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Picosecond optical nonlinearities in symmetrical and unsymmetrical phthalocyanines studied using the Z-scan technique

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Abstract. We present our experimental results on the picosecond nonlinear optical (NLO) studies of symmetrical and unsymmetrical phthalocyanines, examined using the Z-scan technique. Both the open-aperture and closed-aperture Z-scan curves for three samples were recorded and the nonlinear coefficients were extracted from the theoretical fits. The nonlinear absorption/refraction contribution from the solvent was also identified. The observed open aperture behaviour for these molecules is understood in terms of the absorption coefficients of these molecules near 800 nm and the peak intensities used. It is established that these phthalocyanines exhibit large optical nonlinearities and, hence, are suitable for optical limiting applications.

Keywords. Z-scan; unsymmetrical phthalocyanines; picosecond; two-photon absorption.

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1. Introduction

Organic compounds such as porphyrins and phthalocyanines possess several advantages over their counterpart inorganic materials as far as their third-order nonlinear optical (NLO) properties are concerned. Some of the important characteristics of these classes of compounds are their (i) planar structure, (ii) excellent chemical and thermal stabilities, (iii) large optical nonlinearity, (iv) response time in the picosecond and femtosecond time domains and (v) ease of preparation/purification. Among the conjugated organic molecules possessing large third-order NLO properties, phthalocyanines and their derivatives occupy a prominent position owing to these properties [1–10].

The Z-scan method, introduced by Sheik-Bahae *et al* [11], is a standard tool for determining nonlinear index of various materials because of its simplicity and accuracy. The intensity-dependent nonlinear phase-front distortions of the beam

are measured in terms of the variations of the transmittance through an aperture placed in the transmitted beam as a function of Z. The knowledge of ultrashort pulse nonlinear refractive index aids in deciding appropriate materials for optical switching applications. Molecules with strong nonlinear absorption coefficient (two-photon or three-photon) find applications in imaging and lithography. Herein we present some of our results on the NLO measurements of three phthalocyanines (herewith denoted as A: PCH001, B: PCH003; C: ZnOCPc) in solution studied using Z-scan technique employing ∼2 ps pulses at 800 nm. The nomenclatures for the compounds are 2-(3-(butane-1,4-dioic acid)-9(10),16,(17),23(24)-tri tert-butyl phthalocyanine zinc(II) (unsymmetrical PCH001; MW = 862.3), 2-(3-(butane-1,4-dioic acid)-8,11,15,18,22,25-hexakis-(butyloxy) phthalocyanine zinc(II) (unsymmetrical PCH003; MW = 1126.6) and 2(3),9(10),17(18),23(24)-((1,2-(dicarboxyethyl))-phthalocyanato zinc(II) (symmetrical ZnOCPc; MW = 1042.2). Details of the structures for PCH001 and PCH003 are reported in [12]. ZnOCPc was synthesized and purified as per the techniques reported in [13]. From the ps open-aperture Z-scan data we derived the magnitude of nonlinear absorption. We estimated the sign and magnitude of third-order refractive nonlinearities from closed aperture data.

2. Experimental details

Z-scan measurements were performed using the amplified Ti:sapphire laser system (LEGEND, Coherent) delivering nearly transform-limited pulses with a duration of ∼2 ps and a repetition rate of 1 kHz at 800 nm. The amplifier was seeded with ∼15 fs pulses from the oscillator (MICRA, Coherent). Laser pulse energies in the range of ∼few μJ with a repetition rate of 1 kHz were used for the measurements. The input beam was spatially filtered to obtain a pure Gaussian profile in the far field. The beam was focussed using 200 mm focal length lens into the sample, placed

Table 1. Summary of the NLO coefficients obtained from the present study.

