CHAPTER 7
Chapter 7

Multiphoton absorption properties

Abstract

In this chapter, we present our results on nonlinear optical properties of $2(3), 9(10), 16(17), 23(24)$ tetra tert-butyl phthalocyanine and $2(3), 9(10), 16(17), 23(24)$ tetra tert-butyl Zinc phthalocyanine studied using Z-scan technique with 800 nm femtosecond and 532 nm nanosecond pulses. Nonlinear absorption behavior in both femtosecond and nanosecond domains was studied in detail. We observed three-photon absorption with femtosecond laser excitation and strong reverse saturable absorption with nanosecond pulse excitation. We have also evaluated the sign and magnitude of the third-order nonlinearity. Further, we carried out investigation of ultrafast nonlinear optical properties including the time response of studied using degenerate four-wave mixing technique at a wavelength of 800 nm with 100 fs pulses. We recorded large off-resonant second hyperpolarizability ($\gamma$) for these molecules with ultrafast nonlinear optical response in the femtosecond domain. Our studies on their figures of merit indicate these molecules possess enormous potential for photonic switching applications. The performance of these molecules vis-à-vis other molecules, in general, and phthalocyanines, in particular, is discussed.
Multiphoton absorption and ultrafast nonlinear optical properties of alkyl phthalocyanines

7.1 Introduction

The high intensities associated with fs pulses can induce profound changes in the optical properties of a material leading to a nonlinear response of the real and imaginary parts of polarization. The imaginary part of the nonlinear polarization is associated, for instance, with multiphoton transitions and will exhibit a \( n \)-photon resonance when two levels of an atomic or molecular system can be connected by \( n \) optical quanta. Nonlinear absorption refers to the change of transmittance of a material as a function of intensity or fluence. At sufficiently high intensities, the probability of a material absorbing more than one photon before relaxing to the ground state can be greatly enhanced. As early as 1931, Göppert-Mayer derived the two-photon transition probability in a system using the second order quantum perturbation theory [1]. With the availability of high intensities with fs pulses, in addition to numerous investigations into this phenomenon of the simultaneous absorption of two photons, multiphoton (\( >2 \)) absorption has also been widely studied. Multiphoton absorption processes are highly promising for a number of processes including optical limiting [2], 3D microfabrication [3], and optical data storage [4].

Porphyrins and phthalocyanines systems have received particular attention in the context of multiphoton absorption because of their large \( \pi \) electron delocalization, flat structure, and high thermal stability with applications in optical processing devices, practical optical limiters, and biomedical applications [5-8]. In organic materials three-photon absorption (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 [7]. Such materials will have a broad impact in biology and medicine through three-photon induced photodynamic therapy (PDT) in cancer treatment. Recently novel materials including organic fluorophores like halogenated fluorine molecules, polydiaectomylenes, semiconductor nanoparticles have been investigated for their 3PA properties using femtosecond (fs) and picosecond pulses in the NIR spectral regions [9-14]. 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 polydiaectomylenes in the excitation wavelength region from $\lambda_{ex} = 800$ to 1600 nm [9]. Phthalocyanines are versatile because they offer enormous structural flexibility with the capacity of hosting ~70 different elements in the central cavity. One of the major drawback with these molecules is majority of them are insoluble in common solvents. However, incorporation of substituents at the peripheral and non-peripheral positions has established to improve the solubility [15]. Recent studies have extracted a large variety of peripheral substituents for improving the poor solubility of unsubstituted phthalocyanines. New molecules with high two-photon (2PA) and three-photon absorption (3PA) cross-sections are interesting for their potential applications in photonics and biomedical applications [16]. Significant studies on application of phthalocyanines in PDT [7] have motivated us further to identify materials, especially phthalocyanine derivatives, with appropriate absorption in the UV region along with a transmission window in the NIR range contributing to multi-photon absorption.

Typically, the presence of nonlinear absorption in molecules like phthalocyanines augments their capability for optical limiting applications while the presence of nonlinear refraction facilitates all-optical switching applications.
Though nonlinear optical properties of variety of phthalocyanines have been investigated till date there are further opportunities and avenues to explore novel structures with superior figures of merit [17]. It is well established that for a third-order nonlinear material to be attractive for optical switching applications the nonlinear response has to be strong (a high value of the effective nonlinear refractive index $n_2$) and instantaneous time response of the induced refractive-index change (typical response is expected in the sub-picosecond range) along with the requirement of minuscule material losses due to one-photon, multiphoton absorption. Furthermore, scattering losses are to be minimal for any signal processing devices application [18]. Accurate determination of the merit factors is imperative for deciding the applicability of third-order NLO materials for optical switching. Unfortunately many reports which dealt with the NLO properties of organic materials in general, with phthalocyanines in particular, furnish fragmentary information about these parameters.

