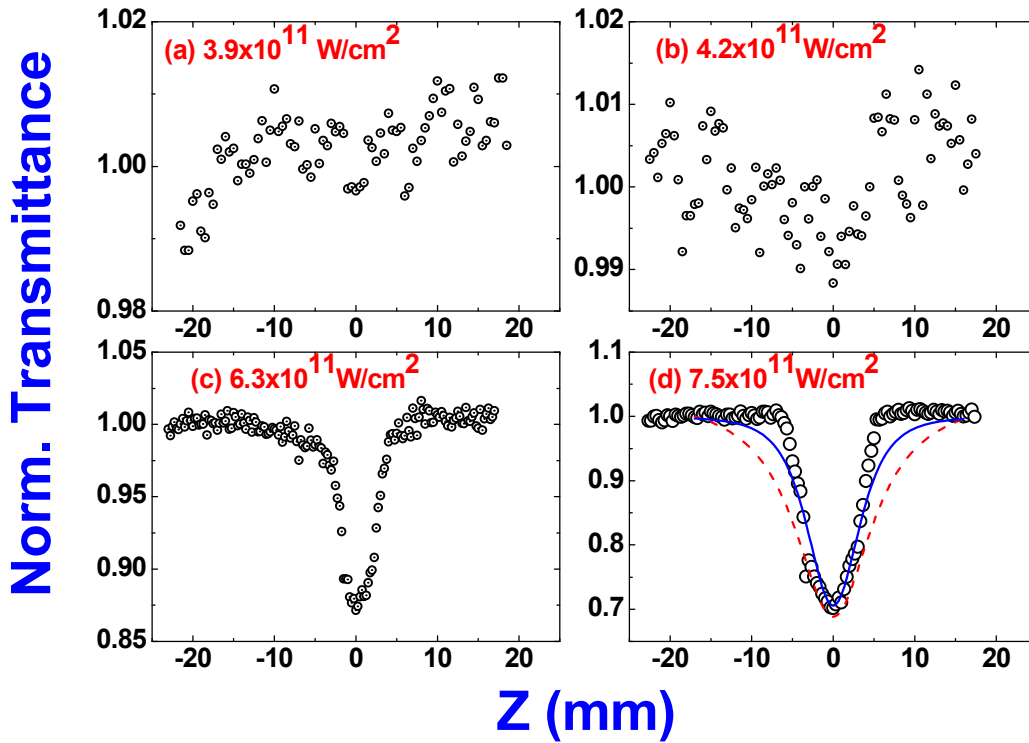
Figure 5 Open aperture Z-scan data for phthalocyanine III obtained at various input intensities. Solid line is the 3PA fit while the dashed line is obtained with 2PA fitting in (d).

Figure 6 shows the closed aperture Z-scans recorded for all the samples. It is apparent that all of them possessed positive nonlinearity. The data was fitted with standard closed aperture equations for retrieving the $\Delta\phi$ and thereby the magnitudes of nonlinear refractive index, n_2. The values obtained were **5.0×10^{-15} cm^2/W** for I, **1.8×10^{-15} cm^2/W** for II, and **1.93×10^{-15} cm^2/W** for III, respectively. Again, the nonlinear RI obtained for I is higher than those of II and III implying the role of porphyrin groups in the molecular structure of $(H_2)_2SnPc$. We also expect the solvent contribution to the overall fit value. A detailed estimate provided us some insight into the extent of solvent contribution which was <25%. Separate closed aperture Z-scan experimental studies are in progress with solvent alone to quantify the exact contribution and will be reported at a later stage. High nonlinear refractive index is useful for optical switching applications. Figures of merit based on nonlinear and linear absorption, nonlinear refractive index are being estimated and we expect them to higher when compared to alkyl and alkoxy phthalocyanines.


I II III
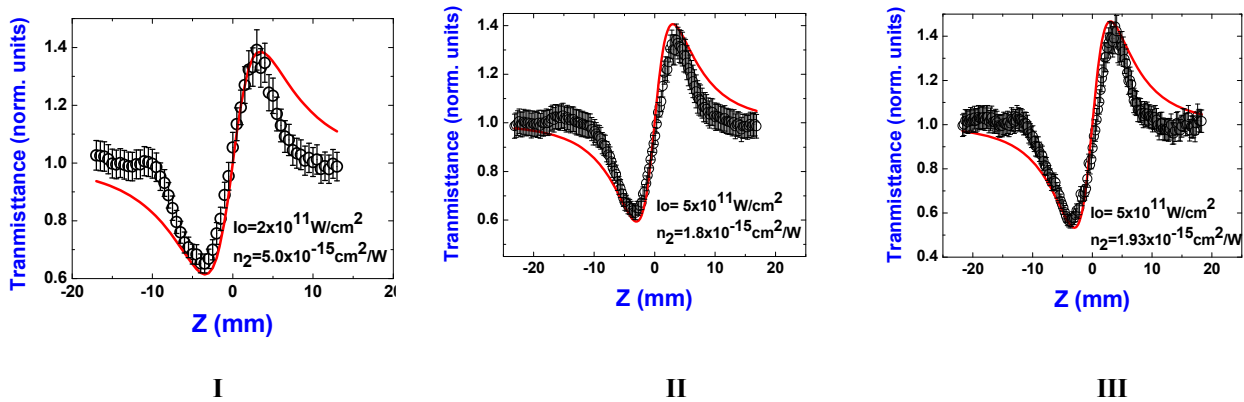
Figure 6. Closed aperture Z-scan data for I, II, and III using 100 fsec pulses near 800 nm.