Sample	n_2 (m^2/W) $\times10^{-19}$	n_2 (esu) $\times10^{-12}$	Re$\lvert\chi^{(3)}\rvert$ (m^2/V^2) $\times10^{-21}$	Re$\lvert\chi^{(3)}\rvert$ (esu) $\times10^{-13}$	β (m/W) $\times10^{-12}$	Im$\lvert\chi^{(3)}\rvert$ (m^2/V^2) $\times10^{-21}$	$\lvert\chi^{(3)}\rvert$ (m^2/V^2) $\times10^{-21}$	$\lvert\chi^{(3)}\rvert$ (esu) $\times10^{-13}$
PCH001	−2.95	−0.95	−2.9	−1.3	1.06	0.53	2.90	2.13
PCH003	−3.75	−1.2	−3.69	−1.76	2.75	1.72	4.07	2.91
PCH001 (I_{oo} = 154 GW/cm^2)					0.075 Is = 30 GW/cm^2			
PCH003 (I_{oo} = 405 GW/cm^2)					0.08 Is = 35 GW/cm^2			
ZnOCPc	−1.3	−0.42	−1.2	−0.61	α_3 (cm^3/W^2) 4.5×10^{-22}	Im$\lvert\chi^{(5)}\rvert$ (m^4/V^4) 4.6×10^{-29}		

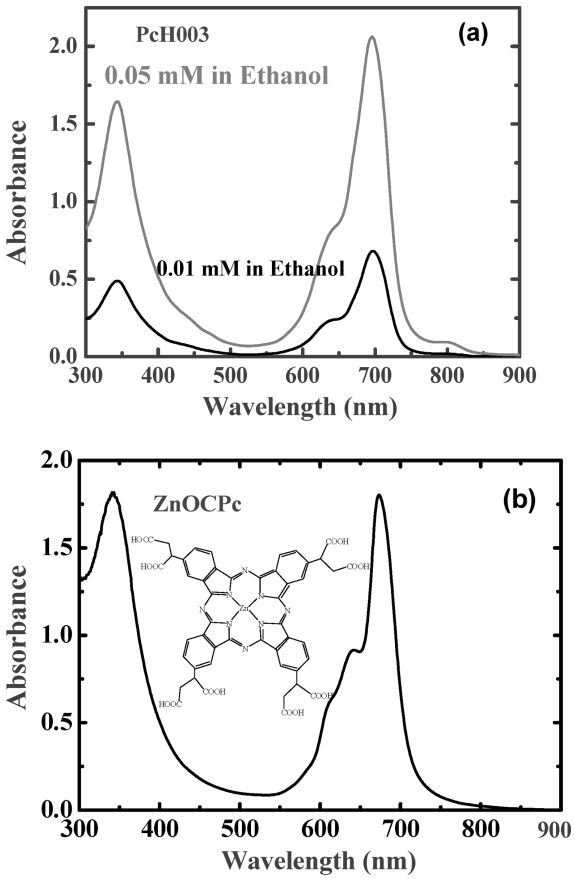

Figure 1. Absorption spectra of (**a**) PCH003 dissolved in ethanol and (**b**) ZnOCPc dissolved in water. Inset shows the structure.

in 1-mm path length quartz/glass cuvettes. All the experiments were carried out with samples having concentrations in the range of $2–3\times10^{-4}$ M. The beam waist (ω_0) at the focal plane was estimated to be $\sim$30 μm with a corresponding Rayleigh range $\sim$3.3 mm. Pulse energies were kept low in order to avoid contribution from higher-order nonlinearities. The sample position was scanned and the transmittance was recorded, along the z-axis, in open-aperture and closed-aperture configurations. The translation stage (Newport; ILS 250PP) had a resolution of 0.5 μm. The transmitted power was measured using a power meter (PS19, Coherent).