In the light of above mentioned objective to investigate phthalocyanines as a potential candidate with good 3PA cross-section and ultrafast nonlinear optical behavior we concentrated our efforts on the nonlinear optical properties of 2(3), 9(10), 16(17), 23(24) tetrabutyl phthalocyanine (referred to as pc1) and 2(3), 9(10),16(17), 23(24) tetrabutyl Zinc phthalocyanine (referred to as pc2). The multiphoton absorption properties of pc1 and pc2 are obtained using Z-scan with 800 nm, 100 fs and 532 nm, 6 ns laser pulse excitation. From the fs 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 (ns) 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 both ns and fs data.

Further, by utilizing the technique of degenerate four-wave mixing technique (DFWM) near 800 nm with ~100 femtosecond (fs) pulses we investigated the nonlinear optical response of pc1 and pc2. We observed large...
third order nonlinear susceptibility $\chi^{(3)}$ and second order molecular hyperpolarizability $\gamma$ for these molecules. Time-resolved degenerate four wave mixing (DFWM) measurements in the box-car geometry revealed instantaneous response from these molecules. Our detailed DFWM studies suggest that these molecules are potential candidates for photonic switching applications. We have also tried to establish the competence of these molecules, compared to some of the recently reported molecules [19-27], through their figures of merit evaluation.

### 7.2 Molecular structure and spectroscopic characterization:

Alkyl phthalocyanines were synthesized according to the procedures reported in literature1 and both pc1 and pc2 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 7.1. The molecular weights of pc1 and pc2 are 748 gm/M and 804 gm/M respectively.

![Fig.7.1: Structures of the phthalocyanines used (a) tetra tert-butyl phthalocyanine (pc1) (b) Zinc tetra tert-butyl phthalocyanine (pc2)](image)

The absorption spectra were recorded using an UV-visible spectrometer for $\sim 10^{-4}$ M solutions and are depicted in figure 7.2(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 7.3, 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.

Excited state lifetimes for these molecules were measured using the fluorescence decay measurements and were 6.31 and 3.18 ns for pc1 and pc2, respectively. Fluorescence decays shown in figure 7.4 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°) 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).

![Fluorescence decay curves for pc1 and pc2 with TCSPC measurements](image)

7.3 Multiphoton absorption studies by Z-scan technique:

7.3.1 Theoretical considerations for multiphoton absorption processes:

Assuming a spatial and temporal Gaussian profile for laser pulses we derive
the general equation for open aperture (OA) normalized energy transmittance
below:

Two photon absorption (TPA) involves a transition from ground state (1) of
a material to a higher-lying state (2) by the simultaneous absorption of two
photons via an intermediate virtual state, as schematically shown in figure 7.5(a).
In this case, the attenuation of the incident light is described by

\[
\frac{dl}{dz} = -\beta l^2
\]

where \( \beta \) is the two-photon absorption coefficient.
Three photon or multi photon absorption involves a transition from the ground state to a higher-lying state by the simultaneous absorption of three or more number photons via multiple numbers of virtual states as shown in figure 7.5(b). In this case, the attenuation of the incident light is described by

\[
\frac{dI}{dz} = -\alpha_n I^n
\]

where \(\alpha_n\) is the n-photon absorption coefficient.

Fig. 7.5: Schematic energy level diagram for (a) Two-photon absorption (TPA); (b) Multi-photon absorption (MPA).

\[
\alpha_n L = \frac{1}{(n-1)I_{in}^{n-1}} \left[ \frac{1}{1 + \alpha_n L(n-1)I_{in}^{n-1}} \right], \text{ where } T = \frac{I_{out}}{I_{in}}, \quad T^{n-1} = \frac{1}{1 + \alpha_n L(n-1)I_{in}^{n-1}}
\]
$T = \frac{1}{1 + \alpha_n L(n-1)I_{in}^{n-1}}$ 

$\frac{I_{in}}{\omega_0^2} = \frac{I_{00}}{\omega_Z^2}$, where $I_{in} = \frac{I_{00}}{1 + \frac{Z^2}{Z_0^2}}$ and $\omega_Z^2 = \omega_0^2 \left( 1 + \frac{Z^2}{Z_0^2} \right)$

$T = \frac{1}{\left[ 1 + (n-1)\alpha_n L \left( \frac{I_{00}}{\left( 1 + \left( \frac{Z}{Z_0} \right)^2 \right)} \right)^{n-1} \right]^{\frac{1}{n-1}}}$

$\Rightarrow T_{OA(nPA)} = \frac{1}{\left[ 1 + (n-1)\alpha_n L \left( \frac{I_{00}}{\left( 1 + \left( \frac{Z}{Z_0} \right)^2 \right)} \right)^{n-1} \right]^{\frac{1}{n-1}}}$

where $\alpha_n$ is the effective MPA coefficient ($n = 2$ for 2PA; $n = 3$ for 3PA, and so on), $I_{00}$ is the peak intensity (at $Z=0$), $I_{in}$ is intensity at sample position (if $Z$- is the distance from focal point $I_{in}$ ($I_Z$) is the intensity at that point), $Z_0 = \frac{\pi \omega_0^2}{\lambda}$ is Rayleigh range, $\omega_0$ is the beam waist at the focal point ($Z=0$), $dz$ is small slice of the sample, $I_{in}$ is input intensity and $I_{out}$ is output intensity of the sample.

