

Ultrafast nonlinear optical properties and excited state dynamics of phthalocyanine thin films

S. Venugopal Rao,* P.T. Anusha, T. Shuvan Prashant, D. Swain, Surya P. Tewari
Advanced Center for Research in High Energy Materials (ACRHEM)
University of Hyderabad 500046, India

* Corresponding author's e-mail: svrsp@uohyd.ernet.in or soma_venu@yahoo.com

ABSTRACT

We have investigated the nonlinear optical properties, optical limiting thresholds, and figures of merits for five different phthalocyanine thin films, achieved through doping in PMMA, using the Z-scan technique at 800 nm with 2 ps laser pulses. From the open-aperture Z-scan data we established that these molecules exhibit strong two photon absorption (2PA) with the nonlinear coefficients in the range of 15-200 cm/GW. We have also estimated the sign and magnitude of real part of third order nonlinearity through the closed aperture scans. Preliminary femtosecond pump-probe data suggests that the lifetimes of excited states are in the sub-100 ps regime for all the molecules in film form. Our studies provide tangible evidence that these phthalocyanines are potential candidates for multi-photon imaging and optical limiting applications.

Keywords Z-scan, phthalocyanines, ultrafast, thin films, nonlinear absorption.

1. INTRODUCTION

Novel moieties with strong two-photon (2PA) and three-photon absorption (3PA) crosssections/coefficients are attractive for potential applications in the fields of photonics and bio-medicine [1-4]. Studies on a variety of molecules with strong 2PA/3PA have been established to be relevant in fluorescence spectroscopy, 3D imaging, and lithography because of high spatial resolution achieved through intensity dependent processes [3-7]. Additionally, they can be used for optical data storage and optical limiting purposes. Several materials such as porphyrins and phthalocyanines that possess such properties have been investigated extensively in recent times by several groups including ours [8-26]. Especially, phthalocyanines have been examined by chemists, material scientists, and physicists alike since these are ubiquitous materials in which an alteration in molecular configuration allows the engineering of both linear and nonlinear optical (NLO) properties for specific applications. These organic polymeric systems contain conjugated π electron structure and show large optical nonlinearities combined with nonlinear response time is in the femtosecond time domain [7, 8]. Due to the large, ultrafast third-order nonlinearities and the ease with which one can derive several new compounds through peripheral and axial substitutions, these molecules have generated a great deal of interest in nonlinear optics [10-26]. The third order NLO properties of phthalocyanines are closely dependent on the central metal ion and other modifications to the core and peripheral substitution. However, phthalocyanines are hardly soluble in organic solvents and do not crystallize easily in matrices. Moreover, the molecule aggregation of phthalocyanines greatly influences the third order nonlinearity, $\chi^{(3)}$. To circumvent these problems modification of phthalocyanines such as the introduction of peripheral substitutions or attaching them to polymer chains have been carried out. The latter approach has the advantage that a high concentration of nonlinear chromophores can be incorporated into the polymer system without crystallization, phase separation, or formation of concentration gradients.

Several earlier reports [10-26] on the optical and NLO properties have been in various forms of thin films. We have recently reported the NLO studies of novel phthalocyanines using continuous wave, nanosecond (ns), picosecond (ps), and femtosecond (fs) laser pulses [27-37]. Our recent efforts have been towards understanding the nonlinearities in all the time domains, albeit in solution form and in one case in nanoparticles form [36]. Our wide-ranging studies strongly suggest these are prospective molecules with strong nonlinearities and figures of merit in each time domain. In this paper we report two photon absorption and the nonlinear refraction studies of phthalocyanine thin films achieved using ps pulses. The standard Z-scan technique was utilized to investigate the third order NLO properties of the film. The knowledge of ultrashort pulse nonlinear refractive index aids in deciding appropriate materials for optical switching

applications. Herein we present the results of our investigations on the NLO properties of five films of phthalocyanines studied using 2 ps pulses.

