

Femtosecond and nanosecond nonlinear optical properties of alkyl phthalocyanines studied using Z-scan technique

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Abstract

We report 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.

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1. Introduction

Among the conjugated organic molecules possessing third-order nonlinear optical (NLO) properties phthalocyanines and their derivatives occupy a prominent position owing to their versatility, high thermal and chemical stability along with the ease of preparation and purification [1–6]. 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 [7]. Recent studies have extracted a large variety of peripheral substituents for improving the poor solubility of unsubstituted phthalocyanines. The large optical nonlinearities of phthalocyanines due to delocalized π electrons are envisaged in applications such as optical processing devices, practical optical limiters,

and all-optical switches [1–6]. 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 [8–12]. Recent studies suggest phthalocyanines possess strong two-photon absorption [2PA] cross-sections. In organic materials 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. Such materials will have a broad impact in biology and medicine through three-photon induced photodynamic therapy (PDT) in cancer treatment. In recent times novel materials including organic fluorophores like halogenated fluorine molecules, polydiaetylenes, semiconductor nanoparticles have been investigated for their 3PA properties using femtosecond (fs) and picosecond pulses in the NIR spectral regions [13–18]. However, we discovered that there are sporadic reports on organic molecules exhibiting 3PA in the

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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 polydiaecylenes in the excitation wavelength region from $\lambda_{\text{ex}} = 800$ to 1600 nm [13]. Significant studies [19,20] on application of phthalocyanines in PDT 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. In this Letter we present results of our studies on the nonlinear optical properties of 2(3), 9(10), 16(17), 23(24) tetra *tert*-butyl phthalocyanine [herewith referred to as pc1] and 2(3), 9(10), 16(17), 23(24) tetra *tert*-butyl Zinc phthalocyanine [herewith referred to as pc2] in solution 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. Our study concludes that these alkyl phthalocyanines are prospective candidates for multi-photon applications in the fs regime.

2. Experimental details

Alkyl phthalocyanines were synthesized according to the procedures reported in the literature [21] and were purified before use. The details of molecular structure and the absorption spectra have been reported elsewhere [22]. All the experiments were performed with samples dissolved in chloroform and placed in 1-mm glass/quartz cuvettes. Femtosecond laser pulses were obtained from a conventional chirped pulse amplification system comprising of an oscillator (MaiTai, Spectra-Physics Inc.) that delivered ~ 80 fs, 82 MHz at 800 nm and a regenerative amplifier (Spitfire, Spectra Physics Inc.), from which we obtained 1 kHz amplified pulses of ~ 100 fs, with output energy of ~ 1 mJ. 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. Z-scan studies [21] 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/cm² and 10–150 MW/cm² range for fs and ns pulse excitation, respectively. All the studies were performed with solution concentrations of 5×10^{-4} M providing $\sim 75\%$ linear transmission for 532 nm and 85% for 800 nm. We maintained similar intensity levels ensuring identical experimental conditions for both the samples.

3. Results and discussion

3.1. Theoretical consideration for order of absorption process using Z-scan studies

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. [23,24] we have the general equation for open aperture (OA) normalized energy transmittance given by

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

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 with an analytical expression for OA scans for only three-photon absorbers.

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

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

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 $L_{\text{eff}} = \frac{1-e^{-\alpha_2 L}}{\alpha_2}$, $L'_{\text{eff}} = \frac{1-e^{-2\alpha_3 L}}{2\alpha_3}$.

3.2. Three-photon absorption with 800 nm, 100 fs pulses Z-scan studies

Fig. 1 shows representative open aperture scans for pc1 and pc2 recorded at 800 nm using ~ 100 fs pulses with an input irradiance of ~ 387 GW/cm². We observed strong reverse saturable absorption (RSA) kind of behavior in the intensity range of 200–400 GW/cm². Obtained experimental data was fitted using Eqs. (1) and (2) and we found the best fit was obtained with the transmission equation for three-photon absorption (3PA). The dashed line in the figure represents the theoretical fit with Eq. (1) and the solid line with Eq. (2). It is evident that 3PA is the dominant mechanism for the observed RSA kind of behavior. The dashed line in the Fig. 1 represents the fit using Eq. (1) confirming that the process has to be other than 2PA. To verify the presence of 3PA in the OA data we carried out the least square fitting test and obtained a value of $\chi^2 \sim 0.0002$ for pc1 and pc2. Owing to large peak intensities at the focal point with fs laser excitation 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

