

## Central metal ion enhances the excited state optical nonlinearity of naphthalocyanine compound

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**Abstract:** The third-order optical nonlinearities of lead and palladium naphthalocyanine compounds were studied comparatively using Z-scan technique with ns laser pulses at 532 nm. The experimental results showed that the two kinds of naphthalocyanine compounds also indicated strong nonlinear absorption (reverse saturable absorption) and nonlinear refraction (self-focusing) characteristics. Nonlinear absorption coefficient  $\beta$  for lead and palladium naphthalocyanine compounds by theoretical fitting were  $6.54 \times 10^{-10}$  m/W and  $3.90 \times 10^{-10}$  m/W, respectively. Nonlinear refractive index coefficient  $n_2$  were  $1.68 \times 10^{-10}$  esu and  $8.04 \times 10^{-11}$  esu, respectively. The second-order molecular hyperpolarizabilities  $\gamma$  were  $3.44 \times 10^{-28}$  esu and  $2.57 \times 10^{-28}$  esu, respectively, which were approximately about  $10^5$  order in magnitude than that of  $\text{CS}_2$  ( $4.32 \times 10^{-33}$  esu). The experimental results show that the lead naphthalocyanine compound exhibits great optical nonlinearities than palladium naphthalocyanine compound results from the heavy metal atoms as central atom of naphthalocyanine lead compounds enhance the optical nonlinearities of naphthalocyanine compounds.

**Key words:** third-order optical nonlinearity; naphthalocyanine; heavy atom effect

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## 中心金属原子对酞菁化合物激发态的光学非线性增强效应

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**摘 要:** 应用 Z-扫描技术对比研究了酞菁铅和酞菁钡化合物在波长为 532 nm 纳秒激光脉冲作用下的三阶非线性光学特性。实验结果表明, 两种酞菁化合物均显现出较强的非线性吸收特性(反饱和吸收)和非线性折射特性(自聚焦)。理论拟合得出酞菁铅和酞菁钡的非线性吸收系数  $\beta$  分别为  $6.54 \times 10^{-10}$  m/W 和  $3.90 \times 10^{-10}$  m/W; 非线性折射系数率  $n_2$  分别为  $1.68 \times 10^{-10}$  esu 和  $8.04 \times 10^{-11}$  esu; 二阶分子超极化率系数  $\gamma$  分别为  $3.44 \times 10^{-28}$  esu 和  $2.57 \times 10^{-28}$  esu,  $\text{CS}_2$  二阶分子超极化率系数为  $4.32 \times 10^{-33}$  esu; 两种酞菁化合物的二阶分子超极化率强于  $\text{CS}_2$  近 5 个数量级。实验结果表明, 酞菁铅化合物具有较强的非线性吸收和非线性折射特性, 且大于酞菁钡化合物的光学非线性特性是由于酞菁铅化合物的重原子效应提高了其光学非线性特性。

**关键词:** 三阶光学非线性; 酞菁; 重原子效应

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## 0 Introduction

With the development of nonlinear optical techniques, nonlinear optical materials are widely used in laser protection, frequency conversion, optical communication and other fields<sup>[1]</sup>. Metallic phthalocyanine compounds (MPcs) are planar molecules with D<sub>4h</sub> symmetry containing 18 $\pi$  electrons per ring. They exhibit strong nonlinear optical properties, which have attracted considerable interest over these years<sup>[2-4]</sup>. However, a major drawback of the metallic phthalocyanine compounds is absorption peaks in visible range that influence the visible transmittance and limit the wavelength bandwidth. It was reported that the Q band absorption peaks of zinc naphthalocyanine compounds are moving from visible range to near-infrared range<sup>[5]</sup>. It is to be noted that the effect of metal atom has been actively investigated nearly such as phthalocyanine with Al, In, Zn, Mg, Fe<sup>[6-8]</sup>. In this paper, the third-order optical nonlinearities of naphthalocyanine compounds with Pb and Pd were studied using Z-scan technique under ns laser pulses.

