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Crystal Structure and Third-Order Nonlinear Optical Properties Study of Tetraphenylporphyrin and Its Nickle Complex at Wavelength 532 nm and 1064 nm

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Tetraphenylporphyrin (TPP) and its nickel(II) (NiTPP) complex have been synthesized, their crystal structures have been determined by means of X-ray single crystal diffraction. The TPP possesses good planarity in the porphyrin core, while in the complex the planarity disappeared. The central nickel(II) ion coordinates with four nitrogen atoms, which constructed a distorted square environment. Their third-order nonlinear optical properties have been studied using Z-scan technique at wavelength 532 nm and 1064 nm in picosecond (ps) domain. At 532 nm nonlinear absorption were observed, TPP shows two-photon absorption (TPA) combined with saturable absorption (SA), while NiTPP shows SA. At 1064 nm nonlinear refraction were observed, the molecular second hyperpolarizability γ of the NiTPP was about 1.4 times larger than that of the TPP.

Keywords Chemical synthesis; crystal structure; optical materials; optical properties

1. Introduction

Third-order nonlinear optical materials have attracted much attention because of their potential utilities in ultrafast optical switching and modulations, optical power limiting and two-photon upconversion lasing, etc. fields and various types of metal-organic compounds have been synthesized and studied to obtain materials with fine third-order nonlinear optical properties [1]. TPP is a highly π-conjugated planar organic molecule [2] and some of the third-order nonlinear optical properties of this molecule have been investigated previously [3]. In this paper, the synthesis, single crystal structure of TPP and NiTPP are reported, and their third-order nonlinear optical properties are studied using Z-scan technique at wavelength 532 nm and 1064 nm respectively. By comparing their third-order nonlinear optical properties difference the role of center metal factor in the third-order nonlinear optical properties of complexes are studied.

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2. Experimental

General Methods: All reagents and solvents were obtained commercially and used as supplied. The IR spectrum was recorded with Nicolet 6700 spectrometer in the region of 400–4000 cm^{-1} with KBr pellet technique. The linear absorption spectra of TPP and NiTPP in their 1,2-dichloroethane solution (1.272×10^{-4} and 1.296×10^{-4} mol/L) were recorded at 20°C with Helios Alpha spectrometer respectively.

2.1. Synthesis and Recrystallization of TPP and NiTPP

TPP was obtained by condensation of pyrrole and benzaldehyde in propionic acid solution as reported [4]. Purification by chromatography afforded the TPP in 20 % yield. IR (cm^{-1}): $\tilde{\nu} = 3433, 3313.1, 3052.6, 2924.5, 2854.5, 1638.7, 1593.7, 1466.8, 1441.0, 1343.4, 1071.2, 961.4, 795.9, 724.3, 697.8$. The Ni^{II} complex was prepared following a similar refluxing method by mixing one equivalent of TPP with one equivalent of the Ni^{II} salt in DMF. Purification by chromatography afforded the complex in 26% yield. IR (cm^{-1}): $\tilde{\nu} =$ 3050.8, 3020.4, 2922.4, 2361.5, 1795.2, 1594.8, 1439.4, 1349.8, 1176.2, 1069.9, 1006.2, 964.2, 833.4, 791.9, 738.9, 697.4, 520.4, 462.8. Single crystals suitable for X-ray structure determination were obtained by recrystallization in their 1,2-dichloroethane solution.

2.2. X-Ray Crystallographic Study

Structure determination were performed on BRUKER SMART APEX II CCD X-ray diffractometer equipped with a graphite-monochromatic Mo-$K\alpha$ radiation ($\lambda = 0.71073$ Å) for data collection by using an Φ and ω scan mode at 293(2) K. Absorption corrections were applied using the SADABS program [5]. The structure was solved by direct methods and refined by full-matrix least-squares calculations. All the calculations were carried out with SHELXL-97 program [6] with anisotropic thermal parameters for the nonhydrogen atoms. All hydrogen atoms were placed in the calculated positions and refined isotropically using a riding model. Details of the crystal parameters, data collection and refinements are summarized in Table 1.