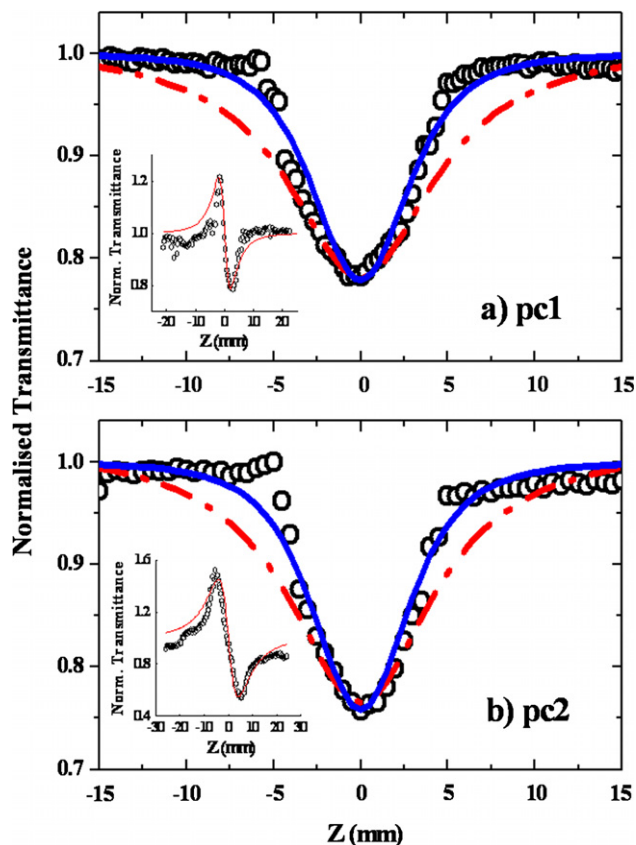


Fig. 1. Open aperture Z-scan curves for obtained with 800 nm, 100 fs pulses. Inset shows the closed aperture scans. Open circles represents experimental data while the solid line represents theoretical fit with three-photon absorption. Dashed-dotted line represents the fit obtained with two-photon absorption.

enhancement for these processes. In order to distinguish the multiphoton process contributing to the present data we performed intensity dependent absorption studies in the OA configuration. We obtained values of α_2 and α_3 for both the phthalocyanines with the theoretical fits with Eqs. (1) and (2) for four different intensities in the range of 200–400 GW/cm².

The intensity dependent behavior of $\alpha_2(\alpha_3)$ is depicted in Fig. 2a and b 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 α_2

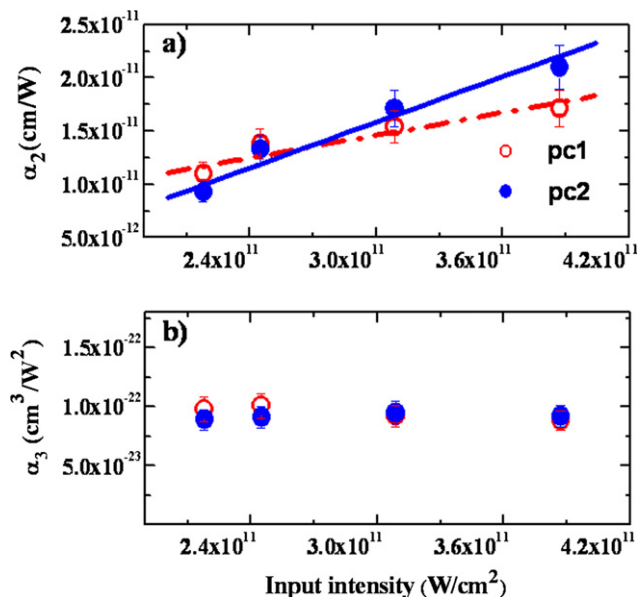


Fig. 2. Plots showing the comparison of intensity dependence of (a) α_2 and (b) α_3 for pc1 (open circles) and pc2 (solid circles) obtained with 800 nm pulses.