## 1 Samples and experiment

The samples used in our experiments were 2-3 naphthalocyanine lead (PbNc) and palladium (PdNc). The molecular structures of the naphthalocyanine compounds were illustrated in Fig.1. The syntheses of them were described previously<sup>[9]</sup>. PbNc and PdNc were respectively dissolved in diethyl sulphoxide (DMSO)

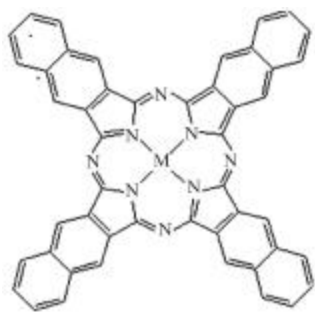


Fig.1 Structure of PbNc and PdNc (M=Pb, Pd)

whose linear transmittance at 532 nm were about 90%. Samples were respectively placed in a 2 mm quartz cell in order to measure their optical nonlinear properties.

The third-order optical nonlinearities of naphthalocyanine compounds were determined by Z-scan technique. Z-scan technique is a single-beam method for measuring the optical nonlinearities through detecting the far-field sample transmittance of a focused Gaussian beam as a function of sample position (z). The open aperture Z-scan curve shows nonlinear absorption alone, and the close aperture Z-scan curve contains both nonlinear absorption and nonlinear refraction. In order to obtain the pure nonlinear refraction we divided the close Z-scan curve by open Z-scan curve.

In the experiments, a Q switched, frequency doubled ns/ps Nd:YAG laser (Continuum Corp.) with pulse width of 8 ns, repetition rate of 1 Hz and wavelength of 532 nm was used as the light source. Incident single pulse energy of source was about 150  $\mu$ J. The spatial and temporal profiles of pulses present an approximately Gaussian distribution. The sample was scanned along the optical axis through the focus of the lens, which has a focal length of 308 mm. The experimental set up was shown in Fig.2. A spectroscopically was used to split the laser beam into two parts. One part was measured by a precision laser detector D1 (818J-09B, Newport Corp.) in order to measure the nonlinear absorption of the samples. Another part was simultaneously measured by another same type detector D2 before which a partially close aperture was placed. The intensity change of D2 contains both nonlinear absorption and nonlinear refraction.

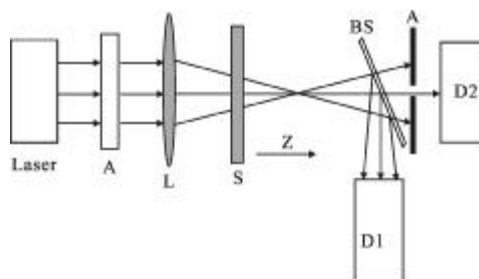


Fig.2 Layout of the Z-scan experiment

## 2 Results and discussion

The open and close aperture Z-scan curves of PbNc and PdNc were shown in Fig.3 and Fig.4 respectively. The Z-scan curves of CS<sub>2</sub> were shown in Fig.5 at the same condition. In Fig.3 and Fig.4, the squares and circles denote the experimental results, the solid and dashed lines indicate the theoretical fitting curves.

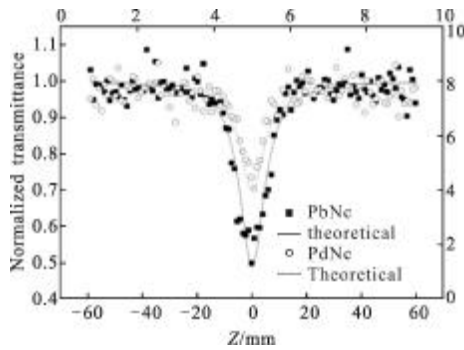


Fig.3 Normalized transmission curves of open aperture Z-scan for PbNc and PdNc solution measured using 8-ns pulses at 532 nm