2.3. Third-Order Nonlinear Optical Properties Measurements

The third-order nonlinear optical properties measurements were performed using single beam Z-scan technique [7]. The light source is a mode-locked Nd:YAG laser (Continuum Leopard D-10, 20 ps, 10 Hz, 1064 nm) and the 532 nm light was obtained by double-frequency technique. The focal-length of the positive lens is $f = 25$ cm. To guarantee the nonlinear optical phenomenon we observed isn't derived from solvent, we performed Z-scan on solvent at the highest pulse energy in our experiments and no obvious nonlinear optical phenomenon was observed. The concentration of TPP and NiTPP in their 1,2-dichloroethane solutions for Z-scan are 6.36×10^{-4} and 6.48×10^{-4} mol L^{-1}.

3. Results and Discussion

3.1. Crystal Structure and Linear Absorption Spectra of TPP and NiTPP

In the TPP (Fig. 1), the four nitrogen atoms of the macrocycle are arranged nearly in a plane. The nickel complex (Fig. 2) shows a square coordination environments of the

Table 1. Crystal data and structure refinement parameters for TPP and NiTPP

	TPP	NiTPP
Empirical formula	$C_{44}H_{30}N_4$	$C_{44}H_{28}N_4Ni$
Formula weight	614.72	671.41
Wavelength/Å	0.71073	0.71073
Crystal system	Triclinic	Tetragonal
space group	P-1	I-42d
a/Å	6.443 (3)	15.0916 (17)
b/Å	10.465 (5)	15.0916 (17)
c/Å	12.394 (6)	13.894 (3)
α/°	95.893 (7)	90.00
β/°	99.271 (7)	90.00
γ/°	101.206 (7)	90.00
Volume/Å^3	801.2 (6)	3164.4 (9)
Z	1	4
Calculated density/g·cm^3	1.274	1.409
Absorption coefficient/mm^{-1}	0.075	0.654
F(000)	322	1392
2θ range/deg	2.79–28.19	2.70–22.69
Limiting indices	$-7 \le h \le 7$	$-19 \le h \le 19$
	$-12 \le k \le 12$	$-11 \le k \le 20$
	$-14 \le l \le 10$	$-17 \le l \le 17$
Total data collected	2819	1925
Unique data	2362	1540
R_{int}	0.0705	0.0501
Goodness of fit (S_{all})	0.991	1.006
R indices [$I > 2\sigma I$]	$R_1 = 0.0490$	$R_1 = 0.0630$
	$\omega R_2 = 0.1377$	$\omega R_2 = 0.2079$
R indices (all data)	$R_1 = 0.0559$	$R_1 = 0.0765$
	$\omega R_2 = 0.1441$[a]	$\omega R_2 = 0.2184$[b]
Largest difference peak/ hole (e/Å^3)	0.243/−0.262	0.309/−0.736
Deposition number [18]	CCDC-904980	CCDC-904978

[a] $\omega = 1/\left[\sigma^2\left(F_0^2\right) + (0.1000P)^2 + 0.0350P\right]$; [b] $\omega = 1/\left[\sigma^2\left(F_0^2\right) + (0.1680P)^2 + 0.1000P\right]$. $P = \left(F_0^2 + 2F_c^2\right)/3$).

metal ion, but the planarity in the porphyrin core were absent. Their bond lengths and angles are in the common range [8]. PLATON program [9] was employed to calculate the weak interactions in the crystals. For the TPP, the formed molecular assembly is further aided by C−H(phenyl)···π-ring(pyrrole) weak interactions (Fig. 3) [C(4)–H(4)···Cg(2): C(4)···Cg(2) 3.573(3) Å, angle at H(4) 135°. Symmetry code: $-1 + X, Y, Z$]. For the NiTPP, the formed molecular assembly is also further aided by C–H(phenyl)···π-ring(pyrrole) weak interactions (Fig. 4) [C(7)–H(7)···Cg(1): C(7)···Cg(1) 3.600(7) Å, angle at H(7) 126°. Symmetry code: $1/2 - X, Y, -1/4 - Z$]. Fig. 5 shows the UV/Vis spectra of TPP and NiTPP. Their linear absorption properties at wavelength 532 nm were listed in Table 2. At 1064 nm, they are transparent.