2. EXPERIMENTAL DETAILS

Z-scan measurements were performed using an amplified Ti:sapphire laser system (LEGEND, Coherent) delivering nearly transform-limited pulses of ~2 ps with a repetition rate of 1 kHz at 800 nm. The amplifier was seeded with ~15 fs pulses from an oscillator (MICRA, Coherent, 1 W average power, 80 MHz repetition rate, 800 nm). Laser pulses with 2-5 μJ energy were used for the experiments. The beam was focused using 200 mm focal length lens into the sample. The beam waist (ω_0) estimated was about 20 μm with a Rayleigh range of 2 mm. The transmittance changes of the sample placed on the translation stage (Newport, ILS250PP), which was controlled by an ESP motion controller, was measured with a sensitive power meter in the far-field. An aperture is placed in front of detector and the power meter was interfaced to the computer. We established that the pulse energies remained low to avoid contribution from higher order nonlinearities. The experiments were repeated more than once and the best data were used for obtaining the nonlinear optical coefficients from the best fits. These molecules are highly soluble in chloroform in which commercially available PMMA (poly methyl methacrylate) was dissolved and the resulting solution was processed into thin films. Such films, upon curing, produced cross linked polymeric system in which phthalocyanine derivative is covalently linked. Typically the concentration of phthalocyanines in polymer was ~1% by weight (of PMMA) though we could put in a maximum of ~5% by weight. PMMA concentration was ~10% by weight in solution. Details of pump-probe experimental set up have been reported earlier [47].

3. RESULTS AND DISCUSSION

The IUPAC nomenclature for the compounds is shown in table 1. The complete details of synthesis of these molecules, their molecular structure, and their absorption spectra are reported elsewhere [27-34]. All the molecules were purified prior to NLO experiments. The molecules were dissolved in a sonicated PMMA+chloroform solution (crystal clear). The solution was then transferred to clean microscopic slides and spin coated to achieve films of various thicknesses. The typical thickness of the films measured using a profilometer were in the 8-12 μm range. The absorption coefficients of all the films were estimated to be in the range of 10^4 m^{-1} for all the films. Linear absorption spectra of typical PC2 and PC3 thin films are shown in figure 1. The slight broadening and splitting observed in Q band (arising from electronic transitions) and broadening of Soret band in the thin film absorption spectra, compared to solutions, could be ascribed to the intermolecular interaction and molecular distortion/deformation [38-39]. In addition there is also the possibility of aggregation in solid state thereby slightly modifying the energy level configuration.

Figures 2(a) to 2(e) show the open aperture data (open stars) of phthalocyanine thin films PC1 to PC5 recorded at 800 nm with 2 ps pulses and input peak intensities in the range of 200 GW/cm^2 . The presence of valley in normalized transmittance in open aperture (OA) scans indicates strong reverse saturation absorption (RSA) at these peak intensities. Inset of figure 2(a) shows the typical closed aperture data for PC1 film. The peak followed by valley in the normalized transmittance data clearly suggests that the sample possesses negative type of nonlinearity and self-defocusing behavior. Similar behavior for n_2 was observed for other thin films also. The n_2 values obtained from the fits for all films were in the range of $2\text{-}15 \times 10^{-4} \text{ cm}^2/\text{GW}$. In order to extract the information of nonlinear refraction alone, the experimental closed aperture Z-scan data was divided by the open aperture data. This greatly eliminated the influence of nonlinear absorption on the nonlinear refraction data.

CA and OA data were fitted using following equations [40]:

$$T_{CA} = 1 + \frac{4\Delta\phi\left(\frac{z}{z_0}\right)}{\left(\left(\frac{z}{z_0}\right)^2 + 9\right)\left(\left(\frac{z}{z_0}\right)^2 + 1\right)} \quad (1)$$