![Schematic diagram of focused laser beam.](image)

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.
Multiphoton absorption properties...

\[ \begin{align*}
T_{OA(2PA)} &= \frac{1}{1 + \alpha_2 L_{\text{eff}} \left( \frac{I_{00}}{1 + \left( z / z_0 \right)^2} \right)} \\
T_{OA(3PA)} &= \frac{1}{1 + 2\alpha_3 L'_{\text{eff}} \left( \frac{I_{00}}{1 + \left( z / z_0 \right)^2} \right)^{1/2}}
\end{align*} \]  

The effective path lengths in the sample of length L for 2PA, 3PA is given as

\[ L_{\text{eff}} = \frac{1 - e^{-\alpha_0 L}}{\alpha_0} \quad L'_{\text{eff}} = \frac{1 - e^{-2\alpha_0 L}}{2\alpha_0} \]

7.3.2 Experimental Details:

Alkyl phthalocyanines were synthesized according to the procedures reported in literature [28] and were purified before use. All the experiments were performed with samples dissolved in chloroform and placed in 1-mm glass/quartz cuvettes. Amplified fs laser pulses of ~100 fs, 800 nm were used from the laser system as described in chapter 2. To make a complete study fo these molecules we also performed z-scan studies with ns pulses. A frequency doubled Nd:YAG laser (Spectra-Physics INDI-40) with 6 ns pulse duration and 10 Hz repetition rate was used for measurements in the ns regime. The Z-scan experimental set up as discussed in chapter 2. Z-scan studies [29] were performed by focusing the input beam using an achromatic doublet (f = 120 mm) for fs excitation and convex lens (f = 60 mm) for ns excitation. The peak intensities used in experiments were in the 200-400 GW/cm\(^2\) and 10-150 MW/cm\(^2\) range for fs and ns 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.
7.3.3 Three photon absorption with 800 nm, 100 fs pulses:

The open aperture scans for pc1 and pc2 recorded at 800 nm using ~100 fs pulses with an input irradiance of ~387 GW/cm² is shown in figure 7.6 and figure 7.7, respectively. We observed strong reverse saturable absorption (RSA) kind of behavior in the intensity range of 200–400 GW/cm² 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 7.1 and 7.2 and we found the best fit was obtained with the transmission equation for three-photon absorption (3PA). The dashed line in the figures 7.7 represents the theoretical fit with equation 7.1 and the solid line with equation 7.2. 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 $\chi^2 \approx 0.0002$ for pc1 and pc2. We obtained values of $\alpha_2$ and $\alpha_3$ for both the phthalocyanines with the theoretical fits with equation 7.1 and equation 7.2 for four different intensities in the range of 200–400 GW/cm².
Fig. 7.7: Open aperture Z-scan curves for pc1 and pc2 obtained with 800 nm, 100 fs pulses. Open circles represent experimental data while the solid line represents theoretical fit with three-photon absorption. Dashed line represents the fit obtained with two-photon absorption.
The intensity dependent behavior of $\alpha_2$ ($\alpha_3$) is depicted in figure 7.8(a) 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 $\sim 20\%$ in our case. We observed that for both phthalocyanines $\alpha_2$ increases linearly with intensity (lines are linear fits). However, as is evident in figure 7.8(b), we find that $\alpha_3$ remained constant with increasing intensities with average magnitudes to be $\sim 0.000091 \text{ cm}^3/\text{GW}^2$ and $\sim 0.000095 \text{ cm}^3/\text{GW}^2$ for pc1 and pc2 respectively. 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/cm² we noted that the sample started degrading.

We have evaluated the three-photon absorption cross-section ($\sigma_3$) using the following relation:

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

(7.3)

where $\omega$ is the frequency of the laser radiation. The values for $pc_1$ and $pc_2$ were $\sim 1.85 \times 10^{-80}$ cm$^6$/s$^2$/photon$^2$ and $\sim 1.93 \times 10^{-80}$ cm$^6$/s$^2$/photon$^2$ respectively.

For evaluating the strength of nonlinear coefficients obtained with our samples we compare them with those reported in literature, which are presented in table 7.1. We note that our values are one order higher than those reported in organic molecules with fs excitation [10, 11]. However, the values reported by He et al. [12] 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.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Wavelength, pulse-width</th>
<th>$\alpha_3$ (cm$^3$/GW$^2$) $\times 10^{-5}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>4,4’-bis(diphenylamino) stilbene (BDPAS) dendrimers</td>
<td>1100 nm, 150 fs</td>
<td>0.51</td>
<td>[10]</td>
</tr>
<tr>
<td>Multi-branched chromophore</td>
<td>1300 nm, 160 fs</td>
<td>0.385</td>
<td>[11]</td>
</tr>
<tr>
<td>ZnS NC’s</td>
<td>800 nm, 120 fs</td>
<td>2400</td>
<td>[12]</td>
</tr>
<tr>
<td>Tetra tert-butyl phthalocyanine (Free base and Zn)</td>
<td>800 nm $\sim 100$ fs</td>
<td>9.1 ($pc_1$) 9.5 ($pc_2$)</td>
<td>This work</td>
</tr>
</tbody>
</table>
7.3.3 Two photon absorption with 532 nm, 6 ns pulses

The open aperture Z-scans for both pc1 and pc2 illustrated a distinct reverse saturable absorption (RSA) behavior with 532 nm, 6 ns 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 ns 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 [6] along with the accurate knowledge of the intersystem crossing times is necessary to pin-point the exact contribution of each of these processes.