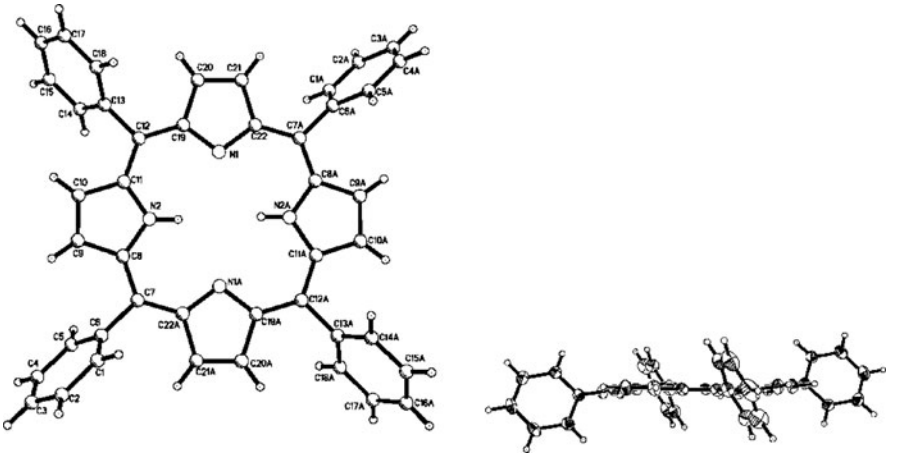

Figure 1. Molecular structure of TPP in two different views showing the overall structure (left) and the planarity in the porphyrin core (right).

3.2. Third-Order Nonlinear Optical Properties Study at 532 nm

Figure 6(a) shows the intensity-dependent open aperture Z-scan study of TPP′s solution in 1,2-dichloroethane. The data contained in these Z-scan plots were analyzed to determine the nonlinear absorption coefficient β. If the nonlinear absorption is the result of a TPA process, β is equal to the TPA coefficient and can be used to determine the TPA cross-section. The analysis is briefly described below. For the open aperture Z-scan measurement results, the normalized transmittance T relates position z through Equation (1):[10]

$$T(z, S=1) = 1/[\sqrt{\pi} \cdot q_0(z,0)] \cdot \int_{-\infty}^{+\infty} \ln\left[1 + q_0(z,0) \cdot e^{-\tau^2}\right] d\tau \tag{1}$$

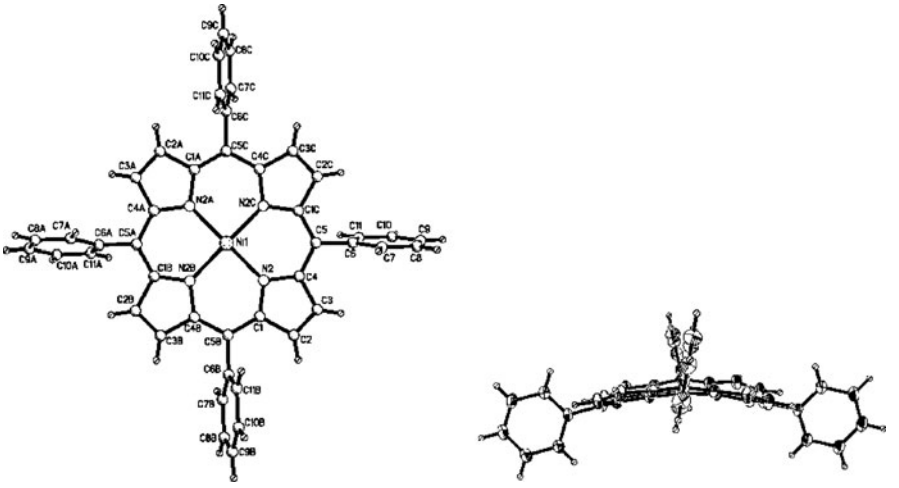

Figure 2. Molecular structure of NiTPP in two different views showing the overall structure (left) and the absence of planarity in the porphyrin core (right).