increases linearly with intensity (lines are linear fits). However, as is evident in Fig. 2b, we find that α_3 remained constant with increasing intensities. 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. For evaluating the strength of nonlinear coefficients obtained with our samples we compare them with those reported in literature, which are presented in Table 1. We note that our values are one order higher than those reported in organic molecules with fs excitation [14,15]. However, the values reported by He et al. [16] 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. We have evaluated the three-photon absorption cross-section (σ_3) using the relation $\sigma_3 = \frac{(h\omega)^2}{N} \alpha_3$, where ω is the frequency of the laser radiation. The values for pc1 and pc2 were $\sim 1.85 \times 10^{-80} \text{ cm}^6 \text{ s}^2/\text{photon}^2$ and $\sim 1.93 \times 10^{-80} \text{ cm}^6 \text{ s}^2/\text{photon}^2$, respectively.

Table 1
Comparison of three-photon and two-photon absorption coefficient (α_3) with values reported in the literature

Three-photon absorption coefficient (fs data)			Two-photon absorption coefficient (ns data)		
Sample	Wavelength, pulse-width	α_3 (cm ³ /GW ²) $\times 10^{-5}$	Sample	Wavelength	α_2 (cm/GW)
4,4'-Bis(diphenylamino) stilbene (BDPAS) dendrimers	1100 nm, 150 fs [14]	0.51	Zn Phthalocyanine	532 nm, 6 ns [23]	47.74
Multi-branched chromophore	1300 nm, 160 fs [15]	0.385	Alkynyl phthalocyanines	532 nm, 6 ns [24]	12–56
ZnS NC's	800 nm, 120 fs [16]	2400	Nd(Pc) ₂	532 nm, 6 ns [25]	42
Tetra <i>tert</i> -butyl phthalocyanine (Free base and Zn)	800 nm, ~ 100 fs this work	9.1 (pc1) 9.5 (pc2)	Tetra <i>tert</i> -butyl phthalocyanine (Free base and Zn)	532 nm, 6 ns	~ 310 (pc1) ~ 420 (pc2)

Inset of Fig. 1a 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} , was fitted to the standard equation for closed aperture transmittance [23]. The magnitude of the nonlinear refractive index n_2 evaluated was $\sim 0.56 \times 10^{-15} \text{ cm}^2/\text{W}$ for pc1 and $\sim 1.14 \times 10^{-15} \text{ cm}^2/\text{W}$ for pc2.

3.3. Two photon absorption with 532 nm, 6 ns pulses Z-scan studies

Fig. 3 shows representative open aperture scans of pc1 and pc2 with 532 nm, 6 ns pulses. We observed reverse saturable absorption (RSA) in these molecules for input intensities in the range of 1–500 MW/cm^2 . For intensities above 10^8 W/cm^2 the normalized transmission dropped below 0.3 indicating 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

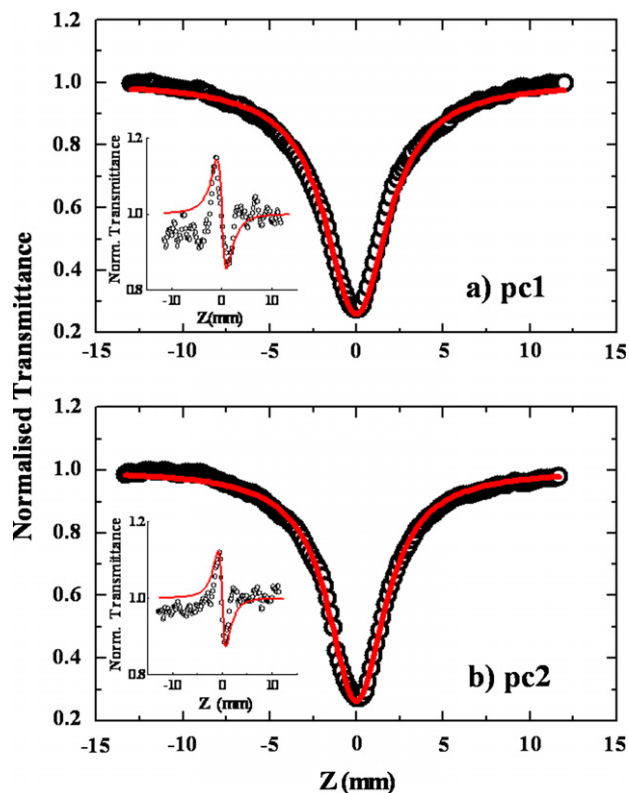


Fig. 3. Open aperture Z-scan curves of with 532 nm, 6 ns pulses. The inset shows the closed aperture scans. Open circles represents experimental data while the solid line represents theoretical fit.