Figure 7.9 shows the representative plots of open aperture Z-scans obtained at three different intensities. The data obtained with ns pulses was fitted using equation 2. The best fit produced an effective nonlinear absorption coefficient ($\alpha_2$) 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.

![Open aperture z-scan plots of pc1 and pc2 at various input intensities upon excitation with 532nm, 6 ns laser pulses. The solid line represents the fitting of equation 7.1 for evaluating the nonlinear absorption coefficient.](image)

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 7.2 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 ns 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.

The two-photon absorption cross-section ($\sigma_{TPA}$) was calculated from the Eq. (7.4) given below:

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

$$N = N_A D$$

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, $\nu$ is the frequency of laser beam used. The two-photon absorption cross-sections ($\sigma_{TPA}$) were estimated to be $3.84 \times 10^{-46}$ and $5.21 \times 10^{-46}$ cm$^4$s photon$^{-1}$ for pc1 and pc2 respectively, which is reasonably high value for organic molecules.

Table 7.2: Comparison of two-photon absorption coefficient ($\alpha_2$) with values reported

<table>
<thead>
<tr>
<th>Sample</th>
<th>Wavelength</th>
<th>$\alpha_2$ (cm/GW)</th>
<th>Intensity (GW/cm$^2$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn Phthalocyanine</td>
<td>532 nm</td>
<td>47.74</td>
<td>-</td>
<td>[30]</td>
</tr>
<tr>
<td>Sm(Pc)$_2$, Eu(Pc)$_2$</td>
<td>596 nm, 604 nm</td>
<td>31, 50</td>
<td>0.143, 0.0835</td>
<td>[31]</td>
</tr>
<tr>
<td>Alkynyl phthalocyanines</td>
<td>532 nm</td>
<td>12 – 56</td>
<td>0.2 – 2.0</td>
<td>[32]</td>
</tr>
<tr>
<td>Nd(Pc)$_2$</td>
<td>532 nm</td>
<td>42</td>
<td>0.09</td>
<td>[33]</td>
</tr>
<tr>
<td>GaPc dimers</td>
<td>532 nm</td>
<td>32 - 35</td>
<td>0.5</td>
<td>[34]</td>
</tr>
<tr>
<td>Octaalkylphthalocyanines and their 15 metallated derivatives</td>
<td>532 nm</td>
<td>15 - 96</td>
<td>0.5</td>
<td>[35]</td>
</tr>
<tr>
<td><strong>Tetra tert-butyl phthalocyanine (Free base and Zn)</strong></td>
<td>532 nm</td>
<td>$\sim 310$ (pc1) $\sim 420$ (pc2)</td>
<td>0.006</td>
<td>This work</td>
</tr>
</tbody>
</table>
7.4 Nonlinear refraction properties with closed aperture Z-scans:

Figures 7.10 (a) and (b) illustrate the typical closed aperture Z-scan curve obtained for pc1 and pc2 with a peak intensity of \( \sim 220 \text{ GW/cm}^2 \). These curves represent normalized data obtained after division of closed aperture data with the open aperture data to eliminate the contribution of nonlinear absorption. The curves were obtained at low peak intensities to avoid contributions to the nonlinearity that are not electronic in origin. It is apparent that both pc1 and pc2 show negative nonlinearity as indicated by the peak-valley structure.

The closed aperture data, \( T_{CA} \), were fitted to the equation 3. [23].

\[
T_{CA} = 1 - \frac{4\Delta\phi_0 (z / z_0)}{[1 + (z / z_0)^2] [9 + (z / z_0)^2]} \tag{7.5}
\]

where \( \Delta\phi_0 \) is the phase change. We have evaluated the nonlinear refractive index using:

\[
n_2 (\text{cm}^2 \text{W}^{-1}) = \frac{|\Delta\phi_0| \lambda}{2\pi d_{oo} L_{eff}} \tag{7.6}
\]

The observed phase change (\( \Delta\phi_0 \)) was less than \( \pi \) (\( \Delta\phi_0 = 1.05 \) and 2.65 for pc1 and pc2 respectively).
The magnitude of the nonlinear refractive index $n_2$ evaluated was $\sim 0.56 \times 10^{-15}$ cm$^2$/W for pc1 and $\sim 1.14 \times 10^{-15}$ cm$^2$/W for pc2. With ns excitation the magnitude of nonlinear refractive index $n_2$ evaluated was $\sim 1.13 \times 10^{-11}$ cm$^2$/W for pc1 and $\sim 0.86 \times 10^{-11}$ cm$^2$/W for pc2. 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 ns laser pulse excitation was very high, possibly owing to the laser energy fluctuation, leading to larger error in the evaluation of the coefficients.