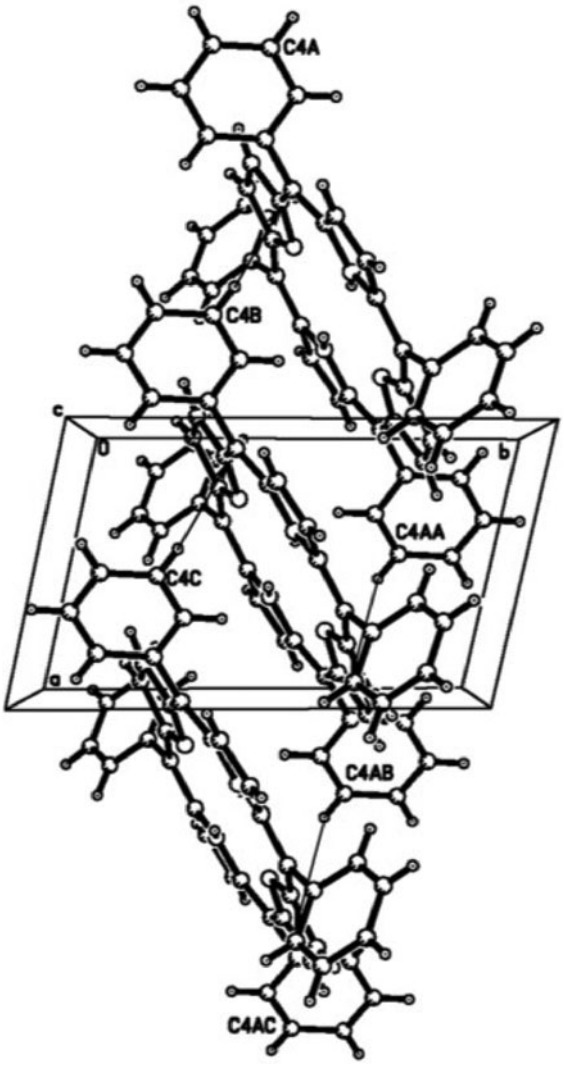

Figure 3. Intermolecular C—H···π-ring interactions in TPP.

where $q_0(z,0) = \beta \cdot L_{\text{eff}} \cdot I_0 / \left(1 + z^2/z_0^2\right)$. I_0 is peak intensity which relates the pulse energy ξ through equation $I_0 = 4\sqrt{\ln 2}\xi/(\pi^{3/2}\omega_0^2\tau)$. $L_{\text{eff}} = \left(1 - e^{-\alpha_0 L}\right)/\alpha_0$ is effect sample length, z is the position of the sample, $z_0 = \pi\omega_0{}^2/\lambda$ is the Rayleigh range of the beam. So, the β can be determined from the theoretical fits, as were shown in Fig. 6(b). The inset

Table 2. Linear absorption characteristics of TPP and NiTPP at wavelength 532 nm

Compound	A	$\alpha_0 = \frac{\text{A}}{0.434\text{L}}$ (cm^{-1})	$\sigma_0 = \frac{\alpha_0}{N_A d_0 10^{-3}}$ (cm^2)
TPP	0.1254	0.277	3.62×10^{-18}
NiTPP	0.1148	0.264	3.38×10^{-18}

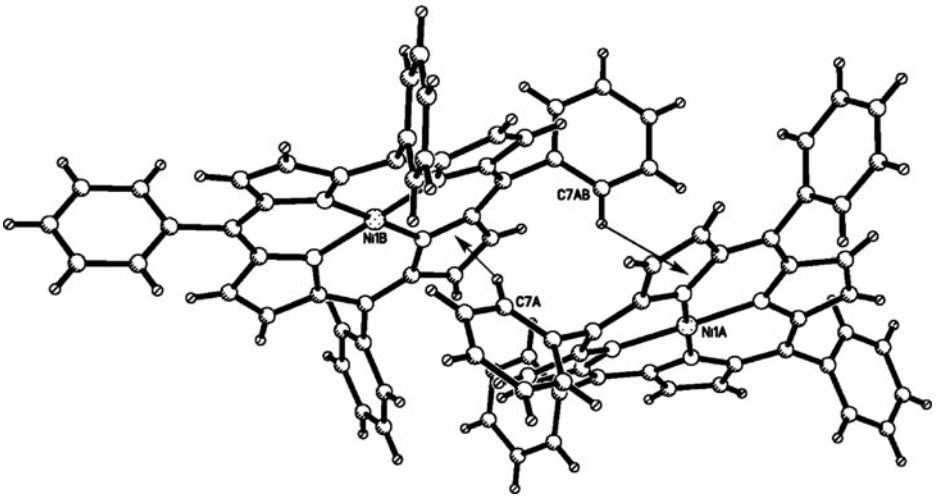

Figure 4. Intermolecular C–H···π-ring interactions in NiTPP.

