



## Octupolar metal complexes for third order nonlinear optical studies

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### ABSTRACT

The octupolar metal complexes [Zn(bpy)(L)] (1), [Cd(bpy)(L)] (2), [Hg(bpy)(L)] (3) (bpy = 2,2'-bipyridyl, L = 4-dimethylamino- $\alpha$ -cyanocinnamic acid) have been synthesized. The third-order nonlinear optical properties of complexes were studied using Z-scan technique at 532 nm with nanosecond laser pulses. The complexes show optical limiting behavior. The values of the effective two-photon absorption (2PA) coefficients ( $\beta$ ), third-order nonlinear susceptibilities ( $\chi^{(3)}$ ) and two-photon absorption cross sections ( $\sigma_2$ ) are calculated. Results show, lewis acidity of metal center and molecular symmetry are two important factors for observed large TPA cross-section of metal complexes.

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### 1. Introduction

Rapid advancements in the field of photonics have increased the demand for novel nonlinear optical (NLO) materials. Particularly, molecules exhibiting strong two photon absorption (TPA) are of practical importance in photonics applications such as frequency upconversion lasing, three-dimensional fluorescence imaging and multi photon microscopy [1–4]. For this purpose, designing the molecule with large TPA cross section plays a vital role. Molecular geometry, strength of electron donor/acceptor groups, molecular planarity and conjugation length affect the TPA cross section [5–7]. In this regard, designing the molecule and understanding the structure–property relationship is of fundamental importance, which is not well established for third order nonlinear materials as compared to that of second-order nonlinear materials.

A wide variety of materials have been investigated for third-order nonlinear optics, among which metal complexes are attractive because of the flexibility they offer in tuning the nonlinear optical properties synthetically. In these class of materials, nonlinear optical response can be enhanced by adopting suitable design strategies, such as donor– $\pi$ -bridge–acceptor (D– $\pi$ -A), donor– $\pi$ -bridge–donor (D– $\pi$ -D), acceptor– $\pi$ -bridge–donor– $\pi$ -bridge–acceptor (A– $\pi$ -D– $\pi$ -A), and donor– $\pi$ -bridge–acceptor– $\pi$ -bridge–donor (D– $\pi$ -A– $\pi$ -D) conjugated structural motifs [8]. Upon excitation, substantial symmetric intramolecular charge redistribution takes place in these molecules, resulting in high TPA cross sections [7]. Compared with the 1D dipolar TPA chromophores, octupolar molecules possess more round-off shapes, which ease their packing in a single crystal-line lattice as opposed to less favorable elongated dipolar rod like

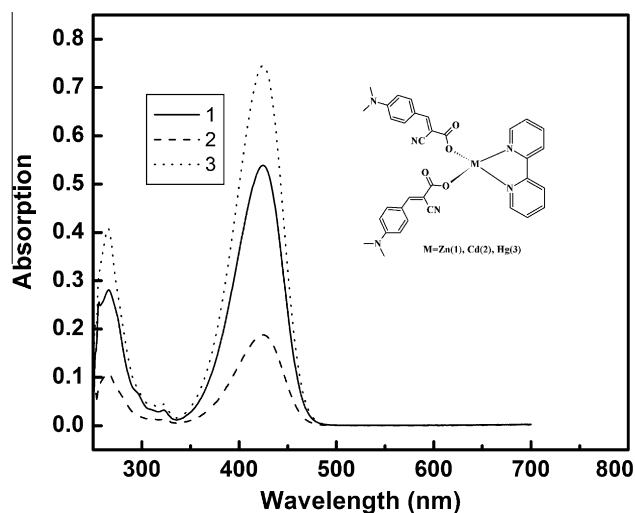
molecules. The absence of dipolar moments in excited as well as ground state makes octupolar molecules more suitable in various optical applications [9–12].

Transition metal chemistry has been proved to be another powerful tool to build up octupolar arrangements. Metal ions can assemble organic ligands in a variety of multipolar arrangements which show interesting electronic and optical properties tunable by virtue of the coordinated metal center. In the UV–Vis region of spectrum of metal complexes, there are often two different transitions, i.e., a strong intraligand charge-transfer (ILCT) transition and a low-energy metal to ligand charge-transfer transition (MLCT), which are often associated with large TPA cross-section. High damage threshold and fast response time that metal complexes have in comparison to organic compounds are important from the perspective of application. Incorporation of metal into the organic chromophore enhances the laser damage threshold, optical quality with high transparency, thermal and photochemical stability [13]. These materials possess additional advantages in that they can be grown as crystals as well as being incorporated into polymers such as poly(methyl methacrylate) (PMMA) to fabricate films [14]. A wide range of metals with different oxidation states and ligands necessarily make metal complexes active research point in design of TPA material [8]. Some reports are available describing the effect of metal ions on TPA-active organic molecules [8,15,16].