3. Results and discussion

The linear absorption spectra of the phthalocyanines studied are shown in figure 1. Two main absorption bands were observed: a Q-band in the vicinity of 700 nm and a B-band in the 350 nm spectral region. These materials have a window,

between these two absorption bands, with high linear transmittance making them attractive as optical limiters for the visible spectral region (∼420–650 nm). The absorption spectra for PCH001/PCH003 and ZnOCPc were recorded with ethanol and water as the solvents, respectively. The linear absorption for all the molecules was minute at the excitation wavelength. Figure 2 shows the closed-aperture Z-scan along with fit for ZnOCPc in water and PCH003 in ethanol at an intensity of 1×10^{11} W/cm^2 and 8.7×10^{10} W/cm^2 respectively. The scattered points (open circles for PCH003 and open triangles ZnOCPc) are the experimental data while solid lines are the theoretical fits. The peak followed by a valley (normalized transmittance obtained from the closed-aperture Z-scan data) indicates that the sign of nonlinear refraction n_2 negative (self-defocusing) at 800 nm. Generally, closed-aperture scans contain contributions from both nonlinear absorption and nonlinear refractive index. The presence of saturation absorption enhances the peak while RSA diminishes the valley intensities in closed-aperture transmittance curves. The closed-aperture data were divided by open-aperture data to eliminate any contribution from nonlinear absorption and retrieved only the nonlinear refraction data. We obtained the best fits for $n_2 = \sim 1.3\times10^{-15}$ cm^2/W and $\sim3.8\times10^{-15}$ cm^2/W for ZnOCPc and PCH003, respectively.

In the present study all the samples were found to exhibit a negative nonlinearity except ethanol which showed a positive nonlinearity ($n_2 = 1\times10^{-15}$ cm^2/W). The valley to peak curve indicated a positive optical nonlinearity (figure 2a). Hence the solvent contribution reduced the actual nonlinear refractive index of phthalocyanines (PCH001 and PCH003). The nonlinear refractive index values for the samples are actually higher than those calculated and presented here. The open-aperture scan for ethanol did not indicate the presence of any significant nonlinear absorption. The nonlinear absorption and refraction observed from water was insignificant at the intensities used in present studies.

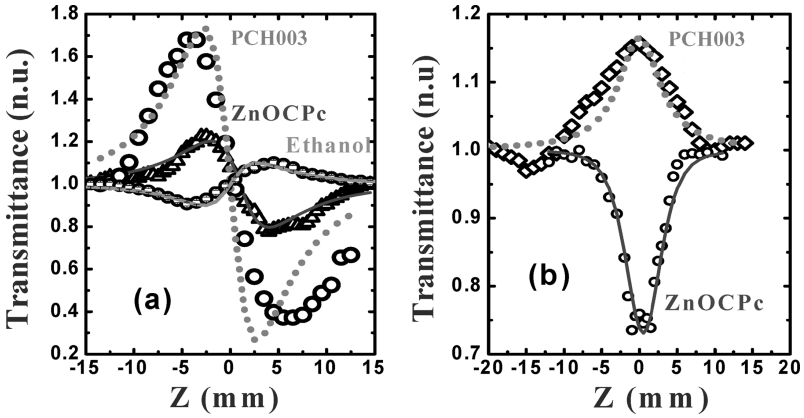

Figure 2. (**a**) Closed- and (**b**) open-aperture Z-scan data for ZnOCPc (in water) and PCH003 (ethanol). Ethanol (solvent) did contribute to the n_2 but not to the nonlinear absorption. The lines (solid for ZnOCPc and dotted for PCH003) are fits to the experimental data. The sign of n_2 was opposite compared to that of the sample.

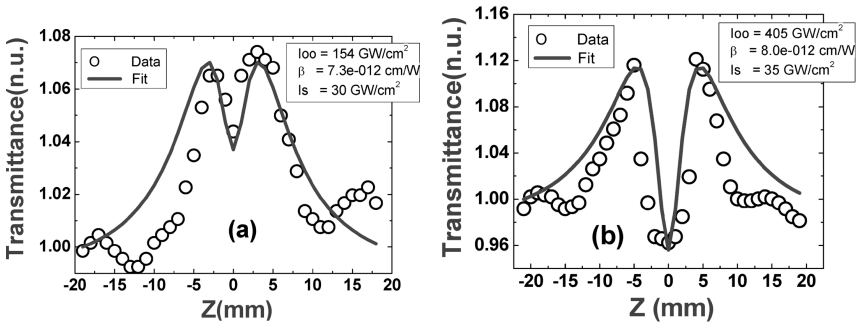

Figure 3. Open-aperture data of (**a**) PCH001 at a peak intensity of 154 GW/cm^2 and (**b**) PCH003 at a peak intensity of 405 GW/cm^2. Solid lines are fits to the experimental data (open circles).