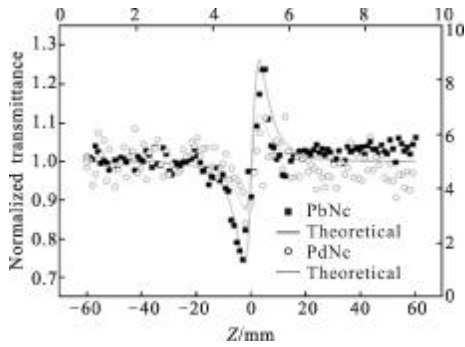
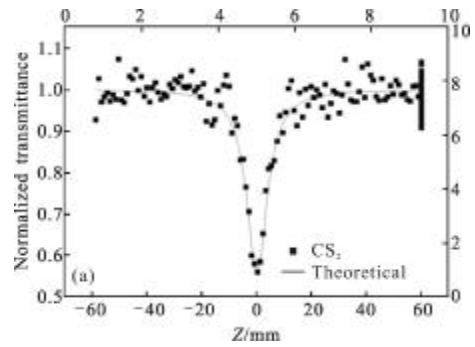


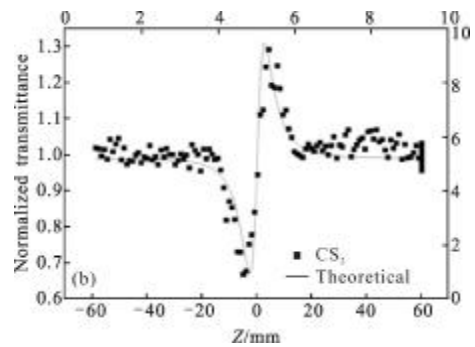
Fig.4 Normalized transmission curves of Z-scan data with an aperture(linear transmission of  $s=0.1$ ) divided by those without aperture for PbNc and PdNc solution measured using 8-ns pulses at 532 nm

In Fig.5, the squares denote the experimental results; the solid lines indicate the theoretical fitting curves.

From Fig.3, we find that PbNc and PdNc all exist nonlinear absorption at 532 nm, and the nonlinear absorption is considered as reserve saturable absorption results from transitions among the singlet states and triplet states.



(a) Normalized transmission curves of open aperture Z-scan for CS<sub>2</sub> measured using 8-ns pulses at 532 nm



(b) Normalized transmission curves of Z-scan data with an aperture (linear transmission of  $s=0.1$ ) divided by those without aperture for CS<sub>2</sub> measured using 8-ns pulses at 532 nm

Fig.5 Z-scan measurement the nonlinear characteristics of CS<sub>2</sub> in nanosecond laser pulses

The normalized transmittance for the open aperture Z-scan experiment is given by<sup>[10]</sup>:

$$T(z, s=1) = \sum_{m=0}^{\infty} \frac{[-\beta I_0 L_{\text{eff}} / (1+z^2/z_0^2)]^m}{(m+1)^{3/2}} \quad (1)$$

Where  $\beta$  is the nonlinear absorption coefficient of the sample,  $I_0(t)$  is the on-axis peak intensity at focus ( $z=0$ ),  $L_{\text{eff}} = \frac{1-\exp(-\alpha l)}{\alpha}$  is the effective thickness of the sample,  $x=z/z_0$  is the diffraction length of the beam,  $\alpha$  is the linear absorption coefficient,  $l$  is the thickness of sample cell. The values of  $\beta$  shown in Tab.1 can be obtained by theoretic fitting using Eq.(1).

From Fig.4, we observe that the scan signal profile with a valley preceding a peak of samples indicate the sign of nonlinear refractive index  $n_2$  is positive. That is characteristic of a self-focusing. Assuming a Gaussian beam traveling in the  $z$

direction, the normalized transmittance for the close aperture is expressed as<sup>[10]</sup>:

$$T(z, \Delta\varphi) = 1 + \frac{4\Delta\varphi_0(t)x}{(x^2+9)(x^2+1)} \quad (2)$$

$$\Delta T_{p-v} = 0.406(1-s)^{0.25}|\Delta\varphi_0| \quad (3)$$

Where  $\Delta\varphi_0(t) = kl_0(t)n_2L_{\text{eff}}$  is the on-axis nonlinear phase shift at the focus,  $\Delta T_{p-v}$  is the difference between the normalized peak and valley transmittance,  $s=0.1$  is the transmittance of the aperture ahead the detector in absence of a sample,  $k$  is the wave vector. The nonlinear refractive index  $n_2$  can be obtained from Eq.(3):

$$n_2 = \frac{\Delta T_{p-v}(-\ln T_0)\omega_0^2\tau\lambda}{(1-T_0)0.406(1-s)^{0.25}\cdot 2E\cdot 1.88I} \quad (4)$$

where  $T_0$  is the linear refractive index of the solution,  $\lambda$  is the laser wavelength,  $\tau$  is the pulse width of beam,  $E$  is the incident energy on the samples. The third-order nonlinear parameters of samples are given in Tab.1.