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 $\chi^{(3)}$ and the imaginary part $\chi^{(3)}$ in terms of the TPA coefficient ($\alpha_2$) of in Gaussian unit’s using the relation\(^{48,49}\)

$$\text{Re}[\chi^{(3)}](\text{esu}) = 10^{-4} \frac{\varepsilon_0 n_0^2 c^2}{\pi} n_2 (\text{cm}^2/\text{W})$$

$$\text{Im}[\chi^{(3)}](\text{esu}) = 10^{-2} \frac{\varepsilon_0 n_0^2 c^2 \lambda}{4\pi^2} \alpha_2 (\text{cm}/\text{W})$$

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

7.5 Optical limiting properties with ns pulses:

An ideal optical limiter, by definition, is a device that exhibits a linear transmittance below a threshold, and clamps the output to a constant above it, thus providing safety to sensors and eye as illustrated in figure 7.11. The limiting...
threshold \( (I_{1/2}) \) of the material is defined as the input intensity/fluence at which the transmittance reduces to half of the linear transmittance.

![Optical limiting diagram](image)

**Fig. 7.11**: Plots showing the optical limiting curves obtained for pc1 and pc2 for ns pumping.

The optical limiting data obtained for pc1 and pc2 at 532 nm using 6 ns pulses are shown in figure 7.11 with both the samples exhibiting limiting thresholds \( (I_{1/2}) \) of \(-0.45\) J/cm\(^2\). The mechanism for optical limiting could be predominantly excited state absorption since with ns 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.

7.6 Investigation of ultrafast nonlinear optical properties by degenerate four-wave mixing studies:

7.6.1. Experimental details

The DFWM set up was configured in the standard box-car geometry described in chapter 2 [36, 37]. The fundamental beam was divided into three nearly equal intensity beams (intensity ratio of 1:1.2:0.8) such that they form three corners of a square and are focused into the nonlinear medium (sample) both spatially and temporally. The resultant DFWM signal was detected at the fourth corner of the box which was generated due to the phase-matched interaction \( k_4 = k_3 - k_2 + k_1 \). All the experiments were performed with samples dissolved in chloroform and placed in 1-mm glass/quartz cuvettes. Sufficient care was observed to reduce the contribution of cuvette signal towards the overall DFWM signal by choosing appropriate focal conditions. The measurement of \( \chi^{(3)} \) values was performed at zero time delay of all the beams. We estimated the magnitude of \( \chi^{(3)} \) by maintaining the same polarization for all the three incident beams. A half-wave plate was introduced in the path of beam 2 to control the polarization required for the estimation of \( \chi^{(3)}_{\text{111}} \).

The transient DFWM profiles were obtained by delaying beam 3 with respect to the other two beams. Through nonlinear transmission measurements the input powers for three mixing pulses were chosen such that the effect of nonlinear absorption was minimal. We believe that the measured \( \chi^{(3)} \) at these intensities is, therefore, purely real in nature without any contribution from the imaginary component arising from multi-photon absorption. Moreover, the choice of low input intensities allowed us to neglect the association of higher order nonlinearities. The intensity measured at the sample due to the three input beams was \( \sim 2.7 \times 10^{10} \text{ W/cm}^2 \). Since all the samples had negligible linear
absorption at the working wavelength of 800 nm we expect the measured \( \chi^{(3)} \) and \( \gamma \) values to be off-resonant. All the studies were performed with solutions possessing concentrations of \( \sim 1 \times 10^{-4} \) M/L.

### 7.6.2 Third order nonlinear optical properties by DFWM measurements

The third order NLO susceptibility \( \chi^{(3)} \) was estimated by comparing the measured DFWM signal of the sample with that of neat CCl\(_4\) as reference \( \left[ \chi^{(3)} = 4.4 \times 10^{-14} \text{ esu} \right] \) measured with the same experimental conditions. The relationship used for \( \chi^{(3)} \) is [36]:

\[
\chi^{(3)}_{\text{sample}} = \left( \frac{n_{\text{sample}}}{n_{\text{ref}}} \right)^2 \left( \frac{I_{\text{sample}}}{I_{\text{ref}}} \right)^{1/2} \left( \frac{L_{\text{ref}}}{L_{\text{sample}}} \right) \alpha L_{\text{sample}} \left( \frac{1}{1 - e^{-\alpha L_{\text{sample}}}} \right) \chi^{(3)}_{\text{ref}} \tag{7.9a}
\]

