



## Picosecond nonlinear optical studies of unsymmetrical alkyl and alkoxy phthalocyanines

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### ABSTRACT

We present our results on picosecond nonlinearities in unsymmetrical alkyl and alkoxy phthalocyanines, studied using the Z-scan technique. Both open and closed aperture Z-scan curves were recorded and nonlinear coefficients were extracted. Solvent contribution to the nonlinearity was identified. We recorded large, off-resonant second hyperpolarizabilities ( $\gamma$ ) at 800 nm with estimated values of  $\sim 6.5 \times 10^{-31}$  esu and  $\sim 8.9 \times 10^{-31}$  esu for unsymmetrical alkyl and alkoxy phthalocyanines, respectively. Evaluated figures of merit indicate that these are potential molecules for photonic applications.

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### 1. Introduction

The pursuit for novel materials with large non-resonant nonlinearities and good figures of merit (small linear absorption and strong nonlinearity), imperative for realization of practical devices in applications such as optical limiting and optical signal processing, continues unabated with variety of materials in different forms being investigated [1–4]. Several materials investigated include organics, organometallics, nanomaterials, semiconductors, etc. [5–17]. The endeavor is to identify materials which suit specific applications by use of studies with different pulse durations. For example, strong nonlinear absorption in the nanosecond domain ensues good optical limiters. Strong multi-photon absorption cross-sections and coefficients are desirable with shorter pulse excitation for applications in biomedicine and imaging. Similarly strong nonlinear refractive index ( $n_2$ ) with ultrafast response time enables all-optical switching. The materials should be robust with essential qualities such as (a) broadband response, (b) easily tailored, (c) should be easily doped in a solid state matrix, and (d) cost-effective to name a few. Some significant characteristics of phthalocyanines comprise (i) planar structure, (ii) excellent chemical and thermal stability, (iii) large optical nonlinearity, (iv) electronic response time in the picosecond (ps) and femtosecond (fs) time domain, and (v) ease of preparation. The foremost advantage is the versatility with which one can alter their optical and nonlinear optical properties. For practical device realization it is imperative that any new molecule should be tested in various forms (solutions, thin films, etc.) and under rigorous

conditions with laser pulses of various energies and durations to arrive at exact figures of merit in each domain. The picosecond nonlinear optical technique is particularly crucial for the studies of electron-phonon interactions [18]. Some of our recent pursuits have been deliberated for understanding the nonlinearities in new class of alkyl and alkoxy phthalocyanines [6–10]. Nonlinear optical (NLO) measurements of two phthalocyanines: 2-(3-(butane-1,4-dioic acid)-9(10),16, (17),23(24)-tri tert-butyl phthalocyanine zinc (II) (unsymmetrical PCH001; MW = 862.3) and 2-(3-(butane-1,4-dioic acid)-8,11,15, 18,22,25-hexakis-(butyloxy) phthalocyanine zinc (II) (unsymmetrical PCH003; MW = 1126.6) were studied using the Z-scan technique [19] and  $\sim 2$  ps pulses near 800 nm. We derived the magnitude of nonlinear absorption, and estimated the sign and magnitude of refractive nonlinearities. Figures of merit and  $\gamma$  were also calculated.

### 2. Experiments

Z-scan measurements were performed using an amplified Ti:sapphire laser system (LEGEND, Coherent) delivering nearly transform-limited pulses of  $\sim 2$  ps and repetition rate of 1 kHz at 800 nm. The amplifier was seeded with  $\sim 15$  fs pulses from an oscillator (MICRA, Coherent,  $\sim 1$  W average power, 80 MHz repetition rate, 800 nm). Laser pulses with  $\sim 3$ – $10$   $\mu$ J energy were used. The beam was focused using 200 mm focal length lens into the sample, placed in 1-mm path length quartz/glass cuvettes. All the experiments were carried out with samples having concentrations of  $\sim 2$ – $3 \times 10^{-4}$  M. The beam waist estimated was  $\sim 30$   $\mu$ m with a Raleigh range of  $\sim 3.3$  mm. We ascertained that the pulse energies remained low to avoid contribution from higher order nonlinearities.

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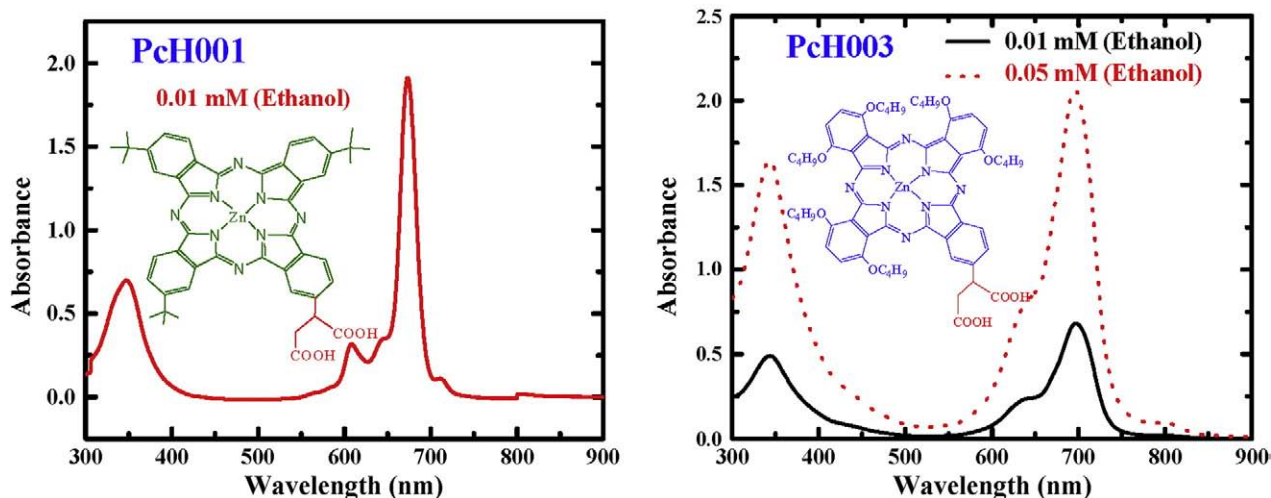


Fig. 1. Absorption spectra of (a) PCH001 and (b) PCH003 in ethanol.

### 3. Results and discussion

Both PCH001 and PCH003 were synthesized and purified according to the methods reported in literature [20,21]. During the synthesis many other isomers were formed along with the desired isomers, which were later isolated by column chromatography method and completely characterized using standard spectroscopic techniques. We performed a re-crystallization procedure just before measuring the NLO properties. This was done to remove any unwanted impurities present in the samples. It is a common technique used extensively in synthetic chemistry. The linear absorption spectra are shown in Fig. 1(a) for PCH001 and Fig. 1(b) for PCH003. The dotted line in Fig. 1(b) represents

0.01 mM spectrum and the solid line represents 0.05 mM spectrum. 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. The absorbance values were  $<0.1$  for these molecules at 800 nm. Fig. 2(a) shows the closed aperture scans, along with the corresponding fits, for PCH001 and the solvent ethanol recorded at  $1 \times 10^{11}$  W/cm<sup>2</sup> intensity. Open squares represent the experimental data for solution and open circles for the solvent while the solid lines are the theoretical fits [9,19]. In PCH001 the sign of nonlinear refraction  $n_2$  was negative. The solvent nonlinearity was positive suggesting the final value of  $n_2$  calculated for the pure solute will be higher than the calculated value. Similarly Fig. 2(b) shows the closed aperture data along with fits for the sample PCH003. We obtained the

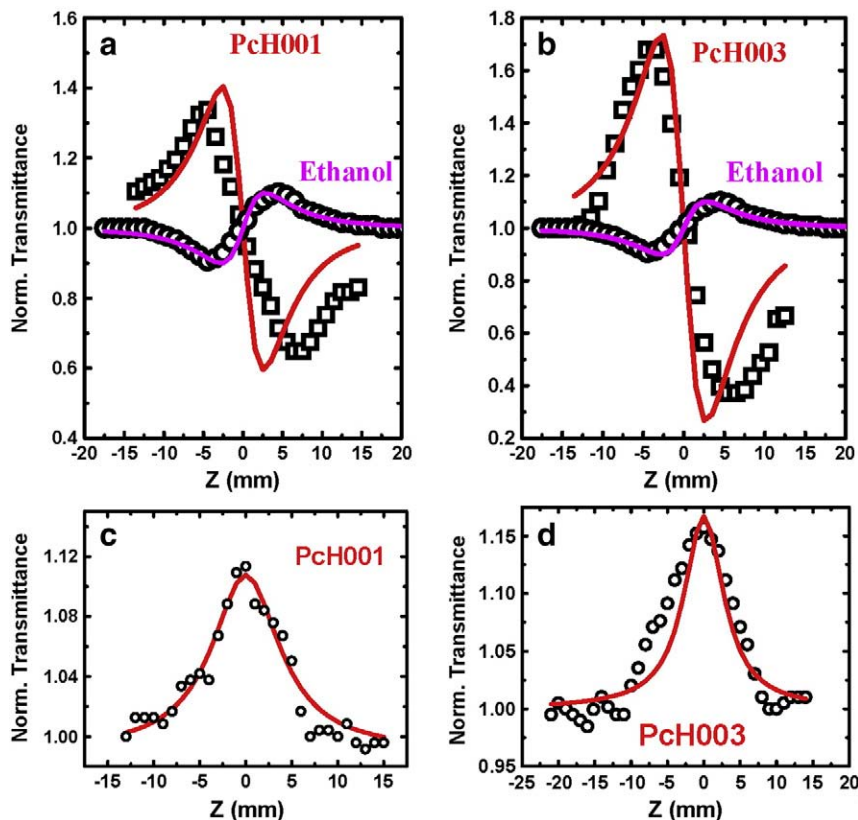


Fig. 2. (a) and (b) Closed aperture Z-scan data for PCH001 and PCH003. Ethanol (solvent) did contribute to the  $n_2$  but not to the nonlinear absorption. (c) and (d) represent typical open aperture Z-scan data for PCH001 and PCH003.

**Table 1**  
Nonlinear coefficients calculated from Z-scan data at a wavelength of 800 nm.

Sample	$n_2$ (m <sup>2</sup> /W) $\times 10^{-19}$	$n_2$ (esu) $\times 10^{-12}$	$\text{Re}[\chi^{(3)}]$ (esu) $\times 10^{-13}$	$\beta$ (m/W) $\times 10^{-12}$	$ \chi^{(3)} $ (m <sup>2</sup> /V <sup>2</sup> ) $\times 10^{-21}$	$ \chi^{(3)} $ (esu) $\times 10^{-13}$	$\langle \gamma \rangle$ (esu) $\times 10^{-31}$	T	W
PCH001	2.95	0.95	1.30	1.06	2.90	2.13	6.51	2.7 (2.1)	65.8 (88.2)
PCH003	3.75	1.2	1.76	2.75	4.07	2.91	8.89	5.8 (4.6)	73.2 (92.8)

best fits for  $n_2$  as  $\sim 2.95 \times 10^{-15}$  cm<sup>2</sup>/W and  $\sim 3.75 \times 10^{-15}$  cm<sup>2</sup>/W for PCH001 and PCH003, respectively. The peak–valley separation was  $\sim 1.7 \times Z_0$ , clearly suggesting the presence of Kerr type of nonlinearity.

Pure solvent ethanol showed a positive nonlinearity with a magnitude of  $n_2 < 1 \times 10^{-16}$  cm<sup>2</sup>/W. Therefore, nonlinear refractive index values of the samples are actually higher by at least 25% than those calculated and presented in Table 1. Fig. 2(c) shows the open aperture data for PCH001 and 2(d) for PCH003 recorded at a peak intensity of  $\sim 2 \times 10^{10}$  W/cm<sup>2</sup> and signatures in both the scans imply saturable absorption. A good fit was obtained for an effective nonlinear absorption coefficient of  $\beta = 0.106$  cm/GW for PCH001 and  $\beta = 0.275$  cm/GW for PCH003. The open aperture scan for ethanol did not indicate the presence of any significant nonlinear absorption. Considering all the unforced random experimental errors (arising from concentration measurement, input power measurement, data fitting, estimation of the spot size at focus, etc.) we have estimated an overall error of  $\pm 20\%$  in our calculations. The absorption spectra of solutions were also recorded after the NLO experiments and no significant changes were observed indicating the photo-stability of these molecules. The solutions were highly homogenous in nature which was confirmed from the absence of any scattering during the experiments.

With the intention of justifying the potential of these molecules we calculated the figures of merit (FOM) and later compared them with other potential molecules reported recently. The merit factor  $W$  is defined as [10]  $W = \frac{n_2 I_{sat}}{\alpha_1 \lambda}$ , where  $\lambda$  is wavelength, and  $I_{sat}$  is the light intensity at which  $n_2$  saturates. The pre-requisite for superior FOM is  $W > 1$ . The corresponding FOM for nonlinear absorption is:  $T^{-1} = \frac{n_2}{\lambda \alpha_1}$ . For photonics device applications  $T < 1$  is desirable.

For PCH001 (PCH003) the FOM calculated were  $T = 2.7$  (5.8) and  $W = 65.8$  (73.2). The corresponding values if the solvent contribution is eliminated are represented in the parentheses of Table 1. It is apparent that FOM ' $W$ ' is  $\gg 1$  and advocates potential applications in photonic devices. The  $\gamma$  values estimated were  $\sim 6.5 \times 10^{-31}$  esu and  $\sim 8.9 \times 10^{-31}$  esu for PCH001 and PCH003, respectively. These represent one of the best values reported recently (see Table 2). Kong et al. [22] report similar magnitudes for the  $\gamma$  values for a ZnPc(OBU)<sub>6</sub>(NCS) with an ultrafast response time. Cheng et al. [23] studied two fullerenes with 38 ps pulses and observed  $\gamma$  values one order of magnitude lower than those presented here. However, higher  $\gamma$  values were obtained in titanium phthalocyanine [25] and rare earth phthalocyanines in polymer [26], possibly due to longer pulses ( $\sim 500$  ps) used in the former case and the polymer host (PMMA) along with excitation wavelength (532 nm) in the latter case enhancing the nonlinearity. Our earlier studies on similar phthalocyanines with 100 fs pulse excitation indicated lower  $\gamma$  value [7]. Higher value of NLO coefficient of PCH003 and PCH001 could be attributed to the lack of symmetry in its structure, resulting from the uneven peripheral substitution. It has been previously suggested that nonlinearity of a molecule increases with asymmetry if the excited states transition moments dominate [27]. We have recently been successful in doping these molecules in PMMA and studied the excited state dynamics with pump–probe technique using ultrashort pulses. Preliminary data suggest that the lifetimes are in the sub-100 ps range. Our future studies will focus on (a) making free-standing thin films and performing NLO studies, (b) investigating the nanosecond/picosecond optical limiting capabilities of these molecules in a polymer matrix, and (c) a comprehensive dispersion NLO study with ns, ps, and fs pulses.

**Table 2**  
Comparison of  $\gamma$  for various molecules studied recently.

Sample(s)	Details	$\gamma$ (esu) at 800 nm	Reference
ZnPc(OBU) <sub>6</sub> (NCS)	130 fs, 800 nm	$2.35 \times 10^{-31}$	[22]
Fullerene derivative 1	38 ps, 532 nm	$0.237 \times 10^{-31}$	[23]
Fullerene derivative 2		$0.202 \times 10^{-31}$	
Lead phthalocyanines	90 ns, 532 nm	$\sim 10^{-34}$	[24]
Alkyl & Alkoxy phthalocyanines	$\sim 100$ fs, 800 nm	$\sim 4 \times 10^{-31}$	[12]
Titanium phthalocyanine	$\sim 500$ ps, 532 nm	$\sim 10^{-29}$	[25]
Rare Earth phthalocyanines in polymer	$\sim 25$ ps, 532 nm	$\sim 10^{-29}$	[26]
Alkyl & Alkoxy phthalocyanines	$\sim 2$ ps, 800 nm	$6.5 \times 10^{-31}$ $8.9 \times 10^{-31}$	This work

4. Conclusions

In summary two phthalocyanines 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 affects the sample nonlinearities. The non-resonant  $\gamma$  values estimated at 800 nm were  $\sim 10^{-31}$  esu. PCH003 and PCH001 were found to be good saturable absorbers.

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