



# Nonlinear optical and optical limiting properties of polymeric carboxyl phthalocyanine coordinated with rare earth atom



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## ABSTRACT

The nonlinear optical properties of the polymeric carboxyl phthalocyanine with lanthanum (LaPPc-COOH), holmium (HoPPc-COOH) and ytterbium (YbPPc-COOH) as centric atom, were investigated by the Z-scan method using a picosecond 532 nm laser. The synthesized phthalocyanines had steric polymeric structure and dissolved well in aqueous solution. The nonlinear optical response of them was attributed to the reverse saturable absorption and self-focus refraction. The nonlinear absorption properties decreased with the centric atoms changing from La, Ho to Yb. The largest second-order hyperpolarizability and optical limiting response threshold of LaPPc-COOH were  $3.89 \times 10^{-29}$  esu and  $0.32$  J/cm<sup>2</sup>, respectively. The reverse saturable absorption was explained by a three level mode of singlet excited state under the picosecond irradiation. The result indicates the steric structure presented additive stability of these polymeric phthalocyanines for their application as potential optical limiting materials.

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## 1. Introduction

Phthalocyanines and its derivatives are fundamental compounds in many important areas associating with the photochemical and photophysical process. The high delocalized, high uniformed conjugated orbital gives phthalocyanine molecule with long-life photochemical excited states and visible light absorptive property. These unique properties are valuable in the research of nonlinear optics [1].

The optical limitation is an important application of nonlinear optics. It suppresses or consumes potentially damaging light of intense irradiation, while allows transmission of low energy light under ambient conditions. Optical limiting materials with good film-formation properties are meaningful to the protection of photo sensors and human eyes under high energy irradiation. Phthalocyanine and its analogue were proved as organic compounds with outstanding nonlinear properties [2,3]. The macrocyclic structure of phthalocyanine is favorable for the modification of their

chemical, physical and soluble properties through changing substitutes and centric atoms in the research of nonlinearity [4,5]. In previous research, the centric atoms of phthalocyanine usually were indium [6], gallium [7] and rare earth elements [8]. These heavy metal atoms help the intersystem crossing (isc) between singlet states and triplet states through enhancing the spin-orbit coupling. The facile intersystem crossing strengthens the reverse saturable adsorption (RSA) in nanosecond nonlinearity [9]. However, the intersystem crossing process (at nanosecond magnitude) does not take more effect in the RSA process under picosecond laser.

Recently, the novel form of phthalocyanine linked with macromolecules, such as bis/tris phthalocyanine [8,10,11], hybrid dyad [12,13] and decked nano-particles [14,15], were intensively reported for their special nonlinear optical properties. The combination of large molecule with heavy metal atoms gives the phthalocyanines with strong nonlinear absorption. As the important macro-molecules, the polymeric phthalocyanines have additional stability than the monomeric forms especially under intense laser irradiation. However, the soluble and film-disperse problems restricted their further research as optical limiting devices. Comparing with their monomeric forms, only a few polymeric

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phthalocyanines were reported of their nonlinear properties. Darwish et al. [16,17] reported the optical limiting property of a polymeric indium phthalocyanine used a planar bis-phthalonitrile as the precursor. We also found the phthalocyanine polymer synthesized from steric tetra-phthalonitrile showed strong third-order hyperpolarizability [18], but it cannot be disperse in organic films. The successive study improved the solubility of the steric polymeric phthalocyanine by the introduction of carboxyl groups [19]. In this work, we investigated the nonlinear optical properties of the polymeric carboxyl phthalocyanine in solution and film using Z-scan method, respectively. The acetate of holmium, ytterbium and lanthanum was used to form rare earth phthalocyanine. The photostability of polymeric carboxyl phthalocyanine dispersed in polymethacrylate (PMMA) film was assessed by repeating optical limiting tests.

## 2. Experimental

### 2.1. Material and methods

The tetrakis-[(2,3-dicyanophenoxy) methyl] methan was synthesized by our lab; La(Ac)<sub>3</sub>, Ho(Ac)<sub>3</sub>, Yb(Ac)<sub>3</sub>, 1,8-diaza bicycle [0,4,5]-undec-7-ene (DBU) and tetrahydronaphthalene was purchased from Sinopharm. Other solvents and reagents used in the experiments were all analytical grade.

Uv–vis absorption spectra recorded on an HP 5324A Uv–vis array Spectrometer; the electronic emission and excitation spectra were recorded by a Hitachi F4500 Spectrometer. In the photophysical study, carboxyl phthalocyanine compounds were dissolved in pH 7.4 phosphate buffer solution at the concentration of 0.1 g/L. All sample solutions were bubbled with argon for 15 min before fluorescent test to minimize the possible quenching of excited singlet states oxygen. NMR was performed on a JOEL JNM-ECA300 Spectrometer. FT-IR was obtained from Avata 360A Spectrometer. Metallic content was measured by an IRIS Intrepid II XS ICP-AES spectrometer. The element analysis was performed on a Vario EL 3 element analyzer. The average viscosimetric molecular weight ( $M_{\eta}$ ) was calculated by the comparative method [19] using PVP-K15 ( $M_{\eta} = 8000$ – $12000$ ) as a standard.

The quantum yield of fluorescence ( $\Phi_F$ ) was measured by the reported method [20] used ZnPc.S<sub>4</sub> ( $\Phi_F = 0.07$ , DMSO [21]) as a standard in pH 7.4 buffer solution. The excited wavelength was 610 nm for both samples and standard. The sample and standard solutions were diluted to the absorbance of 0.05–0.06 at excited wavelength. The  $\Phi_F$  of polymeric phthalocyanine samples was calculated by,

$$\Phi_F^S = \frac{A^S}{A^{Std}} \frac{\phi_F^{Std} Abs^{Std}}{Abs^S} \frac{\eta_s^2}{\eta_{DMSO}^2} \quad (1)$$

where the superscripts s and std represent the sample and standard, respectively.