where \( I \) is the DFWM signal intensity, \( \alpha \) is the linear absorption coefficient, \( L \) is sample path length, and \( n \) is the refractive index. We estimated \( \chi^{(3)} \) values to be \((4.26 \pm 0.43) \times 10^{-14} \text{ esu}\) and \((4.31 \pm 0.43) \times 10^{-14} \text{ esu}\) for pc1 and pc2 respectively for an input intensity of \( \sim 2.7 \times 10^{10} \) W/cm\(^2\). One of the main sources of error that arises in experiments is through the intensity fluctuations of laser pulses. This problem is overcome by taking the averaged data of 1000 pulses. The second major source of error could be from the determination of solutions concentration. Considering all the unforced random experimental errors we estimate an overall error of \( \sim 10\% \) in our calculations by repeating the experiment few times. In an isotropic medium \( \chi^{(3)} \) has three independent components, namely, \( \chi^{(3)}_{1111}, \chi^{(3)}_{1122}, \) and \( \chi^{(3)}_{1212} \). In the case of non-resonant electronic nonlinearity, \( \chi^{(3)}_{1111} = 3 \chi^{(3)}_{1212} = 3 \chi^{(3)}_{1122} \) when the three input beams are all vertically polarized and the corresponding \( \chi^{(3)} \) obtained would be \( \chi^{(3)}_{1111} \). To determine \( \chi^{(3)}_{1212} \), the probe beam has to be orthogonally polarized with respect to the two pump beams. We measured the values for \( \chi^{(3)}_{1212} \) to be \((1.47 \pm 0.15) \times 10^{-14} \text{ esu}\) and \((1.49 \pm 0.15) \times 10^{-14} \text{ esu}\) for pc1 and pc2, respectively, and the obtained ratio of
\( \chi_{111}^{(3)} \) to \( \chi_{1212}^{(3)} \) was \( \sim 2.9 \) suggesting that there was no significant contribution arising from the coherent coupling effects [19]. We estimated the \( \chi^{(3)} \) value of phthalocyanines in a solid film by assuming a density of \( \sim 1 \text{ g/cm}^3 \) using the following relationship [38]

\[
\chi_{\text{thin film}}^{3} = \frac{N}{N_{\text{solution}}} \chi_{\text{solution}}^{3}
\]  

(7.9b)

where \( N \) is the assumed density of the phthalocyanines solid and \( \chi_{\text{solution}}^{3} \) are the value estimated from Eq.1. The estimated values for the solid films of pc1 and pc2 were \((5.74 \pm 0.57) \times 10^{-10}\) esu and \((5.37 \pm 0.54) \times 10^{-10}\) esu, respectively which are among the largest reported values for these types of molecules. The measured \( \chi^{(3)} \) value of chloroform was insignificant compared to the \( \chi^{(3)} \) value of the samples under similar experimental conditions and thus the contribution from pure solvent was neglected.

![Graphs showing the cubic dependence of DFWM signal intensity for pc1 and pc2 as a function of input intensity.](image)

**Fig 7.12:** Plots showing the cubic dependence of DFWM signal for pc1 and pc2 as a function of input intensity
The intensity dependence of the DFWM signal amplitude in both the samples is presented in figure 7.12. At relatively low input intensities (<220 GW/cm²) the DFWM signal amplitude followed a dependence that is essentially cubic (with a slope of ~2.85) clearly indicating that the nonlinearity behaves in a Kerr-like fashion and that origin of DFWM does not have contribution from any multi-photon absorption process in which case the slope of the curve would have been different from 3 [39, 40]. To determine whether our molecules possessed two-photon absorption coefficient $\beta$, which corresponds to the imaginary part of $\chi^{(3)}$, we performed the nonlinear transmission measurements. For both the molecules we obtained straight lines that intercept the ordinate axis and their values were less than unity, suggesting a one-photon contribution to the absorption. This supports our argument that third-order optical susceptibility of our molecules can be attributed to the nonlinear refractive index at 800 nm. Figure 7.13 shows the linearity in the transmission versus the input intensity for the range of intensities from $7 \times 10^9$ to $2.5 \times 10^{11}$ W/cm². The DFWM signal was measured at an input intensity of $I_{in} = 2.7 \times 10^{10}$ W/cm² that was much lower than required for nonlinear absorption which was ~$2.15 \times 10^{11}$ W/cm².

![Fig. 7.13: Plot of output transmittance versus input power, LT represents the linear transmittance at 800 nm.](image)
To estimate the second order hyperpolarizability, $\gamma$, at the molecular level we used the following relation [36]:

$$\gamma_{\text{sample}} = \chi^{(3)} / T^4 N_0 ,$$

(7.10)

where $N_0$ is the number density of the molecules per milliliter, and $T = (n_{\text{sample}}^2 + 2) / 3$ is the local field factor. We assume that the solvent makes negligible contribution to the signal. We estimated the $\gamma$ values to be $(4.27 \pm 0.43) \times 10^{-31}$ esu and $(4.32 \pm 0.43) \times 10^{-31}$ esu for pc1 and pc2 respectively which are reasonably large in the fs regime compared to some of the phthalocyanines and their analogues reported recently [19-26]. The metallic phthalocyanine had marginally higher nonlinearity and the reason could be attributed to the presence of the metal ion.