picture of Fig. 6(b) depicted the β of the TPP as a function of focal intensity. From the plot, it can be seen that the β for TPP decreased linearly as the incident laser irradiance increased, this indicating that the nonlinear absorption process was not simply the result of a TPA process. Instead, it appears more likely that the nonlinear absorption was the result of a TPA process combined with SA process. A fit to the data gives an intercept of 2.69 cm GW^{-1}. This corresponds to the strictly TPA coefficient for TPP. Using this value, the TPA cross-section σ_2 for TPP was determined to be 2.62×10^{-53} $(m^4 \cdot s/photon \cdot molecule)$ according equation: $\sigma_2 = h\nu\beta/2\pi N \left(m^4 \cdot s/photon \cdot molecule\right)$ where $h\nu = 2.343 \times$

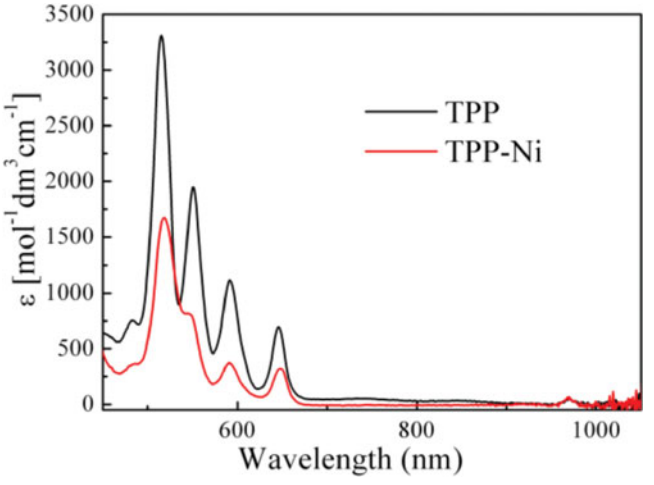

Figure 5. The linear absorption spectra for TPP and NiTPP.