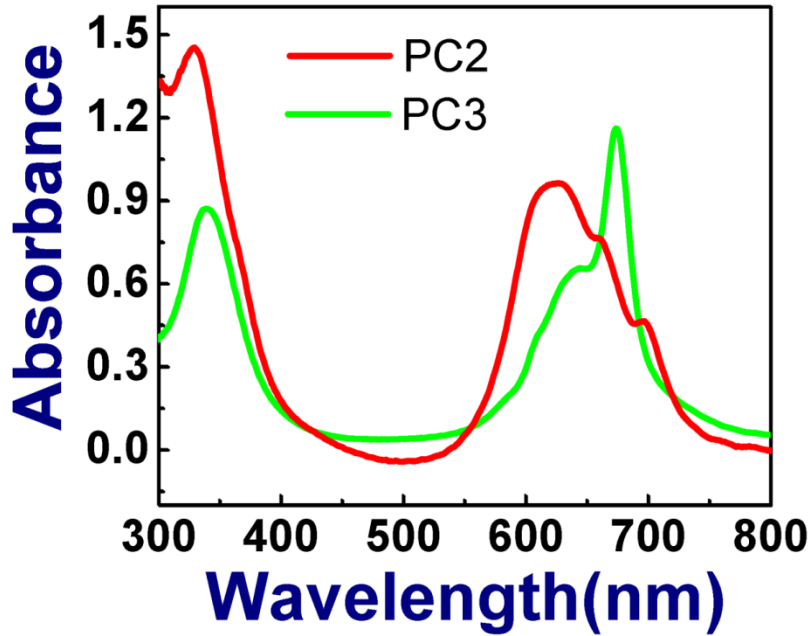


Figure 1 UV-visible absorption spectra of PC2 (top, red color) and PC3 (bottom, green color) doped in PMMA

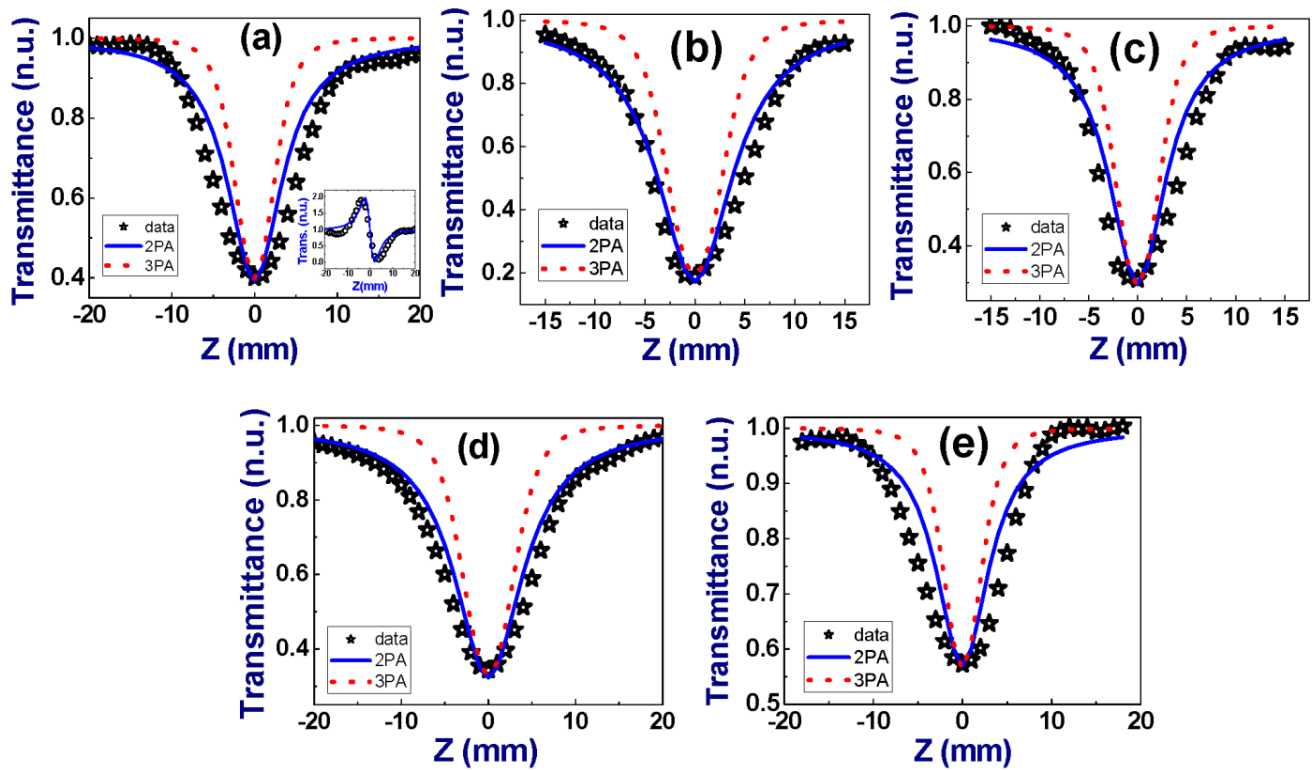


Figure 2(a)-(e) OA Z-scan curves of PC1 to PC5 recorded with peak intensity of 200 GW/cm^2 . Open stars represent the experimental data while the solid lines are fits. Red (dotted) and blue (solid) lines represent theoretical fit for 3PA and 2PA, respectively. Inset of (a) shows CA scan recorded at same intensities.

$$T(z, S = 1) = \frac{1}{\sqrt{\pi}q_0(z,0)} \int_{-\infty}^{\infty} \ln[1 + q_0(z, 0)e^{-\tau^2}] d\tau \quad (2)$$

$$T(z, S = 1) = \frac{1}{\sqrt{\pi}p_0(z, 0)} \int_{-\infty}^{\infty} \ln \left[\sqrt{\ln(1 + p_0^2 \exp(-2\tau^2))} p_0(z, 0) \exp(-\tau^2) \right] d\tau \quad (3)$$

With $q_0 = \beta L_{\text{eff}} I_0$, $p_0 = (2\alpha_3 L'_{\text{eff}} I_0^2)^{1/2}$, β is the 2PA coefficient and α_3 is the 3PA coefficient, I_0 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 $L_{\text{eff}} = \frac{1 - e^{-\alpha_0 L}}{\alpha_0}$.

$$L'_{\text{eff}} = \frac{1 - e^{-2\alpha_0 L}}{2\alpha_0}$$

From all the fits to experimental data it is evident that 2PA is the dominant mechanism for the observed RSA kind of behavior. 2PA absorption coefficients estimated from the fits were in the range of 15-200 cm/GW. 3PA fits are also shown in the figures for comparison and undoubtedly the fits are off from the experimental data. All the samples were checked for presence of any nonlinear absorption losses due to scattering. The transmitted light was devoid of any scattering in the far-field indicating that 2PA was the main mechanism contributing to nonlinear absorption. The values of nonlinear coefficients presented here are accurate within 15% and the errors arise due to uncertainties in the measurements of peak intensity, fitting procedures, unaccounted Fresnel losses, etc. The $\chi^{(3)}$ values, $\sim 10^{-10}$ esu, obtained from our films are comparable to one of the highest reported nonlinearity for Aluminum phthalocyanine films [23]. The best n_2 value was obtained for PC3 (1.44×10^{-16} m²/W) is also comparable to the values obtained in self-assembled multilayer films containing tetrasulfonated iron phthalocyanine [22]. However, in their case due to the multi-layer nature of films the π -electron molecular orbits of macrocycles in the aggregates probably coupled with neighbors so strongly enough to enlarge the conjugation system, thus, changing the electronic structure of the phthalocyanine molecule and improving the third-order optical response. Ma et al. [18] reported $\chi^{(3)}$ values of 10^{-10} esu for their titanylphthalocyanine films which is again comparable to the values obtained in present study. Furthermore we observed strong 2PA in our molecules which find potential applications in bio-imaging and good optical limiting thresholds.

Whilst the solution studies of these molecules, excited with fs pulses exhibited, strong 3PA in alkyl phthalocyanines (PC4 and PC5) [31, 33], an amalgamation of excited state absorption, 2PA, and 3PA in alkoxy phthalocyanines (PC1 and PC2) [30], and saturable absorption behavior with ps pulses in the asymmetric phthalocyanine (PC3) [34, 35, 37] all the films studies obviously pointed to the presence of strong 2PA. This could be explained with the changes in absorption spectra, and thereby the energy level configuration, corresponding to solutions and thin films combined with the aspect of peak intensities used for these studies. With the broadening of Soret band there is a possibility of direct two-photon state existence for the molecule when excited with 800 nm photon in the bulk unlike in solutions. PC3 in solution depicted SA (due to small absorption at 800 nm) when excited with lower peak intensities but immediately switched to RSA with increasing peak intensities [34, 35]. PC1 and PC2 also demonstrated similar behavior of RSA with increasing peak intensities. The nonlinear absorption in such molecules is indeed complex phenomena involving several excited state mechanisms such as 2PA/3PA induced excited state absorption, pure 2PA/3PA, single photon induced excited state absorption etc. [41-46]. Further detailed wavelength and intensity dependent studies are in progress to elucidate the complete nonlinear absorption behavior in these materials.

We have assessed the merit factors W and T for all the thin films studied and defined as

$$W = \frac{n_2 I_{\text{sat}}}{\alpha_1 \lambda} \quad (4)$$

$$T^{-1} = \frac{n_2}{\lambda \alpha_2} \quad (5)$$

where λ is the wavelength and I_{sat} is the light intensity at which the nonlinear refractive index saturates. Ideally W must be >1 and T ought to be <1 for practical device applications.

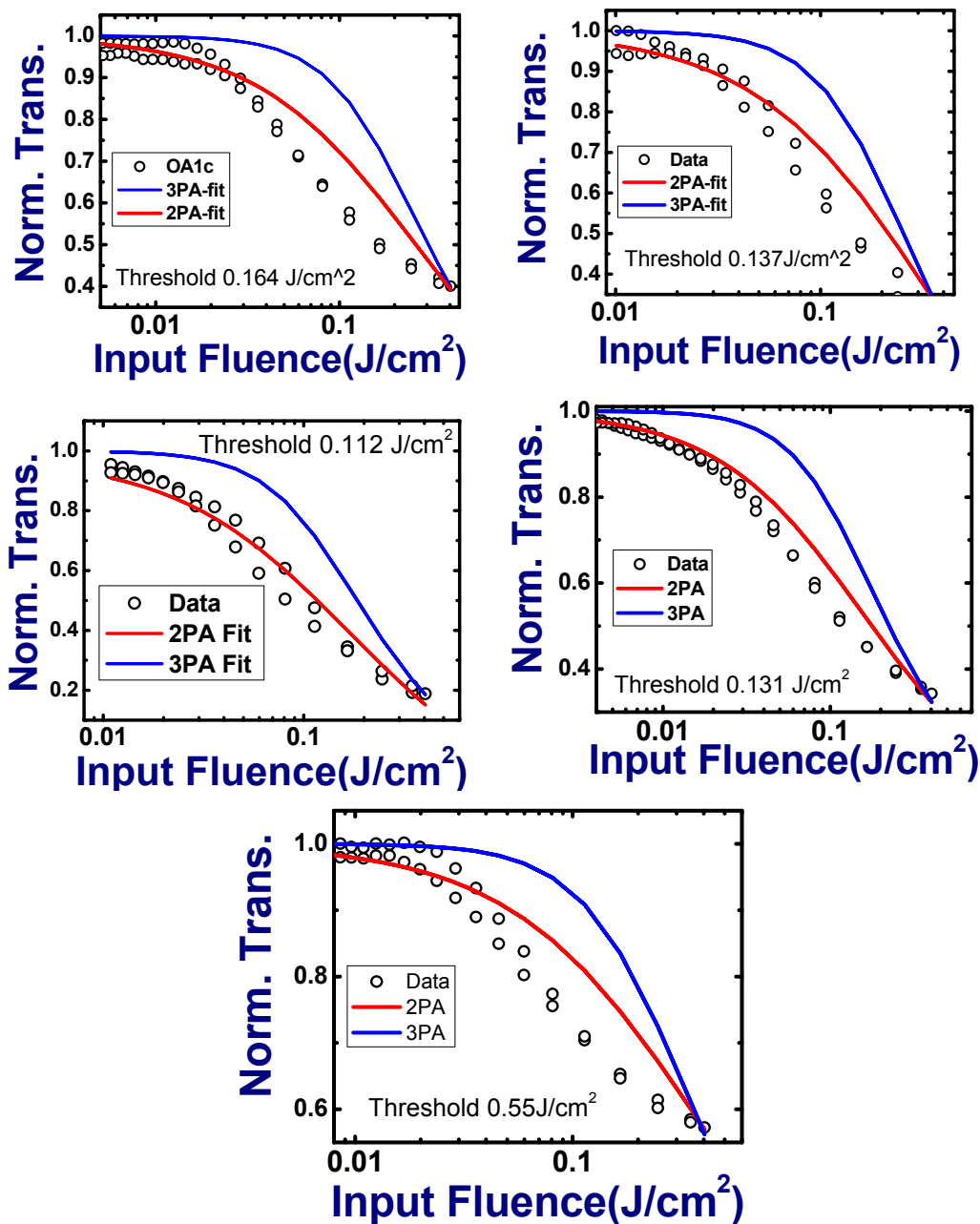


Figure 3 Optical limiting cure recorded for PC3 in PMMA. Blue (solid) line is the fit for 2PA while red (dotted) line is fit for 3PA

In the present case W is certainly >1 for all the films while T is also >1 . We strongly feel that these robust molecules are good for multi-photon absorption based applications due to the presence of strong 2PA. The nonlinear refractive index recorded was also high for these molecules compared to some the recently reported molecules of interest and furthermore the excitation wavelength was non-resonant. However, supplementary wavelength dependent studies will reveal the actual potency of these molecules for optical switching based applications which is strongly dependent on the nonlinear refractive index (n_2).

Figure 3 shows optical limiting curves for PC1 to PC5 depicting the sample transmission as a function of input laser fluence (i.e. energy per area). The input laser energy density was evaluated using the relation $E_{in} = 4\sqrt{\ln 2} E_{in} / \pi^{3/2} \omega(z)^2$, where E_{in} is the input laser pulse energy and $\omega(z)$ is the beam radius. It is evident that under strong irradiance the curve departs from Beer's law leading to optical power limiting in the thin film. The fits were performed using both 2PA and 3PA as the nonlinear absorption mechanism and The limiting thresholds evaluated from the data and fits were in the 0.1-0.6 mJ/cm² range. Table 2 summarizes the nonlinear coefficients of all the films extracted from the present study. The high nonlinearity of PC3 compared to other phthalocyanines can be ascribed to the asymmetry in structure compared to other symmetrical phthalocyanines and is consistent with our earlier results [28-33]. Metal phthalocyanine films exhibited higher nonlinearities when compared to free base phthalocyanine films for both alkyl and alkoxy cases whereas alkoxy phthalocyanine films displayed higher nonlinearity compare to alkyl phthalocyanine films.

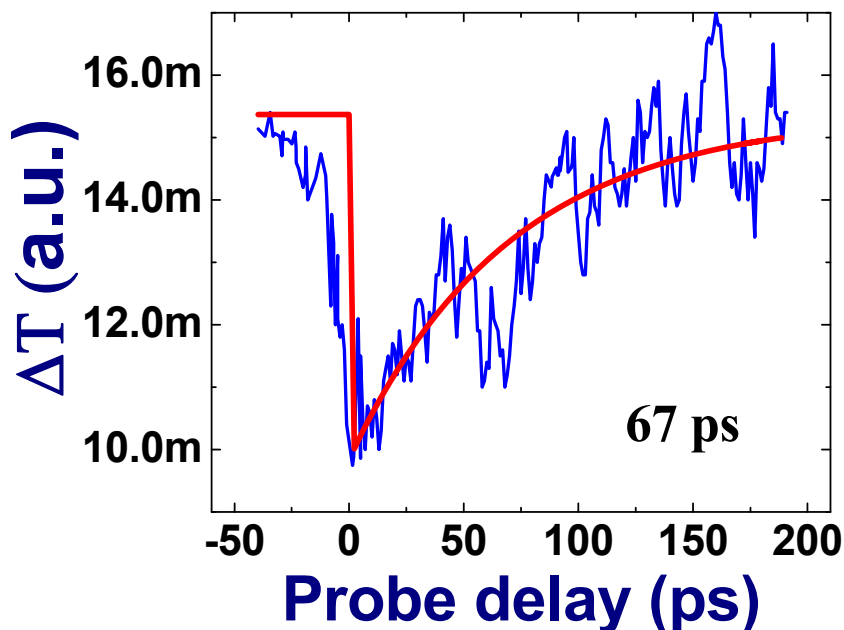


Figure 4 Pump-probe data for PC2 film excited at 610 nm. The decay constant observed from the fit was ~67 ps.

We have also investigated the response time of these films using fs degenerate pump-probe spectroscopy. Our initial fs pump-probe studies offered a testimony for the ultrafast response time with the decay observed in the sub-100 ps time scale [47]. A typical data set obtained for PC2 at a wavelength of ~610 nm (degenerate pump and probe) is shown in figure 4. The lifetime obtained from fit (red solid line) to experimental data (blue line) was ~67 ps. Our earlier studies [47] also suggested lifetimes for PC3 and PC5 in the sub-100 ps regime. Further studies are in progress to achieve better signal noise ratio along with wavelength/intensity dependent life times. Several recent reports too predict the lifetimes of excited states in a number of phthalocyanine thin films to be in the ps time domain [48-52]. Table 3 summarizes the values of third order nonlinearity obtained from our studies with those reported in literature. It is evident that our molecules superior nonlinearity (even with 1% by weight concentration films) compared to most of the others reported. Our future studies will focus on extracting the exact nonlinearity per molecule. Our objective is to obtain a complete perception of these molecules response to cw, ns, ps, and fs excitation in both solution and thin film form by evaluating the nonlinear coefficients, response time, and figures of merit to entirely categorize and utilize their potential in each of these time domains.

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5. CONCLUSIONS

We have investigated the nonlinear optical properties of five different phthalocyanine thin films at 800 nm with short pulses of 2 ps duration. All the samples were found to possess good n_2 values comparing to some of the recently reported values for similar molecules. The sign of the nonlinearity was confirmed to be negative. Open aperture studies demonstrated strong two photon absorption to be responsible for the nonlinear absorption. Initial pump-probe studies using femtosecond pulses near 600 nm indicated sub-100 ps lifetimes for the excited states. Magnitudes of third order nonlinearities and figures of merit have been evaluated for these films and the data suggests these molecules are good for multi-photon imaging and optical limiting applications.

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Sample	Nomenclature
PC1	2,3,9,10,16,17,23,24-octakis (heptyloxy) phthalocyanine
PC2	2,3,9,10,16,17,23,24-octakis-(heptyloxy)phthalocyanine Zinc(II)
PC3	(2-(3-(Butane-1,4-dioic acid)-9(10),16(17),23(24)-tri <i>tert</i> –butyl phthalocyanine Zinc(II)
PC4	2(3),9(10),16(17),23(24) tetra <i>tert</i> -butyl phthalocyanine
PC5	2(3),9(10),16(17),23(24) tetra <i>tert</i> -butyl Zinc phthalocyanine

Table 1 Nomenclature of compounds used in the present study.

Sample	n_2 (m^2/W) $\times 10^{-17}$	n_2 (esu) $\times 10^{-10}$	$Re \chi^{(3)} $ (m^2/V^2) $\times 10^{-19}$	α_2 (m/W) $\times 10^{-10}$	$Im \chi^{(3)} $ (m^2/V^2) $\times 10^{-19}$	$ \chi^{(3)} $ (m^2/V^2) $\times 10^{-19}$	$ \chi^{(3)} $ (esu) $\times 10^{-11}$	Figure of Merit W	Figure of Merit T	Limiting Threshold (J/cm^2)
PC1	4.30	1.53	5.06	6.00	4.50	6.78	4.86	3.7	11.2	0.164
PC2	6.94	2.47	8.17	18.0	13.5	15.8	11.3	7.3	20.7	0.137
PC3	14.4	5.12	17.0	20.0	15.0	22.6	16.2	2.6	11.1	0.112
PC4	2.18	0.78	2.57	6.00	4.50	5.18	3.71	2.3	22.0	0.131
PC5	2.30	0.82	2.71	1.50	1.13	2.93	2.10	3.1	5.2	0.550

Table 2 Summary of the nonlinear coefficients of phthalocyanine thin films extracted from the present study.

Sample	$ \chi^{(3)} $ (esu) $\times 10^{-12}$	Pulse Details	Reference
SiPc	13.3	532 nm, 70 ps	[10]
TiO Pc	100	800 nm	[16]
CoPc(NH ₂) ₄	6.3	2.1 μ m	[17]
VOpc	93	1.907 μ m	[48]
VO(Bu) ₄	6.0	1.907 μ m	[48]
Co Pc	0.7	2.1 μ m	[48]
Cu Pc	1.5	1.907 μ m	[48]
Cu Pc	1.1	2.1 μ m	[48]
Cu Pc(SC ₄ H ₉) ₄	6.2	2.1 μ m	[48]
VOpc	40	2.1 μ m	[49]
VOpc(SC ₆ H ₁₃) ₄	31	2.1 μ m	[49]
Ni Pc(NH ₂) ₄	2.0	1.907 μ m	[49]
Cu Pc	3.4	1.907 μ m	[50]
Co Pc(Co-R) ₂	4	1.5 μ m	[50]
CuPc(NH ₂) ₄	2.0	2.1 μ m	[50]
Ni Pc	1.63	2.1 μ m	[50]
Fe Pc(COOH) ₄	1.18	2.1 μ m	[50]
Azo-Zn Pc	0.23	532 nm, 25 ps	[51]
PC1 PC2 PC3 PC4 PC5	48.6 113 162 37.1 21.0	800 nm, 2 ps (1% concentration by weight in PMMA)	This work

Table 3 Summary of nonlinear coefficients of phthalocyanine thin films reported in literature and extracted from the present study.