Figure 7.14: Temporal profiles of DFWM signals of pc1 and pc2
Figure 7.14 shows the temporal response of the DFWM signal recorded as a function of the probe delay. The signal was fitted with a Gaussian function (solid curve) as given by,

\[ F(t) = \sqrt{\frac{2}{\pi}} \left( \frac{A}{\omega} \right) \exp \left[ -2 \left( \frac{x - x_c}{\omega} \right)^2 \right] \]  

(7.11)

where \( A \) is a weight parameter, \( x \) is a variable that corresponds to the delay and \( \omega \) is the obtained FWHM of the fit. The full width half maximum (FWHM) of the fit was similar to the response signal obtained from pure CCl_4. The signal profiles were nearly symmetric about the maximum (i.e. zero time delay) illustrating that the response times of the nonlinearities were much shorter than the pulse duration (100 fs). Such an instantaneous response is indicative of the Kerr effect (electronic component) from the distortion of the large \( \pi \)-conjugated electron charge distribution of phthalocyanine molecules. This instant response enhances their potential for photonics switching applications. Interestingly, the trapping levels originating from the multi-conformational and polaronic states situated in the HOMO-LUMO gap also play an important role in the DFWM for measurements in solutions [41].

### 7.6.3 Figures of merit (FOM) for photonic switching applications

A convenient way to quantify the losses is to consider the appropriate merit factors formulated by Stegeman for photonic switching applications [21-24]. These figure of merit (FOM) factors are related to the maximum nonlinear phase shift \( \Delta \varphi \) through

\[ \Delta \varphi = \frac{2\pi}{\lambda} \int_0^L n_2 I(z)dz \]  

(7.12)

obtained in a given material within a propagation distance \( L \) corresponding to an absorption length. \( \Delta \varphi \) change of \(~2\pi\) is essential for switching applications. For one-photon absorption as the dominant loss mechanism, the absorption depth can
be defined as $\alpha_i^{-1}$, where $\alpha_i$ is the absorption coefficient. We have the merit factor $W$ defined as

$$W = \frac{n_2 I_{\text{sat}}}{\alpha_i \lambda}$$

where $\lambda$ is the wavelength and $I_{\text{sat}}$ is the light intensity at which the nonlinear refractive-index change saturates. The nonlinear phase shift obtainable on the distance of $\alpha_i^{-1}$ is equal to $1.26 \, \text{W} \, \pi$ rad. Therefore the pre-requisite for superior FOM is:

$$W > 1$$  \hspace{1cm} (7.13)

when the nonlinear losses prevail with materials with strong multi-photon absorption, the nonlinear phase shift will be limited, too. The absorption depth can then be defined as $(\alpha_2 I_0)^{-1}$ and $(\alpha_3 I_0^2)^{-1}$ where $\alpha_2$ and $\alpha_3$ are the two-photon absorption and three-photon coefficient and $I_0$ stands for the incident light. As the absorption depth is intensity dependant, it follows that the obtainable phase shift is now intensity independent. The corresponding FOMs can be presented as:

$$T^{-1} = \frac{n_2}{\lambda \alpha_2}$$  \hspace{1cm} (7.14)

$$V^{-1} = \frac{3n_2}{\lambda \alpha_3 I_0}$$  \hspace{1cm} (7.15)

For a successful operation of a photonics device made of such lossy materials to acquire nominal $2\pi$ phase shift the following inequalities must be satisfied

$$T < 1, \text{ and } V < 0.68$$  \hspace{1cm} (7.16)

To estimate the values of $n_2$ we used the data obtained from the calculation of $\chi^{(3)}$. We estimated $n_2$, which is related to the real part of $\chi^{(3)}$, using the relation [34]:

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\[
 n_2 (\text{cm}^2 / \text{W}) = \frac{0.0395}{n_0^2} \chi^{(3)} \text{(esu)}
\]  

(7.17)

By performing intensity dependent measurements of \(\chi^{(3)}\) we evaluated the corresponding \(n_2\) and observed that \(n_2\) was independent of the input intensity (see figure 7.15) highlighting the existence of pure nonlinearity. We achieved an average \(n_2\) value of \(9.58 \times 10^{-16} \text{ cm}^2 / \text{W}\) and \(9.72 \times 10^{-16} \text{ cm}^2 / \text{W}\) for pc1 and pc2, respectively. For an intensity of \(\sim 190 \text{ GW/cm}^2\), where nonlinear absorption is negligible, and \(\alpha\) for pc1 and pc2 were 0.06 cm\(^{-1}\) and 0.09 cm\(^{-1}\), respectively, we estimated W to be \(\sim 37.9\) and \(\sim 25.6\) for pc1 and pc2 respectively. Though the nonlinearities are higher in pc2 in contrast to pc1 higher linear absorption resulted in lower figure of merit. These are superior to the required values for photonic switching device with one-photon contribution.