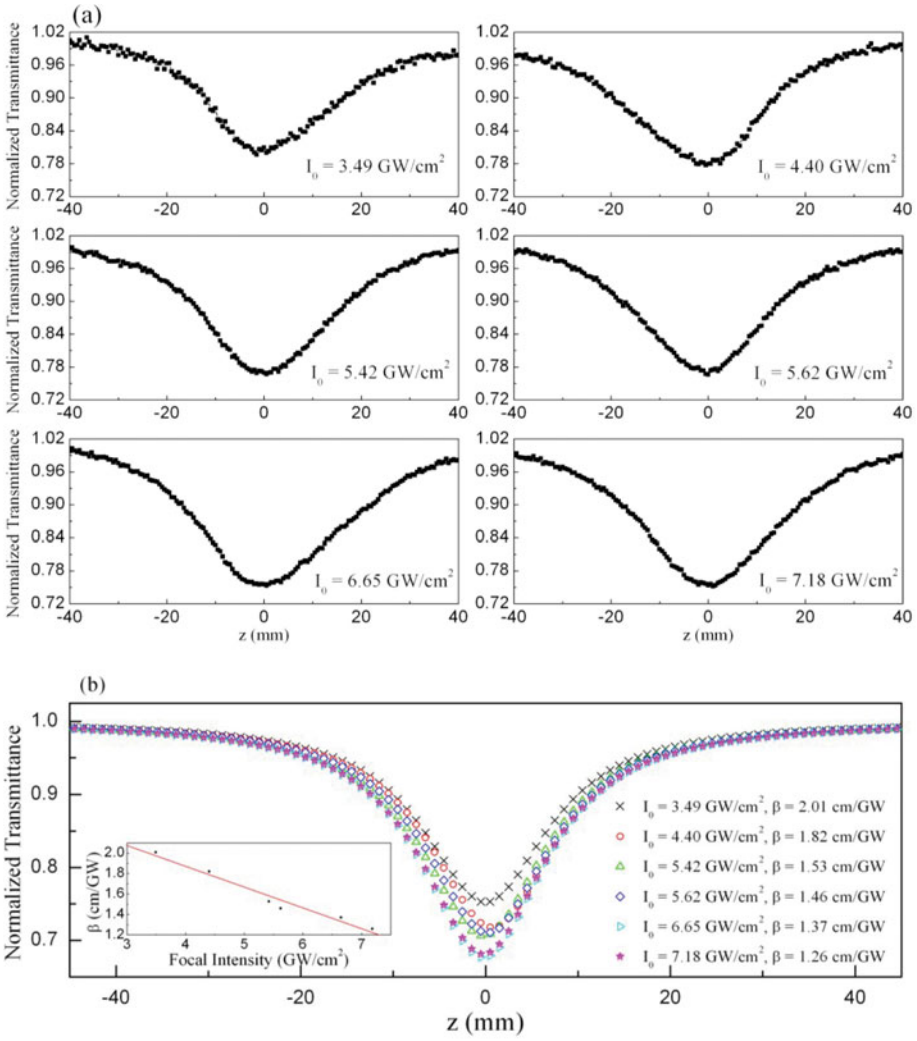

Figure 6. The normalized open aperture Z-scan of TPP's solution in 1,2-dichloroethane (6.36×10^{-4} mol L^{-1}) that were filled in a 1 mm path-length quartz cell using 14 ps pulses as a function of irradiance at $\lambda = 532$ nm, (a) is the experimental results, (b) is the theoretical fitted results.

10^{-18} J is incident photon energy, N is the molecular number of the solute per unit volume (m^{-3}). While in the open aperture Z-scan study of the NiTPP, SA were observed. Fig. 7(a) shows the fluence-dependent open aperture Z-scan study of the NiTPP′s solution in 1,2-dichloroethane. For the excited-state absorption, the normalized transmittance T relates position z through Equation (2):[11]

$$T = \ln\left(1 + q_0/\left(1 + z^2/z_0^2\right)\right) / \left(q_0/\left(1 + z^2/z_0^2\right)\right), \tag{2}$$