Figure 2b shows open-aperture Z-scan data for PCH003 and ZnOCPc at input energies of ∼1.95 μJ, 7 μJ, respectively. The corresponding peak intensities estimated were ∼80 GW/cm^2 for PCH003 and ∼190 GW/cm^2 for ZnOCPc. For ZnOCPc a valley was observed in the scan indicating strong 3PA/ESA behaviour. For ps/fs pulse excitation, depending on the pump intensity and wavelength, nonlinear absorption could be from (a) the ground state S_0 to higher excited singlet states S_n (two-photon or multi-photon absorption) and (b) the first excited singlet state S_1 to higher excited states S_n [14]. The reduction in transmittance about the focus showed a positive nonlinear absorption coefficient. We obtained best fit for three-photon absorption coefficient, $\alpha_3 = 4.5 \times 10^{-22}$ cm^3/W^2. Typical peak intensities at the focus were in the range of 10^{11} W/cm^2. We tried fitting the data with two-photon absorption coefficient but the fit was better in the 3PA case. The open-aperture profile for PCH003 showed an increase in transmission with increasing intensity, which indicated the presence of saturation absorption (SA). A good fit was obtained for an effective nonlinear absorption coefficient of $\beta = 0.275 \times 10^{-9}$ cm/W. Figure 3 shows the open-aperture data of (a) PCH001 (∼3.15 μJ) and (b) PCH003 (∼7.5 μJ) recorded at higher energies. Peak intensity of ∼154 GW/cm^2 was used for PCH001 while a peak intensity of ∼450 GW/cm^2 was used for PCH003. It is evident that the saturable absorption (SA) behaviour changed to reverse saturable absorption (RSA) and the nonlinear coefficients were obtained using the equation $\alpha = \alpha_0 I/[1 + (I/Is)]$. The open-aperture scans were fitted by solving the propagation equation for homogeneous medium $\mathrm{d}I/\mathrm{d}z = \{-\alpha_0 I/[1+(I/Is)]\} - \beta I^2$. Both PCH001 and PCH003 have small absorbance near 800 nm resulting in SA at lower intensities. But, at higher intensities RSA dominated because of the excitation of population to the higher lying states. Such behaviour was observed in similar molecules in our earlier studies using femtosecond pulses [7,8]. In the case of ZnOCPc the absorption was almost negligible near 800 nm and we could observe RSA even at lower peak intensities.

PCH001 and PCH003 are unsymmetrical molecules while ZnOCPc is a symmetric molecule. PCH001 is an alkyl compound while PCH003 is an alkoxy compound. The nonlinear coefficients calculated for these compounds reveal interesting pattern. The unsymmetrical molecules (PCH001 and PCH003) had higher NLO coefficients

compared to symmetrical molecules (ZnOCPc). Between the unsymmetrical molecules alkoxy substitution resulted in higher nonlinearity compared to the alkyl substitution. Higher value of NLO coefficient of PCH003 and PCH001 compared to ZnOCPc could be credited to the lack of symmetry in structure, resulting from the uneven peripheral substitution. It is observed that the nonlinearity of a molecule increases with asymmetry if the excited state transition moments dominate [15]. Similar trends were observed in the nanosecond excitation case.

4. Conclusions

In summary, the phthalocyanines ZnOCPc, PCH003 and PCH001 were characterized for their NLO properties and the nonlinear coefficients were extracted from Z-scan studies at 800 nm using $\sim$2 ps pulses. The solvent effect was also studied which affected the nonlinearities of samples. ZnOCPc exhibited three-photon absorption while PCH003 and PCH001 were found to be good saturable absorbers. It was found that these phthalocyanines, with highly de-localized π-electron system, exhibited large optical nonlinearities. Further studies are in progress to exactly determine the lifetimes, nonlinearities in nanosecond and femtosecond regimes along with their figures of merit for device applications.

Acknowledgements

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