As the M(II) (M = Zn, Cd, Hg) ion usually prefers tetrahedral coordination geometry, it can serve as an excellent 3D template. We describe here the synthesis of three 2,2'-bipyridyl based M(II) complexes (Figure 1) for two-dimensional nonlinear optical response. The complexes show optical limiting behavior. The values of the effective two-photon absorption (2PA) coefficients ( $\beta$ ), third-order nonlinear susceptibilities ( $\chi^{(3)}$ ) and two-photon absorption cross sections ( $\sigma_2$ ) are calculated.

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**Figure 1.** UV-visible absorption spectra of complexes (1–3). Inset shows molecular structures of complexes 1–3.

## 2. Experimental

### 2.1. Materials

All the chemicals used were of analytical grade. Solvents were used as received. 4-Dimethylaminobenzaldehyde, tert-butylcyanoacetate, bipyridine were purchased from Sigma Aldrich and Zn(OAc) $\cdot$ 2H $_2$ O, Cd(OAc) $_2$ ·2H $_2$ O and Hg(OAc) $_2$ ·2H $_2$ O were procured from Merck chemicals. 4-Dimethylamino- $\alpha$ -cyanocinnamic acid was synthesized and characterized by reported procedure [13].

### 2.2. Instrumental

The  $^1$ H NMR spectra were recorded using Bruker AV 400 spectrometer operating at the frequency of 400 MHz. The spectra were recorded in solution with DMSO as internal lock. Electronic spectra were measured on a GBC UV-Vis double beam spectrophotometer with 0.6 nm resolution in DMSO solution of the complexes in the 200–800 nm range. FT-IR spectra were recorded on a Thermo Nicolet Avatar FT-IR spectrometer with 4 cm $^{-1}$  resolution as KBr powder in the frequency range 400–4000 cm $^{-1}$ . The C, H and N contents were determined by ThermoFlash EA1112 series elemental analyzer. The single beam Z-scan technique was used to measure the third-order nonlinear optical susceptibility of the metal complexes. This technique allows simultaneous measurement of nonlinear refraction (NLR) and nonlinear absorption (NLA). Experiment was performed using a Q-switched frequency doubled Nd:YAG laser (Spectra-Physics USA, Model-GCR170) with a temporal pulse width of 7 ns (FWHM) at 532 nm and a repetition rate of 10 Hz. The input pulse energy used was 100  $\mu$ J, which corresponds to an on-axis-peak irradiance of 2.39 GW/cm $^2$ . The transmittance was measured using two Pyroelectric detector (RjP-735) connected with Laser Probe Rj-7620 Energy meter. The output of the laser had a nearly Gaussian intensity profile. A lens of focal length 26 cm was used to focus the laser pulses into a 1 mm quartz cuvette containing the sample solution. The laser was run in the single shot mode using a data acquisition programme, with an approximate interval of 3–4 s between each pulse. This low repetition rate prevents sample damage and cumulative thermal effects [17,18] in the medium.

### 2.3. Synthesis of metal complexes

#### 2.3.1. Synthesis of 4-dimethylamino- $\alpha$ -cyanocinnamic acid (L)

The tert-butylcyanoacetate 1.24 mL (8.8 mmol) was added to the ethanolic (50 ml) solution of 4-dimethylaminobenzaldehyde (1.19 g; 8 mmol) followed by catalytic amount (2 drops) of piperidine. The orange yellow solid that appeared on stirring overnight at room temperature, was collected by filtration, washed thoroughly with ethanol and dried under vacuum. This solid was stirred for 2 h, with 6 mL of trifluoroacetic acid and then poured into 50 mL of water. The orange yellow solid that separated, was collected by filtration, washed with ethanol and finally dried under vacuum. Yield: 90%.  $^1$ H NMR (400 MHz, DMSO, TMS, 25  $^{\circ}$ C):  $\delta$  3.06 (s, 6H), 6.82 (d, 2H), 7.93 (d, 2H), 8.05 (s, 1H), 13.20 (bs, 1H). IR (KBr, cm $^{-1}$ ): 2212, 1662.7. CHN found: C: 67.03, H: 6.03, N: 13.43. C $_{12}$ H $_{12}$ N $_2$ O $_2$  requires C: 66.59, H: 5.54, N: 12.43.