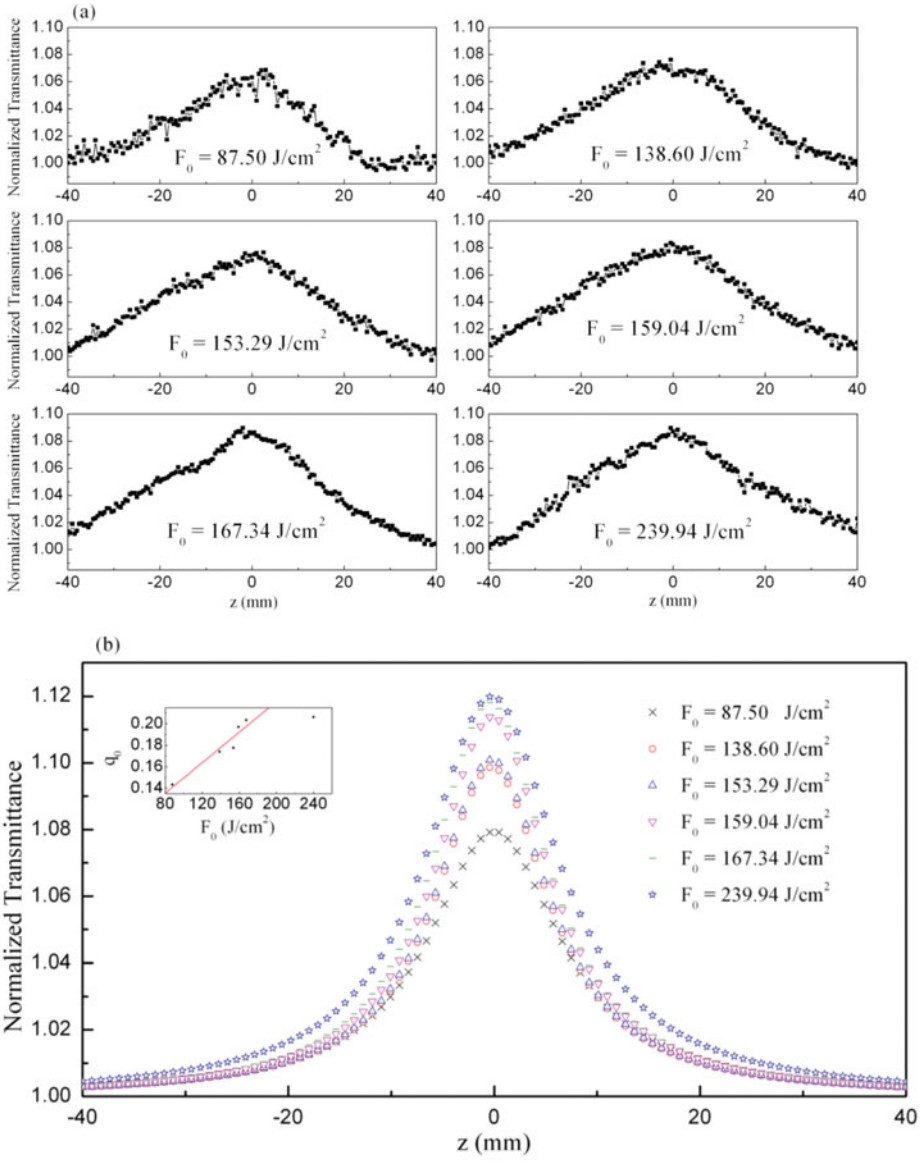

Figure 7. The normalized open aperture Z-scan of NiTPP's solution in 1,2-dichloroethane (6.48×10^{-4} mol L^{-1}) that were filled in a 1 mm path-length quartz cell using 14 ps pulses as a function of irradiance at $\lambda = 532$ nm, (a) is the experimental results, (b) is the theoretical fitted results.

where $q_0 = \pi\sigma_{es}\alpha_0 F_0 L_{eff}/h\nu$, σ_{es} is the excited-state absorption cross section, F_0 is the fluence (J cm^{-2}) of the laser at focus ($z = 0$) which relates the pulse energy ξ through equation $F_0 = 2\xi/\pi\omega_0^2$. Fig. 7(b) are the best fit of the open aperture data for q_0 from Equation (2), which yielded an excited-state absorption cross section value of $\sigma_{es} = 2.01 \times 10^{-20}$ cm^2 for NiTPP. The inset picture of Fig. 7(b) depicted the q_0 as a function of F_0. For NiTPP saturation of the nonlinear absorption above fluences of 167.34 J cm^{-2} was deduced.

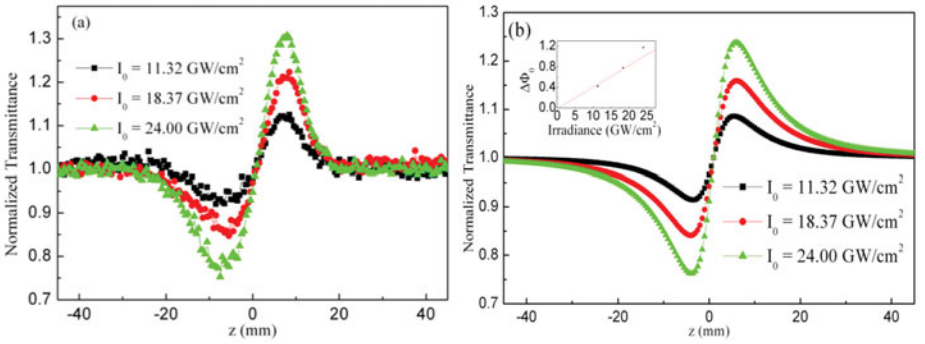

Figure 8. The normalized closed aperture Z-scan of TPP′s 1,2-dichloroethane solution in a 1-mm cuvette using 20 ps pulses as a function of irradiance at $\lambda = 1064$ nm, (a) is the experimental results, (b) is the theoretical fitted results. Inset picture shows the change of $\Delta\Phi_0$ versus the peak irradiance I_0 as measured from the Z-scan experiments. The line represents a cubic nonlinearity, the deviation from the line is indicative of higher order refractive effects.