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	[37]
Multi-branched chromophore	1300 nm, 160 fsec	0.385	[38]
ZnS NC's	800 nm, 120 fsec	2400	[39]
Tetra tert-butyl phthalocyanine (Free base and Zn)	800 nm ~100 fsec	9.1 (pc1) 9.5 (pc2)	[16,17]
(H$_2$)$_2$SnPc (I) Sn(OH)$_2$Pc (II) Sn(Cl)$_2$Pc (III)	800 nm ~100 fsec	**4.0** (8.0) **2.0** (4.0) **1.5** (3.0)	[This Work]

Table 1 Comparison of three-photon absorption coefficient **(α_3)** with other reported values in literature. The values indicated in the parentheses for I, II, and II are the fit values while the actual values, corrected for solvent contribution, are indicated outside the parentheses and in bold

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

Figure 7 illustrates the closed aperture and open aperture Z-scan curves obtained for all the samples with cw excitation at 633 nm. Unambiguous signatures of peak-valley in the closed aperture scans indicate a negative type of nonlinearity in the cw domain. Saturable absorption (SA) type of behavior, evident from open aperture scan, was observed for II. However, for the first time, we observed RSA kind of behavior in II and III with stronger dip in the sample I. The measurements were repeated several times and the outcome was the same. We are analyzing the reason for this behavior. Our initial estimates suggest the nonlinear refractive index to be very high. These are thermal nonlinearities which are a result of the heating of the sample through continuous excitation modifying the refractive index locally. These molecules were also found to be effective optical limiters in the cw domain utilizing the nonlinear refraction. Our future studies include (a) Combining these materials[42,43] with other potential NLO molecules (b) Incorporation into a suitable polymer/glass matrix and (c) Time-resolved studies for evaluating the response times to understand and further enhance their NLO performance
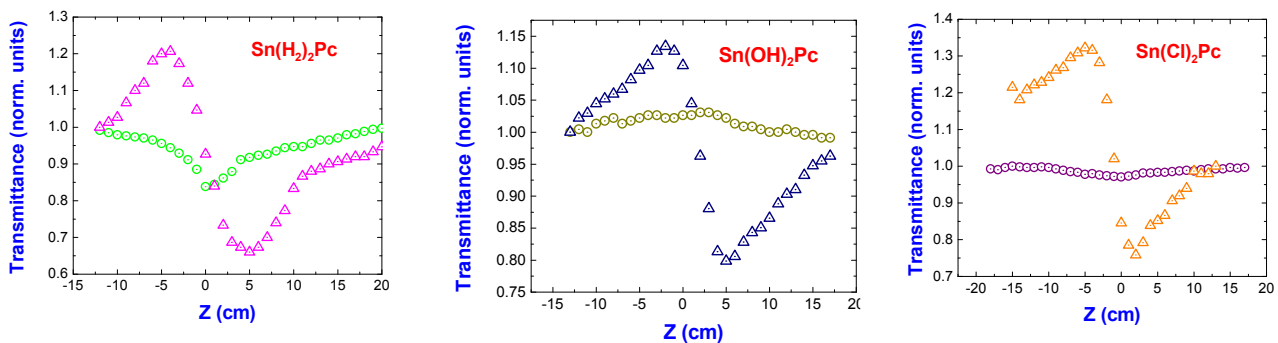
Figure 7 Closed aperture Z-scan data for I, II, and III using cw pulses at 633 nm

4. CONCLUSIONS

We presented our results nonlinear optical properties of (H$_2$)$_2$SnPc (I) , Sn(OH)$_2$Pc (II), and Sn(Cl)$_2$Pc (III) studied

using Z-scan technique with 800 nm, 100 fsec pulses, and 633 nm continuous wave (cw) laser excitation.. From the fsec open-aperture Z-scan data we derived that these molecules exhibited strong 3PA coefficient (α_3) at moderate input intensities. The estimates were obtained after deducting the contribution from solvent (in our case chloroform). The values presented are one of the best amongst the recently reported potential molecules with 3PA. Such molecules find interesting applications in bio-imaging and optical signal processing. Strong nonlinear refractive index was observed with cw excitation and for the first time, to the best of our knowledge, we observed RSA in chloroform solutions of I and III. 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.

Sample	Fsec n_2 (cm^2/W)	3PA coeff (cm^3/GW^3)	Sign n_2 (cw)	Nonlinear absorption type (cw)
1. $(H_2)_2SnPc$ (I)	2.0×10^{-15}	$4.0(8.0)\times10^{-5}$	Negative	RSA
2. $Sn(OH)_2Pc$ (II)	5.0×10^{-15}	$2.0(4.0)\times10^{-5}$	Negative	SA
3. $Sn(Cl)_2Pc$ (III)	1.8×10^{-15}	$1.5(3.0)\times10^{-5}$	Negative	RSA

Table 2 Summary of the nonlinear coefficients obtained for I, II, and III in the present study. The values indicated in the parentheses for 3PA is the fit value while the actual value, corrected for solvent contribution, is indicated outside the parentheses and in bold.

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