A is the integrative areas under the emission curves, Abs is the absorbance and  $\eta$  is the refractive indexes of the solvent.

The triplet quantum yields ( $\Phi_T$ ) were measured on an Edinburgh LP920 laser flash photolysis spectrometer. The third-harmonic output (355 nm) of a Surelite Continuum II Nd: YAG laser (pulse-width 7 ns, repetition rate 1 Hz) was used as the excitation source. The detection source was a xenon lamp (Xe 900, 450 W) with an HAMAMAT-SUPMT R955 amplifier. The sample in DMSO with about  $1 \times 10^{-4}$  mol/L concentration were deoxygenated with nitrogen for at least 30 min before each measurement. The unsubstituted zinc phthalocyanine [22] (ZnPc,  $\Phi_T = 0.65$ ,  $\epsilon_{480nm} = 30\,000$  M<sup>-1</sup>cm<sup>-1</sup>) was used as standard in the calculation of  $\Phi_T$ . The triplet-

triplet absorption coefficients ( $\epsilon_T$ ), quantum yield of triplet states were calculated by,

$$\Phi_T^S = \Phi_T^{Std} \frac{\Delta OD_T^S}{\Delta OD_T^{Std}} \frac{\epsilon_T^{Std}}{\epsilon_T^S} \quad (2)$$

$$\epsilon_T = \frac{OD_T^\infty}{Ns d} \quad (3)$$

where the superscripts s and std represent the samples and standard, respectively.

$\Delta OD$  is optical density of the triplet transient difference absorption spectrum at 480 nm, and  $\epsilon_T$  is the triplet excited-state extinction coefficient.  $Ns$  is the concentration of samples,  $d$  is the thickness of sample,  $OD_T^\infty$  is the saturated absorbance of triplet states of samples at the maximum wavelength of the positive band. Overall uncertainty in the photophysical measurements was estimated to be about 10% by several parallel tests.

The electric susceptibility was calculated by G03W [23] using DFT/B3LYP method with a LANL2DZ basis set. A monomeric unit of the polymeric molecule (shown in Scheme 1) was used to simplify the calculation.

### 2.2. Synthesis

The synthesis and characterization of polymeric carboxyl phthalocyanine (shown in Scheme 1) referred the published document [19]. The tetra-phthalonitriles with a tetrahedral pentaerythritol skeleton was used to introduce the steric structure into the polymeric carboxyl phthalocyanine.

For a typical route, 1.28 g **Pn<sub>4</sub>** (tetrakis-[(2,3-dicyanophenoxy) methyl] methan, 0.002 mol), 0.004 mol metal salt (anhydrate, La(Ac)<sub>3</sub>, Ho(Ac)<sub>3</sub> and Yb(Ac)<sub>3</sub>) and 1 ml 1,8-diaza bicycle [0,4,5]-undec-7-ene (DBU) were refluxed for 5 h under argon ambience in 50 ml tetrahydronaphthalene. The solid product was filtrated out and washed by 6 mol L<sup>-1</sup> hydrochloric acid to remove the residual metallic salt. Then the solid powder was stirred with 50 ml 15% NaOH solution at 80 °C for 12 h. Centrifuge out the insoluble solid and acidify the solution by 6 mol L<sup>-1</sup> HCl to pH 1. The green raw product was acid-out as participate and purified by chromatography on neutral alumina column using DMF/methanol (3:1–4:1) as eluent. The yields were about 40%–50% for the three compounds.

**LaPPc.COOH:** FT-IR(KBr pellet,  $\nu_{max}/cm^{-1}$ ) 1740s (C=O), 3350–3620br (COOH), 1148s, 1313s, 1480s, 1648s (Ph);  $\delta_C$  (300 MHz; DMF): 173–177 (COOH), 101.2116.6118.1, 126.8135.2158.5(Ph), 49.7 (CH<sub>2</sub>), 68.0 (quaternary C); Elemental analysis: Found: C, 69.71; H 4.51; N, 16.24, O, 7.18; La (atom), 4.82%.  $M_{\eta}$ : 8500–11000.

**HoPPc.COOH:** FT-IR(KBr pellet,  $\nu_{max}/cm^{-1}$ ) 1735s (C=O), 3300–3700br (COOH), 1149s, 1321s, 1485s, 1643s (Ph);  $\delta_C$  (300 MHz; DMF): 171–177 (COOH), 103.2115.9117.9125.8136.2156.8 (Ph), 49.5 (CH<sub>2</sub>), 68.4 (quaternary C); Elemental analysis: Found: C, 68.95; H 4.27; N, 16.20, O, 7.10; Ho (atom), 4.89%.  $M_{\eta}$ : 9000–12000.

**YbPPc.COOH:** FT-IR(KBr pellet,  $\nu_{max}/cm^{-1}$ ) 1745s (C=O), 3320–3600br (COOH), 1152s, 1323s, 1487s, 1651s (Ph);  $\delta_C$  (300 MHz; DMF): 175–178 (COOH), 102.2116.2, 118.7, 126.9135.9157.6 (Ph), 49.2(CH<sub>2</sub>), 68.1(quaternary C); Elemental analysis: Found: C, 68.82; H 4.21; N, 16.13, O, 7.02; Yb (atom), 4.95%.  $M_{\eta}$ : 9500–12500.

### 2.3. Z-scan test

Optical nonlinearity was measured by standard Z-scan method (shown in Scheme 2). The carboxyl phthalocyanine was dissolved in pH 7.4 buffer solution with 1.0 g/L concentration and placed in a standard 1 mm quartz cuvette. The apparent molar concentration

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