3.3. Third-Order Nonlinear Optical Properties Study at 1064 nm

Figure 8(a) and 9(a) show the irradiance-dependent closed aperture Z-scan study of the TPP and NiTPP. And the theoretical fitted results were shown in Figs. 8(b) and 9(b). The analysis methods were same as our previously reported [12–14]. All the results were listed in Table 3. Their γ values are in the same magnitude as other metal-porphrin compounds [15]. As was found in the metal-substituted phthalocyanine study [16], a heavy metal in TPP may yield a larger γ value than TPP. The inset picture of Figs. 8(b) and 9(b) shows the plot of $\Delta\Phi_0$ versus peak laser irradiance. At higher irradiance levels in Fig. 8(b), the nonlinear refraction caused by TPA generated charge carriers, an effective fifth-order nonlinearity, becomes important. This is indicated in the inset picture by the small deviation of $\Delta\Phi_0$ at $I_0 = 24$ GW cm^{-2} from the line representing the cubic nonlinearity. In the inset picture of Fig. 9(b), the linear behavior of the plot represents a cubic nonlinearity.

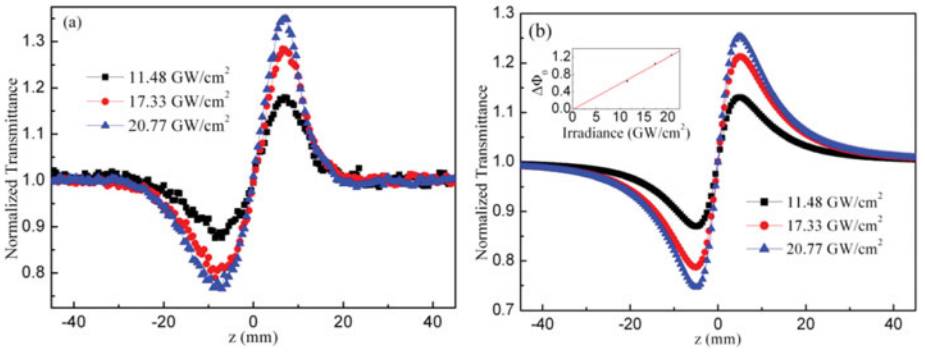

Figure 9. The normalized closed aperture Z-scan of NiTPP′s 1,2-dichloroethane solution in a 1-mm cuvette using 20 ps pulses as a function of irradiance at $\lambda = 1064$ nm, (a) is the experimental results, (b) is the theoretical fitted results. Inset picture shows the change of $\Delta\Phi_0$ versus the peak irradiance I_0 as measured from the Z-scan experiments. The line represents a cubic nonlinearity.

Table 3. Third-order nonlinear optical properties of TPP and NiTPP at wavelength 1064 nm

Compound	n_2^I ($\times 10^{-18}$ m^2 W^{-1})	$\chi_R^{(3)}$ ($\times 10^{-20}$ m^2 V^{-2})	γ ($\times 10^{-56}$ C•m^4 V^{-3})	γ^a ($\times 10^{-30}$ esu)
TPP	0.714	0.791	5.34	0.43
NiTPP	1.02	1.13	7.50	0.61

[a]γ (SI) $= (1/3)^4 \times 10^{-23}\gamma$ (esu).

4. Conclusions

In conclusion TPP and its nickel(II) complex have been synthesized and their crystal structures have been determined by means of X-ray single crystal diffraction, their nonlinear optical properties have been studied using Z-scan technique at wavelength 532 nm and 1064 nm in ps domain. At 532 nm, nonlinear absorption were observed, TPP shows TPA combined with SA, while NiTPP shows SA, this underlines the important role of the metal ion. At 1064 nm nonlinear refraction were observed, the γ value of the NiTPP was about 1.4 times larger than that of the TPP, this certificated that center metal atoms usually enhance the third-order nonlinearity. Beside this strategy by introducing centre metal atoms into organic molecules to form complexes to improve the third-order nonlinearity of materials', some other strategies have been reported, such as it has been reported that a tailored change in the structure of the core of porphyrins can modulate and improve the nonlinear response, and a strongly push-pull molecular structure can also improve the nonlinear response [17].

Acknowledgments

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[18] Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications. CCDC-904980 for TPP and CCDC-904978 for NiTPP. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html.