Tab.1 Third-order optical nonlinear parameters of metallic naphthalocyanine compounds at 532 nm

Samples	PbNc	PdNc	CS <sub>2</sub>
$\beta \times 10^{-11}$ m/W	65.40	39.00	56.90
$\text{Im}\chi^{(3)} \times 10^{-12}$ esu	21.40	12.76	24.30
$n_2 \times 10^{-11}$ esu	16.80	8.04	22.88
$\text{Re}\chi^{(3)} \times 10^{-12}$ esu	4.40	2.00	6.63
$\chi^{(3)} \times 10^{-12}$ esu	21.84	12.88	25.19
$\gamma \times 10^{-29}$ esu	34.4	25.72	$43.2 \times 10^{-6}$

Using Eq.(2), we fit the experimental results of close aperture Z -scan, which are shown in Fig.4. From Fig.4, we find that the values of theoretical calculations are in very agreement with that of experimental results. The results show that the naphthalocyanine compounds exhibit great third-order optical nonlinear properties.

The magnitude of  $X^{(3)}$  is given by<sup>[10]</sup>:

$$X^{(3)} = \left[ (2n_0^2 \varepsilon_0 c n_2)^2 + \left( \frac{\lambda}{2\pi} \cdot n_0^2 \varepsilon_0 c \beta \right)^2 \right]^{1/2} \quad (5)$$

where the value of  $\beta$  and  $n_2$  can be obtained by the Eq.(1) and Eq.(4) respectively,  $c$  is the velocity of light in vacuum,  $\varepsilon_0$  is the permittivity of free space,  $n_0$  is the linear refractive index of sample.

Molecular hyperpolarizability  $\gamma$  is a measure parameter of microscopic third-order nonlinearities. Molecular hyperpolarizability of the solution may be computed<sup>[11]</sup> from the value of  $\chi^{(3)}$ :

$$\gamma = \frac{\chi^{(3)}}{NL^4} \quad (6)$$

where  $N$  is the number density of molecules per  $\text{cm}^3$ ,  $L = (n_0^2 + 2)/3$  is a local field correction factor,  $n_0$  is the refractive index of the medium.

Using Eq. (6), we arrive at the values for the samples at 532 nm of  $\gamma$ (Tab.1). The experimental data show the values for the samples at 532 nm of  $\gamma$  are about  $10^5$  times larger in magnitude than the computed value of  $\text{CS}_2$  in our experiment. This indicates that the two metal naphthalocyanine compounds in our experiments show relatively great third-order optical nonlinearities. The results show that heavy metal atom enhances on the third-order optical nonlinear properties. The reason for such behavior is that the heavy metal atom enhances the intercrossing rate from the lowest excited singlet states to the triplet states due to the larger value of the spin-orbit coupling parameter from singlet states to triplet states. Therefore, the third-order optical non-linear properties are enhanced result from the absorption of triplet excited states which is increased by introducing heavy metal atom. The values of  $\gamma$  for PbNc is larger than that of PdNc due to the atomic number of Pb is larger than that of Pd, which increased the intercrossing rate from the lowest excited singlet states to the triplet states.

### 3 Conclusion

The optical nonlinearities of PbNc and PdNc were studied using Z -scan technique with 532 ns laser pulses. The second-order molecular hyperpolarizabilities were obtained.

The results indicate that the nonlinear absorption and nonlinear refraction of PbNc and PdNc exist at 532 nm, which arise from transitions among the singlet states and the triplet states. The results show that heavy metal atom enhances the third-order nonlinearities of the metal naphthalocyanine compounds.

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