#### 2.3.2. [Zn(bpy)(L) $_2$ ] (1)

A methanolic solution (10 mL) containing 4-dimethylamino- $\alpha$ -cyanocinnamic acid (L), (0.27 g; 1.2 mmol), Zn(OAc) $\cdot$ 2H $_2$ O (0.13 g; 0.63 mmol) and bipyridine (0.098 g; 0.63 mmol) were allowed to stir for 24 h at room temperature. The bright yellow solid that separated upon stirring overnight was collected by filtration, washed with methanol and dried under vacuum. Yield: 88%.  $^1$ H NMR (400 MHz, DMSO, TMS, 25  $^{\circ}$ C):  $\delta$  3.01 (s, 6H), 6.75 (d, 2H), 7.82 (d, 2H), 8.14 (d, 4H), 7.91 (s, 2H), 8.14 (bs, 2H), 8.88 (bs, 2H), 9.16 (bs, 2H). IR (KBr, cm $^{-1}$ ): 2200.1, 554.6, 1600.1. CHN found: C: 63.54, H: 5.78, N: 13.55. C $_{34}$ H $_{30}$ N $_6$ O $_4$ Zn requires C: 62.62, H: 4.63, N: 12.88.

#### 2.3.3. [Cd(bpy)(L) $_2$ ] (2)

Synthesis of this complex is also accomplished following a similar procedure of complex 1 taking Cd(OAc) $_2$ ·2H $_2$ O (0.168 g; 0.63 mmol) in place of Zn(OAc) $\cdot$ 2H $_2$ O keeping other reactants unchanged. The bright yellow solid that separated upon stirring overnight was collected by filtration, washed with methanol and dried under vacuum. Yield: 87%.  $^1$ H NMR (400 MHz, DMSO, TMS, 25  $^{\circ}$ C):  $\delta$  3.00 (s, 6H), 6.79 (d, 2H), 7.56 (d, 2H), 7.85 (d, 4H), 7.94 (s, 2H), 8.03 (bs, 2H), 8.46 (bs, 2H), 8.75 (bs, 2H). IR (KBr, cm $^{-1}$ ): 2207.3, 516.8, 1583.5. CHN found: C: 59.17, H: 4.51, N: 12.73. C $_{34}$ H $_{30}$ N $_6$ O $_4$ Cd requires C: 58.41, H: 4.32, N: 12.02.

#### 2.3.4. [Hg(bpy)(L) $_2$ ] (3)

Synthesis of this complex is also accomplished following a similar procedure of complex 1 taking Hg(OAc) $_2$ ·2H $_2$ O (0.20 g; 0.63 mmol) in place of Zn(OAc) $\cdot$ 2H $_2$ O keeping other reactants unchanged. The bright yellow solid that separated upon stirring overnight was collected by filtration, washed with methanol and dried under vacuum. Yield: 84%.  $^1$ H NMR (400 MHz, DMSO, TMS, 25  $^{\circ}$ C):  $\delta$  3.02 (s, 6H), 6.81 (d, 2H), 7.45 (d, 2H), 7.86 (d, 4H), 8.01 (s, 2H), 8.04 (bs, 2H), 8.56 (bs, 2H), 8.77 (bs, 2H). IR (KBr, cm $^{-1}$ ): 2206.3, 515.1, 1571.2. CHN found: C: 52.06, H: 4.02, N: 10.87. C $_{34}$ H $_{30}$ N $_6$ O $_4$ Hg requires C: 51.87, H: 3.84, N: 10.67.

## 3. Results and discussion

### 3.1. Linear absorption spectra

The molecular structures of the complexes and their linear absorption spectra are displayed in Figure 1. The linear absorption spectra of the complexes were obtained at room temperature in DMSO solvent. The spectra shows an absorption band for complexes around 425 nm, which corresponds to intraligand electronic transition. The spectra also show negligible single photon

absorption at 532 nm wavelength. Therefore, the nonlinear optical measurements carried out in our experiments are under nonresonant excitation.

In presence of high intensity laser irradiation, the nonlinear absorption and refraction are expressed by equations

$$\alpha(I) = \alpha + \beta I \quad (1)$$

$$n(I) = n + n_2 I \quad (2)$$

where  $\alpha$  is the linear absorption coefficient,  $n$  is the linear refractive index,  $\beta$  is the nonlinear absorption coefficient and  $n_2$  is the nonlinear refractive index [19].

According to the basic theory of two photon absorption process (TPA), the change in the intensity of the laser beam, in the unit propagation length can be expressed as [20,21],

$$dI/dz + \alpha I + \beta I^2 = 0 \quad (3)$$

where  $\alpha$  is the attenuation coefficient caused by linear absorption and scattering,  $\beta$  is the attenuation coefficient caused by nonlinear absorption.

### 3.2. Nonlinear absorption

The nonlinear absorption coefficient  $\beta$ , of the complexes were determined from the open aperture Z-scan curves given in Figures 2–4. The model described in [22] was used to determine the magnitude of nonlinear absorption coefficient ( $\beta$ ) of the compounds. If the nonlinear transmissivity change is due to the pure TPA process, then the nonlinear absorption coefficient  $\beta$  should be independent of the input intensity  $I_0$ . However, if there are additional nonlinear absorption mechanisms such as excited state absorption or three photon absorption, the apparently measured values of nonlinear absorption coefficient  $\beta$  will not remain constant [21,23,24]. It is also supported by UV–visible absorption spectra, where the samples show negligible single photon absorption at 532 nm wavelength.

It is known that nonlinear absorption coefficient  $\beta$ , depends on the number of absorptive centers in a unit volume. Assuming that this number is  $N_0$ , in units of  $\text{cm}^{-3}$ , we have [3,21,25]

$$\beta = \sigma_2 N_0 = \sigma_2 N_A d \times 10^{-3} \quad (4)$$

Here,  $N_0$  is the molecular density of the sample (in units of  $1/\text{cm}^3$ ),  $\sigma_2$  is the molecular TPA coefficient (or cross section) (in units of  $\text{cm}^4/\text{GW}$ ),  $d$  is the concentration of the complexes (in units of  $\text{mol}/\text{dm}^3$ ), and  $N_A$  is the Avogadro number. For known  $\beta$  and  $d$ , the value of  $\sigma_2$  can be obtained. In the literature [3,21], molecular TPA cross section (is in units of  $\text{cm}^4 \text{ s}/\text{photon}$ ) is also defined as

$$\sigma'_2 = \sigma_2 h\nu \quad (5)$$

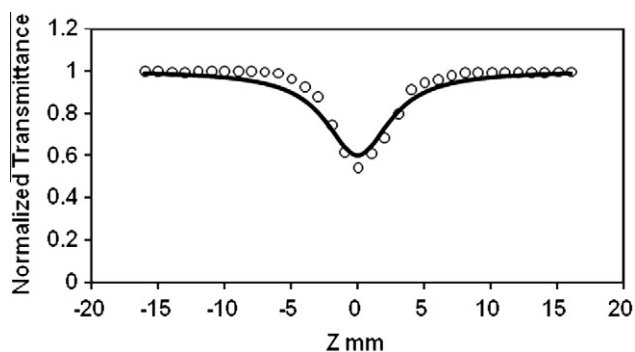


Figure 2. Open aperture Z-scan trace for  $[\text{Zn}(\text{bpy})(\text{L})_2]$ . Solid line depicts theoretical fit.

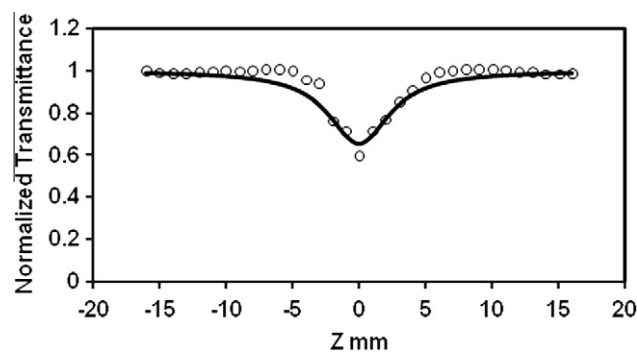


Figure 3. Open aperture Z-scan trace for  $[\text{Cd}(\text{bpy})(\text{L})_2]$ . Solid line depicts theoretical fit.

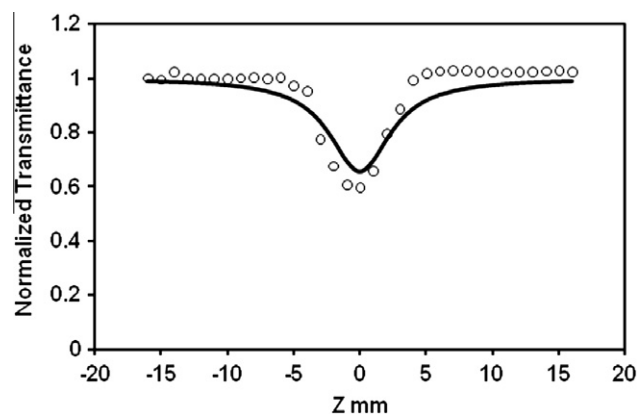


Figure 4. Open aperture Z-scan trace for  $[\text{Hg}(\text{bpy})(\text{L})_2]$ . Solid line depicts theoretical fit.

where,  $\sigma'_2$  is in units of  $\text{cm}^4 \text{ s}$  and  $h\nu$  is the energy (in joules) of an incident photon.

Now the nonlinear absorption coefficient  $\beta$ , is related to the imaginary part of third-order nonlinear optical susceptibility through the equation [22]

$$im\chi = n_0^2 c \epsilon_0 \lambda \beta / 2\pi \quad (6)$$

where  $n_0$  is the linear refractive index,  $\epsilon_0$  is the permittivity of free space and  $c$  is velocity of light in vacuum. The measured values of nonlinear absorption coefficient,  $\beta$ , molecular TPA cross sections  $\sigma_2$  and  $\sigma'_2$ , and the imaginary part of third-order nonlinear optical susceptibility  $\chi^{(3)}$  of the complexes are given in Table 1. The values  $\sigma'_2$  of complexes are nearly two orders of magnitude larger than the Rhodamine 6G which is  $10^{-48}$ – $10^{-50} \text{ cm}^4 \text{ s}/\text{photon}$  [26].

### 3.3. Nonlinear refraction

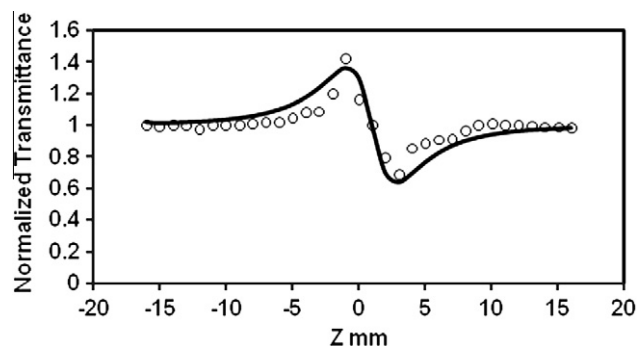
The pure nonlinear refraction curves for complexes shown in Figures 5–7, obtained by dividing closed aperture data by open aperture data exhibit peak-valley characteristic, indicating negative nonlinear refraction or self defocusing effect. The values of nonlinear refractive index  $n_2$  [22] obtained is of the order of  $10^{-11}$  esu. The real part of third-order nonlinear optical susceptibility is obtained through the equation [22],

$$\text{Re}\chi^{(3)} = 2n_0^2 c \epsilon_0 n_2 (\text{esu}) \quad (7)$$

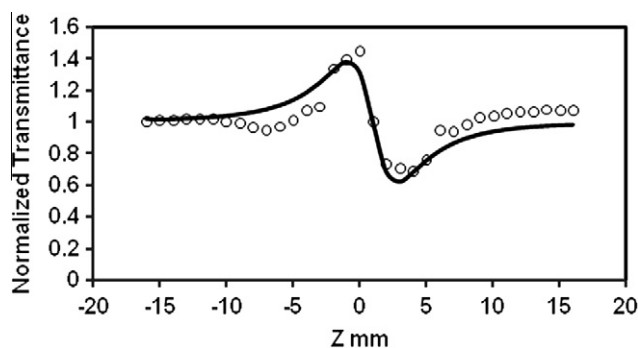
where  $n_0$  is the linear refractive index,  $\epsilon_0$  is the permittivity of free space and  $c$  is velocity of light in vacuum. The values given in Table 1 are of the order of  $10^{-13}$  esu which is well comparable with  $\text{CS}_2$ , a well-known nonlinear refractive material. Free ligand L does not

**Table 1**  
Third-order nonlinear optical parameters of complexes 1–3.

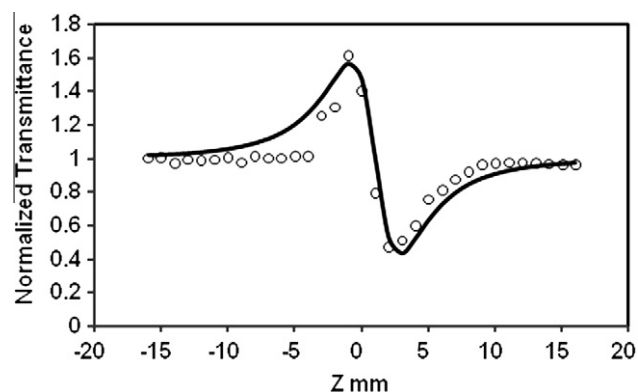
Complex	$\beta$ (cm/GW)	$n_2$ ( $\times 10^{-11}$ esu)	$\text{Im } \chi^3$ ( $\times 10^{-13}$ esu)	$\text{Re } \chi^3$ ( $\times 10^{-13}$ esu)	$\sigma_2$ ( $\times 10^{-19}$ cm <sup>4</sup> /GW)	$\sigma_2'$ ( $\times 10^{-46}$ cm <sup>4</sup> s/photon)
1	6.2557	-2.1640	0.9626	-2.3180	10.390	3.874
2	5.0722	-2.4533	0.7806	-2.6279	8.421	3.141
3	5.0722	-3.3845	0.7805	-3.6255	8.421	3.141



**Figure 5.** Normalized pure nonlinear refraction curve for [Zn(bpy)(L)<sub>2</sub>]. Solid line depicts theoretical fit.



**Figure 6.** Normalized pure nonlinear refraction curve for [Cd(bpy)(L)<sub>2</sub>]. Solid line depicts theoretical fit.



**Figure 7.** Normalized pure nonlinear refraction curve for [Hg(bpy)(L)<sub>2</sub>]. Solid line depicts theoretical fit.

show any nonlinear absorption behavior at 532 nm. In contrast, significant nonlinear absorption performance is observed for each of the complexes (1–3) at the same wavelength. The TPA cross sections of complexes 1–3 are quite similar. The increased interactions between metals and ligands may be responsible for the large

TPA cross sections. The  $\sigma_2$  value of complex 1 is larger compared to complexes 2 and 3, which can be attributed to the greater acceptor strength of Zn(II) in comparison to Cd(II) and Hg(II), leading to an increased ILCT in ligand. The measured values of nonlinear absorption coefficient,  $\beta$ , molecular TPA cross sections  $\sigma_2$ , nonlinear refractive index  $n_2$  and the real and imaginary part of third-order nonlinear optical susceptibility  $\chi^{(3)}$  of the complexes are comparable to those obtained for the organic NLO materials viz polyoxadiazoles [27], polythiophenes [28], copolymer containing oxadiazole and thiophene units [29], chalcones [19,30,31] and hydrazones [32] studied under similar experimental conditions. Since measurement was done in the solution state the NLO properties in this system is not dominated by phonon contributions. The strongest reason being the sample in liquid phase. Also there is no room for sample heating as the repetition rate is low and hence the successive pulses do not see the effect due to the heating caused by the earlier pulse (i.e. typically a few hundreds of microseconds would be enough to relax the sample to the ground state). However the papers by Kityk et al. [17,18] does demonstrate that the second Harmonic generation/absorption in organo-metals get enhanced by one or two orders of magnitude due to phonon interaction. The laser pulse width used is 15 ns and the repetition rate is about 10 Hz. The NLO in organo metalics is strongly affected by phonons, however in the sample system that is under current study, this will not contribute much due to the liquid phase and low repetition rate. This low repetition rate prevents sample damage and cumulative thermal effects in the medium.

The probability for multi-photon absorption (three photon absorption and higher) will be much weaker compared to a two photon absorption. Looking at the absorption spectrum of the present sample, there is a strong absorption corresponding to the two photon wavelength of 266 nm, and hence there exists a strong possibility of two photon absorption in these samples. Moreover the laser excitation intensities used are kept low to avoid influences from higher order absorption. The fact that numerical simulations based on two photon absorption fits well to the experimental data also suggests that contributions from higher order processes are negligible.

#### 4. Conclusions

In summary, the third-order nonlinear optical properties of the complexes have been investigated by Z-scan measurements. The parameters indicate that the complexes exhibits negative nonlinear refractive index. The real and imaginary parts of third-order nonlinear optical susceptibility were found to be as large as  $10^{-13}$  esu. Two photon absorption was found to be the major contributor to the observed nonlinear absorption. Complexes possess large molecular two photon absorption cross section of the order  $10^{-46}$  cm<sup>4</sup> s/photon. Hence, the complexes investigated seem to be promising candidates for future photonic and optoelectronic applications.

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