Table 2

Summary of all the nonlinear optical parameters estimated in this study

Pulses used	Nonlinear coefficient	pc1	pc2
800 nm 100 fs	$\alpha_3 \text{ (cm}^3/\text{GW}^2)$	0.00091	0.00095
	$\sigma_3 \text{ (cm}^6 \text{ s}^2 \text{ photon}^{-2}) \times 10^{-80}$	1.85	1.94
	$n_2 \text{ (cm}^2/\text{W}) \times 10^{-15}$	0.56	1.14
532 nm 6 ns	$\alpha_2 \text{ (cm/GW)}$	310	420
	$n_2 \text{ (cm}^2/\text{W}) \times 10^{-11}$	1.13	0.86
	$\text{Re}[\chi^{(3)}] \text{ (esu)} \times 10^{-10}$	5.93	4.59
	$\text{Im}[\chi^{(3)}] \text{ (esu)} \times 10^{-10}$	0.95	0.71
	$ \chi^{(3)} \text{ (esu)} \times 10^{-10}$	6.02	4.64

depending on the excitation wavelength. A comprehensive five-level modeling [25] along with the accurate knowledge of the excited state life times is necessary to pin-point the exact contribution of each of these processes. However, for 532 nm excitation we can approximate the nonlinear absorption to an effective process and evaluate the nonlinear coefficient [26–31]. 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 data obtained with ns pulses was fitted using Eq. (1). The best fit produced an effective nonlinear absorption coefficient (α_2) of 310 cm/GW for pc1 and 420 cm/GW for pc2 measured with a peak intensity of $6 \times 10^6 \text{ W/cm}^2$. Insets of Fig. 3a and b shows the typical closed aperture Z-scan curve obtained for pc1 and pc2 with a peak intensity of $\sim 6.5 \text{ MW/cm}^2$. The magnitude of nonlinear refractive index n_2 evaluated was $\sim 1.13 \times 10^{-11} \text{ cm}^2/\text{W}$ for pc1 and $\sim 0.86 \times 10^{-11} \text{ cm}^2/\text{W}$ for pc2. The real and imaginary parts of third-order nonlinearity for pc1 and pc2 were also evaluated. $\text{Re}[\chi^{(3)}]$ was estimated to be $\sim 5.93 \times 10^{-10} \text{ esu}$ and $\sim 4.59 \times 10^{-10} \text{ esu}$ and $\text{Im}[\chi^{(3)}]$ to be $\sim 0.97 \times 10^{-10} \text{ esu}$ and $\sim 0.71 \times 10^{-10} \text{ esu}$ for pc1 and pc2, respectively. Table 1 shows the comparison of α_2 obtained in this study with the ones reported recently by other groups and we find that our alkyl phthalocyanines possess at least two orders higher magnitude than other phthalocyanines reported.

We summarize all our evaluated values for the fs and ns nonlinear response of the phthalocyanines in Table 2. Arising from the strong nonlinear absorption property our alkyl phthalocyanines also exhibited strong optical limiting properties in solutions with ns excitation. We recorded limiting thresholds as low as $\sim 0.45 \text{ J/cm}^2$. Recent studies [32,33] established enhanced optical limiting from phthalocyanines in a polymer matrix and we expect superior limiting with our phthalocyanines in thin film form since these are soluble in common solvents implying that they can easily be doped in polymers. A detailed account of optical limiting behavior in solutions and thin films will be reported elsewhere.

4. Conclusions

We presented our results on the NLO properties of a new class of tetra *tert*-butyl phthalocyanines. We carried

out open aperture Z-scan studies with 800 nm, 100 fs and 532 nm, 6 ns pulses to characterize the nonlinear absorption behavior in detail. From the femtosecond data we conclude that these molecules exhibit three-photon absorption (3PA) behavior. The ns data indicated strong reverse saturable absorption and optical limiting. We observed a large nonlinearity using ns pulses while the fs pumping indicated a moderate nonlinearity.

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