**Figure 7.15**: Plot of \(n_2\) as a function of input intensity
For input intensities $> 215 \text{ GW/cm}^2$ we expect substantial contribution from multi-photon absorption. Our earlier studies demonstrated and confirmed these phthalocyanines possessed strong three-photon absorption coefficient (3PA) with fs pulse excitation near 800 nm. The measured 3PA coefficients ($\alpha_3$) were independent of input intensity and the magnitudes were $\approx 0.000091 \text{ cm}^3/\text{GW}^2$ and $\approx 0.000095 \text{ cm}^3/\text{GW}^2$ for pc1 and pc2 respectively. The $V$ parameter calculated from equation 8 and for an input intensity of 230 GW/cm$^2$ was 0.57 and 0.59 for pc1 and pc2, respectively. The combination of instantaneous nonlinear response and excellent figures of merit propels pc1 and pc2 as ideal for photonic switching applications. We summarize the evaluated values of nonlinear coefficients and FOM in table 7.3.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\chi^{(3)}$ esu$^a$</th>
<th>$\gamma$ esu$^a$</th>
<th>$n_2$ (cm$^2$/W)</th>
<th>W $^b$</th>
<th>V $^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>pc1</td>
<td>$(4.26\pm 0.42)\times 10^{-14}$</td>
<td>$(4.27\pm 0.42)\times 10^{-31}$</td>
<td>$(9.58\pm 0.95)\times 10^{-16}$</td>
<td>37.8</td>
<td>0.57</td>
</tr>
<tr>
<td>pc2</td>
<td>$(4.31\pm 0.43)\times 10^{-14}$</td>
<td>$(4.32\pm 0.43)\times 10^{-31}$</td>
<td>$(9.72\pm 0.97)\times 10^{-16}$</td>
<td>25.6</td>
<td>0.59</td>
</tr>
</tbody>
</table>

$^a$ I = 27 GW/cm$^2$; $^b$ I = 190 GW/cm$^2$; $^c$ I = 230 GW/cm$^2$

To put in perspective the merits of our molecules we have tried to compare the coefficients and FOM obtained for our phthalocyanines with some of the other molecules reported recently. Tran et al. [19] reported resonantly enhanced nonlinearities of their squaraine dyes near 700 nm with $\gamma$ values of the order of $10^{-32}$ esu. Fu et al. [20] reported large nonlinearities in naphthalocyanine derivatives near 800 nm with value in the range of $2\times 10^{-29}$ esu to $7\times 10^{-29}$ esu. However, the large values (two orders of magnitude higher) obtained were again attributed to the resonance enhancement. All the molecules they investigated had strong absorption near 800 nm. Li et al. [21] presented their results on centrosymmetric squaraines possessing large nonlinearities studied using fs
DFWM. They achieved $\gamma$ values of $10^{-31}$ esu with fast response times (<100 fs). Their group [22] also reported similar studies on novel diarylethene–phthalocyanine dyads with largest $\gamma$ value for one of the compounds being $10^{-30}$ esu. Kasatani et al. [23] also reported large resonant nonlinearities ($10^{-28}$ esu) for cyanine dyes near 800 nm. Huang et al. [24] measured off-resonant nonlinearities of dihydroxy phosphorus (V) tetrabenzotriazacorroles, which are phthalocyanine analogues, in the range of $10^{-31}$ esu with sub-50 fs response time. Prabhakar et al. presented their results of croconate dyes obtained with 100 fs pulses where off-resonant $\gamma$ values of $10^{-32}$ esu were reported [25]. It is apparent that our molecules possess better or similar values obtained for $\gamma$ and the response times with exception being that reported in reference [28]. We expect further enhancement in the nonlinearities for our sample in the resonant case. In terms of FOM achieved for our molecules, Gu et al. [42] presented their measurements for chalcone derivatives with optimum values for W as 26.6, T as 0.13, and V as 0.64 which are comparable to those obtained for our phthalocyanines.

### 7.7 Conclusions

- From the fs open aperture z-scan data we conclude that these molecules exhibit three-photon absorption (3PA) behavior. The measured 3PA coefficients ($\alpha_3$) were independent of input intensity and the magnitudes were $\sim 0.00091$ cm$^3$/GW$^2$ and $\sim 0.00095$ cm$^3$/GW$^2$ for pc1 and pc2 respectively. This is, to best of our knowledge, first report on the 3PA behavior of phthalocyanines.

- The ns data indicated strong reverse saturable absorption and optical limiting. The nanosecond open aperture Z-scan studies revealed strong effective nonlinear absorption coefficient ($\alpha_2$) of $\sim 310$ and $420$ cm/GW for pc1 and pc2 respectively. These phthalocyanines exhibited strong optical limiting properties in solutions with ns excitation with recorded limiting thresholds of $\sim 0.45$ J/cm$^2$. 

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• We observed a large overall nonlinearity using ns pulses while the fs pumping indicated a moderate nonlinearity. The sign of nonlinearities for both fs and ns-regimes were negative in nature.

• We measured large off-resonant second hyperpolarizabilities ($\gamma$) for these molecules with ultrafast NLO response. The measured values of $\gamma$ were $(4.27 \pm 0.43) \times 10^{-31}$ esu and $(4.32 \pm 0.43) \times 10^{-31}$ esu for pc1 and pc2, respectively.

• The merit factors for photonic switching applications were estimated. For one-photon absorption as the dominant loss mechanism we estimated $W$ to be $\sim 37.9$ and $\sim 25.6$ for pc1 and pc2, respectively. For three-photon absorption as the dominant loss mechanism we estimated $V$ parameter as 0.57 and 0.59 for pc1 and pc2, respectively, for an input intensity of 230 GW/cm².

7.8 References:


