



## Study of the nonlinear optical properties and behavior in phenoxy-phthalocyanines liquid at nanosecond laser pulses



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### ABSTRACT

The nonlinear optical properties of 2,9,16,23-phenoxy-phthalocyanine (Pc1) and 2,9,16,23-phenoxy-phthalocyanine-zinc (Pc2) in solution were investigated under excitation with nanosecond laser pulses at 532 nm. Based on five-level model, the nonlinear absorption in nanosecond regime was theoretically analyzed. The A-OS and OL behavior of Pc1 and Pc2 were further investigated with the pump-probe technique and transmission measurement technique. The results show that the A-OS response time is determined by the lifetime of the first triplet excited state of molecule, and Pc1 and Pc2 exhibit strong optical limiting effect at nanosecond laser pulses. These studies make the samples a promising possibility for device realization.

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### 1. Introduction

The phthalocyanines (Pc) and metallophthalocyanines (MPc) have been studied in great deal for many years. Recently, attentions have been paid on the dynamics of the triplet excited states in phthalocyanines because of their aromatic 18- $\pi$  electron system and ability of containing more than 70 kinds of metallic and non-metallic ions in the ring cavity [1–5]. Furthermore, the large nonlinear optical response of MPc, arising from its two-dimensional conjugated  $\pi$ -electrons system, lends MPc as a candidate in various photonics devices, such as all-optical switching (A-OS) [6], optical limiting (OL) [7,8], and optical bi-stability [9]. A-OS is a fundamental building block of information processing for the future, especially all-optical modulation has attracted much interest, specifically in the field of optical communication. In addition, plethora phthalocyanines performance for optical limiting applications, in general, is quite excellent even though their nonlinear optical properties and derivatives have been investigated [10–14]. The nonlinear optical mechanisms for OL include nonlinear absorption (reverse saturable absorption (RSA), two photon absorption (TPA)), nonlinear refraction and nonlinear scattering [15,16]. Pc and their derivatives have recently attracted considerable scientific attention for OL processes due to their large RSA, fast response times, and ease of chemical modification [17,18]. The RSA mechanism

of Pcs in the optical region comprised between two absorption bands (the Q- and B-bands) involves the population of the excited states which absorb more effectively than the ground state [17]. This leads to the phenomenon of RSA as a consequence of multiphoton absorption. The nonlinear absorption mechanism exhibited by Pc at 532 nm laser irradiation is due to the population of excited states through TPA [19]. The studies above suggest that the effect of the metal ion on the nonlinear optical properties is negligible for phenoxy-phthalocyanines. The advantages of these molecules stem from the fact that they have insignificant linear absorption, especially in the 450–600 nm spectral range which indicates prospective applications in broadband OL [20]. A variety of methods can be used to generate the substituted metal phthalocyanine complexes from corresponding substituted phthalocyanine precursor condensation, but most of them require harsh synthetic conditions, such as high temperature, long reaction time and being sensitive to the water in the solvent or air.

In this work, we synthesized 2,9,16,23-phenoxy-phthalocyanine (Pc1) and 2,9,16,23-phenoxy-phthalocyanine-zinc (Pc2) using mild coordination method. By introducing the acetone oxime or diethyl hydroxylamine as the intermediate reactant, we can simplify the reaction conditions and improve the synthesis efficiency. We present the results of our investigations on the nonlinear optical properties and A-OS/OL behavior of Pc1 and Pc2 under excitation with nanosecond laser pulses at 532 nm. The nonlinear absorption mechanism exhibited by Pc at 532 nm laser irradiation is due to the population of excited states through TPA. The results

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of pump–probe experiments show that the shorter the lifetime of the first triplet excited state of molecule is, the shorter the A-OS response time is. The results OL experiments reveal that the Pc1 and Pc2 exhibited strong OL performance for nanosecond laser pulses.

## 2. Synthesis and experiment

### 2.1. Synthesis of samples

In our experiment, we dissolve the 4-phenoxy Phthalonitrile and acetone oxime with the molar ratio of 1:1 in methanol and refluxes for 5 h, the solution gradually becomes dark green. When the solution is cooled down to room temperature, we can precipitate the crude product Pc1 powder precipitate, with the color of dark green and the yield ratio of 52%. The molar ratio of the synthetic sample is  $\text{ZnCl}_2$ : 4-phenoxy phthalimide nitrile: acetone oxime = 1:4:4. The yield ratio is 65% after precipitation of the crude product. The synthesis of phthalocyanine compounds is shown in Fig. 1. When the peripheral substituent is electron-withdrawing, the reaction cannot be carried out, and forms unknown product. Therefore, we should replace reaction intermediates by using diethylhydroxylamine and using methanol as solvent, and then reflux the reaction. The synthesis mechanism is shown in Fig. 2 (Pc1). When the peripheral substituent is electron-withdrawing, acetone oxime acts as an intermediate reactant oxime while at the same time it acts as the reductant for proton agents involved in the reaction. This reaction does not require special conditions, and all we have to do is to reflux the reaction in the presence of the solvent. After the reaction, sample purification is simple and the yield is high. The synthesis mechanism is shown in Fig. 2 (Pc2). The detailed procedure had been described in [21]. The Pc1 and Pc2 are a hydrogen or zinc connected with four ligands by nitrogen bridges. Fig. 3 shows the Proton Nuclear Magnetic Resonance ( $^1\text{H}$  NMR) of the two synthesized phthalocyanines compounds. The results show that the number and relative intensities of the spectrum peaks, and splitting are identical with the target product (Pc1 and Pc2) structure.

### 2.2. Experiment technique

The Z-scan technique is used to measure the nonlinear optical properties, which is of great advantages due to its simplicity and high sensitivity. The sign and magnitude of nonlinear refractive index is obtained from the closed aperture Z-scan data, while an effective nonlinear absorption coefficient is evaluated from the open aperture Z-scan data. This technique is described in detail by Refs. [22,24,25], the laser source used for the measurement was a frequency-doubled Nd:YAG laser with a pulse width of 10 ns at 532 nm. Basically, in this technique the nonlinear sample is scanned through the focal plane of a tightly focused Gaussian beam and the changes in the far-field intensity pattern with and without aperture are monitored.

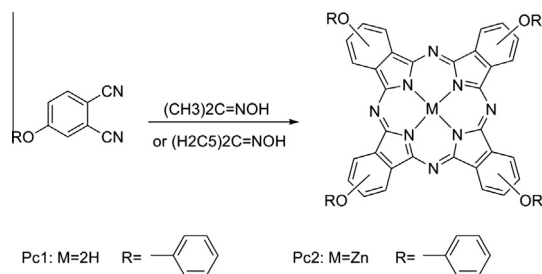


Fig. 1. Synthesis of phthalocyanine compounds.

The characteristics of A-OS of the samples are investigated by two-color pump–probe method. The experimental arrangements have been reported by Refs. [26–30]. The pump light used for the measurement is a frequency-doubled Nd:YAG laser with a pulse width of 10 ns at 532 nm. The probe light used is a He–Ne laser of continuous wave with 632.8 nm. OL measurements were performed using the setup reported by Refs. [17,31,7]. The measurements were done with frequency-doubled Nd:YAG 532 nm laser system. For OL experiments the sample solution in a 1-mm quartz cuvette was placed just after the focus of lens (focal length of 10 cm) where the defocusing occurred. However, for limiting experiments we ensured that there was no ring pattern formation by placing the sample away from focus in the nonlinear regime at room temperature.

## 3. Results and discussion

### 3.1. Linear absorption properties

All the experiments were performed with samples dissolved in N,N-dimethylformamide (DMF). The absorption spectra of Pc1 and Pc2 in ground state ( $S_0$ ) are shown in Fig. 4. For both phthalocyanines in DMF there are two strong broad bands: the B-band ( $\pi \rightarrow \pi^*$ ) in the near-UV ( $\lambda_{\text{max}} = 314$  and 298 nm for Pc1 and Pc2, respectively), and the Q-band ( $n \rightarrow \pi^*$ ) in the red<sup>1</sup> ( $\lambda_{\text{max}} = 712$  nm for Pc1 and 704 nm for Pc2). The results show the molecule in that triplet state may absorb another photon and excited to a higher triplet level  $T_n$ . Moreover, one-photon transfers from  $S_1$  to a higher singlet state  $S_n$  are also possible. This is two-photon absorption for laser radiation at 532 nm. The excited-state linear absorption spectra of MPc with different center metals are similar, which have been reported by Ref. [23]. The results illustrate that the molecules of  $T_1$  do not absorb the pump light at 532 nm, but absorb the probe light at 632.8 nm.

### 3.2. Nonlinear optical properties

In order to further investigate the nonlinear optical properties of sample, we measured the nonlinear optical properties of sample with same concentration ( $2.44 \times 10^{-4}$  mol/L) at different peak intensities. Figs. 5 and 6 show results of the open- and closed-aperture Z-scans for both samples in DMF solution at various peak intensities. For the closed-aperture case, the signal profile shows a peak followed by a valley. This indicates a negative (self-defocusing) optical nonlinearity. The peak-valley characteristic shape is nearly a symmetrical distribution with respect to  $z = 0$ , which means that the influence of nonlinear absorption is deduced. For the open-aperture case, the transmittance curve of open-aperture Z-scans exhibit the valley characteristic shape. The normalized transmittance for the standard open aperture Z-scan [24] is expressed by the relation:  $T(z, s = 1) = ([-q_0]^m / (m + 1)^{3/2})$ , for  $|q_0(0)| < 1$ , where  $q_0(z) = \beta I_0 L_{\text{eff}} / (1 + z/z_0)$  ( $z_0$  is the Rayleigh rang), and  $L_{\text{eff}} = (1 - \exp(-(n - 1)\alpha_0 L)) / ((n - 1)\alpha_0)$  the effective length ( $\alpha_0$  is the linear absorption coefficient and  $L$  is the thickness of the sample). The normalized transmittance for the standard closed aperture Z-scan [24] is expressed by the relation:  $\Delta T_{p-v} = 0.406 (1 - S)^{0.25} |\Phi_0|$ , where  $\Delta T_{p-v}$  is the measured peak-valley transmittance difference,  $\Delta \Phi_0 (= k\gamma I_0 L_{\text{eff}})$  the on-axis phase-shift and  $I_0$ , the peak intensity at focus and  $S$  the linear transmittance of the aperture given by  $S = 1 - \exp(-2(r_a/w_a)^2)$  ( $r_a$  is the radius of the aperture and  $w_a$  is the radius of the laser spot before the aperture). The values of  $\beta$  and  $|\gamma|$  were evaluated from the fitting experimen-

<sup>1</sup> For interpretation of color in Fig. 4, the reader is referred to the web version of this article.

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